ArtDemo:
Reduction of contamination risks at an artificial recharge demonstration site in Denmark and Sweden

Project Publication

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Foreword

Artificial recharge sensu lato, today preferably called ‘Managed Aquifer Recharge’ (MAR), comprises techniques like basin recharge, deep well injection, aquifer transfer recovery (ATR), aquifer storage recovery (ASR) and river bank filtration (RBF). These techniques can partly solve or mitigate the global water crisis, which is deemed to worsen due to climate change and growing water demands. Important advantages of these techniques consist of (1) very high recharge rates utilizing relatively small surface areas; (2) the transformation of unreliable, often polluted surface water into hygienically safe groundwater of much better quality; and (3) subterranean storage which protects the water against evaporation losses, algae blooms, atmospheric fallout of pollutants, and earthquake hazards. Disadvantages may consist of cumbersome clogging phenomena, water losses due to mixing with brackish groundwater, and natural reactions with the porous medium. The latter may raise the concentrations of for instance Fe, As, Mn, NH_4, Ca and DOC and thus necessitate a post-treatment. In addition, surface waters to be infiltrated may contain emerging pollutants like pharmaceuticals, personal care products, xeno-oestrogens and nanoparticles, the behavior of which is still poorly understood.

The introduction of MAR systems therefore raises many technical and scientific questions. Some of these questions have been answered by EU-funded MAR-projects, notably ENV4-CT95-0071 (reported by European Commission 2001, ‘Artificial recharge of groundwater’, Final report EUR 19400, 342p.) and Reclaim water and GABARDINE (both reported by C. Kazner et al. [eds] 2012, ‘Water Reclamation technologies for safe managed aquifer recharge’, IWA Publ. London, 429p).

In between both EU projects and their publication, there was, however, another EU-project, called ArtDemo (Artificial Recharge Demonstration). This report contains the results from that project, which was executed in the period 2002-2006. For various reasons the publication of the ArtDemo results has been delayed for about 11 years, although some parts appeared in 2006 in the proceedings of ISMAR-5 (Proc. 5th Intern. Symp. on Management of Aquifer Recharge, ISMAR-5, Berlin 11-16 June 2005, UNESCO IHP-VI, Series on Groundwater No. 13) and elsewhere. The ArtDemo results reflect, of course, the technological and scientific state-of-the-art of about one decade ago. Nevertheless we judge the information and ideas of high value and actual enough, worth publication. We hope that you share our opinion and enjoy reading.

January, 2018

Anders Lynggaard-Jensen and Pieter J. Stuyfzand

Contact concerning this E-book can be made to Pieter J. Stuyfzand (Pieter.Stuyfzand@kwrwater.nl), and the E-book can be downloaded free of charge from the KWR website following
this link: https://library.kwrwater.nl/publication/55517526/

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Chapter 1: Introduction, ArtDemo Overview and Demonstration Sites

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Abstract: The ArtDemo project objectives are described through the original workplan, and the results obtained are summarized with references to the detailed descriptions given in the following chapters of the publication. Finally descriptions from the three demonstration sites used in the ArtDemo project are compiled into one table for quick reference.

1 INTRODUCTION

The ArtDemo project specifically addresses issues raised by Key action 1: “Sustainable Management and Quality of Water” within the “Energy, Environment and Sustainable Development”. This publication describe the results obtained in the project and constitutes sections 5 and 6 of the final report of the ArtDemo project.

1.1 Problems to be solved

The provision of safe and high quality drinking water is essential and fundamental for having a high quality of life. However, the water resources in Europe are threatened by various sources of contamination. In context of this increasing contaminant pressure, there is an increasing requirement to develop concepts and technologies to create a basis for provision of safe and high quality drinking water.

Drinking water supply companies in Europe use well-proven technologies, which they are familiar with and know how to operate. At the same time, setting up of new plants and implementing new technologies are costly in terms of human resources, technical R&D and investments, although it may be considered cheaper and safer in a longer perspective.

Due to this there is a barrier towards introducing new technologies into water supply. This project demonstrates management tools that will reduce the barriers and show implementation of intelligent operation schemes as well as a way to enable companies and authorities to minimise human impact by waterborne contaminants by increased intelligent surveillance of drinking water resources.

Table 1: ArtDemo Consortium

Partner identification the ArtDemo Consortium		Contact
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1.2 Project objective

The overall objective of the ArtDemo project was to demonstrate a management tool for artificial recharge (AR) plants. The management tool shall use sophisticated monitoring systems linking automatic real-time data acquisition, available on-line/at-line sensor systems and fast field analysis kits with intelligent decision support software, which compile and communicate processed data to specific action protocols.

2 ARTDEMO PROJECT ACTIVITIES

More specific the consortium (Table 1) has addressed the overall objective in the following activities (Work Packages):

2.1 Identification and method development for critical contaminants.

Identification of critical parameters and development and testing of selected on-line/at-line sensor systems and monitoring kits. Target organic analytes will be described. Furthermore, existing sensor systems will be evaluated, and novel technologies used as screening tools for on-line/at-line and field measurements of the described contaminants in water will be developed and evaluated. Traditional water quality parameters like pH, temperature, conductivity, dissolved oxygen (DO) etc. will also be described and quantified.

2.2 Data handling for measuring systems

Integration of on-line/at-line sensor systems and monitoring kits with advanced data handling systems. The measurement systems and test kits developed and evaluated will be integrated with advanced data handling software, to extract the salient analytical data and ensure validated data for the decision support software.

2.3 Buffer capacity of artificial recharge basin infiltration.

The activity will identify the remediation capacity of the artificial recharge production line. Necessary measures to be taken to regenerate the production plant after contamination will be identified, and the risk of building up pollution in the aquifer will be quantified.

2.4 Monitoring strategy.

An integrated management tool, that will be used to semi-automatically control the production based on available information for two specific plants, will be designed. Data validation routines will be introduced to ensure valid and useful data from the selected sensor systems and field test kits.

2.5 Management strategy

Based on the monitoring strategy and the risk assessment a management strategy will be formulated. This strategy will form the basis for development of control protocols to be used for testing various early warning, regeneration and production scenarios.

2.6 Demonstration scenario

All technologies and methodologies will be demonstrated and evaluated by end-users at two artificial recharge plants plants (Arrenæs in Denmark and Dösebacka in Sweden)

3 SUMMARY OF ARTDEMO RESULTS

Beside the two demonstration sites where systems have to be implemented, a third site has been included for reference. The 3 sites are summarised in this chapter and described in detail in chapters 2 to 4.

3.1 Identification and method development for critical contaminants.

The two demonstration sites, Arrenæs (DK) and Gothenborg (GR), have been analyzed for selected pesticides, estrogens, progestogens, antibiotics and VOCs. For these compounds *protocols for the extraction, identification and quantification* in groundwater (all contaminants classes) and soil samples (estrogens, progestogens and antibiotics) have been described. (chapters 5 and 6)

All compounds are found in very low concentrations, and it can be concluded that these two sites are not representative of many other artificial recharge plants in especially Southern Europe.

Investigations concerning microbiological parameters have been added to the sampling and analyses programme. Special focus has been on pathogen removal and microbiological barrier efficiency (chapters 7 to 9).

On the sensor part, the following tasks have been completed (chapter 10).

- Simple at-line sample preparation/ preconcentration methodologies
- Additional usage of surfactant-based preparation systems.
- Examination of alternative materials for the fabrication of disposable electrode devices for the determination of selected heavy metal species in water samples
- Microfabrication
- TOC sensor
- Faecal biomarker analytical method
- Heavy metals determination.
- Spectrofluorimetry
- Hydrocarbons measurement device

3.2 Data handling for measuring systems

Some of the most frequent errors generated by sensors/analysers are missing data, measurement values out of range, peaks (outliers), constant measurement values and drift. It is possible to check the measurement coming from each sensor/analyser for these errors using simple, but still quite reliable methods known as single data validation (chapter 11)

The data analysis models required the use of a range of chemometric techniques in order to aid the interpretation of large data sets and to identify the most relevant characteristics leading to the production of comprehensible and reliable results (chapter 12)

The chemometric approach has proven particularly useful in the de-convolution of overlapping peaks from the electrochemical voltammo-grams and fluorescence spectra (tested with PAH mixtures). Multivariate Calibration (Modelling) proved the most effective data treatment approach.

3.3 Buffer capacity of artificial recharge basin infiltration.

A small database in EXCEL was prepared for the physical and chemical characteristics of various pollutants. In addition 2 fact sheets were prepared, each for a specific pollutant or group of pollutants, giving more detailed information on amongst others emission and immision sources, identity, threshold values, physico-chemical properties, chemical structure, environmental fate, exposure and safety, analytical methods, water treatment processes and sources of information. Also the key parameters for predicting the fate of contaminants in Managed Aquifer Recharge (MAR) systems were described, which also includes parameters which define the aquifer and MAR system.

Kiwa’s expert model Easy-Leacher (EL4.6) was extended with a new modeling approach for micro-organisms, requiring less extensive data than conventional models. EL4.6 was subsequently applied to the 2 demonstration sites Arrenæs and Dösabacka (chapters 13 to 16)

Final description of methodologies for risk assessment has been incorporated in the management schemes.

3.4 Monitoring strategy.

Focus has been on early warning of changes in the water quality of the incoming and recharged water together with an optimal production rate.

The result, an IT based monitoring and management tool exactly addresses these topics, and as it is based on a general and configurable system, it can readily be installed at other locations. Furthermore, developed items (software code) and configured concepts can be used at other application areas (chapter 17).

The IT based monitoring and management tool is implemented as a fully functional demonstrator at the artificial recharge plants located at Arrenæs and Dösebacka All data collected on the plants are available at the two organisations networks in real time.

The IT based monitoring and management tool enables optimisation of daily operation procedures and the use of efficient management strategies by integrating the developments/ investigations done in other project activities.

3.5 Management strategy.

A detailed description of the Arrenæs artificial recharge plant based on data collection and experiences from the operation period of the artificial recharge plant (1995-2004) has been made. Together with a description of the Dösebacka artificial recharge plant, this has formed the basis for the developed management schemes and management plans. The management scheme is linked to the management plan by referring to the protocols within the management plan (chapters 16 to 18 and 24).

The site-specific management plan is build on the operation experiences and knowledge within the two artificial recharge plants. The management plan is divided into two separate parts: Plant Description and Plant Operation Manual.

The first part of the management plan, the “Plant Description”, is a general introduction to the specific artificial recharge plant. This part of the management plan is intended as an informational part to be used as a reference, when using the management plan in the daily operation and management of the artificial recharge plant.

The “Plant Operation Manual” is the second part of the management plan and consists of 21 protocols. The “Plant Operation Manual” is intended as a tool in the daily operation and management of an artificial recharge plant, since all routine situations and actions in alarm situations at the artificial recharge plant are given. The “Plant Operation Manual” is applicable to artificial recharge plants in general.

3.6 Demonstration scenario

A list of the most critical risk scenarios from each plant (Arrenæs and Dösebacka) was produced, and five scenarios were chosen for the test of the the early warning system.

IDAS (Incident, Detection, Action, Surveillance) is new way of assessing the risk management at a certain artificial recharge plant.

The scheme has been defined by and used in the ArtDemo project for determining the risk of potential events that would have a water quality deteriorating effect, and virus removal in unsaturated zone has now been demonstrated (chapters 17 to 26).

4 DEMONSTRATION SITES

The Arrenæs, Dösebacka and Llobregat artificial recharge plants were used throughout the ArtDemo project to demonstrate methodologies for monitoring and managing artificial recharge plants. Table 2 compares key characteristics of the three artificial recharge plants. Detailed descriptions can be found in chapters 2 – 4.

Table 2: Overview of demonstration sites (Ref.: Lars Bennedsen, Måns Lundh, Miren López de Alda)

	Arrenæs	**Dösebacke**	**Llobregat**
Location	Denmark	Sweden	Spain
Start of recharge (Year)	1995	1960-1970	1950 (river bed infiltration) 1969 (recharge wells)
Infiltration method	Basin and irrigation, trial plant	Basin	Recharge wells Combined with induced river bed infiltration
Number of basins/wells	4 basins and an irrigation area	9 basins	7 recharge wells
Number of abstraction wells	4	15	21
Total infiltration area (m^3)	6,000 + irrigation area (20,000)	12,000	-
Maximum recharge capacity (m^3/day)	1,100	7,000	15,120
Abstraction capacity (m^3/day)	900	6,000-6,900	151,200
Aquifer type	Unconfined	Unconfined/confined	Unconfined/confined
Geological setting	Secondary aquifer consisting of glacial sediments dominated by diluvial sand. Separated from the primary limestone aquifer by glacial clay and till deposits.	Glacial stream, sediments and river bed deposits. The aquifer is covered partly by postglacial clay and downwards bounded by the crystalline bedrock.	Fluvial sand and delta deposits. Aquifer is in some locations divided by clay layers in a confined and an unconfined aquifer. The aquifer overlies clay and bedrock.
Source of recharge water	Lake (Arresø)	River (Göta Älv)	River (Riu Llobregat)
Aquifer thickness	Approx. 40 m	10 – 15 m	10 – 40 m
Number of abstraction wells	4	15	21
Main water quality issues	BAM, bacteria, organic matter	Pollution from river water (e.g. relict salt water, faecal contamination, organic matter, algae)	The plant infiltrates treated drinking water.
Residence time	~ 1 – 5 months	<75 days	-

Chapter 2: Description of the Arrenæs Artificial Recharge Trial Plant

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Abstract: Site descriptions for the Arrenæs AR trial plant are presented together with the plans for the proposed large-scale production plant. Geological setting, water quality monitoring, modelling and operational strategies are presented. Generally the Arrenæs site is well suited for artificial recharge, and the produced water is suitable for drinking water production.

1 INTRODUCTION

The Arrenæs Artificial Recharge (AR) Trial Plant is located at the Arrenæs peninsular in the northern part of Zealand, Denmark, as shown in Figure 1. Copenhagen Energy has operated the plant continuously as a trial plan since April 1995, and a large-scale production plant is now proposed at the same location.

The AR trial plant is recharging water from Lake Arresø, which is the largest lake in Denmark with a water volume of 123 million m^3 and the annual discharge from the lake is 30-65 million m^3. The infiltration capacity of the AR trial plant is approximately 350,000 m^3/year.

2 PURPOSE

The purpose of the trial plant is to acquire knowledge on the quality of the infiltrated water and to collect sufficient data on which to base the establishment of the proposed large-scale AR treatment plant. In the ARTDEMO project, various parameters are monitored in order to optimise the management and thereby the sustainable infiltration capacity of the plant.

3 GENERAL PHILOSOPHY CONCERNING ARTIFICIAL RECHARGE

About 99% of all drinking water in Denmark is produced by traditional groundwater abstraction. Unfortunately, pollution and natural contamination resulting from over-exploitation have reduced the available groundwater resource. At the same time, the water quality problems resulting from traditional surface water treatment is getting increased attention, such as disinfections by-products and bacterial re-growth. Therefore, Copenhagen Energy is trying to find alternative sources of drinking water. In this context, artificial recharge is an option, because subsequent disinfection of the artificially recharged water is avoided (Brandt, 1998).

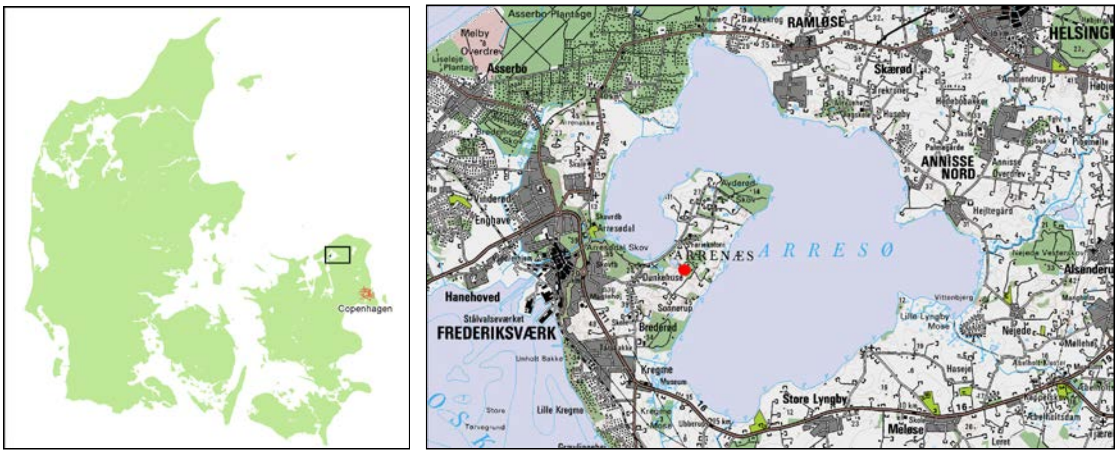

Figure 1: Location of the Arrenæs AR trial plant.

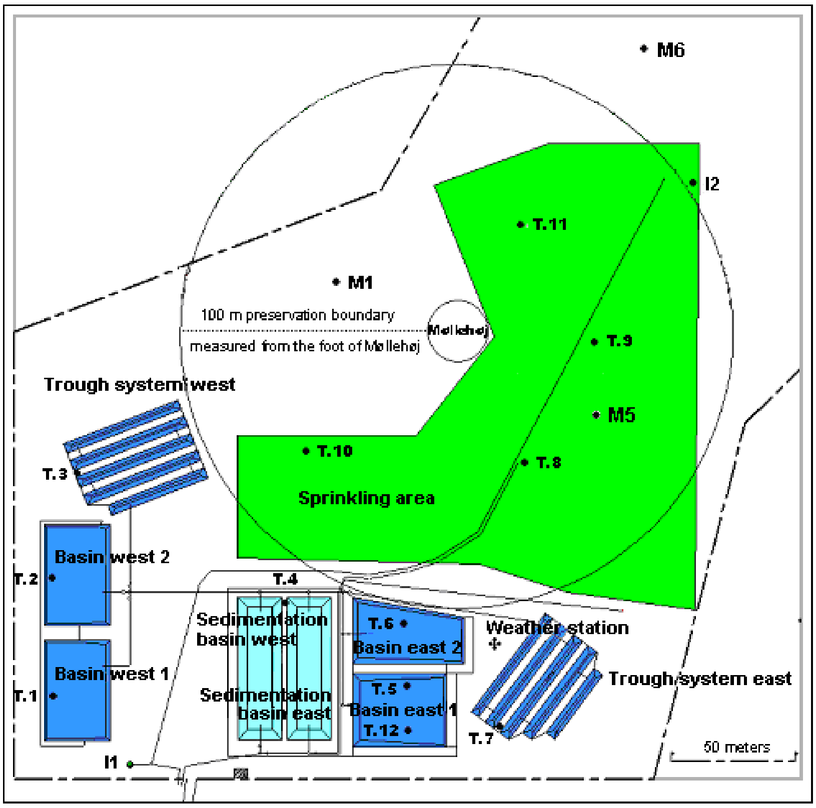

Figure 2: Layout of the Arrenæs AR trial plant.

4 GEOLOGICAL SETTING

The AR trial plant is located approximately 32 metres above sea level at the Arrenæs peninsular, which is about 4 km long. The peninsular is a moraine landscape formed during the last ice age. The resulting glacial deposits are dominated by fine to medium grained sand with a few till intercalations. As a result of glaciotectonic deformation, the sandy glaciofluvial sediments have a thickness of approximately 40 metres and constitute the secondary aquifer of the area, which is affected by the artificial recharge. The secondary aquifer is separated from the primary limestone aquifer by a till layer with a thickness between 5 and 15 metres. The limestone surface is fairly even and is located at a depth of 30 to 37 metres below sea level.

At the site, the groundwater level in the glaciofluvial sand is approximately 5 metres above sea level. The groundwater level falls to about 3.5 metres above sea level at the shore of Lake Arresø and one metre above sea level in the western part near Roskilde Fjord.

The thickness of the unsaturated zone is more than 25 metres at the site and is mostly made up of fine to medium grained sand.

5 INPUT WATER

The input water to the Arrenæs AR trial plant is taken from Lake Arresø. The lake was originally a part of a fjord system in the Postglacial period. Lake Arresø is the largest lake in Denmark with a surface area of 40.7 km^2 and a water volume of 123 million m^3. The lake is relatively shallow with an average depth of 3 metres and a maximum depth of 5.5 metres. Since 1719, the lake has had its outlet to Roskilde Fjord through a canal. The watershed covers an area of 216 km^2, and the runoff from the lake is 30-65 million m^3 per year. The retention time for the water in the lake is approximately 3 years.

The lake is affected by agricultural activity and sewage runoff. Algae growth is a great problem in Lake Arresø due to the high level of nutrient salts in the lake water.

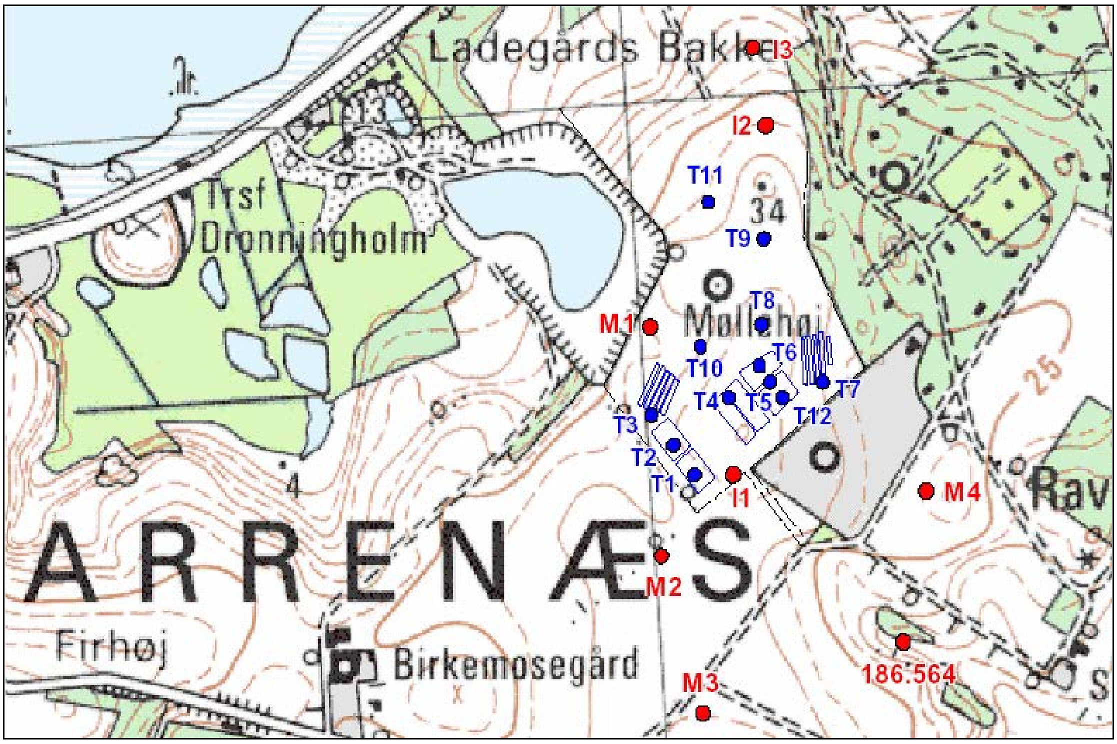

Figure 3: Map of the Arrenæs AR trial plant.

6 DESIGN AND OPERATION

The AR trial plant was established in 1994 and has been in operation since April 1995.

The Arrenæs AR trial plant consists of two parallel infiltration basin/trough systems and two sprinkling areas as shown in Figure 2. The four infiltration basins and the two infiltration trough systems have an area of approximately 1,000 m^2 each and an average depth of 1.5 metres. The sprinkling areas constitute approximately 20,000 m^2 in total.

The lake water for the infiltration basins and trough systems is pre-sedimentated in two sedimentation basins, while the irrigation water is taken directly from the lake without pre-sedimentation.

The infiltration basin and trough systems are used all year, while sprinkling on the grass area is only done from April to December to avoid freezing of the water in the sprinklers. The total amount of water recharged in 2004 was 355,000 m^3, and the total amount of abstracted water was 274,000 m^3. The water abstracted from the trial plant is not used for drinking water purposes, but is returned to Lake Arresø.

The proposed large-scale AR plant at Arrenæs will consists of infiltration basins and sprinkling areas and will not include trough systems. For this reason the trough systems are not dealt with in the investigations performed within the ARTDEMO project.

Throughout the operation period, groundwater levels have been continuously monitored in monitoring wells distributed around the area (M1 – M4 and I2). In 1999 M1 was converted to abstraction well, and in 2002 the monitoring well M4 was abandoned.

Abstraction of recharged groundwater has been performed through the abstraction wells, I1, M1 (since 1999), I3 and DGU 186.564 (since 1999).

Water quality is continuously monitored in the intake water, unsaturated zone through tensiometer wells (T1–T12), in the abstraction wells and in the monitoring wells.

In the ARTDEMO project the monitoring facilities have been extended, so the water flow in the four abstraction wells (I1, I3, M1 and 186.564) is monitored online. In the three abstraction wells I1, M1 and 186.564, also the water level is measured online. Furthermore, two additional monitoring wells (M5 and M6) have been established at the plant.

To measure water flow in the plant, pressure transducers were installed to measure the water level in the 6 Thompson weirs located between the sedimentation basin and the infiltrations basins and the trough systems, and in the 4 infiltration basins. Online measurements in the Thompson overflows are used to determine the flow to each of the basins and trough systems. Thus.

The measurements of flow and water level in the infiltration basins are used to calculate infiltration rate and capacity and thereby determine the optimal time for bed regeneration.

7 DISTRIBUTION OF AR WATER IN THE AQUIFER

The distribution of artificially recharged lake water in the aquifer has been determined using the isotopic composition of the native groundwater and the lake water respectively, and by MIKE-SHE hydrological modelling.

The water in Lake Arresø has a δD- (deuterium) and δ^{18}O-value that is higher than the δD- and δ^{18}O-values of the native groundwater on Arrenæs. Therefore it is possible to map the distribution of artificially recharged lake water in the aquifer by analysing the isotopic composition of the groundwater.

Using the oxygen isotopic compositions, the mixing proportions of groundwater samples collected in the 1998 and 2001 was calculated. The results show that significant amounts of recharged water are only found in two abstraction wells (I1 and M1) and two monitoring wells (I2 and M4), in which surface water represents 45 to 90 % of the collected water samples.

8 HYDROLOGICAL MODELLING

A hydrological model was set up in 1996 using the programme MIKE-SHE. The purpose of the modelling was to evaluate the development of the aquifer receiving artificially recharged lake water from Lake Arresø. The model focuses on catchment areas, distribution and transport times of the AR water, fluctuations in groundwater level and the influence on contaminated sites in the vicinity of the site.

Using the MIKE-SHE model, a number of scenarios have been run to determine the effect of the AR plant at Arrenæs in different production situations.

An example of the model results is the comparison of the efficiency of the four abstraction wells in a scenario with an annual infiltration of 480.000 m^3. The simulation shows that well I1 close to the site will abstract nearly 100% AR water, whereas I3 will only abstract 73% AR water.

In 2005, a new and updated groundwater model has been set up using the programme MIKE-SHE, Nielsen, (2006). This model is going to be used in the future planning of the proposed large-scale AR plant at Arrenæs.

9 WATER QUALITY

There has been an extensive water quality monitoring at the plant throughout the operation period (Hartelius et al., 2001; Jensen et al., 2005).

Table 1: Comparison between native groundwater, lake water, new groundwater, expected groundwater quality and threshold levels for drinking water.

Parameter	Native Groundwater	Lake Water	New Groundwater	Expected Groundwater Quality	Threshold Levels (Drinking Water)
pH	7,3	8,8	7,5	7 – 8	7,5 – 8,5
Chloride (mg/L)	31	65	59	55 – 65	< 250
Sulphate (mg/L)	61	50	47	50	<250
Nitrate (mg/L)	75	10*	4,2	<10	< 50
Dissolved Oxygen (mg/L)	9,2	15,7**	5,0	<5	
NVOC (mg/L)	1,29	17	4,1	<4	< 4
AOC (mg/L)	15	1033***	8,4	< 30	<10*****
Total phosphor (mg/L)	0,031	1,9	0,025	< 0,1	< 0,15
Hardness (dH°)	19	Ca. 8	14,3	8 –16	5 – 30
BAM (mg/L)	Not found.	0,070****	0,059	< 0,1	< 0,1

* Total nitrogen recalculated as nitrate
** Only one measurement, September 1994
*** Values from 1998
**** Values from 2000-2003
***** From van der Kooij, D. et. Al (1989)

The water quality has monitored continuously since 1995 at the intake from Lake Arresø, the unsaturated zone, the aquifer, and the abstracted water. In the beginning, a wide range of parameters was included with high frequency in the monitoring and analyses program. However, the analysis parameters and sampling frequencies have been decreased, as our knowledge of the geochemical processes at the trial plant has increased. An overview of the results is shown in Table 1.

As a part of the ARTDEMO project, an online monitoring unit measuring the quality of the intake water from Lake Arresø was installed in a sedimentation basin at the AR plant in 2004.

The monitoring unit measures temperature, oxygen, pH, electric conductivity, and fluorescence.

The processed data is published once a year to ensure that the knowledge gained from running of the AR plant is readily accessible (Copenhagen Energy, 2000).

Data derived from the continuous monitoring shows changes in the groundwater composition caused by the infiltrating lake water, which is presented in the following:

Chloride: The lake water has chloride levels of about 65 mg/L, whereas the groundwater has a natural background value of about 31 mg/L. As chloride is a conservative tracer, the difference between the chloride content in the lake water and in the newly formed groundwater will be en indicator for the amount of AR water in the groundwater. Figure 4 shows that the difference in chloride content between the lake water and the water from the abstraction wells is decreasing as a result of an increased amount of AR water in the groundwater.

Nitrate: The nitrate level in the native groundwater of the area exceeds the guideline level of 50 mg/L. This is probably due to the washing out of fertilizer from former agricultural activities from the upper soil layers. The nitrate content of the lake water is less than 5 mg/L and the content in the newly formed groundwater is approximately 4 mg/L.

Potassium permanganate consumption: There is a decrease in potassium permanganate consumption with depth from 15-30 mg/L at one metres depth to below 10 mg/L at 15 metres depth. The breakdown of organic matter from the lake water seems to be efficient.

Pesticides: 2,6-Dichlorbenzamid (BAM) has been the most critical substance in the trial period and is the only pesticide that occurs in the lake water in concentrations above the guideline level for drinking water. BAM is the degradation product of the pesticide dichlobenile that was banned in Denmark in 1997. In 1998, BAM was found in Lake Arresø in concentrations of up to 300 ng/L, but the concentration has fallen to an average of approximately 90 ng/L in 2004. The content in the abstracted water was in 2004 between 30 and 70 ng/L in I1, which is below the guideline limit for drinking water of 100 ng/L.

Bacteria: The bacterial content in Lake Arresø is generally low, however there are seasonal variations with high contents during late summer. Investigations of the removal of pathogenic indicator organisms at the AR plant show that these are generally being retained in the clogging layer in the infiltration basins and in the upper part of the unsaturated zone at the sprinkling area. However, the AR plant has a maximum retention capacity that must be respected to avoid bacterial breakthrough in the groundwater zone.

10 THE PROPOSED LARGE-SCALE AR PLANT AT ARRENÆS

The results from the AR trial plant at Arrenæs are to form the basis for a large-scale AR plant at the same location having a production capacity of approximately 4 million m^3 per year. The abstracted water will be added to the existing raw water distribution system, where it will be mixed with native groundwater from 5 other wells fields and treated at the waterworks by simple aeration and filtration through natural sand filters. The consequences of mixing these different water types are discussed in Berg et al. (2004). The future large-scale AR plant is at the planning stage. An Environmental Impact Assessment is currently under way, so the final layout of the plant cannot yet be presented. Figure 5 shows an aerial view of two of the suggested plant layouts.

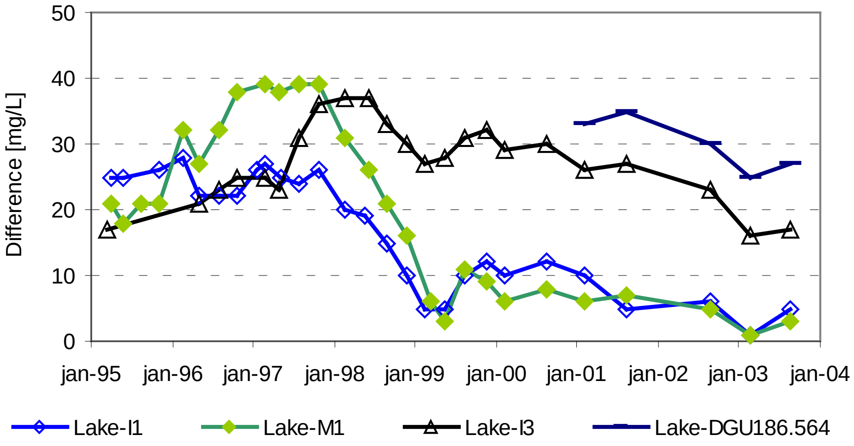

Figure 4: Difference in chloride content between lake water and abstracted water.

Figure 5: Aerial views of the two proposals for the large-scale AR plant at the Arrenæs peninsula.

11 SUMMARY

The results from the trial plant have been positive so far, and the quality of the abstracted water from the Arrenæs AR trial plant is suitable for drinking water production. The proposed large-scale AR plant is therefore a promising alternative drinking water resource. Copenhagen Energy expects artificial recharge of groundwater to become an integral part of the future water supply system to Copenhagen. Within the next couple of years it will be determined by the relevant authorities whether the large-scale AR plant at Arrenæs can be established.

12 REFERENCES

Berg, R.L., Jensen, T.Ø., Bennedsen, L., and Brandt, G. 2004: Investigation of introducing water from an artificial recharge plant to an existing groundwater distribution system. *International Water Association - World Water Congress, Marrakech, 19-24 September 2004.*

Brandt, G. 1998. Arrenæs artificial recharge trial plant, Denmark – Hydrological and chemical aspects. In *Artificial recharge of groundwater, proceedings of the third international symposium on artificial recharge of groundwater – TISAR 98*, Peters H. J. (ed.)

Copenhagen Energy 2000. Arrenaes, Artificial infiltration of lake Arresoe water. Status for 2000 and operational and monitoring plan for 2001. *Reports available for the years 2000-2002. (In Danish)*

Hartelius, E., Bennedsen, L. and Brandt, G. 2001. Arrenæs artificial recharge trial plant, Denmark – hydrological and water quality aspects. *European Water Management* **4**(1), 65-70.

Jensen, T.Ø., Berg, R.L., Bennedsen, L, Brandt, G. & Spliid, H. 2005. Geochemical and microbial processes in the unsaturated zone at the Arrenæs artificial recharge trial plant. *Fifth Int. Symp. on Management of Artificial Recharge (ISMAR), Berlin, 12-16 June 2005. In: Recharge Systems for Protecting and Enhancing Groundwater Resources* (in press).

Nielsen, T. Ø. 2006. Groundwater model in MIKE_SHE for the Arrenæs peninsula. Section for Water Quality, Copenhagen Energy. (In Danish).

Chapter 3: Description of the Dösebacka Artificial Groundwater Recharge Plant

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Abstract: The paper describes the Dösebacka Artificial Recharge plant regarding treatment, geology, hydrogeology and water quality. The Dösebacka Artificial Recharge plant is located in south-west of Sweden. The plant is the water supply for 25 000 inhabitants in the community of Kungälv. The plant produces approximately 6000 m^3/d and consist of 9 infiltration ponds and 15 abstraction wells. The detention time for the water in the aquifer has been estimated to vary between 6 to 60 days depending on abstraction well. The water is pre-treated with sedimentation and the drinking water is pH-adjusted with NaOH for corrosion prevention in the distribution system. Two wells, that abstract water with a higher turbidity and organic content, are post-treated with chemical precipitated using aluminium sulphate. The plant has equipment for disinfection of the drinking water in case of an emergency with microbiological contamination but it is rarely used.

1 INTRODUCTION

The Dösebacka AR-plant, located along the Göta Älv river near Kungälv, Sweden, (Fig.1) participates in the EC-project ARTDEMO with the main objective of demonstrating an early-warning system for monitoring and management. The focus of this paper is to describe the geology, hydrogeology and water-treatment process and performance of the aquifer.

2 GEOLOGY AND GENESIS

In Lundh *et al* (2005) a overview of the geology is presented. The bedrock geology of the region is dominated by Precambrian granite and gneiss broken by two prominent north-south fault/fracture zones; one parallel to the valley occupied by the Göta Älv river. The bedrock was eroded to a peneplain by the end of the Precambrian and covered with sedimentary rocks during the early Palaeozoic. These sedimentary rocks were eroded completely away during the Tertiary, and the re-exposed granite and gneiss was deeply weathered under a tropical climate. The gneiss and granite weathered more quickly and to greater depths along the fracture zones and numerous associated joints. The present topography, consisting of bedrock knobs separated by linear valleys, is merely the result of the removal of this weathered material during the Quaternary Period and the latter part of the Tertiary Period.

Figure 1. The location of the Dösebacka AR plant in Sweden (from Lantmäteriverket, Sweden and Kort & Matrikelstyrelsen, Danmark)

The numerous glaciations of the Quaternary Period did surprisingly little to shape the landscape. Following retreat of the ice, areas now below 100 m above sea level were inundated by the ocean, and marine clay was deposited in thickness up to 80 m in some of the bedrock valleys. The glacier left only a thin layer of till, and bedrock is commonly exposed in upland areas.

The aquifer used by the AR-plant consists of coarse sand and gravel, likely of glacial-stream-sediment origin (Bryllert, 2005). This sand and gravel rests on bedrock (or perhaps on till on bedrock) and is overlain by glacial and post-glacial marine clay that is thick on the river side of the AR-plant, but which wedges out west towards the valley side. Two hypotheses are offered for the origin of the coarse aquifer sediment. (1) The aquifer sediment represents a delta-like deposit that formed at the ice margin during deglaciation when the margin passed over the Dösebacka area. (2) The aquifer sediment may represent wave-washed sediment that was eroded from the above laying drumlin sediments.

A suggested model (Lundh *et al*, 2005) of the Dösebacka aquifer is a 10-15 m single aquifer of sand and gravel, which is sloping from 3-15 m below the bottom of the infiltration pond, to 50-60 m below the ground surface at the river. The aquifer is partly confined with a layer of clay; thin near the ponds and increasing to 20 to 40 m close to the river. In the north the clay is absent. Below the aquifer lies bedrock, probably heavily fractured (Fig.2).

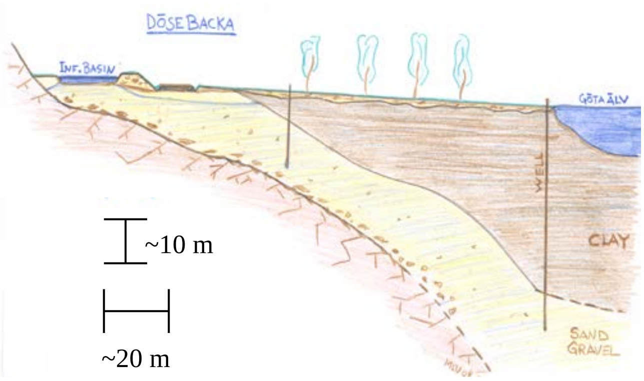

Figure 2. A cross section perpendicular to the river showing the general geological structure of the aquifer in Dösebacka. (from Lundh et al 2005)

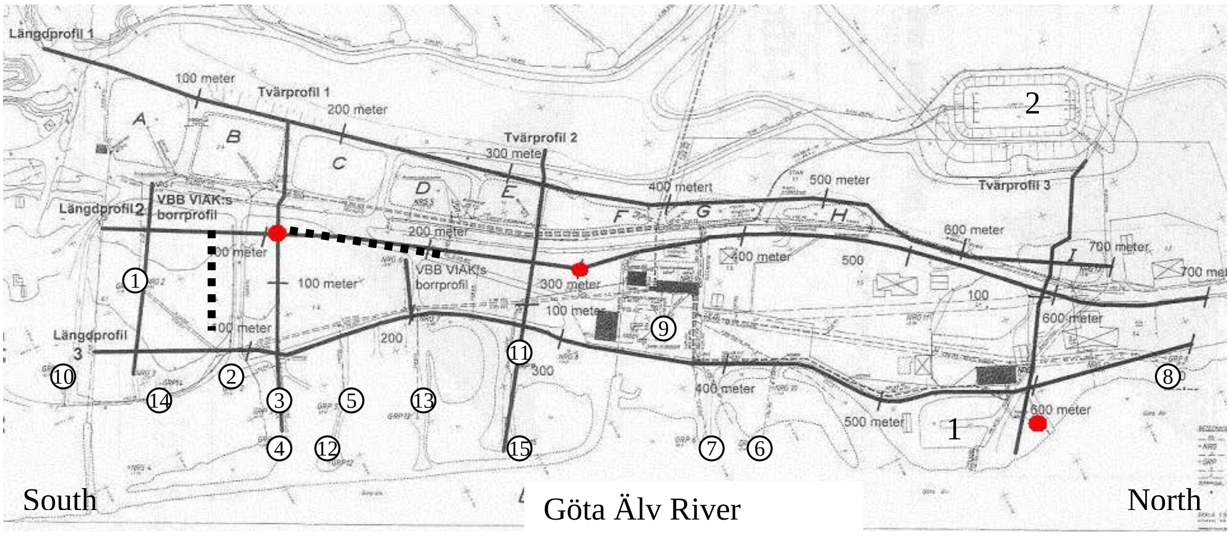

Figure 3 Map over the Dösebacka AR-plant; resistivity soundings (solid lines) in Rhodin (2003), drill holes (red dots) and refraction soundings (dotted lines) in Bryllert (2005), and wells (numbered circles). Upper case letters A-I are infiltration ponds, and the numerals 1 and 2 are referred to in the text.(from Lundh et al 2005)

3 WATER TREATMENT

Dösebacka Waterworks is located 5 km north of Kungälv, Sweden on the west shore of the Göta Älv river just below the Dösebacka drumlin. Raw water from the Göta Älv is pumped from an intake basin (‘1’ in Fig.3) to a sedimentation basin (‘2’ in Fig. 3). The water is distributed to nine infiltration ponds (letters ‘A’ through ‘I’ in Fig. 3). The water infiltrates the filter bed and is transported in the subsurface under unsaturated and saturated conditions. The aquifer water is withdrawn in fifteen abstraction wells (GRP 1-15, Fig. 3) and pumped to a reservoir, where it is pH-adjusted for corrosion prevention. It is also possible to chlorinate the water, but this is rarely done because the water in general has low levels of bacteria. Water from two of the wells (GRP 9 and 11) have high turbidity, and this water is treated chemically to create a precipitate and filtered through sand.

Table 1. Infiltration properties (2003-05-08) for approximately 1 m of water in the ponds (from Lundh et al 2005)

Infiltration pond:	Pond A	Pond B	Pond C	Pond D	Pond E	Pond F	Pond G	Pond H	Pond I
Area (m^2)	2404	1967	1884	1301	1031	1096	787	563	1134
Infiltration rate (cm/h)	1.4	1.3	2.8	2.6	0.8	4.3	1.7	1.9	-

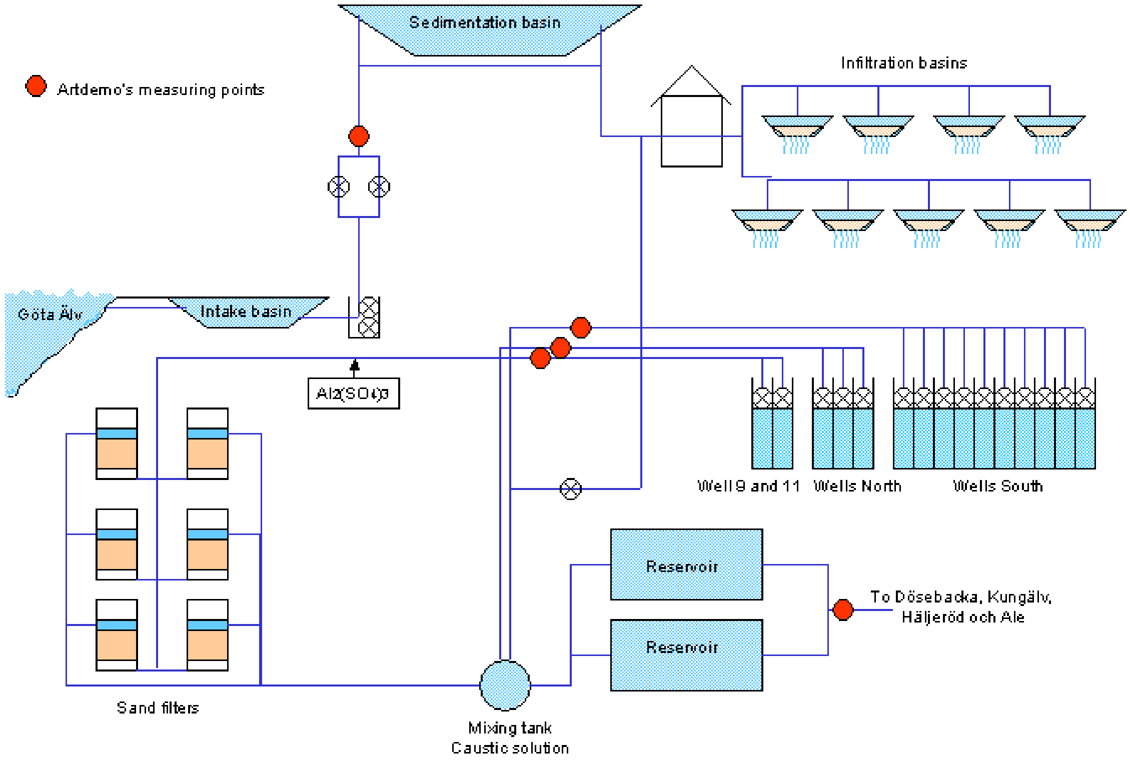

Figure 4. The water treatment process at the Dösebacka AR plant.

The production of drinking water at the plant is 70-80 l/s. A process scheme is presented in Fig.4.

4 GROUNDWATER FLOW AND RESIDENCE TIME

Fig. 5 displays flow paths from the infiltration ponds to the Göta Älv river (MIKE SHE, DHI). Both hydraulic data and seismic investigations suggest a divide at pond C and D, directing the flow into one path from pond D-H towards GRP 9 and 11, and another from A-D towards the wells in the south of the area. This divide is likely made of bedrock or perhaps till. Fig. 5 also reveals a gradient from the river suggesting a transport of water from below the river. In the north, the absence of a confining layer allows induced infiltration from the river.

The bottoms of the infiltration ponds are approximately 4.7-7.7 m above sea level. The water table is about 0-2 m just east of the ponds. The probable presence of shallow bedrock in pond B and high groundwater levels for A-C (Fig. 3) indicate that there is no unsaturated zone below some ponds. These observations imply that the thickness of the unsaturated zone varies between 0 to 7.7 m. The possible crest of the divide beneath ponds C and D is believed to plunge deeply (50 m) towards the river and probably has less influence on the water paths close to the river than higher up towards the ponds.

Investigations of detention time in the subsurface with tracers and calculations of the average hydraulic conductivity suggests a value of 8.4 x 10^{-4} m/s within a range from 1.7 x 10^{-3} m/s (5% percentile) to 3.7 x 10^{-4} m/s (95% percentile) between basin F and GRP9.

Table 2: Converted temperature-based residence time and abstraction rates in Dösebacka.
(from Lundh et al 2005)

Well	Pumping rate (l/s) 2003-06-10 "Typical setting"	Temperature response (d) (Summer peak in raw water – heat peak in well)	Probable residence time (d) Dampening factor 3.2
1	2.5	70	22
2	1.4	180	57
3	1.6	170	53
6	6.8	190	59
7	9.5	140	44
8	3.7	150	47
9	17.9	35	11
10	6.3	240	75
11	6.1	80	25
12	0.9	180	56
13	6.4	175	55
14	7.6	125	39
15	9.3	175	55

The hydraulic gradient could not be exactly determined but a performed sensitivity analysis indicated a range of 3.0 x 10^{-3} to 4.9 x 10^{-4} m/s for a gradient variation of 0.0186 ± 0.0134 m/m.

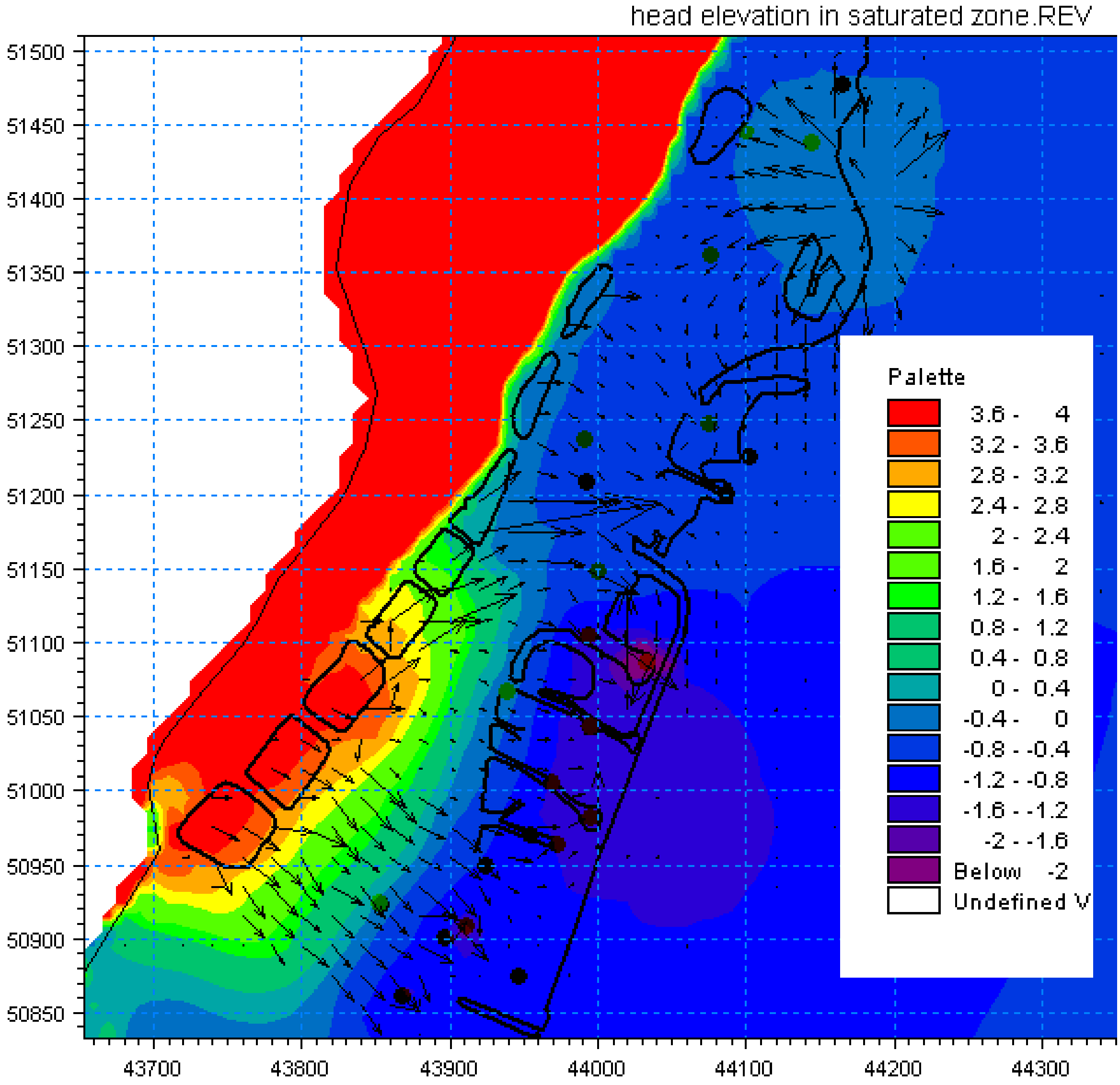

Figure 5. The flow paths at the Dösebacka AR plant generated with numerical calculation in MIKE SHE (from Lundh et al 2005).

However, drillings show that the material in this area consists partly of layers with coarse gravel and thus the permeability should be regarded as high in comparison with the aquifer in general.

The infiltration rates varied between 0.8 to 4.3 cm/h, which gave an infiltration of approximately 62 l/s (Table 1), thus 15-20% of the abstracted water seems to come from other sources. The low rate in pond E might imply a hydraulic feature such as a divide. The residence time for GRP 9 is 11 days according to the tracer experiment and 35 days according to the temperature, giving a conversion factor of 3.2, which suggest residence times less than 75 days for the plant in general (Table 2).

5 GROUNDWATER HYDROCHEMISTRY

River water from Göta Älv and groundwater collected from the wells GRP 1, 2, 3, 5, 9, 10, 11, 13 and 14, are all characterized by mixed water type without dominance of any particularly ions. Groundwater from GRP 4, 6, 7, 8, 12, and 15 are of the Na-Cl/Na-Cl-Ca-HCO_3 types indicating some influence from a saline water body (Fig. 6). The distribution of the electrical conductivity ranges from 90 to 1650 µS/cm and confirms the relatively high concentrations of Na and Cl in these boreholes (Lundh *et al*, 2005).

6 WATER-QUALITY ASPECTS

Turbidity and salt are the two main water-quality problems at the Dösebacka site (Lundh *et al*, 2005). Turbidity is exemplified by GRP 9 (Table 3), which shows high turbidity (but similar organic content as the other wells). The problem is probably related to fines that follow the abstracted water. The problem with salt is believed to do with captured relict water from the period after the deglaciation when the area was inundated by the sea prior to and during the land rise.

The problem is exemplified by GRP 7, which has problems not only with chloride but also with manganese and occasionally nitrite, probably connected to low oxygen concentrations in the relict water. Other wells with similar salt character are GRP 6, 8, 12 and 15. The pretreatment consist of sedimentation for peaks of high turbidity in Göta Älv. This is, however, not observeable in the measurement presented in Table 3.

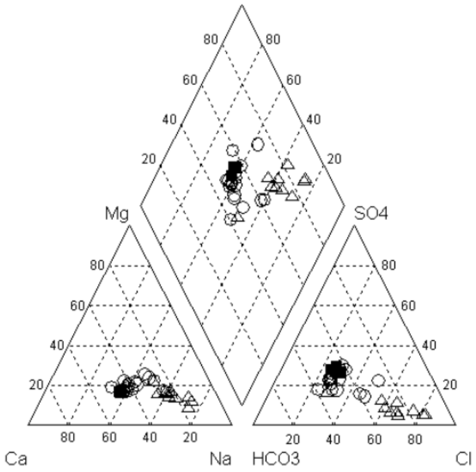

Figure 6. Piper diagram.
■ River water. ○ Mixed water. Δ Na-Cl/Na-Cl-Ca-HCO_3 water types. (from Lundh et al, 2005).

Table 3. Average Water Quality for some parameters (from 4-9 samples over the period) in Dösebacka May 2003-May 2004 * detection level <2 cfu/100 ml (from Lundh et al 2005).

	Unit	Göta Älv	Pond A	GRP 1	GRP 3	GRP 7	GRP 9	Drink W.
Slowly growing bacteria	cfu/ml	3100	>3100	93 - 100	0 - 10.0	48 - 50	5.0 - 13	33 - 38
Microorganisms, 22°C 3d	cfu/ml	1400	>2400	95 - 100	0 - 10.0	0 - 10.0	2.5 - 10.0	5.5 - 5.8
Coliform bacteria 35°	cfu/100ml	>340	>350	0 - 1.0	0.22 - 1.0	0 - 1.0	0 - 1.1*	0 - 1.0
E.coli	cfu/100ml	>46	>38	0 - 1.0	0 - 1.0	0 - 1.0	0 - 1.1*	0 - 1.0
Hardness	°dH	1.5	1.4	1.5	1.5	7.7	1.7	3.3
Fe (++)	mg/l	0.12 - 0.13	0.12 - 0.13	0.014 - 0.053	0.0067 - 0.051	0.086	0.046 - 0.071	0 - 0.050
Cl (-)	mg/l	8.3	8	7.7	8.3	180	9.5	56
EC	mS/m	10	9.9	9.9	11	82	11	33
Mn (++)	mg/l	0.0083 - 0.025	0.0029 - 0.020	0 - 0.020	0 - 0.020	0.23	0 - 0.020	0.034
Nitrite nitrogen	mg/l	0.0028	0.003	0.00078 - 0.0014	0.00044 - 0.0012	0.0076	0.00020 - 0.0011	0.011
Ammonium nitrogen	mg/l	0.025	0.029	0 - 0.0078	0 - 0.0078	0.62	0.0010 - 0.0080	0.07
pH		7.2	7.2	6.9	7.1	7.8	6.9	8.1
Turbidity	FNU	5.2	4.9	0.85	0.72	1.1	1.6	0.54
Alkalinity	mg/l	20	20	21	27	120	22	61
COD-Mn	mg/l	3.7	3.7 - 3.9	0.56 - 1.0	0 - 1.0	0.22 - 1.0	0.70 - 1.1	0.20 - 1.0
Colour		22	22	5.0 - 5.6	5.0 - 8.3	5	9	2.0 - 5.0

Post-treatment consist of chemical precipitation with Al-sulphate for the wells with high turbidity. This results in reduced turbidity, colour and organic matter (COD) in the finally treated water. There is possibly a higher risk of microbiological breakthrough in GRP 9 and 11 due to the shorter residence time, and in fact, coliforms have been detected in GRP 11, but the chemical precipitation constitutes a barrier in that sense. GRP 3 has also indicated coliforms, but this is probably due to leakage into the well during times of flooding of Göta Älv.

7 ACKNOWLEDGEMENT

The authors would like to thank the personnel at the Dösebacka AR plant for their assistance during the study.

8 REFERENCES

Lundh, M., Jonasson, S.A., Jørgensen, N.O. and Johnson, M.D. (2005) Hydrogeology and water treatment performance of the Dösebacka artificial recharge plant – the basis for an efficient system for early warning. In the proceedings of ISMAR2005, the 5th International Symposium on Management of Aquifer Recharge, 12-16 June 2005, KompetenzZentrum Wasser Berlin gGmbh, Berlin, Germany

Rhodin, S. (2003). En geofysisk undersökning av Dösebacka vattentäkt. (Transl: A geophysical examination of the Dösebacka water supply). Master Thesis. Earth Sciences Centre, Göteborg University, B381 (in Swedish).

Bryllert, A. (2005). En litostratigrafisk undersökning av Dösebacka vattentäktsområde. (Transl: A lithostratigraphical investigation of the Dösebacka water supply area). Master Thesis. Earth Sciences Centre, Göteborg University, B447 (in Swedish).

Chapter 4: Artificial Recharging of the Aquifer in the Delta of the Llobregat River

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Abstract: The paper describes how Artificial Recharge is used in the drinking water production for the City of Barcelona using water from the Llobregat River.

1 BACKGROUND

The water supply to the district of the Baix Llobregat and most of the districts in the provinces of Barcelona and the Vallès Occidental depends, as is to be expected given their geographical location (see Figure 1), on the waters of the Llobregat river.

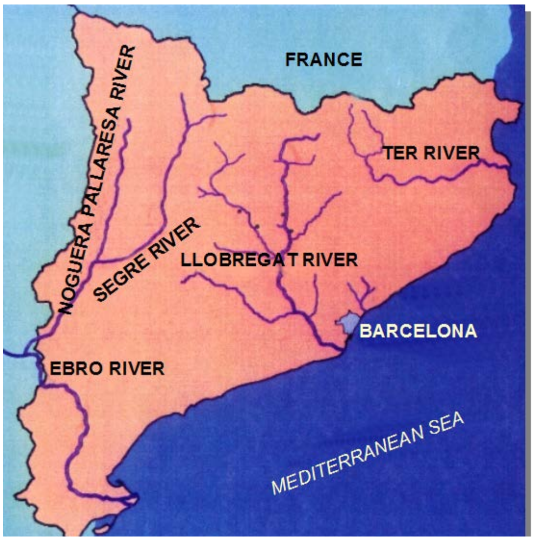

Figure 1. Location and course of the Llobregat river

The Llobregat river is situated in the NE part of Spain. It is 156.5 km long and covers a catchment area of about 4948 km2 which is inhabitated by 3.089.465 persons (in year 1999). It comes from the northwest of Catalonia and flows into the Mediterranean Sea, close to Barcelona (see Figure 1). The headwaters of both the Llobregat river and the Cardener river (a tributary of the Llobregat) are located in a rather unpolluted area of the Eastern Pyrenees. The mid-waters of the rivers flow through a densely populated and industrialised area where three potash mines are very active and strongly increse the salinity of the water resources. The lower course flows through one of the most densely populated areas of the Mediterranean region and, as a consequence, the Llobregat basin receives large inputs from both industry and/or urban origin.

The hydraulic regime of the Llobregat river is of the Mediterranean type with low flows during normal conditions (around 5 m^3/s) and peak events of either absolute dryness or flooding (up to 2000 m^3/s).

Near the mouth of the river, in Sant Joan Despí (a town located 15 km south of Barcelona), there is a waterworks, which is operated by the company “Aguas de Barcelona” (Barcelona’s waters) (AGBAR). In this plant, the water of the Llobregat river (at a flow of about 5.5 m^3/s) is processed through several treatment steps, including prechlorination and pre-dioxichlorination (to minimize subproducts formation), sand filtration, ozonation, granular activated carbon (GAC) filtration and post chlorination, to produce drinking water.

The waterworks supplies approximately 1/3 of the drinking water consumed in Barcelona (with a population of 3.2 million people). In this plant, groundwater from the aquifers located in the lower valley and the delta of the Llobregat river, mixed with river water filtered by sand, is frequently used to produce drinking water, when the water treatment plant is in downtime or the quality of the river water is low. These aquifers are subject to artificial recharge.

Until 1954, when the first treatment plant for surface water was built in Sant Joan Despí, all the resources used in the above mentioned zone were of subterranean origin and came from the aquifers in the lower valley and the delta of the Llobregat river.

The most important of these aquifers is that of the delta, stretching from Pallejà to the Mediterranean sea, and progressively widening into a total extension of about 110 km^2, with fluvial levels being rather thick due to the large variations occurred in the sea level during the Quaternary period (see Figure 2). This stretch constitutes a hydrogeological unit that, in broad terms, has the following characteristics:

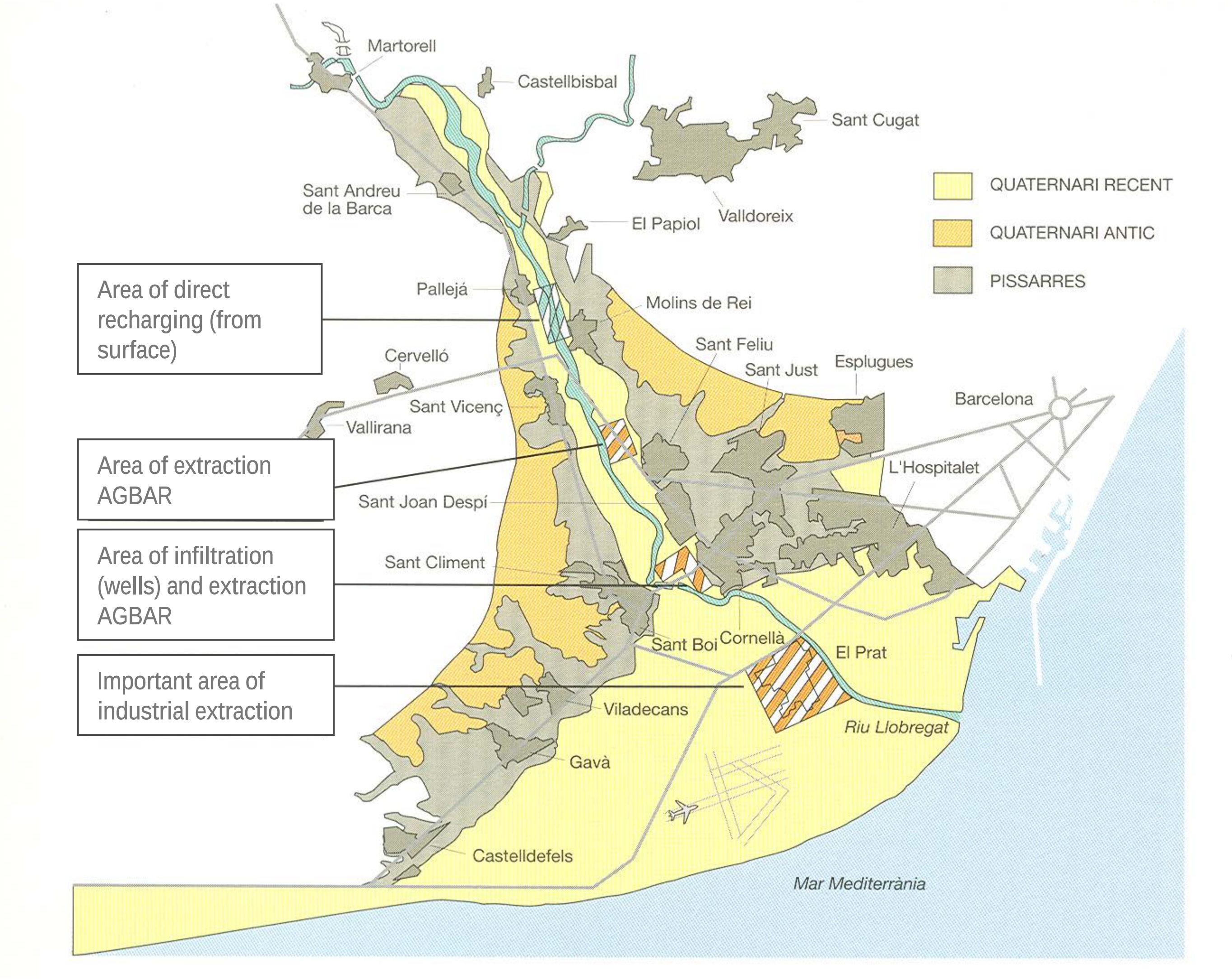

Figure 2: View of the aquifer of the delta of the Llobregat river

In the area between Pallejà and Cornella, the aquifer is free and unified. As it can be seen in Figures 2 and 3, from the Pallejà strait, where it measures some 250 m across, it widens progressively until it is some 2100 m wide between Sant Boi and Cornellà. The thickness of the sediment also increases from 20 m at Pallejà to 40 m at Cornellà.

This sediment is mainly highly permeable porous gravel and granulated sand, although there are also some layers of finer materials. The gravel comes from two or three superimposed Quaternary terraces and the finer materials may come from silt and clay from the flood plain or from lateral or Eolithic additions.

In general, apart from the river-bed, the valley is covered by a layer of silt, which is less than 5 m thick until just before Cornellà.

From Cornellà onwards, significant layers of relatively impermeable materials begin to appear and the aquifer bifurcates into two branches: an upper free branch and a lower confined one.

The deep, confined aquifer is undoubtedly the most important. It occupies the entire central zone of the delta and consists of Quaternary gravels and sands. The impermeable ceiling is formed by a wedge of clayish loams that increase in thickness towards the sea, where it is 40 m thick. The capacity of this confined aquifer varies between 30 m and 45 m and its maximum useful reserve throughout its length is estimated to be 114 hm^3.

The growing demand for water in the zone of the delta of the Llobregat river, much greater than the resources of the aquifer, resulted in a gradual lowering of the levels of the aquifer. In 1950, the *Sociedad General de Aguas de Barcelona (AGBAR, Barcelona Water Company)* considered the possibility of increasing the infiltration of the river water in an artificial way, through the river-bed. Deep artificial recharging in 1969 complemented this step. However, in spite of these efforts, the aquifer is still over exploited: the piezometric level in Cornellà (10 km far from the coastal line and 15 m of altitude) is usually below sea level.

In addition, due to human pressure, the aquifer has suffered frequent pollution episodes by different substances, such as, trichloroethylene, hexavalent chromium, gasoline, and polychlorinated naphthalenes.

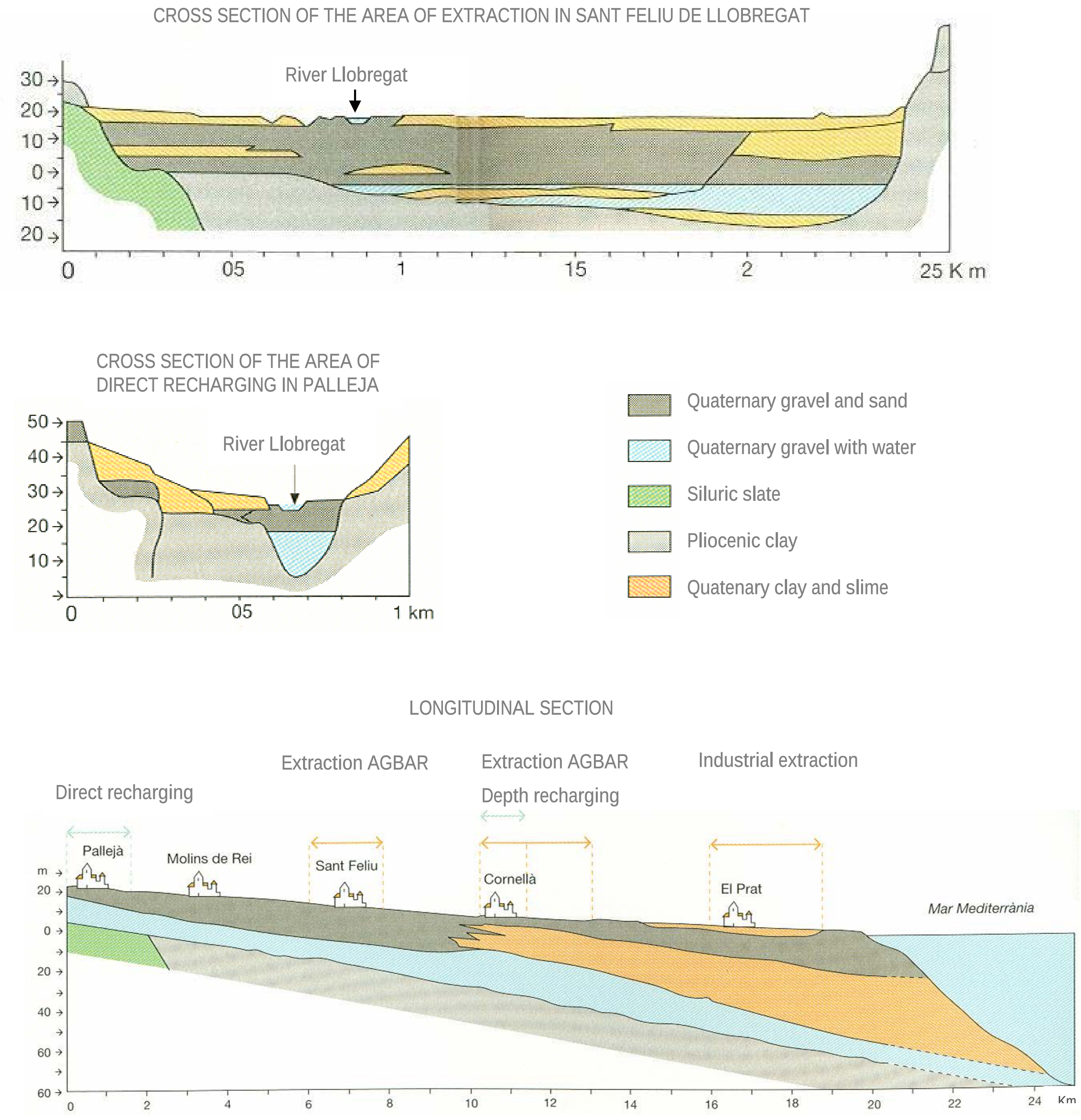

Figure 3: Cross sections and longitudinal section of the aquifer of the delta of the Llobregat river

2 THE AIMS OF ARTIFICIAL RECHARGING

Working any aquifer is a dynamic process in which there is a balance between the volume of water which naturally feeds the aquifer (the water which infiltrates through the river-bed and rain or irrigation water which percolates through the more or less permeable land that covers the aquifer itself) and the volume of water extracted from the wells that are supplied by the subterranean water as well as water loss through any springs in the area.

As an aquifer always has a storage capacity of varying importance, the positive or negative balance between the natural addition and the extraction means that the phreatic levels rise or drop to maintain the hydraulic balance.

This process of artificial recharging has a series of direct or indirect advantages that can be specified as follows:

2.1 Increasing the water reserves

By reducing the exploitation deficit already mentioned, the aquifer acts as a high capacity reservoir. In the case of the Llobregat delta, an increase in level of 3 m makes it possible to store almost 1 hm^3 of water for every km^2 of surface area. This natural reservoir does not require any special construction and, moreover, allows normal use of the land to continue, as opposed to a reservoir created by means of a surface dam that is highly expensive to build and may even be unviable in an area of flat land as it is found in the final stretch of a river. Water loss through evaporation is also much lower.

2.2 Facilitating transport of the water

As the aquifer covers a large area (in the case of the Llobregat delta, some 110 km^2) and is fairly uniform in shape, the water can be extracted, with no need of pipelines, at any site close to the places where it is most used, even though these places may be some distance away from the natural or artificial recharging points.

2.3 Improving the quality of the water

Both in the case of direct infiltration of the river water and recharging with treated water, the aquifer acts as a slow filter that retains suspended matter in the zones of infiltration, so the resulting groundwater has an improved and more constant quality.

2.4 Increasing the phreatic level

If the contribution of water is sufficient to overcome the deficit, it will lead to a general increase in the levels of groundwater, having two obviously important consequences: saving the energy necessary for pumping the water and diminishing the possibility of intrusions of salty water into the aquifer in the coastal zone.

3 DIRECT ARTIFICIAL RECHARGING FROM THE SURFACE

In order to artificially recharge an aquifer from the surface it is necessary to choose a point in the river itself or close to it, where the aquifer comes out next to the river or is only covered by permeable materials. In this zone, natural recharging will obviously take place, either by the river water itself, or by the rain water that falls in this area. This natural recharging can be artificially aided by either preparing the river-bed or constructing shallow pools or ditches that are filled with the water to be recharged.

Rivers usually have muddied waters that, when the aquifers are directly recharged, cause progressive colmations of the permeable river-bed as the materials in suspension are retained in the pores of the gravels that make up the river-bed. This process will result in the clogging of the river-bed if the fluvial currents -during periodic floods- are not strong enough to resuspend the trapped sediment. If this natural process does not occur, it may be necessary to do it artificially. There is no doubt that the colmation process is the most delicate aspect of artificially recharging aquifers.

As previously mentioned, since 1950 the Sociedad General de Aguas de Barcelona has been recharging directly from the surface by scarifying the river-bed of the Llobregat river in the zone where the aquifer is free and in contact with the river. The scarifying operation is carried out always in the same zone, near the city of Pallejà. The procedure has been unchanged for years.

Most of the difficulties are not caused by the technique itself but rather by morphological variations in the river-bed, modifications to the banks and others, caused by periodic floods of the river and sometimes by the holes left by abusive extraction of gravels.

The technique used can be divided into the following steps:

3.1 Preparation of the river-bed

The river-bed has to be conditioned in order for the scarifying to be effective for some time. The accumulations of sludge, mud and waste have to be cleared away, especially at the bottom of the holes left by the above-mentioned extractions of gravels, which have to be substituted by clean gravels that have piled up in the back-waters of the river. In this way, one achieves an even river-bed that can be safely entered by the tractor used for this kind of work.

3.2 Scarification in practice

The tractor has a bucket (for taking out the mud and moving the gravels) and a ripper for working the river-bed. The ripper must not be more than 50 cm deep in a view to ensure that suspended matter doesn't penetrate deeper zones, as they are difficult to recuperate later and, undoubtedly, would end up clogging up the river-bed and making it difficult for the water to enter the aquifer.

It is always necessary to scarify in the same direction as the current. That is to say, from upstream towards downstream so that the water that filtrates into the aquifer is flowing surface water and not the mud or crust that the ripper throws up and is drifted away.

3.3 Limits worth bearing in mind

There are parameters of control that experience has shown to be worth bearing in mind in order not to deteriorate the quality of the water stored in the aquifer and ensure that the colmation process does not become irreversible:

Flow: The river is only scarified when the flow at Pallejà is between 10 and 35 m^3/s. As the Sant Joan Despí Waterworks treats only up to 5.5 m^3/s, when dealing with this range of flow the water that is fed into the aquifer (about a cubic metre per second) would not affect the capacity of the waterworks. With flows higher than 35 m^3/s it is dangerous to enter the river with the tractor, apart from the fact that as we are dealing with extraordinary flows the process of natural recharging increases substantially.

Turbidity: Care must be taken not to scarify the river-bed if the water that has to be filtered has an excess of suspended matter. The established limit allow us working only when the turbidity of the river water at Pallejà is less than 100 N.T.U., usually infiltrating waters with a considerably lower level.

Chemical quality: At the same time, care is taken to ensure the suitability of some indexes of global quality of surface water: ammonia content must be less than 1 mg/L, and chlorine must not surpass the level of 350 mg Cl/L. Other parameters are so that the scarifying process may be postponed if a quality problem is detected in the recharging water.

4 ARTIFICIAL RECHARGING AT DEPTH

When the aquifers are separated from the surface by impermeable, fairly thick layers, it would be very expensive or almost impossible to recharge them directly using infiltration ditches or pools. For this reason an attempt has been made to carry out the operation by recharging through the pumping wells themselves.

The obstacle that has to be overcome when recharging by means of wells is the fact that they clog up, as is the case when dealing with direct recharging. However, the difference is that the phenomenon occurs at great depth, possibly resulting in an increase in the number and magnitude of the difficulties, to such a point that it is impossible to solve them, sometimes resulting in important and expensive facilities becoming inoperative. Therefore, the possibility of carrying out the artificial recharging at depth depends on the ability to carry out an efficient «unclogging» operation of the zone of the relevant aquifer, if, as usually occurs in practice, the water that is infiltrated has particles in suspension.

As of 1966, when Barcelona and the surrounding area received the additional waters of the Ter river for the purpose of providing water, the Water Treatment Plant of surface water of the Llobregat river at Sant Joan Despí often stopped operating at its full capacity although the discharge of the river was sufficient. As a result, the idea of taking advantage of the mentioned excesses of treated, drinking water for artificially recharging the aquifer in the Cornellà pumping zone (as previously mentioned the aquifer is captive at this point), was considered.

The project began in 1969 and uses seven of the existing pumping wells for the purpose of both pumping and recharging, and five additional wells that were constructed for the sole purpose of artificial recharging. However as this water still has some suspended matter, the infiltration zone of the aquifer near the drilling shafts clogs up progressively. This makes it necessary to limit the infiltrated flow and to periodically unclog the area. As experience has shown, this is effectively carried out by means of vigorous pumping with a flow of the order of four times greater than that of the recharging flow.

5 DESCRIPTION OF THE RECHARGING WELLS

The seven existing wells are all similar and are constructed by means of a cased shaft with a diameter of 950 mm and are 35 - 40 m deep, with a section of 10 m of well screen located in the zone of the aquifer. Each one of the sets of pumping equipment installed has a pump with a capacity of about 200 L/s, with a manometric height of 22 m, driven by a 125 horsepower electric engine. Given the fact that these wells were already equipped, the only thing that had to be done was to fit them with a pipe, making possible to introduce the recharge flow of about 50 L/s. A water gauge with a nominal diameter of 200 mm and a regulating valve made possible to maintain the flow within very strict limits.

The installation also has the necessary pipes and valves in order to discard the water during cleaning operations; this must be done periodically in order to unclog the aquifer in the infiltration zone next to the well screen of the drill shaft. In the five new wells constructed specifically for the purpose of recharging, the zone of the well screen was increased up to 15 - 20 m, and as a result of this greater area the recharged flow increased up to 100 L/s; in this case the control gauges have a nominal diameter of 250 mm. The pumping equipment in each one of the five new wells consists of 180 horsepower pumps with a capacity of 400 L/s and a manometric height of 18.5 m.

Practically all of the thirteen recharging wells are located in a transversal section of the aquifer. This layout means that the flow recharged into the aquifer is near the optimal.

6 OPERATING THE SYSTEM

The seven extracting/recharging wells (each with a capacity of 50 L/s), make it possible to recharge the aquifer with an approximate volume of 4000 m^3 per day. Experience has shown that it is worth unclogging the area when 60,000 m^3 of water have been infiltrated per well, that is to say, after being in operation continuously for 15 days. For cleaning purposes, a flow of 200 L/s is pumped for 10 minutes, resulting in losses of about 0.2%.

Similar criteria have been adopted for the wells with a recharging capacity of 100 L/s, proceeding to clean by pumping 400 L/s every 120,000 m^3 of water that is infiltrated per well, that is to say, after being in operation continuously for 15 days. The duration of the cleaning pumping is slightly longer (15 - 20 minutes) and as a result, the losses are of an order of 0,4%. The total infiltration capacity of the system reaches levels of 75,000 m^3 a day. The infiltration cones of each one of the recharging wells are checked in order to clean them more efficiently if the permeability of the aquifer in the zone next to the drilling well screen decreases.

Although the water that is infiltrated comes from the excesses of the water treated at the Sant Joan Despí Water Treatment Plant, in order not to substantially worsen the quality of the subterranean water stored in the aquifer, the treated water is required to have a maximum content of 100 µg Total THM/L.

7 CONCLUSIONS

The combined use of surface and ground water is a key point to ensure the continuity of the drinking water supplied in the Barcelona’s Metropolitan Area. The artificial infiltration of surface river water through the river-bed and the deep recharge of treated water into the aquifer were the strategies chosen to ensure the availability of water at any time, and have been successfully applied since the 1950’s. Unfortunately, the overexploitation of the aquifer is still so important that the water table is consistently under sea level, leading to an almost irreversible salinisation. Possible solutions for this situation are reduction of total abstraction from the aquifer, water importation from France (Rhône River), or sea water desalination.

Chapter 5: The Risk of Organic Contamination during Managed Aquifer Recharge

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Abstract: Population growth and unpredictable climate changes will pose high demands on water resources in the future. Even at present, surface water is certainly not enough to cope with the water requirement for agricultural, industrial, recreational and drinking purposes. In this context, the usage of groundwater has become essential, therefore, their quality and quantity has to be carefully managed. Enhanced groundwater recharge can guarantee a sustainable level of groundwater, whilst strict quality control of waters intended for recharge will minimize contamination of both the groundwater and aquifer area. However, all water resources in the planet are threatened by multiple sources of contamination coming from the extended use of chemicals worldwide. In this respect, the environmental occurrence of organic micropollutants such as pesticides, pharmaceuticals, industrial chemicals and their metabolites has experienced fast growing interest.

In this paper an overview of the priority and emerging organic micropollutants found to be present in surface water, infiltration water and recovered water at managed aquifer recharge sites is presented.

Keywords: artificial recharge, bank filtration, groundwater, managed aquifer recharge, surface water, organic contaminants.

1 INTRODUCTION

The provision of safe and high quality drinking water is essential to preserve human health and ensure a high quality of life. Since the world population is steadily increasing, associated to that there is an increasing demand for water. In addition, potential climatic changes may in the future originate more periods with low rainfall, causing droughts. In many areas of the world, especially the drier ones, groundwater is the main water source[1]. However, when groundwater withdrawal exceeds the groundwater recharge aquifer water depletion occurs, which in coastal regions can lead to seawater intrusion, and then the aquifer will not render drinkable water. Therefore, there is an urgent need for artificial storage of water by suitable facilities. Generally it has been achieved by the construction of different surface reservoirs, such as dams. However, proper sites are getting scarce and an adverse environmental impact on the area is produced. In addition, water stored in surface reservoirs is exposed to evaporation losses, especially important in areas of warm climates. Other drawbacks of dams include potential for structural damage and failure, and the relatively short lifetime due to the accumulation of sediments and other solids[2]. As a suitable alternative, underground storage via different processes avoids evaporation losses and algae growth being sustainable in terms of economical cost and environmental impact[1]. Artificial recharge (AR) is one of the enhanced recharge techniques commonly used in which through man-made systems water is moved from the surface of the earth to underground water-bearing strata where it may be stored for future use[3]. AR is carried out using basins where sedimentation and infiltration of the surface water takes place or through the injection of the recharge water through wells. Enhanced river bank filtration (BF) is used in less extent in enhanced groundwater recharge operations. In general, managed recharge is used in addition to natural bank filtration in sites where surface soils are permeable[4]. BF is dominated by anoxic/anaerobic conditions meanwhile AR is dominated by aerobic conditions. AR has several potential advantages, some of them being the well understood technology by both the technicians and the general population, the easiness of operation of AR systems, the improvement of the aquifer water by recharging with high quality injected water and the significantly increase in the sustainable yield of the aquifer.

The main source of water for groundwater recharge is surface water. Waters that recharge aquifers include mainly relatively poorly treated domestic and industrial wastewaters, floodwaters, agricultural waters, and urban and rural storm water. However, those sources, especially river water, are exposed to permanent and sudden pollution by a wide variety of chemicals that are potentially adverse to the aquifer system. The widespread finding that many groundwater basins have been contaminated by a huge range of pollutants derived from industrial, municipal, and agricultural activities, coupled with the fact that once a groundwater and aquifer area are polluted it is difficult and expensive to restore the aquifer availability, provides justification for concern about the potential impact of transported micropollutants in recharge waters on the aquifer system, especially when the recovered waters are used for drinking water production.

2 SOURCES OF CONTAMINATION

Point source pollution can be controlled and prevented by accomplishing the standing legislation and directives. But even so, there are episodes of uncontrolled (fortuitous or not) chemical spills from industry causing serious water contamination. Agriculture is the main cause of diffuse pollution, which is quite difficult to face and prevent, since pesticides, herbicides and fertilizers are spread on extensive fields. Animal farms are important non-point source pollution since a quite wide variety of phramaceuticals (antibiotics, hormones and other veterinary formulations) are used in the prevention and treatment of microbial infections and as growth promoters. Following medication, the treated organism excretes between 40% and 90% of the dosage applied in the feces and the urine as the parent compound or metabolites, which in some cases can be bioactive residues even more harmful than the parent compound[5]. This manure is commonly used as organic fertilizer and is spread on soils from where the pharmaceutical residues excreted can contaminate groundwater directly by percolation or indirectly via surface water contamination during runoff.

Sewage effluents from STPs and WWTP are also important sources of contamination.Therefore, compounds such as industrial chemicals, pharmaceuticals and personal care products[6], some of them known to be endocrine disrupters, can be present. In areas where there is low-flow surface water, sewage effluents are needed to increase the amount of water to be further treated for drinking water production. This would be the case of Berlin, where a survey of their surface waters revealed that a number of human pharmaceutical residues and metabolites in addition to polar pesticides were found at μg/L level, and that some of them were transferred to the groundwater when these contaminated surface waters were used in groundwater recharge in drinking water production plants[7].

Other sources of contamination can be identified in areas where rain water and roof runoff are used for recharging activities[8]. In rain water pesticides, herbicides, polar compounds photochemically formed in the atmosphere such as halogenated acetic acids and nitrophenols also emitted in fuel combustion, are present. Although pesticides and herbicides are known to be present in rain water, at high concentration during and right after their application in agricultural areas, their contribution to groundwater contamination when infiltration is done is almost irrelevant in comparison with the contribution due to their direct application in agriculture. In addition, a wide variety of chemicals, for instance biocides and anti-corrosion agents, are employed in roof construction and preservation, which can be washed up by the rain water.

3 ORGANIC MICRO-CONTAMINANTS

Whenever AR or BF is used, polar compounds can leach from the surface recharge waters into groundwater. In order to assess the extent of contamination of the aquifer system when surface water is artificially infiltrated, not only the concentrations but also the total loads of the compounds should be considered. In addition to the parent compounds, some metabolites, by-products and enantiomers of optically active substances can also be found.

Pharmaceuticals, pesticides and industrial chemicals have been found to be present in infiltrated waters[9,10,11].

Table 1 lists some of the most usually detected trace organic contaminants in surface waters that are transferred to the aquifer area.

According to an early work by Zoeteman et al.[12], compounds of major concern due to their widespread use, mobility and persistence in ground waters are hydrocarbons, halogenated hydrocarbons and ketones.

Surface water used for enhanced recharge is often contaminated with pharmaceutical residues and their metabolites as consequence of discharges from municipal wastewater treatment plants (WWTP) effluents, where they are not effectively removed. For example, 6 pharmaceuticals belonging to different prescription classes: carbamazepine, primidone, bezafibrate, indomethacine, diclofenac and propyphenazone, and two drug metabolites: clofibric acid and 1-acetyl-1-methyl-2-dimethyl-oxamoyl-2-phenylhydrazide (AMDOPH), were detected in waters from recharging ponds and control wells and 6 of them persisted in the drinking water supply in an artificial groundwater recharge plant in Berlin, replenishing groundwater from the Lake Tegel[13].

Concentrations found in the recharge ponds were in the range 20-455 ng/L, and in the drinking water supplied concentrations between 1570 and 5 ng/L were reported for both metabolites, AMDOPH and chlofibric acid, respectively. The extremely high value corresponding to the metabolite of dimethylaminophenazone seemed to be related with a spill of the parent compound from a close industry. In a recent study, Heberer et al. [14], in addition to these pharmaceuticals, investigated the presence of herbicides, pesticides and flame retardant compounds at the transects of Lakes Teggel and Wannsee, Berlin, whose waters are used for groundwater recharge. Results revealed that the residues of the herbicides mecoprop and bentazone, as well as two metabolites of the banned DDT were detected. Regarding flame retardants, both compounds analyzed, tris(2-chloroethyl)-phosphate and tris(2-chloroisopropyl-9-phosphate, were found to be present, but considerably attenuated.

Other pharmaceuticals, such as antimicrobials have been monitored in managed aquifer recharge sites. Mean concentration of 118 ng/L sulfamethoxazole has been reported in drinking water extracted from the production well in an artificial recharge facilitie also at the Lake Tegel[15]. Under recharge conditions, the analgesic diclofenac has also been detected in groundwater[16,17], but at low concentrations as well as bezafibrate[18].

Hospital wastewater effluents contain in addition to residues of typical prescription drugs, certain pharmaceutical compounds of hospital-use, such as X-ray contrast media. According to Ternes and Hirsch[19] these contrast media in surface waters and in surface water-influenced groundwaters constitute the main fraction of the adsorbable organic iodine.

These compounds are very polar, persistent in the aquatic environment and have been found to be recalcitrant in wastewater treatments. Therefore, compounds such as diatrizoate, iopromide, iopamidol, and amidotrizoic acid were detected up to μg/L concentration level in ground and infiltrated waters [17,19,20]. Recently, the iodinated X-ray contrast agent iopromide, has been searched in extracted raw water from monitoring and production wells of one bank filtration site and one artificial recharge site at the Lake Tegel[15]. In both production wells concentrations found were below the limit of quantification (<20 ng/L).

Triazines, acetamides and phenoxy acids, have been detected in rain water, few of them quite frequently (atrazine 33 ng/L, alachlor 19 ng/L, metholachlor 15 ng/L, R-mecoprop 10 ng/L, R-diclorprop 12 ng/L). In addition, some metabolites (desethylatrazine 29 ng/L, deisopropilatrazine 26 ng/L) and enantiomers (S-mecoprop 10 ng/L, S-diclorprop 9 ng/L) were found to be present[8]. In the same study, roof runoff used for infiltration was also searched for contaminants.

In this case the pesticides detected and their concentrations were in concordance with those found related to direct agricultural use. Moreover, a major portion of the compounds present in such waters were transferred to the ground water without any significant decrease in their concentrations, especially when the infiltration process was carried out in areas with soils of high permeability (rapid infiltration through particles of quite high size), and then can they can be detected in the infiltred water[21].

It has to be pointed out that concentration of metabolites can increase in bank-filtered water in comparison to surface water since the expanded residence time due to the low velocity in groundwater allow the formation of metabolites. After bank filtration increases in the concentration of certain metabolites of triazine and acetamide herbicides, namely cyanazine amide, cyanazine acid and deethylcyanazine have been identified[21]. Heberer et al.[14] in a recent study investigated the behavior of N-(phenylsulphonyl)-sarcosine the metabolite of the anti-corrosion agent N-(phenylsulfonyl)-N-mrthyl-caprionic acid, in surface and in monitoring production wells in an enhanced ground water recharge in Berlin.

Although data on surface water indicated low levels of the metabolite, the concentrations of the production wells were more than 9 folds higher[22].

Alkylphenol ethoxylates (APEOs) are a group of organic micropollutants used in many household and industrial cleaning products, plastic manufacturing, and spermicidal formulations. Their relative concentrations, with respect to other trace organic contaminants, in wastewater are high. During wastewater treatment, these compounds are incompletely degraded and approximately 65% are released into the environment. Moreover, several APEO metabolites (breakdown products) are strogenic and can persist for long periods of time (>1 year) in groundwater environments. Nevertheless, high degradation rates (up to 98%) have been reported in an earlier study by Schaffner et al.[23] for non polar volatile compounds, nonylphenol, nonylphenol ethoxylate, nonylphenol diethoxylate, nitrilotriacetate ethoxylate and diamintetracetic acid in bank filtered water from Switzerland.

Naphthalendisulfonates are intermediates for different industrial proceses that can either be found in industrial and domestic sewage. Some have been found to be quite stable in waste water treatment, as would be the case of the 1,5-naphthalenesulfonic acid[24], which has been reported to occur in extracted water from enhanced recharge sites without any attenuation in its concentration[15]. Estrogenic steroids are not efficiently removed during wastewater treatment[25] and potencially could be introduced in groundwaters through enhanced enrichment; however, because of their physical-chemical properties these esteroids generally tend to adsorbe onto sediments and organic matter, and therefore are unlikely to be transported to the groundwater[26,27].

Table 1. Mean concentrations in ng/L of organic contaminants in surface, infiltrated and supply waters when contaminated surface water is used for groundwater enhanced recharge in drinking water production.

A. Pharmaceuticals and metabolites

Compound	Conc. in Surface water	Conc. in Infiltrated water	Conc in Supply water	Ref.
Diclofenac	15	NR	35	14
	135	NR	10	13
Clofibric acid	40	NR	50	14
	20	NR	5	13
Propyphenazone	230	NR	240	14
	120	NR	40	13
AMDOPH	355	NR	1250	14
	455	NR	1570	13
Carbamazepine	325	NR	60	14
	470	NR	210	13
Primidone	55	NR	40	14
	135	NR	100	13
Indometazine	Nd	NR	Nd	14
	20	NR	nd	13
Bezafibrate	20	NR	<5	15
	30	NR	nd	13
Estrone	1.1	NR	<0.1	26
Iopromide	841	151 (BF)	NR	15
	737	81 (AR)	NR	15
Sulfamethoxazole	485	122 (BF)	NR	15
	463	118 (AR)	NR	15

NR: not reported, BF: bank filtration, AR: artificial recharge.

B. Pesticides and metabolites

Compound	Conc. in Surface water	Conc in Supply water	Ref.
Bentazone	15	10	14
Mecoprop	15	15	14
pp’-DDA	<5	5	14
op’-DDA	nd	nd	14
Deethylatrazine[a]	850	850	21
Deisopropylatrazine[a]	480	410	21
Atrazine amide-I[a]	<200	<200	21
Hydroxyatrazine[a]	610	410	21
Hydroxydeethylatrazine[a]	200	130	21
Hydroxydeisopropylatrazine[a]	120	110	21
Didealkylatrazine[a]	260	210	21
Cyanazine[a]	1360	1150	21
Deethylcyanazine[a]	<10	<10	21
Cyanazine amide[a]	150	500	21
Deethylcyanazine amide[a]	<10	<10	21
Cyanazine acid[a]	130	270	21

Deethylcyanazine acid[a]	<10	270	21
Propazine	120	110	21
Simazine[a]	50	30	21

[a] Data corresponding to year 1999.

C. Industrial chemicals

Compound	Conc. in Surface water	Conc in Supply water	Ref.
N-(phenylsulphonyl)-sarcosine	10	95	14
tris(2-chloroethyl)-phosphate	525	215	14
tris(2-chloroisopropyl)-phosphate	1800	350	14
1,5- naphthalenesulfonic acid	96	77	15
	90	90	15
1,7- naphthalenesulfonic acid	368	191	15
	350	172	15
2,7- naphthalenesulfonic acid	102	47	15
	102	38	15

(Table 1 continued)

For example, according to Zuehlke et al.[27], a short path of few centimeters can substantially decrease the concentration of estrone.

When an excess of drinking water is produced in water works, part of this potable water can be used for recharging the aquifer, which will improve the yield of the aquifer as well as the quality of the groundwater. However, disinfection byproducts such as trihalomethanes and haloacetic acids formed during the chlorination of water for consumption can be introduced.

4 FATE AND REMOVAL

Different mechanisms including adsorption, dispersion and biological transformations are the main processes driving the removal and fate of organic contaminants in groundwater environments during artificial recharge[28], nevertheless, these processes are not sufficiently understood.

Different patterns and kinetics for the removal of the trace organic compounds can be found, however there is a general agreement that significant improvement is achieved in the quality of the recharged waters [13,29]. The behavior of organic chemicals during recharge is affected by different factors, such as geological conditions, permeability of the soil, residence time, T^a and pH, as well as by the physical–chemical properties of every single compound. In general, the behavior of such contaminants is mainly influenced by biological processes[30]. Under anaerobic conditions and $T^a > 5$ ºC a number of halogenated C_1-C_3 aliphatics, nitro- and chloro-benzenes are found to be extensively degraded based on sequential dehalogenation, while at lower temperatures the degradation rate considerably decreases and the formation of by-products occurs, as would be the formation of dichloro- and bromochloro-methane, and dichloroanilines. On the other hand, aerobic processes appeared to be the responsible for the high elimination degree of trihalomethanes and phenoxy pesticides, associated to the unavoidable formation of the hazardous chlorophenols due to the degradation of such class of pesticides.

Redox processes in enhanced grownd water enrichment sites are known to affect the elimination of pharmaceutical residues, as would be the case of sulfamethoxazole, and the X-ray contrast agents such as iopromide, as well as industrial chemical such as the isomers 1,7- and 2,7-naphthalenesulfonic acid[15]. Sulfamethoxazole can be reduced to 20% of the surface concentration by bank filtration (anoxi/anaerobic), however artificial recharge only is able to degrade it to the half[15]. For iopromide results indicate that removal rates at both sites are around 82% and 89%, respectively. More persistent appeared to be both aromatic sulfonates, with degradation rates between 50% and 63% under aerobic conditions[15].

Different elimination rates were reported by Heberer and Adam[13] for a set of compounds, being carbamazepine the most persistent with a 9 % elimination rate, and diclofenac, indomethazine and bezafibrate, last two not detected in the drinking water produced (< 1 ng/L) higly eliminated, with a rate >90%. The elimination of indomethazine and bezafibrate can be explained in terms of their high octanol-water partition coefficient (log Kow), which would be the responsible of adsorption processes onto the soil. Other mechanisms, such as hydrogen bonding, would be related to the removal of more polar organic micropollutants.

Field experiments on bank filtration evidence a significant removal of diclofenac and bezafibrate in the infiltration process as result of their tendency to be adsorbed on the soil/sediment[10,18]. A different behavior was observed for other pharmaceutical residues, such as the antiepileptic drugs carbamazepine and primidone, which are poorly removed during bank filtration, occurring in ground and drinking water where infiltration was carried out[18,31]. According to Heberer et al.[18], medium attenuation is observed for propyphenazone, which was detected in shallow wells as well as in production wells.

The removal of VOCs is strongly concentration-

dependent, therefore can eventually represent a problem in artificial recharge sites located close to a source of such compounds due to their low persistence in surface waters for long distances as a consequence of their high volatility[30].

In addition to the attenuation of organic micro contaminants under natural conditions there are other man-driven processes focused to promote the removal of such trace pollutants from waters intended for underground replenishment activities. For instance, surface waters can be passed through biological activated carbon filters[32].Reverse osmosis has also been successfully applied[14].

5 CONCLUSIONS

Groundwater recharge is an important issue in order to extend the clean water chain and provide major benefits in terms of improving the way in which water is used as a renewable resource, especially to ensure the supply of drinking water of good quality. However, most of the river, lakes, and other sources of water are polluted to some extent. Significant different behaviors of trace organic contaminants during enhanced aquifer recharge –bank filtration and artificial recharge- is found. Findings reported underline the potential of both enhanced groundwater recharge systems to remove them to some degree, however at bank filtration sites the removal of organic micro-pollutants depends on a number of factors, such as the climate, hydro-geological features of the area and on the physical-chemical conditions of the aquifer. Results evidence the leaching of organic contaminants from surface waters used in enhanced recharge operations into groundwater aquifers. Pharmaceuticals, pesticides, herbicides and a number of industrial chemicals have been found to be present in infiltrated waters and supply waters even at the low µg/L level.

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REFERENCES

[1] H. Bouwer, Agricultural Water Management 45 (2000) 217-228.
[2] S. Postel, Pillar of Sand. Worldwatch Institute, Washington DC. 1999.
[3] H. Bouwer, Artificial Recharge of Groundwater: Systems, Designs and Management. In: Mays, L.W. (Ed.), Hydraulic Design HandbBook , McGraw-Hill, New York (1999) Chapter 24.
[4] H. Bouwer, Hydrogeol. J. 10 (2002) 121-142
[5] P.K. Jjemba, Agric. Ecosyst. Environ. 93 (2002) 267.
[6] C.G. Daughton, T.A. Ternes, Pharmaceuticals and Personal Care Products in the Environment: agents of subtle change ?, Environ. Health Perspect. 109 (1999) 907-938.
[7] T. Heberer, K. Schmidt-Bäumler, H.J. Stan, Acta Hydrochim. Hydrobiol. 26 (1998) 272-278.
[8] T.D. Bucheli, S.R. Müller, S. Heberle, R.P. Schwarzenbach, Environ. Sci. Technol. 32 (1998) 3457-3464.
[9] P Hiemstra, R.J. Kolpa, J.M. van Eekhout, van Kessel A.L., E.D. Adamse, J.A.M. van Paassen, J. Water Supply: Res. Technol. 52 (2003) 277-290.
[10] I.M. Verstraeten, T. Heberer, T. Scheytt, Occurrence, characteristics and transport and fate of pesticides, pharmaceutical active compounds, and industrial and personal care products at bank-filtration sites. In.: C. Ray, G. Melin, R.B. Linsky (Eds.) Riverbank Filtration Improving Source Water Quality. Kluwer Academic Publisher, Dordrecht, Netherlands, 2002, Chapter 9.
[11] Th. Heberer, Toxicol. Lett. 131 (2002) 5-17.
[12] B.C.J. Zoeteman, E. De Greef, F.J.J. Brinkmann, Sci. Tot. Environ. 21 (1981) 187-202.
[13] T. Heberer, M. Adam, Environ, Chem. 1 (2004) 22-25.

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[14] T. Heberer, A. Mechlinski, B. Franck, A. Knappe, G. Massmann, B. Fritz, Ground Water Monitoring and Remediation 24 (2004) 70-77.

[15] S. Grünheid, G. Amy, M. Jekel, Water Res. 39 (2005) 3219-3228.

[16] T.H. Heberer, U. Dünnbier, Ch. Reilich, H.J. Stan, Fresenius Environ. Bull 6 (1997) 438-443.

[17] F. Sacher, F. Th. Lange, H.J. Brauch, I. Blankenhorn, J. Chromatogr. A , 938 (2001)199-210.

[18] T. Heberer, I.M. Verstraeten, M.T. Meyer, A. Mechlinski, K. Reddersen, Water Res. Update 120 (2001) 4-17.

[19] T.A. Ternes, R. Hirsch, Environ. Sci. Technol. 34 (2000) 2741-2748.

[20] A. Putschew, S. Wischnack, M. Jekel, Sci. Total Environ. 255 (2000) 129-134.

[21] I.M. Verstraeten, E.M. Thurman, M.E. Lindsey, E.C. Lee, R.D. Smith, J. Hydrol. 266 (2002) 190-208.

[22] P.K. Knepper, F. Kirschho¨fer, I. Lichter, A. Maes , R.D. Wilken 33 (1999) 945-950.

[23] C. Schaffner,M. Ahel, W. Giger, Water Sci. Technol. 19 (1987) 1195-1196.

[24] M. Stüber, T. Reemtsma, M. Jekel, Vom Wasser 98 (2002) 133-144.

[25] C. Baronti, R. Curini, G. D'Ascenzo, A. Di Corcia, A. Gentili, R. Samperi, Environ. Sci. Technol. 34 (2000) 50-59.

[26] I.M. Verstraeten, T. Heberer, J.R. Vogel, T. Speth, S. Zuehlke, U. Duennbier, Practice Periodical of Hazardous, Toxic and Radiactive Waste Management (October 2003) 253-263.

[27] S. Zuehlke, Th. Heberer, U. Duennbier, B. Fritz, Ground Water Monitoring and Remediation, 24 (2004) 78-85.

[28] P.V. Roberts, A.J. Valocchi, Sci. Tot. Environ. 21 (1981) 161-172.

[29] G. Yun, X. Cheng, X. Jian, T. Wu, Y. Pi, Tsingua Sci. Technol. 5 (2000) 333-337.

[30] J. Hrubec, G. den Engeslam, a.C. de Groot, R.S.den Hartog, Intern. J. Environ. Anal. Chem. 58 (1995) 185-198.

[31] W. Kuehn, U. Mueller, J. AWWA (Dec. 2000) 60-69.

[32] P.A.C. Bonné, J.A.M.H. Hofman, J.P. van der Hoek, Water Sci. Technol.: Water Supply, 2 (2002) 139-146.

Chapter 6: Fate of Organic Pollutants in Artificial Recharge Plants Using Surface Waters

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Abstract: The artificial recharge of aquifers has become a valuable tool to increase the source of water for drinking water production. In many northern European countries this technology is being applied to complement other sources. In the scope of the artificial recharge demonstration project (ARTDEMO) several organic pollutants have been monitored in two artificial recharge plants located in Sweden and Denmark. Water and/or sediment samples have been analyzed for pesticides, estrogens, progestogens, antibiotics and volatile organic compounds (VOC's). As a result from two monitoring campaigns conducted in September 2003 and June 2004, the contaminants detected were found to be present at very low levels in both water and sediments, levels which are far from those established in the legislation as maximum admissible concentrations (when existing) and far from those considered as a risk.

1 INTRODUCTION

Due to the widespread pollution and natural contamination of surface waters and the over-exploitation of aquifers, both the quality and quantity of the groundwater resources have decreased. Since the water supply in some countries is mainly based on groundwater abstraction (e.g. Denmark) alternative ways to produce drinking water have to be exploited.

In this study two monitoring campaigns have been performed to evaluate the levels of selected contaminants in two pilot artificial recharge plants.

2 ARTIFICIAL RECHARGE PLANTS STUDIED

2.1 Arrenaes Artificial Recharge Plant, Arrenaes, Denmark

The trial plant has an infiltration capacity of approximately 350,000 m^3/year. The artificial recharge is performed though an unsaturated zone with a thickness of 21 to 28 meters.

The trial plant consists of four large basins, two sets of troughs (with five troughs each), and a grass area where lake water is sprinkled by 40 small water cannons. The basins and trough systems each have an effective area of 1000 m^2, and the grass area covers 20,000 m^2.

2.2 Dösebacka and Gråbo, Göteborg, Sweden

The Gråbo site is located 25 km from Göteborg and supplies the local community of Gråbo with 0.26 Mm^3/year of natural ground water.

The Dösebacka site is situated 10 km from Göteborg. Artificial recharge from the river Göta älv is used to produce 2.2 Mm^3/year of artificial groundwater.

3 MONITORING OF ORGANIC POLLUTANTS

In this study a wide range of organic pollutants going from classical, priority contaminants (e.g. pesticides) to new, emerging contaminants (e.g. estrogens and antibiotics) has been analyzed. In total 48 contaminants have been monitored. Table 1 shows the target analytes chosen in the context of the ARTDEMO project.

Table 1: List of the organic contaminants investigated, grouped by class.

Monitored contaminants			
Pesticides	Estrogens and progestogens	Antibiotics	VOC's
Deisopropylatrazine	Estradiol-17-glucuronide	Sulfadimethoxine	TBA
Desethylatrazine	Estrone-3-sulfate	Sulfamethazine	MTBE
Dimethoate	Estriol	Sulfamethizole	DIPE
Simazine*	Estrone	Sulfamethoxipyridazine	ETBE
Cyanazine	Estradiol	Sulfapyridine	TBF
Chlortoluron	Ethynylestradiol	Sulfisoxazole	Benzene
Isoproturon*	Diethylstilbestrol	Sulfadiazine	TAME
Atrazine*	Norethindrone	Silfathiazole	Toluene
Diuron*	Levonorgestrel	Sulfamethoxazole	Ethylbenzene
Tertbuthylazine	Progesterone	Dicloxacillin	*m*+*p*-Xylene
Linuron		Nafcillin	*o*-Xylene
Molinate			TCE
Metolachlor			DCPD
Alachlor*			
Diazinon			
BAM			

*Compounds included in the list of priority substances in the field of water established in the Decision No 2455/2001/EC. Abbreviations: BAM, 2,6-dichlorobenzamide; TBA, tert.-butyl alcohol; MTBE, methyl tert.-butyl ether; DIPE, diisopropyl ether; ETBE, ethyl tert.-butyl ether; TBF, tert.-butyl formate; TAME, tert.-amyl methyl ether; TCE, trichloroethylene; DCPD, dicyclopentadiene

3.1 Pesticides

The list of pesticides investigated includes 17 compounds belonging to 6 different classes: triazines, organophosphates, the pesticides propanil and molinate used in rice fields, phenyl ureas, anilines and 2,6-dichlorobenzamide (BAM, metabolite of the herbicide dichlobenil (2,6-dichlorobenzonitrile)). Several of these pesticides have been found in groundwater (Spalding et al. 2003).

3.2 Estrogens and progestogens

Among the wide range of substances with endocrine disrupting properties, estrogens are of particular interest due to their high estrogenic potency. Natural steroid estrogens have been shown to exert estrogenic effects in fish at very low concentrations in water (0.1-1 ng/L) (Hansen et al. 1998; Purdom et al. 1994). Target estrogens and progestogens were selected based on their abundance in the human body, their estrogenic potency, and the extent of their use in contraceptive pills. They included the natural estrogen estradiol (E2), its main metabolites estriol (E3) and estrone (E1), the conjugates estradiol-17-glucuronide (E2-gluc) and estrone-3-sulfate (E1-sulf), the synthetic estrogens ethynyl estradiol (EE) and diethylstilbestrol (DES), progesterone and the synthetic progestins norethindrone and levonorgestrel.

3.3 Antimicrobials

Antimicrobials are pharmaceutical compounds widely used in human and veterinary medicine to prevent or to treat microbial infections. They may also find application as growth promoters. The presence of residues of antimicrobial compounds in the environment has caused concern because of the risk of inducing the formation of resistant microorganisms (e.g., sulfonamide- and trimethoprim-resistant bacteria have been detected in rivers in the USA). The antimicrobials studied belong to the families of sulfonamides and penicillins.

3.4 Volatile Organic Compounds (VOC's)

Besides its toxicity at high concentrations, there is much interest in the aesthetic implications of methyl tert.-butyl ether (MTBE) in drinking water. Taste and odour thresholds for this compound in water have been reported at very low concentrations. In the present study the determination of MTBE, its main degradation products, tert.-butyl alcohol (TBA), tert.-butyl formate (TBF), and other gasoline additives, the oxygenate dialkyl ethers ethyl tert.-butyl ether, tert.-amyl methyl ether and diisopropyl ether and the aromatic compounds benzene, toluene, ethylbenzene and xylene (BTEX) was performed in both artificial recharge plants.

4 EXPERIMENTAL

4.1 *Chemicals*

Standards of VOC's were made up from 2000 mg/L or neat stock solutions containing TAME, ETBE, DIPE and a mixture of BTEX and MTBE (Supelco, Bellefonte, PA, USA); TBA and TBF (Fluka, Bucks, Switzerland). Fluorobenzene (Supelco) and deuterated methyl tert.-butyl ether, [2H3] MTBE (MTBE-d3; Aldrich, Germany) were used as internal standards. Each compound was obtained in the highest purity that was commercially available (98.3–99.7%) and used as received within 4 weeks. Working standard solutions (studied compounds and internal standards) were prepared in ultra pure methanol and added on organic-free water (Merck, Darmstadt, Germany).

High purity (98-99.9%) standards of the other target compounds were purchased as powders from Sigma (St Louis, MO, USA). Stock standard solutions for each of the analytes were prepared in methanol at 1 mg mL^{-1} and stored in the dark at 4 ºC. Working solutions of the mixtures of each class of compounds at concentrations ranging between 0.1 and 1000 ng mL^{-1} were prepared by appropriate dilution of the stock solutions in methanol. The standard mixtures were used as spiking solutions and for the preparation of calibration curves. In the on-line procedures, aqueous standard solutions were prepared from the stock solutions and did not contain more than 1‰ of methanol.

Pesticide-grade solvents methanol and acetonitrile and LC-grade water were supplied by Merck (Darmstadt, Germany).

4.2 *Equipment*

Automated on-line solid-phase extraction (SPE), used in the analysis of estrogens, progestogens and pesticides in water, was performed using the sample processor Prospekt-2 (Spark Holland, Emmen, The Netherlands) configured for high sample volumes.

Off-line SPE extraction, used in the analysis of antimicrobials in water, was performed using an automated sample processor ASPEC XL (Automated Sample Preparation with Extraction Columns) fitted with a 817 switching valve and an external 306 LC pump from Gilson (Villiers-le-Bel, France).

In sediments, extraction of estrogens and progestogens was performed by ultrasonication and extraction of antibiotics by pressurized liquid extraction (PLE) in an ASE 200 (Accelerated Solvent Extractor) from Dionex (Sunnyvale, USA). Further clean-up of the extracts was carried out with the above described ASPEC XL system.

Liquid chromatography-tandem mass spectrometry (LC-MS/MS) analyses of estrogens, progestogens, pesticides and antibiotics were carried out in a system consisting of a Waters Alliance 2690 LC pump equipped with an autosampler with the volume injection set to 20 µL and connected in series with a Waters 996 Photodiode Array Detector (all from Waters, Milford, MA,USA) and a Quattro LC triple-quadrupole mass spectrometer from Micromass (Manchester, UK).

For analysis of VOC's in water a commercial Tekmar 3100 purge-and-trap concentrator coupled to an Aquatek 70 liquid autosampler (Tekmar-Dohrmann, USA) was used. Further GC-MS analyses were performed with a Trace GC system coupled to a Voyager MS instrument (ThermoQuest Finnigan, USA).

4.3 *Sample preparation and analysis*

Water samples were collected in glass bottles, and stored and shipped under cooled conditions until analysis, which was performed within 72 hours after collection. If needed samples were acidified with sulfuric acid to pH2 and stored at 4 ºC in the dark for maximum 2 weeks. Sediments were collected in glass bottles, transported under cooled conditions, freeze-dried and stored at -20 ºC.

The analytical methods developed for each compound class and matrix are sumarized in the following scheme and described in more detail in the subsequent tables.

Extraction of water samples.

- Pesticides, estrogens and progestogens: on-line SPE-LC-MS/MS (Table 2)
- Antibiotics: off-line SPE + LC-MS/MS (Table 3)
- VOC's: purge and trap GC-MS (Table 4)

Extraction of sediment samples.

- Estrogens and progestogens: ultrasonication + SPE + LC-MS/MS (Table 5)
- Antibiotics: PLE + SPE + LC-MS/MS (Table 6)

The main MS and MS/MS experimental conditions are listed in Tables 7 to 10.

Table 2: On-line SPE-LC-MS/MS (pesticides, estrogens and progestogens in water)

SPE	LC	(ESI)MS/MS
Prospekt-2	Waters Alliance 2690	Micromass Quatro triple-quad.
-cartridge for pesticides (Borba da Cunha et al. 2004) (Kampioti et al. 2005) Hysphere Resin GP -cartridge for estrogens and Progestogens (Rodriguez-Mozaz et al. 2004): PLRP-s	- Column: Purospher STAR-RP-18e (125×2 mm, 5 µm) - Mobile phase: gradient: acetonitrile/water	-for pesticides and estrogens: SRM (NI) -for progestogens: SRM (PI)
-20 ml sample volume -elution: LC mobile phase	-min 0 to 5: 10% to 50% ACN -min 5 to 25: to 80% ACN -min 26 to 31: 100% ACN -min 32 to 45: 10% ACN	-capillary potential: 3.50 kV -source temperature: 150 ºC -desolvation temperature: 450 ºC

Abbreviations not included in the text: ESI, electrospray; ACN, acetonitrile; SRM, selected reaction monitoring; NI, negative ionization; PI, positive ionization.

Table 3: Off-line SPE + LC-MS/MS (antibiotics in water)

SPE	LC	(ESI)MS/MS
ASPEC	HP1100 MSD	Quatro triple-quadrupole
-cartridges: Isolut ENV+	- Column: Zorbax SB-Aq (4.6x150 mm, 5µm) - Mobile phase: gradient: acetonitrile/water	-SRM (PI)
-20 ml sample volume -elution: 3 ml methanol + 3 ml acetone	-min 0 to 26: 10% to 100% ACN	-capillary potential: 3.50 kV -source temperature: 150 ºC -desolvation temperature: 450 ºC

Abbreviations not included in the text: ESI, electrospray; ACN, acetonitrile; SRM, selected reaction monitoring; PI, positive ionization.

Table 4: Purge and trap GC-MS (VOC's in water) (Rosell et al. 2003)

Purge and trap	GC	(EI)MS
Tekmar 3100	Trace GC-MS Finnigan	
-Trap: Tenax® - Silica gel - Charcoal	-DB-624 (75 m x 0.53 mm ID x 3 mm)	-SIM -see table with transitions
-sample volume: 10 ml -purge time: 13 min. at room temperature -desorption time: 4 min. at 225ºC	-35ºC (5 min.) to 70ºC at a rate of 3ºC/min -70ºC (5 min.) to 210ºC at 6ºC/min -210ºC (5 min.)	-Source temperature: 200 ºC -Interface temperature: 270 ºC Detector voltage: 400 V

Abbreviations not included in the text: EI, electron impact; ID, internal diameter; SIM, selected ion monitoring.

Table 5: Ultrasonication + SPE + LC-MS/MS (estrogens in sediments) (Lopez de Alda et al. 2002)

Sonication	SPE	LC-MS/MS
Ultrasonic bath	Baker	See parameters of method “on-line SPE-LC-MS/MS”
-sample pretreatment: lyophilization + homogenization + sieve	- Sep-Pak Plus C-18 cartridges	
-5g dry weight of sample -extraction with Acetone:MeOH (1:1): 25+15+15 mL	-extract of sonication was reconstituted in 2 mL methanol and 18 mL water and loaded onto cartridge -elution with 8 ml acetonitrile	

Table 6: PLE + SPE + LC-MS/MS (antibiotics in sediments) (Díaz-Cruz et al.)

PLE	SPE	LC-MS/MS
ASE 200	ASPEC	See parameters of method “off-line SPE-LC-MS/MS”
-sample pretreatment: Lyophilization + homogenization + sieve	- Oasis HLB cartridges	
-5g dry weight of sample -extraction with Acetone:MeOH (1:1) -pressure: 1500 psi -temperature: 75 ºC -cycles: 3	-extract of PLE was reconstituted in 1 mL methanol and 19 mL water and loaded onto SPE cartridge -elution with 3 mL methanol + 3 ml acetone	

Table 7: Multiple reaction monitoring (MRM) transitions monitored for pesticides.

Pesticide	Time	MRM transition (m/z)	Cone	Coll.
		Precursor ion → Product ion	(V)	(eV)
Deisopropylatrazine	00.00 -12.40	174 → 104	25	20
		174 → 132	25	15
Desethylatrazine		188 → 146	25	15
		188 → 104	25	25
BAM		190 → 109	30	35
		188 → 146	25	15
Dimethoato		230 → 199	15	10
		230 → 125	15	20
Simazine	12.40 -16.40	202 → 132	30	20
		202 → 124	30	20
Cyanazine		241 → 214	30	15
		241 → 174	30	20
Chlortoluron		213 → 72	25	15
		213 → 140	25	25
Isoproturon		207 → 72	25	15
		207 → 165	25	25
Atrazine		216 → 174	30	15
		216 → 132	30	20
Diuron		233 → 72	15	15
		235 → 72	15	30
Terbuthylazine	16.40 -22.50	230 → 174	20	15
		230 → 132	20	25
Linuron		249 → 160	25	20
		249 → 182	25	15
Molinate		188 → 126	25	10
		188 → 83	25	20
Metalachlor		284 → 252	25	15
		284 → 176	25	25
Alachlor		270 → 238	15	10
		270 → 162	15	25
Propanil		218 → 162	30	25
		218 → 127	30	15
Diazimon	22.50 -30.00	305 → 169	25	20
		305 → 153	25	20

Table 8. SRM transitions monitored for estrogens and progestogens

Compound	**Time (min)**	**SRM transitions (m/z) Precursor ion → Product ion**	**Cone (V)**	**Coll. (V)**
Estradiol -17-gluc.	00.0 -13.25	447 → 113	40	30
		447 → 271	40	50
Estrone -3-sulfate		349 → 269	40	40
		349 → 145	40	40
Estriol		287 → 171	50	40
		287 → 145	50	40
Estradiol	13.25-22.00	271 → 145	50	45
		271 → 183	50	45
Ethynyl estradiol		295 → 145	50	40
		295 → 159	50	40
Estrone		269 → 145	50	40
		269 → 143	50	45
Norethindrone	0-15.30	299 → 171	30	20
		299 → 145	30	20
Levonorgestrel	15.30-17.70	313 → 245	30	20
		313 → 185	30	20
Progesterone	17.70-25.00	315 → 97	30	20
		315 → 109	30	25

Table 9: SRM transitions monitored for the antibiotics

Compound	*Time windows (min.)*	t_R *(min.)*	*SRM transitions* (m/z) Precursor ion → Product ion*	*Cone (V)*	*Coll. (eV)*
Sulfathiazole	0.0 – 8.5	5.39	$[M+H]^+$ 256→ 156	25	15
			$[M+H]^+$ 256→ 92	25	25
Sulfapyridine		5.45	$[M+H]^+$ 250 → 156	30	15
			$[M+H]^+$ 250 → 108	30	25
Sulfadiazine		5.6	$[M+H]^+$ 251→ 156	20	15
			$[M+H]^+$ 251→ 92	20	25
Sulfamethazine		6.6	$[M+H]^+$ 279 → 124	25	25
			$[M+H]^+$ 279 → 204	25	15
Sulfamethoxipyridazine		7.16	$[M+H]^+$ 281 → 156	25	15
			$[M+H]^+$ 281 → 108	25	20
Sulfamethizole		7.26	$[M+H]^+$ 271 → 156	20	15
			$[M+H]^+$ 271 → 108	20	25
Sulfamethoxazole	8.5 – 17.0	11.96	$[M+H]^+$ 254 → 108	30	20
			$[M+H]^+$ 254 → 92	30	25
Sulfisoxazole		12.69	$[M+H]^+$ 268 → 156	25	15
			$[M+H]^+$ 268 → 113	25	15
Sulfadimethoxine		14.24	$[M+H]^+$ 311 → 156	30	20
			$[M+H]^+$ 311 → 108	30	30
Nafcillin	17.0 - 30.0	19.29	$[M+H+MeOH]^+$ 447 → 199	20	20
			$[M+H+MeOH]^+$ 447 → 171	20	40
Dicloxacillin		20.82	$[M+H+MeOH]^+$ 502 → 160	20	15
			$[M+H+MeOH]^+$ 502 → 212	20	35

Table 10: SIM of VOC’s

Compound	Rt (min)	MW (m/z)	Selected ions (m/z)		
			Quantitation	Secondary	Tertiary
TBA	13.11	74	59		
MTBE-d_3	13.43	91	76	57	43
MTBE	13.51	88	73	57	43
DIPE	15.11	102	45	87	59
ETBE	16.30	102	59	87	57
TBF	18.10	102	59	56	57
benzene	20.02	78	78	77	52
TAME	20.52	102	73	55	87
fluorobenzene	21.25	96	96	70	50
TCE	22.88	130	130	132	95
toluene	27.97	92	91	92	65
ethylbenzene	32.96	106	91	106	77
m+*p*-xylene	33.32	106	91	106	77
o-xylene	34.51	106	91	106	77
DCPD	39.43	132	66	132	39
1,2-dichlorobenzene-d	40.35	150	150	152	115

5 RESULTS AND DISCUSSION

Figure 1 shows the levels of pesticides found in the water samples collected at the Arrenaes Artificial Recharge Plant (Arrenaes, Denmark) in both sampling campaigns. As shown in this figure, individual pesticides were at very low concentrations (in the pg/L or low ng/L range) and cummulative pesticide levels never exceeded 25 ng/L. Of the various pesticides investigated, simazine and BAM were the most ubiquitous and abundant compounds. The comparison between the levels obtained in the first and the second monitoring programs shows that the profile of the pesticides detected in each sample is more or less the same in both periods although the concentrations were slightly higher in year 2004. Nevertheless, taking into account the very low levels detected, these differences can be considered negligible. In the water samples from the Swedish plant, the pesticide levels were even lower with cummulative concentrations below 10 ng/L in all samples.

As regards estrogens and progestogens in water, just estrone-3-sulfate was detected in only five samples (from the Danish plant in year 2004) and at very low concentrations (lower than 0.5 ng/L).

In sediments, the levels of the estrogens detected (estrone and estrone 3-sulfate in only two samples of each plant, considering both sampling campaigns) were also very low (< 0.5 ng/g).

In water, none of the antibiotics monitored was detected, regardless of the sampling period or the origin of the samples. However, in sediments there was one compound detected, sulfadimethoxine, which was found in all the samples investigated, although again at very low concentrations (0.04-0.21 ng/g).

As for the VOC’s, none of them was detected in the water samples from the Arrenaes Artificial Recharge Plant. On the contrary, a few VOC’s, namely, toluene, ethylbenzene, benzene, xylene, trichloro-ethylene and tetraclorobenzene, where detected in some of the samples from Göteborg, in either one campaign or another. However, with the exception of toluene, which was found at a concentation of 0.21 µg/L in one of the samples analysed in 2004, all the other compounds were present at levels always lower 0.04 µg/L.

6 CONCLUSIONS

All the chemicals investigated, when detected, were present at very low levels in both water and sediments, levels that are far from those established in the legislation as maximum admissible concentrations (when existing) and far from those considered as a risk.

Individual pesticides concentrations were in the pg/L or low ng/L range. Simazine and BAM were the most ubiquitous and abundant compounds.

The total pesticide concentration was always lower than 25 ng/L. Estrone-3 sulfate and estrone were the only estrogens detected. Progestogens were never found. No antibiotic was detected in water and sulfadimethoxine was the only compound found in sediments. Volatile organic compounds (VOCs) were present only in Swedish water-samples and at concentrations lower than 0.21 µg/L.

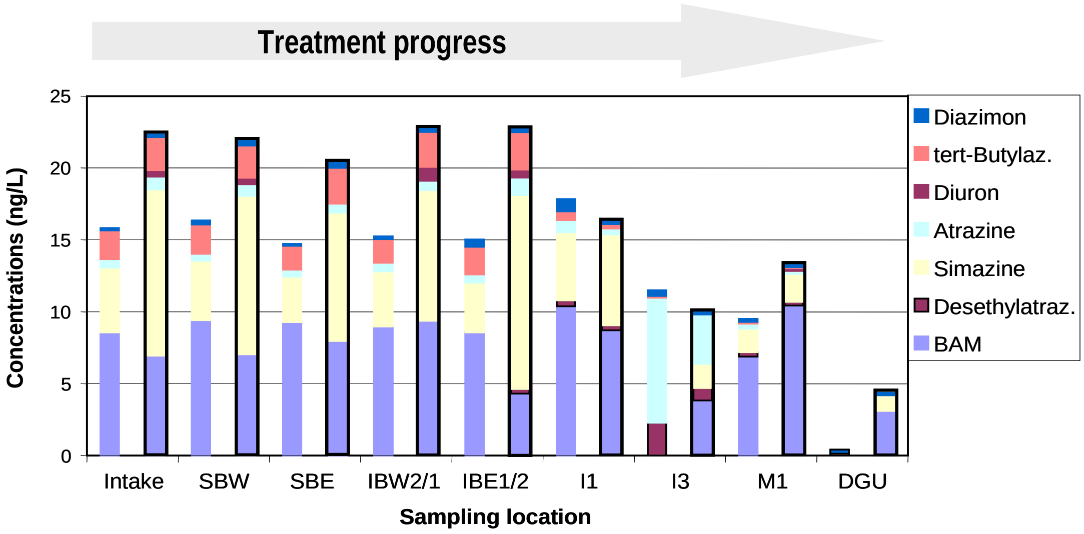

Figure 1. Levels of pesticides found in the water samples along the treament process at the Arrenaes Artificial Recharge Plant (Arrenaes, Denmark) in the first (left bar) and second (right bar) sampling periods.

The similarity of results obtained in both monitoring programs indicates that the levels detected are fairly stable and not affected by seasonal variations.

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8 REFERENCES

Borba da Cunha, A., M. J. López de Alda, D. Barceló, T. M. Pizzolato & J. H. Z. dos Santos. 2004. Multianalyte determination of different classes of pesticides (acidic, triazines, phenyl ureas, anilines, organophosphates, molinate and propanil) by liquid chromatography-electrospray-tandem mass spectrometry. *Anal. Bioanal. Chem.* 378:940-954.

Díaz-Cruz, M. S., M. J. López de Alda & D. Barceló. *J. Chromatogr. A*:(submitted).

Hansen, P.-D., H. Dizer, B. Hock, A. Marx, J. Sherry, M. McMaster & C. Blaise. 1998. Vitellogenin - a biomarker for endocrine disruptors. *Trends Anal. Chem.-TrAC* 17:448-451.

Kampioti, A. A., A. C. Borba da Cunha, M. J. López de Alda & D. Barceló. 2005. Fully automated multianalyte determination of different classes of pesticides, at picogram per litre levels in water, by on-line solid-phase extraction-liquid chromatography-electrospray-tandem mass spectrometry. *Anal. Bioanal. Chem.* 382:1815-1825.

Lopez de Alda, M. J., A. Gil, E. Paz & D. Barcelo. 2002. Occurrence and analysis of estrogens and progestogens in river sediments by liquid chromatography-electrospray-mass spectrometry. *Analyst* 127:1299-1304.

Purdom, C. E., P. A. Hardiman, V. J. Bye, N. C. Eno, C. R. Tyler & J. P. Sumpter. 1994. Estrogenic effects of effluents from sewage treatment works. *Chem. Ecol.* 8:275-285.

Rodriguez-Mozaz, S., M. J. LopezdeAlda & D. Barcelo. 2004. Picogram per Liter Level Determination of Estrogens in Natural Waters and Waterworks by a Fully Automated On-Line Solid-Phase Extraction-Liquid Chromatography-Electrospray Tandem Mass Spectrometry Method. *Anal. Chem.* 76:6998-7006.

Rosell, M., S. Lacorte, A. Ginebreda & D. Barcelo. 2003. Simultaneous determination of methyl tert.-butyl ether and its degradation products, other gasoline oxygenates and benzene, toluene, ethylbenzene and xylenes in Catalonian groundwater by purge-and-trap-gas chromatography-mass spectrometry. *Journal of Chromatography A* 995:171-184.

Spalding, R. F., M. E. Exner, D. D. Snow, D. A. Cassada, M. E. Burbach & S. J. Monson. 2003. Herbicides in Ground Water beneath Nebraska's Management Systems Evaluation Area. *J Environ Qual* 32:92-99.

Chapter 7: Removal of Mycrocystins and Faecal Indicators at the Arrenæs Artificial Recharge Plant

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1 REMOVAL OF MICROCYSTINS

1.1 Introduction

Eutrofication of surface waters is a ubiquitous pollution problem and combined with the right temperature, light and nutrient conditions it may cause blooms of cyanobacteria. A number of the cyanobacteria, such as *Microcystis* sp, produce toxic substances, cyanotoxins. The cyanotoxins are divided into three broad groups: cyclic peptides, alkaloids and lipopolysaccharides, of which the cyclic peptides have received the most attention because they pose a major challenge for the production of drinking water. The cyclic peptides are hepatotoxins affecting the liver of the exposed organisms by inhibition of protein phosphatases. Microcystin LR is highly toxic with a LD_{50} in mice between 25 µg/kg and 150 µg/kg bodyweight, and WHO has adopted a provisional guideline value of 1 µg/l in drinking water.

1.2 Biodegradation of micro-cystins

Microcystins have been shown to be biodegradable by a number of authors. The pathway of biodegradation of Microcystin LR has been studied by Bourne et al. (1996) by the use of a pure culture of a species of *Sphingomonas* isolated from surface water in Australia. The degradation was mediated by at least 3 intracellular hydrolytic enzymes. The first enzyme opens the peptide ring rendering the degradation product much less toxic. Hence, the bacterial degradation not only removes the microcystin but it also reduces the toxicity significantly.

Half lives in batch studies are often less than 1 day (Christoffersen 2002, Saitou, 2002, Chorus et al., 2004) and usually below 4 to 5 days (Saitou 2002; Hyenstrand, 2003; Cousins, 1996; Jones 1994, Chorus et al., 2004). In column studies and studies of sand filters, the kinetics are complicated by the flow of water and interaction between the compounds the solid phase. The most thorough study was conducted by Chorus et al., (2004). Their study included batch studies, column studies as well as large scale studies and field studies to assess the removal processes of microcystins during subsurface transport. In their laboratory studies with 18 cm columns where the water is recirculated they find first order rates of 1.5 day^{-1}. In a slow sand filter they find much higher rates, 17 day^{-1} to 30 day^{-1}.

There is strong evidence that bacteria can grow on microcystin, since bacteria can be isolated by enrichment (Park et al., 2001), biodegradation leads to small organic molecules (Bourne et al., 1996), and mineralisation has been observed (Fedorak and Huck, 1988; Holst et al., 2003). Bacterial growth on cyanotoxins is of importance for the removal efficiency of cyanotoxins during artificial recharge, since the rates of degradation depend on the number of active bacteria and the number of bacteria will increase as the toxin is degraded.

Adaptation can be defined as a change in the microbial community that increases the rate of transformation of a test compound as a result of prior exposure to the test compound (Van Veld, 1983). The adaptation can be characterised by the length of the lag period. The lag period is defined as the length of time during the initial exposure of micro-organisms to a chemical in which the transformation rate is too slow to be measured (Lewis et al.; 1986). Existence of a lag phase is of concern for artificial recharge. The presence cyanotoxins is seasonal and a long lag phase during the first bloom of the season may result in breakthrough of the cyanotoxins. The adaptation and lag period has been studied frequently for the biodegradation of Microcystin (Christoffersen et al., 2002; Saitou et al., 2002; Hyenstrand et al., 2003, Chorus et al., 2004). Lag periods are typically between 0 days and 14 days. However, some studies (Holst et al., 2003) have indicated that in ground water sediments the lag phase may be several months or the potential for degradation may be absent.

1.3 Aim

Previous studies have shown that microcystins can be degraded by at the Arrenæs AR pilot plant (Holst et al., 2003), however it is still a question if the bacterial community is able to maintain its ability to degrade microcystins over the winter, where the microcystins are absent. Therefore the aim of this study has been to examine if the adaptation to degradation of microcystins in the autumn, where recent exposure to microcystins can be expected, and in the spring, where the exposure to microcystins has been absent during the winter. In addition, a field investigation on the occurrence of microcystins was carried out at the Arrenæs AR pilot plant.

1.4 Methodology

The biodegradation of cyanotoxins have been studied by batch experiments. Degradation rates in microcystin-exposed sediments samples and unexposed sediments samples from the Arrenæs AR pilot plant were compared. Toxin-exposed sediment was sampled autumn 2004. Non exposed sediment was sampled in the spring 2005. In order to ensure comparability between the two experiments, filter material from a rapid sand filter (Sjælsø ground water treatment plant no. 2) where the conditions are uniform from year to year was used as a reference. The following experimental conditions were applied:

Sediment samples (50 g w.w.) were taken from a depth of approximately 5 cm below the sediment surface in the West-2 infiltration basin at Arrenæs AR Pilot Plant and added to 1 l of

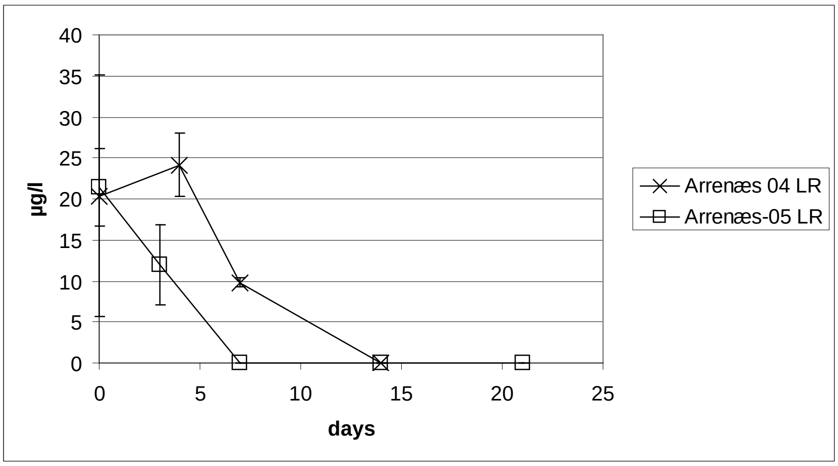

Figure 1: Degradation of Microcystin LR in batch experiments with sediment from the Arrenæs AR pilot plant. Arrenæs 04 is sediment from autumn 2004, which has been exposed to cyanotoxins during the spring and summer period. Arrenæs 05 is sediment which has not been exposed to cyanotoxins during the winter period.

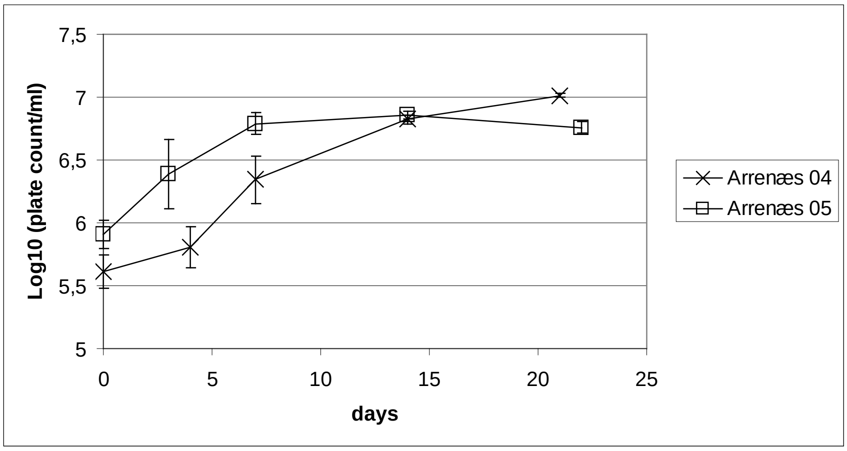

Figure 2: Growth of heterotrophic bacteria in batch experiments with sediment from Arrenæs.

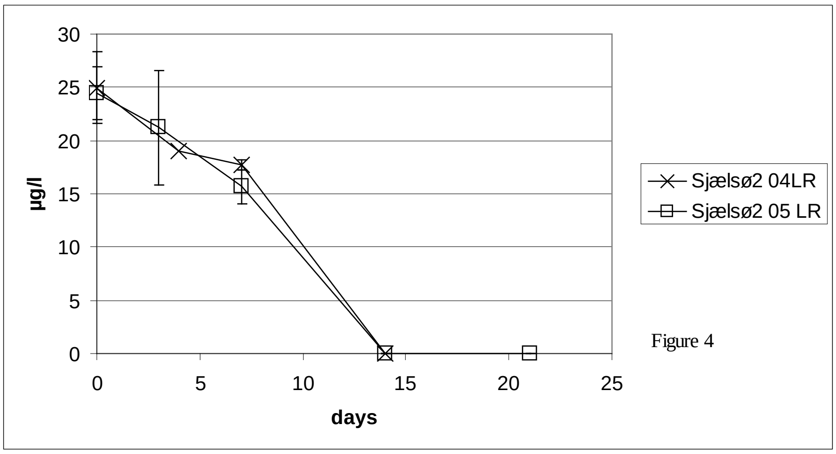

Figure 3: Degradation of Microcystin LR in batch experiments with sediment from the rapid sand filter at Sjælsø water treatment plant 2.

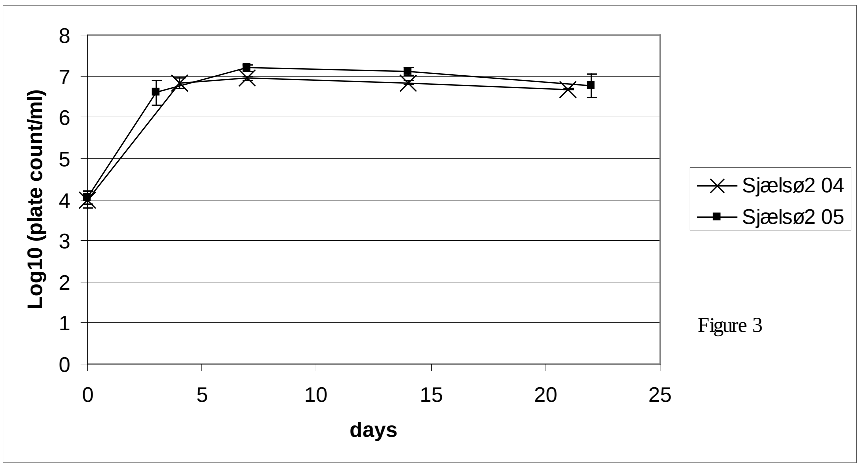

Figure 4: Growth of heterotrophic bacteria in batch experiments with sediment from the rapid sand filter at Sjælsø water treatment plant 2.

water. Triplicate experiments and one autoclaved control were used. The sediment slurries were incubated at 15 °C under slow continuous rotation (~ 1 rpm). 100 ml samples were taken from the slurries on day 0, 4, 7, 14, 21 and analysed for microcystins (HPLC) and heterotrophic plate count (R2A, 15 °C, 14 days). Extract of *Microcystis* PCC 7820, 210203 provided by Jussi Meriluoto, University of Åbo, Finland, was added at to a concentration of approximately 50 µg/l. The extract contained microcystin LR, microcystin LY, microcystin LW and microcystin LF.

The occurrence of microcystins at the Arrenæs AR pilot plant was monitored in the period from 1. June to 10 November 2005. Water samples of the incoming water as well as water sampled approximately 1 m and 25 m below the surface at the Arrenæs AR pilot plant have been analysed by HPLC and ELISA. In addition, samples were analysed for occurrence of algae, by analysing the pigments.

1.5 Results and discussion

The results of the degradation experiments are shown in the Figures 1 to 4

Figure 1 shows that the degradation of microcystin LR progress more rapidly in the batches inoculated with “unexposed” sediment taken in spring 2005 than in the batches inoculated with “exposed” sediment from the autumn 2004. Similar degradation curves were found for microcystin LY, microcystin LW and microcystin LF. This is the opposite of what was expected, since the bacteria in the “exposed”

Table 1: Results from monitoring of the occurrence of Microcystin LR at the Arrenæs AR pilot plant. Concentration in µg/l. Analysed by HPLC in the particulate fraction as well as in solution.

	Arresø		Infiltration basin		Tensiometer	I1
	In solution	particulate	In solution	particulate	In solution	solution
01.06.2005			0,59	< 0,1	0,26	< 0,1
15.06.2005			0,15	0,29	< 0,1	< 0,1
29.06.2005	< 0,1	8,50	< 0,1	1,90		
14.07.2005	< 0,1	0,11	< 0,1	0,16		< 0,1
28.07.2005		0,33	< 0,1	< 0,1		
11.08.2005	< 0,1		< 0,1	< 0,1		< 0,1
25.08.2005	< 0,1	0,74	< 0,1	< 0,1		
14.09.2005	< 0,1	1,09	< 0,1			< 0,1
29.09.2005	< 0,1	0,71				
13.10.2005		< 0,1				< 0,1
27.10.2005		< 0,1				
10.11.2005	< 0,1					

Table 2: Results from monitoring of the occurrence of Microcystins at the Arrenæs AR pilot plant. Concentration in µg/l. Analysed by ELISA in the particulate fraction as well as in solution.

	Arresø		Infiltration basin		Tensiometer
	In solution	particulate	In solution	particulate	In solution
01.06.2005			1,3	0,06	
15.06.2005					< 0,16
11.08.2005				97	
14.09.2005	0,83	77	3,0	25	
29.09.2006		33			
13.10.2005	0,67	36	0,61	36	< 0,16
10.11.2005		28		4,5	1,6

sediment were expected to be better adapted. This could be explained by the higher heterotrophic plate count in the “unexposed” batches as seen in figure 2. Figure 3 and 4 show the degradation and heterotrophic growth in batches inoculated with material from the rapid sand filter at Sjælsø water treatment plant 2. There is not significant difference between the results from 2004 and 2005, showing that the experimental conditions were similar in the two sets of experiments. It can be concluded from the experiments, that the bacterial communities at the Arrenæs AR pilot plant maintain their ability to degrade microcystins during the winter. This strongly indicates that the microcystins will not break through when they appear in the spring.

The analyses of the algal pigments showed that the biomass varied much over the sampling period from approximately 4 µg chlorophyll A in July to 180 µg/l chlorophyll A in August. The distribution of the pigments showed that cyanobacteria were dominant in July and August. However, the pigment myxoxanthophyll, which indicates the presence of *Microcystis* sp., was only present in low concentration. Therefore only a minor part of the algae is considered to have the potential for production of microcystins.

The results of the toxin monitoring are shown in table 1 and table 2.

The HPLC analyses of water in Lake Arresø show a low presence of Microcystin LR from June to September. The toxins are found in the particulate fraction and are considered to be intracellular, i.e. inside the cyanobacteria. Most of the time the concentration is at or below the WHO drinking water guideline value, except in June where a concentration of 8,5 µg/l was recorded. The presence of microcystin in the infiltration basins seems to be lower than in Lake Arresø. This is consistent with the results of Christoffersen (2001), although she found that the toxins were present in October and November as well. Microcystin was found in one occasion in the tensiometer located approximately 1 m below the sediment surface at the same time it was found in solution in the infiltration basin, indicating that the microcystins may travel at least 1 meter through the sediments. In the extraction well (I1) located 25 m below terrain, microcystins could not be detected at any time.

Table 3: Concentration of faecal indicators in the sediment of the west-1 infiltration basin at the Arrenæs AR pilot plant. Sampled 10 october 2005. Numbers pr g. dry weight.

North end	Coliforms	Pres. *E. coli*	Enteroc.	HPC 22 °C	HPC 26 °C	Bacterioph.
Smutzdecke (1)	140	27	6	$1{,}5 \cdot 10^7$	$3{,}1 \cdot 10^6$	Present in 1,6 gram
Smutzdecke (2)	-	-	4	$1{,}4 \cdot 10^7$	$3{,}6 \cdot 10^6$	-
5 cm below sediment surface	24	3,4	3	$1{,}8 \cdot 10^7$	$6{,}0 \cdot 10^6$	n.m
40 cm below sediment surface	0,6	< 0,1	4	$1{,}8 \cdot 10^5$	$9{,}1 \cdot 10^4$	Present in 13 g
South end						
Smutzdecke	11	11	8	$3{,}3 \cdot 10^7$	$9{,}7 \cdot 10^6$	n.m
5 cm below sediment surface (1)	5,0	2	< 3	$2{,}3 \cdot 10^7$	$7{,}0 \cdot 10^6$	n.m
5 cm below sediment surface (2)	13	2	-	-	-	-
40 cm below sediment surface	5	0,7	< 3	$3{,}2 \cdot 10^6$	$9{,}7 \cdot 10^5$	n.m

The ELISA analyses give a picture that is very different from the HPLC analyses. High concentrations up to 97 µg/l was observed in the particulate fraction in the infiltration basin water and 1,6 µg/l was found in the tensiometer. It is believed, that the high concentrations are caused by interference from unknown compounds, since the HPLC analyses give very low results and the pigment analyses indicate that the presence of toxin producing cyanobacteria is low. The low concentrations in the tensiometer shows that the interfering compound is removed during infiltration as well. It is however advisable to identify the interfering parameter. Christoffersen (2001) has found a continuous presence of microcystins in the lake water and in the infiltrated water by ELISA with a lower detection limit. However, the concentrations she found were much lower than those found in this study.

1.6 Conclusion

The degradation studies have shown that the bacterial communities in the sediment of the infiltration basins at the Arrenæs AR Pilot Plant has a well adapted bacterial community also after the winter period, where there has been no or very little exposure to microcystin over a long period. Hence it can be anticipated that the risk of break through, when the toxins first occur in the spring, is very low. This is supported by the very low findings of toxins in the pore-water in this study as well as in the study carried out by Christoffersen (2001).

The monitoring program shows, a continuous presence of toxins in the particulate fraction in the lake water until October and a reduced occurrence in the infiltration basins although at low concentrations. After infiltration toxin was recorded in the 1 m tensiometer, whereas no toxins were detected 25 m below terrain.

2 ANALYSIS OF INDICATORS OF FAECAL CONTAMINATION

2.1 Introduction

Since there are outlets of treated waste water in the catchment area of Lake Arresø, faecal contamination is to be expected, and therefore of concern. To evaluate the penetration of bacteria and viruses, sediment samples from different depths were analysed for faecal indicators. The traditional faecal bacterial indicators were analysed as well as F-specific bacteriophages.

F-specific bacteriophages are bacterial viruses resembling human enteric viruses. Because of the similarities, the F-specific bacteriophages are used as an indicator for the presence of human viruses and to evaluate treatment technologies with respect to removal or inactivation of human viruses.

2.2 Methodology

Three sediment columns from the northern end and two sediments columns from the southern end of the west 1 infiltration basin were obtained by manually forcing an aluminium pipe with a diameter of 7,5 cm into the sediment. Sub samples were taken from the three depths of sediment columns and mixed into one composite sample from the north end and one composite sample from the south end. Coliforms and presumptive *E. coli* were analysed by MPN - method in MacConkey broth and verification by the indole test. Enterococci were analysed by the spread plate method on Slanetz and verified on bile esculin. Heterotrophic plate count was determined by the pour plate method on yeast extract and incubated at 22 °C and 36 °C after extraction by vigorously mixing sub samples in phosphate buffer on a wortex shaker. The F-specific bacteriophages were determined as absent/present using the overlay technique using *Salmonella typhimurium* strain WG49 as host. The results of the F-specific bacteriophages are preliminary results. Duplicate analyses were performed on selected samples.

2.3 Results and discussion

The results of the analyses are shown in table 3. It is seen that the heterotrophic plate count decreases between 1 and 2 orders of magnitude from the smutzdecke to 40 cm below the sediment surface. In the north end the coliforms and the presumptive *E. coli* are reduced more than two orders of magnitude whereas the enterococci are evenly distributed. The bacteriophages could be detected in a depth of 40 cm, however the results are preliminary. In the south end the enterococci can only be detected in the smutzdecke. The presumptive *E. coli* are also reduced significantly, whereas the coliforme bacteria are found at 40 cm.

In general there is a high reduction of the bacterial indicators in the upper 40 cm of the sediment. However, the results show that some coliforms can be expected in this depth. This is not surprising since the coliforms include several environmental species. In the north end, the enterococci are surprisingly more or less uniformly distributed in the sediment column. As with the coliforms, this could be explained by presence of environmental species, but it is more likely that it is due to either transport. However, the numbers are very low and are not of concern. The F-specific bacteriophages are also detected in the 40 cm sample. The results are preliminary and must be interpreted with caution. However, they indicate that the viruses can be transported to this depth.

3 REFERENCES:

Bourne DG, Jones GJ, Blakeley RL, Jones A, Negri AP, Riddles P. 1996. Enzymatic pathway for the bacterial degradation of the cyanobacterial cyclic peptide toxin microcystin-LR. Appl Environ Microbiol;62:4086-4094.

Christoffersen K, Lyck S, Windng A. 2002. Microbial activity and bacterial community structure during degradation of microcystins. Aquat Microb Ecol, 27:125-136.

Christoffersen, K. 2001. Undersøgelser af microcystin I infiltreringsanlæg ved Arrenæs. Ferskvandsbiologisk Laboratorium. Københavns Universitet.

Chorus, I, Böttcher, G., Grützmacher, G., and Pawlitzky, E. 2004. Strategien zur Vermeidung des Vorkommens ausgewählter Algen- und Cyanobakterienmetabolite im Rohwasser Abschlußbericht Teilprojekt: Wirksamkeit der Infiltration/Bodenpassage für die Retention von Algen- und Cyanobakterienmetaboliten. Umweltbundesamt. FG Wasseraufbereitung

Fedorak PM, Huck PM. 1988 Microbial metabolism of cyanobacterial products, batch culture studies with applications to drinking water treatment. Water Res;22:1267-1277.

Holst T, Jørgensen NOG, Jørgensen C, Johansen A. 2003. Degradation of microcystin in sediments at oxic and anoxic, denitrifying conditions. Water Res;37:4748- 4760.

Hyenstrand P, Rohrlack T, Beattie KA, Metcalf JS, Codd GA, Christoffersen K. 2003. Laboratory studies of dissolved radiolabelled microcystin-LR in lake water. Water Res; 37:3299-3306.

Park H-D, Sasaki Y, Maruyama T, Yanagisawa E, Hiraishi A, Kato K. 2001. Degradation of the cyanobacterial hepatotoxin microcystin by a new bacterium isolated from a hypertrophic lake. Environ Toxicology;16:337-343

Saitou T, Sugiura N, Itayama T, Inamori Y, Matsumura M. 2002. Degradation of microcystin by biofilm in practical treatment facility. Water Sci Technol;46:237-244.

Chapter 8: Microbiological Barrier Efficiency at the Dösebacka Artificial Groundwater Recharge Plant

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Abstract: The objective of the ARTDEMO project has been to demonstrate a system for early warning based on on-line instrumentation of relevant parameters and information technology. The microbiological barrier efficiency is recognized to be an important parameter in the operation of waterworks. The barrier efficiency was studied at the Dösecka AR plant in Sweden. The plant consists of 9 infiltration ponds and 15 abstraction wells, producing 6000 m^3 per day for a population of about 25 000. The retention time in the aquifer is estimated to 6-60 days depending on abstraction well. Water samples were taken in one representative infiltration pond and in 4 abstraction wells twice a week for 4 weeks. The study was preceded by 34 days with bad raw water quality regarding indicator organisms for faecal contamination. The water samples were analysed for total Coliforms, E.coli, Enterococci and Cl.perfringens. The result showed that the microbiological barrier Dösebacka AR-plant at least had a 99.9% efficiency, which corresponds to a $3\log_{10}$ reduction.

1 INTRODUCTION

The provision of safe and high quality drinking water is essential and fundamental for having a high quality of life. However, the water resources in Europe are threatened by various sources of contamination. In context of this increasing contaminant pressure, there is an increasing requirement to develop concepts and technologies to create a basis for provision of safe and high quality drinking water (ARTDEMO DoW).

Traditionally, AR plants are operated based on measurements of water quality on a regular basis combined in many cases with real-time measurements of various flow-related parameters. However, water quality of surface waters changes rapidly posing various operational problems, due to the frequency and time lag in traditional laboratory based quality measurements. Consequently, the content of e.g. trace metals, micro organisms, and chemical contaminants can potentially be transported right through the system directly into the drinking water reservoirs or alternatively be accumulated in the aquifer, creating long-term problems (ARTDEMO DoW).

If a plant experiences short travel times of the water in the ground, it might be an idea to install an at-line microbiological detector (on-line does not exist today). However, the alternative of using an optimised programme for manually taken samples might also prove to be sufficient. The choice depends on the plants reduction efficiency, which has to be tested for each plant. In Dösebacka the reduction efficiency of pathogen micro organism is not quantified and the routine manual sampling does not indicate any major problems with micro organisms. In the ARTDEMO-project one important task has been the identification of critical parameters and the remediation capacity of the AR production line. The objective of this study was to identify the microbiological barrier efficiency at the Dösebacka Artificial Groundwater Recharge Plant in order to define the requirements for the management plan.

The Dösebacka Artificial Recharge plant is located in south-west of Sweden, close to Gothenburg. The plant is the water supply for 25 000 people in the community of Kungälv. The plant produces approximately 6000 m^3/d and consist of 9 infiltration ponds and 15 abstraction wells. The detention time for the water in the aquifer has been estimated to vary between 6 to 60 days depending on abstraction well. The water is pre-treated with sedimentation and the drinking water is pH-adjusted with NaOH for corrosion prevention in the distribution net. Two wells that abstract water with a higher turbidity and organic content are post treated with chemical precipitation using aluminium sulphate. There is a disinfection equipment available for the drinking water in case of an emergency with microbiological contamination but it is rarely used. Lundh (2005) in this final report gives more details about the Dösebacka plant.

2 METHOD

The pathogens (infectious microorganisms) were simulated with traditional indicator bacteria of faecal contamination; total Coliforms, E.coli, Enterococci and Clostridium perfringens. The methods for the different analyses are listed in Table 1 (MF=Membrane filtration, MPN=Most Probable Number):

Table 1. The methods for the different analyses. (MF=Membrane filtration, MPN=Most Probable Number, CFU=colony forming unit, No= Number):

Analysis	**Detection level**	**Method**
Coliforms 35ºC MPN	<1 No/100 ml	Colilert18 (Manufacturer: IDEXX)
E.coli 35ºC MPN	<1 No/100 ml	Colilert 18 (Manufacturer: IDEXX)
Coliforms 35ºC MF	<1CFU/100 ml	SS 0281672
E.coli 44ºC MF	<1 CFU/100 ml	SS 0281672 mod
Enterococci 35ºC MF	<1 CFU/100 ml	SS EN ISO 78992 utg 1
Cl.perfringens (pres) MF	<1 CFU/100 ml	ISO/CD 64612 021220

The Colilert is not an approved drinking water method in Sweden, and a national study (National Food Administration Dnr2738/03 Saknr4164 and 2741/03) has indicated that Colilert gives higher Coliform counts and lower E. coli counts compared to the standard method. . As the method has been used extensively in Gothenburg with a good correlation for E.coli, was Colilert used for the first analyses 2004-02-04. The standard method (MF) was used thereafter when the search for a possible breakthrough in the aquifer made it necessary to increase the volume of water to be analysed. The standard method requires 100 ml but the volume was increased up to 2500 ml in an attempt to find bacteria. This approach also decreased the detection level to a minimum of 0.04 CFU per 100 ml, which improved the possibility to find bacteria in a potential breakthrough.

Samples were taken twice a week in infiltration pond F and in 4 abstraction wells; 1, 3, 7, 9, for four weeks in February 2004. The study was preceded by about 34 days of bad water quality, regarding the microbiological aspect. The levels of bacteria were as high as the maximum of a variation in Göta Älv during a typical normal year. Data from Lärjeholm (GÄL) and Southern Nol (S.Nol), measured by the Gothenburg Water and Wastewater Works, were studied in order to verify that the quality indeed had been bad before and during the study and that there were at direct correlation between the levels in Lärjeholm, the Göta Älv just outside Dösebacka (S.Nol) and infiltration pond F at the Dösebacka plant.

In order to detect if any major breakthroughs of bacteria occurred during a year, and to roughly estimate a general directive reduction of bacteria, were measurements performed once a month during 2003-2004 (Lundh *et al* 2005) The samples were taken by the operational staff in Dösebacka and analysed by Alcontrol AB in Uddevalla, Sweden.

The detention time (travel time) for the subsurface water transport is estimated to vary in Dösebacka between 6 days in abstraction well 9 to approximately 60 days in others (Lundh *et al*, 2005). Therefore the period of 60 days from the first of January to last of February 2004, when the study was over, was considered to be long enough to detect a possible breakthrough due to the observed levels of bacteria in Göta Älv.

Abstraction wells for the study were chosen to represents different detention time (well 9 generates short detention time), different areas of the plant, different water characteristics (well 7 has problems with chloride, manganese and iron) and different locations in relation to the river Göta Älv (well 1 and 9 is located farer away from the river than 3 and 7). Infiltration pond F was chosen to represent all ponds and is located in the middle of the chain of ponds (nine in total). Pond F is also the pond that delivers water to GRP 9 and perhaps also to well 7 (not established) and was thus a direct observation for 9 and 7 in the study.

The log reduction in the aquifer, meaning between basin F and the observed wells, was calculated as (negative sign to make the reduction positive):

$$\log_{10} \text{ reduction} = -\text{Log}_{10}(C/C_0) \qquad [-]$$

where C is the measured concentration in a specific well in CFU or No per water volume, C_0 is the initial concentration in pond F in CFU or No per water volume.

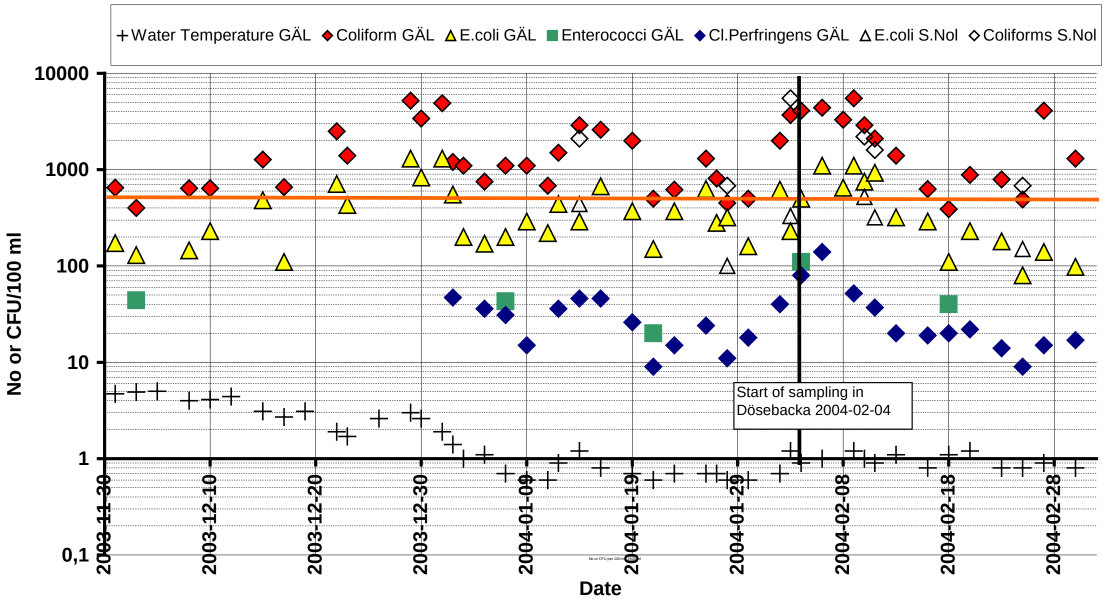

Figure 1. Levels of indicator bacteria in the river Göta Älv in Lärjeholm (GÄL) and at Southern Nol (S.Nol) for the relevant period. S.Nol is located across Göta Älv, just opposite the water intake to the Dösebacka plant.

3 RESULTS AND DISCUSSION

It was important to determine if the analysis of the water quality in Göta Älv before and under the study could be based on data from Lärjeholm that had a frequency of sampling that made a reliable analysis possible. The result (Fig 1) show that there existed a good correlation between the concentration of bacteria in Lärjeholm and the levels in S.Nol, that is located just opposite Dösebacka and represents the raw water quality at Dösebacka. The result show that the concentrations of Coliforms and E.coli bacteria were the same in both Lärjeholm and S.Nol and that the variation at the two locations seemed to have followed each other in real time. The response to an increasing concentration seem to have been immediate for both S.Nol and Lärjeholm; when an increase was detected in Lärjeholm, an increase also occurred in S.Nol. Therefore it should be safe to use the data from Lärjeholm when analysing the concentration prior and under the study in Göta Älv just outside Dösebacka.

The result (Fig.1) verify that the historical raw water quality was clearly worse than average sincefirst of January, even though there existed a variation. Increased levels of E.coli during the observed period, would have initiated the closing of the intake to Gothenburg Waterworks at least three or four times due to microbiological contamination.

Fig.2 show a good correlation between basin F and S.Nol and that the variation was the same in real time for both locations. There was a delay of 1-2 days due to the transport from the intake to Dösebacka to the infiltration pond, but this was not significant to the study.

No bacteria was detected in the abstraction wells except for one occasion in well 3 in 2004-02-09, when 0.08 Cl.perfringens per 100 ml was detected (1 bacteria per 2500 ml sampled water). During a study of the water quality in all wells in 2003/2004 (Table 2), well 3 experienced 1

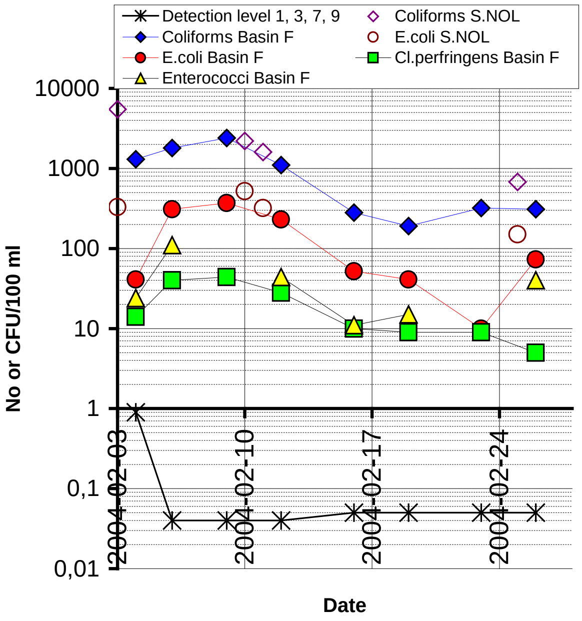

Figure 2. The concentration of the studied bacteria in basin F and the correlation to measurements in S.Nol. No bacteria was detected in the wells and the detection limit for the analysis of bacteria concentration in the abstraction wells are shown. 1, 3, 7 and 9 refers to abstraction well.

Coliform bacteria per 100 ml at two occasions. If these occasions were breakthroughs of bacteria from the infiltration pond was hard to tell. The same study imply a reduction of bacteria of 90%-99% (roughly 1-2 $\log_{10}$ reduction) at Dösebacka, based on the analyses of Coliform, E.coli and micro organisms 3d.

Table 2. Bacteria concentration from 4-9 samples (interval of one month between the samples) in Dösebacka over 2003 to 2004 (* detection level <2 cfu/100 ml) (From Lundh et al, 2005).

	Unit	Göta Älv	Pond A	Well 1	Well 3	Well 7	Well 9	Drink W.
Microorganisms, 22°C 3d	cfu/ml	1400	>2400	95 - 100	0 - 10.0	0 - 10.0	2.5 - 10.0	5.5 - 5.8
Coliform bacteria 35°	cfu/100ml	>340	>350	0 - 1.0	0.22 - 1.0	0 - 1.0	0 - 1.1*	0 - 1.0
E.coli	cfu/100ml	>46	>38	0 - 1.0	0 - 1.0	0 - 1.0	0 - 1.1*	0 - 1.0

Comparing the concentration of bacteria in basin F and the detection level in Fig.2, generates a $\log_{10}$ reduction between 3-4.7 calculated as the difference between the observed maximum in the infiltration pond and the detection limit or the single detections (Table 3). As there were so few detections of bacteria in the wells it has been difficult to quantify the barrier capacity and the experienced values should be considered as minimum values.

Table 3. Observed Log_{10} reduction in the study.

	Log_{10} reduction
Coliform bacteria	4.7
E.coli	3.9
Enterococci	3.4
Cl.perfringens	3.0

E.coli is known to die off rather rapidly and coliforms are found and proliferate in the environment (Water Quality and Treatment, p 2.15) and could thus exist naturally in the wells. However, total coliforms is professionally used to assess water treatment efficiency and the fact that coliform bacteria was not detected in the study makes the results more believable – the high concentration of bacteria observed in the beginning of the period of bad quality do not seem to have breached through the aquifer.

It is not possible to differentiate between die off and sorption as reduction mechanisms. Enterococci or Cl.perfringens, that are more persistent than Coliform and E.coli, were found only at one occasion and in a very low concentration This ought to imply that, regardless of mechanism, a general $\log_{10}$ reduction of about 3 (99.9% reduction) is valid for the Dösebacka plant and might be even higher for certain pathogens, which is indicated by the higher reduction of coliforms. The reduction could also be less for the same reason; the one indication in well 3 of one of the persistent organism could imply that pathogens that are more persistent than Cl.perfringens and Enterococci, might be less reduced. However, this requires more specific studies with other tracer organisms.

Even though the period of four weeks of water sampling was considered as a sufficient observation period for he purpose of the study, the detention time in the subsurface has only been verified in well 9 while the others are estimated from temperature variations in the groundwater (Lundh *et al*, 2005). Therefore there might exist longer transport times in the subsurface for the abstracted water in well 1, 3 and 7. The longer the transport in soil, however, the lower the risk of breakthrough, which makes this aspect less important.

Finally, it should be pointed out that the study has investigated the reduction of indicator organisms for faecal contamination, not any actual pathogen, which means that the reduction is only an indication of the pathogen reduction in Dösebacka, based on the assumption that the indicator organisms studied are behaving similar to the pathogens in die off and sorption.

4 CONCLUSIONS

The conclusion is that the microbiological barrier in the Dösebacka aquifer works relatively well with a efficiency of at least 99.9%. (3 $\log_{10}$ reduction). The study suggests that the plant is capable of handling variations in bacteria concentration in Göta Älv during a normal year. This suggests furthermore that alarms in a system for surveillance should regard 99.9% as an upper limit for an alert situation. That corresponds to a concentration of 999 E.coli per 100 ml in the infiltration pond if the limit for acceptable water quality for drinking water use,<1 CFU per 100 ml, is to be satisfied. However, the reduction is probably higher for those pathogens that resemble the behaviour and die off of coliforms.

5 ACKNOWLEDGEMENT

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6 REFERENCES

ARTDEMO DoW, Artificial Recharge Demonstration Project, Description of work – Annex I to contract no. EVK1-CT2002-00114

Lundh, M. (2005) *Description of the Dösebacka Artificial Groundwater Recharge Plant* . (This Final report)

Lundh, M., Jonasson, S.A., Jørgensen, N.O. and Johnson, M.D. (2005). *Hydrogeology and water treatment performance of the Dösebacka artificial recharge plant – the basis for an efficient system for early warning.* Kompetenzzenter Wasser Berlin,, In press for the proceedings of ISMAR2005, Berlin, June, 2005

SLVFS 2001:30, Livsmedelsverkets föreskrifter om dricksvatten; Swedish regulation on drinking water.

Water Quality & Treatment – A handbook of community water supplies. 5th Edition. Technical Editor: Raymond D. Letterman. AWWA. McGraw & Hill, Inc. ISBN 0-07-001659-3

Chapter 9: Investigation of Pathogen Reduction in Unsaturated Zone in Columns Using Bacteriophages MS-2 and ΦX174 as Model Organisms

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Abstract: A column experiment was performed by the Swedish partner in the EC-project ARTDEMO in order to measure the microbiological barrier efficiency in the unsaturated zone at artificial groundwater recharge. Material from the glacial Gråbodelta in western Sweden, by the lake Mjörn close to Gothenburg, was placed in four columns that were operated with 1, 2 (two columns) and 4 meters of unsaturated zone, and one column with 2 meters of saturated zone. The soil and hydrochemistry were characterised. Two pulse-response and one steady state experiments were performed with bacteriophages MS-2 and ΦX174. The first two had a short pulse of 40 min with peak responses that were used for the determination of the filter factor for each case. In order to check certain parameters and to validate the result from the first two experiments, the third experiment was performed with a 7-day pulse, in order to achieve a steady state with comparable concentration levels. The experiment showed that an unsaturated zone would have the barrier capacity of reducing virus, that correspond to the behaviour of the bacteriophages MS-2 and ΦX175, by 0.73± 0.4 Log_{10}/m,.

1 INTRODUCTION

An increasing population with increasing demands on living standard in combination with societies need to cut costs, put great pressure on the drinking water treatment processes that are today in work or to be constructed. Thus the requirements for a safe drinking water are getting more and more rigorous. An important issue for the drinking water treatment profession is the prevention of contamination of pathogenic microorganisms in the drinking water. In the preface to the Guidelines for drinking water quality (WHO 2004) it is stated that “Experience has shown that microbial hazards continue to be the primary concern in both developing and developed countries. Experience has also shown that the value of a systematic approach towards securing microbial safety”. In e.g. Sweden, 142 water related outbreaks have been reported between 1980-2004 with a total of 63 000 cases of infection. In average 1 outbreak per year was reported with at least 1000 people that became ill (SMI). Diarrhoeal disease alone is responsible for the deaths of 1.8 million people worldwide every year (WHO 2004). It was estimated that 88% of that burden is attributable to unsafe water supply, sanitation and hygiene and that this mostly affected children in developing countries.

A natural reduction of microorganisms is achieved by treating the water with the method of artificial groundwater recharge, which is based on the ongoing re-cycle route of water where the water is naturally treated when passing the soil before becoming groundwater. But how efficient is the method? Traditionally, a groundwater is considered to be microbiologically safe if not contaminated in the vicinity of the well. In Sweden a detention time of 14 days is regarded as sufficient for the water to be considered a groundwater (A guide to the Swedish regulation on drinking water SLVSFS 2001:30) but it has become more common with artificial recharge plants where the water travels for a shorter time in the subsurface. Short detention time could inflict on the removal efficiency as the contact time with the aquifer material becomes less. The shortage of convenient geological formations in the west part of Sweden, e.g., requires that the remaining formation is exposed to a high hydraulic loading which renders the water a shorter detention time. WHO (2004) recommends a strict Log_{10}-reduction of 5 to 6 for rotavirus if there are 10 organisms per litre in the raw water. Consequently, there is a need for more information on the reduction efficiency for all of the processes we use in the treatment of raw water to become drinking water in order to design and operate plants that ensure the safety of the consumer.

In artificial groundwater recharge, there is an early reduction, often located to the initial first meters of subsurface transport (e.g. Pang et al 2003; Shijven 2001; Shijven et al 2000, Deborde et al 1999). Still, studies have reported on detection of indicator organism and pathogens 100 to 1000 m from the source (Pang et al 2003), depending on how coarse the soil was, water velocity in the subsurface, survival, initial concentration of infiltrate, dilution and dispersion. Protozoa and virus are of special interest because of their persistence in the soil. Several studies report on result that show that the unsaturated conditions in the soil seem to influence both removal and die off that contribute to the reduction of microorganisms (Stevik et al 2004, Jörgensen et al 2001, Leclerc et al 2000, Yin et al 2000, Chu et al 2003, WHO 2004). What mechanisms that work in the unsaturated zone are still to be revealed but theories exist on the air-water interface, a shorter distance to the grain media surface and favourable conditions for bacteria to degrade organic matter and microorganisms.

This paper is the presentation of a column experiment that was performed in Gothenburg, Sweden within the EC-project ARTDEMO (EVK1-CT-2002-00114). The objective of the study was to investigate the reduction capacity for virus, simulated with bacteriophags MS-2 and ΦX174 (or simplified as X174 in tables and diagrams), in material from west-Swedish typical glacial deposits for infiltration purposes in order to assess the microbiological barrier efficiency in the unsaturated zone.

2 METHOD

The investigation was performed in five columns in total; four columns with different depth of unsaturated zone; 1, 2 and 4 m, and one column with 2 m saturated zone (Figure 1). The columns were studied with pulse-response experiments by amending the bacteriophages MS-2 and ΦX174, as model virus. The columns were operated with a flow of 25 ml/min, corresponding to an infiltration rate (hydraulic surface loading) of 0.5 m/d. Three experiments were performed Nov/Dec 2004, Feb/Apr and May/Jul 2005. In the first two experiments the columns were amended, during 40 min, with a solution with a concentration of 1.0 x 10^8 pfu/ml of ΦX174 and 1.0 x 10^{10} pfu/ml of MS-2 for period 1 and 1.4 x 10^8 pfu/ml of ΦX174 and 2.0 x 10^8 pfu/ml of MS-2 for experiment 2. Sampling was planned so that the response; incline, peak and decline, was monitored for each column. To learn about the hydraulic retention time (HRT), pulse-response investigations with NaCl were performed (Lundh *et al*), see Table 3. The result from the phage experiments are referred to the HRT when 50% of the recovered NaCl tracer had been detected; t(50%) or length of unsaturated or saturated

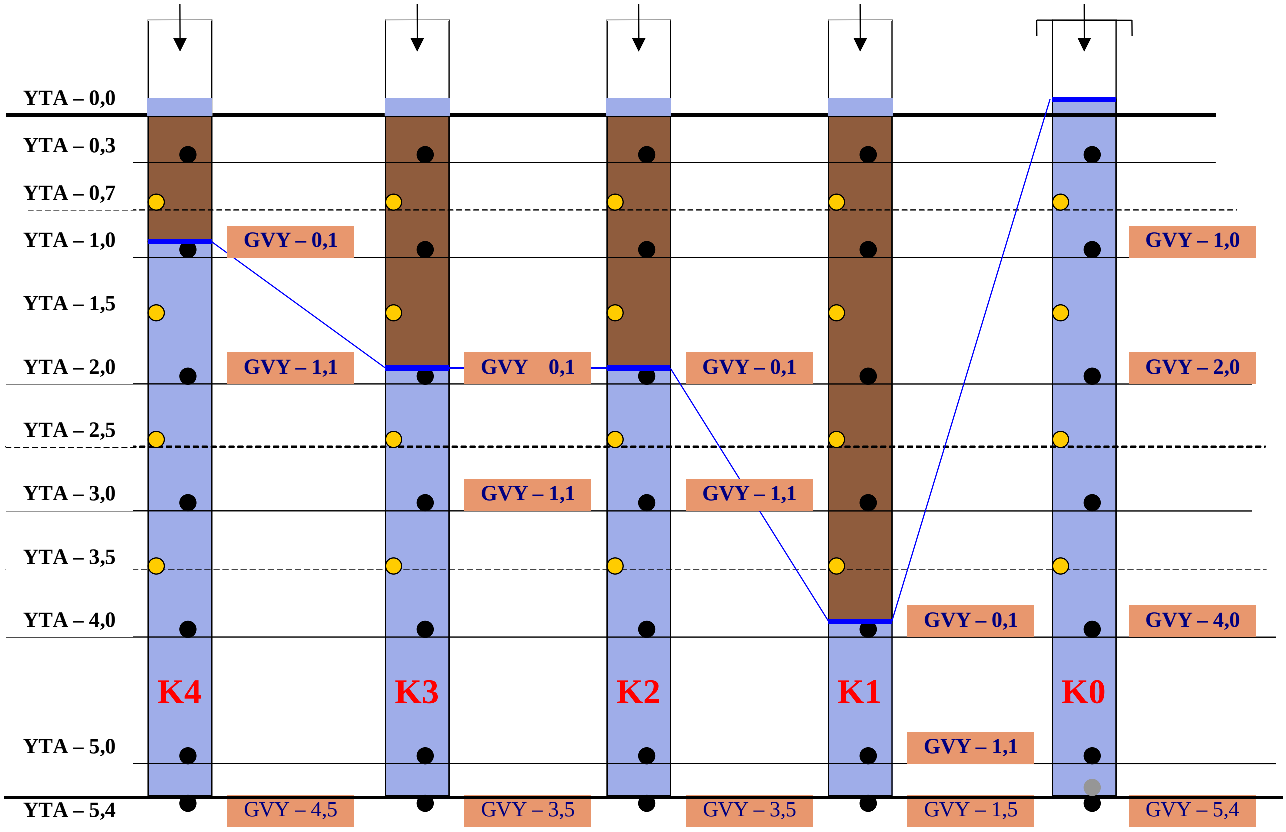

Figure 1. The columns. The sampling points are labelled with the distance (in meters) from the groundwater table (GVY –X) or from the surface of the filter bed (YTA-X) depending on the objective of the specific investigation. K0 is completely saturated. In this study samples were taken in GVY-0,1 for K1 to K4 and GVY-2.0 for the saturated column K0.

zone.

After experiment 1 and 2 the question was if the maximum peak level had been reached, i.e. if the pulse had been long enough for the response to reach a steady state level before wearing off. Moreover, the experiment 2 had shown some discrepancy regarding the mass balance between added and recovered mass (amount of total plaque forming units), indicating a higher recovery than added, which could possibly be due to a high concentration of organic matter (the broth for propagation of bacteriophages) or ionic strength (for the destruction of host bacteria to release the phages) (Lundh *et al*) in the added mixture with phages. This is, however, not further elaborated in this paper.

The aim of the study was to investigate if an identical pulse in all columns would generate a response that would only depend on the depth of zone, providing the same material and packing in all columns. The reduction efficiency was calculated from the relative comparison of the maximum concentration peak of each columns, experiment and organism, generating a log reduction per meter soil, and not on the difference between initial pulse concentration and peak level. In interpreting the result this way the relative difference between peak level for each columns, consequently, becomes more important than the pulse concentration relative to a presumed reached maximum peak level in the effluent. The procedure requires that the same pulse was distributed to all columns from the same batch in real time. The approach thus makes the pulse variance less important; the pulse, being the same for all columns, generates the relative difference in response in the columns.

So, the hesitance regarding the reached steady state was estimated to be of a minor importance for the calculations. However, the approach had to be tested and this motivated an additional experiment with a prolonged pulse in order to reach a steady state to check the reduction achieved with experiment 1 and 2. The mixture, with a concentration of MS-2 and ΦX174 at 10^5 –10^6 pfu/ml was added for 7 days. It was difficult to achieve the same concentration as in experiment 1 and 2 and a more diluted concentration had to be produced. On the other hand, a test with a lower concentration had the advantage of providing an investigation of the result with regard to dependence of added concentration.

3 STUDIED MICROORGANISMS

There are more than several hundreds of species of virus identified in human faeces. Some of them exist in such concentrations that they can infect humans. The most important of them are Hepatitis A and E (HAV/HEV), caliciviruses (including Norwalk virus), rotaviruses and astroviruses (Water Quality&Treatment) Virus has a size of about 20-90 nm and are much smaller than bacteria and protozoa. They only reproduce within other living cells and are without exception intracellular parasites. Virus is different to living cells in three ways; their simple non-cellular construction, the absence of either RNA or DNA and the incapability of reproducing without a host. Because a virus is not consider to live, the die off is referred to as inactivation which is correlated to the inability of infecting due to the destruction of the virus particle.

Methods of analysing specific faecal virus are complicated and expensive. Therefore bacteriophages are used as models in studies on virus reduction. A bacteriophage (or just phage) is a virus that only infect bacteria and not humans. Phages are useful for the studies on the reduction efficiency of different water treatment processes; they are themselves virus, have the same size and the same resistance to disinfection and, finally and most importantly to this study, they seem to behave the same in soil (Leclerc et al 2000).

MS-2 is F^+-specific bacteriophages that are small, hexagonal capsomeres without tails. They are approximately 20–30 nm, containing single-stranded RNA and are referred to as FRNA coliphages (Leclerc et al 2000). Based on a review of studies on affinity to soil and comparison with pathogenic virus regarding inactivation rate Leclerc et al (2000) regard the MS-2 as a conservative microorganism for simulation of the reduction of pathogenic microorganisms from faecal origin. The bacteriophage ΦX174 was used to learn about the range of reduction. The phage has a higher iso-electrical pH than MS-2 which renders it other sorption characteristics.

The propagation and the analysis of water samples of the somatic bacteriophage ΦX174 and the F-RNA bacteriophage MS-2 were performed according to the ISO methods 10705-2 “Detection an enumeration of somatic coliphages” (International Organization for Standardization, 2002a) and ISO 10705-1 “Detection and enumeration of f-specific RNA bacteriophages” (International Organization for Standardization, 2002b).

4 MATHEMATICAL ANALYSIS OF THE DATA

The reduction was analysed by calculating the Log_{10} reduction for each column, giving the $\log_{10}$ reduction for the different settings regarding unsaturated and saturated zone:

Log reduction = $\text{Log}_{10} (C_{max}/C_0)$ [Eq1]

where C_{max}/C_0 is peak concentration of the response curve of the experiment divided with the pulse concentration. C_0 in this study was the maximum concentration of the pulse (Table 3), assumed to give the highest challenge to the material.

During the experiments the spiked concentration decreased due to inactivation of the phages in all experiments and to dilution problems in experiment 3. However, in order to make possible a comparison between the cases, the filter factor was used. If the Log_{10} removal is arranged against column or depth of unsaturated zone, the following expression is achieved, assuming there is a semi-logarithmic linear relationship between the depths :

$\text{Log}_{10} (C_{max}/C_0) = C_f$ x Length + Constant [Eq2]

for which the inclination, C_f, is the uncorrected, with regard to the dispersion in the water, filter constant with the unit Log_{10}/m or Log_{10}/h depending on the parameter set on the x-axis. The Constant is where the linear curve crosses the y-axis. The approach requires of course that the assumption that the relationship is linear is valid, which is probably not the case for a longer length of zone or a longer detention time (Schijvens 2001). In fact, there are trends in the result from this study that also suggest a non-linear relationship. However, if the study is focusing on the same length or detention time, within a reasonable range, the comparison could be based on a linear relationship in a semi-logarithmic graph. This approach also makes the experiment less influenced by variations in incoming concentration as long as all the cases have been spiked with the same solution.

The substance experience dispersion during the transport in the column and in order to be able to compare the result from the columns, the dispersion relationship had to be defined. Tracer experiments with NaCl were performed in all columns and the Log_{10} dilution was calculated with the Eq1 and 2, which produced a dilution factor C_d instead of a C_f. The actual filter factor F was then calculated by adjusting the inclination by $F=C_f - C_d$.

5 SOIL CHARACTERISTICS

The material was taken from the Gråbodelta in western Sweden. The material was analysed with laser beam analysis for the grains less than 2 mm. The result (Fig.2) show a d_{10} between 0.044 mm and 0.074 mm and a d_{60} between 0.210 and 0.500 mm, giving a d_{60}/d_{10} of about 6-7 (Fig. 2). However, about 18% of the material was greater than 2 mm and a complement sieve analysis, excluding the finer material <0.063 mm, displayed a d_{10} between 0.11 and 0.18 mm, and d_{60} between 0.46 0ch 0.86 mm giving d_{60}/d_{10} between 2.6 and 7.8. Common filter material in infiltration ponds in Sweden (Hansson 2000) has a distribution between 0.2-2.0 mm, with d_{10}= 0.35 +/- 0,03 mm and a d_{60}/d_{10}= 2.5 with a maximum 1% less than 0.2 mm. The clay content ($\leq$0.008 mm) according to a laser analysis was between 2 and 3%. The bulk density was measured to 1526 kg/m^3 and the specific yield in the column was estimated to 24% by draining one column (Rådmark and Svensson 2003). Rådmark and Svensson theoretically estimated the specific surface to be 1.23 x 10^5 to 2.51 x 10^5 m^2/m^3.

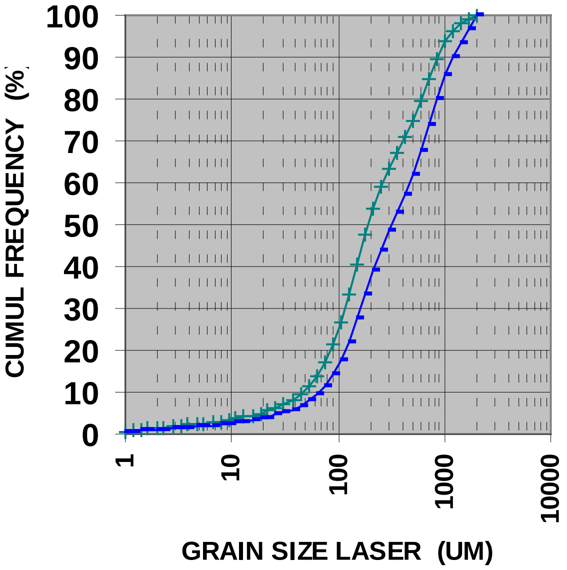

Figure 2. The grain size distribution of two samples from the column material by laser beam analysis

Geochemical data, analysed by KIWA from samples at Dösebacka during the ARTDEMO project, are compiled in Table 2 and 3. The Cation Exchange Capacity (CEC) was 12.81 meq/kg with the largest exchange for Ca followed by Mg. The organic content was low, only 0,03-0,06% (BOM). The mineral composition originates from gneiss and consisted of 40% Quartz, 27% Albite, 16% K-Feldspar, 9% Biotite and 6% Anortite.

6 WATER QUALITY

The raw water to the columns was taken from the lakes Delsjöarna. Analyses of the water is presented in Table 1, performed for a period before the experiments. The result presents an average temperature of about 13ºC, a low turbidity of about 1 FNU, a neutral pH around 7, a low salinity of about 11 mS/m, an alkalinity of about 0.3 mmol/l and a low hardness of about 10 mg/l.

Table 1. Physical and chemical analyses in raw water to the columns 2004-04-13 – 2005-09-14

Parameter	No of samples	Average	Median	Min	Max
Temperature (C)	64	12.6	16.0	2.9	20.5
Turbidity (FNU)	27	1.02	0.83	0.59	2.4
Colour (mg/l Pt)	1	30			
pH	55	7.1	7.1	6.8	7.4
EC (mS/m)	37	11.1	11.2	10.2	14.5
Alk (mmol/l)	23	0.3	0.3	0.21	0.34
Hardness (mg/l)	1	9.9			

The result of the temperature was a bit misleading as the columns were located indoors and did not experience the variations normally existing outside. Thus the temperature in the water distributed to the columns became warmer in the columns, than indicated in the Table 3. The temperature measurements after the passage in the columns ranged from 16ºC to 22ºC (Table 4).

Analyses of the water after the passage in the columns show that the turbidity was much higher than in the raw water. This was probably due to fines of the material that escape the column in the effluent. This was also seen in the analysis colour which had very high levels (not presented here). The salinity did not change, indicating that the contribution of ions was low. Also the alkalinity and the hardness was unchanged, indicating that the material in the columns were conservative for the hydrochemistry in the raw water.

The organic content in the raw water was low (COD_{Mn} =4-5 mg/l water) but there was observed a significant reduction, about 60%, of organic matter in the columns (Table 5), which would indicate a material with an active sorption capacity for organic material and thus probably for microorganisms.

During the experiments the salinity and content of the organic matter increased dramatically. In experiment 1 the organic content in the pulse was COD_{Mn} =2900 mg /l and the UV absorbance was 1.78 ae/cm. The pH was 6.9 and the EC was 1348 mS/m. In experiment 2 the organic content in the pulse was COD_{Mn} =3400 mg /l and the UV absorbance was 8.9 ae/cm. The pH was 7 and the EC was 5500 mS/m. In experiment 3 the organic content in the pulse was in average COD_{Mn} =15 mg /l and TOC =20 mg /l and the UV absorbance was 0.15 ae/cm. The pH was approximately 6.8 and the EC was in average 36 mS/m. COD_{Mn}/TOC was in average 0.8 and UV_{254}/TOC was 0.8 a.e. x l/(mg x m). In the experiments it was observed that the pH decreased significantly during the pulse. In experiment 3 the pH reached just below 6. After the experiments the pH was recovered up towards 7. The organic matter in the experiments seem to have had a character that did not resemble the organic matter in raw water very much as the UV_{254}/TOC was about 2 for the raw water while only 0.8 in the experiment pulse.

Table 2. Geochemistry of the soil from two samples of the column material

	Mean Grain Size	Clay Size Fraction	pH-H_2O	EC-H_2O	BOM	PYR-C	PYR-N	$CaCO_3$	S_{tot}	FeS_2
Description	(<2 mm)	laser≤8um		20 ºC		C-org	N-total			Max
Unit	um	%	-	uS/cm	%	%	mg / kg	%	mg / kg	mg / kg
Sample 1	202	3.08	6.80	46	0.03	0.00	15	0.229	61	112
Sample 2	299	2.27	6.44	47	0.06	0.02	5	0.144	20	33

Table 3. Cation exchange capacity (CEC) and mineral composition of the soil

	CEC	Na	K	Ca	Mg	Fe	Ca- Silicate	Na- Silicate	K- Silicate	Mg- Silicate	Quartz/ Opal
Description	ACTUAL	EXCH	EXCH	EXCH	EXCH	EXCH	ANORTITE	ALBITE	K-FELDSPAR	BIOTITE	SiO2
Unit	meq / kg	meq / kg	meq / kg	meq / kg	meq / kg	meq / kg	%	%	%	%	%
Sample 1	12.81	0.12	0.09	9.81	2.75	0.024	5.66	27.08	16.35	9.03	40.14
Sample 2	9.95	0.09	0.07	7.62	2.14	0.019	5.70	26.14	16.07	8.70	41.83

Table 4. Physical-Chemical analyses of filtrate (average from 1, 2 and 4 m) from the columns during 2004-06-08 to 2004-10-27, which is before the experiments were performed.

Parameter	No of samples	Saturation	Average	Median	Min	Max
Temperature (C)	65	Unsaturated	19.6	19.2	16.5	22.5
	34	Saturated	19.8	20	18	22
Turbidity (FNU)	56	Unsaturated	52.6	60	7.3	105
	33	Saturated	77.2	72	22	140
pH	66	Unsaturated	7.0	7.0	6.7	7.6
	35	Saturated	6.9	6.9	6.7	7.1
EC (mS/m)	60	Unsaturated	11.4	11.5	10.7	12.7
	34	Saturated	11.5	11.4	11.1	11.9
Alk (mmol/l)	20	Unsaturated	0.31	0.31	0.26	0.33
	11	Saturated	0.31	0.31	0.28	0.33
Hardness (mg/l)	20	Unsaturated	9.6	9.7	8.1	10.1
	10	Saturated	9.5	9.5	8.6	9.9

Table 5. Median before experiments during period 2004-06-08 to 2004-10-27. Samples were taken according to a schedule every second week. Less samples were taken for saturated zone 1 and 4 m.

Column	Unsaturated zone (m)	HRT (h)	COD_{Mn} (mg O_2/l)	TOC (mg/l)	UV254 nm (ae/cm)
Raw water	0	0	4.3	4.4	0.116
K4	1	13	2.8	3.1	0.115
K3	2	20	2.5	2.7	0.093
K2	2	24	2.4	2.6	0.101
K1	4	44	1.6	2.1	0.053
	Saturated zone (m)				
K0	1	<39*	-	-	0.130
K0	2	39	2.8	2.8	0.094
K0	4	>39*	1.8	2.3	0.084

* Not measured

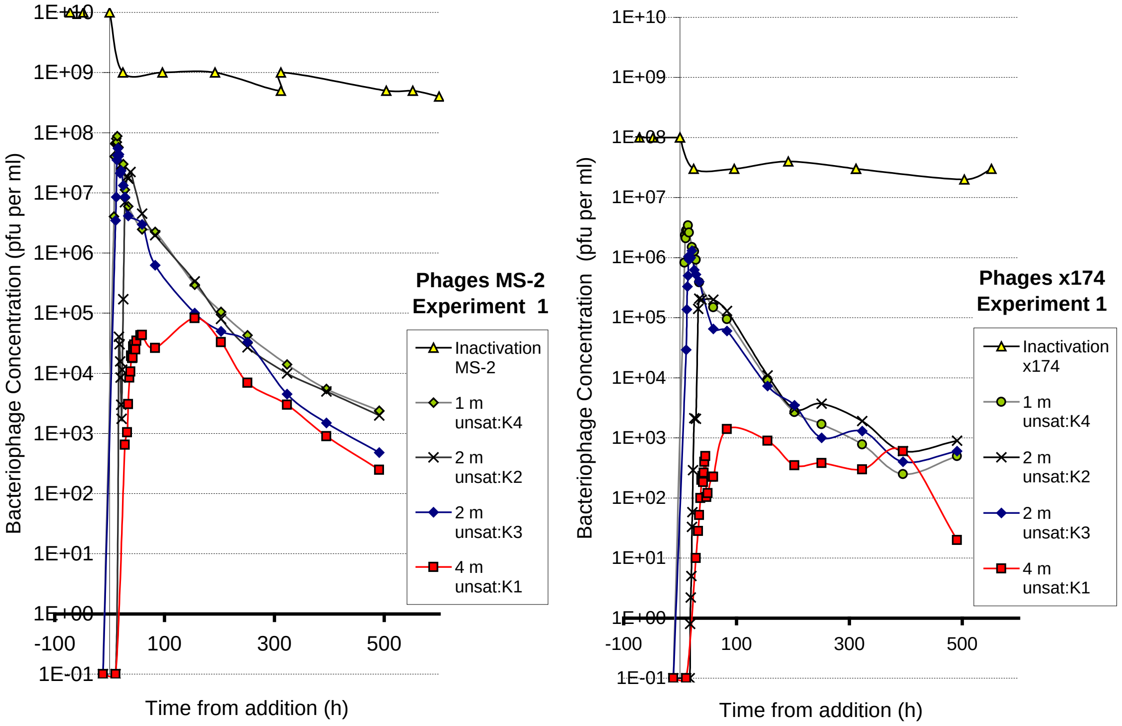

Figure 3. Response curves of bacteriophage X174 and MS-2 in pulse-response experiment 1. The pulse solution was added for 40 min.

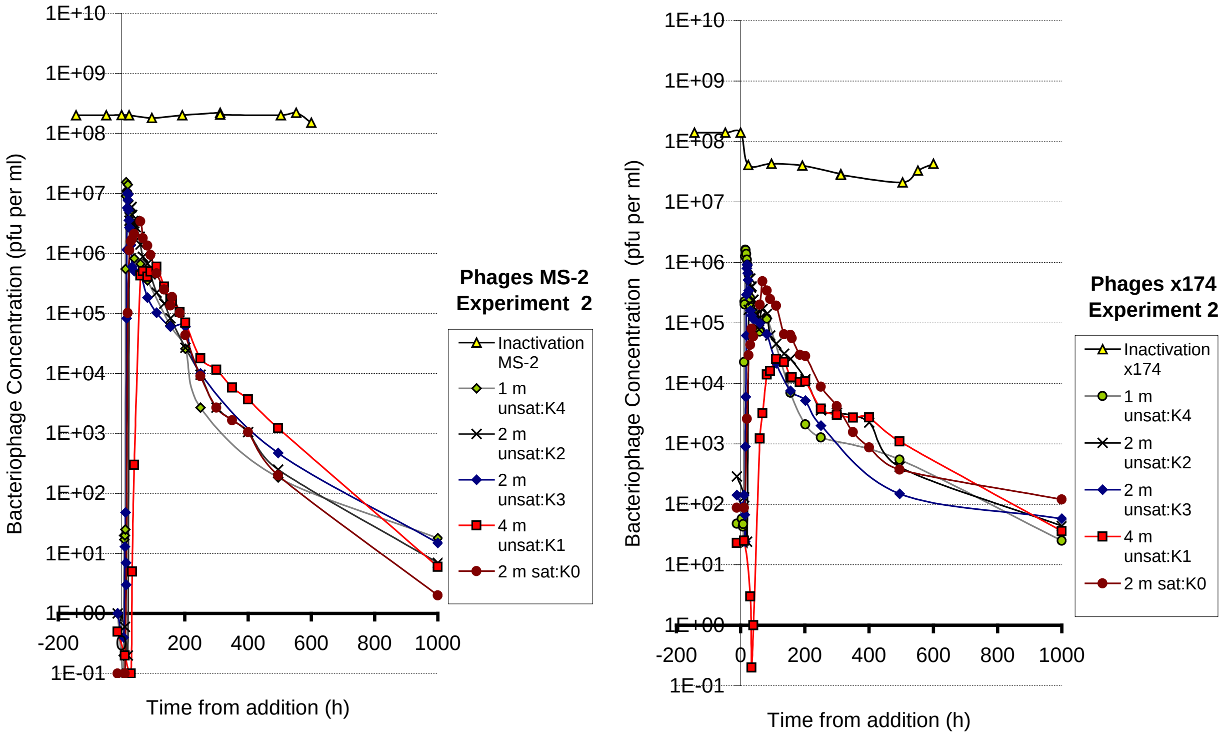

Figure 4. Response curves of bacteriophage X174 and MS-2 in pulse-response experiment 2. The pulse solution was added for 40 min.

Table 6. Peak concentration in experiment 1 and 2 and steady state concentrations in experiment 3. Rounded off to two numbers. High and low refers to highest and lowest detected concentration during steady state in experiment 3. Steady state occurs depending on the case specific HRT during the period 2005-05-26 –31 prior to the peak (Figure 6)

All concentrations in pfu/ml	Depth (m)	HRT t(50%) (h)	Experiment 1 ΦX174	Experiment 1 MS2	Experiment 2 ΦX174	Experiment 2 MS2	Experiment 3:High ΦX174	Experiment 3:Low ΦX174	Experiment 3:High MS2	Experiment 3:Low MS2
Pulse Conc.Max* (C_0)			1.0×10^8	1.0×10^{10}	1.4×10^8	2.0×10^8	7.0×10^5	7.0×10^5	3.6×10^6	3.6×10^6
Pulse Conc.Min*			3.0×10^7	1.0×10^9	2.1×10^7	1.5×10^8	1.5×10^5	1.5×10^5	6.4×10^4	6.4×10^4
K1: 4 m unsaturated	4	44	1.4×10^3	8.3×10^4	2.5×10^4	6.0×10^5	0.75	0.05	2.1×10^2	15
K2: 2 m unsaturated	2	24	2.1×10^5	2.2×10^7	5.4×10^5	6.0×10^6	0.67	0.05	8.2×10^4	2.3×10^4
K3: 2 m unsaturated	2	20	1.3×10^6	5.5×10^7	9.2×10^5	1.0×10^7	26.0	0.67	2.2×10^4	5.5×10^3
K4: 1 m unsaturated	1	13	3.4×10^6	8.7×10^7	1.6×10^6	1.5×10^7	1.1×10^2	30	3.9×10^5	7.7×10^4
K0: 2 m saturated	2	39	Failed**	Failed**	4.9×10^5	3.4×10^6	1.3×10^4	5.8×10^3	1.7×10^6	8.5×10^5

*Added maximum and minimum concentration are the maximum and minimum (due to die off, mixing etc) concentration for the pulse.

**The column K0 was clogged and produced a water flow too small to be compared with the other columns..

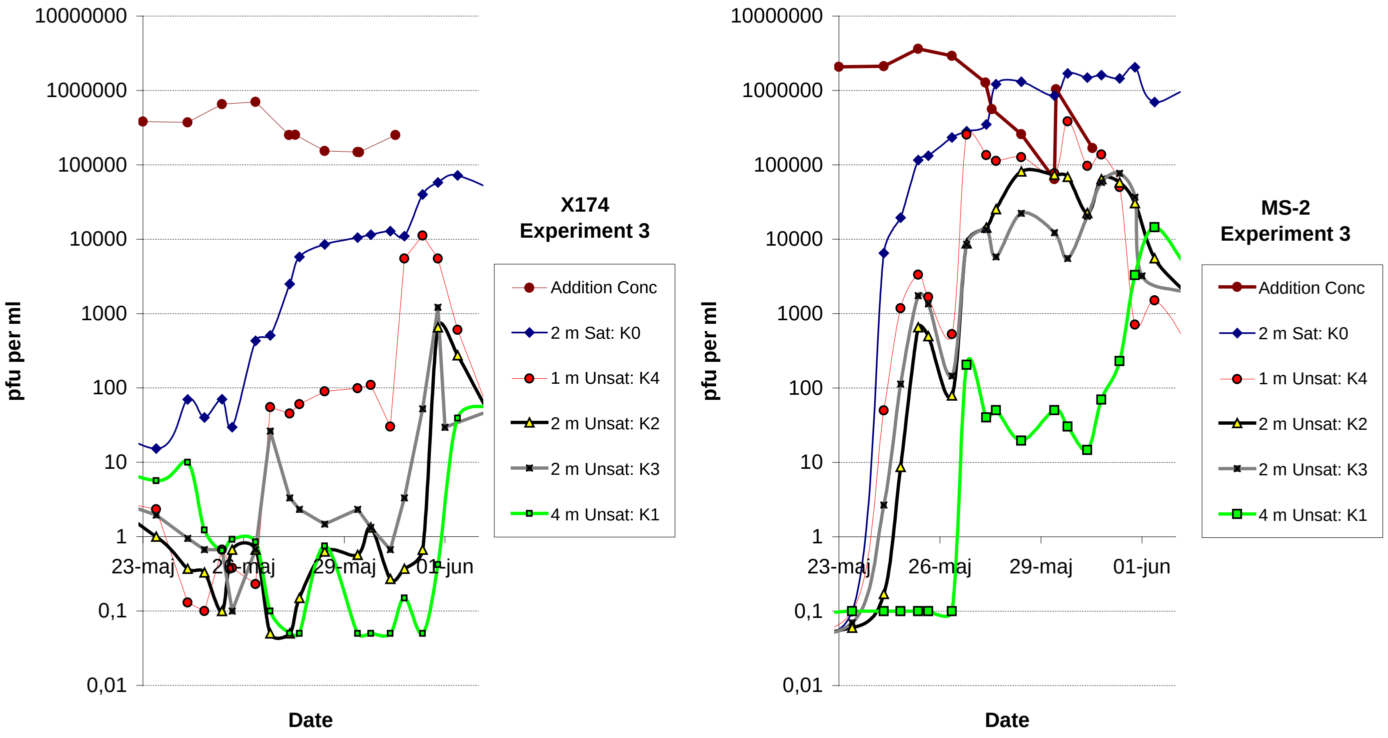

Figure 5. Effluent concentration from the columns in addition experiment 3; continuous addition for 7 days to achieve steady state. K0 is 2 m saturated zone, K1 is 4 m unsaturated zone, K2 and K3 are 2 m unsaturated zone and K4 is 1 m unsaturated zone. The detection limit varied between <0.03 to <0.1 depending analysis procedure. A detection = detection limit (e.g. 0.1 or <0.1) is not distinguished in the diagram. The detection level was between <0.1 and <0.04 pfu/ml.

Table 7. Linear relationships (regression analysis) in a semi-logarithmic graph based on the Log$_{10}$ reduction for each column and bacteriophage

Experiment (Line colour in Fig. 6)	**Experiment Type**	**y Log$_{10}$(C$_{max}$/C$_0$)**	**R2**	**C$_f$ Log$_{10}$/m**	**F =C$_f$-C$_d$ Log$_{10}$/m**
1 MS-2 (Blue)	Pulse response	1.0717x + 0.602	0.93	1.07	0.90
1 ΦX174 (Red)	Pulse response	1.163x + 0.1045	0.94	1.16	0.99
2 MS-2 (Turquoise)	Pulse response	0.4872x + 0.5197	0.96	0.49	0.32
2 ΦX174 (Purple)	Pulse response	0.6275x + 1.1571	0.96	0.63	0.46
3:1 MS-2 (Green)	Steady state	1.1056x - 0.217	0.97	1.11	0.94
3:2 MS-2 (Yellow)	Steady state	1.2781x + 0.1458	0.96	1.28	1.11
3:1 ΦX174 (Black)	Steady state	0.6488x + 3.5953	0.54	0.65	0.48
3:2 ΦX174 (Light blue)	Steady state	0.7904x + 4.392	0.57	0.79	0.62

					Filter Factor F$_f$ Log$_{10}$/m		
Dispersion exper.		**y (Log$_{10}$(C$_{max}$/C$_0$))**	**R2**	**C$_d$ (Log$_{10}$/m)**	**min**	**average**	**max**
NaCl (Grey)	Pulse	0.1749x + 0.7426	0.85	0.17	0.32	0.73	1.11

7 RESULT AND DISCUSSION

The result are presented in figure 3, 4 and 5. The diagrams gives a overview of the result and a more detailed analysis is given by Lundh *et al*, which the following presentation is based on.

The response curves for experiment 1 and 2 indicate a reduction of concentration (phage number) for all columns, observed as the difference between added concentration and peak. The highest reduction was achieved for column 1 which had the deepest unsaturated zone (4 m). In experiment 1 the saturated column K0 failed to work due to clogging. In experiment 2 the 2-m saturated zone (K0) showed a similar reduction of phages as 1 and 2 meter of unsaturated zone but a lesser reduction than the 4-m unsaturated column. The reduction in the 4-m unsaturated case also seem to be lower in experiment 2, possibly due to a higher ionic strength in the pulse observed in experiment 2 (Lundh et al).

The pulse concentration was different between the experiments and was also varying in inactivation rate (Figure 3 and 4). The curve showing the inactivation (die off) of the phages, refers to the concentration control program of the phage inactivation in the pulse solution, covering a longer period than the 40 minutes of added pulse.

The calculations on reduction efficiency has been based on the relative comparison of the results from each column for each case, using the inclination of the relationship between the depth of unsaturated zone and the logarithmic of the relative concentration C$_{max}$/C$_0$, see “Mathematical Analysis of the Data”, for the calculation of the filter factor F**.** The peak concentration that was used for each case is compiled in Table 6. The information from experiment 3 was compared with experiment 1 and 2 with the same mathematical approach using the steady state levels for each column to calculate the filter factor F.

Experiment 3 showed distinct differences in the concentration of phages in the filtrate (Figure 5). The result also clearly show that the saturated 2-m case (K0) produced the highest concentration, up to 1-4 Log$_{10}$ higher than the corresponding 2-m unsaturated case. The results in experiment 3 also show that the reduction was improved with depth of unsaturated zone, with the 1-m unsaturated zone (K4) producing a higher concentration than the 2-m unsaturated cases (K2 and 3), which in turn were producing, in general, a higher concentration than the 4-m unsaturated zone (K1). The steady state levels are presented in Table 6 and the results from the calculation of the filter factor F are presented in Table 7.

The results from the calculations are presented in Figure 6. The average reduction efficiency, expressed as the filter factor was measured in the study to 0.73±0.4 Log$_{10}$/m. The reduction efficiency, shown as the inclination in Figure 6, in experiment 1 (0.90-0.99 Log$_{10}$/m), was higher than in experiment 2 (0.32-0.46 Log$_{10}$/m). It could possibly be explained by the organic matter and virus in the previous experiment 1 that might have occupied sorption sites before experiment 2, thus generating a lower efficiency in experiment 2. In both experiments, a lower efficiency in the reduction of the MS-2 was observed, which was expected because of the higher iso-electric point of the phage.

In experiment 3 the filter factor is lower for ΦX174 (0.48-0.62 Log$_{10}$/m) than for MS-2 (0.94-1.11 Log$_{10}$/m), even though a higher total reduction was achieved for ΦX174 (approx. 4-7

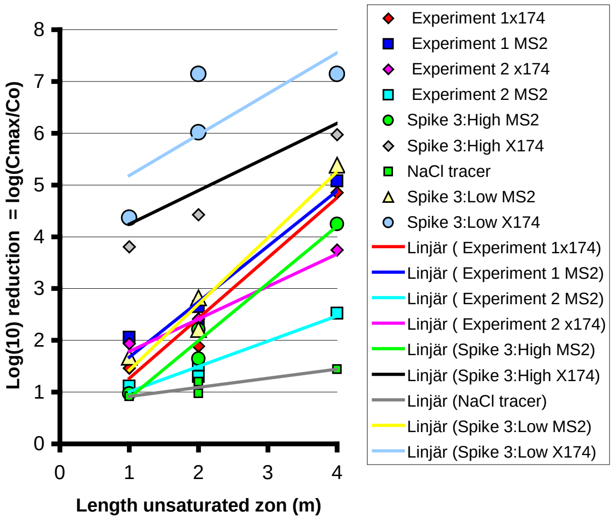

Figure 6. The semi-logarithmic linear Log_{10} reduction as a relationship of the length of unsaturated zone in meters.C_0 is the maximum concentration of the pulse (Table 3).

Log_{10}) compared with MS-2 (approx. 1-5 Log_{10}). The filter factor is based on the removal from 1 meter to 4 meter, thus it seems that ΦX174 was reduced more efficiently in the first meter and then to a lesser extent for an increasing depth of unsaturated zone. MS-2 seems to have been reduced more proportional to the depth. This phenomenon was not readily observed for experiment 1 and 2 when the concentration of phages, ionic strength and organic matter was 2-4 fold higher (2 to 4 log).

8 CONCLUSION

The experiment showed that an unsaturated zone, in material from the glacial delta deposit in Gråbo, would have the barrier capacity of reducing virus of 0.73± 0.4 Log_{10}/m. That would correspond to a total average barrier efficiency of about 1.5 Log_{10} for 2 meter and 3 Log_{10} for 4 m of unsaturated zone. In this study that would correspond to a hydraulic retention time of 44 hours.

The result is valid down to a depth 4 m of unsaturated zone in material and for conditions defined in this study. The result imply a linear behaviour in a semi-logarithmic graph but other studies have suggested a non-linear behaviour along with the subsurface transport in saturated zone, which makes a prognosis for the reduction in deeper zones difficult.

9 ACKNOWLEDGEMENT

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10 REFERENCES

A guide to the Swedish regulation on drinking water SLVFS 2001:30.

Chu Y., Jin Y., Baumann T., Yates M.V., 2003. Effect of Soil Properties on Saturated and Unsaturated Virus Transport through Columns. Journal of Environmental Quality 32, 2017–2025.

DeBorde D., Woessner W.W., Kiley Q.T., Ball P. 1999. Rapid transport of viruses in a floodplain aquifer, Water Research 33, 2229-2238

Hanson G., 2000. Konstgjord grundvattenbildning: 100-årig teknik inom svensk dricksvattenförsörjning, VA-forsk Rapport 2000-5.

Jin Y., Chu Y., Li Y., 2000. Virus removal and transport in saturated and unsaturated sand columns. Journal of Contaminant Hydrology 43, 111–128.

Jörgensen C., Peters J., Eschweiler B., 2001. Removal of pathogens and monitoring of microbial changes during artificial recharge. Artificial recharge of groundwater, EC project ENV4-CT95-0071 Final report, Kapitel 8.

Leclerc H., Edberg S., Pierzo, V., Delattre J.M., 2000. Bacteriophages as indicators of enteric viruses and public health risks in groundwater. Journal of Applied microbiology 88, 5-21.

Lundh et al. Reduction of Bacteriophages MS-2 and ΦX174 in Pilot-Scale Columns with Unsaturated Zone. Manuscript

Pang L., Close M., Goltz M., Sinton L., Davies H., Hall C., Stanton G., 2003. Estimation of setback distances based on transport of E.coli and F-RNA phages. Environment International 29, 907-921.

Rådmark and Svensson 2003. Reningspotentialen av främst organiskt material i omättad zon vid konstgjord grundvattenvbildning – Uppstart av kolonnförsök för att studera Gråbo isälvsdelta. Report 2003:21. Master Thesis at the WET, Chalmers Technical University, Sweden (in Swedish).

Schijven J.F., Medema G., Vogelaar A.J., Hassanizadeh S.M., 2000. Removal of microorganisms by deep well injection. Journal of Contaminant Hydrology 44, 301–327.

Schijven J.F., 2001. Virus removal from groundwater by soil passage, Modelling, field and laboratory experiments. Ponsen & Looijen B.V, Wageningen.

Smittskyddsinstitutet, 2005. http://www.smittskyddsinstitutet.se/SMItemplates/Article____2376.aspx (2005-08-12)

Stevik T-K., Aa K., Ausland G., Hanssen J.F., 2004. Retention and removal of pathogenic bacteria in wastewater percolating through porous media: a review. Water Research 38, 1355-1367.

Water Quality & Treatment – A Handbook of community water supplies. 5th Edition. AWWA. McGraw-Hill Handbooks. Ed: Raymond D Letterman. ISBN 0-07-001659-3.

WHO 2004. Guidelines for Drinking-Water Quality. Third Edition. Recommendations. World Health Organization, Geneva, ISBN 92 4 154638 7 (NLM Classification: WA 675).

Chapter 10: Sensors for Water Quality Monitoring in Recharge Plants

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Abstract: Increasing industrialisation and end-user demand is putting greater pressure on the water supplier with respect to the delivery of clean, high quality drinking water. Whilst there are many sophisticated laboratory-based techniques for analysing the composition of water samples, logistical and cost-constraints are leading to a greater interest in the deployment of simple, robust, reliable and low-cost tools within the water processing operation in order to identify the presence of pollutants at the earliest possible point within the process. This chapter reviews the current state of the art with respect to current at-line/on-line water quality monitoring as well as introducing a number of new and emerging approaches within this field, a number of which have been assessed and demonstrated within the ARTDEMO project.

1 INTRODUCTION

Man is making an ever increasing impact on the environment. In addition to the extra burden placed on the ecosphere by humankind's increasing demands for raw materials, there is an ever greater quantity of waste material being generated which must be appropriately treated before release into the environment. Coupled to this issue, is the increasing demand for clean, reliable and high quality water supplies. It is therefore evident that there is a rapidly growing demand for simple, robust and reliable tools capable of assessing drinking water quality and identifying and quantifying pollutants at all points in the supply stream. A vital component in the safeguarding of water supplies is the use of simple measurement tools that can be deployed where needed, in an at-line or on-line capacity, in the water supply chain.

The ideal measurement tool should be low-cost, robust and reliable, capable of performing the same analytical function without the need for any extensive sample treatment or operator intervention. Few current measurement tools fulfil these criteria. Sensor devices, in which the analyte is both' recognised' and quantified with minimal operator intervention and beginning to make an impact in the field. Ion Selective Electrodes (ISEs) are widely used in the field to measure critical factors such as pH or dissolved oxygen (DO), whilst other electrochemical probes can be used to determine general quality descriptors such as conductivity or oxidation-reduction potential (ORP). Certain simple optical probes may also be used to assess water quality.

However, in many cases, the nature, location and susceptibility of the water sample demands that the measurement methods used should be capable of determining more specific target species. In such cases, the information offered by simple probes is often insufficient, necessitating the requirement for new or improved measurement tools coupled to suitable sample preparation methodologies.

This chapter briefly reviews the main methods currently in use for the measurement of contaminants in water samples, before introducing some new or emerging concepts in the decentralised water quality analysis field, a number of which have been developed or examined within the ARTDEMO programme. During this review, reference is made to at-line, on-line and in-line measurement tools. On-line tools involve the use of a measurement probe or sensor that is able to collect information from the process stream and report the data in real, or near-real, time. In-line tools are those that are actually deployed within the process stream, whilst at-line tools are those in which the measurement is effected at the point at which the sample is collected, and as such may involve the intervention of an end-user with basic liquid handling skills.

2 GENERAL SENSORS AND MEASUREMENT DEVICES

2.1 Currently used methods

As with any water treatment process, the measurement of simple physical parameters can provide much useful information regarding water quality. Measurement processes need not just be confined to the liquid phase; assessment of solid and gas phases may also provide valuable information. In this section those sensors commonly used for monitoring of key water quality parameters are briefly described. A more detailed review is provided by Vanrolleghem and Lee (2003). Table 1 summarises those sensors/measurement devices routinely used to determine general on-line or at-line indicators of water quality.

Table 1: Sensors and measurement tools used for the monitoring of general water quality parameters.

Measurement device	Comment
Temperature	Typically measured using a thermistor
Liquid level	On/off level detection using floats with switches or conductivity switches; pressure/capacitance measurement, ultrasonic level detection
Gas/liquid flow	Liquid: Venturi measurement or electromagnetic sensors. Gas: rotameters
pH	pH electrodes with appropriate cleaning regimes (hydraulic, mechanical, chemical, ultrasonic)
Ion-selective electrodes (ISEs)	Electrochemical probes towards arrange of commonly encountered ions of water quality concern. See below.
Conductivity	Numerous commercial probes available
Biomass/suspended solids	Optical measurement (scattering of incident light). Measurement of light scattered by >90° is known as nephelometry). Ultrasound (measurement of differences in velocity of ultrasonic sound in suspension and particle-free suspension) Dielectric spectroscopy (Electric field applied to test suspension, resulting in movement of ions in solution and biological cells, leading to charge separation across cell membrane. Measurement of capacitance equates to biomass content).
Pressure transducer	Control/alarm functions
Calorimetry	Measure of biological activity by production of heat
Conductivity/resistivity	Measure of the ability for a sample to transport electricity and hence may be used as a general physico-chemical descriptor of sample properties.
Dissolved oxygen	For measurement of biochemical oxygen demand (BOD) and chemical oxygen demand (COD). Further details below.
Salinity	Measurement of total dissolved salt by conductimetry
Turbidity	Measurement of total suspended solids (TSS). May be determined by optical instrumentation or by eye. Related to chlorophyll and phytoplankton fluorescence.
Acoustic Doppler Velocimeter	Velocimeters using acoustic sensing techniques to measure flow in remote sampling volumes
ORP (Oxidation Reduction Potential)	Electrochemical-based measure of the oxidising or reducing potential of a sample (e.g. ORP electrodes are commonly used to determine the oxidizing ability of chlorine in swimming pools)
Total dissolved solids	Normally determined by gravimetric means (evaporation of sample and weighing of residue), but can be estimated by conductivity and/or filtration.
Respirometry	Primarily aimed at waste-treatment sector – involves measurement and interpretation of respiration rate of activated sludge.. Involves oxygen measurement (gas/liquid) + gas/liquid flow rate.

It should also be noted that many other sensor/measurement systems have been designed to determine water quality parameters as applied to the water treatment/processing industry. Many water treatment processes require the destruction of high levels of organic species, as is the case with anaerobic digestion, where the goal is to achieve the complete mineralization of organic material into gaseous products, such as CO_2, CH_4, H_2 and H_2S. Specific gas analysers are available on the market that can be used to determine such gases, although there appears to be no on-line measurement tools for a number of these gases (e.g. H_2S, CH_4 in the liquid phase).

2.2 Ion selective electrodes

An Ion-selective electrode (ISE) is essentially a transducer which converts the activity of a specific ion dissolved in a solution into a measurable electrical potential. The voltage is dependent on the logarithm of the ionic activity, as governed by the Nernst equation and provides data output in real time. Electrode selectivity is usually achieved by means of an ion-specific membrane. Both the pH electrode (hydrogen ion specific) and dissolved oxygen probe are examples of ISEs.

Certain types of glass exhibit good ion exchange properties towards certain singly and doubly charged cations, allowing the construction of ISEs, notably for H^+, Na^+, Ag^+, Pb^{2+}, and Cd^{2+}. Certain crystalline membranes may be fabricated from mono- or polycrystallite materials and have good selectivity, since only certain ions (both cationic and anionic) may introduce themselves into the crystalline structure and hence alter the electrode response. A good example is the fluoride selective electrode based on LaF_3 crystals. The most widely type of ISE is that employing ion-exchange resin membranes which permit the passage of specific ions. However, such electrodes have low chemical/physical durability and lifetime. An example is the potassium selective electrode based on the ion exchange agent valinomycin

2.3 Dissolved oxygen measurement and BOD/cod

Dissolved oxygen is an important parameter in order to calculate the BOD (Biological oxygen demand) and COD (Chemical oxygen demand) of a sample, as well as facilitating respirometric measurements, and thus is perhaps the most widely used sensor for examination of water quality. Dissolved oxygen measurement is based on the electrochemical reduction of oxygen diffusing from the liquid phase across a gas permeable membrane in an amperometric or polarographic measuring cell.

BOD is an indicator of the concentration of biodegradable organic matter present in an aqueous sample and is used to ascertain general water quality and degree of pollution. The BOD of asample is determined by measuring the rate of uptake of oxygen by micro-organisms in a sample of water at a fixed temperature and over a given period of time. In a typical procedure, samples are diluted in de-ionised water saturated with oxygen, sealed and stored in the dark 20°C for 5 days prior to determination of the dissolved oxygen concentration. The apparent BOD of a blank control is subtracted from the test result to provide a corrected BOD_5 value. Another useful global indicator of water quality is Chemical oxygen demand (COD). It is similar in function to BOD, in that it also measures the levels of organic compounds in water, but it is less specific since it measures total organic levels rather than just the levels of biologically active organic matter.

3 SAMPLE PREPARATION ISSUES

3.1 Introduction

By definition, on-line and at-line analytical methodologies should follow a simple operating procedure, thus any additional processing operations should involve minimal operator intervention (i.e. user-friendly/automatable) and rely on robust and reliable methodologies. Sample preparation methods for at-line/on-line operation in the water industry should adhere to these guidelines.

When considering the sample preparation issue, the first question that must be asked is if sample preparation is actually necessary. A sample requires preparation when (a) the complexity of the sample is such that the selected determination methodology is unable to distinguish the selected analyte(s) from the bulk medium and (b) when the analyte(s) are present at concentrations above or below the dynamic range of the chosen determination method. Ideally, presentation of the device to the sample would involve no sample preparation. This is certainly possible when analysing water samples allied to the use of more 'global' determinative methods where the general physico-chemical properties of the sample are sought. Examples here would be the use of optical techniques to assess sample turbidity or adsorption maxima at selected wavelengths. However, even in these simplistic situations, it may be necessary to filter the samples prior to analysis to remove larger sized contaminants and suspended solids.

3.2 Selective determinative methodologies

Sample preparation may be kept to a minimum when utilising high-specificity determinative methodologies. For example, ion-selective electrodes achieve specificity using, for example, ion-specific sensing surfaces, such as the pH electrode which employs a particular grade of glass that is able to interact primarily with protons in solution, or the oxygen electrode that uses a membrane to allow the preferential passage of dioxygen to the transducer device. The determination of more complex molecular species, such as pesticides, herbicides and other organic species can be achieved using immuno-analytical methodologies. This approach will be discussed in more detail in Section 5.3, but in effect high-specificity biologically-derived binding entities (antibodies) are used to selectively bind target species, based on a combination of structural 'fit' and physico-chemical binding. In this way, target species may be selectively separated from the bulk solution by, what is in effect, an *in situ* sample preparation procedure.

3.3 Established sample preparation procedures

The techniques that can be deployed in the field for environmental sample preparation are necessarily limited, primarily by logistical constraints such as speed, robustness, reliability and simplicity. A well utilised method is that of solvent extraction, whereby a solvent of the required polarity is used to extract the analyte, usually resulting in removal of many matrix components and analyte pre-concentration. For example, extraction of a relatively non-polar analyte from an aqueous sample is relatively straightforward by use of a suitable water immiscible non-polar solvent. Similar approaches may be employed to remove analyte classes from soil and sediment samples.

Alternative approaches rely on sorption phenomena. The use of solid-phase extraction (SPE) is becoming more established in decentralised locations. The principle is simple – a sorptive solid-phase media is used to selectively trap analyte (or contaminant) from applied sample streams, resulting in both matrix simplification and analyte (or contaminant) concentration. In the case of analyte entrapment, a small volume of suitable solvent is then required to recover the analyte. The media is typically supplied in pre-packed or flat disc cartridges through which the sample is passed. By the nature of the material, it is possible to pass large volumes of liquid sample material through the cartridges, hence significant analyte concentrations are possible. Many different sorption matrices are now readily commercially available, so that a high degree of selectivity is possible with respect to recovery of particular analyte classes. Whilst it is possible to automate this method (this is done routinely in centralised laboratories), cost and complexity make this a less attractive option in the field. In most cases it is not considered best-practice to regenerate the sorbent material, so some form of carousel-based cartridge dispensing system is required for stand-alone operation – cost and robustness issues then apply.

3.4 A novel method: surfactants

Ideally the sample pre-treatment system adjunct to the actual sensor should be able to exploit the physico-chemical characteristics of the target analyte (e.g. laboratory-based Soxhlet, Solid Phase and Supercritical Fluid.

A promising alternative method that is considered as an ‘environmentally benign separation technology (Huddleston *et al.*) is that presented by amphiphilic species (species exhibiting both hydrophilic and hydrophobic properties) resulting in the development of a novel liquid-liquid extraction method. Surface active agents, such as surfactants or detergents, are water soluble chemical species that form structural molecular aggregates within the water lattices. Used for their solubilisation properties in our everyday washing-up liquid, some surfactant systems can lead to the ready formation of bi-phasic systems (Aqueous Two-Phases Systems - ATPS), from previously single phase predominantly aqueous solutions in which a surfactant rich phase and a surfactant depleted phase are formed. (Figure 1)

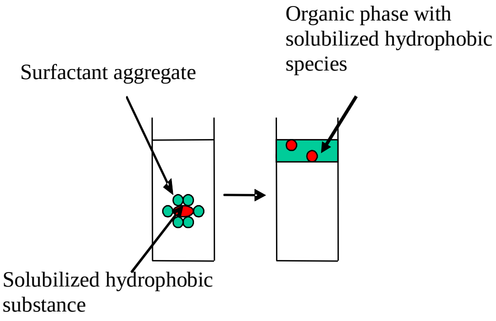

Figure 1: Schematic extraction principle of Aqueous Two-Phase Systems (ATPS)

Amphiphilic molecules are made of two moieties, an hydrophobic alkyl chain and an hydrophilic head group. The nature of this latter moiety determines the particular nature of the surfactant, whilst the balance between these two moieties defines the physical-chemical properties of the detergent.

Alklyl ethylene oxides surfactants such as Triton TX-100 has already been used (Watanabe and Tanaka, 1978) to extract chelated metals from aqueous samples. Nevertheless their application in analytical applications (e.g. chromatography) has proven difficult due to their high UV-fluorescence coupled to long retention times (Silia *et al.*, 1999).

Ionic surfactants are commonly used in electrophoretic and micellar chromatographic analytical systems, as not only do they not interfere with electrochemical or optical detection, they can be advantageously used in analytical separation schemes.

During ARTDEMO, a novel surfactant-based extraction scheme was developed to extract water contaminants. Mixed surfactant systems (e.g. anionic/cationic species) were of interest due to their intrinsic synergistic properties. Indeed, it has been shown that by careful selection and optimisation of mixed media preparations, it is possible to effect high efficiency separations, coupled to subsequent simple phase separation and concentrated analyte recovery, through the simple manipulation of a single system parameter such as pH, temperature or ionic strength. Such systems are also compatible with chromatographic separation and electrochemical and optical detection modes.

3.5 Surfactant-based extraction of sterols

Steroids and estrogens are a classical example of where these novel surfactant extraction approaches may be employed. Currently, their analysis is either carried out by time-consuming assays or costly mass spectrometry (Ottosson,2000).

Sterols determination is a useful tool with respect to the faecal contamination of water sources. Faecal discharges represent a serious health hazard whilst also having a widespread economic impact through medical treatment, damage to marine/fresh water farming concerns and restrictions in recreational activities. The rapid identification as to whether a faecal pollution is human or animal in origin can be achieved by examining the ratio of certain sterol indicators (notably coprostanol and 24-ethylcoprostanol) in water samples and gives an indication as to the types of pathogens that maybe expected, the infection risk and the treatments that may be required to control resultant diseases.

However both coprostanol and 24 ethylcoprostanol are structurally and chemically very similar, differing only by the alkyl chain at the C25 position. Both sterols exhibit minimal absorption and fluorescence in the ultraviolet/visible region and thus are difficult to determine by chromatographic means. Extensive sample preparation and pre-concentration is required in order to provide sterol-containing samples of sufficient concentration to be determined by these instrumental methods. Analysis of the prior art suggests that improved methods of analysis, particularly with respect to rapid sample preparation and downstream detection are required in order to maximise the application of the sterol-based approach.

For this purpose, a simple derivatisation procedure has been coupled to the mixed surfactant based extraction system. Derivatization is a common analytical procedure, whereby an optical or electrochemically active compound is allowed to react with a specific target analyte or analyte family. An acyl chloride based dye was used to effect an easy analytical determination of these key faecal biomarkers.

With the growing interest towards the lab-on-chip concept, where both separation and detection operations are carried out on the same miniaturised platform, surfactant systems can be employed within the development of Micro Total Analytical Systems. Coupled with Marangoni, electrophoretic or liquid chromatographic systems, they offer an opportunity to develop a novel class of totally automated at-line measurement tools.

4 AT-LINE/OFF-LINE MEASUREMENT METHODS

4.1 Bioassays

The term bioassay generally refers to assays in which living organisms are used to ascertain the biological effect of a substance or group of substances and thus may be considered *in vivo* experiments. Bioassays may either qualitative or quantitative in nature and can provide valuable information concerning the concentration or potency of a substance or mixture of substances on the concomitant biological response. The biological entities used may range from animal to fish, to microorganism, the latter often being favoured for ethical and cost reasons.

In the very crudest form, an indication of a water contamination event can be evidenced by the presence of dead aquatic organisms, as would be the case of high BOD leading to oxygen depletion in a body of water.

More targeted tests involve the use of microorganisms, in which the toxicity of a sample is assessed by the effect of that sample upon microbial respiration. A good example of this approach is that espoused by the Microtox test system[1], a leading commercial product in the bioassay toxicity testing field. The Microtox system employs luminescent bacteria, specifically the strain *Vibrio fischeri* NRRL B-11177, to measure toxicity from environmental samples. Luminescent bacteria produce light as a by-product of their cellular respiration, the degree of bioluminescence being directly related to cell respiration. Inhibition of cellular activity (toxicity) results in a decreased rate of respiration and a corresponding decrease in bioluminescence intensity, thus, the more toxic the sample, the greater the diminishment of light from the microbial test suspension. The method is simple, rapid (as little as 15 min.) and requires minimal operator skill and has proven to be a reliable method for determining the presence of toxic chemicals in aquatic samples. The bacteria are provided in freeze-dried form and are easily reconstituted, making the process amenable to at-line/on-line operation Strain 11177 is favoured due to its high sensitivity towards a broad range of chemicals.

4.2 Immunoassays

Immunoassays make use of antibodies, binding proteins formed as part of the vertebrate immune response to invasion of a foreign macromolecule. The fundamental principle of the immunoassay process is to use antibody of the required specificity to selectively bind to the analyte(s) in solution. The extent of this binding is then addressed either directly (by measurement of changes in local physico-chemical conditions, such as refractive index) or indirectly, by use of labelled reagents. The latter approach is more suited to decentralised applications and thus will be discussed further here.

There is considerable interest in the use of immunoassays as at-line analytical measurement tools. Antibody binding is via structural fit within the binding pockets on the antibody molecule, a process governed by physico-chemical factors, such as ionic, hydrophobic, hydrogen bonding and Van der Waal’s forces. The nature of the antibody-antigen interaction is generally such that the process has high specificity and high affinity, thus highly specific assays, offering very low detection limits, can be constructed. Other benefits include relatively low-cost (as minute amounts of antibody are required), ease to use (essentially a number of simple liquid handling operations) and high throughput (multiple assays can be performed at the same time if desired).

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[1] http://www.azurenv.com/mtox.htm

Most commercially available immunoassay products utilise immunoglobulin G (IgG). In order to develop a new immunoassay, access to antibody of the desired binding specificity is required. This can be achieved by simply injecting an animal host with target analyte and subsequently recovering the desired IgG from a blood sample (in which case the antibody preparation will be *polyclonal*). With the advent of sophisticated cell culturing techniques, it is now possible to isolate those cells responsible for antibody production (plasma cells) and fuse them with tumour cells to form a *hybridoma* that is effectively an immortal cell line capable of producing the specific antibody desired (in which the antibody produced by a given hybridoma cell are monoclonal). A large scale screening process follows, in which those hybridomas producing the required antibody are identified.

Antibody generation in the body is triggered by the presence of foreign material above a certain molecular weight (usually ~5000). However, many analytes, particularly those of interest to the water supplier, are of a much lower molecular weight. In this case, the procedure is to attach the target analyte to a larger carrier protein and use this to trigger antibody formation. Such a preparation is termed an immunogen.

Many immunoassay formats exist, but perhaps that which is most readily amenable to at-line operation is that of the competitive immunoassay. A typical competitive immunoassay procedure is summarised in Figure 2. In this case, tubes or wells are supplied in which an analogue of the analyte (usually in the form of the immunogen) has been physically pre-adsorbed onto the surface of the vessel. The operator adds the sample and antibody, conjugated to a suitable label. Labelled antibody will either bind to free analyte in solution, or immobilised analyte analogue – hence the term *competitive* immunoassay. Following this incubation step, the vessel is washed to remove all unbound species and the residual antibody-linked signal addressed. It follows that if there is little free analyte present, then the majority of the antibody label will bind to the immobilised analogue and a high signal will be obtained – and *vice versa*. Thus an inverse proportionality exists between analyte concentration and signal response. Typical labels include optically active compounds such as chromophores, fluorophore, or enzymes, the latter being used to amplify signals due to their biocatalytic activity. Enzymic products may be optically or electrochemically active and thus can be simply determined using low cost robust and portable instruments.

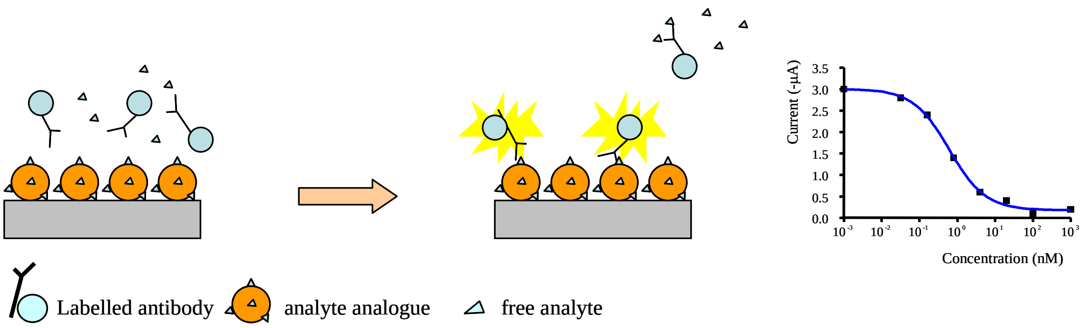

Figure 2: Operating principle of a competitive indirect immunoassay. Details are provided in the text.

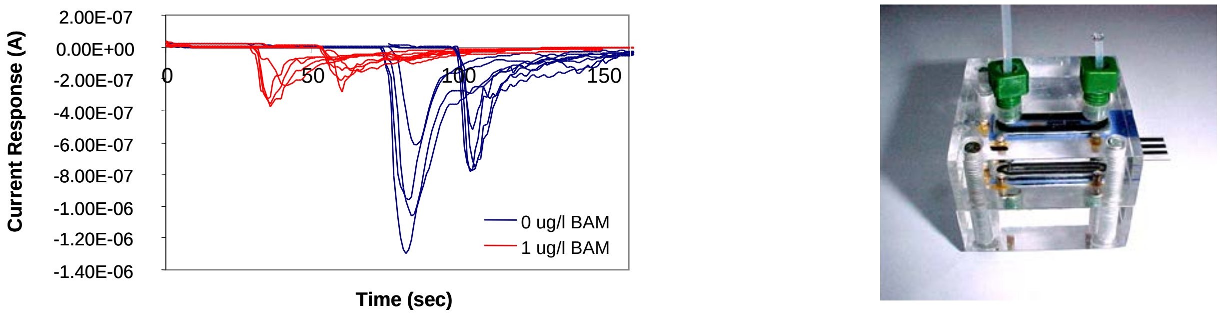

Figure 3: BAM immunoassay electrochemical flow cell detector and typical time versus response electrochemical profile in the presence of 0 and 1 µg/l BAM.

An at-line automatable optical immunoassay against the pesticide residue BAM (2,6-dichlorobenzamide – a breakdown product of the widely used domestic herbicide diclobenil), developed by ARTDEMO partner Cranfield University has been evaluated within the project. The method centres on the immobilisation of a BAM analogue, that is a BAM molecule linked to a suitable carrier protein that is used to 'tether' the BAM structure to the walls of a microtitre well. The system is configured such that a detection cell, consisting of an electrode assembly within a flow-cell is located downstream of the microtire well incubation chamber. A pump is used to remove solution from the wells as required, and deliver product to the detection cell. (Figure 3).

During the assay, antibody, attached to an enzyme label (in this case, the well known diagnostic enzyme horseradish peroxidase) and the sample itself (containing free BAM as analyte) is introduced to the microtitre well. A competitive immunoassay follows in which the labelled antibody either binds to the free BAM, or immobilised BAM analogue. The wells are then washed, to remove all unbound material, including free BAM-antibody complexes. Enzyme substrate is then introduced into the wells where it reacts to form HRP product that is subsequently delivered to the downstream flow-cell and the amount of electroactive product determined.

5 FUTURE TRENDS

5.1 Biosensors

A biosensor may be described as an analytical device that incorporates a biologically derived recognition molecule (or biomimetic equivalent), in intimate association with a transducer, capable of converting the biorecognition event into a measurable electronic signal. Biological recognition agents include enzymes, antibodies, cell fragments, whole cells, nucleic acid segments and receptor binding proteins. The commonest transduction mechanisms include electrochemistry, optical detection, acoustic wave (by exploitation of the piezoelectric effect) and calorimetry. The biosensor field is vast and has widespread applications across many sectors, including medical, food, environmental, health and process monitoring, thus including the water processing. The best known biosensor to date is the hugely commercially successful glucose biosensor used by diabetics to measure their blood glucose levels. An immobilised enzyme (glucose oxidase) oxidises the glucose, generating stoichiometric quantities of hydrogen peroxide as a by-product that is electrochemically oxidised (and hence measured) at an underlying screen-printed electrode assembly.

The current interest in biosensors within the water processing industry centres on the attractiveness of the approach. In essence, biosensors represent a complete measurement solution to a problem. Biologically derived binding ligands have the capability of recognising and binding target species in often complex media. Furthermore, binding is often at high affinity, allowing highly sensitive devices, with low detection levels to be developed. Coupling of this recognition process with a suitable transducer shifts the emphasis of measurement from the end-user to the device, thus allowing their operation by minimally trained personnel. Biosensor response times are also often very rapid, again as a result of the integration of the recognition process with the transducer, rendering biosensors compatible with on-line/at-line applications.

5.2 Respirometric biosensors

Respirometric biosensors, typically in which the metabolic profile of entrapped whole cell microbial preparations are determined during exposure to water samples, has received much interest over recent years, particularly for measurement of biodegradable organic species and hence biological oxygen demand (BOD). The transduction mechanism is typically a dissolved oxygen probe with microorganisms genrally of a single type, entrapped within the vicinity of the transducer by means of membranes of suitable properties and pore size. A number of these devices are now becoming commercially available (Lynggaard-Jensen, 1999).

Whilst gaining greater industry acceptance, limitations of respirometric biosensors should be borne in mind. Whilst respirometric biosensors undoubtedly offer the end-user valuable information regarding the organic loading and nature of the test solutions, the measurement process resports the levels of dissolved oxygen diffusing through the immobilsed biological material and membrane and compares this with standard BOD check solutions and therefore do not necessarily represent the true conditions during water processing operations (Bourgeois *et al.*, 2001). Furthermore, some reservations regarding their use, particularly from the prespective of the utilisation of 'foreign' microbial populations within the water treatment environment have been raised (Qian and Tan, 1999). Given that the operating principle depends upon the metabolic activity of the entrapped microbial population, care must be taken to maintain stable operating conditions, such as pH and temperature. Live cells require careful maintenance when not in-use and reactivation of dormant populations after delivery and long term storage also demands time and care. These type of biosensor also have limited lifetimes.

5.3 Target specific biosensors (Immunosensors)

A respirometric biosensor measures the global state of a sample, since there may be a number of sample components that can have an effect on one or more metabolic processes within the entrapped microbial preparation. However, by utilising *specific* biorecognition components, information on a particular analyte, or analyte groups can be obtained. For example, the enzyme acetyl choline esterase (AChE) is known to be inhibited by a broad range of organophosphate pesticides (OPs). Thus, by monitoring the sensor output from an AChE-transducer immobilised preparation in the presence of acetyl choline substrate and OP containing sample allows the highly sensitive determination of OPs in environmental samples.

Generally, biosensor devices developed to determine specific target analytes make use of antibodies, utilising methodologies similar to those described for the immunoassays above, but in which the transducer is intimately associated with the immuno-mediated recognition process. Thus the advantage of an immunosensor over an immunoassay is ease-of-use, in that recognition and determination are associated. Ease-of-use is, of course, a key criterion in establishing any in-line/at-line detection method.

A representative example of an immunosensor for the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D), with electrochemical transduction is that previously developed in our laboratories (Kroger et al., 1998). The basal transduction device is a screen-printed electrode, produced in-house. Screen-printed electrodes (SPEs) excellent example of how promising immunosensor devices developed in the laboratory can be translated to at-line field-based usage. Screen-printing is a process whereby layers of conducting and insulating materials can be precisely deposited onto cheap plastic backing materials (substrates) and is highly amenable to mass-production. A typical SPE consists of a carbon working and counter electrodes and a silver/silver chloride reference electrode.

The immunosensor was constructed by immobilising a 2,4-D analogue (2,4-D immobilised to bovine serum albumin carrier protein) directly to the working electrode surface by simple physical adsorption. A competitive immunoassay was then performed in which an antibody conjugated to glucose oxidase (GOx) enzyme was used. Following incubation and washing, residual GOx was determined by adding glucose substrate and electrochemically (amperometrically) determining the oxidation of hydrogen peroxide generated as a by-product during glucose oxidation. The performance of the sensor was assessed in buffer, 30% methanol, and methanolic soil extracts and was capable of quantifying 2,4-D in all three matrixes at the low ppm (µg/kg) level with coefficient of variation values of 6.2-33.6%. The sensor, tested in parallel with a commercial 2,4-D immunoassay test kit, yielded comparable quantitative data and detection limits whilst exhibiting greater assay simplicity

5.4 DNA-based biosensors

DNA based biosensors are an area of growing interest for environmental analytical applications. The determination of foreign DNA material in a given sample may be indicative of a biologically related pollution incident (e.g. microbial contamination, animal matter, human faecal contamination). DNA-based biosensors make use of the complimentarity between the individual strands of a double stranded DNA molecules.

A typical DNA-based assay therefore would involve the use of platforms in which target-relevant sections of DNA are immobilised to a suitable support, such that the specific DNA-base sequence is free to interact with complimentary DNA strands from the applied sample. Visualisation of the bound material is then required and there are many ways of achieving this. Since the immobilised DNA fragment is relatively short relative to the target DNA fraction, a significant portion of the target DNA molecule will be available for complimentary binding. Therefore, one well utilised visualisation approach is to subsequently add a probe material – essentially a short strand of DNA exhibiting complimentarity towards the residual single stranded portion of the immobilised target DNA, coupled to a suitable label, typically a fluorophore. Such methods are more aimed at qualitative, as opposed to quantitative determinations.

DNA determination methods are increasingly being supplied in array form, in which a multitude of DNA fragments are spotted and immobilised to a single chip in a 2-dimensional format. Specialised readers are also supplied that can simultaneously address the optical properties of each spotted fragment to indicate if target DNA material is present. The market leader in this field is affymetrix (www.affymetrix.com). Such methodologies are more assay, rather than sensor-based.

In order for DNA-based methods to be successful, a degree of sample preparation is required. The preparation method should include protocols to cleave open cells to release the nucleic materials, and the use of suitable denaturing conditions to allow double stranded nucleic acids to exist in their single stranded form. Furthermore, the amount of genetic material to be detected is often extremely low, thus some form of amplification of the relevant segments of the DNA strands is required. This can be achieved routinely by employment of the PCR (Polymerase Chain Reaction) technique, in which the desired fractions of the DNA material are specifically targeted and amplified using primer DNA sequences, polymerase enzymes and DNA building block materials. Whilst such methods are still primarily used in centralised laboratories, there is an increasing drive towards miniaturising the method, offering the benefits of portability, reduced cost, reduced reagent consumption and, importantly, speed.

5.5 *Determination of chemical entities using nucleic acid-based approaches*

Scope for the construction of simple field-enabled DNA-based biosensor systems do exist. These types of system are not based on recognition of nucleic acid fragments, rather they are used to identify particular toxicogenomic compounds that disrupt the complimentary binding of double-stranded DNA. Certain compounds are able to intercalate within the double-stranded DNA helix, inducing a change that can be measured at a suitable transducer. An elegant method is that proposed by Mascini and coworkers (Bagni *et al.*, 2005, Lucarelli *et al.*, 2001) in which double stranded DNA (e.g. from calf thymus) is immobilised to screen-printed electrodes. On addition of certain chemical entities (e.g. daunomycin, PCBs, aflatoxin B1, and aromatic amines) the immobilised double stranded DNA is disrupted, resulting in the exposure of guanine bases in the nucleic acid structure to the underlying electrode surface. The oxidation of guanine, and hence an indication of the level of genotoxicity can be determined by the standard electrochemical methods of chronopotentiometry or square wave voltammetry. The approach has been successfully used to analyse river and waste water samples.

5.6 *Biosensors - conclusion*

Biosensors are not yet the panacea sought by the water industry for on-line/at-line measurement. Whilst holding considerable promise, issues regarding sensor robustness and reliability require addressing, before there is widespread up-take of this technology by the industry. It is hoped that the growing commercial success of the respirometric biosensors is matched by the more ‘target-specific’ sensors in the near future.

5.7 *TOC sensor*

Total Organic Carbon (TOC) is becoming an increasingly important parameter with respect to the true level of organic pollution in a water sample, primarily due to the relative ease-of-use of the method, particularly when compared with BOD and COD measurements. The essential aspect of any TOC measurement is the complete mineralization of organic carbon to carbon dioxide. Wet chemical oxidation (WCO) represents the more traditional method, in which persulphate reagent is added to the sample followed by low-temperature UV radiation. Inorganic carbon is first removed from the sample by acidification coupled to aeration. The more recent method of High Temperature Catalytic Oxidation (HTCO), utilises a catalyst and temperatures in the region of 650-900°C. However, discrepancies have been observed between the 2 methods, rendering interpretation difficult (Thomas *et al.*, 1999; Sharp *et al.*, 1993). It is also important to note that TOC only measures the organic content of a sample and should not be correlated to BOD data substances other than organic matter may influence BOD readings.[2] In line with the other developments reported in this chapter and in response to the ARTDEMO project partner’s needs, research was carried out towards the development of rapid, cost-effective and reliable on-/at-line TOC sensor.

Recently, water treatment companies have exhibit interest towards the so-called ‘Advanced Oxidation Processes (AOPs) (Table 2), as they have been proven promising with respect to elimination of toxic and bio-resistant organic and inorganic compounds from wastewater, by transformation into innocuous species. Within ARTDEMO an opportunity was identified in which the photocatalytic capability of certain semiconductor materials could be exploited for the development of novel, simple, low cost miniaturised TOC sensors. Unlike classical oxidation processes, i.e. combustion and persulfate methods, that are time and energy extensive, photo-catalytic semiconductors such as titanium dioxide can promote the photomineralization of organic and inorganic compounds to carbon dioxide (CO_2) and acid minerals (Figure 3)

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[2] Stuetz 33-35

Table 2: Comparison of different Advanced Oxidation Process

Advanced Oxidation Processes		
Ozone based (Peroxones, O_3/catalyst, O_3/UV)	(Fe^{II}/H_2O_2)Fenton (Fe^{II}/H_2O_2/UV) photo-Fenton systems	TiO_2 semiconductor (TiO_2/UV)
• Process efficiency depends on pH, temperature, oxydant dosage • Possible new waste generation • Not cost effective due to the generation of O_3	• High dosage of oxidant • Problem of catalyst removal from the sludges • Not cost effective	• cheap material and source of energy • non-specific degradation • efficiency depends on the surface area and quality of the photo-catalyst • Cost effective

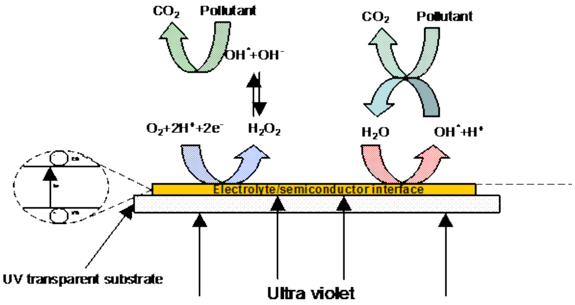


Figure 3: Semiconductor photocatalysis principle

In the same manner that the light absorption properties of organic chromophores and metallic species forms the basis of molecular and atomic spectroscopy, semiconductor can also absorb light. Under illumination of appropriate energy, electrons within the semiconductor can be promoted from the ground state valence band to the more energetic conduction band, provided the energy of the illumination matches the energy gap between these two energy bands.

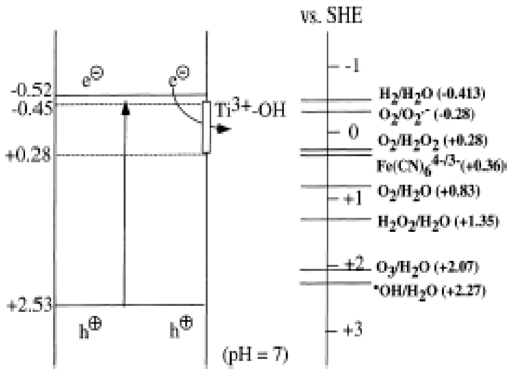


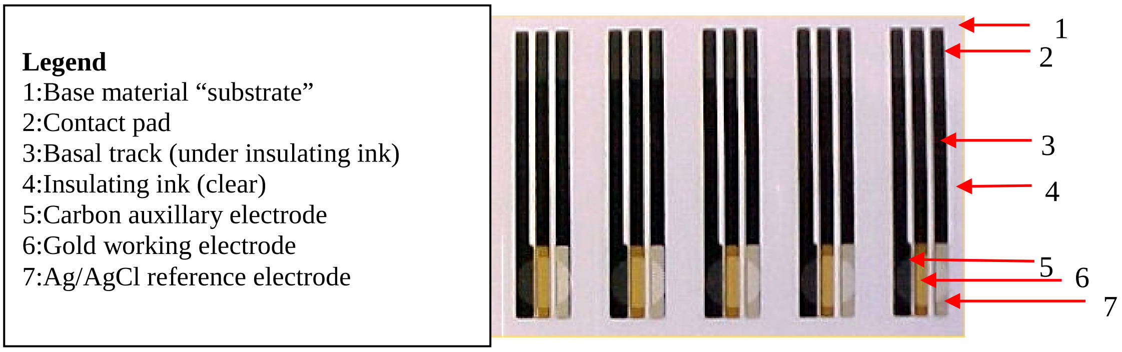
Figure 4: Redox potential of photogenerated holes and electrons on TiO_2 surface

Among all the known semiconductors, only titanium dioxide possesses a band gap (Figure 4) where photogenerated reducing surface electrons and highly oxidising photogenerated holes drive the radical degradation of organics. However, in order to prevent undesirable separation steps, the photocatalyst should be immobilised onto a support. A chemical approach was employed here over more conventional physical immobilisation methods for cost reasons. The total organic content of the sample is simply determined by measuring the sample impedance change before and after the photocatalytic oxidation process.

In order to produce a uniform semi-conductor film, both sol-gel (Paez et al., 2003) and reverse micellar (Stathatos et al., 1997) routes have been examined, in which the degree of polycondensation of the organic precursor dictates the thickness of the film. Typically films thickness produced by dip- or spin-coating range between 10-100 nm. Alternatively films may be formed from inorganic metal precursor material using the so-called Doctor Blade technique (Zhang et al., 2003).

The photocatalytically active TiO_2 thin film is however subject to some limitations. An intrinsic problem of the catalyst is that the charge recombination process shortens the lifetime of the surface photogenerated holes and available electrons. However, chemical doping strategies and electrical bias have proven effective in minimising this phenomenon. The surface area of the film, which defines the effective area of the catalyst, may be maximised using agents such as poly(ethylene) glycol 1000 (Bu *et al.*, 2004) or inert porous silica support such as MCM (Van Grieken *et al.*, 2002).

The photocatalytic efficiency of such films will also be relying on the mass-transfer of reactants or degradation products at the semiconductor/ electrolyte interface. Such



Legend
1:Base material “substrate”
2:Contact pad
3:Basal track (under insulating ink)
4:Insulating ink (clear)
5:Carbon auxillary electrode
6:Gold working electrode
7:Ag/AgCl reference electrode

Figure 5: example of low-temperature curable gold electrodes used within ARTDEMO. In a standard procedure, a small volume of water sample (~100 µl) is pre-mixed with an acid/electrolyte mixture. A 100 µl volume is then applied as a droplet to the electrode surface. A negative potential is applied, resulting in reduction and depositioning of metal ions at the working electrode surface. Depositioning is allowed to continue until sufficient metal ions have been removed from the sample solution.

parameters can be minimised depending on the volume of sample applied the TOC sensor.

5.8 *Heavy metals determination*

Traditionally, heavy metals analysis is performed in centralised laboratories using specialised techniques such as Flame Atomic Absorption Spectroscopy and Inductively Coupled Plasma Atomic Emission Spectroscopy – methodologies that are not amenable to at-line/on-line testing. This has led to the need for rapid and cost-effective *in situ* methods of analysis for a range of contaminants. Heavy metals, such as lead (Pb), copper (Cu), cadmium (Cd), arsenic (As) and mercury (Hg) are of particular concern as they are non-biodegradable, persistent and, even at extremely low concentrations, can produce undesirable effects to human health and the environment.

Anodic stripping voltammetry (ASV), coupled with screen-printed electrodes (SPE) offers a convenient technique for at-line analysis.

This approach is favoured for reasons of cost, simplicity, speed (<4 min) and sensitivity (µg l^{-1}). The use of single-use disposable sensors also negates the need for solution stirring, de-aeration and lengthy electrode cleaning procedures. Consequently, a chemical sensor utilising Differential Pulse ASV (DPASV) and screen-printed carbon and gold electrodes has been developed and evaluated within the ARTDEMO programme. Examples of the electrodes produced in this study are shown in Figure 5.

The potential of the working electrode is then swept at a linear rate (mV s^{-1}) to a more positive potential. Metal ion species, depending upon their electrochemical properties, are stripped (oxidised) back onto solution at certain specific potentials. The oxidation process results in transfer of electrons from the metal to the working electrode, resulting in a current flow, the magnitude of which is related to the metal ion concentration. Observation of current, as a function of potential (a voltammogram), provides both quantitative (peak current area) and qualitative (stripping potential) information regarding the metal species present (Figure 6).

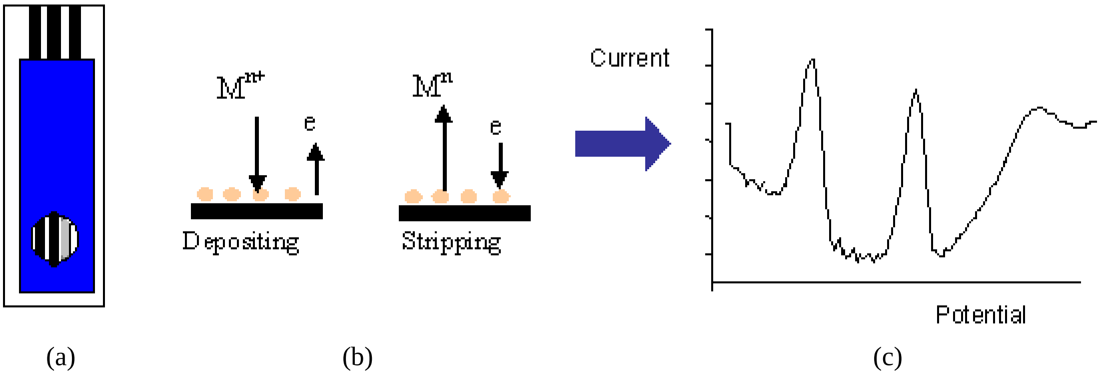


Figure 6: A typical SPE is shown in (a), the circular aperture defining the 3-electrode assembly. At a suitably negative working electrode potential (b), metal ions are reduced (depositioning), accepting electrons from the working electrode. During stripping, metal species are oxidised at characteristic potentials, passing electrons back to the working electrode. The resultant voltammogram (c) provides both qualitative and quantitative data regarding the metal species present.

In the last few years, SPEs have been widely promoted for field-based ASV applications to satisfy the increasing demand for rapid, simple low-cost *decentralised* analytical testing. All such devices utilise carbon as the working electrode material. As such, samples must also be pre-mixed with mercuric salts, such that, on application of the depositioning potential, the mercuric ions are reduced to form an elemental mercury film over the working electrode - necessary for metal ion depositioning at the working electrode.

Work on ARTDEMO has focussed on 2 types of screen-printed indicator electrode materials: Carbon and low temperature curable gold.

Carbon working electrodes: These sensors allow *simultaneous* detection of cadmium, copper and lead at µg kg^{-1} range (parts per billion) with a total assay time of around 4 min. Repeatability is generally below 10% (RSD), with the method showing a high degree of correlation (>0.9700) compared to standard ICP methods. Low levels of mercury salts are required in the sample mixture. The use of mercury to assist metal ion depositioning limits this approach to those species that are stripped back into solution prior to the stripping of mercury itself.

Mercury free electrodes: SPEs, incorporating a novel, proprietary low-temperature curable gold ink have been evaluated within ARTDEMO. The low-temperature curable aspect of the gold formulation allows printing of gold layers onto plastic substrates, rendering the assembly low-cost to manufacture, and hence may be considered disposable. These sensors do not require the addition of mercuric ions since the apparatus and methodology employed allows direct metal ion depositioning. As such, the approach negates the requirement to work with toxic mercury materials and allows detection of metals otherwise stripped back into solution at a potential greater than that of mercury. The method is particularly amenable to mercury and arsenic measurement (detection limits of <1 µg l^{-1} in water for mercury), but also shows promise for measurement of copper, cadmium and lead.

Two typical voltammograms recorded on the carbon- and gold-based screen-printed electrodes are illustrated in Figures 7 and 8 respectively.

As can be seen in Figure 8, there is a severe overlap with the mercury (Hg) and copper (Cu) components which would make their respective determinations rather difficult under normal conditions. Special mathematical applications in the form of chemometrics can be applied to deconvolute (and thus resolve) the two components instead of applying further laboratory processes (Chapter 11). This will lead to the amount present in a given sample being accurately and confidently determined.

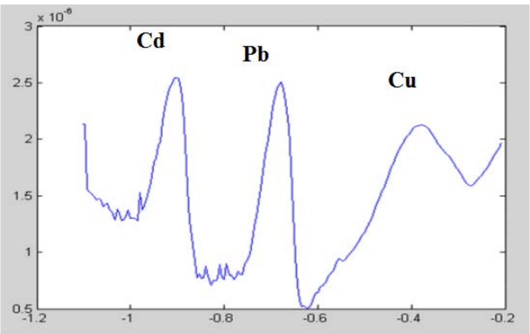


Figure 7: A typical voltammogram acquired on a carbon-based screen-printed electrode under the following conditions: Components: 100 ppb cadmium (Cd), 100 ppb lead (Pb), 200 ppb copper (Cu); Reagents: 2 ppm mercuric (II) nitrate, 1% (v/v) nitric acid, 0.1M potassium chloride (KCl); Experimental Conditions: Deposition time: 165s; Deposition potential: -1.1V; Range: -1.1 to -0.2V; Scan rate: 10mV/s

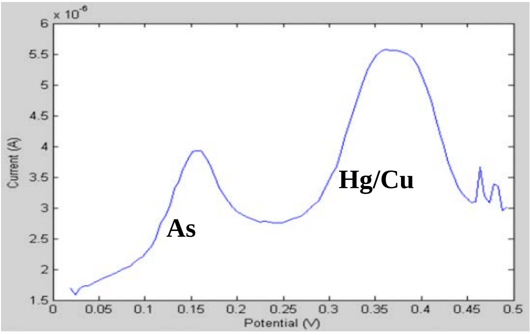


Figure 8: A typical voltammogram acquired on a gold-based screen-printed electrode under the following conditions: Components: 300 ppb arsenic (As), 300 ppb mercury (Hg) and 300 ppb copper (Cu); Reagents: 4M hydrochloric acid (HCl), 1mM hydrazinium chloride; Experimental Conditions: Deposition time: 30s; Deposition potential: 0V; Range: 0.0 to 0.5V; Scan rate: 10mV/s

Chemometrics: An issue to overcome when performing electrochemical measurements is that non-target species exhibiting electroactivity in the vicinity of the working electrode will induce a matrix effect. To a certain extent, use of the mercury film and gold electrodes reduce certain matrix effects in that they are more pre-disposed to the accumulation of metallic species during the depositioning step. Furthermore, peak overlap may be an issue when several different types of metal species are present in the sample. In certain situations, this problem may be overcome by manipulation of measurement parameters (e.g. stripping potential range) or by adjustment to ‘wet’ chemistry conditions.

However, as part of the ARTDEMO programme, the usage of data treatment tools to deconvolute complex voltammograms has been examined, as is elaborated on in ArtDemo Chapter 12.

Multiplex potentiostat: In order to extend the capability of the on-line metals detection aspect of the ARTDEMO programme, a 4 channel multiplex potentiostat has been developed and successfully trialled within the programme. The device has been designed as a portable and flexible instrument capable of carrying out a wide variety of electrochemical tests in the laboratory and in the field. The device is battery operated and ruggedised, and can operate in a stand-alone mode or with an attached PC or PDA. The device has been configured to perform heavy metal detection, but the flexibility afforded by its software configuration makes it suitable for a wide range of other electrochemical applications. The device is illustrated in Figure 9 along with an example voltammogram generated by the device.

Other design aspects of the device relating to at-line/on-line measurement include : Electrochemical drive voltages fully synthesised in software to 1mV with 5µsec resolution; PicoAmp resolution with full auto ranging; Onboard Microcontroller – fast, low current consumption; Structured software design, implemented in ‘C’ language; On board data storage, or real time transmission over RS232 / Bluetooth link to PC/PDA; Calibration data stored in on-board EEPROM, allows low cost hardware components to be used; Battery operated, robust, portable for field use; On board or PC based data analysis

The device has 4 completely independent potentiostat channels, thus 4 electrochemical measurements can be performed simultaneously. This has the advantage of increasing sample throughput, or alternatively, utilising different sensors (e.g. gold and carbon sensors), coupled to alternative applied electrochemical conditions (variation of depositioning times and potentials and metal stripping regimes) to allow more complex measurements to be performed, or to analytically deconvolute complex voltammograms. This multi-data collection capability, allied with chemometric data treatment (ArtDemo Chapter 12) provides a powerful tool for on-line/at-line multiple heavy metals determination.

The data files generated by the PDA application can be transferred to a desktop PC and analysed with specialised in-house built multivariate analysis applications. Alternatively, they can be analysed at-site on the PDA itself. The PDA software is developed to determine the amounts of components present in any given sample, and thus determine whether any problems have arisen.

Figure 9: (upper) Metals analysis software loaded onto PDA; (middle) multiplex potentiostat; (below) typical voltammetric response for lead and copper using multiplex potentiostat.

In brief, the first step involves importing the model that has been generated on a desktop PC. The model will contain the regression factors which liaises the concentrations of the target components to the voltammograms acquired along with the chemometric algorithm employed to generate these factors. In addition, it contains information on whether any pre-treatment techniques had been applied to the data such as range-scaling or mean-centring. As the next step the acquired voltammograms are imported, and finally the ‘predictions’ are carried out.

5.9 Machine Olfaction – ‘the electronic nose’

Machine olfaction is a term used to describe instrument-based methods of mimicking the underlying principle of the sense of smell. This concept has attracted recent attention within the water processing industry since it may be used as an at-line method for the identification of undesirable odours within water samples, by recognising patterns of volatile species emanating from a given water sample.

The biological olfaction principle centres on the presence of an array of cells that are capable of reacting to specific volatile compounds drawn into the olfactory system. The specific interaction between the cell and target compound, results in the generation of an electrical signal that is sent to the brain for processing. In most cases, a ‘smell’ consists of a number of individual compounds – thus different cells in the olfactory array will respond to these different compounds. The brain therefore receives a multi-signal input from a single sensing event. The brain employs a neural network approach, in which the overall signal response is interrogated and specific parameters recognised, culminating in the identification of a particular smell. The neural network approach is essentially one of learning, in which the biological host develops a recognition capability based on previous exposure. Given this learning approach, the olfactory system is sufficiently flexible to allow new ‘smells’ to be examined and information obtained as to the particular composition of that smell without prior exposure. The popular concept of having an in-built library is incorrect, since no two smells may be exactly alike.

The machine olfaction principle mirrors the biological approach, but with less sophistication. An array of sensors is required in order to generate the odour ‘signature’. However, unlike the biological system where there are ~1000 individual types of recognition cell, the machine-based approach typically employs a limited multiple of 4 or 8 sensors (8, 12, 16, 24 being most common). Essential to this operation is the fact that each sensor is different (either materially or via the applied operating parameters) and should react reversibly with the target species, such that the sensor array may be repeatedly reused. The sensors should exhibit partial specificity, which should differ but overlap between sensors across the array.[3] Data from the sensor response (typically a response versus time profile) is fed to a processor, for data pre-treatment and evaluation. Typically, the data is processed by 1 of 2 methods – either by chemometric evaluation (the term used for statistical data treatment of chemical data) or by machine learning techniques (typically by the application of artificial neural networks, ANNs). The output from the system is essentially a classification, often graphical, in which particular odour compositions can be grouped according to their compositional similarity.

In principle, any suitable sensor device could be used in the construction of the array. In practice, three types of sensor predominate. Sensor arrays based on mixed metal oxide semi-conductor (MOS) sensors(most commonly tin oxide) require sensor operation at high temperature and effect a resistance change in the presence of reactive species. Conducting polymer sensors rely on the adsorption of analyte into a polymer film which induces swelling that in turn generates a measurable resistance change. Acoustic wave (AW) sensors exploit the phenomenon of acoustic waves generating a stable radio frequency resonance in piezoelectric crystals, such as quartz. A shift in oscillation frequency , directly related to the mass of adsorbed compound, is induced by the adsorption of gaseous species onto a surface coating. Variations to the AW approach include bulk acoustic wave (BAW) and surface acoustic wave (SAW) sensors. Sensors may be coated in different sorbents to modulate sensor selectivity.

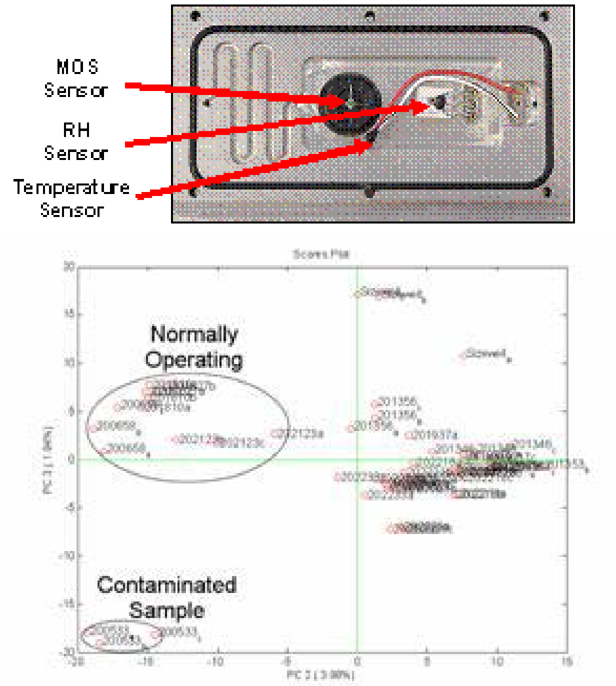


Figure 10: (upper) Single gas element sensor chamber showing position of metal oxide semi-conductor sensor. (lower) Typical PCA scores plot showing diagnostic/differentiating power of gas sensor system allied to on-board data analysis capability.

Single element sensing systems: A variant to the machine olfaction approach is that offered by the single element sensing system, recently innovated within the laboratory of ARTDEMO partner Cranfield University (UK). Whilst

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[3] JLD, 124

having some similarity with the machine olfaction approach, a fundamental difference exists in that the volatilised sample is passed over a single gas sensing element (in this case a MOS sensor; Figure 10). Key features of the resistance versus time response from the sensor is collected and analysed by the Principal Components Analysis (PCA) chemometric method, the output being a PCA scores plot that can be used to group those samples exhibiting similar response features and hence volatiles component composition. This method potentially offers improved at-line performance for the processing industries, due to improvements in robustness and reliability over conventional machine olfaction systems by virtue of the single, as opposed to multiple, sensor composition. To date the device has been used for environmental applications, notably aging of oil, and medical applications (bacterial identification).

There is growing interest in the usage of the electronic nose for at-line monitoring of water quality, due to its non-invasive nature, generic nature and the fact that no sample preparation is required. Preliminary studies have shown that electronic noses are capable of distinguishing samples containing low levels of organic pollutants and tainting compounds in both waste and potable water. Furthermore, it is possible to distinguish between wastewater samples of different types and origins (Stuetz *et al*., 1999a; Fenner and Stuetz, 1999). The generic nature of the electronic nose approach is illustrated by the fact that these devices correlate well with more standard water analysis tests, such as the 5-day BOD test, where method agreement was observed over periods of up to 4 weeks (Stuetz *et al*., 1999b; Stuetz *et al*., 1999c). Such data suggests that the electronic nose is in its infancy with respect to the sheer scope and applicability towards the measurement of a range or water quality parameters and will represent an increasingly valuable tool for identifying abnormal sample profiles.

In our laboratories, we are currently adapting the single element sensor approach for near real-time monitoring of water processing operations (pre- and post sewage treatment), with the aim of developing a near-real time volatiles measurement device for the water processing industries. This work is at an early stage.

5.10 Optical/fluorescence

Interrogation of the interaction of radiation energy with a test sample is the fundamental aspect underpinning a wide array of analytical methodologies, the most widely used methods being those based on ultraviolet (UV), fluorescent, visible (vis) and infrared (IR) radiation. Instruments employing these approaches are commonplace in the laboratory, and there is a growing trend towards the usage of simplified, more robust versions of these types of device for at-line/on-line water quality applications.

Uv-vis spectrometers are readily available on the market and have some benefits in determining the more global aspects of a sample's nature, such as presence of suspended solids, humic acids etc. and a limited sample evaluation may be drawn from such data.

IR detection: IR methods are characterised by radiation with wavelengths between 700nm and 1mm and is most suited to the interrogation of samples containing organic compounds. Clues as to the composition and structure of a sample can be gained by observing both the percentage transmission of IR radiation thorough a sample, coupled to the frequencies of the radiation absorbed by that sample as a result of the stretching of molecular bonds induced by the incident IR radiation. For example, C-H bonds exhibit a characteristic absorption band that can be used to indicate the levels of hydrocarbons in a sample.

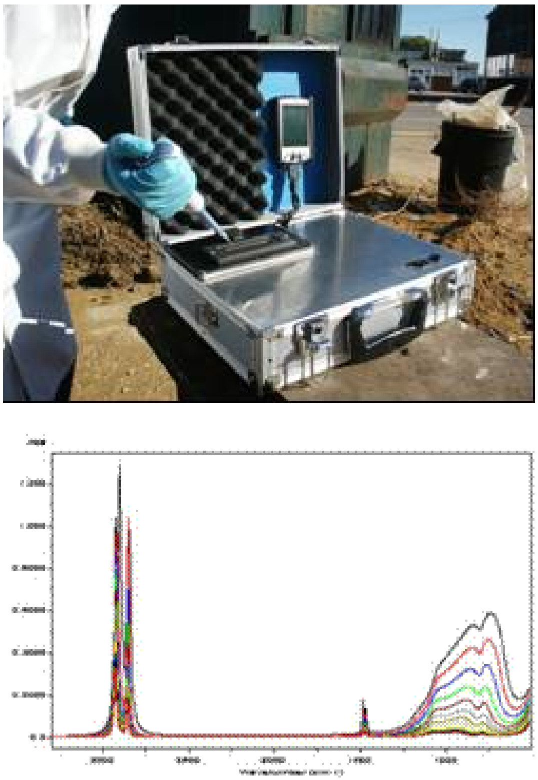

Figure 11: (Upper) Petrosense device for determining hydrocarbon contamination in environmental samples; (Lower) Typical IR spectral response at differing levels of hydrocarbon contamination.

A number of field-enabled IR measurement devices are commercially available. A method developed in our laboratory (the 'Petrosense' device) features an ATR (attenuated Total Reflectance) crystal to facilitate the construction of a compact, robust and reliable at-line tool for total hydrocarbon measurement. The device is shown in Figure 11.

The operating principle is simple. Hydrocarbon species are extracted from the environmental sample (soil, sediment or water) using a simple solvent extraction procedure. In the case of a soil sample, the soil must first be weighed out (e.g. 5g) and dried. This can simply be achieved by the addition of a suitable drying agent such as powdered magnesium sulphate and stirring for ~2 min. A fixed amount of extraction solvent is then added to the vessel (e.g. 2ml/gramme solid). Acetone is suitable for soil samples, having the necessary solvation properties, coupled to high volatility, low toxicity and non-chlorinated. The vessel is then shaken manually for 3 min. Solids are allowed to begin to settle in the vessel (~1 min.) and a 100 ml volume of the emerging clearing supernatant is applied to the ATR crystal after filtration. The solvent rapidly evaporates on addition to the crystal, due to its high vapour pressure and the small amount of solution applied, leaving an 'oily' hydrocarbon-rich film on the crystal surface.

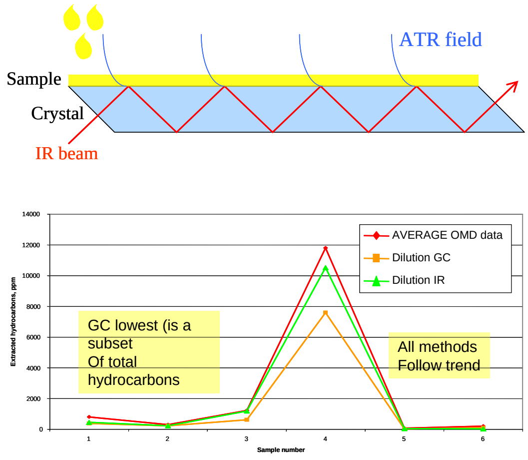

Figure 12: (a) Propagation of IR radiation along an ATR crystal previously exposed to hydrocarbon sample extract. (b) Comparison of Petrosense device for measurement of hydrocarbon contaminated soils with standard laboratory based IR and GC-MS methods.

An IR beam is propagated along the crystal via multiple total internal reflections (Figure 12a). The presence of a hydrocarbon film at the crystal surface results in the selective absorption of C-H bond specific wavelengths of the IR radiation spectrum. Thus, the light emerging at the end of the crystal will reflect the amount of hydrocarbon species present in the original sample. The process is highly rugged and amenable for at-line usage (5 min. extraction time + 10 min. analysis time). The method compares well with the USEPA approved laboratory-based IR methods and also shows similarities with the USEPA approved gas chromatographic methods with mass-spectrometric (GC-MS) detection in which all C10 to C40 compounds are determined and quantified (Fig. 12b). The method can quantify across the range 500-10,000 mg/kg, with a limit of detection of 50 mg/kg.

Fluorescence: An alternative optical methodology of increasing usage within the field-based context is that of fluorescence, in which the sample is irradiated with light of appropriately short wavelength (usually in the UV region) to allow interrogation of the fluorescent properties of a sample. Sample molecules absorb the high energy photons and re-emit them as lower energy longer wavelength light, the energy difference being dissipated as molecular vibrations (i.e. heat). Usually the emitted light is in the visible region, but this will depend upon the particular optical properties of the sample, including the Stokes shift, and the wavelength of incident light used. Fluorescence is a powerful detection tool since the method may be highly sensitive and can yield both quantitative and qualitative data with minimal operator intervention.

Many components of crude and refined petroleum products exhibit fluorescence, most notably the polyaromatic hydrocarbons (PAHs) and heterocyclic hydrocarbons. Under optimum conditions, detailed spectral fingerprints can be obtained from oil contaminated environmental samples which is useful in identifying pollution incidents and also relating the pollution incident to a particular contamination source or event.

A typical fluorescence spectrum is created by placing a sample in a suitable optically transparent vessel, such as a quartz cuvette, and irradiating with a broad wavelength excitation source, such as a xenon lamp. An excitation monochromator is placed between the light source and sample to allow light of a narrow bandwidth to interact with the sample at any given point in time and is manipulated during the measurement procedure such that the sample is scanned across the required excitation wavelength window during the measurement procedure. The emission wavelength profile is collected during this procedure and provides valuable information relating to the fluorescent properties of the sample.

Field-based fluorescent probes: A number of field-enabled fluorescent probes are now available to the water analysis sector. For example, Robertson Geologging Ltd[4] report a new borehole UV fluorescence probe (UVFP) to detect hydrocarbon contamination in water wells (9 cm diameter). The UVFP uses a powerful xenon light source that emits UV radiation at a peak wavelength of 239nm that is collimated and focussed through a window in the probe onto a small volume of the surrounding fluid or vapour. Resultant fluorescence is detected at a sensitive photomultiplier. An optical filter centred on 360nm is used to discriminate hydrocarbon fluorescence from that produced by organic decay. The probe response is standardised against a known concentration of carbazole, an organic compound with a similar fluorescent fingerprint to common oils.

Synchronous scanning fluorimetry: The emission profiles from fluorophores are typically relatively broad. In many cases, additional useful data can be obtained by performing synchronous scanning fluorescence, in which both an excitation and emission monochromator is used, such that the wavelength at which the emission profile is collected is offset by a relatively small bandwidth (e.g. 5-8 nm) relative to the excitation wavelength and both monochromators are scanned across the chosen wavelength window in a synchronous manner. Using this approach, it is possible to generate fluorescence fingerprints from which much useful data can be extracted. This approach was examined within the ARTDEMO programme and the additive information obtained by the resultant data analysis programme is discussed in more detail in ArtDemo Chapter 12.

Three dimensional fluorimetry: A drawback of standard fluorescence techniques is that, typically, the output data is in the form of an emission-intensity versus wavelength spectrum. However, when dealing with samples containing components of widely differing fluorescence characteristics, this resultant ‘two-dimensional’ spectrum can be difficult to interpret. In such cases, it is usual to employ rapid scanning techniques to create excitation-emission matrices (EEMs) in which an array of emission spectra are collected across a range of incrementally increasing excitation wavelengths.

Within the ARTDEMO programme, we have evaluated the use of a ‘three-dimensional’ spectrofluorimeter (SPEX 3-D, Jobin Yvon/Horiba, Edison, NJ, USA) as a means of rapidly interrogating PAH containing samples for fluorescence activity. This device utilises both an excitation and emission polychromators (spectrographs) to allow the instantaneous generation of EEM data. The first polychromator is used to disperse excitation radiation such that it is incident in a vertical plane upon the sample contained in the measurement vessel (a piece of quartz tubing). The emitted light is dispersed horizontally using a second polychromator to yield two-dimensionally dispersed radiation that is subsequently collected at a CCD detector (Figure 13). The third dimension is represented by the intensity of the signal, thus the output from the system is in the form of an excitation vs. emission vs. intensity profile. (Figure 14).

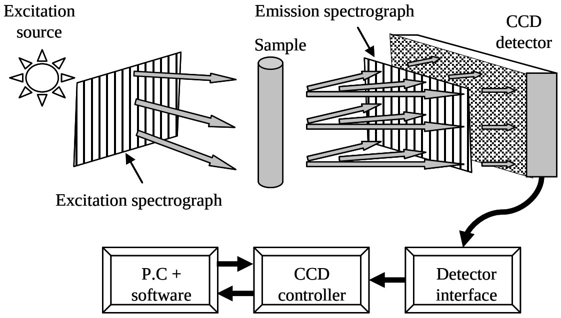

Figure 13: Schematic of the operating principle of the 3-dimensional spectrofluorimeter. Full details in text.

The benefits of this approach for on-line water quality assessment are significant – the entire fluorescent properties of a water sample can be captured instantaneously in an on-line format. Coupling this approach to sophisticated data treatment methodologies allows a degree of spectral deconvolution and valuable information concerning the composition of water samples is promised. The applicability of this approach to water samples analysis is explored further within ArtDemo Chapter 12.

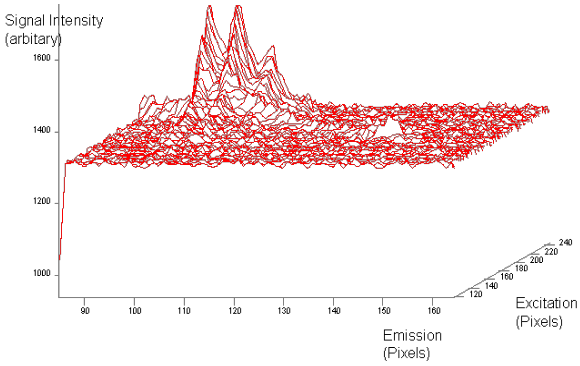

Figure 14: Three-dimensional isometric contour diagram of the polynuclear aromatic hydrocarbon perylene. X-axis: emission wavelength (pixels); y-axis: signal intensity at CCD recorder; z-axis: excitation wavelength.

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[4] http://www.geologging.com/english/downloads/uvfinal.pdf

6 CONCLUSION

Current methods of at-line/on-line water quality monitoring are relatively limited, either using standard non-specific probes to measure gross sample properties (pH, temperature, conductivity etc.) or general devices for determination of certain key physico-chemical characteristics (dissolved oxygen, specific ions, total dissolved solids, absorption maxima). However, considerable research is on-going in areas related to on-line/at-line quality in areas as diverse as biosensors (immunosensors) and inorganic (metals) analysis. Novel technologies developed during the ARTDEMO project are introduced: a microsensor for total organic carbon measurement, electrochemical methods for heavy metals analysis using disposable gold sensors, surfactant-based sample extraction techniques and a rapid method for sterols determination.

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8 REFERENCES

Bagni G, Hernandez S, Mascini M, et al. DNA biosensor for rapid detection of genotoxic compounds in soil samples. Sensors 5 (6-10): 394-410 Jun-Oct 2005

Bourgeois, W., Burgess, J.E., Stuetz, R.M. 2001. On-line monitoring of wastewater quality: a review. J. Chem. Technol. Biotechnol 76:337-348.

Bu S.J., Jin Z.G., Liu X.X.,Yang L.R., Cheng Z.J., Journal of the European Ceramic Society, 2004, *In Press*

Fenner, R.A., Stuetz, R.M. 1999. The application of electronic nose technology to environmental monitoring of water and waste-water treatment activities. Water Env. Res. 71:282-289

Huddelston J.G., Willauer H.D., Griffin S.T., Rogers D.R.. Aqueous polymeric solutions as environmentally benign liquid liquid extraction media. Ind.Eng.Chem.Res., 1999, 38, 2523-2539

Kröger, S. Setford, S.J. Turner, A.P.F. An immunosensor for 2,4-Dichlorophenoxyacetic acid in aqueous/organic solvent soil extracts. Analytical Chemistry, Vol. 70, 5047-5053, 1998.

Lucarelli F, Marrazza G, Mascini M. Enzyme-based impedimetric detection of PCR products using oligonucleotide-modified screen-printed gold electrodes. Biosensors and Bioelectronics 20 (10): 2001-2009 (2005).

Lynggaard-Jensen, A. 1999. Trends in monitoring of waste water systems. Talanta 50:707-716.

Mascini, M. Affinity electrochemical biosensors for pollution control Pure Appl. Chem. 73(1), pp. 23–30, 2001.

Qian, Z., Tan, T.C. 1999. Response characteristics of a dead cell BOD sensor. Water Res.. 32:801-807.

Ottosson, J. 2000. Hygiene Aspects of Greywater and Greywater Reuse, thesis TRITA-LWR LIC 2011, ISBN 91-7283-436-6.

Paez L.R., Matousek J., 2003. Preparation of TiO2 sol-gel layers on glass. Ceramics-Silikaty, 47 28-31.

Sharp, J.H., Suzuki, Y., Munday, W.L. 1999. A comparison of dissolved organic carbon in North Atlantic ocean near foreshore waters by high temperature combustion and wet chemical oxidation. Marine Chemistry 41:253-260

Silia, D., Rubio, S. Perez-Bendito, D. Maniasso, N. Zagatto, E.A.G. (1999). Anionic surfactants in acid media: a new cloud point extraction approach for the det. of polycyclic aromatic hydrocarbons in environmental samples A. Chem. Acta, 392 29-38.

Stathatos E., Lianos P., Del Monte F., Levy D., Tsiourvas D. (1997). . Formation of TiO2 nanoparticles in reverse micelles and their deposition as thin films on glass substrates Langmuir 13 4295-4300.

Stuetz, R.M., Fenner, R.A., Engin, G. 1999a. Assessment of odours from sewage treatment works by an electronic nose, H_2S analysis and olfactometry. Water Res. 33:453-461.

Stuetz, R.M., Fenner, R.A., Engin, G. 1999b. Characterisation of water using an electronic nose. Water Res. 33:442-452.

Stuetz, R.M., Georges, S., Fenner, R.A. 1999c. Monitoring wastewater BOD using a non-specific sensor array. J. Chem. Technol. Biotechnol. 74:1069-1074.

Thomas, O., El Khorassani, H., Touraud, E., Bitar, H. 1993. TOC versus UV spectrophotometry for wastewater quality monitoring. Talanta. 50:743-749.

Van Grieken R., Aguado J., Lopez-Munoz M.J., Marugan J. (2002) Synthesis of size controlled silica supported TiO2 photocatalysis. Journal of Photochemistry and Photobiology A: Chemistry, 148 315-322.

Vanrolleghem, P.A., Lee, D.S. 2003. On-line monitoring equipment for wastewater processes: state of the art. Wat. Sci. Tech. 47:1-34.

Watanabe H., Tanaka H, (1978). Nonionic surfactant as a new solvent for liquid-liquid extraction of zinc(II) with 1-(2-pyridylazo)-2-naphthol. Talanta 25, 585-589.

Zhang D., Yoshida T., Minoura H. (2003). Low-temperature fabrication of efficient porous titania photoelectrodes by hydrothermal crystallization at the solid/gas interface Advanced Materials, 15(2003)814-817.

Chapter 11: Real Time Data Validation and Filtration of Sensor and Analyser Measurements

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Abstract: Increased availability of sensors/analysers for a wide range of different parameters in water and waste water have led to an increased use of sensors/analysers for monitoring/control of treatment plants - resulting in better operating safety and better operational economy. However, the possibilities to carry out well performing real time online monitoring and/or process control of treatment plants depend of course on the quality of the incoming data from sensors/analysers applied. Some of the most frequent errors generated by sensors/analysers are missing data, measurement values out of range, peaks (outliers), constant measurement values and drift. It is possible to check the measurement coming from each sensor/analyser for these errors using simple, but still quite reliable methods.

1 INTRODUCTION

Single data methods are applied each time a new measurement value is logged (meaning that this is done in real time) and each of them gives as a result a confidence value between 0 and 100. An overall assessment of the confidence in the measurement can be made, and if this is lower than a preset threshold different actions can be taken (avoid to use measurement for control, calibrate/repair sensor/analyser, etc.).

The single data methods are designed to work within minutes and therefore other methods working over hours and days to look for drift of the measurement over a longer period have to be designed. However, one part these methods can be based on the same principles as the more simple methods, but are using data from a much longer period of time – typically looking days back from the actual time. The other part of the methods will need other measurements for comparison in order to distinguish between instrument drift and a real drift in the determinand measured. These methods are known as cross validation methods.

As described validated data are a prerequisite for using the data in real time for either closed loop process control or decision support. However, it might also be necessary to apply filtering methods in order to use the validated data, because correctly measured data still can show too high variation for closed loop feed back control procedures.

2 SINGLE DATA VALIDATION

This section describes some simple methods for single data validation and demonstrates (figure 1 and table 1) these on a typical sensor measurement in a process showing an hourly variation and a trend. The measurement is logged and validated every minute and the confidence generated by each method, the overall confidence and the measurement itself is plotted for a 3 hour period. The parameters used for each method has to be adjusted to the nature of the process monitored and the sensor/analyser used.

2.1 Gap Filling

Missing data is of course a big problem in RTC (real time control) applications where the control actions are based directly on sensor/analyser measurements, but it is also a problem in applications where the measurements are used either directly or indirectly (real time calculation of operation indexes) for decision support by operators.

Every time a single data point is missing it has to be considered if a possible control action should use a default option or it is possible to use an estimate for the missing value and then continue normal operation based on this. Depending on the variability and knowledge of the process measured, several possibilities exists for estimation of missing data (gap filling). The most simple is of course to use the value from the last measurement or use the trend from previous values of the measurement. However, if a correlation with other measurements exists or a process model is available, better estimates can be obtained.

No matter what method used it shall be reflected that confidence in an estimate is lower than confidence in a value from a real measurement. Furthermore, confidence shall decrease more and more for each consecutive value missing - eventually resulting in zero confidence. How fast confidence shall reach zero and if the decrease in confidence shall be linear or decrease faster for each value missing depends on the belief in the estimates.

The gap filling method used in the example is using the previous value of the measurement as an estimate and a linear confidence function, which simply is adjusted by giving the decrease in confidence per minute (eg. per time step). In order to demonstrate the method data have been deleted in the test data set between 00:15 and 00:20 and around 00:30

2.2 *Range Check*

Values out of range can be related to either the sensor/analyser itself or knowledge concerning the process monitored. The sensor/analyser is having a normal working range, where – if properly calibrated - values are believed to be true. This working range should fit the normal variation band of the determinand monitored.

A validation method taking into account also the fact that, the working range of a sensor/analyser is not necessarily the same as the full scale (often the quality of a measurement is lower at the ends of the full scale) suggests that confidence in the measurement shall be maximum within the normal working range and decrease gradually to zero through two “warning bands” on each side of the working range.

The example shows a method with a sensor/analyser having a full scale of 0 – 25 and a normal working range for the determinand monitored of 20 to 80 % of full scale (low and high limit for the confidence function in the example being 5 and 20 respectively). Values higher 95 % and lower than 5 % of the full scale are not expected to occur so confidence in these measurement values shall be zero (minimum and maximum limit for the confidence function in the example being 1.25 and 23.75 respectively).

The decrease in confidence is in the example designed to have a linear behaviour, but of course other functions could have been chosen. The demonstration (figure 1) shows unexpected values in the start of the period, but after a few minutes the values are only triggering a warning. Due to the hourly variation and the drift in the measurement a warning is again issued after an hour (values too low but might be valid) and after 2.5 hours (values too high but might be valid).

The range check also detects the second peak in the data, but the first peak, the estimates of missing data and the constant sensor/analyser value passes the check unattended because the measured values are within the working range.

2.3 *Rate of Change Check*

Peaks (outliers) of a much higher (lower) value than the current measurement values are usually caused by a disturbance of the sensor/analyser and are easily detected because the rate of change normally is much bigger than the true variations in the determinand monitored and the random error (noise) in the measurement value generated by the sensor/analyser. The confidence in peak values shall of course be zero (and an estimate of the measurement value could be the previous value).

Table 1: Single data validation methods and parameters used in example

Method	Confidence function	Parameters used
Gap Filling (GF); N = no. of time steps	$= 100 * (1 - n_i * (100 / N)$; $n_i < N$ ($n_i = 1, 2, ...N$) $= 0$; $n_i >= N$	$N = 5$
Range Check (RC); x = measurement value	$= 0$; $x > L_{max}$ $= 100 * ((L_{max} - x) / (L_{max} - L_{high}))$; $L_{high} <= x <= L_{max}$ $= 100$; $L_{low} < x < L_{high}$ $= 100 * ((x - L_{min}) / (L_{low} - L_{min}))$; $L_{min} <= x <= L_{low}$ $= 0$; $x < L_{min}$	$L_{max} = 23.75$ $L_{high} = 20.0$ $L_{low} = 5.0$ $L_{min} = 1.25$
Rate of Change Check (RCC); x = change of measurement per minute	$= 0$; $x > L_{max}$ $= 100 * ((L_{max} - x) / (L_{max} - L_{high}))$; $L_{high} <= x <= L_{max}$ $= 100$; $L_{low} < x < L_{high}$ $= 100 * ((x - L_{min}) / (L_{low} - L_{min}))$; $L_{min} <= x <= L_{low}$ $= 0$; $x < L_{min}$	$L_{max} = 2.5$ $L_{high} = 2.0$ $L_{low} = -2.0$ $L_{min} = -2.5$
Running Variance Check (RVC); x = running variance of last n measurements	$= 100$; $L_{low} < x$ $= 100 * ((x - L_{min}) / (L_{low} - L_{min}))$; $L_{min} <= x <= L_{low}$ $= 0$; $x < L_{min}$	$L_{low} = 0.025$ $L_{min} = 0.01$ $n = 5$
Overall Assessment	$= Min (C_{GF}, C_{RC}, C_{RCC}, C_{RVC})$	-

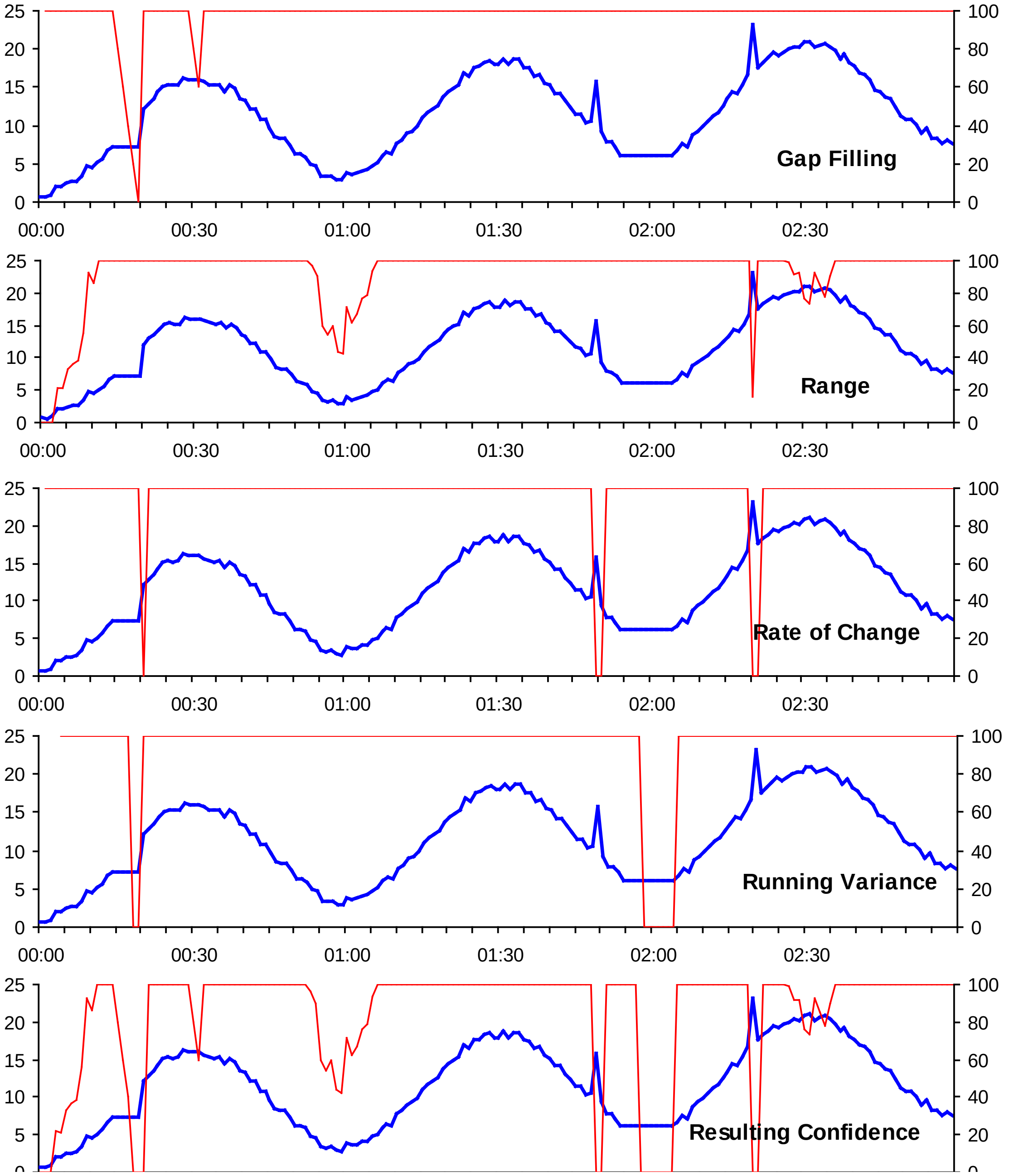

Figure 1: Single data validation methods - example

Smaller outliers and unexpected process rates can also be detected but as it can be difficult to distinguish between these with a simple method, confidence shall be calculated using a “warning band” as in the method used for range check.

The measurement value used in the example vary with approximately 15/half hour corresponding to 0.5/minute and the random component is not bigger than 1.5/minute. Therefore, values of the difference between two consecutive measurement values inside the range from –2 to 2 shall have maximum confidence. The band width of the “warning band” has been set to 0.5, allowing for an increase in the variation of the determinand monitored of a factor of two (assuming that the size of the random component of the measurement value will not increase) before the calculated rate of change is declared as a peak value

The demonstration shows that the peaks are detected without any problem. Also the shift from estimates to real measurement values is detected, but as this is already known from the gap filling it can safely be neglected. However, this shows that a sudden shift in measurement values also will be detected by this method

2.4 Running Variance Check

Constant measurement values are typically a result of planned (automatic calibration) or unexpected (failure) sensor/analyser performance, because a normally functioning sensor/analyser always have a small variation in its measurement value even if it measures in a standard solution (the random component usually referred to as precision or repeatability, which is the precision under repeatability conditions).

None of the above methods are able to detect if a sensor/analyser fails and “locks” on a fixed measurement value, if this value is within the working range. Furthermore, it is often seen that a sensor/analyser measurement shifts towards a smaller variation when it needs cleaning.

Therefore, the need for a validation method allowing a certain variation as the normal is obvious. Furthermore the method shall decrease the confidence if the expected variation decreases and end up with a zero confidence when the variation nearly has disappeared (still allowing for bits to shift in A/D converters).

The running variance of a number of previous measurement values shall serve as a measure of the variation in the actual measurement value and again a simple way of calculating the confidence shall be a linear decrease over a “warning band”. In order to not have a too “sluggish” running variance calculation, the calculation period is in the example kept down to 5 time steps. Typically the running variance for the measurement used in the example is always higher than 0.05 so the method low limit is set to 0.025, whereas the minimum limit is set to 0.01.

The demonstration of the method (figure 1) shows that the constant measurement values primed into the data set around 02:00 are nicely detected together with the estimates in the start of the dataset. However, it also shows that with the actual variation a certain number of constant values is needed – the two estimates just after 00:30 are not detected

2.5 Overall Assesment

Overall assessment of the confidence in the measurement value is done by calculating a resulting confidence as the minimum of all confidence functions, and as figure 1 shows this simple single data validation scheme nicely detects the type of errors searched for.

As the simple single data validation scheme described has focus on sensor/analyser performance here and now without any comparison with reference values, it will not be able to express anything about the trueness (measured as bias) or long term drift of the measurement values

3 CHECKING FOR LONG TERM DRIFT

A known bias is not a problem as this can be compensated and preferably an unknown bias should be avoided by proper calibration procedures. However, a bias in the measurement value can slowly develop in time typically caused by fouling of the sensor. Therefore, a validation method detecting long term drift in the measurement value is needed.

The method is divided into two steps, where the first step is using two different methods to detect the long term drift. The second step is used to determine whether it is a drift caused by the Sensor/analyser itself, or it is a true long term trend in the determinand value monitored.

Detection of long term drift can be done using two different methods, Expected Mean Check and Acceptable Trend Check, both of them demonstrated in figure 2 and table 2 on a measurement having a range of 0 – 100 and logged every 12th minute (5 times per hour).

Data from a period of 14 days shows a process variable with a periodic variation of half a day, an expected mean value of approximately

Table 2: Methods for detection of long term drift and parameters used in example

Method	**Degree of Compliance with Limits**	**Parameters used**
Expected Mean Check (EMC); x = moving average of last n measurements	$= 0;\ x > L_{max}$ $= 100 * ((L_{max} – x) / (L_{max} – L_{high}));\ L_{high} <= x <= L_{max}$ $= 100;\ L_{low} < x < L_{high}$ $= 100 * ((x – L_{min}) / (L_{low} – L_{min}));\ L_{min} <= x <= L_{low}$ $= 0;\ x < L_{min}$	Expected Mean = 50 $L_{max} = 55.0$ $L_{high} = 52.5$ $L_{low} = 47.5$ $L_{min} = 45.0$ $n = 60$
Acceptable Trend Check (ATC); x = moving slope (slope determined by linear regression of last n moving average values)	$= 0;\ x > L_{max}$ $= 100 * ((L_{max} – x) / (L_{max} – L_{high}));\ L_{high} <= x <= L_{max}$ $= 100;\ L_{low} < x < L_{high}$ $= 100 * ((x – L_{min}) / (L_{low} – L_{min}));\ L_{min} <= x <= L_{low}$ $= 0;\ x < L_{min}$	$L_{max} = 1.0$ $L_{high} = 0.75$ $L_{low} = -0.75$ $L_{min} = -1.0$ $n = 240$

50 and a drift in the measurement starting approximately after a week.

3.1 *Expected Mean Check*

The Expected Mean Check method is based on a calculation of a moving average of the last n measurements of the determinand monitored. The moving average is compared to the expected mean value. It is important that n is chosen in such a way that the moving average is able to accommodate possible periodical variations in the process monitored.

3.2 *Acceptable Trend Check*

The Acceptable Trend Check method is based on a calculation of a moving slope. The slope is calculated from the last n values of the moving average calculated above. The moving slope is compared to an acceptable trend. It is important that n is chosen in such a way that the moving slope in fact shows long term drift, and the n for this method is typically 2 - 5 times higher than for Expected Mean Check method.

Five times an hour both methods generate a degree of compliance (100 for full compliance and 0 for non-compliance) with the set limits (table 2). The calculations of the degree of compliance for the methods are comparable to the calculations of the confidences for the range check method and the rate of change method respectively, and as for these single data validation methods, it is important that the parameters used for each method are adjusted to the nature of the process monitored and the sensor/analyser used.

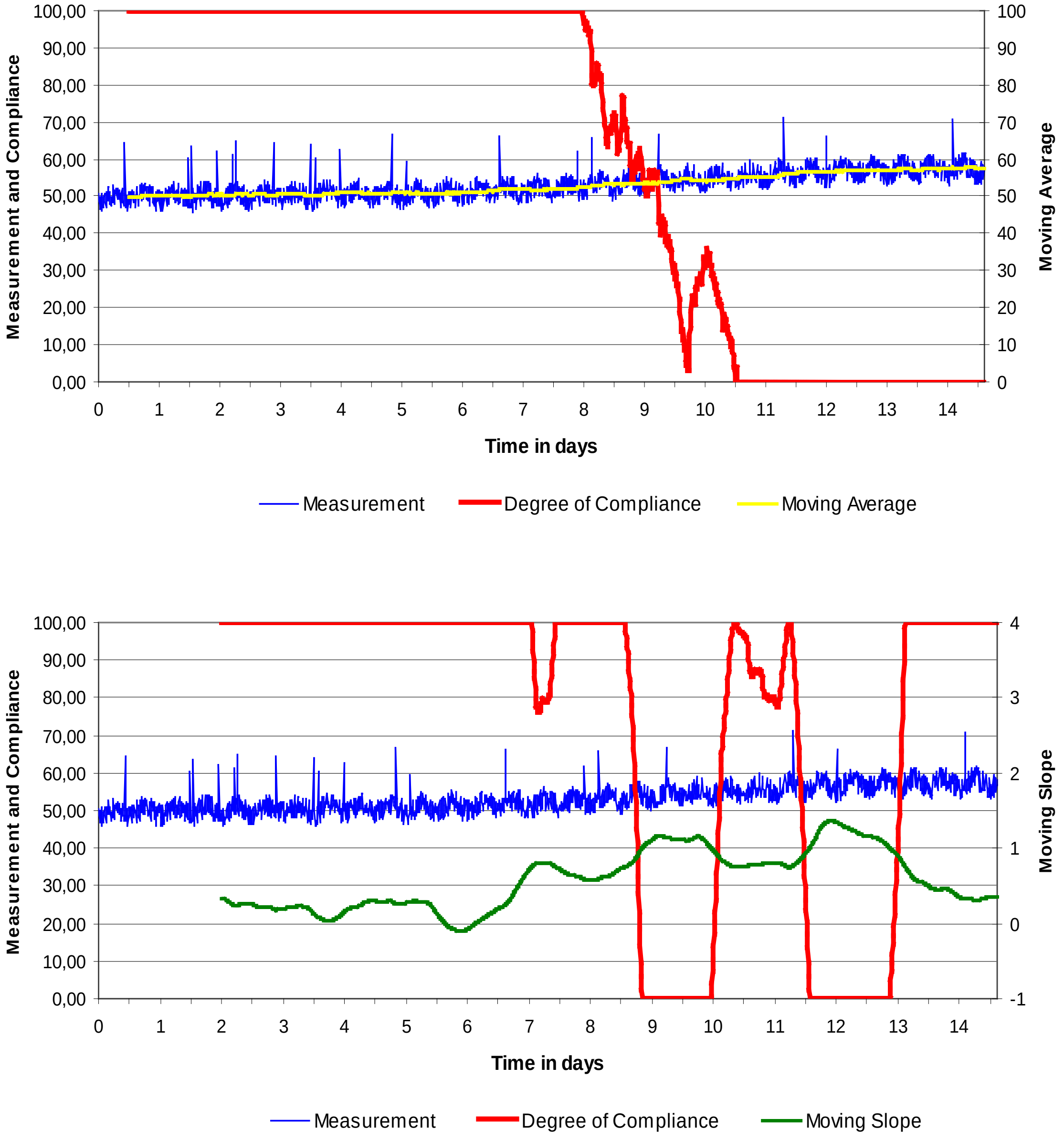

Figure 2: Methods for detection of long term drift - example

As can be seen in figure 2 a drift is detected and a warning given after 7 days by the moving slope. However, the moving average shows that the resulting bias (or drift in the process variable) is still within acceptable limits. During day 8 the drift becomes unacceptable and the resulting bias increases over the next two days to an unacceptable level. After day 13 the drift disappears again but leaves the measurement with an unacceptable bias.

As described, using both methods, will enable an operator to assess the warnings given by the methods, and even if both methods works in real time, they are (at least in this example) not so time critical as the single data validation methods. Therefore, actions taken do not necessarily have to be started automatic (even if they could), and the operator can therefore proceed to the next step

3.3 The Nature of the Drift

Determination of the nature of the drift (instrument or real drift of the determinand monitored) can be done either manually or automatically. The operator can decide to analyse a grab sample or he can invoke a cross validation method (see next section). The result from either method can then be compared to the measurement from the monitor, and it can be judged if the drift is instrument or process based.

The cross validation method can of course also be started automatically at a given degree of compliance, calculated by either of the two detection methods, and give an estimate of the measurement value, compare it to the measurement from the monitor and decide if the difference is significant (ie. a bias).

If the detected drift is instrument based the on-line monitor will need a recalibration, and if the drift is process based the operator will need to assess the causes to the change in the process

4 CROSS VALIDATION METHODS

A cross validation method exploits the possible correlation between on-line measurements and is therefore a multi data validation method. If the measurements are highly correlated, it is possible to build and calibrate a model (simple or complex) describing the relation between two or more measurements. It can be a deterministic or statistic model or a combination (known as a grey-box model) and it can have one or more measurements from different on-line monitors/sensors as input and one or more of measurement(s) as output.

If such a model is running in real time giving a new estimate every time data are logged from different sensors/analysers, the estimate can be regarded as a measurement with the same properties as other measurements. Such an estimate is also known as a software sensor or a virtual sensor.

Some of the more simple examples of software sensors are: a flow sensor based on a level measurement and a Q/H relation (one input, one output), a mass sensor based on a flow and a concentration measurement (two inputs, one output), a process rate sensor based on several consecutive measurements of a concentration (at least two inputs, one output). The more complex examples of software sensors ends up as real time modelling of treatment processes, sewer systems, etc. (multiple inputs, multiple outputs).

If a software sensor which “measures” the same as an on-line sensor/analyser is available, cross validation is quite straightforward, because the difference of the two measurements then can be regarded as a new measurement with an expected mean at zero. This new measurement can undergo a range check with narrow limits or directly give an estimate of a bias, which can be followed by the expected mean check. Such a software sensor is also very useful in the case of missing data, because the estimate of the measurement then can be used instead.

The most simple cross validation can of course be performed, if an application (for operational security) uses redundant (two or more of the same type of sensors/analysers. Another simple cross validation can be set up in a situation where a flow meter, a level measurement and a Q/H relation are available.

However, also more complex cross validations can be easily be done using neural networks with two or more inputs and one output. Neural networks have become more and more easy to use, and if they are properly trained, using measurements which are known to be correlated, they are a very good tool for building virtual sensors corresponding to the real sensors/analysers in a given application.

5 DATA FILTRATION

Data filtration is a necessary step in the process of turning on-line sensor/analyser data into useful information. On-line measurements can be rather noisy and fluctuating, which can make them difficult to overlook and difficult to use in calculation of set-points for control (closed loop or as a decision support function).

Table 3: Data filters to be used in real time on measurements from sensors and analysers. x_t: raw measurement at time t; y_t: filtered measurement at time t; n: number of time steps involved

Filter	General expression	Comment
Moving average	$y_t = \sum_{i=0}^{n-1} \frac{1}{n} x_{t-i}$	Also called a rectangular filter. All measurements included are given the same weight. Filters out periodical events with a period equal to the time period covered.
Parzen filter	$y_t = \sum_{i=0}^{n-1} w_{t-i} x_{t-i}$	Also called low-pass filter if weights calculated to decrease with age. Filters out events occurring more often than the time period covered.
Robust filter	$y_t = \frac{1}{n-2} \sum_{i=0}^{n-1} x_{t-i} - x_{\max} - x_{\min}$	Filters out the max and min value in the time period covered and calculates the mean of the rest.
Exponential filter	$y_t = y_{t-1} + a(x_t - y_{t-1})$	An auto regressive filter remembering past measurements according to the exponential factor a. If a=0.5 an abrupt change in a measurement will have reached 97% of its value after 5 steps.

Filtering gives a more smooth signal which is better suited for control purposes. However, it has to be remembered, that filtering add to the response time of an on-line measurement

Four of the more commonly used (and simple) filters are described in table 3, and figure 3 shows two of these filters working on a suspended solids measurement (top) in the bottom outlet from a clarifier and a sludge blanket measurement (bottom) in the clarifier. Both measurements are used for real time control of the clarifier, but as can be seen fluctuations in the measurements makes it necessary to use filters before the measurements can be used for calculations of set points.

The Suspended Solids measurement has a periodic behavior due to a sludge scraper passing every 16th minute. Therefore a moving average with a period of 16 minutes has been selected to filter this measurement. The sludge blanket measurement shows a more random behavior, therefore an exponential filter has been selected for this measurement.

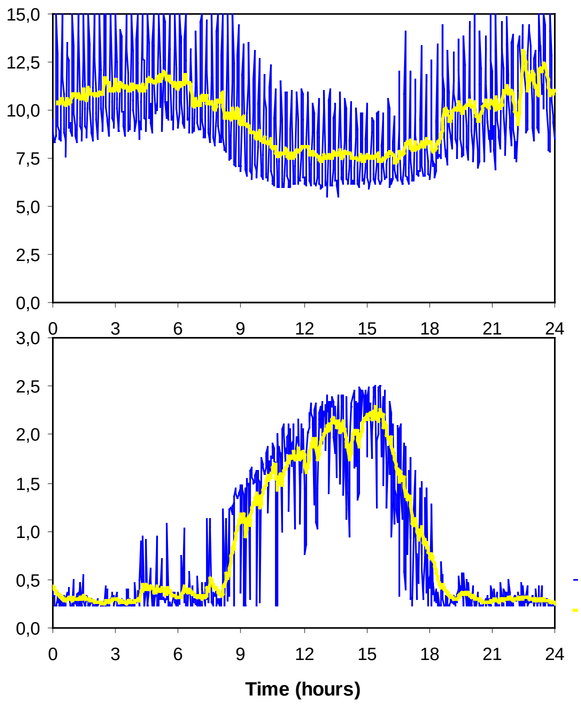

Figure 3: Filters used on clarifier measurements

Chapter 12: Chemometrics for Environmental Analysis

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Abstract: Chemometrics can briefly be defined as the application of mathematical and statistical techniques to extract the maximum relevant chemical information from analytical data. Although the discipline has been around for some decades, it is the capability of modern analytical instruments to routinely generate large multivariate data sets that has secured chemometrics as an essential part of the environmental analyst's armoury. This chapter introduces the three main branches of chemometrics – data exploration, sample classification and multivariate calibration. It goes on to describe the general approach used to generate a calibration model, using as example the simultaneous determination of three polyaromatic hydrocarbons (PAHs) in water using data acquired by fluorescence spectroscopy, and the simultaneous determination of multiple metal pollutants in water using electroanalysis.

1 INTRODUCTION

Modern analytical methods are capable of extracting large amounts of chemical data from a given environmental sample. For example, a fluorimeter can provide us with a feature packed spectrum from water contaminated by polyaromatic hydrocarbons, but what is the nature of the contamination? What pollutants are present? What is the concentration of the pollutants? How confident can we be in this information? Fundamental theory tells us that the wavelength at which a compound fluoresces is related to its chemical structure and the intensity of the fluorescence is related to its concentration, but the theory tends to break down in real analytical situations, because instruments are not totally error free and sample matrices can be complex. The solution to this problem is chemometrics, the science of extracting relevant information from analytical data. There are many definitions, but the most meticulous is arguably that proposed in one of the first textbooks on the subject [Massart et al., 1988]:

"Chemometrics is the discipline that uses mathematical, statistical, and other methods employing formal logic (a) to design and select optimal measurement procedures and experiments, and (b) to provide maximum relevant chemical information by analysing chemical data".

Although the experimental design aspects covered in part (a) of this definition are important (as mentioned later in section 1.3.1), this chapter focuses primarily on the second part of the definition, which occurs after data has been collected. The key factor differentiating chemometrics from more prevalent forms of statistical data analysis is that we are usually looking at multivariate data. That is, data acquired from instruments that measure more than one variable for each sample, for example:

- Spectroscopy: intensity is measured at multiple wavelengths.
- Electronic nose: data is acquired from an array of sensors.
- Chromatography: measurements are acquired at different elution times.

Furthermore, we are also usually looking at analyses in which the sample being analysed is a mixture of two or more compounds. This is important, because this is what we usually want to do in the real world – very few samples contain only a single analyte.

2 REPRESENTATION OF DATA

Before going into detail about chemometric methods, it is important to examine how multivariate data from analytical devices is usually organised. In the case of a single sample, we simply have a list of measurements for each variable. In the case of an eight-sensor array, in which each sensor provides one value, the data captured by the array from a given sample might look something like this:

Sensor 1	Sensor 2	Sensor 3	Sensor 4	Sensor 5	Sensor 6	Sensor 7	Sensor 8
74.5	98.0	70.4	83.1	47.6	69.5	127.3	46.2

In chemometrics, we refer to this using the mathematical term, vector, and it is written in vector notation:

$x = (74.5\ \ 98.0\ \ 70.4\ \ 83.1\ \ 47.6\ \ 69.5\ \ 127.3\ \ 46.2)$

In a scientific study, we will generally have multiple samples, the results of which are usually arranged in a table of variables against sample names. The data acquired from a collection of five samples like the one above might look like this:

	Sensor 1	Sensor 2	Sensor 3	Sensor 4	Sensor 5	Sensor 6	Sensor 7	Sensor 8
Sample 1	74.5	98.0	70.4	83.1	47.6	69.5	127.3	46.2
Sample 2	6.9	5.1	14.6	3.9	3.1	4.8	5.1	5.1
Sample 3	58.1	73.7	56.8	62.4	35.8	53.1	93.6	36.0
Sample 4	5.7	4.6	12.6	3.4	2.5	4.2	5.2	4.3
Sample 5	7.2	5.4	15.5	4.1	3.6	5.1	5.3	5.2

In mathematical terms, this is referred to as a matrix, and is written in matrix notation, which simply collects together the measurement vectors for all the samples:

$$\mathbf{X} = \begin{pmatrix} 74.5 & 98.0 & 70.4 & 83.1 & 47.6 & 69.7 & 127.3 & 46.2 \\ 6.9 & 5.1 & 14.6 & 3.9 & 3.1 & 4.8 & 5.1 & 5.1 \\ 58.1 & 73.7 & 56.8 & 62.4 & 35.8 & 53.1 & 93.6 & 36.0 \\ 5.7 & 4.6 & 12.6 & 3.4 & 2.5 & 4.2 & 5.2 & 4.3 \\ 7.2 & 5.4 & 15.5 & 4.1 & 3.6 & 5.1 & 5.3 & 5.2 \end{pmatrix}$$

The size of the data matrix is n rows by p columns, where n is the number of samples and p is the number variables collected for each sample. Storing data as a matrix is advantageous as matrices are easily extensible to large numbers of variables and samples, and the adoption of such a consistent way of representing data allows chemometric techniques to be easily adapted to different applications. For example, if the data were spectroscopic, we would use a matrix similar to that shown above, but with the columns representing individual wavelengths rather than individual sensors, as shown in Figure 1.

3 BRANCHES OF CHEMOMETRICS

Chemometrics is a mature and multi-faceted discipline, covering many different methods, and many variations on each method. Different people group the methods in different ways, typically according to underlying mathematical principles. For our purposes, it is most appropriate to break chemometrics down into the following three branches, according to application:

- Exploration and visualisation of a collection of analytical data.
- Classification of samples according to their analytical response.
- Calibration of acquired data to provide quantitative information about a sample.

These three branches of chemometrics are introduced individually in the following sections.

3.1 *Exploratory Analysis*

The purpose of exploratory data analysis is to simplify a data matrix so that we can more easily comprehend it. The ultimate aim is usually to convert a large data matrix into a visual representation from which relationships between different samples can be observed. This can help us to answer pertinent analytical questions such as:

- Are there sufficient differences between the data from different sample types to use it for sample identification?
- How much variation is there between

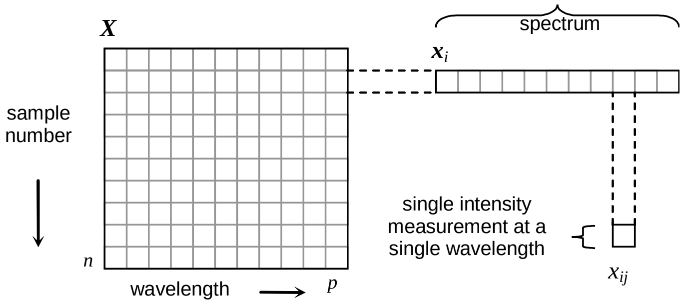

Figure 1: Organisation of spectroscopic data into a data matrix, X

samples of the same type?

- Are all samples correctly labelled?
- Are there any rogue results (outliers)?

The most popular exploratory data analysis method is principal components analysis (PCA) which reduces the many variables in data matrix into a much smaller number of combined variables, called principal components [Jackson, 1980]. Samples can then be plotted on a simple 2D or 3D scatter plot, at positions dictated by these principal components, making the relationships between the samples easy to see. An example PCA plot is shown in Figure 2. The alternative approach of hierarchical cluster analysis (HCA) produces tree diagrams (dendrograms) in which the level of similarity between samples is depicted by the length of the branch by which the sample is represented [Otto, 1999, Ch. 5], and is particularly useful for data sets with very large numbers of samples. Techniques such as PCA and HCA are often referred to as unsupervised methods because no prior knowledge is incorporated into the analysis – the samples are simply organised according to their level of similarity.

3.2 *Classification*

The aim of classification is to convert the numeric data provided by an analytical instrument into qualitative information of use to the analyst. For example, we might want to acquire a spectrum from a water sample, and classify that sample as ‘polluted’ or ‘clean’ according to the content of that sample. This is achieved by building a classification model – a mathematical equation capable of transforming

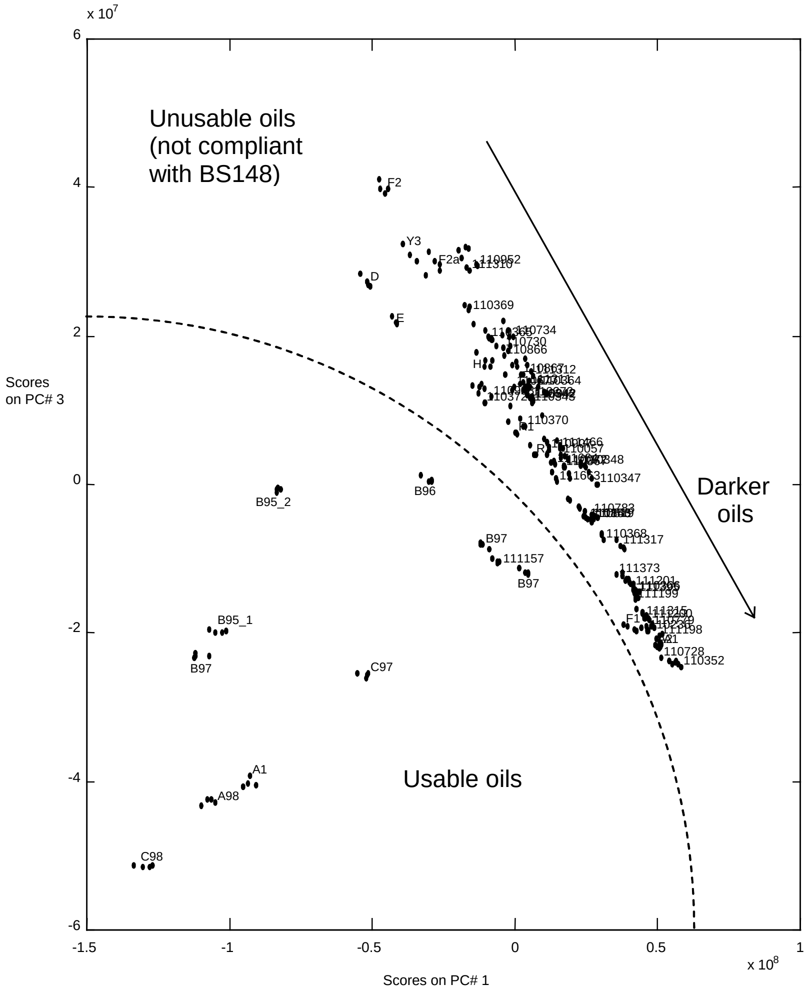

Figure 2: Principal components plot showing the relationship between insulation oils according to their synchronous scan fluorescence spectra [from Bessant, 2001]. Each point on the figure represents a 250 element spectrum acquired from a particular oil. The plot clearly reveals that the data acquisition technique is very repeatable – the four repetitions for each oil fall within small clusters. More importantly, all the oils conforming to the British environmental standard BS148 fall within one area of the figure, delineated manually on the plot by the dotted line. These results clearly indicate that the synchronous scan analysis protocol can be used to determine regulatory conformance.

an unseen measurement vector (x) in a single variable (y) representing its class. Linear discriminant analysis (LDA) and SIMCA (Soft Independent Modeling of Class Analogies) are two well-established chemometric methods for building classification models [Otto, 1999, Ch. 5]. Essentially, these methods use data from known samples (so-called training data) to build a mathematical definition for each class. Unseen samples can then be classified according to the definition that they match most closely. In simple terms this is analogous to drawing boundaries around the clusters in a PCA plot and identifying unseen samples by determining which bounded cluster they fall into. A more complex, and often more effective, alternative is to use artificial neural networks (ANNs) which can basically be trained to recognise particular spectral or other analytical patterns, despite the presence of noise and other variations, by means analogous to those that the brain uses to recognise shapes [Hagan et al., 2003].

3.3 *Calibration*

The aim of calibration is to extract quantitative information from a measurement. Every scientist is familiar with this concept, typically in terms of the calibration of a measured value, x, to a value of interest, y using the equation of a straight line, $y = mx + c$, where m is a scaling factor and c is an offset. However, as modern analytical techniques are capable of generating more than one measured value per sample, more complicated – multivariate - calibration techniques may be applied. The remainder of this chapter deals with this subject, as this is most applicable to one of the key applications in environmental analysis – quantification of multiple analytes from a complex analytical response.

4 MULTIVARIATE CALIBRATION

Multivariate calibration is achieved by generating a calibration model - a mathematical equation capable of transforming a multivariate analytical response acquired from a sample into one or more quantitative values of interest. Typically the quantitative information sought is the concentration of one or more chosen analytes. In the following sections, we explain the processes used to generate and validate a calibration model, using work carried out in the ARTDEMO project as an example. In this case, we are interested in determining the concentration of three potentially polluting polyaromatic hydrocarbons (anthracene, phenanthrene and napthalene) in water samples analysed using fluorescence spectroscopy. The responses obtained for the three PAHs when analysed individually are shown in Figure 4. Although each compound gives a distinct response following excitation, the overlapping nature of the responses would clearly make them difficult to resolve individually in a mixture without chemometic assistance.

4.1 *Building and Using a Calibration Model with Multiple Linear Regression*

The starting point for building a calibration model is a set of analytical responses acquired from a set of samples of known composition. These samples may be synthetic mixtures, or real samples for which the concentration of analytes of interest has previously been accurately determined using standard laboratory protocols. This data set is referred to as the training set, because it is used to train the model to carry out the required calibration task. The composition of the training set is crucial to the generation of an accurate calibration model because it needs to

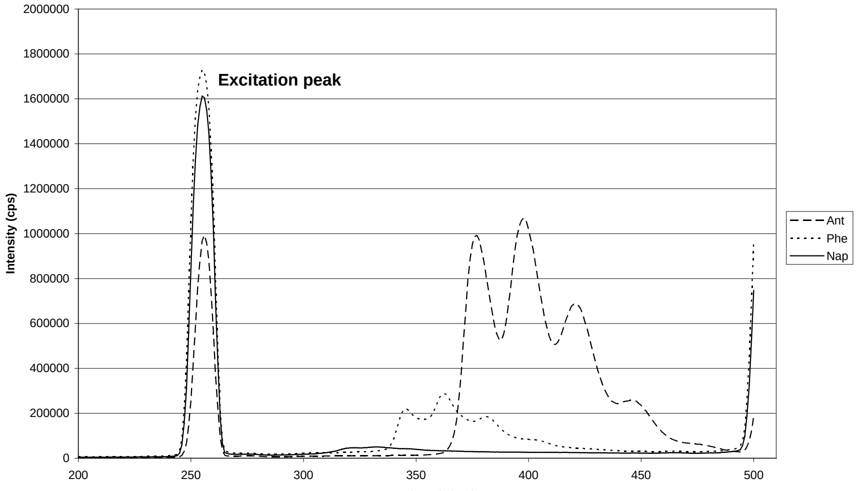

Figure 4: Fluorescence spectra collected from three different PAHs: anthracene, phenanthrene and naptheline.

capture all the key aspects of the data. In particular, the data should:

- Contain all the analytes at the maximum and minimum concentrations expected.
- Contain enough concentration steps to allow fitting of a non-linear model if necessary.
- Contain representative mixtures of the analytes – not just individual responses.
- Capture a representative amount of expected experimental variability.

In the example described here, the input data comprised a 301 element spectrum for each sample, where each element represents the fluorescence intensity at a given wavelength. The samples were generated synthetically, by adding the three PAHs to acetyl nitrile in the required proportions. This was done according to the full factorial design with five levels (0, 100, 200, 400, 600 ppb) shown in Figure 4. As is common practice, samples were produced and analysed in a random order, to separate the effect of the different concentrations from possible time dependent factors such as sensor drift. This data set was collected using a particularly thorough design, as every possible combination of compounds with the concentrations listed above has been analysed – resulting in 125 unique mixtures. Various experimental design approaches are available for producing designs which meet the requirements for a good training set, using considerably fewer samples [Brereton, 2003, Ch. 2; Otto, 1999, Ch. 4].

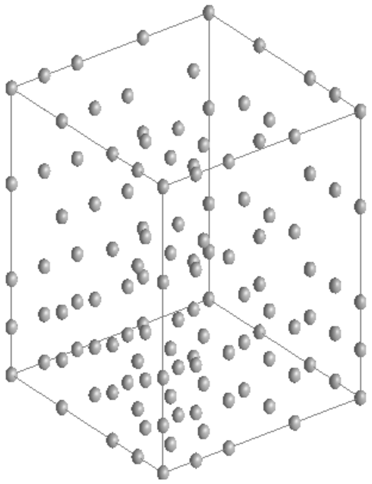

Figure 4: A schematic representation of the training data set. Each sphere represents a mixture of the three compounds at the concentrations indicated by the position of the sphere. Three spectra were obtained from each mixture, giving a total of 375 spectra in the training set.

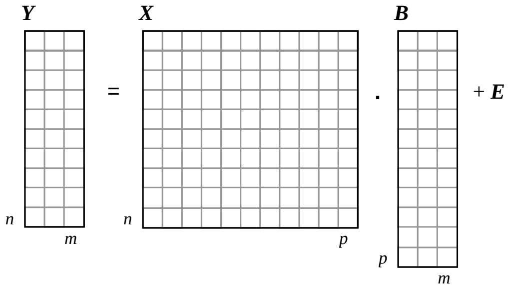

Figure 5: A schematic representation of multivariate calibration using multiple linear regression.

In addition to the matrix of training data, we also have a n×m matrix, Y, containing the concentrations of the m analytes of interest for each of the n samples. In our example, m = 3 and n = 375. The aim of building the calibration model is to develop a mathematical equation capable of transforming the training data matrix, X, to the concentration matrix, Y. The simplest way of achieving this is multiple linear regression (MLR), shown diagrammatically in Figure 5, in which a regression matrix, B, is calculated which, when multiplied by X, yields as close an approximate of as possible Y. Given a known X and Y, calculation of B can be achieved relatively easily using the method of least squares [Otto, 1999, Ch. 6]. Because experimental variability always prevents a perfect fit, the residual matrix, E, is needed to balance the equation. The magnitude of E gives a good indication of quality of the model.

Once the regression matrix has been determined, prediction of the analyte concentrations in trivial. We simply multiply the measurement vector for a sample by the regression vector. The results in a m element vector, ŷ, representing the concentrations of the m analytes in that sample.

4.2 Partial Least Squares

A major disadvantage of MLR is that all variables are given equal weight when determining the regression matrix. This tends to limit the accuracy of the calibration models produced, as the model is compromised by trying to map noise to analyte concentration. One way round this is to use PCA to reduce the training data set to its principal components before calculating the regression matrix – this combined approach is known as principal components regression (PCR). Partial least squares (PLS) takes this a step further by weighting the variables according to the impact they have on the concentrations, i.e. the covariance between the X and Y matrices [Gelad & Kowalski, 1986]. This generally results in more accurate models than both MLR and PCR, so tends to be the most widely used of the three techniques. Indeed, it is

PLS that we used to calibrate the systems in the ARTDEMO project.

4.3 Other approaches

Given good quality training data, PLS usually produces good quality calibration models, provided the relationship between acquired data and concentration is linear, or can be made linear by a simple transformation of the ***X*** or ***Y*** matrix. In some cases, for example where quenching or other complex interactions between analytes occur, this is not possible, and more advanced modeling techniques are required. A particularly popular solution is ANNs, which are able to model virtually any relationship between ***X*** and ***Y***, provided such a relationship exists in the data. Extensive work has been done in this area in both in spectroscopy [Long *et al.*, 1990] and electrochemistry [Richards *et al.*, 2002].

4.4 Model validation

Essentially, we can produce a model to map any ***X*** matrix to any ***Y*** matrix, particularly using a selectively chosen training matrix or a very powerful neural network. For this reason, it is essential that a calibration model is properly validated before being used to determine analyte concentrations in unknown samples. This must always be done with known samples that were not included in the training data set, ideally at concentrations other than those used during training. The predicted concentration vector, $\hat{\boldsymbol{y}}$, produced by multiplying the validation data matrix by the regression matrix can then be compared with the actual concentration vector, $\boldsymbol{y}$, to see how accurate the model is for a given sample. These results are often plotted graphically, as for our example in Figure 6, or used to calculate an overall error score for the model, such as the root mean square (RMS) error:

$$RMSE = \sqrt{\frac{\sum_{j=1}^{n}\left(y_j - \hat{y}_j\right)^2}{n}}$$

The number of samples in the validation set is denoted by n in this equation. For our example calibration, the RMS error for the validation data is a very respectable ±32 ppb averaged across all three analytes, which varies according to compound and concentration as shown in the figure.

5 ELECTROANALYSIS CASE STUDY

To illustrate the generic applicability of the multivariate calibration methodology described above, we present here another example from the ARTDEMO project, where PLS was used to build a model for the determining the concentration of three metallic contaminants in water samples, from data acquired using anodic stripping voltammetry (ASV). Typical voltammograms acquired using this technique are shown in Figure 7 of Chapter 10, along with details of how they were obtained. The voltammograms are the starting point for our data analysis, so are in that respect analogous to the spectra seen in Figure 4. The calibration process that follows is also very similar, with the same requirement to collect a representative set of training data, and a validation set on which to test the model. The results of validating a PLS calibration model trained to determine the concentration of three metals – cadmium, lead

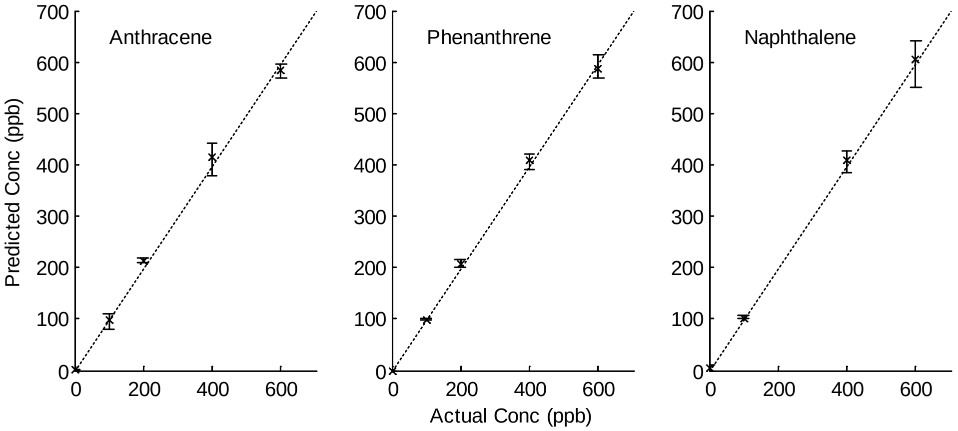

Figure 6: Output of PLS calibration model for validation data comprising a total of 15 spectra from sample mixtures. Error bars indicate maximum and minimum predictions, revealing the worst performance of the model. The dotted lines indicate the ideal relationship between actual and predicted concentrations.

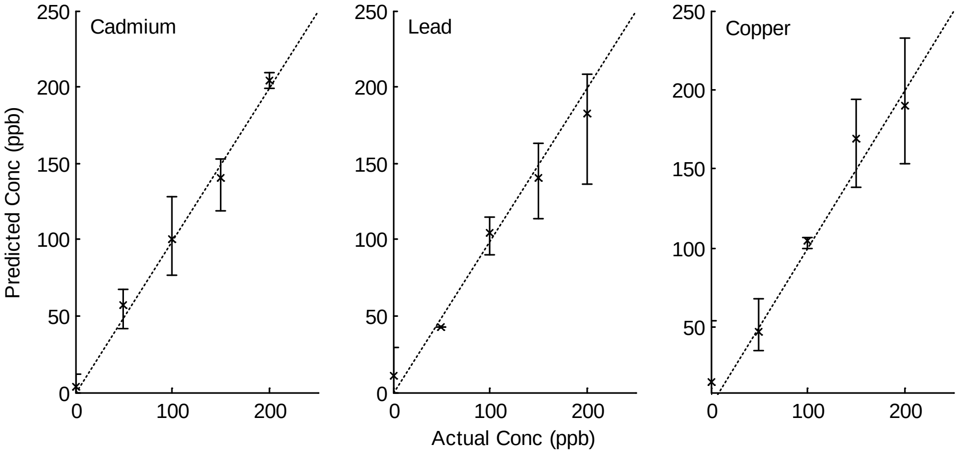

Figure 7: Calibration performance of a PLS model trained to determine the concentration of cadmium, lead and copper from anodic stripping voltammograms. Key as Figure 6.

and copper – from ASVs is shown in Figure 7.

Calibration of voltrammetric data is generally more challenging than calibrating spectra, because the surface chemistry of the electrode can change as the potential sweep progresses, so an analyte that appears early in the scan can have a considerable impact on the response of an analyte that occurs later. This is particularly common for organic analytes, whose oxidation or reduction at the electrode can result in breakdown products adsorbing to the electrode surface. For those cases, it can be necessary to use ANNs to account for the added complexity. In this example the model is clearly capable of simultaneously determining the concentration of the three analytes, but the variance of predicted concentration is high, suggesting that it may be worth pursuing the ANN route.

6 CHEMOMETRICS IN PRACTICE

For most applications, exploratory data analysis and model building can be achieved using an entry level personal computer (PC) running appropriate software. At the time of writing, there are several off the shelf chemometrics packages on the market, most notably Simca (Umetrics, Sweden) and Unscrambler (Camo, Norway). Many other packages also provide multivariate statistical functionality, such as Statistica (Statsoft, USA), and there are a number of toolboxes and other add-ins for general mathematical environments such as R (freely available from www.r-project.org) and Matlab (Mathworks, USA).

Once a model has been built, the computational requirements of running that model are minimal. Since most analytical instruments are controlled by some kind of computer or microcontroller, there is no additional equipment overhead. We have found LabVIEW (National Instruments, USA) to be a very useful environment for deployment of chemometrics applications in the ARTDEMO project, as it allows direct integration of the chemometrics and instrument control software, and can be easily ported to palmtop computers for deployment in the field.

7 CONCLUSIONS

This chapter has provided a high level introduction to how chemometrics can be of use in environmental analysis, and the basic process followed to generate and test a calibration model for a given analytical technique. Clearly it is impossible to cover many important details such as data pre-treatment and model optimisation here, so for this the interested reader is directed to the references, or one of the excellent chemometrics textbooks now available [Brereton, 2003; Otto, 1999].

It is important to remember that it is only possible to extract information from a measurement if that information is present within the measured data, so chemometrics cannot be seen a substitute for good laboratory practice. Similarly, chemometric models cannot be expected to cope with the unexpected – if a sample contains an impurity that was not present in the training data used to build the model then the model may yield erroneous results if that impurity is manifested in the analytical response. However, if it is used responsibly, chemometrics can be an immensely powerful tool. Indeed, such techniques are becoming essential for the comprehension of the large amounts of data that are produced by contemporary laboratory instrumentation. Chemometrics also opens up new possibilities in areas such as autonomous devices for environmental monitoring, as it can help us get the most out of very basic instrumentation. For example, if we can measure multiple analytes simultaneously by separating their responses mathematically, we can do away with a potentially bulky and labour intensive physical separation stage.

8 REFERENCES

Bessant, C., Ritchie, L.J., Saini, S., Pahlavanpour, B. & Wilson, G.,2001, A Chemometric Evaluation of Synchronous Scan Fluorescence Spectroscopy for the Determination of Regulatory Conformance and Usage History of Insulation Oils., Applied Spectroscopy 55: 840-846

Brereton, R.G., 2003, Chemometrics: Data Analysis for the Laboratory and Chemical Plant. Wiley, ISBN 0471489786.

Geladi, P. & Kowalski, B. R., 1986, Partial Least Squares Regression: A Tutorial. Anal. Chim. Acta, 185: 1-17.

Hagan, M.T., Demuth, H.B., Beale, M.H., 2003, Neural Network Design, Martin Hagan, ISBN 0971732108

Jackson, J.E. 1980. Principal components for factor analysis: Part I - Principal Components, J. Qual. Tech. 12: 201-213.

Long, J.R. Gregoriou, V.G., Gemperline, P.J., 1990, Spectroscopic calibration and quantitationusing artificial neural networks, Anal. Chem., 62: 1791-1797.

Massart, D.L., Vendeginste, B.G.M., Deming, S.N, Michotte, Y., Kaufman, L., 1988, Chemometrics: A Textbook, Elsevier Science Publishers. ISBN 0444426604.

Otto, M., Chemometrics: Statistics and Computer Application in Analytical Chemistry, Wiley-VCH 1999. ISBN 352729628X.

Richards, E., Bessant, C. & Saini, S., 2002, Multivariate Data Analysis in Electroanalytical Chemistry, Electroanalysis, 14: 1522-1542.

Chapter 13: Key Parameters for Predicting the Fate of Contaminants in Managed Aquifer Recharge Systems

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1 INTRODUCTION

In order to predict the behaviour of contaminants during managed aquifer recharge (MAR), we need to know enough about their physico-chemical properties, the hydrogeological and geochemical characteristics of the aquifer system, the hydrology and management of the MAR system, and the hydrochemistry of both the native groundwater and the infiltration water. All this information is indeed needed as input for running any reactive transport model, like Easy-Leacher 4.8 (Stuyfzand et al., this volume).

In this chapter the required information is further specified with the aim to provide the key parameters that need to be addressed in (a) prospective research for new MAR systems, (b) retrospective research on operating MAR systems, and (c) regular monitoring systems for MAR systems.

Contaminants can roughly be divided into 2 groups: macropollutants (mg/L-level, like NO_3, Cl, SO_4, PO_4, NH_4, Na, TOC, DOC) and micropollutants (μg/L down to pg/L). The latter can be further subdivided into trace inorganics (like As, B, Br, Cd, Hg, Pb, Se, Zn, chlorite, chlorate, bromate, perchlorate), organic micropollutants (OMPs, like PAHs, chlorinated hydrocarbons, BTEX, pharmaceuticals, complexing agents, and pesticides), radionuclides, and pathogenic micro-organisms (bacteria and viruses).

The focus here is directed on micropollutants and relatively simple prediction models mainly involving retardation factors and the half life approach (see for instance Stuyfzand, 1998a), with a low level of data hunger and without parameters that require very specialized equipment and laboratories. We therefore exclude parameters like iron(hydr)oxides, zeta potential, trace element composition of carbonates and pyrite, reactivity of bulk organic material and pyrite, which are usefull but not analysed on a routine basis.

2 PHYSICO-CHEMICAL PROPERTIES OF POLLUTANTS

The physico-chemical key properties are listed for 4 groups of contaminants in Table 1.

Values of the Ion Exchange coefficient ($K_{Na\backslash X}$), which are needed to calculate the retardation coefficient of trace elements and radionuclides, are listed by Appelo & Postma (2005). The parameter %silt-bound (f) is equal to the percentage which is retained by a 0.45 μm membrane filter. These values can be easily obtained. Half lifes of radionuclides (T1/2) are listed by Haberer (1989).

Schwarzenbach et al. (1993), Stuyfzand & Lüers (1996, 2000) Appelo & Postma (2005) present data on the Henry coefficient (K_{Henry}), partition coefficient for octanol-water (K_{OW}) or organic carbon–water (K_{OC}), dissociation constants (pKa), and half lifes related to photochemical degradation (T1/2-photo) and biodegradation (T1/2-biodeg). The latter strongly depend on the redox environment (Stuyfzand, 1998b) and temperature. Most critical are the T1/2-biodeg values which very often derive from laboratory experiments or field data obtained under uncomparable conditions (if they were described at all).

If K_{oc} is unknown, calculate by:

$$K_{OC} = 10^{b} K^{a}_{OW} \qquad (1)$$

with: K_{OW} = octanol water distribution coefficient, a and b = regression parameters (see Appelo & Postma, 2005). Or calculate K_{OC} by:

$$K_{OC} = 10^{3.64} S^{-0.55} \qquad (2)$$

with: S = solubility OMP in water [mg/L].
If K_{Henry} is unknown, approximate by:

$$K_{H} \approx \{ M P_{VAP} \} / S \qquad (3)$$

With: P_{VAP} = vapour pressure of OMP [Pa].

Essential is also the TOC/DOC-ratio in the infiltration water, which is easily determined by analyzing an unfiltrated sample, which yields TOC (Total Organic Carbon = POC + DOC), and a 0.45 µm filtrated sample (yielding DOC = Dissolved Organic Carbon, thus without Particulate Organic Carbon).

Data on inactivation coefficients of bacteria and viruses are given by Matthess et al. (1988) and Schijven (2001). Data on the first and second bow point in a concentration versus ‘distance in aquifer’ plot (X_1 and X_2) and the corresponding Decimal Elimination Capacity at these points (resp. DEC_1 and DEC_2) should be measured on site or at a similar site (see Stuyfzand et al., this volume). For a more traditional approach to model virus or bacteria transport reference is made to Matthess et al. (1988) and Schijven (2001). These models require data on at least the pathogen diameter, average grain size diameter and the collision efficiency. The latter, however, strongly depends on many factors which are still ill known.

2.1 *Fact sheets and data bases*

More extensive information on organic micropollutants can be presented in so-called fact sheets, which for one specific compound or group of compounds present information on amongst others: emission and immision souces, identity, threshold values, physico-chemical properties, chemical structure, environmental fate, exposure and safety, analytical methods, water treatment processes and sources of information. Mons & Heringa (this volume) give 2 examples on respectively MTBE (annex 1) and NDMA (annex 2).

In a more compact way, physico-chemical and other data can be ordered for a large variety of compounds in spread-sheets or data base systems. As an example an abbreviated listing is given for 26 organic micropollutants in Table 2. It can be seen that not all needed parameters are known (or could be found in the databases consulted).

Table 1. Physico-chemical key parameters for 4 groups of contaminants. For explanation see text.

CONTAMINANT GROUP	KEY PARAMETERS
Trace elements	AW or MW, valence (m), Ion Exchange coefficient ($K_{ca\backslash x}$), %silt-bound (f)
Radionuclides	As above, T1/2
Organic micropollutants	MW, TOC/DOC, K_{Henry}, K_{OW} or K_{OC}, pK_a, T1/2-photo, T1/2-biodeg (depending on redox and temp.
Bacteria and viruses	Inactivation coefficient (redox and temp. dependent), X1, X2, DEC1, DEC2

AW, MW = Atomic or Molecular Weight; T1/2 = half life connected with (bio)degradation

Table 2. Listing of the most important physico-chemical parameters for 26 organic micropollutants.

	K_{HENRY}	Molecular	T½			Vapour	Water		T½ - biodegradation		
NAME	20'C	Weight	Photolysis	log K_{OW}	log K_{OC}	pressure	Solubility	pKa	(sub)oxic	anoxic	deep ano
COMPOUND	Pa.m3/mole	g/mole	d			Pa	mg/L 20'C		days	days	days
VARIOUS OMPs											
1,2-dichlorobenzene (1,2-DCB)	126	147	40	3.39	2.49	1.3-2 E5	140		180	720	10
1,2-dichloroethane (1,2-DCEa)	94.26	99		1.45	1.51				180	720	720
1,2-dichloroethylene (1,2-DCEe)	4276	96.9		2.55	2.18				28	720	360
1,2-dichloropropane	193	112.99		2.28E+00	1.66E+00	4600	2700		167-1280	668-5150	
Benzo(a) pyrene (BAP)	0.0355	252.3		6.04	6.4				530	2120	2120
Bromodichloromethane (CCl2Br)	162	163.8		1.88	2.07				20	4	0.1
Chloroform (CCl3)	304	119.4	5.1	1.97	1.6	2.1 E+04	9000		80	16	0.2
Dibuthylphtalate	0.047	278.4	75	4.91	3.7				5	10	23
Hexachlorobenzene (HCB)	41	284.8	1500	5.73	4.6				969	3876	8356
MTBE	44-59	88,15		0.94-1.2	1.049	3.22E+04	42-59 E+03	3.7			
Tetrachloroeth(yl)ene (per)	841	165.8	94	2.53-2.60	2.32-2.60	1.9 E+06	155		183-365	98-1644	
Phenanthrene (phen)	3.95	178.2		4.56	4.36				28	200	800
Trichloroethylene (tri)	1035	131.4	7.29	2.35	2.2				360	1653	31
PESTICIDES											
AMPA	1	111		2	2				40	20	10
Atrazine	3.08E-04	215.7		2.33	1.85	4.00E-05	28		140	20	10
Bentazone	2.10E-04	240.28		0.3	0.3	<1E-05	500	2.91	1830	100000	100000
Dichlobenyl	6.98E-04	172.02		2.10E+00		7.30E-05	18				
Dinoseb (DNBP)		240.22					52				
Diurone	2.30E-03	233.1		2.81	2.6	4.10E-04	42		240	25	12
Isoproturone	9.45E-06	206.29		2.81	2.6	3.30E-06	72		240	25	12
Lindane (gamma-HCH)	4.90E-02	290.85		3.69	3.3	5.60E-03	7.3		240	30	6
Mecoprop (MCPP)		214.65		1.00E-01		<1E-05	620				
Methyl bromide	1.61E+03	94.94		3.77E-01		2.27E+05	13400				
Metolachlor	9.10E-04	283.8		2.01E+00		1.70E-03	530				
Pentachlorophenol (PCF)		266.34				16; 100'C	80				
Simazine	4.00E-08	201.7		2.84	2.12	8.10E-07	3.5		90	10	5

3 AQUIFER CHARACTERISTICS

The key parameters to define the target aquifer or aquifer system involved in artificial recharge are listed in Table 3. Hydrogeological, geochemical and hydrochemical data are distinguished.

It is of paramount importance to identify the stratification of the aquifer system, i.e. to identify spatially significant units/layers.

The density of the aquifer matrix (ρ_S) can be estimated as follows:

$$\rho_S = (1 - BOM/100)*2.65 + BOM/100 \qquad (4)$$

with: BOM = Bulk Organic Material = 2*C_{ORG} (% dry weight).

The effective cation exchange capacity (CEC, in meq/kg d.w) can be calculated according to the following formula, which combines the approach by Appelo & Postma (2005) with the pH-dependence of the CEC of organic matter according to Scheffer & Schachtschabel (2002):

$$CEC_{CALC} = 7\ L + 5.1\ (pH - 1.16)\ C_{ORG} \qquad (5)$$

with:

L = clay size fraction, i.e. content of particles < 2 μm [% d.w.]; C_{ORG} = organic carbon [% d.w.], either measured or calculated from Bulk Organic Material (BOM) by taking:

$$C_{ORG} = 0.5\ BOM \qquad (6)$$

With both parameters in % d.w.

It is advised, also for economical reasons, to analyse aquifer cores at least on:

their grain size distribution by seeving over 2 mm and the fraction <2 mm by a laser particle sizer;

the total content of ca. 30 elements by XRF (X-ray fluorescence);

residues at 105ºC (dry weight residue), 450ºC (loss on ignition, a measure for total organic material), and 1000ºC (burning residue: measure for total carbonates), by thermogravimetry; and

total C and total organic C, total N and total S by pyrolysis and gas detection.

Table 3. Key parameters to define the target aquifer.

AQUIFER PROPERTIES	KEY PARAMETERS
Hydrogeology	Depth to top and base of each sublayer, hydraulic conductivity (K_H), porosity, depth to groundwater table
Geochemistry	$CaCO_3$ (or total carbonates), FeS+FeS_2, bulk organic material or C-organic, density of solids, CEC (or size fraction < 2 um, BOM or C-org, pH-H_2O)
Native hydrochemistry	Temp, pH, EC, macro-ions, trace elements, OMPs, Rads, B&V

EC = Electrical Conductivity; OMPs = Organic MicroPollutants; Rads = Radionuclides; B & V = bacteria and viruses.

Table 4. Key parameters to define the Managed Aquifer Recharge system.

MAR-SYSTEM	KEY PARAMETERS
Layout of MAR-system	Recharge type (basin, injection, trench, ASR), distance between recharge and recovery facilities, number of basins and wells, mean width of basins, depth of basins, injection well and recovery
Management	Selective intake, pretreatment, periodical or continuous recharge, sludge removal (or declogging), algae, reed and fish control
Hydrology	Annual totals of water recharged and recovered, infiltration intensity, periodical or continuous recharge, evaporation, rainfall, water depth in basins, detention time in basins, presence and thickness of unsaturated zone, travel times, flux contributions and distances of all (representative) flowpaths in saturated aquifer layers, steady admixing of native groundwater
Hydrochemistry of input	Bulk atmospheric deposition (incl. dust and gases) and infiltration water, both on: Temp., pH, EC, macro-ions, trace elements, OMPs, Rads, B&V
Redox environment of aquifer system	To be determined for each flowline by interpreting analyses on O2, NO3, NH4, Fe, Mn, SO4 and CH4 (procedure in Table 5)

4 PARAMETERS OF THE MAR SYSTEM

The key parameters to define the Managed Aquifer Recharge system are listed in Table 4. There is a clear distinction between parameters defining the lay-out of the MAR-system, the management of the Iartificial recharge, the hydrology and hydrochemistry of the input, and the redox environment during artificial recharge in full operation.

The infiltration intensity, detention time in basins, travel times and distances of flowpaths in saturated aquifer layers and the amount of steadily admixed native groundwater can be either calculated using hydrological models (like MODFLOW) or measured using (semi)natural tracers (already present in the infiltration water).

Knowing the quality of the infiltration water, means to have an understanding of the annual mean, trends, seasonal fluctuations (with their temperature and discharge relationship), incidental peaks by spills, and the effects of pretreating the intake water (especially regarding suspended solids, pH, O_2, NO_3, EC and DOC).

The most important macroparameters for modeling the transport of micropollutants are: temp, pH, EC, Na, Ca, en those parameters that indicate the redox environment (see below).

4.1 The Redox environment

The redox environment or redox level is defined as a specific range of the redox potential (degree of aerobicity) with a specific cluster of dissolved ions and gasses with characteristic concentration levels; ions and gasses that remain stable only within those ranges of the redox potential.

For practical purposes we discern only the following 3 (not 7) levels (Fig.1 and Table 5):

(sub)oxic, which is redox cluster 0-2. For criteria see Table 5. Clastic sediment colour also is an excellent indicator: needs to be yellow in case of sandy material.

Anoxic, being redox cluster 3-4. For criteria see Table 5. Clastic sediment colour in combination with smell are also good indicators: colour needs to be gray or black in case of sandy material, and smell should be without rotten eggs (H_2S).

Deep anoxic, the redox cluster 5-6. For criteria see Table 5. Clastic sediment colour in combination with smell are also good indicators: colour needs to be gray or black in case of sandy material, and smell should be with rotten eggs (H_2S).

Table 5 Practical criteria for determining the redox environment (after Stuyfzand, 1993; concentrations in mg/L).

Level	Environment	Criteria			
0	Oxic	$O_2 \geq 0.9\ (O_2)_{sat}$			
1	Penoxic	$1 \leq O_2 < 0.9\ (O_2)_{sat}$			
2	Suboxic	$O_2 < 1$,	$NO_3^- \geq 1$		
3	Transition	$O_2 < 0.5$,	$NO_3^- < 0.5$,	$Mn^{2+} \geq 0.1$,	$Fe^{2+} < 0.1$.
4	Sulphate-stable	$O_2 < 0.5$,	$NO_3^- < 0.5$,	$Fe^{2+} \geq 0.1$,	$SO_4^{2-} \geq 0.9\ (SO_4)_O$
5	Sulphate-reducing	$O_2 < 0.5$,	$NO_3^- < 0.5$,	$0.1\ (SO_4)_O < SO_4^{2-} < 0.9\ (SO_4)_O$	$CH_4 < 1$.
6	Methanogenic	$O_2 < 0.5$,	$NO_3^- < 0.5$,	$SO_4^{2-} \leq 0.1\ (SO_4)_O$	$CH_4 \geq 1$.
Redox clusters					
0-2	(sub)oxic	$O_2 \geq 1$ or	$NO_3^- \geq 1$		
3-4	anoxic	$O_2 < 0.5$ and	$NO_3^- < 0.5$,	$SO_4^{2-} \geq 0.9\ (SO_4)_O$	$CH_4 < 0.5$
5-6	deep anoxic	$O_2 < 0.5$ and	$NO_3^- < 0.5$,	$SO_4^{2-} \geq 0.9\ (SO_4)_O$	$CH_4 > 0.5$
0-2	aerobic	as (sub)oxic (0-2)			
3-6	anaerobic	as anoxic (3-4) or	deep anoxic (5-6)		

$(O_2)_{sat}$ = oxygen saturation concentration, with t = temp [°C] and Cl^- = chloride [mg/L]:

= $14.594 - 0.4\ t + 0.0085\ t^2 - 97\ 10^{-6}\ t^3 - 10^{-5}\ (16.35 + 0.008\ t^2 - 5.32/t)\ Cl^-$

$(SO_4)_O$ = sulphate concentration in influent (prior to aquifer passage; to be calculated by linear regression with chloride).

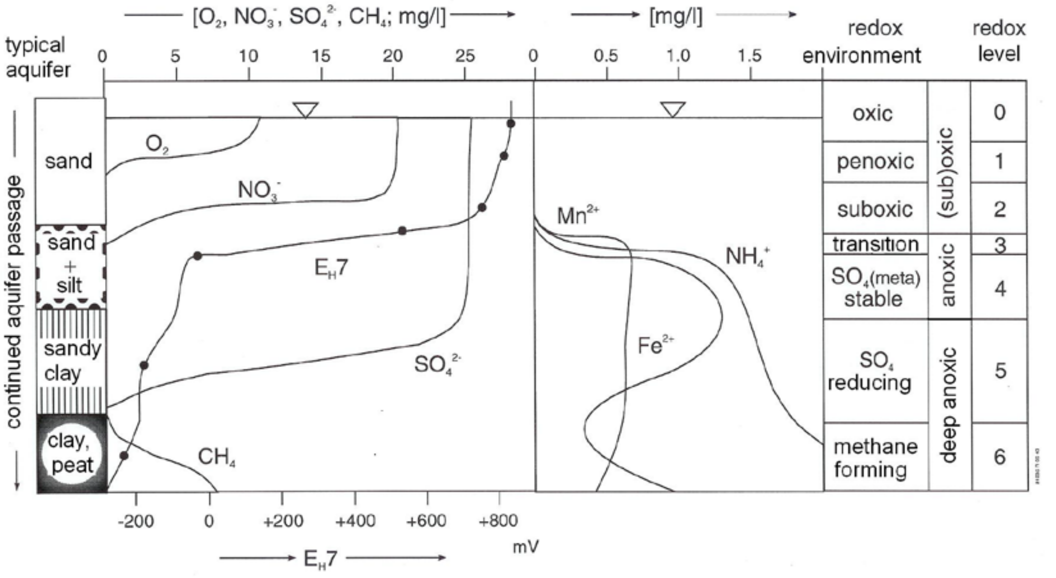


Figure 1: The ideal redox sequence for a system closed from the atmosphere like groundwater, where no mixing occurs and first all oxygen, then all nitrate and subsequently all sulphate is used to oxidise dead organic material, and finally methane appears (after Stuyfzand, 1993).
Also indicated are the theoretical redox potentials at pH7 (E_H7), the concentration logs for iron, manganese, hydrogen, hydrogensulphide and ammonium, and a subdivision into redox environments. Criteria for subdivision are presented in Table 5.

5 REFERENCES

Appelo, C.A.J. & D. Postma 1993. Geochemistry, groundwater and pollution. 2nd edition, Balkema, Rotterdam, 649p.

Haberer, K. 1989. Umweltradioaktivität und Trinkwasserversorgung. R. Oldenbourg Verlag, München, 142p.

Matthess, G., A. Pekdeger & J. Schröter 1988. Persistence and transport of bacteria and viruses in groundwater: a conceptual evaluation. J. Contaminant Hydrol 2, 171-188.

Mons, .& M. Heringa 2006. Fact sheet MTBE, Methyl Tert-butyl ether. This volume.

Mons, .& M. Heringa 2006. Fact sheet NDMA, N-Nitrosodimethylamine. This volume.

Scheffer, F. & P. Schachtschabel 2002. Lehrbuch der Bodenkunde, 15th ed, Elsevier, Amsterdam, 607p.

Schijven, J.F. (2001) Virus removal from groundwater by soil passage; modeling, field and laboratory experiments. Ph.D. Thesis Techn. Univ. Delft, the Netherlands, 262p.

Schwarzenbach, R.P., P.M. Gschwend & D. Imboden 1993. Environmental organic chemistry. J. Wiley & Sons, NY.

Stuyfzand, P.J. 1993. Hydrochemistry and hydrology of the coastal dune area of the Western Netherlands. Ph.D Thesis Vrije Univ. Amsterdam, published by KIWA, ISBN 90-74741-01-0, 366 p.

Stuyfzand, P.J. 1998a. Simple models for reactive transport of pollutants and main constituents during artificial recharge and bank filtration. In: Peters J.H. (ed), Artificial recharge of groundwater, Proc. 3rd Intern. Symp. on Artificial Recharge, Amsterdam the Netherlands, Balkema, 427-434.

Stuyfzand, P.J. 1998b. Fate of pollutants during artificial recharge and bank filtration in the Netherlands. In: Peters J.H. (ed), Artificial recharge of groundwater, Proc. 3rd Intern. Symp. on Artificial Recharge, Amsterdam the Netherlands, Balkema, 119-125.

Stuyfzand, P.J. & F. Lúers 1996. Behavior of environmental pollutants after river bank filtration and artificial recharge; effects of aquifer passage as measured along flow paths. Kiwa-Meded. 125, 272p (in dutch).

Stuyfzand, P.J. & F. Lüers 2000. Environmental balance for pollutants in nature reserves with and without artificial recharge. Kiwa-Meded. 126 (in dutch), 241p.

Stuyfzand, P.J., T.O. Jensen, R.J. Berg & M. Lundh 2006. Quantification of the chemical and microbiological retention capacity and sustainability of basin recharge systems Arrenaes (Denmark) and Dösebacka (Sweden), by Easy-Leacher 4.8. This volume.

Annex 1: Info Sheet MTBE: METHYL TERT-BUTYL ETHER

ir. Margreet Mons and ir. Minne Heringa

Kiwa Water Research

INTRODUCTION

In order to boost up the octane number of gasoline, MTBE is used as a additive in the USA (15%) since 1979. In the Netherlands addition of MTBE has started in the eighties (~5%). In the presence of MTBE the combustion of gasoline is better which decreases the lead emission to the environment. MTBE, introduced as a solution to air pollution caused by combustion engines now appears to be a large scale water pollutant itself. Annualy, $21.4 \cdot 10^6$ tons of MTBE is produced worldwide. In the Netherlands this amounts to $1.17 \cdot 10^6$ tons a year.

Since groundwater as well as surface water in the United States has become polluted with TBE, this compound receives a lot of attention since 1995.

The use of MTBE is already prohibited in a number of the United States.

SOURCES

In groundwater MTBE occurs especially near gasoline storage tanks as a result of leaks, overflowing tanks and spilling during storage. MTBE contamination of surface water is mainly due to motorized recreational watercraft, accidental fuel spills, and minimally, runoff and precipitation from the atmosphere [2]. Recreational watercraft is believed to be the major source of MTBE contamination of surface water.

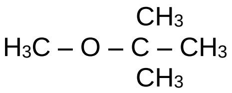
IDENTITY

IUPAC name	Methyl tertiair-butyl ether
Synonyms	MTBE; 2-methoxy-2-methyl propane
Chemical formula	$C_5H_{12}O$
Molecular Weight (g/mole)	88.15
CAS-number	1634-04-4

PHYSICOCHEMICAL PROPERTIES

Appearance	volatile colorless liquid with a strong white spirit smell
Solubility (g/l)	42 – 59, solubility increases with lower temp.
Melting point (°C)	-109
Boiling point (°C)	55.2
Density (g/ml)	0.7405 (20 °C)
Henry's constant (atm.m^3.mol^{-1})	$4.4 \cdot 10^{-4}$
log Kow	1.20
log Koc	1.049
Vapour pressure (mg Hg, 25 °C)	245
Mobility/Attachement to soil particles	very mobile / low partitioning coefficient water to soil
Biodegradation (anaerobic/aerobic)	Slowly
Threshold value odor (µg/L) [8]	15
Thershold value taste (µg/L) [8]	39
Organoleptic standard (µg/L, USEPA)	20 – 40
UV absorbance	

STRUCTURE



$$H_3C - O - \overset{CH_3}{\underset{CH_3}{C}} - CH_3$$

ENVIRONMENTAL FATE

Occurrence in raw water sources and drinking water - United States

General (no date, no reference data)

Source	MTBE concentration (µg/L)
Groundwater (rural)	≤ 2
Groundwater (urban)	0.2 - 23000
Surface water	≤ 30
Drinking water prepared from groundwater	< 20

State of California (August 1, 2002) #

Source	Number of samples	MTBE detections	– MTBE ≥ 3 µg/L	MTBE > 5 µg/L	MTBE > 13 µg/L
Groundwater	9,715	60 (0.6%)	52 (0.5%)	36 (0.4%)	20 (0.2%)
Surface water	705	31 (4.4%)	17 (2.4%)	8 (1.1%)	2 (0.3%)
Total	10,420	91 (0.9%)	69 (0.7%)	44 (0.4%)	22 (0.2%)
Public Water Systems	3,319	53 (1.7%)	42 (1.3%)	33 (1.1%)	14 (0.4%)

Data taken from www.dhs.ca.gov/ps/ddwem/chemicals/MTBE/mtbeindex.htm

Occurrence in raw water sources and drinking water - The Netherlands (RIVM)

	Concentration (µg/L)				– Number		
Source	Number of samples	Minimum	Maximum	Average	≥ GSD	≥ SGW	≥ RG
Surface water	35	< 0.01	3.2	0.16	0	1	30
Ground water	21	< 0.01	11.9	0.14	1	1	41
Bank filtrate	109	0.01	0.41	0.14	0	0	21
Drinking water	52	< 0.01	2.9	0.09	0	1	38

≥ GSD: number of samples above the most critical odor and taste threshold value (7.3 µg/L)

≥ SGW: number of samples above the signal value for halogenated monocyclic hydrocarbons, halogenated alifatic hydrocarbons and monocyclic hydrocarbons and aromats as given in the Dutch water directive from 2001 (1.0 µg/L)

≥ RG: number of samples above the detection limit (0.01 µg/L)

EXPOSURE & SAFETY

Especially people working with gasoline during distribution and storage are exposed to MTBE. Common people inhale MTBE during tank refueling and in a parking garage. For people living in the United States the concentration of MTBE inhaled is calculated at 2 – 5 µg/kg body weight. If MTBE occurrs in drinking water, exposure may proceed by swallowing, by inhalation and it may be taken up via the skin during showering. Based on the results of experiments with animals, MTBE is a moderate acute toxic. It may cause irritation to eyes and skin.

A risk assessment has been performed (Clary, 1997; USEPA, 2000):

– LC50	– inhalation: 85,000 mg/m^3
⁻ LOAEL (rats)	– inhalation: 10,899 mg/m^3
⁻ LOAEL (mice)	– inhalation: 3,000 ppm
⁻ NOAEL (rats)	– inhalation: 1,145 mg/m^3

ORGANOLEPTIC PROPERTIES

After exposure for a longer period of time (doses ≥440 mg/kg of body weight) effects on liver and kidneys were found with laboratory animals. EPA has classified MTBE as a possible (or potential) carcinigen. It may cause cancer to the liver and kidneys of rodents.

HEALTH-RELATED ASPECTS AND GUIDELINES

Since 1999, California Department of Health Services (DHS) uses a secondary Maximum Contaminant Level (MCL) of 5 μg/L to address taste and odor. Also since 1999 DHS uses a primary MCL of 13 μg/L to address the public health aspects of MTBE.

In 2001 or 2002, the Dutch (VEWIN) has set a guideline of 1 μg/L in drinking water (Vewin, internal paper). According to the European Commission, there is no need for changing the content of MTBE in gasoline. It is to be trusted that producers and distributors take the responsibility and liability towards pollution of groundwater and therefore will take suitable measures.

ANALYTICAL METHODS

USEPA method 524.2

Purge-and-trap gas chromatography – mass spectrometry for VOC analysis. A 25-ml sample is purged with helium to a sorbent trap for 11 minutes. The trap was then heated and backflushed directly to the GC analytical column (30 m., 1.4 μm film, 0.25 mm inside diameter), which is temperature programmed to separate the method analytes. The analytes were then detected by electron impass mass spectrometry and quantified by linear regression calibration curves (Dale et al., 2000; Chang et al., 2000).

This method is also applicable for the determination of BTEX consituents (see ‘Other compounds in same class’) and other VOC’s.

REMOVAL/DEGRADATION - EFFICIENCY OF WATER TREATMENT PROCESSES

Activated carbon filtration and advanced oxidation (AOP) may be affective in removing MTBE from water (Dale et al., 2000). Combination of these methods renders the best effects (Vewin, internal paper).

GAC filtration is an effective remediation technology for the removal of MTBE in concentrations ranging from 10 to 100 μg/L. Above 100 μg/l conventional water treatment processes have only moderate success. Waters with such concentrations can effectively treated with advanced oxidation: UV/H_2O_2 and O_3/H_2O_2 (Safarzadeh-Amiri et al., 2000). A disadvantage of the O_3/H_2O_2 process over the UV/H_2O_2 process is formation of carcinogenic bromate if the water to be treated contains bromide.

Airstripping, although conventionally reliable for VOC removal, only renders acceptable results at high air to water ratio’s and multiple airstrippers in series. The disappointing results are caused by the low Henry’s constant of MTBE. Airstripping has proven to remove MTBE successfully, but at relatively high costs.

REMOVAL/DEGRADATION – METABOLITES

Application of the UV/H_2O_2 oxidation process resulted primarily in the formation of tert-butyl formate TBF), 2-methoxy-2-methyl propionaldehyde (MMP), formaldehyde, acetone, tert-butyl alcohol and methylacetate. Also carbonyl compounds like hydroxy-iso-butyraldehyde, hydroxyacetone, pyruvaldehyde) and organic acids (hydroxy-iso-butyric, formic, pyruvic, acetic, oxalic) were detected (Stefan et al., 2000).

REMOVAL/DEGRADATION – OPERATING AND/OR CAPITAL COSTS

Reducing 10 mg/L MTBE in groundwater to 0.01 mg/l, the costs (both capital and operation) of the O_3/H_2O_2 and UV/H_2O_2 processes range between US$ 0.26 – 0.52 and US$ 0.64 – 0.85, respectively (Safarzadeh-Amiri, 2002).

OTHER COMPOUNDS IN SAME CLASS

(Van der Vaart, 2002)

TBA (tertiary-butyl alcohol)
TAME (tertiary-amyl methyl ether)
ETBE (ethyl tertiair-butyl ether)
TAEE (tertiary-amyl ethyl ether)

DIPE (di-isopropyl ether)

Although they are not compounds from the same class, soils contaminated with MTBE generally are also contaminated with benzene, toluene, ethtylbenzene, and xylene (BTEX).

OCCURRENCE IN DRINKING WATER - FUTURE EXPECTATIONS

No information available.

REFERENCES

Chang, P.B.L., Young, T.M., Kinetics of methyl tert-butyl ether degradation and by-product formation during UV/hydrogen peroxide water treatment, Wat. Res., vol. 34(8), 2000, pp. 2233 – 2240.

Clary, John J. "Methyl tert Butyl Ether Systematic Toxicity," Risk Analysis 17, 661 – 672 (1997).

Dale, M.S., Koch, B., Losee, R.F., Crofts, E.W., Davis, M.K., MTBE in Southern California water, J. AWWA, Vol. 92(8), 2000, pp. 42 – 51.

MTBE: Methyl Tertiar Butyl Ether, unknown reference.

Safarzadeh-Amiri, A., Cater, S.R., Stefan, M.I., Bolton, J.R., UV/H_2O_2 treatment of methyl-tert-butylether in contaminated waters, Environ. Sci. Technol., 2000, 34, pp. 659 – 662.

Safarzadeh-Amiri, A., O_3/H_2O_2 advanced oxidation treatment of MTBE in contaminated groundwaters, Proceedings of the IOA Pan American Group, Rayleigh-Durham, North Carolina, May 18 – 22, 2002, session 6B, pp. 312 – 321.

Stefan, M.I., Mack, J., Bolton, J.R., Degradation pathways during the treatment of methyl tert-butyl ether by the UV/H_2O_2 process, Environ. Sci. Technol., vol. 34, 2000, pp. 650 – 658.

USEPA: UATW (Unified Air Toxics Website) Health Effects Notebook for Hazardous Air Pollutants: METHYL tert-BUTYL ETHER, January 5, 2000.

Vaart, J. van der, Effects of the use of methyl tertiairy-butyl ether (MTBE) in fuel on public water supplies in the Netherlands, Master of Science Dissertation, Hydron Advies & Diensten, December 2002.

Vewin, internal report.

Annex 2: Info sheet NDMA: N-NITROSODIMETHYLAMINE

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INTRODUCTION

Already in the seventies of the last century NDMA was found in dried sludge from 14 wastewater plants in the United States. In 1974 Ayanaba and Alexander reported that NDMA formed in wastewater as a result of biological and chemical transformation of alkylamines in the presence of nitrite. Since the concern about NDMA started as an air contaminant, drinking water MCLG (Maximum Contaminant Level Goal) or MCL have not been established yet. Nowadays NDMA receives even more attention since NDMA may be formed during water treatment producing drinking water.

SOURCES

- manufactured as an intermediate in the production of 1,1-dimethylhydrazine (1950 – 1976), which is stored as a liquid rocket fuel (contains ~ 0.1% NDMA)
- inhibitor of nitrification in soil, plasticizer for rubber and polymers, solvent in fiber and plastics industry, antioxidant, softener of copolymers, additive to lubricants
- by-product in the manufacturing of some pesticides
- present in food: cheeses, soybean oil, canned fruit, meat, fish
- present in tobacco smoke

IDENTITY

IUPAC name	N-Nitrosodimethylamine
Synonyms	NDMA; N-methyl-N-nitroso Methamine; N-methyl-N-nitroso Methanamine
Chemical formula	$C_2H_6N_2O$
Molecular Weight (g/mole)	74.08
CAS-number	62-75-9

PHYSICOCHEMICAL PROPERTIES

Appearance	viscous yellow liquid
Solubility	very water-soluble
Melting point (°C)	
Boiling point (°C)	151 – 153
Density (kg/m^3)	1.0048 (20 °C)
Henry’s constant (atm.m^3.mol^{-1})	$2.63 \cdot 10^{-7}$
pKa-value	
log Kow	-0.57 (estimated) [7]
log Koc	
Vapour pressure (mg Hg, 25 °C)	
Mobility/Attachement to soil particles	NDMA is very mobile in water
(Bio)degradation	rapid degradation on soil surfaces, but degrades slowly in sediment (½-life=5500 h)
Threshold value odor	
Threshold value taste	
UV absorbance	200 – 270 nm, max. at ~ 232 nm

STRUCTURE

$$\mathrm{O = N - N}\begin{array}{l}\mathrm{CH3}\\ \\ \mathrm{CH3}\end{array}$$

ENVIRONMENTAL FATE

Occurrence in raw water and drinking water – United States/Canada

- found in 37 (out of 101) Ontario raw water plants: >0.001 µg/L, c_{max} = 0.008 µg/L.
- found in drinking water in California: <0.01 µg/L
- two wells in San Gabriel Basin closed: 0.07 µg/L
- two Orange county wells removed from service at 0.04 µg/L (contaminated by wastewater injection)

Occurrence in raw water and drinking water – The Netherlands

Data on the occurrence of NDMA in raw water sources and drinking water are not available.

EXPOSURE & SAFETY

Health & safety information: R 45 25 26 48/25 51/53; S 45 61 53.

ORGANOLEPTIC PROPERTIES

In 1991 NDMA was classified a Class 1 carcinogen (Lewis, 1991). Exposure to NDMA at high levels has been shown to cause hepatocellular carcinomas (primarily liver, kidney, and lung tumors) in mice, rats, hamsters, rabbits and guinea pigs.

It has a high acute toxicity: LD50 in rats is 23 – 40 mg/kg body weight. It is mutagenic and clastogenic [2]. In 1997 USEPA classified NDMA as a probable human carcinogen (B2). According to the National Toxicology Programm NDMA is considerd a human carcinogen (NTP, 2000)

HEALTH-RELATED ASPECTS AND GUIDELINES

- no standard yet; the current action level established by the California Department of Health Services (DHS) is 0.01 µg/L (2002)
- DHS recommends to take the drinking water system out of service if the NDMA level is more than 10 times the action level.
- cancer risk level (10^{-6}) in drinking water: 0.007 µg/L (USEPA, 1997) and 0.002 µg/L (10^{-6} risk level, OEHHA, 2000)
- MAC: 9 ng/L (Ministry of Environment of Ontario Canada, 1998)

ANALYTICAL METHODS

The current method has a detection limit of 0.4 ng/L NDMA and a reporting limit of 1 ng/L. This method which is based on GC-MS provides reliable data in the 1 – 200 ng/L range [3].

Current location in the Netherlands for NDMA analysis is Kiwa Water Research

REMOVAL - EFFICIENCY OF WATER TREATMENT PROCESSES

Removal and treatment of NDMA is difficult. NDMA does not biodegrade significantly, so it persists in the environment. It does not air strip nor stick to activated carbon. The only effective treatment up till now is direct ultraviolet photolysis (Bolton, 2001).

Application of direct UV photolysis degrades NDMA into dimethylamine and nitrite. Since dimethylamine does not photolyze, it persists in the system. However, NDMA may be formed using UV photolysis on water with dimethylamine and nitrate forming nitrite.

On application of UV/H_2O_2 nitrate is the most important degradation product of NDMA, and the level of dimethylamine is significantly lower than that produced during UV photolysis [6].

FORMATION DURING WATER TREATMENT AND WATER DISTRIBUTION

- Besides resulting from industrial sources NDMA may be formed as a by-product during water treatment by biological and chemical transformation of alkylamines in the presence of nitrite.
- Treatment of water containing pesticides and fungicides like thiram may enhance the formation of NDMA
- Treatment of raw (ground) water with ion exchange resins containing trimethyl or dimethyl-ethanol quaternary functional groups may lead to NDMA formation.
- Application of free chlorine (treatment) and chloramines (distribution) may enhance the formation of NDMA.
- Highest levels were associated with the use of pre-blended alum/polymer coagulants [1].

REMOVAL – METABOLITES

No information available

REMOVAL – OPERATING COSTS

Costs for the removal of NDMA from a broad range of waters with UV photolysis have been published to vary between €0.11 (0.1 ppb ⇨ <0.005 ppb) and €0.27 (37 ppb ⇨ <0.1 ppb) per m^3 water [4].

OTHER COMPOUNDS IN SAME CLASS

NDEA (N-Nitrosodiethylamine) and NDPA (N-Nitrosodipropylamine) may be formed treating water with resins containing triethyl and tripropyl functional groups. Safety and exposure data on these compounds are not available yet.

FUTURE EXPECTATIONS ENCOUNTERING NDMA IN DRINKING WATER

Additional information on the occurrence of NDMA in raw water sources is not available. With respect to the formation of NDMA during water treatment, UV photolysis of water containing dimethylamine and nitrate may cause NDMA formation.

REFERENCES

Najim, I., Trussell, R.R., *NDMA formation in water and wastewater*, J. AWWA, February 2001, pp. 92 – 99.

Bergman, J., *NDMA Briefing notes*, Buffalo Pound WTP, Canada.

Andrews, S.A., Taguchi, V.Y., *NDMA – Canadian issues*, AWWA, Water Quality Technology Conference Proceedings, 2000.

Calgon Carbon, *UV-photolysis of N-Nitrosodimethylamine (NDMA) in contaminated water*, www.calgoncarbon.com/bulletins/UV-photolysis_of_NDMA.htm

Davis, M.K., Barrett, S.E., Hwang, C.J., Guo, Y., Liang, S., *N-Nitrosodimethylamine (NDMA) in surface water*, AWWA, Water Quality Technology Conference Proceedings, 2000.

Bolton, J.R., Stefan, M.I., *UV Photodegradation as a treatment technology for N-Nitrosodimethylamine (NDMA)*, AWWA, Water Quality Technology Conference Proceedings, 2000.

Hansch,C et al., (1995), internet.

Chapter 14: Aggregated Quality Parameters and Their Radar Plots, for Concise Quality Communication to Authorities: Principles

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1 INTRODUCTION

Aggregated quality parameters like pollution indices help to summarize a large amount of chemical and physical characteristics of water or soil, into a single number or figure which is understandable and informative to both layman and specialist. However, such a parameter or index normally addresses only one specific target (for instance the suitability of water for either consumption, irrigation or deep well injection) and very often it is valid for only one type of water or group of soils (for instance either fresh surface water, groundwater or sea water). This explains why there are in fact so many indices in use (Stuyfzand, 1993; BKH, 1994).

The aim of this study is to quantify the quality of water and soil in systems with and without MAR, in such a way that the resulting number is based on many quality aspects.

2 THE WATER POLLUTION INDEX: WAPI

The Water Pollution Index WAPI is calculated according to Stuyfzand & Lüers (2000) with minor modifications according to Stuyfzand (2005), as indicated in Tables 1 and 2. WAPI is the square root of the quadratic mean of subindices A-J, each of which covering a specific water quality aspect. Most sub-indices consist of the unweighted mean of scores for related quality parameters, on the basis of the ratio of the measured value and the natural background (or target) value (NB) or maximum permissible concentration for drinking water (MPC). In the Netherlands we use NBs according to LBB (1998), and MPCs according to WLB (2001), also valid in EU.

The use of such ratio's is advantageous thanks to (a) their clear environmental significance, e.g. 3 meaning 3 times more polluted than natural background, and (b) the possibility to plot each subindex in a radar plot (section 4).

Subindices A-J cover the following water quality aspects: esthetics (A), acidity (B), oxidation or reduction capacity (C), nutrients (D), total salt content (E), inorganic micropollutants (F), organic micropollutants, pesticides excluded (G), pesticides (H), radioactivity (I) and microbiology (J).

WAPI can be easily adapted to embrace the available data on water quality and natural backgrounds.

The parameter B was squared and the

Table 1: Determination of the Water Pollution Index WAPI by averaging quality aspects A – J
(modified after Stuyfzand & Lüers, 2000; Stuyfzand, 2005). Values >1 indicate that natural background (or target) levels are exceeded.
N.B.:If parameters are omitted or added, then the final division factor should change accordingly (C excluded).
The natural background of each parameter equals its individual division factor (if indicated).

WAPI = sqrt $[(A^2 + B^2 + C^2 + D^2 + E^2 + F^2 + G^2 + H^2 + I^2 + J^2)/10]$		
with:		Example (unit see Table 2)
A =	Esthetics	(suspended solids + colour/20 + taste/2 + odeur/2 + turbidity/4)/5
B =	Acidity	$(pH - 7)^2$
C =	Oxidation or reduction capacity	$\lvert MOC \rvert /2.7$ [me/L] with: $MOC = 4O_2 + 5NO_3 + 7SO_4^{2-} - 3NH_4^+ - Fe^{2+} - 2Mn^{2+} - 8CH_4$
D =	Nutrients (eutrophication potential)	$(PO_4\text{-}P/0.02 + ?\ [NO_3\text{-}N + NO_2\text{-}N + NH_4\text{-}N]/0.3)/2$
E =	Total salt content	(CI'/12 + EC/350)/2
F =	Inorganic micropollutants (trace elements)	(As/5 + Ba/50 + Cd/0.05 + Cr/5 + Cu/3 + Hg/0.02 + Ni/9 + Pb/4 + Zn/9)/9
G =	Org. micropollutants (excl. pesticides)	(ΣBTEX + ΣLUMP + Σothers + ΣPAH + ΣVOCI)/5 (see Table 2)
H =	Pesticides	(atra + sima + diur + α-HCH + γHCH + HCB + bent)/0.07
I =	Radioactivity	$(\text{rest}\beta/10 + {}^3H/8)/2$
J =	Microbiology	$([Colc_{22}]/10000 + [Coli_{44}]/10 + [Fs]/10)/3$

logarithm of J was taken, in order to obtain a range of scores comparable to the other 8 quality aspects.

WAPI is based on total concentrations, because only these data are usually available. This means that there are no corrections of for instance heavy metals and PAHs for suspended solids or particulate organic carbon (POC).

A_{WAPI}: esthetics

Included are the content of suspended solids, turbidity, color, taste and odor. The natural backgrounds of suspended solids (1 mg/L), turbidity (4 FTU), color (20 mg/L Pt/Co), taste (2 dilutions) and odor (2 dilutions) derive from MPCs for drinking water according to WLB (2001). Missing parameters are to be declared as such, which automatically reduces the division factor (max = 5, min = 1).

B_{WAPI}: acidity

The pH is a measure for the degree of acidification on the one hand (pH <7) and alkalinisation on the other (pH >7). pH-values of 6-8 are within the range of natural backgrounds (target values). A lower pH is regarded as undesirable in connection with the leaching of bases from the soil and the mobilization of heavy metals in soil and transport mains. A higher pH is undesirable as well because of (a) promoting the deposition of a.o. carbonates and phosphates, (b) its relation with algae blooms in surface water, and (c) enhancing the dissolution of silicate minerals and various metals.

C_{WAPI}: oxidation or reduction capacity

This capacity is calculated with MOC (Modified Oxidation Capacity) as indicated Table 1. MOC is a new parameter developed by Stuyfzand (in prep) with the unit milli-electron/L (me/L). A positive value indicates oxidizing, a negative value reducing capacity. In fact the total electron transfer is added up, resulting from the reduction of O_2 to H_2O, NO_3^- to N_2 and SO_4^{2-} to H_2S, and from the oxidation of NH_4^+ to NO_3^-, Fe^{2+} to $Fe(OH)_3$, Mn^{2+} to MnO_2 and CH_4 to CO_2. The factor -3 for ammonium is based on the fact that nitrate is formed upon oxidation of NH_4^+ (-8 me/L) and can subsequently be reduced (+5 me/L).

A MOC-value in between +2.7 and -2.7 is considered as the natural background because this agrees with respectively. (a) oxygen saturation at 11°C (11,3 mg O_2/L yielding 4*11,3/32 = 1,4 me/L) in absence of NO_3^- which is considered as largely anthropogenic, and with natural SO_4^{2-} ≤15 mg/L (dissolution of gypsum is thus considered as undesirable), and (b) modal concentration levels of natural NH_4^+, Fe^{2+}, Mn^{2+} and CH_4 in anoxic water which are easily removed by conventional water treatment systems.

Strongly positive MOC-values are associated with: (a) nitrate pollution for instance by agricultural activities, (b) sulfate pollution by for instance pyrite oxidation as a result of lowered water tables or nitrate pollution, or (c) gypsum dissolution which is natural but quite problematic for drinking water supply.

Strongly negative MOC-values normally result from deep anoxic conditions by strong interaction of water with unstabilized organic matter and iron minerals. Deep anoxic conditions can be purely natural and even advantageous for the (bio)degradation of various organic micropollutants and for immobilizing heavy metals (Schwarzenbach et al., 1993; Stuyfzand & Lüers, 1996; Appelo & Postma, 1996). The resulting raised concentrations of NH_4^+, Fe^{2+}, Mn^{2+} and methane are, however, disadvantageous for (1) the air compartment (oxidation of CH_4, Fe^{2+} and Mn^{2+} leading to CO_2 emissions, and methane also contributing itself to the greenhouse effect), (2) the acidity of seepage water (oxidation of Fe^{2+} with precipitation of $Fe(OH)_3$ and oxidation of NH_4^+ ,both producing a lot of acidity), and (3) water supply companies (lots of purification sludges being produced). Concentrations of Fe^{2+}, Mn^{2+} and methane in surface and rain water are assumed to be zero.

D_{WAPI}: nutrients

Orthophosphate and TIN (= Total Inorganic Nitrogen = NO_3^- + NO_2^- + NH_4^+) are regarded as the most prominent and critical nutrients for plants and plankton, as other nutrients usually do not pose limits to growth (SiO_2 sometimes excluded). The natural background for orthophosphate is set at 0.02 mg P/L, for TIN at 0.9 mg N/L. These values are close to the upper limits for mesotrafent environments (Vollenweider, 1976; Schindler, 1981). Higher values are undesirable due to increased risks on surface water eutrophication.

Table 2: Survey of parameters involved in the determination of the Water Pollution Index WAPI, with their natural backgrounds (division factor in WAPI), and various water quality standards applied in the Netherlands.

Quality	Quality	Unit	WAPI	Target	Drinking	Artificial
Aspect	Parameter		applied	quality	Water	Recharge
			background	Groundwater	Standard	MACs Neths
				LBB, 1998	WLB, 2001	IB, 1993
A (esthetics)	Colour	mg/l Pt/Co	20		20	
A (esthetics)	Odour	N*	2		2	
A (esthetics)	Suspended solids	mg/l	0.5			0.5
A (esthetics)	Taste	N*	2		2	
A (esthetics)	Turbidity	FTE	1		1	
B (acidity)	pH	-	7		7-9.5	
C (ox/red cap)	CH4	mg/l	4.8			
C (ox/red cap)	Fe(II)	mg/l	11		0.2 (tot)	
C (ox/red cap)	Mn(II)	mg/l	1.1		0.05 (tot)	
C (ox/red cap)	O2	mg/l	11		>2	
C (ox/red cap)	SO4	mg/l	15	150	150	150
C + D	NH4	mg/l	0.4	2.6-12.9#	0.2	3.23
C + D	NO2	mg/l	0.1		0.1	
C + D	NO3	mg/l	2.5	24.8	50	24.8
D (nutrients)	ortho PO4	mg/l	0.06	1.22-9.2$	6.1 (tot)	1.22 (tot)
E (total salt)	Cl	mg/l	12	100	150	200
E (total salt)	Electr. Conductivity	uS/cm	350		1250	
F (IMPs)	As	ug/l	5	10	10	10
F (IMPs)	Cd	ug/l	0.05	0.4	5	0.4
F (IMPs)	Cr	ug/l	2	1	50	2
F (IMPs)	Cu	ug/l	3	15	2 (plateau)	15
F (IMPs)	Hg	ug/l	0.02	0.05	1	0.05
F (IMPs)	Ni	ug/l	10	15	20	15
F (IMPs)	Pb	ug/l	4	15	10	15
F (IMPs)	Zn	ug/l	10	65	3	65
G (OMPs, BTEX)	benzene	ug/l	0.2	0.2	1 (sum BTEX)	
G (OMPs, BTEX)	toluene	ug/l	0.2	0.2	1 (sum BTEX)	
G (OMPs, Lump)	AOX	ug Cl/l	5			30
G (OMPs, Lump)	EOX	ug Cl/l	0.5			
G (OMPs, others)	4-nitrofenol	ug/l	0.01			
G (OMPs, others)	benzothiazole	ug/l	0.01			
G (OMPs, others)	isobuthylfuranone	ug/l	0.01			
G (OMPs, others)	tributylphosphate + -iso-	ug/l	0.01			
G (OMPs, PAHs)	anthracene	ug/l	0.02	0.02	0.05	0.02
G (OMPs, PAHs)	benzo(a)anthracene	ug/l	0.002	0.002	0.05	
G (OMPs, PAHs)	benzo(a)pyrene (Borneff)	ug/l	0.001	0.001	0.01	0.1(ΣB)
G (OMPs, PAHs)	benzo(ghi)perylene (Borneff)	ug/l	0.002	0.002	0.05	0.1(ΣB)
G (OMPs, PAHs)	benzo(k)fluoranthene (Borneff)	ug/l	0.001	0.001	0.05	0.1(ΣB)
G (OMPs, PAHs)	chrysene	ug/l	0.002	0.002	0.05	0.02
G (OMPs, PAHs)	fluoranthene (Borneff)	ug/l	0.005	0.005	0.05	0.1(ΣB)
G (OMPs, PAHs)	indeno(123cd)pyrene (Borneff)	ug/l	0.0004	0.0004	0.05	0.1(ΣB)
G (OMPs, PAHs)	naphtalene	ug/l	0.1	0.1		0.1
G (OMPs, PAHs)	phenanthrene	ug/l	0.02	0.02	0.05	0.02
G (OMPs, THMs)	chloroform	ug/l	0.1	0.01	25 (sum THM)	
G (OMPs, VOCs)	trichloroethene	ug/l	0.01	0.01	10 (+tetra)	0.5
H (Pesticides)	alpha-HCH	ug/l	0.01	0.01	0.1	0.05
H (Pesticides)	atrazine	ug/l	0.01	0.0075	0.1	0.1
H (Pesticides)	bentazone	ug/l	0.01		0.1	0.1
H (Pesticides)	gamma-HCH (lindane)	ug/l	0.01	0.00002	0.1	0.05
H (Pesticides)	hexachlorobenzene	ug/l	0.01	0.01	0.1	0.05
H (Pesticides)	simazine	ug/l	0.01		0.1	0.1
I (Radioactivity)	rest-beta	mBq/l	10		1	
I (Radioactivity)	tritium	TU	8		840	
J (Microbiology)	colony counts 22`C	CFU/l	10000			
J (Microbiology)	faecal streptococs	CFU/l	10			
J (Microbiology)	thermotolerant coli counts	CFU/l	10			

E_{WAPI}: total salt content

This parameter combines the total amount of dissolved solids, for which Electrical Conductivity (EC) forms an excellent indicator, with the share in this of sodium chloride, with Cl^- concentration as indicator. Natural backgrounds of resp. 350 µS/cm and 12 mg Cl^-/L are based on (i) natural backgrounds for Rhine River water and old groundwater in the Netherlands, and (ii) the adverse effects of higher levels. Higher levels may lead to (1) adverse effects on plants bound to fresh water ecosystems, sensitive crops, cattle and man, and (2) corrosion of water treatment plants and transport mains. Of course natural backgrounds can be both higher and lower, necessitating adjustments in the division factors.

F_{WAPI}: inorganic micropollutants

The heavy metals Cd, Cr, Cu, Hg, Ni, Pb and Zn as well as As belong to the environmentally hazardous inorganic micropollutants. Natural backgrounds of resp. 0.05, 5, 3, 0.02, 9, 4, 9 and 5 µg/L derive from those for surface water according to MILBOWA (1991). These values are, Cr excluded, considerably lower (more severe) than those for groundwater. The parameter F_{WAPI} can, if appropriate, be easily extended with for instance Al, B, Ba, F, Sb and Se (for which MPCs for drinking water are available).

G_{WAPI}: organic micropollutants, non-pesticide

Included are here 4 groups of organic microcontaminants, which have been measured on a very frequent basis: 10 PAHs, 2 sum parameters (ΣLUMP), 4 VOlatile hydroCarbons (VOCs) and 4 other OMPs. Natural backgrounds (0.001-3 µg/L; see division factor in Table 1 and 2) derive from those for surface water according to MILBOWA (1991) with several deviations when necessitated by MDLs of analysis and with few additions (AOX and Σothers).

G_{WAPI} can be assumed zero, when data on all OMPs are lacking and if tritium <2 TU, because the groundwater than normally infiltrated before 1954 (when the use of many OMPs still was rather limited). The parameter G_{WAPI} can be easily modified by regarding other OMPs, or be extended with more OMPs (within each of the 4 groups or with more groups).

H_{WAPI}: pesticides

This category includes 7 pesticides, amongst which 2 triazines (atrazine and simazine), 3 organochlorine pesticides (α-HCH, γHCH and HCB), a phenylureum-herbicide (diuron) and bentazone. The choice of these pesticides was determined by their availability in data records and their frequent presence.

Natural backgrounds (0.01 µg/L; see division factor in Table 1 and 2) derive from those for surface water according to MILBOWA (1991), with as a deviation higher values for atrazine and above all α- and γ-HCH due to their higher MDL of the current analysis..

For water with tritium < 2 TU we can assume that H_{WAPI}, if measurements are lacking, equals zero, because the water in that case normally infiltrated prior to 1954 (when the use of pesticides mostly was at minimum). The parameter H_{WAPI} can be easily extended with other or more pesticides.

I_{WAPI}: radioactivity

Rest-β and tritium have been taken together as a measure for radioactive contamination, because of their frequent measurement. Rest-β is equal to the total beta-radiation after subtracting a calculated contribution of natural ^{40}K (ca. 0.02 Bq/L per mg K^+/L) and after excluding tritium. Tritium (^3H) is a beta-radiating element as well and has a half life of 12.43 years. This heaviest isotope of hydrogen (part of the water molecule and therefore an excellent tracer) mainly originated from above ground nuclear tests (especially in the period 1954-1970), regular discharges by nuclear power plants, reactor incidents and cosmic radiation.

Natural backgrounds for Rest-β and tritium are estimated at respectively. 10 mBq/L and 8 TU, which are considerably lower than the target values [posed by MILBOWA (1991). Tritium also constitutes, for groundwater, an indicator of potential contamination with modern, anthropogenic organic micropollutants. The parameter I_{WAPI} can be easily extended with for instance total alpha and gamma radiation.

J_{WAPI}: microbiology

The number of colony forming units (CFU) of cultivable cells on PCA at 22°C ($Colc_{22}$; also called colony counts), thermotolerant bacteria of the coli group ($Coli_{44}$) and faecal streptococci (Fs) have been taken together as a measure for bacteriological infection of water. One of the arguments to take these is the availability of their measurement. The natural backgrounds of respectively 10000, 10 and 10 CFU/L are based on data regarding surface water (RIWA, 1971-1996), dune infiltrate (Hoekstra, 1984) and Rhine bank filtrate (Van der Kooij, 1985). J_{WAPI} can be set standard at 0.3 in case of groundwater, if there are no measurements at all, because groundwater does not contain any $Coli_{44}$ nor Fs, while showing a median $Colc_{22}$ of ca. 10^4 CFU/L (Hoekstra, 1984; Van der Kooij, 1985).

The parameter J_{WAPI} can be easily extended with sulfite reducing clostridia, aeromonas, giardia etc.

3 THE SOIL POLLUTION INDEX: SOPI

The SOil Pollution Index (SOPI) is calculated according to Stuyfzand & Lüers (2000) with minor modifications, as indicated in Table 3. As in WAPI (section 2) unweighted means and the ratio of measured values and natural backgrounds or target values are used. Values normalised to natural backgrounds (X_N) are defined as:

$$X_N = X / X_{NB} \quad (1)$$

With: X = measured content of X in soil or aquifer [mg/kg d.w.]; X_{NB} = natural background (or target level) for micropollutant X in sediments (in the Netherlands: LBB, 1998)

[mg/kg d.w]. X_{NB} is equated to the content of particles < 2 μm and organic matter (loss on ignition) as indicated in Table 3.

4 RADAR PLOTS OF WAPI AND SOPI

The pollution indices WAPI and SOPI have the advantage that they (a) group various quality parameters and (b) relate analytical results to natural backgrounds or target values. This enables to directly plot each subindex into a radar plot, which is a standard plotting facility in spread sheets like EXCEL.

Such a radar plot is similar to the so-called 'AMOEBE'-approach (Ten Brink & Hosper, 1989; Baptist & Laane, 1996). AMOEBE is the acronym for 'Algemene Methode voor OEcosysteem BEoordeling' (General Method for Ecosystem Evaluation). It consists of a circular plot of many parameters with natural background or environmental target values forming the central circle. A kind of amoeba results when each parameter is plotted as a percentage of its natural background or environmental target value.

The principle of the WAPI and SOPI radar plots is shown in respectively Fig.1 and Fig.2. These plots differ from the AMOEBE-approach by using a logarithmic scale, styling into radar instead of circles, and addressing other parameters.

All calculations and plots have been programmed in EXCEL-spreadsheet. A radar plot similar to our SOPI radar was presented by Mannaerts et al. (1995).

Table 3: Determination of SOil Pollution Index SOPI and micropollutant contents normalized to their natural background or target level (X_{NB} in Eq.1), in sediments (in Netherlands as given by LBB 1998).
L = clay fraction (<2μm; % d.w.); NOM = Natural Organic Material (% d.w.).
N.B.: If parameters are omitted, then the final division factor should decrease accordingly

	$SOPI = 0.5\,(\Sigma TE_N / 9 + \Sigma OMP_N / 4)$	
TE_N: INORGANIC MICROPOLLUTANTS NORMALISED TO NATURAL BACKGROUNDS in mg/kg d.w.		
$As_N = As/(15+0.4(L+NOM))$ $Ba_N = Ba/(30+5L)$ $Cd_N = Cd/(0.4+0.007\,(L+3\,NOM))$	$Cr_N = Cr/(50+2L)$ $Cu_N = Cu/(15+0.6(L+NOM))$ $Hg_N = Hg/(0.2+0.0017\,(2L+NOM))$	$Ni_N = Ni/(10+L)$ $Pb_N = Pb/(50+L+NOM)$ $Zn_N = Zn/(50+1.5\,(2L+NOM))$
OMP_N: ORGANIC MICROPOLLUTANTS NORMALISED TO NATURAL BACKGROUNDS in mg/kg d.w.		
PAK_N = (naf + ant + fen + fla + baa + chry + bap + bpe + bkf + ipy)/(0.1 NOM)		
$EOX_N = EOX/(0.01\,NOM)$		
PCB_N = (PCB28+PCB52+PCB101+PCB118+PCB138+PCB153+PCB180)/(0.0024 NOM)		
OCP_N = (3ΣDDT+aldrin+5 dieldrin+2.5 endrin+αHCH+2.5 βHCH+0.05 γHCH)/(0.0225 NOM)		
ΣDDT = op-DDE + pp-DDE + op-DDD + pp-DDD + op-DDT + pp-DDT		

naf = naphtalene; ant = anthracene; fen = phenantrene; fla = fluoranthene; baa = benzo(a)anthracene; chry = chrysene; bap = benzo(a)pyrene; bpe = benzo(ghi)perylene; bkf =benzo(k)fluoranthene; ipy = indeno(1,2,3cd)pyrene.
NB: if content of specific TE or OMP < Minimum Detection Limit (MDL), then to be filled in zero value.

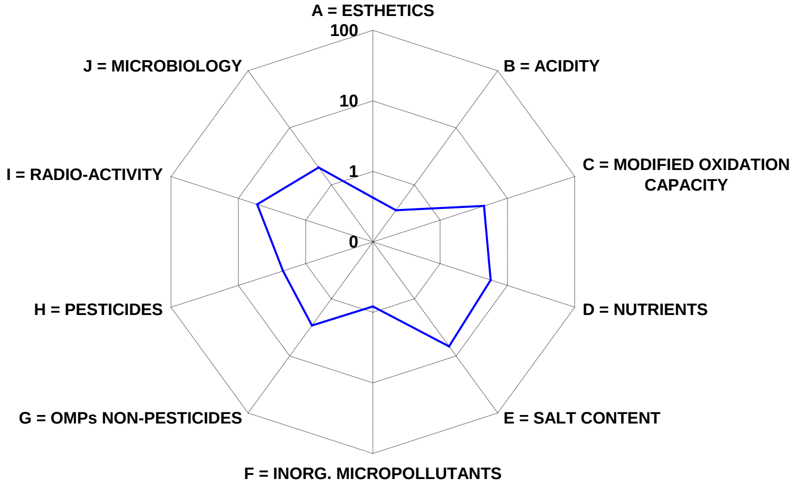

Figure 1 Principle of the WAPI radar plot (WAPI = WAter Pollution Index).
0, 1, 10, 100 = number of times the natural background value.

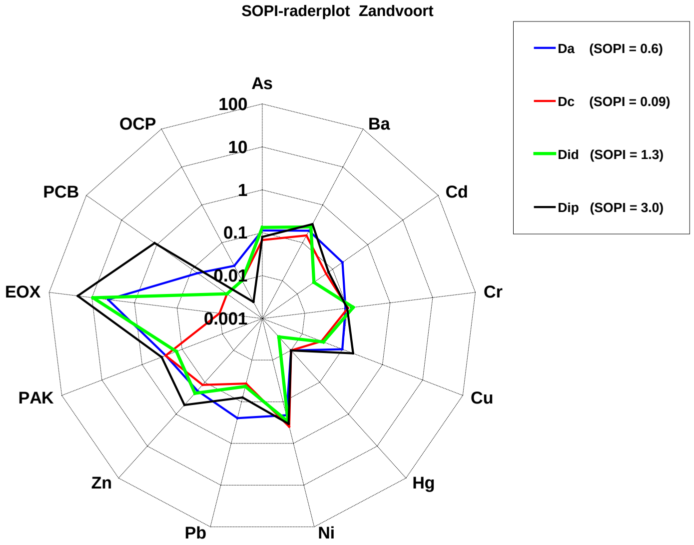

Figure 2 Principle of the SOPI radar plot (SOPI = SOil Pollution Index).
0, 1, 10, 100 = number of times the natural background value.

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6 REFERENCES

Appelo, C.A.J. & D. Postma 1993. Geochemistry, groundwater and pollution. Balkema, Rotterdam, 536p.

Baptist, H.J.M. & W.E.M. Laane 1996. AMOEBE'S in WSV. H_2O 29, 743-595 en 598.

BKH 1994. Chemische waterkwaliteitsindices; internationale inventarisatie van technieken en methodieken voor de aggregatie en presentatie van chemische waterkwaliteitsgegevens. Rapport bkh adviesbureau, Delft, 67p.

Hoekstra, A.C. 1984. Microbiologische aspecten van duininfiltratie. KIWA-Meded. 81, 217-259.

Mannaerts, S.H.W.M., B.W. Raterman & J. Blok 1995. Bodemkwaliteitsdiagram, een extra hulpmiddel voor de weergave van bodemkwaliteit. Bodem 4, 176-177.

LBB 1998. Guide for soil protection, No 4, Ministerie VROM, Netherlands (in dutch).

Schindler, D.W. (1981) : Interrelationships between the cycles of elements in freshwater ecosystems. Ch. 7 in "Some perspectives of the major biogeochemical cycles", G.E. Likens (ed), SCOPE, 113-123.

Schwarzenbach, R.P., P.M. Gschwend & D. Imboden 1993. Environmental organic chemistry. J. Wiley & Sons, NY.

Stuyfzand, P.J. 1993b. Hydrochemistry and hydrology of the coastal dune area of the Western Netherlands. Ph.D Thesis Vrije Univ. Amsterdam, published by KIWA, ISBN 90-74741-01-0, 366 p.

Stuyfzand, P.J. 1998. Decalcification and acidification of coastal dune sands in the Netherlands. Water-Rock Interaction, Proc. 9th Intern. Symp. on WRI, Taupo New Zealand, G.B. Arehart & J.R. Hulston (eds), Balkema, 79-82.

Stuyfzand, P.J. 2001 Modelling the quality changes upon artificial recharge and bank filtration; principles and user’s guide of Easy-Leacher 4.6. Kiwa report SWI 99.199, 3^{rd} edition, 150p.

Stuyfzand, P.J. 2002. Modelling the accumulation rate and chemical composition of sludges in recharge basins. This volume.

Stuyfzand, P.J. 2005. Mapping groundwater bodies with artificial or induced recharge, by determination of their origin and chemical facies. Proc ISMAR-5, Berlin, 12-17 June 2005, in prep.

Stuyfzand, P.J. & F. Lúers 1996. Gedrag van milieugevaarlijke stoffen bij oeverinfiltratie en kunstmatige infiltratie; effecten van bodempassage gemeten langs stroombanen. Kiwa-Meded. 125, 272p.

Stuyfzand, P.J. & F. Lüers 2000. Environmental balance for pollutants in nature reserves with and without artificial recharge. Kiwa-Meded. 126 (in dutch), 241p.

Ten Brink, B.J.E. & S.H. Hosper 1989. Naar toetsbare ecologische doelstellingen voor het waterbeheer: de AMOEBE-benadering. H_2O 22, 612-617.

Van der Kooij, D. 1985. Microbiologische aspecten van oevergrondwater. Ch.6 in KIWA Meded. 89, 24p.

Vollenweider, R.A. (1976) : Advances in defining critical loading levels for phosphorus in lake eutrophication. Mem. Inst. Ital. Idrobiol. (33), 53-83.

WLB 2001. Herziene Waterleidingbesluit. . Staatsblad 2001, 31, 1-28 (in dutch).

Chapter 15: Quantifying the Chemical and Microbiological Retention Capacity and Sustainability of Basin Recharge Systems Arrenæs and Dösebacka by Easy-Leacher 4.8®

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Abstract: The chemical and microbiological retention (buffer) capacity of an aquifer, as part of a managed aquifer recharge (MAR) system, was evaluated by predicting the quality evolution with time, of both the water recovered after aquifer passage, and the aquifer used. To this purpose the 2D reactive transport code Easy-Leacher 4.8® (EL4.8) was used. EL4.8 was extended with a simple approach to predict the retention of pathogenic micro-organisms by a series of 3 exponential elimination rates. This approach requires data on pathogen concentrations in the input and at various distances in the aquifer, on a reference site, and – for extrapolation to other sites or aquifer layers – data on (1) groundwater flow velocity, (2) temperature, pH and concentrations of O_2, NO_3 and SO_4 of the infiltrate, and (3) horizontal hydraulic conductivity and CEC of each aquifer layer.

Prior to applying EL4.8 to 2 basin recharge systems, resp. Dösebacka in Sweden and Arrenaes in Denmark, essential data are presented for each site, regarding the recharge process, hydrogeology, native hydro- and geochemistry, quality of the infiltration water, hydrology and chemical interactions between water and aquifer. The retention capacity of these 2 MAR sites was evaluated on the basis of model predictions of (a) the behaviour of amongst others NO_3, 9 trace elements, 17 organic micropollutants, 6 radionuclides and 5 pathogens, and (b) the leaching of aquifer constituents like $CaCO_3$, Bulk Organic Material, and MnO_2-like minerals. It is concluded that both systems, Dösebacka more than Arrenaes, are vulnerable to potential, long lasting, raised inputs of nitrate, trace elements, organic micropollutants and radionuclides, which justifies the current efforts to implement a sensitive on-line early-warning system to prevent the intake of polluted river/lake water.

1 INTRODUCTION

Managed Aquifer Recharge (MAR) operations are sustainable when all resulting beneficial processes are renewable and continue indefinitely, without undesirable effects on adjacent systems. The following criteria should be met in order to earn the mark “hydrogeochemically sustainable” (Stuyfzand, 2002a): (1) the receiving aquifer system and, if present, recharge basins and recollection wells, drains or canals remain multifunctional (fit for other uses when MAR operations should be abandoned); (2) the beneficial physical and (bio)chemical processes in the recharge facilities and receiving aquifer system continue indefinitely; (3) criteria 1 and 2 last as long as they last in adjacent or comparable background areas; and (4) recharge operations do not change the chemical environment of the adjacent area (including surface water and groundwater).

In this study the focus is on the quantification of the current and future chemical and microbiological retention (buffer) capacity of the aquifer system. This is done by evaluating the effects of the MAR operation on the quality evolution with time, of both the water recovered after aquifer passage, and the aquifer used. A rapid and high-level break-through of fluvial pollutants in the water recovered would indicate a low retention (buffer) capacity, and a rapid and high-level accumulation of pollutants in muds or aquifer, and a rapid leaching of natural aquifer constituents, would demonstrate a low hydrogeochemical sustainability.

These processes are evaluated by using Kiwa’s expert-system Easy-Leacher 4.8® (EL4.8; Stuyfzand, 1998, 2001, 2002b), for modeling the quality changes during MAR (like artificial recharge).

The use of EL also allows for a preliminary screening of pollutants on their behaviour in basins and aquifers, and thus on their potential impact on drinking water quality (or on the required post-treatment) and the environment, notably the aquifer. This holds for organic micropollutants like pesticides, endocrine disruptors and pharmaceuticals, heavy metals, and pathogenic micro-organisms. In addition, also the load of acidifying (NH_4, DOC, CO_2) or oxidizing substances (O_2, NO_3, SO_4) is evaluated by calculating the resulting rate of leaching of valuable aquifer constituents like acid buffering calcium carbonate ($CaCO_3$) and redox buffering pyrite (FeS_2) and Bulk Organic Matter (BOM).

The resulting knowledge can be used to: (a) selectively exclude thus polluted or highly corrosive water as much as possible by closing the water intake upon an early warning; (b) improve the pretreatment such that the pollutant or leaching agent is eliminated there; (c) sanitate the fluvial basin from which the infiltration water derives, by political means; and (d) shift the undesired or harmful pollutants or agents to the black list leading to a politically imposed embargo on use and production.

The economic benefits of avoiding the infiltration of surface water polluted with substances that contaminate or leach the aquifer or affect the drinking water, are enormous. First of all, if drinking water consumers lose their faith in tap water, more money is spent on bottled water. This leads to raised costs of living, and thus to economic damage. On the other hand, a polluted aquifer system needs to be cleaned-up, in case of abandoning an AR site, by virtue of the EU law on AR of surface water. This clean-up can be extremely expensive, and if aquifers are completely leached of their natural, buffering components, the post-treatment may need expensive extensions.

Within the ARTDEMO project, EL4.8 has been applied to the two field sites; Dösebacka AR plant and Arrenæs AR trial plant.

2 PRINCIPLES OF EASY-LEACHER

2.1 General Features

Easy-Leacher (EL) is a 2D reactive transport code, developed by Stuyfzand (1998, 2005) and set in EXCEL spreadsheet, which makes it relatively easy to apply. El4.8 combines chemical principles with empirical rules in an expert system. These rules are based on 30 years of intensive Kiwa research on numerous experimental and productive sites with Artificial Recharge (AR, using either basins or injection wells) and River Bank Filtration (RBF), in the Netherlands, Germany, UK and Australia. The leaching of aquifers is important because of high fluxes in AR and RBF systems. The quality of the input water (e.g. river water), flow and mud conditions are assumed more or less constant since the start of AR or RBF.

2.2 The model is mainly based on:

- Microsoft's spreadsheet EXCEL for Windows (≥95);
- the straw approach, which simplifies 3D groundwater flow into a 2D set of maximum 50 flow tubes through a maximum of 10 horizontal aquifer layers;
- hydrological key parameters (from separately run hydrological models or field data);
- the chemical mass balance approach;
- equilibrium of the Ca-CO_2-H2O system (if relevant);
- empirical rules for sequence of reactions, reaction kinetics and behaviour of specific dissolved species and bacteria and viruses.

By including these empirical rules EL can be considered an expert system. Chemical transport is in fact calculated on the basis of pore flushes (time scale), retardation and leach factors (superimposed on the pore flushes), $CaCO_3$ equilibrium (if relevant), mass balancing and many if/else statements (expert rules).

2.3 Compartments and processes

EL addresses the following processes in the 4 compartments depicted in Fig.1:

1. basin or river: admixing of rain water (+ dry deposition), evaporation, nutrient uptake, biogenic hardness reduction, volatilisation, photolysis and (bio)degradation;
2. water sediment interface: filtration, additional O_2 and CO_2 inputs (unsaturated zone or root respiration), mineralisation of organic matter, dissolution of $CaCO_3$, precipitation of sulphides, nitrification and DOC oxidation;
3. aquifer: displacement of native groundwater, cation exchange, oxidation of pyrite and organic matter, dissolution of $CaCO_3$ and MnO_2, sorption of trace elements and Organic Micro Pollutants (OMPs), radioactive decay, degradation of OMPs and elimination of bacteria and viruses;
4. recovery system: mixing of max. 50 different flowlines starting in basin, river or well, with native groundwater, from max. 10 aquifer layers.

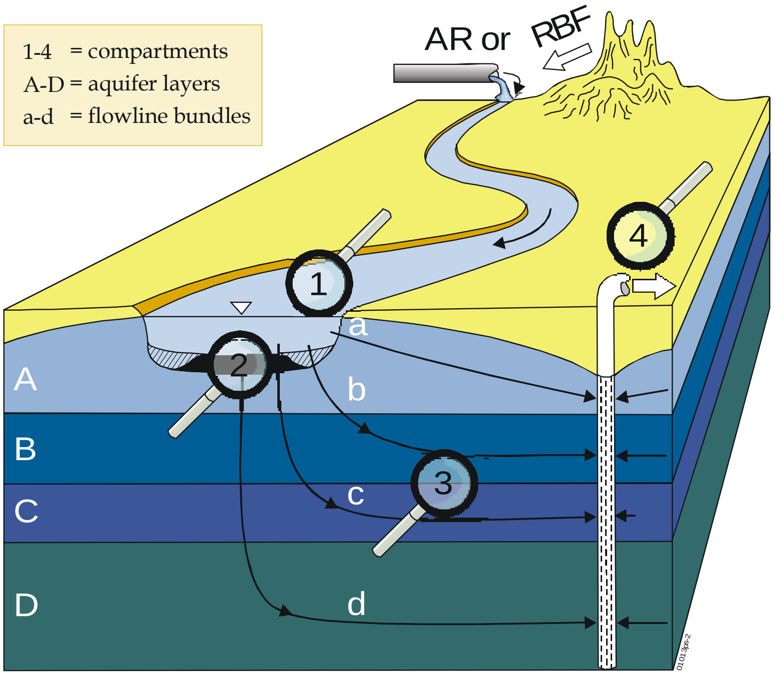

Figure 1. The 4 compartments in EASY-LEACHER, with schematisation of the aquifer system, flow, mud interaction and recovery. AR = Artificial Recharge; RBF = River Bank Filtration.

2.4 *Easy-Leacher calculates*

- Quality changes in: recharge basins (or fluvial compartment or injection well), clogging layer and aquifer
- Quality development in recovered water, with position of fronts (leaching or breakthrough) in aquifer
- Clogging layer: accumulation rate, chemical composition
- All this is calculated for main constituents (21), trace elements (9), radionuclides (6), organic micropollutants (17) and pathogens (3 groups: viruses, bacteria without oocysts, and bacteria with oocysts). EL can be easily extended with other quality parameters.

2.5 *Recent adaptations and extensions to EL4.6*

EL4.8 was upgraded for ARTDEMO from the former version 4.6, mainly by expansion with pathogenic micro-organisms, and with AR systems with an unsaturated zone, and by coupling EL to the calculation of the aggregated quality parameter WAPI (Water Pollution Index) and SOPI (Soil Pollution Index), which is elucidated by Stuyfzand & Lüers (2000) and Berg et al. (2006, this volume).

3 PATHOGEN TRANSPORT

3.1 *Fitting observations to equations*

The original, simple formula that best describes the exponential decreasing concentration of bacteria and viruses in infiltrated surface water during aquifer passage is, according to Iwasaki (1937) and Matthess et al. (1988):

$$C_X = C_0 \exp(-\lambda_X X) \qquad (1A)$$

$$C_T = C_0 \exp(-\lambda_T t) \qquad (1B)$$

With:
C_X = content at distance X = X [CFU/L or n/L]
C_T = content after travel time in aquifer t = T [CFU/L or n/L]
C_0 = input content at distance X = 0 and at travel time t = 0 [CFU/L or n/L]
λ_X = filter factor, including the combined effects of filtration, sedimentation, sorption, decay etc. [m^{-1}];
λ_T = elimination factor = λ_X X / t [d^{-1}];
X = distance travelled in porous medium since infiltration [m]
t = travel time in porous medium since infiltration [d]
exp() = $e^{()}$

In microbiology it is common use to define the Decimal Elimination Capacity (DEC) as:

$$DEC_X = \log_{10} (C_0 / C_X) \qquad (2A)$$

$$DEC_T = \log_{10} (C_0 / C_T) \qquad (2B)$$

Thus, the filter or elimination factor λ relates to DEC as follows:

$$\lambda_X = 2.303\ DEC_X / X \qquad (3A)$$
$$\lambda_T = 2.303\ DEC_T / t \qquad (3B)$$

The approach in EL4.8 forms an extension to Eq.1A by discerning a series of 3 exponential elimination rates in specific aquifer zones (Fig.2). The method is similar, in a way, to models describing DOC-removal (Mälzer et al., 1992; Schoenheinz, 2004). Those models, however, relate the elimination rates to time, and need the input of 3 DOC-fractions: highly, moderately and not degradable.

In our approach the first, high elimination rate (DEC_{S1}) is connected with the recharge proximal zone (several metres wide; S1), the second, moderately high elimination rate (DEC_{S2}) with the main aquifer zone beyond the proximal zone (S2), and the third, low elimination rate (DEC_{S3}) with the most remote zone where only inactivation processes operates (S3). So we obtain (see Fig.2):

If $X \leq S1$:

$$C_X = C_0\ E\ (-DEC_{S1}\ X / S1) \qquad (4)$$

If $S1 < X \leq S2$:

$$C_X = C_0\ E\ -(DEC_{S1} + DEC_{S2}\ (X - S1) / (S2 - S1)) \qquad (5)$$

If $X \geq S2$:

$$C_X = C_0\ E\ -(DEC_{S1} + DEC_{S2} + DEC_{S3}\ (X - S2) / (S3 - S2)) \qquad (6)$$

With:

$E\ () = 10^{()}$

S1 = first bow point in a concentration versus distance in aquifer plot [m]

S2 = second bow point in a concentration versus distance in aquifer plot, or the most downgradient observation point [m]

S3 = the terminal point of aquifer passage, just prior to exfiltration or abstraction by a pumping well [m]

DEC_{S1} = total DEC observed at point S1 [-];

DEC_{S2} = total DEC observed at point S2 minus DEC_{S1} [-];

DEC_{S3} = total DEC observed at point S3 minus DEC_{S2}, or to be calculated as follows from known λ_T :

$$DEC_{S3} = \lambda_{T3}\ (S3 - S2) / (2.303\ v_{23}) \qquad (7)$$

where:

λ_{T3} = inactivation rate coefficient in water [d^{-1}], and v_{23} = mean flow velocity in between S3 and S2 [m/d];

The inactivation rate coefficient in water strongly depends on temperature and redox conditions.

3.2 Extrapolation to the whole MAR plant, same aquifer layer

Ideally the experimental data within a specific MAR plant allow for the construction of a concentration-distance plot like in Fig.2. From this plot the data for applying Eq. 4-6 can be

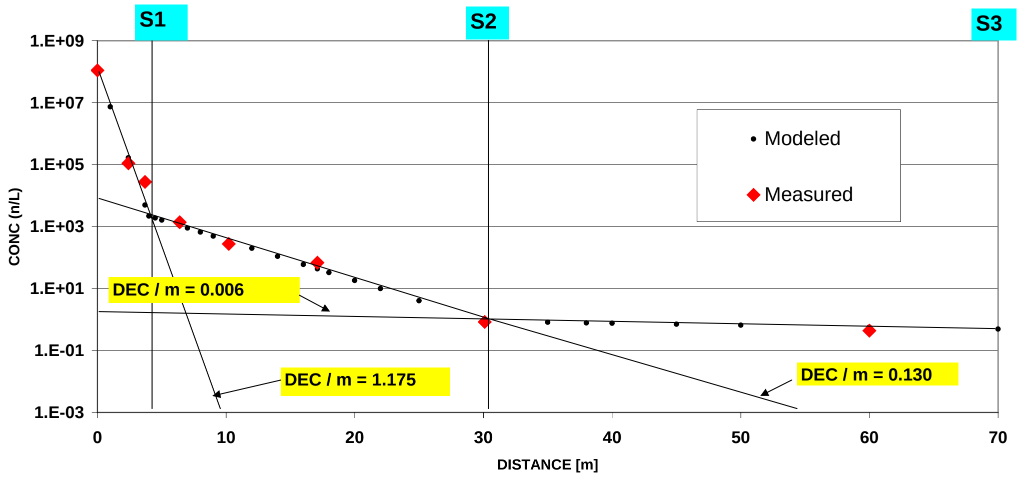

Figure 2. Principles and parameters of 1D transport modelling of bacteria and viruses in aquifers. DEC = Decimal Elimination Capacity (see Eq.2A); S1, S2 = respectively first and second bow point in the plot; S3 = water abstraction point. If observations at S2 are lacking, then – in a conservative estimate – the most remote observation well (beyond S1) should be assigned as S2.

easily derived to calculate the elimination rates at all other distances within the same specific aquifer layer within the same MAR area, assuming a homogeneous porous medium and recharge process.

In several field studies the exact position of bow point S2 is not known, but situated anyhow beyond the most remote observation well. In that case the worst case approach applies: the distance to this most remote observation well is taken as S2, beyond which the conservative ‘low’ elimination factor holds, equal to the inactivation rate coefficient.

3.3 Extrapolation to other aquifer layers or another MAR plant

The above field data can in several cases be extrapolated to other aquifer layers on the same MAR site, or even to a site with a comparable artificial recharge and aquifer system. In both cases some corrections are needed to account for deviations in temperature, pH and redox, aquifer characteristics (like CEC, grain size distribution and bulk organic carbon) and flow velocity.

As a first intuitive approximation, to be further calibrated by comparing measured data on various field sites, it is assumed that the bow points S1 and S2 linearly increase with (a) the square root of the hydraulic conductivity (in horizontal direction) of the aquifer matrix, (b) the square root of the groundwater flow velocity, and (c) the dynamic viscosity of water:

$$(S1)_Y = (S1)_A \ \mathrm{sqrt}[(K_H)_Y / (K_H)_A] \ \mathrm{sqrt}[v_Y / v_A] \ (\eta_Y / \eta_A) \qquad (8A)$$

$$(S2)_Y = (S2)_A \ \mathrm{sqrt}[(K_H)_Y / (K_H)_A] \ \mathrm{sqrt}[v_Y / v_A] \ (\eta_Y / \eta_A) \qquad (8B)$$

with:

$(S1)_Y$, $(S1)_A$ = S1 on respectively site Y to be modelled, and site A from which the field data derive;
$(K_H)_Y$, $(K_H)_A$ = K_H = hydraulic conductivity in horizontal direction [m/d], respectively on site Y and A.
v_Y , v_A = velocity of groundwater flow in zone X = 0 to X = S1 [m/d] on respectively site Y to be modelled, and site A from which the field data derive
η_Y , η_A = dynamic viscosity of the water [Pa s)] on respectively site Y to be modelled, and site A from which the field data derive:

$$\eta = 0.5268 \ [1 + 8.05\ 10\text{-}7\ (0.69778\ EC) - 6.5\ 10\text{-}6\ (t - 4 + 2.2\ 10\text{-}4\ EC)^2]\ 0.947 / (t + 42.5)^{1.5} \qquad (9)$$

And as a first approximation, the DEC_{S1} and DEC_{S2}-values are assumed to depend on the actual Cation Exchange Capacity (CEC), the mean pH of the infiltrated water, and the redox and temperature dependent decay rate coefficient (rBOM) of organic matter in the aquifer:

$$(DEC_{S1})_Y = (DEC_{S1})_A \ (CEC)_Y / (CEC)_A \ E\ (pH_Y^{-0.75} - 0.7) / E\ (pH_A^{-0.75} - 0.7) + \log[(rBOM_Y / rBOM_A)] \qquad (10A)$$

$$(DEC_{S2})_Y = (DEC_{S2})_A \ (CEC)_Y / (CEC)_A \ E\ (pH_Y^{-0.75} - 0.7) / E\ (pH_A^{-0.75} - 0.7) + \log[(rBOM_Y / rBOM_A)] \qquad (10B)$$

with:

$$rBOM = f_T \ \{k_{O2}\ [C_{O2} / (2.94\ 10^{-4} + C_{O2})] + k_{NO3}\ [(C_{NO3} / (1.55\ 10^{-4} + C_{NO3})] + k_{SO4}\ [C_{SO4} / (10^{-4} + C_{SO4})]\} \qquad (11)$$

$$f_T = \exp(-6758.1 / [t + 273.15] + 16.1) / \exp(-6758.1 / [10 + 273.15] + 16.1) \qquad (12)$$

with:
f_T = correction factor for temperature deviating from standard temp = 10oC [-];
k_{O2} = 1.57 10^{-9} mol L-1 s-1 = rate constant for oxygen;
k_{NO3} = 1.67 10^{-11} mol L-1 s-1 = rate constant for nitrate;
k_{SO4} = 1.00 10^{-13} mol L-1 s-1 = rate constant for sulphate;
C_{O2} = mean concentration of oxygen in the involved aquifer segment [mol / L]
C_{NO3} = mean concentration of nitrate in the involved aquifer segment [mol / L]
C_{SO4} = mean concentration of sulphate in the involved aquifer segment [mol / L]

The pH-correction factor is based on data in Schijven (2001).

The redox and temperature dependent decay rate coefficient (rBOM) is based on Prommer & Stuyfzand (2005).

3.4 Validation

The above approach was validated by comparing 2 extensively studied artificial recharge sites A and Y in the Netherlands, both in unconsolidated sandy sediments and both with MS2 and PRD-1 bacteriophage challenge tests including detailed monitoring of piezometers at various distances from the recharge facility. Site A is a basin recharge plant near Castricum with a (sub)oxic aquifer (calcareous dune sand) and relatively high pH (7.8), and site Y is deep well injection site DIZON near Someren with a largely anoxic aquifer (Miocene decalcified, pyritiferous sand) and relatively low pH (6.6).

The test results on site A were published by Peters et al. (1998) and Schijven et al. (1999), and those on site Y by Medema et al. (2000) and Schijven et al. (2001).

4 APPLICATION OF EL4.8 TO DÖSEBACKA AR PLANT

4.1 Schematization of the recharge process and hydrogeology

The artificial recharge plant Dösebacka is described in further detail in Lundh (2005). The whole plant has been schematized here as shown in Fig.3, mainly on the basis of data in Lundh & Bergstedt (2003) and Lundh et al. (2005b). The 9 recharge basins and 15 recovery wells are schematized into one average basin and one recovery well at 120 m distance. The hydrogeology is simplified by the 4 aquifer layers specified in Table 1, maintaining a constant thickness (20 m) and tilting them into a horizontal position. The observed variation in travel times between the 9 infiltration basins and the 15 recovery wells is accounted for in the response curve of the schematized recovery well. The percentage of native groundwater that is admixed in the recovery (20%), is based on calculations using Cl- as a tracer.

4.2 Native hydrogeology and geochemistry (Dösebacka)

The native hydrogeological and geochemical characteristics of the 4 discerned aquifer layers at Dösebacka are given in Table 1. These results are based, among others, on 3 recently drilled wells (I - III), which were extensively analysed on their grain size distribution and geochemistry. The crude geochemical data were processed by the program GEO-CHEMCAL 5.2 (Stuyfzand, 2005a), a geochemical calculator and data base, to correct the data for undesired and desired contributions, and to attribute elemental data to mineral phases.

It can be concluded from Table 1 that the following minerals are or seem to be present: quartz (33-82%), albite (8-30%), K-feldspar (4-19%), biotite (4-8%), anorthite (2-6%), various clay minerals (0.6-2.9%), $CaCO_3$ (0-0.4%), $FeCO_3$ (0.1-0.4%), (hydr)oxides of Fe, Mn and Al (respectively 900-3000, 30-50 and 325-1375 ppm, as element), and FeS_2 (25-45 ppm). However, the following drawbacks should be made:

- The various silicate minerals were assigned assuming them to be the dominant end-members. This does not exclude the presence of other silicate minerals (which normally are numerous in diversity).
- The content of the carbonate minerals (only present in layers B-D) is very low. Coatings may prevent these small amounts to react.
- The derived pyrite content is extremely low, and could be erroneous due to the presence of other sulphur species like barite, or due to proximity of the minimum detection limit.

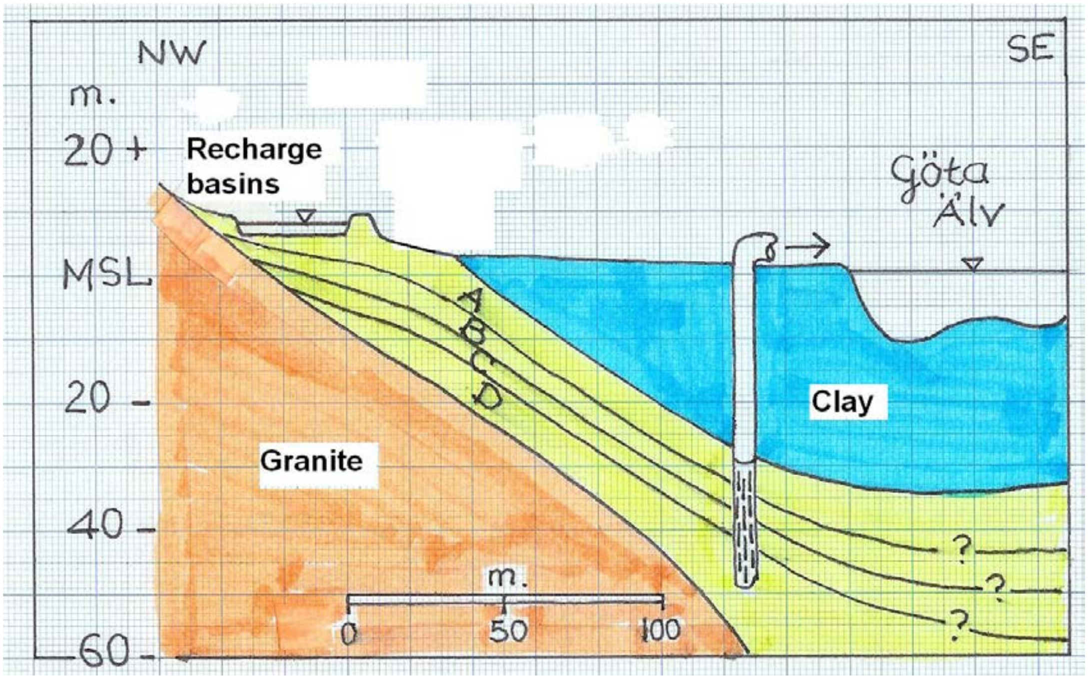

Figure 3. EL4.8 model cross section of Dösebacka, with indication of the 4 clastic aquifer layers (A-D).

The above drawbacks and the observed water quality changes (section 4.6) justify to insert in EL4.8, zero contents for $FeCO_3$ and FeS_2, and to reduce the amount of CO_2 reacting with $CaCO_3$ in layers B-D (set at 20%). The silicate minerals are not included in EL4.8, because they normally are not/hardly reactive when flushed by surface water that equilibrated with these minerals prior to becoming surface water. Most important for the modelling is the input of CEC and organic carbon (or bulk organic matter). Their input in EL4.8 is specified in Table 1.

4.3 Native hydrochemistry (Dösebacka)

The native hydrochemistry within each aquifer layer (Table 2) was estimated, as data were lacking, by comparing the Göta Älv input with the output of both the whole well field and individual wells. A significant amount of brackish groundwater should be present, especially in layer D, in order to explain the clear salinity increase in the output. This especially holds for the wells close to the river, which receive more native groundwater than the ones upgradient closer to the infiltration basins.

4.4 Quality of the infiltration water (Dösebacka)

The mean quality (period 2002-2004) of the Göta Älv River water, which is only treated by sedimentation before infiltration at the AR plant, is given in Table 2. Clearly, this is one of the cleanest surface waters to recharge! In the period 1950-1975 the river was rather polluted by a.o. spills from sewage water plants and industries like paper mills, and surface runoff from farm land.

Most health hazards are currently related to microbiological quality, which still indicates a faecal contamination. The mean suspended solids content of Göta Älv River is, expressed as turbidity, 6-18 FNU and very little seems to settle out in the sedimentation basin However, the infiltration basins are cleaned only once per year, indicating that suspended solids may be hampering the infiltration process.

In order to still get an impression of the elimination capacity of the aquifer, the input of those micropollutants that were either always below detection (organic micropollutants) or not analysed (radionuclides, viruses and several bacteria) was set at 100% in EL4.8. This approach does not conflict with chemical principles, because the inherent trace concentrations are well below any solubility control, and endogenic sources can be neglected.

4.5 Hydrological parameters (Dösebacka)

Table 1. Hydro(geo)logical and geochemical characteristics of the aquifer zones discerned in the target aquifer of Dösebacka (corresponding with Fig.3) and Arrenæs (corresponding with Fig.7).

Site			DOSEBACKA					ARRENAES						
Layer		Unit	Sludge	A	B	C	D	Sludge	UNSAT		A	B	C	D
Depth	from	m+LS	0	0.0	-6.0	-10.0	-13.5	0.0	0.0	-1.5	-27.0	-32.5	-37.9	-44.1
Depth	to	m+LS	0.02	-6.0	-10.0	-13.5	-20.0	0.02	-1.5	-27.0	-32.5	-37.9	-44.1	-47.0
Hydr Cond		m/d	29	45	120	30	90	33	2	40.1	35	22	78	3
Mean grain size	<2000 um	um	820	841	1177	480	1059	517	221	430.5	492	440	487	175
Clay size (<2um)	<2000 um	%	2.29	1.54	2.52	3.79	1.53	2.56	18.63	1.44	1.10	1.81	0.93	2.50
Siliceous gravel	>2000 um	%	4.3	4.8	77.5	16.8	49.5	0.0	2.2	2.0	4.4	1.8	1.0	0.0
BOM		%	0.624	0.301	0.053	0.030	0.001	1.910	0.79	0.06	0.05	0.05	0.06	0.08
C-organic		%	0.312	0.151	0.026	0.015	0.001	0.955	0.40	0.03	0.02	0.02	0.03	0.04
N / C	pyrolysis	mol/mol	0.12	0.13	0.11	0.03		0.07	0.10	0.11	0.11	0.11	0.13	0.06
P / C	C-best	mol/mol	0.04	0.13	1.41	1.76		0.01	0.01	0.09	0.01	0.11	0.10	0.14
CEC	actual	meq / kg	25.1	15.0	5.3	20.7	5.4	47.4	139.9	11.1	8.3	13.5	7.8	19.1
Na-Exch		meq / kg	0.23	0.14	0.05	0.19	0.05	0.85	2.52	0.20	0.15	0.24	0.14	0.34
K-Exch		meq / kg	0.17	0.10	0.04	0.14	0.04	0.52	1.54	0.12	0.09	0.15	0.09	0.21
Ca-Exch		meq / kg	19.2	11.5	4.1	15.9	4.2	39.4	113.1	9.4	7.1	11.5	6.7	16.0
Mg-Exch		meq / kg	5.4	3.2	1.1	4.5	1.2	4.9	14.9	0.8	0.6	0.9	0.5	1.3
Fe-Exch		meq / kg	0.048	0.029	0.010	0.040	0.010	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Base Saturation		%	100.0	100.0	100.0	100.0	100.0	100.0	98.8	100.0	100.0	100.0	100.0	100.0
CaCO3 #	(max)	%	0.00	0.00	0.14	0.40	0.28	0.31	3.96	2.55	1.88	2.53	2.88	3.18
Dolomite #	(max)	%	0.00	0.00	0.00	0.00	0.00	0.99	1.29	0.28	0.44	0.11	0.13	0.62
FeCO3	(max)	%	0.25	0.39	0.08	0.34	0.19	0.85	0.69	0.15	0.12	0.15	0.13	0.27
Ca / Sr	XRF	mol/mol	88	98	157	138	159	230	93	191		233	265	314
Fe-Oxalate		mg / kg	2432	1653	874	3040	2031	850						
Mn-Oxalate		mg / kg	79	48	32	51	53	100						
Al-Oxalate		mg / kg	427	327	550	1378	945	200						
FeS2	(max)	mg / kg	76	41	26	24	45	237	0	0	0	0	0	0
Ca-silicate	as Anortite	%	4.5	5.4	2.1	6.4	5.4	7.0	0.9	2.6		3.2	3.0	5.8
Mg-silicate	as Biotite	%	5.6	6.1	3.6	7.0	8.4	0.5	0.4	0.6		0.5	1.3	0.3
Na-silicate	as Albite	%	30.1	29.7	7.6	25.2	17.0	16.2	11.9	11.3		15.9	16.1	14.0
K-silicate	as K-feldspar	%	19.1	18.0	4.3	14.4	9.3	11.9	12.0	7.7		10.1	10.9	11.2
Quartz/opal	as SiO2	%	33.3	33.8	81.9	42.8	59.5	53.6	57.2	45.0		63.5	61.3	60.9
Clay minerals	(max)	%	2.18	1.46	0.64	2.88	0.77	2.49	17.53	1.4	1.02	1.74	0.89	2.39

1 = max if dolomite = 0, else minimum

The most important hydrological parameters in modelling with EL4.8 are given in Table 3. An important clue on the indicated travel times was given by observations in the recovery wells, on the time shift of seasonal temperature peaks in the infiltration water (Lundh et al., 2005). The temperature's retardation factor was set by them at 3.2, on the basis of a comparison, in well GRP.9, of temperature variations and the response curve from a NaCl tracer experiment. From this value we calculated the porosity of the aquifer as follows:

$$\mathrm{RTEMP} = 1 + (1 - n)\, k_S / (n\, k_W) \qquad (13A)$$

$$n = k_S / (k_W\, (R_{TEMP} - 1) + k_S) \qquad (13B)$$

With: n = porosity [-];

k_S , k_W = heat capacity of respectively solid phase (assuming all silicates, neglecting organic matter) and water, respectively 1925 and 4184 [J/ (L °C)]

Eq.13B yields, after inserting R_{TEMP} = 3.2, a porosity of 0.173, which is typical for gravel and till deposits.

The response curve for the Dösebacka well field (Fig.4) was constructed on the basis of travel time and pumping rate data for all wells as listed by Lundh et al. (2005). It has been approximated as much as possible in the EL4.8 simulation by varying the hydraulic conductivities (K_H) between the 4 aquifer layers with the constraint, however, to remain close to the mean value for the whole aquifer of 72.5 m/d, a value mentioned by Lundh et al. (2005).

The percentage of native groundwater that is admixed in the recovery (20%), is based on calculations using Cl^- as a tracer. Lundh et al. (2005) estimated the admixed quantity at 15-20% by comparing the mean infiltration rate (62 L/s) with the mean pumping rate (70-80 L/s).

Lundh et al. (2005) mention the presence of a 0-7.7 m thick unsaturated zone under basins D-I.

Table 2. Mean chemical composition of the native groundwater, infiltration and recovered water at recharge sites Dösebacka and Arrenæs. Dösebacka: native hydrochemistry in the individual aquifer layers A-D was postulated on the basis of the observed quality in all individual pumping wells and the raw water abstracted. The groundwater recovered includes 20% admixed natural groundwater. Arrenæs: both native and recovered groundwater as observed in Well I1 (receiving water mainly from the recharge basins).

		Dosebacka							Arrenaes		
		Native					Input	Output	Native	Input	Output
		A	B	C	D	Mix	Gota Alv	Mix	Well I1	Lake Arresoe	Well I1
		0-6	6-10	10-13.5	13.5-20	0-20		0-20			
EC20 (US)	uS/cm	296	419	612	1252	748	92	289	451	431	505
TEMP (C)	oC	9.0	9.1	9.2	9.3	9.2	9.0	9.1	9.1	10.5	10.2
pH		7.80	7.80	7.80	7.80	7.80	7.20	7.27	7.44	8.26	7.45
O2	mg/L	0.0	0.0	0.0	0.0	0.0	9.0	9.0	6.2	9.4	5.3
CH4	mg/L	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	<0.01	<0.01
DOC	mg/L	0.5	0.5	0.5	0.5	0.5	3.5	1.0	1.0	13.0	4.0
SI-calcite		-0.31	-0.26	-0.26	-0.24	-0.25	-2.16	-1.45	0.12	0.66	0.08
Cl	mg/L	30	60	120	320	164	8	52	29	64	60
SO4	mg/L	4	8	17	45	23	13	16	51	39	48
HCO3	mg/L	120	140	145	155	143	20	64	225	194	237
NO3	mg/L	3.0	1.0	0.0	0.0	0.9	2.1	2.3	40.6	2.1	4.3
PO4	mg/L	0.03	0.03	0.03	0.03	0.03	0.06	<0.03	0.022	0.24	0.023
Na	mg/L	27.9	44.6	78.0	189.2	102.7	7.2	41.9	12	40	36
K	mg/L	5.3	5.9	7.2	11.3	8.1	1.4	3.1	1.3	5.8	3.6
Ca	mg/L	29.2	29.9	31.2	35.4	32.1	7.9	12.9	107	64	88
Mg	mg/L	5.3	7.3	11.3	24.7	14.3	1.7	5.3	5.5	9.1	8.4
NH4	mg/L	0.10	0.55	1.10	1.20	0.77	0.03	0.13	0.05	0.32	0.031
Fe	mg/L	0.05	0.05	0.10	0.20	0.11	0.12	0.04	0.09	0.063	0.09
Mn	mg/L	0.05	0.16	0.18	0.20	0.16	0.01	0.05	0.04	0.093	0.094
SiO2	mg/L	10.0	15.0	20.0	32.0	21.3	5.0	8.0	20	5.4	16
As	ug/L	2.0	2.0	2.0	2.0	2.0	0.3		<0.2	0.11	0.66
B	ug/L	25	25	25	55	37	10			127	88
Ba	ug/L	10.0	10.0	20.0	25.0	16.8	14	30		27	27
Cd	ug/L	0.00	0.00	0.00	0.00	0.00	0.01	0.06	<0.01	0.01	
Cu	ug/L	1.2	0.7	0.5	0.2	0.6	1.3	2.0	<2	1	
F	ug/L	180	200	250	350	261	100	0.20	0.11	230	220
Ni	ug/L	0.5	0.3	0.2	0.1	0.2	0.8	2.4	<2	0.9	1.7
Pb	ug/L	0.3	0.3	0.3	0.1	0.2	0.3	1.0	<2	0.4	
Zn	ug/L	3.0	3.0	4.0	5.0	3.9	3.0	<5	18	3.1	
AMPA	ug/L	0.0	0.0	0.0	0.0	0.0			<0.01	0.044	<0.01
atrazine	ug/L	0.0	0.0	0.0	0.0	0.0	<0.01			<0.01	<0.01
diurone	ug/L	0.0	0.0	0.0	0.0	0.0	<0.01			<0.01	<0.01
dibuftal	ug/L	0.0	0.0	0.0	0.0	0.0	<0.1			<0.1	<0.01
1,2-DCEa	ug/L	0.0	0.0	0.0	0.0	0.0	<0.02		<0.02	<0.02	<0.02
tri	ug/L	0.0	0.0	0.0	0.0	0.0	<0.05		<0.01	<0.05	<0.05
CCl3	ug/L	0.0	0.0	0.0	0.0	0.0	<0.05		0.15	<0.05	<0.05
phenanthrene	ug/L	0.0	0.0	0.0	0.0	0.0					
BAP	ug/L	0.0	0.0	0.0	0.0	0.0					
3H	TU	20.0	5.0	0.0	0.0	5.4				100	
Th37 Coli	CFU/L	0.0	0.0	0.0	0.0	0.0	4200		<1	190	
faec streptococs	CFU/L	0.0	0.0	0.0	0.0	0.0	330				
SO3-r Clos	CFU/L	0.0	0.0	0.0	0.0	0.0					

Taking into account the infiltration rate of each basin, this means that 50% of the water is infiltrating without an unsaturated zone. In EL4.8 we incorporated the presence of this unsaturated zone, by only adding an additional amount of O_2 (3.8 mg/L) to the infiltration water. The effects of an unsaturated zone on pathogen transport (normally resulting in an improved removal rate) has been neglected.

4.6 *Water aquifer interaction and aquifer leaching (Dösebacka)*

Reactions of the infiltrating water with the aquifer can be deduced by comparing the mean input water quality (of the infiltration water) with the mean output water quality (of the well field or one pumping well or a monitoring well). However, corrections are needed to account for: (a) quality changes in the infiltration ponds, (b) a time shift between the in- and output corresponding to the travel time in the system; and (c) the admixing of native groundwater (if relevant).

Application of this method to Dösebacka in Table 2 yields the following conclusions:

- Most quality changes are mainly dictated by the admixing of relatively saline native groundwater;
- Calcite and MnO_2 are slowly dissolving, yielding some additional Ca, HCO_3 and Mn; and
- Bulk organic material in the aquifer (BOM) is slowly oxidizing, which explains the decrease in concentrations of O_2 and NO_3.

Another method is to analyse the geochemistry of the aquifer in detail, looking for decreasing contents of minerals and BOM upgradient towards the recharge basins, from where the leaching starts. In the case of Dösebacka there can only be clearly deduced that $CaCO_3$ is indeed leached close to the recharge basin (even in the mud layer; Table 1).

Results with EL4.8 (Fig.5) predict the following situation after 100 years of artificial recharge (i.e. anno 2005): (a) the labile BOM (ca 10% of the total amount) has already been leached completely, but only 10-15% of the more difficult to mineralize fraction of BOM has leached; (b) calcium carbonate has been leached completely from layer A, and for about 5-20% from layers B, C and D; and (c) the MnO_2 phase has been leached for 3-15% only.

Table 3. Hydrological parameters of the Dösebacka recharge system.

Native	**Depth**	**porosity**	**Travel time**	**Flux-tot**	**Flux-mix**	**Kh**	**KD**
Aquifer	**m-LS**	**%**	**d**	**%**	**%**	**m/d**	**m2/d**
Layer A = Sand	**0-6**	**0.3**	**77.2**	**18.8**	**3.8**	**45**	**270**
Layer B = Gravel/stones	**6-10**	**0.175**	**22**	**33.3**	**6.7**	**120**	**480**
Layer C = Coarse sand	**10-13.5**	**0.3**	**88**	**7.3**	**1.5**	**30**	**105**
Layer D = Sand and gravel	**13.5-20**	**0.175**	**44.1**	**40.6**	**8.1**	**90**	**585**

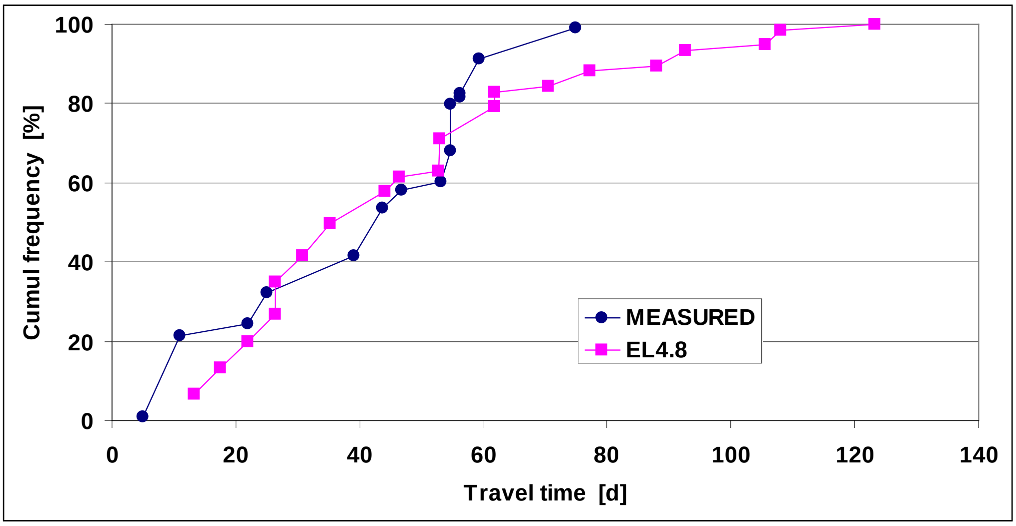

Figure 4. The 'measured' response curve for Dösebacka, showing the cumulative travel time distribution as based on data in Lundh et al. (2005). The response curve as entered in EL4.8 is also shown.

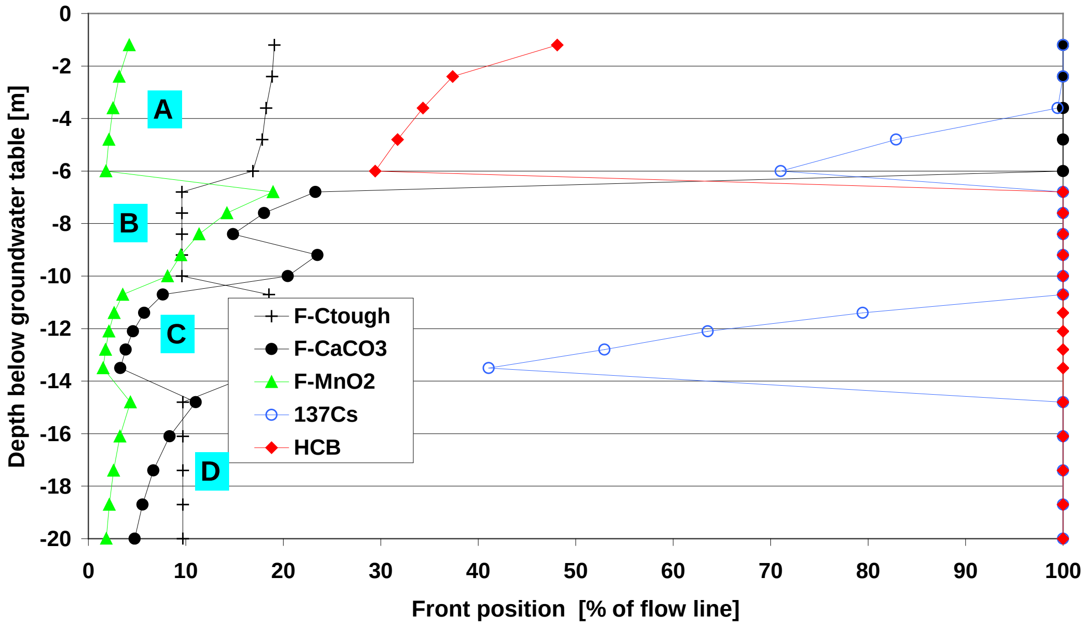

Figure 5. Calculated position of (i) the leaching front of organic material relatively hard to biodegrade (C-tough), calcite ($CaCO_3$) and MnO_2, and (ii) the breakthrough front of radiocaesium (^{137}Cs) and hexachlorobenzene (HCB), both 100 years after the start of artificial recharge at Dösebacka. Five flow lines are depicted within each aquifer zone (A-D, see Table 1), sorted top–down on the basis of increasing travel time. A front position of 10% means that after 100 years the front is situated at 1/10 of the total distance between recharge basin and recovery well. F-X = leaching front of solid phase X.

Thus leaching is relatively rapid for $CaCO_3$, and slow for tough BOM and MnO_2. The leaching of BOM causes the pool of sorption sites for organic micropollutants to decrease and the penetration distance of oxidants like O_2 and NO_3 to increase (see Table 5).

4.7 Prediction of pollutant behaviour (Dösebacka)

The concentrations of pollutants in the infiltration water are, and during the past years, have been so extremely low that there is no chance to validate the model predictions. The invalidated results of EL4.8 modelling, with a realistic input of inorganic micropollutants and a 100% input of organic and radioactive micropollutants are shown in Fig.6. In addition, Table 4 offers a view on the behaviour of various other pollutants during a constant input for 0-10,000 years.

It can be concluded that the recharge system is quite vulnerable to potential, long lasting, raised inputs of nitrate, trace elements, organic micropollutants and radionuclides. The retention capacity of the aquifer system is quite low for these inputs, which justifies the current efforts to implement a sensitive on-line monitoring system to prevent the intake of polluted river water.

4.8 Prediction of pathogen removal (Dösebacka)

In the model predictions it is, at present, assumed that redox conditions remain stable, and that pathogens are not or hardly retarded during aquifer transport. The first assumption is not valid (see O_2 and NO_3 in Table 4), which means that the model predictions are a bit on the pessimistic side on the long term. This is so because an increasing oxygenation of the aquifer conduces to higher inactivation rates of pathogens.

Anyhow, it can be concluded from Table 4 that viruses, for which the bacteriophages MS-2 and PRD-1 are model organisms, are best removed (4-5 log units), and thermotolerant Coli, faecal streptococci and sulphite reducing clostridia much less (2.5-3 log units). These conclusions do not conflict with observations by Lundh et al (2005a) because of the low inputs and relatively high analytical minimum detection limits.

These DEC values may incidentally be insufficient, especially in winter time when temperatures are low (and inactivation rates low as well). This means that also on microbiological grounds, MARS facility Dösebacka is quite vulnerable, requiring an effective on-line early warning system.

Table 4. Predicted raw water quality from the pumping wells of Dösebacka, as calculated by EL4.8. Years since the start of artificial recharge; input is Göta Älv River water with indicated quality (period 2002-2003); and admixed groundwater with indicated quality is fixed at 20%.

		NATIVE	INPUT	OUTPUT after:				
		Groundwater		1	10	100	1000	10000
		20% admix		year	year	year	year	year
EC20 (US)	uS/cm	748	92	257	257	257	257	257
TEMP (C)	oC	9.2	9.0	9.0	9.0	9.0	9.0	9.0
pH		7.80	7.20	7.10	7.10	7.24	7.41	7.41
O2	mg/L	0.0	9.0	2.0	2.0	4.0	5.5	5.7
CH4	mg/L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DOC	mg/L	0.5	3.5	1.0	1.0	1.0	1.0	1.0
SI-calcite		-0.25	-2.16	-1.69	-1.69	-1.57	-1.41	-1.42
Cl	mg/L	164.4	8.3	39.6	39.6	39.6	39.6	39.6
SO4	mg/L	23.0	13	15.1	15.1	15.1	15.1	15.1
HCO3	mg/L	143	20	51	51	50	49	49
NO3	mg/L	0.90	2.13	0.5	0.5	1.2	1.7	1.8
PO4	mg/L	0.03	0.06	0.03	0.06	0.06	0.06	0.06
Na	mg/L	102.7	7.2	55.6	26.3	26.3	26.3	26.3
K	mg/L	8.09	1.4	3.6	2.7	2.7	2.7	2.7
Ca	mg/L	32.1	7.9	13.5	13.5	13.1	12.9	12.7
Mg	mg/L	14.3	1.7	10.6	4.7	4.2	4.2	4.2
NH4	mg/L	0.77	0.03	0.20	0.16	0.16	0.15	0.15
Fe	mg/L	0.11	0.12	0.07	0.02	0.02	0.02	0.02
Mn	mg/L	0.16	0.01	0.07	0.07	0.04	0.03	0.03
SiO2	mg/L	21.3	5.0	14.5	8.6	8.3	8.3	8.3
As	ug/L	2.0	0.3	1.8	0.7	0.5	0.4	0.4
B	ug/L	37	10	15	15	15	15	15
Ba	ug/L	16.8	14	14	14	15	15	15
Cd	ug/L	0.000	0.01	0.001	0.004	0.005	0.005	0.005
Cu	ug/L	0.6	1.3	0.8	1.2	1.2	1.2	1.2
F	ug/L	261	100	151	133	148	133	133
Ni	ug/L	0.2	0.8	0.4	0.7	0.7	0.7	0.7
Pb	ug/L	0.2	0.3	0.3	0.3	0.3	0.3	0.3
Zn	ug/L	3.9	3.0	3.5	3.1	3.1	3.1	3.1
atrazine	%	0.0	100.0	42.0	42.3	52.5	62.2	62.2
diurone	%	0.0	100.0	40.9	41.3	50.1	65.5	65.6
lindane	%	0.0	100.0	28.5	29.5	34.8	53.4	54.0
dibuftal	%	0.0	100.0	0.0	0.0	0.0	0.0	0.0
1,2-DCB	%	0.0	100.0	29.9	31.8	28.2	31.8	31.8
tri	%	0.0	100.0	30.8	30.9	29.3	30.2	30.2
CCl3	%	0.0	100.0	15.0	15.1	18.3	21.1	21.1
phenanthrene	%	0.0	100.0	0.0	0.0	0.0	0.0	0.0
BAP	%	0.0	100.0	0.0	0.0	0.0	0.0	0.0
3H	TU	5.4	100.0	80.5	80.5	80.5	80.5	80.5
60Co	%	0.0	100.0	30.0	59.7	59.7	59.7	59.7
90Sr	%	0.0	100.0	0.0	61.3	70.8	70.8	70.8
137Cs	%	0.0	100.0	0.0	0.0	16.9	17.5	17.5
MS-2	%	0.0	100.0	0.002	0.002	0.002	0.002	0.002
PRD-1	%	0.0	100.0	0.005	0.005	0.005	0.005	0.005
Th37 Coli	%	0.0	100.0	0.04	0.04	0.04	0.04	0.04
faec streptococs	%	0.0	100.0	0.13	0.13	0.13	0.13	0.13
SO3-r Clos	%	0.0	100.0	0.25	0.25	0.25	0.25	0.25

4.9 Accumulation of pollutants (Dösebacka)

With EL4.8 the accumulation rate of mud and the accumulation of main constituents (BOM, $CaCO_3$, silicates), trace elements and organic micropollutants can be calculated (Stuyfzand, 2002). However, without data on suspended solids and on the DOC/TOC-ratio in the infiltration water this is more or less useless.

So here we have to rely on measurements of the mud and underlying aquifer layers, which were sampled in autumn 2004. It should be

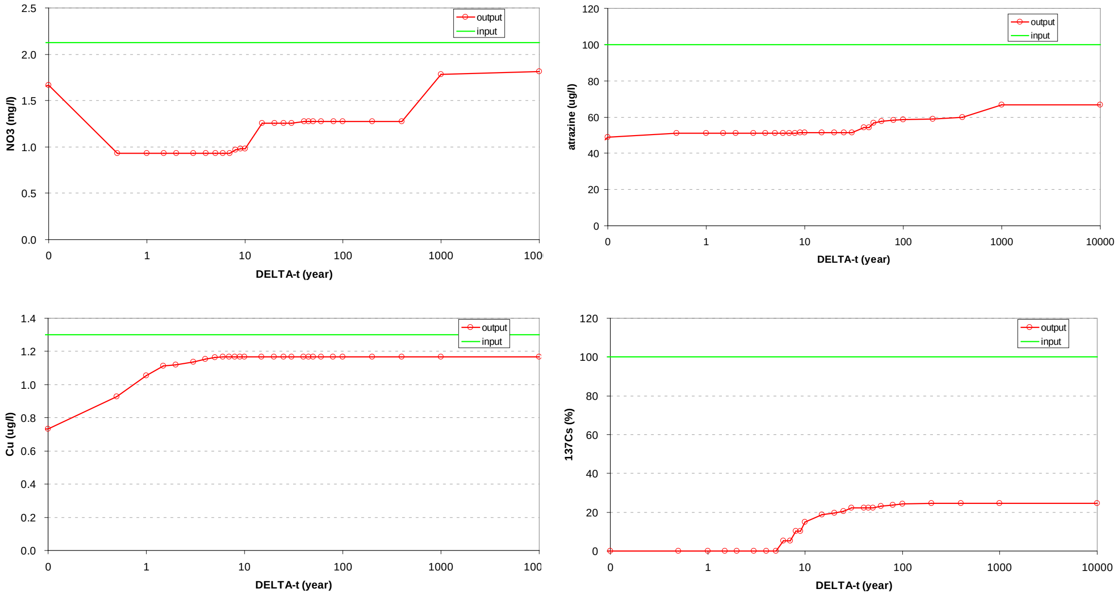

Figure 6. Predicted concentrations (by EL4.8) of 4 micropollutants in the water pumped from well field Dösebacka, since the start of artificial recharge (t = 0).

Table 5. Trace element content (incl. Fe, Mn, P and Ti) of mud at the bottom of the recharge basins, and of sand and sandy gravel in the discerned aquifer layers A-D at Dösebacka, and in the unsaturated zone at Arrenæs.

Site			DOSEBACKA					ARRENAES						
Layer			Sludge	A	B	C	D	Sludge	UNSAT		B	C	D	E
Depth	from	m+LS	0.00	0.00	-6.00	-10.00	-13.50	0.00	0.00	-1.5	-1.5	-9.0	-16.5	-25.0
Depth	tot	m+LS	-0.02	-6.00	-10.00	-13.50	-20.00	-0.02	-1.5	-27.0	-9.0	-16.5	-25.0	-29.0
As	XRF	mg / kg	0.6	0.8	0.5	0.4	0.2	1.4	3.2	1.1	0.9	1.1	1.2	1.3
Ba	XRF	mg / kg	638	607	138	486	306	446	436	341	162	402	417	403
Cr	XRF	mg / kg	20	21	4	14	10	13	36	17.4	5.7	12	30	22
Cu	XRF	mg / kg	13.0	20.1	2.3	8.5	6.0	2.8	10.6	15.8	2.3	7.8	39.7	4.9
Fe	XRF	%	1.12	1.16	0.43	1.15	1.02	0.71	1.24	0.45	0.30	0.47	0.44	0.70
Ga	XRF	mg / kg	14.1	13.6	3.4	10.8	7.7	7.6	8.8	5.9	3.1	6.8	7.1	7.2
La	XRF	mg / kg	22.3	21.7	5.0	18.6	11.2	14.4	18.6	11.0	9.6	10.2	11.3	14.3
Mn	XRF	%	0.024	0.024	0.009	0.025	0.021	0.018	0.032	0.014	0.010	0.015	0.015	0.018
Nb	XRF	mg / kg	9.9	9.7	1.7	7.3	4.4	4.9	8.2	4.6	4.9	4.0	4.0	6.6
Nd	XRF	mg / kg	12.4	11.0	2.8	10.7	9.2	8.2	10.6	5.7	4.2	3.6	5.2	13.2
Ni	XRF	mg / kg	8.8	8.7	2.3	7.2	5.7	4.6	11.4	4.2	2.1	4.5	4.5	7.0
P	XRF	%	0.028	0.026	0.010	0.026	0.023	0.032	0.037	0.016	0.012	0.014	0.018	0.026
Pb	XRF	mg / kg	16.6	16.0	3.7	15.1	8.6	11.9	20.1	9.1	4.8	9.8	11.1	11.7
Rb	XRF	mg / kg	107	99	24	73	51	58	69	41	18	48	51	50
Sc	XRF	mg / kg	4.7	5.6	1.6	6.4	4.2	3.5	5.0	3.1	1.9	3.9	2.8	4.8
Sn	XRF	mg / kg	2.2	3.2	0.6	0.8	1.4	1.3	2.8	3.7	11.2		2.1	
Sr	XRF	mg / kg	220	231	65	224	154	163	104	148	121	154	165	153
Th	XRF	mg / kg	4.8	5.1	0.8	4.7	2.2	4.2	5.3	2.3	1.6	2.5	2.5	2.9
Ti	XRF	%	0.14	0.15	0.05	0.14	0.11	0.10	0.21	0.09	0.07	0.09	0.08	0.16
U	XRF	mg / kg	1.4	1.6	0.5	1.5	1.4	1.5	1.7	0.8	0.4	0.7	0.9	1.1
V	XRF	mg / kg	27.5	30.2	10.3	27.4	23.5	18.0	34.4	13.7	8.9	15.2	12.8	21.9
Y	XRF	mg / kg	18.2	19.8	4.6	18.9	12.5	11.6	16.4	10.4	7.4	10.4	10.5	15.9
Zn	XRF	mg / kg	43.0	39.1	7.7	17.8	16.6	15.7	36.8	15.2	6.9	8.6	28.1	15.6
Zr	XRF	mg / kg	111	127	29	108	78	101	252	166	165	130	132	308

mentioned that mud is regularly removed (once a year on average) in order to keep infiltration rates high. This excludes the presence of old mud deposits, which were formed during periods with higher pollution loads of the infiltration water.

The data shown in Table 1 (main constituents) and Table 5 (trace elements), reveal the following: (a) the mud sampled was strongly diluted with material from aquifer layer A, and was thus relatively clean and decalcified; (b) it was clearly enriched with respect to BOM, probably due to algae; and (c) the mud contained only little more Ba, Ga, La, Nb, Nd, Ni, P, Pb, Rb and Zn than the other layers (with respect to layer A less than 10% more), probably reflecting the deposition of clay minerals from Göta Älv water.

So the present pollution level of the mud is very low, which is also due to a lack of old mud remnants from the more polluted past, thanks to frequent mud removal.

5 APPLICATION OF EL4.8 TO ARRENÆS AR TRIAL PLANT

5.1 Schematization of the recharge process and hydrogeology

The artificial recharge trial plant Arrenæs is described in further detail by Bennedsen et al. (2005). EL4.8 is applied here only to one part of this composite plant, which combines sprinkling, trough and basin recharge: namely to the basin recharge scheme with well I1 as its main recovery. This implies that a complete model for Arrenæs, including all 3 recharge types (of which the troughs can quantitatively be neglected) and the total recovery system by 4 wells, would necessitate to (a) build a separate model for the sprinkling system, and subsequently (b) combine the results of both models.

So, only the basin recharge system has been schematized as shown in Fig.7, mainly on the basis of data supplied by Copenhagen Energy. The 4 recharge basins West 1, West 2, East 1 and East 2 and the main recovery well I1 are schematized into one average basin and one recovery well at a weighted average distance of 112 m. The hydrogeology is simplified by identifying a thick one layer unsaturated zone and 4 aquifer layers with specifications in Table 1. A median shortest travel time of 120 days between basins and recovery well I1, as based on data in Jørgensen & Helleberg (2002), in combination with the measured distances to all basins, yielded an estimate of the response curve of the schematized recovery well. The percentage of native groundwater that is admixed in the recovery (14%), is based on calculations using Cl^- as a tracer.

5.2 Native hydrogeology and geochemistry (Arrenæs)

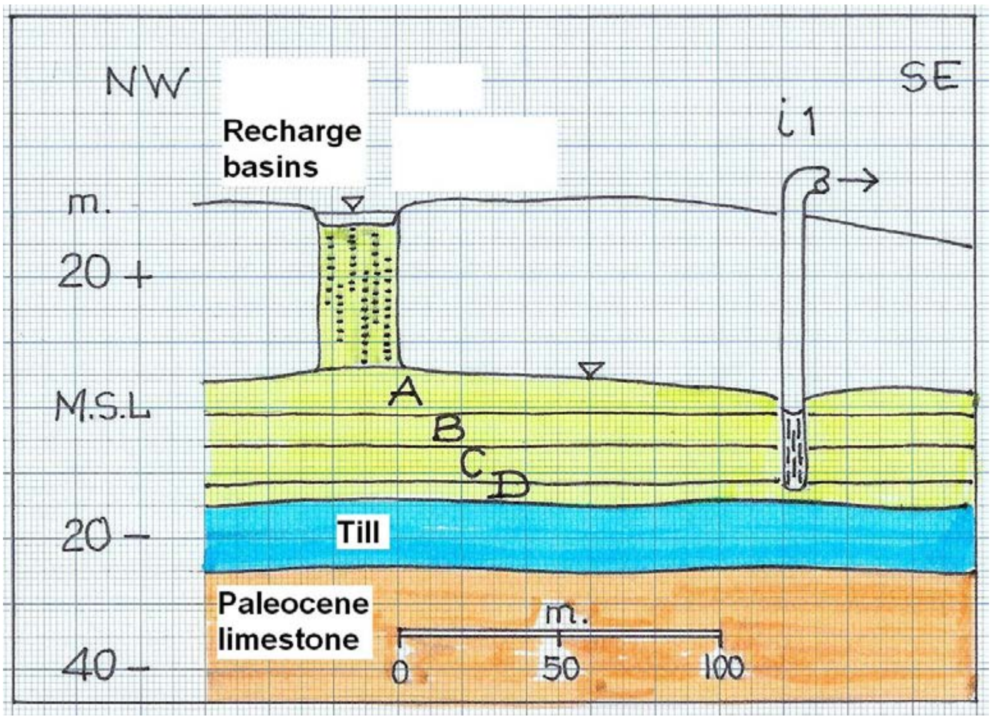

Figure 7. EL4.8 model cross section of the basin recharge subsystem of pilot plant Arrenæs, with indication of the 4 aquifer layers (A-D).

The native hydrogeological and geochemical characteristics of the approximately 27 m thick, unsaturated zone and the 4 discerned aquifer layers at Arrenæs are given in Table 1. These results are based on the following. The mean characteristics of the unsaturated zone are fully based on 2 shallow and 2 deep bore holes (Nielsen et al., 2005), which were extensively analysed on their grain size distribution and geochemistry. The crude geochemical data on 35 sediment samples in total, were processed by the program GEO-CHEMCAL 5.2 (Stuyfzand, 2005a), a geochemical calculator and data base, to correct the data for undesired and desired contributions, and to attribute elemental data to mineral phases.

As sufficient data on the saturated (aquifer) zone are lacking (one sample from each of the 2 deep boreholes was from the saturated zone), the results of the unsaturated zone were used to characterize the aquifer between 27 and 47 m-LS (Land Surface). The upper 1.5 m were, however, skipped, and the differentiation of the originally identified zones in between 1.5 and 29 m-LS, was maintained. So it is assumed that the stratification in the saturated zone is a copy of the one in the unsaturated zone.

It can be concluded from Table 1 that the following minerals are or seem to be present: quartz (54-64%), albite (12-16%), K-feldspar (10-12%), biotite (0.3-1.3%), anorthite (1-7%), various clay minerlals (1-18%), calcite ($CaCO_3$ min. 0.3-4%), dolomiet ($CaMg(CO3)_2$ max. 0.1-1.3%), siderite ($FeCO_3$ max 0.1-0.8%), and (hydr)oxides of Fe, Mn and Al (order of magnitude estimated at respectively 1000, 50-100 and 200-1000 ppm, as element). Pyrite (FeS_2) is virtually absent (<20 ppm).

However, the following drawbacks should be made:

The various silicate minerals were assigned assuming them to be the dominant end-members. This does not exclude the presence of other silicate minerals (which normally are numerous in diversity).

The content of the carbonate minerals is relatively high (except for the mud layer where it is low). Calcium carbonate is by far the dominant carbonate mineral. The presence of dolomite is highly questionable, because the groundwater quality does not reflect a significant dissolution of dolomite, as the Mg^{2+} concentration in native groundwater is low (5.5 with Ca^{2+} = 107 mg/L) and deriving for 37% from sea spray (Cl^- = 29 mg/L). Of course, the calcium carbonate may contain impurities of $MgCO_3$ and $FeCO_3$, which are more resistant to dissolution. Additionally, coatings may prevent the small amounts of $FeCO_3$ to react.

The above data, drawbacks and observed water quality changes (section 5.6) justify to insert in EL4.8, zero contents for dolomite, siderite and pyrite. The silicate minerals are not included in EL4.8, because they normally are not/hardly reactive when flushed by surface water that equilibrated with these minerals prior to becoming surface water. Most important for the modelling is the input of $CaCO_3$, CEC and organic carbon (or bulk organic matter). Their input in EL4.8 was conform Table 1.

5.3 *Native hydrochemistry (Arrenœs)*

The native hydrochemistry within each aquifer layer (Table 2) was set equal to the mean groundwater quality from pumping well I1 prior to the start of artificial recharge in April 1995. Clearly, the high NO_3 concentrations reflect strong agricultural imprints. The reason for the raised chloroform content is unknown.

5.4 *Quality of the infiltration water (Arrenœs)*

The mean quality (period 1997-1999) of Lake Arresø water, which is only treated by sedimentation before infiltration at the Arrenæs

AR trial plant, is given in Table 2. Most health hazards are currently related to microbiological quality, which still indicates a faecal contamination.

In order to still get an impression of the elimination capacity of the aquifer, the input of those micropollutants that were either always

Table 6. Hydrological parameters of the Arrenæs recharge system. Travel time in saturated layers incl. 55 days in unsaturated zone.

Native	Depth	porosity	Travel time	Flux-tot	Flux-mix	Kh	KD
Aquifer	m-LS	%	d	%	%	m/d	m2/d
Unsaturated zone	0-27	0.3	55	100	0	30	810
LAYER A= Sand, coarse	27-32.5	0.32	301	23.8	3.3	35	191
LAYER B = Sand, medium coarse	32.5-37.9	0.32	479	15.0	2.1	22	120
LAYER C = Sand, very coarse	37.9-44.1	0.32	135	60.1	8.4	78	482
LAYER D = Sand, fine	44.1-47	0.32	3510	1.1	0.2	3	9

below detection (organic micropollutants) or not analysed (radionuclides, viruses and several bacteria) was set at 100% in EL4.8. This approach does not conflict with chemical principles, because the inherent trace concentrations are well below any solubility control, and endogenic sources can be neglected.

5.5 *Hydrological parameters (Arrenæs)*

The most important hydrological parameters in modelling EL4.8 are given in Table 6.

The response curve for recovery well I1 (Fig.8) was constructed on the basis of the following data.

The median travel time in the unsaturated zone is about 55 days, according to Jørgensen & Helleberg (2002), who measured the delay in seasonal 18O peaks. They also mentioned that travel times in the saturated zone to the closest recovery wells, like I1, are in the order of 2-3 months (calculated with MODFLOW). So in total, travel times along the relatively short flowlines from basin West 1 are estimated at about 135 days. The travel times from the other 3 basins (t_X; Table 7) were calculated by:

$$t_X = 55 + (135-55)\ R_X / R_{W1} \qquad (14)$$

And the flux contribution (in %) from basin X to the discharge of well I1 (Table 7) was estimated by:

$$\mathrm{Flux}_X = 100\ (1/R_X) / (1/R_W + 1/R_X + 1/R_Y + 1/R_Z) \qquad (15)$$

With: R_X = distance from recovery well I1 to the inner basin bank of basin X [m].

The percentage of native groundwater that is admixed in the recovery (14%), is based on calculations using Cl^- as a tracer (65, 60 and 29 mg/L in respectively infiltrated, recovered and native water). Jørgensen & Helleberg (2002) mention a value of 17% as based on $\delta^{18}O$ values in 2001.

5.6 *Water aquifer interaction and aquifer leaching (Arrenæs)*

Comparison of the mean quality of Lake Arresø water with the mean output water quality of well I1 in Table 2 yields the following conclusions:

- The quality changes are only little influenced by the admixing of native groundwater;
- DOC (Dissolved Organic Carbon) in the infiltration water is partly oxidized (69%), which explains the decrease in O2 concentrations. This process mainly occurs in the unsaturated zone, as evidenced by detailed data in Brun & Broholm (1998).
- The ammonium in the infiltration water is largely nitrified (90%), probably in the unsaturated zone as well;
- Calcite is clearly dissolving, yielding additional Ca and HCO_3. Obviously the supersaturated infiltration water gains a lot of CO_2 from the oxidizing DOC, NH_4 and BOM in the basin proximal, unsaturated zone; and
- Several exchange reactions are still ongoing, which explains the lowering of K, PO_4 and B concentrations and the remarkable rise for SiO_2.

The high O_2 concentration of the water recovered (5.3 mg/L) testifies of a very low redox buffer capacity of the saturated zone of the aquifer. However, there also might be a bias, for instance due to sample conservation problems (introduction of air in bottle), or the introduction of air from the unsaturated zone through the well screen when the groundwater table declined too much around the well. The small SO_4 increase might indicate that pyrite is oxidizing somewhere in the saturated zone as no FeS_2 was detected in the unsaturated zone. But it could also indicate that the admixing native groundwater changed.

Another method is to analyse the geochemistry of the aquifer in detail, looking for decreasing contents of minerals and BOM upgradient towards the recharge basins, from

Table 7. Data used to calculate the response curve for recovery well I1, on the basis of a modal travel time of 55 days from basin West 1, and the measured distances to the inner bank of the other 3 contributing recharge basins.

Recharge	**mean**	**travel**	**contrib**	**cumul**
Basin	**distance**	**time**	**(1/R)**	**contrib**
scale	**m**	**d**	**%**	**%**
West 1	**26**	**135**	**53.0**	**53.0**
West 2	**68**	**261**	**20.6**	**73.6**
East 1	**101**	**362**	**13.8**	**87.4**
East 2	**111**	**392**	**12.6**	**100.0**

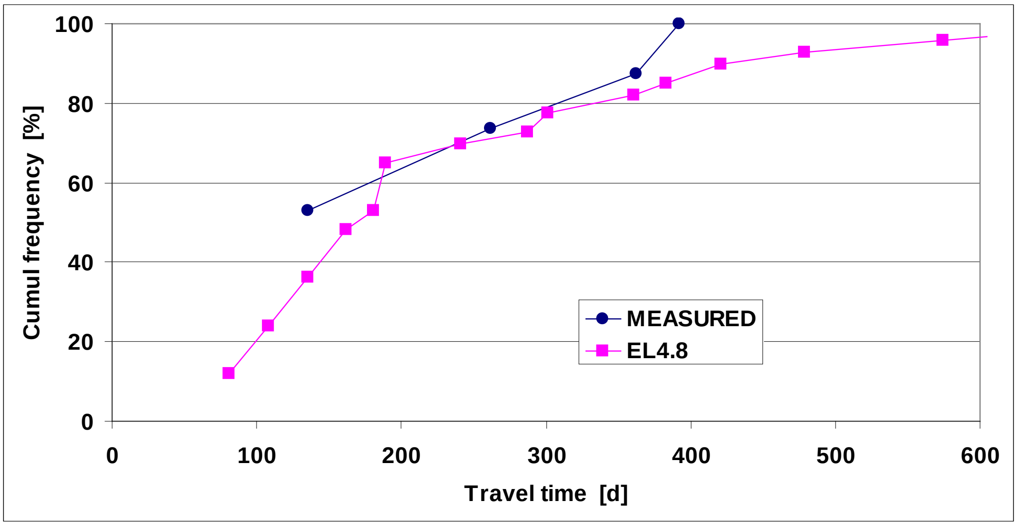

Figure. 8. The ‘calculated’ response curve for Arrenæs, showing the cumulative travel time distribution. The response curve as entered in EL4.8 is also shown.

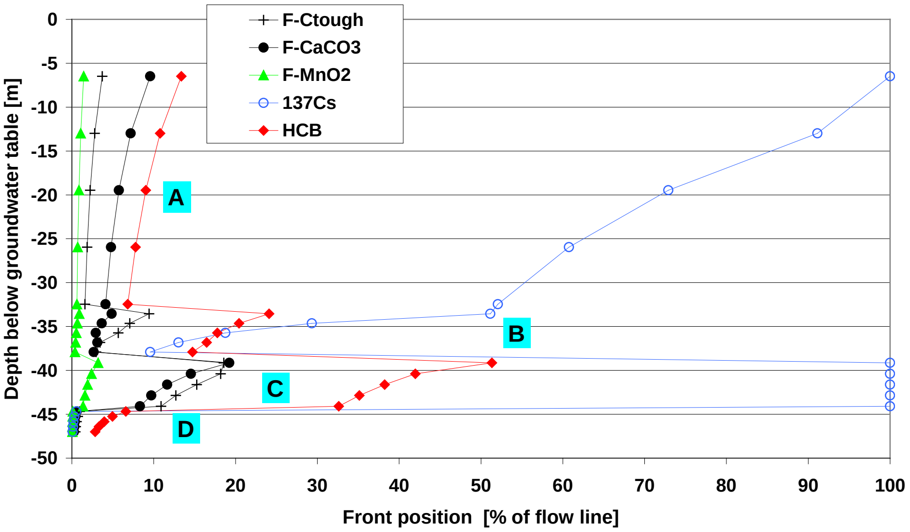

Figure 9. Calculated position of (i) the leaching front of organic material relatively hard to biodegrade (C-tough), calcite ($CaCO_3$) and MnO_2, and (ii) the breakthrough front of radiocaesium (^{137}Cs) and hexachlorobenzene (HCB), 100 years after the start of artificial recharge at Arrenæs (thus prediction for the year 2095). Five flow lines are depicted within each aquifer zone (A-D, see Table 1), sorted top–down on the basis of increasing travel time. A front position of 10% means that after 100 years the front is situated at 1/10 of the total distance between recharge basin and recovery well. F-X = leaching front of solid phase X.

where the leaching starts. In the case of Arrenæs there can only be clearly deduced that $CaCO_3$ is indeed leached close to the basin (especially in the mud layer; Table 1). For further details on leaching at the sprinkling area, see Nielsen et al. (2005).

Results with EL4.8 (Fig.9) predict the following for the situation after 100 years of artificial recharge (i.e. anno 2095): (a) the labile BOM (ca 1% of the total amount) has already been leached completely, but only 10-15% of the more difficult to mineralize fraction of BOM has leached; (b) calcium carbonate has been leached only from the first 2-20 meters in the unsaturated zone; and (c) the MnO_2 phase has been leached for <2% only.

Thus leaching is relatively rapid for labile BOM, and slow for $CaCO_3$, tough BOM and MnO_2. The leaching of BOM causes the pool of sorption sites for organic micropollutants to decrease and the penetration distance of oxidants like O_2 and NO_3 to increase (see Table 8).

5.7 Prediction of pollutant behaviour (Arrenæs)

The concentrations of pollutants in the infiltration water are, and during the past years, have been low, and the period of artificial recharge is still rather short (10 years), so that there is no chance to validate the model predictions. The unvalidated results of EL4.8 modeling, with a realistic input of inorganic and a 100% input of organic and radioactive micropollutants are shown in Fig.10, together with the results for Ca and NO_3. In addition, Table 8 offers a view on the behaviour of various other pollutants during a constant input for 0-10,000 years.

It can be concluded that the recharge system is less vulnerable than Dösebacka to potential, long lasting, raised inputs of nitrate, trace elements, organic micropollutants and radionuclides. The retention capacity of the aquifer system is relatively good for the organic micropollutants studied. It is, however, not so high for nitrate, trace elements (incl. heavy metals), and radionuclides. This justifies the current efforts to implement a sensitive on-line monitoring system to prevent the intake of polluted river water.

5.8 Prediction of pathogen removal (Arrenæs)

In the model predictions it is, at present, assumed that redox conditions remain stable, and that pathogens are not or hardly retarded during aquifer transport. The first assumption is not valid (see O_2 and NO_3 in Table 8), which means that the model predictions are a bit on the pessimistic side on the long term. This is so because an increasing oxygenation of the aquifer conduces to higher inactivation rates of pathogens.

Anyhow, it can be concluded from Table 8 that viruses, for which the bacteriophages MS-2 and PRD-1 are model organisms, are very well removed (8-10 log units), and thermotolerant Coli, faecal streptococci and sulphite reducing clostridia less but still good (3.5-8 log units). These conclusions do not conflict with observations by Berg et al. (2005) because of the low inputs and relatively high analytical minimum detection limits.

Table 8. Predicted raw water quality from recovery well I1 of Arrenæs, as calculated by EL4.8. Years since the start of artificial recharge; input is Lake Arresø water with indicated quality (period 2002-2003); and admixed groundwater with indicated quality fixed at 14%.

		NATIVE	INPUT	OUTPUT after:				
		Groundwater		1	10	100	1000	10000
		20% admix		year	year	year	year	year
EC20 (US)	uS/cm	451	431	602	613	613	598	542
TEMP (C)	oC	9.1	10.5	9.5	10.3	10.3	10.3	10.3
pH		7.44	8.26	7.44	7.44	7.44	7.34	7.05
O2	mg/L	6.2	9.4	2.2	1.0	1.0	2.3	6.8
CH4	mg/L	0.04	0.00	0.01	0.01	0.01	0.01	0.01
DOC	mg/L	1.0	13.0	2.6	4.0	4.0	4.0	4.0
SI-calcite		0.12	0.66	0.12	0.13	0.13	-0.01	-0.48
Cl	mg/L	29.0	64.0	51.6	59.2	59.3	59.3	59.3
SO4	mg/L	51.0	39	43.3	40.8	40.7	40.7	40.7
HCO3	mg/L	225	194	265	277	277	262	209
NO3	mg/L	40.60	2.13	14.5	5.8	5.7	6.3	7.8
PO4	mg/L	0.02	0.24	0.02	0.10	0.23	0.22	0.19
Na	mg/L	12.0	40.0	21.2	35.9	36.0	36.0	36.0
K	mg/L	1.30	5.8	2.3	5.1	5.1	5.1	5.1
Ca	mg/L	107.0	64.0	95.5	91.3	91.3	86.5	68.8
Mg	mg/L	5.5	9.1	5.8	8.5	8.6	8.6	8.6
NH4	mg/L	0.05	0.32	0.06	0.07	0.07	0.05	0.01
Fe	mg/L	0.09	0.063	0.09	0.02	0.01	0.01	0.01
Mn	mg/L	0.04	0.093	0.03	0.04	0.04	0.03	0.01
SiO2	mg/L	20.0	5.4	19.6	8.3	7.3	7.3	7.3
As	ug/L	0.1	0.11	0.1	0.1	0.1	0.1	0.0
B	ug/L	25	127	55	112	113	113	113
Ba	ug/L	16.2	27	14	19	25	25	25
Cd	ug/L	0.005	0.01	0.005	0.009	0.011	0.011	0.011
Cu	ug/L	1.0	1.0	1.0	1.1	1.1	1.1	1.1
F	ug/L	110	230	137	213	238	214	214
Ni	ug/L	1.0	0.9	1.0	0.9	0.9	0.9	0.9
Pb	ug/L	1.0	0.4	1.0	0.8	0.5	0.5	0.5
Zn	ug/L	18.0	3.1	18.0	9.2	5.2	5.2	5.2
atrazine	%	0.0	100.0	0.2	4.8	5.0	12.4	21.1
diurone	%	0.0	100.0	0.0	3.2	3.6	14.7	22.6
lindane	%	0.0	100.0	0.0	0.4	0.5	7.9	8.5
dibuftal	%	0.0	100.0	0.0	0.0	0.0	0.0	0.0
1,2-DCB	%	0.0	100.0	3.2	6.1	4.5	6.6	5.5
tri	%	0.0	100.0	5.1	12.3	10.8	11.8	9.5
CCl3	%	0.2	100.0	0.1	0.7	0.7	1.7	2.3
phenanthrene	%	0.0	100.0	0.0	0.0	0.0	0.0	0.0
BAP	%	0.0	100.0	0.0	0.0	0.0	0.0	0.0
3H	TU	4.3	100.0	64.6	82.8	82.9	82.9	82.9
60Co	%	0.0	100.0	0.0	49.9	50.4	50.4	50.4
90Sr	%	0.0	100.0	0.0	44.4	68.4	68.4	68.4
137Cs	%	0.0	100.0	0.0	0.0	4.6	5.3	5.3
MS-2	%	0.0	100.0	1.85E-08	1.85E-08	1.85E-08	1.85E-08	1.85E-08
PRD-1	%	0.0	100.0	5.76E-07	5.76E-07	5.76E-07	5.76E-07	5.76E-07
Th37 Coli	%	0.0	100.0	3.04E-07	3.04E-07	3.04E-07	3.04E-07	3.04E-07
faec streptococs	%	0.0	100.0	4.61E-04	4.61E-04	4.61E-04	4.61E-04	4.61E-04
SO3-r Clos	%	0.0	100.0	4.09E-02	4.24E-02	4.24E-02	4.24E-02	4.24E-02

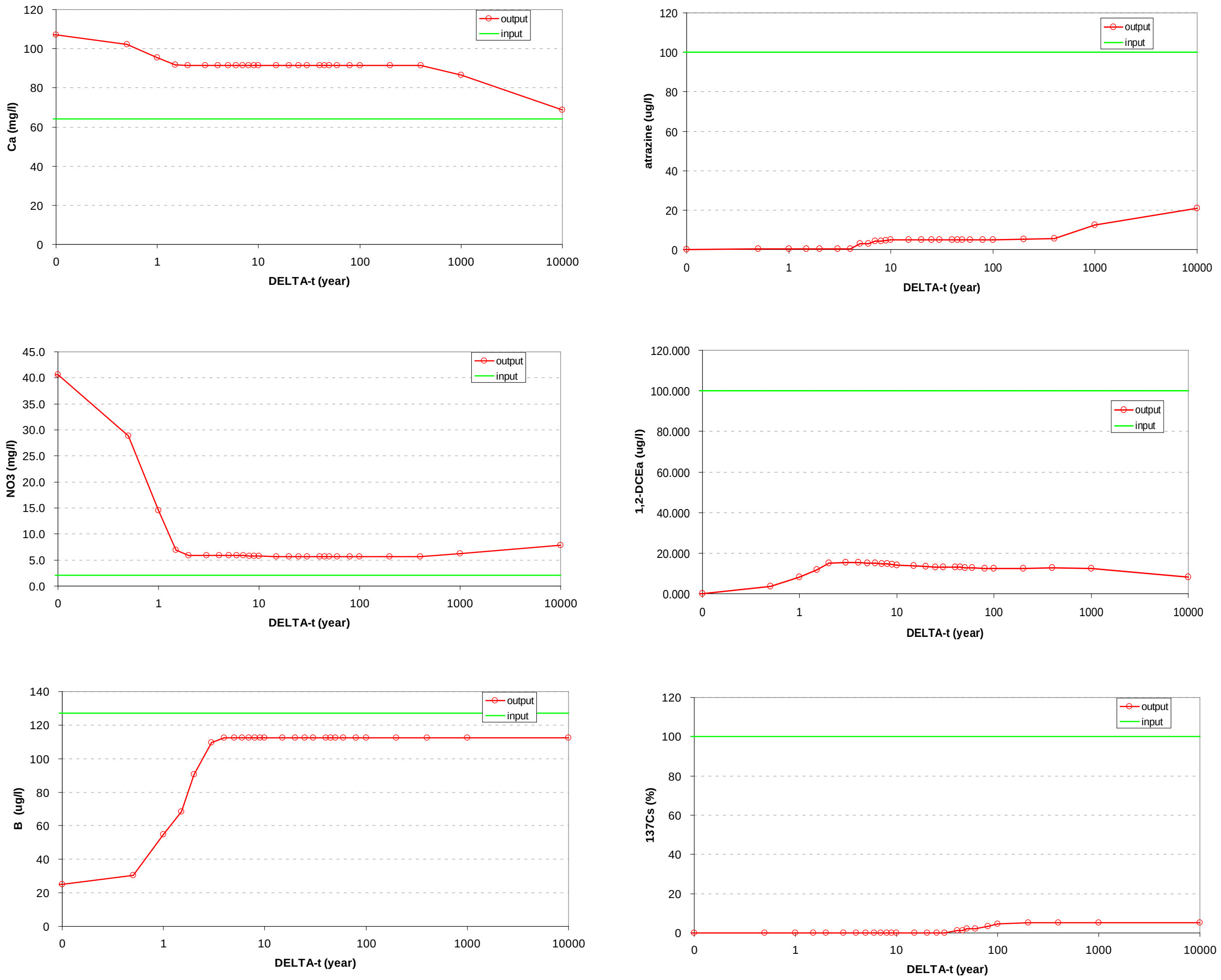

Figure 10. Predicted concentrations (by EL4.8) of Ca and NO_3 plus 4 micropollutants in the water pumped from recovery well I1 at Arrenæs, since the start of artificial recharge in April 1995 (t = 0).

The DEC values for sulphite reducing clostridia might incidentally be insufficient, especially in winter time when temperatures are low (and inactivation rates low as well). This means that on microbiological grounds, MARS facility Arrenæs can still be somewhat vulnerable, requiring an effective on-line alarm system.

5.9 Accumulation of pollutants (Arrenæs)

With EL4.8 the accumulation rate of mud and the accumulation of main constituents (BOM, $CaCO_3$, silicates), trace elements and organic micropollutants can be calculated (Stuyfzand, 2002). However, without data on suspended solids and on the DOC/TOC-ratio in the infiltration water this is more or less useless.

So here we have to rely on measurements of the mud and underlying aquifer layers, which were sampled in autumn 2004. It should be mentioned that mud is regularly exposed to air (once a year on average) in order to keep infiltration rates high. Removal has only occurred once (in 2001) during the 10 years of operation. This was done to make the bottoms sloping and not for regeneration purposes. This excludes the presence of older mud deposits, which were formed during periods with somewhat higher pollution loads of the infiltration water.

The data shown in Table 1 (main constituents) and Table 5 (trace elements), reveal the following: (a) the mud sampled was strongly diluted with material from the unsaturated sandy zone, and was thus relatively clean and partly decalcified; (b) it was clearly enriched with respect to BOM, probably due to algae; and (c) the mud contained did not contain more trace elements (incl. heavy metals) than the other layers. The upper layer in the unsaturated zone (0-1.5 m-LS) has the highest contents of clay minerals and therefore also shows the highest contents of many clay-bound trace elements. If there should be some accumulation of pollutants in that layer, then it is hard to demonstrate this against the natural backgrounds!

So the present pollution level of the mud at the bottom of the infiltration basins and of the unsaturated zone below them is very low. This is also due to a lack of older mud remnants from the more polluted past, thanks to mud removal in 2001.

6 CONCLUSIONS

It can be concluded that both recharge systems at Dösebacka AR plant and Arrenæs AR trial plant are vulnerable to potential, long lasting, raised inputs of nitrate, trace elements, organic micropollutants and radionuclides. The retention capacity of the aquifer systems is low for these inputs, which justifies the current efforts to implement a sensitive on-line monitoring system to prevent the intake of polluted river/lake water. Dösebacka is much more vulnerable than Arrenæs because of shorter travel times and less buffer capacity of the coarser sediments.

It should be emphasized, however, that the actual quality of both infiltration waters, Göta Älv and Lake Arresø, is extremely good. In this respect Dösebacka has a more profitable position than Arrenæs.

The DEC values for pathogenic micro-organisms may incidentally be insufficient for both sites, especially in winter time when temperatures are low (and inactivation rates low as well). This means that also on microbiological grounds, both AR sites are vulnerable, requiring an effective on-line alarm system. Again, in this respect Dösebacka needs more attention than Arrenæs.

7 REFERENCES

Appelo, C.A.J. & D. Postma 1993. Geochemistry, groundwater and pollution. Balkema, Rotterdam, 536p.

Bennedsen, L.; Berg, R.L.; Brandt, G.; Nielsen T.Ø. 2005. Description of Arrenæs AR trial plant (In this Final Scientific Report).

Berg, R.L.; Nielsen, T.Ø.; Bennedsen, L.; Brandt, G. 2005. Microbiological barrier efficiency at the Arrenæs AR trial plant and risk of pathogenic break through (In this Final Scientific Report).

Berg, R.L.; Stuyfzand, P.J., Nielsen, T.Ø.; Bennedsen, L., Brandt, G., Engblom, K., Lundh, M. & Holmström, E. 2006. Formulation of aggregated water quality information to authorities (In this scientific Report).

Brandt, G. 2005. Brandt, G. 1998. Arrenaes artificial recharge plant, Denmark; hydrological and chemical aspects. In: Peters J.H. (ed), Artificial recharge of groundwater, Proc. 3rd Intern. Symp. on Artificial Recharge, Amsterdam the Netherlands, Balkema, 217-222.

Brun, A. & K. Broholm 1998. Basin infiltration at the Arrenaes site, Denmark: tracer test and quality changes during aquifer passage below infiltration basins. In 'Artificial recharge of groundwater', Final report EC project ENV4-CT95-0071, ISBN 92-894-0186-9, European Commission EUR 19400, 177-181.

Hoekstra, A.C. 1984. Microbiologische aspecten van duininfiltratie. KIWA-Meded. 81, 217-259.

Iwasaki, T. 1937. Some notes on sand filtration. J. Amer. Water Works Assoc., 29, 1591-1609.

Jensen, T.Ø., Berg, R.L., Bennedsen, L., Brandt, G. & Spliid, H. (2005): Geochemical and microbial processes in the unsaturated zone at the Arrenæs artificial recharge trial plant. Fifth Int. Symp. on Management of Artificial Recharge (ISMAR), Berlin, 12-16 June 2005. In: Recharge Systems for Protecting and Enhancing Groundwater Resources (in press).

Jørgensen, C. 2001. Migration and survival of bacteria during artificial recharge. In 'Artificial recharge of groundwater', Final report EC project ENV4-CT95-0071, ISBN 92-894-0186-9, European Commission EUR 19400, 231-234.

Jørgensen, N.O. & B.B. Helleberg 2002. Stable isotopes (2H and 18O) and chloride as environmental tracers in a study of artificial recharge in Denmark. In Dillon, P. J. (ed), Management of Aquifer Recharge for Sustainability, Proc. 4th Internat. Symp. on Artificial Recharge, Adelaide, Australia, 22-26 Sept. 2002, Balkema, 245-250.

Lundh, M. 2005. Description of Dösebacka Artificial Groundwater Recharge Plant (In this Final Scientific Report).

Lundh, M., Rydberg,H. and Holmström, E. 2005a Microbiological barrier efficiency at the Dösebacka Artificial Groundwater Recharge Plant. (In this Final report).

Lundh, M., S.A. Jonasson, N.O. Jorgensen & M.D. Johnson 2005b. Hydrogeology and water treatment performance of the Dösebacka artificial recharge plant; the basis for an efficient system for early warning. Kompetenzzenter Wasser Berlin. In press for the proceedings of ISMAR2005, Berlin, June, 2005.

Lundh, M. & O. Bergstedt 2003. Description of the Dösebacka artificial groundwater recharge plant; method, operation and treatment. Report Gothenborg Region Association of Local Authorities (GR).

Lundh, M., S.A. Jonasson, N.O. Jorgensen & M.D. Johnson 2005. Hydrogeology and water treatment performance of the Dösebacka artificial recharge plant; the basis for an efficient system for early warning.

Mälzer, H.J., M. Gerlach, & R. Gimbel 1992. Entwicklung von Testfiltern zur Simulation von Stossbelastungen bei der Uferfiltration. Vom Wasser 78, 343-353.

Matthess, G., A. Pekdeger & J. Schröter 1988. Persistence and transport of bacteria and viruses in groundwater: a conceptual evaluation. J. Contaminant Hydrol 2, 171-188.

Medema, G.J. & P.J. Stuyfzand 2002. Removal of micro-organisms upon basin recharge, deep well injection and river bank filtration in the Netherlands. In Dillon, P.J. (ed), Management of Aquifer Recharge for Sustainability, Proc. 4th Internat. Symp. on Artificial Recharge, Adelaide, Australia, 22-26 Sept. 2002, Balkema, 125-131.

Nielsen, T.Ø.; Berg R.L.; Bennedsen L.; Brandt, G. 2005. Geochemical processes in the unsaturated zone at the Arrenæs artificial recharge trial plant (In this Final Scientific Report).

Peters, J.H. et al. 1998. Fate of pathogens and consequences for the design of artificial recharge. In: Artificial recharge of groundwater, (ed. J.H. Peters) Proc. 3rd Intern. Symp. on Artificial Recharge, Balkema publ., Amsterdam the Netherlands, pp. 141-146.

Prommer, H. & P.J. Stuyfzand 2005. Identification of temperature-dependent water quality changes during a deep well injection experiment in a pyritic aquifer. Environ. Sci. & Technol. 39, 2200-2209.

Schijven, J.F. 2001 Virus removal from groundwater by soil passage; modeling, field and laboratory experiments. Ph.D. Thesis Techn. Univ. Delft, the Netherlands, 262p.

Schijven, J.F., Medema, G.J., Vogelaar, A.J. and Hassanizadeh, S.M. (2000) Removal of microorganisms by deep well injection. J. Contam. Hydrol.44, 301-327.

Schoenheinz, D. 2004. DOC als Leitparameter, zur Bewertung und Bewirtschaftung von Grundwasserleitern mit anthropogen beeinflusster Infiltration. PhD Thesis Technical University Dresden, 117p + 47p annexes.

Schwarzenbach, R.P., P.M. Gschwend & D. Imboden 1993. Environmental organic chemistry. J. Wiley & Sons, NY.

Stuyfzand, P.J. 1998. Simple models for reactive transport of pollutants and main constituents during artificial recharge and bank filtration. In: Peters J.H. (ed), Artificial recharge of groundwater, Proc. 3rd Intern. Symp. on Artificial Recharge, Amsterdam the Netherlands, Balkema, 427-434.

Stuyfzand, P.J. 2001. Modelling chemical reactions during deep well injection at Langerak and Nieuwegein with EASY-LEACHER. In 'Artificial recharge of groundwater', Final report EC project ENV4-CT95-0071, ISBN 92-894-0186-9, European Commission EUR 19400, 270-277.

Stuyfzand, P.J. 2002a. Quantifying the environmental impact and sustainability of artificial recharge systems. In Dillon, P. J. (ed), Management of Aquifer Recharge for Sustainability, Proc. 4th Internat. Symp. on Artificial Recharge, Adelaide, Australia, 22-26 Sept. 2002, Balkema, 77-82.

Stuyfzand, P.J. 2002b. Modelling the accumulation rate and chemical composition of sludges in recharge basins. In Dillon, P. J. (ed), Management of Aquifer Recharge for Sustainability, Proc. 4th Internat. Symp. on Artificial Recharge, Adelaide, Australia, 22-26 Sept. 2002, Balkema, 221-224.

Stuyfzand, P.J. 2005a. GEO-CHEMCAL, a geochemical database and calculator in EXCEL, for storing, retrieving, correcting and calculating geochemical analyses, to arrive at a soil pollution index and to quantify the mineralogical composition. Kiwa Water Research.

Stuyfzand, P.J. 2005b. Mapping groundwater bodies with artificial or induced recharge, by determination of their origin and chemical facies. Proc ISMAR-5, Berlin, 12-17 June 2005, in press.

Stuyfzand, P.J. & Lüers, 2000. Environmental balance for pollutants in nature reserves with and without artificial recharge. Kiwa-Meded. 126 (in dutch), 241p.

Chapter 16: Bed Regeneration Handbook for the Arrenæs and Dösebacka Artificial Recharge Plants

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Abstract: In the ARTDEMO project, the methods for bed regeneration at Arrenæs and Dösebacka artificial recharge plants have been described. The descriptions are compiled in a Bed Regeneration Handbook that compares similar methods from the two plants and gives recommendations for the practical implementation of the methods. Generally the methods are comparable, but variations in recharge conditions and plant design cause differences in the methods used. The handbook can be used as an inspiration for other recharge plants, but it is important to adapt the methods to the actual conditions at the site and the plant operation.

1 INTRODUCTION

Methods for continuous regeneration of the soil layers are important to insure a stable and sustainable operation of artificial recharge plants. In normal operation, the primary cause of bed regeneration is clogging of the infiltration basins. Clogging is caused by a complex interaction of physical, chemical and biological processes in the uppermost soil layers. The processes are described in the Clogging Handbook by Pérez-Paricio and Carrera (1999). The methods described in the Bed Regeneration Handbook are mostly aimed to solve this problem.

2 OPERATION PROCEDURES AT ARRENÆS

The Arrenæs Artificial Recharge (AR) Trial Plant consists of four infiltration basins, two sets of infiltration troughs and a grass covered irrigation area, see figure 1and 2. The four infiltration basins and the two infiltration trough systems have an area of approximately 1,000 m2 each and an average depth of 1.5 metres. The sprinkling areas constitute approximately 20,000 m2 in total.

The lake water for the infiltration basins and trough systems is pre-sedimentated in two sedimentation basins, while the irrigation water is taken directly from the lake without pre-sedimentation.

In normal operation a basin is emptied when the infiltration rate for the basin falls below 5 m3/h. However in winter periods the basins are preferably not taken out of operation and in this period a flow as low as 1 m3/h is accepted. The basin is subsequently emptied, dried and cultivated. The operation period for a basin is between 2 – 3 months depending on the season.

Sprinkling takes place at the irrigated areas from April to October, and the sprinkling capacity to is approximately 35-42 m3/h. Grass is harvested from the area twice a year.

More detailed descriptions of plant operation

Figure 1: Infiltration basin at the Arrenæs AR Plant

and water quality aspects can be found in Bennedsen et al. (this publication), Brandt (1998) and Hartelius et al. (2001).

Figure 2: Irrigated grass area, Arrenæs AR Plant.

3 OPERATION PROCEDURES AT DÖSEBACKA

The Dösebacka AR plant consists of nine infiltration basins, and the water is pre-treated in a sedimentation basin. The total infiltration area is approximately 12,000 m2.

Infiltration basins are scraped once a year – just before the winter, e.g. in October. A couple of centimetres of sand are removed. New sand is evened out on the bottom of the basin when the sand layer has been reduced approximately 0.5 m. The removed sand undergoes further treatment before reuse. Scraping is normally only needed once a year due to the existence of a sedimentation unit at the plant. To ensure proper water treatment efficiency, it is important that the biological filter skin is developed before the winter. The time for this process must be permitted when scheduling bed regeneration activities.

4 BED REGENERATION PROCEDURES

The bed generation procedures have been compiled in Table 1.

At Dösebacka, regular bed regeneration is performed by drying the basins. After drying, the basin bottoms are scraped. The removed sand is stored, regenerated by an external contractor, and reapplied to the basins. Every 5 to 10 years deep sand replacement is performed down to approximately two meters under the basin floor (fugure 3).

The regular bed regeneration at Arrenæs is very similar to Dösebacka though using slightly different methods. After drying the basin bottoms, tillage is performed. Experiments have been performed, where the upper soil layer was removed and left in small dykes for regeneration in a period of 30 days. The irrigated areas at Arrenæs are maintained by grass harvesting.

Table 1: Bed regeneration procedures

	Arrenæs	Dösebacka
Desiccation (Drying)	*	*
Tillage	*	
Scraping		*
”Vacuum cleaning”	(*)	
Deep sand replacement		*
Algae clogging remediation	(*)	*
Dykes	(*)	
Regeneration of infiltration sand		*
Harvesting at irrigated areas	*	

Figure 3: Excavator replacing slow filter sand after deep sand replacement at Dösebacka.

At the Arrenæs trial plant, experiments have been made using a slurry pump to “Vacuum clean” the basin bottoms. The slurry pump is mounted in a frame that automatically sweeps the basin bottom in a regular pattern. The contraption is originally designed for fish farms.

The primary cause of clogging in infiltration basins is algal growth (figure 4). Occasional lowering of the water level in the basins causing the algae to die naturally and float to the surface helps prevent algal clogging at Dösebacka. Several experiments have been performed at Arrenæs amongst others using microfiltration and application of mussels. Chemical algae removal by $KMnO_4$ or $Ca(OH)_2$ have been evaluated in the Arrenæs AR trial plant but were rejected because of various negative side effects.

Figure 4: Algae in one of the basins at Dösebacka Waterworks

5 SUMMARY

Various bed regeneration methodologies are used at the Dösebacka and Arrenæs AR plants. The methods are primarily based on physical treatment of the basin floors to prevent clogging. These methods include drying, scraping, tillage and deep sand replacement.

The methods have been compiled in a Bed Regeneration Handbook for the two plants. The handbook can be used as a source of inspiration for other AR plants, but the methodologies should always be individually adapted to the specific sites.

6 REFERENCES

Brandt G. (1998).Arrenæs artificial recharge trial plant, Denmark – Hydrological and chemical aspects. In *Artificial recharge of groundwater, proceedings of the third international symposium on artificial recharge of groundwater – TISAR 98*, Peters H. J. (ed.)

Copenhagen Energy (2000) Arrenaes, Artificial infiltration of lake Arresoe water. Status for 2000 and operational and monitoring plan for 2001. *Reports available for the years 2000-2002. (In Danish)*

Hartelius, E., Bennedsen, L. and Brandt, G. (2001) Arrenæs artificial recharge trial plant, Denmark – hydrological and water quality aspects. *European Water Management* **4**(1), 65-70.

Holmström, E., Lundh, M. Management Plan, Waterworks of Dösebacka, *Will be presented in the final report of the ArtDemo project 2005.*

Lundh, M., (2005) Hydrogeology and water treatment performance of the Dösebacka artificial recharge plant – the basis for an efficient system for early warning. In *Abstract, Ismar 5, 5th International Symposium on Managemant of Aquifer Recharge, 2005*, Berlin, Germany

Pérez-Paricio A., Carrera J. (1999): Clogging Handbook, *Technical University of Catalonia (UPC), Barcelona, Spain.*

Villson, Sölve, Operator at Dösebacka Waterworks, Interview 2005

Chapter 17: Real Time Monitoring and Management of Artificial Recharge Plants

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Abstract: Secure and stable water supply is not a given thing in areas with water scarcity and/or polluted water source. Artificial recharge of groundwater from surface waters is a method to help/overcome this problem. However, early warning of changes in the water quality of the recharged water and intake protection are issues, which has to be dealt with together with an optimal production rate during the periods with less scarcity. The developed distributed information system exactly addresses these topics, and as it is a general and configurable system it can readily be installed at other locations

1. INTRODUCTION

The objective of this work is to create the basic structure for an integrated monitoring and management tool, that will be used to semi-automatically control the water production based on available information from artificial recharge plants. The basic structure shall be based on an existing monitoring and management software package (DIMS) extended with data validation routines to ensure valid and useful data from the selected sensor systems and field test kits.

Based on the basic structure the system shall be configured and implemented as an early warning system and a management tool for artificial recharge plants, linking automatic real-time data acquisition, available on-line/at-line sensor systems and fast field analysis kits with intelligent decision support, which compile and communicate processed data to specific action protocols.

Implementation will take place at artificial recharge plants located at Arrenæs, DK and Dösebacka, SE. These plants are operated by Copenhagen Energy (KE) and Göteborg VA-verk (GV) respectively. All data collected on the plants shall be available at the two organisations networks in real time in order to be processed for decision support. Further, and it has been decided, that data and information shall be available for all other project partners in near real time as well, in order to facilitate the common developments to be done during the project lifetime.

The basic system design and communication are described below for both the Arrenæs and the Dösebacka artificial recharge plants, whereas the more detailed configuration of the system is described using examples from the Arrenæs artificial recharge plant only.

2. BASIC SYSTEM DESIGN AND COMMUNICATION

The detailed description of the artificial recharge plants at Arrenæs and Dösebacka are given in chapters 2 and 3 (by Bennedsen *et al.* and Måns Lundh respectively). Although the existing systems at KE and GV (see figure 1 and 2) are quite different, the resulting monitoring and management systems built on top of these have the same functionality and “look and feel” of the user interfaces.

2.1 Arrenæs

The designed system setup is given in figure 1, and includes functionalities at 3 locations:

- Arrenæs artificial recharge plant
- Copenhagen Energy Network
- DHI network

Measurements (timeseries) included in the DIMS database on the DIMS server (sensor signals, manual readings, laboratory analyses, etc.) are:

- Total no of timeseries: 3092
- Distributed over the period 1993-2005 (all historical data transferred)
  - incl. 238 parameters at 73 locations
  - hereof 59 on-line
    - 41 on new general I/O system (flows, levels, pump status, alarms)
    - 7 on Water Quality station
    - 11 on Meteorological station

It should be noted that no SCADA system was available at the Arrenæs artficial recharge

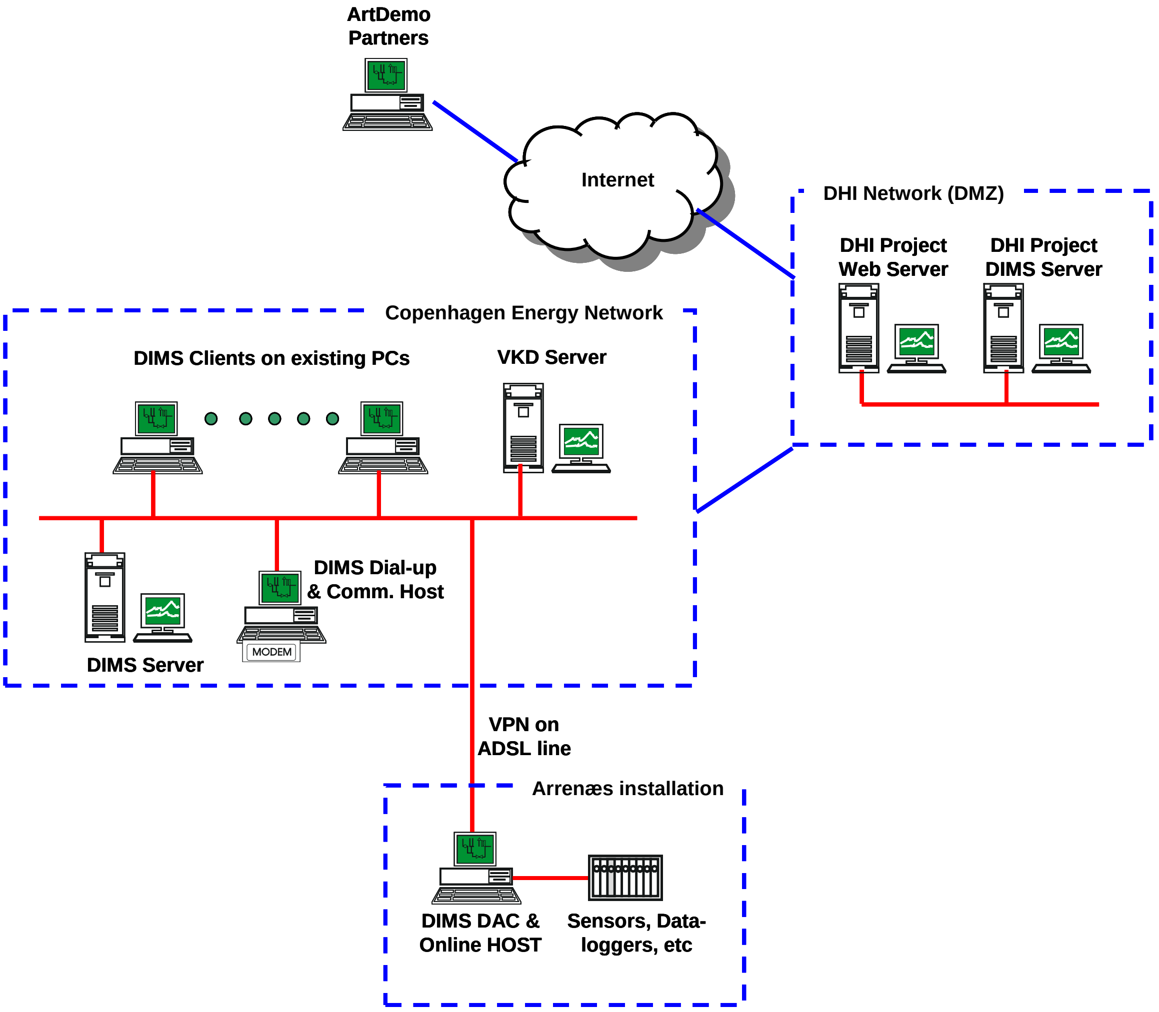


Figure 1: System setup for Arrenæs

plant. Therefore, the implementation started with the quite heavy basic task of connecting existing analog signals to a new general I/O system consisting of A/D converter boards controlled by the DIMS DAC and On-line Host PC.

Available functionality at the Arrenæs demo site:

- Collection of measurements through interface to:
    - new I/O system for existing and new analog signals and counters,
    - weather station,
    - DHI-WQ monitoring station in the inlet
- Manual input of readings performed by the operator (a daily operations journal)
- Visualisation of current operation for the operator (plots, reports, etc)
- Communicate all data to DIMSserver at KE network

Available functionality at the Copenhagen Energy network:

- Automatic transfer of relevant data from the VKD (the normal WQ database used at KE) system to DIMS database
- Automatic datatransfer via GSM from and online communication with BAM and MTBE sensors
- Daily (or more frequent) automatic transfer of new data to DIMS server at DHI
- Online curves of operational data from Arrenæs at desk
- All DIMS functionalities like:
    - Configuration tools for user interface, measurements, reports, etc.
    - Datavalidation
    - Aggregation
    - Automatic calculations (software sensors)
    - Automatic reporting (to the local web-site on the DIMS server)

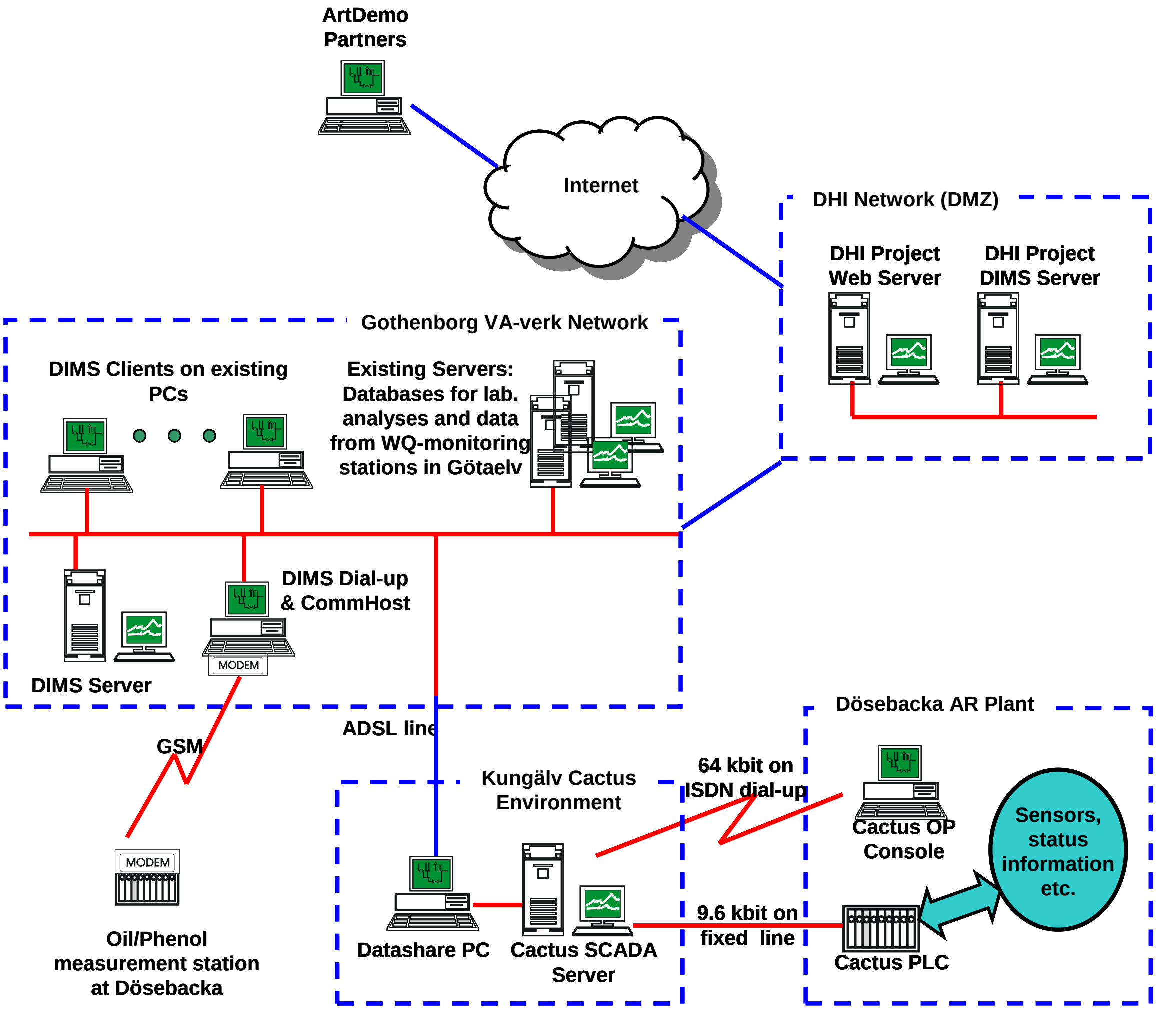


Figure 2: System setup for Dösebacka

Available functionality at the DHI network:

As restricted access to the network of KE made it impossible for the other ArtDemo partners to access information to be used in their tasks, the system has been designed to mirror all data in a DIMS database located at DHI. Data is pushed from the database at KE through the firewall to the databases at DHI, and the same reports, etc, as in the original system was made available on the ArtDemo project homepage. The partners could also extract data through a web based version of the DIMS client – all they needed was an internet connection, a browser and a login/password.

2.2 Dösebacka

The designed system setup is given in figure 2, and includes functionalities at 4 locations:

- Dösebacka
- Kungälv
- Göteborg VA-verk Network
- DHI network

A location more than at Arrenæs is needed here due to an older existing SCADA system with a relatively complex setup.

Measurements (timeseries) included in the DIMS database on the DIMS server (sensor signals, manual readings, laboratory analyses, etc.) are:

- Total no of timeseries: 279
- Distributed over the period 1992-2005
    - incl. 41 parameters at 19 locations
    - hereof 24 on-line
        - 22 on general system
        - 2 on fluorescence measurement system (Oil and Phenols)
        - 1 raingauge

Available functionality at the Dösebacka demo site:

- Collection of measurements by Cactus PLC:
    - Operation related measurements/status information,
    - New sensor WQ measurements,
- Communication of collected data from Cactus PLC to Cactus SCADA at Kungälv

- Operation of plant via Cactus OP-Console
- Visualisation of current operation for the operator on Cactus OP-Console

Available functionality at the Kungälv Cactus Environment:

- Transfer of data from Cactus SCADA to Datashare PC
- Data on Datashare PC available for DIMS via the internet (restricted access)

Available functionality at the Göteborg VA-verk network:

- Automatic request of data from the Datashare PC to DIMS database
- Automatic datatransfer via GSM from DHI Oil/Phenol measurement station and transfer of data from WQ-stations on the Göta Elv from a database at the internal network
- Manual and automatic input of data from laboratory analyses
- Daily (or more frequent) automatic transfer of new data to DIMS server at DHI in order to share data with other project partners
- Online curves of operational data from Dösebacka at desk
- All DIMS functionalities like:
    - Configuration tools for user interface, measurements, manual datainput, reports….
    - Data validation
    - Aggregation
    - Automatic calculations (software sensors)
    - Automatic reporting (to the local web-site)

Available functionality at the DHI network:

As restricted access to the network of GV made it impossible for the other ArtDemo partners to access information to be used in their tasks, the system has been designed to mirror all data in a DIMS database located at DHI. Data is pushed from the database at GV through the firewall to the databases at DHI, and the same reports, etc, as in the original system was made available on the ArtDemo project homepage. The partners could also extract data through a web based version of the DIMS client – all they needed was an internet connection, a browser and a login/password.

3. MONITORING AT ARRENÆS

Implementation of the real time monitoring at Arrenæs is based on both hardware (sensors, PCs, communication, etc.) and software (basic configuration of the DIMS system). The real time data included in the implementation can be seen in table 1.

Table 1: Real time data at Arrenæs connected via the general system and the meteorological and water quality stations

General system		
Flow measurements	**Level measurements**	**Alarms and status information**
Sedimentation Basin East	Basin East1	Max. level intake pump at lake
Sedimentation Basin West	Basin East2	Min. level intake pump at lake
Well nr. I1, pump1	Basin West1	Pump1 Well nr. I1, failed
Well nr. I3, pump2	Basin West2	Pump2 Well nr. I3, failed
Well nr. M1, pump3	Well DGU	Pump3 Well nr. M1, failed
Well nr. DGU, pump4	Well nr. I1	Sprinkler system East, failed
Sprikler System East	Well nr. M1	Sprinkler system West, failed
Sprikler System West	Thompson weir Basin East1	Infiltration Trough 5 west, failed
Basin East1 (SW-sensor)	Thompson weir Basin East2	Status Pump1 Well nr. I1
Basin East2 (SW-sensor)	Thompson weir Trough East	Status Pump2 Well nr. I3
Trough East (SW-sensor)	Thompson weir Trough West	Status Pump3 Well nr. M1
Trough West (SW-sensor)	Thompson weir Basin West1	Status Sprinkler system East
Basin West1 (SW-sensor)	Thompson weir Basin West2	Status Sprinkler system West
Basin West2 (SW-sensor)		Status water Trough 5 west

Meteorological station		**WQ-station**
Air temperature	Solarimeter	Conductivity
Relative humidity	Solarimeter net	Fluorescence
Pressure - atmospheric	Solarimeter reflected	Dissolved oxygen
Rain fall accumulated during day	Negative Solarimeter reflected	pH
Soil temperature		Temperature
Windspeed		Sensor depth
Wind direction		Battery voltage

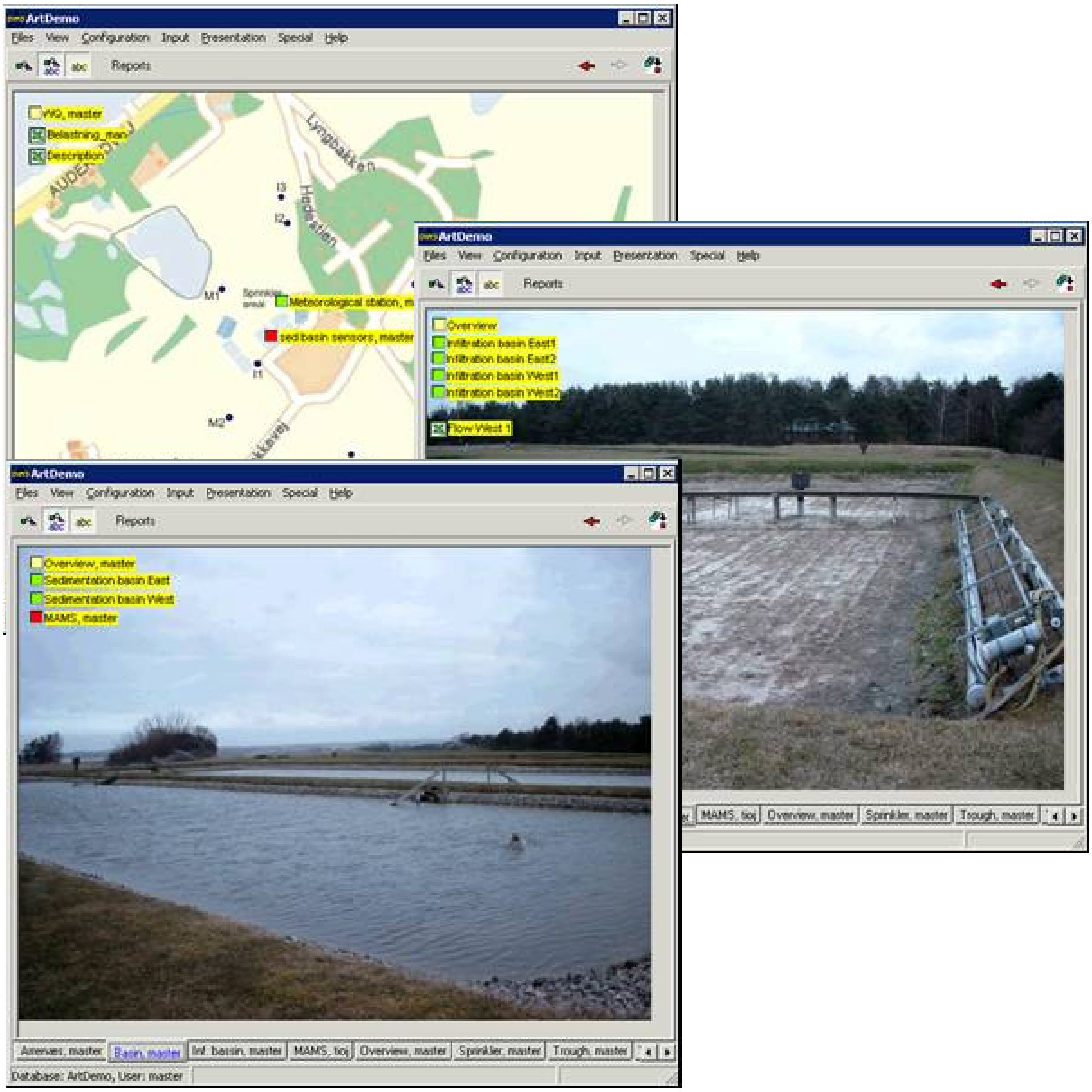


Figure 3: Examples from user interface at Arrenæs

3.1 Configuration

The main user interface has been configured using maps and photos from the site - figure 3 - The squares on the user interface having different colors are active links placed by the users. (Yellow: link to another image (can also be done using the tabs), Green: link to graphs, tables and properties of a group of time series according to a logical criterion chosen by the user. Red: link to graphs, tables and properties of a group of time series according to a geographical location (measuring place) chosen by the user. Excel logo: link to user configured reports setup in the embedded Excel .

Clicking on Configuration in the menu and then selecting Server configuration, gives access to the database setup and configuration of the basic elements of the system, which are time series of sensor values, lab. analyses, registrations, aggregated values, on-line calculations (software sensors), etc.

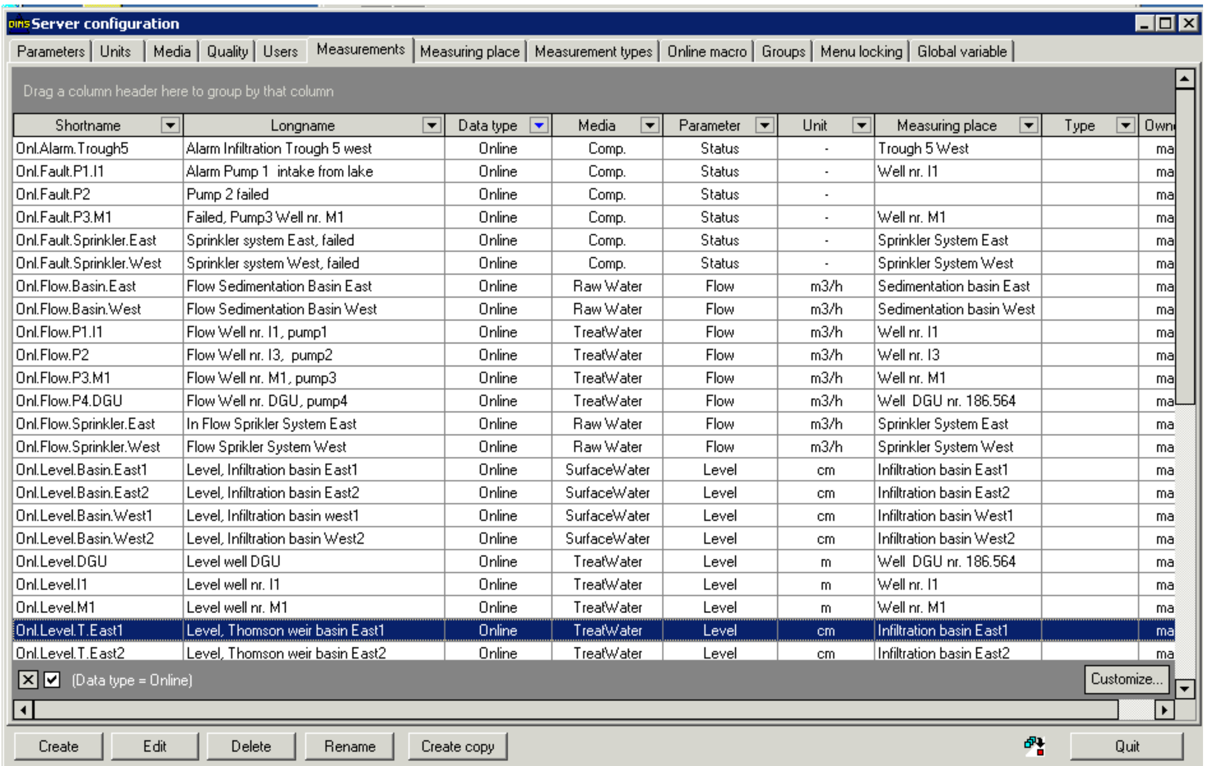
Figure 4 shows User interface for server configuration – tab-sheet: Measurements selected – showing a part of the list of measurements (time series) included in the database and their properties. The list can be sorted after each property – the figure shows that the property “Data type” has been selected to Online.

Clicking on the highlighted measurement - which is a level measurement behind a Thompson weir in infiltration basin East 1 – brings forward the propereties dialog for the measurement (figure 5).

This dialog shows how easy it is to configure new measurements (time series) in the DIMS system at Arrenæs. Measurement properties to the left and selection of Data type Online on tab-sheet: Source to the right – giving the necessary information of addressing the attached I/O system through its device driver.

3.2 Software Sensors

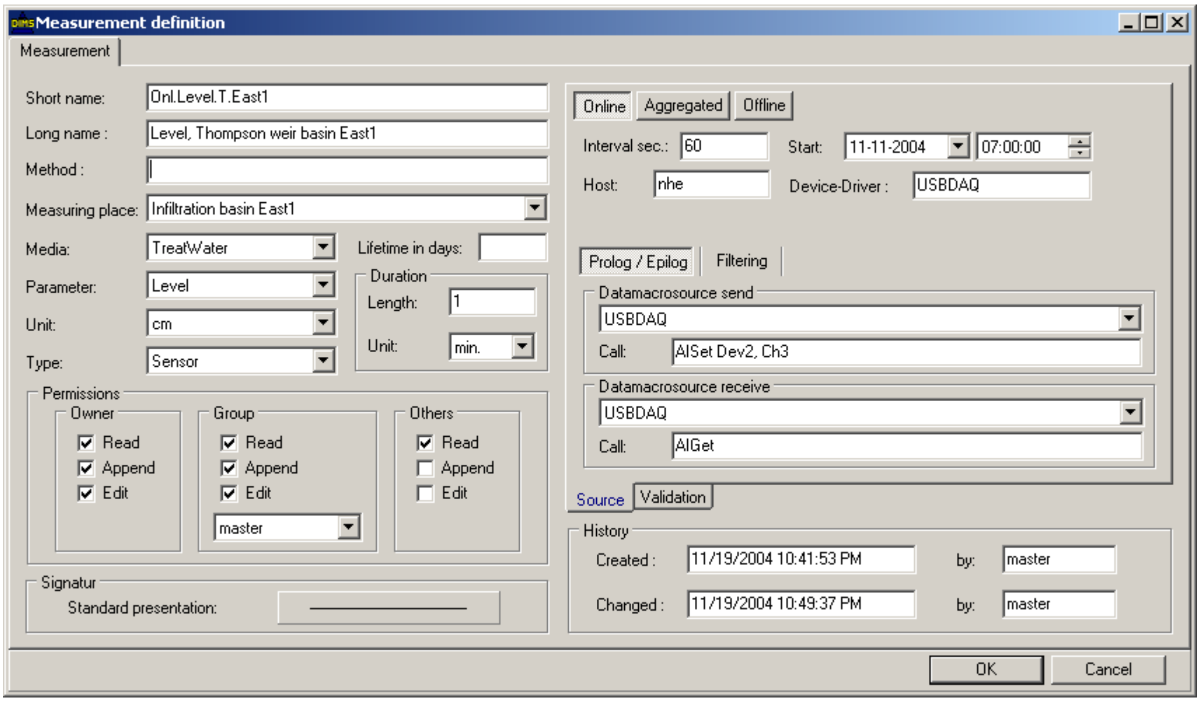
Real time calculations based on one or more measurements – also known as software sensors, as the results of the calculations has the same properties as a normal measurement – is a very important system entity. At Arrenæs it has among other been used to implement "virtual flowmeters" using the installed level



Shortname	Longname	Data type	Media	Parameter	Unit	Measuring place	Type	Own
Onl.Alarm.Trough5	Alarm Infiltration Trough 5 west	Online	Comp.	Status	-	Trough 5 West		ma
Onl.Fault.P1.I1	Alarm Pump 1 intake from lake	Online	Comp.	Status	-	Well nr. I1		ma
Onl.Fault.P2	Pump 2 failed	Online	Comp.	Status	-			ma
Onl.Fault.P3.M1	Failed, Pump3 Well nr. M1	Online	Comp.	Status	-	Well nr. M1		ma
Onl.Fault.Sprinkler.East	Sprinkler system East, failed	Online	Comp.	Status	-	Sprinkler System East		ma
Onl.Fault.Sprinkler.West	Sprinkler system West, failed	Online	Comp.	Status	-	Sprinkler System West		ma
Onl.Flow.Basin.East	Flow Sedimentation Basin East	Online	Raw Water	Flow	m3/h	Sedimentation basin East		ma
Onl.Flow.Basin.West	Flow Sedimentation Basin West	Online	Raw Water	Flow	m3/h	Sedimentation basin West		ma
Onl.Flow.P1.I1	Flow Well nr. I1, pump1	Online	TreatWater	Flow	m3/h	Well nr. I1		ma
Onl.Flow.P2	Flow Well nr. I3, pump2	Online	TreatWater	Flow	m3/h	Well nr. I3		ma
Onl.Flow.P3.M1	Flow Well nr. M1, pump3	Online	TreatWater	Flow	m3/h	Well nr. M1		ma
Onl.Flow.P4.DGU	Flow Well nr. DGU, pump4	Online	TreatWater	Flow	m3/h	Well DGU nr. 186.564		ma
Onl.Flow.Sprinkler.East	In Flow Sprikler System East	Online	Raw Water	Flow	m3/h	Sprinkler System East		ma
Onl.Flow.Sprinkler.West	Flow Sprikler System West	Online	Raw Water	Flow	m3/h	Sprinkler System West		ma
Onl.Level.Basin.East1	Level, Infiltration basin East1	Online	SurfaceWater	Level	cm	Infiltration basin East1		ma
Onl.Level.Basin.East2	Level, Infiltration basin East2	Online	SurfaceWater	Level	cm	Infiltration basin East2		ma
Onl.Level.Basin.West1	Level, Infiltration basin west1	Online	SurfaceWater	Level	cm	Infiltration basin West1		ma
Onl.Level.Basin.West2	Level, Infiltration basin West2	Online	SurfaceWater	Level	cm	Infiltration basin West2		ma
Onl.Level.DGU	Level well DGU	Online	TreatWater	Level	m	Well DGU nr. 186.564		ma
Onl.Level.I1	Level well nr. I1	Online	TreatWater	Level	m	Well nr. I1		ma
Onl.Level.M1	Level well nr. M1	Online	TreatWater	Level	m	Well nr. M1		ma
Onl.Level.T.East1	Level, Thomson weir basin East1	Online	TreatWater	Level	cm	Infiltration basin East1		ma
Onl.Level.T.East2	Level, Thomson weir basin East2	Online	TreatWater	Level	cm	Infiltration basin East2		ma

☒ ☑ (Data type = Online)

Figure 4: User interface for server configuration – tab-sheet measurements selected



Short name: Onl.Level.T.East1
Long name : Level, Thompson weir basin East1
Method :
Measuring place: Infiltration basin East1
Media: TreatWater
Lifetime in days:
Parameter: Level
Duration
Length: 1
Unit: min.
Unit: cm
Type: Sensor

Permissions
Owner: ☑ Read ☑ Append ☑ Edit
Group: ☑ Read ☑ Append ☑ Edit
master
Others: ☑ Read ☐ Append ☐ Edit

Signatur
Standard presentation:

Interval sec.: 60
Start: 11-11-2004 07:00:00
Host: nhe
Device-Driver : USBDAQ

Datamacrosource send
USBDAQ
Call: AISet Dev2, Ch3

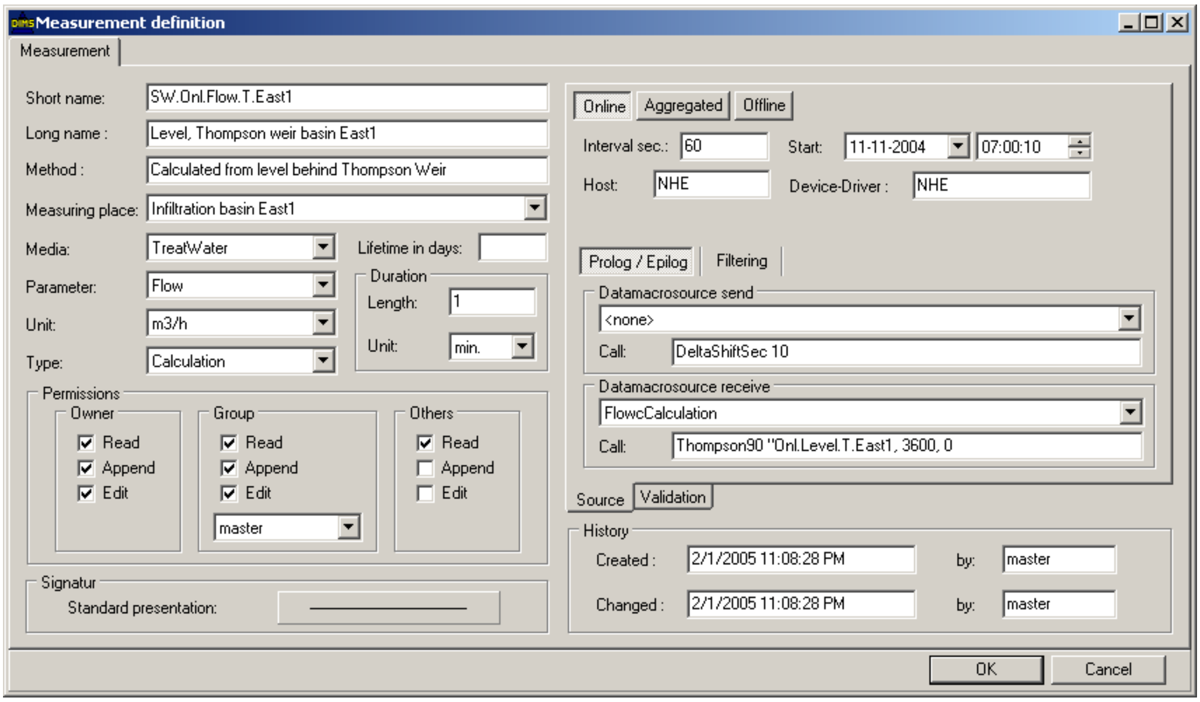
Datamacrosource receive
USBDAQ
Call: AIGet

History
Created : 11/19/2004 10:41:53 PM by: master
Changed : 11/19/2004 10:49:37 PM by: master

Figure 5: Configuration of a measurement (time series) in the DIMS system at Arrenæs

$$Q = C_e \frac{8}{15} \operatorname{tg} \frac{\alpha}{2} \sqrt{2g}\, h_e^{2,5}$$

Figure 6: Level measurement upstream Thompson Weir – and the Flow vs. Level relationship



Measurement definition

Short name: SW.Onl.Flow.T.East1
Long name : Level, Thompson weir basin East1
Method : Calculated from level behind Thompson Weir
Measuring place: Infiltration basin East1
Media: TreatWater
Parameter: Flow
Unit: m3/h
Type: Calculation
Lifetime in days:
Duration
Length: 1
Unit: min.
Permissions
Owner: ☑ Read ☑ Append ☑ Edit
Group: ☑ Read ☑ Append ☑ Edit master
Others: ☑ Read ☐ Append ☐ Edit
Signatur
Standard presentation:

Interval sec.: 60
Start: 11-11-2004 07:00:10
Host: NHE
Device-Driver : NHE
Datamacrosource send: <none>
Call: DeltaShiftSec 10
Datamacrosource receive: FlowcCalculation
Call: Thompson90 "Onl.Level.T.East1, 3600, 0
History
Created : 2/1/2005 11:08:28 PM by: master
Changed : 2/1/2005 11:08:28 PM by: master

Figure 7: Methods for detection of long term drift - example

measurements located upstream the Thompson Weirs (figure 6) and infiltration rates based on the “virtual flowmeters” together with the level measurements in the infiltration basins.

The “virtual flowmeters” are a quick, easy and inexpensive method to get more flow measurements at the demo site. The existing wells with Thompson Weirs were simply supplied with pressure transducers, and the levels measured were used as input for as many software sensors calculating the flows.

The configuration is shown in figure 7 using the measurements dialog box. Properties (left side) are set up as for any other measurement. To the right Online is selected as the data type and no request is sent to an I/O system. Instead a macro, Thompson90 (in a built in makro library FlowCalculation), using the formula from figure 6 is referred to with the name of the level measurement to be used (and a factor and an offset for calibration).

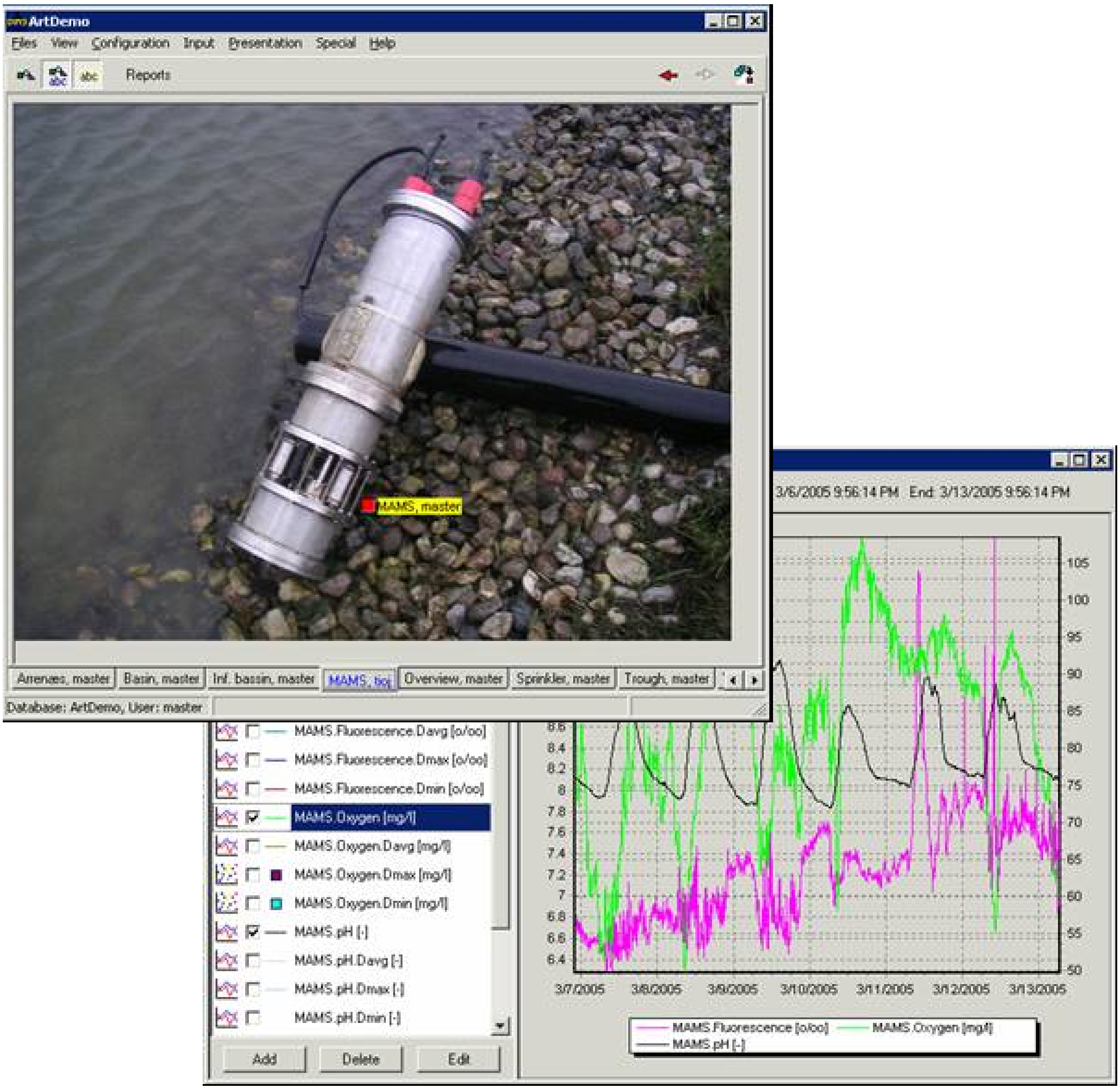


Figure 8: Water Quality station at Arrenæs – LinkPlot of selected measurements from the WQ-station measurements

3.3 Real time information at the desk

Real time information is available on any PC attached to the KE network and having the DIMS Client software installed. Figure 8 shows this possibility using information from the water quality station located in the inlet to the sedimentation basins.

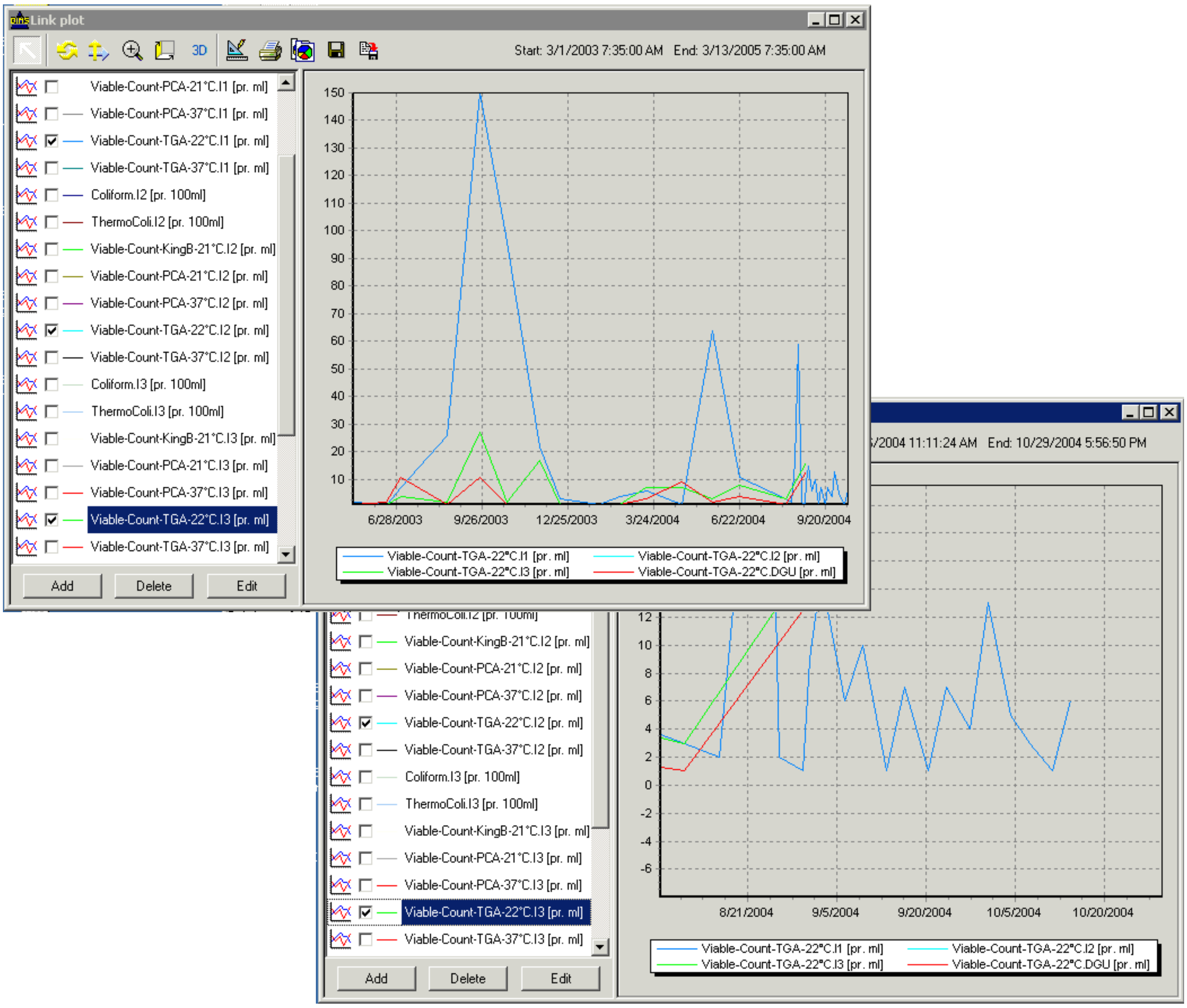
Left clicking on a link on the user interface opens a configurable plot – the LinkPlot - of measurements grouped during configuration (or added to the group at a later stage).

If a relative time line is chosen the plot will always open with the right edge representing time equal now and then reach a predefined period back in time. Setting more marks immediately extracts the corresponding values for the measurements from the database in the given period. Further, the plot – if left open - is updated in real time with the chosen logging frequency of the system providing real time information at every desk.

The Water Quality station measures temperature, conductivity, pH, dissolved oxygen, fluorescence, level and power status, and is installed in order to give early warning concerning changing status of the incoming water quality (see also the management section).

Especially the fluorescence is important, as this parameter indicates the level of algae in the lake water. High levels of algae, which passes through the sedimentation can cause clogging of the infiltration basins quite rapidly – and during springtime the eutrophic lake have an algae bloom, which can be detected at a very early stage, giving the possibility to stop the inlet pumps and avoid the clogging.

The link plot shows the sensor values for oxygen, pH and fluorescence. The pH clearly



☐ Viable-Count-PCA-21°C.I1 [pr. ml]
☐ Viable-Count-PCA-37°C.I1 [pr. ml]
☑ Viable-Count-TGA-22°C.I1 [pr. ml]
☐ Viable-Count-TGA-37°C.I1 [pr. ml]
☐ Coliform.I2 [pr. 100ml]
☐ ThermoColi.I2 [pr. 100ml]
☐ Viable-Count-KingB-21°C.I2 [pr. ml]
☐ Viable-Count-PCA-21°C.I2 [pr. ml]
☐ Viable-Count-PCA-37°C.I2 [pr. ml]
☑ Viable-Count-TGA-22°C.I2 [pr. ml]
☐ Viable-Count-TGA-37°C.I2 [pr. ml]
☐ Coliform.I3 [pr. 100ml]
☐ ThermoColi.I3 [pr. 100ml]
☐ Viable-Count-KingB-21°C.I3 [pr. ml]
☐ Viable-Count-PCA-21°C.I3 [pr. ml]
☐ Viable-Count-PCA-37°C.I3 [pr. ml]
☑ Viable-Count-TGA-22°C.I3 [pr. ml]
☐ Viable-Count-TGA-37°C.I3 [pr. ml]

Figure 9: Link plot of a group configured to contain microbiological parameters

have a daily variation – typically caused by an eutrophic lake producing or consuming oxygen according to light conditions. The variation can be seen in the oxygen data as well, however, these data are affected by the pumping (even more than the pH data)

From the list to the left in the LinkPlot window it can be seen that the online measurements also are aggregated into daily average, minimum and maximum values (other aggregation methods are available like the sum and numeric integration – and all methods can be used in a selected period of time).

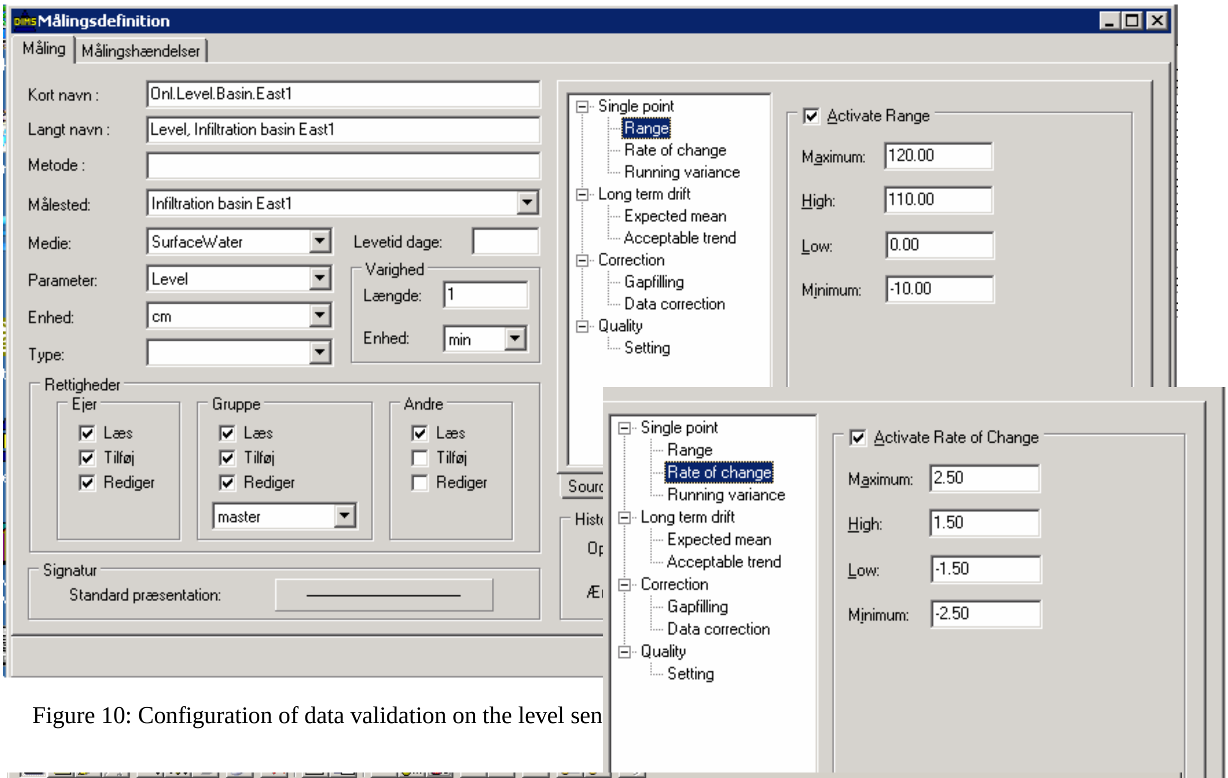
Aggregated values are stored in the database as well, as these are quite valuable to have at hand for the automatic reporting described in the management section.

The main part of the time series in the database are analyses on samples taken at different locations and depths – now automatically transferred from the the normal WQ database used at KE - and figure 9 shows some of the viable counts from some of the producing wells over the last couple of years. The time line when opened is 2 years, but Link Plot also supports zoom and pan with dynamic update enabling further inspection of details in the time series. Access to all time series are quite straightforward, if each time series is configured with the correct properties.

3.4 Data validation

The developed and implemented data validation functions (see chapter 11) have been configured to perform data validation of the on-line measurements. Figure 10 shows the configuration of range check and rate of change check on the level sensor in infiltration basin East1 using the measurement dialog and selecting the tab “Validation” on the right hand side of the dialog.

The measured values from the basin levels must be above 0 cm and below 110 cm as values outside this range are not physical possible. Further, the water level can not change fast. Therefore the rate of change check is used to find



Kort navn : Onl.Level.Basin.East1
Langt navn : Level, Infiltration basin East1
Metode :
Målested: Infiltration basin East1
Medie: SurfaceWater
Parameter: Level
Enhed: cm
Type:
Levetid dage:
Varighed
Længde: 1
Enhed: min

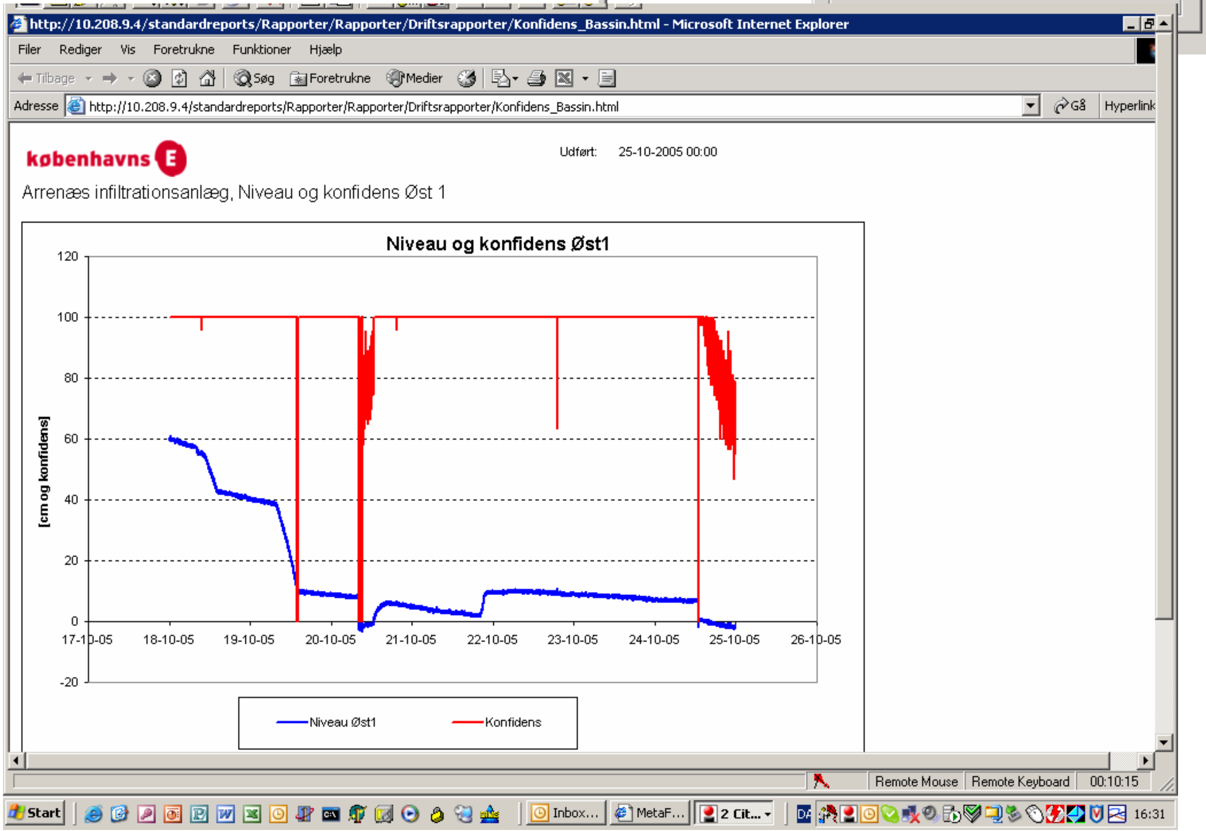
Rettigheder
Ejer
☑ Læs
☑ Tilføj
☑ Rediger
Gruppe
☑ Læs
☑ Tilføj
☑ Rediger
master
Andre
☑ Læs
☐ Tilføj
☐ Rediger

Signatur
Standard præsentation:

☑ Activate Range
Maximum: 120.00
High: 110.00
Low: 0.00
Minimum: -10.00

☑ Activate Rate of Change
Maximum: 2.50
High: 1.50
Low: -1.50
Minimum: -2.50

Figure 10: Configuration of data validation on the level sen



Udført: 25-10-2005 00:00

Arrenæs infiltrationsanlæg, Niveau og konfidens Øst 1

Figure 11: Automatic produced report showing the level in infiltration basin East 1 and the corresponding confidence

peaks in data allowing a change less than 1.5 cm/min to be acceptable.

Confidences are calculated in real time (as described in chapter 11) and the resulting confidence is the minimum value of the two calculated confidences.

Beside the possibility of having an alarm when the confidence passes a threshold, figure 11 shows a daily report automatically produced every morning (see management section), which presents the level measurement and the

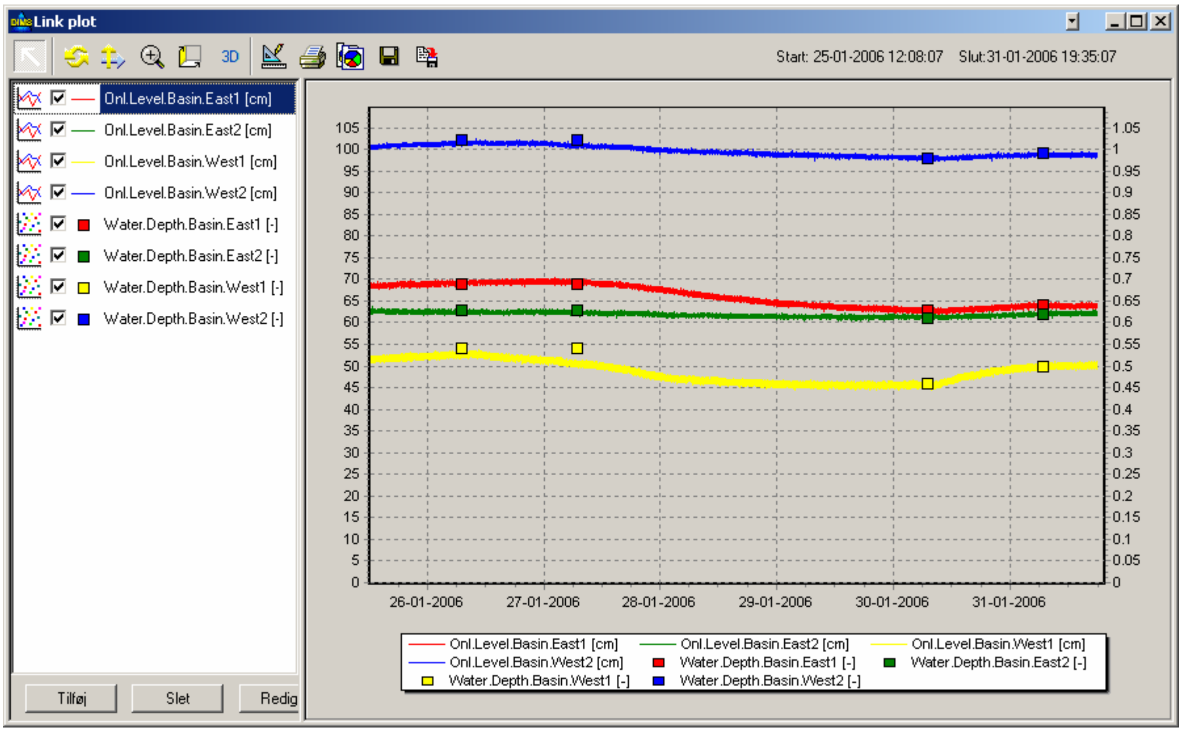
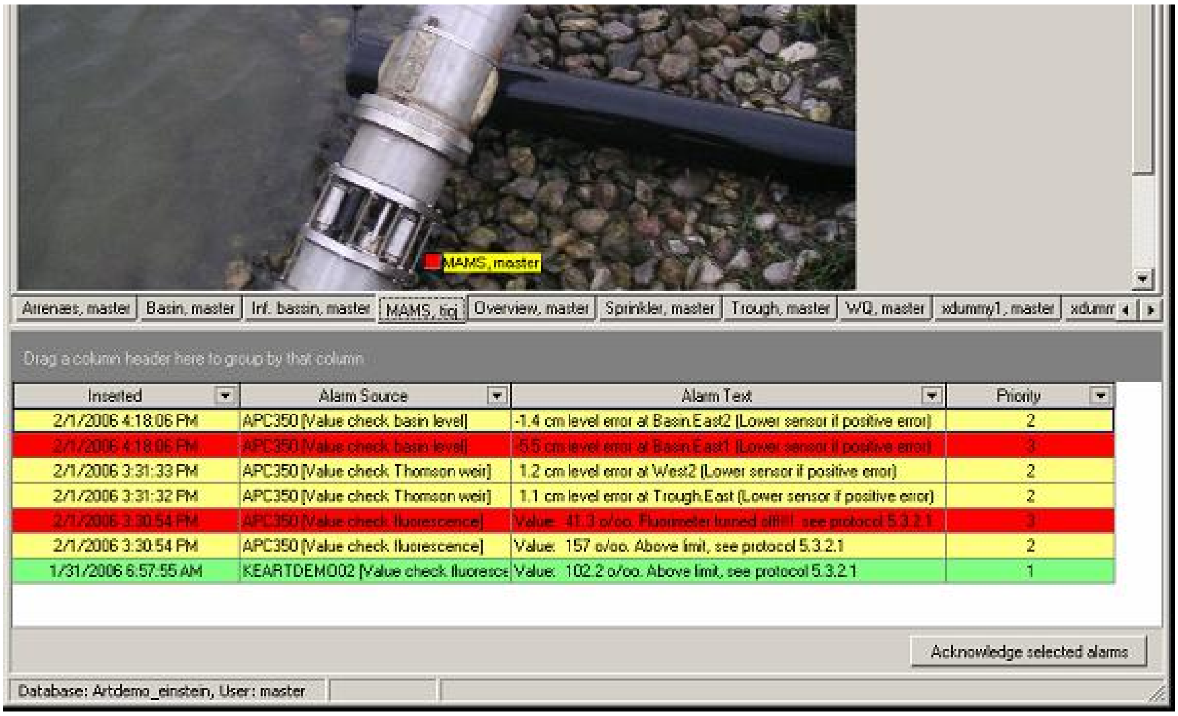


Figure 12: Configured Link plot showing a comparison between on-line level measurements in four infiltration basins and the manual readings of the levels



Inserted	Alarm Source	Alarm Text	Priority
2/1/2006 4:18:06 PM	APC350 [Value check basin level]	-1.4 cm level error at Basin.East2 (Lower sensor if positive error)	2
2/1/2006 4:18:06 PM	APC350 [Value check basin level]	-5.5 cm level error at Basin.East1 (Lower sensor if positive error)	3
2/1/2006 3:31:33 PM	APC350 [Value check Thomson weir]	1.2 cm level error at West2 (Lower sensor if positive error)	2
2/1/2006 3:31:32 PM	APC350 [Value check Thomson weir]	1.1 cm level error at Trough.East (Lower sensor if positive error)	2
2/1/2006 3:30:54 PM	APC350 [Value check fluorescence]	Value: 41.3 o/oo. Fluormeter turned off!!! see protocol 5.3.2.1	3
2/1/2006 3:30:54 PM	APC350 [Value check fluorescence]	Value: 157 o/oo. Above limit, see protocol 5.3.2.1	2
1/31/2006 6:57:55 AM	KEARTDEMO02 [Value check fluoresce	Value: 102.2 o/oo. Above limit, see protocol 5.3.2.1	1

Figure 13: The user interface with open alarm list

confidence in the measurement for the last week (example in Danish – as all operation reports).

When the basin is empty there is a small off set in the measured values, which results in a reduced confidence, but also the rate of change check can be seen to be active giving confidences at zero.

The operator also makes daily readings of the levels in the basins and behind the Thompson weirs. These readings are typed into the system and together with the on-line measurements they can be presented in a Link plot (figure 12) giving a direct visual comparison. The Link plot gives the operator of the plant a quick overview of any problems with the pressure transducers.

3.5 Alarms and early warning

In combination with this, a notice in the alarm list is produced if the difference between the on-line values and the manual readings are above a certain limit. The user can specify whether the colour of the alarm shall be green, yellow or red - according to the size of the error.

Figure 13 shows the user interface with open alarm list. The lines in the alarm list notify the operator of the plant, that there is a problem and give a hint of what to do to fix the problem – either as a direct advice or as a reference to the operation protocol (see management section).

After the alarm information is seen, the user has to acknowledge the selected alarm to remove it from the list of actual alarms. A list of acknowledged alarms can also be seen in the DIMS system, but in the short list, only a user specified number of the newest alarms are present

Another type of alarm is also shown in figure 13. In this case a low value of the fluorimeter system indicates, that the flashlamp in the sensor is not running, so this gives a red alarm. If the sensor signal is above a certain level, it indicates that there is an algae bloom starting (green) and if the value still increases it will turn to yellow and finally to red – early warning via the alarm list.

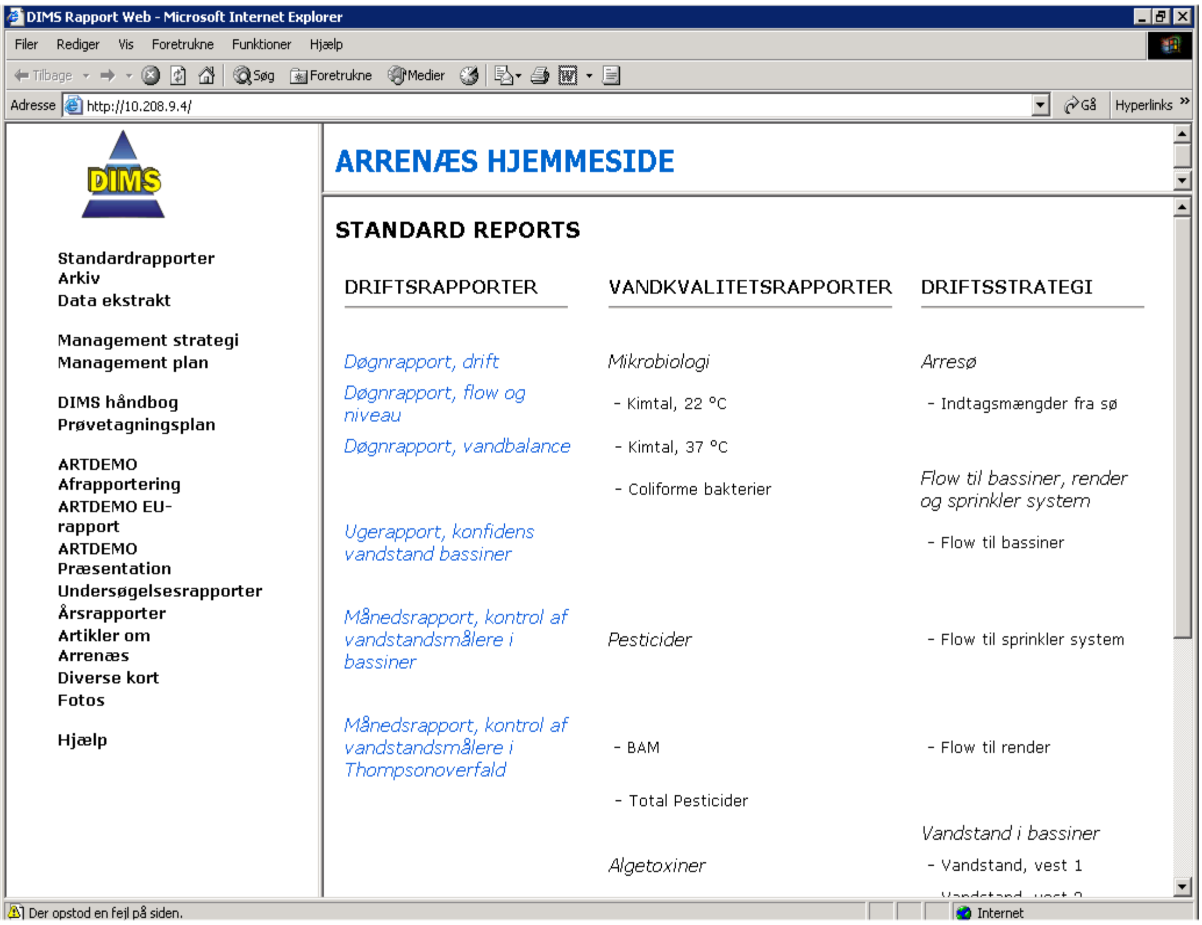
4. MANAGEMENT AT ARRENÆS

Implementation of the real time management at Arrenæs is based on automatic reporting to the Arrenæs website created on the DIMS server on the KE network.

4.1 The Arrenæs Website

However, other information than data and automated reports is available for the Arrenæs artificial recharge plant and therefore included on the website, as all staff both at the network in KE in Copenhagen and at the plant at Arrenæs can access the website including the reports – just using their normal browser.

Figure 14 shows the start page of the website – which is in Danish Language, as it is implemented as the normal tool used by operators and other staff in their daily work. The left hand frame gives the overview and the links to navigate on the website – a translation is given



Standardrapporter
Arkiv
Data ekstrakt

Management strategi
Management plan

DIMS håndbog
Prøvetagningsplan

ARTDEMO Afrapportering
ARTDEMO EU-rapport
ARTDEMO Præsentation
Undersøgelsesrapporter
Årsrapporter
Artikler om Arrenæs
Diverse kort
Fotos

Hjælp

ARRENÆS HJEMMESIDE

STANDARD REPORTS

DRIFTSRAPPORTER	VANDKVALITETSRAPPORTER	DRIFTSSTRATEGI
Døgnrapport, drift	*Mikrobiologi*	*Arresø*
Døgnrapport, flow og niveau	- Kimtal, 22 °C	- Indtagsmængder fra sø
Døgnrapport, vandbalance	- Kimtal, 37 °C	
	- Coliforme bakterier	*Flow til bassiner, render og sprinkler system*
Ugerapport, konfidens vandstand bassiner		- Flow til bassiner
Månedsrapport, kontrol af vandstandsmålere i bassiner	*Pesticider*	- Flow til sprinkler system
Månedsrapport, kontrol af vandstandsmålere i Thompsonoverfald	- BAM	- Flow til render
	- Total Pesticider	
		Vandstand i bassiner
	Algetoxiner	- Vandstand, vest 1

Figure 14: The start page of the Arrenæs website at KE

Table 2: Overview of the content of the Arrenæs website at KE

Link	Explanation
Standardrapporter	Standard reports. All reports configured in the system using the embedded excel functionality and produced automatically using updated extracts from the database
Arkiv	Archive. Monthly backup of all standard reports - easy access to historical events
Data ekstrakt	Web based client software to extract specific data from the database
Management strategi	The management strategy for the AR plants
Management plan	The developed management plan for AR plants including operation protocols to be followed during detected events
DIMS håndbog	User manual and tutorials
Prøvetagningsplan	Planning schedule for sampling and analyses
ARTDEMO afrapportering	ARTDEMO project reports
ARTDEMO EU-rapport	ARTDEMO final scientific report – finished contributions
ARTDEMO Præsentation	ARTDEMO presentations
Undersøgelsesrapporter	Various reports from specific investigations carried out at Arrenæs AR plant
Årsrapporter	Yearly reports showing the aggregated results from the operation of Arrenæs AR
Artikler om Arrenæs	Various papers concerning the Arrenæs AR plant
Diverse kort	Various maps of the Arrenæs AR plant and its surroundings
Fotos	Pictures of the Arrenæs AR plant and its technical installations
Hjælp	Help to navigate and use the website/distributed information system

in table 2 together with an explanation of the content of the site.

Although focus of the website originally was to share the automated operation reports – it soon became important to establish links from the automated reports to other sources on the website like operation dependent links to the management plan (operation protocols), configure automated versions of the standardised overviews for artificial recharge plants (WAPI, SOPI,…). In other words the management overview, planning and reporting has been automated as well. Examples are:

- "Belastning" (Load) , executed on daily basis
- "Driftsrapport" (Operation), executed on daily basis – links to management plan
- "NVOC " (Water Quality Report), executed on daily basis
- "Vandbalance" (Water Balance), executed on daily basis
- "WAPI" WAter Pollution Index, executed manually when data is available

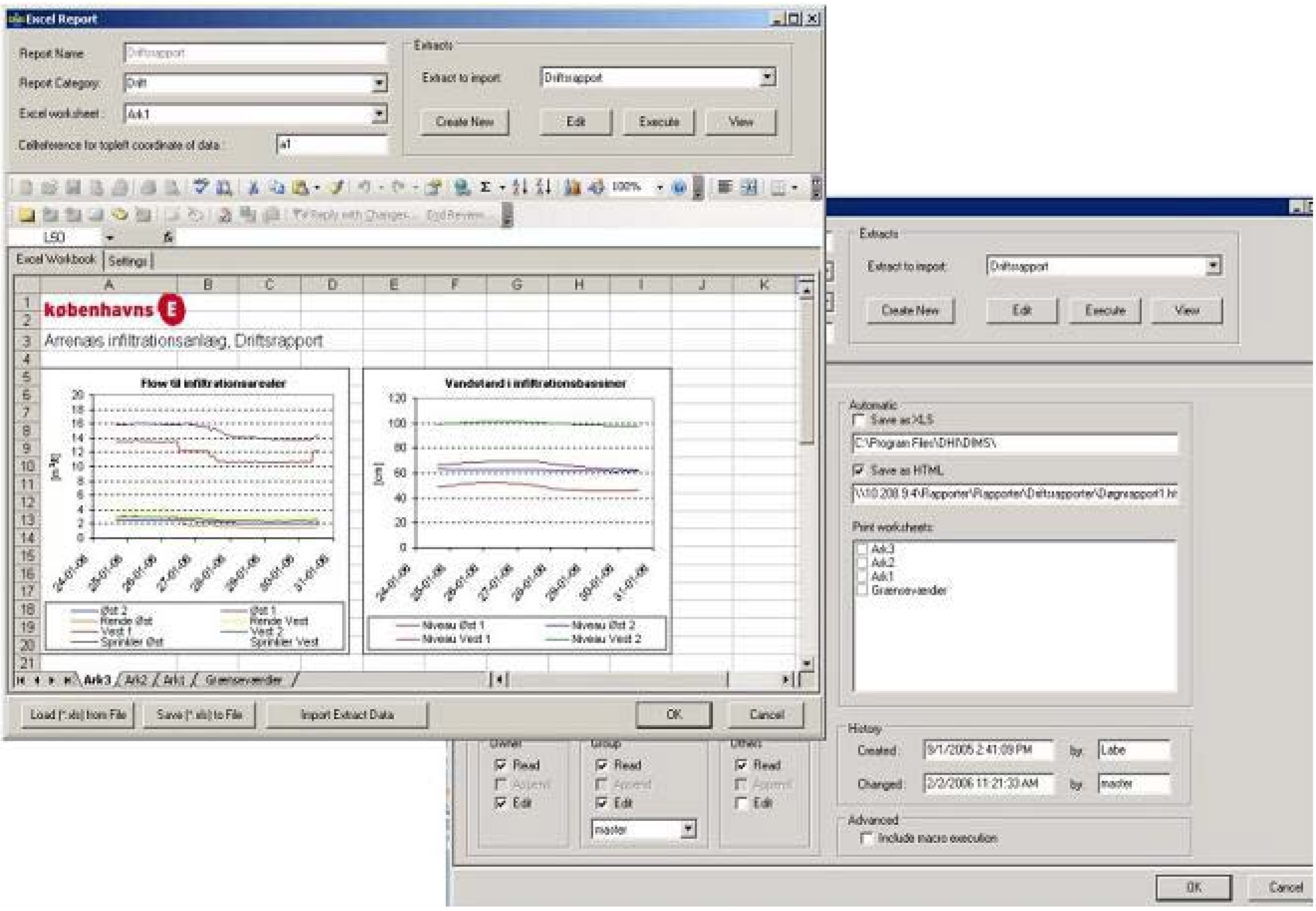
4.2 Configuration of automated reports

Using the "Driftsrapport" (Operation) as an example shows the quite straightforward configuration steps the user has to carry out in order to produce an automated daily report with operation dependent links to the management plan. A prerequisite for this is that measurements and calculations are available in an extract from the database defined with a moving time period – here measurements of levels/flows, automatic calculations of flows/infiltration rates (software sensors) and aggregated values of these, in a time window going one week back from the actual time where the extract is carried out.

As DIMS has Excel as a built in tool, it is quite easy to make reports (tables and graphs) containing further calculations on the data – which of course can be a combination of any of the data types defined (online, analyses, aggregated…). The Excel sheets themselves also are contained in the database, and therefore can be shared across the network – even for configuration purposes.

Figure 15 shows the layout for configuring of the automated report Driftsrapport. The report is based on the database extract definition Driftsrapport, which at user selected points in time (weekly, daily, etc.) will be executed and stored in the embedded excel file under the sheet Ark1, starting in the cell a1.

Tables and plots are configured as usual in Excel under sheets Ark3 and Ark2 using the data under sheet Ark1. The configured excel file is stored in the database together with report settings – here defined to be saved as html on the website when the report is executed.



Report Name: Driftsrapport

Report Category: Drift

Excel worksheet: Ark1

Cellreference for topleft coordinate of data: a1

Extracts

Extract to import: Driftsrapport

Create New | Edit | Execute | View

Arrenæs infiltrationsanlæg, Driftsrapport

Load (*.xls) from File | Save (*.xls) to File | Import Extract Data | OK | Cancel

Owner: ☑ Read ☐ Append ☑ Edit

Group: ☑ Read ☐ Append ☑ Edit master

Others: ☑ Read ☐ Append ☐ Edit

Automatic

☐ Save as XLS

C:\Program Files\DHI\DIMS\

☑ Save as HTML

\\10.208.9.4\Rapporter\Rapporter\Driftsrapporter\Dagsrapport1.ht

Print worksheets:

☐ Ark3

☐ Ark2

☐ Ark1

☐ Grænseværdier

History

Created: 9/1/2005 2:41:09 PM by: Labe

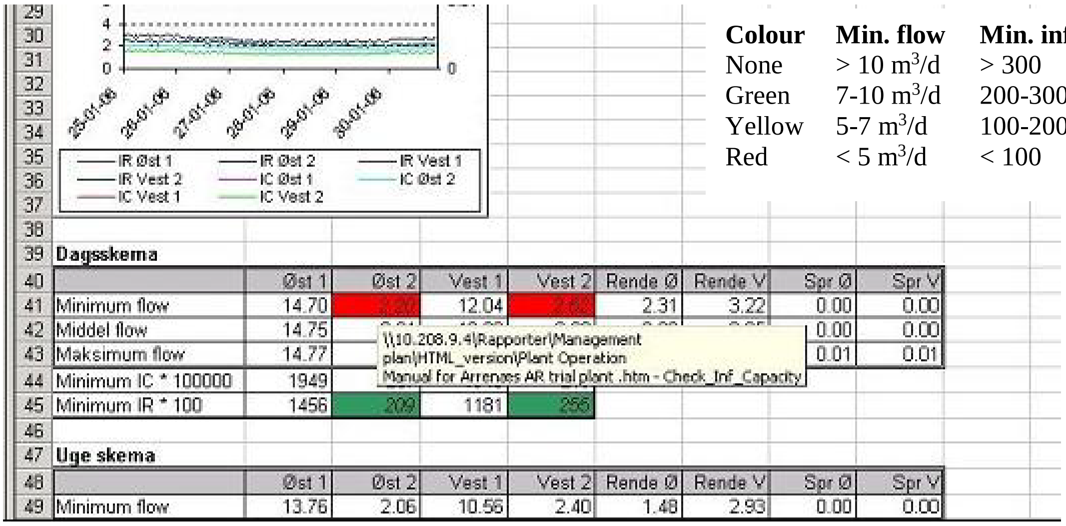
Changed: 2/2/2006 11:21:33 AM by: master

Advanced

☐ Include macro execution

OK | Cancel

Figure 15: Configuration of the tables and plots and the destination at the website in the report “Driftsrapport” (Operation) - Excel worksheet and Settings



Colour	**Min. flow**	**Min. infiltration rate**
None	> 10 m^3/d	> 300
Green	7-10 m^3/d	200-300
Yellow	5-7 m^3/d	100-200
Red	< 5 m^3/d	< 100

Dagsskema

	Øst 1	Øst 2	Vest 1	Vest 2	Rende Ø	Rende V	Spr Ø	Spr V
Minimum flow	14.70	[illegible]	12.04	[illegible]	2.31	3.22	0.00	0.00
Middel flow	14.75	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.00	0.00
Maksimum flow	14.77	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.01	0.01
Minimum IC * 100000	1949	[illegible]	[illegible]	[illegible]				
Minimum IR * 100	1456	209	1181	256				

\\10.208.9.4\Rapporter\Management plan\HTML_version\Plant Operation Manual for Arrenæs AR trial plant .htm - Check_Inf_Capacity

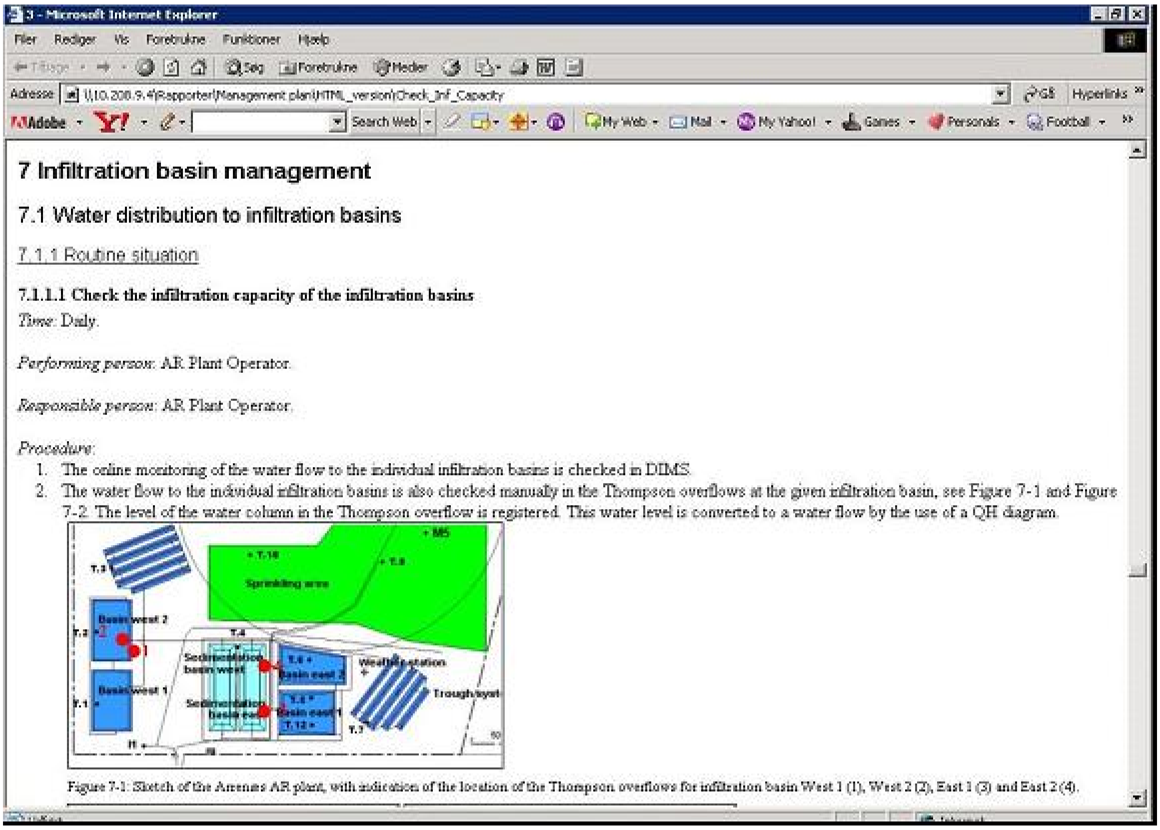
Uge skema

	Øst 1	Øst 2	Vest 1	Vest 2	Rende Ø	Rende V	Spr Ø	Spr V
Minimum flow	13.76	2.06	10.56	2.40	1.48	2.93	0.00	0.00

Figure 16: Configuration of conditional formatting and links to the management plan in the report “Driftsrapport” (Operation)

4.3 Configuration of links to management schemes

The tables in the report described above show daily and weekly minimum, average and maximum values for flows and infiltration rates. In order to keep focus on the capacity and optimised operation of the infiltration basins, the cells showing the minimum values for flow and infiltration rates are configured with conditional formatting giving different colours depending of the value in the cell according to the shown colour table:



7 Infiltration basin management

7.1 Water distribution to infiltration basins

7.1.1 Routine situation

7.1.1.1 Check the infiltration capacity of the infiltration basins

Time: Daily.

Performing person: AR Plant Operator.

Responsible person: AR Plant Operator.

Procedure:
1. The online monitoring of the water flow to the individual infiltration basins is checked in DIMS.
2. The water flow to the individual infiltration basins is also checked manually in the Thompson overflows at the given infiltration basin, see Figure 7-1 and Figure 7-2. The level of the water column in the Thompson overflow is registered. This water level is converted to a water flow by the use of a QH diagram.

Figure 7-1: Sketch of the Arrenæs AR plant, with indication of the location of the Thompson overflows for infiltration basin West 1 (1), West 2 (2), East 1 (3) and East 2 (4).

Figure 17: Screen dump from the website showing the activated link to the management plan when clicking on the cell in the report "Driftsrapport" (Operation)

Finally the cells are configured to link to the part of the management plan, which describes the actions needed according to the colour shown. The report is executed automatically every day using the updated data extract and written to the website (figure 16). On the website the user can click on the coloured cell, and thereby activate the configured link to the management plan (figure 17).

4.4 Managing the water balance

Managing the water balance in an artificial recharge plant requires an overview of the different components contributing to the balance (figure 18) in order to alow daily operation to secure that the water level is "constant" – meaning that the demand is balanced by the production – seen over a period of time – and still keeping the required water quality in the

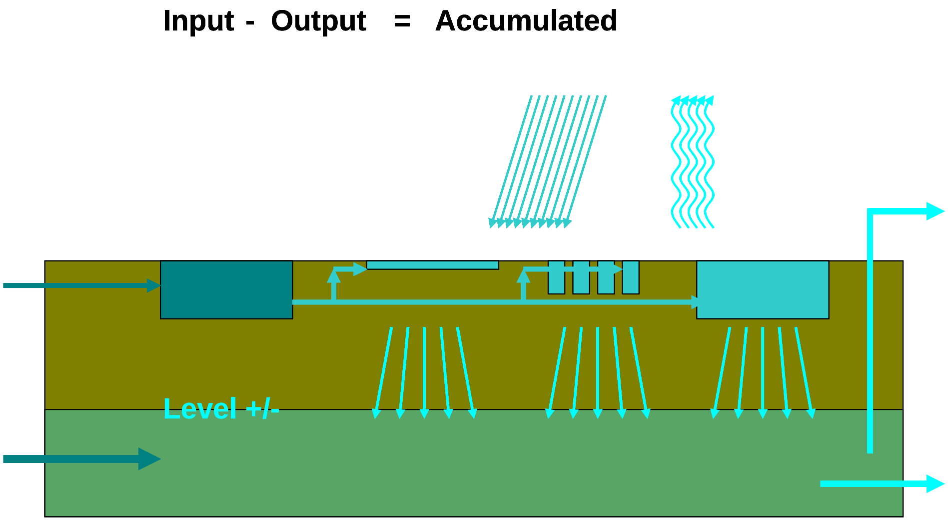
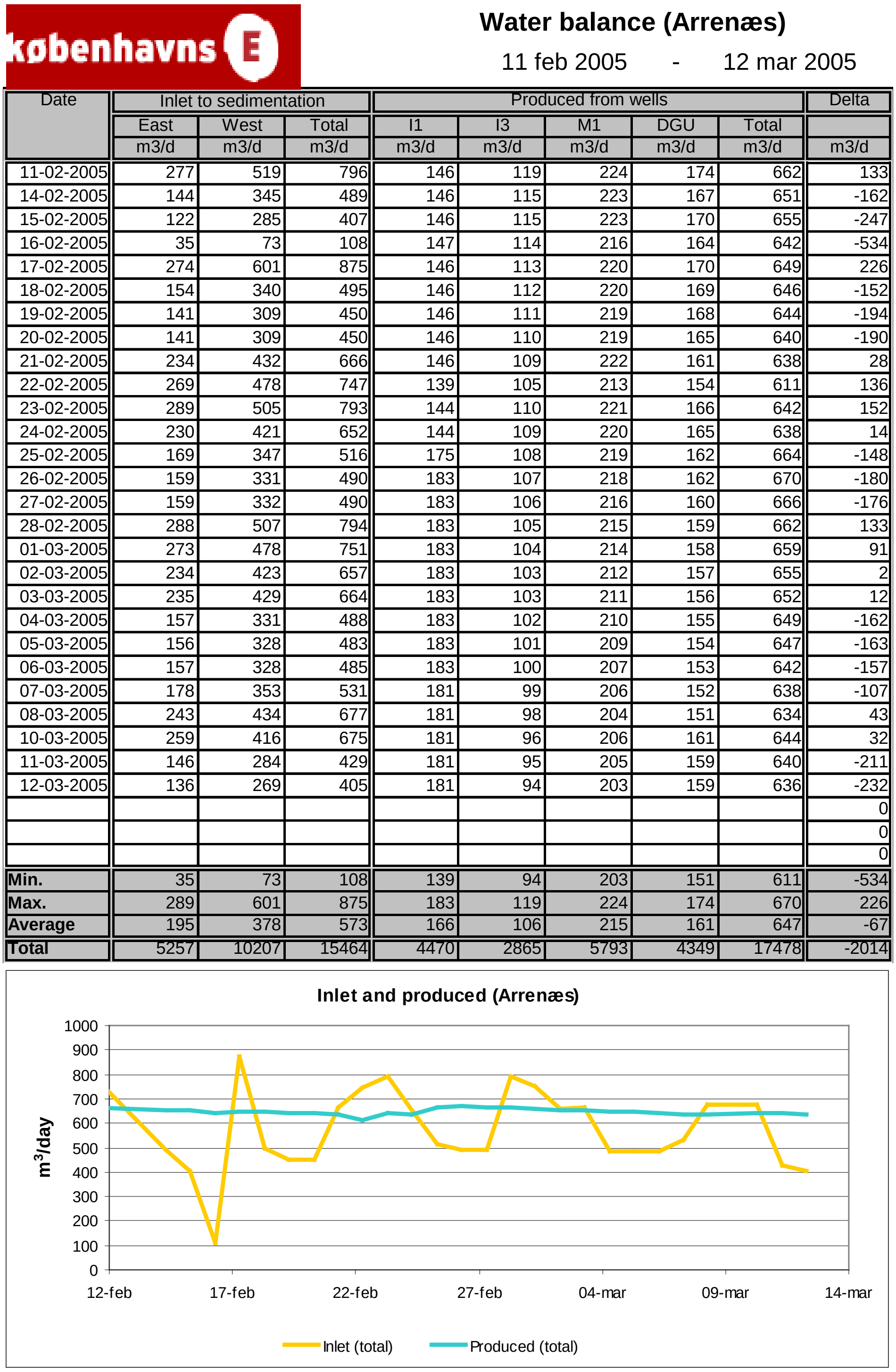


Figure 18: Water balance diagram for Arrenæs artificial recharge plant showing the flows to be monitored



københavns E

Water balance (Arrenæs)

11 feb 2005 - 12 mar 2005

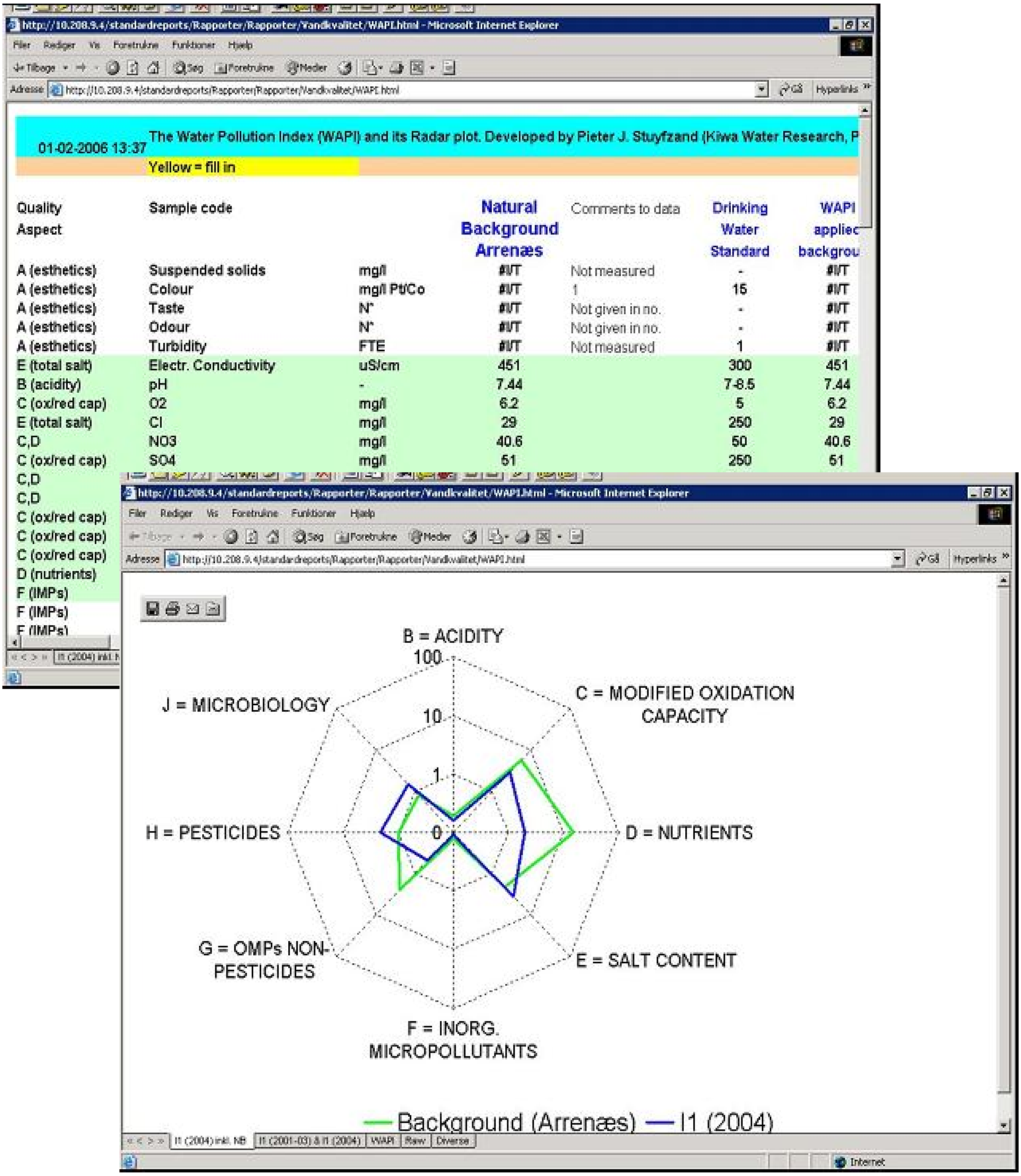
Date	Inlet to sedimentation			Produced from wells					Delta
	East	West	Total	I1	I3	M1	DGU	Total	
	m3/d	m3/d	m3/d	m3/d	m3/d	m3/d	m3/d	m3/d	m3/d
11-02-2005	277	519	796	146	119	224	174	662	133
14-02-2005	144	345	489	146	115	223	167	651	-162
15-02-2005	122	285	407	146	115	223	170	655	-247
16-02-2005	35	73	108	147	114	216	164	642	-534
17-02-2005	274	601	875	146	113	220	170	649	226
18-02-2005	154	340	495	146	112	220	169	646	-152
19-02-2005	141	309	450	146	111	219	168	644	-194
20-02-2005	141	309	450	146	110	219	165	640	-190
21-02-2005	234	432	666	146	109	222	161	638	28
22-02-2005	269	478	747	139	105	213	154	611	136
23-02-2005	289	505	793	144	110	221	166	642	152
24-02-2005	230	421	652	144	109	220	165	638	14
25-02-2005	169	347	516	175	108	219	162	664	-148
26-02-2005	159	331	490	183	107	218	162	670	-180
27-02-2005	159	332	490	183	106	216	160	666	-176
28-02-2005	288	507	794	183	105	215	159	662	133
01-03-2005	273	478	751	183	104	214	158	659	91
02-03-2005	234	423	657	183	103	212	157	655	2
03-03-2005	235	429	664	183	103	211	156	652	12
04-03-2005	157	331	488	183	102	210	155	649	-162
05-03-2005	156	328	483	183	101	209	154	647	-163
06-03-2005	157	328	485	183	100	207	153	642	-157
07-03-2005	178	353	531	181	99	206	152	638	-107
08-03-2005	243	434	677	181	98	204	151	634	43
10-03-2005	259	416	675	181	96	206	161	644	32
11-03-2005	146	284	429	181	95	205	159	640	-211
12-03-2005	136	269	405	181	94	203	159	636	-232
									0
									0
									0
Min.	35	73	108	139	94	203	151	611	-534
Max.	289	601	875	183	119	224	174	670	226
Average	195	378	573	166	106	215	161	647	-67
Total	5257	10207	15464	4470	2865	5793	4349	17478	-2014

Figure 19: Automated daily water balance report

produced water.

The installed monitoring system shall be able to give an overview – with proper configuration of automated calculations and reports. An overview, which together with management schemes for the infiltration basins – based not only on time but also on calculation of infiltration rates – will secure that demands can be met.

Figure 19 shows the daily updated water balance report for the last 30 days for two of the components: inlet to the plant and produced water. Other components - like rainfall and evaporation - has not been included yet, but the system has the measurements to support these. Further, the groundwater level is available as a measurement giving the possibility to check the balance with the change in level, which is



01-02-2006 13:37 The Water Pollution Index (WAPI) and its Radar plot. Developed by Pieter J. Stuyfzand (Kiwa Water Research, P

Yellow = fill in

Quality Aspect	Sample code		Natural Background Arrenæs	Comments to data	Drinking Water Standard	WAPI applie backgrou
A (esthetics)	Suspended solids	mg/l	#I/T	Not measured	-	#I/T
A (esthetics)	Colour	mg/l Pt/Co	#I/T	1	15	#I/T
A (esthetics)	Taste	N*	#I/T	Not given in no.	-	#I/T
A (esthetics)	Odour	N*	#I/T	Not given in no.	-	#I/T
A (esthetics)	Turbidity	FTE	#I/T	Not measured	1	#I/T
E (total salt)	Electr. Conductivity	uS/cm	451		300	451
B (acidity)	pH	-	7.44		7-8.5	7.44
C (ox/red cap)	O2	mg/l	6.2		5	6.2
E (total salt)	Cl	mg/l	29		250	29
C,D	NO3	mg/l	40.6		50	40.6
C (ox/red cap)	SO4	mg/l	51		250	51
C,D						
C,D						
C (ox/red cap)						
C (ox/red cap)						
C (ox/red cap)						
D (nutrients)						
F (IMPs)						
F (IMPs)						
F (IMPs)						

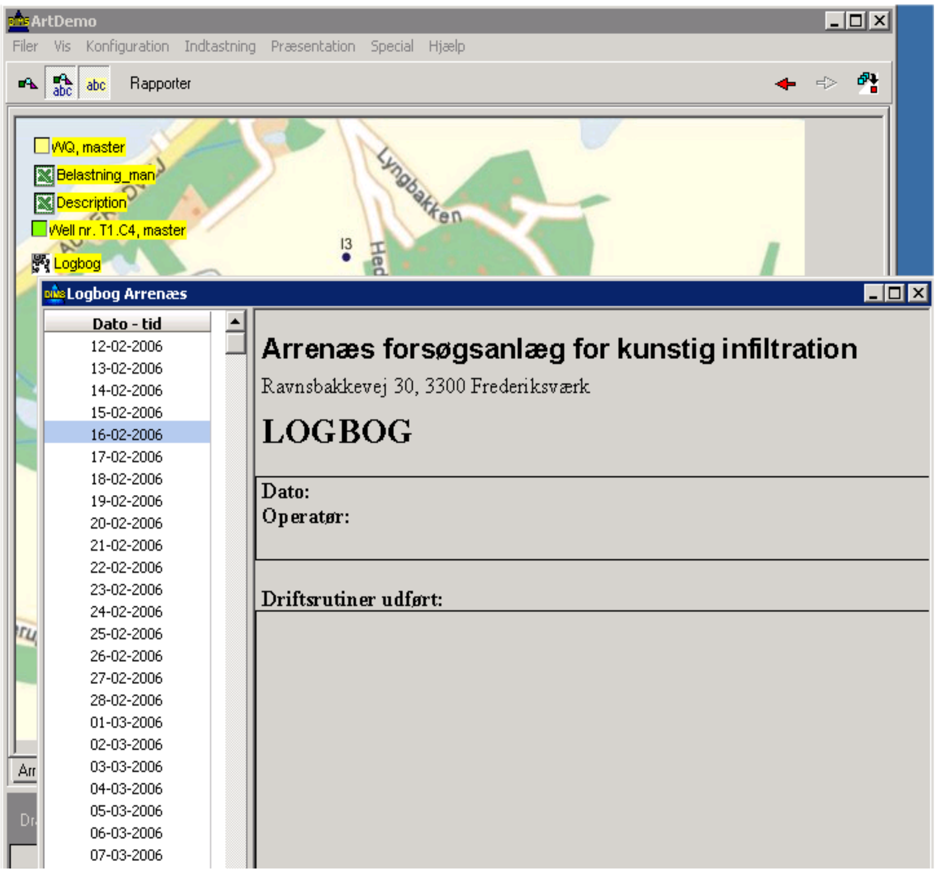
Figure 20: The Water Pollution Index calculations and the WAPI Radar plot, screen dumps from the website

important as the flow of groundwater to and from the aquifer still are unknown components

4.5 Long term management of water quality

The WAter Pollution Index (WAPI) report described by Kiwa is another example of how methods, procedures/protocols and management schemes developed during the project has been made operative.

The WAPI report is configured to be calculated and written to the website when the report is executed by the user by clicking on a link in the user interface (once a year or when ever new data are available).



Dato - tid
12-02-2006
13-02-2006
14-02-2006
15-02-2006
16-02-2006
17-02-2006
18-02-2006
19-02-2006
20-02-2006
21-02-2006
22-02-2006
23-02-2006
24-02-2006
25-02-2006
26-02-2006
27-02-2006
28-02-2006
01-03-2006
02-03-2006
03-03-2006
04-03-2006
05-03-2006
06-03-2006
07-03-2006

Arrenæs forsøgsanlæg for kunstig infiltration

Ravnsbakkevej 30, 3300 Frederiksværk

LOGBOG

Dato:
Operatør:

Driftsrutiner udført:

Figure 21: User interface to a configured daily log based on Word documents stored in the system database (template in Danish language from Arrenæs demosite)

Database: ARTDEMO, Bruger: master

The WAPI calculations are based on average values per year, so the report calculates these average values and place them in the correct cells for WAPI calculation (figure 20). The report also produces the WAPI Radar plot based on the calculations (figure 20).

4.6 Daily log – a shared function

During the work it became clear that the system needed a common location for time referenced unformatted information related to the daily operation of the artificial recharge plants – a daily log. Therefore, it was decided to use the system database ability to store time stamped objects rather than values. The objects should be Word documents, which should be available for all users - just like any measurement in the database is available to all users (respecting the permissions given).

User interface and integration to Word was developed, and it is now possible to configure one or more daily "measurements", which instead of values in the database has word documents – each document being a time referenced sheet in a log book. The sheets can be configured using a template produced in Word, and the daily sheets can be accessed from the database by clicking on the preferred date in the log book user interface, which is activated by clicking on a link on the basic user interface (figure 21).

5. CONCLUSION

The major target for the system design has been to standardise and automate the platform for the management system, in order to make it independent of the dataacquisition methods used and to enable partners to concentrate on optimisation of operation procedures, management schemes, sampling programmes, process investigations and sensor development.

Implementation of the system design has resulted in the completion of distributed information systems for operation and management of the artificial recharge plants at Arrenæs and Dösebacka.

The distributed information systems enable optimisation of daily operation procedures and the use of efficient management strategies by integrating the developments/investigations from the other work packages in the ArtDemo project with the established monitoring systems at the artificial recharge plants via websites at KE and GV.

Chapter 18: Introduction to the Management Plan for the Dösebacka AR Plant

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Abstract: The production of a management plan has been a part of the objective of the EC-project Artificial Recharge Demonstration Project. The overall objective of the ARTDEMO-project was to demonstrate an early-warning system for Artificial Groundwater Recharge plants based on on-line monitoring and information technology, which was to be applied to a full-scale plant. The paper is an introduction to the management plan of the Dösebacka AR plant, which is one of the test sites. It shows that the structure of the plan has been constructed on a follow-the-flow concept and an early-warning strategy. The plan is divided into a Part 1-Plant Operation Description, that describe in general the management of the plant, and a Part 2- Plant Operation Manual that compile in a systematic order the protocols for routine and alarm situations in the operation of the plant. By using a generalising approach to the set-up, a flexible structure has been achieved that allow an easy modification of the plan to comply with any other plant. Experience from the construction of the plan suggest several changes to the management of the plant, regarding instrumentation, equipment, monitoring and control.

1 INTRODUCTION

The production of a management plan has been a part of the objective of the EC-project Artificial Recharge Demonstration Project (ARTDEMO), EVK1-CT-2002-00114. The overall objective of the ARTDEMO-project was to demonstrate an early-warning system for Artificial Groundwater Recharge plants based on on-line monitoring and information technology (IT), which was to be applied to a full-scale plant. One test site has been the Dösebacka AR plant for the City of Kungälv in Sweden. Subsequently, the objective of the production of the management plan has been to demonstrate how a management plan could be designed following a management strategy based on a early-warning strategy model. This paper introduces the management plan for the Dösebacka plant and how it was produced. The demonstration and the test of the function of the plan is presented in Engblom et al (2005) in this ARTDEMO Scientific Report. The details of the management plan is found on the ARTDEMO Final Report CD appended to the report and this paper will only describe the structure of the plan.

After a short description of the plant, the method of how the management plan was constructed is presented. Then the management strategy is presented followed by a presentation of the management plan structure is shown. Possible changes to the strategy and plan, based on gained experience when constructing the plan and the evaluation with the different scenarios Engblom et al (2005), are discussed in one chapter. Finally, the paper is concluded in a summary.

It should be pointed out that the management of the Dösebacka AR plant has not used the ARTDEMO system during the project, as the work was a test and demonstration of a new arrangement. The evaluation has been preformed by the staff in the ARTDEMO-project.

2 GENERAL DESCRIPTION OF THE AR PLANT IN DÖSEBACKA

The Dösebacka Artificial Recharge plant is located in south-west of Sweden. The plant is the water supply for 25 000 people in the community of Kungälv. The plant produces approximately 6000 m3/d and consist of 9 infiltration ponds and 15 abstraction wells. The detention time for the water in the aquifer has been estimated to vary between 6 to 60 days depending on abstraction well (Lundh et al 2005c). The water is pre-treated with sedimentation and the drinking water is pH-adjusted with NaOH for corrosion prevention in the distribution system. Two wells that abstract water with a higher turbidity and organic content, are post-treated with chemical precipitated using aluminium sulphate. The plant has equipment for disinfection of the drinking water in case of an emergency with microbiological contamination but it is rarely used. For more details about the Dösebacka plant, the reader is advised to the site description (Lundh 2005) in this report.

3 METHOD OF CONSTRUCTING THE PLAN

The main structure of the plan has been developed in several workshops with the ARTDEMO partners. The concept was to approach the construction of the plan from an early-warning point of view and a strategy model was defined called IDAS (Incident, Detection, Action, Surveillance) in order to identify the relevant check points for the monitoring of the water quality Lundh et al (2005a). Moreover, it was decided to follow the water transport through the plant when arranging the relevant units of the plant into a logical structure.

The details of the management plan have then been built on the routines for the actual operation at the Dösebacka plant. Information for routines and alarms have been gathered from the existing Dösebacka AR-plant operation manual and from interviews with the personnel involved in the operation and management of the plant. The protocols specifically connected to the ARTDEMO measurement station has been invented to fit the principal of IDAS and the set up of the measurement station. Therefore, several protocols that are presented in the management plan is a mixture of the standard procedure at the plant (original plant operation manual), the Swedish regulation for drinking water (SLVFS 2001:30) and new thinking in relation to the early-warning strategy model IDAS.

4 MANAGEMENT STRATEGY

The overall objective of a management plan, as defined in this project, was to give directives for the management of the plant to ensure that the right quantity of water is produced with the right quality, which also includes protecting the plant from damage – a crucial issue when it comes to groundwater and artificial recharge. This could be systemized in the following quality management:

- Sustainable water quality (SWQ) - meaning maintaining a continuous, good water quality according to regulations
- Sustainable water production (SWP) - meaning maintaining a continuous water production according to community requirements
- Sustainable plant operation (SPO) - meaning protecting the plant from unmanageable damage.

So, considering the objectives of the management, the management strategy should be:

A. to equip the plant with the right tools for monitoring and control.
B. to produce routine protocols that instruct the operators at the plant how to handle the daily operation.
C. to produce action protocols that instruct the operators at the plant how to handle alarm situations.
D. to monitor the plant operation and water quality with a sufficient frequency, so that a quality deterioration, or an event that could cause problems that inflict on the production demands, or an event that would severely damage the plant for a long time, will be detected in time for the plant operation to take action to ensure a safe and reliable drinking water production.

1.1.1.1.1.1.1 Part 1 – Plant Operation Description

A General description of the plant
- A.1 Plant Design
    - A.1.1 Location
    - A.1.2 Geology and Hydrogeology
        - A.1.2.1 Geology
        - A.1.2.2 Hydrogeology
    - A.1.3 Plant operation data
    - A.1.4 Raw Water Source
    - A.1.5 Raw water intake and intake pond
    - A.1.6 Pre-Treatment
        - A.1.6.1 Sedimentation pond
    - A.1.7 Infiltration pond
    - A.1.8 Abstraction wells 1-15
    - A.1.9 Ground Water Level
    - A.1.10 Internal piping
    - A.1.11 Protection zones
    - A.1.12 Post-treatment
        - A.1.12.1 Overview
        - A.1.12.2 Adjustment of pH
        - A.1.12.3 Chemical coagulation and filtration
        - A.1.12.4 Disinfection with chlorine
    - A.1.13 Reservoirs 1 and 2
    - A.1.14 External distribution
- A.2 Security
- A.3 General supply
- A.4 IT-communication
- A.5 Water Quality Monitoring
    - A.5.1 Alarm

B Management scheme
- B.1 Public authorities
- B.2 Organisation

C Documentation

D List of responsible and performing persons
- D.1 Larger consumers

E Early warning system - IDAS

Figure 1. Part 1 Plant Operation Description

5 STRUCTURE OF THE MANAGEMENT PLAN

The management plan is divided into two separate parts:

1. Plant operation description
2. Plant operation manual

The Part 1 (Figure 1) is a description of the plant and its management in general. The document does not include any protocols for routines and alarm situations and is meant to inform the operation and others about the plant and the general management. The details are found in the management plan in the appended Final Report CD.

Part 2 lists in a systematic order the routine and alarm instructions for the operation of the plant. The plan has been arranged with the intention of creating a structure that could be applied on any plant. A plant is in many ways specific in its kind; requiring specific management, and routines and alarms need to be set accordingly. Therefore the titles in the head structure is more general in its character and the plant specific information appears in the subtitles. The plan structure was also arranged in such a way that parts that dont fit with the plant in question can be taken out. Parts in grey were not applicable for the Dösebacka plant at the time and have therefore been left empty in the plan.

Part 2 is not complete regarding the protocols; you will find that several protocols, that should normally exist for the operation of an AR plant, are empty. This is an ARTDEMO project-related strategy to focus on the early-warning objective of the project, which has been set on the main structure of the plan - pointing out the strategy of early warning and significant head and subtitles to be address - and on the chosen scenarios that was used to test the plan and system of early warning. The protocols for the routines and actions connected to the scenarios have thus been fully described in the management plan, while the others have been left empty to be filled in and adapted to the condition for a plant in question.

Below is the structure of the Dösebacka plant. The structure is based on the strategy model IDAS (Lundh et al 2005a). The head titles of the plan that are correlated to the activity locations in the IDAS Scheme are labelled with the column number in [brackets]. The water in the Göta Älv river, referring to [1] in the IDAS Scheme, is not handled in the management plan. The [11] and [12] refers to the water distribution system and end consumer of the drinking water and are also not handled in the plan.

Part 2 - Plant Operation Manual

1. Operational Control
    - 1.1. General maintenance
    - 1.2. Security
    - 1.3. General supply
    - 1.4. IT-communication
    - 1.5. Maintenance of measurement stations
    - 1.6. Maintenance of grass areas and roads
    - 1.7. Electric fence
    - 1.8. Internal reporting
    - 1.9. External reporting
2. Early warning - water quality upstream the intake **[2]**
    - 2.1. Manual water quality monitoring, upstream the intake
    - 2.2. On-line water quality monitoring, upstream the intake
3. Water level in raw water source **[2]**
    - 3.1. On-line monitoring of water level in raw water source
4. Raw water intake **[3]**
    - 4.1. Maintenance
    - 4.2. Pump function
5. Early warning - water quality in the raw water **[4]**
    - 5.1. Maintenance of measurement station
    - 5.2. Manual water quality monitoring, raw water
    - 5.3. On-line water quality monitoring, raw water
6. Pre treatment **[5]**
    - 6.1. Sedimentation basin management
    - 6.2. Water level in sedimentation basin **[6]**
    - 6.3. Accumulation of sludge in sedimentation basin
    - 6.4. Pump function, sedimentation basins
7. Infiltration basin management **[5]**
    - 7.1. Water distribution to infiltration basins
    - 7.2. Water level in infiltration basins
    - 7.3. Regeneration of infiltration basins
8. Early warning - water quality in infiltration basins **[6]**
9. Sprinkling areas **[5]**
10. Early warning – water quality in the unsaturated zone **[6]**
11. Monitoring well management
12. Early warning water quality in monitoring well **[6]**
13. Abstraction well management **[7]**
    - 13.1. Maintenance
    - 13.2. Pump function
14. Early warning - water quality in abstraction wells **[8]**
    - 14.1. Manual water quality monitoring, abstraction wells
    - 14.2. On-line water quality monitoring, abstraction wells
15. Groundwater level measurement and control **[8]**

    - 15.1. Online monitoring and management of the groundwater level
16. Internal pipelines
    - 16.1. Maintenance
    - 16.2. Flow in pipelines at the AR plant
17. Protection zones
    - 17.1. Maintenance of unused wells and holes into the unsaturated zones
    - 17.2. General monitoring of the area
18. Post treatment at the plant **[9]**
    - 18.1. Adjustment of pH
    - 18.2. Chemical coagulation
    - 18.3. Filtration
    - 18.4. Chlorination (optional)
19. Reservoirs at the plant
    - 19.1. Maintenance
20. Early warning – water quality in distributed water **[10]**
    - 20.1. Manual water quality monitoring, distributed water
    - 20.2. On-line water quality monitoring, distributed water
21. External distribution
    - 21.1. Pump function
    - 21.2. Flow in external pipelines

6 REFORMULATION OF THE MANAGEMENT STRATEGY AND PLAN

Does the management strategy need a reformulation? The following discussion is on the result from the integrated work with the management plan in WP5 and the set-up of the early warning system and evaluation test of the whole system including the management plant that has been performed in WP6.

I. Based on information gathered in studies in ARTDEMO, it has been found that the groundwater in some high-producing abstraction wells have a detention time less than 14 days, which ought to be regarded as a relatively short time for such a process. Thus, the plant perhaps should be considered as a surface water treatment plant rather than a groundwater treatment plant, which changes the requirements according to Swedish regulations. Then the monitoring of the microbiological quality would have to be significantly increased from once a month, which is the case today, to once a week.

II. The use of on-line measurements has been regarded in the ARTDEMO-project as a way of bringing the operators attention to a situation which is deviating from a normal one, not as direct verified information on what has gone wrong or has polluted the water. Generally, especially at the end of the plant process, the alarms from the instruments should be followed up by manually taken water samples in the drinking water to ensure the safety of the end-consumer at the tap. This is relatively satisfied in this version of the management plan but might require an additional pitch for completion.

III. In the evaluation of the instruments it has been found that the chosen instruments have major limitations regarding the detection/identification of microbiological contamination. In a future up-dated version of the management plan a different set up of instruments will have to be chosen or developed. If a plant experiences short travel times of the water in the subsurface, it might be an idea to install an at-line microbiological detector (on-line does not exist today). However, the alternative of using a optimised programme for manually taken samples will also probably prove to be sufficient. The choice depends on the plants removal efficiency, which has to be tested for each plant. In the case with Dösebacka it is probably sufficient with a more optimised manual water sampling programme.

IV. Today the control of the groundwater table is handled by adjusting the valves in the distribution system to the infiltration ponds. These valves are not on-line monitored and is adjusted by hand. The arrangement does not provide any information on the water flow distributed to the infiltration ponds. It is advisable to add flow meters to the pipes supplying the infiltration ponds and to the abstraction pumps. That would provide the operation of the plant with information that could be linked to the groundwater levels. Would this system also be complemented with electrical devices that drives the valves for the distribution of water to the infiltration ponds and remote controlled valves for the abstraction pumps, the plant would have a system that is more easy to overview and control and with the possibility of adding automatic control. It could be an good idea to monitor the temperature and the EC in each well, enabling an early action towards increasing salt concentration and temperature. Not only would such a system make easier the operators task in smoothing out the variations due to precipitation, water level in Göta Älv, temperature, salt and clogging, it would also make data available on long term deviations.

V. The instrumentation in the measurement station were used for all water types at the Dösebacka plant. It was found that there were some negative consequences by using the same system for both drinking water and raw water, regarding biofilm growth and detection levels. Thus it might be an good idea to use separate instrumentation for water with significant differences in character.

VI. It became more and more evident that the different subsystems; early warning, measurement station, DIMS, management plan, etc, in the complete management set-up for the plant, depended very much on the location of the monitoring. This aspect could possibly be interpreted through the formulation ".. in time …." In point D) in the strategy, but it is probably a clarification if "location" is also added to the strategy.

Based on the discussion above it is concluded that the management strategy, as defined in the *Formulation of Management Strategy*, does not have to be changed in its general construction with the exception of the point D) that should also include the location of the monitoring, which refers to aspect 6 above (change in bold letters):

D) to monitor the plant operation and water quality **in relevant locations and** with a sufficient frequency, so that a quality deterioration, or an event that could cause problems that inflict on the production demands, or an event that would severely damage the plant for a long time, will be detected in time for the plant operation to take action to ensure a safe and reliable drinking water production.

Furthermore, the discussion suggests several aspects that could be implemented in the management plan to comply better with the management strategy.

7 SUMMARY

The introduction of the management plan for Dösebacka MAR plant have shown that the structure has been constructed on a follow-the-flow concept and an early-warning strategy. The plan is divided into a Part 1-Plant Operation Description that describe in general the management of the plant, and a Part 2- Plant Operation Manual that consist of routine and alarm protocols for the operation of the plant. By using a generalising approach to the set-up, a flexible structure has been achieved that allow an easy modification of the plan to comply with any other plant. Experience from the construction of the plan suggest several changes to the management of the plan, regarding instrumentation, equipment, monitoring and control.

8 ACKNOWLEDGEMENT

The authors would like to thank the personnel at the Dösebacka AR plant for their assistance during the study.

9 REFERENCES

Engblom, K. (2005) Risk Analysis of the Dösebacka Waterworks, Master Thesis at KTH, Stockholm, Sweden.

Engblom, K., Lundh, M. and Holmström, E. (2005), Scenario Management and Expert system for the Dösebacka Waterworks. This final Report.

Lundh, M (2005) Description of the Dösebacka Artificial Grouindwater Recharge Plant. This final report.

Lundh, M., Engblom, K., Holmström, E., Bennedsen, L., Brandt, G., Linding Berg, R. and Ørbæk Jensen, T. (2005a) IDAS: Connecting the Detection of an Incident with the resulting Action and the follow-up Surveillance in an early warning strategy model, This final report.

Lundh, M., Engblom, K and Holmström, E (2005b) Early Warning System at the Dösebacka MAR Plant, This final report.

Lundh, M., Jonasson, S A, Jørgensen, N. O., Johnson, M. D. (2005c). Hydrogeology and water treatment performance of the Dösebacka artificial recharge plant – the basis for an efficient system for early warning. Kompetenzzenter Wasser Berlin,, In press for the proceedings of ISMAR2005, Berlin, June, 2005

Chapter 19: Scenario Management and Expert System for the Dösebacka AR Plant

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Abstract: The early warning system; the measurement station and DIMS, and the management strategy and plan for Dösebacka AR plant have been tested and evaluated. The testing was based on three risk scenarios that could occur at the plant and that had been assessed as the most critical. The measurement station was tested with a simulation in a laboratory and the management strategy and plan were tested and demonstrated fictively and are presented in a PowerPoint show. In the evaluation of the measurement station it was found that the monitoring strategy had major limitations regarding the detection of microbiological contamination, but regarding petroleum products and substances that can cause clogging, it worked satisfactory. In general, the management strategy and plan are well organized regarding the control of the process at Dösebacka waterworks. The management plan proved to work satisfactorily for the test with the scenarios with some minor exceptions and improvements are suggested in order to make the plan more efficient.

1 INTRODUCTION

The overall objective of the ARTDEMO-project (EVK1-CT-2002-00114) has been to demonstrate an early-warning integrated management system for Aquifer Recharge plants (Lundh et al, 2005a and b). An early-warning system has been developed based on on-line monitoring in a measurement station connected with an advanced data handling system (DIMS – presented in chapter 17 in this report). A strategy model (IDAS – presented by Lundh et al(2005c)) has also been developed for the management of the early-warning system and incorporated in the work with the measurement station and DIMS. To evaluate the management system from a realistic perspective a risk analysis was performed at the Dösebacka waterworks to find the three most critical risk scenarios. These were used as a base for the testing of the early-warning system, the measurement station and DIMS, and testing of the management strategy and plan. The aim and goals with the scenario testing were to demonstrate the Management Strategy and Management Plan of the Dösebacka waterworks, to find problems and limitations and give future recommendations and suggestions of improvement. Certain aspects could not be implemented to refine the strategy and the early warning system and they are instead discussed in Conclusions.

The expert system is made up by the interaction between the online monitoring, the data treatment by the DIMS-system, the operator and his/her use of the management strategy and plan in order to operate the plant. The system is used by the operator/manager in arranging the data so that the essential information on water quality, operation and groundwater conditions can give insight to relationships between different parameters that can be used for optimising the early warning and operation system.

Due to possible problems and hazards as a result of bringing in contaminants to a functioning AR plant the testing has to a large extent been done theoretically by experience and shown in a PowerPoint presentation, a flow chart or simulated in a laboratory, by so called detection identification tests.

2 THE DÖSEBACKA AR PLANT

Dösebacka Waterworks is an infiltration plant for artificial recharge of groundwater and is located 5 km north of Kungälv, on the west shore of Göta Älv. The geological formation is of a glacial/fluvial origin with a partly clay-confined sand and gravel aquifer located along the Göta Älv river. A more expanded description of the plant is presented by Lundh (2005).

Raw water from the Göta Älv is pumped from an intake pond, in direct contact with the river, up to a sedimentation pond where larger particles settle. This saves the infiltration ponds from an acute or too early clogging. The water is then distributed through fall by hydraulic gradient to the 9 infiltration ponds. In the infiltration ponds the water infiltrates the filter bed and is transported in unsaturated and saturated ground for approximately 6-60 days, depending on abstraction well. The aquifer water is abstracted in up to 15 wells and distributed to the reservoir, where it is pH-adjusted for corrosion prevention. There is also the possibility of chlorination but in general the water has such high quality that this is not necessary. Two abstraction wells have problems with turbidity and is chemically precipitated and filtrated in upwards-directed sand filters.

The plant is situated in an area that is exposed to possible accidents and hazards that can affect the production process and the plant. The industries and the heavy traffic along and on Göta älv is a potential threat as will be described further in the following sections.

3 EXPLANATION OF THE POWERPOINT PRESENTATION FOR DÖSEBACKA

The measurement station is tested through detection identification tests for two of the scenarios, but the complete test of the early warning system and management strategy and plan is tested fictively and demonstrated in a PowerPoint presentation on a CD in this Final report. A PowerPoint presentation has been put together to easily describe how the testing has been carried out. The use of pictures and schematic diagrams demonstrates the required procedures and actions for handling the risk scenario.

The presentation is based on DIMS, which informs the operator about the conditions at the plant, and on the action protocols, which are the base for the operations manual of the Management plan for Dösebacka. The concept and structure of IDAS can be followed throughout the test and the presentation shows the following strategies and systems:

- Normal operation strategy
- Early warning strategy

Three risk scenarios are demonstrated under the early warning strategy, covering the following situations:

- Barrier removal effect – the plants ability to remove microbiological and chemical contaminants
- Closure strategy – closing of the intake of raw water
- The regeneration strategy – the regeneration of the infiltration ponds

4 SCENARIOS FOR THE DÖSEBACKA AR PLANT

4.1 *Identification of risk scenarios*

Identification of potential risks that can affect the water quality at the Dösebacka artificial recharge plant was carried out through a study of literature that consisted of several general risk analyses regarding the Göta älv area and drinking water production. Statistics covering incidents and accidents in Göta älv and at other water works, as well as problems with raw and drinking water quality was collected and analysed. Further information was given by interviews of experts at two different artificial recharge plants.

An internal scenario is defined as an incident occurring at the AR trial plant, that affect the water while it is in the plant being processed, but the influence can derive from outside the plant. External scenario is defined as an incident occurring outside the AR trial plant but affecting the operation and/or the water quality at the AR plant, e.g. they affect the raw water before it has entered the plant. Further subdivision of the identified risks is done in the subchapters below.

Internal risks

1. Contamination of sedimentation and infiltration ponds
   - Chemical/petroleum products from transportation on or close to the plant
   - Leakage from sewage close to the plant, animal drops
   - Algae production in the ponds
2. Contamination of abstraction wells
   - Chemical/petroleum products from transportation on or close to the plant
   - Göta älv water due to inundation (flooding)
3. Saltwater penetration into the aquifer
   - From captured ancient salt water in the aquifer
4. Process interruptions
   - Dosage of aluminium sulphate, NaOH
   - Pump break down
   - Freezing of or damage on pipes
   - Clogging of sand filters in post treatment
5. Power failure
   - General power cut, including emergency power supply set-up
   - Power cut to different parts of the process due to wire problems
6. IT
   - Interruption or failure of process and data handling
7. Sabotage
   - Deliberate actions to damage the process or plant
8. Clogging of infiltration ponds (result of external scenario 3)

External risks

9. Microbiological contamination of raw water
   a. Due to heavy rains, inundations and runoff from agricultural land

   b. Overflows from sewage treatment plants
   c. Manure discharge
   d. Sludge deposit from pulp/paper industries
   e. Algae, algae toxin
10. Chemical contamination of raw water
    a. Chemical/petroleum products from transportation on or close to Göta älv by ships, trains or trucks
    b. Chemical/petroleum products from industry discharge or accident
    c. Harbour work
    d. GMO, micro-pollutants, pesticides
11. Contamination of raw water with algae, fibres, clay, sediment (which results in an internal risk - clogging of infiltration ponds)
    a. Pulp/paper industries
    b. Mudslide of the banks of Göta älv (could lead to microbiological and/or chemical contamination depending on if the soil is contaminated)
    c. Increased amount of algae and production of algae toxins.

4.2 *The most critical (high risk) scenarios*

To define the most critical (high risk) scenarios to the water quality at Dösebacka AR plant, the same means and resources mentioned above for the identification of risk scenarios were taken into consideration as well as the inputs from discussions with Artdemo partners KE and DHI (Artdemo meeting 2-3/2 2005). Even though all the identified situations and consequences are of significance, and are most likely to cause problems for the Dösebacka plant at some time, and which the management of the plant has to be capable to handle, the study had to be limited down to just a few in order to optimise the time and project resources. In the choice of scenarios to follow up, the focus was set on the early-warning strategy including mainly water quality deterioration that was to be tested in the project.

Another goal of the selection was to cover the three important areas of quality management that are incorporated in the management strategy and plan of Dösebacka:

1. Sustainable water quality (SWQ) - meaning maintaining a continuous, good water quality according to regulations
2. Sustainable water production (SWP) - meaning maintaining a continuous water production according to community requirements
3. Sustainable plant operation (SPO) - meaning protecting the plant from unmanageable damage

The three chosen risk scenarios for Dösebacka were:

- Microbiological contamination of raw water (SWQ, SPO)
- Chemical contamination of raw water with petroleum products (SWQ, SPO)
- Contamination of the raw water with fibres, sediment, clay or algae (SWP)

These three scenarios were chosen because the raw water quality is of great importance to an AR plant and therefore it is interesting to investigate the early warning systems ability to handle the different scenarios. The Dösebacka AR plant is located in an environment that is exposed and vulnerable to external risk scenarios, which has influenced the choice of scenarios to test the early warning system. The different scenarios will affect the AR plant differently and the cause is also varying which is described in the following chapters.

5 SCENARIO 9: MICROBIOLOGICAL CONTAMINATION OF RAW WATER

5.1 *Scenario description and assumptions*

The prevention of potential microbiological contamination is regarded as one of the highest priorities for drinking water production. Therefore the monitoring and surveillance of the raw water quality concerning pathogens is important. Possible microbiological contamination sources in Göta älv are overflows from wastewater treatment plants and pumping stations, runoff from agricultural and stock-rising land or manure discharge. Other origins of high pathogen concentration could be process interruptions at one of the pulp- and paper industries along Göta älv or mudslides of the banks of Göta älv. High bacterial numbers (represented by >1000 E.coli/100 ml) occurs in Göta älv with a frequency of about 4-5 times a year (Wångsell 2004).

5.2 *Critical substances and consequences*

Pathogenic virus, bacteria, protozoa exist to a certain amount in Göta älv. Since analysis of specific pathogens is limited due to difficult, time consuming and expensive analysing methods, indicator bacteria are used to indicate faecal contamination. At the moment there are no regulations for maximal concentrations of indicator bacteria in the raw water. But the drinking water has strict regulations (see table 1) and requires a high standard of the production means to reach the demanded quality.

Table 1. Swedish regulation regarding the distributed drinking water from the plant (Livsmedelsverket, 2001).

	Acceptable with remark	**Not acceptable (Unfit)**
Coliform bacteria	Found (in 100ml)	10 No./100ml
E.coli		Found (in 100ml)
Enterococci		Found (in 100ml)
Clostridium perfringens	Found (in 100ml)	
Heterotr. Platecounts 22º	10 (in 100ml)	

Other parameters that are believed to possible contribute to indirect detection of microbiological contamination are: Colour/Absorbance 436 nm, Turbidity, UV organic material (Extinction) 254 nm, Temperature, pH and Electrical conductivity.

Substantial microbial contamination could cause deterioration of the water quality by contamination of the aquifer due to e.g. persistent protozoa and there is the possibility of transmission of infection by the drinking water due to short travel time for specific abstraction wells (GRP 1, 9 and 11 at the Dösebacka AR plant). The areas of quality management: Sustainable water quality and Sustainable plant operation are therefore affected.

5.3 Testing the early warning system and the management plan with scenario 9

Since there were no possibilities in using wastewater with high concentrations of microorganisms for experiments at the Dösebacka AR plant, the demonstration of the scenario was performed by a “detection identification experiment” in an accredited laboratory. Wastewater was diluted to different concentrations in Göta älv water and analysed with regard to the same parameters that are a part of the measurement station; absorbance 436 nm, turbidity, UV organic material 254 nm, pH and electrical conductivity. The traditional parameter colour was also analysed. Since the simulation was supposed to represent a mix of different influences on the raw water (e.g. run-off and overflows from wastewater treatment plants) the concentrations of wastewater could be quite high compared to the possible concentrations in Göta älv, and chosen to 0,1 %, 1 % and 5 %.

The bacterial concentrations are increased by approximately one log10 when the wastewater concentration increases from 0,1 % to 1 % and app. 1 log10 when the concentration is increased to 5 % (Fig.1). This implies that the concentrations are well above the possible natural concentrations in Göta älv, which are about 2 log10 lower than the most diluted solution.

The tested parameters in the detection identification experiment, responded insignificantly for the two lowest concentrations of wastewater and raw water solutions and they are not above maximal concentrations found in Göta älv in 2004 for the tested solution of 5 % (Fig.2) . The response of the tested parameters increased only marginally with a further increase of sewage concentration and bacterial concentration. Turbidity, absorbance, conductivity and colour showed a greater response; but the response did not increase above the yearly normal variation in Göta älv for situations when the bacterial concentrations are generally much lower than observed in the experiment. The sewage does not affect pH and extinction 254 nm. Since the microorganisms obviously do not influence the parameters, the measurement station will have little possibility to detect microbiological contamination. A similar experiment at the measurement station would give similar results and would not contribute further to the demonstration.

The result show that the instruments in the measurement station does not work satisfactory in detecting and giving alarms for microbiological contamination of raw water. However, periods with maximum bacterial concentration during a normal year in the Göta älav river are often related to periods with high flows in the river and heavy rain. Therefore, the instruments could possibly be used for the detection of microbiological contamination due to exceptional incidents (leakage from manure storage, overflows from damaged wastewater treatment plants, etc) during dry weather periods. This approach was used, even though it was never verified to work, as an example of how an expert function could be developed in DIMS by the formulation of an expert protocol. The protocol in the management plan makes use of the aggregated information from several measured parameters that are collected and evaluated with macros in DIMS. The operator does not need to do advanced calculation on relationships between rain, temp, EC, turbidity, UV253nm etc, but is informed by DIMS about the situation and he/she can now act according to procedure.

The alarm that starts the procedure of monitoring for microbiological contamination constitutes of the different parameters that are slightly affected by wastewater in the detection

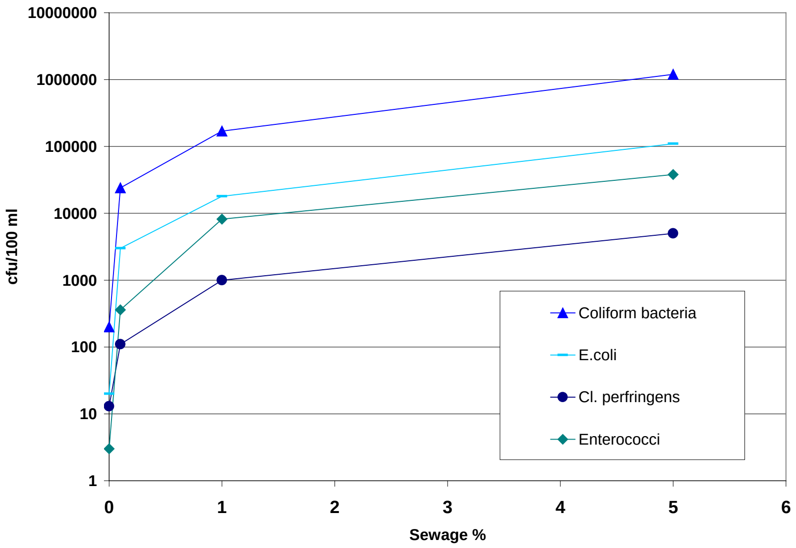

Figure 1. Bacterial concentration in sewage solutions. The 0 %-case is the original Göta älv water.

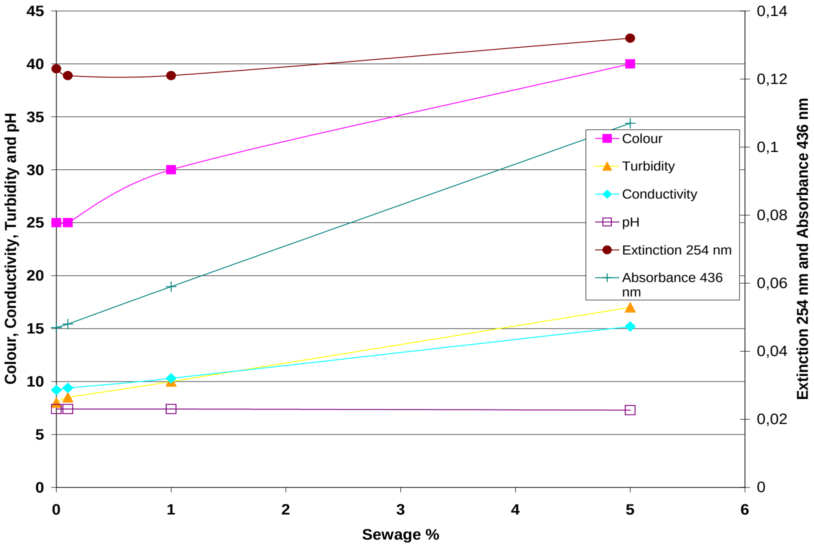

Figure 2. Parameters depending on sewage concentration. The 0 %-case is the original Göta älv water.

identification experiment and rain. If the parameters absorbance, turbidity and conductivity increase and it has not rained an alarm is generated in DIMS. Together with very careful assessment of when the intake should be closed, according to a “worst case” approach, and the robust barrier effect at the plant – the risk scenario can be handled. To further develop the early-warning system an on-line/at-line instrument for detection of microbiological contamination might be a valuable complement to the plant.

The measurement station was tested by the detection identification test, but the complete test of the early warning system was tested fictively and demonstrated in the PowerPoint presentation. The practical procedure at Dösebacka when an incident has happened is shown in the PowerPoint show. The action protocol in the management plan regarding this risk scenario, “5.3 Online water quality monitoring, raw water” and the subprotocol “5.3.2.2 High turbidity (> 20 FNU)” are evaluated and the strategies for normal operation, early warning and barrier removal effect were tested. From these action protocols there are further references to other routine and action protocols according to the build up and thinking of IDAS.

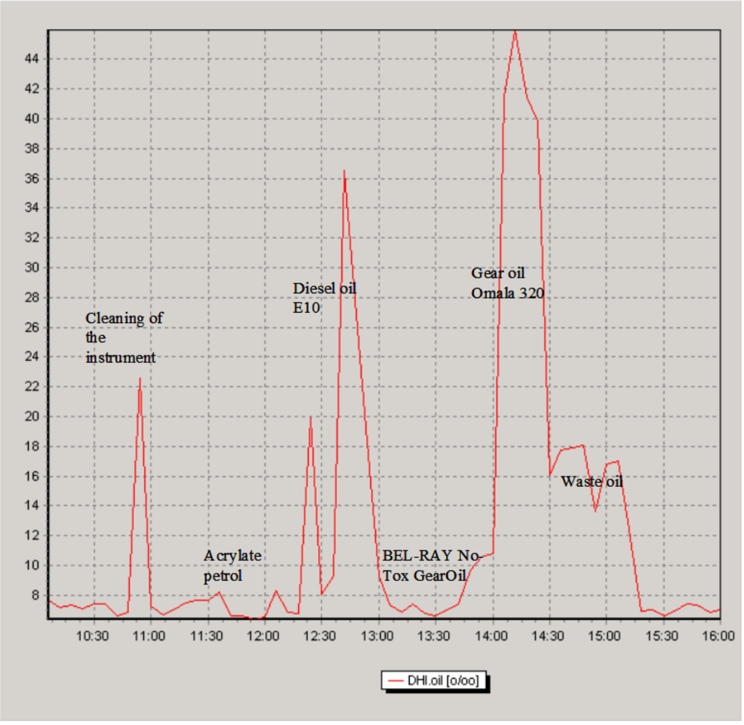

Figure 3. Response from the oil-fluorescence instrument at addition of different oils.

6 SCENARIO 10: CHEMICAL CONTAMINATION OF RAW WATER WITH PETROLEUM PRODUCTS

6.1 *Scenario description and assumptions*

Chemical contamination of the raw water can be caused by several different incidents. There are a number of industries close to Göta älv and in the catchment area and the transport of hazardous substances on the river and close to the river is extensive. Every day there are approximately ten ships travelling on Göta älv, with three of them containing petroleum products or other chemicals. There are about 2-3 reported petroleum discharges per year in the raw water source. They often occur in or close to the harbours during loading and unloading (Wångsell 2004).

6.2 *Critical substances and consequences*

There are quality limits for the drinking water on substances and parameters directly or indirectly related to petroleum products; colour, taste and smell, turbidity, benzene, bens(a)pyrene, and poly aromatic carbons (PAH) (Swedish drinking water regulation - SLV FS 2001:30). The limit on the relative parameter from the oil-phenol fluorescence instrument is set to 10 ‰ according to empirical experience during the last half year.

This scenario is an external scenario, the risk derives from outside the plant but develops to an internal scenario since the surface located processes such sedimentation ponds and infiltration ponds can be damaged as well as there is possible deterioration of the water quality. The aquifer can be ruined by only a small amount of petrol, 1 l in 2•106 l of water is enough to contaminate the water according to U.S. EPA (Nadim 2000). The additives in oil, MTBE and TBA are carcinogenic and a low concentration (10-20 µg/l) can influence the taste and smell of the water. The affected areas of quality management are Sustainable water quality and Sustainable plant operation.

6.3 *Testing the early warning system and the management plan with scenario 10*

Five different types of oil were added to the measurement area of the instrument with tools for 1 µl and 10 µl, with the water flow turned of. After adding the oil it was left for 20 minutes to ensure a sufficient time for the read off. The chemicals tested were: Alkylate petrol, diesel oil (E10), BEL-RAY No-Tox GearOil, Gearoil OMALA 320 and waste oil from a waterworks. These were chosen since they are likely to appear in the Göta älv river, and for the possibility to relate the oils to earlier tests of the instrument. Most of the oils were detected but the result depended on the amount of fluorescing bindings.

The response (Fig.3) show that there was a difference in how the different oils were detected by the instrument. The first peak (app. 22 ‰) is from cleaning the cylinder were the measurements are performed. Alkylate petrol was not detected since the amount of fluorescing bindings is low. Diesel oil, Gearoil OMALA 320 and waste oil were distinctly detected. A limitation to the experiment was the difference in the oil’s viscosity and density which contributed to an uncertainty of the added amount. The oils with large viscosity had a tendency of not releasing from the tool used for adding the oil in the experiment and the detection was therefore smaller.

It should be possible to see concentrations down to 20 µg/l, but it depends on other fluorescing content in the water (discussion with Niels Eisum, April 2005). At Dösebacka the instrument normally shows 5,5-9 ‰ for the raw water. The amounts of oil used in the experiment gave low concentrations of oil, but the alarm in DIMS was set relative to the normal value to indicate when a change from normal values is observed. In the case of an alarm there should be an ocular assessment and further manual water quality samples sent to the laboratory.

The concentration at which the oil becomes a danger to the AR plant depends on several factors, e.g. which type of oil it is and the temperature at which the oil is taken into the process. The raw water intake to the plant was installed approximately one meter below the water surface and as oil mostly is transported on the surface of the water, this arrangement may prevent the oil from coming into the plant.

The measurement station was tested through this test with different oils, but the complete test of the early warning system was tested fictively and is demonstrated in the PowerPoint presentation appended to the final report in the Final Report CD. The practical procedure at Dösebacka when an incident has happened is shown in the PowerPoint show. The action protocol in the management plan regarding this risk scenario, “5.3 Online water quality monitoring, raw water” and the sub protocol “5.3.2.3 Oil-phenol measuring system (>10 ‰)” are used and evaluated and the strategies for normal operation, early warning and closure strategy were tested. From these action protocols there are further references to other routine and action protocols according to the build up and thinking of IDAS.

7 SCENARIO 11: CONTAMINATION OF THE RAW WATER WITH FIBRES, SEDIMENT, CLAY OR ALGAE

7.1 Scenario description and assumptions

The fibres in this scenario can derive from the four paper and pulp industries upstream from Dösebacka waterworks. According to reports of deviations and problems at the paper- and pulp industries along Göta älv, discharge of process water and sludge happens at a frequency of 1-4 times per year. Algae can derive from the raw water and from growth in the sedimentation and infiltration ponds. Increased amount of algae is dependent on season and nutrition concentrations, which are affected by run-off from fertilized land and overflows from wastewater treatment plants. High concentration of sediments and clay can be a cause of landslides of the banks along Göta älv river. The Göta älv valley is a potential risk area due to the geology of the region and several slides have happened in the valley the last 50 years (Wångsell 2004; SGU 2005).

7.2 Critical substances and consequences

The critical substances in this scenario are high amount of fibres, sediment, clay and algae. As for the second scenario there exists a Swedish quality regulation for the drinking water on colour and turbidity, that are related to the substances fibres, algae, sediment and clay. Other parameters at the measuring station that could indicate contamination are particle counting and UV organic material. There are also parameters indirect related to the clogging of the infiltration ponds. One parameter to consider is the ground water level. If the level is lowered for no apparent reason, clogging might be the possible cause. Temperature affects the velocity of the infiltrating water and at low temperatures there should be an awareness of this effect. However, not to be confused with clogging.

This scenario is also an external scenario that develops into an internal scenario since the contamination in this case contributes to a potential clogging of the infiltration ponds. Fibres, algae, humic substances, mud or clay can all contribute to the building up of an impermeable filter skin and eventually the clogging of the infiltration ponds. As the infiltration decreases, the abstraction of water might also have to be decreased to keep the groundwater level at a controlled level. This inflicts on the water production ability of the plant.

7.3 Testing the early warning system and the management plan with scenario 11

The test of the early warning system regarding this scenario was tested fictively and demonstrated in the PowerPoint presentation. The practical procedure at Dösebacka, when an incident has happened, is demonstrated in the PowerPoint show. The action protocols in the management plan regarding this risk scenario, “5.3 Online water quality monitoring, raw water”, “7.3 Regeneration of infiltration ponds” and the subprotocol “5.3.2.2 High turbidity (> 20 FNU)” are used and evaluated and the strategies for normal operation, early warning and regeneration strategy were tested. From these action protocols there are further references to other routine and action protocols according to the build up and the thinking of IDAS.

8 CONCLUSIONS

In general, the management strategy and plan works satisfactory regarding the control of the process at Dösebacka waterworks. The handling of the scenarios by the early warning system is efficient but there are improvements to make. Within the framework of the management plan there is a great possibility of developing and building further action protocols, and to extend the expert system that can be developed to increase the potential of monitoring. Some adjustments have already been made to the early warning system but some have not been possible to carry out within this project.

The use of on-line measurements has been regarded in the ARTDEMO-project as a way of bringing the operators attention to a situation that is deviating from a normal one, not as direct verified information on what has gone wrong or has polluted the water. Generally, especially at the end of the plant process, the alarms from the instruments should be followed up by manually taken water samples in the drinking water to ensure the safety of the end-consumer at the tap. This is relatively satisfied in this version of the management plan but might require an additional pitch for completion.

In the evaluation of the measurement station it has been found that the chosen instruments have major limitations regarding the detection/identification of microbiological contamination. In a future up-dated version of the management plan a different set up of instruments will have to be chosen or developed. If a plant experiences short travel times of the water in the subsurface, it might be an idea to install an at-line microbiological detector (on-line does not exist today). However, the alternative of using an optimised programme for manually taken samples will also probably prove to be sufficient. The choice depends on the plants removal efficiency, which has to be tested for each plant. In the case with Dösebacka it is probably sufficient with a more optimised manual water-sampling programme.

The demonstration of the scenarios and the evaluation of the management plan revealed some missing links between included protocols. A further update of the management plan could include a reference between the protocols about an alarm on high turbidity and regeneration of the infiltration ponds. There should also be updates of the action protocols if the expert system is extended with more alarms. There could also be an improvement to the management plan if an “opening strategy” of the intake was to be defined more explicit, i.e. how, what, and how many manual samples should be taken before the intake can be opened after an incident.

9 ACKNOWLEDGEMENT

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10 REFERENCES

Lundh, M. (2005) Description of the Dösebacka Artificial Groundwater Recharge Plant . (This Final report)

Lundh, M., Engblom, K and Holmström, E (2005a) Introduction of the Management Plan for the Dösebacka AR Plant. This final report.

Lundh, M., Engblom, K and Holmström, E (2005b) Early Warning System at the Dösebacka AR Plant. This final report.

Lundh, M., Engblom, K., Holmström, E., Bennedsen, L., Brandt, G., Linding Berg, R. and Ørbæk Jensen, T. (2005c) IDAS: Connecting the Detection of an Incident with the resulting Action and the follow-up Surveillance in an early warning strategy model. This final report.

Nadim, F., Hoag, G., Liu, S., Carley, R., och Zach, P., 2000. Detection and remediation of soil and aquifer systems contaminated with petroleum products: an overview. Journal of Petroleum Science and Engineering 26 (2000) 169-178

SGU, Statens geologiska undersökning, Skred och Ras, http://www.sgu.se/sgu/sv/geologi_samhalle/skred_s.htm (2005-11-24) (In Swedish)

SLV FS 2001:30 Statens livsmedelsverks föreskrifter om dricksvatten. Swedish drinking water regulations (In Swedish)

Wångsell, Claes, Uppföljning-Avvikelser, VA-verket, Göteborg 1999-2004 (In Swedish)

Interviews:

Niels Eisum, DHI 2005-04-25

Chapter 20: IDAS: Connecting the Detection of an Incident with the Resulting Action and the Follow-up Surveillance in an Early Warning Strategy Model for AR Applications

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Abstract: The production of an early-warning integrated management plan has been a part of the objective of the EC-project ARTDEMO (Artificial Recharge Demonstration Project). The set-up of the management plan and early-warning system have been based on, among other things, a strategy model called IDAS (Incident, Detection, Action, Surveillance), which has been defined in ARTDEMO. The paper presents the structure and function of the model.

1 INTRODUCTION

The production of an early-warning integrated management plan has been a part of the objective of the EC-project Artificial Recharge Demonstration Project (ARTDEMO), EVK1-CT-2002-00114. The overall objective of the ARTDEMO-project was to demonstrate an early-warning system for Artificial Groundwater Recharge plants based on on-line monitoring and information technology (IT), which was to be applied to full-scale plants. The set-up of the management plan and early-warning system have been based on the principal of “follow-the-flow” and a strategy model called IDAS (Incident, Detection, Action, Surveillance), which has been defined in ARTDEMO. This paper describes the early-warning strategy model IDAS.

2 MODEL CONSTRUCTION

The IDAS model suggests a stepwise monitoring and handling of a problem through the plant. The idea of keeping track of a contaminant in drinking water facilities is perhaps not a new approach in water treatment operation but in ARTDEMO the aim has been to introduce the concept to the infiltration application, such as the basin infiltration. The idea is to follow the transport of water through the plant, monitor essential parameters in critical locations in the treatment process, take actions depending on the incident and observe the consequence of an incident or action.

The early warning system is based on the principle shown in the scheme in the IDAS-scheme, see figure 1. The main idea is that the type and location of an incident determine the critical points in the early warning system, i.e. where measurements and actions should be taken. By assessment of the treatment process, the essential points for measuring locations are decided; the early warning procedure is built around this key monitoring locations. The soil passage is considered to be one treatment step among the others.

The activities in the model are:

I: *Incident*

An incident occurs e.g. in the raw water source, which affect one or several of the on-line-monitored parameters.

D: *Detection*

The incident is detected in the monitoring of the raw water source.

A: *Action*

Action is taken.

S: *Surveillance*

An intensified surveillance program comes into action. This program monitors the effects of the incident and taken actions in the subsequent treatment step at the AR plant.

N: *Normalisation*

If there are no effects of the incident in the subsequent treatment step the situation is considered normalised. The condition for normalization could be that the incident did not cause any measurable effects or that the chosen action was proven to be sufficient.

In figure 1 is also a suggestion of at mathematical interpretation of the model, shown as a diagram with a decreasing relative concentration along with the travel time of the substance through the plant. The risk for the consumer increases the closer to the consumer the incident occurs, which means that there is less time for remedy actions. The risk that the consumers are affected by an incident is related to how long time it takes the water to get from the critical treatment step to the tap at the consumer and the possible remedy during that time. The more time available the more time to detect the problem and to take actions, and therefore the smaller the risk that the consumer will experience any water quality deterioration.

The activities performed at the locations defined in the scheme (list number refers to column number in the IDAS-scheme):

1. Raw water source
2. Measurement in raw water source or reporting of incidents
3. Intake facility to the plant
4. Measurement in incoming water in the water intake arrangement
5. Pre-treatment units such as settling, rapid filtration, oxidation ponds, infiltration ponds, etc.
6. Measurement in pre-treatment units or reporting of incidents.
7. System connected to the geological formation (infiltration, aquifer, abstraction)
8. Measurement in abstraction well water or reporting of incidents
9. Post treatment at the plant, such as oxidation ponds, filtration, chemical precipitation, etc.
10. Measurement in treated water or reporting of incidents
11. Distribution system
12. Measurement in the consumers tap or reports from consumers.

3 AN EXAMPLE FOR DEMONSTRATION

To demonstrate IDAS the following example from Dösebacka is presented. The activity locations are presented in row 2 in the scheme given in figure 1. As can be seen in the IDAS-scheme in figure 1, an incident (I) might occur in the Göta Älv river (column 1). Lets say that due to heavy rain (the incident) the concentration of bacteria increases as the fields with tame animals are drained into the river and up-stream located wastewater treatment plants deliberately by-passes wastewater into the river in order to save the function of the wastewater treatment plants. In the system at the Dösebacka AR plant, the increased concentration could be indirectly detected (D) with a redox electrode in measurement stations located up-stream the river (column 2). The information from the measurement stations alerts the operator through the DIMS-system (not applied in the ARTDEMO project) and the operator can now choose to close the intake (A), or closely monitor (S) the plug of pollution as it is transported in the Göta Älv down towards the intake of Dösebacka, and also in the intake to Dösebacka. If the concentration of bacteria still is high in the intake, due to an action of not closing the intake, the detection of the high levels of bacteria is now bringing the pollution management procedure down to the next row and the incident – open intake - which has caused a detection of high levels of bacteria in the intake water (column 3), and so forth.

IDAS – Scheme

1	2	3	4	5	6	7	8	9	10	11	12
Raw water	**Monitoring**	**Raw water intake**	**Monitoring**	**Pre-treatment**	**Monitoring**	**Water in Aquifer**	**Monitoring**	**Post treatment**	**Monitoring**	**Distribution**	**Monitoring**
I	**D**	**A**	**S**	**N**	**N**	**N**	**N**	**N**	**N**	**N**	**N**
		I	**D**	**A**	**S**	**N**	**N**	**N**	**N**	**N**	**N**
				I	**D**	**A**	**S**	**N**	**N**	**N**	**N**
						I	**D**	**A**	**S**	**N**	**etc**

I = Incident, D = Detection, A = Action, S = Surveillance, N = Normalisation

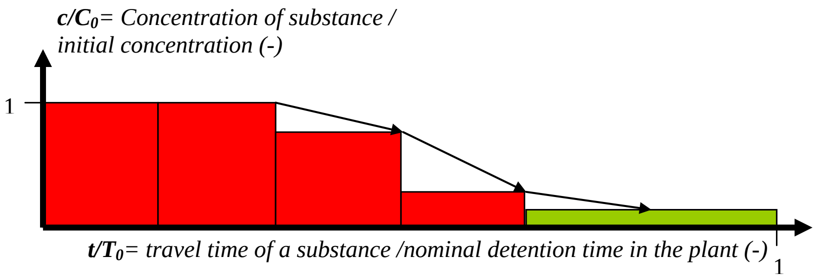

Figure 1. The IDAS scheme (above) and a diagram suggesting how the model could be interpreted in mathematical terms by using the relative concentration of the critical substance (c/C0), the removal efficiency in specific parts of the plant and the relative travel time(t/T0) of the water through the plant.

Chapter 21: Early Warning System at the Dösebacka AR Plant

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Abstract: The overall objective of the ARTDEMO-project has been to demonstrate an early-warning system for AR plants, based on on-line monitoring and information technology, which was to be applied on a full-scale plant. This paper presents the early-warning system that was applied to the Dösebacka AR plant. The system consisted of existing monitored data from the plant, a measurement station that measured water in different locations with the same instruments according to the early-warning strategy model IDAS and a software for data storage, data handling and expert analysis.

1 INTRODUCTION

The overall objective of the ARTDEMO-project (EVK1-CT-2002-00114) has been to demonstrate an early-warning system for Artificial Groundwater Recharge plants, based on on-line monitoring and information technology (IT), which was to be applied on a full-scale plant. Subsequently, two early-warning systems has been built for the test sites Dösebacka and Arrenæs. Each system has been constructed to meet the special requirements at the specific plant, depending on e.g. raw water source and localisation. The Dösebacka plant is situated on the shore of the river Göta Älv in Sweden and abstracts water from a confined aquifer that reaches down under the river itself. The raw water comes from the same river. Arrenas is situated on a peninsula in the lake Arresø, using the lake as raw water source. This paper will describe the early warning system set up at the Dösebacka AR plant.

The early warning system was built on the idea of monitoring the parameters that were considered to be critical to the plants objective. In order to be in control of the plant, the contamination should be detected wherever it appears before and inside the plant, making it possible to take the correct action in preventing the contamination to reach the consumer. Therefore an early-warning strategy model, IDAS (Incident, Detection, Action, Surveillance), was developed (Lundh et al 2005) to be use in the work of producing the management plan and consequently the early warning system of the plant.

First, the site is briefly described. Thereafter there is a presentation of the management strategy of the plant and the rationale for the choice of parameters that were used in the monitoring. The components of the system is then described and finally a summary concludes the paper.

2 GENERAL DESCRIPTION OF THE AR PLANT IN DÖSEBACKA

The Dösebacka Artificial Recharge plant is located in south-west of Sweden. The plant is the water supply for 25000 inhabitants in the community of Kungälv. The plant produces approximately 6000 m3/d and consists of 9 infiltration ponds and 15 abstraction wells. The detention time for the water in the aquifer has been estimated to vary between 6 to 60 days depending on abstraction well. The water is pre-treated with sedimentation and the drinking water is pH-adjusted with NaOH for corrosion prevention in the distribution system. Two wells that abstract water with a higher turbidity and organic content, are post-treated with chemical precipitated using aluminium sulphate. The plant has equipment for disinfection of the drinking water in case of an emergency with microbiological contamination but it is rarely used. For more details about the Dösebacka plant, the reader is advised to the site description (Lundh 2005) in this final report.

3 MANAGEMENT STRATEGY

The overall objective of a management plan, as defined in this study, is to give directives for the management of the plant to ensure that the right quantity of water is produced with the right quality, which also includes preventing the plant from damage – a crucial issue when it comes to groundwater and artificial recharge. This could be summarized in the following quality management:

- Sustainable water quality (SWQ) - meaning maintaining a continuous, good water quality according to regulations

- Sustainable water production (SWP) - meaning maintaining a continuous water production according to community requirements
- Sustainable plant operation (SPO) - meaning protecting the plant from unmanageable damage.

Considering the objectives of the management, the management strategy should thus be:

- to equip the plant with the right tools for monitoring and control.
- to produce routine protocols that instruct the operators at the plant how to handle the daily operation.
- to produce action protocols that instruct the operators at the plant how to handle alarm situations.
- to monitor the plant operation and water quality with a sufficient frequency so that a quality deterioration, or an event that could cause problems that inflict on the production demands, or an event that would severely damage the plant for a long time, will be detected in time for the plant operation to take action to ensure a safe and reliable drinking water production.

4 DESCRIPTION OF THE RELEVANT PROBLEMS AND HOW THE SYSTEM REACTS

So what are the risk contaminations for the Dösebacka? A risk analysis of Dösebacka Waterworks (Engblom 2005) identified several potential scenarios. Parts of the thesis is presented in the ARTDEMO Final report (Engblom et al. 2005). The results from the risk analysis gave input on how the management strategy should satisfy the monitoring need with the set-up of instruments and IT arrangement. The study had to be limited down to a few risk scenarios in order to optimise the time and project resources, even though the risk analysis resulted in several risk scenarios with consequences that are of significance and are most likely to cause problems at some time for the Dösebacka plant, and which the management of the plant has to be capable of handling. In the choice of scenarios to follow up, the focus was set on the early-warning strategy including mainly water quality deterioration, that were to be tested in the project. The risk assessment is described more in detail in Engblom et al (2005) in this final report. The three chosen risk scenarios that were tested for Dösebacka are (quality management in brackets, see Management Strategy):

1. Microbiological contamination of raw water (SWQ, SPO)
2. Chemical contamination of raw water with oil (SWQ, SPO)
3. Clogging of infiltration ponds (SWP)

Consequences and remedy feasibility of the three scenarios:

1. Pathogenic virus, bacteria, protozoa
    a. Possible contamination of the aquifer due to e.g. persistent protozoa (difficult remedy)
    b. Possible transmission of infection due to short detention time for specific abstraction wells (action possible)
2. Petroleum products
    a. Damaging surface located processes such sedimentation basins and infiltration ponds (manageable remedy)
    b. Damaging the aquifer (difficult remedy)
    c. Possible deteriorating water quality (action possible)
3. Fibres, algae, humic substances, mud or clay, impermeable filter skin
    a. Clogging of infiltration basins (easy remedy)
    b. Reduced water production (actions possible).

Remedy refers to the actions needed to bring the plant into operation after an incident that damages the plants treatment function. Action (as in action possible) refers to those actions needed to prevent water with bad quality to reach the consumer. The definition of easy remedy refers to a situation when it is possible to take actions within a reasonable time span and budget. If e.g. the infiltration pond is clogged with fibres or silt particles or if the filter skin becomes impermeable, the pond can be taken out of operation and the top-layered filter material can be either removed or cleaned. The definition of manageable remedy refers to a situation when it is possible to take actions, but the actions might require considerable time and cost in order to accomplish the remedy. If the infiltration pond is polluted with oil in the top layers of the filter bed, the pond can be taken out of operation and filter material can be removed and replaced with new material. However, if the incident were of a more severe character, if e.g. the contaminant had penetrated deep down (several meters) into the filter bed, the remedy might require that large amounts of material were replaced, which is costly and time consuming. The definition of difficult remedy refers to a situation when it is very difficult or impossible to take actions within reasonable time and for a manageable cost to accomplish the remedy.

5 DEFINITION OF RELEVANT PARAMETERS

Parameters that were used for the detection of the defined critical scenarios were:

1. Pathogenic virus, bacteria, protozoa
   a. On-line Colour
   b. On-line Turbidity
   c. On-line UV organic material
   d. On-line Temperature
   e. On-line pH
   f. On-line Electrical conductivity

2. Petroleum products
   a. On-line Oil fluorescence

3. Fibres, algae, humic substances, mud or clay, impermeable filter skin
   a. On-line Colour
   b. On-line Turbidity
   c. On-line Particle counting
   d. On-line UV organic material
   e. On-line Temperature
   f. Valve manoeuvre
   g. nfiltration rate
   h. On-line Monitored ground water level

Parameters 3f and 3g are today not on-line measured as there are no instrumentation for that purpose. However, it is fairly easy to implement them into the system.

6 COMPONENTS OF THE EARLY WARNING SYSTEM

In accordance to the management strategy the following components were used to build up the early-warning system:

1. A measurement station that made possible a monitoring of the water quality according to the early-warning strategy model IDAS
2. A system for data handling and expert analysis, DIMS, that was connected to the existing SCADA system (Cactus) at the plant. The system enabled a systematic display of the monitored parameters and made possible expert functions for the analysis of the data.
3. Data that were logged from equipment and instruments in the monitoring system that existing on the plant before the ARTDEMO project started.

7 ON-LINE MONITORING AT THE DÖSEBACKA AR PLANT

An intermittent on-line measurement station (Fig.1) monitored the water quality on several locations in the system at the plant (Fig.2 and 3). The idea was to cover several important process steps according to the strategy model IDAS (Lundh et al. 2005) in order to follow a contaminations transport through the plant and the effect of actions in preventing it from reaching the consumer (example of measured time in brackets):

1. Raw Water Göta Älv (4h)
2. North (4h)
3. South (4h)
4. Raw water Göta Älv (4h)
5. Well 9, which also covered well 11 (4h)
6. Distributed Drinking Water (4h)

The water monitored was pumped from the incoming pipes to the measurement station. The instruments covered pH, Electric conductivity (EC), Oxygen, Turbidity , Temperature, Particle count (1-2, 2-15, 15-50, >50 nm), UV-absorbance at 254 nm (organic substance), Absorbance (colour) at 436 nm and Fluorescence for oil.

Figure 1. The measurement station in Dösebacka.

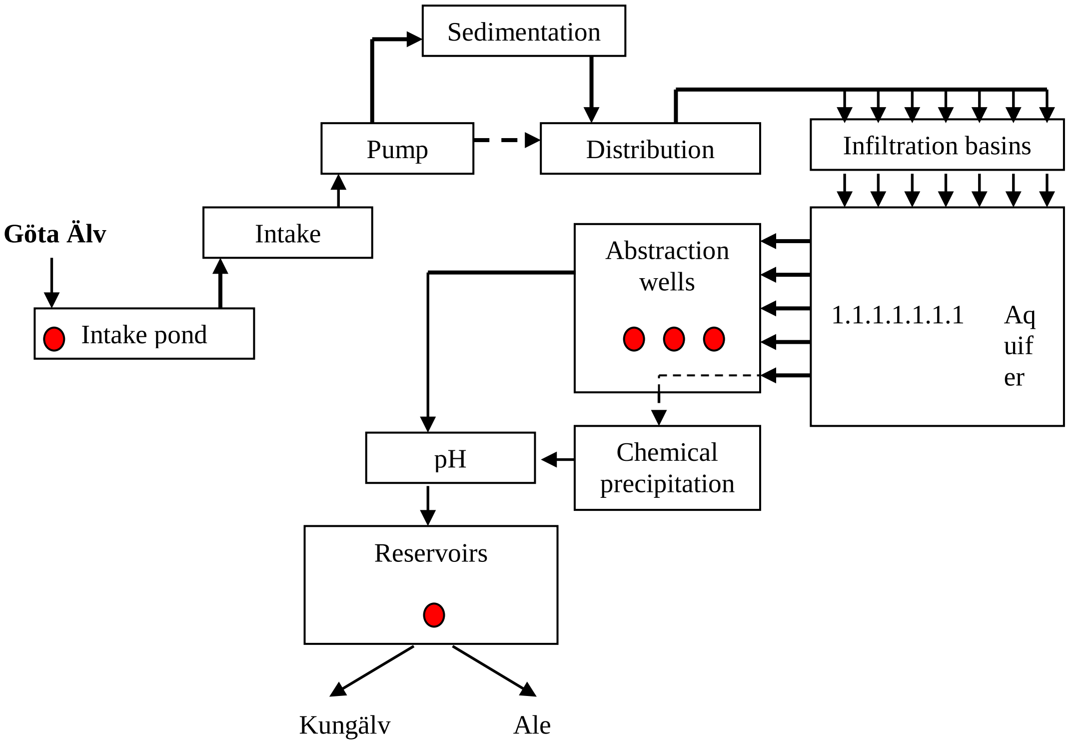

Figure 3. The process scheme at the Dösebacka AR plant. The location where water is monitored is shown with red dots.

As the ARTDEMO measurement station only monitor pH and turbidity on-line for certain periods (intermittent) the stations did not meet the Swedish regulation on on-line monitoring of pH and turbidity in the finally produced drinking water. The regulation was satisfied by using the existing on-line monitoring at the plant that complemented the measurement station.

The on-line monitoring was used as an attention calling function, meaning that the parameters were considered as indirect indicators of contamination that need to be verified by standardised analysis methods in the laboratory. Parameters that deviate below or above the limits set for that specific parameter is a signal for starting an action. The type of deviation determines what action to be taken, for example if there are required changes in the process, closing of the intake, additional manual sample takings, instrument calibration or other checks, etc. The manual samples are sent to an approved accredited laboratory, which make the evaluation according to the Swedish drinking water regulations.

8 DATA COLLECTION AND FOLLOW UP AT THE DÖSEBACKA AR PLANT

Nearly 200 different parameters are registered in DIMS from Dösebacka. The details of the system is described elsewhere in this final report of ARTDEMO. The data, an average value over 6 minutes, was stored in the local SCADA-system, Cactus, and transferred automatically every hour by the SCADA system via a router to the Gothenburg network. The data were stored in the DIMS server located in Gothenburg and from which the operators/managers of the plant can reach the DIMS application by DIMS-clients on their personal computers. DIMS was arranged with a lay-out that worked for the monitoring of the Dösebacka plant and adjusted according to the management strategy and plan.

The arrangement of locating the data equipment in Gothenburg was a project-related solution as the project was performed by others (GR) than the plant owner. If the owner of Dösabacka would have the system installed, the equipment would naturally be placed in Kungälv municipality. The system set-up nicely demonstrates the possibility of arranging a remote-controlled system for infiltration plants.

9 SUMMARY

The system of the early warning system at the Dösebacka MAR plant demonstrated in the project ARTDEMO, was based on an early-warning strategy model, IDAS, and constituted of on-line instruments, a monitoring computer based system and a software, DIMS, for

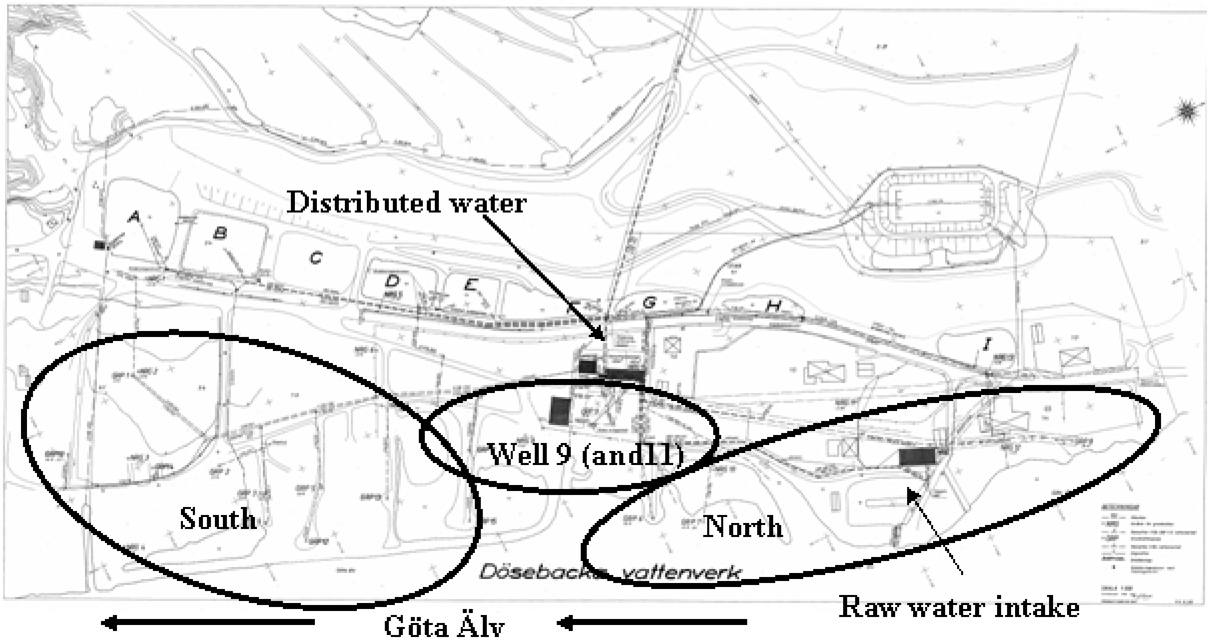

Figure 2. Spatial distribution of the monitoring at the Dösebacka AR plant

handling data and expert system. The on-line instruments were used for monitoring in several crucial locations at the plant in order to cover the transport of a potential contamination throughout the plant. Consequently, the on-line monitoring for a certain water was interrupted on a regular basis and has thus to be considered intermittent. When regulation requires on-line monitoring, other on-line instruments have to complement the system. However, the arrangement made possible the use of the same instruments for monitoring of several locations separated apart by a great distance. The data from the instruments was saved in the existing monitoring and control system at Dösebacka and subsequently delivered to the DIMS system. The DIMS was arranged with a lay-out that worked for the monitoring of the Dösebacka plant and adjusted according to the management strategy and plan.

10 ACKNOWLEDGEMENT

The authors would like to thank the personnel at the Dösebacka AR plant for their assistance during the study.

11 REFERENCES

Engblom, K. (2005) Risk analysis of the Dösebacka Waterworks, Master Thesis at KTH, Stockholm, Sweden.

Engblom, K., Lundh, M. and Holmström, E. (2005), Scenario management and expert system for the Dösebacka AR plant. This Final Report.

Lundh, M (2005) Description of the Dösebacka Artificial Groundwater Recharge Plant. This final report.

Lundh, M., Engblom, K., Holmström, E., Bennedsen, L., Brandt, G., Linding Berg, R. and Ørbæk Jensen, T. (2005) IDAS: Connecting the Detection of an Incident with the resulting Action and the follow-up Surveillance in an early warning strategy model, This final report.

Chapter 22: Early Warning System at the Arrenæs Artificial Recharge Trial Plant

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Abstract: At the Arrenæs AR trial plant, an early warning system has been installed as a part of the ARTDEMO project. A management strategy for the AR plant together with identification of possible risk to the sustainability of the AR plant formed the basis for setting up the early warning system at Arrenæs AR trial plant. This early warning system includes both off- and online monitoring, which is collected, reported and validated in the data handling system DIMS (Dynamic Integrated Monitoring System). It has been demonstrated that online monitoring is an efficient tool in the management of the AR plant. Real-time data on water quality and water quantity are accessible and can be used to optimise the operation of the AR plant and to avoid unexpected contamination events affecting the sustainability of the AR plant. Online monitoring of the water flow at the Arrenæs AR trial plant is performed in all parts of the plant. On-line monitoring of water quality is performed on the intake water from Lake Arresø. This early warning system is, however, not sufficient to cover the transport of a potential contaminant through the AR plant. In a production situation, it is therefore important to complement the existing early warning system at the Arrenæs AR trial plant with additional on-line instruments measuring water quality in other parts of the AR plant.

1 INTRODUCTION

A system for early warning and follow up has been established at the ARTDEMO demonstration site Arrenæs AR trial plant, Denmark. The aim has been to develop a surveillance system, where both water quality and water quantity are closely monitored to obtain the most stable and secure production of artificially recharged water from the AR plant. Thus at the site, the necessary monitoring equipment and data handling system have been installed to obtain an efficient early warning system based on an early warning model called IDAS (Incident, Detection, Action, Surveillance). The IDAS model is described in more details in Lundh et al. (2005a). The early warning system for the Arrenæs AR trial plant has subsequently been tested as a part of the expert system described in Berg et al. (2005).

The planning tools used in the establishment of the early warning systems have been developed through a close cooperation between the ARTDEMO personal from Gothenburg Region Association of Local Authorities (GR) in Sweden and Copenhagen Energy (KE) in Denmark. Thus the same tools are used for both Dösebacka AR plant and Arrenæs AR trial plant even though the two sites are characterised by having different raw water sources. The general construction of the tools makes the process of establishing an early warning system at any AR plant straightforward, as described in this present paper for the Arrenæs AR trial plant and in Lundh et al. (2005b) for the Dösebacka AR plant.

This paper presents the process of defining and establishing an early warning system for the Arrenæs AR trial plant followed by a description of the established early warning.

2 GENERAL DESCRIPTION OF THE ARRENÆS AR TRIAL PLANT

The Arrenæs Artificial Recharge (AR) trial plant located at the Arrenæs peninsular in the northern part of Zealand, Denmark is a preliminary test site for a proposed large-scale AR plant for drinking water production at the same locality. The AR trial plant was established in 1994 and has been functioning since 1995. KE runs the plant.

In figure 1, one of the four infiltration basins (in total 4,000 m^2) and the sprinkling area (in total 20,000 m^2) is shown. The AR trial plant also includes two trough systems (in total 2,000 m^2).

The Arrenæs AR trial plant is recharging water from Lake Arresø, which has a water volume of 123 million m^3 and an annual discharge of 30-65 million m^3. Lake Arresø is surrounded by agricultural land and no industries are located close to the lake. Point source pollution is therefore not an immediate threat to Lake Arresø and the Arrenæs AR trial plant. However, diffusive pollution from the agricultural activity might be a threat to the AR plant when recharging the lake water, due to the risk of contamination of the unsaturated zone and the recharge aquifer.

Figure 1: Infiltration basin West 1 and the sprinkling area at the Arrenæs AR trial plant.

The infiltration capacity of the AR trial plant is 350,000 m^3/year. The abstracted water is presently not used for drinking water purposes but is instead led back to Lake Arresø.

The water quality through the system has been monitored continuously since 1994 by manual collection and analysis of water samples from the intake to the AR plant, from the unsaturated zone (T1-T12), from the monitoring wells (I2, M2, M3, and M4), and from the abstraction wells (I1, M1, I3, and DGU186.564), see Figure 2. For detailed information on the Arrenæs AR trial plant, see the site description in Bennedsen et al. (2005) within this Final Scientific Report.

3 MANAGEMENT STRATEGY

The quality of the management of an artificial recharge plant can be summarized in the following three important issues, which was defined within the ARTDEMO project:

- Sustainable water quality (SWQ) - meaning maintaining a continuous, good water quality according to regulations
- Sustainable water production (SWP) - meaning maintaining a continuous water production according to community requirements
- Sustainable plant operation (SPO) - meaning protecting the plant from unmanageable damage.

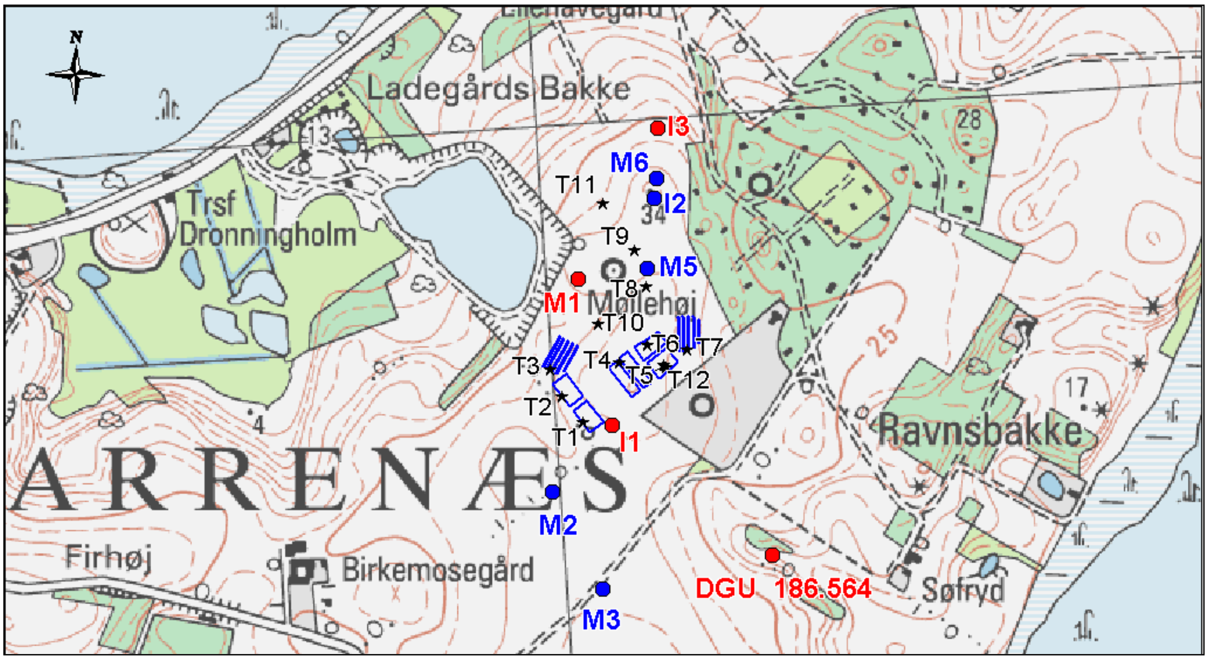

Figure 2: The Arrenæs AR trial plant (red dots indicate location of abstraction wells, blue dots give the location of monitoring wells, and black stars indicate location of tensiometer wells)

The management of the Arrenæs AR trial plant is based on these three quality issues. The management strategy for the Arrenæs AR trial plant is formulated as follows:

1. Water Quality Management Strategy for AR plants (WQMS-AR): *The main aim of the WQMS-AR is to achieve a sustainable use of the aquifer at the AR plant by a continuous, online monitoring of water quality in intake water and abstracted water – as a minimum. In this way it must be ensured that water quality regulations are always fulfilled, that water quality in the aquifer is not deteriorating, and that unmanageable damage to the recharge area and aquifer is not occurring.*

2. Water Production Management Strategy for AR plants (WPMS-AR): *The objective of the WPMS-AR is to enhance a sustainable production of artificially recharged groundwater for drinking water purposes by a plant operation that ensures a constant water production and a stable water flow through the plant by use of online monitoring equipment to monitor the water flow in all parts of the MAR plant. In this way it is assured that the amount of abstracted artificially recharged water is not exceeding the amount of water infiltrated.*

This management strategy is a reformulation of a preliminary management strategy formulated on basis of the operation of Arrenæs AR trial plant prior to the ARTDEMO project. The elaboration of the management strategy is discussed in Nielsen et al. (2005). The management strategy encourages the use of online monitoring, as it was realized through the experiences of setting up the early warning system described in this paper and the work with the elaboration of the management plan described in Nielsen et al. (2005), how important and valuable online monitoring is to the management of the AR plant.

4 DESCRIPTION OF THE RELEVANT PROBLEMS AND HOW THE SYSTEM REACTS

Within the ARTDEMO project, all thinkable risks (both internal and external) towards Arrenæs AR trial plant were identified (Berg et al., 2005). The background for this identification was the knowledge from 10 years of operation of the AR trial plant, and the problems that have arisen during this period.

For Arrenæs AR trial plant, three risks were selected as the most critical. Each of the risks affects one or more of the three important quality management areas defined during the formulation of the management strategy. A detailed discussion of the risks is given in detail in Berg et al. (2005). However, it should be stated that all the defined risks are of significance, and are most likely to cause problems at some time at the Arrenæs AR trial plant. The selected risks are:

- Power failure, general power cut at the AR plant area (SWP)
- Increased amount of algae in the raw water source (SWP, SPO)
- Production of algae toxins in the raw water source (SWQ, SWP, SPO)

The following lists the possible consequences to the Arrenæs AR system for the three selected risks:

<u>Power failure</u>

a. No water is recharged from lake Arresø
b. No water production

<u>Increased amount of algae in the raw water source</u>

a. Clogging of the infiltration basins
b. Reduced water production

<u>Production of algae toxins in the raw water source</u>

a. Contamination of the clogging layer in the infiltration basins with algae toxins
b. Break through of algae toxins in the groundwater and thereby possible deteriorating quality of the abstracted water.

In the present operation of the Arrenæs AR trial plant, water production stops in a power failure situation. From the risk “Power failure”, it was found in Berg et al. (2005) that an emergency power supply could be installed to limit the consequences of a power failure and ensure a stable water production from the AR plant. However, as the cause of a total power failure at the AR plant is assumed to be external, the risk is not dealt with in more detail here.

By evaluating the risks “Increased amount of algae in the raw water source” and “Production of algae toxins in the raw water source”, a need for a continuous online monitoring of the water quality through the AR system was identified, as manual monitoring of the water quality is not adequate to ensure the sustainability of the AR plant. Online monitoring of the water quality will be a useful tool in the management of the AR plant, as it will be possible to have an early warning of a given risk to the plant. E.g. a fluorescence sensor can warn about an increased amount of algae in the raw water source and thereby clogging of the infiltration basins can be prevented, as it is possible for the operator to take action and close the intake.

Online equipment measuring the water flow through the AR system is also found to be very useful in managing the AR plant. Having real-time quality data of the water flow through the plant, makes it possible for the operator to have an overview of the operation, and in this way it is easier to control the operation and e.g. prevent an unintended clogging of the infiltration basins.

5 DEFINITION OF RELEVANT PARAMETERS

Parameters used in the detection of the defined critical risks, “Increased amount of algae in the raw water source” and “Production of algae toxins in the raw water source”, are:

<u>Algae</u>

a. On-line fluorescence
b. On-line temperature
c. On-line pH
d. On-line oxygen
e. On-line monitored water flow to infiltration basins
f. On-line monitored water level in infiltration basins

<u>Algae toxins</u>

a. On-line fluorescence
b. On-line temperature
c. On-line pH
d. On-line oxygen
e. Off-line algae toxin measurements

6 COMPONENTS OF THE EARLY WARNING SYSTEM

The management strategy together with an identification of risks to Arrenæs AR trial plant formed the basis for identifying the components that were used in building up the early warning system for the Arrenæs AR trial plant. To establish an efficient early warning system at the Arrenæs AR plant, online monitoring of both water flow and water quality were of decisive importance. The functions within the system at the Arrenæs AR trial plant include:

1. A measurement station monitoring the quality of the intake water from Lake Arresø.
2. Pressure transducer in Thompson overflows measuring the water level from which the flow to the infiltration basins and troughs are calculated.
3. Pressure transducers in the infiltration basins monitoring water level.
4. Pressure transducers in the abstraction wells monitoring water level and flow.
5. A weather station.
6. A system for data handling and expert analysis, DIMS (see chapter 8: Data collection and follow up at the Arrenæs AF Trial Plant), automatically collects data from the online installations at Arrenæs AR trial plant, thereby enabling a systematic display of the monitored parameters, data aggregation, data validation, automatic calculations, and alarm handling.
7. Manual inputs from the plant operator (operation journal).
8. Transfer of relevant data from the water quality database (VKD) within Copenhagen Energy to the DIMS database.
9. Automatic reporting of data to the Arrenæs web page on the internal network within KE.

The system for early warning includes both online monitoring of water flow and water quality and a system for data handling. As a part of the early warning system for detection of contaminants at Arrenæs AR trial plant, continuous online monitoring of selected parameters in the intake water is an important management tool and it is of decisive importance to the operation of the AR plant, because pollution incidents in the lake, seasonal variations in the content of e.g. organic matter, and the general quality of the lake water may affect the operation of the AR plant. By monitoring both water quantity and quality, it is possible to make a fast response in case of unexpected findings in e.g. the intake water, as the amount of water led to each part of the plant is controlled.

To ensure an optimum operation and to avoid pollution of the AR plant, it is necessary, besides online monitoring, to collect and analyse water samples continuously from the intake. At present, manually collected water samples are analysed once a month for algae toxins and pesticides; twice a year for general geochemical parameters, trace elements and microbiology; and once a year for organic micro pollutants. The frequency of analyses is in some ways different from a production plant, since the monitoring consists of a limited normal monitoring program extended with a number of special investigations with close monitoring of specific parameters.

7 ON-LINE MONITORING AT ARRENÆS AR TRIAL PLANT

During the establishment if the early warning system at the Arrenæs AR trial plant within the ARTDEMO project, online monitoring of water flow through the AR plant was expanded, and online monitoring of water quality was introduced. Further, the AR plant was equipped with the automatic data collection and reporting system DIMS (Dynamic Integrated Monitoring System).

7.1 On-line monitoring of the water flow through the AR plant

The online monitoring of water flow through the Arrenæs AR trial plant includes: Flow in the intake well from Lake Arresø pumping the water to the AR plant, flow to infiltration basins, flow to trough systems; flow to sprinkling area and amount of water abstracted from abstraction well I1, I3, M1, and DGU186.564. In addition, water level is online measured in infiltration basins and abstraction wells I1, M1, and DGU186.564. A number of online alarms are defined at the AR plant and include: Alarm on water level in intake well, alarm on pumps in the intake well, alarm on sprinkler pumps, alarm on overflow, and operation of and alarm on pumps in abstraction wells. Some of the online sensors were installed at the Arrenæs AR trial plant during the ARTDEMO project. This include pressure transducers in Thompson overflows, pressure transducers in infiltration basins, and a weather station giving information on temperature, soil temperature, precipitation, barometric pressure, relative humidity, solar radiation, wind direction and wind speed. Photos of these new installations are given in figure 3.

The online measurements and alarms are in general used to improve the daily operation of the plant and handle possible alarm situations. Online measurements in the Thompson overflows are used to determine the flow to each of the infiltration basins and the trough systems. Together with water levels measurements in the infiltration basins, it is possible to control the water flow through the system. E.g., in an alarm situation where a pollutant is introduced to the AR plant, damage to the AR plant can be minimised, as the water flow through the plant can be controlled online.

7.2 Online monitoring of water quality at the AR plant

Within the ARTDEMO project, an online monitoring unit measuring the quality of the intake water from Lake Arresø was installed in sedimentation basin east in the immediate vicinity of the intake of the lake water, see figure 3. The monitoring unit measures oxygen, pH, electric conductivity, fluorescence, and temperature, and the online data is collected using the DIMS system. This makes it possible to have an indication of e.g. peaks of algae, as fluorescence is a measure of the chlorophyll content in the intake water and thereby an indirect measure of the amount of algae. Measurements of algae are important in the operation of the plant, as e.g. a fluorescence sensor can warn about an increased amount of algae in the raw water source, and thereby clogging of the infiltration basins or clogging of the filters in the sprinklers can be prevented, as it is possible for the operator to take action and close the intake. Additionally, if the fluorescence measurements are combined with measurements of algae pigment, the presence and content of toxic producing algae can be estimated, and contamination of the AR site with algae toxins can thereby avoided.

The early warning system at the Arrenæs AR trial plant is summarised in the flow scheme given in figure 4, where the boxes with red outline indicate locations with online monitoring at the AR plant.

8 DATA COLLECTION AND FOLLOW UP AT THE ARRENÆS AR TRIAL PLANT

The monitoring and data handling system at the Arrenæs AR trial plant is based on DIMS. The integrated management tool DIMS was been adopted to fit the specific requirements at the Arrenæs AR plant, and it is used to semi-automatically control the operation based on available information for the Arrenæs AR plant. The information system supports all the existing components of the monitoring system at the AR plant and allows for use of online as well as offline data. The application of the system to an AR plant was a part of the ARTDEMO project, and it is described in more detail in Lynggard-Jensen et al. (2005).

In DIMS, 3187 time series for water quality parameters and water flow exist including 238 parameters at 73 locations, hereof 59 online. The time series for offline data is for most of the parameters available for the time period from 1995 until today, as a large number of historical data from the Arrenæs AR plant were transferred to DIMS during the process of building up the DIMS database within KE.

At the Arrenæs AR plant, all online data signals are collected using DIMS. Also the manual inputs from the plant operator group are added to DIMS by using a "key in" function within DIMS. The data processed at the AR plant is communicated via the local PC at Arrenæs to the DIMS server on the internal network of KE. This online storage of data on the DIMS server is performed every minute for the water level and flow data. For the water quality measurement station, measurements are performed every tenth seconds and an average of these values is stored locally in the data logger in the measurement station every fifth minute. Water quality data is transferred directly to the DIMS server within KE once every day - in a production situation, data should be transferred directly to DIMS every fifth minute. Meteorological data is stored locally in the weather station every minute and averaged over ten minutes. Data is transferred to DIMS every hour. The results of the analyses of the water samples manually collected at the Arrenæs AR plant are entered into the water quality database (VKD) within KE. Once every week, this database is synchronised with DIMS.

Through the ARTDEMO project, the DIMS system for Arrenæs AR trial plant was continuously extended with new functionalities that include: Configuration of user interface, measurements and reports; data validation; data storage; automatic calculations; alarm handling; data validation and control. In last phase of the ARTDEMO project, an operational orientated management system including alarm handling was constructed within DIMS based on the results from the evaluated management plan. This coupling is described in Nielsen et al. (2005).

The staff within KE has access to the DIMS application through a DIMS client installed locally the personal computer. The online data within the DIMS database is also available at the web site (http://teams.dhi.dk/ARTDEMO/) for all partners within the ARTDEMO project.

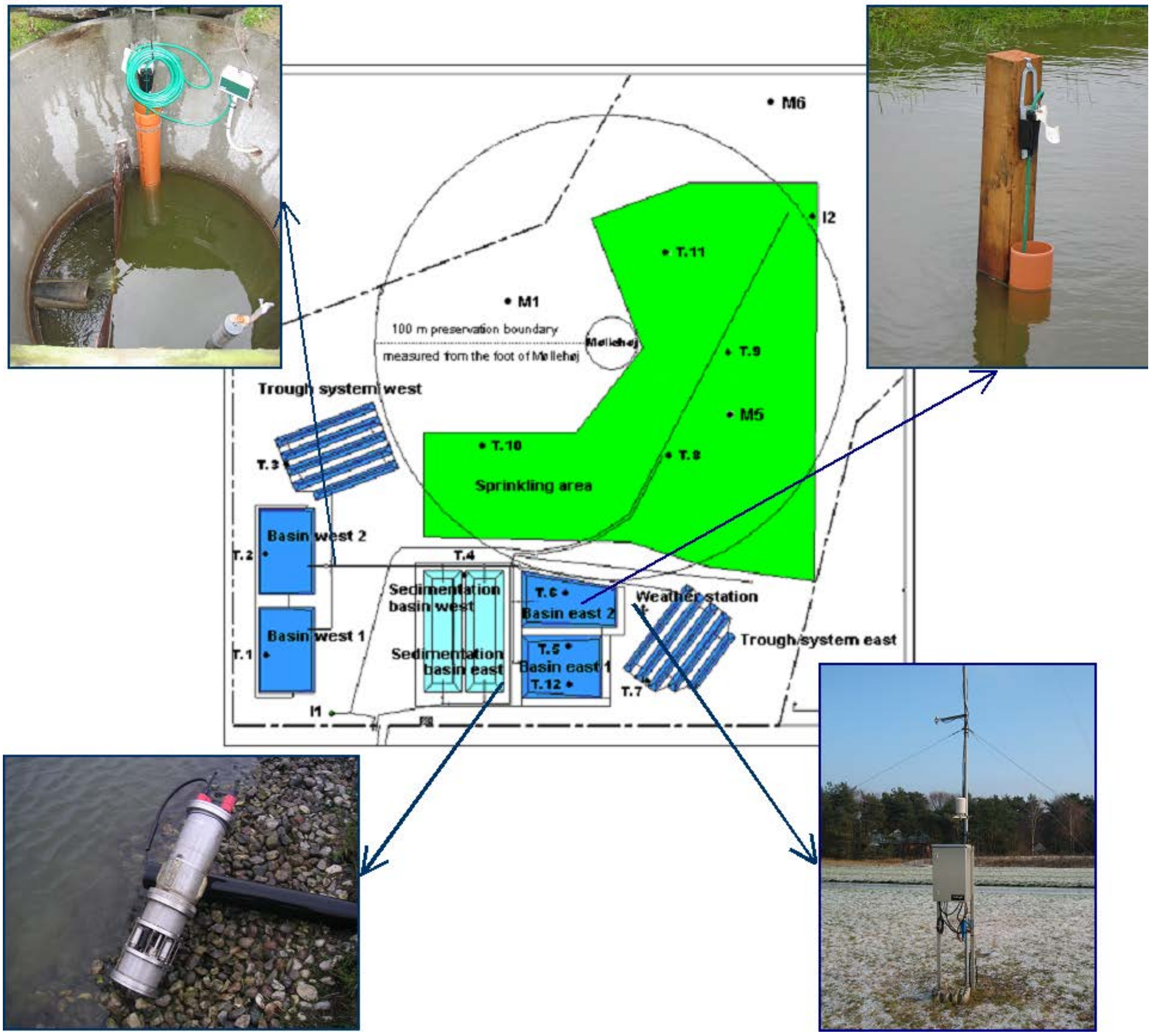

Figure 3: The Arrenæs AR trial plant with photos of the installed pressure transducers in the Thompson overflows and in the infiltration basins, the water quality monitoring unit (is submerged in sedimentation basin East), and the weather station

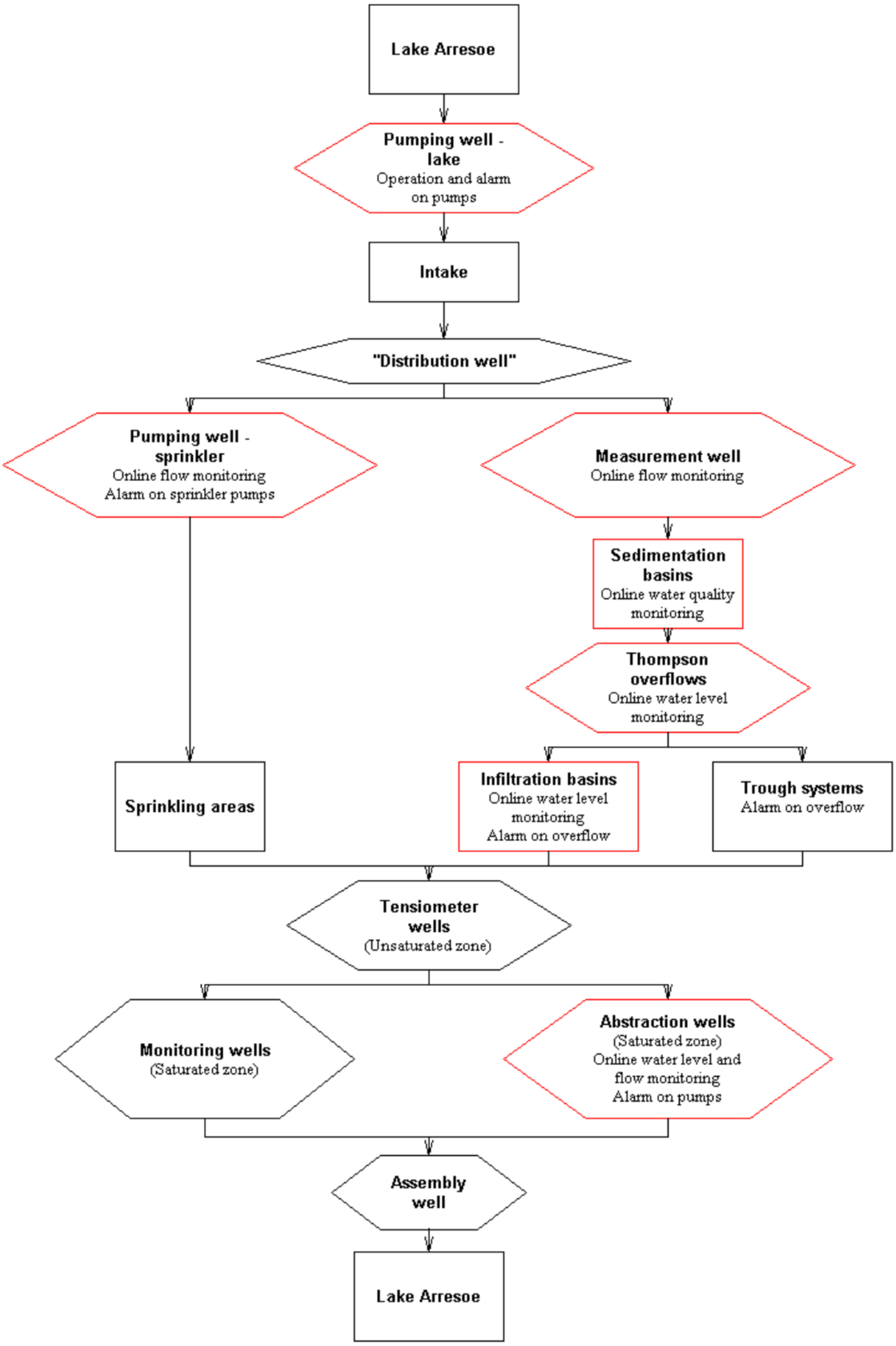

Figure 4: Flow scheme for the early warning system at the Arrenæs AR trial plant. The red boxes illustrates from where online data is collected in DIMS

9 SUMMARY

The early warning system installed at the Arrenæs AR trial plant within the ARTDEMO project is an efficient management tool. The interaction between the early warning system and the plant operator's use of the management plan (Nielsen et al., 2005) constitutes an expert system (Berg et al., 2005) for the Arrenæs AR trial plant.

The early warning system for Arrenæs AR trial plant includes both off- and online monitoring, and the data handling system DIMS. It has been demonstrated that online monitoring is important in the management of the AR plant. Real-time data on water quality are accessible and can, together with online data on water flow, be used to optimise the operation of the AR plant and also to prevent unexpected contamination events in destroying the sustainability of the AR plant.

Online monitoring of the water flow at the Arrenæs AR trial plant is performed in all parts of the plant. On-line monitoring of water quality is performed on the intake water from Lake Arresø. In the establishment of the proposed large-scale production plant at Arrenæs, it is important to complement the existing early warning system with additional on-line instruments measuring water quality in other parts of the AR plant, as it is presently not possible to cover the transport of a potential contaminant through the plant with the present early warning system.

10 ACKNOWLEDGEMENT

The authors would like to thank the personnel at the Arrenæs AR trial plant for their assistance in setting up the early warning system at the AR plant, and for their efforts in making online monitoring and DIMS a part of the normal operation of the AR plant.

11 REFERENCES

Bennedsen, L., Berg, R.L., Brandt, G. & Nielsen, T.Ø. 2005. Description of the Arrenæs Artificial Recharge Trial Plant. (Chapter 2 in this Final Scientific Report).

Berg, R.L., Nielsen, T.Ø., Bennedsen, L. & Brandt, G. 2005. Scenario Management and Expert System for the Arrenæs Artificial Recharge Trial Plant. (Chapter 26 in this Final Scientific Report).

Lundh, M., Engblom, K., Holmström, E., Bennedsen, L., Brandt, G., Berg, R.L. & Nielsen, T.Ø. 2005a. IDAS: Connection the Detection of an Incident with the resulting Action and the follow-up Surveillance in an early warning strategy model for MAR applications (Chapter 20 in this Final Scientific Report).

Lundh, M., Engblom, K. & Holmström, E. 2005b. Early Warning System at the Dösebacka AR Plant. (Chapter 21 in this Final Scientific Report).

Lynggaard-Jensen, A., Eisum, N.H. & Rasmussen, I. 2005. Real Time Monitoring and Management of Artificial Recharge Plants. (Chapter 17 in this Final Scientific Report).

Nielsen, T.Ø., Berg, R.L., Bennedsen, L. & Brandt, G. 2005. Introduction of the Management Plan for the Arrenæs Artificial Recharge Trial Plant. (Chapter 24 in this Final Scientific Report).

Chapter 23: Geochemical Processes in the Unsaturated Zone at the Arrenæs Artificial Recharge Trial Plant

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Abstract: At the Arrenæs Artificial Recharge (AR) trial plant, Denmark, investigations of the geochemical processes occurring in the unsaturated zone when recharging water from Lake Arresø have been performed. Focus has been on ensuring a sustainable operation of the AR plant and a continuously stable quality of the abstracted water. The investigations revealed that the primary changes in geochemical composition in the sediment below an irrigated area and an infiltration basin occurred in the uppermost part of the soil, and that the location of the groundwater table is reflected in the geochemical properties. The difference in the decalcification front between the irrigated and a non-irrigated area was approximately 3 metres. Simulations using PHREEQC show that after 60 years of operation of the AR trial plant, the decalcification front in the unsaturated zone at the irrigated area has moved approximately 2 metres downwards compared to the present situation, indicating that the calcite buffer capacity is not depleted even in a long-term perspective. Problems with formation of aggressive CO_2 in the abstracted water should therefore not be expected.

1 INTRODUCTION

Since 1995, Copenhagen Energy has run the Arrenæs trial plant based on Artificial Recharge (AR) to determine the potential for use of this technology in Denmark to ensure the supply of drinking water to Copenhagen. The results of running the AR trial plant have been positive and a large-scale production plant is therefore proposed at the same location.

When operating an AR plant it is important that the operation is sustainable and that short- and long-term undesirable changes and damage to the AR site is avoided. The influence of the artificial recharge depends on the quantity and quality of the infiltrating water and the buffer capacity of the recharge areas. The Arrenæs AR trial plant infiltrates water from Lake Arresø, which is an organic and nutrient rich lake.

With focus on ensuring a long-term sustainable operation of the Arrenæs AR trial plant and a continuously stable quality of the abstracted water, the geochemical processes occurring in the unsaturated zone at the recharge areas have been investigated. This includes an investigation of the changes over depth in the geochemical composition of sediment samples from an irrigated area, an infiltration basin, and a non-irrigated area (reference area), as well as an investigation of the differences between the areas. The result of these investigations have been used in the establishment of the early-warning system, the management strategy, and management plan developed for the Arrenæs AR trial plant within the ARTDEMO project (Nielsen et al. 2005a; Nielsen et al. 2005b).

2 THE ARRENÆS AR TRIAL PLANT

The Arrenæs AR trial plant is located in the Northern part of Zealand, Denmark. The trial plant consists of four infiltration basins and two trough systems (1,000 m^2 each - in operation all year), and a grass-covered irrigation area (20,000 m^2 - in operation from April to November), see figure 1.

Raw water for infiltration is taken from Lake Arresø. The amount of runoff water used as recharge water is approximately 100,000 m^3/year to the irrigation area and 300,000 m^3/year to the infiltration basins and trough systems. This results in a production of approximately 270,000 m^3/year, which is currently not used for drinking water purposes, but led back to Lake Arresø. The unsaturated zone consists of glaciofluvial sand and is approximately 26-27 metres thick. A detailed description of the Arrenæs AR trial plant is given in Bennedsen et al. (2005) within this Final Scientific Report.

3 METHODS

The investigations include continuous monitoring (1994-2005) of the quality of the input water, soil water, and abstracted water. Additionally, sediment samples from 0-30 meters below surface (mb.s.) were collected in October 2004, while establishing two monitoring wells; one at an irrigated area (M5) and one at a non-irrigated area (M6), where recharge of lake water has not been performed, see figure 1. The two monitoring wells were made using the solid flight auger drilling method, which made it possible to collect depth specific samples.

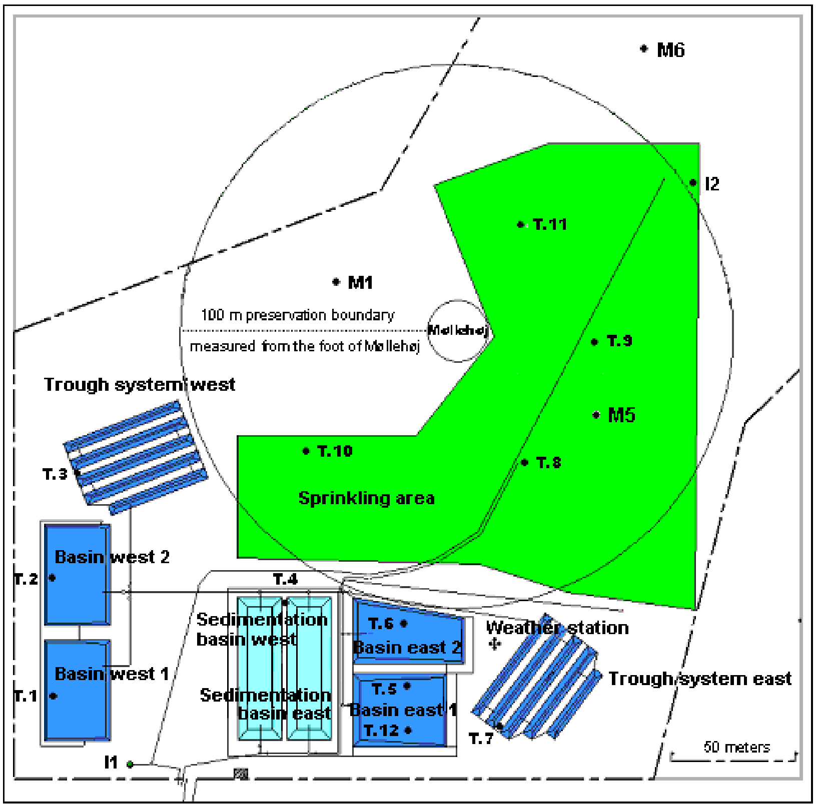

Figure 1: Layout of the Arrenæs AR trial plant.

Additionally, in March 2004, sediment samples were collected from the bottom of an infiltration basin (West 1, see figure 1) at the end of an operation period of the infiltration basin. The sediment samples were collected as cores using a plastic pipe at depths of 0.01 (filter skin), 0.07, and 0.35 meters below basin bottom (mb.b.).

Geochemical analyses performed on the soil material included pH (NEN 6411), electric conductivity (EC) (NEN 6412), non-silicate bound calcium (ICP-MS analysis on HNO_3 extract), organic carbon (pyrolysis of decalcified sample and subsequent gas detection by LECO analyzer), iron (Fe_{ox}), manganese (Mn_{ox}), and aluminium-oxalate (Al_{ox}) (AAS analysis on ammonium oxalate and 0.2 M oxalic acid, pH 3, extract from sample <2mm), and clay (<2mm, by a FRITSCH Laser Particle Sizer A22). Chemical modelling (PHREEQC) was done using chemical parameters analysed in water samples according to the Danish Standards.

4 GEOCHEMICAL PROPERTIES OF THE UNSATURATED AND SATURATED ZONE

The results of the sediment samples (0-30 mb.s.) collected at the irrigated and non-irrigated area at Arrenæs AR trial plant show that the primary changes in the geochemical composition at the two areas occurred in the upper 2 metres of the unsaturated zone. In the deeper parts from 2-26 mb.s., the geochemical parameters show less variation. However, the location of the groundwater table in approximately 26 mb.s. is reflected in the geochemical properties.

Additionally, the difference in the geochemical properties between the two areas was most significant in the upper 2 metres of the unsaturated zone. Figure 2 shows the results of the analyses for clay (<2µm), organic carbon, cation exchange capacity (CEC), pH, and calcium at the irrigated and non-irrigated area.

The clay fraction (<2 µm) given in figure 2 shows that at both locations the sediment in the upper 2 metres was finer grained than in the deeper parts of the unsaturated zone, especially at the non-irrigated area, where the amount of clay was approximately 3 times higher compared to samples from the upper metres at the irrigated area. This influences CEC, and thereby also the content of cations. At the groundwater table in approximately 25 metres depth, the clay fraction (<2 µm) increased at both locations, indicating that finer particles is transported with the groundwater flow.

Accumulation of organic carbon is occurring in the topsoil, see figure 2. Due to bioturbation and degradation, the content of organic carbon is decreasing in the upper 2 mb.s. The degradation

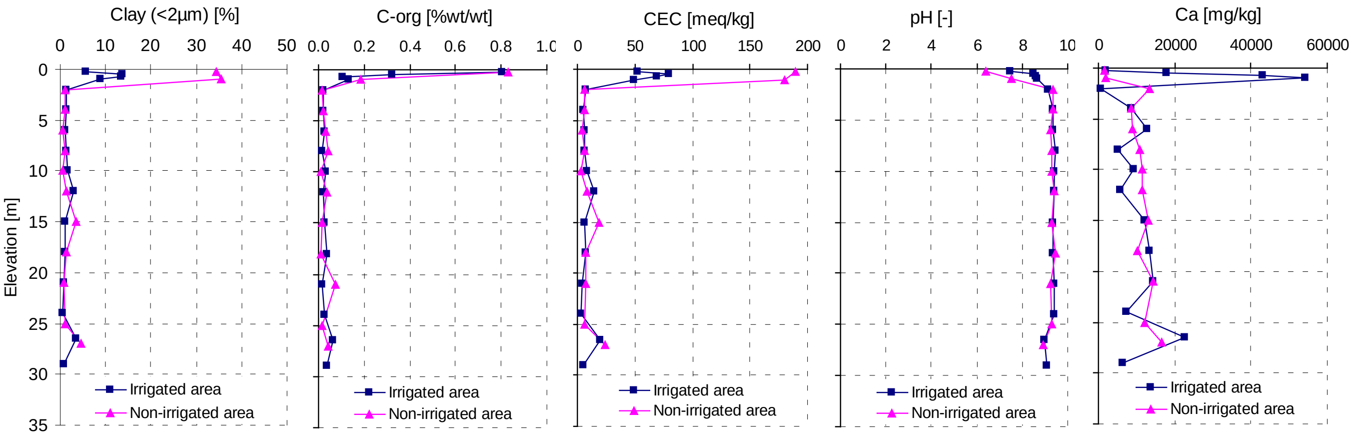

Figure 2: Clay (<2µm), organic carbon, cation exchange capacity (CEC), pH, and calcium at the irrigated and the non-irrigated area

of organic carbon is reflected in a decreased pH compared to the deeper layers, where pH is controlled by calcite equilibrium.

Data show a significant increase in the content of calcium from 0-2 mb.s. at the irrigated area. This calcium was primarily present as calcite. From the cation exchange capacity, figure 2, it is estimated that ion exchange does not have a significant influence on the calcium content in the sediment. The accumulation of calcite in the upper 2 metres is primarily a result of irrigation with lake water supersaturated with calcite, and evaporation. In addition, algae growth in the topsoil and loss of CO_2 gas may cause precipitation of calcite. Figure 2 indicates a decalcification front located approximately 1-2 mb.s. at the non-irrigated area and below the calcite rich soil horizon in approximately 3-4 mb.s. at the irrigated area. Whether this difference can be explained by artificial recharge needs further investigations of the location of the decalcification front, as natural geological heterogeneities also have an impact on the difference shown in figure 2. Below the leaching front, geological variations may influence the carbonate equilibrium.

The results of Fe_{ox} and Mn_{ox} are given in figure 3. The acidified oxalate extracts iron and manganese in organic complexes and poorly ordered (non-crystallized) oxides and silicates (Holm et al., 2003). Fe_{ox} and Mn_{ox} show the highest concentrations in the upper sediment samples decreasing in 2 mb.s. The elevated content of organic material in the upper 2 metres at both locations indicates that Fe_{ox} and Mn_{ox} may be present in complexes with organic material. Additionally, if oxic conditions are present in the upper metres, the accumulation of Fe_{ox} and Mn_{ox} in 0-2 mb.s. may be caused by accumulation of iron- and manganese oxides. However, as the content of Al_{ox}, which is primarily controlled by the content of organic material, show a similar trend over depth (figure 3), it is most likely that the accumulation in the upper layers is affected by the formation of complexes with the organic material.

From 2 mb.s. to the groundwater table in approximately 26-27 mb.s. Mn_{ox} was not present at any of the locations, whereas Fe_{ox} was present at both locations showing some variation

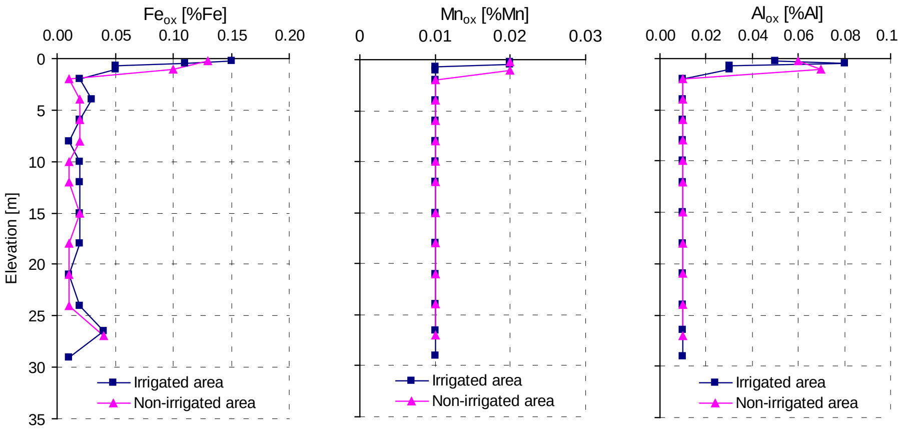

Figure 3: Fe_{ox} (iron-oxalate), Mn_{ox} (manganese-oxalate) (detection limit 0.01%), and Al_{ox} (detection limit 0.01%) at the irrigated and the non-irrigated area

between 0.01-0.03% Fe. The content of Fe_{ox} increased at the level of the groundwater table, which might be caused by iron present in the groundwater precipitating as oxides. This occurs when the groundwater table varies and iron in the groundwater mixes with oxygen in the unsaturated zone.

The geochemical processes in the unsaturated zone may also be affected by complicated flow patterns such as preferential flow, as revealed in studies at the Arrenæs AR trial plant by Brun & Broholm (2001).

Similar investigations were performed in the upper 0.35 metres of the soil below infiltration basin West 1. Figure 4 shows the results of the analyses for clay (<2µm), organic carbon, CEC, pH, calcite, and EC.

It is evident from this figure that also in the soil material below infiltration basin West 1, the primary changes occurred in the uppermost part of the soil (0.01-0.07 mb.b.). Homogeneous material was added to the bottom of the infiltration basins when establishing the AR trial plant. The clay fraction (<2µm) is therefore approximately 10 times less than at the irrigated area. However, the amount of clay (<2µm) is slightly decreasing, which together with a decrease in the content of organic material is reflected in a slightly decrease in the CEC. The high calcite content in the filterskin (0.01 mb.s.) may be explained by algae growth in the infiltration basin causing a decrease in CO_2 and thus increasing the calcite saturation index (Schuh, 1990). The organic carbon content in the sediment below the infiltration basin decreased from 0.095 to 0.031%w/w in the upper 0.07 metres of the soil, see figure 3. The degradation of organic carbon is reflected in a concurrent decrease in calcite content and electrical conductivity. It would have been expected that the vertical distribution of calcite would be reflected in pH, this is however not observed, se figure 4.

5 DEPLETION OF THE CALCITE BUFFER CAPACITY IN THE UNSATURATED ZONE

The results presented in the previous section indicate that the primary changes in geochemical composition of the soils occurs in the upper 2-4 metres at the irrigated area and in the upper part of the soil below the infiltration basins. However, in a long-term perspective, recharging water from Lake Arresø may cause geochemical

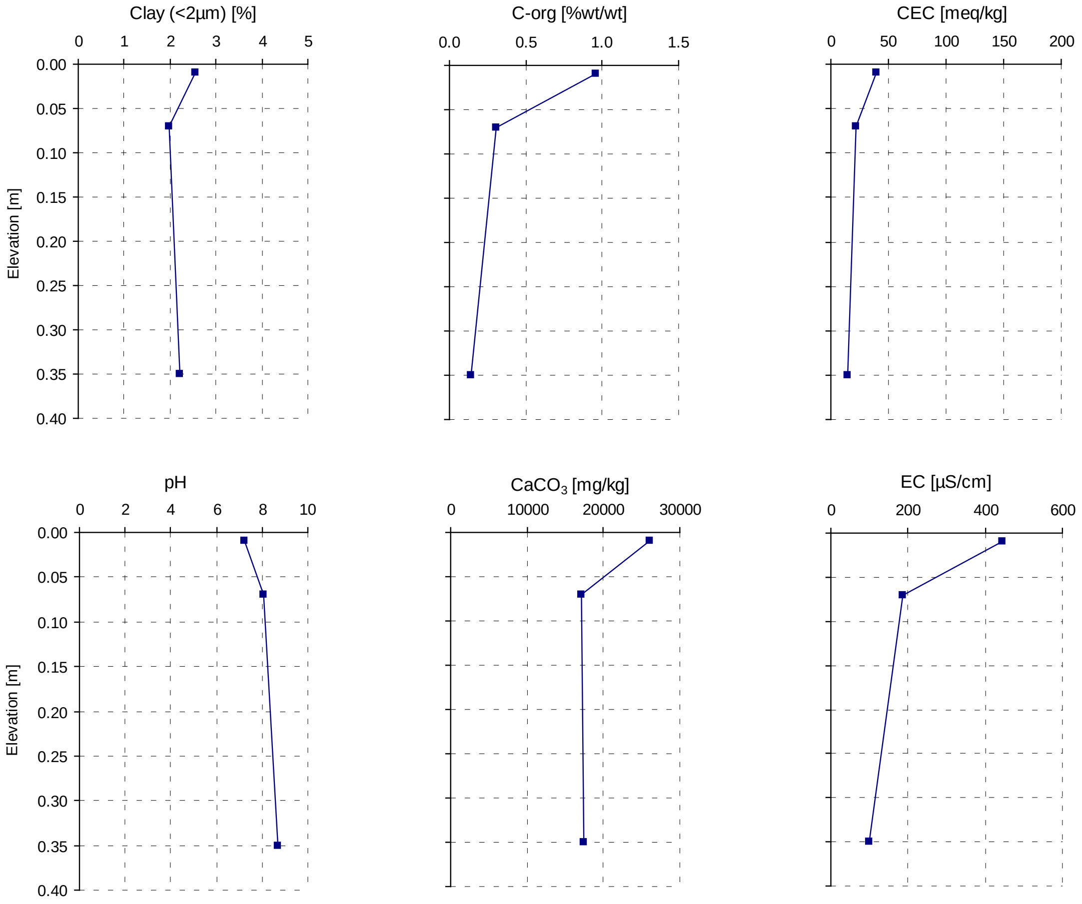

Figure 4: Clay (<2µm), organic carbon, CEC (cation exchange capacity), pH, calcite, and EC (electrical conductivity) in the soil below infiltration basin West 1 (n=2)

Table 1: Selected water quality parameters in the input water, soil water, and abstracted AR water

Parameter [mg/L]	**Arresoe - input water** Average 1995-2005 (excl. Nov.-March.)	**Tensiometer well T9 - 1m** (soil water) 19/04/1995	**Tensiometer well T9 - 5m** (soil water) 19/04/1995	**Tensiometer well T9 - 15m** (soil water) 19/04/1995	**Abstracted AR water** Average 2001-2005
pH at 12°C	8.9	9.1	7.6	7.5	7.5
O_2	9.3	-	-	-	4.7
Ca	46	26	38	55	87
Cl	65	29	6	35	59
HCO_3	132	140	184	132	236
NO_3	0.269	3.7	10	80	4.7
NO_2	0.03	0.17	0.42	0.19	<0.01
NH_4	0.1	0.48	0.25	0.1	0.03
NVOC	15.2	-	-	-	3.9

changes at increased depth in the unsaturated zone, e.g. depletion of the calcite buffer capacity and thereby problems with formation of aggressive CO_2.

The analyses of sediment samples from the Arrenæs AR trial plant have shown that the soil has a large calcite buffer capacity. In addition, the input water from Lake Arresø is supersaturated with calcite. However, table 1 shows that there is a significant difference in the organic carbon content between the input water and the abstracted water, indicating degradation of organic carbon in the unsaturated zone, which induces calcite dissolution. This was also evident from the sediment samples as discussed previously. The abstracted water has fairly constant pH, calcium, and bicarbonate levels, indicating that buffering processes occur in the unsaturated zone.

The risk of depletion of the calcite buffer capacity in the unsaturated zone at the irrigated area was investigated using the programme PHREEQC and data are given in table 1. In the calculations, equilibrium with calcite, and oxidation of organic matter by oxygen and nitrate using first order reaction kinetics is assumed. Ion exchange is not included in the calculations.

The composition of the soil water in the unsaturated zone at the irrigated area after 10 years of operation was simulated in PHREEQC and shows results similar to the field data from 2-30 mb.s. Simulation of the processes occurring in the upper 2 metres has, however, not been possible using the assumptions given above. Additionally, alternating calcite content over depth due to geological variations cannot be reflected in the simulation, as the unsaturated zone is assumed uniform in the simulations.

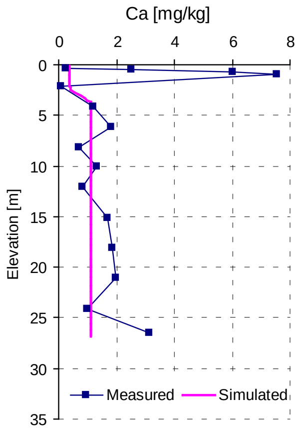

Figure 5: Measured and simulated decalcification front at the irrigated area at Arrenæs AR trial plant

Simulations show that the decalcification front will move approximately 2 metres downwards after 60 years of operation of the AR trial plant compared to the present location of the front in approximately 3-4 metres, see figure 5. Problems connected with production of aggressive CO_2 due to a depletion of the calcite buffer capacity are therefore not expected in a time perspective of 60 years.

6 CONCLUSIONS

The investigations in this study show that the primary changes in geochemical properties at the Arrenæs AR trial plant occur in the uppermost part of the soil. Interpretation of the geochemical data shows that the primary changes occurred in the upper 2 mb.s. at the irrigation area and in the upper 0.07 mb.b. in infiltration basin West 1, and that only minor changes occurred in depth of 2-27 mb.s. at the irrigated area. The difference in the decalcification front between the irrigated and non-irrigated area is approximately 3 m.

Simulations in PHREEQC show that the decalcification front after 60 years of operation of the Arrenæs AR trial plant will move approximately 2 metres downwards compared to the present location. This shows that the calcite buffer capacity in the unsaturated zone is not depleted even in a long-term perspective, indicating that problems with aggressive CO_2 should not be expected. To further examine the geochemical processes occurring in the uppermost part of the soil at the recharge areas, detailed investigations need to be performed from 0-1.5 mb.s.

7 ACKNOWLEDGEMENTS

The authors would like to thank the personnel at the Arrenæs AR trial plant for their assistance in the collection of the sediment samples.

8 REFERENCES

Bennedsen, L., Berg, R.L., Brandt, G. & Nielsen, T.Ø. 2005. Description of the Arrenæs Artificial Recharge Trial Plant. (In this Final Scientific Report).

Brandt, G. 1998. Arrenæs artificial recharge trial plant, Denmark - Hydrological and chemical aspects. In Proceedings of the third International Symposium on Artificial Recharge of Groundwater – TISAR 98 Amsterdam, Netherlands, 21-25 September, pp. 217-222.

Brun, A. & Broholm, K. 2001. Basin infiltration at the Arrenæs site, Denmark: Tracer test and quality changes during aquifer passage below infiltration basins. In: Final report from the EC project ENV4-CT95-0071 Artificial recharge of groundwater, pp. 177-181.

Copenhagen Energy. 2000. Arrenæs, Artificial infiltration of Lake Arresø water. Status for 2000 and operational and monitoring plan for 2001. Reports available for the years 2000-2003. (In Danish).

Copenhagen Water Supply & County of Frederiksborg (1995). Arrenæs, Artificial infiltration of Lake Arresø water. Status for 1995 and operational and monitoring plan for 1996. Reports available for the years 1995-1999. (In Danish).

Hartelius, E., Bennedsen, L. & Brandt, G. 2001. Arrenæs artificial recharge trial plant, Denmark – hydrological and water quality aspects. European Water Management 4(1), pp. 65-70.

Holm, P.E., Rootzén, H., Borggaard, O.K., Møberg, J.P. & Chrsitensen, T.H. 2003. Correlation of Cadmium Distribution Coefficients to Soil Characteristics. J. Environ. Qual. 32:138-145.

Nielsen, T.Ø., Berg, R.L., Bennedsen, L. & Brandt, G. 2005a. Early Warning System at the Arrenæs Artificial Recharge Trial Plant. (In this Final Scientific Report).

Nielsen, T.Ø., Berg, R.L., Bennedsen, L. & Brandt, G. 2005b. Introduction of the Management Plan for the Arrenæs Artificial Recharge Trial Plant. (In this Final Scientific Report).

Passow, J. 1996. The Arrenæs artificial recharge plant - design and operation. In Proceedings of an International Symposium on Artificial recharge of groundwater, Helsinki, 3-5 June, pp. 99-104.

Schuh. W.M. 1990. Seasonal variation of clogging of an artificial recharge basin in a northern climate. In: Journal of hydrology, vol. 121, pp. 193-215.

Chapter 24: Introduction of the Management Plan for the Arrenæs Artificial Recharge Trial Plant

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Abstract: Establishing a management plan is a part of the objective of the EU-project ARTDEMO. In this paper, the concept of the management plan has been applied to the Arrenæs AR trial plant, Denmark. The plant is a trial plant prior to a proposed large-scale AR plant at the same location. The structure of the management plan is based on a “follow-the-flow” concept and the basis for the plan is a management strategy based on the early warning model IDAS. The management plan is divided into a Part 1 – Plant Operation Description, and a Part 2 – Plant Operation Manual. In the process of establishing and evaluating the management plan for the Arrenæs AR trial plant, structure and contents of the management plan were evaluated by testing it against a number of situations that may constitute a risk to the operation of the AR plant. The evaluation revealed that some adjustments and improvements should be performed regarding equipment, monitoring and the management plan. Some of these adjustments were easy to implement in the management plan, whereas some changes required new installations to be set up at the AR plant and new procedures, which were not possible to include in the management plan of the present AR trial plant. These non-easily implemented adjustments are given in a “List of Suggestions”. When establishing the proposed large-scale Arrenæs AR production plant, it should be considered to include the improvements given in the “List of suggestions”. The result of the work is an evaluated management plan for the Arrenæs AR trial plant, which can be found on the CD – Final Report.

1 INTRODUCTION

Establishing a management plan is a part of the objective of the EU-project ARTDEMO. The objective has been to demonstrate how a management plan can be designed following a management strategy based on an early warning model called IDAS (Incident, Detection, Action, Surveillance). The IDAS model is described in detail in Lundh et al., 2005, and the concept of the management plan is described in Brandt et al., 2005.

The management plan will be a part of an expert system. The aim of the expert system has been to develop a surveillance system, where both the water quality and the water quantity is closely monitored to obtain the most stable and secure production of artificially recharged groundwater for drinking water purposes at the Arrenæs AR trial plant.

The quality of the management of an artificial recharge (AR) plant can be summarized in three important issues, which has been defined within the ARTDEMO project. The management of the Arrenæs AR trial plant is based on these quality issues:

- **Sustainable water quality (SWQ)** meaning maintaining a continuous, good water quality according to regulations
- **Sustainable water production (SWP)** meaning maintaining a continuous water production according to community requirements
- **Sustainable plant operation (SPO)** meaning protecting the plant from unmanageable damage

These issues were included in the preliminary management strategy for the Arrenæs AR trial plant that formed the basis for the management plan for Arrenæs AR trial plant and was formulated as follows:

1. Water Quality Management Strategy for AR plants (WQMS-AR)
   The main aim of the WQMS-AR is to achieve a sustainable use of the aquifer at the AR plant by a continuous, manual monitoring of water quality in intake water and abstracted artificially recharged water – as a minimum. In this way it must be ensured that water quality regulations are always fulfilled, that water quality in the aquifer is not deteriorating, and that unmanageable damage to the recharge area and aquifer is not occurring.
2. Water Production Management Strategy for AR plants (WPMS-AR)
   The objective of the WPMS-AR is to enhance a sustainable production of artificially recharged groundwater for drinking water purposes by a plant operation that ensures a constant water production in which the amount of abstracted artificially recharged

water is not exceeding the amount of water infiltrated.

In the present paper, the concept of the management plan is applied to the Arrenæs AR trial plant to evaluate structure and contents of the plan, and its applicability on the AR plant.

2 GENERAL DESCRIPTION OF ARRENÆS AR TRIAL PLANT

The Arrenæs AR Trial Plant is located at the Arrenæs peninsular in the northern part of Zealand, Denmark. The trial plant is a preliminary test site for a proposed production plant at the location. The AR trial plant was established in 1994 and has been operated continuously since April 1995. The plant consists of four infiltration basins (in total 4,000 m^2), two trough systems (in total 2,000 m^2) and a sprinkling area (in total 20,000 m^2). The multi supplier (water, gas, district heating, sewage) for the city of Copenhagen, Copenhagen Energy (KE), runs the plant.

The AR trial plant is recharging water from Lake Arresø with a water volume of 123 million m^3 and an annual discharge of 30-65 million m^3. The infiltration capacity of the AR trial plant is 350,000 m^3/year. The abstracted AR water is presently not used for drinking water purposes but is instead led back to Lake Arresø. The proposed large-scale infiltration plant at the site aims at a capacity of 4-5 million m^3/year. For detailed information on the Arrenæs AR trial plant, see the site description (Bennedsen et al., 2005) within this Final Scientific Report

3 MANAGEMENT PLAN FOR ARRENÆS AR TRIAL PLANT

As part of the ARTDEMO project, a concept for a general management plan was developed. This management plan presented in Brandt et al. (2005) consists of two parts:

- Part 1: Plant Operation Description
- Part 2: Plant Operation Manual

To illustrate how this management plan can be applied to a specific AR plant, the management plan concept was applied to the Arrenæs AR trial plant.

A contingency plan exists for each well field within KE, where communication paths and responsible persons in an alarm situation are listed. For this reason, the delimitation of the management plan is determined by the action plan, and situations mentioned in the contingency plan are not included in the management plan.

The management plan for the Arrenæs AR

A. General description of the plant
    A.1. Plant design
        A.1.1 Geology
        A.1.2 Input water
        A.1.3 The AR trial plant
        A.1.4 The proposed large-scale AR plant
    A.2. Security
    A.3. General supply
    A.4. IT-communication
        A.4.1 Functions within the system of the Arrenæs AR trial plant
        A.4.2 Functions on the internal network of Copenhagen Energy
    A.5. Water Quality Monitoring
        A.5.1 Sample locations
        A.5.2 Parameters analysed in water samples from Arrenæs
        A.5.3 Manual Water Quality Monitoring
        A.5.4 Online monitoring

B. Management scheme
    B.1. Organisational structure
    B.2. Linking to protocols

C. Documentation
    C.1. Annual operation and monitoring report
    C.2. External reporting

D. Responsible and performing persons

E. Early warning system
    E.1. Description of the early warning system at Arrenæs
    E.2. Early warning in the management plan

Figure 1: Outline of the Plant Operation Description, which is Part 1 in the management plan

trial plant is based on operational experiences and knowledge within this specific AR plant. No operation manual existed for Arrenæs AR trial plant, and one of the tasks when writing the management plan was therefore to accumulate these experiences from the trial period into the management plan. This was done through interviews with the operators of the AR plant and by investigating results of several experiments and tests performed at the trial plant.

The result of this work is a site-specific management plan consisting of a Plant Operation Description with information on the Arrenæs AR trial plant and a Plant Operation Manual, where only protocols of relevance to the Arrenæs AR trial plant are included. The management plan is delimited geographically to the AR site. The management plan for the Arrenæs AR trial plant is included on the CD – Final Report.

3.1 Part 1 - Plant Operation Description

The Plant Operation Manual for Arrenæs AR trial plant gives an introduction to the AR plant and management of the AR plant in general. The Plant Operation Manual includes the information shown in figure 1.

3.2 Part 2 – Plant Operation Manual

The Plant Operation Manual in the general management plan presented in Brandt et al. (2005) is based on a “follow-the-flow” concept and consists of 21 protocols, which describe all parts of the management of an AR plant. Within each protocol, a number of sub-protocols are given - including both routine and alarm situations. To handle these routine and alarm situations, it is a condition that the operator has a basic knowledge of the operation of the AR trial plant, either from reading the Plant Operation Manual or from experiences in operating the AR plant.

When applying the general management plan to a specific AR plant, one of the first tasks is to select protocols and sub-protocols relevant for the plant in question, and omit not applicable protocols and sub-protocols.

The resulting Plant Operation Manual for Arrenæs AR trial plant comprises the protocols/sub-protocols shown in figure 2.

The structure of this Plant Operation Manual is consistent with the general list given in Brandt et al. (2005). However, a comparison reveals that protocols no. 17-21 concerning post treatment are not included in the Plant Operation Manual for the Arrenæs AR plant, because post treatment of the AR water in a production situation will be performed at a waterworks several kilometres from the AR plant.

When reading the Plant Operation Manual for the Arrenæs AR trial plant, one should be aware that the plant is only a test plant. The operation is therefore in some ways different from a typical production plant.

As focus in the ARTDEMO project has been to set the main structure of the general management plan, the management plan for the Arrenæs AR trial plant is not complete. There are several protocols that are left empty, as only selected protocols have been compiled to test and evaluate possible lacks in the structure or content of the plan.

1. Operational Control
    - 1.1. General maintenance
    - 1.2. Security
    - 1.3. General supply
    - 1.4. IT-communication
    - 1.5. Maintenance of measurement stations
    - 1.6. Maintenance of grass areas and roads
    - 1.7. Electric fence
    - 1.8. Internal reporting
    - 1.9. External reporting
2. Early warning - water quality upstream the intake
    - 2.1. Manual water quality monitoring, upstream the intake
3. Water level in raw water source
    - 3.1. Manual monitoring of the water level in raw water source
4. Raw water intake
    - 4.1. Maintenance
    - 4.2. Pump function, intake
5. Early warning - water quality in the intake water
    - 5.1. Maintenance of measurement station
    - 5.2. Manual water quality monitoring, intake water
    - 5.3. Online water quality monitoring, intake water
6. Pre treatment
    - 6.1. Sedimentation basin management
    - 6.2. Water level in sedimentation basin
    - 6.3. Accumulation of sludge in sedimentation basins
7. Infiltration basin management
    - 7.1. Water distribution to infiltration basins
    - 7.2. Water level in infiltration basins
    - 7.3. Regeneration of infiltration basins
8. Early warning - water quality in infiltration basins
    - 8.1. Manual water quality monitoring, infiltration basins
9. Sprinkling areas
    - 9.1. Management of sprinkling areas
10. Early warning – water quality in the unsaturated zone
    - 10.1. Manual water quality monitoring, unsaturated zone
11. Monitoring well management
    - 11.1. Maintenance
    - 11.2. Pump function, monitoring wells
12. Early warning – water quality in monitoring wells
    - 12.1. Manual water quality monitoring, monitoring wells
13. Abstraction well management
    - 13.1. Maintenance
    - 13.2. Pump function, abstraction wells
14. Early warning - water quality in abstraction wells
    - 14.1. Manual water quality monitoring, abstraction wells
15. Groundwater level measurement and control
    - 15.1. Online monitoring and management of the groundwater level
16. Internal pipelines
    - 16.1. Maintenance
    - 16.2. Flow in pipelines at the AR plant

Figure 2: Outline of the Plant Operation Manual, which is Part 2 in the management plan

4 COUPLING OF MANAGEMENT PLAN AND MANAGEMENT SYSTEM DIMS

To obtain an efficient management tool, the management plan was coupled with the results from the monitoring strategy presented in Lynggaard-Jensen et al. (2005). This was done within ARTDEMO in the management system DIMS (Dynamic Integrated Monitoring System).

In DIMS, an alarm appears at the computer screen, if any defined abnormality occurs, see figure 3. The alarm will be followed by a description of the problem and a link to the specific alarm protocol in the Plant Operation Manual within the management plan in which actions to be performed in the given situation is described. An electronic version of the management plan can be reached from DIMS.

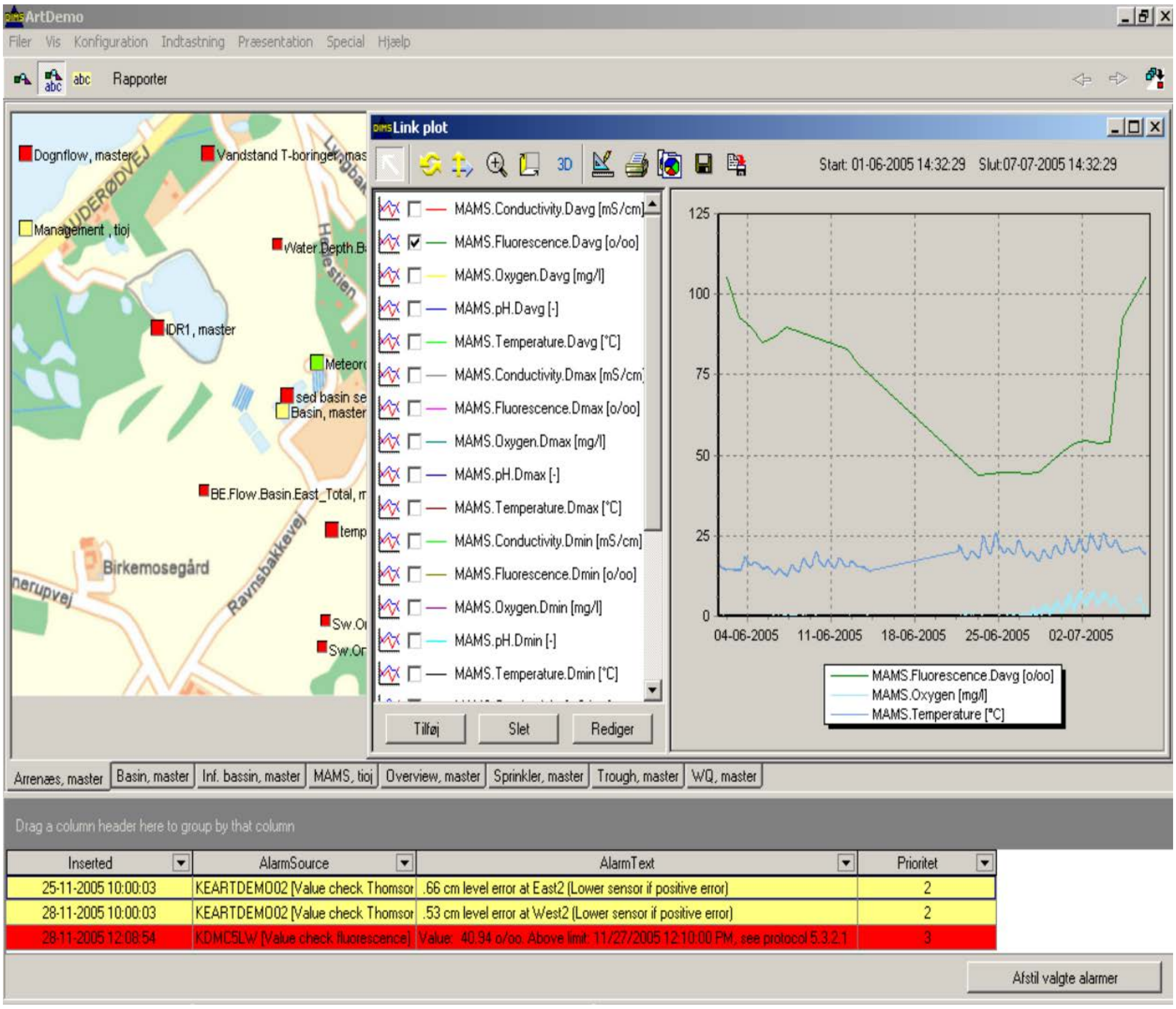
In the operation of the Arrenæs AR trial plant, a “Daily report” is used to optimise the daily management. The “Daily Report” consists of a number of excel reports with information on flow and water level, which is automatically updated every day and reported on the internal website for the Arrenæs AR trial plant developed within the ARTDEMO project, see figure 4. In the “Daily report”, a notice will appear if e.g. regeneration of the infiltration basins is needed in near future. In this situation, there will be a link to the relevant sub-protocol within the Plant Operation Manual in the management plan.

Within the ARTDEMO project, a trial version of an interactive management plan was developed, see figure 5. This is included on the CD - Final Report.

5 EVALUATION OF THE MANAGEMENT STRATEGY AND MANAGEMENT PLAN FOR ARRENÆS AR TRIAL PLANT

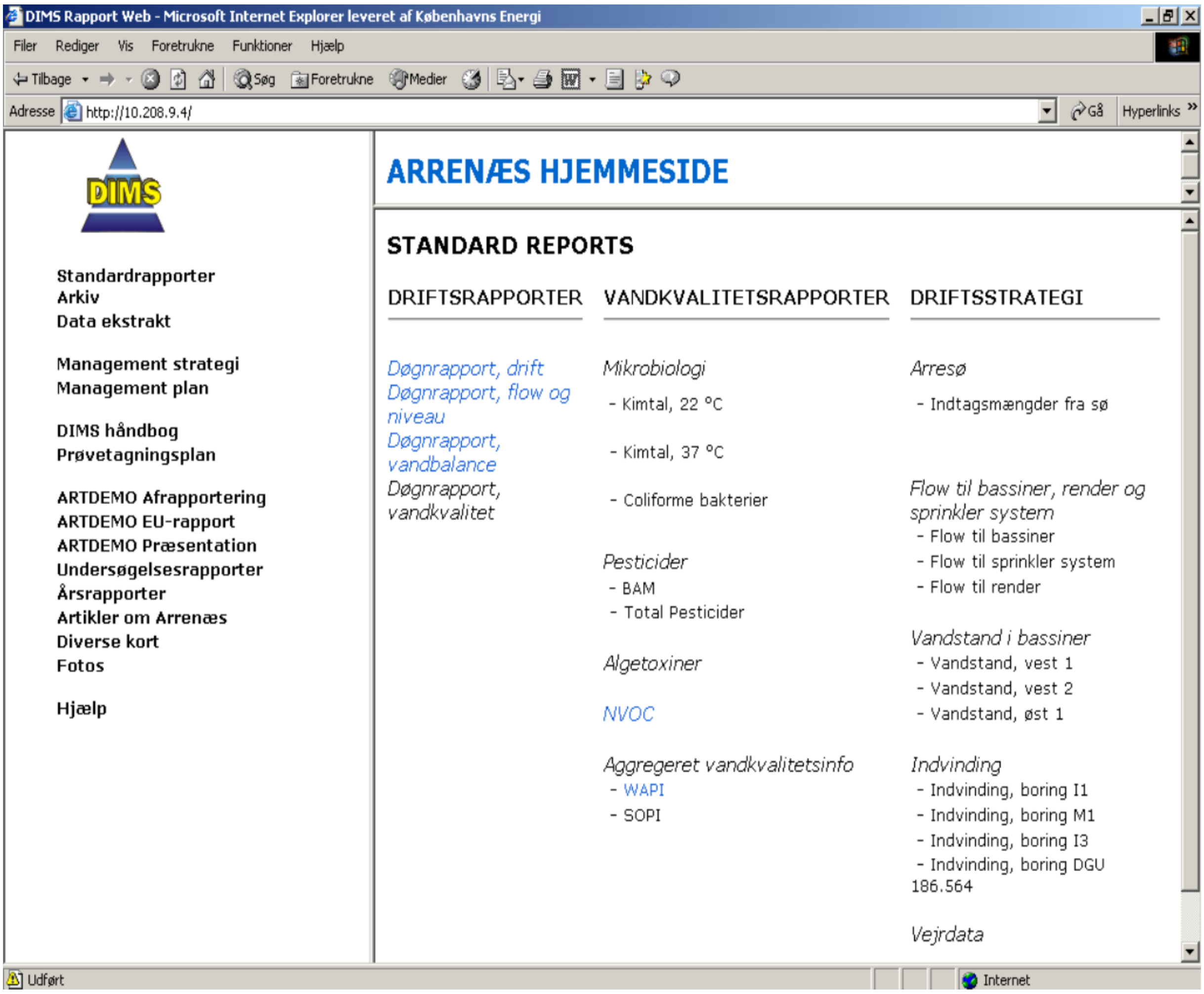
The objective of the management plan is to guide the operator of the plant through the process of performing routine work and handle alarm situations in the best possible way.

In the evaluation of the management plan for the Arrenæs AR trial plant it was tested how robust the management plan is in a number of situations that can cause a risk to the sustainability of the AR plant. This was done by



Inserted	AlarmSource	AlarmText	Prioritet
25-11-2005 10:00:03	KEARTDEMO02 [Value check Thomsor	.66 cm level error at East2 (Lower sensor if positive error)	2
28-11-2005 10:00:03	KEARTDEMO02 [Value check Thomsor	.53 cm level error at West2 (Lower sensor if positive error)	2
28-11-2005 12:08:54	KDMC5LW [Value check fluorescence]	Value: 40.94 o/oo. Above limit: 11/27/2005 12:10:00 PM, see protocol 5.3.2.1	3

Figure 3: The DIMS system with an alarm message in the bottom of the screen



Standardrapporter
Arkiv
Data ekstrakt

Management strategi
Management plan

DIMS håndbog
Prøvetagningsplan

ARTDEMO Afrapportering
ARTDEMO EU-rapport
ARTDEMO Præsentation
Undersøgelsesrapporter
Årsrapporter
Artikler om Arrenæs
Diverse kort
Fotos

Hjælp

ARRENÆS HJEMMESIDE

STANDARD REPORTS

DRIFTSRAPPORTER

Døgnrapport, drift
Døgnrapport, flow og niveau
Døgnrapport, vandbalance
Døgnrapport, vandkvalitet

VANDKVALITETSRAPPORTER

Mikrobiologi
- Kimtal, 22 °C
- Kimtal, 37 °C
- Coliforme bakterier

Pesticider
- BAM
- Total Pesticider

Algetoxiner

NVOC

Aggregeret vandkvalitetsinfo
- WAPI
- SOPI

DRIFTSSTRATEGI

Arresø
- Indtagsmængder fra sø

Flow til bassiner, render og sprinkler system
- Flow til bassiner
- Flow til sprinkler system
- Flow til render

Vandstand i bassiner
- Vandstand, vest 1
- Vandstand, vest 2
- Vandstand, øst 1

Indvinding
- Indvinding, boring I1
- Indvinding, boring M1
- Indvinding, boring I3
- Indvinding, boring DGU 186.564

Vejrdata

Figure 4: Internal website of the Arrenæs AR trial plant (in Danish)

using online sensors, the management system DIMS and the trial version of the interactive management plan. A detailed discussion on three selected potential risks to Arrenæs AR trial plant is given in Berg et al. (2005).

The evaluation of the management plan revealed that in general the alarm situations tested were handled as would be required by the expert system (DIMS/ management plan). However, in the evaluation of the management plan, limitations were detected and adjustments were made to the plan. This included problems in the interaction between different protocols, missing links between sub-protocols, addition of new sub-protocols, and extension of sub-protocols with supplementary contents.

A number of adjustments to the management plan were not easily implemented, as they required e.g. installation of new equipment at the Arrenæs AR trial plant. These adjustments are given in a "List of suggestions".

The use of online measurements was found to be very useful in the management of the Arrenæs AR trial plant, since it is a way to give the operator an overview of the operation of the plant and makes it possible to quickly detect an alarm situation and perform the required actions. During the ARTDEMO project, online monitoring equipment measuring flow through the AR plant, water levels in infiltration basins and abstraction wells, and water quality in the intake water were installed. However, through the evaluation of the expert system, further needs for online monitoring were identified. Especially installation of online water quality monitoring equipment in abstractions wells would be relevant to monitor the quality of the abstracted AR water. These improvements were included in "List of suggestions".

Additionally, improvements to the management of the Arrenæs AR trial plant concerning manually collected water samples were included in "List of Suggestions". These improvements are not implemented in the management plan for the Arrenæs AR trial plant, as the plant is presently run as a test site. However in a large-scale operation situation, these adjustments should be made, e.g. water sampling for algae toxins in intake water to the AR plant and in infiltration basins when detecting high amounts of algae in the raw water source, should be standard procedure. And if algae toxins are detected in intake water and/or infiltration basins, water samples should be collected from tensiometer wells.

During the process of preparing the management plan for the Arrenæs AR trial plant, a number of optimisation possibilities for the operation of the Arrenæs AR trial plant were identified and included in the List of Suggestions. An example is the operation of the infiltration basins. At present, a high amount of water is lead to the infiltration basins in the beginning of an operation period to obtain a high infiltration rate. This can be critical, as an active clogging layer has to be developed before algae toxins and bacteria can be efficiently retarded in the upper soils layers. A change in the operation would therefore be advisable to avoid breakthrough of bacteria in abstraction wells, which has been identified at the plant. In this connection it is also important to investigate the travel time from a basin to an abstraction well, as problems with break through of bacteria can arise if the travel time is insufficient.

The not easily implemented adjustments to the management of the Arrenæs AR trial plant together with relevant optimisation possibilities are given in the “List of suggestions” that can be found on the CD - Final Report. In the future operation of the proposed large-scale AR plant, it should be considered to include the improvements to the management plan given in “List of Suggestions”.

The need for continuous monitoring of water flow and water quality determined through the work with the management plan and the testing of the expert system, in Berg et al. (2005), have led to a reformulation of the management strategy defined in the introduction of this paper, as new approaches to a stable and secure production of artificially recharged groundwater for drinking water purposes have been defined.

The management strategy for the Arrenæs AR trial plant is therefore reformulated as follows:

1. Water Quality Management Strategy for AR plants (WQMS-AR)
   The main aim of the WQMS-AR is to achieve a sustainable use of the aquifer at the AR plant by a continuous, online monitoring of water quality in intake water and abstracted water – as a minimum. In this way it must be ensured that water quality regulations are always fulfilled, that water quality in the aquifer is not deteriorating, and that unmanageable damage to the recharge area and aquifer is not occurring.
2. Water Production Management Strategy for AR plants (WPMS-AR)
   The objective of the WPMS-AR is to enhance a sustainable production of artificially recharged groundwater for drinking water purposes by a plant operation that ensures a constant water production and a stable water flow through the plant by use of online monitoring equipment to monitor the water flow in all parts of the MAR plant. In this way it is assured that the amount of abstracted artificially recharged water is not exceeding the amount of water infiltrated.

It should be noticed that at present, the Arrenæs AR trial plant actually do not fulfil the aim set in the WQMS-MAR, as there is no online monitoring of the quality of abstracted AR water. In a large-scale production situation, this should of course be implemented.

6 SUMMARY

The application of the management plan concept to the Arrenæs AR trial plant has illustrated, that the concept of “follow-the-flow” is operating very well, as the management plan was easy to implement at the AR plant and easy to understand due to the simple structure.

The management plan for the Arrenæs AR trial plant was evaluated by setting up a number of possible risks to the plant. The evaluation resulted in some adjustments to the management plan and a “List of Suggestions” for adjustments that was not easily implemented in the operation of the present AR trial plant but needed to have an optimal management of the plant. The management plant together with the “List of Suggestions” is included on the CD - Final Report.

As the Arrenæs AR plant is a trial plant, the management plan should be considered more as an accommodation of experiences, than an actual operation manual. The present management plan should therefore not be applied directly to an AR production plant without adjusting it to the actual situation.

In a production situation at the Arrenæs AR plant, especially the monitoring programme will be extended significantly to ensure a sustainable production of AR water, and the suggested improvements included in “List of Suggestions” should be considered implemented at the AR plant.

7 ACKNOWLEDGEMENTS

The authors would like to thank the personnel at the Arrenæs AR trial plant for providing information on operational experiences and knowledge gained from 10 years of operation of

the AR plant. This has been valuable for the preparation of the management plan.

8 REFERENCES

Bennedsen, L., Berg, R.L., Brandt, G. & Nielsen, T.Ø. 2005. Description of the Arrenæs Artificial Recharge Trial Plant. (In this Final Scientific Report).

Berg, R.L., Nielsen, T.Ø., Bennedsen, L. & Brandt, G. 2005. Scenario Management and Expert System for the Arrenæs Artificial Recharge Trial Plant. (In this Final Scientific Report).

Brandt, G., Nielsen, T.Ø., Berg, R.L., Lundh, M., Holmström, E. & Engblom, K. 2005. Establishment of a Management Plan for Artificial Recharge Plants (In this Final Scientific Report).

Copenhagen Energy. 2000. Arrenæs, Artificial infiltration of Lake Arresø water. Status for 2000 and operational and monitoring plan for 2001. Reports available for the years 2000-2003. (In Danish).

Lundh, M., Engblom, K., Holmström, E., Bennedsen, L., Brandt, G., Berg, R.L. & Nielsen, T.Ø. 2005. IDAS: Connection the Detection of an Incident with the resulting Action and the follow-up Surveillance in an early warning strategy model for MAR applications (In this Final Scientific Report).

Lynggaard-Jensen, A., Eisum, N.H. & Rasmussen, I. 2005. Real Time Operation and Management system at Arrenæs Artificial Recharge Plant. (In this Final Scientific Report).

Chapter 25: Microbiological Barrier Efficiency at the Arrenæs Artificial Recharge Trial Plant and Risk of Pathogenic Break Through

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Abstract: The Arrenæs Artificial Recharge (AR) trial plant, Denmark, recharges water from Lake Arresø. In the operation of the AR trial plant, it is of uttermost importance that pathogenic bacteria present in the lake water are removed during infiltration to secure the quality of the abstracted AR water, as bacteria are not necessarily removed in the following water treatment, which only include simple aeration and filtration. As part of the ARTDEMO project, removal of bacteria at the Arrenæs AR trial plant has been investigated. Analysis of the bacterial content of sediment samples collected at the recharge areas show that 91-99% of the bacteria were removed in the upper 0.4 metres in an infiltration basin and in the upper 2-4 metres at the irrigated area. Analysis of the bacterial content of water samples collected at the Arrenæs AR trial plant did, however, show 5 occasions of break through of coliform bacteria in two abstraction wells. Using the results from these investigations, statistical calculations show that only 17% of all possible break through with coliform bacteria in the abstraction wells are discovered using the present sample collection frequency.

1 INTRODUCTION

In the operation of an AR plant, a sustainable quality of the abstracted water is of uttermost importance. The quality of the abstracted AR water may be affected by the quality of the raw water source, if undesirable parameters present in the raw water source are not removed during infiltration. In the operation of an AR plant it is thus important to identify the barrier efficiency and thereby removal of undesirable parameters.

At the Arrenæs Artificial Recharge (AR) trial plant, located at the Arrenæs peninsular in the Northern part of Zealand, Denmark, raw water for infiltration is taken from Lake Arresø. The intake water contains various organisms, among these pathogenic bacteria, and it is of highest importance that these bacteria are removed during infiltration. The present AR plant at Arrenæs is a trial plant, and the produced water is currently not used for drinking water purposes, but is led back to Lake Arresø. However, results of running the trial plant have been positive and a large-scale production plant is proposed at the same location. In a potential future production situation at the Arrenæs AR plant, a high quality of the abstracted AR water is a necessity, as bacteria are not removed in the following water treatment at the waterworks, which only includes simple aeration and filtration through natural sand filters.

As a part of developing the early warning system within the ARTDEMO project (Nielsen et al., 2005), removal of bacteria at the Arrenæs AR trial plant has been investigated. In the investigation of the removal of pathogens, focus has been on the fate of pathogenic indicator organisms. The investigations include collection and analyses of both sediment- and water samples from the Arrenæs AR trial plant. Using these results, risk of break through of pathogenic indicator organisms in the abstraction wells has been estimated

2 THE ARRENÆS AR TRIAL PLANT

The Arrenæs AR trial plant recharges water from Lake Arresø, which has a large surface area (40.7 km^2) and low depth (average 3.1 m). The lake is therefore often fully mixed. The catchment area is mostly agricultural areas, but also several cities and forest areas are included. Lake Arresø is therefore affected by both agricultural activity and sewage runoff and is an eutrophic lake.

The Arrenæs AR trial plant has been in operation since April 1995 and consists of four infiltration basins, two trough systems (1,000 m^2 each), and a grass-covered irrigation area (20,000 m^2), see figure 1. The lake water for the infiltration basins and trough systems is pre-sedimentated in two sedimentation basins. The water for the irrigation areas is taken directly from the lake without pre-sedimentation. The basins and trough systems are in operation all year, while the irrigation area is in operation from April to November. The unsaturated zone is approximately 25-27 metres thick and consists primarily of glaciofluvial sand.

Four abstraction wells are located around the Arrenæs AR trial plant; I1, M1, I3, and DGU 186.564, see figure 1, where also the

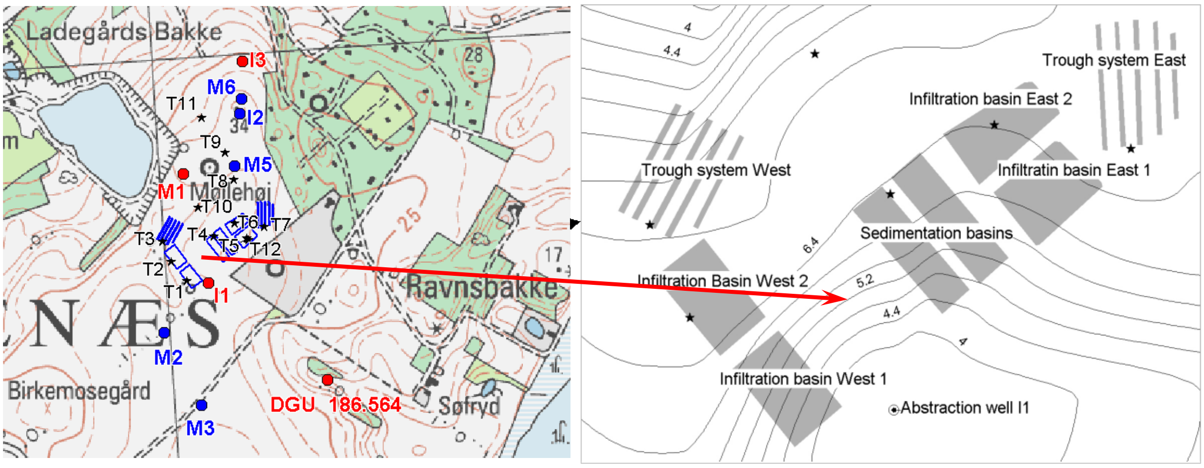

Figure 1: Map of the Arrenæs AR trial plant. Abstraction wells are indicated by red dots, monitoring wells by blue dots, and tensiometer wells by black stars.

groundwater table is given. Figure 1 shows that the hydraulic heads are affected by abstraction well I1 located close to infiltration basin West 1 (approximately 15 metres) and abstraction well M1 located just north of trough system West. The hydraulic heads indicates that water infiltrating in infiltration basin West 1 and West 2 is primarily abstracted in well I1. A detailed description of the Arrenæs AR trial plant is given in Bennedsen et al. (2005) within this Final Scientific Report.

3 METHODS

Sediment samples were collected from an infiltration basin (West 1) in March 2004 and October 2005. The samples from infiltration basin West 1 were collected at the end of an operation period of the infiltration basin, just before the basin bottom was to be regenerated. The bottom of the infiltration basin is sloping, and sediment samples were collected from both the shallow and deep end. In March 2004 sediment samples were collected as cores using a plastic pipe, at 0.01, 0.07, and 0.35 meters below basin bottom (m.b.b.). In October 2005 sediment samples were collected as cores using an aluminium pipe, at 0.01, 0.05, and 0.4 m.b.b. The upper samples at 0.01 m.b.b. (filterskin) primarily consisted of sludge, whereas samples at 0.07/0.05 and 0.35/0.4 m.b.b. primarily consisted of sand. Additionally, sediment samples from 0-30 metres below surface (m.b.s.) were collected in October 2004, while establishing two monitoring wells; one at the irrigated area (M5) and one at a non-irrigated area (M6), where recharge of lake water has not been performed. The two monitoring wells were made using the solid flight auger drilling method, which made it possible to collect depth specific sediment samples.

The sediment samples were analysed for colony-forming units (CFU), coliform bacteria, thermotolerant coliform bacteria, and enterococci. Additionally, sediment samples collected from infiltration basin West 1 in March 2004 and at the irrigated and non-irrigated area in 2005 were analysed for sulphite-reducing clostridia and *Clostridium perfringen*s. The total amount of bacteria was determined in sediment samples from the irrigated and non-irrigated area. In table 1, the methods for the bacterial analyses are listed.

Table 1: Methods for the bacterial analyses of sediment and water samples. (In 2005 a new method (Colilert Quanty-Tray) for analysing groundwater samples for coliform bacteria and E. coli was introduced, and this method was therefore used for some water samples collected from abstraction well I1 and M1 during the monitoring program in August-September 2005)

Parameter	Sample	Method
Total amount of bacteria	Sediment	AODC
CFU at 22°C and 37°C	Water and sediment	DS/EN ISO 6222
Coliform bacteria, 37°C, MPN	Water and sediment	DS 2255
Coliform bacteria, 37°C	Water	Collilert Quanty-Tray [1]
Thermotolerant coliform bacteria, 44°C, MPN	Water and sediment	DS 2255
E. coli, 37°C	Water	Collilert Quanty-Tray [1]
Enterococci	Water	ISO 7899/2 mod.MST98
Enterococci	Sediment	DS 2401
Sulphite reducing *Clostridia*	Water and sediment	NMKL 56
Clostridium perfringens	Water and sediment	DS 2256

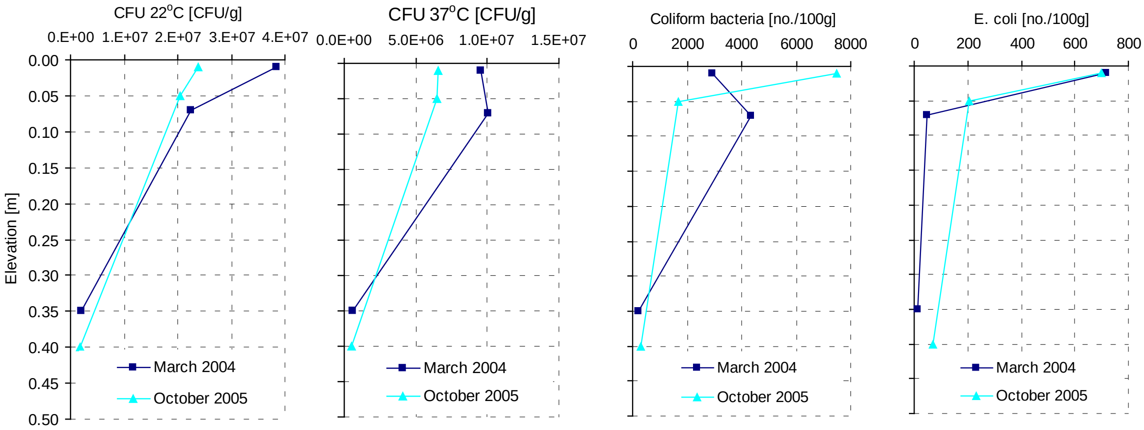

Figure 2: CFU at 22°C and 37°C, coliform bacteria, and thermotolerant coliform bacteria (E. coli) in the soil below infiltration basin West 1. Sediment samples were collected in March 2004 and October 2005.

Analyses of water samples include continuous monitoring (1994-2005) of the quality of the input water from Lake Arresø, and water from monitoring- and abstraction wells. Additionally, specific monitoring programs were established in 2004 and 2005, where water samples were collected twice a week from the intake from Lake Arresø, infiltration basin West 1, and abstraction wells I1 and M1 during 2-2½ month. The samples were collected during late summer/autumn, where the content of bacteria in Lake Arresø is highest. The first monitoring period was August 2, 2004 until October 14, 2004, and the second monitoring period was August 4, 2005 until September 29, 2005. The aim of the monitoring periods was to investigate the quality of the infiltrating and abstracted water in an operation period of infiltration basin West 1. Both monitoring periods were started when the operation of infiltration basin West 1 was initiated after a period of regeneration of the basin bottom. Due to the regeneration there was no clogging layer in the basin bottom retarding the bacteria.

Microbiological analyses of water samples included CFU, coliform bacteria, and thermotolerant coliform bacteria. Additionally, water samples from the monitoring program in 2004 were analysed for enterococci, sulphite-reducing clostridia, and *Clostridium perfringens*, see table 1. Water samples collected from the abstraction wells I1 and M1 during this monitoring program in 2004 were only analysed for enterococci and *Clostridium perfringens* at every second sample collection.

4 REMOVAL OF BACTERIA – SEDIMENT SAMPLES

The capacity of the AR system for removing bacteria from the recharged water has been investigated by collecting and analysing sediment samples from infiltration basin West 1, the irrigated, and a non-irrigated area. The samples from the non-irrigated area were used as reference representing the background levels in the area.

4.1 *Infiltration basin*

The results of the analyses of sediment samples collected from infiltration basin West 1 in March 2004 and October 2005 are presented as average values of the samples from the shallow and deep end at the specific depths and year. Figure 2 shows the results of the analyses of CFU at 22°C and 37°C, coliform bacteria, and thermotolerant coliform bacteria.

Figure 2 shows that CFU, coliform bacteria, and thermotolerant coliform bacteria were primarily present in the upper 0.07 m.b.b. in 2004 and an the upper 0.05 m.b.b. in 2005. This is similar to findings at the Arrenæs AR trial plant by Jørgensen (2001) and Jørgensen et al. (2001). The contents of the bacteria show, however, both decreasing and increasing trends with depth in the upper 0.07/0.05 m.b.b.

Generally, the levels of the bacteria in sediment samples collected in March 2004 were higher than in sediment samples collected in October 2005. The content of coliform bacteria in 0.01 m.b.b. and thermotolerant coliform bacteria in 0.01-0,07 m.b.b. do, however, deviate from that, as the highest values are detected in October 2005.

Enterococci and *Clostridium perfringens* were not detected above the detection limit of 10 / 100 no. per g in the sediment samples collected in March 2004. Only the upper samples in 0.01 m.b.b. were analysed for sulphite-reducing clostridia, and the analyses result showed an average amount of 1000 sulphite-reducing clostridia/g. The content of enterococci in the samples collected in October 2005, varies between <3 and 8 enterococci/g dw. It was possible to measure this content as the detection

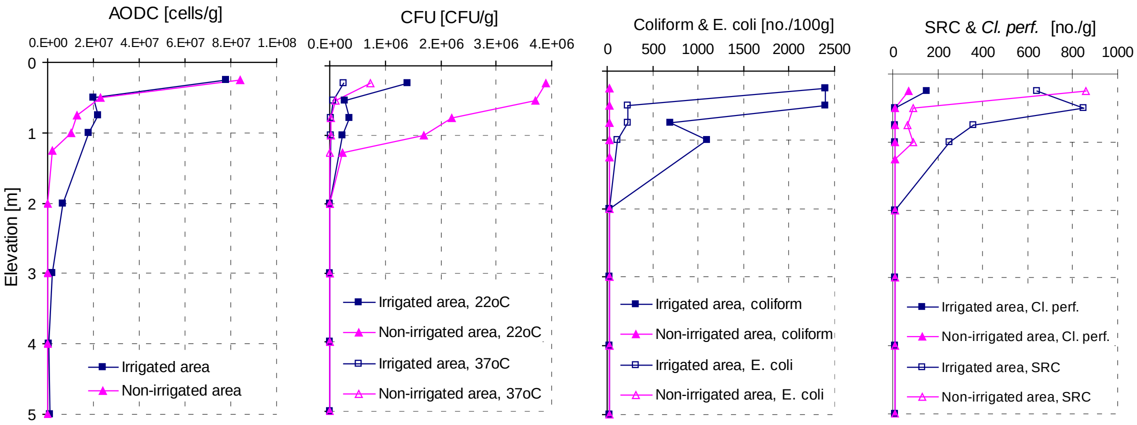

Figure 3: AODC, CFU, coliform bacteria, thermotolerant coliform bacteria (E. coli), sulphite-reducing clostridia (SRC), and *Clostridium perfringens* from 0-5 m.b.s. at the irrigated area and the non-irrigated area.

limit for the sediment samples collected in 2005 was 3 enterococci/g dw.

4.2 Irrigation area and reference area

The microbiological results of the sediment samples collected at the irrigated area and the reference area (0-30 m.b.s.) revealed that the bacteria were primarily present in the upper 2 m.b.s. and measured below detection limit from 2 until approximately 26-27 metres depth (except AODC, which was found in the upper 4 metres at the irrigated area). The content of AODC and CFU was higher in samples from the reference area compared to samples from the irrigated area, whereas the content of pathogenic indicator organisms, as expected, generally were higher in samples from the irrigated area compared to the reference area.

Figure 3 includes the upper 5 metres of the unsaturated zone, where the primary microbiological activity occurred. From this figure it is evident that the total number of bacteria (AODC) and CFU at 22°C and 37°C (detected using the yeast extract agar) were higher at the reference area compared to the irrigated area in the upper 0.5-1 meters. The content of bacteria measured as CFU was less than the total amount of bacteria (AODC) at both the irrigated and non-irrigated area, which indicates that bacteria cultures not accounted for using yeast extract agar were present at both locations.

The higher total amount of bacteria and CFU in the upper 0.5-1 meter at the reference area compared to the irrigated area may result from the difference in the geology between the two locations. At the reference area, the samples from the upper meter were more fine-grained compared to samples from the upper meter at the irrigated area, which may cause a higher degree of retention of bacteria in the sediment at the non-irrigated area. In addition, the lower content of bacteria at the irrigated area may be a result of the increased water flow at this area compared to the reference area, causing leaching of the bacteria. However, a higher amount of bacteria in the deeper layers at the irrigated area would then have been expected.

Coliform bacteria, thermotolerant coliform bacteria, and enterococci (not showed) were only detected at the irrigated area from 0-2 m.b.s., see figure 3. This is a result of irrigating with water from Lake Arresø, which has average contents of 68 coliform bacteria/100mL (2000-2005), 34 thermotolerant coliform bacteria/100mL (2000-2005), and 7 enterococci/100mL (2002-2004). Sulphite-reducing clostridia and *Clostridium perfringens* were, however, present in the upper 2 meters at both the irrigated area and the reference area.

4.3 Bacterial removal capacity at the recharge areas

The results of the bacterial analyses of sediment samples from infiltration basin West 1 and the irrigated area were used to calculate the degree to which these bacteria were removed. The bacterial removal in infiltration basin West 1 was calculated by using the content of bacteria in the sludge layer (0.01 m.b.b.) and in a depth of 0.35/0.4 m.b.b., whereas the bacterial removal at the irrigated area was calculated using the content of bacteria in 0.25 m.b.s. and 2 m.b.s. The results are shown in table 2. Except for coliform bacteria and enterococci measured in samples from infiltration basin West 1 in October 2005, the results show a removal of bacteria between 91 and 99% in both infiltration basin West 1 and at the irrigated area. It should be noticed that the minimum concentration of the bacteria is given as "less than detection limit", and the removal will therefore always be less than 100%.

Table 2: Removal of bacteria in the upper 0.35 m.b.b. (2004) and 0.4 m.b.b. (2005) in infiltration basin West 1 and in the upper 2 m.b.s. at the irrigated area. The removal in infiltration basin West 1 is given as an average of the removal in the shallow and deep end of the infiltration basin.

Parameter	Average removal at 0.35 m.b.b., West 1, March 2004 [%]	Average removal at 0.4 m.b.b., West 1, October 2005 [%]	Removal at 2 m.b.s., irrigated area [%]
AODC	Not measured	Not measured	91.3
CFU at 22°C	95.8	94.5	99.4
CFU at 37°C	94.2	93.6	99.1
Coliform bacteria	96.2	76.2 [1]	99.2
Thermotolerant coliform bacteria	97.3	93.4 (deep end)	99.2
Enterococci	Not detected	41.3 [2]	92.3
Clostridium perfringens , cells	Not detected	Not measured	93.3
Clostridium perfringens , spores	Not detected	Not measured	Not detected
Sulphite reducing *Clostridia*	Only measured in 0.01 m.b.b.	Not measured	98.4

[1] The removal of coliform bacteria in the *shallow* end was 99.6%, whereas it was 52.4% in the *deep* end.

[2] The removal of enterococci in the *shallow* end was 20%, whereas it was 62.5% in the *deep* end.

To further investigate the removal efficiency in the sediments below the infiltration basins, detailed investigations of the bacterial content of sediment samples from e.g. 0.4-2 m.b.b. need to be performed before finally calculating the removal capacity of the infiltration basins.

5 REMOVAL OF BACTERIA – WATER SAMPLES

The removal of bacteria in the upper parts of the recharge areas was 91-99.9%, as described in section 4.3. However, if the remaining parts of the pathogen indicator organisms are not removed in the deeper part of the unsaturated

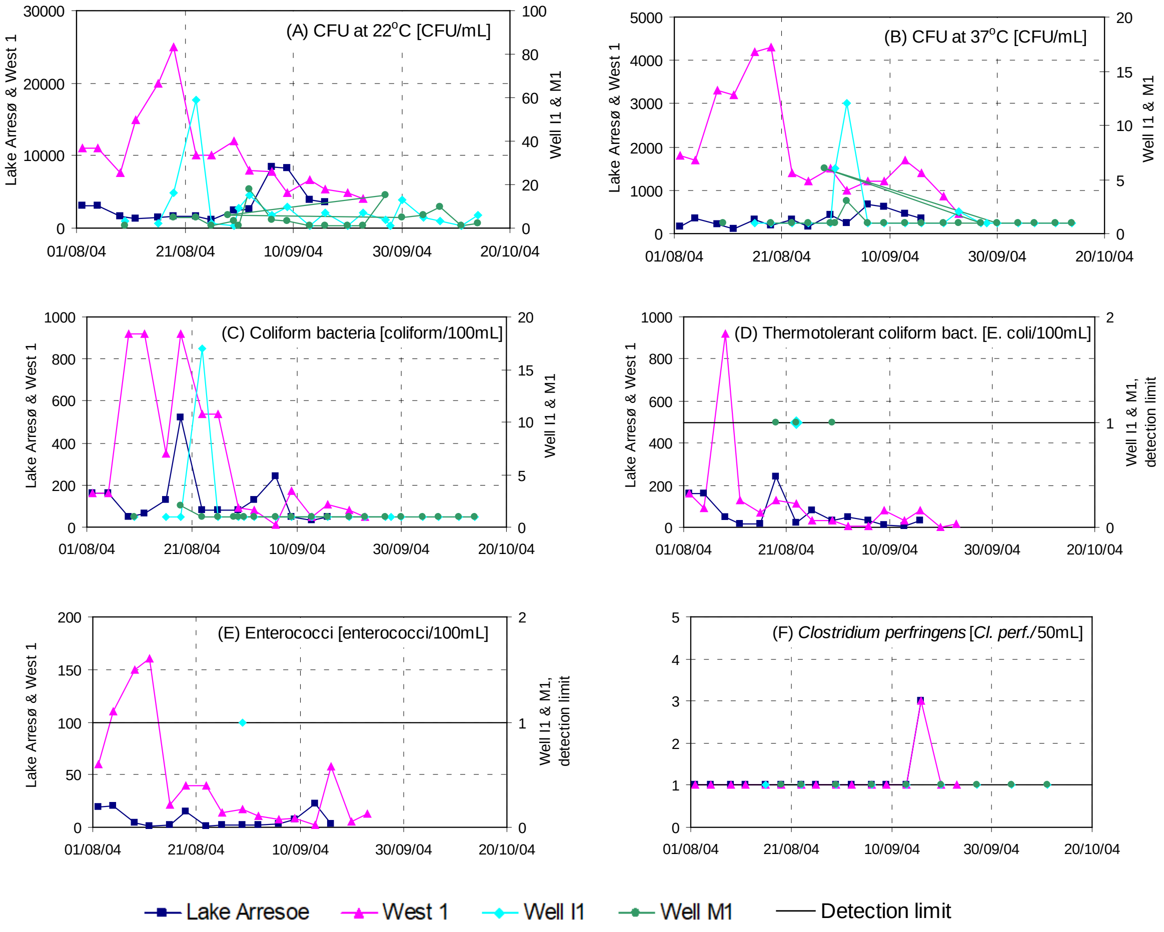

Figure 4A-F: CFU at 22°C and 37°C, coliform bacteria, thermotolerant coliform bacteria, enterococci, and *Clostridium perfringens* (cells) in water samples from the intake from Lake Arresø, infiltration basin West 1, and the abstraction wells I1 and M1 (2004) zone, there is a risk of a break through in the abstracted AR water. This risk has been investigated since the beginning of the operation of the Arrenæs AR trial plant in 1995 by continuously collecting and analysing water samples. Additionally, the risk of break through was investigated during water quality monitoring periods in 2004 and in 2005.

The following figure 4A-F show the results of the bacterial analyses from August-October 2004. The results of the two abstraction wells are shown on the secondary y-axis.

Figure 4A-F show that - except for *Clostridium perfringens* - the content of the bacterial parameters in water samples from Lake Arresø and infiltration basin West 1, were highest in the beginning of the monitoring period followed by decreasing concentrations. The content of CFU at both 22°C and 37°C as well as coliform bacteria and enterococci were higher in infiltration basin West 1 compared to Lake Arresø, which indicates that growth conditions for these bacteria might be present in infiltration basin West 1, due to elevated temperatures of the basin water of up to 25.6°C in this period. The increased concentrations in infiltration basin West 1 compared to Lake Arresø could also be caused by local faecal contamination. However, then it would be expected that also an increased content in infiltration basins West 1 of e.g. thermotolerant bacteria would have occurred.

Additionally, figure 4A-F show that the high content of bacteria in the water in infiltration basin West 1 was generally removed during infiltration. Concentrations of CFU, thermotolerant coliform bacteria, enterococci, and *Clostridium perfringens* did not exceed the guideline levels for raw water in water samples from the abstraction wells I1 and M1. However, break through of coliform bacteria occurred in both abstraction wells; in abstraction well M1 August 19, 2004 (2 coliform bacteria/100 mL) and in abstraction well I1 August 23, 2004 (17 coliform bacteria/100 mL).

The following figure 5A-D show the results of the bacterial analyses of the water samples collected in August-September 2005. The results of the abstraction wells I1 and M1 are shown on the secondary y-axis.

Figure 5A and B show that the content of CFU (22°C and 37°C) varied a lot in both samples from Lake Arresø and infiltration basin West 1, however showing an increasing trend in the second half of the monitoring period. Some of the variation in the content of CFU at 22°C is due to some of the samples being registered as >3000 CFU/mL. The content of CFU (22°C) in infiltration basin West 1 was similar to or higher than the content in Lake Arresø. The content of coliform bacteria and thermotolerant coliform bacteria was generally higher in infiltration basin West 1 compared to Lake Arresø, and both parameters showed some variation (figure 5C and D).

The levels of CFU at 22°C, coliform bacteria, and thermotolerant coliform bacteria measured during the monitoring period in August-September 2005 were much lower compared to the results from the monitoring period in August to October 2004. This might be a result of

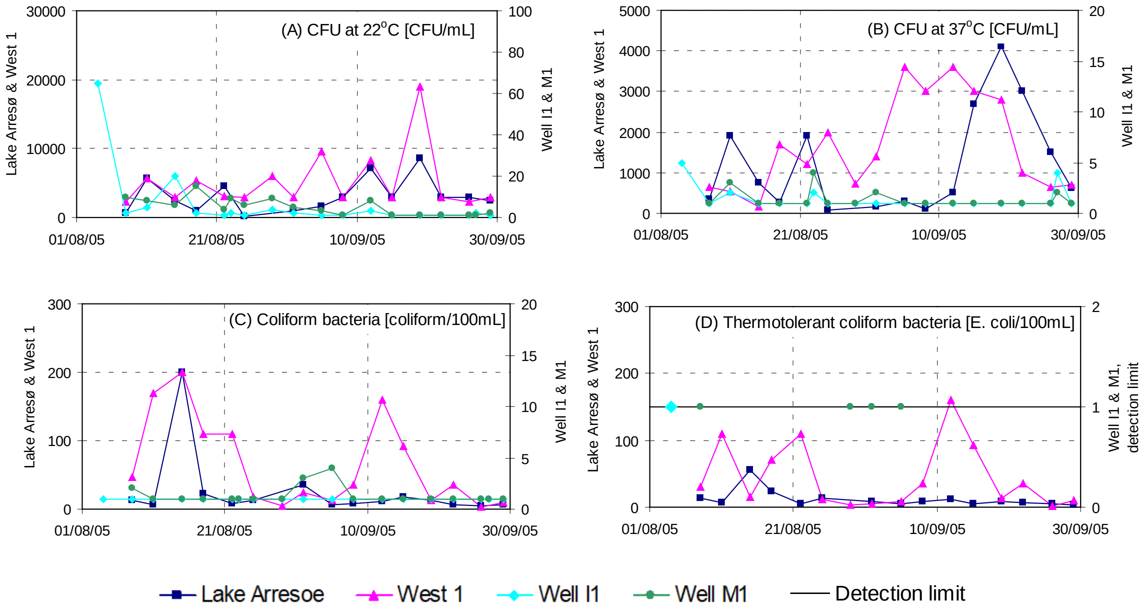

Figure 5: CFU at 22°C and 37°C, coliform bacteria, and thermotolerant coliform bacteria in water samples from the intake from Lake Arresø, infiltration basin West 1, and the abstraction wells I1 and M1 (2005). (The sample collected August 29 from Lake Arresø showed extremely high levels CFU and coliform bacteria. As these high levels were only occurring in this sample, the results from this date are omitted from the figures).

different weather conditions. The water temperatures measured in Lake Arresø and infiltration basin West 1 in 2004 were on average 18°C, whereas the water temperatures in 2005 were on average 16.5°C. This decreased water temperature in 2005 compared to 2004 might cause a decrease in the measured content of bacteria.

Except for the sample collected from abstraction well I1 August 4, 2005, the CFU at both 22°C and 37°C in samples from abstraction well I1 and M1 showed low levels, similar to the measured concentrations found in the monitoring period in 2004 (figure 5A and B). Coliform bacteria in water from abstraction well I1 was below detection limit during the measurement period. In abstraction well M1 break through of coliform bacteria was, however, detected three times; August 8 (2 coliform bacteria/100mL) and September 1 and 5 (3 and 4 coliform bacteria/100 mL), see figure 5C. Thermotolerant coliform bacteria were not detected in any of the samples (figure 5D).

6 INVESTIGATION OF THE POTENTIAL RISK FOR PATHOGENIC BREAK THROUGH IN THE GROUNDWATER

Break through of pathogens was investigated in Jensen et al. (2005) using the results of analysing the pathogenic indicator organism coliform bacteria. The following is based on results from this work. Break through of coliform bacteria in abstraction well I1 has, as mentioned, been registered three times (in 2002, 2004, and 2005), however, the following calculations are based in the break through registered in 2002 and 2004. Unregistered contamination of the abstraction wells may, however, have occurred. The probability of a contamination of an abstraction well being found is estimated as discussed by Boe-Hansen et al. (2003). It is assumed that a contamination has a duration of N days with probabilities $P(N)$, $N = 1,2,...$ and as an example, it is assumed, that N varies between 1 and 13 days with equal probabilities $P(N) = 1/13$ (mean(N) = 7). The annual rate of contaminations is called λ_y, and the sampling frequency is S_y (currently 12 samples/year). To repeat a positive test d days (in this study d=2) are needed, and the detection limit is 1 bacterium in a 100 mL sample. The mean number of bacteria per 100 mL in a contamination is called μ_c.

Under these assumptions the proportion of contaminations detected and confirmed can be

$$Q(S_y, \mu_c) \cong (1-\exp(-\mu_c))^2 \cdot S_y \sum_{N>d} P(N)\cdot(N-d)/365$$

estimated:

where,

$$\sum\nolimits_{N>2} P(N)\cdot(N-2)/365 = 5.076/365 = 0.0139$$

in the given example. If further $\mu_c > 3$,

$$(1-\exp(-\mu_c))^2 > 0.90 \cong 1,$$

the variation of μ_c between contaminations is thus of little consequence, except for very low-level contaminations. The contaminations experienced in 2002 and 2004 have shown $\mu_c >> 3$ in both cases. The annual rate of confirmed findings is $\lambda_y \cdot Q(S_y, \mu_c)$. The formulas apply for moderate S_y and moderate length of contamination, that is when the time between sampling is long compared to the mean duration of contamination (365/S_y >> mean(N)) and the occurrence rate is low. Using the above $P(N)$ and d, the detection proportion, $Q(S_y, \mu_c)$ is computed, see table 3.

Table 3: The proportion of detected and confirmed contaminations using $P(N)$=1/13 and d=2.

Contamination	Samples per year = S_y		
	12	18	24
μ_c = 1.0	0.07	0.10	0.13
μ_c = 2.0	0.12	0.19	0.25
μ_c = 3.0	0.15	0.23	0.30
μ_c >> 3.0	0.17	0.25	0.33

As the detection rate is proportional to the occurrence rate λ_y, the table can be applied to estimate λ_y. If, for example, 2 contaminations are found in a year using the present S_y = 12 and μ_c >> 3, the contamination rate may be as high as $\lambda_y = 2/0.17 \cong 12$ per year or more.

It should be noticed that these calculations are based on a sample collection frequency of two samples per week, which was used in the monitoring periods in August-October 2004 and August-September 2005. However, the routine sample collection frequency at the AR trial plant is presently one sample per month. The calculations in this section show that it is important to increase the sample collection frequency to detect a possible break through. Additionally, it is important to encourage researchers to develop methods for online monitoring of pathogenic bacteria. This could be used as a management tool in the operation of the AR plant. Contamination of the abstraction wells could thereby be limited. In addition, operational changes must be made to avoid pathogens in the abstracted water.

7 CONCLUSIONS

The investigations in this study show that the primary removal of the bacteria at the Arrenæs AR trial plant occurs in the uppermost part of the soil. A removal capacity of 91-99% of the microbial content was observed in both infiltration basin West 1 and at the irrigated area. However, to further examine the bacterial processes in the deeper part of infiltration basin West 1, investigations need to be performed at depths below approximately 0.4 meters. Additionally, detailed investigations need to be performed from 0-1.5 m.b.s. at the irrigated area to further examine the microbiological processes occurring in the uppermost part of the soil.

Despite the high removal of the bacterial content during infiltration, break through of coliform bacteria was observed twice in abstraction well I1 and three times in abstraction well M1. This shows that break through of coliform bacteria in the abstraction wells constitutes a risk to the quality of the abstracted water. It is therefore recommended that the operation of the AR plant is adjusted to avoid pathogenic break through, e.g. by lowering the water flow to the infiltration basins in the beginning of an infiltration period until a clogging layer in the basin bottom is formed.

Based on a sample collection frequency of two samples per week, statistical calculations in this study indicate that only 17% of all possible break through with coliform bacteria in the abstraction wells will be discovered. It may therefore be relevant to increase the sample collection frequency of the abstracted water at the Arrenæs AR trial plant and to develop methods for online monitoring of pathogenic bacteria, which could be used as a management tool in the operation of the proposed large-scale AR plant at Arrenæs.

8 ACKNOWLEDGEMENTS

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9 REFERENCES

Bennedsen, L., Berg, R.L., Brandt, G. & Nielsen, T.Ø. 2005. Description of the Arrenæs Artificial Recharge Trial Plant. (In this Final Scientific Report).

Boe-Hansen, R., Albrechtsen, H.-J., Arvin, E. & Spliid, H. 2003. Microbial pollutions - we only see the tip of the ice (in Danish). In: Dansk Vand, vol. **3**, pp. 86-90.

Jensen, T.Ø., Berg, R.L., Bennedsen, L., Brandt, G. & Spliid, H. 2005. Geochemical and microbial processes in the unsaturated zone at the Arrenæs artificial recharge trial plant. Fifth Int. Symp. on Management of Artificial Recharge (ISMAR), Berlin, 12-16 June 2005. In: Recharge Systems for Protecting and Enhancing Groundwater Resources (in press).

Jørgensen, C., Peters, J. & Eschweiler, B. 2001. Removal of pathogens and monitoring of microbial changes during artificial recharge. In: Final report from the EC project ENV4-CT95-0071 Artificial recharge of groundwater, pp. 221-225.

Jørgensen, C. 2001. Migration and survival of bacteria during artificial recharge. In: Final report from the EC project ENV4-CT95-0071 Artificial recharge of groundwater, pp. 231-234.

Nielsen, T.Ø., Berg, R.L., Bennedsen, L. & Brandt, G. 2005. Early Warning System at the Arrenæs Artificial Recharge Trial Plant. (In this Final Scientific Report).

Chapter 26: Scenario Management and Expert System for the Arrenæs Artificial Recharge Trial Plant

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Abstract: An "expert system" has been developed within the ARTDEMO project for the Arrenæs AR trial plant, Denmark. The expert system is made up by the early warning system (online monitoring and DIMS) and the plant operator’s use of the management plan in the operation of the AR plant. The expert system has subsequently been tested and evaluated using three selected risks considered as the most critical to the operation of the AR plant. The evaluation was performed theoretically using flow charts and a PowerPoint presentation, and was based on experiences of operating the AR plant. The evaluation revealed that the expert system in general handled the risks as required. However, some improvements for the early warning system and the management plan were identified and either included in the present expert system or suggested for future improvements.

1 INTRODUCTION

A part of the ARTDEMO project has been to develop and integrate an early warning management strategy at the Arrenæs Artificial Recharge (AR) trial plant, Denmark. The objective has been to develop an "expert system", which forms the basis for a sustainable and optimal management and operation of the AR trial plant.

The expert system is based on an early warning model called IDAS (Incident, Detection, Action, Surveillance) described in Lundh et al. (2005), which illustrates how incidents affecting the AR plant are detected and handled to limit possible damage. The early warning system includes both off- and online monitoring and the data handling system DIMS (Dynamic Integrated Monitoring System) as described in Nielsen et al. (2005a) and Lynggaard-Jensen et al. (2005). The management and operation of the Arrenæs AR trial plant is described in the management strategy and the management plan developed for the Arrenæs AR trial plant within the ARTDEMO project (Nielsen et al., 2005b). The interaction between the online monitoring, DIMS, and the plant operator’s use of the management plan in the operation of the AR plant forms the basis of the expert system. This system can be used by the plant operator to get essential information on the operation of the AR plant, which can be beneficial for optimising the operation.

To evaluate the expert system developed for the Arrenæs AR trial plant, a number of risks towards the operation of the AR plant have been identified. The three most important risks within the area of sustainable water quality, water quantity, and plant operation have been selected for the evaluation. The aim of this evaluation is to use the risks to reveal if the early warning system and the management plan can handle a given situation as required. The evaluation is performed using strategies for "normal operation" and "early warning" and the three selected risk covers the situations of "closure", "regeneration", and "barrier removal effect". If lacks and/or limitations to the developed expert system are revealed, the expert system should be improved, if possible, or suggestions should be included for future improvements.

2 THE ARRENÆS AR TRIAL PLANT

The Arrenæs AR Trial Plant is located at the Arrenæs peninsular in the northern part of Zealand,Denmark. The AR trial plant is recharging water from Lake Arresø, which is the largest lake in Denmark with a surface area of 40.7 km^2 and an average depth of 3.1 metres. The annual discharge of Lake Arresø is 30-65 million m^3 and the retention time for the water in the lake is approximately 3 years. The catchment area for Lake Arresø is mostly agricultural areas, but also several cities and forest areas are included.

The Arrenæs AR trial plant consists of four infiltration basins and two trough systems (1000 m^2 each) and a sprinkling area (20,000 m^2 in total). The thickness of the unsaturated zone is more than 25 metres at the site. At the AR plant 12 tensiometer wells, 6 monitoring wells, and 4 abstraction wells have been established, and it is thereby possible to measure the quality of the water passing through the unsaturated zone as well as the quality of the newly formed groundwater. The abstracted water is presently not used for drinking water purposes but is let back to Lake Arresø. However, a large-scale AR plant for drinking water purposes has been proposed at the location. For a detailed description of the Arrenæs AR trial plant see Bennedsen et al. (2005) in this Final Scientific Report

3 SCENARIOS FOR THE ARRENÆS AR TRIAL PLANT

3.1 Identification of risk scenarios

A list containing all relevant risk scenarios for the Arrenæs AR trial plant has been set up. The list is divided into two parts describing internal and external risks. An *internal risk* is defined as an incident occurring at the AR trial plant, e.g. clogging of the infiltration basins due to algae growth in sedimentation and/or infiltration basins (scenario 3). An *external risk* is defined as an incident occurring outside the AR trial plant, but affecting the operation and/or the water quality at the AR plant, e.g. algae growth in Lake Arresø resulting in clogging of the infiltration basins (scenario 9).

The list was produced using both experiences from the 10 years of operation of the Arrenæs AR trial plant, experiences gained from running a public water supply, as well as considering possible risks caused by the land use in the surrounding areas. The list contains what is presently thought to be the most critical situations that could affect the operation of the Arrenæs AR trial plant. If additional risks are identified in the future, these should be added to the list and it should be checked that the early warning system, as well as routine procedures and alarm actions defined in the management plan, account for the given situation. In the following, the internal and external risks are listed.

Internal risks:

1. Contamination of sedimentation basins
    - Production of algae toxins in the sedimentation basins
    - Increase in the content of pathogens in the sedimentation basins
    - Spill of chemical/petroleum products from a vehicle on the AR plant
2. Contamination of infiltration basins
    - Production of algae toxins in the infiltration basins
    - Increase in the content of pathogens in the infiltration basins
    - Spill of chemical/petroleum products from a vehicle on the AR plant
3. Clogging of infiltration basins
    - Algae production in the sedimentation/infiltration basins
4. Overflow of infiltration basins caused by heavy rainfalls
5. Contamination of abstraction wells
6. Process interruptions
    - Pump break down
    - Freezing of or damage on pipes/ sprinklers
7. Power failure
    - General power cut at the AR plant area
    - Power cut to different parts of the processes at the AR plant
8. IT
    - Data collection and data handling error.

External risks:

1. Increased amount of algae in the raw water source
2. Production of algae toxins in the raw water source
3. Microbial contamination of the raw water source
    - Overflows from wastewater treatment plants
    - Leaching of manure from agricultural land to the raw water source due to heavy rainfall
4. Increased content of nutrients in the raw water source
    - Overflows from wastewater treatment plants
    - Leaching of manure from agricultural land to the raw water source due to heavy rainfall
5. Contamination of the raw water source with micro-pollutants and/or pesticides
    - Overflows from wastewater treatment plants
    - Leaching of manure from agricultural land to the raw water source due to heavy rainfall
    - Additional discharge to the raw water source from industries
6. Chemical contamination of the raw water source
    - Overflows from wastewater treatment plants
7. Contamination of the raw water source with GMO
    - Overflows from wastewater treatment plants
8. Power failure
    - General power cut in the local area/region.

3.2 The most critical (high risk) scenarios

The risk scenarios given in the previous two lists are all relevant in testing of the expert system. Within ARTDEMO three scenarios have been selected to test and evaluate the expert system for Arrenæs AR trial plant. In the selection of these three risk scenarios, focus was to choose the most critical risks within the area of water quality, water quantity, and the operation of the AR plant, as these are crucial factors in the management and operation of an AR plant. Within the ARTDEMO project, the following three important areas of quality management have therefore been defined:

- **Sustainable water quality** (SWQ) meaning maintaining a continuous, good water quality according to regulations
- **Sustainable water production** (SWP) meaning maintaining a continuous water production according to community requirements
- **Sustainable plant operation** (SPO) meaning protecting the plant from unmanageable damage

The three risk scenarios selected for the evaluation of the early warning system and the management plant for the Arrenæs AR trial plant are:

- Scenario 7: Power failure, general power cut at the AR plant area (SWP)
- Scenario 9: Increased amount of algae in the raw water source (SWP, SPO)
- Scenario 10: Production of algae toxins in the raw water source (SWQ, SWP, SPO)

Each of the scenarios affects one or more of the three quality management areas. However, it should be noticed that all the defined internal and external risk scenarios are of significance, and are most likely to cause problems at some time at the Arrenæs AR trial plant. To perform a complete test and evaluation of the expert system all defined risks should therefore be used.

4 TESTING THE EARLY WARNING SYSTEM AND MANAGEMENT PLAN USING THE SELECTED RISK SCENARIOS

In the evaluation of the expert system performed with the three selected risk scenarios, the concept and structure of the IDAS model (Lundh et al., 2005) was used as discussed in details within the ARTDEMO Deliverable 6.3. As described in section 3, the risk scenarios were selected within the areas of sustainable water quality, quantity, and plant operation. The evaluation includes a test of the strategies for "normal operation" and "early warning" as defined within the ARTDEMO project, and the three risk scenarios covers the situations of "barrier removal effect" (the ability of the AR system to remove contaminants), "regeneration strategy" (regeneration of infiltration basins) and "closure strategy" (closing down all or a part of the AR plant, e.g. the intake). It is assumed that the AR plant is operated according to the normal operation strategy, when the risk scenarios are initiated. Table 1 shows relevant parameters in the three selected scenarios, how the risks are detected, possible consequences for the AR

Table 1: Overview of three selected risk scenarios regarding relevant parameters, detection, possible consequences together with situations and operation strategies to be tested.

Risk scenarios	Relevant parameters	Detection (D) and possible consequences (C) of risks	Situations and operation strategies to be tested
Scenario 7: Power failure	Water	D: All electricity dependent functions are out of operation	Closure strategy
		C: No water is recharged from Lake Arresø	
		C: No water production	
Scenario 9: Increased amount of algae in the raw water source	Algae	D: High content of algae in Lake Arresø	Normal strategy, early-warning strategy, closure strategy
		C: Clogging of the infiltration basins	Regeneration strategy
		C: Reduced water production	
Scenario 10: Production of algae toxins in the raw water source	Algae toxins	D: High concentration of algae toxins in Lake Arresø	Normal strategy, early-warning strategy, closure strategy
		C: Contamination of the clogging layer in the infiltration basins with algae toxins	Barrier removal effect
		C: Break through of algae toxins in the groundwater and thereby possible deteriorating quality of the abstracted water	Early warning strategy

system, together with situations and operation strategies to be tested.

The evaluation of the three scenarios was performed theoretically based on experiences. For each of the three scenarios, a flow chart has been made to test and evaluate the expert system. The flow chart gives an overview of the given situation, the early warning system and protocols within the management plan involved in the scenario, and the links between relevant protocols. Additionally, for scenario 9, a PowerPoint presentation was made (see the CD - Final Scientific Report) illustrating the required procedures and actions in the given situation.

In the following short descriptions are given for the evaluation performed using scenario 7 and 10. For scenario 9, the description of the evaluation processes is more detailed to illustrate the concept of the evaluation process. To have a fully evaluated expert system, all defined risks should be used, and the evaluation should be performed continuously, when new risks are identified.

A detailed description of the evaluation for all three risks scenarios is given in the ARTDEMO Deliverable 6.3, and changes to the early warning system and the management plan is described in Nielsen et al. (2005b).

5 SCENARIO 7: POWER FAILURE

Supply of power is crucial in the operation of the Arrenæs AR trial plant, as several essential functions are dependent on electricity: pumps; alarm signals; online measurements of water quality, -flow and -level; and the control system in the operator house. There is no emergency power supply set up at the present AR trial plant. Therefore, if a power failure occurs, water will not be pumped from Lake Arresø to the AR plant or recovered from the abstraction wells

The risk scenario starts when a fictitious power failure occurs at the Arrenæs AR trial plant and all electricity dependent functions stop. The early warning system - online monitoring and DIMS – is not involved in detecting this risk scenario, as alarms and DIMS is out of operation. The AR plant operator will discover the power failure in various other ways; no water is let to the sedimentation basins or sprinkling areas, the control board does not show the displays, the light is turned off, etc.

Testing the early warning system and the management plan, using scenario 7, revealed that overall the situation was handled as required. However, links between the protocols included in the testing were lacking and new sub-protocols at level 4 in the management plan were required. Power failure has only occurred infrequently at the Arrenæs AR trial plant and investigations of the most expedient procedures and actions should therefore be performed and included in the management plan in the future. An improvement in the operation of the AR plant would be to install an emergency power supply, which would limit the consequences of a power failure.

6 SCENARIO 10: PRODUCTION OF ALGAE TOXINS IN THE RAW WATER SOURCE

An important factor affecting a sustainable management and operation of an AR plant is the quality of the intake water. Contaminated intake water may result in contamination of the

clogging layer in the infiltration basins, the unsaturated zone, the aquifer, and in the end the abstracted water. This may cause undesirable changes in the operation of the AR plant for shorter or longer periods. Scenario 10 focuses on production of the algae toxins, microcystins, in Lake Arresø. Microcystins are produced by Cyanobacteria (blue-green algae), which may be the dominating phytoplankton in Lake Arresø in August-September (Christoffersen, 2000). Microcystins are liver toxins and therefore undesirable in drinking water (advisable limit value in drinking water given by WHO: 1 µg/L). Investigations at the Arrenæs AR trial plant have shown that microcystins are removed during infiltration through the unsaturated zone. However, attention should be paid to the removal of microcystins, as it is crucial that these are not present in the abstracted water, since they will not be removed in the following treatment (simple aeration and filtration) at the waterworks.

The scenario starts with an fictitious alarm occurring in DIMS, due to the detection of algae toxins in the intake water from lake Arresø above a given attention value. When detecting algae toxins in the intake water above this given attention value, procedures and actions described in the management plan need to be performed in accordance to the IDAS model as described in Lundh et al. (2005) to minimise the consequences in the given alarm situation.

In the testing of the early warning system and the management plan using scenario 10, it was revealed that overall the alarm situation of detecting algae toxins in the raw water source above the attention value was handled as required. However, as for scenario 7, links between protocols were lacking, and new sub-protocols at level 4 in the management plan were required. Furthermore, additionally laboratory experiments and field investigations of the occurrence and behaviour of microcystins are needed before determining the attention value for microcystins in the intake water and the exact procedures and actions to be included in the management plan.

7 SCENARIO 9: INCREASED AMOUNT OF ALGAE IN THE RAW WATER SOURCE

7.1 Scenario description and assumptions

The amount of water infiltrating from the recharge areas, e.g. the infiltration basins, is an important factor in having a sustainable water production at an AR plant. The intake water from Lake Arresø contains algae, especially during summer months. Algae cause clogging of the infiltration basins, which reduces the water production, and when an infiltration basin is fully clogged, regeneration of the basin bottom is needed. This is a time and resource-consuming task, which lasts for approximately one month. The optimum operation of the infiltration basins is to lower the regeneration frequency by making the operation periods as long as possible, while still having a satisfactory water production.

An online water quality measurement station has therefore been installed at the Arrenæs AR trial plant, measuring the quality of the intake water from Lake Arresø. One of the parameters is fluorescence, which is an indicator for the content of algae in the water. An attention value is set for the fluorescence level. If the content of algae is measured above the attention value, it is advisable to close the intake of water to reduce/avoid clogging of the infiltration basins.

Risk scenario 9 starts with a fictitious alarm in DIMS caused by a fluorescence level in the intake water above the attention value. During the testing of this situation, several assumptions were made to limit the testing and make it clear. Most important, it is assumed that the intake of water is closed for maximum one week, and that this will not cause a lowering of the groundwater table, even if the abstraction of AR water continues.

7.2 Critical substances and consequences

The critical substance in this scenario is a content of algae in the intake water above the attention value. Since November 2004 a fluorescence sensor has been installed at the Arrenæs AR trial plant measuring the content of algae in the intake water, see figure 1. In the period from November 2004 to May 2005 the results were, however, very unstable. A preliminary attention value for the fluorescence level is therefore based on results from May to October 2005 and is set to 100‰. Additionally experiences and investigations of the fluorescence level is, however, needed before finally selecting the attention value.

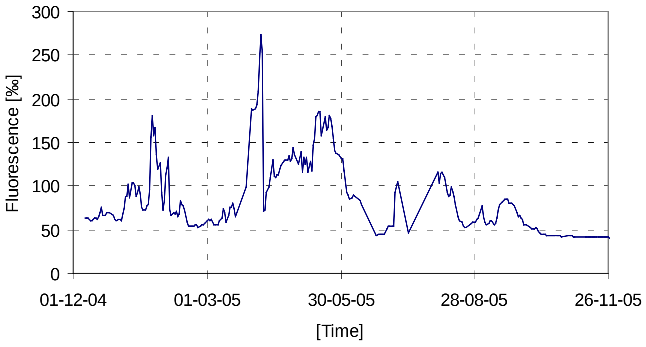


Figure 1: Fluorescence measurements of the intake water from Lake Arresø from Nov. 2004 to Oct. 2005.

The critical substance is a water quality parameter, but does however, affects the operation of the AR plant and the water production, as it causes clogging and thereby a reduction of the water production. In the management of the AR plant it is therefore important to secure that the amount of abstracted water does not exceed the amount of infiltrated water. Depending on the length of the period and the reduction in infiltration rate, the water production at the AR plant may be reduced.

7.3 Testing the early warning system and the management plan with scenario 9

The test of the early warning system and the management plan using scenario 9 is based on experiences and performed theoretically by making a flow chart and a PowerPoint presentation. The flow chart gives an overview of required procedures and actions that should be performed, when an alarm for the fluorescence level in the intake water has occurred in DIMS, see figure 2.

In the flow chart, the squared boxes refer to sub-protocols within the management plan, describing the procedures and actions that must be performed in the given situation. The sub-protocols contain questions (diamond formed boxes) to reveal if the problem has been solved, or if further actions are needed. The overall flow of handling the situation is described in protocol 5.3.2.1, which is made up by questions in the dashed rectangular box. Testing the early warning system and the management plan by making the flow chart gave an overview of the content of related protocols and the links between the protocols.

Additionally, a PowerPoint presentation was made combining the information the AR plant operator gets by using a trial version of the interactive management plan for Arrenæs AR trial plant integrated in DIMS (presented Nielsen et al., 2005) together with pictures of where the procedures and actions are performed.

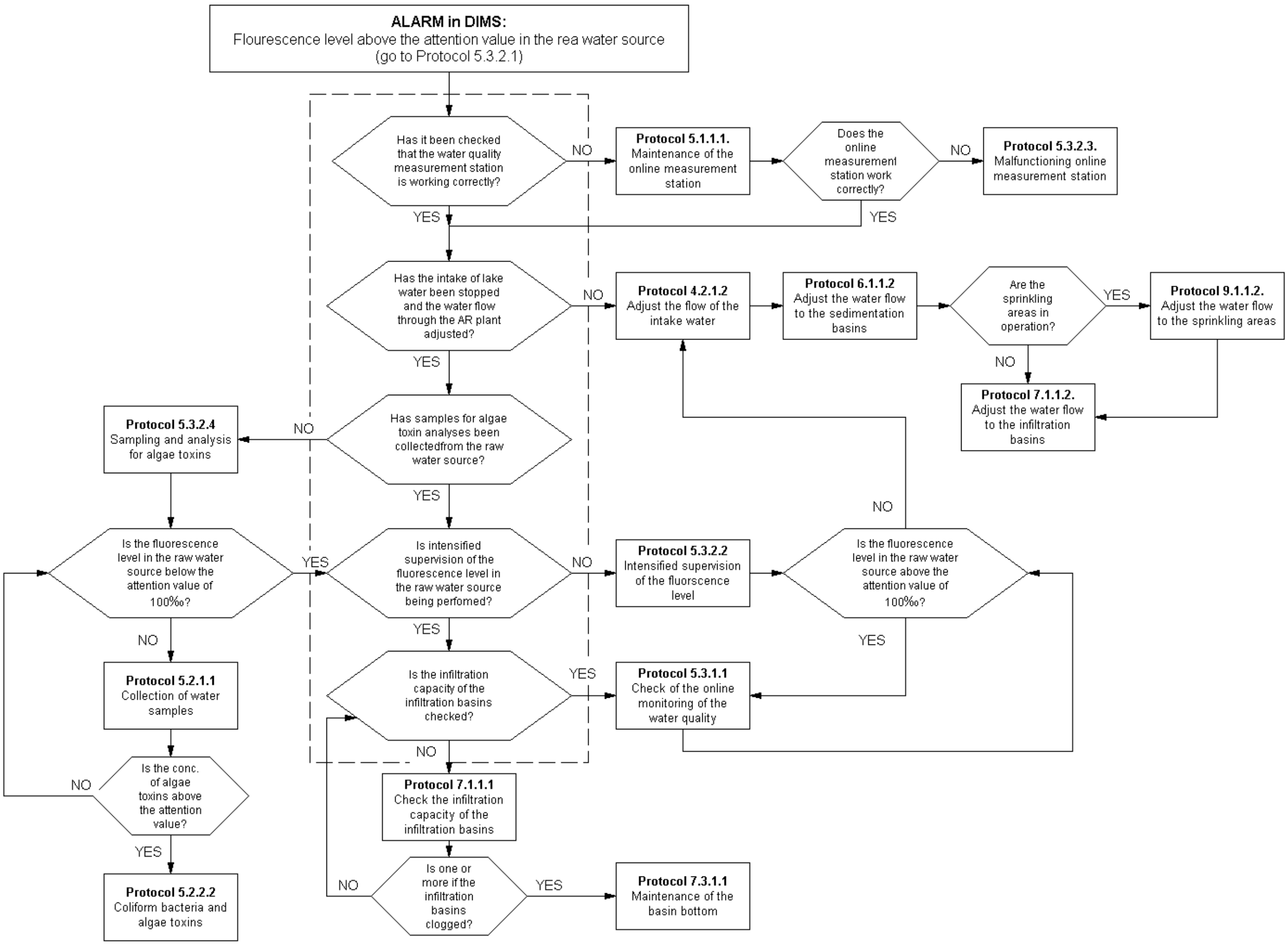


Figure 2: Flow chart of the testing of the expert system using Scenario 9.

The presentation is given on the CD – Final Scientific Report.

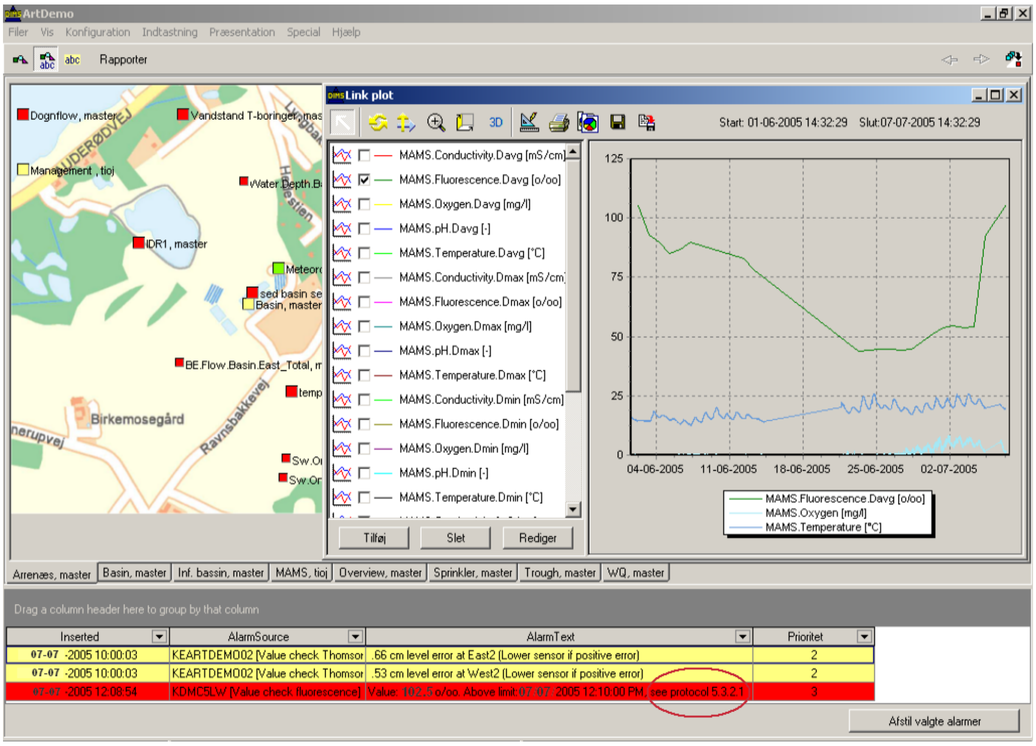
Figure 3 shows how the alarm will display, when the AR plant operator checks the operation in DIMS.

The information connected to this alarm is the level of fluorescence, the time of detection and a reference to protocol 5.3.2.1, which must be checked for further action. Figure 4 shows protocol 5.3.2.1 as a part of the interactive electronic version of the management plant.

Both evaluations methods (flow chart and PowerPoint presentation) revealed that the content in some sub-protocols and links between included sub-protocols were lacking, and that new sub-protocols at level 4 in the management plan were required to handle the situation in an optimal way.

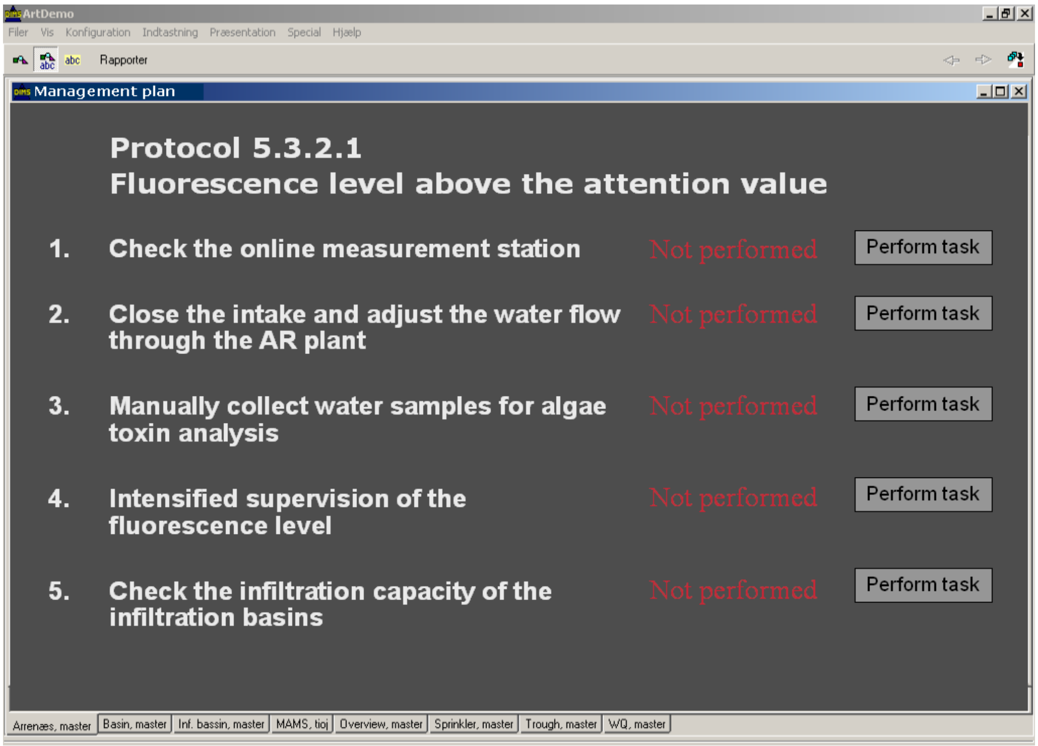
Testing the early warning system furthermore revealed that online measurements of the quality of the intake water are very essential in the operation of an AR plant, where water is being recharged from a nutrient rich lake as Lake Arresø. The scenario reveals that if action is taken when a level of fluorescence is detected above the attention value in the intake water, clogging of the infiltration basins may be avoided. It is therefore recommended to include the fluorescence measurements in the operation of the purposed large-scale AR plant at Arrenæs as a part of an early warning strategy.

Additionally, it would be advisable in an operation situation of the proposed large-scale AR plant to combine the fluorescence measurements with measurements of algae pigment, which identify the amount of selected groups of algae. During the operation of the AR trial plant, it is observed that some algae seem to clog the infiltration basins more efficiently than others. Investigations should be made on this to determine to which degree the different groups of algae will cause problems with clogging. Furthermore, measurements of pigment will give an indication on the presence of algae, which produce toxins and thereby possible future increase in the content of algae toxins. A combination of the measurements of fluorescence and algae pigment will thereby result in a more purposeful effort.



Inserted	AlarmSource	AlarmText	Prioritet
07-07 -2005 10:00:03	KEARTDEMO02 [Value check Thomsor	.66 cm level error at East2 (Lower sensor if positive error)	2
07-07 -2005 10:00:03	KEARTDEMO02 [Value check Thomsor	.53 cm level error at West2 (Lower sensor if positive error)	2
07-07 -2005 12:08:54	KDMC5LW [Value check fluorescence]	Value: 102.5 o/oo. Above limit:07-07-2005 12:10:00 PM, see protocol 5.3.2.1	3

Figure 3: Alarm in DIMS - screen dump from the PowerPoint presentation (scenario 9)



Protocol 5.3.2.1
Fluorescence level above the attention value

1. Check the online measurement station — Not performed
2. Close the intake and adjust the water flow through the AR plant — Not performed
3. Manually collect water samples for algae toxin analysis — Not performed
4. Intensified supervision of the fluorescence level — Not performed
5. Check the infiltration capacity of the infiltration basins — Not performed

Figure 4: Link to the interactive version of the management plan – screen dump from the PowerPoint presentation (scenario 9)

8 CONCLUSIONS

The expert system consisting of the early warning system, data handling in DIMS, and the AR plant operator's use of the management plan have been evaluated by testing three risk scenarios at the Arrenæs AR trial plant. The evaluations were performed theoretically using both flow charts and a PowerPoint presentation, which were very useful tools in the detection of limitations in the expert system. The evaluation revealed that the online monitoring system, DIMS and the management plan overall handled the three risk scenarios as required. The online monitoring system and DIMS made it possible for an early detection of the alarm situations in the scenarios. The evaluation of the protocols in the management plan revealed that some sub-protocols were lacking and that links between sub-protocols were insufficient.

In a future operation of the proposed large-scale AR plant at Arrenæs, it is recommended to extend the expert system compared to the present situation. E.g. it could be useful to install an emergency power supply set up at the proposed large-scale AR plant, to extent the alarms in DIMS with sending an SMS to the responsible person to obtain a faster action, and to include an online monitoring station measuring the quality of the intake water at the AR plant, especially fluorescence, which indicates the algae content in the water. However, further study is needed to set a deliberate attention value for the fluorescence level. The fluorescence measurements may be combined with measurements of algae pigment, or ideally, the fluorescence sensor should be able to distinguish between different kind of algae. This will give information about the potential for clogging of the infiltration basins and production of algae toxins.

9 REFERENCES

Bennedsen, L., Berg, R.L., Brandt, G. & Nielsen, T.Ø. 2005. Description of the Arrenæs Artificial Recharge Trial Plant. (In this Final Scientific Report).

Jørgensen C. 2005. Automatic monitoring and management systems for the Arrenæs AR trial plant. Project description – Microbiological analyses, degradation and transport of pathogens. (In Danish: Automatisk moniterings- og management-system til Arrenæs forsøgsanlæg. Projekt-beskrivelse - Mikrobiologiske undersøgelser, nedbrydning og transport af patogener). DHI – Water and Environment.

Christoffersen K. 2000. Investigation of microcystins the Arrenæs recharge plant – reporting for 2000. (In Danish: Under-søgelser af microcystin i infiltreringsanlæg ved Arrenæs - afrapportering for 2000). Ferskvandsbiologisk Laboratorium. Københavns Universitet.

Lundh, M., Engblom, K., Holmström, E., Bennedsen, L., Brandt, G., Berg, R.L. & Nielsen, T.Ø. 2005. IDAS: Connection the Detection of an Incident with the resulting Action and the follow-up Surveillance in an early warning strategy model for MAR applications (In this Final Scientific Report).

Lynggaard-Jensen, A., Eisum, N.H. & Rasmussen, I. 2005. Real Time Operation and Management system at Arrenæs Artificial Recharge Plant. (In this Final Scientific Report).

Nielsen, T.Ø., Berg, R.L., Bennedsen, L. & Brandt, G. 2005a. Early Warning System at the Arrenæs Artificial Recharge Trial Plant. (In this Final Scientific Report).

Nielsen, T.Ø., Berg, R.L., Bennedsen, L. & Brandt, G. 2005b. Introduction of the Management Plan for the Arrenæs Artificial Recharge Trial Plant. (In this Final Scientific Report).