KWR 2017.009 | February 2017

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Baseline study and batch experiments with $KMnO_4$ and $FeCl_3$ to remove arsenic

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Project manager
Bas Wols

Client
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Quality Assurance
Emile Cornelissen

Author
Arslan Ahmad

Project group
Arslan Ahmad (KWR), Wim Oorthuizen (Dunea), Jordi van Mook (Evides), Bas Schaaf (Evides), Jos Hooft (Waternet)

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Dunea, PWN, Waternet, Evides

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More information
Arslan Ahmad
T +31 6 46 95 02 31
E arslan.ahmad@kwrwater.nl

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

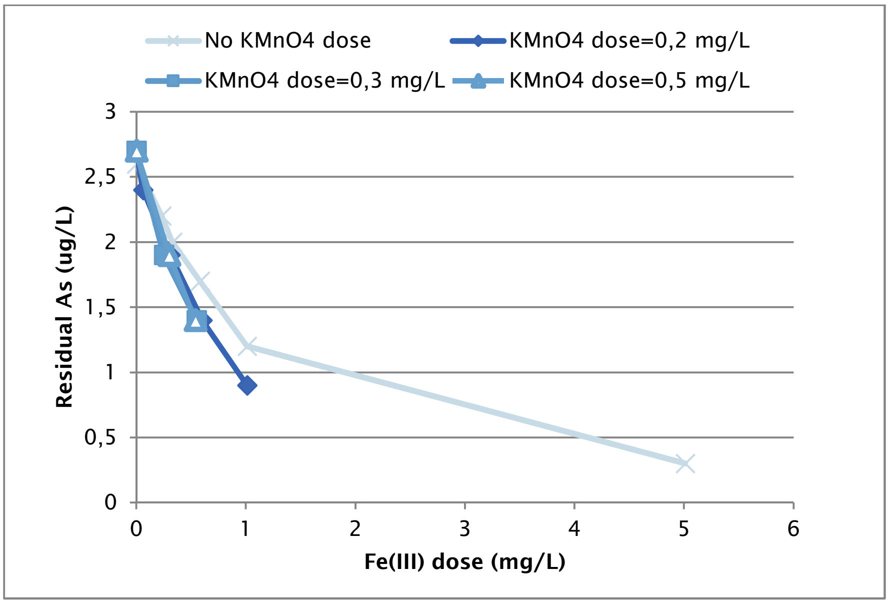
KWR Watercycle Research Institute

Managementsamenvatting

Arseenconcentraties in Katwijk, Ouddorp en Leiduin; methoden om concentraties onder 1 µg/L te brengen

Auteur Arslan Ahmad MSc

De Nederlandse waterbedrijven hebben zichzelf tot doel gesteld de arseenconcentraties in drinkwater te verlagen tot onder 1 µg/L. Voor drie DPWE bedrijven is op drie verschillende locaties gemeten wat de huidige arseenconcentraties van het ruw- en reinwater zijn. Verder is met behulp van laboratoriumtesten onderzocht hoe deze concentraties in het reinwater kunnen worden verlaagd. Toevoeging van ijzer(III), eventueel in combinatie met kaliumpermangaat als oxidator, aan het influent van snelle zandfilters lijkt een effectieve methode te kunnen zijn hiervoor, die relatief eenvoudig kan worden geïmplementeerd.



Invloed van $FeCl_3$ dosering (met en zonder $KMnO_4$) op de As-concentratie in reinwater op locatie Katwijk (Dunea)

Belang: Inzicht in arseenconcentraties en mogelijkheden die te verlagen

De Nederlandse waterbedrijven hebben zich tot doel gesteld de arseenconcentraties in reinwater te verlagen tot onder 1 µg/L. Het is voor de bedrijven belangrijk te weten hoe hoog de huidige concentraties zijn, waar in het proces arseenverwijdering plaatsvindt, en hoe dit proces eventueel, op eenvoudige wijze, verbeterd kan worden.

Aanpak: Inventarisatie arseenconcentraties in ruw- en reinwater, gevolgd door lab-experimenten.

In Katwijk (Dunea), Ouddorp (Evides) en Leiduin (Waternet) zijn arseenconcentraties gemeten in zowel ruw- als reinwater. Hierbij is vastgesteld welk zuiveringsproces het meeste bijdraagt aan de verwijdering. Vervolgens is op het laboratorium onderzocht in hoeverre de verwijdering in deze processtap kan worden verbeterd door co-precipitatie met aanwezig of toegevoegd ijzer en/of toegevoegd $KMnO_4$.

Resultaten: Verlaging van arseenconcentraties in reinwater tot onder 1 µg/L mogelijk.

In alle gevallen bleek arseen voornamelijk samen met ijzer verwijderd te worden in de snelle zandfilters. De aanwezigheid van orthofosfaat kan deze verwijdering hinderen.

Uit het onderzoek bleek dat in Katwijk ruw water gemiddeld 3,8 µg/L bevat en reinwater 2,9 µg/L. Toevoeging van Fe(III) aan het influent van snelle zandfilters levert de gewenste concentratieverlaging, maar wanneer $KMnO_4$ wordt toegevoegd is minder Fe(III)-dosering nodig.

In Ouddorp waren de concentraties in ruw- en reinwater respectievelijk 12 en 2,8 µg/L (met Fe(III)-dosering aan het influent) of 5,5 µg/L (zonder Fe(III)-dosering). Hier bleek een combinatie van $KMnO_4$- en Fe(III)-dosering de gewenste verlaging op te leveren.

In Leiduin werd in het ruwwater gemiddeld 2,7 µg/L aangetroffen, en in het reinwater 1,6 µg/L. Hier kan de beoogde verwijdering worden gerealiseerd door toevoeging van Fe(III) of Fe(II), met of zonder $KMnO_4$, hoewel toevoeging van de oxidator de benodigde ijzerdosering verlaagt.

Implementatie: Arseenconcentraties onder 1 µg/L met behulp van oxidatie en coagulatie.

Door het toevoegen van ijzer (Fe(III)) aan het influent van snelfilters kan de arseenconcentratie in het water worden verlaagd. Dit proces wordt nog effectiever, indien vooraf $KMnO_4$ als oxidator wordt toegevoegd. Hierdoor is het mogelijk de arseenconcentratie onder de streefwaarde van 1 µg/L te brengen bij relatief lage ijzerdoseringen. Deze resultaten zijn gebaseerd op laboratoriumtesten. Het wordt aanbevolen om ook pilottesten uit te voeren om het effect van doseren van ijzer met/zonder $KMnO_4$ op de operatie van de filters en spoelwaterkwaliteit en kwantiteit te onderzoeken.

Rapport

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More information
Arslan Ahmad
T +31 6 46 95 02 31
E arslan.ahmad@kwrwater.nl

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

Summary in English

Introduction

Arsenic (As) is a toxic element which occurs naturally in the earth's crust. It has been reported to cause contamination of drinking water sources in many parts of the world. World Health Organization (WHO) guideline for As in drinking water is 10 µg/L. The drinking water companies in the Netherlands are committed to produce drinking water with impeccable quality and therefore have voluntarily accepted 1 µg/L as the new target for As in drinking water.

This study has been carried out in the joint research program of Dutch dune water companies (DPWE). Three drinking water treatment plants (DWTPs), namely Katwijk (Dunea), Ouddorp (Evides) and Leiduin (Waternet) were included in this study with the aim of investigating the existing As removal efficiency of the existing treatment setups and to pin-point the treatment processes that are responsible for the observed As removal capacity. Furthermore, at each of the locations, the possibility of achieving <1 µg/L of As in the produced drinking water is studied. The technique used is coprecipitation of As with naturally available or artificially added iron (Fe), with or without pretreatment of the water with potassium permanganate ($KMnO_4$).

In order to establish the baseline knowledge regarding As removal the available water quality data from the routine monitoring programs of the DWTPs was analysed. Fresh sampling campaigns were carried out at the full-scale treatment plants whenever required. Jar tests were carried out to investigate the influence of $KMnO_4$ and Fe dosing on As removal, using actual streams of interest from the DWTPs.

Arsenic removal at Katwijk (Dunea)

The results of the baseline study at Katwijk show that the dune effluent contains 3.8 µg/L As [42% As(III) and 58% As(V)] and the produced drinking water contains 2.9 µg/L As [100% As(V)]. The cascade aeration does not oxidize As(III). The rapid sand filter bed oxidizes As(III) to As(V), however it is not yet clear at which depth this transformation takes places and which physicochemical and/or biological processes are the trigger. Iron removal in rapid sand filtration is mainly responsible for the existing As removal capacity of DWTP Katwijk.

The jar tests performed at Katwijk showed that dosing only $KMnO_4$ in the influent of rapid sand filters could not reduce the residual As concentration significantly. Even when As(III) was fully oxidized to As(V) at $KMnO_4$ dose of 0.5 mg/L, the target As concentration of <1 µg/L was not achieved, possibly due to the competition between the produced As(V) and the ortho-PO_4 that was naturally present in the water. Dosing only Fe(III) in the influent of rapid sand filters of Katwijk could lead to residual As concentration of <1 µg/L. The use of $KMnO_4$ for pre-oxidizing As(III) to As(V) is expected to decrease the Fe(III) dose required to achieve <1 µg/L As at Katwijk.

Arsenic removal at Ouddorp (Evides)

The results of the baseline study at Ouddorp show that the average As concentration in the raw water is 12 µg/L [As(III)>70%]. After the treatment, the As concentration in the produced drinking water is averaged at 2.8 µg/L (with 1 mg/L Fe(III) in part of the influent of rapid sand filters) and 5.5 µg/L (without Fe(III) dose before the rapid sand filters). The sprinklers used for aeration of raw water at Ouddorp do not oxidize As(III) to As(V). The oxidation of As(III) takes place in the top half of the filter bed, simultaneously with the removal of As, Fe, Mn and NH_4, however it is not yet clear that which physicochemical and/or biological processes are the trigger for As(III) oxidation to As(V) in the filter bed. The available As removal capacity of the existing treatment process of DWTP Ouddorp can be attributed mainly to the removal of Fe in the rapid sand filters.

The Jar tests performed at Ouddorp showed that dosing of $FeCl_3$ or $KMnO_4$ alone in the combined raw water of DWTP Ouddorp could not reduce residual As concentration to <1µg/L, even at relatively high dosages. Dosing a combination of $KMnO_4$=0.6 mg/L and Fe(III)=1.3 mg/L in the combined raw water could effectively reduce As concentration to <1µg/L (Figure 1).

An alternative option for DWTP Ouddorp is to dose Fe(III) in the influent of ultrafiltration. The jar test shows that this can avoid the need to dose $KMnO_4$.

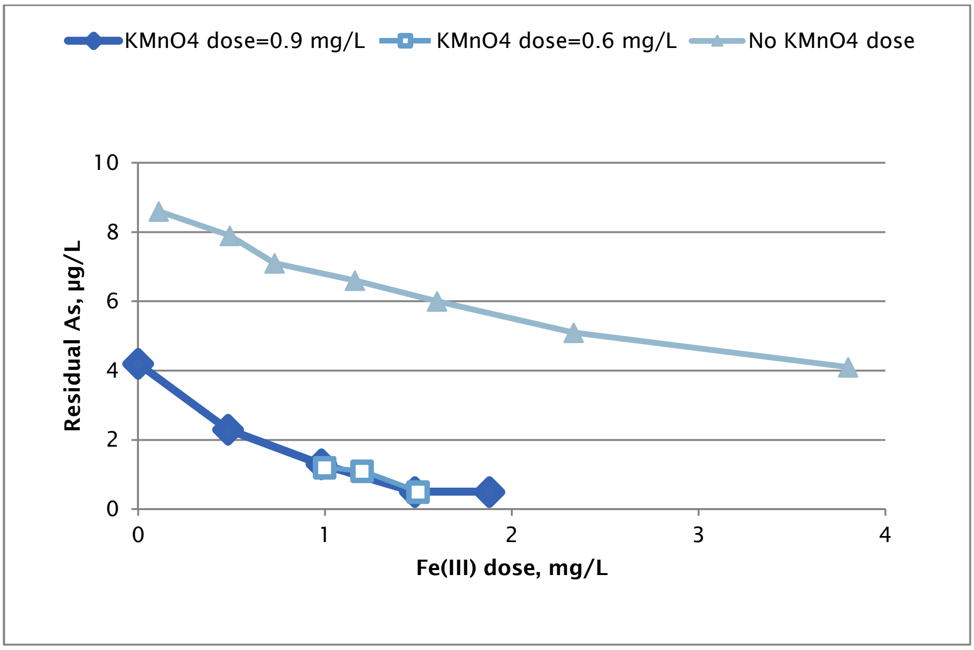

FIGURE 1 ARSENIC REMOVAL BY Fe(III) DOSING, WITH AND WITHOUT PRE-TREATMENT WITH $KMNO_4$. BASED ON THE JAR TESTS PERFORMED WITH THE INFLUENT OF RAPID SAND FILTERS AT OUDDORP (EVIDES).

Arsenic removal at Leiduin (Waternet)

At Leiduin the dune effluent contains 2.7 µg/L As, on average. After the treatment, the As concentration in the produced drinking water is averaged at 1.6 µg/L, representing an average removal of approximately 40 %. The baseline study revealed that the observed As removal at Leiduin can be attributed to Fe removal which principally takes place in the rapid sand filters. The naturally available ortho-PO_4 in the dune effluent seems to compete with As for the sorption sites on Fe-hydroxides.

The jar tests performed at Leiduin show that As removal to <1 μg/L at DWTP Leiduin can be achieved by treating the influent of the rapid sand filters either with Fe(III) or Fe(II), with or without pre-treatment with $KMnO_4$. The use of $KMnO_4$ for pre-oxidizing As(III) to As(V) is expected to lower the coagulant dose required to achieve <1 μg/L As in the drinking water of DWTP Leiduin.

Recommendation for pilot tests at Katwijk, Ouddorp and Leiduin

The current study was based on batch-scale As removal experiments. As a next step, it is recommended to carry out pilot tests. Pilot tests are important to determine the impact of chemical dosing in the operation and performance of filters. They are also important to optimize the filter run time, backwashing frequency etc. and to evaluate the impact of increased As removal on the quantity and quality of the residuals (sludge).

Contents

1 Introduction

1.1 Background

Arsenic (As) is a toxic element which occurs naturally in the earth's crust. It has been reported to cause contamination of drinking water sources in many parts of the world, including (but not limited to) Bangladesh, Chile, China, Hungary, India, Japan, Turkey and the United States of America (USA). Although regulations exist in most of the countries, 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).

World Health Organization (WHO) guideline for As in drinking water is 10 µg/L. World Health Organization denotes this guideline as provisional and states that every effort should be undertaken to keep the concentrations as low as reasonably achievable (WHO, 2011). The drinking water companies in the Netherlands are committed to produce drinking water with impeccable quality and therefore have voluntarily accepted 1 µg/L as the new target for As in drinking water. The decision was made as a precautionary measure based on a two-tiered assessment of As in Dutch drinking water (Van der Wens et al. 2016). In the first tier a conservative estimation on human health effects of As exposure via drinking water was made. In the second tier a removal cost versus health benefit analysis was carried out. Comparison of the treatment costs with modeled health benefits showed that the benefits were approximately twice the costs (Van der Wens et al., 2016).

The spatial distribution of As in raw water in the Netherlands is shown in Figure 1-1 (Stuyfzand et al., 2008; Ahmad, 2015a). Currently, there are 8 public supply well fields (PSWFs) which supply raw water with As concentration >10 µg/L. Fortunately, the raw water contains adequate amount of iron (Fe) by itself to reduce As concentration to < 10 µg/L upon the conventional Fe removal treatment (Ahmad, 2015a). According to REWAB database (the Dutch national database in which the results of the samples reported to the Inspector of Public Health are published), there are 28 drinking water treatment plants (DWTPs) which produce drinking water with >1 µg/L As (Ahmad, 2015a).

When it comes to As removal from water, there is no one "silver bullet". Arsenic removal is challenging and different methods may be appropriate for different situations (Ahmad et al., 2016). Coprecipitation of As with Fe-hydroxides is the most common way to reduce As concentrations at drinking water treatment plants where rapid sand filtration is available. The Fe-hydroxides can be generated in the process water by oxidizing the naturally occurring ferrous iron [Fe(II)] or by dosing an Fe based coagulant, such as iron sulphate ($FeSO_4$) or iron chloride ($FeCl_3$). Operating parameters, such as coagulant type, dose, pH, raw water composition, target arsenic concentration in the effluent, layout of the existing treatment scheme, turbidity/particle removal efficiency of the filters, sludge handling etc. play a vital role in coprecipitation based As removal process (Ahmad et al., 2016).

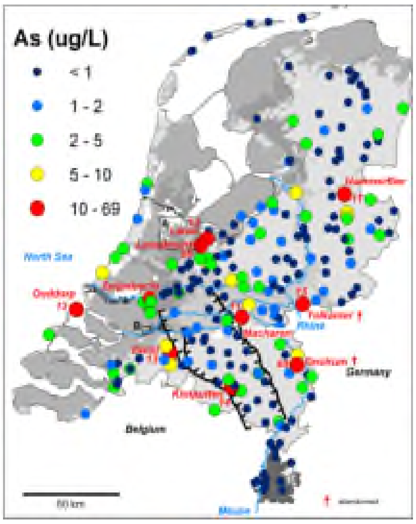

FIGURE 1-1 MEAN As CONCENTRATIONS IN THE RAW WATER PUMPED BY THE 242 PSWFs IN THE NETHERLANDS IN 2008. (*STUYFZAND et al., 2008; AHMAD, 2015a)*

Coprecipitation of As with Fe is more effective in removing arsenate [As(V)] compared to arsenite [As(III)]. This is because, As(V) occurs as a singly or doubly charged specie in the pH range of most natural waters (6-8.5), while, As(III) is predominantly uncharged below pH 9.2 (Smedley and Kinniburgh, 2002). The charge on As(V) facilitates its adsorption onto oppositely charged surfaces and subsequent removal. Therefore, in most cases oxidation of As(III) to As(V) is deemed necessary to achieve satisfactory removal. Chemical oxidants such as chlorine (Cl_2), chlorine dioxide (ClO_2), chloramine (NH_2Cl), sodium hypochlorite (NaOCl), hydrogen peroxide (H_2O_2), ozone (O_3), potassium permanganate ($KMnO_4$) and ferrate (FeO_4^{-2}) can be used to rapidly oxidize As(III) in water (Ahmad et al., 2016). Each oxidant has its own advantages and disadvantages. Brabant Water, a major groundwater company in the Netherlands, uses $KMnO_4$ for oxidizing As(III) at DWTP Dorst (Figure 1-2) because it has proven to be an efficient As(III) oxidant (Ahmad et al., 2014; Ahmad, 2015b), which is easy to store and apply in practice.

1.2 Scope and objectives

This study has been carried out in the joint research program of Dutch dune water companies (DPWE). Three DWTPs, namely Katwijk, Ouddorp and Leiduin were included in this study with the aim of investigating the existing As removal efficiency of these treatment plants, As removal mechanisms at each of these locations and the potential of achieving <1 µg/L of As in the produced drinking water by using coprecipitation with naturally available or artificially added Fe, with or without pretreatment with $KMnO_4$.

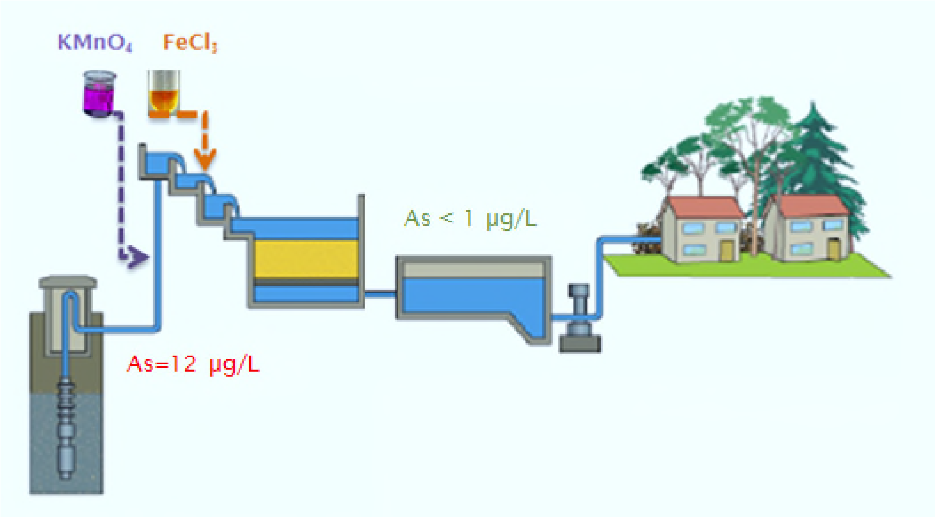

FIGURE 1-2 PROCESS SCHEME OF DWTP DORST (BRABANT WATER), RECENTLY UPGRADED WITH KMNO4 AND FECL3 DOSING FOR ARSENIC REMOVAL TO <1 μg/L .

1.3 Reading guide

This report has been divided into 4 sections. Section 1 (this section) sets the background of the study and describes the aim of the study. Section 2 is focused on the baseline study and jar tests carried out at DWTP Katwijk. Section 3 is focused on the baseline study and jar tests carried out at DWTP Ouddorp. Section 4 is focused on the baseline study and jar tests carried out at DWTP Leiduin.

2 Arsenic removal at Katwijk (Dunea)

2.1 Introduction

The drinking water treatment plant (DWTP) of Katwijk has a production capacity of 24.8 Mm^3/year. It uses surface water from the *afgedamde Maas* (river Meuse) as its raw water. The raw water is pre-treated at Brakel and Bergambacht and then infiltrated in the dune area of Katwijk. The residence time of water in the dunes is approximately 60 days. The average As concentration after the pre-treatment (before dune infiltration) is 0.8 µg/L. During infiltration As gets mobilized and as a result the dune effluent contains 3.8 µg/L As, on average (**Error! Reference source not found.**).

At DWTP Katwijk the dune effluent is treated in a series of steps, including powdered activated carbon (PAC) dosing, cascade aeration, partial pellet softening with caustic soda (NaOH), rapid sand filtration (RSF) and finally slow sand filtration (SSF) (Figure 1-1). After the treatment, the As concentration in the produced drinking water is reduced to 2.9 µg/L on average.

A baseline study was carried out at DWTP Katwijk to determine the share of each treatment system in the existing As removal. Following the baseline study a series of jar tests with RSF influent was carried out at DWTP Katwijk to investigate the removal of As to <1 µg/L.

2.2 Materials and methods

2.2.1 Baseline study

In order to establish the baseline knowledge regarding As removal at DWTP Katwijk the available water quality data from the routine monitoring program of treatment plant was analysed. However, the available data was not adequate to determine As species in the dune effluent and the influence of different treatment steps on the removal and transformation of As species. Therefore, a new sampling campaign was carried out on 03-March-2016. For the sampling campaign 6 sampling points were selected at DWTP Katwijk. These include;

1. Dune effluent
2. Cascade effluent
3. Softening reactor effluent
4. RSF influent (mix of softening effluent + by-pass of softening)
5. RSF effluent
6. SSF effluent (drinking water)

Filtered and unfiltered samples were collected and analysed for total As, Fe, Mn, Ca and Mg concentration. Filtration of samples was carried out onsite, through 0.45 µm disc filters (GE Healthcare Whatman ™ 0.45 µm). For As speciation analysis, the field speciation protocol developed by Clifford et al. (1983) was used and the kits were prepared on site. All the samples collected during the sampling campaign were analysed at Aqualab Zuid.

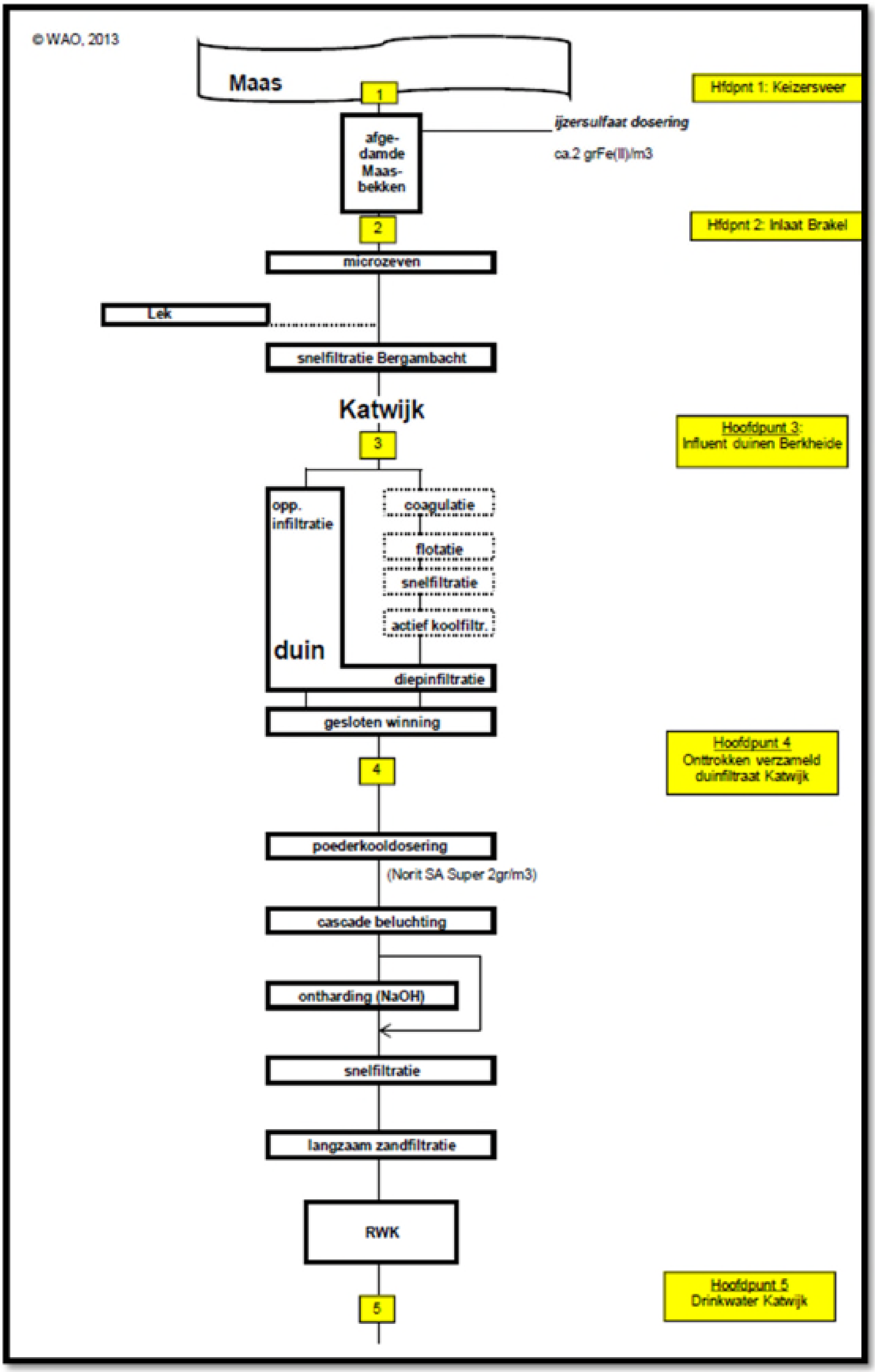

FIGURE 2-1 THE PROCESS SCHEMES OF DWTP KATWIJK.

2.2.2 Jar tests

Three jar tests were performed at DWTP Katwijk. These include:

1. Dosing only $KMnO_4$ in the RSF influent
2. Dosing only $FeCl_3$ in the RSF influent
3. Dosing $KMnO_4$ and $FeCl_3$ in the RSF influent

All the chemicals used in this study were reagent grade. All stock solutions were prepared using distilled water. A standard jar testing device was used to perform the experiments. All the jar tests were carried out at DWTP Katwijk. Figure 2-2 shows the jar testing setup installed at DWTP Katwijk for the experiments. On completion of the desired reaction time between treatment chemicals and given water, samples were collected from the bottom of the jars and immediately filtered through 0.45 µm disc filters (GE Healthcare Whatman ™ 0.45 µm). All the samples were analysed at Aqualab Zuid.

FIGURE 2-2 JAR TESTING SETUP AT DWTP KATWIJK.

2.3 Results and discussion

2.3.1 Baseline study

Table 2-1 presents a comparison between the quality of dune effluent and the produced drinking water at DWTP Katwijk. It is evident that DWTP Katwijk removed approximately 24 % of As. Moreover, the treatment system also removed total and dissolved phosphate (PO4), dissolved organic carbon (DOC), Fe, manganese (Mn), ammonia (NH_4) etc. With the data presented in Table 2-1 it cannot be ascertained that which of the treatment steps were critical for existing As removal at DWTP Katwijk. Moreover, the interaction of As with Fe and Mn was unclear. Therefore, a sampling campaign was required.

Table 2-2 presents the results of the sampling campaign. It shows that the dune effluent contains 0.28 mg/L of total Fe, most of which was available as precipitated Fe-hydroxides. Out of 4 µg/L total As in the dune effluent, 3.1 µg/L was present in dissolved form. Out of 0.44 mg/L of total phosphate, 0.33 mg/L was available as dissolved ortho-phosphate (known from the available data at DWTP Katwijk). It is likely that the precipitated As (0.9 µg/L) and phosphate (0.11 mg/L) in the dune effluent was already co-precipitated with Fe- hydroxides. It can be seen in Table 2-2 that the effluent of RSF contains significantly lower amount of Fe, compared to the influent. With the reduction in total Fe content, As was decreased as well.

This shows that the RSF was the most critical step in the removal of As at DWTP Katwijk. The softening step and SSF does not appear to contribute significantly to As removal at DWTP Katwijk.

Table 2-2 shows that during the treatment the dissolved Fe in the dune effluent (0.08 mg/L) was precipitated to form Fe-hydroxides, however, the dissolved As in the dune effluent was not co-precipitated (further) during the treatment. This can be attributed to the competition between As and ortho-PO_4 for the adsorption sites on the surface of Fe-hydroxides (Manning and Goldberg,1996). The concentration of ortho-PO4 was reduced from 0.33 mg/L to 0.15 mg/L during the treatment of dune effluent at DWTP Katwijk (from the available data at DWTP Katwijk not reported here). It seems that coprecipitation with Fe was not the only mechanism involved in the removal of ortho-PO_4 at DWTP Katwijk.

In the dune effluent 1.3 µg/L of dissolved As(III) and 1.8 µg/L of dissolved As(V) was present. The oxidation (and reduction) of As is fairly a slow process. Therefore, both As(V) and As(III) can exist together in both oxic and reducing conditions (Edwards 1994). It can be observed in Table 2-2 that the ratio between dissolved As(III) and As(V) remained more or less same during various treatment steps of DWTP Katwijk until the process water entered the RSF bed. It is known that conventional aeration techniques e.g. cascade aeration or sprinklers, do not oxidize As(III) (Ahmad et al., 2016). Inside the RSF bed oxidation of As(III) to As(V) took place, as can be seen in Table 2-2. As a result, the dominant form of As in the RSF effluent was As(V).

Oxidation of As(III) to As(V) by atmospheric oxygen is a very slow process. Bissen and Frimmel (2003) studied the oxidation kinetics of As(III) and reported that only 55 % of total As(III) was oxidized in 5 days when the groundwater was purged with air and pure oxygen. The residence time of water in the RSF bed was approximately 10 minutes and in this time frame oxygen alone cannot oxidize As(III). The manganese oxides or biological mechanisms in the RSF beds might be responsible for the observed rapid transformation of As(III) to As(V) (Gude et al., 2016). Similar rapid oxidation of As(III) in rapid sand filters has been observed at other DWTPs in the Netherlands (Ahmad et al., 2014; Ahmad, 2015b, Gude et al., 2016).

TABLE 2-1 COMPARISON OF THE DUNE EFFLUENT AND DRINKING WATER AT DWTP KATWIJK.

Parameter	Unit	Dune effluent	Drinking water
Dissolved oxygen	mg O_2/L	2.6±0.88 (n=26)	9.9±0.38 (n=8)
pH	-	7.67±0.05 (n=106)	8.48±0.09 (n=104)
Turbidity	FTE	1.62±1.83 (n=104)	0.01±0.02 (n=106)
Hardness	mmol/L	2.07±0.09 (n=53)	1.44±0.06 (n=53)
Alkalinity	mg HCO_3/L	204.4±6.25 (n=53)	174.7±5.20 (n=53)
Arsenic	µg As/L	3.8±0.4 (n=8)	2.9±0.4 (n=26)
Ammonia	mg NH_4/L	0.13±0.11 (n=27)	0.006±0.001 (n=53)
Calcium	mg Ca/L	69±3.22 (n=51)	43.9±4.68 (n=105)
Magnesium	mg Mg/L	8.3	8.2
Sodium	mg Na/L	32.9±2.84 (n=27)	52.2±3.7 (n=9)
Iron	mg Fe/L	0.37	0.003
Manganese	mg Mn/L	0.06	0.001
Dissolved organic carbon	mg C/L	2.7±0.13 (n=27)	2.4±0.15 (n=27)
Orthophosphate	mg PO_4/L	0.33±0.12 (n=8)	0.15±0.02 (n=8)
Total phosphate	mg PO_4/L	0.44±0.24 (n=8)	0.17±0.02 (n=8)

TABLE 2-2 RESULTS OF THE SAMPLING CAMPAIGN OF 03 MARCH 2016 (N=1).

Sample point	**Total As**	**Dissolved As**	**Dissolved As(III)**	**Dissolved As(V)**	**Tot Fe**	**Dissolved Fe**	**Total Mn**	**Dissolved Mn**	**Total Ca**	**Total Mg**
	µg/L	µg/L	µg/L	µg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Dune effluent	4	3.1	1.3	1.8	0.28	0.08	0.04	0.03	71	8.33
Cascade effluent	3.7	3.1	1.4	1.7	0.28	0.06	0.04	0.03	71	
Softening reactor effluent	3.9	2.9	1.3	1.6	0.28	0.02	0.01	<0.01	28	8.26
RSF influent (mix of softening effluent + by-pass of softening)	3.7	3.1	1.3	1.8	0.26	0.04	0.02	0.02	48	8.2
RSF effluent	3.1	3	0.5	2.5	0.01	<0.01	<0.01	<0.01	47	-
SSF effluent	3	3.2	0.5	2.7	<0.01	<0.01	<0.01	<0.01	47	8.23

2.3.2 Jar tests

Test 1: Dosing $KMnO_4$ alone in the RSF influent

The baseline study revealed that the influent of RSF contain 1.3 µg/L As(III) (Table 2-2). Jar test 1 was therefore designed to investigate if the uptake of As by the naturally available Fe in the RSF influent could be increased by oxidizing As(III) to As(V) with the help of $KMnO_4$. Figure 2-3 shows the influence of dosing $KMnO_4$ in the RSF influent. It can be seen that dosing $KMnO_4$ in the RSF influent could not reduce the residual As concentration significantly. At none of the studied doses residual As concentration of <1 µg was achieved. The acute drop of residual As to approximately 2.3 µg/L was due to the presence of a slightly higher concentration of naturally available Fe in the start solution of this particular batch.

It is interesting to note that at $KMnO_4$ dose of 0.5 mg/L all the As(III) available in the influent of RSF was oxidized to As(V) (data not shown here). However, the removal of As was not increased. This means that the oxidation of As(III) to As(V) was not shown to increase As removal. This may be attributed to the competition with ortho-PO_4 present in the solution for sorption sites on Fe-hydroxides.

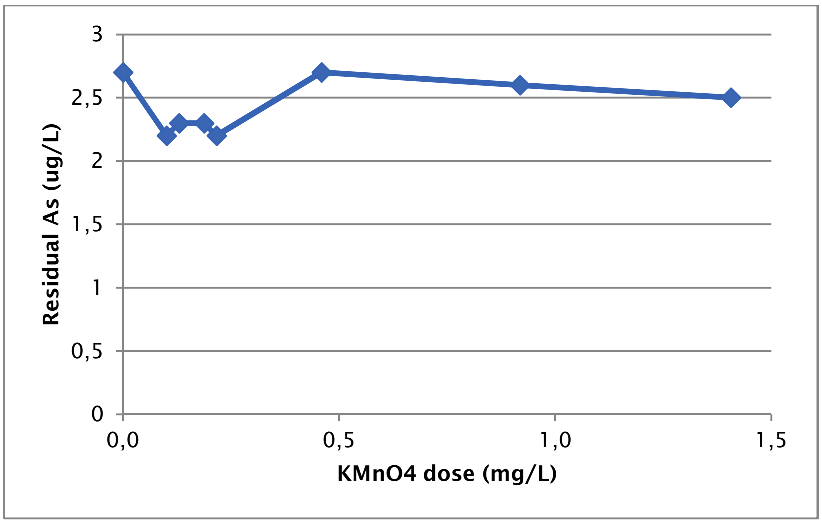

FIGURE 2-3 INFLUENCE OF $KMnO_4$ DOSE ON RESIDUAL As CONCENTRATION.

Test 2 & 3: Dosing $FeCl_3$ (with and without $KMnO_4$) in the RSF influent

Jar test 2 was aimed at investigating the influence on residual As concentration at varying Fe(III) (dosed as $FeCl_3$) dose without pre-treating with $KMnO_4$. On the other hand, Jar test 3 was aimed at investigating the influence on residual As concentration at varying Fe(III) (dosed as $FeCl_3$) dose with $KMnO_4$ pre-treatment. The results have been collectively presented in Figure 2-4. It can be see that the pre-treatment with $KMnO_4$ has a noticeable influence on the residual As concentration. It resulted in a slightly lower residual As concentration compared to Fe(III) dose alone. Figure 2-4 also shows that residual As concentrations remained similar at all the tested $KMnO_4$ dosages. This refers to complete oxidation of As(III) at the lowest $KMnO_4$ dose applied in this test, i.e. 0.2 mg/L.

It can be seen that residual As concentration of <1 µg/L was achieved when the influent of RSF was pre-treated with 0.2 mg/L of $KMnO_4$ and subsequently with 1 mg/L of Fe(III).

Residual As concentration of <1 µg/L was also achieved in the jar test which was performed without pre-treatment with $KMnO_4$, at Fe(III) dose of 5 mg/L. It could also be possible to achieve <1 µg/L at a much lower Fe(III) dose, however Fe(III) doses between 1 and 5 mg/L were not tested in this study.

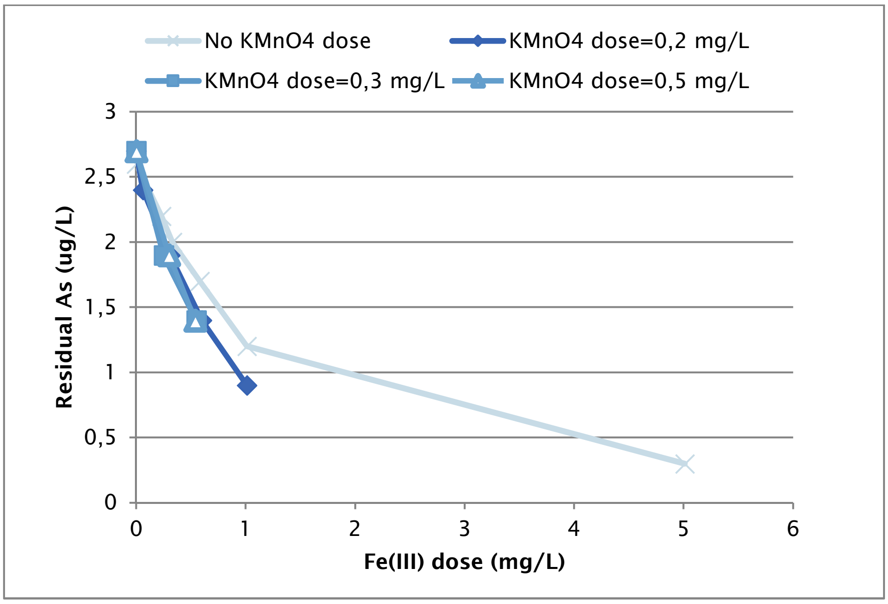

FIGURE 2-4 INFLUENCE OF $FeCl_3$ DOSE (WITH AND WITHOUT $KMnO_4$) ON RESIDUAL As CONCENTRATION.

2.4 Conclucions and recommendations

At drinking water treatment plant Katwijk rapid sand filtration, specifically the Fe removal in the rapid sand filters, is the key process that is responsible for the existing As removal efficiency. The naturally available ortho-PO_4 in the dune effluent seems to compete with As for the sorption sites on Fe-hydroxides because during the treatment uptake of As by already precipitated and freshly precipitating Fe-hydroxides was not increased.

Softening and slow sand filtration do not contribute to existing As removal capacity of DWTP Katwijk. Cascade aeration does not oxidize As(III) which is approximately 42 % of the total dissolved As in the dune effluent. However, the rapid sand filter bed oxidize As(III) to As(V) and the responsible mechanism for this transformation is yet to be ascertained.

Arsenic removal to <1 µg/L at DWTP Katwijk can be achieved by treating the influent of the rapid sand filters with $FeCl_3$, with or without pre-treatment with $KMnO_4$. The use of $KMnO_4$ for pre-oxidizing As(III) to As(V) is expected to decrease the $FeCl_3$ dose required to achieve <1 µg/L As.

Following are the main recommendations:

- To carry out additional sampling campaign, including the determination of total and dissolved PO_4, organics and silicates, besides the constituents which have been taken into account during the sampling campaign of this study.
- To perform an additional batch test with Fe(III) dosages between 1 and 5 mg/L to determine the accurate amount of Fe(III) required to achieve <1 µg/L, without $KMnO_4$ pre-treatment.

- To carry out pilot tests using one or two pilot scale columns, fed with the influent of rapid sand filters in order to optimize (fine-tune) the dosing of chemical(s), to determine the impact of chemical dosing in the operation and performance of filters, in order to optimize the filter run time, backwashing frequency etc. and to evaluate the impact of increased As removal on the quantity and quality of the residuals (sludge).

3 Arsenic removal at Ouddorp (Evides)

3.1 Introduction

The drinking water treatment plant of Ouddorp (DWTP Ouddorp) has a production capacity of 4.8 Mm^3/year. It uses surface water from Haringvliet as its raw water. The raw water is pre-treated and then infiltrated in the dune area of Ouddorp. The residence time of water in dunes is more than 30 days. The As concentration in the source water from Haringvliet is generally <0.5 µg/L. However during the infiltration of water As gets mobilized, resulting in As concentration of higher than 1 µg/L in the dune effluent. Besides the infiltrated water, a limited amount of natural groundwater is also used as raw water. The groundwater also contains As concentration of higher than 1 µg/L. The raw water at DWTP Ouddorp is treated in a series of steps, including sprinkler aeration, iron chloride ($FeCl_3$) dosing, rapid sand filtration (RSF), activated carbon filtration and finally ultrafiltration (Figure 3-1). After the treatment, the As concentration in the produced drinking water is averaged at 2.8 µg/L (with 0.5 mg/L Fe(III)) and 5.5 µg/L (without Fe(III) dose).

It was unclear which treatment step was mainly responsible for As removal at DWTP Ouddorp. Moreover, the distribution of As species in the dune effluent and the variation/interchanging of these species in various treatment steps was not known. Therefore, a sampling campaign was carried out at DWTP Ouddorp. Following the sampling campaign jar tests were performed to determine the removal of As by coprecipitation with Fe, with or without $KMnO_4$ dosing.

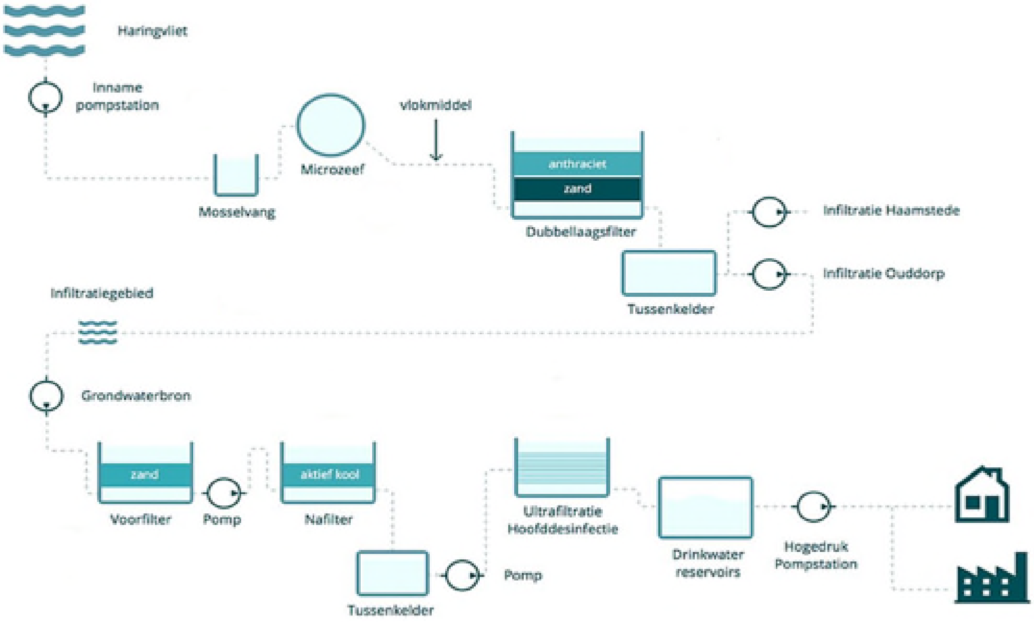

FIGURE 3-1 PROCESS SCHEME OF DWTP OUDDORP.

3.2 Materials and methods

3.2.1 Baseline study

In order to establish the baseline knowledge regarding As removal at DWTP Ouddorp all the water quality data provided by Evides (2006-2016) was studied and wherever required fresh sampling campaigns were carried out at the full-scale installation of Ouddorp. The sampling and analysis was performed by Aqualab Zuid.

3.2.2 Jar tests

Based on the insights gained from the baseline study, two strategies were followed and tested through jar tests for improving arsenic removal efficiency and to achieve <1 µg/l arsenic at DWTP Ouddorp. These were:

1. To treat the combined raw water (influent of the rapid sand filters) by a $KMnO_4$ and then, if necessary, addition of Fe(III). Potassium permanganate would convert As(III) to As(V) in the raw water which would increase the uptake of As by the precipitating Fe-hydroxides, eventually leading to an increase in the overall As removal in the rapid sand filters.
2. To treat the effluent of the activated carbon filters (influent of the UF membranes) by dosing Fe(III), i.e. in-line coagulation before UF. The effluent of activated carbon filters contained only As(V), therefore there would be no need of using $KMnO_4$. Moreover, the As concentration in the effluent of activated carbon filters was much lower and more consistent compared to the combined raw water.

In order to (preliminarily) test the above mentioned strategies, 4 jar tests were performed (Table 3-1) using a jar test apparatus (Figure 2-2). Jar tests 1, 2 and 3 were aimed at investigating the first strategy, i.e. treating the combined raw water of DWTP Ouddorp with $KMnO_4$ and/or $FeCl_3$, and the jar test 4 was aimed at investigation the influence of in-line coagulation on As removal.

The residence time of the process water in each treatment unit of DWTP Ouddorp (e.g. supernatant storage, filter bed etc.) was carefully calculated based on the data provided by Evides. These residence times were then applied in jar tests to simulate/mimic the full-scale process conditions, as much as possible. The protocol of all the jar tests have been provided as Appendix II.

A standard jar testing device (Figure 2-2) was used to perform the experiments. All the jar tests were carried out at DWTP Ouddorp. On completion of the desired reaction time samples were collected from the bottom of the jars and immediately filtered through 0.45 µm disc filters (GE Healthcare Whatman ™ 0.45 µm). All chemicals used in this study were reagent grade. All stock solutions were prepared using distilled water. All the samples were analyzed at Aqualab Zuid. pH, temperature, EC, ORP were measured furing the xperiments with the help of a multimeter (HACH LANGE sensION™+DL portable meter).

TABLE 3-1 OVERVIEW OF JAR TESTS PERFORMED AT DWTP OUDDORP.

Jar tests using the raw water	Jar test using the effluent of activated carbon filter
1. Dosing $FeCl_3$ alone	4. Dosing $FeCl_3$ alone
2. Dosing $KMnO_4$ alone	
3. Dosing both $KMnO_4$ and $FeCl_3$	

3.3 Results and Discussion

3.3.1 Baseline study

Figure 3-2 shows the total As concentrations in the combined raw water (mix of all the instantaneously active drains and wells) and the clear water (drinking water) at DWTP Ouddorp from Feb-2006 to June-2016. It can be seen that in the past significant variations in the raw water quality occurred. These variations affected the drinking water As concentrations as well. The variations in the combined raw water quality can be attributed to one or more of the reasons, such as changes in the infiltration strategy and wells, changes in the pumping rate of dune effluent, erroneous sample collection procedure and the seasonal fluctuation of arsenic. It can be seen in Figure 3-2 that the average As concentration reduced from 5.5 µg/L to 3.1 µg/L in the second half of 2011. This was due to $FeCl_3$ dosing in the combined raw water (influent of rapid sand filters). Lowered As concentration in the drinking water is also evident throughout 2016 because of the $FeCl_3$ dosing (Fe(III)=1 mg/L) in one of the two treatment lines (rapid sand filters 4, 5, 6).

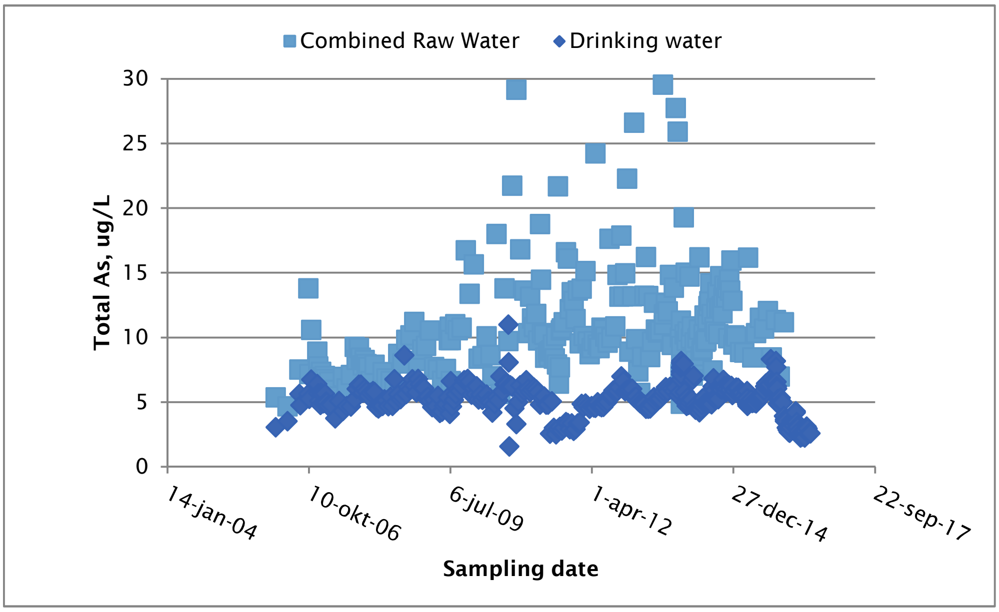

FIGURE 3-2 TOTAL As CONCENTRATION IN THE COMBINED RAW WATER AND THE DRINKING WATER AT DWTP OUDDORP.

Figure 3-3 shows the As concentrations in the combined effluent of the RSF and the drinking water. It can be seen that As concentrations are similar in both streams, implying that the As levels do not decrease further after the RSF at DWTP Ouddorp. In other words, the activated carbon filtration and the UF unit do not remove As at Ouddorp. It's the rapid sand filtration which was mainly responsible for the given As removal at DWTP Ouddorp and this removal of As can be attributed to the coprecipitation and adsorption of As with precipitating Fe-hydroxides and subsequent separation of flocs in the rapid sand filters (Dixit and Hering, 2003; Gude et al., 2016).

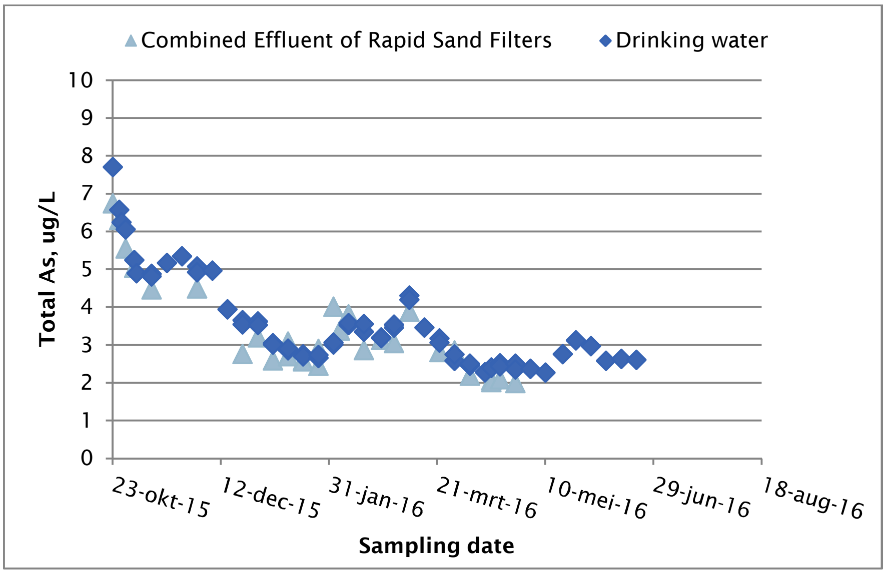

FIGURE 3-3 As CONCENTRATION IN RSF EFFLUENT AND DRINKING WATER AT DWTP OUDDORP.

It can be seen in Figure 3-4 that most of the dissolved As (>70%) in the combined raw water is available as As(III), which is the most difficult to remove specie of As, because of its uncharged nature (Ahmad et al., 2016). In such cases use of a chemical oxidant such as $KMnO_4$ becomes necessary because the oxidation of As(III) by atmospheric oxygen/air is a very slow process (Bissel and Frimmel, 2003).

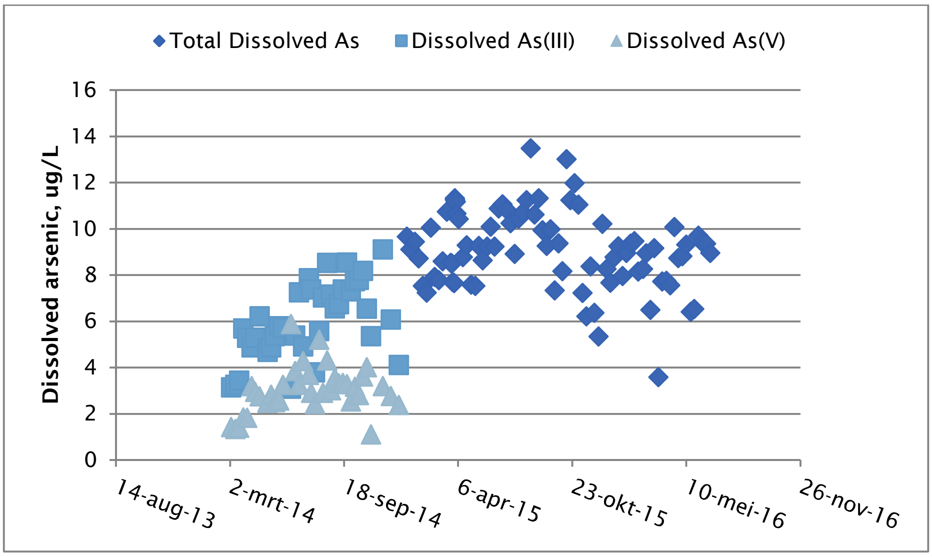

FIGURE 3-4 As SPECIES IN THE COMBINED RAW WATER.

Figure 3-5 shows the distribution of As species in the drinking water at DWTP Ouddorp. It can be seen that the drinking water contained only As(V). It means that the As, while passing through the filter bed, not only gets partly removed, but also the dissolved As(III) gets oxidized to As(V). This phenomenon has also been observed at many other drinking water production locations in the Netherlands, e.g. Dorst, Prinsenbosch, Oosterhout, Katwijk etc. The oxides of manganese or the microorganisms present in the filter bed can be responsible for this transformation (Gude et al., 2016).

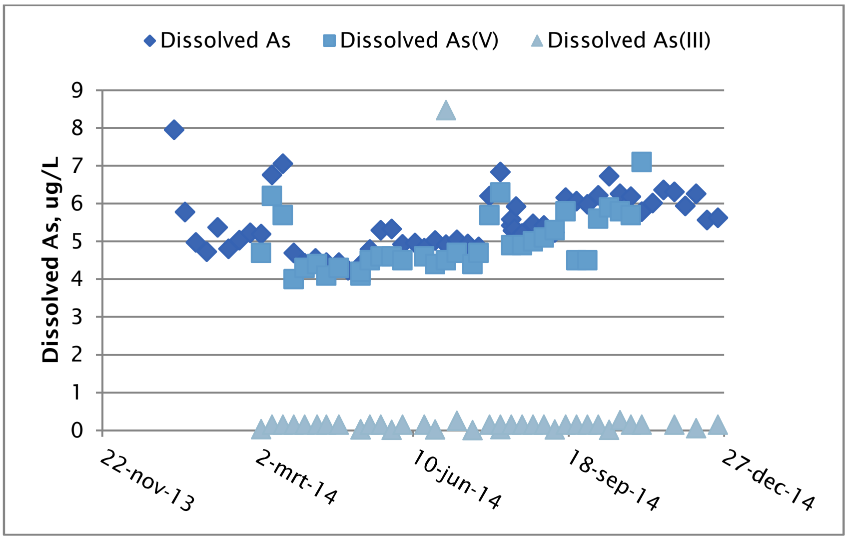

FIGURE 3-5 As SPECIES IN PRODUCED DRINKING WATER AT OUDDORP.

On 19-Feb-2016 an additional sampling campaign was carried out to understand the removal of As and the oxidation of As(III) in the RSF of DWTP Ouddorp. Samples were collected over the bed height of filter 6 and analyzed for total As, Fe and Mn. Moreover, both As(III) and As(V) were determined at all the sampling points. Please note that filter 6 was being dosed with 1 mg/L of Fe(III). FigurE 3-6 shows the profile of As and its species over the complete filter bed height. It can be seen that most of the As removal occurred in the top half of the filter bed, i.e. in the top (800 mm to 1600 mm) of the filter bed. In the bottom half of the filter bed, only a small amount of As, that was already co-precipitated with Fe-hydroxides, was removed. Moreover, it can be seen that it was the top half of the filter bed where the transformation of dissolved As(III) to As(V) took place. Thus, it can be concluded that the top half of the filter bed is critical for As removal and transformations of the As species. Slowing down the rate of Fe(II) oxidation by pH or supernatant depth variation can be investigated to achieve increased removal of As. Another possibility can be to dose iron in the filter bed at the point where As(V) becomes the dominant specie of As.

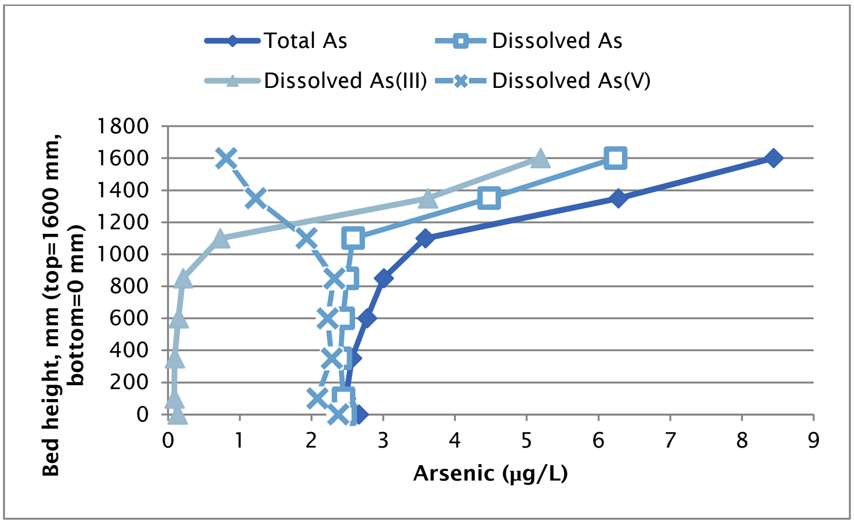

FIGURE 3-6 As PROFILE IN RAPID SAND FILTER 6 OF DWTP OUDDORP.

Samples for the determination of NH_4 and total and dissolved Fe and Mn were also collected during this sampling campaign. The results are shown in Figure 3-7. It can be seen that the top half of the filter bed was the main active zone for the precipitation and separation of Fe and Mn from the aqueous phase. Moreover, NH_4 removal also took place in the same zone. This creates a challenge in attributing the As(III) oxidation to the oxidizing Fe(II), as proposed by Sahai et al., 2007, or the probable presence of manganese oxides in the coating of filter grains, as shown by Driehaus et al., 1995, or due to microbial species that are responsible for nitrification in the filter bed, as shown by Lytle et al., 2007.

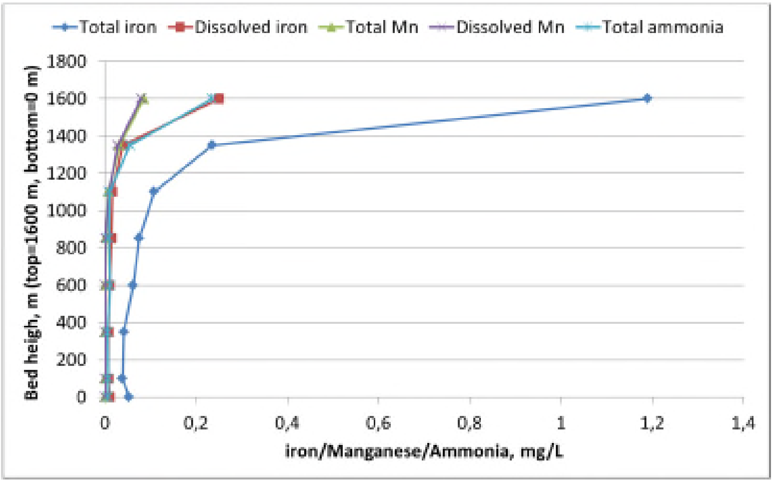

FIGURE 3-7 Fe, Mn AND NH_4 REMOVAL PROFILE IN THE RSF 6 OF DWTP OUDDORP.

Data from 2015 on the quality of combined raw water at Ouddorp shows significant variation of total and dissolved Fe and As concentrations (Table 3-2). However, the particulate arsenic has been observed to correlate with the percentage of precipitated iron in the raw water (Figure 3-8). It means that As, when available in particulate form (un-dissolved form), should be expected to be co-precipitated with Fe-hydroxides. The correlation is expected to hold true also in the supernatant storage of RSFs, i.e. the dissolved As continues to co-precipitate with precipitating Fe-hydroxides. Unlike Fe, Mn is mostly available in the dissolved form in the combined raw water and in the supernatant storage, therefore it can be concluded that before the water enters into the RSFs Mn does not appear to play a role in the uptake of As.

TABLE 3-2 TOTAL, DISSOLVED AND (CO-)PRECIPITATED Fe AND As IN THE COMBINED RAW WATER.

Dates	Total Fe. mg/L	Dissolved Fe. mg/L	Precipitated Fe. mg/L	Precipitated Fe. %	Total As. µg/L	Dissolved As. µg/L	Coprecipitated As. µg/L	Coprecipitated As. %
12-1-2015	0.602	0.438	0.164	27.3	10.060	9.107	0.953	9.5
10-2-2015	0.477	0.265	0.212	44.4	8.887	7.246	1.641	18.5
10-3-2015	0.465	0.411	0.054	11.5	8.823	8.596	0.227	2.6
6-5-2015	0.530	0.390	0.140	26.4	8.461	7.532	0.929	11.0
2-6-2015	0.731	0.659	0.073	9.9	10.330	10.090	0.240	2.3
30-6-2015	0.769	0.684	0.085	11.1	11.520	10.830	0.690	6.0
22-9-2015	0.923	0.522	0.401	43.4	8.448	7.338	1.110	13.1
20-10-2015	0.867	0.817	0.049	5.7	11.360	11.240	0.120	1.1
17-11-2015	0.525	0.442	0.083	15.8	6.977	6.215	0.762	10.9

Figure 3-9 shows the Fe and Mn concentration in the combined effluent of RSF. It can be seen that Mn was consistently reduced to <0.005 mg/L. Probably the mechanism is adsorptive removal. However, total residual Fe mostly stayed >0.03 mg/L. The effluent of RSFs enters the activated carbon filters where the remaining particulate Fe gets removed to <0.01 mg/L.

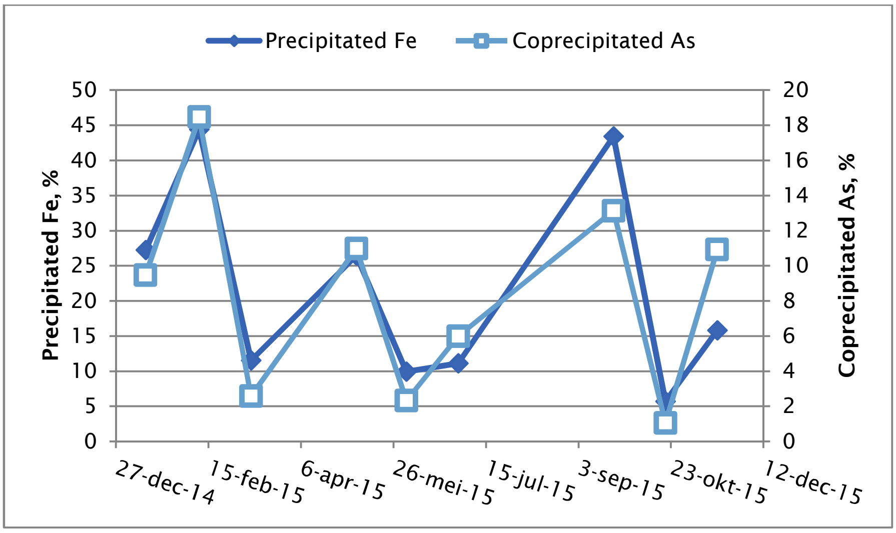

FIGURE 3-8 CORRELATION BETWEEN PRECIPITATED Fe AND PARTICULATE As IN THE COMBINED RAW WATER.

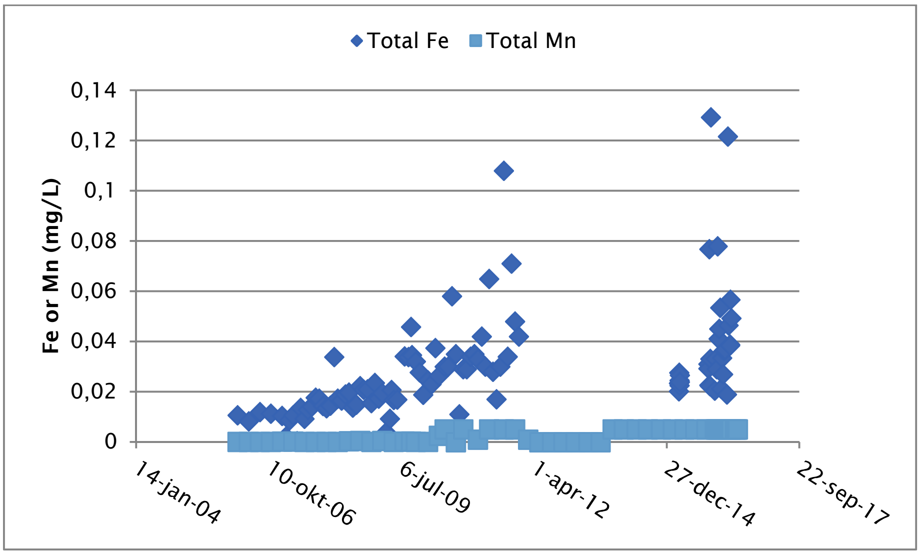

FIGURE 3-9 Fe AND Mn CONCENTRATION IN THE COMBINED EFFLUENT OF RSFs.

3.3.2 Jar tests

Jar test 1: Dosing $FeCl_3$ alone in the combined raw water

As described in section 3.3.1 that , the As removal at Ouddorp increased after the start of $FeCl_3$ dosing before the RSFs 4,5 and 6. However, it had to be determined how much of additional Fe is required to reduce As concentration to <1 µg/L. Therefore, jar test 1 was carried out. In this test varying amounts of $FeCl_3$ were dosed in the combined raw water and afterwards the suspension was processed (mixed at different speeds) in the jars and finally the reaction was stopped by filtering the samples by 0.45 μm filter. Figure 3-10 shows the results of the 2 trials performed on different days. It can be seen that the residual As concentration decreased with increase in Fe(III) dose, however even at 6 mg/L of Fe(III) dose the residual As remained higher than the As concentration of the effluent of filter 6 (the filter which was being dosed with 1 mg/L of Fe(III). In other words, the As uptake by Fe was higher in the full-scale treatment process compared to the simulation in the jar test. This difference can be attributed to the catalytic properties of the (top half of) RSF bed, as discussed in the previous section. Therefore, it is highly likely that a much higher As removal would be achieved when these concentrations of Fe were dosed at the pilot- or full-scale setup.

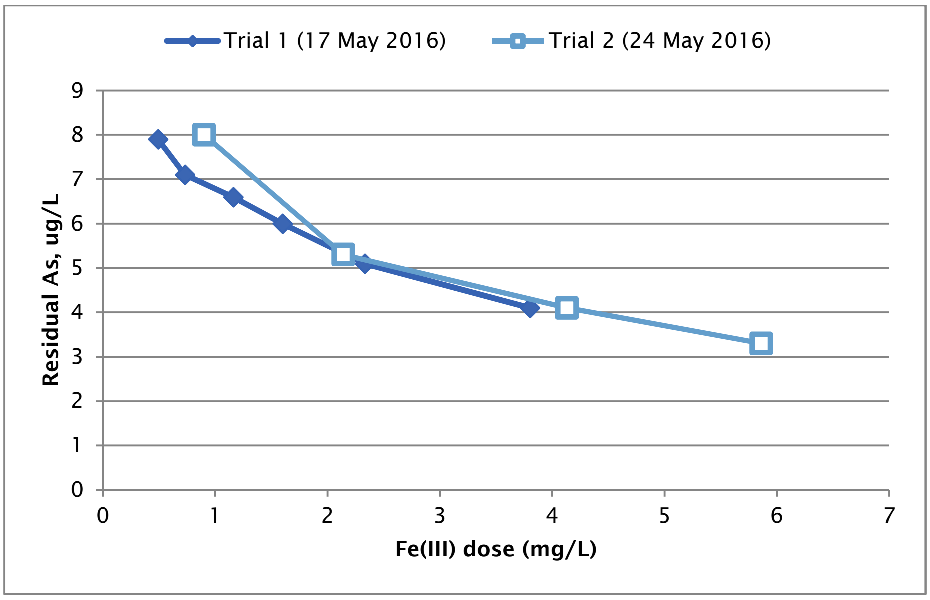

FIGURE 3-10 INFLUENCE ON As CONCENTRATIONS WHEN $FeCl_3$ ALONE WAS DOSED IN COMBINED RAW WATER OF DWTP OUDDORP.

Jar test 2: Dosing $KMnO_4$ alone in the combined raw water

Test 2 was aimed at investigating the influence on As uptake when As(III) in the combined raw water was oxidized by dosing $KMnO_4$ in varying concentration. Figure 3-11 shows the results of the jar test 2. Only one trial of this experiment was performed. It can be seen that the residual As concentration was not decreased after 1 mg/L of $KMnO_4$ dose and became stable around 4.8 μg/L. The effluent of full-scale RSF 1, which was not dosed with Fe, contained an average 6 μg/L of As. It means, by dosing 1 mg/L of $KMnO_4$ As removal could be increased, but the desired level of <1 μg/L could not be achieved.

Dosing of $FeCl_3$ or $KMnO_4$ alone in the combined raw water of Ouddorp could not reduce residual As concentration to <1 μg/L, even at relatively high dosages. Since there was no RSF involved in the jar tests, the catalytic effect of filter bed grains on the oxidation and subsequent removal of As could not be simulated in the jar tests, resulting in underestimation of As removal at different chemical dosages.

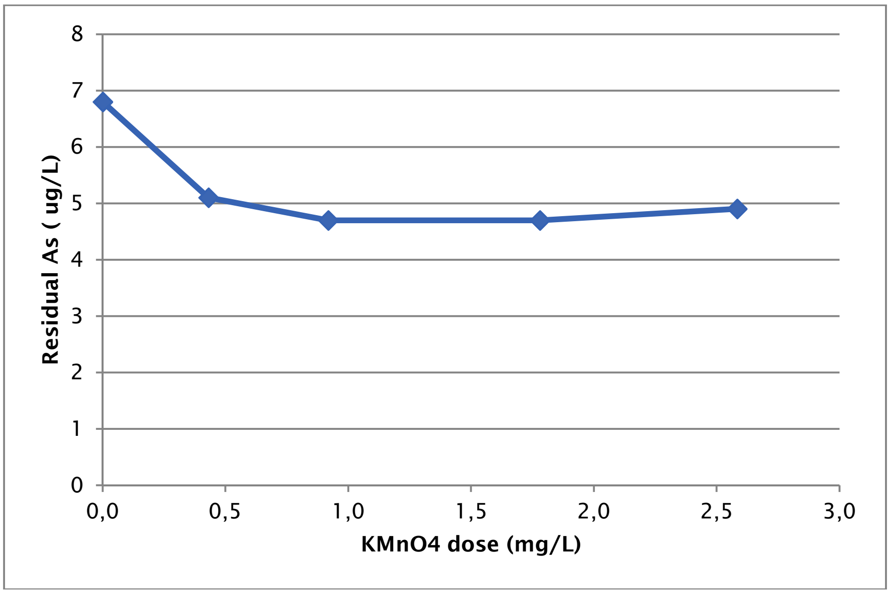

FIGURE 3-11 INFLUENCE ON ARSENIC REMOVAL WHEN KMNO4 ALONE WAS DOSED IN THE COMBINED RAW WATER OF DWTP OUDDORP.

Jar test 3: Dosing both $KMnO_4$ and $FeCl_3$ in the combined raw water

As it is clear from the results of previous two tests that the residual As concentration of <1 µg/l could not be achieved, even at rather high Fe and $KMnO_4$ dosages. Therefore, jar test 3 was carried out to investigate the influence of dosing both the chemicals with a suitable interval (1-2 min) between the dosages. First $KMnO_4$ was dosed and subsequently $FeCl_3$ was dosed. The dosages were optimized using the insights from the previous two experiments. Figure 3-12 shows the influence on As removal when $KMnO_4$ and $FeCl_3$ were dosed in varying concentrations in the raw water. It can be seen that As concentration of <1 µg/L could be achieved by dosing approximately 1.3 mg/l of Fe, when the combined raw water was pre-treated with either 0.6 or 0.9 mg/l of $KMnO_4$. Results of test 3 suggest that both $KMnO_4$ and $FeCl_3$ will be needed to reduce the As concentrations to <1 µg/L at DWTP Ouddorp. As stated before, since there was no RSF involved in the jar tests, the catalytic effect of filter bed grains on the oxidation and subsequent removal of As was not simulated in the jar tests, resulting in a possible overestimation of Fe(III) dose. However, the $KMnO_4$ requirement is expected to remain the same at pilot or full-scale setup.

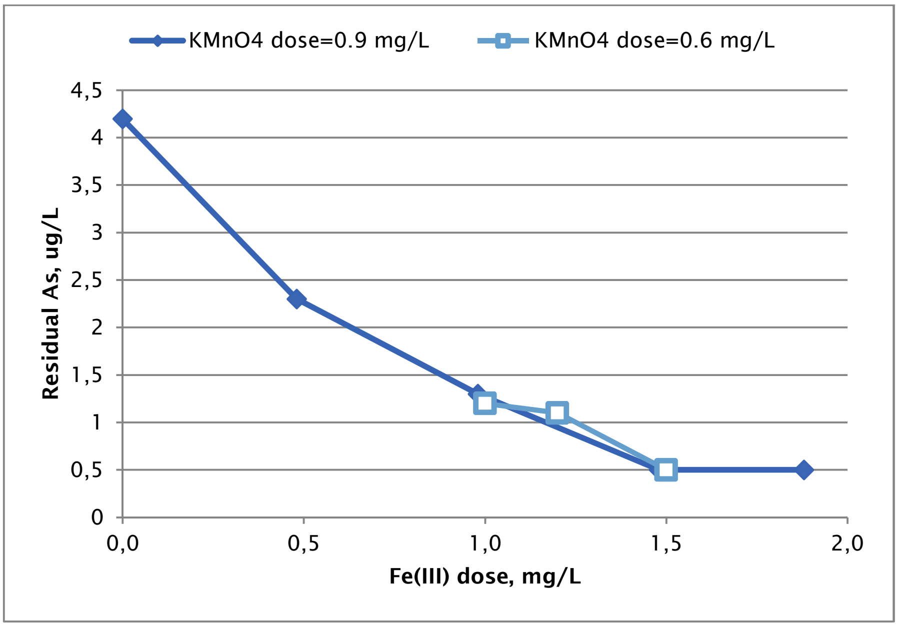

FIGURE 3-12 INFLUENCE ON As REMOVAL WHEN BOTH $KMnO_4$ AND $FeCl_3$ WERE DOSED IN THE COMBINED RAW WATER OF DWTP OUDDORP.

Jar test 4: Dosing $FeCl_3$ alone in the influent of UF membranes

At Ouddorp UF is used as disinfection and final polishing step of the treatment process. The influent of UF membranes is the effluent of the activated carbon filters whose quality in terms of As concentrations remains quite stable, around 3 µg/L. Moreover, the entire concentration of As is available as As(V), implying no need for the dosing of a chemical oxidant. However, dosage of Fe(III) will be required. Jar test 4 was conducted to investigate the scenario of in-line coagulation before UF, using the influent of UF membranes. Figure 3-13 shows the results of jar test 4 in which varying amounts of Fe(III) were added to the influent of the UF membranes and reaction was stopped by filtering with 0.45 um disc filters, after a calculated amount of time (based on the residence time of water between activated carbon filtration and UF). It can be observed that As concentration of <1 µg/l could be achieved by dosing 0.6 mg/L of Fe(III). From the analysis of full-scale water quality data it was clear that no rejection of As takes place at UF step. However, it can now be seen that when coagulation with $FeCl_3$ is introduced before the UF membranes, rejection of As to <1 µg/L can be achieved. The pore size of UF membrane ranges from 25-30 nm. Therefore, the removal of As will get better because in the jar test a pore size of 0.45 µm was used to filter out the precipitates. In-line coagulation with $FeCl_3$ before UF seems promising, however it is still to be determined what will be the influence on the operation (backwashing frequency, minimum flux etc.) and maintenance of UF membranes. Moreover, the floc forming regime, pH effects etc. need to be investigated. It should be noted that the coagulation-UF is not commonly applied in drinking water polishing treatment. It is more common to surface water treatment. Therefore, testing at pilot scale is required to determine the overall impact of Fe(III) dosing before the UF skids. This research will be carried out in a SPO project with Evides in 2017.

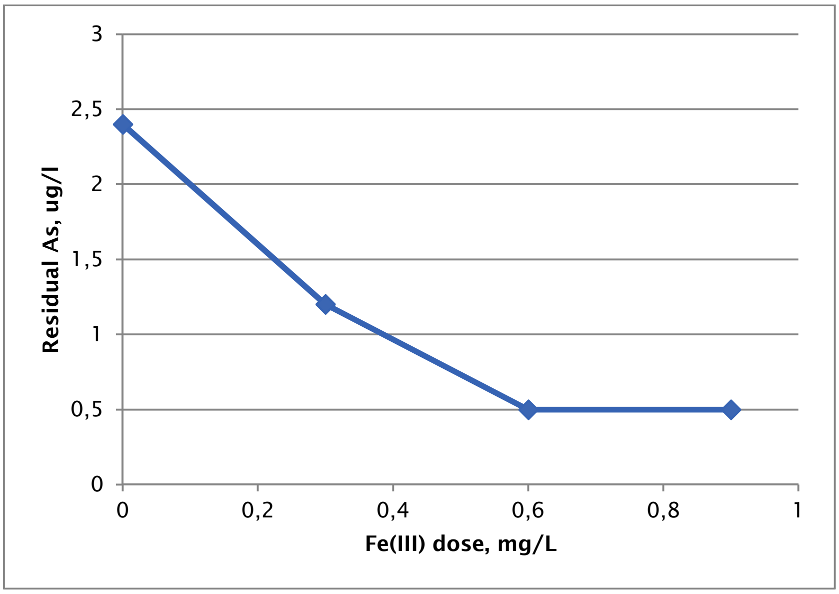

FIGURE 3-13 INFLUENCE ON As REMOVAL WHEN $FeCl_3$ ALONE WAS DOSED IN THE INFLUENT OF UF MEMBRANES.

3.4 Conclusions and recommendations

The main conclusions that can be drawn from the above described baseline study and the jar tests.

- As(III) is the dominant specie of As in the raw water of DWTP Ouddorp. It remains the dominant specie of As in the supernatant storage. The sprinklers used for aeration of raw water at Ouddorp do not oxidize As(III) to As(V).
- The oxidation of As(III) takes place in the top half of the filter bed, simultaneously with the removal of As, Fe, Mn and NH_4.
- The available As removal capacity of the existing treatment process of DWTP Ouddorp can be attributed mainly to the removal of Fe in the treatment plant. The rate of As uptake by Fe-hydroxides is higher in the filter bed compared to the supernatant level and in the cascade aeration step. It means that, the oxidation kinetics of As(III) are slow before the process water enters the filter bed.
- Although the top half of the rapid sand filters oxidizes As(III) to As(V), the lack of adequate amount of Fe is the limiting factor towards achieving additional As removal. There is no Fe left in the water (or very small amount of precipitated Fe is left) in the bottom half of the filter bed that can co-precipitate/adsorb the freshly generated As(V). Slowing down the rate of Fe(II) oxidation or dosing iron will be interesting to investigate.
- Dosing of $FeCl_3$ or $KMnO_4$ alone in the combined raw water of DWTP Ouddorp cannot reduce residual As concentration to <1 µg/L, even at relatively high dosages. Since there was no rapid sand filtration involved in the jar tests, the catalytic effect of the filter bed grains on the oxidation and subsequent removal of As could not be simulated in the jar tests, resulting in a probable underestimation of As removal at different chemical dosages.
- Dosing a combination of $KMnO_4$=0.6 mg/L and Fe(III)=1.3 mg/L in the combined raw water can effectively reduce As concentration to <1 µg/L at Ouddorp. As stated before, since there was no rapid sand filtration involved in the jar tests, the Fe(III)

dose is probably overestimated. However, the amount of $KMnO_4$ required is expected to remain the same for pilot or full-scale setup.

- Dosing of Fe(III)=0.6 mg/L in the influent of the UF step can decrease the As concentration to <1 µg/l in the drinking water produced at Ouddorp.

Following are the main recommendations:

- To carry out pilot tests using one or two pilot scale rapid sand filtration columns, fed with the combined raw water of DWTP Ouddorp to determine the impact of chemical dosing in the operation and performance of RSF, in order to optimize the filter run time, backwashing frequency etc. and to evaluate the impact of increased As removal on the quantity and quality of the residuals (sludge).
- To carry out pilot tests or tests on one full-scale ultrafiltration-skid to investigate in-line coagulation, using effluent of the activated carbon filters as feed and ultrafiltration as floc separation process in order to optimize (fine-tune) the dosing of $FeCl_3$ and to determine the influence on the operation (backwashing frequency, minimum flux etc.).

4 Arsenic removal at Leiduin (Waternet)

4.1 Introduction

The drinking water treatment plant of Leiduin (DWTP Leiduin) has a production capacity of 63 Mm^3/year. It uses surface water from the Lekkanaal as its raw water. The raw water is pre-treated (coagulation-flocculation-rapid sand filtration) at Nieuwegein and then infiltrated in the dune area of Leiduin. The residence time of water in dunes is approximately 90 days. The average As concentration after the pre-treatment (before dune infiltration) is <0.5 µg/L. During infiltration As gets mobilized and as a result the dune effluent contains 2.7 µg/L As, on average. The dune effluent is treated in a series of steps at DWTP Leiduin, including rapid sand filtration (RSF), ozonation, pellet softening with caustic soda (NaOH), activated carbon filtration and finally slow sand filtration. After the treatment, the As concentration in the produced drinking water is averaged at 1.6 µg/L, representing an average removal of approximately 40 %.

It was unclear which treatment step was mainly responsible for As removal at DWTP Leiduin. Moreover, the distribution of As species in the dune effluent and the variation/interchanging of these species in various treatment steps was not known. Therefore, a baseline study was carried out at DWTP Leiduin. Following the baseline study, jar tests were performed to determine the removal of As by coprecipitation with Fe, with or without pre-treatment with $KMnO_4$.

4.2 Materials and methods

4.2.1 Baseline study

In order to establish the baseline knowledge regarding As removal at DWTP Leiduin first the water quality data provided by Waternet (2013-2016) was studied. The regular water quality monitoring program at DWTP Leiduin does not include collection and analysis of filtered (0.45 µm) samples. For this reason the available database was not adequate to differentiate between the total and dissolved concentrations of As, Fe, Mn etc. Furthermore, the information on As speciation was altogether missing. Therefore, additional sampling campaigns were carried out at DWTP Leiduin on 06-Jul-2016, 15-Aug-2016 and 25-Aug-2016. For the sampling campaigns 3 sampling points were selected in one of the treatment trains. These include;

1. Dune effluent (influent of RSF)
2. Supernatant of RSF 47
3. Effluent of RSF

At each sampling point, filtered and unfiltered samples were collected and analysed for total As, Fe and Mn concentration. Filtration of samples was carried out onsite, through 0.45 µm disc filters (GE Healthcare Whatman ™ 0.45 µm) that could be mounted on a 50 mL syringe. Temperature, pH, electrical conductivity (EC) and oxidation-reduction-potential (ORP) were measured onsite with the help of a multi meter (HACH LANGE sensION™+DL portable meter).

For As speciation analysis, field speciation protocol developed by Clifford et al. (1983) was used and the kits were prepared on site. All the samples collected during the sampling campaign were analysed at Aqualab Zuid.

4.2.2 Jar tests

Three jar tests were performed at DWTP Leiduin. These include:

1. Dosing only $KMnO_4$ in RSF influent
2. Dosing only $FeCl_3$ in RSF influent
3. Dosing only $FeSO_4$ in RSF influent

The residence time of the process water in the supernatant and RSF bed of DWTP Leiduin was carefully calculated. This residence time was then applied in jar tests to simulate/mimic the full-scale process conditions, as much as possible. The degree of simulation was monitored during the tests with the help of pH, redox, dissolved oxygen and the concentration of total and dissolved As, Fe and Mn. The detailed protocol of the jar tests is provided as Appendix III.

A standard jar testing device (Figure 2-2) was used to perform the experiments. All the jar tests were carried out at DWTP Leiduin. On completion of the desired reaction time samples were collected from the bottom of the jars and immediately filtered through 0.45 µm disc filters (GE Healthcare Whatman ™ 0.45 µm). All chemicals used in this study were reagent grade. All stock solutions were prepared using distilled water. All the samples were analyzed at Aqualab Zuid. pH, temperature, EC, ORP were measured during the experiments with the help of a multimeter (HACH LANGE sensION™+DL portable meter).

4.3 Results and Discussion

4.3.1 Baseline study

Figure 4-1 shows the total As concentrations in the dune effluent (the combined influent of RSF), combined effluent of RSF and the drinking water at DWTP Leiduin. The data is based on the regular water quality monitoring data (Jan 2013-May 2016) of Waternet. It can be seen that the concentration of As in the dune effluent is mainly removed in the RSFs (1 µg/L removal, on average). A small amount of As (0.13 µg/L removal, on average) is removed in the treatment processes that are present after the RSF at DWTP Leiduin. The dune effluent contains 0.29 mg/L of Fe. The observed As removal at DWTP can be attributed to Fe removal which principally takes place in the RSFs.

Table 4-1 presents the results of the sampling campaigns. The text in red shows the measurements which were not in-line with the results of the routine monitoring program at DWTP Leiduin. The total concentration of As, Fe and Mn should not be higher than the total concentration of these constituents in the influent of rapid sand filters. However, the results of the sampling campaign show that the samples collected from the supernatant storage of the rapid sand filter 47 always contained higher concentration of As, Fe and Mn compared to their concentration in the dune effluent. On the other hand, the dissolved concentrations are approximately similar to those of influent of rapid sand filters.

Moreover, it is surprising to note that in the influent of RSFs 1.4-1.9 µg/L As(III) was present. And during the passage of water through RSF the As(III) content was only slightly reduced, unlike DWTP Ouddorp or Katwijk where the effluents of rapid sand filters contained mainly As(V).

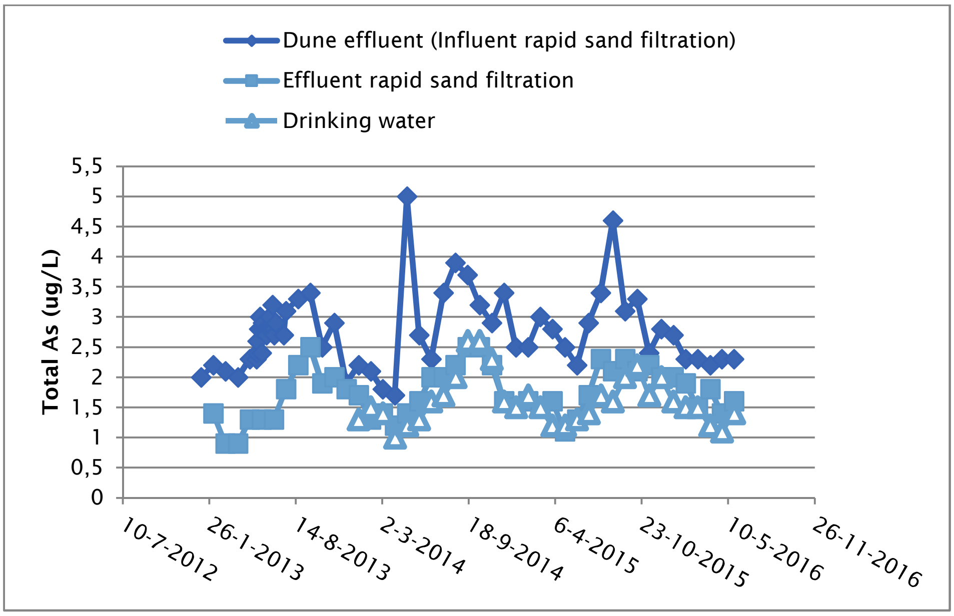

FIGURE 4-1 TOTAL AS CONCENTRATION IN DUNE EFFLUENT, RSF EFFLUENT AND DRINKING WATER AT DWTP LEIDUIN.

TABLE 4-1 TOTAL AND DISSOLVED CONCENTRATION OF As, Fe AND Mn IN THE INFLUENT, SUPERNATANT AND EFFLUENT OF RSF AT DWTP LEIDUIN

Samples			**6-7-2016**			**15-8-2016**			**25-8-2016**
	Arsenic	Iron	Manganese	Arsenic	Iron	Manganese	Arsenic	Iron	Manganese
	μg/l As	mg/l Fe	mg/l Mn	μg/l As	mg/l Fe	mg/l Mn	μg/l As	mg/l Fe	mg/l Mn
Total concentration in dune effluent (influent RSF)	3.5	0.27	0.07	12	3.5	0.73	3.4	0.3	0.14
Dissolved concentration in dune effluent (influent RSF)	2.8	0.05	0.05	2.8	0.042	0.05	2.8	0.02	0.08
Total concentration in supernatant	8.6	1.9	0.27	15	3.7	0.44	11	2.6	0.25
Dissolved concentration in supernatant	2.6	0.06	0.05	2.7	0.05	0.03	2.9	0.06	0.02
Total concentration in rapid sand filter effluent	3.5	0.28	0.07	2.3	0.08	1.1	2.6	0.03	0.07
Dissolved concentration in rapid sand filter effluent	2.7	0.05	0.05	2.2	0.04	1.1	2.6	0.02	0.07
Total concentration in drinking water	1.8	< 0.01	< 0.01						
Dissolved concentration in drinking water	1.7	< 0.01	< 0.01						

TABLE 4-2 DISSOLVED SPECIES OF As IN INFLUENT AND EFFLUENT OF RSF 47.

	Sampling 15-8-2016	**Sampling 25-8-2016**
	μg/L	μg/L
Dissolved As in dune effluent (influent RSF)	2.8	2.8
Dissolved As(III) in dune effluent (influent RSF)	1.9	1.4
Dissolved As(V) in dune effluent (influent RSF)	0.9	1.4
Dissolved As in RSF effluent	2.2	2.6
Dissolved As(III) in RSF effluent	1.7	1.2
Dissolved As(V) in RSF effluent	0.5	1.4

4.3.2 Jar tests

Jar test 1: Dosing $KMnO_4$ alone in the influent of RSFs

The baseline study revealed that the influent of rapid sand filters contain 1.4-1.9 µg/L As(III) (Table 4-2). Jar test 1 was performed to investigate if the As uptake by naturally available Fe in the influent of RSFs could be increased? Figure 4-2 shows the effect of dosing $KMnO_4$ in the RSF influent. It can be seen that dosing $KMnO_4$ alone in the RSF influent did not significantly reduce the As concentration. At none of the studied doses (0-2 mg/L $KMnO_4$) residual As concentration of <1 µg was achieved. It is interesting to note that at $KMnO_4$ dose of 0.5 mg/L all the As(III) available in the influent of RSF was oxidized to As(V). However, the removal of As was not increased further. It means that the oxidation of As(III) to As(V) was not shown to increase As removal to a significant extent. This may be attributed to the competition with ortho-PO_4 present in the solution for sorption sites on Fe-hydroxides. Probably PO_4 ions was already sorbed and As(V) was not able to displace them at this solution pH (8.5).

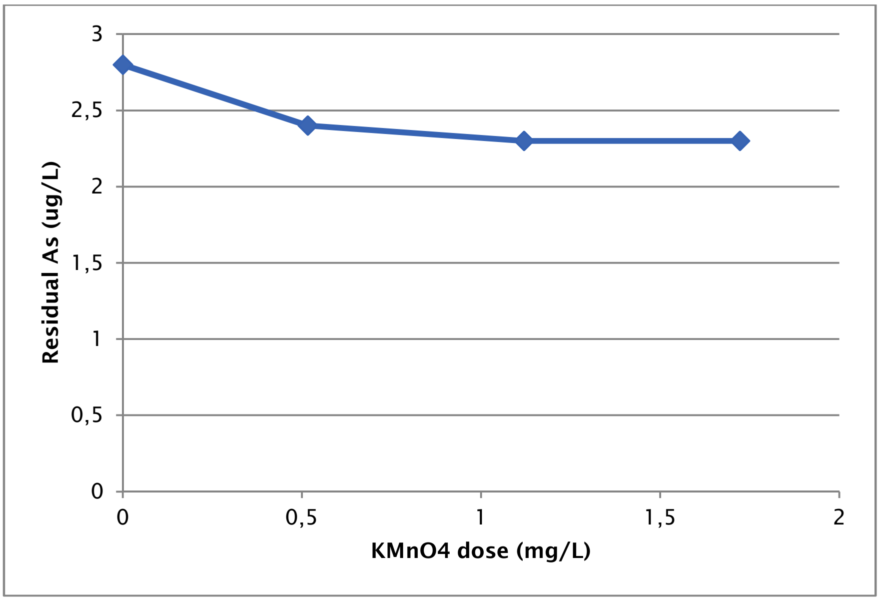

FIGURE 4-2 INFLUENCE OF $KMnO_4$ DOSAGE IN THE INFLUENT OF RSF.

Jar test 2 and 3: Dosing Fe(III) or Fe(II) in the influent of RSFs

Jar test 2 was aimed at investigating the influence on residual As concentration at varying Fe(III) (dosed as $FeCl_3$) dosages without dosing before with $KMnO_4$. Jar test 2 was performed twice, first time on 15-08-2016 and second time on 25-08-2016. Jar test 3 was aimed at investigating the influence on residual As concentration at varying Fe(II) (dosed as $FeSO_4$) dosages. The results have been collectively presented in Figure 4-3. It can be seen that the both Fe(III) and Fe(II) doses resulted in similar performance, i.e., removal of As, in the trials performed on 15-08-2016. None of the Fe dosage studies could achieve the residual As concentration of <1 µg/L. Therefore, the test with Fe(III) dosage was repeated on 25-08-2016. It can be seen that residual As concentration of <1 µg/L was achieved at Fe(III) dosage of 1.5 mg/L. It could also be possible to achieve <1 µg/L at a lower Fe(III) dose, however Fe(III) doses between 0.75 and 1.5 mg/L were not tested in this study. Table 4-1 shows the concentration of total and dissolved concentration of As, Fe and Mn in the influent of RSFs. It is evident that the precipitated Fe and Mn was much higher in the sample collected on 15-08-2016, compared to the sample collected on 25-08-2016. The suspended Fe and Mn particles present in the aqueous phase can influence the coagulant dose significantly. This explains why residual As concentration of <1 µg/L could be achieved at Fe(III) dosage of 1.5 mg/L on 25-08-2016, and why not on 15-08-2016.

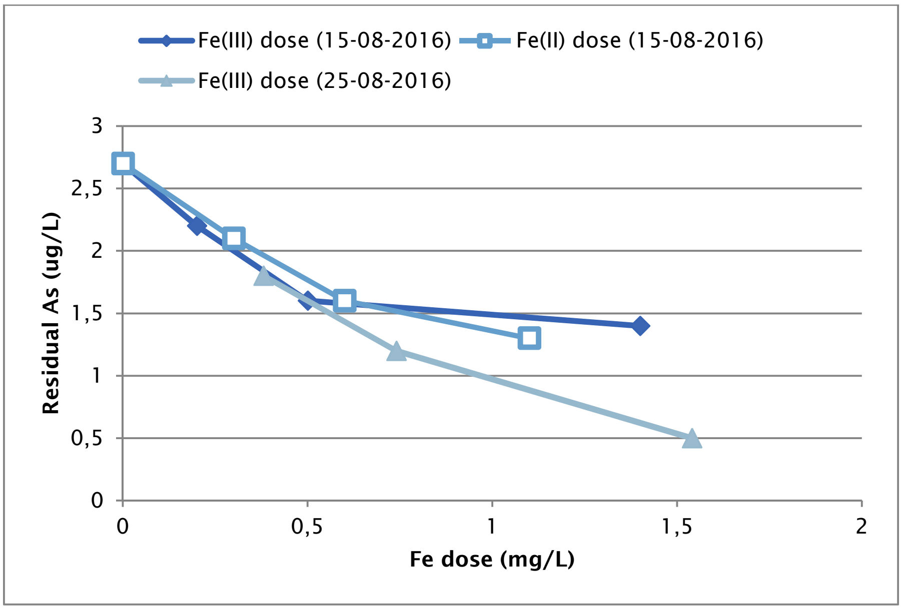

FIGURE 4-3 INFLUENCE OF Fe(II) OR Fe(III) DOSAGE IN THE INFLUENT OF RSFs.

4.4 Conclucions and recommendations

At DWTP Leiduin rapid sand filtration (especially the Fe removal in the rapid sand filters) is the key process step where the existing As removal occurs. The naturally available ortho-PO_4 in the dune effluent seems to compete with As for the sorption sites on Fe-hydroxides because during the treatment uptake of As by already precipitated and freshly precipitating Fe-hydroxides does not increase. DOC might also play a role, however was not investigated.

The rapid sand filters do not oxidize As(III) to As(V). This result is unexpected and strange. This needs further investigation.

Arsenic removal to <1 µg/L at DWTP Leiduin can be achieved by treating the influent of the RSF with either $FeCl_3$ or $FeSO_4$, with or without pre-treatment with $KMnO_4$. The use of $KMnO_4$ for pre-oxidizing As(III) to As(V) is expected to lower the coagulant dose required to achieve <1 µg/L As in the drinking water of DWTP Leiduin.

Following are the main recommendations:

- To carry out a new sampling campaign, including the determination of total and dissolved PO_4, organics and silicates, besides the constituents which have been taken into account during the sampling campaign of this study. The samples should be collected at least 3 times at all the selected sampling points. This sampling campaign is pivitol in order to gain more insights into the transformations happening in the RSFs. Moreover, the overall role of ortho-PO_4 and DOC will become clear.
- Pilot tests using one or two pilot scale rapid sand filtration columns, fed with the influent of rapid sand filters in order to optimize (fine-tune) the dosing of chemical(s), to determine the impact of chemical dosing in the operation and performance of rapid sand filters, in order to optimize the filter run time, backwashing frequency etc. and to evaluate the impact of increased As removal on the quantity and quality of the residuals (sludge) generated from the rapid sand filters.

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Appendix I Protocol for jar tests performed at Katwijk (Dunea)

Jar test 1 : Dosing $KMnO_4$ alone in the influent of Rapid Sand Filter

Time (t), min	Action	Jar 1	Jar 2	Jar 3	Jar 4
t=0	Sample (Unf/Fil) start solution from the jerry can				
t=0	Start solution in	INF RSF	INF RSF	INF RSF	INF RSF
t=0	In-situ measurements in start solution	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP
t=0	pH adjustment	no	no	no	no
t=0	Rapid mix start	150 RPM	150 RPM	150 RPM	150 RPM
t=2	$KMnO_4$ dose	0 mg/L	0,5 mg/L	1,0 mg/L	1,5 mg/L
t=4	Slow mix start	60 RPM	60 RPM	60 RPM	60 RPM
t=22	Sampling	Unf/Fil	Unf/Fil	Unf/Fil	Unf/Fil
t=22-30 min	In-situ measurements in residual solution	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP

Jar test 2 : Dosing $FeCl_3$ alone in the influent of Rapid Sand Filter

Time (t), min	Action	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5
t=0	Sample (Unf/Fil) start solution from the jerry can					
t=0	Start solution in	Influent RSF	Influent RSF	Influent RSF	Influent RSF	Influent RSF
t=0	In-situ measurements in start solution	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP
t=0	pH adjustment	no	no	no	no	no
t=0	Rapid mix start	150 RPM	150 RPM	150 RPM	150 RPM	150 RPM
t=2	Fe(III) dose	0 mg/L	0,3 mg/L	0,6 mg/L	1 mg/L	5 mg/L
t=4	Slow mix start	60 RPM	60 RPM	60 RPM	60 RPM	60 RPM
t=22	Sampling	Unf/Fil	Unf/Fil	Unf/Fil	Unf/Fil	Unf/Fil
t=25 - 30 min	In-situ measurements in residual solution	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP

Jar test 3:Dosing $KMnO_4$ (first) and $FeCl_3$ (later) in the influent to Rapid Sand Filter

Time (t), min	Action	Jar 1	Jar 2	Jar 3	Jar 4
t=0	Sample (Unf/Fil) start solution from the jerry can				
t=0	Start solution in	INF RSF	INF RSF	INF RSF	INF RSF
t=0	In-situ measurements in start solution	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP
t=0	pH adjustment	no	no	no	no
t=0	Rapid mix start	150 RPM	150 RPM	150 RPM	150 RPM
t=2	$KMnO_4$ dose	0,5 mg/L	0,5 mg/L	1 mg/L	1 mg/L
t=4	Fe(III) dose	0,3 mg/L	0,6 mg/L	0,3 mg/L	0,6 mg/L
t=6	Slow mix start	60 RPM	60 RPM	60 RPM	60 RPM
t=22	Sampling	Unf/Fil	Unf/Fil	Unf/Fil	Unf/Fil
t=22-30 min	In-situ measurements in residual solution	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP

Appendix II Protocol for jar tests performed at Ouddorp (Evides)

Test 1:Dosing $FeCl_3$ alone in the Raw water

Time (t), min	Action	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6
t=0	Sample (Unf/Fil) start solution from the jerry can						
t=0	Start solution in	RW (drains+GW)	RW (drains+GW)	RW (drains+GW)	RW (drains+GW)	RW (drains+GW)	RW (drains+GW)
t=0	In-situ measurements in start solution	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP
t=0	pH adjustment	no	no	no	no	no	no
t=0	Rapid mix start	200 RPM	200 RPM	200 RPM	200 RPM	200 RPM	200 RPM
t=0	Fe(III) dose	0 mg/L	0,5 mg/L	1,0 mg/L	1,5 mg/L	2 mg/L	3,5 mg/L
t=2	Slow mix start	70 RPM	70 RPM	70 RPM	70 RPM	70 RPM	70 RPM
t=15	Sampling	Unf/Fil	Unf/Fil	Unf/Fil	Unf/Fil	Unf/Fil	Unf/Fil
t=15 - 20 min	In-situ measurements in residual solution	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP

Test 2:Dosing $KMnO_4$ alone in the Raw water

Time (t), min	Action	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5
t=0	Sample (Unf/Fil) start solution from the jerry can					
t=0	Start solution in	RW (drains+gw)	RW (drains+gw)	RW (drains+gw)	RW (drains+gw)	RW (drains+gw)

t=0	In-situ measurements in start solution	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP
t=0	pH adjustment	no	no	no	no	no
t=0	Rapid mix start	200 RPM	200 RPM	200 RPM	200 RPM	200 RPM
t=0	$KMnO_4$ dose	0 mg/L	0,3 mg/L	0,5 mg/L	1,0 mg/L	1,5 mg/L
t=2	Slow mix start	70 RPM	70 RPM	70 RPM	70 RPM	70 RPM
t=15	Sampling	Unf/Fil	Unf/Fil	Unf/Fil	Unf/Fil	Unf/Fil
t=15-20 min	In-situ measurements in residual solution	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP

Test 3:Dosing $KMnO_4$ (first) and $FeCl_3$ (later) in the Raw water

Time (t), min	**Action**	**Jar 1**	**Jar 2**	**Jar 3**	**Jar 4**	**Jar 5**
t=0	Sample (Unf/Fil) start solution from the jerry can					
t=0	Start solution in	RW	RW	RW	RW	RW
t=0	In-situ measurements in start solution	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP
t=0	pH adjustment	no	no	no	no	no
t=0	Rapid mix start	200 RPM	200 RPM	200 RPM	200 RPM	200 RPM
t=0	$KMnO_4$ dose	0,5 mg/L	0,5 mg/L	0,5 mg/L	0,5 mg/L	0,5 mg/L
t=2	Fe(III) dose	0 mg/L	0,5 mg/L	1,0 mg/L	1,5 mg/L	2 mg/L
t=4	Slow mix start	70 RPM	70 RPM	70 RPM	70 RPM	70 RPM
t=17	Sampling	Unf/Fil	Unf/Fil	Unf/Fil	Unf/Fil	Unf/Fil
t=17-22 min	In-situ measurements in residual solution	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP

Test 4:Dosing $FeCl_3$ alone in the effluent of AKF (inline coagulation scenario before UF)

Time (t), min	**Action**	**Jar 1**	**Jar 2**	**Jar 3**
t=0	Sample (Unf/Fil) start solution from the jerry can			
t=0	Start solution in	Eff AKF	Eff AKF	Eff AKF

t=0	In-situ measurements in start solution	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP
t=0	pH adjustment	no	no	no
t=0	Rapid mix start	200 RPM	200 RPM	200 RPM
t=0	Fe(III) dose	0,3 mg/L	0,6 mg/L	0,9 mg/L
t=2	Slow mix start	70 RPM	70 RPM	70 RPM
t=15	Sampling	Unf/Fil	Unf/Fil	Unf/Fil
t=15 - 20 min	In-situ measurements in residual solution	pH, temp, DO, ORP	pH, temp, DO, ORP	pH, temp, DO, ORP

Appendix III Protocol for jar tests performed at Leiduin (Waternet)

Test 1:Dosing $KMnO_4$ alone in the Raw water

Time (t), min	Action	Jar 1	Jar 2	Jar 3
t=0	Sample (Unf/Fil) start solution from the jerry can			
t=0	Start solution in	RW	RW	RW
t=0	In-situ measurements in start solution	pH, temp, ORP	pH, temp, ORP	pH, temp, ORP
t=0	pH adjustment	no	no	no
t=0	Rapid mix start	300 RPM	300 RPM	300 RPM
t=0	$KMnO_4$ dose	0,5 mg/L	1,0 mg/L	1,5 mg/L
t=2	Slow mix start	70 RPM	70 RPM	70 RPM
t=17	Sampling	Unf/Fil	Unf/Fil	Unf/Fil
t=17-22 min	In-situ measurements in residual solution	pH, temp, ORP	pH, temp, ORP	pH, temp, ORP

Test 2:Dosing Fe(III) alone in the Raw water

Time (t), min	Action	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5
t=0	Sample (Unf/Fil) start solution from the jerry can					
t=0	Start solution in	RW	RW	RW	RW	RW
t=0	In-situ measurements in start solution	pH, temp, ORP	pH, temp, ORP	pH, temp, ORP	pH, temp, ORP	pH, temp, ORP
t=0	pH adjustment	no	no	no	no	no
t=0	Rapid mix start	300 RPM	300 RPM	300 RPM	300 RPM	300 RPM
t=0	Fe(III) dose	0 mg/L	0,3 mg/L	0,6 mg/L	0,9 mg/L	1,2 mg/L
t=	Slow mix	No slow	No slow	No slow	No slow	No slow

	start	mixing	mixing	mixing	mixing	mixing
t=20	Sampling	Unf/Fil	Unf/Fil	Unf/Fil	Unf/Fil	Unf/Fil
t=20-25 min	In-situ measurements in residual solution	pH, temp, ORP	pH, temp, ORP	pH, temp, ORP	pH, temp, ORP	pH, temp, ORP

Test 3:Dosing Fe(II) alone in the Raw water

Time (t), min	**Action**	**Jar 1**	**Jar 2**	**Jar 3**	**Jar 4**	**Jar 5**
t=0	Sample (Unf/Fil) start solution from the jerry can					
t=0	Start solution in	RW	RW	RW	RW	RW
t=0	In-situ measurements in start solution	pH, temp, ORP	pH, temp, ORP	pH, temp, ORP	pH, temp, ORP	pH, temp, ORP
t=0	pH adjustment	no	no	no	no	no
t=0	Rapid mix start	300 RPM	300 RPM	300 RPM	300 RPM	300 RPM
t=0	Fe(II) dose	0 mg/L	0,3 mg/L	0,6 mg/L	0,9 mg/L	1,2 mg/L
t=	Slow mix start	No slow mixing	No slow mixing	No slow mixing	No slow mixing	No slow mixing
t=20	Sampling	Unf/Fil	Unf/Fil	Unf/Fil	Unf/Fil	Unf/Fil
t=20-25 min	In-situ measurements in residual solution	pH, temp, ORP	pH, temp, ORP	pH, temp, ORP	pH, temp, ORP	pH, temp, ORP