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BTO report

The contribution of soil passage in removing pharmaceutical compounds from infiltrated surface water

Towards potential adaption to increasing concentrations due to climate change and ageing

KWR Watercycle Research Institute

BTO

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Summary

Climate change is expected to result in reduced discharge volumes, especially during summer and autumn. Consequently, an increase in pharmaceutical concentrations is expected in surface waters. In addition, an increase in the concentrations of current and newly developed pharmaceuticals is expected following a consumption increase due to population ageing. In many cases, current treatment plants that rely (in part) on surface water for the production of drinking water are facing difficulties removing pharmaceuticals and their transformation products from the water. It is known that part of the removal of these compounds already occurs during soil passage, e.g. during riverbank or dune filtration. The degree to which these substances are removed will depend on the compound characteristics and the site-specific conditions for soil passage, such as redox system and travel times. However, insight into the quantitative extent to which this aquifer-treatment contributes to overall removal and how this varies for various compounds at varying location-specific conditions have been largely lacking so far. In our study, a large database of pharmaceutical concentrations from 5 different recharge systems was used to make a comprehensive estimate of the removal of pharmaceuticals along soil passage after bank or basin filtration.

Quantifying removal of pharmaceuticals under field conditions is, however, hindered by several factors such as scatter of the observed concentrations (temporal heterogeneity of the available data), mixing of different waters, threshold values (concentrations below which there is no removal), different analytical limits of quantification (LOQ) and site specifics like the travel times or the redox conditions (Wiese et al., 2011). Based on the long term dataseries available for some of the systems, it was assumed in our study that the available pharmaceutical concentrations were representative of the variability of the input concentrations. The values under detection limit were given the detection limit value to avoid removal overestimation. The fact that these systems have been in operation for a long time ensures that the biological community responsible for degradation has been allowed to mature and optimize their degradation capacity. Finally, studying five different locations allowed to draw general conclusions (not-site specific) on the behaviour of pharmaceuticals and identification of those pharmaceuticals whose removal will be more site-specific dependent.

To verify the lowering of concentrations through removal processes, pharmaceutical concentrations in the infiltration ponds were compared to those observed in the collected mixed raw water, taking into account the possible dilution with groundwater, This comparison was done through three methods. The first method consisted of the analysis of the differences between the arithmetic averages of the infiltrated and abstracted water. It provided a quantitative answer to the question of how much removal had taken. The second method estimated removal and behaviour of the pharmaceuticals based on the assumption that the correlation of certain compounds in the infiltrated water is expected to change if one of them is degraded relative to another compound. This provided an indication of whether a pharmaceutical is diluted, completely degraded, or it experiences variable removal. The third approach based removal estimation on the differences between the lognormal probability density functions of the infiltrated and abstracted concentrations. This approach provided a quantitative estimate range of the reduction of a given pharmaceutical during soil. This approach proved to give insight on mixing of water that underwent different removal due to different flowpaths and redox conditions. The combination of the three approaches was an effective tool to increase the certainty and understanding of behaviour of pharmaceuticals and it represents a new approach to pharmaceutical, but could be similarly

applied for other water quality parameters. This approach had, to our knowledge, not been used until now.

From the large database of compound concentration measurements, only the compounds that showed concentrations above detection limit in the collected mixed raw abstracted water were taken into account. As a result, the behaviour of a total of 56 pharmaceutical compounds was studied. From the 56 compounds 18 showed a removal percentage higher than 70% in at least one of the sites (Table 5-1): atenolol, bezafibrate, bisoprolol, hydrochlorothiazide, iomeprol, iopamidol, iopromide, Losartan, metformin, metoprolol, naproxen, oxazepam, paracetamol, sotalol, sulfamethoxazole, temazepam, and urotropine (Figure 5-2 and Figure 5-3). From these compounds bisoprolol and iopromide presented removal rates above 70% in three of the sites. Atenolol and losartan showed removal rates above 70% in two of the sites. From the pharmaceuticals above detection limit in the abstracted water, only carbamazepine was analysed at the five sites. The removal extent of carbamazepine was low (<19 %) in all the sites.

For some pharmaceuticals removal percentages differed significantly between sites. These removal differences were influenced by different redox conditions, travel times, geochemistry and length of flowpaths. Scheveningen and well field Heel were the locations where the highest removal was observed (for Scheveningen: 58% overall removal, with 36%compounds with a removal larger than 70% and for Heel 51% overall removal with 18% of the compounds >70% removal). These two locations have notably different travel times and redox zones: Scheveningen is the location with the shortest travel times, minimal dilution with groundwater and soil passage covers oxic to anoxic zones. Heel on the other hand, presents high dilution with groundwater and abstraction through wells instead of drains, with mainly (sub)oxic flowpaths. Waternet had moderate removal but more sampling campaigns would be necessary to draw stronger conclusions. Ouddorp presented lower removal than the other locations and Eijbergen, with immediately anoxic flowpaths showed the poorest performance of all the locations. From the results it is clear that exposure to different redox zones, especially (sub)oxic zones, increases the removal of pharmaceuticals.

Soil passage can be a very efficient way to remove pharmaceuticals when the conditions are adequate. Redox exposure has proven to be a key aspect in pharmaceutical removal. Comparing the different site-specific conditions of the study locations of the present research provides an excellent opportunity to find adaptive measures and operational controls that will ensure enough oxic (and anoxic) exposure along the flowpath and will improve the efficiency of the soil passage as a treatment system.

Contents

1 Introduction

1.1 Context

Climate change is expected to result in reduced discharge volumes, especially during summer and autumn. Consequently, an increase in pharmaceutical concentrations is expected in surface waters. In addition, an increase in the concentrations of current and newly developed pharmaceuticals is expected following a consumption increase due to population ageing. During human consumption, pharmaceuticals are not absorbed completely by the gastro-intestinal tract. This results in a fraction that directly reaches the sewage treatment plants. The pharmaceutical fraction that is absorbed metabolically transforms into a conjugate that reaches the sewage plants as well. These two fractions are not completely eliminated in the course of conventional treatment processes (Schmidt et al., 2007) and they are discharged into the surface water system, mostly as the original active compound. The effluents of sewage plants can contain pharmaceutical concentrations between 0.01 µg/L and more than 1µg/L, and the receiving surface waters between a few ng/L and several µg/L (Schmidt et al., 2007), depending on the sewage water proportion

In many cases, current treatment plants that rely (in part) on surface water for the production of drinking water are facing difficulties removing pharmaceuticals and their transformation products (from here on: pharmaceuticals) from the water. It is known that part of the removal of these compounds already occurs during soil passage, e.g. during riverbank or dune filtration. This water quality improvement during soil passage may result from a combination of dilution with groundwater, peak dampening or removal by sorption and (bio)degradation. The degree to which these substances are removed will depend on the compound characteristics and the site-specific conditions for soil passage, such as redox system and travel times. However, insight into the quantitative extent to which this aquifer-treatment contributes to overall removal and how this varies for various compounds at varying location-specific conditions have been largely lacking so far.

In the Netherlands, managed aquifer recharge (MAR) systems, which use soil passage for water quality improvement, have been used for water supply for more than 70 years and currently account for up to 20% of the total water supply (Stuyfzand 2011). With MAR residence times ranging from 28 to 200 days, recharged water has substituted natural background groundwater between the infiltration area and the abstraction area. It has been repeatedly demonstrated that through the subsurface passage of the infiltrated raw water, quality is significantly improved by means of filtration, sorption and biodegradation (Bakker and Stuyfzand, 1993; Schmidt et al., 2007; Stuyfzand, 1986; Stuyfzand and Lüers, 1996; Stuyfzand, 1993; Stuyfzand, 2011). In addition, the quality improvement in MAR systems may be further supported through extensive pre-treatment systems and controls (Lekkerkerker et al., 2009; Scheideler et al., 2011; Stuyfzand et al., 2007) . In particular, one of the challenges that MAR systems are facing is the removal of emerging organic substances (EOS) from the infiltrating water. Although most of the MAR systems are overall effective in attenuating many of the unregulated trace organic chemicals or EOS (Hoppe-Jones et al., 2010), there are recalcitrant micro pollutants that are only degraded under specific conditions(Maeng et al., 2011). In this report, an analysis and overview of the percentage of removal of pharmaceuticals, is presented for different drinking water production sites in the Netherlands that (in part) rely on infiltrated surface water. Population ageing is expected to bring new pharmaceuticals into the market, however, the

pharmaceuticals here studied are the currently known pharmaceuticals. Making a forecast of possible future new pharmaceuticals and their removal is outside of the scope of this research.

1.2 Scope and objectives of the project

The objective of the present research was, firstly, to provide a quantitative insight into the current removal of pharmaceuticals from infiltrating surface water during soil passage at several Dutch drinking water production sites. For this purpose, 5 locations were selected for which pharmaceutical concentrations in the infiltrated and abstracted water were available. The degree of pharmaceutical removal was then related to the characteristics of each system. The site characterization included the identification of the possible key parameters in the removal of pharmaceuticals such as aquifer type, redox conditions, and residence time. Secondly, based on the different system efficiencies, possible measures to improve pharmaceutical removal are discussed.

Quantifying removal of pharmaceuticals under field conditions is hindered by several factors such as scatter of the observed concentrations (temporal heterogeneity of the available data), mixing of different waters, threshold values (concentrations below which there is no removal), different analytical limits of quantification (LOQ) and site specifics like the travel times or the redox conditions (Wiese et al., 2011). Three approaches were developed in the current study to tackle these difficulties. The first one studied the differences between the averaged concentrations of (long) time series in the infiltrating and abstracted water. The second approach developed consisted of, for each sample, finding correlations in the infiltration water between the different pharmaceuticals. The difference between the correlation ratios before and after soil passage gives information on the processes that affect those pharmaceuticals: conservation, dilution or degradation. The third approach is a probability density analysis by which the cumulative density functions of the infiltrated pharmaceutical concentrations were compared with those of the abstracted water. The cumulative density functions included all available concentration measurements for a particular pharmaceutical for the infiltrated surface water and abstracted water. This comparison provides an additional quantitative approach for the calculation of the removal percentage. To our knowledge it is the first time that these three method have been used in a combined approach to tackle the uncertainties inherent to this type of systems.

By means of these calculations it was possible to determine to which degree the quality of the infiltrated water improves during soil passage in terms of pharmaceutical concentration removal and the similarities and differences between the different soil passage systems. Based on the relation between pharmaceutical removal degree, redox zones and travel times, ways to alter the redox zoning and pathways are discussed to improve the removal efficiency for (particular) pharmaceuticals.

2 Selected locations

2.1 Overview of selected locations

In this chapter an overview of the selected study sites is provided, in which the key characteristics with respect to pharmaceutical removal during soil passage are given. The different types of water and sampling locations of these systems (Table 2-1) are described in more detail per location in the coming sections.

Table 2-1 Types of water and sampling locations common to all the systems. Nomenclature used in the current report.

Source water	**River where the surface water for infiltration is taken from**
Intake	Location in the river where the surface water for infiltration is taken from
Infiltration water	Water sampled prior to infiltration
Mixed raw water	Water collected after soil passage by the drains/wells system
Native groundwater	Groundwater present before the infiltration system. Groundwater that currently surrounds and is not affected by the infiltration system
Groundwater along soil passage	Water sampled in a piezometer with a filter located along an infiltration flowpath

2.1.1 Scheveningen (Water company: Dunea)

Water company Dunea provides water to The Hague and surrounding area, delivering around 75Mm^3 of drinking water per year. The most important water production location of Dunea is the basin artificial recharge (BAR) system Scheveningen located in the Meijendel dune area, to the North of The Hague, in operation since 1955. This BAR system targets a stratified aquifer composed of Holocene and Pleistocene unconsolidated sands (with dunes on top), with a total thickness of ca. 75m with a hydraulic conductivity of 10-20 m/day. Yearly, 45 Mm^3 of water from the Meuse river (from the intake point Brakel) are being infiltrated with a modal residence time of 70 days. The abstraction is done by wells or drains located at, on average, 65m away from the infiltration basin banks. The system is composed of 12km of drains and 1200 phreatic wells (Figure 2-1).

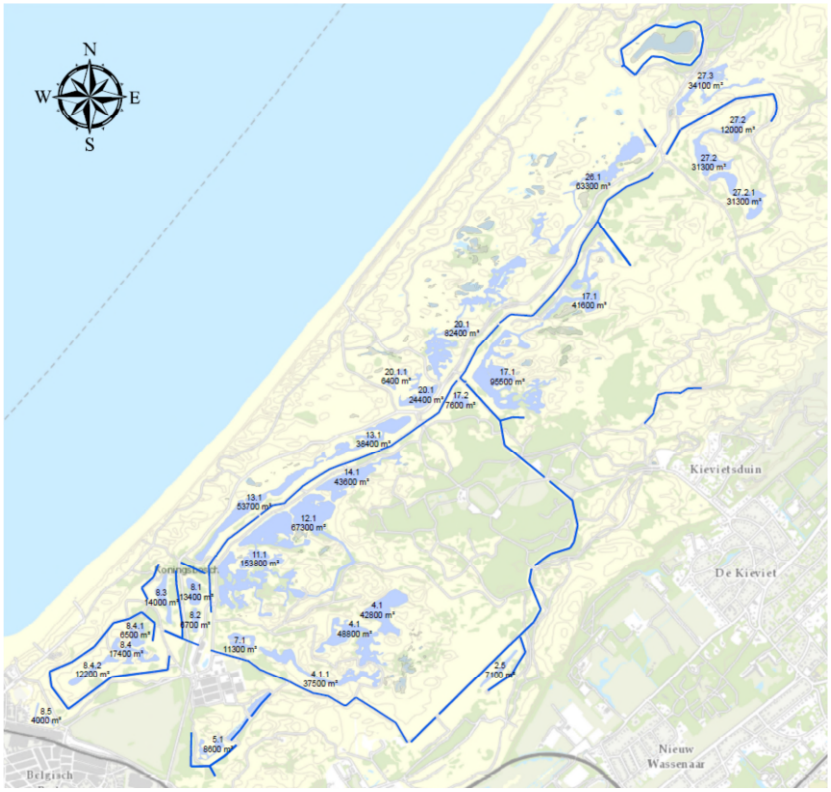

Figure 2-1: Infiltration ponds and drains in the BAR (Basin Artificial Recharge) system Scheveningen. The ponds are labeled with their number and the surface they occupy. The drains are indicated with blue lines.

The infiltration water originates from the river Meuse (intake point Brakel) where it undergoes coagulation, microsieving and rapid sand filtration. It is subsequently transported to the dune area for infiltration. After the water is infiltrated in the dune area, it gradually gets reduced along its flowpath (de la Loma González et al., 2013) rendering a redox zonation approximately like the one depicted in Figure 2-2. The recharged water has substituted the natural background groundwater between the infiltration area and the abstraction area and the abstracted groundwater is recently infiltrated water, according to the spatial distribution of the ponds and drains (de la Loma González et al., 2015).

To study the pharmaceutical's behaviour the sampling points depicted in Figure 2-2 were used. These comprise the measurements performed in the intake of the infiltration water, the measurements of the mixed raw water collected from all drains and wells, and the measurements of groundwater from observation wells during aquifer passage soil passage.

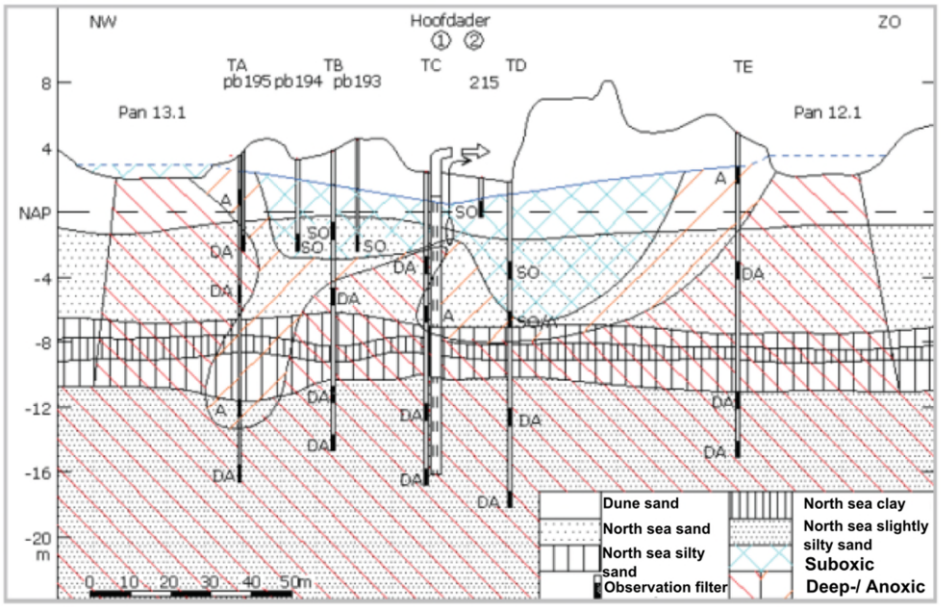

Figure 2-2: Profile of hydrogeology and redox zonation along with observation wells, recovery wells from Stuyfzand et al. (2007) Pan13.1 and 12.1 are the infiltration ponds, TA-TE the deep multilevel observation wells and pb the shallow observation wells. (SO = suboxic, DA = deeply anoxic; A = anoxic; NAP = mean sea water level)

In addition to the sampling points in the artificial recharge system, data from the intake point at Brakel was also used for the present research. From the data available, 67 pharmaceuticals were identified in the samples taken in the dune area and 56 in the samples taken at the intake point. A list with these pharmaceuticals is available in Attachment I.

The variability of the infiltrating water coming from the river Meuse is clear in Figure 2-3 where the concentrations of different pharmaceuticals over time are shown. This variability hampers the possibility of backwards interpolation of the concentrations observed in the abstracted water from the MAR systems. Averages of short periods are also not reliable, since a long enough period to make an average should be used and this will also depend on the substance.

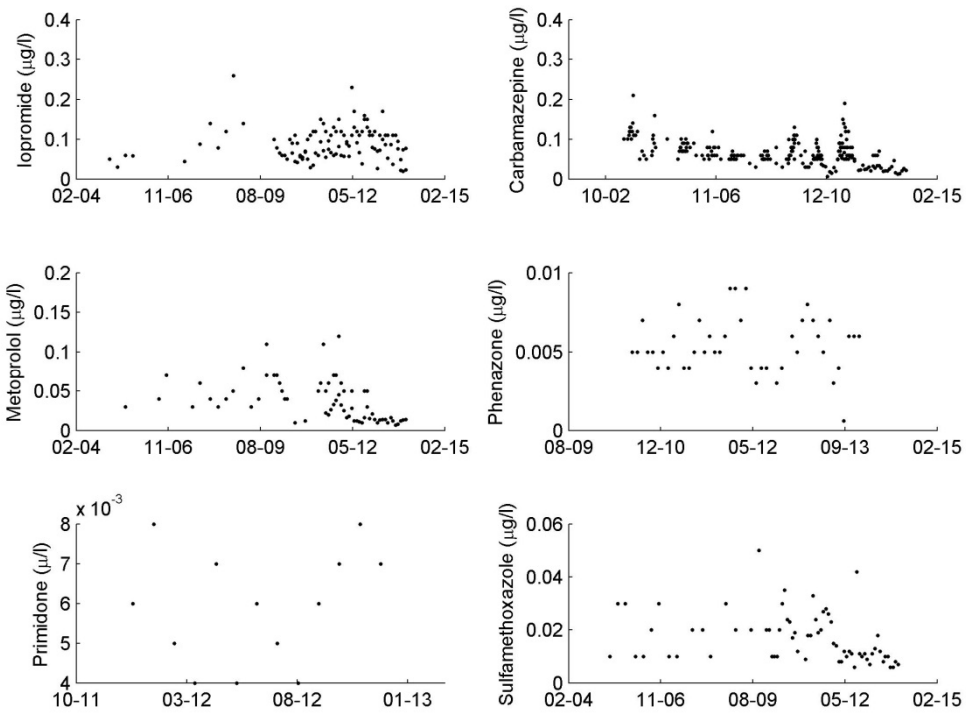

Figure 2-3. Concentrations over time (month-year) of selected EOS measured at Brakel intake (not treated).

2.1.2 Well field Heel (Water Company: WML)

WML produces drinking water from well field Heel since 2002. The wells of this well field are located along the man-made basin "Lange Vlieter" (Figure 2-4), which was formerly a gravel pit for the cement industry. The capacity of the well field increased over time until 2007, when the production stabilized at 16.10^6 m^3/year, with a maximum capacity of 25.10^6 m^3/year. The Lange Vlieter is fed by surface water from the river Meuse through the lateral canal (Figure 2-4) and this water has an average residence time in the infiltration pond of approximately 1.5 years (Hartog, 2014) before it gets infiltrated. After approximately 1 year of soil passage (modelled travel times by Bustos Medina et al. (2013), the infiltrated water is abstracted through the 29 wells surrounding the infiltration basin and thereafter treated for its distribution as drinking water.

Due to the topography of the area, with an elevated surface level in the NorthWest (24m + NAP) relative to the SouthEast and around the lateral canal (15m + NAP), the basin acts like a flow-through lake: groundwater enters the basin through the Northwest and leaves the basin mainly in the Southeast. This results in dilution of the infiltrated water from the river Meuse with local groundwater in the basin. Also, the "Boschmolenplas" occasionally contributed with water (until 2013) to the Lange Vlieter if the water level in the Boschmolenplas exceeded the maximum level of 21.30 m+NAP. The Boschmolenplas" is located at the West side of the Lange Vlieter and mainly fed by groundwater seepage The contribution by the "Boschmolenplas" occured mainly in winter. In summer the water volume abstracted from the lateral canal increases to keep the water level of the Lange vlieter

constant. The yearly contribution of groundwater to the Lange Vlieter is estimated at 30% of its volume, 10% of the volume would correspond to the contribution of the Boschmolenplas and 60% of the lateral Canal (de la Loma González et al., 2013). Since 2009 this yearly contribution has remained more or less stable but it does vary per season.

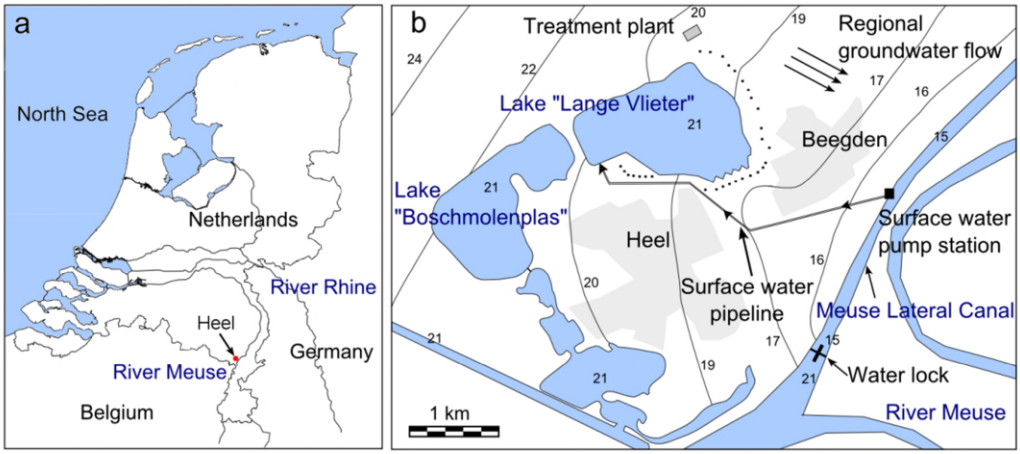

Figure 2-4 Location of well field Heel. The wells are located along the southern and eastern shore of the basin "Lange Vlieter" (adapted from Bustos Medina et al., 2013).

The well field around the lake abstracts the infiltrated water after soil passage between the lake as well as groundwater with a local origin. Four main geological formations are distinguished (de la Loma González et al., 2013): a) the Twente formation, in the upper 10 meters, mainly consisting of fine sands and loams or loamy sands, b) the Kreftenheye and Veghel formation, from 10 to 30 meters, which consist of gravel with a hydraulic conductivity of around 250 m/d, c) the Sterksel formation, till 50 meter, consisting of medium coarse sand with fine and coarse gravel with a hydraulic conductivity of 70 m/day and d) the Kedichem formation, deeper than 50 m, consisting of fine to coarse sands and clays.

The groundwater immediately surrounding the infiltration lake primarily consists of water from the Lange Vlieter (Bustos Medina et al., 2013) and, as is common in lake bank filtration systems with organic rich bottom sediments, the infiltrated oxic water is quickly reduced by degradation of organic matter. There is however a coarse gravel around 17-25 m bls where the infiltrated water remains slightly oxic (Figure 2-5). The redox zonation is therefore horizontally stratified in well field Heel, especially during pumping (Bustos Medina et al., 2013). The extent of the oxic zone depends on the pumped volume, its depth and neighbouring wells. This contrasts with the usual redox zonation during soil passage where oxic zones are found near recharge and more reduced conditions are found further downstream.

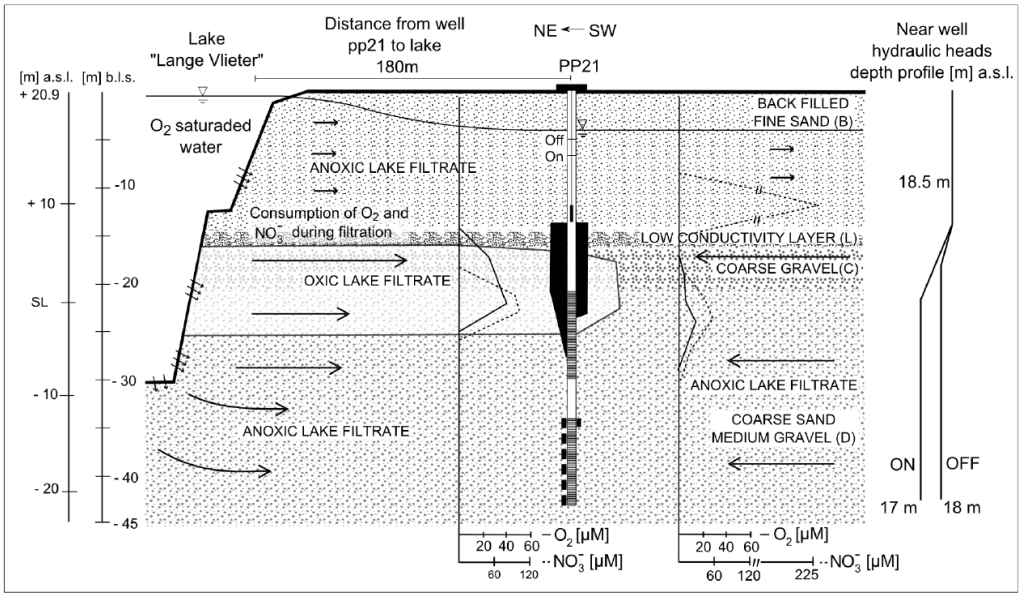

Figure 2-5 Cross section of lake bank filtration at well-field Heel (well PP21) (Bustos Medina et al., 2013). Shadowed zones on the well indicate screen sections. Longer arrows indicate flowlines with higher groundwater velocity. Black zones on the sides of the well indicate incrustation distribution. Hydraulic head depth profiles are shown on the right.

Pharmaceuticals are known to be present in the river Meuse water (ter Laak et al., 2013) and WML has therefore performed several sampling campaigns to determine the presence of these pharmaceuticals in the infiltrated and the collected mixed raw water water in Heel from 2010 to 2013. In the present study, only the infiltration water measured at the intake from the lateral canal and the collected mixed raw water from section Galgenberg (East side of the basin) and De Reut (West side of the basin) (figure 2-6) are taken into account when performing the removal analysis. The abstracted water is diluted with groundwater and according to Hartog (2014) the fraction of infiltrated surface water in the abstracted water for these well sections is 61%.

figure 2-6. overview of well-field heel and the sampling locations used in the research by Hartog (2014).

Fourty six pharmaceuticals were screened for the well clusters Langven and de Reut (Fig.2-6). A list with these pharmaceuticals is included in Attachment I.

2.1.3 Eijbergen (Water company: Vitens)

The Vitens well field Eijbergen is located in the East of the Netherlands, close to the border with Germany. The total water abstracted at Eijbergen is up to 1.34 million m^3/year which partly infiltrates from the Berkel, a tributary of the river Ijssel, via Haninkgoot (Figure 2-7) with an intake of 210 l/s in winter and 350 l/s in summer. In addition Vitens pumps 10 l/s from dewatering canal (Afw.) Van Zaterdag (Figure 2-7) for the infiltration basin to maintain local groundwater levels. Overall the total surface water infiltration is 300,000 m^3/year.

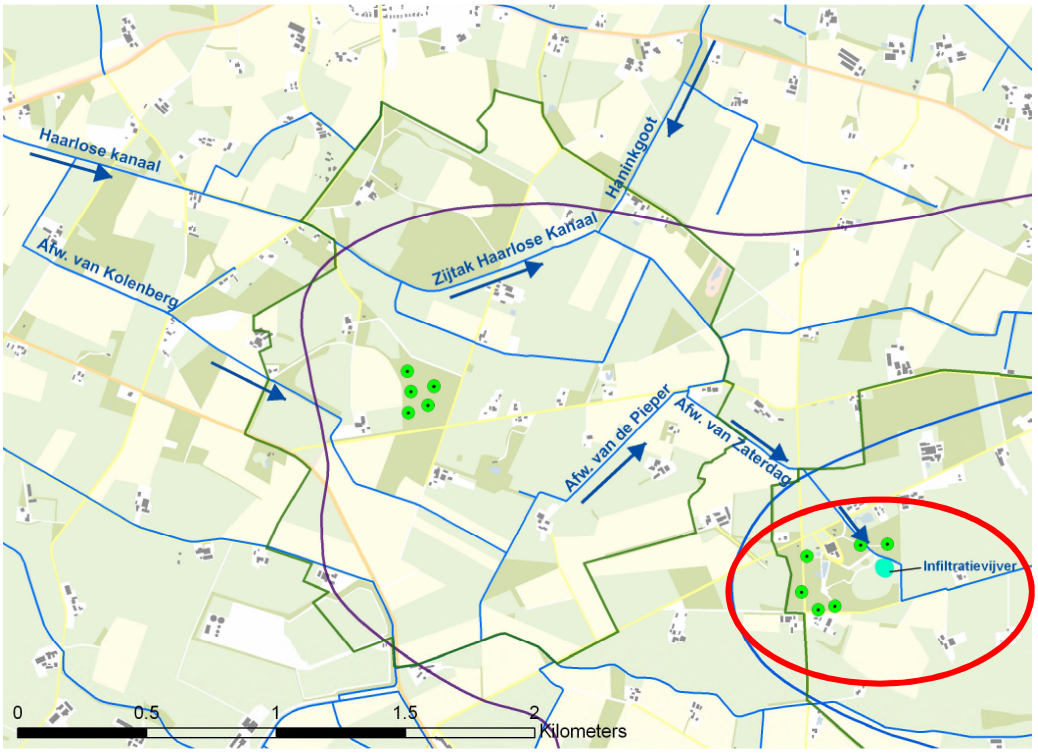

Figure 2-7. Water supply in Olden Eijbergen well field, demarcated by a red circle. The green dots represent the production wells and the blue circle the infiltration basin.

Water is produced with 6 wells that abstract groundwater at 25-30m^3/h from the coarse sand of the Kreftenheye formation and the fine sand of the Twente formation. The depth of the aquifer used for water production is around 25-30 mbl (meters below surface) and it is intercalated with several loam layers. The system is mostly phreatic and it lacks a continuous sealing layer.

Preliminary results of a tracer test recently performed (March 2016) at the site by Gijsbert Cirkel (KWR) for Vitens suggest that the travel time from the infiltration pond to the abstraction wells is around 150 days. According to the measurements in the observation wells surrounding the pond the oxic infiltrating water gets quickly reduced (in less than 3m of soil passage) with in most cases complete NO_3 reduction (anoxic zone) and in some other cases even the complete? SO_4 reduction (deeply anoxic). This is due to the organic matter

layer in the bottom muds of the pond, the presence of pyrite in the aquifer and the thin organic loam layers in the aquifer.

The pumping wells surrounding the infiltration basin in Eibergen (Figure 2-8) abstract infiltrated water that is mixed with groundwater in different degrees. The abstracted water is thus a mixture of infiltrated surface water and ambient groundwater.

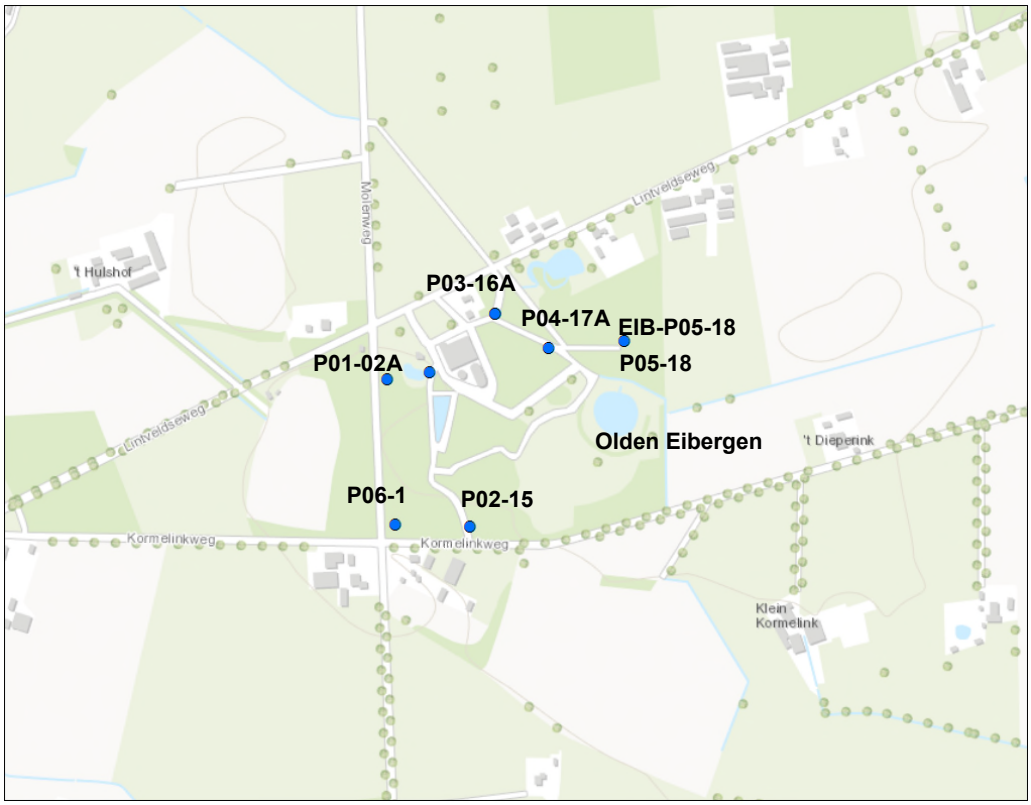

Figure 2-8 Water extraction in Olden Eibergen. The pumping wells are represented by light blue dots (18 to 30 meters deep below ground level).

The river Berkel has several sewage treatment plants (STPs) that discharge into it, and its water quality is measured on the German side of the border. Between that monitoring location and the infiltration pond there are no further STP discharges into the Berkel River, so that the quality measured in the Berkel is comparable to that measured in the infiltration pond. German measurements indicate that organic micropollutants, including pharmaceuticals, should be present in the infiltrating surface water at Olden Eijbergen. Figure 2-9 illustrates the temporal variability of the concentrations for diclofenac measured in the Berkel.

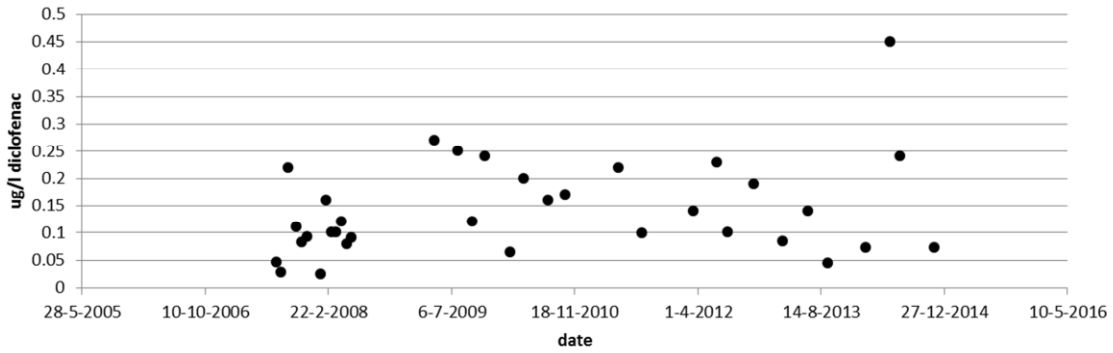

Figure 2-9: Diclofenac concentrations in the surface water measured at the intake point in Berkel ,

Data from the infiltration pond and the 6 production wells is used in the current analysis, also the new well P07 is included in the analysis.

2.1.4 Ouddorp (Water company: Evides)

Evides has applied artificial recharge via basins, in the dunes of Ouddorp for their drinking water production since 1955. The number of infiltration channels (Figure 2-10) grew over time with the increase in water demand. The artificially recharged water comes, since 1994, entirely from the Haringvliet, which is a mixture of river Rhine water and river Maas water (Stuyfzand et al., 2007). From 2001 the infiltration area follows the OINS concept (Open Infiltration New Style) aiming for a sustainable infiltration system with a nature-friendly design, reducing also the abstraction of pure dune groundwater to 0.25 Mm3 / year .

The 2 most relevant aquifers of Ouddorp consist of Holocene and Pleistocene sands respectively, with dunes on top (Figure 2-11). The phreatic, upper dune aquifer is separated from the semiconfined second aquifer by a confining layer of clay and fine sand layer found from 0 to 4m –NAP. The travel times (Figure 2-11) are indicative of the limited hydraulic connection between both aquifers. In the study area, the groundwater flow in the first aquifer is dominated by the artificial recharge system. Water flows from the infiltration canals towards the drains situated around 5 m deep (around NAP level) and distant enough (Figure 1 1) so as to ensure microbiologically safe groundwater. The travel time from the infiltration to the abstracting drain is around 90 days, according to the groundwater model of the infiltration area (de la Loma González et al., 2013).

The redox zoning in the upper aquifer is depicted in Figure 2-12 , where anoxic and deeply anoxic areas are depicted based on the results from the monitoring performed in 2008 (de la Loma González et al., 2013). The infiltrated water gets reduced during its passage through the dunes, being oxic in the infiltration canal, suboxic in the first 40 meters and anoxic in the last 50 meters of its passage through the soil. The drains abstract 100% infiltrated water.

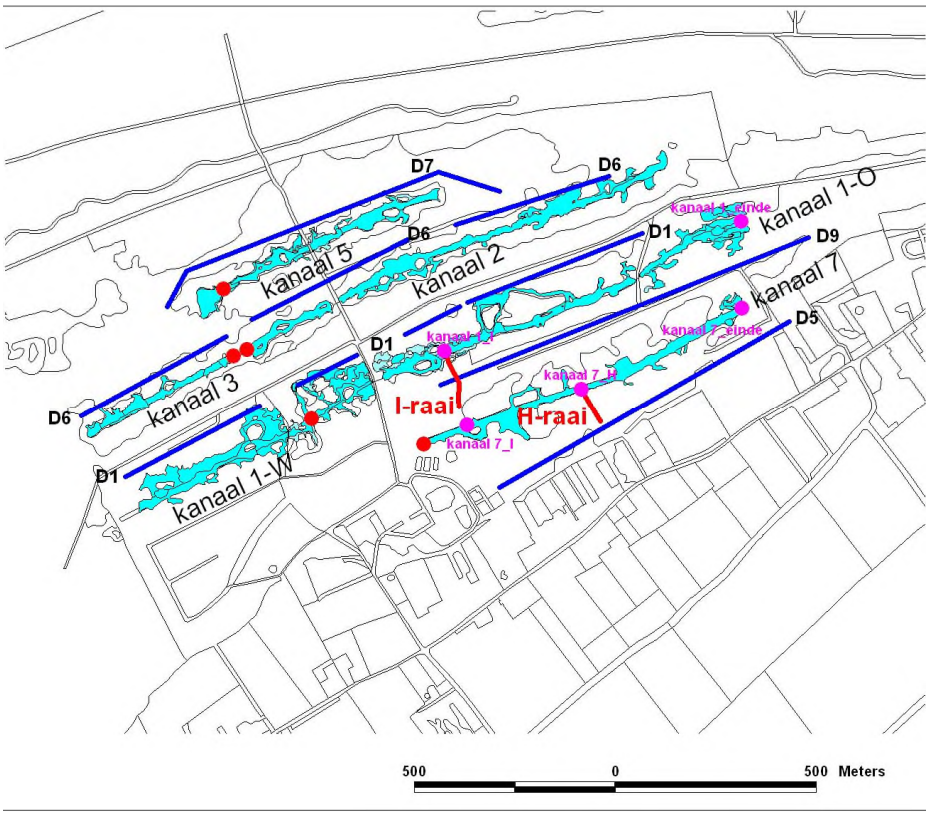

Figure 2-10. Infiltration field Oostduinen. Legend: infiltration channels (light blue), intake point of infiltration water (red points), drains (dark blue lines), and surface water monitoring points (pink dots) .

	Depth m-LS	Travel time (d)	Kh (m/d)
Dune Sand	1-6	135	10
Fine Sand	6-7	190	4
Sea Sand	7-8	220	15
Clay and peat	8-10	2200	0.001
Pleist. Sand	10-35	4500	30
Deep Pleist. Sand	35-45	9000	20

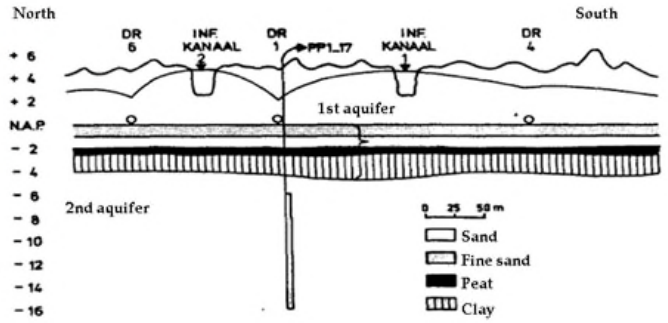

Figure 2-11. Left: Layers and averaged hydraulic parameters in Ouddorp (Aggenbach et al, 2012). The surface level in the dunes (LS) is around 6m+NAP. Right: Geological schematization of a N-S cross section in the dunes of Ouddorp

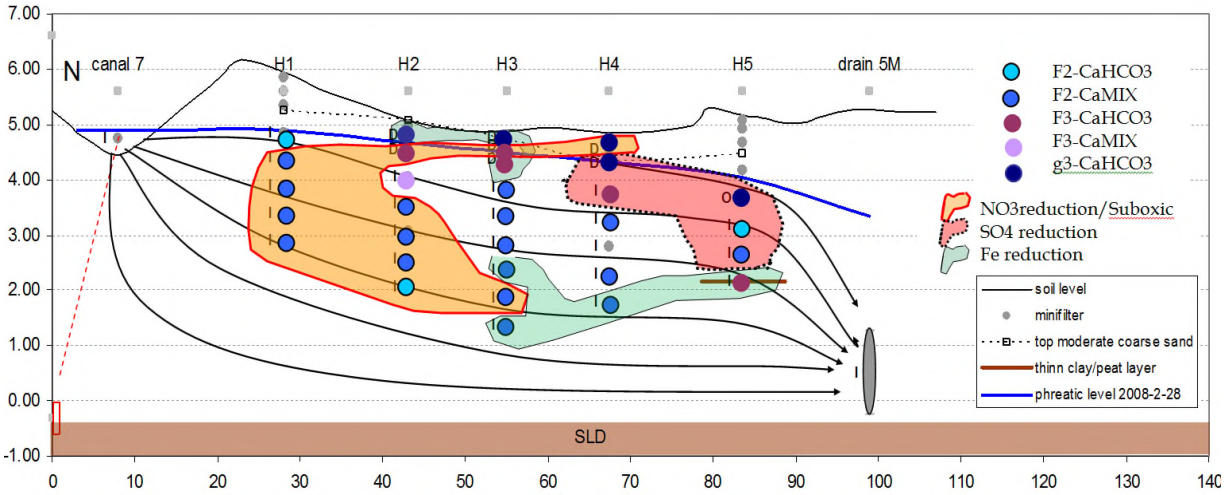

Figure 2-12 Transect showing the 5 piezometers and the minifilters sampled in autumn of 2012. This figure shows the chemical water types (according to Stuyfzand's classification (Stuyfzand, 1993) and the redox status in each of the miniscreens as observed during that sampling campaign.

As previously cited for the river Meuse, the Rhine river is known to carry different organic micropollutants (Eschauzier et al., 2010; Segers and Stuyfzand, 2007) and some of these have been found back in Ouddorp after soil passage in the broad screening (LC-MS and GC-MS) perfomed in 2012 (de la Loma González et al., 2013). The water transported from the Haringvliet undergoes a pre-treatment process before it is infiltrated in the dunes (Figure 2-13), and a post-treatment after dune passage. In the period 2009 -2015 Evides has screened its water for pharmaceuticals, 29 times before infiltration and 30 times after its passage through the dunes. Pharmaceuticals were also analysed at the intake point (location code: POUD13INNA) and after treatment, location code: POUD80UITG. The distribution and coding of these sampling locations is indicated in Figure 2-13

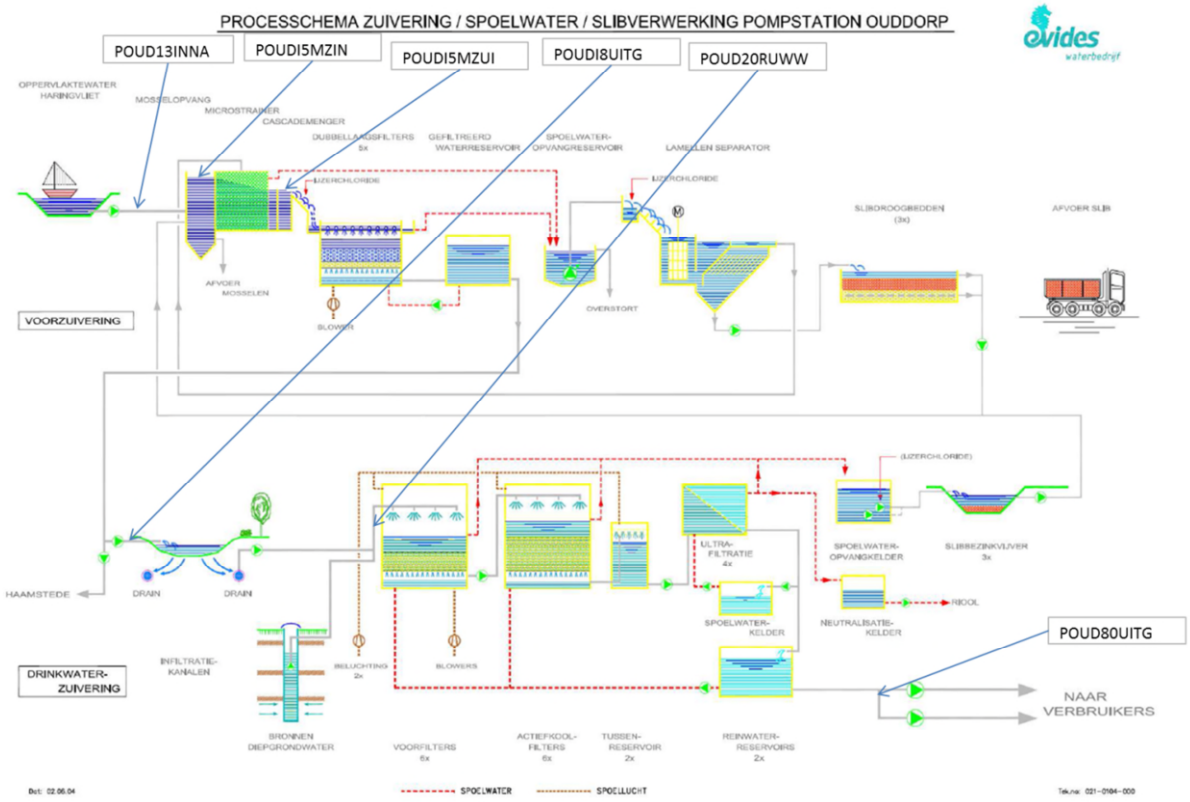

Figure 2-13 treatment process of the water produced by Evides in ouddorp

2.1.5 Amsterdam Water Supply Dunes (Water company: Waternet)

The Amsterdam Water Supply Dunes (AWD) managed by Waternet are situated in the coastal dune area in the western part of the Netherlands. The AWD contain an artificial recharge network of supply canals, infiltration ponds, drains and extraction canals, which has allowed sustainable drinking water production for the Amsterdam area since 1957. Water from the Lek Canal, a tributary branch of the river Rhine, is transported over 55 km by pipeline after pretreatment through coagulation, sedimentation and rapid sand filtration, to reach the dunes and be distributed through the network to the 86 ha of infiltration ponds.

The upper lithology is of Holocene eolian and marine origin. Dune sands with some pockets of peat are found from the surface down to mean sea level (MSL), and are underlain by beach and shallow marine sands rich in calcite, and subsequently by silty fine marine sands, silty marine sands and marine sandy clays. Both the silty fine marine sands and marine sandy clays are classified as aquitards by Stuyfzand (1993). Fluvial and eolian fine sands, followed by marine coarse sands down to 30 m below MSL, both of the Pleistocene era, are underlying the sandy clays and are the deepest sediments of relevance for this study. A rain fed dune water lens exists on top of the Rhine water lens, and remains fairly stable (Stuyfzand and Stuurman, 1985).

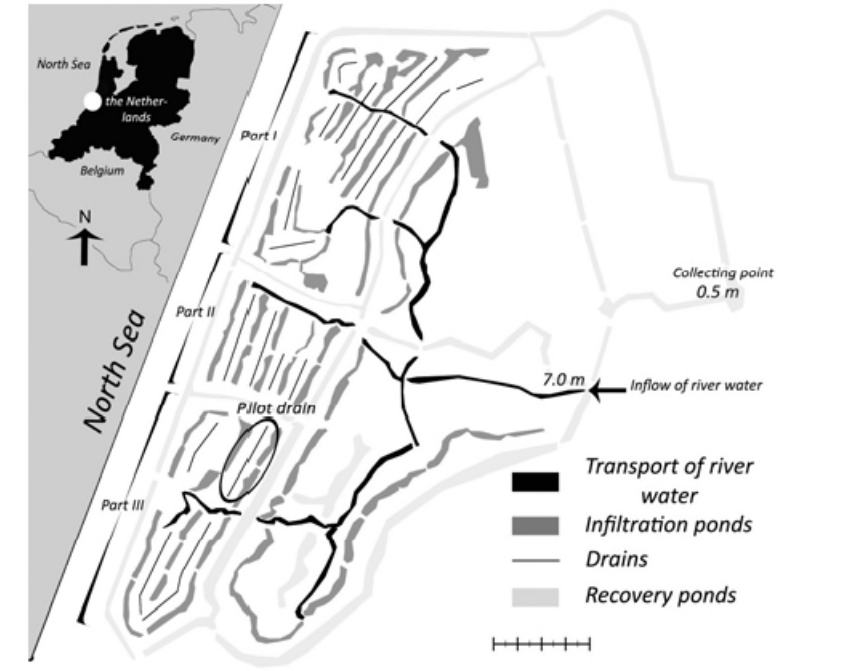

Figure 2-14 Plan view of the infiltration ponds in the Amsterdam water supply dunes (after (Houde, 2010))

The water from the river Rhine is transported to the infiltration basins and after a modal residence time of 5 days in the basins, it gets infiltrated and then abstracted through the drains after 80 days of travel time. During underground flow the infiltrated water passes different redox zones: oxic, anoxic (nitrate reducing) and deeply anoxic (sulphate reducing) depending on the flowpath (Figure 2-15), before it is being abstracted by the drains. Not all the flow paths are exposed to the same redox sequence and this can be a relevant factor when it comes to compound removal. The data available from the Amsterdam Water Supply Dunes is minimal, with two sample dates at the infiltration point and two at the recovery point.

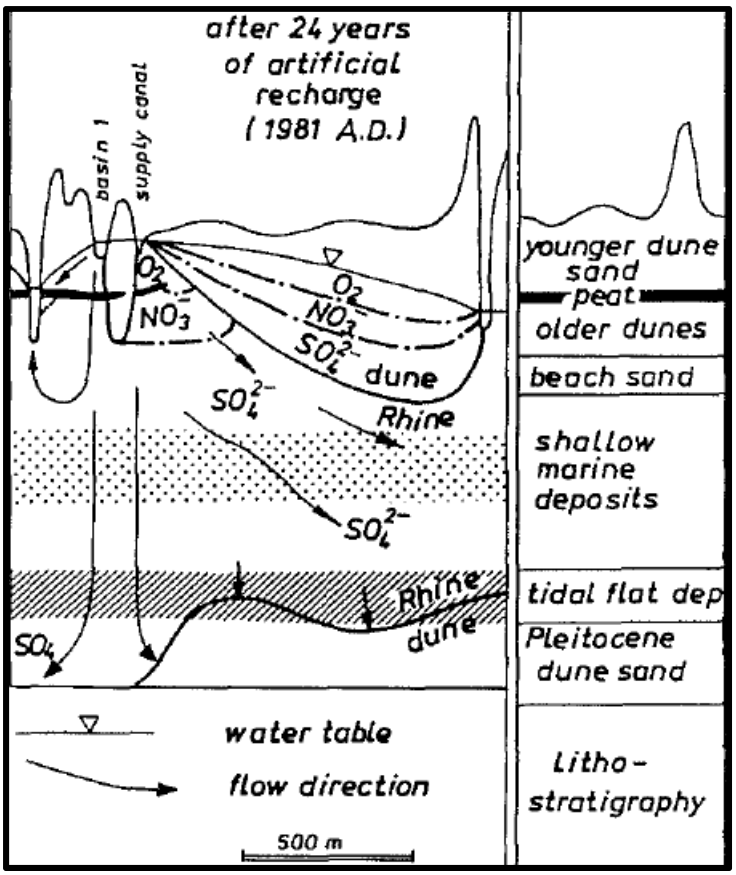

Figure 2-15 Cross section and redox zones of the Amsterdam water supply dunes

2.2 Overview of data available

For each drinking water production location studied, the number of available data and the frequency with which it has been collected vary, there is a wide range in data availability (Table 2-2). In addition, the period for which data is available and the surface water infiltration conditions vary depending on the site characteristics (Table 2-2, Table 2-3, Table 2-4). This influences the type of approach that can be taken to calculate the removal percentage. Table 2-2 provides an overview of the data available per field site included in the present research. Table 2-3 and Table 2-4 provide a summary of the specific site conditions per location that may influence the removal of pharmaceuticals. The databases available per location were scanned for 303 different pharmaceuticals as presented in Attachment I.

Table 2-2 Data available per location. GW= groundwater

		Min Date	Max Date	Frequency	nr sample dates
Scheveningen (Dunea)	Infiltration water (input)	4-1-2005	10-12-2013	weekly	396
	Mixed Raw Water (output)	7-1-2003	24-12-2012	weekly (+2013: 2 meas in March & May)	531
	Groundwater along soil passage	1-5-1990	28-8-2012	monthly until 1998, then twice per year	155

Well field Heel (WML)	Infiltration water (input)	15-2-2011	29-7-2013	bimonthly in 2011, monthly in 2012-2013	25
	Mixed Raw Water (output)	31-1-2012	13-8-2013	bimonthly	13
	groundwater along soil passage	13-3-2012	21-6-2013	2015 5 times, 2013 bimonthly	10
Ouddorp (Evides)	Infiltration water (input)	3-1-2008	29-9-2015	weekly	384
	Mixed Raw Water (output)	3-1-2008	29-9-2015	Monthly since 2013	65
	Groundwater along soil passage	-	-		
Eijbergen (Vitens)	Infiltration water (input)	30-1-2007	17-12-2015	from 2009 bimonthly, before monthly. In 2015 monthly	62
	Mixed Raw Water (output)	15-3-2013	17-6-2015	1 in 2013,5 in 214,5 in 2015	7
	Groundwater along soil passage	-	-		
AWD (Waternet)	Infiltration water (input)	27-7-2005	6-9-2006		2
	Mixed Raw Water (output)	-	-		0
	Groundwater along soil passage	27-7-2005	6-9-2006		2

Table 2-3 Surface water input conditions and data available per location and methods used (CDF = cumulative probability function, Correl = correlation method, Boxplot = arithmetic average method)

	Mixing before infiltration	Infiltration system	Recovery system	Time series (years)	Method used
Scheveningen	Yes	Canals	Drains + wells	8	Boxplot + Correl+ CDF
Well field Heel	No	Pond	Wells	3	Boxplot + Correl + CDF
Eijbergen	Yes	Pond	Wells	8	Boxplot + Correl + CDF
Ouddorp	Yes	Canals	Drains	7	Boxplot + Correl + CDF
AWD	Yes	canals	drains	2	Boxplot

Table 2-4 Summary of the specific site conditions per location described in detail in the previous chapter.

	Redox	Travel time	Mixing during abstraction
Scheveningen	A – SO	70 days	Minimal
Well field Heel	O – A	1.5 years	Yes
Eijbergen	A – DA	150 days	Yes
Ouddorp	A – DA	90 days	Yes
AWD	O-A-DA	80 days	No

3 Methods used and developed

In the current investigation an analysis of pharmaceutical removal along soil passage in five different locations was made. The sites are drinking water production sites where surface water infiltration into an aquifer takes place. Depending on conditions, the passage of the surface water through the soil in these sites improves the quality of the resulting recovered (abstracted) water. The sites were selected for the data availability of pharmaceutical concentrations both in the infiltrated and abstracted water. Several sites were selected to link different site characteristics to pharmaceutical removal and so that the databases and pharmaceuticals measured would complement each other and could be compared.

Pharmaceutical removal estimation per site was estimated using three different methods in an attempt to circumvent the uncertainties and complexities inherent to these types of systems and this type of research. In the first part of the methodology chapter the different complexity factors that the estimation of pharmaceutical removal along soil passage has to deal with are described. The second part of the methodology comprises the methods used to tackle these obstacles and to calculate pharmaceutical removal as accurate as possible.

3.1 Complexities of pharmaceutical removal calculation during soil passage

Estimating pharmaceutical removal along soil passage is not a straight-forward task due to different complexity factors inherent to the type of groundwater system and the type of data available. These were taken into account and dealt with in different ways. In this section these complexity factors are described.

3.1.1 Highly variable input concentration, measurement frequencies and pharmaceuticals analysed

Most field studies on the removal of organic micro-pollutants during soil passage use a flow-path approach. This approach provides a snapshot of the pharmaceutical concentrations measured along the flow-path at a given time and, based on these concentrations, pharmaceuticals removal is calculated. Due to the scattering of observations and to the temporal variations in the input , rarely there is information of the concentration at the corresponding moment of infiltration, resulting in a tentative calculated removal percentage. Some studies calculated pharmaceutical removal efficiency through statistics: in an infiltration transect decreasing mean values would mean that removal processes are taking place, typically represented with box plots (Massmann, et al., 2008; Eschauzier et al., 2010), or using frequency of detection combined with concentration distance plots (Stuyfzand et al., 2007). Recent studies estimated, for particular monitoring wells, the time of infiltration using estimated travel times. The concentrations at the time of infiltration were then determined by linear interpolation between surface water measurements since in most of the cases no measurement was available for exactly the estimated moment of infiltration (Wiese et al., 2011, Segers and Stuyfzand 2007). In addition to uncertainties in estimating travel times, surface water concentrations are highly variable. Therefore, interpolation is prone to yield inaccuracies in the estimated infiltrated concentrations and consequently also in the calculated removal fractions, when comparing the input concentrations with those observed in (abstracted) groundwater.

The large variability of pharmaceutical concentrations is reflected in the data of the infiltration water from the river Meuse or Rhine. Houtman et al. (2013) studied the variation and trend of pharmaceuticals and pesticides measured in Meuse river water at the intake Brakel every four weeks from August 2010 to August 2012. The concentrations varied significantly between seasons

depending on fluctuations in (i) the discharge of the river Meuse, (ii) the human consumption rate (for instance of caffeine or ibuprofen), and (iii) environmental biodegradation.

In some artificial recharge cases, the seasonal variations in the input are dampened by mixing in the recharge basins or recharge lakes, resulting in abstracted concentrations with average values of the conservative tracers concentrations measured in the source waters. This is the case for well field Heel, where the infiltration water in the Lange Vlieter basin has a residence time of 1,5 year (Hartog, 2014). For the other sites studied, however, the residence time in the ponds is not sufficient to assume homogenization of temporal variation.

Unlike the flow-path approach, in the current research the soil passage system is considered as a whole, where the input concentrations are compared with the output concentrations and (long) time series of data are used, assuming they are representative of the possible input variations.

In some of the study sites the type of pharmaceuticals analysed for the infiltration ponds were not always the same as for the abstracted drains or wells. This reduced the number of compounds for which removal could be calculated. In these cases, if concentration data measured at the intake or at the post-treatment was used, if available. In the calculated removal for during soil passage, possible changes in pharmaceutical concentration. before infiltration and after abstraction are then neglected.

3.1.2 Varying detection limits

Not only the measured concentrations vary greatly temporally, but also the detection limits (DL) due to the evolution in analytical techniques. This can lead to “false positives” of removal. For instance, for a given input concentration of 0.10 µg/l and two different DL such as 0.02 and 0.03 µg/l, two different removal fractions of 90% and 85% would be calculated respectively. This calculated removal decrease responds only to the increase in DL. In this study the “detectability” of each pharmaceutical is considered depending on the DL.

Also, when pharmaceutical concentrations are below detection limit it cannot be said that the pharmaceutical has been completely removed since there is no information of its real concentration under the detection limit value. Many studies (Wiese et al., 2011) calculate removal based on DL/2 or LOQ/2 which may lead to overestimation of removal. Some other studies set below detection limit values to zero or neglect those measurements altogether due to the uncertainty that they pose. In the current research, however, when performing the statistical analysis for removal estimation, the measurements under detection limit are taken as the detection limit concentration value. This ensures that pharmaceutical removal is not overestimated while still the information that below detection limit measurements provide is not neglected. Since the extent to which removal can be quantified depends on the height of the detection limit, the calculated removal extents are therefore considered as minimal removal extents.

3.1.3 Mixing with different water types and retardation

In addition to the highly variable concentrations input, mixing with other sources of water during infiltration or abstraction increases the uncertainty regarding the original infiltrating concentration that the removal should be calculated with. In some of the field sites the infiltration ponds are fed as well with groundwater and in some others the water abstracted through wells or drains contains partly native groundwater. This native groundwater and water feeding the infiltration ponds is here assumed as pharmaceutical-free. To determine the degree of mixing, the chloride/sulphate ratios of the intake water, the infiltration pond(s), the groundwater and abstracted water are compared per site. This analysis is shown as a Cl/SO4 plot for each site inside of the results chapter per location.

Retardation during soil passage may affect observed pharmaceutical concentrations in abstracted water. However, most pharmaceutical compounds are typically hydrophilic and mobile. In addition,

since the selected study sites have been functioning for numerous years and (long) time series of data are used we consider the impact of adsorption to the calculated removal extent negligible in the current study

3.2 Methods used for estimation of pharmaceutical removal along soil passage

3.2.1 Method 1: times series averaging

It is considered that long time series are representative of the variability in input concentrations and therefore can be used for comparing infiltrated and abstracted pharmaceutical concentrations.

For each sampling location the maximum, minimum and mean (arithmetic average) concentration per parameter were calculated. The arithmetic average is calculated including those measurements below detection limit by including them with the detection limit value as their concentration. This provides a conservative estimate of actual removal and limits it to what can actually be detected. The averages were corrected for the degree of dilution with native groundwater

In those cases were the infiltrated or abstracted water were diluted the removal percentage was calculated as follows

$$\%\, removal = \frac{[Cinfiltration\ diluted] - [Cabstracted]}{[Cinfiltration\ diluted.]}$$

Where

$$[Cinfiltration\ diluted] = f_{infiltrated\ water\ in\ abstracted\ water}[Cinfiltration]$$

With $f_{infiltrated\ water\ in\ abstracted\ water}$ as the fraction of infiltrated surface water.

The fraction of infiltration source water present in recovered water is calculated based on chloride concentrations, using the available contrast between the infiltration water and ambient (or native) groundwater, as follows

$$f = \frac{[Cl]\ measured - [Cl]ambient}{[Cl]inf - [Cl]ambient}$$

This was the case for the site study Eijbergen, where the average of the native or ambient groundwater Cl concentrations was used.

For well field Heel, dilution with native groundwater also occurs. Due to the wider range in Cl concentrations the fraction of infiltrated water was calculated using fitted functions for the observed Cl-SO_4 correlation for the infiltrated water and native groundwater endmembers (Hartog, 2014, and illustrated in Fig 4-1) as follows:

$$f = \frac{[SO_4]_{measured} - c\,[Cl]_{ambient} - d}{a[Cl]_{inf} - c\,[Cl]_{ambient} + b - d}$$

Where

$$a, b = constants\ of\ the\ linear\ function\ with\ the\ form: [SO_4]_{inf} = a[Cl]_{inf} + b$$

$$c, d = constants\ of\ the\ linear\ function\ with\ the\ form: [SO_4]_{ambient} = c[Cl]_{ambient} + d$$

The dilution-corrected pharmaceutical concentration is then calculated using a correction factor that is described as follows:

$$[CPHARM]corrected = \frac{[CPHARM]measured - (1-f)[CPHARM]ambient}{f}$$

Where

$[CPHARM]measured$ = averaged concentrations measured, including detection limit values

$[CPHARM]ambient$= averaged concentrations measured in wells where no infiltrated water is abstracted, including detection limit values.

The detection limit in the abstracted water limits the removal percentage that can be calculated per substance. In those cases where all the concentrations in the abstracted water were below detection limit, the removal percentage will be:

$$Removal\ (\%) = \frac{\overline{[pharm_{abstracted}]}}{\overline{[pharm_{infiltrated}]}} * 100 = \left(1 - \frac{DL_{abstracted}}{\overline{[pharm_{inf}]}}\right) * 100$$

3.2.2 Method 2: pharmaceutical correlation analysis

The second method is based on the correlation of concentrations for certain pharmaceuticals, e.g. because they are typically consumed together and therefore their concentrations will be highly correlated in the infiltration water. Under conservative conditions, it is expected that their correlation ratio in the abstracted water will not change due to dilution with groundwater. Therefore, in the absence of other contaminant sources, the ratio will change if different degradation or elimination of one compound relative to the other takes place. Previous studies regarding urban groundwater affected by waste water sources, already introduced the concept of co-tracers to identify groundwater affected by waste water (Scheurer et al., 2011) or to identify single and multiple waste water sources (Van Stempvoort et al., 2013). In the current study a correlation analysis was run for pairs of compounds found in the infiltrating water more than 10 times. The combination of parameters that showed Pearson coefficients higher than 0.6 were plotted against each other (with all the individual measurements) and visually inspected. The concentrations measured in the abstracted (recovered) water were plotted as well and the change in the correlation ratio was examined to identify the changes in the relationships between them.

3.2.3 Method 3: probability density function analysis.

Due to the variability of the input and output signals, the pharmaceutical concentrations in these infiltration systems can be considered as stochastic or random variables that can take on a set of possible different values, each with an associated probability. Stochastic variables can be described through probability density functions (PDF). In this case, due to the nature of the concentrations, the observed data was first fitted to a lognormal distribution and based on this fit the cumulative density function (CDF) was calculated. Comparing the CDF of the input and the output can give insight in the

removal extent (Vanderzalm et al., 2013). In the following paragraphs it is described in detail how this was done.

Firstly, for a given parameter (pharmaceutical) the empirical cumulative distribution function (ECDF) of the infiltrated concentrations was computed by ordering the data available from smaller to larger including detection limits. The same was done for the abstracted concentrations. A two-sample Kolmogorov–Smirnov test with a significance level of 0.005 was run to test whether the two underlying one-dimensional probability distributions (empirical infiltrated and empirical abstracted) differed statistically (Massey Jr, 1951). This method provides the advantage in comparison to other methods that it checks for differences independently from the type of distribution that the data set might present. It would not be possible to compare and calculate removal fractions from two distributions that are not significantly different.

Secondly, the resulting CDFs for the infiltration and abstraction data were fitted to a lognormal distribution and the parameters of this distribution were used to calculate the associated cumulative density function. By running again a two-sample Kolmogorov–Smirnov test (alpha = 0.005), it was tested whether the two distributions, empirical and fitted, differed. The same was done for the abstracted concentrations. If the Kolmogorov-Smirnov tests indicated that the fitted and empirical distributions did not statistically differ from each other, the fitted CDF were used to calculate the removal efficiency. This was done for concentrations associated to the mean and the 10th, 50th and 90th percentiles of the concentration distribution. These provide the range for the statistical range for the removal extent per pharmaceutical.

4 Results

4.1 Well field Heel

At well field Heel, surface water is transported from the lateral canal to the analysis pond and after a short residence time (Bustos Medina et al., 2013) it is transferred to the infiltration basin, the Lange Vlieter, where.it stays approximately 18 months (Hartog, 2014). In this basin the water gets mixed with in flowing groundwater. After soil passage, the water is then subsequently abstracted by the surrounding wells. Additional mixing with local groundwater occurs to variable extents depending on how much native groundwater is co-extracted. To discern the degree of mixing, the Cl/SO_4 of the infiltrated, abstracted and ambient groundwater are compared (Figure 4-1) which yields different dilution factors per sampling location. Hartog (2014) studied this in his research and Table 4-1shows the resulting contribution percentages per location.

The Cl/SO_4 (Figure 4-1) plot Indicates the degree of homogenization that happens in the Lange Vlieter. Figure 4-1 shows Cl concentration ranges of the concentrations measured in the intake. The SO_4/Cl ratio of the Lange Vlieter plots higher than the ones measured at the intake, which gives an insight into the degree of mixing with groundwater and water from the Boschmolenplas, which is mainly fed by groundwater. The production wells show SO_4/Cl concentrations that plot in many cases between the Boschmolenplas ranges and the intake SO_4/Cl ranges. The fraction of groundwater and surface water abstracted per well and sampling location is summarized in Table 4-1 according to what Hartog (2014) calculated based on the Cl and SO_4 of samples for which also pharmaceuticals were analysed. The formula used for this calculation is included in the methodology chapter, section 3.2.1.

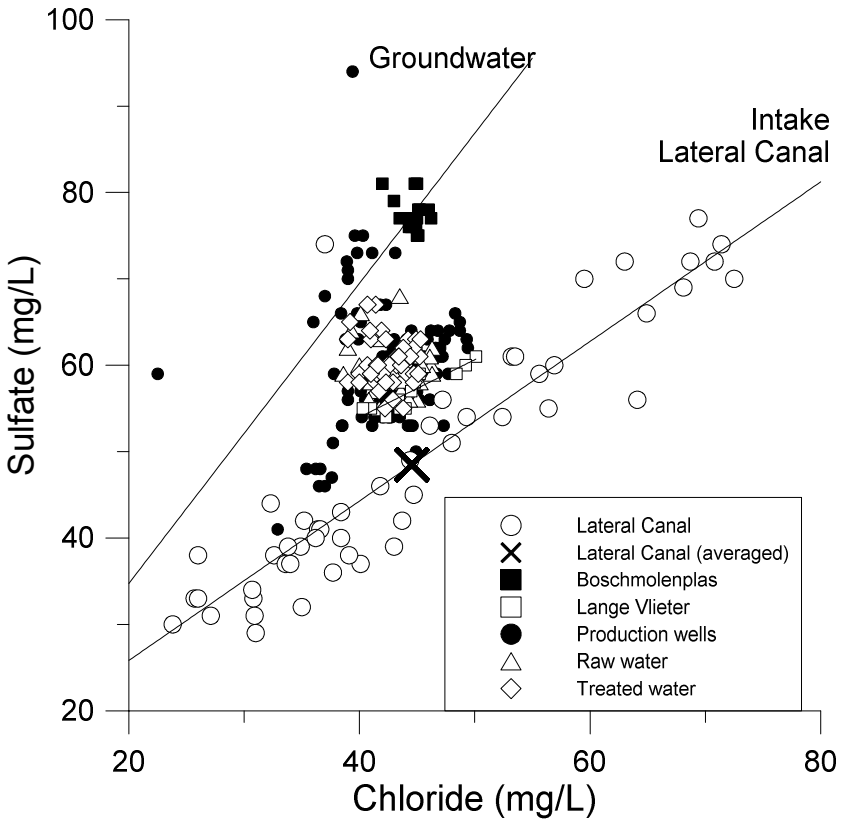

Figure 4-1 Chloride and sulfate concentrations measured in the intake (Lateral Canal), infiltration pond (Lange vlieter), groundwater fed pond beside the infiltration pond (Boschmolenplas), production wells and treated water that is used for drinkwater distribution from 2010 to 2013. The lines indicate the average sulfate concentration for a certain groundwater chloride concentration (SO4=1.754*Cl) and for the Lateral Canal intake water (SO4 = 0.92*Cl + 7.36). Figure as presented in Hartog (2014).

From the sampling locations used by Hartog (2014) only the measurements performed at the intake in the Lateral Canal, the Lange Vlieter, the collected mixed raw water in well clusters Galgenberg, Langven en de Reut (figure 2-6) were used in this research to determine pharmaceutical removal during soil passage. 46 different pharmaceuticals were analysed, in well field Heel.

Table 4-1 Calculated relative fraction of intake water from the Lateral Canal and groundwater at the different sample locations in well field Heel. The calculations are based on the chloride and sulphate concentrations, Hartog (2014).

Sample location	Lateral Canal	Groundwater
	%	%
Lange Vlieter	74	26
PP 3	69	31
PP 5	48	52
PP 13	62	39
PP 24	76	24
PP 27	70	30
PP 42	80	20
PP 45	--	-
Mixed Raw Water (output) water Galgenberg	66	34
Mixed Raw Water (output) water Langven and De Reut	56	44
Average Galgenberg & Langven		39
Post-treatment water	60	40

4.1.1 Concentration averages Heel

The averaged concentrations of the pharmaceuticals measured at least once above detection limit in the infiltration water (39 out of 46), are plotted in decreasing order in Figure 4.2. The arithmetic averages include the concentration values of the detection limit for those samples that showed concentrations below detection limit. Since the actual concentration below DL is unknown, the extent of removal of a pharmaceutical can only be determined down to its detection limit. The average abstracted concentrations (average of the collected mixed raw water at Galgenberg and de Reut) are plotted as well. Just by dilution with groundwater, a decrease of 39% (Table 4-1) in the input concentrations is expected in the abstracted water, according to the fraction of infiltrated water expected in both well clusters (Table 4-1).

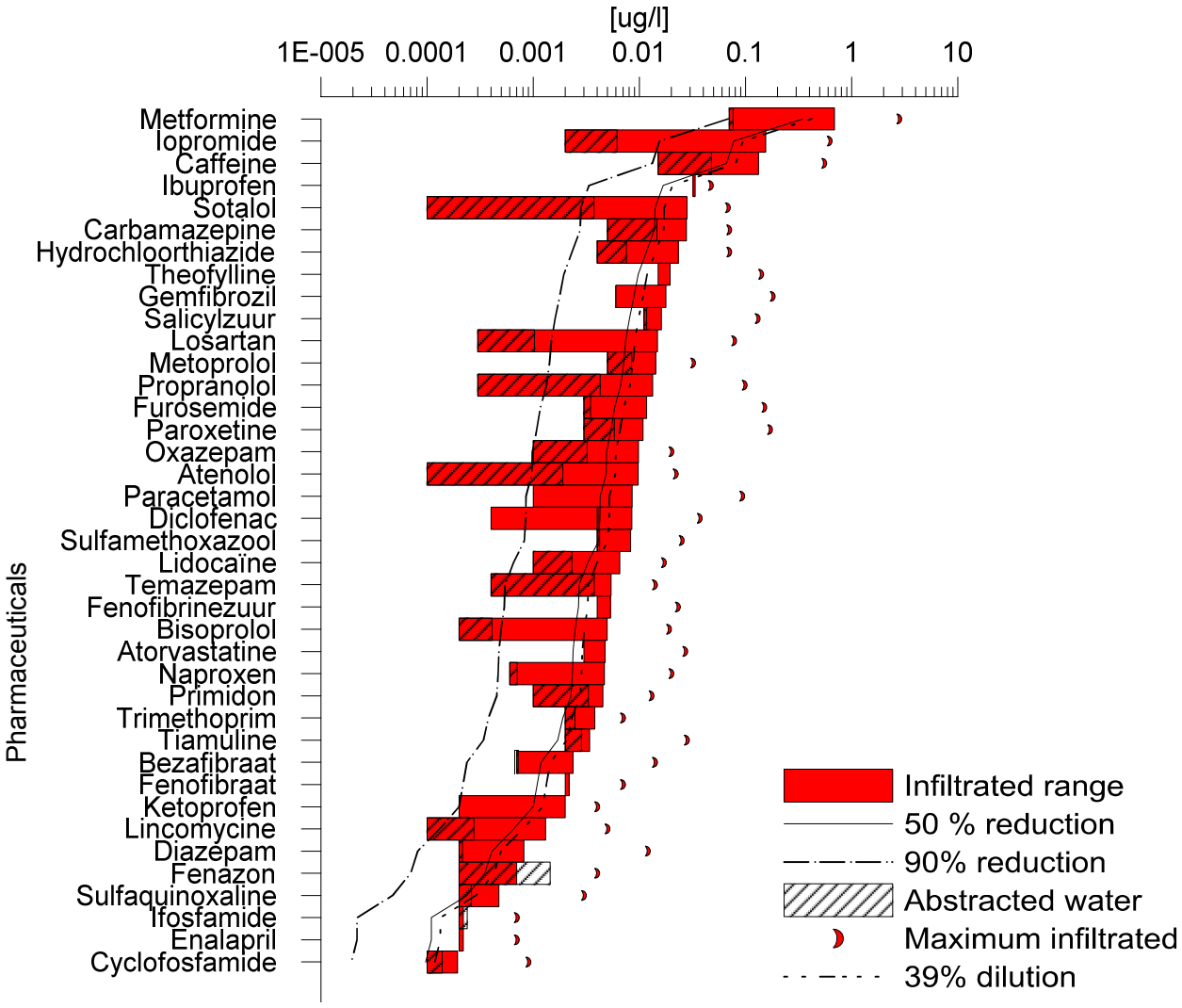

Figure 4-2 Averaged concentrations of the pharmaceuticals measured in the infiltration pond Lange Vlieter and in the abstraction (or production) wells in well field Heel (diagonally-stripped bars). This figure includes the concentrations expected by dilution with 39% of groundwater, where no pharmaceuticals are expected. The figure indicates as well

Some of the compounds in the plot show concentration values in the abstracted water that are very close to the range of concentrations that would be expected due only to dilution (39% dilution plot line) or higher. This is the case for metoprolol, temazepam, primidone, tiamuline trimethoprim, fenazone, sulfaquinoxaline and cyclofosfamide. These parameters do not experience considerable removal (Figure 4-2 and Table 4-2) during soil passage or have relatively high detection limits that do not allow quantification at the degree of dilution. The concentrations of some other compounds were however noticeably reduced more than 75% such as metformin, iopromide, sotalol, losartan, paracetamol, bisoprolol and lincomycin. It is not possible to say however, due to the detection limit threshold, that they are completely removed. Table 4-2 shows in detail what the averaged concentrations in the Lange Vlieter were and what were the averaged concentrations in the production well clusters Galgenberg and de Reut. This table shows negative removal values for those parameters of which the fraction of the detection limit concentration per infiltrated concentration is higher than the assumed dilution fraction. This is the case of ibuprofen, theophylline, salicylic acid, fenofibric acid, fenofibrate, ketoprofen, lifosfamide and enalapril. The removal values for these parameters were therefore not included in the table. Some of the other calculated removals are negative and this is due to higher concentrations in the abstracted water than those expected after

dilution, this could be a sign of contamination or of insufficient data with respect to the remaining variability in the infiltration water and the relatively low sampling frequency.

Table 4-2 Averaged concentrations measured in the infiltrated and recovered water in well field Heel (2010-2013). The averages of the abstracted water are not corrected for dilution. This table includes the detection limits and number of samples above the detection limit. The minimum and maximum detection limit are included for the infiltrated and the abstracted water (the latter only showed a minimum detection limit) and the fraction that the detection limit measured in the abstracted water represents with respect to the mean infiltration water. If there is no information on the detection limit of the abstracted water, then the detection limit of the inifiltrated water is used to calculate this fraction.

	unit	INF max	INF min	INF mean	**INF min DL (max DL)**	Nr samples INF >DL/all	ABS mean	ABS Min DL max	Nr samples ABS >DL/all	Fraction DLinf /INF	% removal
Metformin	µg/l	2.8	0.07	6853	0.07	23/31	0.0762	0.07	2/13	0.10	81.8%
Iopromide	µg/l	0.62	0.002	1546	0.002	27/31	0.0062	0.002	7/13	0.01	93.5%
Caffeine	µg/l	0.55	0.015	1326	0.015	19/24	0.0478	0.015	9/13	0.11	40.9%
Ibuprofen	µg/l	0.047	0.032	0335	0.032	4/31	0.0320	0.032	0/13	0.95	
Sotalol	µg/l	0.068	0.0001	0281	0.0001	29/32	0.0037	0.0001	8/13	0.00	78.3%
Carbamazepine	µg/l	0.07	0.005	0277	0.005	30/32	0.0145	0.005	11/13	0.18	13.9%
Hydrochlorothiazide	µg/l	0.07	0.004	0232	0.004	23/32	0.0075	0.004	2/13	0.17	46.7%
Theophylline	µg/l	0.14	0.015	0194	0.015	4/32	0.0150	0.015	0/13	0.77	
Gemfibrozil	µg/l	0.18	0.006	0177	0.006	10/27	0.0060	0.006	1/13	0.34	44.6%
Salicylic acid	µg/l	0.13	0.011	0161	0.011	4/31	0.0117	0.011	1/13	0.68	
Losartan	µg/l	0.078	0.0003	0148	0.0003	23/32	0.0010	0.0003	2/13	0.02	88.7%
Metoprolol	µg/l	0.032	0.005	0142	0.005	25/32	0.0085	0.005	2/13	0.35	2.4%
Propranolol	µg/l	0.098	0.0003	0133	0.0003	22/30	0.0043	0.0003	5/13	0.02	47.7%
Furosemide	µg/l	0.15	0.003	0117	0.003	8/32	0.0035	0.003	1/13	0.26	51.4%
Paroxetine	µg/l	0.17	0.003	0108	0.003	2/24	0.0058	0.003	4/13	0.28	11.6%
Oxazepam	µg/l	0.02	0.001	0098	0.001	25/32	0.0032	0.001	3/13	0.10	46.0%
Atenolol	µg/l	0.022	0.0001	0097	0.0001	25/31	0.0019	0.0001	3/13	0.01	68.1%
Paracetamol	µg/l	0.093	0.001	0085	0.001	13/31	0.0010	0.001	1/13	0.12	80.8%
Diclofenac	µg/l	0.037	0.0004	0085	0.0004	11/29	0.0041	0.004	3/13	0.47	21.2%
Sulfamethoxazole	µg/l	0.025	0.004	0083	0.004	22/32	0.0042	0.004	1/13	0.48	15.9%
Lidocaine	µg/l	0.017	0.001	0065	0.001	25/32	0.0023	0.001	2/13	0.15	42.1%
Temazepam	µg/l	0.014	0.0004	0054	0.0004	29/32	0.0037	0.0004	11/13	0.07	-13.3%
Fenofibric acid	µg/l	0.023	0.004	0053	0.004	7/32	0.0040	0.004	0/13	0.75	
Bisoprolol	µg/l	0.019	0.0002	0050	0.0002	25/31	0.0004	0.0002	6/13	0.04	86.6%
Atorvastatin	µg/l	0.027	0.003	0048	0.003	5/28	0.0030	0.003	1/13	0.63	
Naproxen	µg/l	0.02	0.0006	0047	0.0006	18/32	0.0007	0.0006	1/13	0.13	75.2%
Primidone	µg/l	0.013	0.001	0045	0.001	31/32	0.0033	0.001	12/13	0.22	-19.7%
Trimethoprim	µg/l	0.007	0.002	0038	0.002	23/32	0.0025	0.002	4/13	0.53	-6.7%
Tiamulin	µg/l	0.028	0.002	0034	0.002	6/28	0.0028	0.002	3/13	0.59	-37.5%
Bezafibrate	µg/l	0.014	0.0007	0024	0.0007	19/32	0.0007	0.0007	1/13	0.30	50.0%
Fenofibrate	µg/l	0.007	0.002	0022	0.002	1/28	0.0020	0.002	0/13	0.92	
Ketoprofen	µg/l	0.004	0.0002	0020	0.0002 (0.002)	1/32	0.0020	0.002	0/13	1.00	

	unit	INF max	INF min	INF mean	**INF min DL (max DL)**	Nr samples INF >DL/all	ABS mean	ABS Min DL max	Nr samples ABS >DL/all	Fraction DLinf /INF	% removal
Lincomycin	µg/l	0.005	0.0001	0013	0.0001 (0.0004)	27/31	0.0003	0.0001	8/13	0.08	65.6%
Diazepam	µg/l	0.012	0.0002	0008	0.0002	10/31	0.0002	0.0002	1/13	0.25	56.7%
Phenazone	µg/l	0.004	0.0002	0007	0.0002	16/32	0.0014	0.0002	8/13	0.29	-238.7%
Sulfaquinoxaline	µg/l	0.003	0.0002	0005	0.0002	5/30	0.0003	0.0002	1/13	0.42	9.4%
Iifosfamide	µg/l	0.000	0.0002	0002	0.0002	2/32	0.0002	0.0002	1/13	0.91	
Enalapril	µg/l	0.000	0.0002	0002	0.0002	4/32	0.0002	0.0002	0/13	0.91	
Cyclophosphamide	µg/l	0.000	0.0001	0002	0.0001	13/32	0.0001	0.0001	2/13	0.52	-17.2%

4.1.2 Correlation analysis approach Heel

Correlation analysis provided an additional approach to assess the occurrence of pharmaceutical removal for certain pharmaceuticals for which their concentrations were observed to be correlated in the infiltrated water. Five pairs of compound showed correlation in the infiltrated water and the change in the correlation rate for the abstracted concentrations indicated the removal or dilution that these compounds went through. For carbamazepine and oxazepam the correlation found in the infiltration water (**Error! Reference source not found.**) , is lost in the abstracted water. While the downward shift of the concentration range for the abstracted water of carbamazepine is partly due to dilution, the removal of oxazepam is most pronounced as most of the measurements were below detection limit (**Error! Reference source not found.** and Table 4-2).

In contrast, the correlation between carbamazepine and primidone (Figure 4-4) indicates no removal of primidone relative to carbamazepine in the abstracted water. The correlation of temazepam with carbamazepine indicated partial temazepam removal (**Error! Reference source not found.** and Table 4-3) as the concentrations of temazapan generally decreased relative to those for carbamazepine. This is contrary to the indication based on the arithmetic averages, which was influenced by the 2 high outliers in observed temazepam concentrations measured in the abstracted water.

For the correlation between iopromide and lincomycin (Figure 4-6), there was clear removal of iopromide except for one sample. Sotalol and atenolol (**Error! Reference source not found.**) were highly correlated in the infiltration water but they were only measured three times in the abstracted water with lower concentrations except for two outliers. This variable removal means that some samples experience removal and some others not, this can be dependent on site-specific conditions such as travel time or exposure to different redox-zones.

Table 4-3 Correlated parameters in the infiltration water and the conclusions drawn from plotting them for the infiltrated and abstracted water. Reduction means reduction more than by dilution alone.

Correlation	**Parameter 1 (Y)**	**Parameter 2 (X)**	**Reduction of:**
0.633	Oxazepam	carbamazepine	Param 1+2
0.667	Primidone	Carbamazepine	Partial Param 2
0.729	Temazepam	Carbamazepine	Partial Param 1+2
0.614	Iopromide	Lincomycin	Param 1+ 2

0.84399	Atenolol	Sotalol	Partial Param 1+ 2

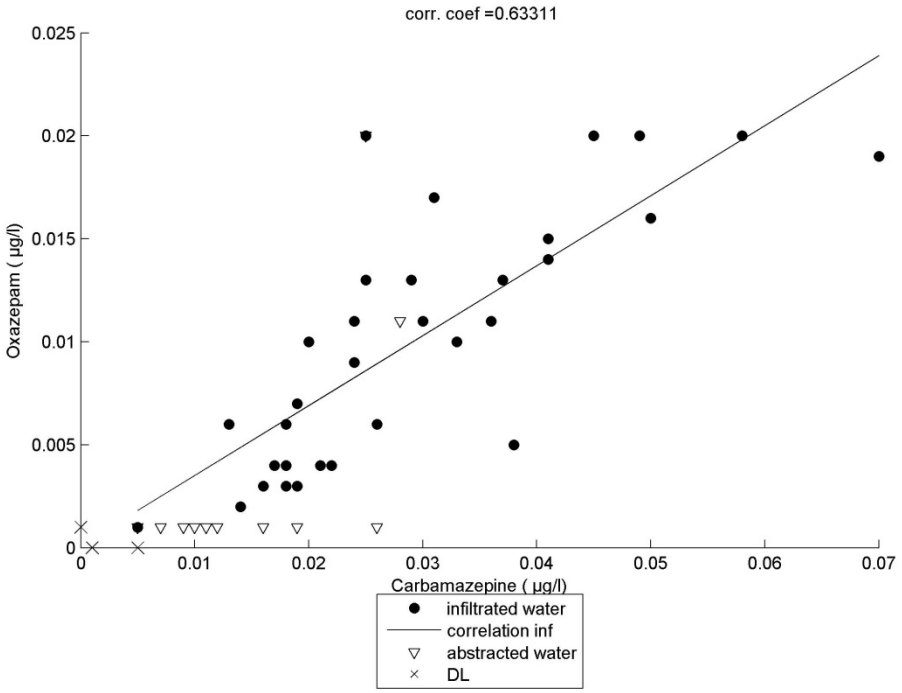

Figure 4-3. Carbamazepine concentrations versus oxazepam. Where DL = DETECTION LIMIT for both compounds. The markers indicate single measurements

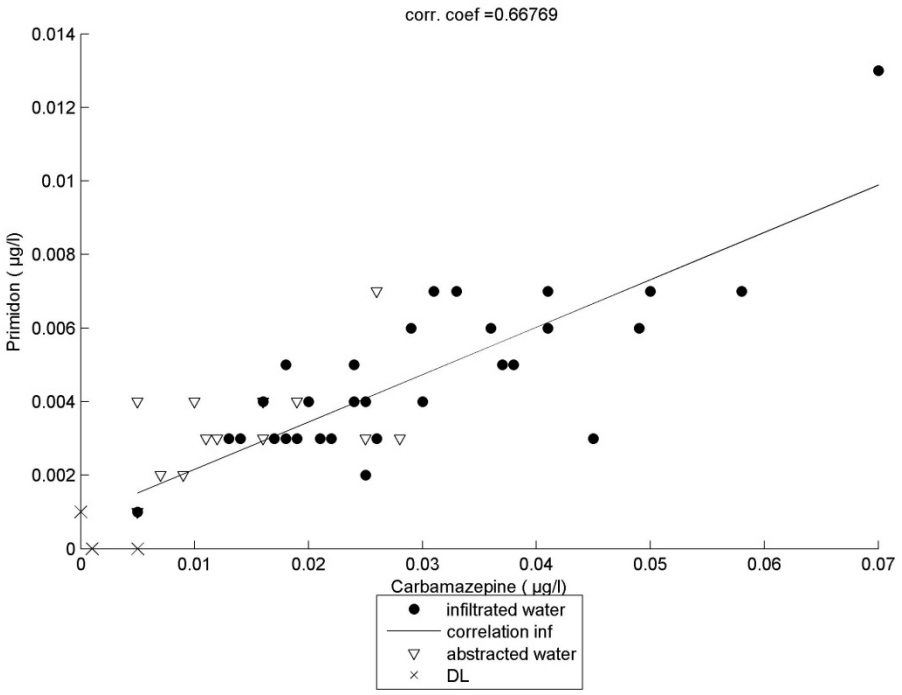

Figure 4-4. Carbamazepine concentrations versus Primidone. Where DL = DETECTION LIMIT for both compounds. The markers indicate single measurements

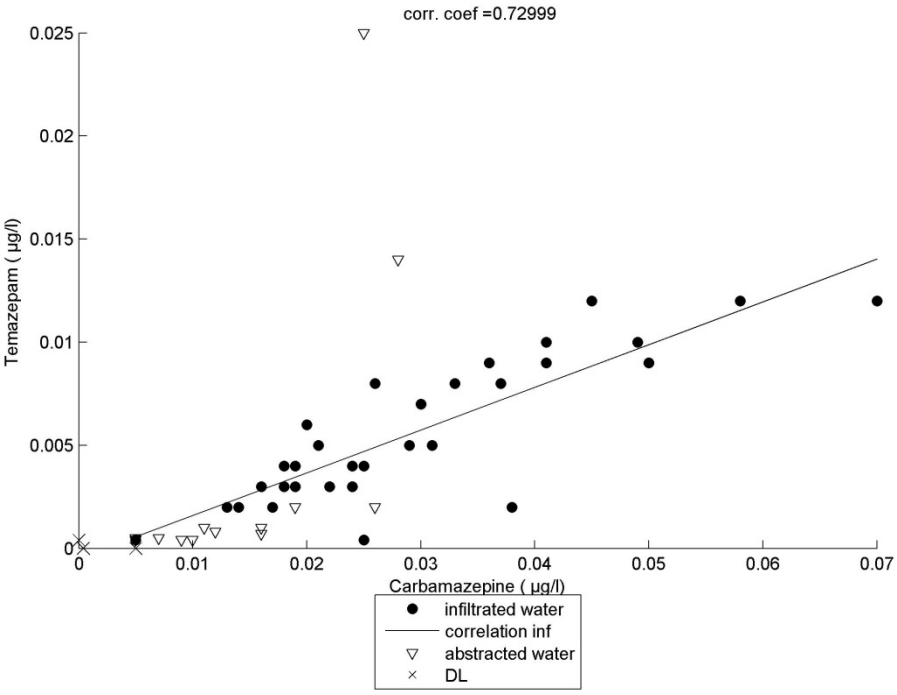

Figure 4-5. Carbamazepine concentrations versus Temazepam. Where DL = DETECTION LIMIT for both compounds and the markers indicate single measurements

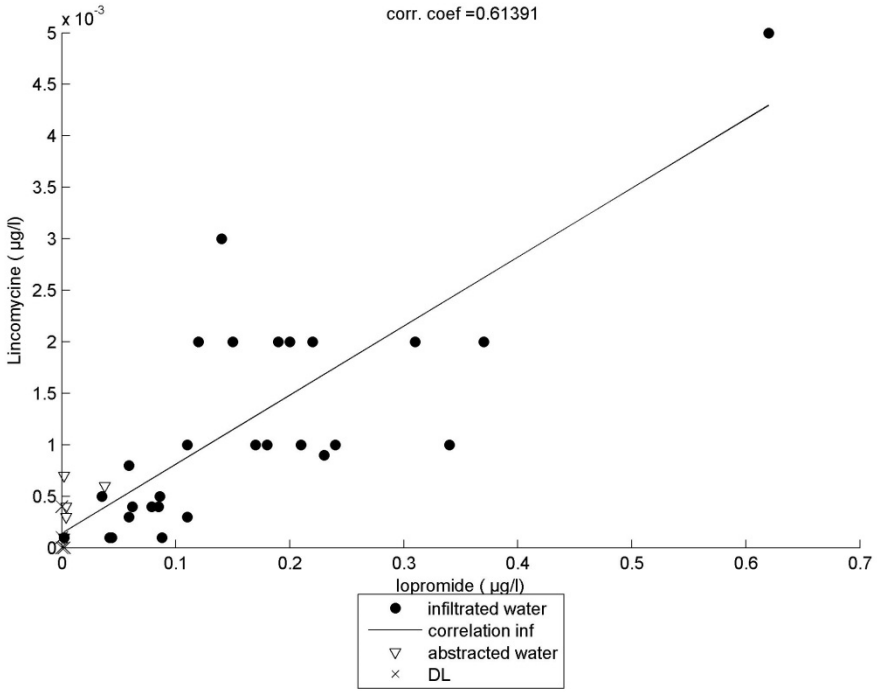

Figure 4-6. Iopromide concentrations versus lincomyccine. Where DL = DETECTION LIMIT for both compounds and the markers indicate single measurements

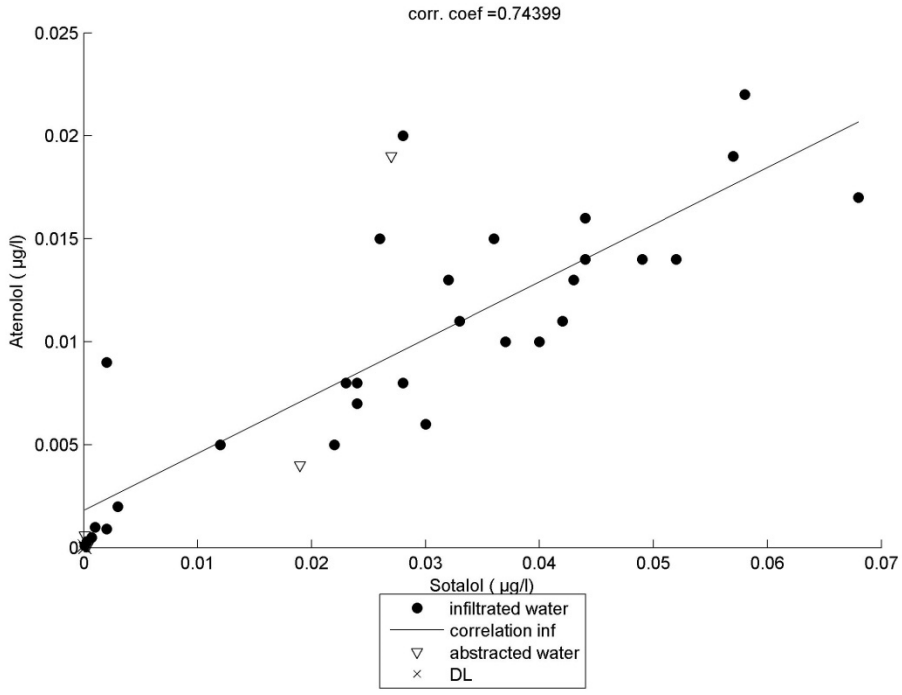

Figure 4-7. Sotalol concentrations versus atenolol. Where DL = DETECTION LIMIT for both compounds and the markers indicate single measurements

4.1.3 Cumulative probability analysis Heel

The cumulative probability density (CPD) analysis provides further information on the degree of removal per compound and confirms what was seen through the correlation method. From the pharmaceuticals with at least 5 measurements above detection limit (29 out of 46) in the infiltration water the (empirical) cumulative functions were calculated. This calculation did take into account the non-detects and the plots hereafter include the concentrations of the detection limits and how many samples were found below the detection limit providing further information on the removal. The CPD analysis was performed on the available raw concentration data, without correction for dilution. In this way, the mean average removal obtained through the probability density analysis can be compared to the removal obtained through the arithmetic averages and to confirm the effects of dilution.

The results from running a Kolmogorov-Smirnov test show that 8 out 29 compounds present empirical cumulative distributions that are significantly different (alpha = 0.05) during infiltration and during abstraction (Table 4.4). For these 8 compounds, metformin did not have enough concentrations above detection limit in the abstracted water to fit a lognormal distribution to them and therefore its removal is not calculated. Table 4-4 presents these compounds in decreasing order of concentration reduction calculated. These percentages include dilution (34-44%), therefore the effective removal is lower. Iopromide and sotalol are the compounds that undergo the most reduction, followed by atenolol, bisoprolol, lincomycin, temazepam, hydrochlorothiazide. These last 2 compounds show a wide range of reduction % (it can vary from 10th percentile = 45% to around 75% - 90th percentile), which is linked to the fact that in some cases there was removal and in some others no removal at all. This could be again a case of variable removal dependant on redox conditions or travel times. Carbamazepine shows a reduction percentage similar to the one obtained

through the arithmetic averages when, subtracting the effects of dilution (39%)..On the other hand, temazepam shows a wide range of removal percentage, which indicates variable removal and it results in a different mean than the one obtained through arithmetic averages. If 39% would be subtracted from the removal due to dilution, some temazepam would be expected to be persistent and some reduced, while from the averages calculations it would be deduced that all temazepam is persistent. Through these graphs it is also possible to extrapolate which concentrations would be expected if there would not be a detection limit concentration threshold.

For atenolol, lincomycin, and hydrochlorothiazide the fact that the non-detected values were included in the calculation of the fitted cumulative density function could result in an underestimation of the removal.

Table 4-4 Removal ranges (%), including effects of dilution (on average 39%), for those pharmaceuticals found to be significantly different in the injection and in the abstraction according to a Two-sample Kolmogorov-Smirnov test with a 0.005 confidence level.The removal % is calculated based on the lognormal cumulative distribution functions associated to each data set (infiltration and abstraction). This removal includes the effects of dilution.

	10th	90th	Mean
Iopromide	96.8%	97.5%	97.2%
Sotalol	97.2%	96.9%	97.1%
Atenolol	96.7%	94.5%	95.7%
Bisoprolol	69.0%	95.6%	88.4%
Lincomycin	69.0%	82.4%	76.7%
Temazepam	84.9%	46.8%	71.6%
Hydrochlorothiazide	46.4%	76.7%	64.6%
Carbamazepine	55.6%	47.2%	51.5%

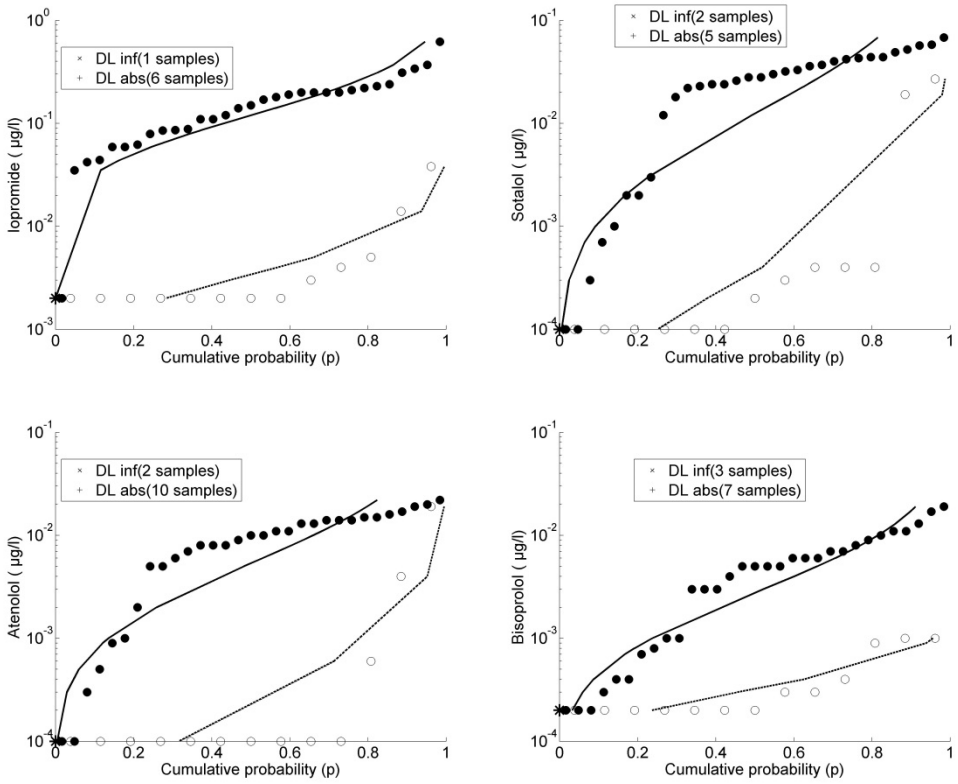

Figure 4-8 Empirical cumulative distribution (ECDF) of iopromide, sotalol, atenolol and bisoprolol based on the concentrations measured at the infiltration (filled circles) and abstraction (empty circles) location . The fitted lognormal cumulative distributions of the infiltration and abstraction are plotted as well. The detection limits identified for the infiltration data (DL inf) and the abstraction data (DL abs) are indicated above the Y axis. The legend indicates how many samples are below detection limit.

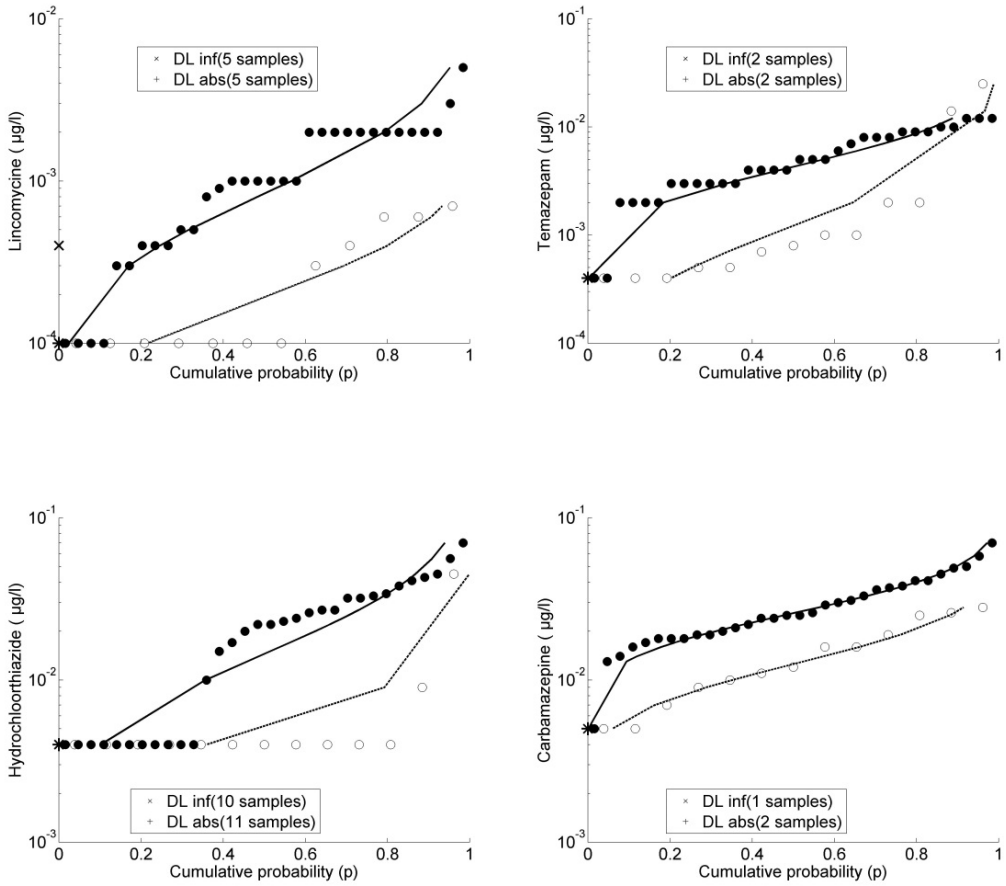

Figure 4-9 Empirical cumulative distribution (ECDF) of lincomycin, temazepam, hydrochlorothiazide and carbamazepine at the infiltration (filled circles) and abstraction (empty circles) location . The fitted lognormal cumulative distributions of the infiltration (continous line) and abstraction (dotted line) are plotted as well. The detection limits identified among the infiltration database (DL inf) and the abstraction database (DL abs) are indicated above the Y axis.

Iopromide, sotalol, and lincomycin have shown a high degree of removal during soil passage consistently for the three different data analysis methods. Temazepam and carbamazepine have shown variable removal also with the three methods. The removal of bisoprolol and metformin has been confirmed through probability analysis and comparison of input and output averages.

4.2 Scheveningen

The water taken from Brakel and infiltrating in Dunea's Scheveningen infiltration area undergoes a pre-treatment consisting of coagulation, microsieving and rapid sand filtration. This results in an 8% higher average sulphate concentration in the infiltration water (Figure 4-10) compared to the water

in Brakel due to the coagulation treatment with $FeSO_4$. The average abstracted Cl falls within the average infiltrated Cl, however the average abstracted SO_4 is notably lower due to its reduction during soil passage. Based on the spatial distribution of the ponds and the contribution of deep wells to the raw water, dilution of the infiltrated water with local groundwater in the abstracted water is expected to be less than 10% (Stuyfzand and Lüers, 2000). According to the Cl and SO_4 concentration (see Figure 4 5) most of the reduction in concentration seen in the abstracted water should be due to removal during soil passage.

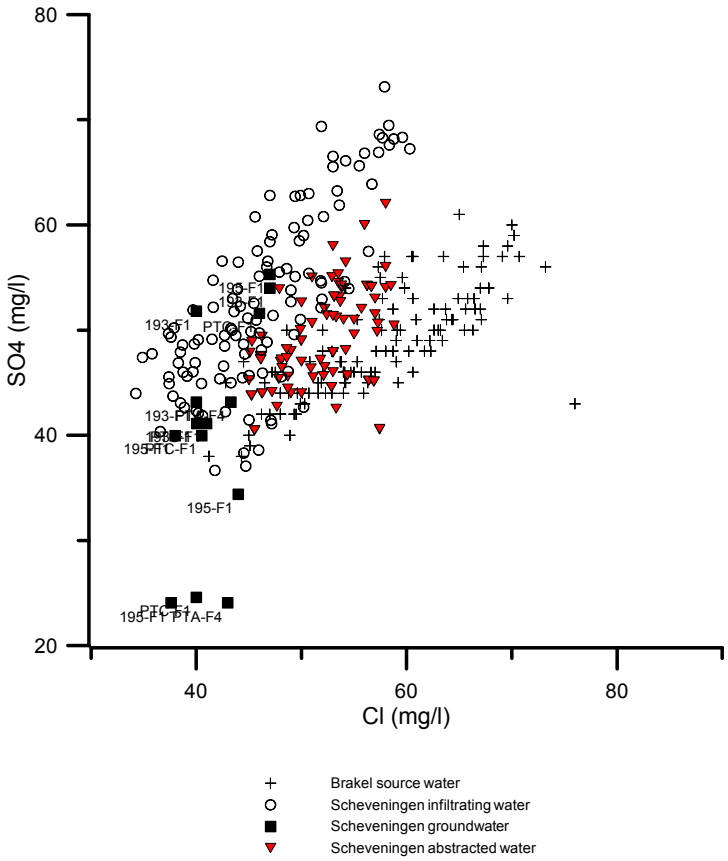

Figure 4-10 Chloride and sulfate concentrations measured in the intake, infiltration ponds, observations wells and drains of the BAR system in Scheveningen.

There are 396 sampling dates available of the infiltration water in Scheveningen (from which 67 were taken to analyse for pharmaceuticals) and 531 from the collected mixed raw water, from which 131times it was sampled for pharmaceuticals.

4.2.1 Concentration averages Scheveningen

The pharmaceuticals for which the concentration in the infiltration water was more than once above detection limit are displayed in decreasing order of mean infiltrated concentration in Figure 4-11. The blue bars correspond to the concentrations measured in Brakel and the red bars to the concentrations measured prior to infiltration. According to the plot and based on the concentrations measured in the abstracted water tribromomethane, bromodichloromethane, p-isopropylmethylbenzene, gemfibrozil, propranolol, paroxetine and sulfaquinoxaline did not show

removal during soil passage. Even in some cases the average abstracted concentration was higher than the maximum measured at the infiltration, this is the case of paroxetine and gemfibrozil, which is due to the low number of measurements above detection limit in both cases at the infiltration location.

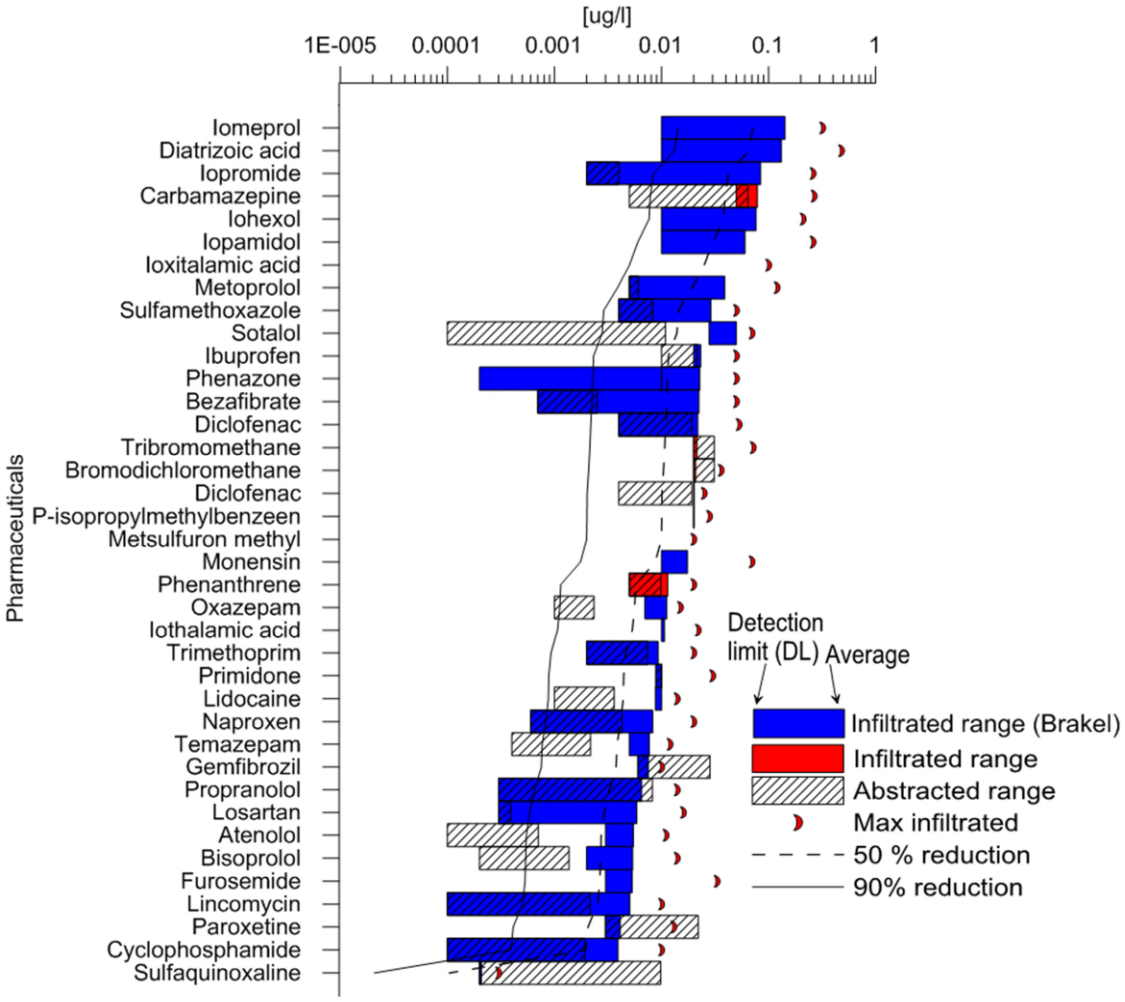

Figure 4-11 Pharmaceuticals measured in the intake at Brakel (blue bars), infiltration ponds (red bars) and in the abstraction wells (transparent bars with diagonal stripes) at Scheveningen MAR system.

Table 4-5 includes in detail the average infiltration and abstraction concentrations of those compounds with concentrations above the detection limit at least once in the infiltration water.

Since the concentration reduction due to dilution with groundwater is expected to be minimal, all concentration reduction was attributed to removal (Table 4-5). However, relatively high detection limits with respect to the concentration in the infiltrating water yielded negative removal percentages, when detection limits varied over time. So, if the detection limit used for the abstracted water was much higher than that of the infiltrated surface water, the average (that will be calculated with the detection limit value) will be higher than the infiltrated average even though the compound might have been removed. From the analysed compounds the biggest removal takes place for iopromide, sulfamethoxazole, metoprolol, sotalol, oxazepam, temazepam, losartan, atenolol and bisoprolol (Table 4-5).

Table 4-5 Averaged concentrations measured in the infiltrated and recovered water in well field Heel. This table includes the detection limits and number of samples above detection limit. The minimum and maximum detection limit are included for the infiltrated and the abstracted water (the latter only showed one detection limit along the time series) and the fraction that the detection limit measured in the abstracted water represents with respect to the mean infiltration water. If there is no information on the detection limit of the abstracted water then the detection limit of the inifiltrated water is used to calculate this fraction.

	INF max	INF min	INF mean	Brakel mean	Nr samples INF>>DL	INF min DL max DL	ABS mean	ABS Min DL max DL	Nr samples ABS >DL	Fraction DL_{abs}/INF	% removal
Iomeprol	0.32	0.010		0.142	61/ 66	0.01	-	-	-	0.07	
Diatrizoic acid	0.48	0.010		0.132	67/ 68	0.01	-	-	-	0.08	
Iopromide	0.260	0.002		0.084	106/ 113	0.002 0.01	0.004	0.002	17/32	0.02	95%
Carbamazepine	0.266	0.050	0.078		55/ 164	0.05 0.1	0.064	0.005 0.1	67/304	0.06	18%
Iohexol	0.210	0.010		0.076	65/ 68	0.01	-	-	-	0.13	
Iopamidol	0.260	0.010		0.060	61/ 68	0.01	-	-	-	0.17	
Ioxitalamic acid	0.100	0.020		0.050	18/ 18		-	-	-	0.00	
Metoprolol	0.120	0.005		0.039	75/ 124	0.005 0.06	0.006	0.005 0.01	1/38	0.13	84%
Sulfamethoxazole	0.050	0.004		0.029	79/ 134	0.004 0.05	0.0083	0.004 0.01	32/39	0.14	71%
Sotalol	0.070	0.001		0.028	56/ 82	0.05	0.011	0.0001 0.1	27/39	1.80	61%
Ibuprofen	0.050	0.020		0.023	9/ 86	0.02 0.032	0.022	0.01 0.032	1/227	0.86	7%
Phenazone	0.050	0.000		0.023	49/ 134	0.0002 0.05	0.01003	0.01	36/39	0.01	56.1%
Bezafibrate	0.050	0.001		0.022	10/ 34	0.0007 0.05	0.0025	0.0007 0.01	1/39	0.03	
Diclofenac	0.053	0.004		0.022	16/ 361	0.004 0.05	0.019	0.004 0.02	2/228	0.18	12%
Tribromomethane	0.072	0.020	0.021		9/ 132	0.02 0.03	0.031	0.02 0.1	0/117	0.47	-45%
Bromodichloromethane	0.036	0.020	0.021		1/ 133	0.02 0.03	0.031	0.02 0.1	0/117	0.48	-49%
Diclofenac	0.025	0.020	0.020		6/ 109	0.02	0.019	0.004 0.02	2/228	0.20	4%
P-isopropyl methyl benzene	0.028	0.020	0.020		3/ 106	0.02	0.020	0.02	3/63	0.99	-1%
Metsulfuron methyl	0.02	0.020	0.020		1/ 43	0.02	0.020	0.02	0/39	1.00	0%
Monensin	0.07	0.010		0.018	1/ 8	0.01	0.010	0.01	0/7	0.57	43%
Phenanthrene	0.02	0.005	0.011		3/ 69	0.005 0.02	0.010	0.005	1/39	0.17	14%
Oxazepam	0.015	0.007		0.011	13/ 13	0.007 0.0002	0.002	0.001	31/32	0.62	79%

	INF max	INF min	INF mean	Brakel mean	Nr samples INF>>DL	INF min DL max DL	ABS mean	ABS Min DL max DL	Nr samples ABS >DL	Fraction DL_{abs}/INF	% removal
Iothalamic acid	0.022	0.010		0.011	1/ 18	0.01	-	-	-	0.94	
Trimethoprim	0.02	0.002		0.009	6/ 21	0.002 0.02	0.007	0.002 0.02	8/39	0.22	20%
Primidone	0.03	0.004		0.009	13/ 20	0.01 0.03	0.0089	0.001 0.02	8/39	1.13	-0.5%
Lidocaine	0.014	0.005		0.009	16/ 18	0.01	0.0036	0.001 0.01	28/39	1.14	58.8%
Naproxen	0.02	0.001		0.008	2/ 21	0.0006 0.02	0.004	0.0006 0.02	1/39	0.07	48%
Temazepam	0.012	0.005		0.008	13/ 13	0.005 0.0002	0.002	0.0004	30/32	0.65	72%
Gemfibrozil	0.01	0.006		0.008	2/ 21	0.006 0.01	0.028	0.006 0.01	4/38	0.80	-277%
Propranolol	0.014	0.000		0.007	10/ 21	0.0003 0.01	0.008	0.0003	11/31	0.05	-26%
Losartan	0.016	0.000		0.006	9/ 13	0.0003	0.000	0.0003	3/32	0.05	93%
Atenolol	0.011	0.003		0.005	13/ 13	0.003 0.0002	0.001	0.0001	11/32	0.55	87%
Bisoprolol	0.014	0.002		0.005	13/ 13	0.002	0.001	0.0002	12/31	0.37	75%
Furosemide	0.033	0.003		0.005	1/ 13	0.003	0.003	0.003	0/32	0.57	43%
Lincomycin	0.01	0.000		0.005	47/ 84	0.0001 0.01	0.0021	0.0001 0.01	24/39	0.02	57%
Paroxetine	0.013	0.003		0.004	1/ 9	0.003	0.022	0.003	4/19	0.73	-436%
Cyclophosphamide	0.01	0.000		0.004	7/ 21	0.0001 0.01	0.00192	0.0001 0.01	10/39	0.03	51%
Sulfaquinoxaline	0.0003	0.000		0.0002	1/ 13	0.0002	0.010	0.0002 0.05	7/39	0.96	-4632%

4.2.2 Correlation analysis Scheveningen

The large amount of data available from the Brakel intake yielded significant correlations for many parameters. Following these correlations in the infiltration data also in the abstracted water proved to be more difficult since fewer parameters are regularly scanned. All the correlations found in the intake or infiltration water higher than 0.6 were visually inspected. The following figures contain the pharmaceuticals and other organic tracers that showed linear relationship in the input and were analysed in the groundwater or in the abstracted water of the MAR system. PFBS, sotalol and diotrizoic acid were analysed in the abstracted water in Scheveningen but not in the infiltration water. Therefore those infiltration concentrations were taken from Brakel.

Table 4-6 Correlated parameters in the infiltration water and the conclusions drawn from plotting them for the infiltrated and abstracted water.

Correlation	Parameter 1 (Y)	Parameter 2 (X)	Removal of:	Comments
0.66	Carbamazepine	Sulphate	Param 1	Removal in anoxic zone
0.60	Sulfamethoxazole	Carbamazepine	Param 1+2	Ubiquitous decrease
0.62	Sotalol	PFBS	Param 1	Complete removal except in suboxic
0.74	PFBS	Amidotrizoic acid	None	

When plotting carbamazepine versus sulphate (Figure 4-12), there is a general trend of decreased sulphate and carbamazepine in the abstracted water. The samples that show decreased sulphate compared to the input signal are accompanied by a stronger reduction of carbamazepine, which suggests removal under SO_4 reducing conditions or admixing with SO_4-depleted groundwater. At higher sulphate concentrations, in suboxic groundwater samples, the ratio with carbamazepine of the infiltration is however conserved.

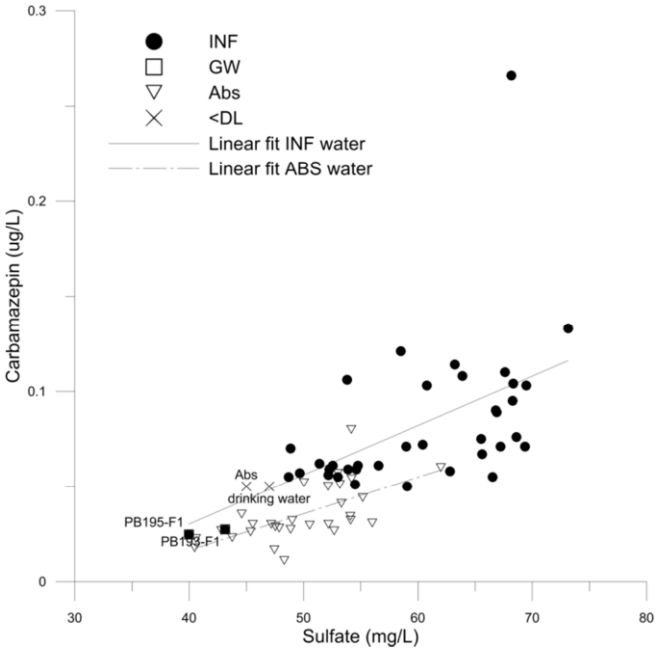

Figure 4-12. Carbamazepine versus sulfate concentration. Where INF= source infiltrating water, GW=groundwater and abs = water from the recovery wells.

When plotting carbamazepine versus sulfamethoxazole the relationship found in the infiltrating water is replicated for many samples, although for the abstracted water the concentrations are in the lower range of the infiltrated concentrations for both carbamazepine and the sulfamethoxazole. Overall, the removal of sulfamethoxazole seems similar to that of carbamazepine with removal primarily under sulphate reducing conditions (or partly admixing with SO_4 reducing water) (Figure 4-13).

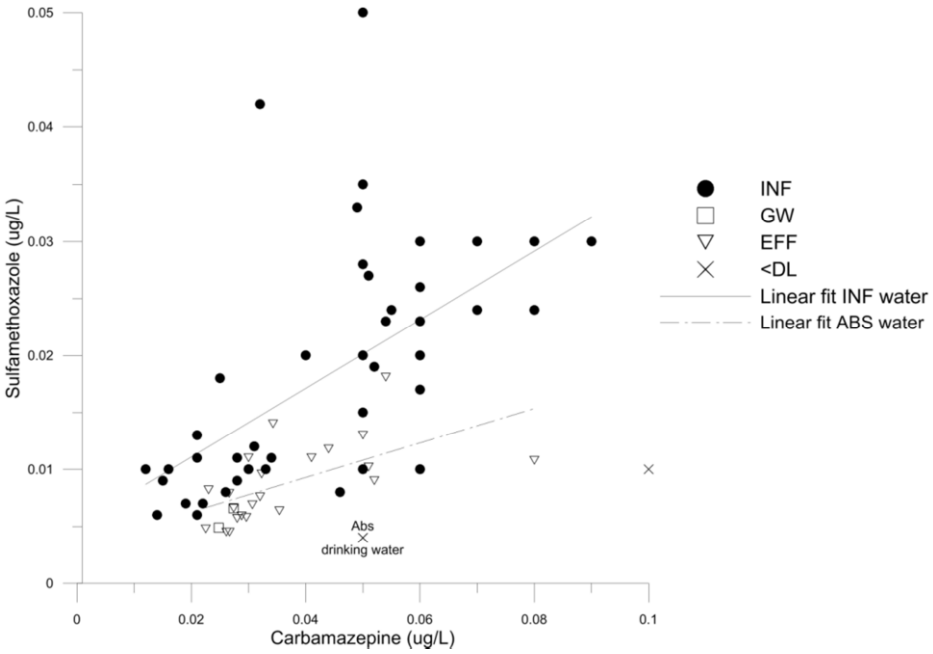

Figure 4-13. Carbamazepine concentrations versus sulfamethoxazole concentrations. Where INF= source infiltrating water, GW=groundwater, EFF= water from the recovery wells.

PFBS is used as a conservative tracer to investigate the behaviour of sotalol. In the study by (de la Loma González et al., 2015), where the same database was used as here, it was found that PFBS was among the emerging contaminants that behaved conservatively. Considering this, the strongly lowered sotalol concentrations during soil passage point towards removal of sotalol (**Error! Reference source not found.**).

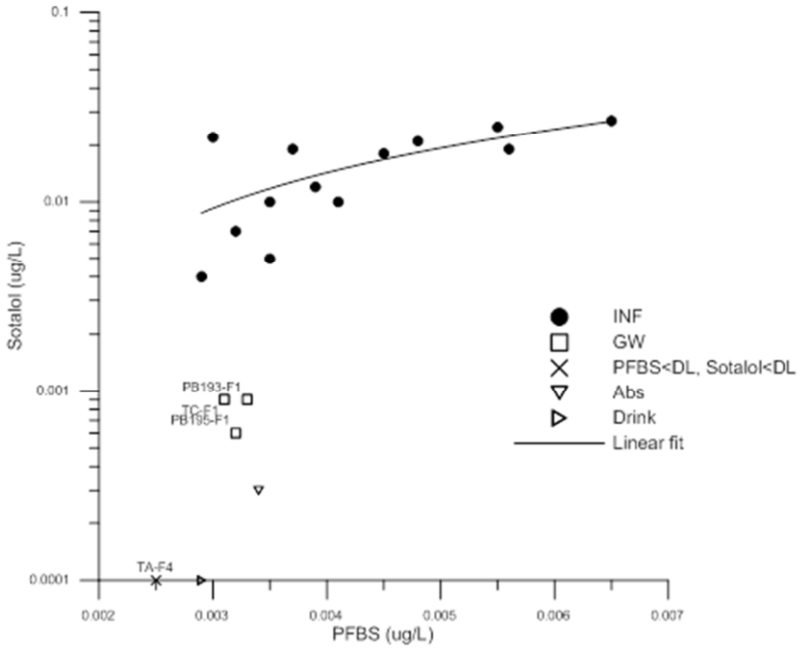

Figure 4-14. PFBS concentrations versus sotalol concentrations. Where INF= source infiltrating water, GW=groundwater, EFF= water from the recovery wells.

The ratio PFBS/Amidotrizoic acid is similar along the different groundwater, abstraction and drinking water samples (**Error! Reference source not found.**) indicating that in addition to PFBS, also amidotrizoic acid behaves conservatively (de la Loma González et al., 2015) and that it might experience dilution to a small extent.

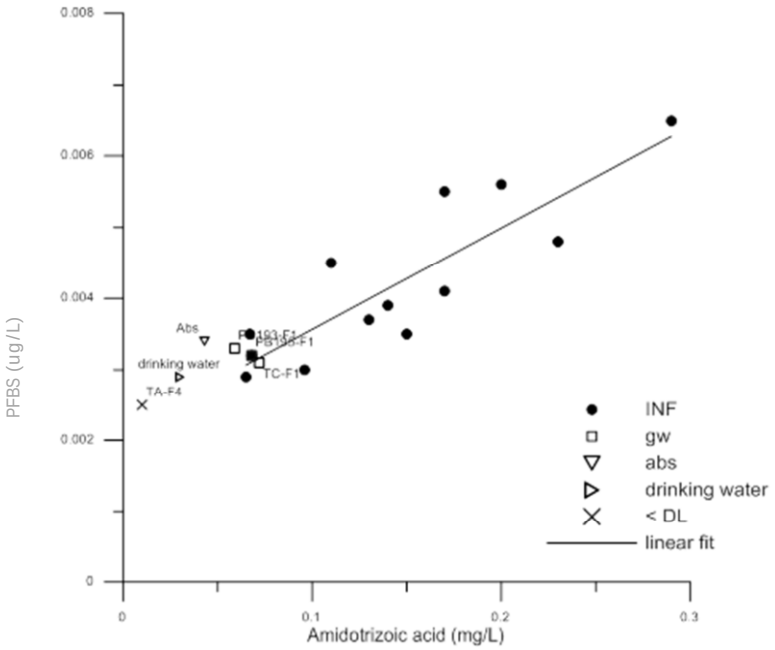

Figure 4-15. PFBS concentrations versus amidotrizoic acid. Where INF= source infiltrating water, gw=groundwater, drinking water= water after post-treatment and abs= water from the recovery wells.

4.2.3 Cumulative probability analysis Scheveningen

When performing a cumulative probability density analysis, from the 56 pharmaceuticals screened for in Brakel, only four show significant differences with the concentrations measured during abstraction. Iopromide and Sotalol prove to be highly reduced (with removal percentages ranging from 94% and 95%) followed by oxazepam and temazepam. From the 67 pharmaceuticals measured at the infiltration ponds only carbamazepine shows significant differences with the abstracted concentrations but the removal ranges from 10% to 30% (Figure 4-16, Figure 4-17,Table 4-7).

Table 4-7 Removal ranges (%) for those pharmaceuticals found to be significantly different in the infiltration water and in the abstraction according to a two-sample Kolmogorov-Smirnov test with a 0.005 confidence level. The removal % is calculated based on the lognormal cumulative distribution functions associated to each data set (infiltration and abstraction).

	10th	90th	Mean	Infiltration concentration measured at
Iopromide	94.6%	96.1%	95.4%	Brakel
Sotalol	98.5%	76.8%	94.0%	Brakel
oxazepam	86.1%	74.7%	81.2%	Brakel
temazepam	82.4%	63.3%	74.5%	Brakel
Carbamazepine	30%	10%	20%	Scheveningen

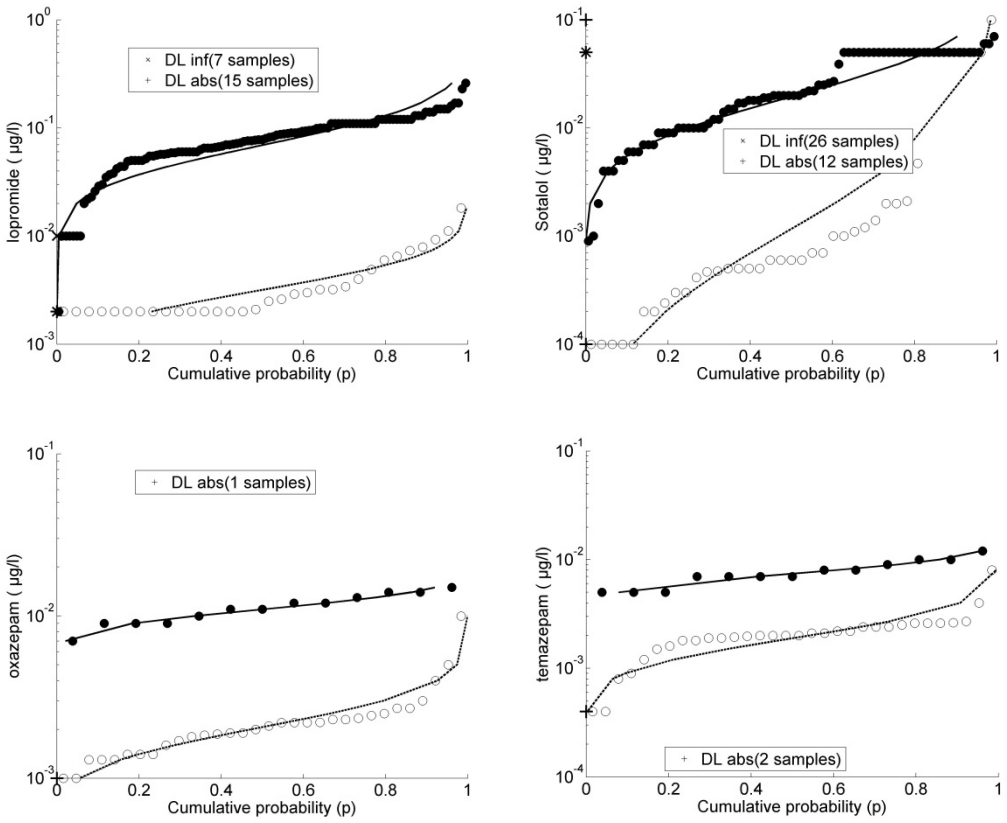

Figure 4-16 Empirical cumulative distribution (ECDF) of iopromide, sotalol, oxazepam and temazepam based on the concentrations measured in Brakel (filled circles) and abstraction system (empty circles) location. The fitted lognormal cumulative distributions of the infiltration (continous line) and abstraction (dotted line) are plotted as well. The detection limits identified among the infiltration database (DL inf) and the abstraction database (DL abs) are indicated above the Y axis. The legend indicates how many samples are below detection limit.

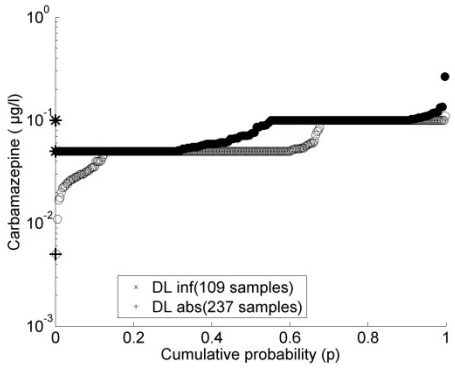

Figure 4-17 Empirical cumulative distribution (ECDF) of carbamazepine based on the concentrations measured above detection limit at the infiltration ponds (filled circles) and abstraction (empty circles) location . The fitted lognormal cumulative distributions of the infiltration (continous line) and abstraction (dotted line) are plotted as well. The detection limits identified among the infiltration database (DL inf) and the abstraction database (DL abs) are indicated above the Y axis. The legend indicates how many samples are below detection limit.

4.3 Eijbergen

The water abstracted in Eijbergen through the various pumping wells is mixed with groundwater in different degrees. The fraction of native groundwater in the abstracted water ranges from 100% in observation well WP 02-15C, to around 25% for well WP 04-17A. The Cl concentrations of the native water are quite restricted compared to those of the infiltration water (Figure 4-18), in contrast to what was observed in well field Heel or Scheveningen, this allows for a calculation of the dilution factor based solely on chloride concentrations, such as described in Chapter 3. The resulting dilution factors per pumping well in Eijbergen are shown in Table 4-8.

Table 4-8 Dilution coefficiens per well according to the fraction of infiltrated surface water expected in each of them

Dilution coefficient	
P04	0.78
P07	0.45
P03	0.68
P05	0.21
P02	0.00

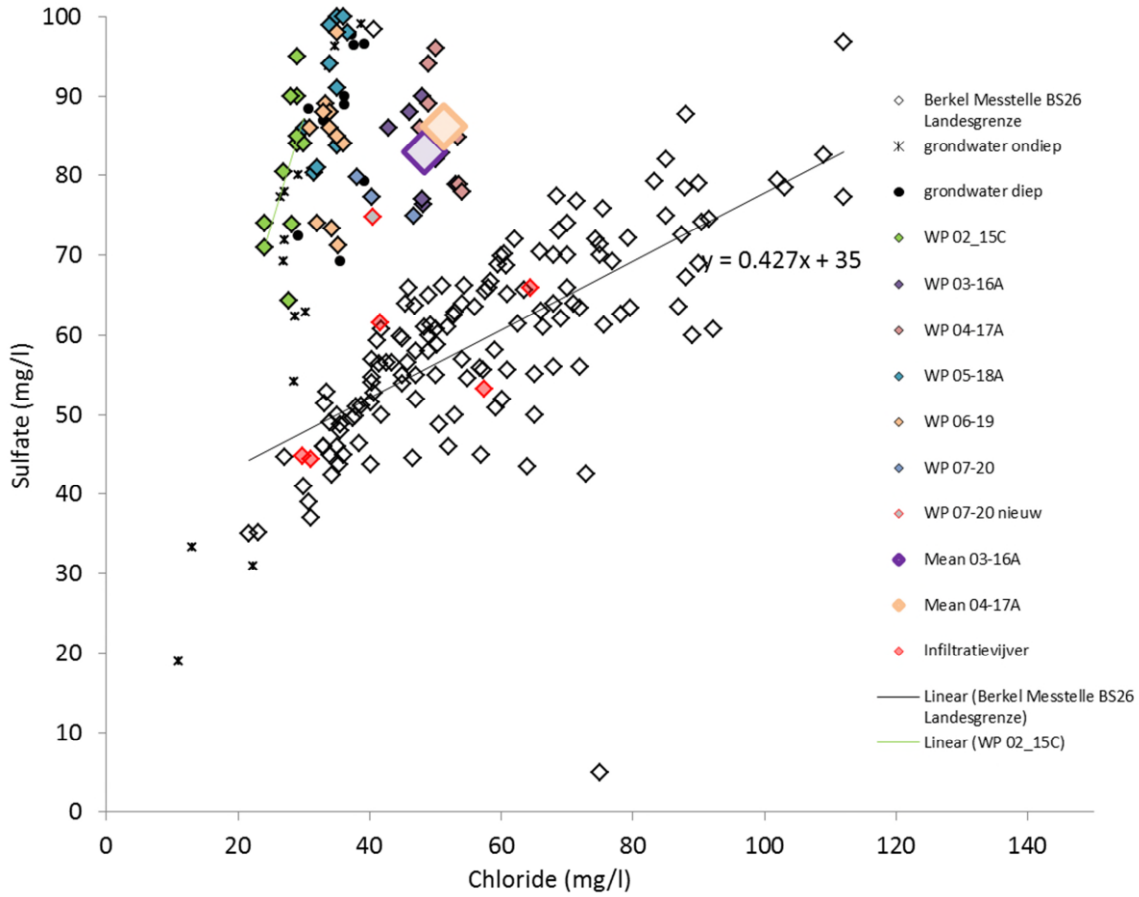

Figure 4-18. Chloride (mg/l) versus sulphate (mg/l) measured in Eibergen.

4.3.1 Concentration averages Eijbergen

The abstracted concentrations were firstly multiplied by the dilution coefficient as described in chapter 3. The pharmaceuticals measured in the infiltration water are displayed in Figure 4-19 in decreasing order. The average abstracted concentrations of wells P04, P07, P03 and P05 are also displayed corrected for dilution. The removal percentages were calculated as well taking into account the dilution factors as described in chapter 3. This as result gives in some cases negative removal values (Table 4-9, Table 4-10 and Table 4-11) if the dilution factor was higher than the detectability determined by the detection limit, like in the case of well field Heel. Table 4-10 provides also the average of the concentrations measured in the wells where infiltration water is expected to be abstracted (P03, P05; P04 and P07) and the average removal per compound is calculated as the average of the removal of those wells where that compound was measured at least once above detection limit. The average concentrations measured in well P02 are also given and they provide an overview of the native water quality.

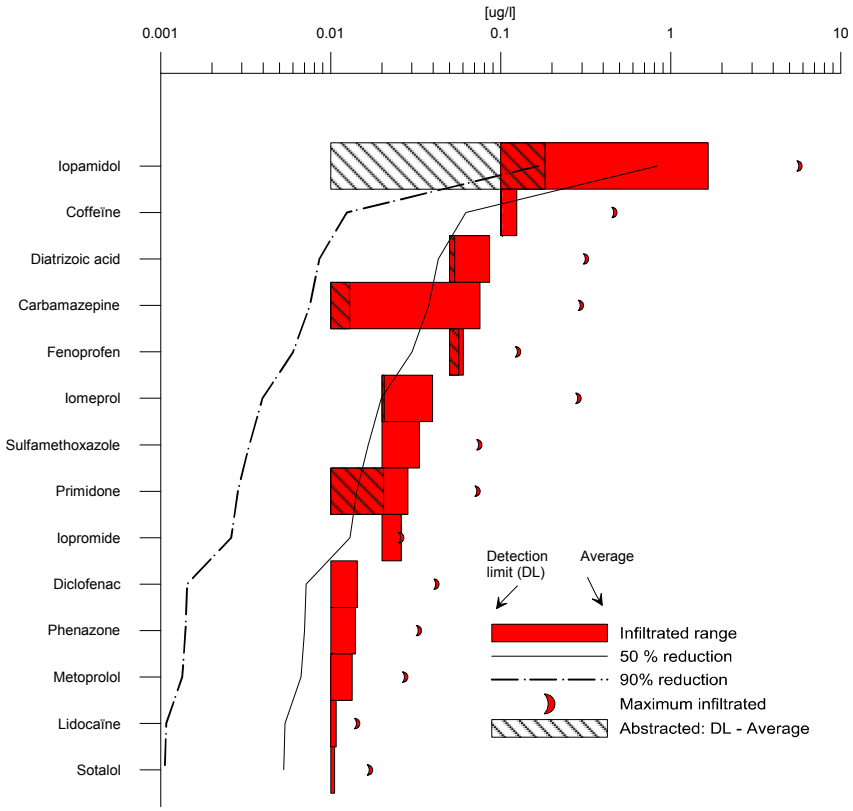

Figure 4-19 Pharmaceuticals measured in the infiltration pond and in the abstraction wells in Eijbergen.

Figure 4-19 suggests the removal of iopamidol, caffeine, diatrizoic acid, carbamazepine, iomeprol, primidone and iopromide. However, when analysing the removal percentage according to the expected dilution, only positive removal values are obtained for iopamidol and carbamazepine (low removal, persistent). The maximum removal of iopamidol is observed in well P04 (68%) and of carbamazepine in well P07 (16%) (Table 4-11). Fenoprofen and primidone on the other hand do not show clear removal in any of the wells especially when considering the expected reduction by dilution. Sulfamethoxazole, Iopromide, diclofenac, phenazone, metoprolol, lidocaine and sotalol were measured under the detection limit in all the abstracted water samples.

Table 4-9 Averaged concentrations measured in the infiltration water in Eijbergen. This table includes the detection limits and number of samples above detection limit. The minimum and maximum detection limit are included and the fraction that the detection limit represents with respect to the mean infiltration water.

Parameter	units	Max INF	Min INF	Mean INF	Min DL	Max DL	Fraction DL_{inf} / $Mean_{INF}$	Samples <DL	Total nr of samples
Iopamidol	µg/l	5.7075	0.0146	1.6587	0.1	0.1	0.06	0	14
Caffeine	µg/l	0.4657	0.1	0.1244	0.1	0.1	0.80	14	15
Diatrizoic acid	µg/l	0.317	0.05	0.0858	0.05	0.05	0.58	9	14
Carbamazepine	µg/l	0.296	0.01	0.0754	0.01	0.01	0.13	6	15
Fenoprofen	µg/l	0.1265	0.05	0.0602	0.05	0.05	0.83	13	15
Iomeprol	µg/l	0.286	0.02	0.0397	0.02	0.02	0.50	12	14
Sulfamethoxazole	µg/l	0.0748	0.02	0.0332	0.02	0.02	0.60	7	13
Primidone	µg/l	0.073	0.01	0.0285	0.01	0.01	0.35	6	15
Iopromide	µg/l	0.026	0.026	0.026	0.02	0.02	0.77	0	1

Parameter	units	Max INF	Min INF	Mean INF	Min DL	Max DL	Fraction DL_{inf}/ $Mean_{INF}$	Samples <DL	Total nr of samples
Diclofenac	µg/l	0.0418	0.01	0.0143	0.01	0.01	0.70	12	15
Phenazone	µg/l	0.033	0.01	0.014	0.01	0.01	0.71	9	15
Metoprolol	µg/l	0.0274	0.01	0.0134	0.01	0.01	0.75	10	15
Lidocaine	µg/l	0.0143	0.01	0.0108	0.01	0.01	0.93	12	15
Sotalol	µg/l	0.017	0.01	0.0106	0.01	0.01	0.95	10	15

Table 4-10 Averaged concentrations measured in the infiltrated and recovered water in Eijbergen. This table includes the detection limits and number of samples above the detection limit. The fifth column gives the average of the concentrations measured in the wells that are expected to abstract infiltration water: well P04, P07, P05 and P03, corrected for dilution. Max DL or Fraction…?? provides the averages measured in well P02, expected to be 100% groundwater.

Parameter	units	Mean INF	INF Min DL	Fraction DL_{abs}/ $Mean_{INF}$	average P04-07-03-05	% Removal average	P02 (100% gw)	% Removal	samples with values over DL/total
Iopamidol	µg/l	1.6587	0.1	0.06	0.182	33%	0.0104	-1%	2/14
Caffeine	µg/l	0.1244	0.1	0.80	0.101	-63%	0.1		0/14
Diatrizoic acid	µg/l	0.0858	0.05	0.58	0.053	-30%	0.05		0/14
Carbamazepine	µg/l	0.0754	0.01	0.13	0.013	16%	0.01		0/14
Fenoprofen	µg/l	0.0602	0.05	0.83	0.057	-53%	0.05	-83%	2/14
Iomeprol	µg/l	0.0397	0.02	0.50	0.021		0.02		0/14
Sulfamethoxazole	µg/l	0.0332	0.02	0.60	0.02		0.02		0/12
Primidone	µg/l	0.0285	0.01	0.35	0.0204	-19%	0.01		0/14
Iopromide	µg/l	0.0260	0.02	0.77	0.005				0/0
Diclofenac	µg/l	0.0143	0.01	0.70	0.01		0.01		0/14
Phenazone	µg/l	0.0140	0.01	0.71	0.01		0.01		0/14
Metoprolol	µg/l	0.0134	0.01	0.75	0.01		0.01		0/14
Lidocaïne	µg/l	0.0108	0.01	0.93	0.01		0.01		0/14
Sotalol	µg/l	0.0106	0.01	0.95	0.01		0.01		0/14

Table 4-11 Averaged concentrations measured in the infiltrated and recovered water in Eijbergen. This table includes the averages of the concentrations measured in the abstraction wells corrected for dilution.

Parameter	units	Mean INF	INF min DL	Fraction DL_{abs}/ $Mean_{INF}$	P04	% Removal	samples with values over DL	P07 (35%gw)	% Removal	samples with values over DL/total
Iopamidol	µg/l	1.6587		0.006	1.33E-01	68%	4/16	2.96E-01	22%	1/1
Caffeine	µg/l	0.1244	0.1	0.80	0.1		0/16	0.1		0/1
Diatrizoic acid	µg/l	0.0858	0.05	0.58	0.05		0/16	6.10E-02	-30%	1/1
Carbamazepine	µg/l	0.0754	0.01	0.13	0.01		0/16	1.90E-02	16%	1/1

Parameter	units	Mean INF	INF min DL	Fraction DL_{abs}/ $Mean_{INF}$	P04	% Removal	samples with values over DL	P07 (35%gw)	% Removal	samples with values over DL/total
Fenoprofen	µg/l	0.0602	0.05	0.83	5.77E-02	-22%	2/16	0.05		0/1
Iomeprol	µg/l	0.0397	0.02	0.50	0.02		0/16	0.02		0/1
Sulfamethoxazole	µg/l	0.0332	0.02	0.60	0.02		0/14	0.02		0/1
Primidone	µg/l	0.0285	0.01	0.35	2.10E-02	-7%	2/16	1.90E-02	-31%	1/1
Iopromide	µg/l	0.0260		0.77			0/0	0.02		0/1
Diclofenac	µg/l	0.0143	0.01	0.70	0.01		0/16	0.01		0/1
Phenazone	µg/l	0.0140	0.01	0.71	0.01		0/16	0.01		0/1
Metoprolol	µg/l	0.0134	0.01	0.75	0.01		0/16	0.01		0/1
Lidocaïne	µg/l	0.0108	0.01	0.93	0.01		0/16	0.01		0/1
Sotalol	µg/l	0.0106	0.01	0.95	0.01		0/16	0.01		0/1

Table 4-12 Averaged concentrations measured in the infiltrated and recovered water in Eijbergen. This table includes the averages of the concentrations measured in the abstraction wells corrected for dilution. .

Parameter	units	Mean INF	INF minDL	Fraction DL_{abs}/ $Mean_{INF}$	P03	% Removal	samples with values over DL	P05	% Removal	samples with values over DL/total
Iopamidol	µg/l	1.6587		0.06	1.18E-01	59%	4/16	2.82E-02	19%	4/16
Caffeine	µg/l	0.1244	0.1	0.80	0.1		0/16	1.03E-01	-63%	2/16
Diatrizoic acid	µg/l	0.0858	0.05	0.58	0.05		0/16	0.05		0/16
Carbamazepine	µg/l	0.0754	0.01	0.13	0.01		0/16	0.01		0/16
Fenoprofen	µg/l	0.0602	0.05	0.83	5.28E-02	-21%	2/16	6.02E-02	-84%	2/16
Iomeprol	µg/l	0.0397	0.02	0.50	0.02		0/16	2.25E-02		0/16
Sulfamethoxazole	µg/l	0.0332	0.02	0.60	0.02		0/14	0.02		0/14
Primidone	µg/l	0.0285	0.01	0.35	2.14E-02	-19%	2/16	1.10E-02	-19%	2/16
Iopromide	µg/l	0.0260		0.77			0/0			0/0
Diclofenac	µg/l	0.0143	0.01	0.70	0.01		0/16	0.01		0/16
Phenazone	µg/l	0.0140	0.01	0.71	0.01		0/16	0.01		0/16
Metoprolol	µg/l	0.0134	0.01	0.75	0.01		0/16	0.01		0/16

Parameter	units	Mean INF	INF minDL	Fraction DL_{abs} / $Mean_{INF}$	P03	% Removal	samples with values over DL	P05	% Removal	samples with values over DL/total
Lidocaïne	µg/l	0.0108	0.01	0.93	0.01		0/16	0.01		0/16
Sotalol	µg/l	0.0106	0.01	0.95	0.01		0/16	0.01		0/16

4.3.2 Correlation analysis Eijbergen

Correlations were found for four different set of pharmaceuticals for the infiltration water. Their concentrations and the concentrations measured at wells P03, P04, P05 and P07 are displayed in the following figures; these concentrations were not corrected for dilution as to avoid any bias that can come from that calculation. Carbamazepine and primidone were highly correlated (r^2 = 0.91,Table 4-13,Figure 4-20) in the infiltration water and in the abstracted water all the carbamazepine concentrations plotted on top of the detection limit concentration value, indicating carbamazepine removal. The correlation for the abstracted water shifted towards a vertical line parallel to the Primidone axis where the concentration ranges for Primidone got also reduced, which in part is attributed to dilution. Iopamidol showed partial removal with respect to primidone (Figure 4-21**Error! Reference source not found.**).

Sulfamethoxazole and primidone concentrations were highly correlated in the infiltrating water while for the abstracted water sulfamethoxazole is more strongly removed during soil passage. The same applies for the correlation found for primidone and diatrizoic acid (Figure 4-23), where diatrizoic acid gets preferentially removed. Iopamidol and sulfamethoxazole (Figure 4-24) showed a correlation of 0.785 in the infiltrating water. This correlation changed for the abstracted water and the measurements for both of the parameters shifted towards the origin indicating removal and dilution of both of them.

Table 4-13 Correlated parameters in the infiltration water and the conclusions drawn from plotting them for the infiltrated and abstracted water.

Correlation	Parameter 1 (Y)	Parameter 2 (X)	Removal of:	Comments
0.9	Primidone	Carbamazepine	Param 1	Primidone has decreased the maximum concentration reached
0.8	Sulfamethoxazole	Primidone	Param1	(Same as above)
0.768	Primidone	Diatrizoic acid	Param 2	
0.785	Iopamidol	Sulfamethoxazole	Param1 + 2	

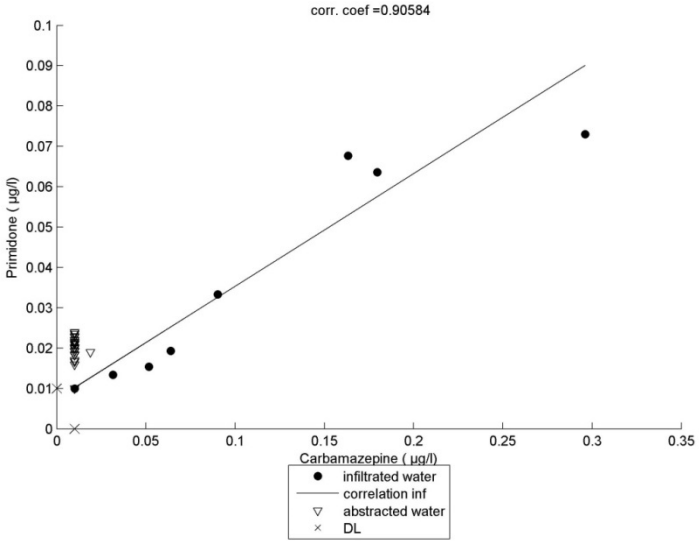

Figure 4-20. Primidone versus carbamazepine concentrations measured in eijbergen for all the infiltration and abstraction sampling locations.

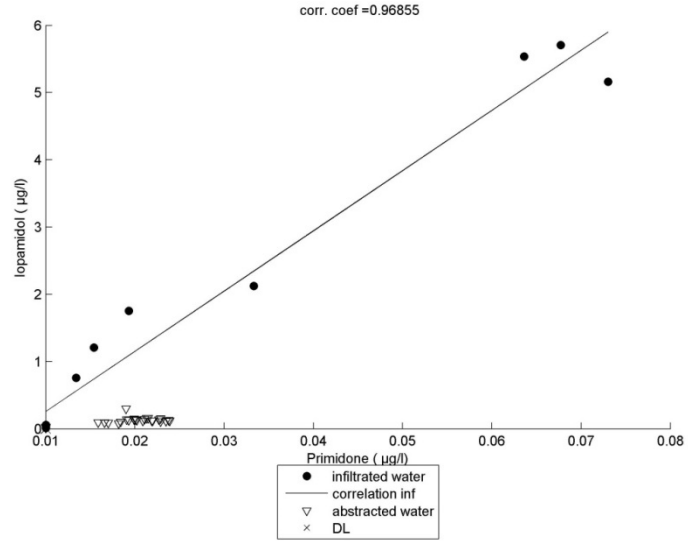

Figure 4-21. Iopamidol versus primidone concentrations measured in eijbergen for all the infiltration and abstraction sampling locations.

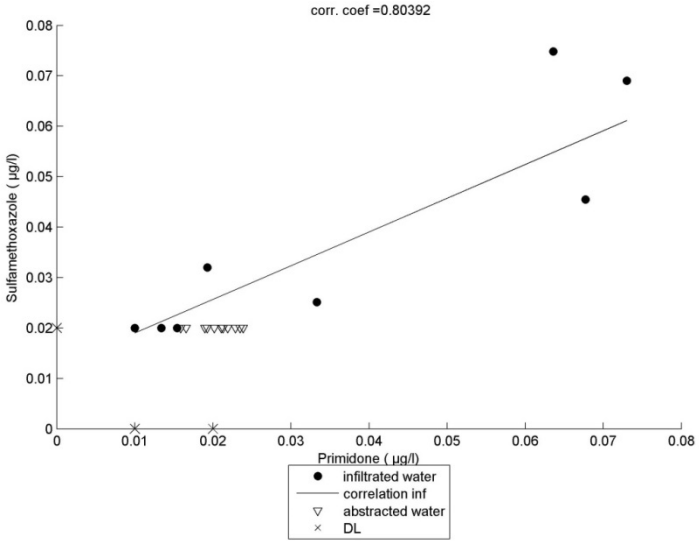

Figure 4-22. sulfamethoxazole versus primidone concentrations measured in eijbergen for all the infiltration and abstraction sampling locations.

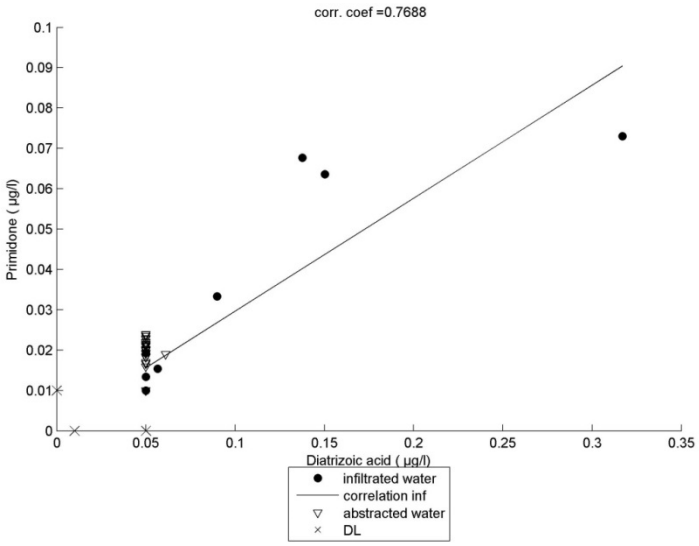

Figure 4-23. primidone versus diatrizoic acid concentrations measured in eijbergen for all the infiltration and abstraction sampling locations.

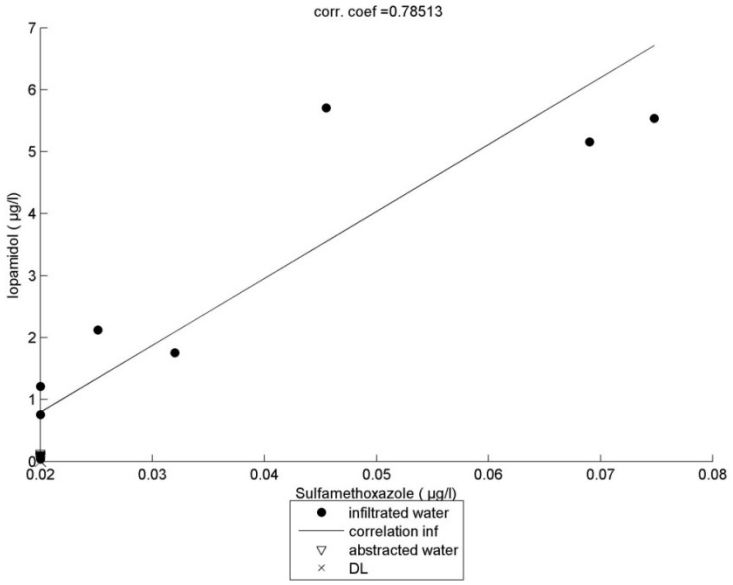

Figure 4-24. iopamidol versus sulfamethoxazole concentrations measured in eijbergen for all the infiltration and abstraction sampling locations.

4.3.3 Cumulative probability analysis Eijbergen

Only for Iopamidol the empirical cumulative concentration distribution was significantly different between the abstraction and the injection water (Table 4-14). However the removal percentages calculated from the cumulative distribution functions give wide ranges. The wide ranges could indicate that the abstracted water results from a mixture flowpaths where removal takes place and where it does not. Figure 4-25 shows that the cumulative distribution functions for the infiltrated and abstracted water even cross each-other.

Table 4-14 Removal ranges (%) for the pharmaceuticals found to be significantly different in the injection and in the abstraction according to a Twosample Kolmogorov-Smirnov test with a 0.005 confidence level.The removal % is calculated based on the lognormal cumulative distributions functions associated to each data set (infiltration and abstraction).

	10th	90th	Mean
Iopamidol	-32.0%	96.6%	78.9%

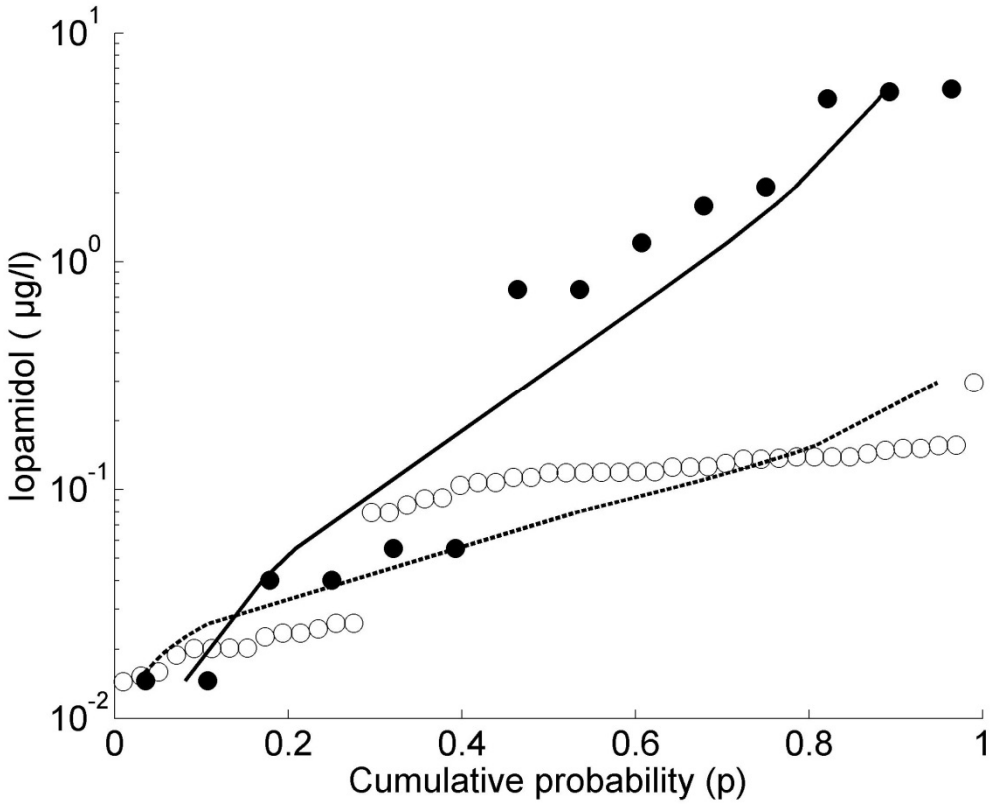

Figure 4-25 Empirical cumulative distribution (ECDF) of iopamidol based on the concentrations measured at the infiltration (filled circles) and abstraction (empty circles) location . The fitted lognormal cumulative distributions of the infiltration (continous line) and abstraction (dotted line) are plotted as well.

4.4 Ouddorp

After the intake, the surface water taken from the Haringvliet undergoes a treatment process after which is being infiltrated through the infiltration ponds. This infiltrated water has a residence time of 108 days before it is being abstracted again through drains and treated again prior to its distribution.

To calculate the degree of dilution of the abstracted water, the sulphate and chloride concentrations at the intake, infiltration ponds and abstraction wells are plotted. The measurements in the infiltration water and at the intake present a similar range of Cl/SO_4 ratio Figure 4-26, however the Cl average for the infiltrating water is higher than that of the intake and this has to do with the coagulation pre-treatment process by which FeCl3 is added to the water. The Cl/SO_4 ratio is higher for the abstracted than for the infiltration water due to the SO4 reduction along the dune passage and performing a linear fit to these two data sets indicates that the abstracted SO_4 concentrations are 50% lower with regard to Cl concentrations.

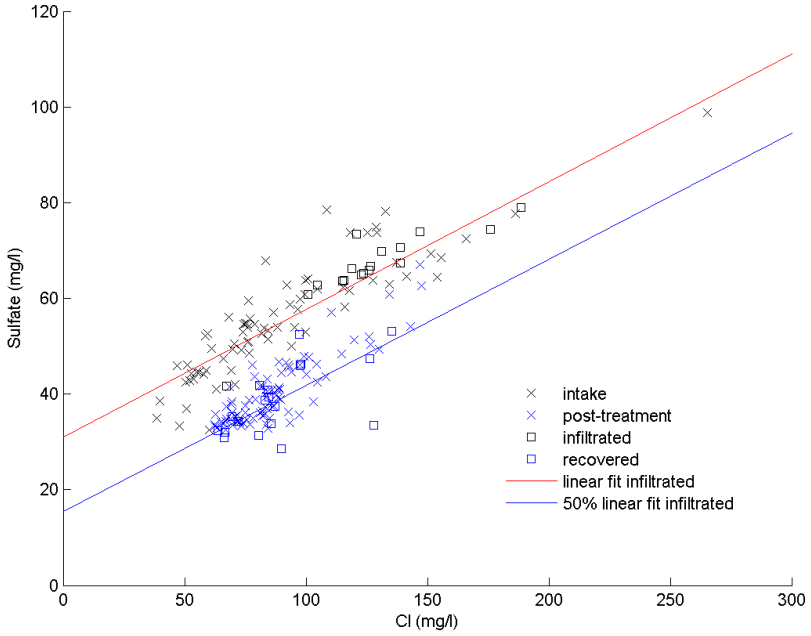

Figure 4-26 Sulfate and chloride concentrations measured both in the intake and in the collected mixed raw water .

4.4.1 Concentration averages Ouddorp

An analysis of the concentrations measured before infiltration (after the pre-treatment process) and after the soil passage (Figure 4-27 and Table 4-15), indicates low or no removal for sotalol, carbamazepine, phenazone, propranolol and lyncomicine. Removal was observed for urotropine, hydrochlorothiazide, bisoprolol, oxazepam, metoprolol, sulfamethoxazole and temazepam. Some removal percentages give negative values and this is due to the higher detection limit of the abstracted water than that used in the analysis of the infiltration water.

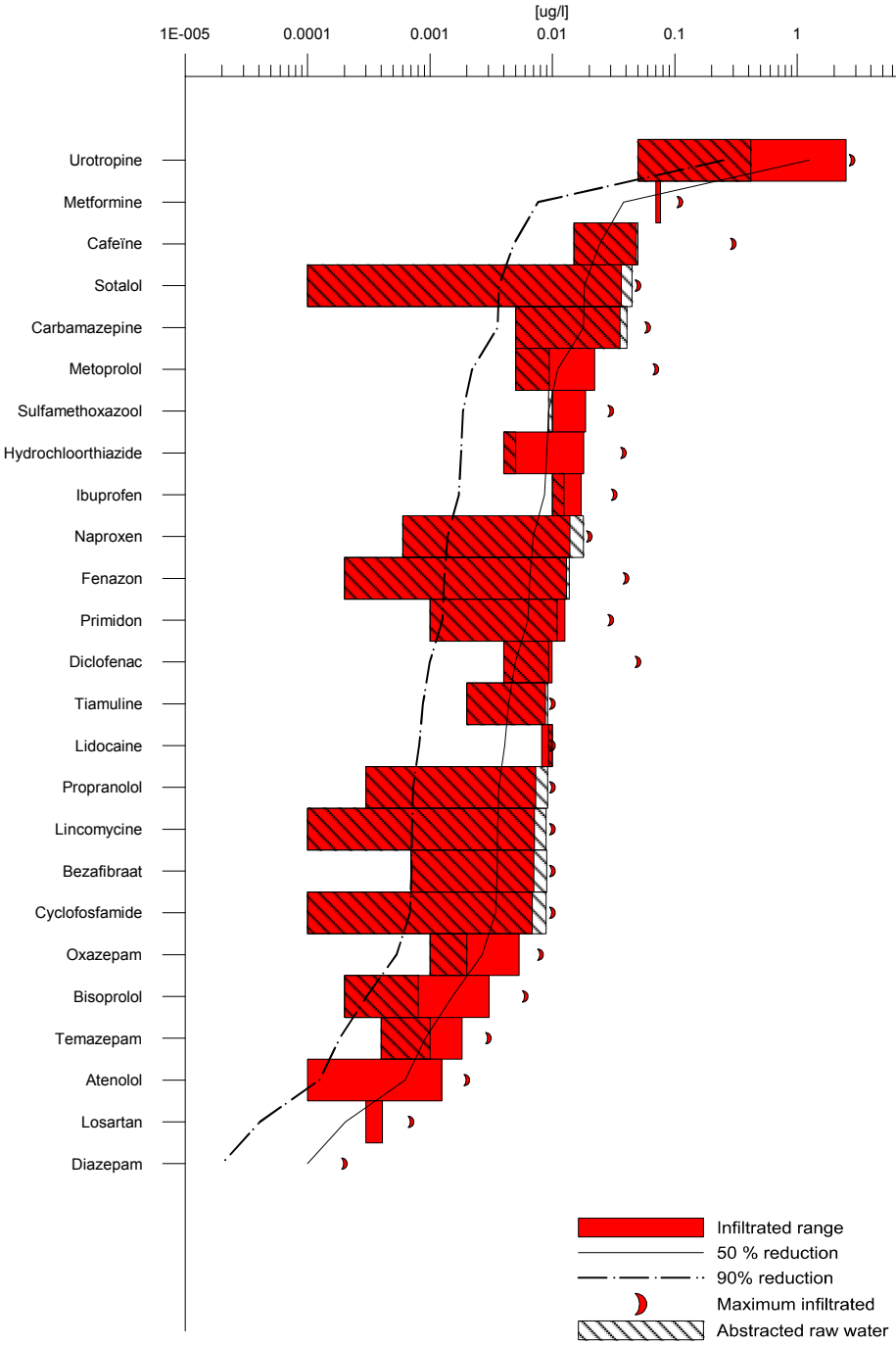

Figure 4-27 Pharmaceuticals measured in the infiltration ponds and in the abstraction wells in Ouddorp .

Table 4-15 Averaged Concentrations measured in the infiltrated and recovered water in Ouddorp. This table includes the detection limits and number of samples over the detection limit. The minimum and maximum detection limit are included for the infiltrated and the abstracted water and the fraction that the detection limit measured in the abstracted water represents with respect to the mean infiltration water. If there is no information on the detection limit of the abstracted water then the detection limit of the inifiltrated water is used to calculate this fraction.

parameters	units	INF max	INF min	INF mean	INF Min DL	Samples INF > DL/total	Mixed Raw Water (output) mean	ABS min DL	Nr samples collected >DL /total	Fraction DL abs/ INFmean	% removed
Urotropine	µg/l	2.8	2.3	2.5		3/3	0.4176		25/25		83%
Metformin	µg/l	0.11	0.07	0.0763	0.07	3/12	0.07	0.07	0/1	0.92	
Caffeine	µg/l	0.3	0.015	0.0485	0.015	7/38	0.05	0.05	0/9	1.03	
Sotalol	µg/l	0.05	0.006	0.0366	0.0001	12/25	0.0448	0.003	1/9	1.37	-22%
Carbamazepine	µg/l	0.06	0.019	0.0358	0.005	38/38	0.0408		9/9	0.00	-14%
Metoprolol	µg/l	0.07	0.005	0.0221	0.005	26/38	0.0094	0.005	0/9	0.23	
Sulfamethoxazole	µg/l	0.03	0.01	0.0186	0.01	37/38	0.0093	0.004	0/9	0.21	
Hydrochlorothiazide	µg/l	0.038	0.004	0.0180	0.004	9/12	0.0050		1/1	0.22	72%
Ibuprofen	µg/l	0.032	0.01	0.0172	0.01	1/38	0.0124	0.01	0/9	0.58	
Naproxen	µg/l	0.02	0.0006	0.0139	0.0006	4/38	0.0178	0.0006	0/9	0.04	
Phenazon	µg/l	0.04	0.0002	0.0131	0.0002	21/38	0.0138	0.01	3/9	0.77	-5%
Primidone	µg/l	0.03	0.004	0.0127	0.001	12/38	0.0109	0.01	1/9	0.79	14%
Diclofenac	µg/l	0.05	0.004	0.0099	0.004	5/38	0.0093	0.004	0/9	0.40	
Tiamuline	µg/l	0.01	0.002	0.0088	0.002	2/38	0.0091	0.002	0/9	0.23	
Lidocaine	µg/l	0.01	0.003	0.0082	0.01	12/25	0.0093	0.01	1/9	1.23	-14%
Propranolol	µg/l	0.01	0.0003	0.0073	0.0003	11/38	0.0091	0.01	1/9	1.37	-25%
Lincomycin	µg/l	0.01	0.0002	0.0071	0.0001	12/38	0.0089	0.01	1/9	1.40	-25%
Bezafibrate	µg/l	0.01	0.0007	0.0071	0.0007	1/38	0.0090	0.0007	0/9	0.10	
Cyclophosphamide	µg/l	0.01	0.0001	0.0069	0.0001	5/38	0.0089	0.0001	0/9	0.01	
Oxazepam	µg/l	0.008	0.003	0.0053	0.001	12/12	0.002		1/1		63%
Bisoprolol	µg/l	0.006	0.0006	0.0030	0.0002	12/12	0.0008		1/1		74%
Temazepam	µg/l	0.003	0.001	0.0018	0.0004	12/12	0.001		1/1		45%
Atenolol	µg/l	0.002	0.0005	0.0013	0.0001	12/12	0.0001	0.0001	0/1	0.08	
Losartan	µg/l	0.0007	0.0003	0.0004	0.0003	11/12	0.0003	0.0003	0/1	0.73	
Diazepam	µg/l	0.0002	0.0002	0.0002	0.0002	3/12	0.0002	0.0002	0/1	1.00	

4.4.2 Correlation analysis Ouddorp

Sotalol and hydrochlorothiazide concentrations showed a strong correlation in the inifltrating water (Table 4-16, Fig. 4-27). However, in the abstracted water there were few samples where these two parameters were measured and were in all cases below detection limit. Lidocaine and sotalol correlate in the infiltration water (Fig. 4-28) and most of the measurements are below detection limit in the abstracted water. Bisoprolol and atenolol (Fig. 4-29) also resulted in values under detection limit after soil passage for both.

Table 4-16 Correlated parameters in the infiltration water and the conclusions drawn from plotting them for the infiltrated and abstracted water.

Correlation	Parameter 1 (Y)	Parameter 2 (X)	Removal of:	Comments
0.91	Sotalol	Hydrochlorothiazide	Param 1 + 2	Infiltrated - Abstracted
0.91	Lidocaine	Sotalol	none	Infiltrated – Abstracted
0.84	Bisoprolol	Atenolol	Param 1+2	Infiltrated – Abstracted

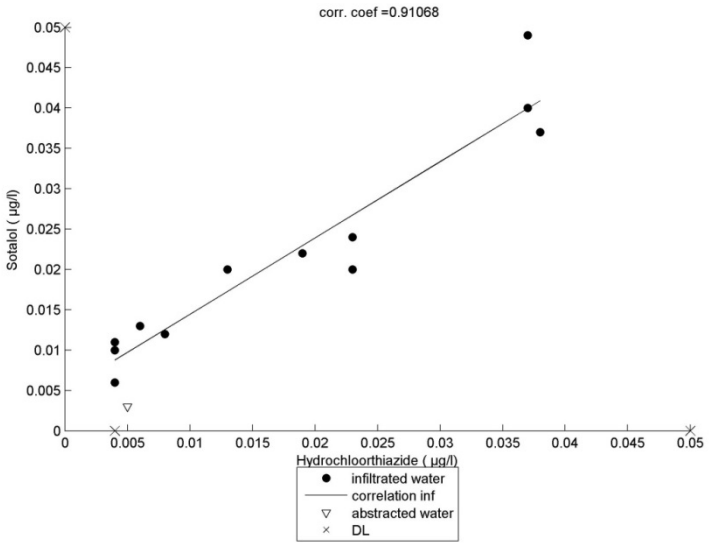

Figure 4-28 Sotalol concentrations versus hydrochlorothiazide. Where DL = DETECTION LIMIT for both compounds. The markers indicate single measurements

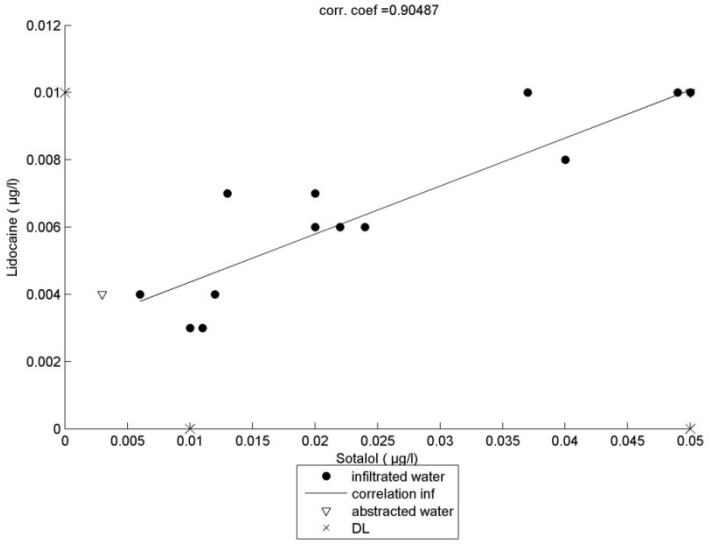

Figure 4-29 Lidocain concentrations versus sotalol. Where DL = DETECTION LIMIT for both compounds. The markers indicate single measurements

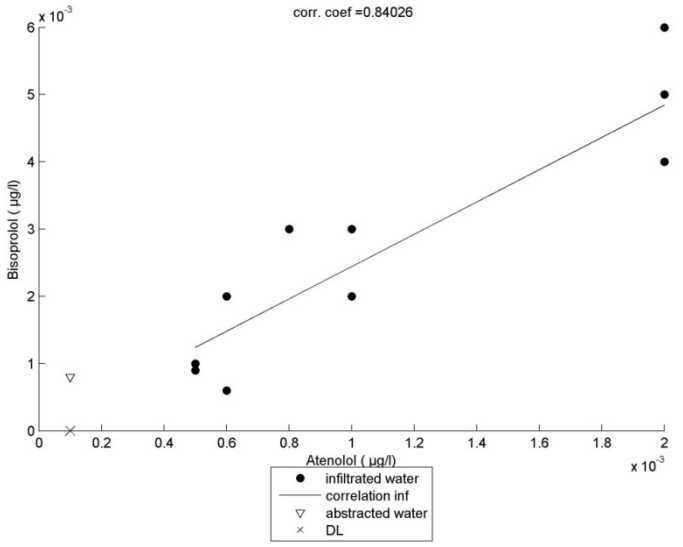

Figure 4-30 Bisoprolol concentrations versus atenolol concentrations measured in Ouddorp. Where DL = DETECTION LIMIT for both compounds. The markers indicate single measurements

4.4.3 Cumulative probability analysis Ouddorp

In the comparison of cumulative probability distribution functions, there were only significant differences found between the infiltrated and abstracted concentration distributions for metoprolol. However the wide range of removal percentages indicates variable removal (Table 4-17).

It was also possible to fit lognormal distributions to both the measurements of the infiltrated and abstracted water for Carbamazepine and these two distributions were not significantly different, which could be concluded as a sign of no removal. (Figure 4-31). Note the high and diverse values of the detection limits in the case of metoprolol.

Table 4-17 Removal ranges (%) for the pharmaceuticals found to be significantly different in the injection and in the abstraction according to a Twosample Kolmogorov-Smirnov test with a 0.005 confidence level.The removal % is calculated based on the lognormal cumulative distributions functions associated to each data set (infiltration and abstraction).

	10th	90th	Mean
Metoprolol	8.8%	69.9%	47.6%

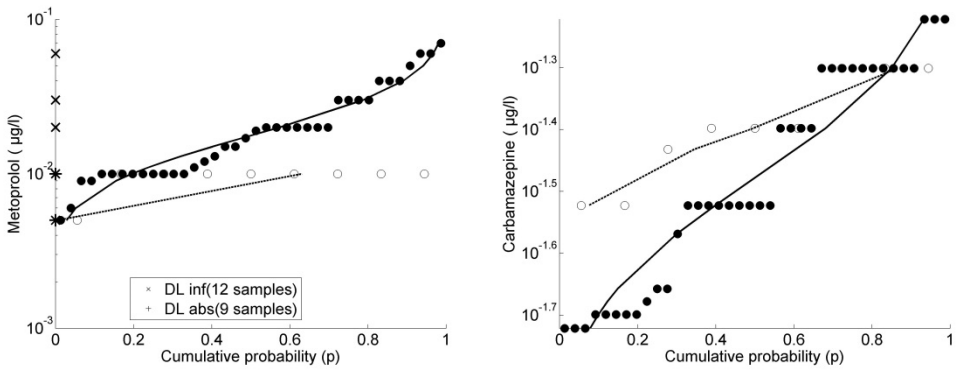

Figure 4-31 Empirical cumulative distribution (ECDF) of metoprolol and carbamazepine based on the concentrations measured at the infiltration (filled circles) and abstraction (empty circles) location . The fitted lognormal cumulative distributions of the infiltration (continous line) and abstraction (dotted line) are plotted as well. The detection limits identified among the infiltration database (DL inf) and the abstraction database (DL abs) are indicated above the Y axis. The legend indicates how many samples are below detection limit.

4.5 Amsterdam Water supply Dunes

The abstracted water in the Amsterdam Water supply dunes is 100% infiltrated water according to several studies done here (Stuyfzand, 1986; Stuyfzand, 1993; Stuyfzand, 2011; Stuyfzand et al., 2007).

A statistical analysis of the arithmetic averages in the infiltrated and abstracted water indicates that iopromide, iohexol and iomeprol decreased their concentrations along the soil passage (Table 4-18 and Figure 4-32). Carbamazepine does not show a clear removal, and sulfamethoxazole shows what could be considered partial removal. The data is insufficient to perform a correlation or a probability analysis. However the difference between the infiltration concentrations and the concentrations measured after the passage are consistent with what was found in the other sites. Chapter 5 provides a more in-depth comparison between sites.

Table 4-18 Averaged Concentrations measured in the infiltrated and recovered water in AWD. This table includes the detection limits and number of samples over the detection limit. The removal percentage is calculated as described in chapter 3.

	INF	Abs	min DL	INF samples	ABS samples	% removal
Diethyl phthalate (DEP)	0.5	0.571	0.5	0	2/10	-14%
iopamidol	0.17	0.043	0.01	1/1	11/14	74%
diatrizoic acid	0.14	0.069	0.01	1/1	7/14	51%
iopromide	0.093	0.010	0.01	1/1	1/14	89%
iomeprol	0.0695	0.010	0.01	1/1	1/14	86%
carbamazepine	0.0575	0.049	0.01	1/1	11/14	14%
Iso-Nonylphenol	0.032	0.051	0.025	0	8/10	-59%
iohexol	0.021	0.010	0.01	1/1	1/14	52%
sulfamethoxazole	0.02	0.012	0.01	1/1	2/14	38%
Acid ioxitalamic	0.01	0.010	0.01	1/1	0/14	0%

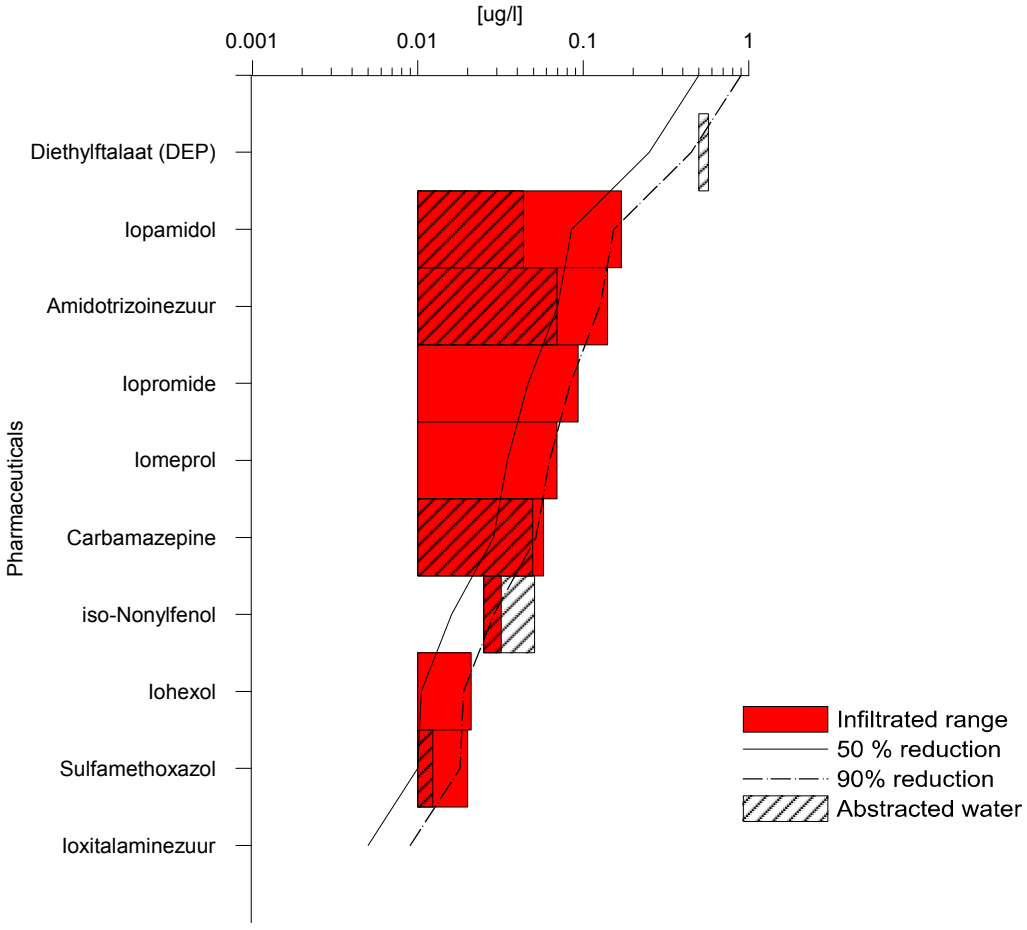

Figure 4-32 Pharmaceuticals measured in the infiltration ponds and in the abstraction wells in AWD .

5 Discussion

5.1.1 Performance of the study sites

Comparing the different sites provides an overview of the overall removal of pharmaceuticals along soil passage for different conditions. For the same pharmaceutical, different removal percentages were found per site (Figure 5-2 and Figure 5-3). This difference is influenced by diverse redox conditions, travel times, geochemistry and length of flowpaths. The location with the highest average removal is Scheveningen (58%) followed by Amsterdam Water supply dunes (AWD) (51%) and well field Heel (51%) (Table 5-5). These locations have different travel times and redox zones. Scheveningen is the location with the shortest travel time (70 days) and minimal dilution with groundwater. In our study 36% of the pharmaceuticals in Scheveningen were removed more than70%. The water infiltrated in the Amsterdam Water supply Dunes undergoes an 80-day passage through the soil before it is abstracted with no groundwater contribution and 30% of the pharmaceuticals were removed more than 70%. Well field Heel, on the other hand, presents high dilution with groundwater and long residence time with abstraction through wells instead of drains with 18% of the measured pharmaceuticals being removed more than 70%. Ouddorp presented a removal fraction over 70% for only 16% of the pharmaceuticals, which was not expected due to the relatively long residence time (90 days). In Eijbergen none of the pharmaceuticals measured was removed more than 70%.

Removal of compounds along soil passage has been associated by many authors (Hamann et al., 2016; Henzler et al., 2014; Maeng et al., 2011) with their passage through different redox zones. Well field Heel presents less redox zones than those observed in Scheveningen and AWD and this could explain the lower amount of compounds removed. Since the flowpaths go mainly through oxic and suboxic zones, only those compounds removed under oxic conditions are expected to change. In Eijbergen the water gets immediately depleted after infiltration, presenting flowpaths that are mainly anoxic, this is expected to render the lowest removal fractions for most of the compounds, and good removal for some of them, like sulfamethoxazole (Heberer et al., 2008), which only showed abstracted concentration values under detection at this site. In Eijbergen only two compounds presented positive low and moderate removal fractions: carbamazepine and iopamidol, respectively. Finally Ouddorp is expected to present all types of redox zones, but it is dependent on the flowpath that the infiltration water undertakes. This could be the reason for the lower removal fractions if the flowpath is mainly anoxic or (sub)oxic. The approaches taken to determine pharmaceutical removal were efficient in finding trends and differences. Even in sites with minimal data availability, such as Waternet, the results are consistent with what was found in other sites. The following section describes the differences in removal fractions between the sites per pharmaceutical.

5.1.2 Removal efficiencies of pharmaceuticals grouped according to therapeutic uses

A summary of the behaviour of the pharmaceuticals is here provided grouped by therapeutic use. The analysis follows a decreasing removal order: first the compounds with the highest removal are discussed together with the behaviour of the other compounds that fall in the same group, even if they presented lower removal fractions. Subsequently, the second compound with the highest removal is analysed together with other compounds inside the same group. Like this, the differences inside every group are clearer, contrary to the common practice of assigning a general removal behaviour per group (Maeng et al., 2011).

5.1.2.1 X-Ray agents

Iopromide is the substance with the highest average removal based on the difference between the arithmetic averages in the input and output of the systems. The mean of the three sites where it was analysed is 93% (95% in Scheveningen, 93% in Heel and 89% in Waternet). Iopromide falls inside the group of X-ray contrast agents and the removal fractions found here are in agreement with previous studies (Grünheid et al., 2005; Hamann et al., 2016; Maeng et al., 2011; Nham et al., 2015). Iopromide to be strongly removed, especially under oxic conditions (Wiese et al., 2011),(Burke et al., 2014). This is supported by the change in correlations observed in Well Field Heel, with oxic pathways, where the correlation between Iopromide and lincomycin changes indicating removal of iopromide. In addition, the probability analysis shows that the removal percentage in this location is constrained between 96.8% (10^{th} percentile) and 97.5 (90^{th} percentile) (Table 5-4 and Figure 5-1).This indicates complete removal, in contrast with wider percentile ranges which would indicate partial or redox/time-dependent removal.

The second highest removal mean was from **iomeprol**, also an X-ray contrast agent, which showed a removal fraction of 86% in AWD. In Scheveningen and in Eijbergen all the samples were below detection limit in the abstracted water. In addition to the literature mentioned for iopromide, where iomeprol was said to be highly removed through soil passage, (Engelhardt et al., 2013) showed that iomeprol was removed under nitrate-reducing conditions. Its good removal in these two sites corresponds with the nitrate reducing conditions present.

Iopamidol and iohexol, presented high to moderate removal fractions (74% and 52%, respectively) in well field Heel. **Iopamidol** showed high removal in the AWD (74%) and variable moderate removal in Eijbergen (33%), with a wide range for the cumulative probability of the removal percentage (Table 5-4). On one hand, literature stated until now that iopamidol was well removed much like the rest of the x-ray agents (Maeng et al., 2011; Nham et al., 2015), especially in (sub)oxic conditions, showing slower rates in anoxic environments (Hamann et al., 2016). On the other hand, the study of long time series of long-distance RBF showed iopamidol as a substance only partially removed. Our study corroborates both hypotheses: the removal of iopamidol seems to be favourable in most of the sites and partially removed in Eijbergen, which is mainly anoxic. Iohexol was, in order of decreasing infiltration, the 5^{th} compound in Scheveningen, however, there are no measurements performed in the abstracted water. In the AWD 52% of iohexol was removed in contrast to the full removal found in earlier studies (Hamann et al., 2016)

Diatrizoic acid has also been found as one of the compounds with the highest infiltrating concentrations in Scheveningen, Eljbergen and AWD but its removal fractions. The diatrizoic acid was not measured in the abstracted water in Scheveningen and in Ejbergen was always under detection limit except for one measurement in well P07. In AWD it was removed to around 51%, although this fraction is highly dependent on only one sample of the infiltrating water. In his review, (Storck et al., 2012) considered this compound as persistent and (Schmidt et al., 2007) observed that the removal efficiency increased significantly in anoxic environments which fits with what was observed in Eijbergen.

5.1.2.2 Antibiotics

Urotropine was the third compound most removed with an 83% removal in Ouddorp. This agrees with the significant removal observed by (Brauch et al., 2000) in the RBF Dusseldorf-Flehe waterworks, associated with biological degradation. (Schmidt et al., 2003). However, estimated urotropine removal was lower in RBF in Germany (around 20%). Within the antibiotic group, lincomycin, was well removed in Scheveningen and well field Heel (57% and 66% respectively) and badly removed in Ouddorp (-24.8%). The good removal under oxic conditions (Heel) is supported by the correlation analysis and probability density function. The somewhat broad 10^{th} to 90^{th} percentile interval of removal (69.0% to 82.4%) suggests that there is partial removal depending on the flow

path. These findings contradict what was observed in lab column tests(Bertelkamp et al., 2012; Bertelkamp et al., 2014) where lincomycine seemed to be persistent. No other research has been found regarding field degradation fractions of lincomycine.

Sulfamethoxazole is an antibiotic that, according to the literature, is removed in anoxic environments (Grünheid et al., 2005; Schmidt et al., 2007) or with long travel times (Laws et al., 2011). The highest removal is seen in Scheveningen (71%), followed by Ouddorp(49.9%), the Amsterdam Water supply dunes (38%) and well field Heel (16%). This could indicate that the flowpath of Scheveningen and Ouddorp goes through both oxic and anoxic redox zones while for the Heel production site it is known that part of the abstracted water is still oxic. The correlation analysis in Scheveningen also points to decreasing concentrations due to admixing with SO4-reduced water.

The most persistent antibiotic of the compounds measured seemed to be trimethoprim, with only 20% removal in Scheveningen and no removal in well field Heel. this is in contrast with the good removal observed by (Heberer et al., 2008). (Liu et al., 2010) linked anaerobic conditions to longer half-life and also corroborated that the presence of biota resulted in higher degradation fractions. According to (Liu et al., 2010) trimethoprim behaves similarly to Sulfamethoxazole, but field measurements indicate that it is more persistent.

5.1.2.3 Beta-blockers

Atenolol was the 4th compound most removed in several locations; Scheveningen 87%, Ouddorp 92%, and well field Heel 68%. This is in agreement with what was found in literature, that shows that beta-blockers, pharmaceuticals for heart diseases that lower blood pressure, have a high tendency for removal (Burke et al., 2013; Maeng et al., 2011). In well field Heel also the cumulative probability function analysis showed a removal fraction fairly constrained around 96% (Table 5-4).

Bisoprolol, also a beta-blocker, presented high removal degree in three of the locations; 75% in Scheveningen, 73% in Ouddorp and 87% in well field Heel (Figure 5-3), in accordance with what was found in the literature (Maeng et al., 2011; Schmidt et al., 2007). This was supported as well by the correlation analysis performed in Ouddorp (Table 5-4). Losartan, another antihypertensive, was strongly removed (93%) in Scheveningen, and well field Heel (89%) (the low removal observed in Ouddorp -26.5%- was due to the fact that it was only analysed once and was under detection limit). There are two other beta-blockers, however, that were expected (Burke et al., 2014; Hamann et al., 2016; Lekkerkerker-Teunissen et al., 2012) to be removed more than what they proved to be: metroprolol and propranolol with an average removal of 48%. This is, metoprolol was removed 84% in Scheveningen, 57.3% in Ouddorp (10th percentile 9% ,90th percentile 70%), and 2% in Heel (Table 5-4), Meanwhile propranolol did not show real removal in Scheveningen nor in Ouddorp and was removed about 48% percent in well field Heel. This could mean that metoprolol has dependant removal and is best removed when it goes through several redox zones, including anoxic areas, and propranolol when the pathway is fully oxic. It can be noted too that the infiltration concentrations of propranolol were significantly lower than those of metoprolol in Scheveningen and Ouddorp.

Sotalol is the beta blocker with the highest average concentrations between 2010 and 2012 in the river Rhine (Houtman et al., 2013) and it is one of the pharmaceuticals with the highest concentrations measured in the infiltration basins of Scheveningen, well field Heel and Ouddorp. Sotalol presented high removal fractions in Well field Heel and Scheveningen, both through arithmetic average calculation (Figure 5-3) and through the probability analysis (Figure 5-1). In the analysis of Figure 5-1 it should be taken into account that ECDF-calculated removal in Heel includes the effects of dilution, this result in an effective removal about 40% lower. In Scheveningen the probability analysis showed considerably wide removal ranges (Table 5-4), all this could indicate redox

sensitivity and favourable removal in fully oxic pathways. This is supported by the findings of (Bertelkamp et al., 2016), who linked a full removal of sotalol to the presence of micro-biota in oxic soil. The negative removal of sotalol observed in Ouddorp responds to lower detection limits in the abstracted water than in the infiltrated water, with most of the samples under detection limit. This coincides with what was observed by Schmidt et al. (2007) where sotalol removal was more than 80% in oxic, suboxic, anoxic and deep anoxic riverbank filtration zones.

Hydrochlorothiazide, also a drug used to treat high blood pressure, presents good to moderate removal fractions in Ouddorp (72%) and in well field Heel (47%) contrasting with the persistent behaviour observed in lab columns by (Bertelkamp et al., 2014). In her study, Bertelkamp studied the biodegradation of organic micropollutants in soil columns representative of the first metes of soil passage, that is, under oxic conditions, this combined with our results, could suggest removal of hydrochlorothiazide under suboxic and anoxic conditions. The correlation analysis of the data available in Ouddorp (Table 5-4) suggests complete removal and the probability density function performed in Heel regarding hydrochlorothiazide suggests partial removal due to a broad 10th to 90th-percentile interval, which could be linked to different pathways.

Propanolol is the beta-blocker with the lowest removal fractions in Scheveningen and Ouddorp except for in Heel where it is removed to 48%. This could suggest removal of propranolol under strictly oxic conditions. The removal extents close to 50% are in agreement with what was found by (Bertelkamp et al., 2012) in lab experiments under oxic conditions.

5.1.2.4 Lipid regulators

From the lipid regulators bezafibrate presented high removal in Scheveningen (97%), half-removal in Heel (50%) and no removal (-27%) in Ouddorp (Figure 5-3). According to (Nham et al., 2015), bezafibrate experiences some biodegradation and a good to moderate removal along soil passage, being this removal highly dependent on the site-specific conditions and bacterial community. This could explain the differences between the sites. Note that bezafibrate infiltration concentration is also variable between sites, being the 13th compound in Scheveningen and the 34th in well field Heel. (Maeng et al., 2011) observed significant removal of bezafibrate during bank filtration and so did (Schaffer et al., 2015) in his study. Schaffer links the removal of bezafibrate to residence time, this could also explain the differences between Heel and Scheveningen. Gemfibrozil, on the other hand, showed somewhat lower removal fractions in Heel (45%) but no removal at all in Scheveningen. According to (Schaffer et al., 2015) gemfibrozil is expected to be biodegradated and sorbed, the differences here observed might be due to the small amount of samples above detection limit of this compound both in the infiltrating and abstracted water.

5.1.2.5 Psychoactive drugs

From the tranquilizers oxazepam is the best removed one with 79% removal in Scheveningen, 62.5% in Ouddorp and 46% in well field Heel. This is supported by what was seen through the correlation analysis in well field Heel. Previous literature states that oxazepam seems to be or either persistent (Löffler et al., 2005) or sorbed (Burke et al., 2013). Considering that the data available of oxazepam in Scheveningen extends from 2010 to end of 2012, we could rule out sorption as the main removal process if the retardation factors are between the 1.6 (experimental) and the 4.3 (estimated) values given by (Burke et al., 2013). In well field Heel the residence time is longer and given that the data available corresponds to three years we can not rule out sorption as a process. Diazepam is the other psychoactive drug that according to literature has a high retardation factor (from 1.8, (Nham et al., 2015) to a 5.8 estimated value (Burke et al., 2013)) and that shows removal of 57% in well field Heel with only one value over detection limit, with the same concentration as the value for the concentration limit. In this case the removal seen in Heel might have to do with sorption.

Carbamazepine, an anti-convulsion drug is known for being recalcitrant (Lekkerkerker-Teunissen et al., 2012; Maeng et al., 2011),which is what was observed in the present research, with low removal fractions in all the sites. Some other studies stated that carbamazepine removal was dependent on the residence time in the soil (Maeng et al., 2011). This could explain why in Scheveningen the cumulative probability density functions of infiltrated and abstracted water crossed and showed conservative and non-conservative behaviours.

5.1.2.6 Analgesics

The analgesics and anti-inflammatory drugs (NSAIDs) found in the infiltrating water above detection limits are, in decreasing order of site-average removal, paracetamol (80% removal), naproxen, phenazone, ibuprofen and diclofenac (13%).

Paracetamol showed only values above detection limits in well field Heel and proved to be well removed (80%), meanwhile naproxen experienced removal between 45% and 75% in Scheveningen and Heel and no removal at all in Ouddorp. Phenazone only showed positive removal fractions in Scheveningen (56%) and no removal in Heel. In Ouddorp, due to higher detection limits in the abstracted water than in the infiltrated water, there is negative removal and it is not possible to know whether there is real removal. Ibuprofen was removed in Scheveningen (7%), Ouddorp (27.7%) and none (negative removal) in Heel. Diclofenac was removed 12% in Scheveningen, 6% in Ouddorp and 21% in Heel.

Prior literature attributed the removal of diclofenac, naproxen, phenazone, and ibuprofen to sorption associated with their moderately high octanol water partition coefficients (Maeng et al., 2011; Massmann et al., 2008; Schmidt et al., 2007). One explanation of the lower effective removal fractions than expected due to sorption processes could be that at the production locations studied, the natural sorption capacity of the soil for these compounds is already saturated as these all have been in operation for years already. Some other studies link the removal of some of these compounds, like ibuprofen, to biodegradation (Winkler et al., 2001), low removal of ibuprofen could thus be linked to the existent biota.

In the more specific case of phenazone and phenazone-type pharmaceuticals literature states that they are best removed under oxic conditions (Maeng et al., 2011; Massmann et al., 2008), which does not explain the low removal fractions in well field Heel, which would be explained better by the recalcitrant behaviour also observed by (Lekkerkerker-Teunissen et al., 2012). Based on the differences between Scheveningen and well field Heel, our findings would suggest that removal of phenazone is favoured by finer sediments and passage through diverse redox conditions.

Lidocaine has different behaviour depending on the site, in Scheveningen and in Heel the removal is 59% and 42% respectively meanwhile in Ouddorp there is no removal, much the contrary, there were higher concentrations present in the abstracted water than in the infiltrated. This is supported as well by the correlation analysis where lidocaine is plotted versus sotalol. In their experiment (Bradley et al., 2014) showed that concentrations of lidocaine were found after 20 m of soil passage from a wastewater landfill. This could indicate a persistent behaviour of this compound, which should, however, be taken cautiously since 20 m is only a small distance compared with distances in the artificial recharge systems.

5.1.2.7 Chemotherapy

Cyclophosphamide, a medication used in chemotherapy was found present in Scheveningen, Ouddorp and Heel and showed quite a persistent behaviour in the last two. In Scheveningen the removal corresponded to around half of the infiltrated concentrations. There was no literature found regarding the removal of this compound during soil passage.

5.1.2.8 Hypoglycemic agents (anti-diabetic medication)

Metformin is the first compound in terms of infiltrating concentration in well field Heel and the second in Ouddorp. It is removed well at Heel (82%). At Ouddorp average removal was 8.3% but this was caused by just one sample of the abstracted water analysed for metformin below detection limit (0.007 µg/L). This relatively high detection limit limited the extent to which removal could be quantified (8%) at Ouddorp. The removal of metformin is in line with what was observed by (Scheurer et al., 2012): the soil passage works very efficiently removing metformin through biodegradation, this could be the case in well field Heel.

5.1.2.9 Others

Caffeine was removed in well field Heel (41%) and in Ouddorp (with no concentrations measured above detection limit in the abstracted water). Eijbergen showed no removal at all but this had to do with the high detection limits for that location. Removal of caffeine through soil passage under aerobic and anaerobic conditions has already been described before, for instance by (Regnery et al., 2015) in her 3-year test.

Table 5-1 Summary of the removal (%) calculated through the arithmetic averages of the infiltrated and abstracted water per location. Per site the % of removal is given and the order of appearance of the pharmaceutical when ordering it in decreasing average infiltration concentration.

		Scheveningen		Ouddorp		Eijbergen		Well field Heel		AWD	
		%reduction	order	%reduction	order	%reduction	order	% reduction	order	% reduction	order
1	Amidotrizoic acid										
2	atenolol	87%	32	92.0%	23			68%	20		
3	atorvastatin							-4%	29		
4	bezafibrate	100%	13	-26.9%	18			50%	34		
5	bisoprolol	75%	33	73.7%	21			87%	28		
6	bromodichloromethane		16								
7	Caffeine			-3.0%	3	-63.00%	2	41%	3		
8	carbamazepine	18%	4	-14.0%	5	16.00%	4	14%	8	14%	6
9	cyclophosphamide	51%	37	-29.4%	19			-17%	44		
10	Diatrizoic acid		2			-30.00%	3			51%	3
11	diazepam			0.0%	25			57%	39		
12	diclofenac	12%	14	6.2%	13		10	21%	22		
13	Diethyl phthalate (DEP)									-14%	1
14	enalapril							-50%	43		
15	phenanthrene	14%	21								
16	phenazone	56%	12	-5.5%	11		11	-239%	40		
17	fenofibric							-23%	26		
18	fenofibrate							-50%	35		
19	fenoprofen					-53.00%	5				
20	furosemide		34					51%	16		
21	gemfibrozil	-277%	29					45%	11		
22	hydrochlorothiazide			72.2%	8			47%	9		
23	ibuprofen	7%	11	27.7%	9			-57%	6		
24	ifosfamide							-79%	42		
25	iohexol		5							52%	8
26	iomeprol		1				6			86%	5
27	iopamidol		6			33.00%	1			74%	2
28	iopromide	95%	3				9	93%	2	89%	4
29	iso-Nonylphenol									-59%	7
30	iothalamic acid		23								
31	Ioxitalaminezuur		7							0%	10
32	ketoprofen							-63%	36		
33	Lidocaine	59%	26	-14.4%	15		13	42%	24		
34	lincomycin	57%	35	-24.8%	17			66%	38		
35	losartan	93%	31	26.5%	24			89%	13		
36	metformin			8.3%	2			82%	1		
37	metoprolol	84%	8	57.3%	6		12	2%	14		
38	metsulfuron methyl		19								
39	monensin		20								
40	naproxen	48%	27	-28.0%	10			75%	30		
41	oxazepam	79%	22	62.5%	20			46%	19		
42	p-isopropylmethylbenzeen	-1%	18								
43	Paracetamol							81%	21		
44	paroxetine	-436%	36					12%	18		
45	primidone			14.0%	12	-19.00%	8	-20%	31		
46	Propranolol	-26%	30	-24.8%	16			48%	15		
47	sotalol	61%	10	-22.5%	4		14	78%	7		
48	sulfamethoxazole	71%	9	49.9%	7		7	16%	23	38%	9
49	Sulfaquinoxaline	-4632%	38					9%	41		
50	salicylic acid							-19%	12		
51	temazepam	72%	28	45.5%	22			-13%	25		
52	theophylline							-27%	10		
53	tiamulin			-3.8%	14			-38%	33		
54	tribromomethane		15								
55	trimethoprim	20%	24					-7%	32		
56	Urotropine			83.3%	1						

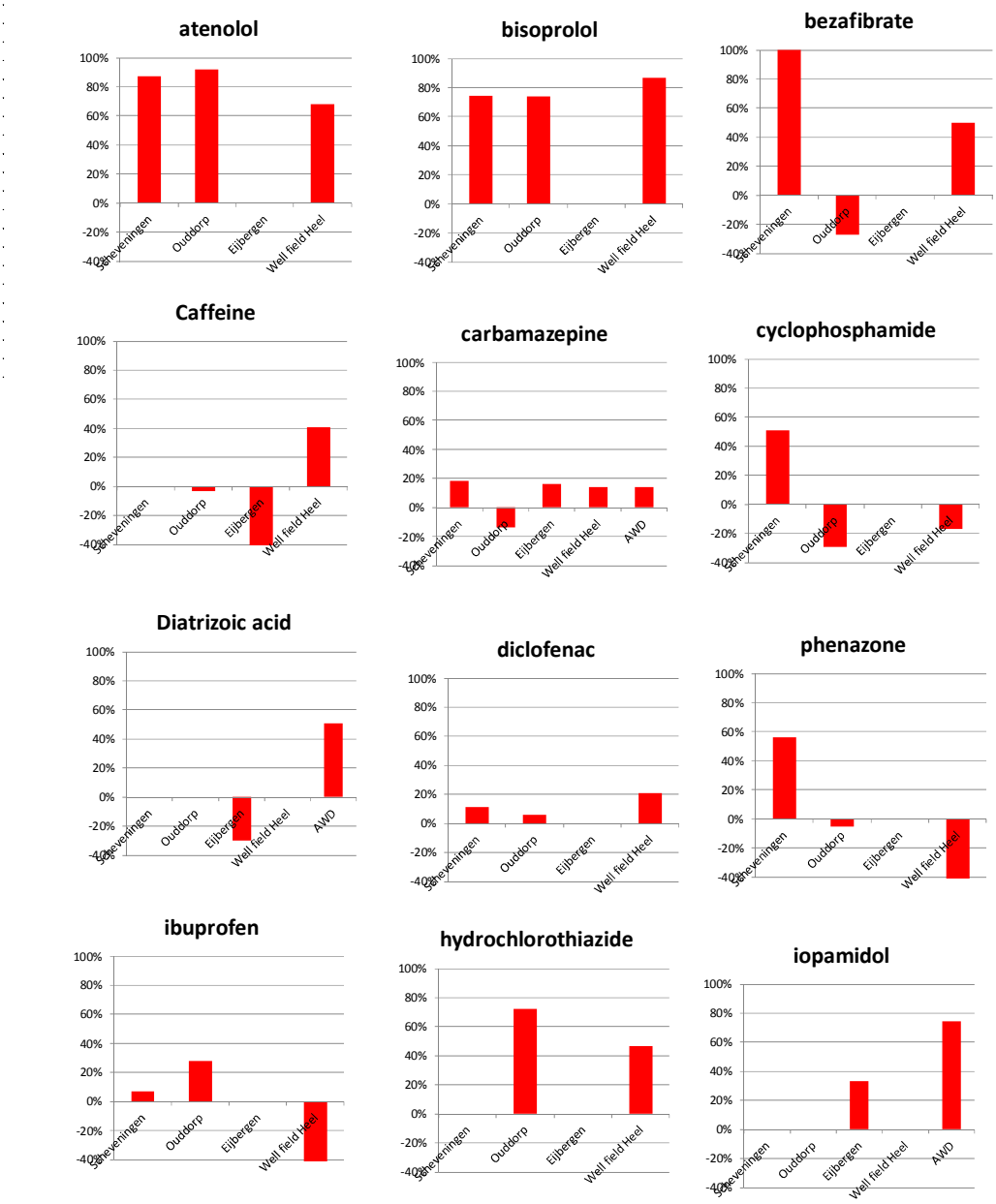

Figure 5-2 Summary of the removal (%) calculated through the arithmetic averages of the infiltrated and abstracted water per location.

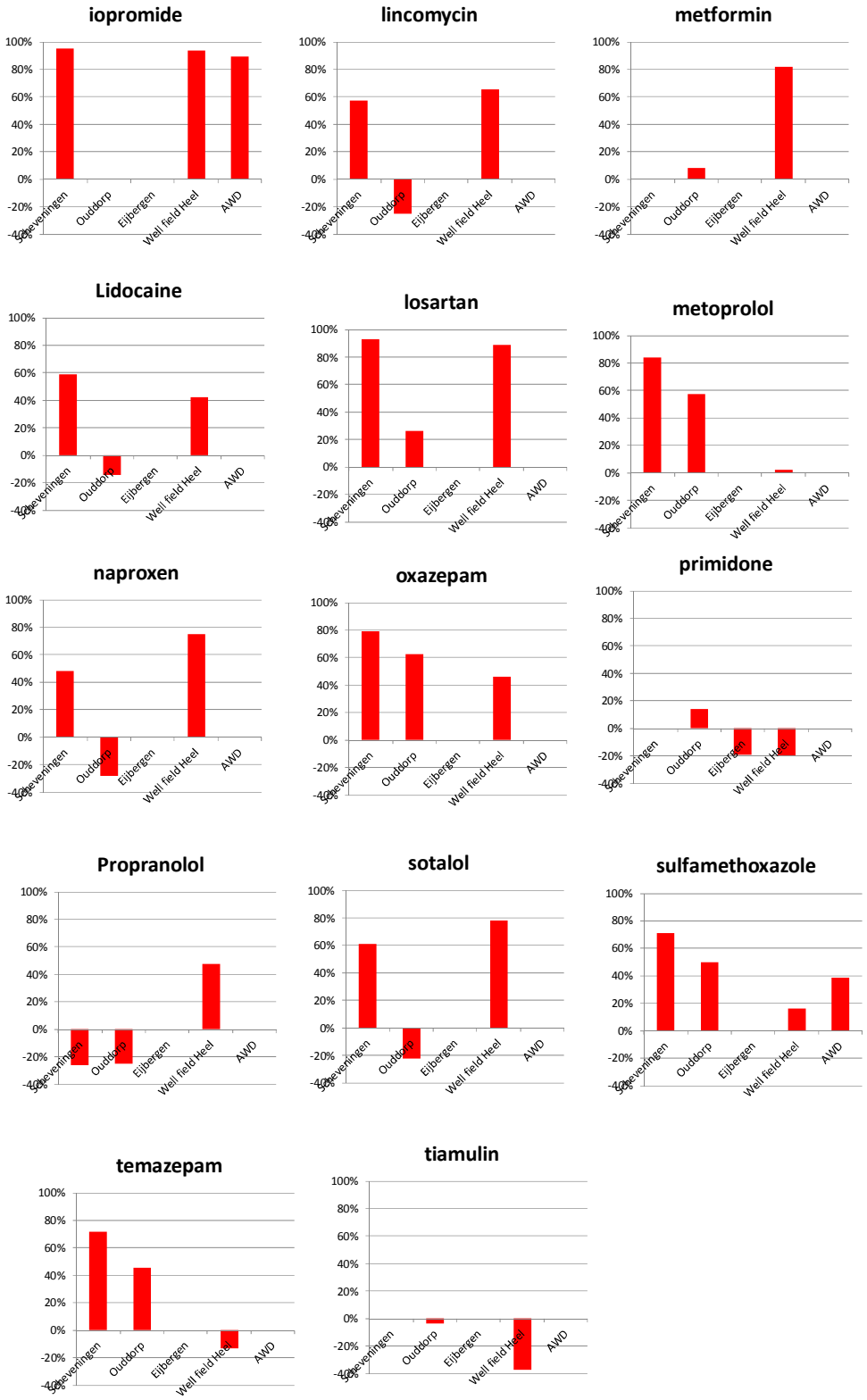

Figure 5-3 Summary of the removal (%) calculated through the arithmetic averages of the infiltrated and abstracted water per location.

Table 5-4 Removal percentages calculated through the different methods in each of the locations where these were applied. The amsterdam water supply dunes are not included since only arithmetic averages were calculated. The Per location, the removal (%) calculated through the averages of the infiltrated and abstracted water is displayed on the first column. The removal (none, partial or complete) observed through the correlation plots is included in the second column. The third column displays the percentage of reduction observed when comparing the distribution fitting the infiltrated concentrations and the abstracted ones if they proved to be statistically different. Columns 4th and 5th include the 10th and 90th percentiles of the removal. For Ouddorp no results of the probabilistic analysis were displayed since no compound showed statsitically different distributions in the infiltration and abstraction.

	Scheveningen					**Ouddorp**					**Eijbergen**					**well field Heel**				
	%removal	correl	ECDF (mean)	10th	90th	%removal	correl	ECDF (mean)	10th	90th	%removal	correl	ECDF (mean)	10th	90th	%removal	correl	ECDF (mean)	10th	90th
diatrizoic acid		none										complete								
atenolol	87%					92.0%										68%	variable	95.7%	96.7%	95%
bisoprolol	75%					73.7%	complete									87%		88.4%	69.0%	95.6%
carbamazepine	18%	variable(oxic)				-14.0%					16.00%	variable				14%	low(variable)	51.5%	55.6%	47.2%
hydrochlorothiazide						72.2%	complete									47%		64.6%	46.4%	76.7%
iopamidol											33.00%	variable	79%	-32%	97%					
iopromide	95%		95%	95%	96%											93%	complete	97.2%	96.8%	97.5%
Lidocaine	59%					-14.4%	dilution									42%				
lincomycin	57%					-24.8%										66%	variable	76.7%	69.0%	82.4%
metoprolol	84%					57.3%		48%	9%	70%						2%				
oxazepam	79%		81%	86%	75%	62.5%	variable									46%	complete			
primidone		low(variable)				14.0%					-19.00%	none				-20%	none			
sotalol	61%	complete	94%	98%	77%	-22.5%	complete									78%	variable	97.1%	97.2%	96.9%
sulfamethoxazole	71%	variable				49.9%						complete				16%				
temazepam	72%		75%	82%	63%	45.5%										-13%	low(variable)	71.6%	84.9%	46.8%

Table 5-5 Average of the positive removals (%) per location and percentage of pharmaceuticals found to be removed more than 70% per location.

	Average positive removal	**Removal > 70%**
Scheveningen	58%	**36%**
Ouddorp	44%	**16%**
Eijbergen	25%	**0%**
Well field Heel	51%	**18%**
AWD	51%	**30%**

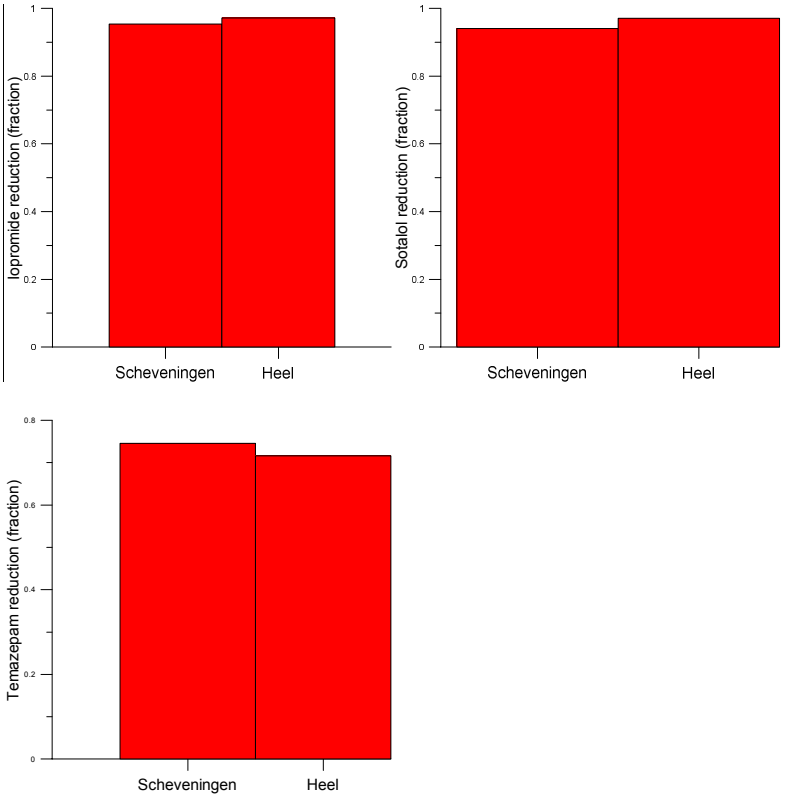

Figure 5-1Comparison of the reduction fractions calculated through comparison of the CDF's that fit the ECDF of the infiltrated and abstracted water in those locations where this approach could be applied for those parameters of which this information was available. The removal calculated in Heel includes the effects of dilution, therefore around 0.39 should be substracted. The water abstracted in Scheveningen is also expected to experience dilution, but to a maximum of 10%.

5.2 Conclusions

Much of the research on pharmaceutical removal during soil passage has been done through column laboratory studies (Bertelkamp et al., 2014; Burke et al., 2014; Grünheid et al., 2008; Mersmann et al., 2002; Schaffer et al., 2015) or small-scale field experiments (Bradley et al., 2014; Grünheid et al., 2005; Heberer et al., 2008; Massmann et al., 2006; Nham et al., 2015). Some field studies that focussed on flow-path removal failed to address the variability of the input concentrations and its impact on the removal estimation, due to constrained time frame that was considered. Even with the use of longer time-series, however, pharmaceutical removal based on a one location cannot be simply extrapolated to other locations due to site-specific conditions. Although in the laboratory conditions can be controlled their representativeness for site-specific conditions life of field conditions in soil passage systems is difficult to establish. In most lab studies it could be accurately assessed the removal extent since sufficiently high concentrations were used to minimize below detection limit measurements. In contrast, in most field studies detection limits were dealt with by assuming that those concentrations under detection limit were 0 ug/l (Massmann et al., 2006) or half of the detection limit value (Bradley et al., 2014), which could lead to an overestimation of the removal rates, particularly for compounds with a relatively high detection limit. As a conservative estimate for the removal capacity of soil passage systems we therefore preferred the use of detection limit values.

In our study, a large database of pharmaceutical concentrations from 5 different recharge systems was used to make a comprehensive estimate of the removal of pharmaceuticals along soil passage after bank or basin filtration. Based on the long term dataseries available for some of the systems, it was assumed that the available pharmaceutical concentrations were representative of the variability of the input concentrations. The fact that these systems have been in operation for a long time ensures that the biological community responsible for degradation has been allowed to mature and optimize their degradation capacity. Studying five different locations allowed drawing general conclusions (not-site specific) on the behaviour of pharmaceuticals and identification of those pharmaceuticals whose removal will be more site-specific dependent.

In this study soil passage was considered as an overall treatment step for which the total output concentrations of pharmaceuticals are compared with the input concentrations in the system. To verify the lowering of concentrations through removal processes, pharmaceutical concentrations in the infiltration ponds were compared to those observed in the collected mixed raw water, taking into account the possible dilution with groundwater, through three different methods . The first method consisted of the analysis of the differences between the arithmetic averages of the infiltrated and abstracted water. It provided a quantitative answer to the question of how much removal had taken place although in some cases could underestimate removal since the averages included the measurements below detection limit with their detection limit value. This aspect was addressed by comparing it with the other methods. The second method estimated removal and behaviour of the pharmaceuticals based on the assumption that the correlation of certain compounds in the infiltrated water is expected to change if one of them is degraded relative to another compound. This provided an indication of whether a pharmaceutical is diluted, completely degraded, or it experiences variable removal. The limitation of this method proved to be the scarce measurements available above detection limit in the abstracted water and the low correlation coefficients for many pharmaceuticals. The third approach based removal estimation on the differences between the lognormal probability density functions of the infiltrated and abstracted concentrations. This approach provided a quantitative estimate range of the reduction of a given pharmaceutical during soil passage if there were significant differences between the infiltrated and abstracted water and if a lognormal distribution could be fitted to both. This approach proved to give insight on mixing of water that underwent different removal due to different flowpaths and redox conditions. The combination of the three approaches was an effective tool to increase the certainty and understanding of behaviour of pharmaceuticals and it represents a new approach to pharmaceutical, but could be similarly applied for other water quality parameters. This approach had, to our knowledge, not been used until now.

From the large database of compound concentration measurements, only the compounds that showed concentrations above detection limit in the collected mixed raw abstracted water were taken into account. As a result, the behaviour of a total of 56 pharmaceutical compounds was studied. From the 56 compounds 18 showed a removal percentage higher than 70% in at least one of the sites (Table 5-1): atenolol, bezafibrate, bisoprolol, hydrochlorothiazide, iomeprol, iopamidol, iopromide, Losartan, metformin, metoprolol, naproxen, oxazepam, paracetamol, sotalol, sulfamethoxazole, temazepam, and urotropine (Figure 5-2 and Figure 5-3). From these compounds bisoprolol and iopromide presented removal rates above 70% in three of the sites. Atenolol and losartan showed removal rates above 70% in two of the sites. From the pharmaceuticals above detection limit in the abstracted water, only carbamazepine was analysed at the five sites. The removal extent of carbamazepine was low (<19 %) in all the sites.

Summary of the findings per location - highlights

- At Heel iopromide, losartan, bisoprolol, metformin, paracetamol, sotalol and naproxen (in decreasing order of removal) showed high (>75%) degrees of removal during soil passage. Primidone, temazepam and carbamazepine, showed low (<20%) removal and a more persistent behaviour.
- At Scheveningen bezafibrate, iopromide, losartan, atenolol, metoprolol, oxazepam and bisoprolol proved to be removed (>75%) . Carbamazepine, phenanthrene, diclofenac, ibuprofen, propranolol, gemfibrozil and paroxetine (in decreasing removal order) were removed less than 20%..
- At Eijbergen there was no pharmaceutical removed more than 75% and carbamazepine, primidone, diatrizoic acid, fenoprofen and caffeine proved to behave conservatively (<20% removal).
- At Ouddorp, according to the analysis performed atenolol, urotropine, bisoprolol, and hydrochlorothiazide showed removal fractions larger than 70%. Meanwhile primidone, metformin, diclofenac, diazepam, caffeine, tiamulin, phenazone, carbamazepine, lidocaine, sotalol, propranolol, lincomycin, bezafibrate, naproxen and cyclophosphamide presented removal fractions <20%.

For some pharmaceuticals removal percentages differed significantly between sites. These removal differences were influenced by different redox conditions, travel times, geochemistry and length of flowpaths. Scheveningen and well field Heel were the locations where the highest removal (For Scheveningen: 58% overall removal, 36%compounds >70% removal and for Heel 51% overall removal with 18% of the compounds >70% removal) was observed. These two locations have notably different travel times and redox zones. Although Scheveningen is the location with the shortest travel times, minimal dilution with groundwater, soil passage covers oxic to anoxic zones. Heel on the other hand, presents high dilution with groundwater and abstraction through wells instead of drains, with mainly (sub)oxic flowpaths. Waternet had moderate removal but more sampling campaigns would be necessary to draw stronger conclusions. Ouddorp presented lower removal than the other locations and Eijbergen, with immediately anoxic flowpaths showed the poorest performance of all the locations. From the results it is clear that exposure to different redox zones, especially (sub)oxic zones, increases the removal of pharmaceuticals.

The conclusions regarding the individual behaviour of each pharmaceutical are included under the discussion chapter 5.1.2. The difference between this analysis and the literature values obtained from lab experiments supports the need of comparing always the removal extents obtained from lab experiments with field measurements, in line with what (Bertelkamp et al., 2012) did. In addition, our research contributed to a better understanding of the behaviour of each pharmaceutical under different field mature conditions and provides a basis for assessing the removal conditions at other soil passage locations and the consideration of possible measures that can be taken to improve the removal capacity of soil passage systems at specific sites.

It is suggested as good practice to make sampling campaigns on a regular basis for a set of pharmaceuticals in the infiltrated and in the abstracted water in these locations. Long time series of data proved to be key in the understanding of pharmaceutical concentrations. Ideally, this set of pharmaceuticals could be agreed on by different water companies so that they all could benefit from the comparison of the results.

Soil passage can be a very efficient way to remove pharmaceuticals when the conditions are adequate. Redox exposure has proven to be a key aspect in pharmaceutical removal. Comparing the different site-specific conditions of the study locations of the present research provides an excellent opportunity to find adaptive measures and operational

controls that will ensure enough oxic (and anoxic) exposure along the flowpath and will improve the efficiency of the soil passage as a treatment system.

6 References

Attachment I List of pharmaceuticals

WML	Well field Heel
1	atenolol
2	atorvastatin
3	bezafibrate
4	bisoprolol
5	caffeine
6	carbamazepine
7	chloramphenicol
8	clofibrate
9	clofibrinizuur
10	cyclophosphamide
11	diazepam
12	diclofenac
13	enalapril
14	phenazone

WML	Well field Heel
15	fenofibrate
16	fenofibric
17	fluoxetine
18	furosemide
19	gemfibrozil
20	hydrochlorothiazide
21	ibuprofen
22	ifosfamide
23	indomethacin
24	iopromide
25	ketoprofen
26	lidocaine
27	lincomycin
28	losartan
29	metformin
30	metoprolol

WML	Well field Heel
31	naproxen
32	oxacillin
33	oxazepam
34	paracetamol
35	paroxetine
36	pravastatin
37	primidone
38	propranolol
39	salicylic acid
40	sotalol
41	sulfamethoxazole
42	sulfaquinoxaline
43	temazepam
44	theophylline
45	tiamulin
46	trimethoprim

	Scheveningen (Dunea)
1	4-dimethylaminoantipyrine
2	Carbamazepine
3	Diclofenac
4	Ibuprofen
5	Iohexol
6	Iomeprol
7	Iopamidol
8	Iopromide
9	Metoprolol
10	Sotalol
11	atenolol
12	atorvastatine
13	bezafibraat
14	bisoprolol
15	chloramphenicol

	Scheveningen (Dunea)
16	clarithromycine
17	clofibraat
18	clofibrinezuur
19	cloxacilline
20	coffeïne
21	cyclofosfamide
22	dapson
23	diazepam
24	dicloxacilline
25	enalapril
26	erythromycine
27	phenazon
28	fenofibraat
29	fenofibrinezuur
30	fenoprofen
31	fenoterol

	Scheveningen (Dunea)
32	fluoxetine
33	furazolidon
34	furosemide
35	gemfibrozil
36	ifosfamide
37	indomethacine
38	ketoprofen
39	lidocaïne
40	lincomycin
41	losartan
42	monensin
43	nafcilline
44	naproxen
45	oestron
46	oleandomycine
47	oxacilline

	Scheveningen (Dunea)
48	oxazepam
49	paracetamol
50	paroxetine
51	pentoxyfilline
52	pravastatine
53	primidon
54	propanolol

	Scheveningen (Dunea)
55	propranolol
56	roxithromycine
57	salicylzuur
58	spiramycine
59	sulfadimethoxine
60	sulfadimidine
61	sulfamethoxasol

	Scheveningen (Dunea)
62	sulfaquinoxaline
63	temazepam
64	theophylline
65	tiamuline
66	tolfenaminezuur
67	trimethoprim

	Brakel
1	Carbamazepine
2	Lidocaine
3	Estrone
4	Chloramphenicol
5	Clarithromycin
6	Cloxacillin
7	Dicloxacillin
8	Erythromycin
9	Oleandomycin
10	Oxacillin
11	Roxithromycin
12	Spiramycin
13	Sulfamethazine
14	Sulfamethoxazole
15	Trimethoprim
16	Cyclophosphamide
17	Atenolol
18	Bisoprolol
19	Metoprolol

	Brakel
20	Propranolol
21	Sotalol
22	Pentoxifylline
23	Diatrizoic acid
24	Iohexol
25	Iomeprol
26	Iopamidol
27	Iopanoic acid
28	Iopromide
29	Iothalamic acid
30	Ioxitalamic acid
31	Bezafibrate
32	Clofibric acid
33	Fenofibrate
34	Gemfibrozil
35	Diclofenac
36	Fenoprofen
37	Ibuprofen
38	Ketoprofen

	Brakel
39	Naproxen
40	Phenazone
41	Lincomycin
42	Fenoterol
43	Monensin
44	Primidone
45	Sulfaquinoxaline
46	Clofibrate
47	theophylline
48	Iosartan
49	enalapril
50	oxazepam
51	temazepam
52	pravastatine
53	paracetamol
54	furosemide
55	paroxetine
56	Azithromycin

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