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Arsenic and chromium concentrations and their speciation in groundwater resources and drinking water supply in the Netherlands

BTO

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Quality Assurance

Emile Cornelissen

Roberta Hofman-Caris

Stephan van de Wetering (Brabant Water)

Ron Jong (Vitens)

Authors

Arslan Ahmad (Chapters 1, 3, 4)

Stefan Kools (Ch 1)

Merijn Schriks (Ch 1)

Pieter Stuyfzand (Ch 2)

Bas Hofs (Managementsamenvatting, Ch 5)

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More information

dr.ir. Bas Hofs

T 030 60 69 697

E bas.hofs@kwrwater.nl

Keywords

speciation, heavy metals, as(III), cr(VI)

PO Box 1072
3430 BB Nieuwegein
The Netherlands

T +31 (0)30 60 69 511

F +31 (0)30 60 61 165

E info@kwrwater.nl

I www.kwrwater.nl



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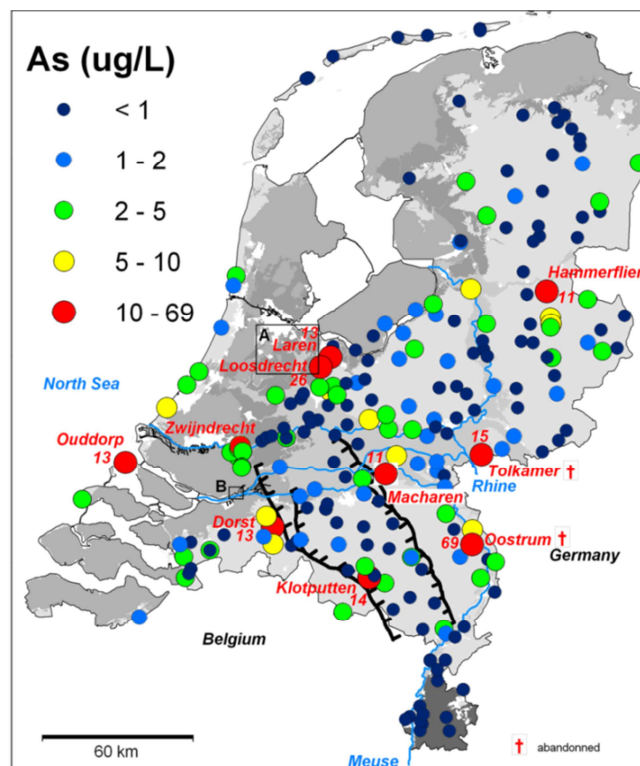
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BTO Managementsamenvatting

Inventarisatie van arseen en chroom in bronnen en zuivering

Auteurs Arslan Ahmad MSc, dr. Stefan Kools, dr. ing. Merijn Schriks, prof. dr. Pieter Stuyfzand, dr. ir. Bas Hof

De wetenschappelijke discussie over gezondheidskundige normen voor arseen en chroom is recent in meerdere landen aangewakkerd op basis van voortschrijdend inzicht. Dit is waardevol, omdat de 'provisional guideline values' van de WHO uit 2011 (resp. 10 en 50 µg/l) gebaseerd zijn op wat meetbaar en zuiveringstechnisch haalbaar is, en niet op toxicologische gronden. De wetenschappelijke discussie rondom herziening gaat richting lagere streefwaarden dan de huidige WHO streefwaarden. Daarom is de aanwezigheid onderzocht van de verschillende vormen van arseen (As(III) en As(V)) en chroom (Cr(III) en Cr(VI)) in de bronnen en zuiveringen van de Nederlandse drinkwaterbedrijven; hierbij zijn o.a. de REWAB database gebruikt en is in 2014 een gerichte meetcampagne uitgevoerd. De inventarisatie laat zien dat arseen- en chroomconcentraties in resp. 47% en 8% van de bronnen een voorlopige indicatieve streefwaarde van 1 µg/l (Schriks, M. en Baken, K., Streefwaarde arseen voor drinkwater. Een verdiepend onderzoek naar de actuele stand van zaken – deel I toxicologische evaluatie. KWR, 2014, niet gepubliceerd) overschrijden. Voor ongeveer 20 zuiveringen voldoet ook het geproduceerde drinkwater op dit moment niet aan deze voorlopige indicatieve streefwaarden. Na de zuivering heeft praktisch al het aanwezige arseen de vorm van As(V) en chroom de vorm van Cr(VI). Meer onderzoek naar mogelijkheden om arseen en chroom te verwijderen, zodat lagere concentraties dan 1 µg/l overblijven, is een logische eerste vervolgstap.



Figuur: Gemiddelde arseenconcentratie in het ruwe grondwater uit puttenvelden voor de drinkwatervoorziening in Nederland (gebaseerd op data uit 2008, arseenconcentratie te Ouddorp gebaseerd op metingen in 2013)

Belang: kennis nodig over toxicologie en verwijderingsmogelijkheden arseen en chroom

De wetenschappelijke basis voor de huidige streefwaarden van arseen en chroom in drinkwater staat in diverse landen ter discussie door nieuwe toxicologische inzichten. In Nederland gelden momenteel de streefwaarden van de WHO. Nederlandse drinkwaterbedrijven hebben om hun eigen positie en mogelijkheden te bepalen een goed beeld nodig van (i) deze wetenschappelijke discussie, (ii) het voorkomen van arseen en chroom in (de bronnen voor) Nederlands drinkwater en (iii) de verwijderingsmogelijkheden voor deze stoffen. Arseen- en chroomconcentraties in bronnen en drinkwater zijn doorgaans laag (orde $\mu\text{g/l}$ of minder). Daarnaast is er behoefte aan analysemethoden die onderscheid maken tussen de verschillende vormen (As(III) en As(V), Cr(III) en Cr(VI)) en gegevens over waar deze vormen voorkomen.

Aanpak: inventarisatie van toxicologische inzichten en meetgegevens in bronnen en zuiveringen

De meest recente wetenschappelijke inzichten op toxicologisch gebied zijn samengevat om een beeld te krijgen of herziening van de streefwaarden gewenst is. Daarnaast is met behulp van o.a. de REWAB database (aangeleverd door het RIVM) en een meetcampagne, het voorkomen geïnventariseerd van arseen (As(III) en As(V)) en chroom (Cr(III) en Cr(VI)) in de bronnen en zuiveringen. Ook zijn de beschikbare verwijderingsmogelijkheden geïnventariseerd.

Resultaten: wetenschap streefwaarden ter discussie, voorkomen en vorm As en Cr geïnventariseerd

As(III) is toxischer dan As(V), maar in het menselijk lichaam wordt As(V) omgezet in As(III) zodat beide vormen bijdragen aan toxicologisch relevante effecten. Voor chroom is in drinkwater Cr(VI) de meest toxische variant, en dit is ook de variant die in drinkwater wordt aangetroffen. De wetenschappelijke discussies rondom nieuwe indicatieve streefwaarden komen uit rond $1 \mu\text{g/l}$ voor arseen en $0,3 \mu\text{g/l}$ voor Cr(VI).

In de bronnen voor drinkwater ligt de arseenconcentratie in 47% van de grondwaterputtenvelden boven $1 \mu\text{g/l}$ en de chroomconcentratie in 8% van de puttenvelden). Arseen komt vooral voor in de vorm van opgelost As(III) en chroom in de vorm van opgelost Cr(VI). In het algemeen geldt: 'arsen komt niet alleen', omdat arseenmobilisatie in de bodem gepaard gaat met mobilisatie van andere bestanddelen. In de zuiveringen wordt As(III) omgezet naar As(V) en door co-precipitatie met Fe verwijderd. In het geproduceerde drinkwater zit op 28 drinkwaterproductielocaties meer dan $1 \mu\text{g/l}$ arseen, en op ongeveer 20 locaties meer dan $0,5 \mu\text{g/l}$ chroom. Arseenverwijdering tot minder dan $1 \mu\text{g/l}$ is technisch mogelijk, zoals recente aanpassingen bij Dorst laten zien. De verwijdering van opgelost Cr(VI) tot deze lage concentraties vormt nog een uitdaging.

Advies: internationale discussie volgen, monitoring verbeteren, onderzoek verwijdering en voorkomen

De diverse wetenschappelijke discussies kunnen leiden tot herziening van streefwaarden. Zo is in Amerika een nieuwe norm voor totaal chroom afgesproken, en in Duitsland een nieuwe streefwaarde voorgesteld. Voor chroom geldt dat de huidige monitoring waarschijnlijk niet voldoende nauwkeurig is (te hoge kwantificatielimiet), terwijl er wel degelijk betere methodes beschikbaar zijn. Daarnaast is verwijdering van arseen tot een laag niveau technisch mogelijk; voor chroom is daarvoor nog verder onderzoek nodig.

Hoge As en Cr concentraties kunnen bovendien voorkomen worden door betere aansturing van puttenvelden, ondergrondse ontijzering, ASR-toepassing en fine-tuning van ecohydrologische optimalisaties.

Rapport

Dit onderzoek is beschreven in rapport *Arsenic and chromium concentrations and their speciation in groundwater resources and drinking water supply in the Netherlands* (BTO-2015.017).

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More information

dr.ir. Bas Hof's
T 030 60 69 697
E bas.hofs@kwrwater.nl

Keywords

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PO Box 1072
3430 BB Nieuwegein
The Netherlands

T +31 (0)30 60 69 511
F +31 (0)30 60 61 165
E info@kwrwater.nl
I www.kwrwater.nl

KWR Watercycle
Research
Institute

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1 The global challenge of arsenic and chromium in drinking waters – An introduction

Authors: Arslan Ahmad, Stefan Kools, Merijn Schriks

1.1 Arsenic

1.1.1 Arsenic poisoning of drinking water – a global issue

Arsenic (As) contamination of drinking water sources is a worldwide issue. Scientists long ago linked high As concentrations in ground waters of Taiwan, Bangladesh, and South America to cancer and other human illnesses. Today, As is the main priority on the US Agency of Toxic Substances and Disease Registry's Substance Priority List (ATSDR, 2013). As concentrations in food and drinking water are regulated worldwide. Although regulations exist in almost every corner of the inhabited world, more than 226 million people are still exposed to above acceptable As concentrations around the globe (Murcott, 2012). The most serious case of As poisoning through drinking water is currently ongoing in Bangladesh where an estimated 77 million people have been chronically exposed to As in their drinking water (Flanagan et al., 2012). Other As affected countries include, but are not limited to, Argentina, Brazil, Canada, Chile, China, Hungary, India, Italy, Pakistan, Serbia, Iran, USA and the list continuous (Fig. 1.1). A list of countries (and continents) with reported cases of As contamination has been synthesized from various literature sources and has been shown in (Table 1.1). According to the United Nations Synthesis report, arsenic poisoning is the second most important health hazard related to drinking water after the contamination by pathogenic microorganisms (Johnston et al., 2001).

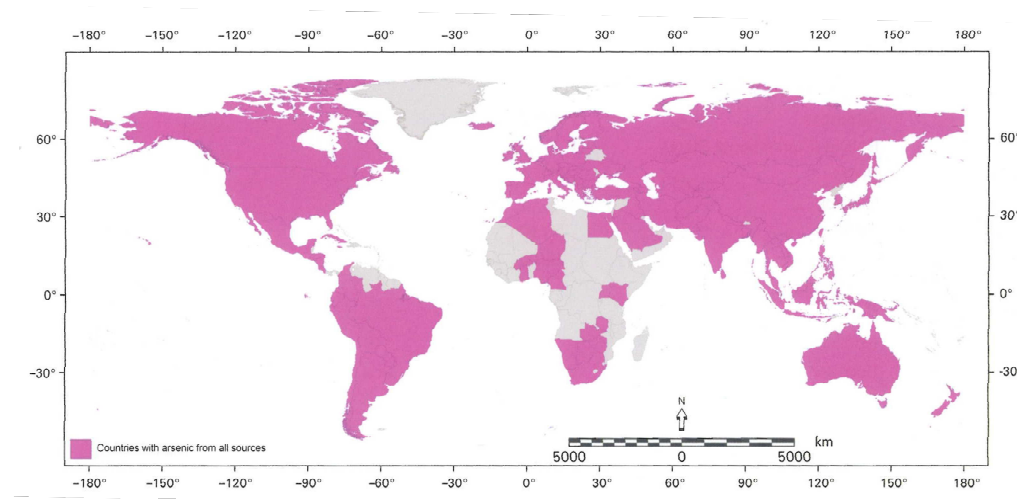


Figure 1.1: Arsenic affected parts of the world (shaded parts) (from Murcott, 2012).

Both natural and anthropogenic processes have been identified to be responsible for the introduction of As into groundwater sources. In Poland, Korea and in Brazil, As contamination of groundwater due to anthropogenic mining activities have been reported

(Marszalek and Wasik, 2000; Woo and Choi, 2001; Borba et al., 2003). In contrast, in parts of Turkey elevated As in groundwater is attributed to natural geothermal factors (Gunduz et al., 2009) and in Bangladesh geogenic sources are considered major cause of large scale As contamination.

Table 1.1: List of As affected countries of the world.

Asia	Bangladesh, Pakistan, Cambodia, China, Taiwan, India, Iran, Japan, Myanmar, Nepal, Thailand, Vietnam, Korea
Americas	Alaska, Argentina, Brazil, Chile, Canada, Dominica, El Salvador, Honduras, Mexico, Peru, Unites States of America
Europe	Austria, Croatia, Finland, France, Germany, Greece, Hungary, Italy, Poland, Romania, Russia, Serbia, United Kingdom, the Netherlands
Africa	Ghana, South Africa, Zimbabwe
Pacific	Australia, New Zealand

Source: Smedley and Kinniburgh (2001); Stuyfzand et al. (2006); Petrusevski et al. (2007); Smedley et al. (2007); Gunduz et al. (2009); Jovanovic et al. (2011).

1.1.2 Exposure and related health effects

Arsenic toxicity strongly depends upon the chemical form in which it is present in water. In water, it is mostly present as As(V), but in anaerobic conditions, it is likely to be present as As(III) (WHO, 2011). The concentration of As in natural surface and groundwater is generally about 1 µg/L but may exceed 1 mg/L in mining areas where As levels in soil are high. Groundwater is far more likely to contain high levels of As compared to surface water. Estimates of the minimum lethal oral dose in humans ranges from 1 to 3 mg/kg bodyweight/day (GR, 2012), although it has been recognized that there may be considerable variation between individuals. Acute lethality as caused by the ingestion of inorganic arsenic is usually attributed to cardiopulmonary collapse (GR, 2012). Arsine (the gas AsH₃) is considered as the most toxic form, followed by the As(III), As(V) and organic As compounds (WHO, 2011). The most commonly observed signs of chronic As exposure include skin lesions such as hyperpigmentation and hypopigmentation. Analysis of numerous epidemiological studies of skin lesions suggest that most persons with skin lesions had consumed water with As concentrations of 100 µg/L, although lesions have been reported at lower concentrations (Naukokas et al., 2013).

Arsenic is a known carcinogen in skin, lung, bladder, liver and kidney, with evidence suggesting lung cancer is the most common cause of arsenic-related mortality (Naukokas et al., 2013). In a Chilean cohort that was exposed to high As in drinking water (>850 µg/L) for a limited period of time (1958-1971), the peak mortality rate ratio (MRR) for lung cancer was 3.61 for men in 1992-1994, suggesting a 34-36 years latency period (Marshall et al., 2007). According to the Health Council of the Netherlands (2012), it is becoming increasingly evident that the toxicity and carcinogenicity of As is likely to be closely associated with metabolic processes. Absorbed As(V) is rapidly reduced to As(III), at least partially in the blood. Because As(III) is known to be more toxic than As(V), this reduction step may be considered as bioactivation rather than detoxification. Because As(III) has greater reactivity and toxicity compared to As(V), it is generally believed that As(III) is the carcinogen. Arsenic is not a mutagen but inhibits DNA repair and inactivates tumor suppressor genes (US EPA, 1997; GR, 2012).

1.1.3 Occurrence and global circulation

Arsenic is the 20th most abundant element in earth's crust. It is found in at least 200 different mineral forms including sulfides and sulfo salts, and as minor amounts of

arsenides, As(V)s, oxides, and silicates (Greenwood and Earnshaw, 1989; Bissen and Frimmel, 2003). Some of the As bearing minerals are : arsenopyrite (FeAsS), realgar (As_4S_4), orpiment (As_2S_3), arsenolite (As_2O_3), loellengite (FeAs_2), nicolite (NiAs), saffrolite (CoAs), enargite (Cu_3AsS_4), cobaltatite (CoAsS) and glaucodote ($(\text{Co,Fe})\text{AsS}$) (Greenwood and Earnshaw, 1989; Bissen and Frimmel, 2003). Typical As concentrations in crustal are presented (Table 1.2).

Table 1.2: Natural abundance of As in crystalline materials

Rock type	Arsenic concentration (mg/kg)
<u>Igneous rocks</u>	
Ultrabasic	0.3 - 16
Basalts	0.06 - 113
Andesites	0.5 - 5.8
Granites	0.2 - 13.8
<u>Sedimentary rock</u>	
Shales and clays	0.3 - 490
Phosphorites	0.4 - 188
Sand stones	0.6 - 120
Limestones	0.1 - 20
<u>Coal</u>	
Bituminous	9 ± 0.8
Lignites	7.4 ± 1.4
Peat	16 - 340

Source: Jacks and Bhattacharira (1998).

Arsenic is one of the most mobile elements in the environment. It readily changes its oxidation states through chemical or biological reactions which are common in the natural environments. From its origin in the bed rock, inorganic As enters into the soil where its average concentration depends upon various factors such as the type of parent rock, anthropogenic activities, local climate, forms or speciation, and redox conditions of the soil and water (Yan Shu, 1994). The principal mechanism of As release from the rocks and soil to the environment is weathering, depending upon the redox environments. Further, the main mode of transport of As in the environment is either by dissolution in rain, river or groundwater or with dust particles through air. Volatile forms of As enter the atmosphere from land and water and then they are returned to soils and sediments by precipitation processes e.g. rain and snow. When, somehow, anaerobic and further anoxic conditions develop, the oxidized forms of As are reduced to sulfides in soils and sediments and become immobile again (Pontius et al., 1994).

Apart from the natural processes, anthropogenic activities are also responsible for the release of As to the environment (Bhattacharya et al., 2007). For example, waste streams from metallurgical industry, glass and ceramic industries, dye and pesticide manufacturing industries, petroleum refining, rare earth industry and other organic and inorganic chemical industries have been reported to be the major anthropogenic sources of As (Mudhoo et al., 2011). Other industries which may introduce As to the environment include wood preservative, lead shot manufacturing, phosphate detergent industry and fertilizer manufacturers (Viraraghavan et al., 1999). Mining activities and smelters also discharge As rich wastes into natural environments (Bissen and Frimmel, 2003). Burning of fossil fuels in the household and power plants may also be considered as a source of As pollution. A scheme (adopted from Bumbala and Keefer, 1994; Shih, 2005) of As circulation among different elements of the environment i.e., land, air, and water, is presented (Fig. 1.2).

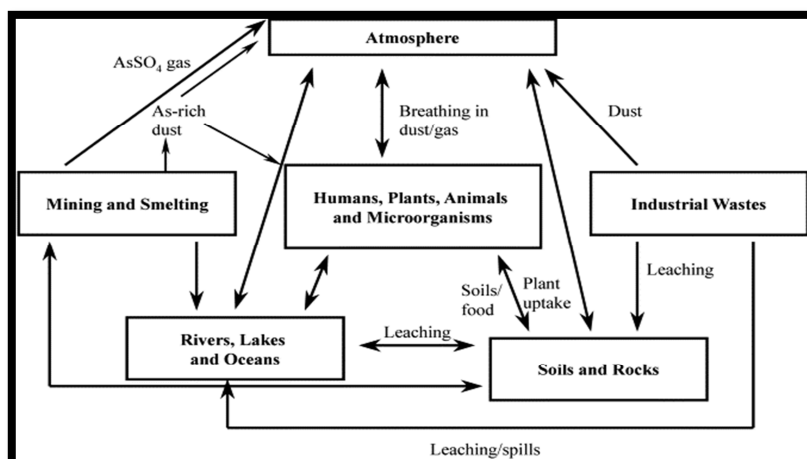


Figure 1.2: As cycling in the environment (from Bumbla and Keefer, 1994).

1.1.4 Hydrogeochemistry

Arsenic is a metalloid, chalcophilic (accumulating in sulphide form) and siderophilic (accumulating in iron form), with atomic number 33, atomic weight 74.922 and a density of 5.73 kg/L. There is only one isotope (^{75}As). The chemistry of As in aqueous environments is of principle importance because it directly affects the type and extent of remediation measures. In aqueous environments, As can exist both in organic and inorganic forms, however, the organically bound As exhibits relatively low toxicity. Depending upon the redox environment, inorganic As can exist as two species; trivalent As (As(III) or As(III)) and pentavalent As (As(V) or As(V)). The more mobile and much more toxic As(III) mainly occurs in anoxic or deeply anoxic environments, i.e., where oxygen and nitrate are virtually absent and where iron is reduced (anoxic) or sulphate is reduced with or without methanogenesis (deeply anoxic). On the other hand, As(V) occurs mainly in (sub)oxic environments (where oxygen is present or where nitrate and nitrite are (meta)stable). Within a particular oxidation state (+3 or +5), pH controls the nature of inorganic As species (Figure 1.3). As(V) can exist as H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} and/or AsO_4^{3-} . In the pH range of 6 to 9, HAsO_4^{2-} and H_2AsO_4^- dominate with a relatively low concentration of AsO_4^{3-} . Below pH 6, H_2AsO_4^- and H_3AsO_4 dominate while above pH 9 AsO_4^{3-} mostly occurs (Figure 1.4). As(III) can exist as H_3AsO_3 , H_2AsO_3^- and/or HAsO_3^{2-} . Below pH 9, H_3AsO_3 is the dominant specie whereas H_2AsO_3^- and HAsO_3^{2-} dominate above pH 9.

The oxidation (and reduction) of As is fairly a slow process even in well-aerated streams, therefore both As(V) and As(III) frequently exist together in both oxic and reducing conditions (Edwards, 1994). Most of the As removal technologies are more effective in removing As(V) compared to As(III) . This is because As(V) occurs as a monovalent or divalent ion in the pH range of most natural waters (6-8.5), on the other hand, As(III) is predominantly uncharged below pH 9.2. The charge on As(V) facilitates its adsorption onto the oppositely charged surfaces and subsequent removal. Therefore, in most cases it is advisable to oxidize As(III) to As(V) , if the prior one dominates the raw water As fraction. Once again, it is worth mentioning that As(III) is much more toxic than As(V) (WHO, 1993; Pontius et al., 1994).

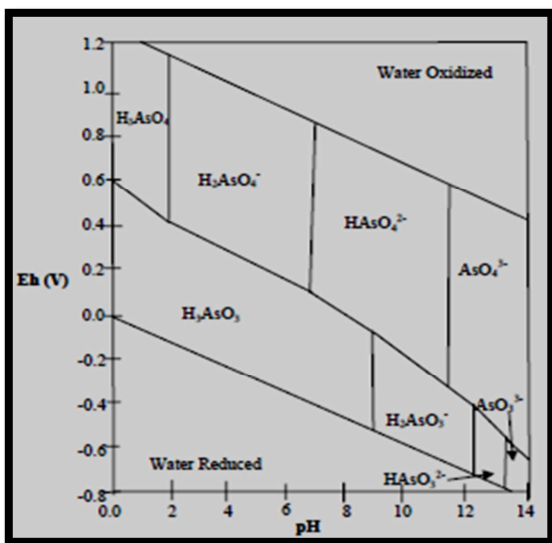


Figure 1.3: Eh-pH diagram for aqueous As (Smedley, 2008)

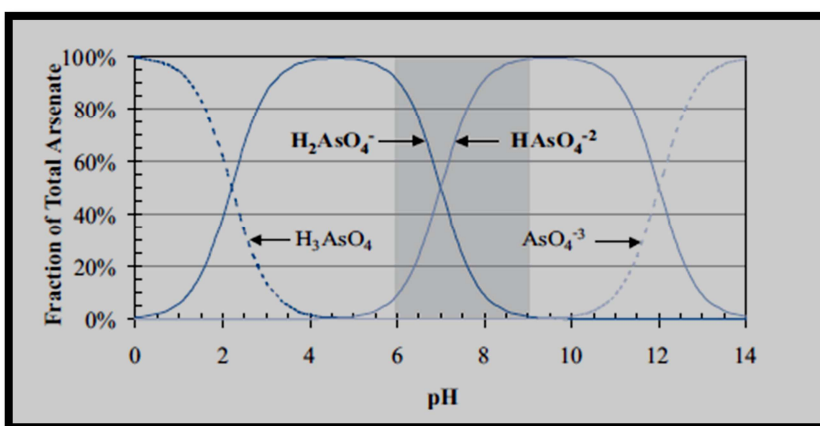
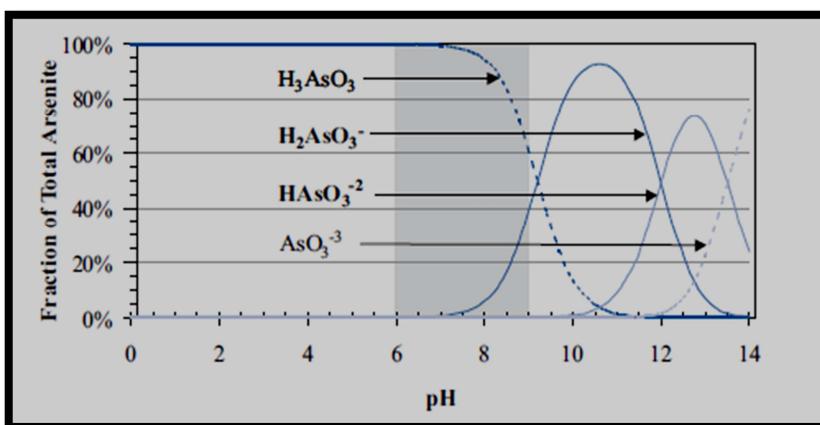


Figure 1.4: Distribution of As(III) and As(V) species as a function of pH (Wilson et al., 2003; USEPA, 2005).

1.1.5 Mobilization processes in groundwater

During the last decade a significant amount of research has been dedicated to understand the underlying mechanisms which are responsible for naturally caused (geogenic) elevated As levels in groundwater. Several theories have been proposed in this context; however, there is still a limited understanding of all the active processes. It is known that the occurrence of As in groundwater is mainly controlled by iron (Fe) oxide and sulfide dominated minerals. Iron oxides have the ability to bind As onto their surface, whereas sulphide minerals take up As into their structure. Iron oxides are generally formed under oxic conditions and dissolved in an anaerobic environment, while sulfide minerals are generally stable under anaerobic conditions and break down by oxidation (Ravenscroft et al., 2009). As long as Fe-oxides or sulphide minerals are present in the aquifers, As can be immobilized under either oxidizing or reducing conditions, for example, by a sub-surface As immobilization technique which will be discussed later in this study. The processes involved in underground As mobilization vary from one place to another depending upon the hydrogeochemical conditions of the soil environment. Based on the wide range of literature focused on As contamination, Ravenscroft et al. (2009) distinguished four principle mechanisms which are believed to control the mobility of As in ground water. These mechanisms include: reductive dissolution, alkali desorption, sulphide oxidation, and mobilization under the influence of geothermal factors. A brief description of these mechanisms is provided below.

1.1.5.1 Reductive dissolution

Reductive dissolution mobilizes As by the reduction of solid Fe-oxides so that both the aqueous Fe(II) and As(III) are released into the solution. Many Fe-oxide minerals are commonly found in groundwater aquifers, for example, ferrihydrite ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$), goethite ($\alpha\text{-FeOOH}$), lepidocrocite ($\gamma\text{-FeOOH}$) and hematite (Appelo and Postma, 1994). The mobilization process of As takes place due to the gradual depletion of oxygen in an aquifer. Bacterial decomposition of organic matter consumes all the available oxygen which is followed by a well-defined sequence of reactions, going from O_2 reduction, NO_3^- reduction and reduction of manganese oxides to the reduction of Fe-oxides. After the reduction of Fe-oxides, reaction continues towards sulphate reduction and methanogenesis. The reduction of As(V) is expected to occur between the reduction of Fe(III) and sulphates (Ravenscroft et al., 2009; Smedley and Kinniburgh, 2001). The groundwaters dominated by reductive dissolution are characterized by the presence of As(III) and are always strongly reducing with a near-neutral pH. Other indicators are high concentrations of Fe, Mn and ammonium (NH_4^+), a high alkalinity and possibly a high dissolved organic carbon (DOC) content. Nitrates and sulphates, however, are nearly absent (Smedley and Kinniburgh, 2001; Ravenscroft et al., 2009).

1.1.5.2 Alkaline desorption

In aerobic groundwaters (phreatic aquifers) when conditions are acidic to near-neutral, As(V) is strongly adsorbed by Fe-oxide minerals. However, when the pH increases (≥ 8) As(V) starts to desorb from the Fe-oxide surfaces and the groundwater becomes contaminated with As. At pH values above 9, significant desorption of As(V) is expected because of the decreased electrostatic attraction between the Fe-oxide surface and the charged As(V) species. Actually, the point of zero charge (PZC) of Fe-oxides occurs below pH 9 and the net surface charge of the oxide becomes negative above the PZC. The uptake of protons by mineral weathering and ion-exchange reactions in combination with evaporation can possibly be the trigger for the rise in pH (Smedley and Kinniburgh, 2001; Ravenscroft et al., 2009). If the water produces sulphates or nitrates in the presence of dissolved oxygen, pH may rise as well. Besides a high pH, other indicators of alkaline desorption are an increased salinity and possibly high concentrations of fluorine, uranium, boron, selenium and molybdenum, while

concentrations of Fe and Mn remain generally low (Smedley and Kinniburgh, 2001; Ravenscroft et al., 2009).

1.1.5.3 Sulphide oxidation

Arsenic mobilization can also occur when As bearing sulphide minerals, for example pyrite, are exposed to oxygen as a result of a lowered groundwater table due to heavy withdrawal of water. For example, during mining activities large quantities of groundwater are pumped out in order to lower the water table which exposes As-bearing sulphide minerals to aerated conditions. Subsequently, As contamination of groundwater occurs during the post-mining groundwater rebound (Smedley and Kinniburgh, 2001; Ravenscroft et al., 2009).

Groundwaters influenced by sulphide oxidation are typically acidic (pH 1-6) and contain high concentrations of sulphates and, but not necessarily, Fe. Other trace metals like copper, nickel, lead, zinc, aluminum, cobalt, and cadmium might also be present (Smedley and Kinniburgh, 2001; Ravenscroft et al., 2009).

1.1.5.4 Geothermal influence

Groundwater may also get elevated As concentrations when geothermally influenced water streams, for example from active volcanic areas, enter into the groundwater aquifers. The geothermally influenced waters usually have an increased salinity with high concentrations of chloride and sodium. Other indicators may be high concentrations of boron, lithium, fluorine, silica and a pH higher than 7 (Smedley and Kinniburgh, 2001).

1.1.6 Regulatory status

Drinking water standards have been set in the USA and the EU, with provisional guidelines also given by the World Health Organization (WHO). The WHO recommendation of 10 µg/L has been adopted as a national standard by many countries, including Japan, Jordan, the Netherlands, Mongolia, Namibia, Syria, USA, and the European Union (EU) (Table 1.3). For a number of low income countries, implementation of 10 µg/L is not currently feasible. Therefore, countries including Bangladesh, India and Pakistan still maintain the 50 µg/L limit. The most stringent drinking water quality standard for As in drinking water is set in Denmark namely 5 µg/L at the entrance of the property. However, the value at the users tap is 10 µg/L (personal communication Jens Stockmarr, GEUS).

At present, there is an ongoing debate about the standard for arsenic in drinking water (Schmidt, 2014). This debate will likely continue on two fronts: (i) how to apply mechanistic findings from animal and in vitro research to human responses, and (ii) how to address fundamental uncertainties in the human data. As stated by Schmidt, a key question is whether the recent epidemiological literature supports estimates of cancer risk predicted from linear dose-response models. If so, the risks are huge and herein lies the controversy.

Table 1.3: Drinking water As standards of various countries.

Countries/States	MCL (µg/L)
Denmark, New Jersey (US)	5
Australia	7
WHO, EU, Japan, US, Canada, Taiwan	10
Mexico	35
Bahrain, Bangladesh, Bolivia, China, Egypt, India, Indonesia, Pakistan	50

Source: WHO (2011).

1.2 Chromium

1.2.1 Chromium in drinking water – a global issue

Chromium (Cr) is the 21st most abundant element in the earth's crust. In natural environments, Cr occurs typically as Cr(III) and/or Cr(VI). Trivalent chromium is considered as an essential human nutrient and does not pose any potential health threat at the concentrations found in fresh water environments (low concentrations). On the other hand, Cr(VI) is toxic and a potent carcinogen (IARC, 2011; Linos et al., 2011). Elevated Cr(VI) concentrations in groundwater sources have been reported in many parts of the world, e.g. in Canada (Izbicki et al, 2008), in USA (USEPA 2000; USGS 2004), in Mexico (Armienta-Hernandez & Rodriguez-Castilo 1995), in Italy (Fantoni et al. 2002) and in India (Bellander & Peterson 2001; Blacksmith Institute, 2006). In the Netherlands, a mean concentration of 0.7 µg/L has been measured, with a maximum of 5 µg/L (Fonds et al. 1987).

Chromium can be introduced into drinking water supplies by natural weathering of chromium-bearing minerals and/or by uncontrolled emissions from a variety of industrial processes. Natural sources of chromium include various iron and aluminium minerals, natural ores like eskolaite (Cr_2O_3), chromite ($\text{Fe(II)Cr}_2\text{O}_4$), crocoite (PbCrO_4), and the sorption complex of clay minerals (Wedepohl, 1978). Waste streams from chemical industry, metal alloying and plating industry, wood treatment, and leather tanning may introduce significant levels of Cr to drinking water sources (Kimbrough et al, 1999; Jongh et al., 2012). Other sources of Cr release are landfills and roadways.

1.2.2 Cr(VI) exposure and related health effects (based on the German report of DVGW, 2013).

According to Kats and Salem (1994), the toxicity of Cr strongly depends on its oxidation state. Hexavalent Cr is classified by the IARC as a human carcinogen (IARC group 1), whereas trivalent Cr is not classifiable as to its carcinogenicity (IARC group 3). Cr(III) compounds are essential to normal glucose, protein and fat metabolism. Most quantitative studies of the gastrointestinal absorption of Cr in humans have estimated that the absorption fraction <10% of the ingested dose (ATSDR, 2012). In part, Cr(VI) is reduced in the stomach by gastric juice (at low pH) to Cr(III), which lowers the absorbed dose from ingested Cr(VI) (De Flora et al., 1987). Absorption is also affected by nutritional status. The carcinogenic action of Cr(VI) is already known for a long period (IARC, 1990; IRIS, 2008; ATSDR, 2012). The development of lung cancer among workers exposed to Cr(VI), has been demonstrated by numerous epidemiological studies (ATSDR, 2012, McLean et al., 2012). Studies of associations between oral exposures to Cr and cancer outcomes in humans are limited to several ecological studies (ATSDR, 2012). Actual exposures to individuals have not been determined and therefore uncertainties remain between exposure and outcomes. However, ecological studies strongly support associations between cancer mortality and exposures to Cr. The latter is also supported by recent studies in mice and rats which provided unequivocal evidence that chronic exposure to Cr(VI) in drinking water resulted in increased incidence of neoplasms in the digestive tract (NTP, 2008). In vitro studies have demonstrated that Cr(VI) enters the cells faster as compared to Cr(III). Therefore, Cr(VI) is of greater concern with regard to health effects. Hexavalent and trivalent chromium have been shown to be genotoxic in human cells (ATSDR, 2012). However, ATSDR notes that in positive genotoxicity studies, the potency of Cr(III) was several orders lower compared to Cr(VI). The main reason underlying this difference is that Cr(III) is less able to cross cell membranes.

1.2.3 Hydrogeochemistry

Chromium is a heavy metal, lithophilic (accumulates in rock and is not well soluble in water), with atomic number 24, atomic weight 51.996 and a density of 7.19 kg/L. There are 4 stable isotopes: ^{50}Cr (4.4%), ^{52}Cr (83.8%), ^{53}Cr (9.5%) and ^{54}Cr (2.4%). Chromium forms a number of salts which are characterized by a variety of colors, solubilities and other properties (de Jongh, 2012). In aqueous environments, Cr occurs predominantly in two forms, Cr(III) and Cr(VI). The distribution of Cr(III) and Cr(VI) depends mainly on the redox potential and the solution pH (Fig. 1,5). As a general rule, Cr(VI) is expected to predominate in highly oxygenated conditions or when strong oxidants such as chlorine or even moderately strong oxidants like chloramine are present in water. The mobility of Cr(VI) in water considerably exceeds the mobility of Cr(III), because Cr(VI) exists as an anion and Cr(III) as a cation (WHO, 2003). At the predominating pH-values anions adsorb less and cations much more to the negatively charged soil or aquifer. Cr(VI) is reduced to the much less soluble Cr(III) in (deeply) anoxic environments, especially by Fe^{2+} , organic material, pyrite and H_2S (Breit et al. 1992; Yao-Tung & Ching-Pao 2008). In groundwater Fe^{2+} and Cr(VI) appear to be antagonists.

Depending upon pH, Cr(III) occurs as a cation that forms aqueous complexes and hydroxide precipitates. The simplest ionic form of Cr(III) is Cr^{3+} which predominates at $\text{pH} < 4$ (Fig. X-X). At $\text{pH} > 4$, Cr(III) forms hydroxide complexes in a stepwise manner as pH increases ($\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3^+$, $\text{Cr}(\text{OH})_3$ and $\text{Cr}(\text{OH})_4^-$) (AWWARF, 2004). $\text{Cr}(\text{OH})_2^+$ is the dominant specie in natural groundwater with a pH between 6 and 8 (Calder 1988). Cr(III) tends to be extremely insoluble between pH 7 and pH 10, with minimum solubility at pH 8 (Rai et al, 1987). Cr(VI) exists in aqueous solutions as monomeric species: H_2CrO_4^0 , HCrO_4^- (hydrogen chromate) and CrO_4^{2-} (chromate); or as the dimeric ion $\text{Cr}_2\text{O}_7^{2-}$ (dichromate—only exists in very strongly acidic solution or when Cr concentration is higher than 1000 mg/L) (AWWARF, 2004). In the pH range (1–10) and at low concentrations, Cr(VI) is present in groundwater as either monovalent HCrO_4^- or divalent chromate CrO_4^{2-} . The monovalent form predominates in acidic water while the divalent form predominates at neutral pH or above. Under certain conditions, Cr(III) can be oxidized to Cr(VI) and vice versa. Based on these trends of inter-conversions, it is desirable that water quality standards should be based on total chromium concentration as well as the concentration of the more toxic species Cr(VI) (Sharma et al., 2008).

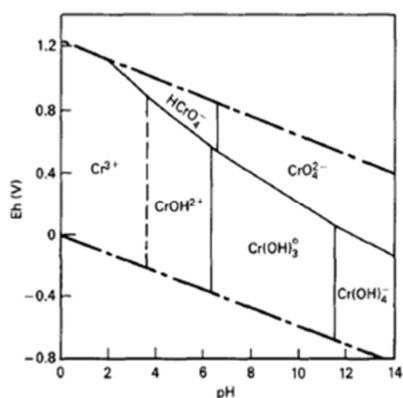


Figure 1.5: Eh-pH diagram of aqueous Cr species without solid phases (from Rai et al., 1989).

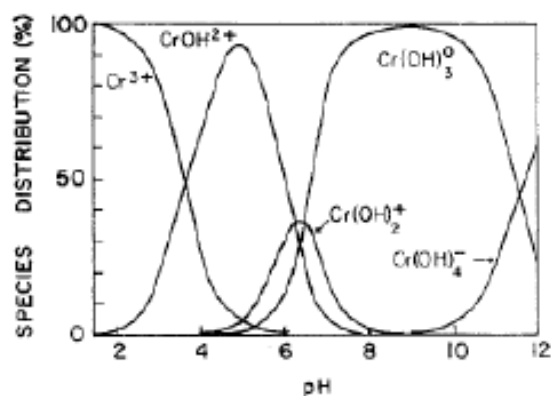


Figure 1.6: Distribution of Cr(III) species in water as a function of pH at 25 °C and 1 bar (Richard & Bourg, 1991).

1.2.4 Mobilization of chromium from the treatment and distribution infrastructure

Several studies report an increase in Cr concentration as the water is treated and distributed. One study reported that 17% of water samples had “pickup” of Cr, meaning that tap water samples had more Cr than water leaving the treatment plant (Craun & McCabe, 1975). Another study observed an increase in the Cr concentrations during water travels from the source to the tap (Frey et al., 2004). The increase in Cr concentrations during treatment and supply is an important subject. It needs further research and identification of the sources with the treatment and supply infrastructure. At the consumer’s tap Cr may arise from a variety of sources. For example, Chromium may be added from the treatment chemicals (McNeill et al. 2012). Moreover, leaching from the material of the distribution network or house plumbing may also increase Cr concentration in the drinking water (McNeill et al. 2012). The build-up of Cr in the sediment layer in the distribution network may also serve as a potential Cr source for the drinking water at the consumer’s tap. Understanding of Cr mobilization from the infrastructure is immensely important to safeguard public health.

1.2.5 Regulatory status

The WHO recommends 50 µg/L as the guideline value for total Cr in drinking water. The guideline is designated as provisional because of uncertainties in the toxicological database. The EU Drinking Water Directive, California EPA and Health Canada recommend the same guideline value (Table 1.4). These regulations do not distinguish between the presence of trivalent and hexavalent Cr. At present a Maximum Residue Level (MRL) of 0.9 µg/Cr(VI)/kg bw/d has been derived for chronic oral duration to Cr(VI) compounds (NTP, 2008). This would translate to a total of 63 µg Cr(VI)/day for an adult person of 70 kg. In addition a Reference Dose (RfD) of 3 µg/Cr(VI)/kg bw/d has been derived and verified by the US EPA. This would translate to 210 µg/hexavalent chromium/kg bw/d for an adult person of 70 kg. The Environmental Protection Agency of California has explicitly taken the position that Cr(VI) in drinking water should be regulated separately. In 2011 the California EPA’s Office of Environmental Health Hazard Assessment (OEHHA) released a Public Health Goal (PHG) for Cr(VI) in drinking water of 0.02 µg/L based on potential carcinogenic effects. The PHG is a level of drinking water contaminant at which adverse health effects are not expected to occur on lifetime exposure. This PHG was intended to guide the California Department of Public Health in developing a MCL of 10 µg/L for Cr(VI) in drinking water (California Environmental Protection Agency, 2011). In 2013 the California Department of Public Health set the first drinking water standard specifically for Cr(VI) and that is 10 µg/L (Water21, 2013). The State of New Jersey has also considered whether to propose a state MCL for Cr(VI), with a health-based MCL estimated at 0.07 µg/L (New Jersey Drinking Water Quality Institute, 2010).

Following the discussion in the United States, a debate on the evaluation of the occurrence of Cr(VI) in drinking water has recently started in Germany. Up to now a regulatory value of 50 µg/L for total Cr was set in the German Drinking Water Ordinance but in the ongoing discussion the German Ministry of Health has proposed a new target value for Cr(VI) in drinking water as low as 0.3 µg/L with an additional cancer risk of 10^{-6} (TZW, 2014). In the Netherlands a provisional guideline value for drinking water of 0.2 µg/L was derived on similar grounds (de Jongh et al. 2012).

Table 1.4: Current guideline values for total Cr in drinking water

Authority	Total Chromium (µg/L)
EU (Drinking water directive 98/83/EC)	50
WHO (Guidelines for drinking water quality)	50
USEPA (MCL)	100
California Dept. of Public Health (MCL)	50
Health Canada	50
De Jongh et al., 2012	

1.3 Mitigation for elevated arsenic and chromium concentrations

Once elevated As and/or Cr(VI) concentrations are confirmed in the drinking water sources, the immediate priority should be either to find a safe alternative source of water or to apply suitable treatment measures to remove the contaminant to a level that is considered safe. Removal of As and Cr(VI) from water is not an easy task. It may require sophisticated and expensive treatment which is not always attractive in areas with low economic resources. On the other hand, finding an alternative drinking water source may also become a challenge, especially in the water scarce regions of the world. Therefore, the options must be carefully evaluated with a long-term vision before any sort of practical implementation.

1.3.1 Source substitution

An existing unsafe source can be substituted by a safe groundwater, rainwater or surface water source, however various technical, economic and social factors determine the suitability of any of these options in practice. For example, rain water can serve as a potential alternative to a problematic drinking water source, however, this option is better suited to individual households or small scale rural water supply systems which supply drinking water to a small number of households. It must be noted that poorly stored rainwater has a high potential for bacteriological contamination and cleanliness of collection surfaces (roofs) and storage tanks is one of the critical considerations in maintaining good quality.

At most large scale centralized water production locations, groundwater is pumped through a number of tube wells installed in one or more aquifers. In such situations, the water quality data from each individual well should be carefully evaluated and switching the “problematic” wells from full-time use to seasonal or peaking use can be considered to obtain safe water. The option of blending surface and groundwater to produce a diluted raw water stream can also be probed, however, this kind of strategy may require additional treatment step(s) in the downstream treatment train of the centralized treatment system.

Most surface waters receive pollutants from agricultural, industrial, domestic and municipal sources, therefore may require intensive treatment before consumption. In case use of surface water is the only available option to obtain As or Cr(VI)-safe water, affordable treatment strategies should be adopted and maximum benefit should be taken from the natural cleansing processes. River bank infiltration and Dune infiltration are excellent pre-

treatment techniques for surface water purification. As the water infiltrates through a layer of soil/sand, it becomes significantly free from a wide range of impurities. It must be noted that infiltration of surface water through geological formations may sometimes introduce heavy metals in to the infiltrating stream.

1.3.2 Treatment of water

Treatment of As or Cr(VI) contaminated water is an alternative option to make use of available sources which are likely to be declared abandoned otherwise. There are several well-established methods available for As and Cr(VI) removal from potable water. The most commonly used technologies include; precipitation/co-precipitation, adsorption onto sorptive media, ion exchange resin treatment and membrane techniques. Chapter 4 of this report provides an overview of the technologies and their limitations.

1.4 Other metals and current risk limits

The WHO has published its latest guideline values in 2011 (WHO, 2011). For most compounds detailed chemical fact sheet information has been collated for this review. Besides arsenic and chromium, other metals are also included in monitoring and risk assessment: the list contains several metals: Al, As, Ba, B, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Mb, Ni, Ag, U, Zn.

Table 1.5 gives an overview of the methodology how WHO guideline values were derived and how these compare to European and Dutch standards (EU, 1998; Drinkwaterbesluit, 2011). Based on this overview, attention could go to metals that have limited data in the current assessment, or towards metals that are known to have local background values (either naturally or by use in treatment). In general, metals that may be present in a certain oxidative state, like arsenic and chromium, may also ask for a more in-depth evaluation of health aspects.

For some metals, provisional WHO guidelines exist (As, Cr, Pb, Hg, Se, U). For some others, no values exist (Al, Fe, Mn, Mb, Ag, Zn). Reasons for not having a guideline value may be that these elements are considered not relevant for human health (Al, Fe, Zn), or that the data are not suitable for deriving a guideline (e.g. silver (Ag)). For manganese (Mn), the acceptability problems with drinking water are at levels not of health concern. Nevertheless, for some elements the assessment has been made longer than several years ago, which could indicate that new data may be available. Also the practice may have changed in developing new water treatment concepts. For example, use of metals as water treatment agents different than iron and aluminum may give reasons to reassess the guideline values, such as the use of manganese in treating arsenic rich water.

In the Netherlands, current risk limits are described in table II of the drinking water law (Drinkwaterbesluit, 2011) and included the following elements; As, Cd, Cr, Cu, Hg, Pb, Se, Sb, and Ni. These metals are regularly monitored during the drinking water treatment process and at tap water points. Other metals are used as indicative limits in the monitoring (table III), including Al, Fe, Zn.

In the drinking water quality report of last two reported years (2011-2012), Mn, Ni and Pb were reported above limits (ILT, 2011; ILT, 2012). Here, elevated Pb was most probably caused by lead parts of the in-house installation. In the Netherlands, most distribution systems have been changed from lead to other materials. Only 900 distribution systems still exist, while over 400.000 existed before. Iron and manganese are sometimes above indication values, mostly after construction works or due to well-specific water quality.

Besides these metals, Ni and Al are also incidentally above indication values, either caused by sub-optimal treatment or changing water supply.

US-EPA has published the 3rd Contaminant Candidate List containing compounds a) that are currently not subject to any proposed or promulgated national primary drinking water regulations, b) that are known or anticipated to occur in public water systems, and c) which may require regulation under the Safe Drinking Water Act (SDWA). From this list, cobalt, molybdenum, strontium, vanadium were included, while the fourth list is due soon (expected in 2014) (reference <http://www2.epa.gov/ccl/contaminant-candidate-list-3-ccl-3>). Detailed information on the speciation of these elements and their respective toxicity and specific behavior has not been evaluated in detail in this study.

Table 1.5: Overview of metals and guidelines from WHO, EU and Dutch drinking water law.

Metal	WHO Guideline values	Remarks on derivation methodology (see WHO, 2011 for details)	Last assessment (as stated in WHO, 2011)	EU drinking water standards	Dutch drinking water law. Guideline value.
As (Arsenic)	Provisional guideline: 0.01 mg/L	Provisional guideline on the basis of uncertainties in the toxicological database	2011	0.01 mg/L	0.01 mg/L
Cr (Chromium)	Provisional guideline: 0.05 mg/L	Provisional guideline on the basis of treatment performance and analytical achievability	1993	0.05 mg/L	0.05 mg/L
Aluminium (Al)	No value	Health based guideline value: 0.9 mg/L Practical guidelines are max. 0.2 mg/L, used for prevention of microbiological risks.	2003	<i>Monitoring in case of use as flocculant 0.2 mg/L</i>	0.2 mg/L *)#
Barium (Ba)	0.7 mg/L	WHO: Derived from NOEL 7.3 mg/L, factor 10 uncertainty	2003		
Boron (B)	2.4 mg/L	0.17 mg/kg body weight, based on a BMDL05 of 10.3 mg/kg body weight/day for developmental toxicity and an uncertainty factor of 60	2009	1.0 mg/L	0.5 mg/L
Cadmium (Cd)	0.003 mg/L	Derived from PTMI of 25 microg/kg.body wt.	2011	0.005 mg/L	0.005 mg/L
Copper(Cu)	2 mg/L	Protective guideline to gastrointestinal effects	2003	2 mg/L	2 mg/L
Iron (Fe)	No value	No health concern, may affect acceptability of water	1993	<i>Monitoring in case of use as flocculant 0.2 mg/L</i>	0.2 mg/L *)
Lead (Pb)	Provisional guideline: 0.01 mg/L	The guideline is provisional on the basis of treatment performance and analytical achievability	2011	0.01 mg/L	0.01 mg/L

Manganese (Mn)	No value	Not of health concern at levels found in drinking water	2003, revision 2011	<i>n/a</i>	*) 0.05 mg/L
Mercury (Hg)	0.006 mg/L (inorganic)	Derived via 2 µg/kg body weight based on a NOAEL of 0.23 mg/kg body weight per day	2004	0.001 mg/L	0.001 mg/L
Molybdenum	No value	Occurs in drinking-water at concentrations well below those of health concern	1993, revised in 2011	No value	No value
Nickel (Ni)	0.07 mg/L	Derived via RDI from LOAEL value	2004	0.02 mg/L	0.02 mg/L
Selenium	0.04 mg/L	The guideline value is designated as provisional because of the uncertainties inherent in the scientific database.	2010	0.01 mg/L	0.01 mg/L
Silver (Ag)	No Value	Available data inadequate to permit health-based guideline value	1993		
Uranium (U), chemical (not radiological)	Provisional value: 0.03 mg/L	Provisional because of scientific uncertainties surrounding uranium toxicity	2003, WHO, 2011		
Zink (Zn)	No Value	Not of health concern at levels found in drinking water	1993 WHO, 2003		*) 3 mg/L

*) Dutch drinking water law: refers to indicator parameters ("Table III").

Is already reported to proper authorities in case of exceeding 0.03 mg/L, due to the possible use of drinking water for renal dialysis.

1.5 The need and goal of this project

In the Netherlands, the total As and total Cr concentrations in drinking water supply are well below the national maximum concentrations limits (MCLs), thanks to its compliant drinking water treatment systems that are producing world's highest quality drinking water. As discussed earlier in this chapter the debate emphasizing the health effects of much lower As and Cr concentrations is ongoing in many parts of the world. These concentrations are those that many Europeans, Americans and Canadians live with every day. Although nothing concrete may be concluded yet, researchers across the world increasingly believe that the risks associated to As and Cr are more widespread than previously recognized and concentrations lower than the current guidelines may pose risk to the health and lives of consumers. Previous studies in the Netherlands reported that As and Cr occur as trace elements in Dutch groundwaters, with As concentrations in the range of <0.1 to ~1,500 µg/L (Stuyfzand et al. 2008), and Cr concentrations in the range of <0.1 to ~15 µg/L (De Jongh et al. 2012). If the current MCLs of As (10 µg/L) and Cr (50 µg/L) in drinking water would be lowered in the near future, the exact number of Dutch drinking water production locations that may become non-compliant is still unknown. Furthermore, it has to be determined yet how many Public Supply Well Fields (PSWFs) will deliver raw water with serious As or Cr norm exceedances and that may necessitate serious adaptations of the current drinking water treatment systems.

The overall goal of this project was to investigate the As and Cr concentrations and their speciation in the drinking waters produced across the Netherlands and their sources. Data on As and Cr speciation in drinking water are even more scarce. This is primarily because species are not regulated in drinking water and accurate speciation methods for measuring low levels of As and Cr have only recently been developed. A review of conventional As and Cr treatment technologies has also been carried out within this study that may be applied to optimize the treatment systems. This project work has been carried out within the framework of the Joint Research Program (BTO) of the Dutch Waterworks and is guided by the theme group Drinking Water Technology of the Future (TG DTT).

1.6 Segments of the report (The reading guide)

Chapter 1 focuses on setting the background of the occurrence and toxicological aspects of As and Cr in drinking water supplies from a global perspective and also on explaining the rationale and goal of this project.

Chapter 2 focuses on As and Cr in the source waters of the Netherlands and their speciation. This chapter discusses the results of the data analysis from previous years and sampling campaign performed in 2014.

Chapter 3 focuses on As and Cr concentrations in the treated waters of the Netherlands and their speciation. This chapter discusses the results from the data analysis from previous years and sampling campaign held in 2014.

Chapter 4 provides an overview of the treatment technologies available for the removal of As and Cr. The overview is based on literature research.

Chapter 5 summarized the main findings of the project and provides recommendations to the BTO for effective management of As and Cr challenge.

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2 Arsenic and Chromium Concentrations and Speciation in Raw Water Sources for Drinking Water Supply in the Netherlands

Author: Pieter Stuyfzand

Abstract

An inventory was made of arsenic and chromium concentrations in groundwater resources for drinking water supply in the Netherlands, as based on various data bases and a sampling campaign by KWR in August 2014. Bias by suspended particles and corrosion of stainless steel was observed, necessitating removal of some data from the data bases.

Total dissolved arsenic concentrations of raw groundwater in the Netherlands, pumped for public drinking water supply, ranged in 2013 from 0.1-21 µg/L, and those for total dissolved chromium ranged from <0.1-3 µg/L. The REWAB database reveals that 47, 13.5, 6.7 and 4 % of 190 public supply well fields (PSWFs) showed As levels in 2013 above 1, 3, 5 and 10 µg/L, and 44, 8 and 0.5% showed Cr levels above 0.3, 1 and 2 µg/L.

The summer 2014 sampling campaign demonstrates that the higher As and Cr concentrations mainly refer to arsenite (As(III) as H_3AsO_3) in (deeply) anoxic environment, and chromate (Cr(VI) as CrO_4^{2-}) in (sub)oxic environment.

Arsenic hotspots (up to 1,500 µg/L) and Cr hotspots (up to 12 µg/L) in groundwater without local pollution sources are discussed, together with the conditions under which As and Cr become mobilized.

2.1 Introduction

Arsenic (As) and chromium (Cr) normally occur as trace elements in fresh groundwater resources of the Netherlands. The dissolved As concentrations range from <0.1 to ~1500 µg/L (Stuyfzand et al. 2008) and the dissolved Cr concentrations range from <0.1 to ~15 µg/L (De Jongh et al. 2012). Their concentrations varied much less, however, in the raw groundwater pumped for drinking water supply in the Netherlands, namely between <0.1 and 70 µg As/L, and <0.1 and 8 µg Cr/L, in the period 1989-2002.

If the current maximum concentration limits (MCLs) of As (10 µg/L) and Cr (50 µg/L) in drinking water would be lowered in future, then many Public Supply Well Fields (PSWFs) may deliver raw water with seriously elevated As and/or Cr concentrations. And that in turn may necessitate serious adaptations of the current drinking water treatment processes in the Netherlands. Furthermore, in establishing new MCLs for As and Cr in the Netherlands, their speciation may play an important role, because arsenite (As(III) mainly as H_3AsO_3) is much more toxic than arsenate (As(V) mainly as AsO_4^{3-}), and chromate (Cr(VI) mainly as CrO_4^{2-}) is much more toxic than Cr(III). As discussed in Chapter 1, there are ongoing discussions on the health based limits of As and Cr in different parts of the world and recommendations on setting the MCL for As and Cr(VI) to lower levels have been provided at 1-3 and 0.3 µg/L for As and Cr(VI) respectively.

In this chapter, we therefore investigate the current total dissolved concentration levels of As and Cr in the raw water sources used for drinking water production while also paying attention to speciation (As(III) versus As(V), and Cr(III) versus Cr(VI)).

2.2 Material and methods

The inventory has been based on 2 national databases (REWAB and KIDAP), 3 isolated national sampling campaigns in the period 1998-2014, and various data records of Pieter Stuyfzand. The investigated PSWFs are shown in Fig.2.1, and the discerned types are explained in Table 2.1.

2.2.1 The REWAB database

Database REWAB (Registratie opgaven van Drinkwaterbedrijven) contains information on the quality of raw water, drinking water and water at the tap, from all the public supply well fields (PSWFs) and the Surface Water Treatment Plants (SWTPs) in the Netherlands. It is managed jointly by the Dutch National Institute of Public Health and the Environment (RIVM) and KWR Watercycle Research Institute, based on data supplied by all the Dutch drinking water companies since 1992. In this study, the data on the annual mean inorganic quality of raw water from all PSWFs in the period 2008-2013 have been used. The As and Cr concentrations in this database refer to total dissolved concentrations, with minimum quantification limits (MQLs) of 0.1-1 µg/L for both As and Cr.

2.2.2 The KIDAP database

Igor Mendizabal and Stuyfzand constructed KIDAP (Kiwa Database Pompstations), a database for PSWFs, containing information on all well fields in the Netherlands, including their technical and hydrogeological characteristics and their mean annual inorganic water quality data in the period 1898-2008. The PSWFs in the Netherlands have been classified in 5 groups, namely, Phreatic, (Semi)confined, AR (Artificial Recharge), RBF (River Bank Filtrate) and limestone. Their main properties are summarized in Table 2.1 and their spatial distribution is given in Fig 2.1. According to the KIDAP database, most AR is located in the coastal dunes, RBF in the Rhine Delta, and limestone in Southern Limburg. Most PSWFs in Twente and the Achterhoek are phreatic and pump water from a shallow aquifer, while most PSWFs in the Central Graben (area within the faults) pump from deep Tertiary aquifers, at 100-200 m-MSL (meters below Mean Sea Level). For more details see Mendizabal & Stuyfzand (2009).

2.2.3 Sampling campaigns in 1998, 2008 and 2014

In 1998, RIVM conducted a drinking water monitoring program in which several non-routine parameters were sampled. Cr(VI) was also the part of the sampling campaign (Jonker et al., 1999). Cr(VI) was analyzed in the raw water and drinking water from a selection of 17 PSWFs and 2 SWTPs. The 0.5 L water samples were not filtrated nor acidified, and analyzed by ion chromatography with MQL < 0.2 µg/L.

In the first trimester of 2008, Igor Mendizabal from KWR organized a national sampling campaign, in which all active PSWFs were sampled for a broad scan of the inorganic chemical composition, including isotopes, trace elements (including As and Cr) and main constituents. A total of 241 samples were obtained from the 206 active PSWFs at that time, thus also including separate sections of specific well fields (for instance, remote well clusters or wells from different aquifer layers). Unlike the 1998 sampling campaign, this time the samples for metals (including As and Cr) were filtrated in the field over 0.45 µm, acidified and cooled in the dark for preservation, and their total dissolved concentrations were analyzed via ICP-MS and ICP-OES techniques with a MQL of 0.5 µg/L for As and Cr. Mendizabal et al., (2011) supplies more detail.

In August 2014, KWR organized a restricted national sampling campaign, in which a selection of 14 active PSWFs were sampled for a broad scan of the inorganic chemical composition, including trace elements (including As(III), As(VI), As-total, Cr(III), Cr(VI) and Cr-total) and main constituents. The selection was based on a pre-selection of the 2008-2013 REWAB top 10 As PSWFs, top 10 Cr PSWFs and a group of PSWFs showing both, i.e., an elevated As and Cr concentration, and a post-selection to minimize sampling efforts and costs. The samples for metals (including As and Cr) were filtrated in the field over 0.45 µm, acidified and cooled in the dark for preservation, and their total dissolved concentrations were analyzed via ICP-MS after destruction. Furthermore, the speciation of As was determined in the samples from all 14 locations and the speciation of Cr was determined in samples from 10 locations. The other 4 locations were not sampled for Cr speciation analysis because the RIVM database (2008-2013) did not indicate > 0.5 µ/L of total Cr at these locations. The samples for As and Cr speciation were filtrated over 0.45 µm filter and collected in especially designated bottles provided by Aqualab Zuid (As speciation) and the laboratory of Vitens (Cr speciation). More information on the methods for the determination of As and Cr species may be obtained from the mentioned laboratories.

2.2.4 Various datafiles of Stuyfzand

Extensive data on the concentration of trace elements in the Netherlands have been systematically collected by the author (e.g. Stuyfzand, 1987, 1991, 1993, 2010, 2012, 2014) in his hydrogeochemical research. The data cover nearly the whole periodic table of elements, and refer to total dissolved concentrations as measured by various techniques such as instrumental neutron activation analysis (INAA), AAS graphite furnace (incl. matrix modifiers, metal hydride conversion, deuterium background correction; Van der Jagt & Stuyfzand, 1987), and ICP-MS + ICP-OES. Samples were always filtrated in the field over 0.45 µm (a series in 1980 excluded), and acidified for preservation.

TABLE 2.1: Hydrological classification of PSWF-types in The Netherlands, with data referring to the year 2008. The number of PSWFs corresponds to the number of samples obtained during sampling (phreatic and confined parts of a PSWF pumping both aquifers were sampled separately and further considered as two PSWFs) (Mendizabal & Stuyfzand (2011)).

PSWF type	Unit	Sand and gravel				Lime-stone
		G		AR	RBF	
		Phreatic	Confined			
First year of operation of first PSWF		1853	1893	1940	1890	1904
Number of active PSWFs		67	126	12	27	9
Mean raw water production per PSWF ^a	Mm3/y	2.8	3.7	16.0	2.7	2.6
Total amount of drinking water produced ^a	Mm3/y	187	449	192	74	23
% of total amount of drinking water produced ^a	%	20	49	21	8	3
Mean number of wells / sampling points		11	12	131	17	7
Mean land surface	m ASL	18	14	9	3	68
Mean abstraction level	m BLS	26-60	82-135	10-31	24-56	24-74
Mean depth to brackish groundwater [m]	m	154	204	65	142	197
Age spectrum	y	2-200	20-25000	0.1-0.3	1-50	2-200

^a Water production in year 2004; G = fresh, autochthonous, actual groundwater; AR = artificially recharged water; RBF = river bank filtrate; ASL = Above Sea Level; BLS = Below Land Surface.

2.3 Review of hydrogeochemical behavior of arsenic

Arsenic is a metalloid, chalcophilic (accumulating in sulphide form) and siderophilic (accumulating in iron form), with atomic number 33, atomic weight 74.922 and a density of 5.73 kg/L. There is only one isotope (⁷⁵As). In nature it mainly occurs as pentavalent As(V)

and/or trivalent As(III), of which As(III) is the predominant form. The more mobile and much more toxic As(III) only occurs in anoxic or deeply anoxic environment (Fig.2.2), i.e. where oxygen and nitrate are virtually absent and where iron is reduced (anoxic) or sulfate is reduced with or without methanogenesis (deeply anoxic). As(V) is mainly restricted to (sub)oxic environments (where oxygen is present or where nitrate and nitrite are (meta)stable). The predominant natural sources of As in groundwater are iron sulfides (mainly pyrite = FeS_2) and iron (hydr)oxides (mainly ferrihydrite = $\text{Fe}(\text{OH})_3$), as indicated by Smedley (2008). The various mobilization processes in the Netherlands have been discussed in Chapter 1 and are also listed in Table 2.2. Pyrite oxidation, the reduction of ferrihydrite and anion exchange are the most common mobilization processes. Appelo (2008) demonstrated that As(V) is strongly sorbed to ferrihydrite at $\text{pH} < 9$, and that PO_4 at $\text{pH} < 9$, HCO_3 at $\text{pH} 3-7.5$ and SO_4 at $\text{pH} < 7$ may drive AsO_4^{3-} from the exchanger.

2.4 Review of hydrogeochemical behavior of chromium

Chromium is a heavy metal, lithophilic (accumulates in rock and is not well soluble in water), with atomic number 24, atomic weight 51.996 and a density of 7.19 kg/L. There are 4 stable isotopes: ^{50}Cr (4.4%), ^{52}Cr (83.8%), ^{53}Cr (9.5%) and ^{54}Cr (2.4%). In nature it occurs as Cr(VI) and Cr(III), of which Cr(III) is the predominant. The better soluble and much more toxic Cr(VI) only occurs in (sub)oxic environment, i.e. where oxygen is present or where nitrate and nitrite are (meta)stable (Fig.2.3). Cr(VI) is reduced to the much less soluble Cr(III) in (deeply) anoxic environments, especially by Fe^{2+} , organic material, pyrite and H_2S (Breit et al. 1992; Yao-Tung & Ching-Pao 2008). In groundwater Fe^{2+} and Cr(VI) appear to be antagonists (Fig.2.3).

The mobility of Cr(VI) in water considerably exceeds the mobility of Cr(III), because Cr(VI) exists as an anion and Cr(III) as a cation. At the predominating pH-values anions adsorb less and cations much more to the negatively charged soil or aquifer. Richard & Bourg (1991) state that Cr(III) will migrate under acidic conditions and/or if present as dissolved organic matter complexes, while Cr(VI) generally migrates rapidly but its mobility is inhibited when the Fe(II) and organic matter concentrations are high and when sorption processes are favored (low pH). It is remarkable that Cr(III) at pH7 is still relatively immobile notwithstanding its uncharged character ($\text{Cr}(\text{OH})_3$). Specific Cr minerals are relatively rare and in the Netherlands they are practically absent. Chromium frequently replaces Fe^{3+} and Al^{3+} in other minerals, which in the Netherlands yields the highest contents in sediments rich in clay minerals.

The most important human activities that raise the environmental concentrations of Cr (VI), are composed of industrial activities producing chemicals, leather and textile, electro paints and various other Cr(VI) applications in industry. Metallurgical industrial spills mainly discharge Cr(III) to surface and ground water. Chromium is used there, among others, to galvanize metal surfaces or to produce stainless steel, which contains 12-15% Cr(III).

RIVM (2008) states that soil emissions of Cr are mainly related to industry (65%) and consumers (30%, significant part by using wolmanized wood) and others (5%). Water is polluted by chromium (directly and indirectly) mainly via sewage (42%) and industrial effluents (37%), and in addition by the construction sector (3%), waste processing industries (3%), traffic (1%) and others (14%). For more details see De Jongh et al. (2012).

2.5 Overview of total dissolved As and Cr data from REWAB

From the REWAB database the cumulative frequency distribution was constructed for each of the years 2008 – 2013. There was little difference between them. Therefore, data from 2008 and 2013 are presented (Fig.2.4). It can be concluded that in 2013 approximately 47, 13, 6.5

and 4% of 180 PSWFs showed As levels above 1, 3, 5 and 10 $\mu\text{g/L}$ respectively, and 44, 8, and 0.5% showed Cr levels above 0.3, 1, and 2 $\mu\text{g/L}$ respectively. The percentages for Cr > 0.3 are rather inaccurate due to relatively high MQLs (0.5 $\mu\text{g/L}$).

The top 31 PSWFs regarding their As and Cr concentration in the raw groundwater produced in 2013, are listed in Table 2.3. All of the PSWFs selected for KWR's sampling campaign are on this list, except the Plasmolen.

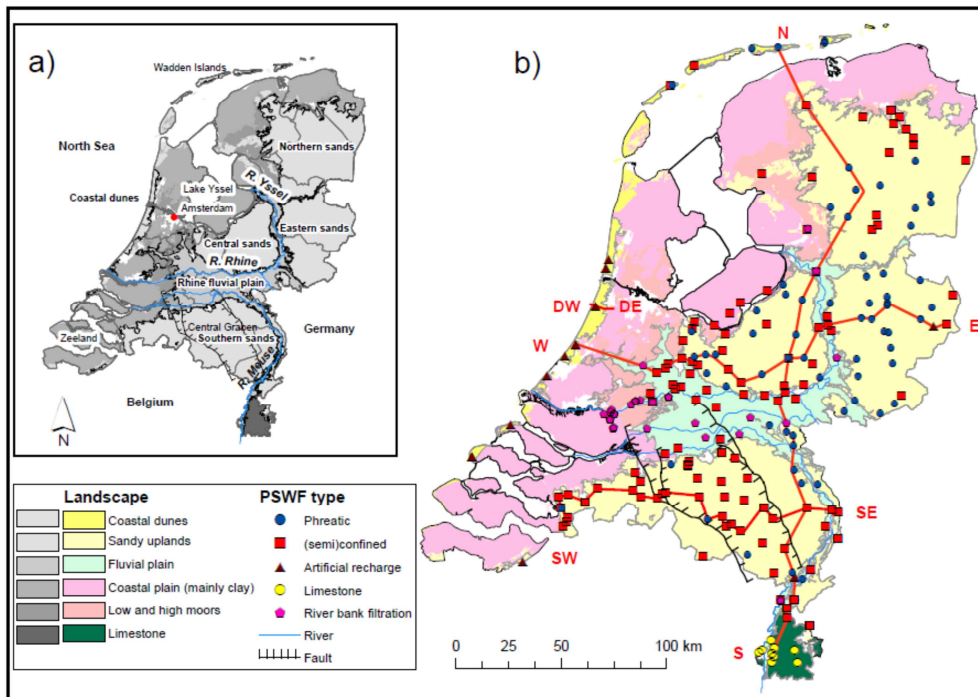


FIG. 2.1: Location map of (a) The Netherlands and (b) the 206 PSWFs active in 2008, their hydrological type (according to Table 2.1) and the main recharge areas of groundwater pumped for public drinking water supply (Mendizabal & Stuyfzand (2011)).

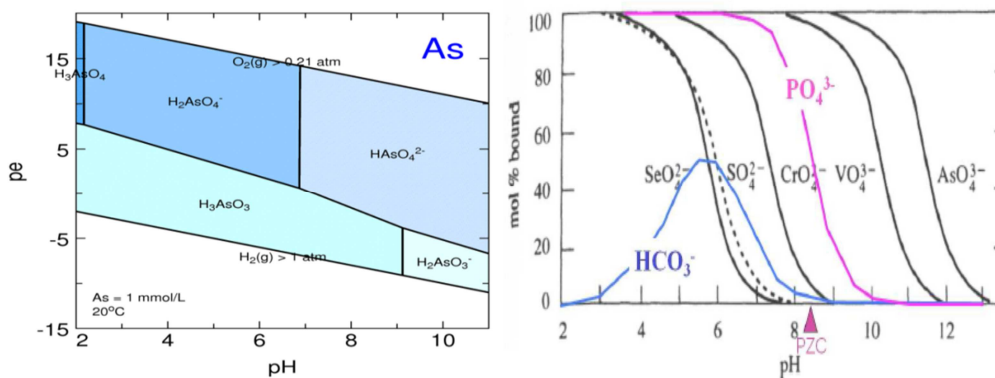


FIG. 2.2: Arsenic speciation and arsenate sorption. Left panel: Eh-pH diagram of aqueous As species in the indicated environment (from Smedley, 2008). Right panel: sorption of oxyanions (among which arsenate), to ferrihydrite as function of pH (Appelo 2008).

TABLE 2.2: Overview of the most probable arsenic mobilization processes in the Netherlands (modified after Stuyfzand et al. 2008).

No.	Mobilizing process	Trigger	Freq
1	Desorption	pH-increase, temp. increase, ?clay+peat compaction?	C
2	Ripening of ironhydroxides	Time, Increase of temp.	CC?
3	Anion exchange	Flushing with water high in PO ₄ , HCO ₃ or SO ₄ (low pH)	CC
4	Dissolution of As-minerals (like As ₂ S ₃)	Input CO ₃ ²⁻ in reduced environment --> complexation as: As(CO ₃) ₂ ⁻ , As(CO ₃)(OH) ₂ ⁻ , AsCO ₃ ⁺	RR
5	Oxidation of Fe-sulphide minerals + Elimination other O ₂ +NO ₃ -consumers + Prevention of sorption	High input of O ₂ and/or ##, Fe ²⁺ escaping from oxidation Low input of DOC, NH ₄ High input of PO ₄ , H ₄ SiO ₄ , HCO ₃ , SO ₄ , DOC, ?F?	CC
6	Reduction of AsO ₄ to H ₃ AsO ₃	High input of CH ₄ , H ₂ , labile DOC, H ₂ S (Fe ²⁺ low),	CC
7	Reduction of iron(hydr)oxides		

C? = probably frequent; C = frequent; CC = very frequent; RR = very rare.
= NO₃, O₃, Cl₂, NH₂Cl etc.

Iron and Cr(VI) are antagonists:

$$3 \text{Fe}^{2+} + \text{CrO}_4^{2-} + 5 \text{H}_2\text{O} \rightarrow 3 \text{Fe}(\text{OH})_3 (\text{s}) + \text{Cr}^{3+} + \text{H}^+$$

$$(1-x) \text{Fe}^{3+} + x \text{Cr}^{3+} + 3 \text{H}_2\text{O} \rightarrow \text{Fe}_{1-x}\text{Cr}_x(\text{OH})_3 (\text{s}) + 3 \text{H}^+$$

Oxidation of Cr³⁺ by O₂ very slow, catalysts needed, e.g.

$$\text{Cr}^{3+} + 1.5 \text{MnO}_2(\text{s}) + \text{H}_2\text{O} \rightarrow \text{HCrO}_4^- + 1.5 \text{Mn}^{2+} + \text{H}^+$$

Mobility high if: low pH for Cr(III), but high pH for Cr(VI)

Sources:

- Nat. ores (not in Neths): eskolaite (Cr₂O₃), chromite (Fe(II)Cr₂O₄), crocoite (PbCrO₄),
- Envir. Pollution: indus. Waste, stainless steel
- Clay minerals (Cr = 0.3 + 0.0016 Al, R² = 0.82): filtration bias

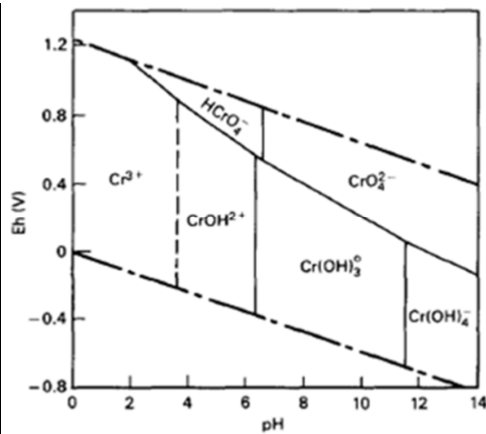


FIG.2.3: Chromium behavior in groundwater. Left panel: some facts and figures derived from Stuyfzand 2012). Right panel: Eh-pH diagram of aqueous Cr species without solid phases (from: Rai et al., 1989)

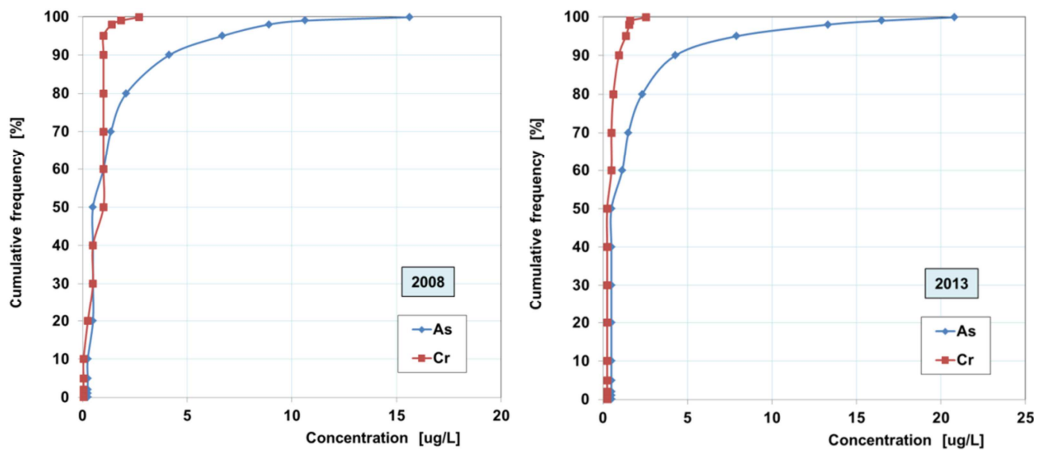


FIG. 2.4: Cumulative frequency distribution of total dissolved arsenic and chromium concentrations in the raw groundwater from 190 PSWFs in 2008 and 180 PWSFs in 2013. Data from REWAB database.

2.6 Overview of total dissolved As and Cr data from the 2008 campaign

2.6.1 Arsenic

The spatial distribution of As is shown in Fig.2.5 and the mean composition of the 5 groundwater resources in Table 2.4. The mean values for each groundwater type (0.3-

2.9 µg/L) were quite low, but there were 8 well fields with As concentrations >10 µg/L (Fig.2.5). These higher concentrations are observed in anoxic sand aquifers and deeply anoxic river bank filtration systems. The maximum value at the abandoned PSWF Oostrum (Fig.2.5) was associated with pyrite oxidation through excessive manure and fertilizer applications on an agricultural catchment area (Broers & Buijs, 1997). This situation was encountered in more well fields, like in Vierlingsbeek (a phreatic well field, discussed in detail by Stuyfzand et al., 2008).

Relatively high As concentrations (>10 µg/L) also correlate with abstraction from glauconitic sand aquifers of Late Tertiary age, such as Dorst and Klotputten in Fig.2.5. The exact mechanism behind this correlation is still unclear (Flink, 1985; Coetsiers, 2007), but the reductive dissolution of iron seems to be involved. Well fields pumping from cretaceous limestone typically have very low As concentrations (Table 2.4).

There are no clear relations between As on the one hand and PO_4 , SO_4 , HCO_3 , Fe, Cl, Mn and DOC on the other hand, but maximum concentrations correspond with pH 6-7.5, $\text{NO}_3 < 2$ and screen depths of 0-50 m-MSL (Stuyfzand et al., 2008).

The cumulative frequency distribution of total dissolved As concentrations in the raw water pumped by the 242 PSWFs in the Netherlands in 2008 for the 5 PSWF types discerned is shown in Fig.2.6.

TABEL 2.3: The top 31 PSWFs regarding their As and Cr concentration in the raw groundwater produced in 2013. Data based on REWAB. Green colored PSWFs were included in the 2014 sampling campaign, but ranked only for either As or Cr in the top 31; Orange = ditto but ranked for both As and Cr.

Rank	PSWF name	Type	As	PSWF name	Type	Cr
1	Almelo - Wierden	A	21.3	Pinkenberg	A	1.63
2	Loosdrecht	B	17.4	Zeist	B	1.58
3	Manderveen	A	14.3	Wezep (Boele)	A	1.55
4	Ouddorp	i	12.6	Arnhem - la Cabine	B	1.52
5	Breda - Dorst	B	12.0	Oldeholtpade	B	1.39
6	Hammerflïer	A	10.1	Epe	A	1.37
7	Laren I	A	9.4	De Haere	A	1.32
8	Oosterhout	B	6.6	Oosterbeek	B	1.14
9	Druten	U	6.0	Ruinerwold	A	1.00
10	Tilburg - Gilzerbaan	B	5.1	Havelterberg	A	0.97
11	Rhenen - Lijsterengh	B	4.8	Hammerflïer	A	0.92
12	Hooge Hexel	A	4.8	Harderwijk II	A	0.92
13	Beerschoten	B	4.4	Amersfoort Berg	A	0.82
14	Engelse Werk	U	4.3	Vlieland	A/B	0.81
15	Leersum	A	4.3	Amersfoortseweg - Ape	A	0.80
16	Lekkerker-Schuwacht	U	3.8	Archemerberg	A	0.78
17	Wageningse Berg	B	3.8	Leersum	A	0.77
18	St.Jansklooster	B/U	3.2	Doorn	A	0.72
19	Scheveningen	i	3.1	Ameland - Hollum	A	0.67
20	Zeist	B	3.1	Enschede-Weerselosew	i	0.66
21	Heumensoord	A	3.1	Driebergen	A	0.66
22	Sellingen	B	2.7	Putten	A	0.66
23	Bunnik	B	2.7	St.Jansklooster	B/U	0.62
24	Oldeholtpade	B	2.6	Hoenderlo	A/B	0.60
25	Ridderkerk - Kievitsweg	i	2.5	Rodenmors	B	0.54
26	Nieuw Lekkerland - de	i	2.5	Kamerik - Zegveld	U	0.54
27	Goor	A	2.4	Soestduinen	A	0.52
28	Veenendaal	B	2.4	Dalen - de Loo	A	0.50
29	Olden Eibergen	A	2.3	Assen	B	0.50
30	Havelterberg	A	2.2	Beilen	A	0.50
31	Arnhem - la Cabine	B	2.1	Leggeloo	A	0.50

A = phreatic groundwater; B = semiconfined groundwater; i = Artificially Recharged surface water; U = River Bank Filtrate.

2.6.2 Chromium

Chromium concentrations in the raw water of the Dutch PSWFs varied between <0.5 and 3.0 µg/L (Table 2.4). The highest values were observed for semi-confined PSWFs (type B; Eerbeek deep) and the lowest for PSWFs with artificial recharge (type I). Concentrations in pretreated infiltration waters for artificial recharge were already very low (≤ 1 µg/L), and clearly remained low during and after aquifer passage (Stuyfzand, 1991c, 2014).

The cumulative frequency distribution of the total dissolved Cr concentrations in the raw water pumped by the 242 PSWFs in the Netherlands in 2008 is shown for the discerned 5 PSWF types in Fig.2.7. The following outliers in the database were eliminated:

- 31.2 µg Cr/L for PSWF Hoenderloo shallow and 35.4 µg Cr/L for PSWF Hoenderloo deep, because (i) both also showed elevated levels of Mo (42-4.6 µg/L) and Ni (21.4-22.8 µg/L), indicating corrosion of stainless steel, and (ii) earlier data were always ~0.5 µg/L;
- 7.4 µg Cr/L for PSWF Schijf, because earlier data were always ~0.5 µg/L, while also an anomalously high Cr concentration of 0.64 µg/L was found (in all other PSWFs Cr <0.05 µg/L); and
- 3.5 µg Cr/L for PSWF Haren, because earlier data were always ~0.5 µg/L.

TABEL 2.4: Overview of composition of total-dissolved concentrations of arsenic and chromium in groundwater extracted by Dutch well fields for drinking water supply, in 2008. Based on sampling campaign by Mendizabal.

PSWF type	Unit	Sand and gravel				Lime-stone
		G		AR	RBF	
		Phreatic	Confined			
Number of samples		70	119	13	9	30
Mean land surface [m ASL]		20	12	11	2	80
Mean abstraction level [m BLS]		26-65	62-112	9-41	24-54	19-60
Age spectrum [y]		2-200	20-25000	0.1-0.3	1-50	2-200
EC 20oC	uS/cm	371	389	584	687	771
pH		7.01	7.25	7.60	7.25	7.03
Temp	oC	11.0	11.6	12.3	12.5	10.4
O2	mg/L	2.2	0.8	3.5	0.7	3.8
CH4	µg/L	0.7	2.7	0.0	1.1	0.3
Cl	µg/L	26.9	24.8	69.4	80.6	31.2
HCO3	µg/L	141	206	178	258	367
SO4	µg/L	41.1	11.6	58.9	40.1	62.8
NO3	µg/L	5.3	0.1	3.9	1.5	22.2
PO4	µg/L	0.44	0.71	0.30	1.70	0.16
Fe	µg/L	3.8	3.8	0.5	3.3	0.4
Mn	µg/L	0.23	0.17	0.11	0.47	0.01
Al	µg/L	23.5	1.9	1.8	2.2	0.7
As	µg/L	1.8	1.5	2.9	2.0	0.3
As-max	µg/L	13.2	26.3	7.6	7.4	<0.5
Cr	µg/L	0.6	0.4	0.3	1.1	0.4
Cr-max	µg/L	2.2	3.0	<0.5	1.9	0.9

G = fresh, autochthonous, actual groundwater; AR = artificially recharged; RBF = river bank filtrate.

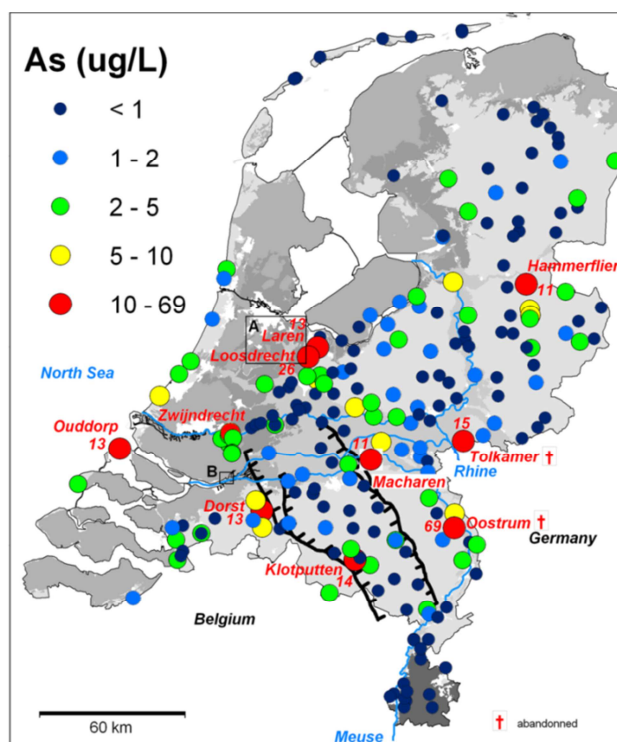


FIG. 2.5: Mean As concentrations in the raw water pumped by the 242 PSWFs in the Netherlands in 2008. Based on data from 2008 sampling campaign. Oostrum was abandoned around 2001 (As in 1997) and Tolkamer was abandoned around 2005 (As in 2003). As Ouddorp in 2013.

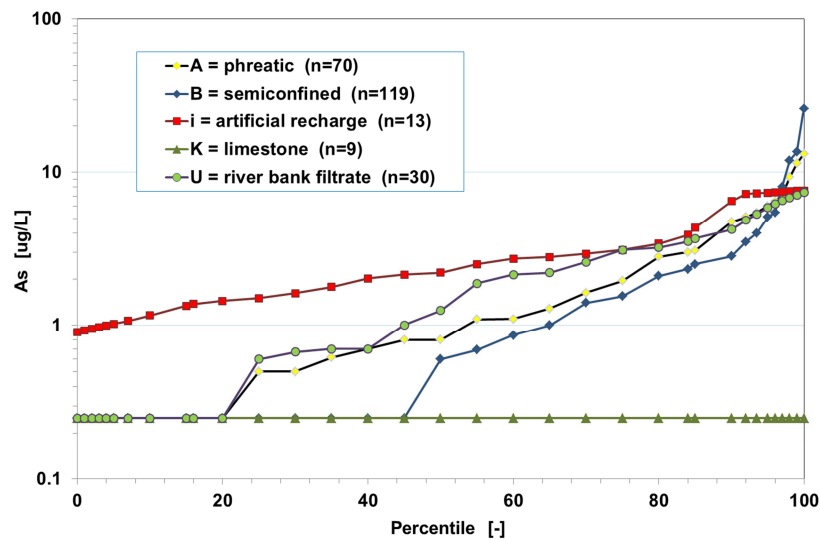


FIG. 2.6: Cumulative frequency distribution of total dissolved As concentrations in the raw water pumped by the 242 PSWFs in the Netherlands in 2008. Based on data from 2008 sampling campaign.

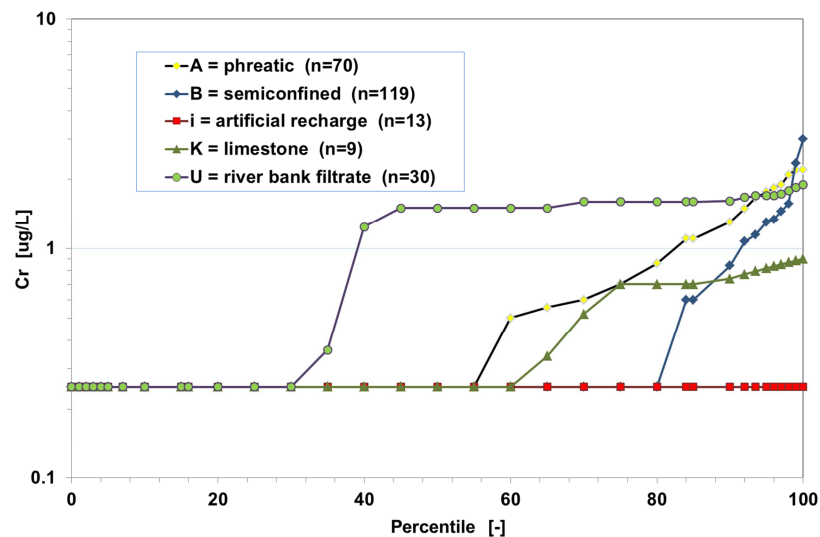


FIG. 2.7: Cumulative frequency distribution of total dissolved Cr concentrations in the raw water pumped by the 242 PSWFs in the Netherlands in 2008. Based on data from 2008 sampling campaign.

2.7 Chromium speciation data from RIVM's 1998 campaign

Cr(VI) data on the raw and treated water in the Netherlands were published by Jonker et al. (1998), and were further elaborated by Stuyfzand (2012). Their results are shown in Table 2.5, with distinction between water abstracted by PSWFs and surface water. Data were added on the main constituents, total dissolved Cr and Al and Ni, from the KIDAP database.

The following conclusions can be drawn from Table 2.5:

1. Iron and Cr form antagonists: PSWFs with Fe > approx. 1 mg/L show Cr-total \leq 0.5 and Cr(VI) < 0.2 µg/L.

- Cr(VI) in raw water is only present when O₂ and NO₃ are >1 mg/L, which is in line with the previous conclusion;
- Concentrations in raw and treated water do not differ much in most cases, indicating that aeration and rapid sand filtration do not remove Cr(VI). The data show that these processes might even convert Cr(III) into Cr(VI) by oxidation. More data are needed, however, to corroborate such an important conclusion. Doubts about this conclusion are based on the fact that possibly reduction of Cr(VI) also result from Table 2.5, and bias in sampling cannot be excluded because the sampling procedure was not clearly described in the RIVM report.
- Cr(VI) and total chromium do not differ much in most samples, indicating that Cr(VI) is the principal species there;
- The maximum Cr(VI) concentration encountered in the 17 PSWFs was 2.1 µg/L;
- In most cases where Cr(VI) was detected, the treated water contained a little more than the raw water;
- Surface water (only 2 samples) showed lower chromate contents than groundwater.
- PSWF Hoenderloo showed an anomaly in Cr, Ni and Mo in 2008, probably due to dissolution of stainless steel.
- The data set does not show a relation between pH and Cr, nor between depth and Cr.

TABLE 2.5: Overview of total dissolved chromium (Cr-tot) and total (unfiltered) chromate (Cr(VI)) concentrations in the raw water of 17 public supply well fields and 2 surface water intake points, with some further chemical characteristics. Chromate data derive from Jonker et al. (1998), the other data from the KIDAP database.

Raw waters for drinking water supply			Well screen			Cr(VI) ug/L		Raw (black = 2008; red = 1998)										
Name	Company	Type	LS	From	To	Raw	Treated	Cr-tot	pH	O ₂	NO ₃	SO ₄	Cl	HCO ₃	Fe	Al	Ni	
	1998		m ASL	m ALS	1998	1998	ug/L											mg/L
<i>Public Supply Well Field</i>																		
Arnhem, La Cabine	NUON	B	30	80	120	2.0	1.3	1.5	7.0	5.5	<0.06	14.8	16	87	0.04	1	0.4	
Baarn-van Reenenlaan	WMN	A	6	24	48	0.3	0.6	0.7	7.6	2.6	7.3	16.5	27	122	0.3	1	0.5	
Bilthoven	WMN	A	6	23	100	0.4	<0.2	<0.5	7.2	<1	2.3	18.3	20	78	0.76	12	0.8	
Boxmeer	WOB	A	15	9	15	<0.2	<0.2	0.5	6.7	-	0.5	101.3	40	241	8.94	2	1.7	
Driebergen mix	WMN	B	7	41	172	1.8	1.5	1.2	7.3	1.9	7.2	18.3	37	49	0.01	<1	0.2	
Grubbenvorst conv	WML	B	20	25	45	<0.2	<0.2	<0.5	6.6	0.1	<0.06	15.3	34	126	5.95	<1	2.1	
Herkenbosch	WML	B	49	60	170	<0.2	<0.2	-	6.8	<0.5	<0.5	<5	15	251	3.6	9	-	
Hoenderloo ondiep	NUON	A	60	40	70	<0.2	0.3	35.4	6.7	3.2	14.8	15.4	15	49	0.13	1	22.8	
Laren Mix	WMN	A	10.5	15	67	<0.2	<0.2	<0.5	7.3	1.6	0.1	12.7	31	185	3.34	2	4.1	
Leersum	WMN	B	10	42	68	<0.2	2.1	0.7	6.9	2.6	8.0	17.2	14	39	0.53	1	0.7	
Lichtenvoorde	WG	A	19	25	35	<0.2	<0.2	0.5	7.1	0.5	0.9	83.0	45	431	11.2	<5	<5	
Montferland, Galgenberg	WG	A	50	50	62	0.9	0.6	0.6	7.0	6.7	38.2	36.4	19	101	0.22	1	<0.2	
Oosterbeek	NUON	B	10	55	75	<0.2	1.1	1.1	7.3	2.0	<0.06	12.0	12	111	0.04	3	<0.2	
Soestduinen	WMN	A	7.5	33	93	0.4	0.6	1.3	7.1	2.2	4.2	21.1	17	88	-0.01	8	0.5	
Susteren diep	WML	B	30	95	230	<0.2	<0.2	<0.5	6.3	0.23	<0.06	5.1	4	90	3.94	<1	<0.2	
Vierlingsbeek	WOB	A	20	8	28	<0.2	<0.2	<0.5	5.9	2.0	15.5	154.6	29	25	9.18	920	90.0	
Zeist	WMN	B	6	60	76	<0.2	1.6	2.5	7.5	<1	3.8	21.4	20	90	0.36	1	1.6	
<i>Surface water</i>																		
WRK III (Prinses Juliana)	WRK	O				0.3	-	-	-	-	-	-	-	-	-	-	-	
A'dam-Weesperkarspel	GWA	O	-1.1	-2	-2	<0.2	<0.2	-	-	-	-	-	-	-	-	-	-	

ASL = Above Sea Level

ALS = Above Land Surface

LS = Land Surface

2.8 As and Cr speciation data from KWR's 2014 campaign

The results of the summer 2014 sampling campaign of 14 PSWFs are given in Table 2.6. They demonstrate that the higher As concentrations mainly refer to As(III) in (deeply) anoxic environment, and the higher Cr concentrations in most cases to Cr(VI) in (sub)oxic environment. It should be noted that low pH samples with potentially raised Cr(III) concentrations, were not included. A relatively high percentage of As(V) and Cr(VI) corresponds in most cases with a significant NO₃ and negligible Fe(II) concentration, as

expected. This is not true in all the samples, which could be explained by the mixing of aerobic with anaerobic groundwater in the PSWF, insufficient sample preservation, discrepancies between analytical techniques, and the filtration bias.

TABLE 2.6. Main results of the summer 2014 sampling of 14 PSWFs, in order of decreasing total dissolved As concentration. Cr-t1, Cr-t2 = total dissolved Cr analyzed by KWR and Vitens respectively. Green cells = Strong correspondence between As-tot and {As(III) + As(V)}, or between Cr-t1 and Cr-t2 values; Red cells = Weak correspondence between Cr-t1 and Cr-t2 values.

Loc	Type	Depth		EC	pH	NO ₃	Fe	Mn	Al	As-t	As(III)	As(V)	Cr-t1	Cr-t2	Cr(VI)	As(V)	Cr(VI)	
		m	+NAP															uS/cm
Loosdrecht	B	-35	-88	216	7.4	0.5	4.88	0.23	28	20.0	20	3.5	0.68					15
Breda - Dorst	B	-118	-183	366	7.6	0.5	1.43	0.04	13	10.0	10	0.9	0.22	0.51	0.03			8
Ouddorp	i	2	1	573	7.9	0.5	0.49	0.10	11	8.7	6.2	2.1	0.20	1.07	0.03			25
Oosterhout	B	-135	-190	383	7.6	0.1	1.19	0.05	15	5.3	5.7	0.4	0.16					7
Wageningse Berg	B	-37	-67	165	8.0	0.5	0.34	0.15	15	3.7	3.4	0.2	0.36					4
Leersum	A	-35	-60	225	6.8	31.3	0.32	0.02	31	3.6	2.7	1.4	0.62	0.71	0.53			34
Zeist	B	-51	-69	226	6.8	7.8	0.57	0.16	19	3.4	1.6	1.0	2.08	1.98	1.01			38
Scheveningen	i	0	-14	482	7.6	2.6	0.12	0.08	21	3.4	1.1	1.2	0.20	0.25	0.03			52
Lekkerker-Schuwacht	U	-14	-29	658	7.2	0.5	4.74	0.52	12	3.2	3.4	0.4	0.30	0.21	0.03			11
Plasmolen	A	5	-15	203	7.5	0.5	1.18	0.11	11	2.7	2.6	0.3	0.28	0.01	0.01			10
Veenendaal	B	-39	-116	351	7.9	0.5	0.37	0.05	16	2.4	1.6	0.2	0.30					9
Arnhem - la Cabine	B	-39	-93	201	7.3	14.1	0.05	0.04	25	2.0	0.4	0.5	1.42	1.25	1.09			56
De Haere	A	-17	-136	161	8.2	3.7	0.09	0.01	41	1.7	0.6	0.9	0.38	0.609	0.03			60
Pinkenberg	A	-41	-94	122	7.2	4.4	0.03	0.02	25	0.5	0.151	0.7	1.38	1.64	1.67			82

A = phreatic groundwater; B = semiconfined groundwater; i = Artificially Recharged surface water; U = River Bank Filtrate.

2.9 Capita selecta

2.9.1 Arsenic hotspots in the Netherlands

Stuyfzand et al. (2008) concluded that As did not menace drinking water supply at the scale of well fields, because (i) the drinking water MCL was 10 µg/L at that time (and still is), and (ii) groundwaters with higher As levels contained sufficient Fe(II) to get the As concentration of the treated waters below that MCL, upon aeration and rapid sand filtration. It was also concluded, however, that there were several situations, on a local scale, that were clearly pointing at a strong As mobilization (up to 1,500 µg/L) which could affect drinking water or its treatment on the long term. This field evidence was derived from detailed studies of the following young hydrological systems in sandy aquifers of Quaternary age: (i) a partly decalcified, pumped aquifer system with strong agricultural inputs (PSWF Vierlingsbeek); (ii) artificial recharge using basins (PSWF Leiduin and Scheveningen), (iii) artificial recharge using injection wells (a pilot near Langerak), (iv) river bank filtration in the Hollandsch Diep, and (v) a polder system south of Amsterdam City, composed of a reclaimed lake surrounded by an influent eutrophic river, and underlain by Holocene peat.

The most probable As mobilizing processes in the systems i-v were: raised NO₃ inputs on agricultural plots underlain by a pyritiferous aquifer (i); the introduction of O₂ and NO₃ containing surface water into deeply anoxic aquifers containing pyrite (ii-iii); (sub)recent changes in quality of infiltrating river water (ii, iv), especially regarding rises of PO₄, SO₄, HCO₃, DOC, F and temperature (which all contribute to desorption of As); (sub)recent mud accumulations in infiltrating parts of lakes, rivers and recharge basins (ii, iv) where the oxidation of fresh organic matter is producing a lot of CH₄ which may reduce iron(hydr)oxides and arsenate (to arsenite), and is also producing a lot of PO₄, HCO₃ and DOC which compete for sorption sites with As; and the reductive dissolution of iron(hydr)oxides plus desorption in peat rich polder areas (v) where the oxidation of peat is also producing elevated quantities of CH₄, PO₄, HCO₃ and DOC.

2.9.2 Chromium hotspots in the Netherlands

Shallow, coastal dune groundwaters (<5 m below groundwater table) normally show low Cr concentrations (<1 µg/L), but in decalcified dunes with pH<6 Cr concentrations were observed to rise up to 12 µg/L (Stuyfzand, 1991d). These values correspond with Cr concentrations observed in LMG, the national monitoring network of groundwater between 9 and 25 m below ground level (RIVM, 1992). According to Boumans & Fraters (1993) Cr concentrations in shallow groundwaters in the Netherlands show a positive correlation with land use by (intensive) agriculture, mixed forests and grass lands, atmospheric SO_x deposition, total dissolved solids and concentrations of SO₄, DOC and Al, and a negative correlation with depth and pH.

2.9.3 Filtration and corrosion bias

Stuyfzand (1987) observed that total dissolved Cr is very susceptible to filtration bias. When water samples are preserved for later analysis by acidification, suspended material has not always been sufficiently eliminated by filtration over a 0.45 µm membrane filter. Filtration bias is easily identified by raised dissolved Al concentrations in samples that otherwise should have a very low Al concentration (<10 µg/L), as is normally the case with pH 6-8. The Al is an indicator then of Al-silicates like clay minerals, that passed the filtration step and (partly) dissolved in the acidified sample. Elevated levels of Ni and Cr should be mistrusted in case of stainless steel wells due to corrosion effects (Oakley & Korte, 1996).

Stuyfzand et al. (2014) noticed that also total dissolved As is also very susceptible to filtration bias. This is not linked to Al, however, but to iron which is an indicator of iron hydroxide flocks (Fe(OH)₃), that passed the filtration step and (partly) dissolved in the acidified sample. This situation arises most frequently when those pumping wells or drains are sampled, that discharge a mix of aerobic (O₂ containing) and anaerobic (Fe(II) containing) groundwater.

2.9.4 Raised arsenic levels in basin recharge PSWF Ouddorp

At PSWF Ouddorp, AR has been applied as of 1955. The infiltration water was composed of untreated polder water (1955-1972), an untreated mixture of polder and Haringvliet water (1972-1993), untreated Haringvliet water (1993-1995) and pretreated Haringvliet water (1995-today). In 2007 an alarming rise of As concentrations was noticed in the raw water, which is continuing till today. The level rose from ~3 µg/L in the year 2000 to ~13 µg/L in 2013, and simultaneously the Fe, Mn, NH₄ and PO₄ concentrations increased as well (Fig. 2.7). A very similar As peak concentration had shown up already in 1983, also together with high Fe, Mn, NH₄ and PO₄ concentrations (Fig. 2.7). The As increase in the period 2000-2013 could be linked to ecological renovation works in 2000, which aimed at the creation of broader and morphologically more varied recharge basins and at a rise of groundwater tables in the recharge area. The groundwater table rise caused the recharged aquifer to become more anoxic, as evidenced by the increasing Fe, Mn, NH₄ and PO₄ concentrations. This resulted in increasingly more reductive dissolution of iron (hydr)oxides from which the As was mobilized. A nice seasonal pattern in this reductive dissolution can be observed, showing As peaks in late summer or autumn when temperature is highest and NO₃ lowest due to more denitrification (Fig. 2.8).

The upward trend in As concentrations also correlated with a decreasing trend in O₂ concentrations, an upward trend in temperature, HCO₃ and TOC concentrations, and a decreased infiltration rate. Concentrations of As, Fe and PO₄ increased by about the same factor (4) in the period 2000-2013: As from 3 to 13 µg/L, Fe from 0.25 to 1.0 mg/L and PO₄-total from 0.06 to 0.24 mg/L. Mo and V showed a positive correlation with As peaks, in 12 observation wells, contrary to Co and Zn which showed a negative correlation. This indicates

that Mo and V (both oxyanions) could be bound to $\text{Fe}(\text{OH})_3$ and codissolve with it under reducing conditions. See Stuyfzand et al. (2014) for more details.

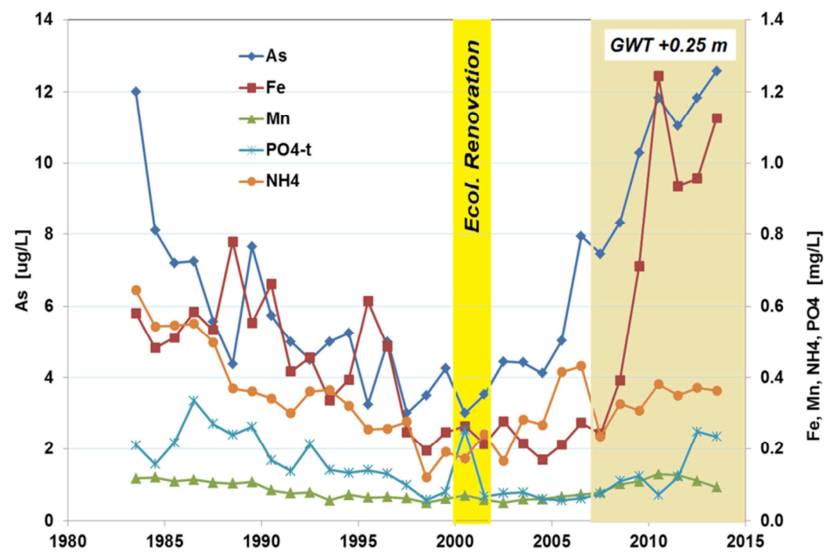


FIG. 2.7: Annual mean concentrations of As, Fe, Mn, NH_4 and PO_4 in the period 1983-2013, for the raw water recovered from artificial recharge area Ouddorp (from Stuyfzand et al., 2014)

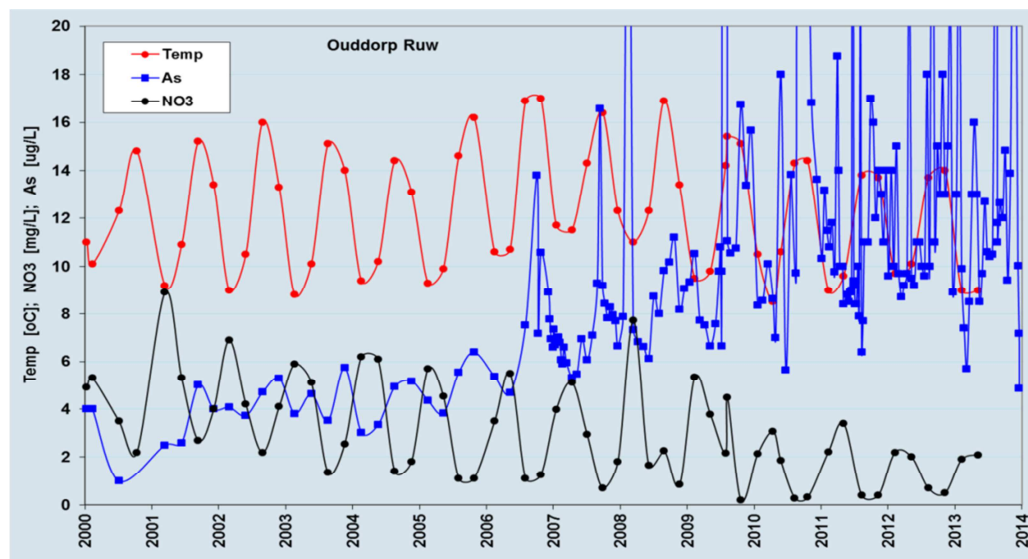


FIG. 2.8: Seasonal fluctuations in concentrations of As, Fe, Mn, NH_4 and PO_4 in the period 2000-2013, for the raw water recovered from artificial recharge area Ouddorp (from Stuyfzand et al., 2014)

2.9.5 Arsenic does not come alone!

The above discussed Ouddorp case showed that As did not come alone, but was accompanied by various water quality parameters that indicate more anoxic conditions: a rise of $\text{Fe}(\text{II})$, $\text{Mn}(\text{II})$, NH_4 , PO_4 , HCO_3 and DOC concentrations and a decline of O_2 , NO_3 and SO_4 concentrations. In addition, the concentrations of Mo and V (oxyanions as As) increased where As peaked.

In another artificial recharge area, the one south of Zandvoort (PSWF Leiduin), the reductive dissolution of ferrihydrite formed a very strong source of As as demonstrated by the synchronous As and Fe mobilization and denitrification in infiltrated Rhine water (Fig.2.9). The Mo pattern in Fig.2.9, however, does not show such behavior, because the main source is the infiltrated Rhine River water. The migration of both As and Mo is clearly halted where SO_4 reduction is taking place, As at an earlier stage than Mo (Fig.2.9). Their coprecipitation with pyrite in deeply anoxic environments is well documented (Edmunds & Shand 2008; Smedley et al. 2014). While pyrite is still being formed in aquifer layers b, 1B, c and 2, it is oxidized upgradient in the suboxic parts of aquifer 1A (below the dune sand). This pyrite is known to contain significant amounts of As, Co, Ni and Zn, that upon pyrite oxidation are immobilized directly at the current pH (7-8) by sorption to the neofomed ferrihydrite precipitate (Stuyfzand 1998; Stuyfzand et al. 2008). Indeed, no mobilization of these TEs is noticed where pyrite is being oxidized in a calcareous environment.

At shallower depth, where the presence of NO_3^- is indicating (sub)oxic conditions, a clear U peak is found, deriving from Rhine River water and from a geogenic source (probably $\text{Fe}(\text{OH})_3$). This U is probably mobilized as $\text{UO}_2(\text{CO}_3)_2$ in the suboxic zone and immobilized as UO_2 after complete denitrification (Fig.2.9).

It can be concluded from the patterns displayed in Fig.2.9, that As and Mo may show up together in AR systems with a significant Mo input, but that As is showing a more restricted zone of peaking because it is more sensitive to sorption in (sub)oxic environment and more sensitive to coprecipitation with iron sulfides.

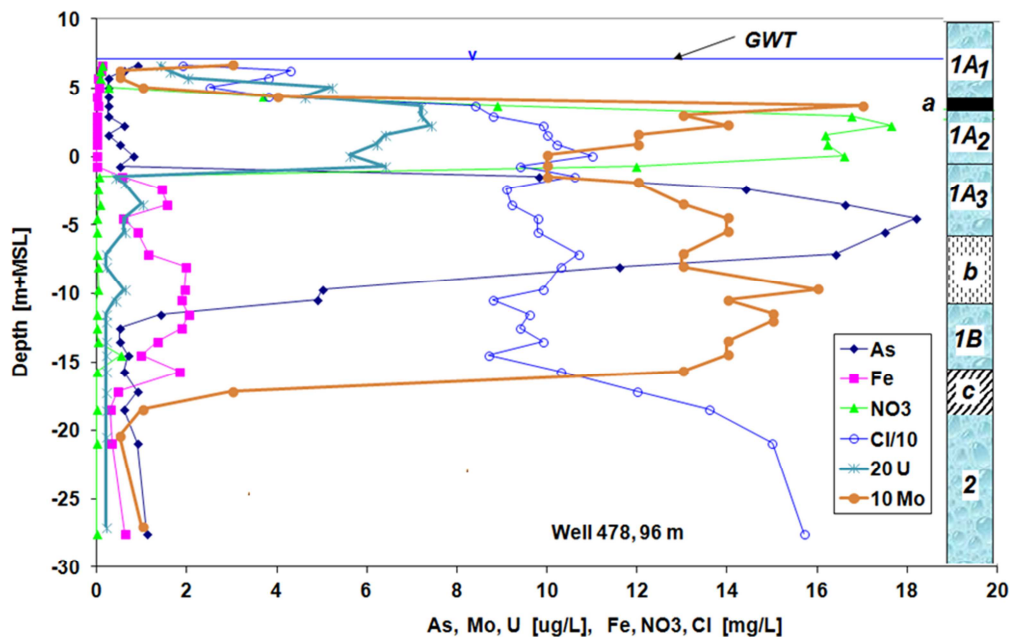


FIG. 2.9: Hydrochemical profile in monitor well 478 at 96 m from an infiltrating supply channel in the Amsterdam dune catchment area, sampled in 2007 (from Stuyfzand, 2014). Suboxic dune groundwater is observed in layer 1A1, on top of infiltrated Rhine River water in all layers below. Nitrate reduction is completed near the boundary between layers 1A2 and 1A3, and partial sulfate reduction is taking place mainly in layers b, 1B and c. GWT = Ground Water Table. Legend to lithological column: 1A1-1A3, 1B, 2 = sand; a = peat; b = silt; c = clay.

2.10 Conclusions

Total dissolved As concentrations in raw waters in the Netherlands, pumped for public drinking water supply, ranged in 2013 from 0.1-21 µg/L, and those for total dissolved Cr ranged from <0.1-3 µg/L. The REWAB database reveals that, in 2013, 47, 13.5, 6.7 and 4 % of 190 public supply well fields (PSWFs) showed As levels above 1, 3, 5 and 10 µg/L, and 44, 8 and 0.5% showed Cr levels above 0.3, 1 and 2 µg/L. Consequently, if the MCL of drinking water would be lowered from 10 to 3 µg As/L and from 50 to 0.3 µg Cr(VI)/L, then the percentage of PSWFs with As and Cr(VI) concentrations above the MCL would rise from 4 to 13.5% (As) and from 0 to maximum 44% (Cr). The strong rise for Cr(VI) is biased, however, by the high number of PSWFs with Cr concentration below the reported minimum detection limit (often 0.5 µg/L).

The summer 2014 sampling campaign demonstrates that the higher As and Cr concentrations mainly refer to arsenite (As(III) as H_3AsO_3) in (deeply) anoxic environment, and chromate (Cr(VI) as CrO_4^{2-}) in (sub)oxic environment. This is in line with earlier studies and expected hydrogeochemical behavior.

Arsenic hotspots are mainly localized where the hydrological system was (sub)recently disturbed, mainly by (1) a drawdown or rise of the groundwater table, (2) a quality change of the infiltration water (especially an increase of PO_4 , SO_4 , HCO_3 , DOC, F, temp), (3) accumulation of anoxic muds in infiltrating rivers, basins, lakes etc., and (4) the genesis of reducing gasses, notably CH_4 . Glauconite containing aquifers may also form an As hotspot.

Arsenic does not come alone. Most cases of As peaking relate to reductive dissolution of iron (hydr)oxides, producing concomitant, high concentrations of Fe, Mn, SiO_2 , PO_4 , HCO_3 and DOC, and also of Mo and V in case of AR or RBF when the infiltration water showed a relatively high input concentration. In case of pyrite oxidation, As peaks can be accompanied by Ni, Co and Zn if pH is 5-6, but the area affected is relatively small.

Chromium hotspots are mainly related to (1) local pollution sources such as steel, textile, leather or cement industries, and (2) a low pH in connection with intensive agriculture, forest stands and shallow groundwater.

Bias was observed for both Cr and As data, in several cases. Too high concentrations were due to insufficient filtration of suspended fines (clay particles in case of Cr, and iron (hydr)oxide flocks in case of As), and due to corrosion of stainless steel in case of Cr.

2.11 Recommendations

The following research questions on trace elements in groundwater are considered relevant:

1. Are there any trends in the Fe/As-ratio in the groundwater recovered? The Fe/As ratio is an important parameter in the removal potential of aeration followed by rapid sand filtration.
2. Are there important spatial patterns in the concentrations of As and Cr within well fields? If so, then their concentration could be influenced by changing the spatial pumping regime.
3. How does As behave in SIR (Subterranean Iron Removal) and ASR (Aquifer Storage Recovery) systems, and can this behavior be influenced?
4. How can we reduce conflicting interests of ecohydrological optimization measures within a groundwater catchment area and measures to minimize the As response of a well field? This is especially relevant to basin artificial recharge areas.
5. Can we develop a risk index and screening parameter for As and Cr?

6. Which concentrations are observed for less studied trace elements like Hg, Mo, Se, U, and V in groundwater resources, and under which conditions do their concentrations peak or decline to below MCL.

2.12 Acknowledgements

This study was carried out within the framework of the Joint Research Program (BTO) of the Dutch Waterworks, which is carried out by KWR Watercycle Research Institute (KWR). Harald Dik and Ans Versteegh, both from RIVM, are greatly acknowledged for their help in providing the 2008-2013 data from the REWAB database. Meindert de Graaf took the samples during KWR's sampling campaign in 2014.

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3 Arsenic and Chromium Concentrations and Speciation in the Drinking Waters supplied in the Netherlands

Author: Arslan Ahmad

3.1 Introduction

Elevated arsenic (As) and/or chromium (Cr) concentrations in drinking water supplies is a serious issue. The toxicity of both As and Cr depends upon the oxidation state in which these substances are present in water. The World Health Organization (WHO) and other prominent authorities such as United States Environmental Protection Agency (USEPA) and the European Union (EU) regulate total As and total Cr in drinking water supplies, irrespective of in whatever speciation they are present in water. At present, the WHO recommends 10 µg/L as a guideline value for total As in drinking water and 50 µg/L as a guideline value for total Cr in water. Both these guidelines are designated as provisional because of the uncertainties in the toxicological databases.

In the Netherlands, drinking water is of top quality and As and Cr concentrations in the produced drinking water are well below the Dutch maximum concentration limits (MCLs). The subject of exposure to low As and Cr concentrations is currently in discussion and the latest toxicological findings are being reviewed to find a threshold below which the As and Cr concentrations do not pose any risk to the health of the consumers. Although nothing concrete may be concluded yet from these developments and more information is still needed on the potential adverse health effects of low As and Cr concentrations, obtaining an overview of the drinking water quality in relation to As and Cr concentrations is pertinent.

This chapter provides an overview of the As and Cr concentrations and speciation in the drinking water supply in the Netherlands. The inventory has been based on the REWAB (Registratie opgaven van Drinkwaterbedrijven) database (2008-2013), input from the Dutch drinking water companies and a dedicated sampling campaign which was undertaken in August 2014 by KWR.

3.2 Materials and methods

The inventory has been based on REWAB national database, recent sampling (independent research) data from the drinking water companies and a dedicated sampling campaign at 14 selected locations performed by KWR in 2014. To start with, the REWAB database (2008-2013) was analyzed and the DWPLs with As concentrations > 1 µg/L and Cr concentrations > 0.5 µg/L were screened-out. Since the REWAB database did not include information on the speciation of As and Cr, a post selection of DWPLs was made in consultation with the drinking water companies to investigate the speciation and gain most recent As and Cr effluent levels. The post-selection resulted in a group of 14 DWPLs across the Netherlands where either effluent As concentration was > 1 µg/l or effluent Cr concentration was > 0.5 µ/L or both were above the indicated thresholds. Treated water samples were collected at the 14 locations for a broad scan of the inorganic chemical composition, including trace

elements (including As(III), As(VI), As-total, Cr(III), Cr(VI) and Cr-total) and the main constituents.

3.2.1 The REWAB national database

The REWAB database contains information on the quality of raw water, drinking water and water at the tap, from all drinking water production locations (DWPLs)/drinking water treatment plants (DWTPs) in the Netherlands. It is based on the data supplied by all the Dutch drinking water companies since 1992 and is managed jointly by RIVM and KWR. In this project the data on the annual mean inorganic quality of raw water from all the active DWPLs in the period 2008-2013 have been used. The data on As and Cr refer to total dissolved concentrations, with minimum quantification limits (MQLs) of 0.1-1 µg/L for both As and Cr. The database does not provide information on the speciation of As and Cr.

3.2.2 Data from the water companies

Many of the Dutch drinking water companies have recently initiated independent research activities focusing on As and Cr concentrations in their drinking water supplies. For example, Brabant Water and Evides carried out independent sampling campaigns for As at Dorst and Ouddorp respectively. Similarly, Vitens is monitoring both As and Cr concentrations and speciation in the drinking water streams. In order to support the inventory in this study, the drinking water companies were requested to share the results of their independent sampling campaigns at the selected location. Furthermore, a Questionnaire (see Appendix) was sent to the water companies which included specific questions about the raw water sources and the treatment processes applied at the 14 selected locations. Data on As and Cr concentrations and responses to the Questionnaire were received from all the locations.

3.2.3 The sampling campaign of 2014

In August 2014, KWR organized a restricted national sampling campaign, in which 14 active DWPLs were visited and samples were obtained from treated waters/plant effluents (Fig. 3.1) for subsequent broad scan of the inorganic chemical composition, including trace elements (As(III), As(VI), As-total, Cr(III), Cr(VI) and Cr-total) and the main constituents. The selection was based on a pre-selection of the 2008-2013 REWAB and a post-selection to minimize sampling efforts and costs, in consultation with the drinking water companies. The treated water samples for the determination of metals (including As and Cr) were not filtrated in the field over 0.45 µm, however, acidified and cooled for preservation, and their total dissolved concentrations were analyzed via ICP-MS after destruction. The treated water samples for the speciation of As and Cr were filtered over the 0.45 µm filters and then preserved in especially designated bottles supplied by AquaLab Zuid (for As speciation) and Vitens laboratory (for Cr speciation). The description of the speciation methods used may be obtained from the respective laboratories.

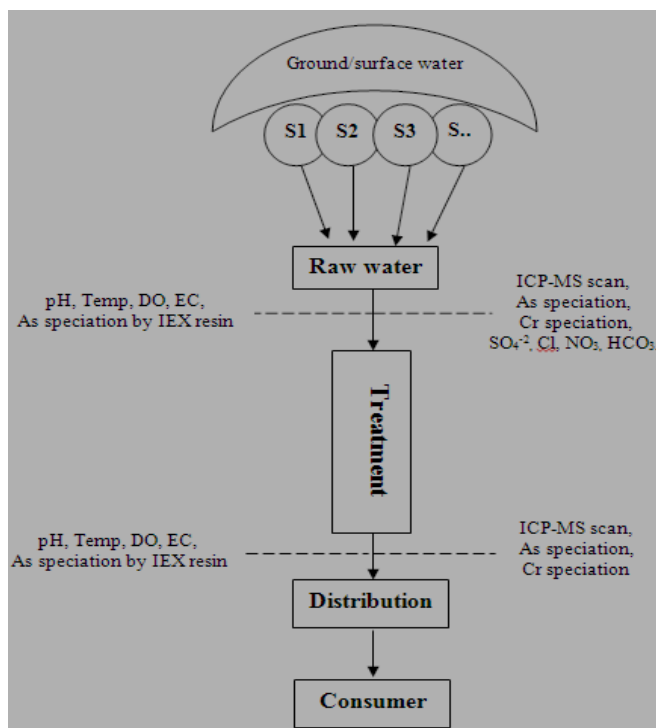


Figure 3.1: Sampling points and measured parameters

3.3 Results and discussion

3.3.1 Overview of arsenic concentrations based on REWAB database (2008-2013)

The REWAB database was reviewed to obtain an overview of total As concentrations in the effluents of the DWPLs across the Netherlands. The database included drinking water quality data from 189 locations in 2008, 182 locations in 2009, 179 locations in 2010, 177 locations in 2011, 176 locations in 2012 and 172 DWPLs in 2013 (Table 3.1). The mean total As concentration is quite consistent in the reviewed period (2008-2013) and is $<1 \mu\text{g/L}$. The minimum and maximum total As concentrations in these years also remain consistent (Table 3.1). The maximum total As concentration in the effluents of Dutch DWPLs is $6.1 \mu\text{g/L}$ which is lower than the MCL of As in the Netherlands, EU and the current WHO recommendation ($10 \mu\text{g/L}$).

The REWAB database shows that from the 180 DWPLs (average), 28 produce drinking water with $>1 \mu\text{g/L}$ total As, 10 produce drinking water with $>2 \mu\text{g/L}$ total As, 4 produce drinking water $>3 \mu\text{g/L}$ total As and 2 DWPLs produce drinking water with $>5 \mu\text{g/L}$ total As (Fig. 3.2). In other words, 16 % of the total number of DWPLs produce effluent with $>1 \mu\text{g/L}$ As, 6 % produce effluent with $>2 \mu\text{g/L}$ As, 2 % produce effluent with $>3 \mu\text{g/L}$ As and only about 1 % of the total number of DWPLs produces effluent water with $>5 \mu\text{g/L}$ As.

In general, the Dutch drinking water companies maintain an internal MCL of 50 % for any regulated substance in the drinking water. It means that for As the drinking water companies voluntarily aim at maintaining an arsenic level of $\leq 5 \mu\text{g/L}$. This is well-reflected in the statistics shown (Fig 3.2), however, at DWPLs Dorst and Ouddorp the effluent As concentrations are above $5 \mu\text{g/L}$. Based on the REWAB database, a list of all the DWPLs with the effluent As concentrations above $1 \mu\text{g/L}$ was formed (Table 3.2). DWPL Dorst (Brabant Water) is currently being optimized with a target to produce drinking water with a total As

concentration below 1 µg/L (for details, see Ahmad, 2014 and Ahmad et al., 2014). The situation at the DWPL Ouddorp has been described in chapter 2 of this report.

An overview of As removal (in terms of percentage) at the 28 DWPLs with effluent As concentration > 1 µg/L has been provided (Table 3.3). It was noticed that the DWPLs having higher iron (Fe) content in the source waters removed As to a greater extent compared to the DWPLs using raw waters with low Fe content. For example, at the DWPL Loosdrecht, where the source water contains the highest Fe content in the Netherlands, approximately 90 % of the total As gets removed during conventional groundwater treatment. Figure 3.3 further demonstrates the relationship between the raw water Fe content and the As removal achieved. The data points in Figure 3.3 represent (selected) DWPLs in the Netherlands. In general, Fe-(hydr)oxides are considered as a resource for removing As from the drinking water supplies. A detailed description on Fe based As removal technologies has been provided in chapter 4 of this report.

In relation to the REWAB database, it must be noted that during the period 2008-2013, the minimum quantification limit (MQL) for As was lowered from 2 µg/L to 1 µg/L by the laboratories. It resulted in a challenging situation during data interpretation and gaining a concrete statistical overview. For the sake of statistical overview the concentrations reported in the database as <x µg/L were converted to x/2 µg/L and then used in the calculations.

Table 3.1: Total arsenic concentrations in the effluents of Dutch drinking water production locations (DWPLs) from 2008 to 2013.

Arsenic (µg/L)	Year 2008	Year 2009	Year 2010	Year 2011	Year 2012	Year 2013
N*	189	182	179	177	176	172
Min	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Mean	0.71	0.75	0.75	0.75	0.75	0.76
Max	6.00	5.4	6.0	6.10	5.9	5.9
*Number of sampled locations						

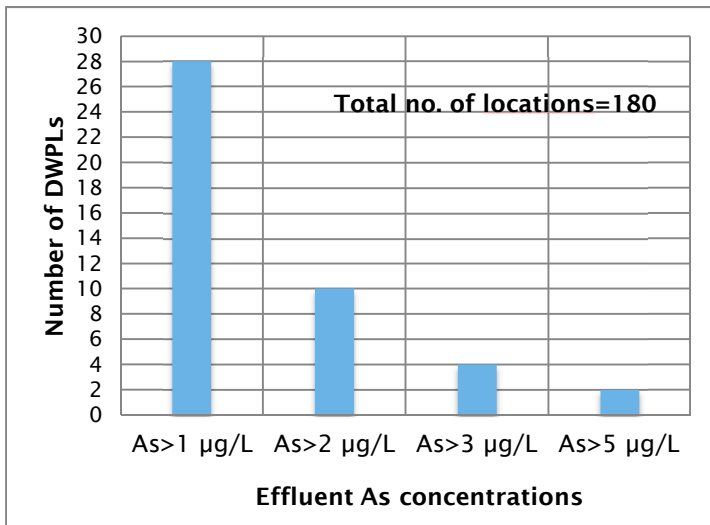


Figure 3.2: Number of DWPLs with elevated As concentrations in the produced water in the Netherlands.

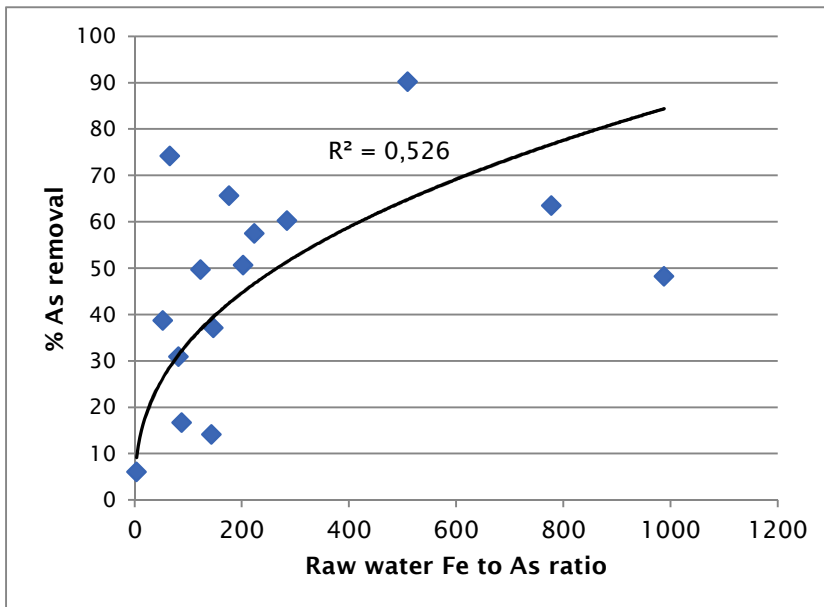


Figure 3.3: Relation between raw water Fe/As ratio and % As removal at selected Dutch DWPLs.

Table 3.2: List of 28 DWPLs with effluent As > 1 µg/L.

DWPLs	Year 2008	Year 2009	Year 2010	Year 2011	Year 2012	Year 2013	Average effluent As (µg/L)
Breda - Dorst	5.6	5.4	5.8	6.1	5.9	5.9	5.8
Ouddorp	6.0	5.0	6.0	4.2	5.2	5.5	5.3
Oosterhout	3.6	3.4	3.9	3.7	3.3	3.2	3.5
Wageningse Berg	3.1	3.1	3.3	2.9	2.9	3.0	3.1
Leersum	3.1	3.1	2.6	3.0	2.9	2.8	2.9
Monster	3.3	3.1	2.8	2.6	2.6	2.6	2.8

Speuld	2.5	2.6	2.4	2.5	2.6	2.4	2.5
Katwijk	2.6	2.4	2.5	2.4	2.5	2.2	2.4
Prinsenbosch	1.9	2.1	2.4	2.7	2.5	2.3	2.3
Manderveen	0.5	1.4	1.8	2.9	2.7	3.2	2.1
Loosdrecht	1.7	1.9	1.8	2.0	1.9	2.0	1.9
Elburg	1.6	2.1	1.7	1.8	NA*	NA	1.8
Scheveningen	1.9	1.7	1.7	1.7	1.8	1.8	1.8
Tilburg - Gilzerbaan	1.5	1.6	1.8	1.6	1.8	1.9	1.7
Veenendaal	1.9	1.8	1.6	1.5	1.5	1.6	1.6
Beerschoten	1.2	1.3	1.5	1.6	1.9	1.7	1.5
Lekkerker-Schuwacht	1.5	1.3	1.5	1.4	1.5	1.4	1.4
Plasmolen	0.5	1.7	1.7	1.4	1.7	1.5	1.4
Nieuw Lekkerland - de Put	1.5	1.7	1.2	1.4	1.2	1.3	1.4
Bilthoven	1.4	1.5	1.3	1.3	1.2	NA	1.4
Zeist	1.4	1.0	1.3	1.4	1.4	1.4	1.3
Arnhem - la Cabine	1.1	1.5	1.0	0.5	1.8	1.8	1.3
Haamstede	1.0	1.0	1.0	1.4	1.5	1.5	1.2
Welschap	NA	1.1	NA	1.4	1.5	0.5	1.1
Edese Bos	0.5	0.5	1.6	1.4	1.3	1.3	1.1
Zwijndrecht - Ringdijk	1.5	1.4	NA	NA	0.5	NA	1.1
Soestduinen	1.3	1.2	1.2	1.3	0.5	1.2	1.1
Harderwijk II	0.5	1.3	1.3	1.3	1.1	1.0	1.1
Montferland (dr.J.v.Heek)	1.3	0.5	1.3	1.2	0.5	1.5	1.0

*NA=Data not available

3.3.2 Overview of chromium concentrations based on REWAB database (2008-2013)

The REWAB database was reviewed to obtain an overview of total Cr concentrations in the effluents of the DWPLs across the Netherlands. The database included drinking water quality data from 189 locations in 2008, 182 locations in 2009, 179 locations in 2010, 177 locations in 2011, 176 locations in 2012 and 172 DWPLs in 2013 (Table 3.4). The mean Cr concentration is quite consistent in the period of 2009-2013 and is <0.5 µg/L. However, in 2008, a mean concentration of 0.63 µg/L has been observed which is higher than the rest of the reviewed period. This can be attributed to the higher MQL for total Cr (2 µg/L) that was lowered by the laboratories to 1 µg/L and subsequently to 0.5 µg/L after 2008. The minimum Cr concentration in these years has been consistently <0.5 µg/L. A much lower minimum Cr concentration of 0.05 µg/L in the 2008 corresponds to measurements at Vitens Laboratories where sometimes special analysis methods are used during internal research activities. As discussed in case of arsenic, for total Cr also the changing MQLs in the period 2008-2013 resulted in difficulties to obtain the statistical overview. It can be observed from Table 3.4 that the maximum total Cr concentrations in the effluents of DWPLs range from 1.6 µg/L to 3.1 µg/L. These concentrations are much lower than the MCL of total Cr in Dutch drinking waters, EU and the current WHO recommendation.

Table 3.3: Arsenic removal efficiency of the 28 DWPLs with > 1 µg/L effluent As concentration.

DWPLs	Average As conc. in the source water (µg/L)	Average As conc. in the treated water (µg/L)	As removal (%)

Breda - Dorst	11.5	5.8	49.7
Ouddorp	12.5	5.3	57.5
Oosterhout	6.6	3.5	46.7
Wageningse Berg	3.7	3.1	16.7
Leersum	4.2	2.9	30.9
Monster	4.5	2.8	37.0
Speuld	NA*	2.5	-
Katwijk	3.6	2.4	32.4
Prinsenbosch	3.9	2.3	40.6
Manderveen	8.1	2.1	74.2
Loosdrecht	18.9	1.9	90.2
Elburg	3.4	1.8	46.5
Scheveningen	2.4	1.8	27.0
Tilburg - Gilzerbaan	4.3	1.7	60.3
Veenendaal	1.9	1.6	14.1
Beerschoten	4.4	1.5	65.6
Lekkerker-Schuwacht	3.9	1.4	63.5
Plasmolen	NA	1.4	-
Nieuw Lekkerland - de Put	2.7	1.4	48.2
Bilthoven	2.5	1.4	45.2
Zeist	2.7	1.3	50.7
Arnhem - la Cabine	2.1	1.3	38.7
Haamstede	NA	1.2	-
Welschap	3.3	1.1	65.9
Edese Bos	NA	1.1	-
Zwijndrecht - Ringdijk	4.3	1.1	74.2
Soestduinen	1.2	1.1	8.3
Harderwijk II	1.2	1.1	6.1
Montferland (dr.J.v.Heek)	1.7	1.0	37.1
*NA=Data not available			

Table 3.4: Chromium concentrations in Dutch drinking waters from 2008 to 2013.

Cr (µg/L)	Year 2008	Year 2009	Year 2010	Year 2011	Year 2012	Year 2013
N*	189	182	179	177	176	172
Min	0.05	<0.5	<0.5	<0.5	<0.5	<0.5
Mean	0.63	0.46	0.45	0.45	0.44	0.44
Max	2.09	3.10	2.19	2.02	1.63	1.80
*Number of sampled locations						

From 180 DWPLs, 29 produce effluent with >0.5 µg/L total Cr, 6 produce effluent with >1 µg/L total Cr and only 1 DWPL produce effluent with >1.5 µg/L total Cr concentration (Fig. 3.4). In other words, 16 % of the total number of DWPLs produce drinking water with >0.5 µg/L Cr, 3 % produce >1 µg/L Cr, and only 0.6 % produce drinking water with >1.5 µg/L Cr. The RIVM database (2008-2013) did not provide information on the speciation of Cr.

A list of all the 29 DWPLs with the effluent total Cr concentrations above 0.5 µg/L has been provided (Table 3.5). Pinkenberg (Vitens), Epe (Vitens) and Zeist (Vitens) consistently show the highest total Cr concentrations in their effluents i.e., 1.5 µg/L, 1.2 µg/L and 1.2 µg/L respectively. In order to gain insight into the Cr removal efficiency of the Dutch treatment systems, the Cr removal at the DWPLs with >0.5 µg/L total Cr in the effluent has been provided (Table 3.6). It can be observed that the removal of total Cr removal at the Dutch DWPLs is in general quite low. Table 3.6 shows negative removal efficiencies at various DWPLs. The negative values can be partly explained by measurement uncertainty, but for some locations the change is large, and most likely due to the release (mobilization) of Cr within the treatment system. Of course the bias due to changing MQLs and sampling and measurement techniques should not be overlooked. However, there is a significant number of studies from other parts of the world where a similar increase in Cr concentrations has been observed (Craun & McCabe, 1975; Frey et al., 2004). The increase in Cr concentrations during the distribution is also a very important subject and at some locations an increase in the Cr concentration has also been observed during the distribution to the consumers. This subject needs further research and identification of the sources within the treatment and supply infrastructure.

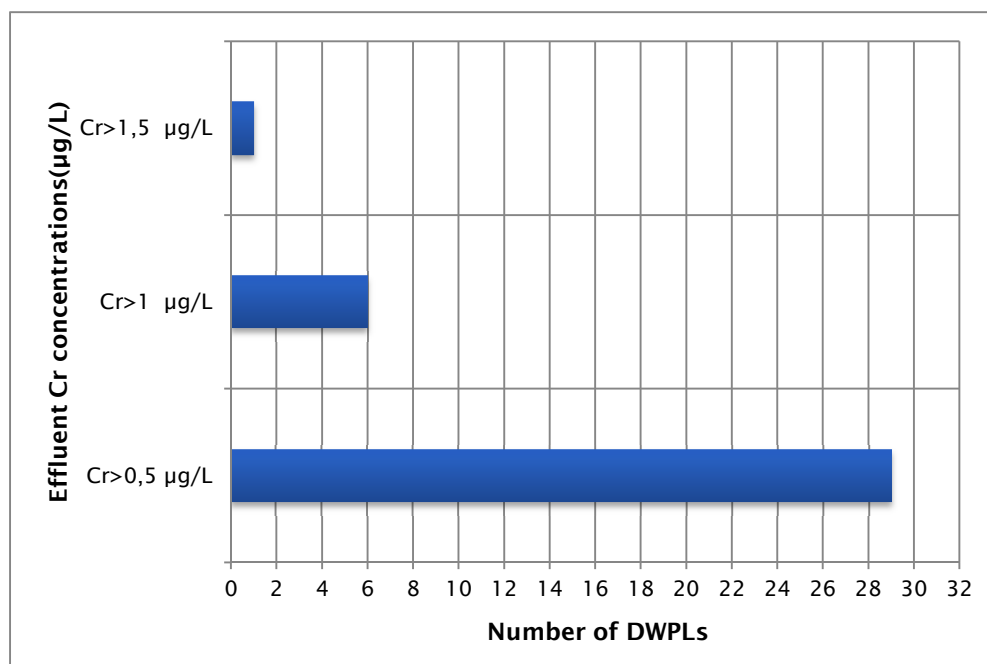


Figure 3.4: Number of DWPLs with elevated Cr concentrations in the produced water in the Netherlands.

Table 3.5: List of 29 drinking water production locations with effluent Cr > 0.5 µg/L.

DWPLs	Year 2008	Year 2009	Year 2010	Year 2011	Year 2012	Year 2013	Average effluent Cr (µg/L)
Pinkenberg	1.0	1.5	1.3	2.0	1.6	1.8	1.5
Epe	1.0	1.0	1.1	1.5	1.5	1.4	1.2
Zeist	1.6	1.3	0.8	0.9	1.5	0.9	1.2
De Haere	1.0	1.0	1.1	1.4	1.1	1.1	1.1
Wezep (Boele)	1.0	0.7	1.5	1.4	0.9	1.0	1.1
Oosterbeek	1.0	0.9	1.3	0.8	1.1	1.0	1.0

Harderwijk II	1.0	0.9	1.0	0.9	1.0	0.9	0.9
Soestduinen	1.0	2.4	0.6	0.5	0.3	0.3	0.9
Driebergen	1.4	1.2	1.2	0.6	0.3	0.3	0.8
Arnhem - la Cabine	1.0	0.8	1.0	1.1	0.3	0.8	0.8
Doorn	0.8	0.7	0.7	0.8	0.9	0.9	0.8
Speuld	1.0	0.3	0.6	0.7	0.9	0.9	0.7
Kruidhaars (Sleen)	0.5	0.5	0.5	0.5	1.5	0.5	0.7
Noordbergum	0.5	1.4	0.5	0.5	0.5	0.5	0.6
Nijverdal	1.0	0.3	0.6	0.7	0.5	0.8	0.6
Hasselo	1.0	0.5	0.6	0.6	0.7	0.3	0.6
Ps. de Punt - Grondwater	1.0	0.3	0.5	0.6	0.7	0.6	0.6
Amersfoort Berg	0.5	0.5	0.5	0.5	1.1	0.5	0.6
Witharen	0.1	0.8	0.3	0.6	0.8	1.0	0.6
Hoenderlo	1.0	0.3	0.3	0.7	0.7	0.7	0.6
Beilen	1.0	0.3	0.3	0.9	0.5	0.6	0.6
de Groeve	0.5	0.5	0.5	1.0	0.5	0.5	0.6
Nietap	0.5	0.5	1.0	0.5	0.5	0.5	0.6
Amersfoortseweg- Apeldoorn	1.0	0.5	0.5	0.5	0.5	0.5	0.6
Leersum	1.0	0.6	0.5	0.6	0.3	0.6	0.6
Velddriel	0.4	1.1	0.6	0.6	0.3	0.6	0.6
Putten	1.0	0.3	0.5	0.7	0.3	0.7	0.6
Ellecom	1.0	0.6	0.6	0.6	0.3	0.3	0.5
De Muntberg	1.0	0.3	0.6	0.5	0.3	0.6	0.5

Table 3.6: Chromium removal efficiency at the DWPLs with > 0.5 µg/L effluent Cr concentration.

DWPLs	Average Cr conc. in the source water (µg/L)	Average Cr conc. in the treated water (µg/L)	Cr removal (%)
Pinkenberg	1.69	1.55	8.5
Epe	0.93	1.25	-34
Zeist	0.96	1.17	-21.6
De Haere	1.23	1.13	7.9
Wezep (Boele)	1.33	1.09	18.4
Oosterbeek	0.89	1.02	-14.7
Harderwijk II	0.67	0.85	-27.4
Heumensoord	0.38	0.85	-123.7
Soestduinen	0.81	0.83	-3.1
Driebergen	1.05	0.82	21.5
Arnhem - la Cabine	1.05	0.82	22.1
Doorn	0.72	0.80	-11
Speuld	NA	0.74	NA
Kruidhaars (Sleen)	0.5	0.67	-33.3
Seppe	NA	0.65	NA
Noordbergum	0.38	0.64	-69.3
Nijverdal	0.56	0.61	-9.4
Hasselo	0.38	0.60	-58.6
Ps. de Punt - Grondwater	0.5	0.60	-20
Amersfoort Berg	0.93	0.59	36.1
Witharen	0.42	0.59	-41.2

Hoenderlo	0.6	0.59	1.5
Beilen	0.5	0.58	-16.7
de Groeve	0.5	0.58	-16.7
Nietap	0.58	0.58	-0.6
Amersfoortseweg - Apeldoorn	0.57	0.58	-1.6
Leersum	0.78	0.57	27.2
Velddriel	0.38	0.56	-47.5
Lekkerker-Schuwacht	0.22	0.56	-153
Beerschoten	0.22	0.54	-145.5
Putten	0.7	0.54	23.4
Ellecom	0.44	0.54	-21.7
De Muntberg	0.49	0.53	-7.5
NA= Data not available			

3.3.3 Arsenic and chromium concentrations and speciation based on the sampling campaign of 2014

In the summer of 2014, a sampling campaign at 14 selected DWPLs was undertaken. The main motivation for the sampling was to double check the outcomes of the analysis of RIVM database (see previous section) and to investigate the nature of As and Cr species in the effluents of Dutch DWPLs. Although the most desired strategy would be to investigate the As speciation at all the 28 DWPLs with total As concentration of $>1 \mu\text{g/L}$ and Cr speciation at all the 29 DWPLs with total Cr concentration of $>0.5 \mu\text{g/L}$, the budget and time limitations did not allow this. Nevertheless, the outcomes of the sampling campaign (Table 3.7) provide important insights into different forms of As and Cr which exist in Dutch drinking water supplies.

The total As and total Cr concentrations in the effluents of the selected DWPLs as indicated in Table 3.7 correspond well to the total As and total Cr concentrations listed in Table 3.2 and 3.5 respectively. The organic fraction of total As in the samples was not reported by AquaLab Zuid. In general, the organically bound As is expected to be very low in the treated drinking waters. However, the absence of DMA and MMA fractions in speciation results of As may include slight inconsistencies when As(III) and As(V) are added to obtain total As concentration in any sample. In other words, Total As is $[\text{As(III)} + \text{As(V)}]_{\text{inorganic}} + [\text{organic-As}]$. However, Table 3.7 only shows As(III) and As(V) concentrations and the organically bound fraction of As has not been reported which induces a slight bias, that fortunately is not significant in this particular case. It can be observed from Table 3.7 that in the effluents of all the 14 DWPLs As exists mainly as As(V) and As(III) in all the cases was found $<0.3 \mu\text{g/L}$. This finding of the sampling campaign was somewhat expected. Because, it has been well reported that the predominant form of As in well-aerated conditions is As(V) (see chapter 1). From the toxicology point of view, although As(V) is considered less toxic than As(III), still both forms of As are known carcinogens.

The total Cr and Cr(VI) concentrations in the effluents of 10 DWPLs have been reported in Table 3.7. The symbol "NM" indicates the locations where sampling for Cr concentrations and speciation was not carried out. It can be observed from the results of the sampling campaign that at most of the samples DWPLs Cr exist as Cr(VI) – the toxic and carcinogenic form of the element. At the DWPL of Dorst, the occurrence of Cr as Cr(III) in the effluent is an exception. The source groundwater of Dorst contains $0.5 \mu\text{g/L}$ of Cr and most part of it exists at Cr(III) (see chapter 1). It means that the influent Cr(III) at Dorst could not be oxidized to Cr(VI) during the treatment process. Further research at Dorst is recommended to investigate why the influent Cr(III) does not oxidize during the treatment process, while on

the other hand, influent As(III) oxidizes completely to As(V). Chapter 2 of this document reports that the raw water sources at most of the selected 10 DWPLs contain Cr as Cr(VI). Therefore, it may be concluded that in most cases Cr(VI) is the dominant species in Dutch drinking water streams and it passes through the treatment systems without being reduced to Cr(III) and without significant removal.

Table 3.7: Arsenic and chromium concentrations and speciation in the effluents of selected DWPLs based on the sampling campaign of 2014.

DWPLs	Total As (µg/L)	As(III) (µg/L)	As(V) (µg/L)	Total Cr (µg/L)	Cr(VI) (µg/L)
Loosdrecht	2.1	<0.3	1.7	NM	NM
Wageningse Berg	2.9	<0.3	2.9	NM	NM
Veenendaal	2.0	<0.3	1.6	NM	NM
Pinkenbergh	<1.0	<0.3	0.5	1.8	1.8
De Haere	<1.0	<0.3	1.1	1.3	1.0
Zeist	1.6	<0.3	1.4	1.0	0.9
La Cabine	1.3	<0.3	0.9	1.0	1.0
Leersum	2.4	<0.3	2.4	0.6	0.4
Dorst	5.4	<0.3	5.3	0.4	<0.02
Oosterhout	3.4	<0.3	3.1	NM	NM
Ouddorp	4.9	<0.3	5.2	0.3	0.2
Scheveningen	2.3	<0.3	1.8	0.2	0.1
Lekkerkerk schuwacht	1.6	<0.3	1.4	0.3	0.2
Plasmolen	1.4	<0.3	1.6	<0.05	<0.02

NM= Not measured.

3.3.4 Arsenic treatment at Dorst to achieve < 1 µg/L effluent As concentrations – a case study

Drinking water production location of Dorst produces drinking water with an average As concentration of 5.8 µg/L. Brabant Water, the public water supply company in the Brabant province of the Netherlands, has started optimizing this DWPL in collaboration with KTH-International Groundwater Arsenic Research Group (GARG) and KWR Watercycle Research Institute for enhanced As removal, targeting effluent As concentrations below 1 µg/L. Dorst produces 10 Mm³ of drinking water per year from deep groundwater. The treatment includes ten parallel treatment trains, each consisting of a raw water intake from a common reservoir (As ~ 12 µg/L), a cascade aerator, a rapid sand filter and an effluent discharge to a common reservoir (As ~ 6 µg/L) from where the water is subsequently distributed to communities in the southern part of the Netherlands. Brabant Water has studied the feasibility of a hybrid technique, Advanced Oxidation-Coagulation-Filtration (AOCF), by extensive laboratory, pilot and demonstration scale investigations. By laboratory jar testing, the most suitable coagulant for the raw water quality and the existing setup at Dorst was determined from three commonly used metal salts (ferrous sulphate, ferric chloride and alum). In accordance with what has been reported in literature, ferric chloride showed the highest As removal efficacy at the operational pH of Dorst (7.5-8). After selecting ferric chloride as the coagulant, its optimum combination dose with KMnO₄ oxidant was also determined through jar tests. Experiments led to various oxidant-coagulant dose combinations that could achieve a residual As concentration of lower than 1 µg/L (Table 3.8).

Table 3.8. Optimized dosing combinations at different pH values obtained from the bench scale study.

pH	mg L ⁻¹	
	KMnO ₄	FeCl ₃
7.0	1.0	1.5
7.5	1.0	2.0
8.0	1.5	2.0

Arsenic, if present in trivalent form (arsenite or As(III)), is more of a challenge to remove compared to its pentavalent form (arsenate or As(V)). This is because As(III) mainly exists as an uncharged species within the pH window of natural waters (6-8). In order to avoid lower As removal efficacy and higher coagulant doses Brabant Water is using KMnO₄ to pre-oxidize As(III). The cascade aerators are not able to oxidize As significantly, because the oxidation of As(III) is fairly a slow process in the presence of atmospheric oxygen only. Sorption is central to most of the As removal technologies. In order to eliminate As from water it is basically adsorbed to oppositely charged surfaces and then these surfaces are removed from the aqueous phase. Fixed bed columns, with naturally available or engineered adsorptive media and metal (hydro)oxide mobile phases generated when a metal coagulant is added to water, frequently provide sites for As sorption in many treatment methods. For Dorst, Brabant Water is using ferric (hydro)oxides surfaces, which are formed in the aqueous phase when ferric chloride is dissolved in water with an oxidant. Besides the dosed ferric chloride, the natural iron content of raw water itself also contributes to the overall As removal.

After the lab investigations, the As removal by AOCF was further evaluated at pilot scale and optimized where required. An optimum combination dose of KMnO₄ and FeCl₃ was added in the pilot plant, that was especially designed to represent a physical model of the full scale Dorst. The pilot setup included two treatment trains, each consisting of a cascade and a rapid sand filter. In one of the filters we used metal oxide coated sand (MOCS), collected from the full scale filters of Dorst. In the other filter we used virgin sand (VS) of equal particle size. Before starting the evaluation of AOCF, both the filters were ripened (Fig. 3.5). The suitable dosing points had been determined during the extensive jar testing phase of the project. As soon as the AOCF was implemented at the pilot plant, levels of As in both the effluents significantly decreased (Fig. 3.5). In the effluent of VS media residual As concentration of lower than 1 µg/L was obtained consistently for several weeks; however, the effluent from MOCS contained a slightly higher concentration of As (1-1.5 µg/L). The application of AOCF did not disturb the pre-existing removal processes of CH₄, Fe, Mn and NH₄⁺. However, a decrease in average filter run time from 96 to 24 h was noticed for both the filters. In order to optimize the filter run time, dual media/double layer filtration with anthracite (1-1.6 mm) and finer sand (0.5-0.8 mm) was evaluated with the optimum chemical dosing combination. Average filter run time increased to more than 48 h.

Currently Brabant Water is involved in the final phase of research project, i.e., dedicated filter trials at the Dorst. The company has separated one complete treatment train for the final trials. The filter media has been changed and the same strategy for start-up has been adopted as was followed in the pilot scale. We first ripened the filter for about 2 months and subsequently we started dosing the chemicals in the cascade with a little adjustment of the existing setup. Effluent As concentration turned steadily below 1 µg/L one day after the start of dosing. An average filter run time of 50+ hours at 130 m³/h (5 m/h) has been successfully achieved which fulfills the operational criteria of Brabant Water.

Based on the experience at Dorst, AOCF appears to be an efficient, simple and affordable technology which can guarantee As concentrations below 1 µg/L in drinking water supplies.

The technology was easily implemented at the conventional groundwater treatment system of Dorst requiring only an addition of a chemical dosing setup and replacement of the filtration media. No evidence of disturbance has been noticed for the pre-existing removal processes of common groundwater undesirable constituents e.g. CH_4 , Fe, Mn and NH_4^+ . Knowing this, Brabant Water has approved the implementation of AOCF on the full scale. Dorst will be the first full scale prototype in the Netherlands based on AOCF. The total costs associated with the application of AOCF technology at the DWTP Dorst have been estimated at approximately 0.02 €/m³, half of which is related to the cost of chemicals.

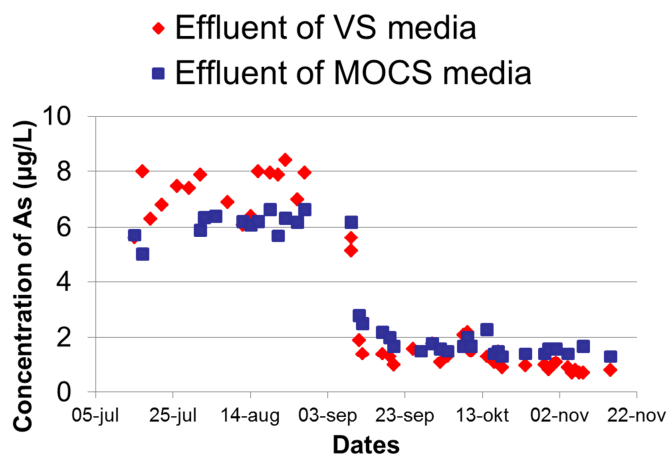


Figure 3.5: Effluent As concentration (µg/L) during pilot plant experiments at DWPL Dorst. Start date of chemical dosing: 13 Sep 2013.

3.4 Conclusions

- All the drinking water production locations in the Netherlands are in compliance with Dutch MCLs for arsenic and chromium in drinking water.
- Approximately 16 % of the total number of drinking water production locations in the Netherlands produce effluent with >1 µg/L total As, 6 % produce effluent with >2 µg/L total As, 2 % produce effluent with >3 µg/L total As and 1 % produces effluent with >5 µg/L total As.
- Only 2 locations, Dorst and Ouddorp, produce drinking water with >5 µg/L total As, i.e., >50% of the Dutch MCL.
- The drinking water production plants using raw waters with high dissolved iron remove arsenic to a greater extent compared to the locations using raw waters with low Fe content.
- Based on the experience at Dorst, achieving effluent arsenic concentration <1 µg/L is feasible with the appropriate treatment technique.
- Approximately 16 % of the total number of drinking water production locations produce drinking water with >0.5 µg/L total Cr, 3 % produce >1 µg/L total Cr, and only 0.6 % produce drinking water with >1.5 µg/L total Cr.
- At some drinking water production locations a “pick-up” of Cr has been observed during the treatment process, however, further investigation is necessary to support this conclusion and to determine the cause.
- In the effluents of all 14 sampled locations, arsenic exists mainly as As(V). As(V) is a known carcinogen.
- In 9 of the 10 sampled locations, chromium exists as Cr(VI) which is the toxic form of chromium.

3.5 Recommendations

This study recommends further research on arsenic and chromium speciation at the drinking water production locations across the Netherlands to remove even minor uncertainties. Drinking water companies should investigate especially the chromium concentrations in the effluents of all their drinking water production locations.

The removal of low arsenic and chromium concentrations from the drinking water supplies needs attention from the end-users, like the drinking water companies. In literature a knowledge gap exists and investigations at bench and pilot scale are needed to obtain guidelines for removing low arsenic and chromium concentrations.

The release of chromium in trace concentrations from within the drinking water treatment and distribution infrastructure is a very serious issue. The sources should be identified by further research and appropriate measures should be investigated to mitigate this challenge.

Finally, the laboratories in the Netherlands should coordinate and prepare themselves to measure and report precisely low concentrations of trace metals in water samples.

3.6 References

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4 Treatment of drinking water for removal of arsenic and chromium

Author: Arslan Ahmad

4.1 Introduction into arsenic removal

In recent years a pressing need for the optimization of conventional arsenic (As) removal processes and development of new techniques has been unavoidable, especially after the mass poisoning case of Bangladesh came into highlights in 90s (Chen et al., 2006; Mohan and Pittman, 2007). Presence of As in drinking water is a very serious issue since it is a known carcinogen and even trace levels of it in water may harm human health. Historically, the most common method for As removal has been precipitation, for example, coagulation with metal salts and Fe/Mn removal by aeration, however, in many circumstances precipitative processes are not able to remove As to the desired safe levels (Litter et al., 2010; Mudhoo et al., 2011). When, in 1993, WHO established 10 µg/L as the new provisional guideline value for As in drinking water, the development of various alternative As removal technologies was prioritized in many parts of the world. Many of the removal technologies which recently have been developed have been reported capable of removing As very effectively to trace levels in well-controlled conditions of laboratory and pilot scale, however, there are only few technologies which have been demonstrated (implemented) at full-scale treatment (Johnston and Heijnen, 2001; Mudhoo et al., 2011).

Most of the As removal methods, either conventional or emerging, rely on a few basic physical-chemical processes. These include oxidation/reduction, precipitation, adsorption and ion exchange, solid/liquid separation and physical exclusion (Johnston and Heijnen, 2001; Duarte et al., 2009). The treatment technologies can be classified accordingly as well. Almost all of the As removal technologies possess an added benefit of removing many other undesirable compounds from water. A detailed description of different mechanisms central to most As removal technologies has been provided below. It must be noted that some biological mechanisms may also play an important role in catalyzing many of the As removal processes, however relatively little is known about the potential for biological removal of As from water. Therefore, this chapter does not discuss the biological removal of As from water.

4.2 Water treatment and arsenic removal

4.2.1 Oxidation/Reduction

Oxidation/Reduction is not a removal technique; however, it plays a vital role in optimizing several As removal processes. Most of the As removal technologies are effective at removing As(V) (Hering et al., 1996; Hering et al., 1997). This is because, As(III) is predominantly non-charged below pH 9.2. On the other hand, As(V) occurs as monovalent or divalent ions in the pH range of natural waters (Ferguson and Gavis, 1972). The charged nature of As(V) facilitates its removal by adsorption onto oppositely charged surfaces.

The oxidation of As(III) by air is fairly a slow process. Hug et al. (2003) performed laboratory air oxidation experiments with As(III) at pH values typical of natural groundwater and found that As(III) oxidation by air occurred on a time scale of tens of minutes. Bissen and Frimmel (2003) studied As(III) oxidation kinetics and reported that only 55 % of total As(III) was

oxidized in 5 days when the groundwater was purged with air and pure oxygen. For the advanced oxidation of As(III), chemical oxidants are generally required. Some common oxidants which may be used include; gaseous chlorine, hypochlorite, ozone, permanganate and hydrogen peroxide. Ultraviolet radiations (UV) may also play a role to catalyze the oxidation of As(III) in the presence of oxygen. It is worth-mentioning that chlorine is a rapid and effective As(III) oxidant, however it may lead to the production of toxic trihalomethanes in the presence of organic matter in water. Although oxygen assisted conversion of As(III) to As(V) is generally slow, solid-liquid interfaces in the presence of dissolved oxygen may catalyze the process. For example, the Fe(III) deposits on the surface of filter sand grains, may facilitate the conversion of As(III) to As(V) by catalytic effects and direct reactions (Sarkar and Rehman, 2001).

Besides the physicochemical processes, biological mechanisms may also play a role in the oxidation of As(III). A wide range of bacteria have been reported for their ability to enzymatically synthesize and oxidize As(III) (Duarte et al., 2009). They include heterotrophic bacteria as well as chemoautotrophic bacteria in which As(III) serves as an electron donor reducing oxygen or nitrate (Duarte et al., 2009). Besides oxidation, bacterial reduction of As(V) to As(III) has also been reported in literature according to Duarte et al. (2009).

4.2.2 Precipitation/Co-precipitation

The precipitation based As removal methods commonly include coagulation/filtration, Fe/Mn removal by aeration or advance oxidation, coagulation assisted microfiltration, enhanced coagulation, lime softening and enhanced lime softening (USEPA, 2000; Mudhoo et al., 2011). The frequently applied precipitative techniques have been discussed below in detail.

4.2.2.1 Coagulation/Filtration

Coagulation followed by rapid sand filtration is a commonly applied water treatment method. For As removal it is one of the most extensively investigated and implemented techniques. It has traditionally been used to remove solids from drinking water, however, this treatment can effectively remove many dissolved constituents from water such as As. According to USEPA (2000), coagulation/filtration can successfully achieve As(V) removal efficiency of higher than 90 percent and if optimal operating conditions are adopted, effluent levels of less than 3 µg/L may be obtained. In this method, the major mechanism of As elimination is adsorption onto the charged sites provided by polymerising metal oxy-hydroxide molecules (Sancha, 2006). However, incorporation of soluble As species into growing precipitates (metal hydroxide phase) contributes significantly to As removal as well. This kind of entrapment of As is due to occlusion, inclusion and adsorption, which is sometimes collectively known as co-precipitation. Arsenic removal by direct precipitation i.e, as $\text{Al}(\text{AsO}_4)$ or $\text{Fe}(\text{AsO}_4)$, is generally considered less contributing towards the overall removal of As during coagulation (Johnston and Heijnen, 2001).

The most commonly used coagulants (precipitants) for As removal are aluminum (Al) salts such as alum, and Fe salts such as ferric chloride (FeCl_3) or ferrous sulfate (FeSO_4) (USEPA, 2000; Johnston and Heijnen, 2001). As(III) removal during coagulation has been shown to be less efficient than As(V) under comparable conditions (Table 4.1) (Hering et al., 1996; Hering et al., 1997). The added benefit of coagulation/filtration technique for As removal would be an enhanced removal efficiency for turbidity, natural organic matter (NOM), synthetic organic compounds (SOCs), Fe, Mn, phosphates and fluoride (USEPA, 2000; Johnston and Heijnen, 2001). The factors affecting the removal of As by coagulation/filtration are widely investigated. Major factors include: coagulant type, coagulant dose, pH, As speciation, initial As concentration and the nature of co-occurring inorganic solutes. Many studies have reported Fe(III) based salts as the most appropriate coagulants for As removal (USEPA, 2000).

However, the availability, downstream processes carried out at the treatment plant and above all, the raw water quality must be taken into account before the selection of a coagulant for As removal.

A promising modification of the conventional coagulation/filtration technology is the coagulation assisted microfiltration. Microfiltration replaces conventional rapid sand filters and serves as a more effective barrier to small floc sizes. As a result total plant capacity is increased and coagulant dose can be reduced (USEPA, 2000). Membrane fouling because of particulate oxides of Fe and Mn may be a potential disadvantage of coagulation assisted microfiltration (Sevil, 2005).

Table 4.1: As(III) and As(V) removal efficiency of different coagulants.

As form	Coagulant	
	Al ₂ (SO ₄) ₃	FeCl ₃
As(III)	0-20%	40-70%
As(V)	70-80%	80-100%

Source: Chwirka et al. (2000).

4.2.2.2 Combined removal with iron and manganese

Ground waters which contain high concentrations of dissolved Fe and/or Mn are generally treated by aeration followed by one or two stage rapid sand filtration. These metals, when oxidized, form solid metallic oxides and hydroxides which can sorb significant amounts of As (USEPA, 2000; Hug et al., 2003). The production of oxidized Fe and Mn species and their subsequent precipitation as hydroxides and oxides is similar to an in situ coagulant addition, with the quantity of Fe or Mn removed translating into a “coagulant dose”.

The Fe removal in conventional aeration-filtration systems follows two physicochemical mechanisms which most of the times work simultaneously. One mechanism is the aqueous phase oxidation of Fe(II) to Fe(III) and immediate hydrolysis to form iron oxyhydroxide (FeOOH or Fe(OH)₃) flocs. For simplicity, this mechanism can be named as flocculative removal mode. The second mechanism is adsorption of Fe(II) on the surface of the filter media, followed by its oxidation to Fe(III) while being adsorbed at the media grains. This mechanism can be regarded as an adsorptive removal mode. Arsenic gets removed by both processes i.e., adsorption onto Fe(OH)₃ flocs and by the dense Fe-oxide coating developed gradually over time on filter media grains. When source water pH is below 9, the oxidation of influent Mn(II) to solid Mn₃O₄ and/or MnO₂ is generally very slow in the presence of atmospheric oxygen only. Therefore, Mn enters the rapid sand filter beds as dissolved Mn(II) even after the water is aerated in the cascades. Manganese removal thus occurs either by addition of strong oxidants like KMnO₄, by bacteria that are capable of oxidizing Mn(II), and/or by auto-catalytic adsorptive removal on (biologically) formed manganese oxides (Buamah, 2008; Bruins et al. 2014). The adsorbed and subsequently oxidized Mn acts as a newly created adsorbent for the incoming Mn(II). In this way, the thickness of the coating keeps increasing and Mn removal continues. The Mn-oxide coatings formed on the surface of the filter media grains may contribute to the oxidation of As(III).

4.2.2.3 Lime softening

Ground water softening with lime is very effective in reducing As from drinking water (USEPA, 2000; Fields et al., 2000). Water hardness is primarily due to the presence of calcium and magnesium ions. The lime is added to provide hydroxide ions which increase the pH of water. At increased pH bicarbonate is converted to carbonate which results in calcium and magnesium removal due to the formation of CaCO₃ and Mg(OH)₂ precipitates. If insufficient

carbonate is present in the water, soda ash is added to remove hardness to the desired levels. Softening for only calcium removal is typically accomplished at pH between 9 and 9.5 (USEPA, 2000). However if magnesium removal is desired, excess lime is added to raise the pH above 10.5 so that magnesium precipitates as $Mg(OH)_2$ (USEPA, 2000). Fields et al., (2000) reported that As removal during lime softening is pH dependent and removal of As(III) and As(V) are low at pH less than 10; however, As(V) removal approaches 100% and As(III) removal approaches to 75% at pH values greater than 10.5. It means that when pH is high enough to precipitate $Mg(OH)_2$, As adsorption and subsequent removal increases. Post treatment pH adjustment may be accomplished by recarbonation with CO_2 . Softening can also be accomplished by caustic soda (NaOH).

4.2.3 Adsorption and ion exchange

Adsorption is a key process in many As removal techniques and may be regarded as the most important As removal mechanism. Four principal types of adsorption have been identified: namely, ion exchange, chemical adsorption, physical adsorption and specific adsorption (Yang 1999; Buamah, 2009). Arsenic removal by adsorptive processes can be accomplished in two ways, i.e., adsorptive media filtration or flow through a column of ion-exchange resin. The effectiveness of As treatment by adsorption and ion exchange is more likely to be affected by characteristics and contaminants other than As compared to precipitative processes discussed in the previous section. Therefore, adsorption and ion exchange media treatment techniques tend to be used more often when As is the only contaminant to be treated, for relatively smaller systems, and as an auxiliary process for treating effluent from larger systems (Petrusevski et al., 2007). Different adsorptive and ion-exchange medias are discussed below.

4.2.3.1 Adsorptive media

In the past, the most commonly used adsorptive media for As removal had been Activated Alumina (AA). However, in recent years, several new granular adsorptive filter media have been developed which have shown high effectiveness in As removal from water (Petrusevski et al., 2007). These media can be categorized into two major groups i.e., metal oxide coated media and metal oxide based media. In aqueous systems the surfaces of metal oxide adsorptive media grains get covered with hydroxyl groups. Anions such as As(V) are then adsorbed onto metal oxide based media via a ligand exchange reaction in which hydroxyl surface groups are replaced by the sorbing ions (Buamah et al., 2008). In the complex adsorptive environment of media As(III), which exists as an uncharged species in the pH range of 6-9, may also be removed because of physical and specific adsorption mechanisms.

Latest research regarding As removal has been more focused on the development of Fe based/coated As adsorptive media. One such promising adsorption media is Iron Oxide Coated Sand (IOCS) (Fig. 4.1). IOCS has shown efficient As(III) and As(V) removal capacity during field trials in Bangladesh and at centralized applications in Greece and Hungary (Petrusevski et al., 2007). Natural geological materials have also demonstrated strong affinity for both As(III) and As(V) (Bundschuh et al., 2011). Pretreatment of the zeolite with copper has shown to enhance As adsorption capacity of the zeolite (Beamguard, 2006). Naturally occurring glauconitic sand after being treated with $KMnO_4$ (known as green sand) (Fig. 4.1) can also remove As from water. The principle behind the As removal by green sand is multifaceted, including oxidation, ion exchange and adsorption (USEPA, 2000). Some other commercial adsorptive media include Aquamandix (Figure 4.1) Aqua-Bind MP, ArsenX, Bayoxide E33 ferric oxide, GFH, MEDIA G2 etc.

4.2.3.2 Ion exchange resins

For As removal from water synthetic anion exchange resins are proven to be very effective. According to USEPA (2000) a consistent removal to below 3 µg/L can be achieved by anion exchange technology. Conventional sulphate and nitrate selective resins are well suited for As(V) removal (Johnston and Heijnen, 2001). The removal through an ion-exchange resin involves short-range forces which occur within the porous lattice of resin grains which contain a fixed charge. The electrostatic attachment of ionic species to sites of opposite charge at the surface of an ion exchange media grain occurs with a subsequent displacement of these species by other ionic adsorbates of greater electrostatic affinity. The ion exchange treatment procedure includes continuous passage of feed water through a packed bed of ion exchange resin beads until the resin is exhausted. At that stage, the bed is regenerated by rinsing with a regenerant. The principle challenge with ion exchange resin treatment is the absence of removal for As(III). This is because of the uncharged nature of As(III). Therefore, waters containing As(III) typically require a pre-oxidation step before contact with ion exchange resin bed. Another problem in this treatment is the potential interference from other anions. If the feed water contains sulphates, nitrates, chloride or other anions, the As removal may be significantly reduced (Johnston and Heijnen, 2001). Some commercially available ion exchange resins include Dowex 11, Ionac ASB-2 and Dowex SBR-1 (USEPA, 2000).



Figure 4.1: Different types of adsorptive media. a) Aquamandix b) IOCS c) Manganese greensand d) A stone of iron ore which can be crushed and pulverized (Buamah, 2009).

4.2.4 Membrane separation processes

A water treatment membrane is a selective barrier which allows some constituents to pass while blocking the passage of others. Membranes split a feed stream into two parts i.e., retentate and permeate fractions. Membrane processes can remove As very effectively through filtration, electric repulsion and adsorption of As bearing compounds (Petrusevski et al., 2007). Membrane filtration is capable of removing both As(III) and As(V), however As(V) removal efficiency is higher than As(III) (Petrusevski et al., 2007). Membrane processes produce a large volume of residuals and tend to be more expensive compared to other As removal methods. They are therefore used less frequently than precipitative/coprecipitative, adsorptive and ion exchange processes.

4.2.5 Subsurface immobilization

The application of subsurface treatment for the removal of As from groundwater is a relatively new approach (Sarkar and Rahman, 2001; van Halem 2011). In contrast, for removing Fe from groundwater, a subsurface immobilization method (Fig. X-X) has been used in central Europe for many decades. In strongly reducing environments As gets

mobilized into groundwater because of the reductive dissolution of As bearing minerals. The process can be reversed and loose As can be immobilized again by pumping aerated water periodically into an anoxic aquifer. The injected water oxidizes dissolved Fe(II) which is then precipitated on the soil grains, resulting in the formation of adsorptive surfaces of iron hydroxides. Arsenic ions get adsorbed on these surface sorption sites and become immobile. When the flow is reversed (abstraction mode), As free water can be obtained. Apart from As adsorption, there may also be As immobilization through coprecipitation while Fe(II) changes to ferrihydrite (van Halem, 2011). Subsurface As removal has the potential to be a cost-effective way to provide safe drinking water in rural areas in decentralized applications (van Halem, 2011). A remarkable advantage of this process is no production of As-rich waste above surface.

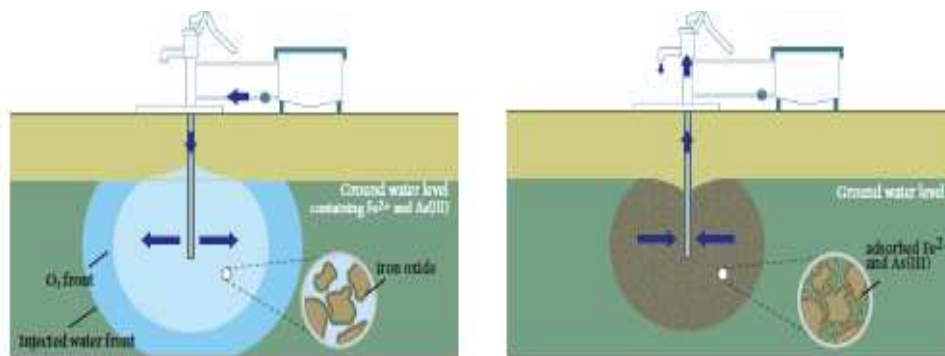


Figure 4.2: Principle of subsurface iron removal. Injection (left) and abstraction (right) (van Halem, 2011).

4.3 Introduction into chromium removal

The presence of hexavalent chromium [Cr(VI)] in source waters (raw waters) can be a problem for the drinking water production facilities. As discussed earlier, the toxicity of chromium (Cr) strongly depends on the form in which it is present in water, i.e., Cr(III) or Cr(VI). Although Cr(III) is considered non-toxic in the concentrations encountered in drinking waters, its presence in the effluent of the treatment plant may pose risks to the health of the consumers. This is because Cr(III) can be oxidized to Cr(VI) in the distribution network, before it reaches the consumer's tap. Therefore, total Cr should be removed from water to a level at which the complete conversion to Cr(VI) would not exceed the treatment objective (Brandhuber et al., 2004). The remediation measures may be applied in-situ (sub-surface), at centralized scale and/or at the point-of-use level.

The conventional techniques to remove Cr from water have mainly been applied to remove and recover high Cr concentrations from the wastewater of various industrial processes. Under conditions where Cr concentrations are much lower, such as the groundwater resources for drinking water supply, only few studies provide guidance on the efficacy of the conventional removal processes. The complex chemistry of Cr in aqueous environments (see chapter 1) provides various possibilities that have been exploited for developing efficient Cr removal technologies. These treatment methods may be classified into five main groups, as done by Sharma et al., 2008, namely; coagulation & precipitation, adsorption onto different media, ion exchange, membrane technology and biological removal. This chapter discusses these methods (except biological removal) in detail and reviews their suitability and limitations for the removal of low Cr concentrations.

4.4 Chromium removal methods, their suitability and limitations

4.4.1 Coagulation and precipitation

Chromium metal can be removed from water by precipitation (Blais et al., 2008). However, Cr(III) is relatively easier to remove than Cr(VI). This is because Cr(III) is predominantly present as a cation and readily forms complexes with hydroxides, chlorides, fluorides, sulfates, ammonium salt, cyanides, sulfocyanides, oxalates and citrates (de Jongh et al., 2012). On the other hand, Cr(VI) is extremely soluble. Coagulation using alum ($\text{Al}_2\text{SO}_4)_3$ and ferric based coagulants (e.g. ferric chloride, FeCl_3) has been extensively applied for Cr(III) removal in conventional treatment of wastewater streams contaminated with Cr. In coagulation, removal is mainly due to the precipitation of Cr as $\text{Cr}(\text{OH})_3$ and co-precipitation with the hydrolyzing metal species, such as $\text{Fe}(\text{OH})_3$, resulting in the formation of complexes, e.g. $\text{Fe}_x\text{Cr}_{1-x}(\text{OH})_3$ (Sharma, 2008; Hashim, 2011). Chromium removal by precipitation is strongly dependent on pH, and thus it sometimes is possible to achieve precipitation of Cr(III) just by adding NaOH or $\text{Ca}(\text{OH})_2$ (de Jongh et al., 2012).

Contrary to Cr(III), Cr(VI) is not effectively removed by conventional coagulation because Cr(VI) occurs predominantly as anionic complexes in aqueous solutions. Its complexes are extremely soluble (Brandhuber et al., 2004; de Jongh et al., 2012; Sharma et al., 2012). In order to gain an increased Cr(VI) removal, the Cr(VI) fraction of the total Cr should be reduced to Cr(III) through the use of chemical reducing agents such as ferrous sulphate (FeSO_4), sodium bisulfite, zero-valent iron, or stannous chloride (Brandhuber et al., 2004; McNeill et al., 2012). The reduction of Cr(VI) to Cr(III) and subsequent removal of Cr(III) by the use of coagulants is a two-stage process that may increase the overall treatment cost. Furthermore, precipitated Cr may form small particles that do not settle readily. As a result, a large settling basin may be required to collect the precipitates. Moreover, the subsequent filtration step should be carefully designed to effectively catch the carry-over flocs.

Another technique to remove Cr from water is lime softening. Like coagulation, lime softening is best suited for the removal of Cr(III) (Brandhuber et al., 2004). Softening is normally carried out at higher pH levels which may hinder Cr(VI) reduction to Cr(III). Therefore, the reduction of Cr(VI) to Cr(III) is done under acidic conditions and then precipitation of hydrated Cr-oxide is achieved by raising the pH by adding NaOH or lime. Drinking water treatment plants should expect larger sludge volumes when implementing precipitative Cr removal techniques. Furthermore, if the sludge is counted as toxic waste due to high accumulated Cr(VI) levels, safe disposal options such as toxic waste landfills should be arranged.

4.4.2 Adsorption onto different media

Adsorption on different media is an extensively applied treatment technique for the removal of dissolved metals from water. It can also remove inorganically and organically complexed metals, as well as oxyanions such as CrO_4^{2-} , that might not be effectively removed by precipitative treatment techniques (Benjamin et al., 1996; Sharma et al., 2008). Activated carbon (AC) treatment has been reported to remove relatively higher concentrations of Cr, however, there exists a knowledge gap for the treatment of drinking water streams where Cr concentrations are considerably low (Brandhuber et al., 2004; Mohan and Pittman, 2006). Although AC is effective for the removal of both forms of [Cr(III) and Cr(VI)], various studies report a higher removal of Cr(VI) compared to Cr(III) (Hung and Wu, 1997; Yoshida et al., 1977). Anupam et al. (2011) found that with powdered activated carbon (PAC) the maximum adsorption could be obtained with high PAC dosage and at a low pH. The adsorption capacity of AC may be enhanced artificially. For example, Cho et al., (2011) described the use of granular activated carbon (GAC), modified with a cationic polymer, to enhance its

adsorption capacity for Cr(VI) adsorption. An added benefit of AC treatment is the removal of other heavy metals and organic micro-pollutants (OMPs), besides Cr(III) and Cr(VI). More research is needed to investigate the optimal conditions for Cr removal in drinking water treatment.

Apart from AC, scientists have also studied the effectiveness of various other (cost-effective) adsorbents for the removal of Cr in batch, fixed bed and fluidized bed processes. For example, iron-oxide-coated sand (IOCS), produced by coating quartz sand with ferric nitrate, has proven to be effective for removal of Cr from wastewater effluents (Edwards & Benjamin, 1989). Other tested adsorbents include, but are not limited to, treated and untreated zeolites (Kurniawan et al., 2006), clay minerals (Gupta and Bhattacharyya, 2011), manganese oxide coated sand (Guha et al., 2001) and peat moss (Kurniawan et al., 2006). After these adsorptive media have reached their adsorption capacity, either regeneration or replacement of the exhausted media becomes necessary. This may pose environmental concerns.

4.4.3 Ion exchange resin treatment

Ion exchange is one of the “best available technologies for Cr removal”, as indicated by the United States Environmental protection Agency (USEPA) (USEPA, 2003). Bahowick et al., (1996) showed that ion exchange could consistently reduce groundwater Cr(VI) concentrations from 30 µg/L to lower than 2 µg/L. Cation exchangers are effective for Cr(III), while anion exchangers are appropriate for Cr(VI) removal. If both Cr species are present in the stream to be treated, a two-step ion exchange process would be needed. For the removal of Cr(VI) from water under (slightly) acidic conditions, a weak-base anion exchange resin can be used. These can be regenerated with a concentrated (5-8%) sodium chloride (NaCl) solution (de Jongh et al., 2012). The efficiency of the regeneration process can be improved by adding sodium hydroxide (NaOH). The main limitations of the ion exchange treatment technique are the requirements for regular regeneration and concentrate disposal, potential fouling of the resins, and the effect on removal efficiency when other ions are present in the water. Knowledge gaps in the literature exist on the removal of low Cr concentrations by ion exchange.

4.4.4 Membrane treatment

The use of membrane technology, specifically reverse osmosis (RO), is also considered as one of the best available technologies for Cr removal by USEPA (USEPA, 2003). A number of studies have shown that RO can achieve excellent removal of both the Cr species, i.e., Cr(III) and Cr(VI) (Sharma et al., 2008). Hamann et al., 1990 showed that RO was slightly more effective in removing Cr(III) than Cr(VI) in the pH range of natural waters. Electrodialysis (ED) is comparable to RO and therefore should also be an appropriate technology for removing Cr (Brandhuber et al., 2004). Not much has been reported on the Cr removal potential of nano-filtration (NF) in literature. An important challenge in applying membrane technology for Cr removal is to prevent fouling and corrosion of well casings and entrapment of air that could cause oxidation of iron and sulfur compounds (which also causes severe fouling of membranes) (Sharma et al., 2008). Applying membrane treatment generally needs a higher investment. Operational costs are also high because of the continuous energy requirements of the process. The process generates concentrated brine that needs to be disposed appropriately.

4.5 Conclusions

Several methods have been reviewed in this chapter to deal with the presence of low concentrations of As and Cr in drinking water supply. Removal of As and Cr from water depends upon the overall source water quality, pre-existing treatment processes,

concentrations and speciation of As and Cr, water scarcity in the region, residuals handling concerns, and the origins of both these trace metals.

High As concentrations in groundwater need not be problematic, as As can be removed efficiently by co-precipitation with iron. When insufficient iron is available however, other options need to be explored to reduce As concentrations into the low $\mu\text{g/L}$ range. In general As(V) is easier to remove than As(III) because of As(V)'s ability to readily adsorb to positively charged surfaces. However, in (deeply) anoxic groundwaters As(III) is the dominant form of As. Unfortunately, atmospheric oxygen alone does not oxidize As(III) fast enough. In that case, it is highly recommended to oxidize the anoxic groundwater with the help of a strong oxidant. All the conventional treatment methods for arsenic removal discussed in this chapter (precipitation, adsorption, ion exchange, membranes) are able to remove arsenic from high concentrations to very low concentrations. However, there is a need for research in the area where arsenic levels in raw waters are relatively low ($< 10 \mu\text{g/L}$) and the target effluent concentrations are even lower ($< 1 \mu\text{g/L}$).

Cr(III) is insoluble at neutral and higher pH, therefore its removal is relatively easy compared to Cr(VI) removal. Coagulation, adsorption on different media, ion exchange and membrane filtration processes have been traditionally applied for the removal of Cr from water. Of the different methods, precipitation (including redox-assisted coagulation) and adsorption based removal techniques are the most effective methods of Cr removal from water. Ion exchange and reverse osmosis are proven technologies for the removal of both Cr species, however, additional costs for treating and/or disposing of large volumes of liquid toxic waste may render these processes expensive.

The conventional methods discussed in this chapter have been investigated in the past mainly for high Cr concentrations and from the perspective of Cr recovery and reuse. The applicability of these methods for waters with relatively low Cr concentrations (drinking water) is not well-documented. There is still a need for a process-efficient and cost-effective treatment method for Cr removal from drinking water supply sources that could be used at different treatment scales.

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5 Conclusions and recommendations

Author: Bas Hof's

5.1 Conclusions

5.1.1 Toxicology

A short inventory was made of current guidelines and current efforts to generate new guidelines. For both arsenic (As) and chromium (Cr), the current 'provisional guideline values' (PGV) for drinking water as set by the WHO (WHO, 2011) are not based purely on toxicological data.

For As the PGV is 10 µg/L and was dictated by the current analytical techniques and uncertainties in the toxicological data (WHO, 2011). Currently, a PGV for As is also being evaluated at KWR on the basis of toxicological data alone. This appears to lead to a guideline value that is an order of magnitude lower than the PGV from the WHO. The speciation of As may ultimately not be very relevant from a toxicological point of view due to bioactivation upon ingestion, where the less toxic dissolved As(V) is transformed into the more toxic dissolved As(III).

For Cr the PGV is 50 µg/L and was dictated by the removal technologies, source protection methods, etc. (WHO, 2011). Dissolved Cr(VI) is more toxic than dissolved Cr(III). A PGV for Cr(VI) of 0.2 µg/L was derived by KWR (De Jongh, 2012), and a very similar new target value for Cr(VI) of 0.3 µg/L was recently proposed in Germany (TZW, 2014).

5.1.2 Raw water sources

An inventory was made of arsenic and chromium concentrations in groundwater resources for drinking water supply in the Netherlands, based on various data bases and a new sampling campaign in 2014 (for 14 well fields).

According to data from the REWAB database 47% of 190 public supply well fields (PSWFs) showed As levels in 2013 above 1 µg/L, and 44% Cr levels above 0.3 µg/L. This last value is determined only approximately, as the quantification limit of the methods used were often higher than 0.3 µg/L, and some data are simply missing. The 2014 sampling campaign demonstrates that the higher As and Cr concentrations mainly refer to arsenite (As(III) as H_3AsO_3) in (deeply) anoxic environment, and chromate (Cr(VI) as CrO_4^{2-}) in (sub)oxic environment.

Thus, in the Netherlands the presence of elevated levels (with respect to possible new stricter PGVs) of As and Cr in the sources for drinking water production are widespread. Arsenic hotspots are mainly localized where the hydrological system was (sub)recently disturbed, mainly by (1) a drawdown or rise of the groundwater table, (2) a quality change of the infiltration water (especially an increase of PO_4 , SO_4 , HCO_3 , DOC, F, temp), (3) accumulation of anoxic muds in infiltrating rivers, basins, lakes etc., and (4) the genesis of reducing gasses, notably CH_4 . Glauconite containing aquifers may also form an As hotspot. Arsenic does not come alone. Most cases of As peaking relate to reductive dissolution of iron (hydr)oxides, producing concomitant, high concentrations of Fe, Mn, SiO_2 , PO_4 , HCO_3 and DOC, and also of Mo and V in case of AR or RBF when the infiltration water showed a relatively high input concentration. In case of pyrite oxidation, As peaks can be accompanied by Ni, Co and Zn if pH is 5-6, but the area affected is relatively small.

Chromium hotspots are mainly related to (1) local pollution sources such as steel, textile, leather or cement industries, and (2) a low pH in connection with intensive agriculture, forest stands and shallow groundwater.

Bias was observed for both Cr and As data, in several cases. Too high concentrations were due to insufficient filtration of suspended fines (clay particles in case of Cr, and iron (hydr)oxide flocks in case of As), and due to corrosion of stainless steel in case of Cr.

5.1.3 Drinking water production plants

The above-mentioned REWAB database and the sampling campaign were also used for an inventory of the concentrations and speciation of the drinking water as freshly produced in the drinking water production plants (DWPPs). The REWAB database showed that for 28 DWPPs the As concentration in the drinking water is above 1 µg/L, and that for 29 DWPPs the Cr concentration is above 0.5 µg/L. The exact number is not known (uncertainty estimated at about 20%) due to the reported quantification limit for Cr. The sampling campaign at 14 locations showed that after treatment the As is present in the form of arsenate (dissolved As(V)), and Cr mostly in the form of chromate (dissolved Cr(VI)). Removal of As in the DWPPs was highly variable, depending amongst other things on the iron concentration of the source water. Cr was usually not removed in the DWPPs, an increase could even be observed for some DWPPs.

5.1.4 Mitigation strategies and treatment options

Protection of the source, subterranean iron removal or optimization of well field management can be important measures to reduce As concentrations. For example, a recent increase in influent As concentrations at DWPP Ouddorp (thus in raw water) could be attributed to recent changes in groundwater levels with subsequent changes in redox chemistry. Different interests (for example ecohydrological benefits of raised water tables versus potential release of As) should be weighed carefully.

Treatment options to reduce As concentration in produced drinking water down to 1 µg/L are only just becoming available. At DWPP Dorst a combination of KMnO_4 and FeCl_3 dosing has recently been successfully applied to decrease the concentration of As in drinking water from about 6 to <1 µg/L (Water21, 2014). This shows that treatment down to these low As levels is in principle possible.

As far as we know, for removal of Cr to <0.3 µg/L no options are readily available. In principle all forms of Cr should be removed by reverse osmosis, but this may be considered a kill or cure remedy (in Dutch: 'paardemiddel'). Dissolved Cr(III) can be removed by coagulation and co-precipitation with FeCl_3 , but unfortunately most of the Cr is already in the form of dissolved Cr(VI) in the public supply well fields. For removal of dissolved Cr(VI) anion exchange can be used, but here competition with all other anions and NOM is the limiting factor.

5.2 Recommendations

- Keep an up-to-date view on the ongoing discussions for PGVs of As, Cr, and other heavy metals.
- Decrease the quantification limit for Cr (to well below 0.3 µg/L) in the methods that are used to obtain data for input in the REWAB database, in order to get better data on the concentration of Cr in the produced drinking water.
- Carefully weigh potentially conflicting interests of ecohydrological optimization measures and changes in subsoil water redox chemistry (potential change in As concentrations).
- Investigate the origin of Cr in sources, treatment (increase at some DWPPs) and distribution (tendency to increase in the distribution system).

- Investigate removal technologies (either subsoil or above ground) for both Cr and As, that can achieve low levels in treated water (<1 µg/L As, <0.3 µg/L Cr).
- Investigate how well field management can assist in preventing the peaking of As and Cr in water resources.

5.3 References

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Attachment I Information request

De volgende vragenlijst is naar alle bedrijven verstuurd om voor de uitgevoerde monstercampagne voor elke locatie een goed beeld te krijgen van de lokale omstandigheden.

5.4 Information request

Selected drinking water production sites for sampling campaign

Table 1 presents 14 drinking water production locations which have been selected for further As and Cr investigation. Please note that the As and Cr concentrations mentioned in table 1 are average of past 6 years (2008-2013) and taken from RIVM database.

In case both As and Cr speciation analysis is to be undertaken, several samples will be collected from each water production location, both from raw water (verzameld ruw) and from the finished drinking water (rein water). Planned analysis: ICP-MS scan (after destruction), As speciation, Cr speciation, and anions for raw water. All the samples for speciation analysis will be collected after filtration through 0,45 µm membrane filter in order to measure only the dissolved fraction of different As and Cr species. The raw water samples for ICP-MS scan will also be collected after filtration through 0,45 µm filter. The treated water samples will be unfiltered.

Table: Selected drinking water production locations from the Netherlands for As and Cr investigation

Location	As (Raw)	As (Treated)	As removal	Cr (Raw)	Cr (Treated)	Cr removal	Water companies	Speciation	
	µg. L ⁻¹	µg. L ⁻¹	%	µg. L ⁻¹	µg. L ⁻¹	%		As	Cr
Loosdrecht	18,93	1,85	90,23	<0,5	<0,5	-	Vitens	1	0
Ouddorp	12,5	5,32	57,44	1,17	<1	57,3	Evides	1	1
Breda-Dorst	11,5	5,78	49,74	?	<1	?	BW	1	1
Oosterhout	6,6	3,52	46,67	?	<1	?	BW	1	0
Wageningse Berg	3,67	3,06	16,62	<0,5	<0,5	-	Vitens	1	0
Veenendaal	1,92	1,65	14,15	<0,5	<0,5	-	Vitens	1	0
Monster*	0,92	2,83	-207	0,87 (2,7 in 2013)	<0,5	72	Dunea	1	1
Plasmolen	?	1,42	?	?	<1	?	WML	1	1
Lekkerker-Schuwacht	3,95	1,5	62,1	<0,5	0,56	-124	Oasen	1	1
Pinkenberg	<1	<1	-	1,69	1,55	8,48	Vitens	1	1
De Haere	1,4	<1	-	1,23	1,13	7,86	Vitens	1	1
Zeist	2,68	1,32	50,7	0,96	1,17	-21,60	Vitens	1	1

Arnhem la Cabine	2,1	1,29	38,73	1,05	0,82	22,3	Vitens	1	1
Leersum	4,21	2,91	31,2	0,78	0,57	26,9	Vitens	1	1

1=Speciation analysis planned

0=Speciation analysis not planned

* Initially DWPP Monster was selected for sampling, but this was changed to DWPP Scheveningen after conferring with Dunea

Information required/questions to be answered by the water companies Vitens, Brabant Water, Dunea, Evides and WML:

Abstraction

Production capacity of the facility? Total production in 2013?

Number of pumping wells?

Abstraction depth and average pumping rate (2013) for each individual well?

Information regarding aquifer from which groundwater is being abstracted: depth, type (phreatic, semi-confined, confined), single aquifer or >1 aquifer?

Is there a raw water reservoir or the raw water is treated directly after abstraction without storage?

Please specify/confirm the raw water source (location) of every water production location in the list! For instance, from where Monster pumps in its raw water...

Treatment

Please provide the process scheme of the water production facility!

What type of aeration is applied?

Dissolved oxygen level before and after aeration?

Redox potential before and after aeration?

Use of chemical oxidants, coagulants or any other chemicals? Type, dose (mg/L) and point of dosing in the treatment train?

Type of mixing equipment used?

Type of filtration media (particle type, size in mm, single or double)?

Single step or two step filtration?

Filtration velocity?

Filter bed height?

Supernatant depth?

Filter run time?

Backwashing criteria (Breakthrough or pressure drop)?

Backwashing procedure?

Please provide details of any post treatment applied (pH adjustment, UV etc.)

Your specific views about this drinking water production location?

Data from recent As and Cr measurements

Please share As and Cr (total and/or speciation) measurement results in the source and treated waters of the mentioned facilities if you have any from the latest sampling.

Please share also the water quality data (incl. main constituents and trace elements [incl. As, Cr]) of the individual pumping wells, in order to evaluate effects of mixing of different qualities.

