

## Arsenic removal in rapid sand filters

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# **Arsenic removal in rapid sand filters**

Proefschrift

ter verkrijging van de graad van doctor aan de Technische Universiteit Delft,  
op gezag van de Rector Magnificus, prof. dr. ir. T.H.J.J. van der Hagen, voorzitter van het  
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Voor Cees en René Gude, mijn grootvader en vader.



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## 1. Introduction

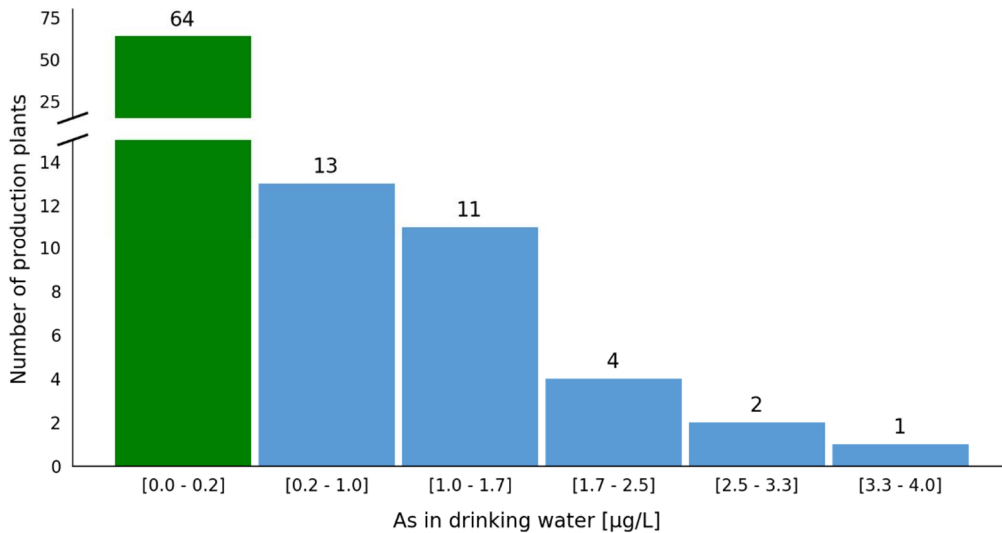
### 1.1 Arsenic in water

Arsenic (As) is a very toxic, naturally occurring element, and it ranks as the twentieth abundant element in the earth's crust. In the ground, As is mainly associated with sulphide minerals (Bissen et al., 2003), but is easily solvable in water until high concentrations, while remaining tasteless and odourless. The highest As concentrations in water can be present in mine drainage and can range up to 850 mg/L. Also geothermal waters can contain high As concentrations, in the range of 50 mg/L. These sources would be the last choice for safe drinking water production considering the World Health Organisation (WHO) guideline for drinking water of 0.01 mg/L. However, globally there are some As-rich areas where drinking water is produced from groundwater containing up to 5 mg/L, e.g. the Bengal Basin, Argentina, Mexico, northern China, Taiwan and Hungary (Smedley and Kinniburgh, 2002). Recently, Pakistan was added to this list and, worldwide, the WHO estimated that 200 million people rely on drinking water with concentrations of As higher than the recommend 10 µg/L (Guglielmi, 2017).

The main adverse effects associated with long-term ingestion of As in humans are skin lesions, (lung-)cancer, developmental toxicity, neurotoxicity, cardiovascular diseases, abnormal glucose metabolism, and diabetes. Additionally there is emerging evidence of negative impacts on foetal and infant development, particularly reduced birth weight (WHO, 2011). The fact that As has detrimental effects on human health is known for decades and was reflected in the first standard on As in drinking water as early as 1954 at a concentration of 50 µg/L. In 1993, the WHO guideline value for As in drinking water was reduced, up to the present 10 µg/L. This value was based on the increasing awareness of the toxicity of As, particularly its carcinogenicity, and on the ability to measure it quantitatively at lower concentrations (WHO, 1993).

However, due to adverse health effects, even at concentrations below 10 µg/L (Roh et al., 2017; WHO, 2011), some developed countries have lowered their national guideline for As further. Conclusions from van Halem et al. (2009) have been the inducement for the Netherlands to target As concentrations in drinking water even to be less than 1 µg/L.

In the Netherlands, groundwater used for drinking water production contains As in the range from 0 – 70  $\mu\text{g/L}$  (Stuyfzand et al., 2006). Currently, all groundwater treatment plants reduce As in drinking water below the WHO standard of 10  $\mu\text{g/L}$ . However, the new target value would cause a small percentage of the groundwater treatment plants with trace amounts of As exceeding the 1  $\mu\text{g/L}$ . 31 of the 95 water production locations of Vitens, the largest drinking water company in the Netherlands, are confronted with measurable ( $>0.1 \mu\text{g/L}$ ) As concentrations in their raw water, from these facilities the drinking water As concentrations are visualised in a histogram depicted in Figure 1.1 (Vitens, 2014).



**Figure 1.1** Six bin histogram of As concentrations in the filtrate of the 95 groundwater treatment plants of Vitens drinking water company of which 31 contained (traces) of As in the raw water (Vitens, 2014).

Thus 58% of the treatment plants with measurable As in the raw water (19% from total) would need some sort of adjustment to their treatment scheme to comply with the new As target value. Preferably this is done by only changing operational settings (e.g. supernatant level and filtration velocity), at minimum additional costs, that could aid in removing the additionally required removal of As.

## 1.2 Groundwater water treatment

Aeration and rapid sand filtration are probably the most frequently used processes to bring anoxic or anaerobic groundwater to drinking water quality. Aeration will saturate the water with oxygen ( $O_2$ ), and remove (a part of the) dissolved gasses carbon dioxide ( $CO_2$ ), hydrogen sulphite ( $H_2S$ ) and methane ( $CH_4$ ).  $O_2$  facilitates the oxidative removal of iron (Fe), manganese (Mn) and ammonium ( $NH_4$ ) subsequently in the rapid sand filter.

The aerated water is supplied to the supernatant water of a rapid sand filter, see Figure 1.2, that typically consists of a filter bed with a height of 1.5–2.5 m and is commonly operated with a downward filtration velocity of 3–8 m/h. Various filter media can be used; sand and anthracite are the most common and often applied together in a so-called double media filter. The grainsize of sand is normally in the range of 0.5–2.0 mm at the bottom, while anthracite, with a lower density, makes up the top layer with larger grainsizes, in the range 1.5–4.0 mm. The applied grainsize and filtration velocity are the main contributors to the initial resistance in the filter bed (causing pressure drop over the filter media), commonly referred to as 'clean bed resistance'. Media size and filtration velocity are generally determined experimentally or by experience.

During operation, the filter bed fills up with the filtered particles, resulting in clogging and thus a decreased filter porosity. The runtime is mainly influenced by the incoming water quality, filtration velocity, media size and height of the filter bed. Finally, at the end of the filter runtime, the filter is backwashed. The backwash frequency is commonly between 24 and 60 hours. Various air scouring and water flush programs are used to remove most clogging, taking about 30 min in total. The backwash sequence is usually triggered by a maximum pressure drop of about 1.5 m over the filter bed caused by the retained solids or decreased effluent water quality (Moel et al., 2006).

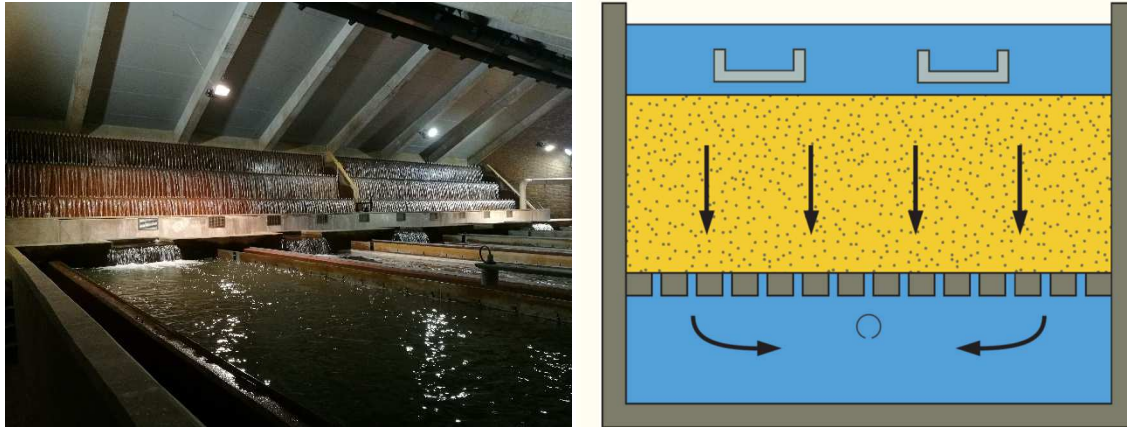


Figure 1.2 left: a photograph of an aeration and rapid filtration system in the Netherlands. Right: a schematic view of a rapid filter system.

### 1.3 Arsenic removal

As removal, for the purpose of drinking water production, can be achieved in various ways, e.g. by reverse osmosis, softening or ion-exchange (Mondal et al., 2013). However, these solutions are expensive, energy intensive and/or consume chemicals, and should therefore be avoided, if possible. The least invasive method for As removal is oxidation-coagulation-filtration (Bissen and Frimmel, 2003), since this can largely be applied in existing installations to treat groundwater (Ngo et al., 1999). However, also in this concept challenges exist, which have mainly to do with the oxidation state of As.

As is commonly present in water as either As(III) or As(V), where the Roman numerals refer to their oxidation state. The oxidation state of As determines to a great extent the efficiency of the adsorption process. As, when dissolved in anoxic or anaerobic groundwater of near neutral pH, is typically present as As(III) ---  $\text{H}_3\text{AsO}_3^*$  ---, the reduced, uncharged, trivalent form of As (Smedley and Kinniburgh, 2002; Stuyfzand et al., 2006). In contrast, the oxidised pentavalent form of As, As(V), is, at neutral pH, a negatively charged anion ---  $\text{H}_2\text{AsO}_4^-$  ---, leading to a more efficient removal via adsorption onto e.g. hydrous ferric oxides (HFO) (Bissen and Frimmel, 2003), being the main removal mechanism during rapid sand filtration (Katsoyiannis et al., 2008; Wu et al., 2015).

HFO in the filter bed originates from the oxidation of Fe(II) present in the anoxic or anaerobic groundwater. Fe(II) can be removed via homogeneous, heterogeneous and biological oxidation, depending on operational parameters such as, supernatant water

level, filtration velocity, pH and O<sub>2</sub> concentration (van Beek et al., 2015). Fe is efficiently removed in the top layer of the filter bed in most installations.

To oxidise As(III) a strong oxidant, such as e.g., ozone gas, MnO<sub>4</sub> or chlorine can be used (Ghurye and Clifford, 2004). In addition, these oxidant oxidise other reduced substances present in the raw groundwater, such as Fe(II) and Mn(II). The formed As(V) will then rapidly adsorb onto the simultaneous precipitated HFO, which can be subsequently retained in a rapid sand filter (Guan et al., 2009). However, chemical oxidation has disadvantages, as it leads to: (1) increased operational costs, (2) stricter safety procedures for handling the highly reactive oxidants, (3) shorter runtimes of the rapid sand filters as a result of larger HFO flocs, (4) reduced iron sludge density, which is undesirable for backwash water treatment, and (5) possibly reduced biological stability of the produced drinking water due to the formation of biodegradable organic matter, see Park et al. (2016) and Zhang et al. (2016) for studies on biological stability.

However, the prior mentioned Vitens data (see Figure 1.1) showed that in the 31 treatment plants with As in the raw water, also spontaneous, unintentional, As removal occurred, ranging from 15% - 95%; just by aeration and rapid filtration. Given that the removal percentages vary greatly and the amount of As removal that is required is small, more knowledge on As removal mechanisms in rapid sand filters could result in improved removal performance by better operation of these filters, avoiding the use of strong oxidants. Full understanding of the As removal mechanisms could thus aid in the enlargement of the natural As removing capacity of groundwater treatment plants and save water companies from expensive, undesirable additional water treatment processes.

#### **1.4 Research questions and methods**

Currently, the exact interactions that are involved in As removal in rapid sand filter treating aerated groundwater remain unknown. There are many intricate and inter-dependable processes occurring simultaneously or sequentially (Jessen et al., 2005; Katsoyiannis and Zouboulis, 2004; Niu et al., 2013; Sharma et al., 2001). Some of these processes include biological and/or abiotic oxidation of multiple components (e.g. Fe(II), As(III), Mn(II) and ammonium (NH<sub>4</sub>)), followed by the adsorption of various oxyanions, cations and anions and mineral precipitation. The difficulty is that many of the processes

can occur via multiple mechanisms, e.g. Fe(II) can be transformed into HFO via homogeneous, heterogeneous and biological oxidation pathways.

Therefore this thesis aims to discern the relevant As removal processes that occur during aeration and rapid filtration and to establish a 'toolbox' to increase the natural removal capacity of the aeration – rapid filtration process.

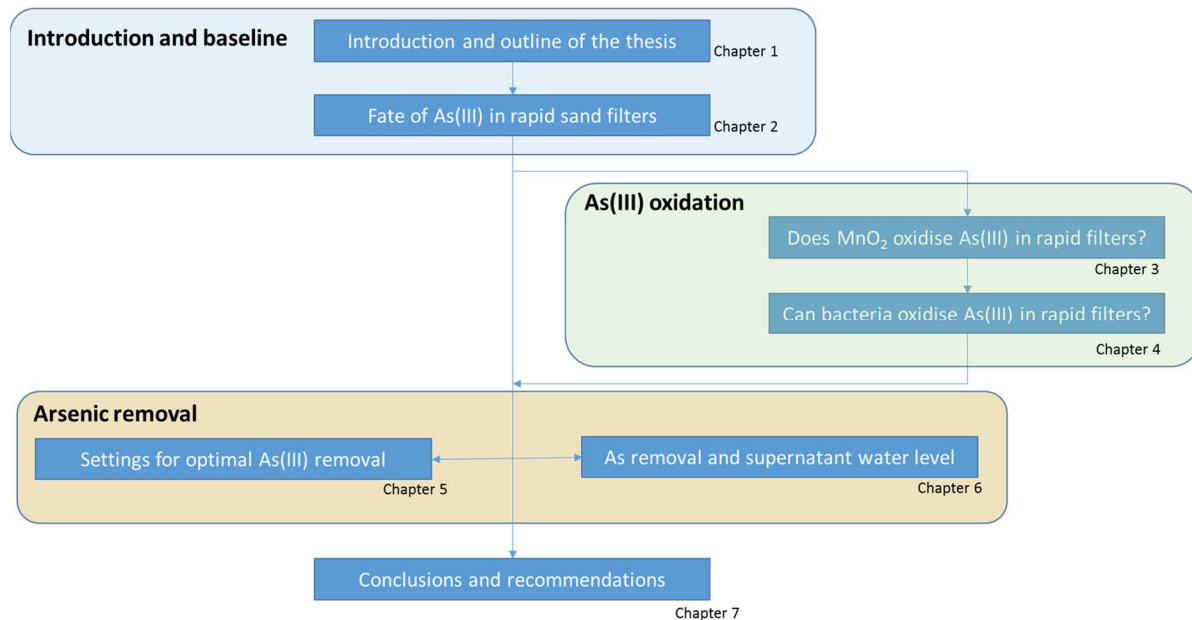
In order to achieve this this main objective, the following research questions are:

- I. What are the main contributors in reducing As mobility during full-scale aeration and rapid sand filtration?
- II. To what extent can MnO<sub>2</sub> be responsible for rapid oxidation of As(III) in the top of the filter bed?
- III. What is the role of arsenic-oxidising bacteria (AsOB) in rapid sand filters for the removal of arsenic?
- IV. Can As removal be improved by optimising operational settings: filter media size, Fe oxidation state entering the filter bed or pH value?
- V. Could As removal be influenced by supernatant level, hence Fe(II)/Fe(III) ratio entering the rapid sand filter?

The answering of these research questions will bring new evidence on the mobility of not only As, but also on Fe, Mn and NH<sub>4</sub> during groundwater treatment. Therefore water samples, obtained from full-scale drinking water treatment plants, pilot plants, column set-ups and jar tests, run with As containing or added to demineralised water and natural groundwater, were analysed.

## 1.5 Outline of the thesis

The outline of the thesis is depicted in Figure 1.3.



**Figure 1.3** Outline of the thesis.

In **chapter 2**, the mechanisms behind adventitious As removal are determined at three full-scale groundwater treatment filters. Main finding concerning As(III) oxidation in the filter bed will be elaborated on in chapter 3 and chapter 4. **Chapter 3** scrutinises the potential of MnO<sub>2</sub> to oxidise As(III) in the top of the filter bed, while **chapter 4** describes the possible role of As(III) oxidising bacteria in rapid filters. Combining the knowledge gained in prior chapters, **chapter 5** gives a look into the role of filter media size, filtration velocity, pH and Fe species in their contribution to maximise As adsorption to HFO in rapid filters. **Chapter 6** sheds light on the role of the supernatant level above the filter and the interactions of Fe and biological As(III) oxidation. Finally, conclusions and recommendations for future research are made in **chapter 7**.

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## 2. Fate of low arsenic concentrations during full-scale aeration and rapid filtration

J.C.J Gude, L.C. Rietveld and D. van Halem

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### Abstract

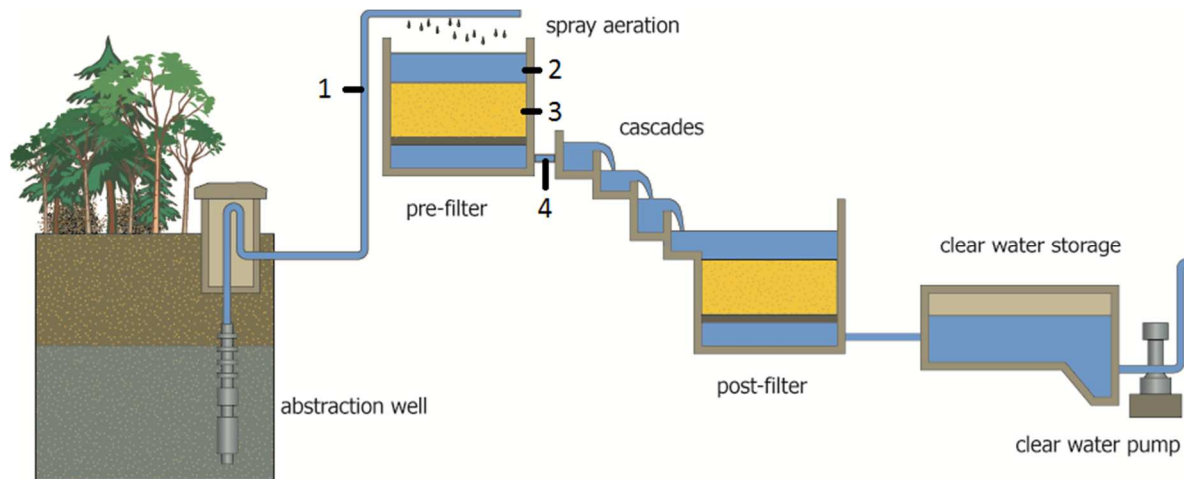
In the Netherlands, groundwater treatment commonly consists of aeration, with subsequent sand filtration without using chemical oxidants like chlorine. With arsenic (As) concentrations well below the actual guidelines of 10 µg As/L, groundwater treatment plants have been exclusively designed for the removal of iron (Fe), manganese and ammonium. The aim of this study was to investigate the As removal capacity at three of these groundwater treatment plants (10-26 µg As/L) in order to identify operational parameters that can contribute to lowering the filtrate As concentration to <1 µg/L. For this purpose a sampling campaign and experiments with supernatant water and hydrous ferric oxide (HFO) flocs were executed to identify the key mechanisms controlling As removal.

Results showed that after aeration, arsenic largely remained mobile in the supernatant water; even during extended residence times only 20 - 48% removal was achieved (with 1.4 - 4.2 mg/L precipitated Fe(II)). Speciation showed that the mobile As was in the reduced As(III) form, whereas, As(V) was readily adsorbed to the formed HFO flocs. In the filter bed, the remaining As(III) completely oxidised within 2 minutes of residence time and As removal efficiencies increased to 48 - 90%. Filter grain coating analysis showed the presence of manganese at all three treatment plants. It is hypothesised that these manganese oxides are responsible for the accelerated As(III) oxidation in the filter bed, leading to an increased removal capacity. In addition, pH adjustment from 7.8 to 7.0 has been found to improve the capacity for As(V) uptake by the HFO flocs in the filter bed. The overall conclusion is, that during groundwater treatment, the filter bed is crucial for rapid As(III) removal, indicating the importance to control the oxidation sequence of iron and As for improved As removal efficiencies.

## 2.1 Introduction

Arsenic (As) mobility in water is worldwide studied since its toxicity was proven in 1888 (Smith et al., 1992). Intake of As can lead to skin disease, cancer, kidney and heart failure, diabetes and paralysis (Mandal et al., 2002; Duker et al., 2005; WHO 2011). As naturally occurs in groundwater and in the Netherlands concentrations range from 0.01 – 70 µg/l. The As is related to subsurface oxidative and reductive dissolution of iron (Fe) minerals containing As (Stuyfzand et al., 2006). Under typical reducing groundwater conditions As is predominantly found in the arsenite (As(III)) form (Smedley et al., 2002) which is a fully protonated oxyanion at neutral pH. The other common form of As in the aquatic environment is arsenate (As(V)), which is oxidised and a charged oxyanion at neutral pH. Although all (groundwater) treatment plants in the Netherlands provide drinking water below the European standard of 10 µg As/L, Dutch drinking water companies investigate implications of distributing water with As concentrations below 1 µg/L to their customers (WHO 2011; Halem et al., 2009).

In the Netherlands, groundwater treatment commonly consists of aeration, with subsequent sand filtration processes without using chemical oxidants like chlorine, as depicted in Figure 2.1 (Moel et al., 2006; Huisman 2004). Aeration typically consists of cascade or spray aeration, and rapid filters are generally submerged with supernatant water and operated under gravity. In this process, completed within 15 minutes of residence time, As is co-precipitated and partially adsorbed during treatment. However, water quality data from 21 typical groundwater treatment plants (WTPs) in the Netherlands indicate that As removal efficiencies vary greatly: 15-96% (Vitens, 2014). The variety in As removal efficiency can be attributed to the different aeration and filtration designs, as well as different raw water qualities.



**Figure 2.1.** Typical set-up for groundwater treatment in the Netherlands. Numbers 1 to 4 indicate the following sample points: (1) raw water, (2) aerated supernatant water (3) multiple sample points over the height of the filter bed and (4) filtrate.

For the removal of As, As(III) oxidation has been studied extensively because of the charge neutrality of As(III) at neutral pH. Homogeneous oxidation of As(III) by oxygen is thermodynamically possible but can be slow, taking up to seven days for complete oxidation, thus being an insignificant process for drinking water treatment (Kim et al., 2000; Bissen et al., 2003; Oscarson et al., 1981). Strong oxidants like chlorine, potassium permanganate and ozone can oxidise As(III) to As(V) within a few seconds to a minute of residence time (Ghurye et al., 2004; Guan et al., 2009a). However, a study of Pettine et al. (1999) into hydrogen peroxide as an oxidant, showed that As(III) oxidation time is pH dependant in a range from minutes (pH 10) to multiple hours (pH 6). This reaction time is too long to be beneficial for groundwater treatment processes. In addition, strong oxidants also oxidise other reduced groundwater constituents, are costly and dangerous to handle and are therefore preferably not used during groundwater treatment. Since Fe(II) is present in virtually all groundwater matrices, a more promising oxidation mechanism was provided by Hug et al. (2003): As(III) was catalytically oxidised by intermittent Fe(IV) species during Fe(II) oxidation, following the oxidation kinetics of Fe. Unfortunately in excess of Fe, only 25-30% As(III) was oxidised, leaving the majority of As(III) reduced and uncharged. Bisceglia et al. (2005) showed the same process in a sand filter and modelled the process with a reactive-transport model. In sand filters, where Fe oxides are present on the filter grains, As(III) can be oxidised catalytically by heterogeneous Fe(II) oxidation on Fe oxides (Amstaetter et al., 2010; Wang et al., 2015),

Bruins et al. (2014) showed with Raman spectroscopy, XRD and SEM analyses that manganese (Mn) removal during rapid filtration resulted in the presence of poorly crystalline  $\text{MnO}_2$  in the grain coatings, in addition to amorphous Fe oxides (Sharma, 2001). These Mn and Fe oxides are formed either by biotic oxidation (de Vet et al., 2011; Katsoyiannis et al., 2004) or abiotic oxidation (Stumm et al., 1996). Spiro et al. (2010) found that biotically produced  $\text{MnO}_2$  has excellent oxidative power and a high surface area. The effects of  $\text{MnO}_2$  in the filter grain coating on As(III) oxidation has not been studied in detail, but rapid As(III) oxidation in a filter bed was observed at a treatment plant in Denmark (Jessen et al., 2005) and an increased concentration of mobile Mn(II) adduced the reactivity of  $\text{MnO}_2$  present on the filter grains. Studies on abiotic oxidation of As(III) by synthetic birnessite ( $\text{MnO}_2$ ) showed rapid oxidation as well (Manning et al., 2002). Lafferty et al. (2010) showed passivation of Mn oxides during oxidation of As(III) and states that Mn oxidation by poorly crystalline  $\text{MnO}_2$  is of mayor influence on the oxidation process. Driehaus et al. (1995) showed that  $\text{MnO}_2$  can directly oxidise As(III) and is unaffected by pH in the range of pH 5 to pH 10. Apart from Mn oxides, also hydrous ferric oxides (HFO) are formed during groundwater treatment from the precipitating Fe(II) and are known to accumulate on sand grains and in the pore volume of rapid filters. Equilibrium adsorption studies of As on HFO have been executed quite extensively and for example Dixit et al. (2003) found that both As(III) and As(V) have strong affinity for Fe hydroxyl sorption sites. Manning et al. (1998) showed higher equilibrium adsorption of As(III) than As(V) at pH >5 on goethite and, using EXAFS, demonstrated that both As(III) and As(V) form innersphere complexes. Raven et al. (1998) found similar As behaviour on ferrihydrite. This study indicated that at high As/Fe ratios (13.3 mol / kg Fe) also kinetics were faster for As(III) than As(V), at both investigated pHs; pH 4.6 and pH 9.2. Only at pH 4.6 and a low As/Fe ratio (0.267 mol / kg Fe) stronger and faster adsorption of As(V) occurred. However, this low As/Fe ratio is still about four times larger than the common As/Fe ratio during groundwater treatment in the Netherlands. Therefore, although equilibrium studies adduce that both As(III) and As(V) adsorb to HFO flocs, it is generally accepted that for efficient groundwater treatment, where kinetics play a crucial role, As must be in the anionic As(V) form (Jessen et al., 2005; Katsoyiannis et al., 2008; Bissen et al., 2003; Lee et al., 2003).

Apart from pH and ionic strength, also specific cations like calcium (Ca) and magnesium (Mg) promote anion adsorption to Fe hydroxides by positively influencing the surface charge (Guan, et al., 2009b). Meanwhile, anions like phosphate ( $\text{PO}_4$ ), sulphate ( $\text{SO}_4$ ), silicate ( $\text{SiO}_4$ ) and bicarbonate ( $\text{HCO}_3$ ) are able to compete for the same adsorption sites as As.  $\text{PO}_4$  and As(V) are, for example, equally adsorbed on goethite at  $\text{pH} > 6$  (Lui et al., 2001), but, since concentrations of  $\text{PO}_4$  are generally 10 to 20 times higher than As in groundwater,  $\text{PO}_4$  can seriously inhibit As removal. Apart from blocking adsorption sites,  $\text{PO}_4$  can also precipitate with Fe and inhibit further flocculation due to the negative surface charge of the  $\text{FePO}_4$  precipitates (Voegelin et al., 2013; Gunnars et al., 2002). Roberts et al. (2004) showed this process prevents Fe(II) to form HFO flocs that create adsorption sites for As.

Groundwater treatment plants in the Netherlands have exclusively been designed for the removal of Fe, Mn and ammonium ( $\text{NH}_4$ ). With As concentrations well below the guidelines, this parameter has not yet influenced treatment set-ups nor operational parameters like aeration type, supernatant water level, filtration velocity and grain size. Current research, as mentioned above, mainly focusses on As removal at higher concentrations and removal by use of costly sorbents or dosage of chemicals, targeting the WHO standard of  $10 \mu\text{g/L}$ . The overall aim of this study was to investigate the natural As removal capacity at three groundwater treatment plants ( $10\text{-}26 \mu\text{g As/L}$ ) in order to identify operational parameters that can contribute to lowering the filtrate As concentration to  $<1 \mu\text{g/L}$ . Therefore, the interactions between As, Fe,  $\text{PO}_4$ , Mn and  $\text{NH}_4$  after aeration and during rapid filtration in the natural groundwater matrix were investigated at low As concentrations. A differentiation was made between the processes in the supernatant water storage after aeration, and the filtration process. For this purpose a WTP sampling campaign, supernatant water experiments, experiments with HFO flocs, collected from the top of a rapid filter, and filter grain analyses were executed to identify the key mechanisms controlling As removal during full scale drinking water production.



## 2.2 Materials and methods

### 2.2.1 Treatment plants

The research was executed at three different WTPs in the Netherlands. Table 2.1 provides details on the WTPs and the relevant water quality parameters.

Table 2.1 Details of investigated groundwater treatment plants

	Unit	WTP 1		WTP 2		WTP 3	
<b>Aeration type</b>		Spray		Cascade		Spray	
<b>Filter height and media</b>		2.0 m sand		2.17 m sand		1m anthracite 1 m sand	
<b>Filter media age</b>	years	>22		19		8	
<b>Grain diameter (D50)</b>	µm	3200		1300		1600 / 1000	
<b>Specific surface area<sup>1,2</sup></b>	A/V m <sup>-1</sup>	1163		2862		2325 / 3720	
<b>Filtration rate</b>	m/h	5.0		4.8		6.8	
<b>Supernatant level</b>	m	0.4		0.25		0.6	
<b>Residence time<sup>2</sup> during aeration-filtration</b>	min	13.9		13.4		12.4	
<b>Temperature</b>	°C	11.2		12.4		10.5	
<b>pH supernatant water</b>		7.55		7.88		7.98 <sup>3</sup>	
		<b>Raw</b>	<b>Filtrate</b>	<b>Raw</b>	<b>Filtrate</b>	<b>Raw</b>	<b>Filtrate</b>
<b>pH</b>		7.29	7.23	7.54	7.69	7.39	7.66
<b>HCO<sub>3</sub></b>	mg/L	n.m.	n.m.	246	241	115	119
<b>Conductivity</b>	µS/cm	399	389	440	432	250	253 <sup>3</sup>
<b>ORP</b>	mV	50	300	-134	232	-139	274
<b>As</b>	µg/L	10.2	1.50	13.2	6.18	26.1	2.44
<b>As(III)</b>	µg/L	8.23	0.57	12.7	0.76	22.4	0.26
<b>Fe</b>	mg/L	1.97	0.04	1.40	0.01	4.33	0.14
<b>Mn</b>	mg/L	0.93	0.001	0.04	0.001	0.178	0.001
<b>NH<sub>4</sub></b>	mg N /L	0.27	0.001	0.42	0.011	0.29	0.004

<b>PO<sub>4</sub></b>	mg P /L	0.023	0.003	0.15	0.03	0.19	0.024
<b>TOC</b>	mg C /L	1.53	1.54	2.22	2.13	2.56	2.16
<b>SO<sub>4</sub></b>	mg/L	15.5	15.6	0	0.37	7.72	7.74

\*n.m. = not measured; <sup>1</sup>Calculated with porosity and grain size (no BET measurement); <sup>2</sup> Calculated with a filter bed porosity of 0.38; <sup>3</sup> Increased value due to caustic soda (NaOH) dosage;

### 2.2.2 Analyses

pH, conductivity, oxidation-reduction potential (ORP), oxygen and temperature were measured with WTW electrodes (SenTix 940, SenTix ORP 900, TerraCon 925 and FDO925). Water samples of 50 mL were analysed for Fe, As, Mn, Si, P, Ca, and Mg, both unfiltered and filtered over a polyethersulfone 0.45 µm filter (25 mm, VWR). Both filtered and unfiltered samples were acidified with 0.6 mL 5M H<sub>2</sub>SO<sub>4</sub> and analysed with Inductively Coupled Plasma Mass Spectrometry (ICP-MS). HCO<sub>3</sub> was determined with a titrimetric measurement, SO<sub>4</sub> by spectrophotometry and TOC by high temperature combustion and infrared detection.

As speciation was done by letting 100 mL filtered water pass a syringe of 30 mL filled with 20 mL Amberlite® IRA-400 chlorite form anion ion-exchange resin. The As concentration that remained after contact with the resin was considered to be the uncharged As(III) (Clifford et al., 2005). As(V) was calculated by subtracting As(III) from the concentration of mobile As. Results were in compliance with results obtained by IC coupled with ICP-MS (n=10). Additionally, a control solution of 2 mg/L As(V) was effectively retained by the resin.

### 2.2.3 WTP sampling campaign

At the three selected WTPs, a water sampling campaign was executed with 10-12 sampling points in the raw water, supernatant water, multiple sample points in the filter bed and filtrate of one filtration step, as depicted in Figure 2.1. Before sampling, the rotation of the groundwater well circuit was stopped to ensure a constant flow and water quality during the complete runtime of the sampled filter. All data was collected between a filter runtime of 16 – 22 hours to ensure optimal working conditions and minimal pore blocking by already retained HFO flocs. Supernatant water level was regulated and kept

constant. The sampling was concluded with filter backwashing to collect the accumulated sludge that was retained in the filter during the sampling campaign.

Three types of samples were taken for each sampling point: unfiltered, 0.45  $\mu\text{m}$  filtered and As-speciated. For sampling over the height of the filter bed, a short tube was connected to the sampling tap and led to the bottom of a 2 L jar. In this jar the WTW electrodes were placed and the samples were taken. The filtered water and speciated samples were taken from the bottom of the jar using a 60 mL syringe, and were directly filtered.

#### **2.2.4 Supernatant water experiments**

Jar tests experiments were executed to simulate As behaviour in the supernatant water with extended residence times. 12 L of supernatant water was collected and distributed evenly over six jars containing magnetic stirrers. Three jars were spiked with extra 22  $\mu\text{g/L}$  As(V), consequently three jars contained mainly As(III) and three jars contained both As(III) and As(V). The jars were continuously stirred at 20 rpm and analysed for pH, ORP, conductivity, oxygen and temperature. Samples were taken after 10, 20 and 60 minutes contact time.

#### **2.2.5 HFO floc experiments**

As adsorption onto HFO flocs extracted from the filter bed of WTP2 was investigated by collecting filter material from the top 10 cm of the filter bed after a filter runtime of +/- 40 hour. Subsequently, 1750mL filter material was flushed with 2L of filtrate. The sludge-containing solution was left to settle for 30 min, leaving 700mL dense HFO flocs from the top of the filter bed, containing 50 mg/L Fe and 340  $\mu\text{g/L}$  As. For the experiments 20 mL of this HFO flock suspension was added to 2L of filtrate, with or without an additional spike of As(III) or As(V). The experiments were executed at pH 7 by adding HCl, pH 7.8 (no pH adjustment) and pH 8.2 by adding NaOH. The filtrate was put into contact with the HFO for exactly 20 min while being stirred with a magnetic stirrer at 20 rpm keeping the HFO flocs homogenously suspended. The pH was measured in all jars at the start and end of the experiment and showed no drift in 20 min. After 20 min each jar was sampled

unfiltered and filtered and analysed for Fe, Mn, Ca and As speciation. Each experiment was performed in duplicate.

### **2.2.6 Characterization of filter sand grains and backwash water analysis**

Grains were removed from the top of the filter bed with a stainless steel device during the last rinse of the backwash procedure. The grain diameter was analysed and the coating of 0.5 g of the grains was dissolved in 25 mL demi water and 6.25 mL concentrated HNO<sub>3</sub> (69-70%) by heating the suspension to 98 °C for 4 hours. After cooling down, the acidified water was filtered through a cellulose acetate filter of 0.45µm (Whatman) and analysed for dissolved As, Fe, Mn, Si, P and Ca. Backwash water was sampled directly from the backwash gutter after 20 seconds of overflow during the first rinse.

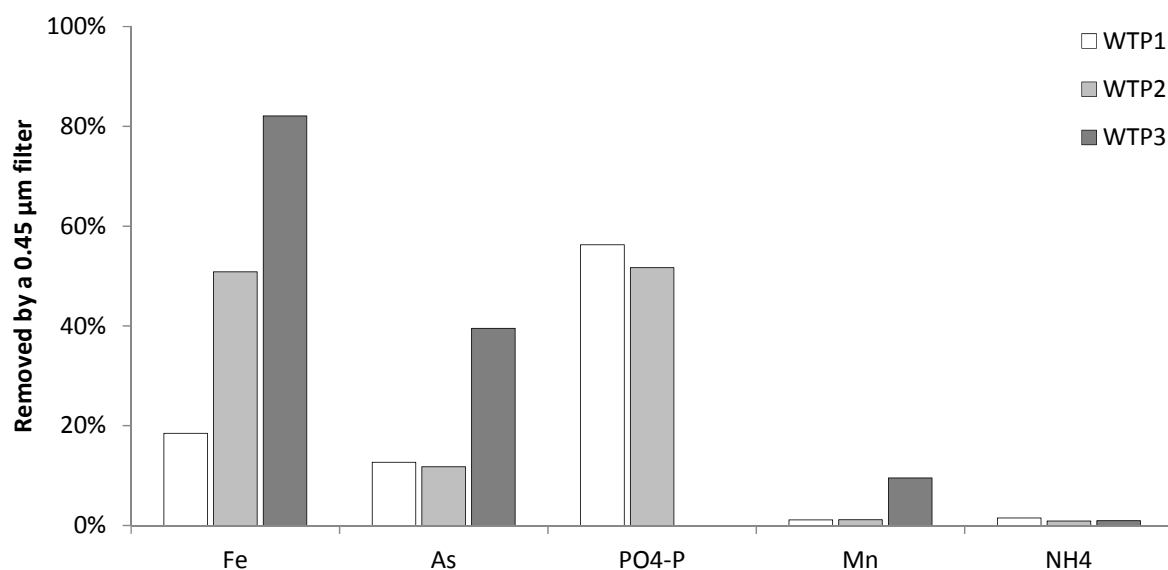
### **2.2.7 Chemical additions**

Sigma Aldrich As(III) solution 0.1M was diluted in ultra-pure water to 0.4 mg/L As(III) and Sigma Aldrich Na<sub>2</sub>HAsO<sub>4</sub> crystals were dissolved in ultra-pure water to obtain a concentration of 44 mg/L As(V). NaOH and HCl were diluted to 0.1M in ultra-pure water prior to dosing.

## **2.3 Results and discussion**

### **2.3.1 Filterability due to oxidation processes in the supernatant water**

To study As mobility in the aerated supernatant water at the three WTPs, the removability of the groundwater components of interest by a 0.45 µm filter are depicted in Figure 2.2. The Figure shows that a proportion of Fe, As and PO<sub>4</sub> was retained by the filter due to the oxidation processes in the supernatant water, whereas Mn (1-10%) and NH<sub>4</sub> (0-1%) remained largely dissolved in the water.



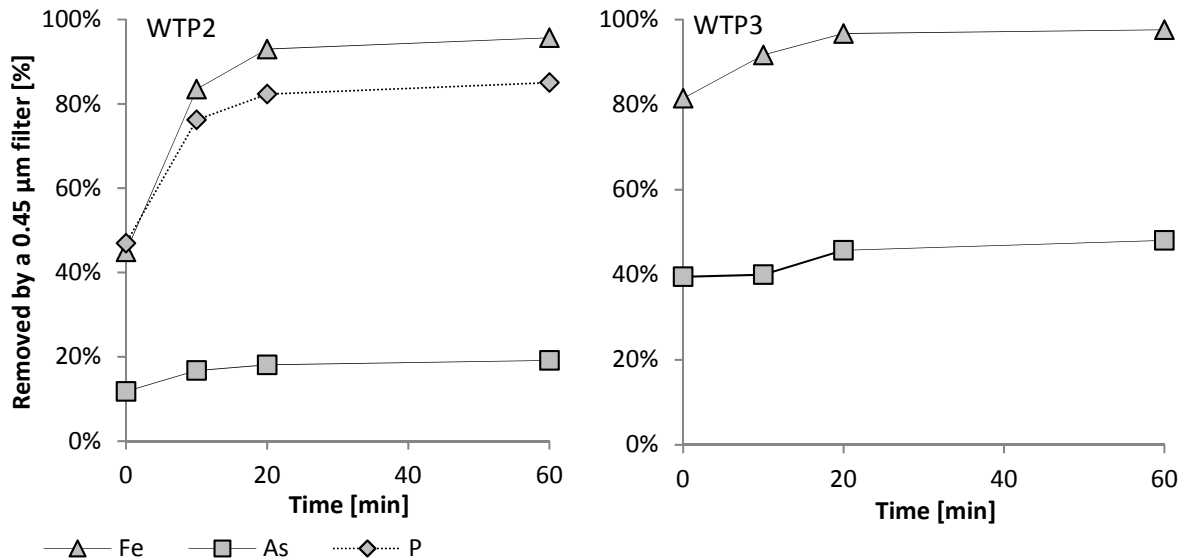
**Figure 2.2** Percentage of Fe, As, PO<sub>4</sub>, Mn and NH<sub>4</sub> removed by a 0.45 µm filter of aerated supernatant water at WTP1, WTP2 and WTP3. Initial concentrations for the WTPs were respectively (Table 2.1): Fe 2.0, 1.4, and 4.3 mg/L; As 10, 13 and 26 µg/l; PO<sub>4</sub> 23, 150 and 190 µg P /L; Mn 0.93, 0.04 and 0.18 mg/L; NH<sub>4</sub> 0.27, 0.42 and 0.29 mg N /L.

Fe removability due to aeration of the raw water varied from 18-82%. This difference in efficiency can mainly be attributed to the oxidation kinetics of Fe(II) since residence times and pH in the supernatant water were not similar. The precipitating Fe(II) incorporated part of the As and PO<sub>4</sub> by (co-)precipitation and/or adsorption and made them filterable too. Compared to PO<sub>4</sub> (52 - 85%) only a small proportion of As (12 - 40%) was removed. A potential explanation could be that As removal may have been limited by insufficient residence time or insufficient As(III) oxidation in the supernatant water.

### 2.3.2 Supernatant water experiments

Whether the residence time in the supernatant water was limiting As removal, was investigated by extending the storage step during jar test experiments. The supernatant water on top of the filter bed had an approximate residence time of 3.1 and 5.5 minutes at the moment of sampling for WTP2 and WTP3, respectively. The Fe that precipitated in this period (45-81%) resulted in 12% and 40% As removal for WTP2 and WTP3, respectively. In this period the pH drifted for WTP2 from 7.97 to 7.90 and for WTP3 from 8.83 to 8.03. The moment of supernatant water sampling was considered as the start of the jar test experiments (t=0). Figure 2.3 depicts Fe, PO<sub>4</sub> and As filterability of the

supernatant water of WTP2 and Fe and As of WTP3 during the extended supernatant water experiments (60 minutes).



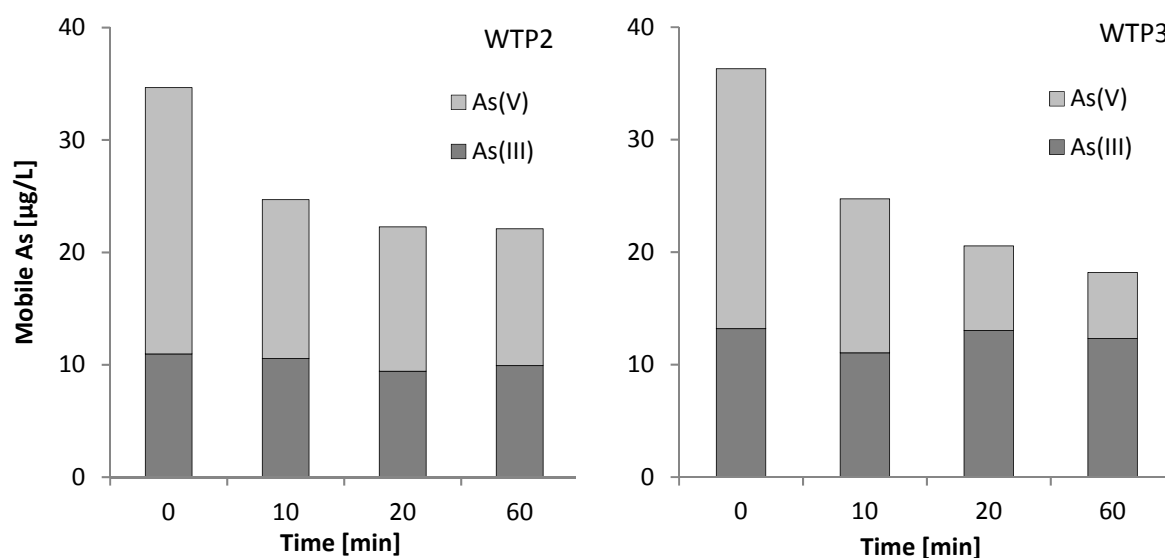
**Figure 2.3** Fe and As removed by 0.45 µm filtration after extending the oxidation time of the supernatant water in jars at WTP2 (left) with initial concentrations Fe 1.4 mg/L, As 13 µg/L and P 150 µg P/L and WTP3 (right) with initial concentrations Fe 4.3 mg/L and As 26 µg/L.

At WTP3 the Mn filterability during supernatant storage was 10%, this slightly increased by extending residence times to 11%, 12% and 12% after 10, 20 and 60 minutes respectively (not depicted in Figure 2.3). The increased filterability of Mn during the first 5.5 minutes can only be attributed to a short period that the pH was above 8.6 due to the NaOH dosage in the raw water.

While Mn remained mobile, during the 60 min retention time, complete Fe filterability, and thus oxidation was achieved for both WTPs. However, the concentration of already precipitated Fe (HFO flocs) in the supernatant water was not comparable; WTP2 had 0.7 mg/L (51%) and WTP3 had 3.5 mg/L (82%) of HFO flocs at  $t=0$ . During the 60 minutes extended residence time As removal increased 7% (from 12 to 19%) for WTP2 and 8% (from 40 to 48%) for WTP3. Therefore, it may be concluded that lengthening the storage time in the supernatant water only marginally improved the As removal. The dotted line depicted in Figure 2.3 is  $PO_4$  removal at WTP2, so in contrast to arsenic,  $PO_4$  removal did increase during this experiment with 38% (from 47% to 85%), indicating that As removal

may have been outcompeted by  $\text{PO}_4$  in the supernatant water. Measurements indicated the mobile As was in the As(III) form at both WTPs at all the sampling intervals.

In order to investigate whether the precipitating Fe(II) in the supernatant water had residual adsorptive capacity for As(V), the previous experiment was repeated with an As(V) spike of  $23 \mu\text{g/L}$ , in addition to the naturally occurring As(III) in the WTP2 and WTP3 supernatant water. The uptake of As(III) and As(V) in the supernatant water during this 60 minutes jar experiment is depicted in Figure 2.4.

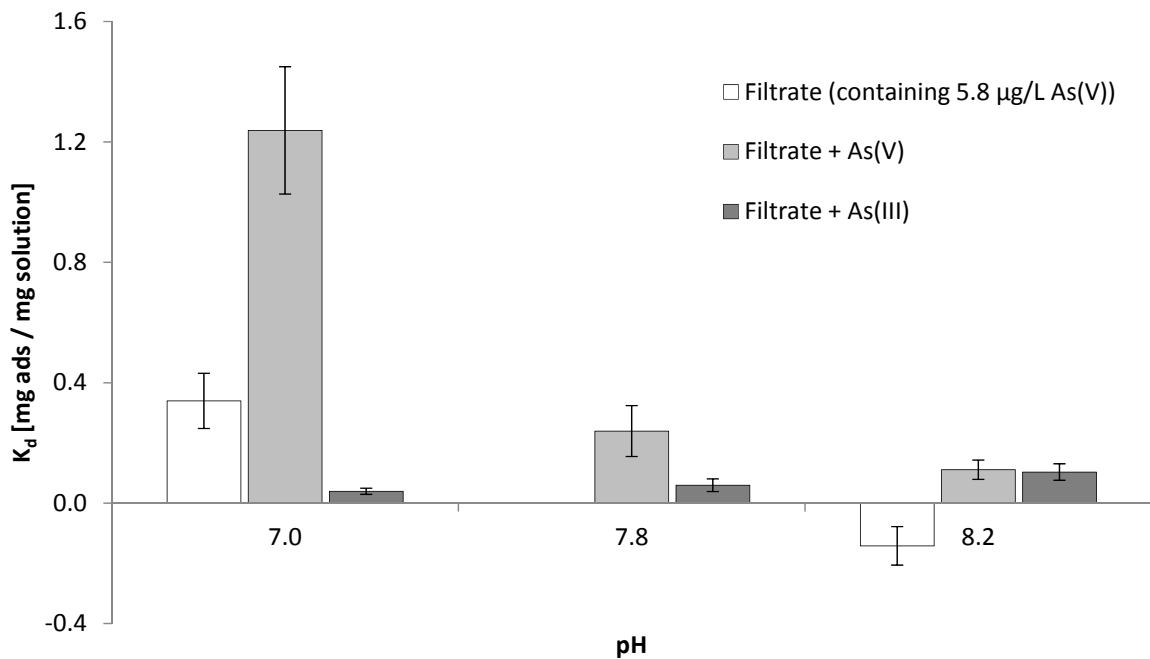


**Figure 2.4.** Addition of  $23 \mu\text{g/L}$  As(V) to supernatant water of WTP2 (left) and WTP3 (right) with naturally occurring As(III). Graphs show As species over time, with at  $t=0$  for WTP2  $0.7 \text{ mg/L}$  Fe(II) and  $0.7 \text{ mg/L}$  HFO flocs and for WTP3  $0.7 \text{ mg/L}$  Fe(II) and  $3.5 \text{ mg/L}$  HFO flocs.

At the start of this experiment both WTPs had similar levels of As(III) and Fe(II) in the aerated supernatant water, namely about  $12 \mu\text{g/L}$  As(III) and  $0.7 \text{ mg/L}$  Fe(II) for WTP2 and WTP3. HFO flock concentrations were  $0.7 \text{ mg/L}$  and  $3.5 \text{ mg/L}$  respectively. The As(III) concentration of both WTP2 and WTP3 showed a limited drop ( $1 \mu\text{g/L}$  and  $2 \mu\text{g/L}$ ) during the 60 minutes. In the same jar, the spiked As(V) was readily immobilised ( $10 \mu\text{g/L}$  and  $16 \mu\text{g/L}$ ), making oxidation of As(III) imperative for complete As removal.

### 2.3.3 HFO flocs experiments

To scrutinize whether the accumulated HFO flocs during a filter run contribute to the adsorption of As in the top layer of a filter, (de)sorption experiments of As(III) and As(V) onto accumulated HFO flocs were performed. The pH effect on the remaining adsorption capacity was investigated, as well as As speciation. This experiment was performed with HFO flocs collected from the top layer of the filter bed at WTP2; results are depicted in Figure 2.5. Three experiments were performed: (1) with natural As(V)-containing filtrate, (2) filtrate with an additional As(V) spike of 90  $\mu\text{g/L}$ , and (3) filtrate with an As(III) spike of 900  $\mu\text{g/L}$ . The observed As adsorption is expressed as the distribution coefficient ( $K_d$ ). This coefficient equals the amount of adsorbed As divided by the equilibrium solute concentration, as commonly used by geochemists (Appelo et al., 2005).



**Figure 2.5** Amount As adsorbed onto HFO flocs from top filter bed over As solution at pH 7.0, 7.8 and 8.2, during 20 min jar test experiments.

Adding an excess amount of HFO flocs (50 mg/L Fe) to the filtrate, containing 5.8  $\mu\text{g/L}$  As(V) did not result in any As adsorption in 20 min at the unaltered filtrate pH of 7.8. Acidifying to pH 7 resulted in a reduction of mobile As(V) to 4.6  $\mu\text{g/L}$  ( $K_d=0.34$  mg/mg), indicating adsorption. When increasing the pH of the filtrate to 8.2 the As(V) concentration increased to 7.2  $\mu\text{g/L}$  and a negative  $K_d$  value was observed, indicating



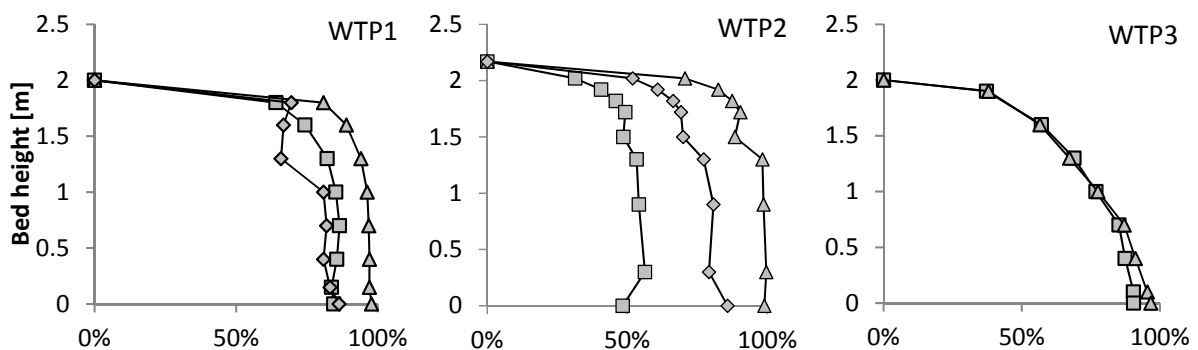
desorption. As(V) forms inner-sphere surface complexes with HFO, and the intrinsic surface constants are pH dependent (Dixit et al., 2003), lowering the pH results in increased adsorption. The lower pH also results in an increased negative surface charge of the HFO which is beneficial for anion sorption (Dzombak et al., 1990).

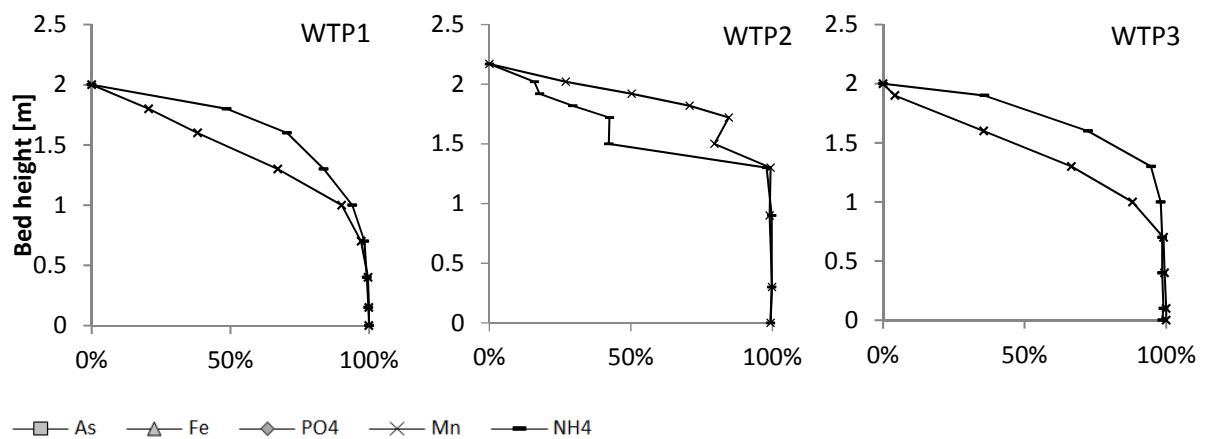
An As(V) spike of 90 µg/L to the filtrate resulted in adsorption of 17.2 µg/l As(V) and increased the  $K_d$  to 0.24 at the natural filtrate pH. When acidifying the filtrate to pH 7, more adsorption sites became available and 57 µg/L was adsorbed in 20 min ( $K_d=1.24$ ). When increasing the pH of the filtrate to pH 8.2 only 9.2 µg/L of the added 90 µg/L was adsorbed but no desorption occurred. Inverted behaviour was observed for As(III) compared to As(V), because when spiking filtrate without pH adjustment only 53 µg/L adsorbed ( $K_d=0.06$ ). At pH 7 the  $K_d$  value dropped to 0.04 and at pH 8.2, the  $K_d$  value increased to 0.1 (88 µg/L adsorption).

Based on these results it can be concluded that no residual adsorption capacity on the accumulated HFO flocs were observed for the remaining As in the filtrate. This can be attributed to the saturated nature and the reduced surface area of the aggregated HFO flocs. Only lowering the pH and/or an additional spiked concentration of As(V) resulted in extra uptake of As(V) on the HFO flocs indicating reversible pH dependent sorption.

### 2.3.4 Arsenic removal in the filter bed

As observed in the supernatant water experiments, most of the As was still mobile before entering the filter bed, predominantly consisting of As(III) (>90%). Upon entering the filter bed, the water quality changed rapidly, as depicted for Fe, As, PO<sub>4</sub>, Mn and NH<sub>4</sub> in Figure 2.6.





**Figure 2.6** Removal percentages over the bed height in the rapid filters: on the x-axis removal percentage; on the y-axis bed height in meters. Initial concentrations for WTP1, WTP2 and WTP3 were respectively: Fe 2.0, 1.4, and 4.3 mg/L; As 10, 13 and 26  $\mu\text{g/l}$ ;  $\text{PO}_4$  23, 150 and 190  $\mu\text{g P /L}$ ; Mn 0.93, 0.04 and 0.18 mg/L;  $\text{NH}_4$  0.27, 0.42 and 0.29 mg N /L.

Removal of As in the rapid filters was more efficient than removal of As on Fe flocs in the supernatant water. WTP1, WTP2 and WTP3 removed 86%, 48% and 90% As in the filter bed respectively.  $\text{PO}_4$  and As were removed simultaneously with Fe and removal stopped when Fe removal was finished. At WTP1 and WTP2 >97% Fe was removed within the first meter of the filter bed. However, the Fe profile in the WTP3 filter bed was inconsistent with the other two WTPs, which can be explained by the dual filter bed at this location. The HFO flocs (3.5 mg/L) formed in the supernatant water above the filter penetrated deeper into the filter bed because of the larger size of the anthracite in the top layer of the filter bed, subsequently, resulting in more elevated As concentrations in the filter bed compared to WTP1 and WTP2.

The mobile As in the filtrate of WTP1, WTP2 and WTP3 was in the As(V) form. This means that As(III) oxidation was completed in the filter bed within 10 min residence time.

In contrast to As,  $\text{PO}_4$  removal is not enhanced by the filter bed. The P/Fe ratio varied between the WTPs, being 0.01, 0.11 and 0.04 for WTP1, WTP2 and WTP3 respectively. Previous research has shown that even at P/Fe ratios below 0.2, part of the precipitating Fe(II) transforms into amorphous  $\text{FePO}_4$  (Voegelin et al., 2013).  $\text{FePO}_4$  precipitates are more mobile, due to the negative surface charge (Gunnars et al., 2002), but do not offer surface complexation sites for anion adsorption (Kaegi et al., 2010).  $\text{PO}_4$  does thus not only directly compete for the same adsorption sites as As (Lui et al., 2001), but may also inhibit the creation of surface complexation sites. Hence, formation of  $\text{FePO}_4$  precipitates

and surface complexation of  $\text{PO}_4$  with HFO during groundwater treatment may prevent effective As removal.

Figure 2.2 shows no  $\text{NH}_4$  and Mn (10% Mn removal at WTP3 due to NaOH dosage) removal in the supernatant water. In the filter bed however, removal starts instantly. The profile over the filter bed is similar for both constituents, and clearly different from the Fe, As and  $\text{PO}_4$  profiles: the initial removal rate is lower and complete removal occurs deeper in the filter bed, but on contrary to As and  $\text{PO}_4$ , both constituents are completely removed.  $\text{NH}_4$  removal in the top of the filter bed indicates biological activity throughout the complete filter bed, since the oxidation of  $\text{NH}_4$  to  $\text{NO}_3$  with oxygen is biotic in groundwater treatment. Mn(II) oxidation and removal can either be biotic (Katsoyiannis et al., 2004) and abiotic in the presence of Mn oxides (Stumm et al., 1996). The Mn oxidation in the top layer of the filter bed shows the formation of Mn oxides in the top of the filter bed, which is confirmed by the destruction analyses (Table 2.2) and the absence of Mn in the backwash water (Table 2.3). These Mn oxides are able to oxidise As(III) (Driehaus et al., 1995; Manning et al., 2002; Lafferty et al., 2010), and potentially explain the rapid As oxidation and subsequent adsorption in the top layer of the filter bed.

### **2.3.5 Characterization of filter sand grains and backwash water analysis**

The three WTPs consisted of aged filter material (>8 years). The grains were coated with natural precipitates over the years. Table 2.2 contains the elements found by dissolving the grain coating of the filter grains from the three WTPs.

**Table 2.2 Constituents of the filter material coating measured after destruction (% is relative abundance)**

Element	Unit			WTP 3	WTP 3
		WTP 1	WTP 2	Anthracite	Sand
Arsenic (As)	mg/kg ds	83 (<1%)	230 (<1%)	1,400 (1%)	97 (<1%)
Calcium (Ca)	g/kg ds	32 (15%)	4.5 (9%)	11 (5%)	1.7 (6%)
Iron (Fe)	g/kg ds	96 (46%)	30 (57%)	190 (80%)	15 (57%)
Magnesium (Mg)	g/kg ds	0.57 (<1%)	0.42 (1%)	0.30 (<1%)	0.30 (1%)
Manganese (Mn)	g/kg ds	64 (31%)	9.5 (18%)	18 (8%)	7.4 (28%)
Phosphorus (PO <sub>4</sub> )	g PO <sub>4</sub> /kg ds	7.2 (3%)	4.7 (9%)	n.m.	n.m.
Silicium (Si)	g/kg ds	8 (4%)	3.5 (7%)	16 (7%)	1.7 (6%)

As, Ca, Fe, Mg, Mn, PO<sub>4</sub> and Si were all present in the filter grain coating. Fe and Mn contributed most to the mass of the grain coating at the three WTPs. Considering the Fe concentrations were 2, 20 and 40 times higher than the Mn concentration in the raw water of WTP1, WTP2 and WTP3 respectively, the concentration of Mn found on the grains of WTP2 and WTP3 was relatively high. Table 2.3 quantifies the same elements, mobile and filterable by 0.45 µm, in the backwash water. Fe concentrations were considerably higher in the backwash water than in the raw water, indicating retention in the rapid filter as backwashable HFO flocs. Concentrations of As and PO<sub>4</sub> were also increased multiple times because of precipitation and/or adsorption with Fe. Mn, on the other hand, was barely found in the backwash water, but abundantly in the grain coating and must therefore preferably be accumulated on the filter grains. Figure 2.7 depicts two digital microscope images (Keyence VHX5000) of filter grains of WTP1, WTP2 and WTP3, clearly showing black Mn oxide and brown Fe oxide surfaces on the grain coating.

Table 2.3. Backwash water unfiltered (unf) and filtered (0.45  $\mu\text{m}$ )

Element	Unit	WTP1		WTP2		WTP3	
		unf	0.45 $\mu\text{m}$	unf	0.45 $\mu\text{m}$	unf	0.45 $\mu\text{m}$
<b>Arsenic (As)</b>	$\mu\text{g/l}$	255	1.96	159	4.32	517	6.69
<b>Calcium (Ca)</b>	$\text{mg / l}$	57	53	67	62	48	37
<b>Iron (Fe)</b>	$\text{mg/l}$	90	0.07	44	0.11	138	0.68
<b>Manganese (Mn)</b>	$\text{mg / l}$	1.1	0.19	0.2	0.01	0.6	0.06
<b>Phosphorus (PO<sub>4</sub>)</b>	$\text{mg P / l}$	1.27	0.003	5.9	0.02	n.m.	n.m.



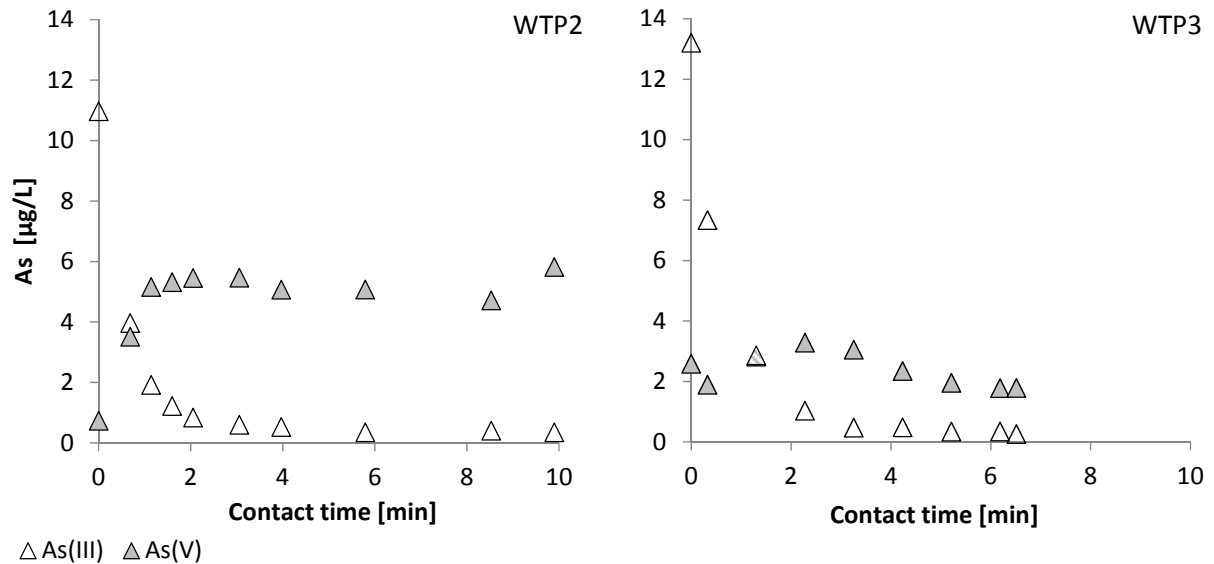
Figure 2.7. Digital microscope image of sand grain coating extracted from WTP1 (left), WTP2 (middle) and WTP3 (Right)

In order to investigate the mobility of the As found in the filter sand coating, filtrate of WTP1 (1.5  $\mu\text{g/l}$  As) with adjusted pH, 7.3, 8.5 and 9.2, was brought into contact with an excess amount of coated filter sand grains from the top of the filter of WTP1 for 24 hours. As mobilization occurred with an increase in pH (after 24 hours As concentrations were increased by 0.66  $\mu\text{g/l}$  0.92  $\mu\text{g/l}$  and 1.17  $\mu\text{g/l}$ , for pH 7.3, 8.5 and 9.2, respectively), showing the same desorption mechanism as the HFO flocs and being in line with the study of Jessen et al. (2005).

### 2.3.6 As(III) oxidation in the filter bed

In the supernatant water, the As(III) concentration remained constant after the initial concentration drop during first minutes (or seconds) of contact with oxygen (Figure 2.4). Additionally it was shown that the HFO flocs and filter grains from the filter bed had little or no affinity for adsorbing extra As. Assuming that As removal in the filter bed could only occur after As(III) oxidation to As(V), the oxidation kinetics of As(III) in the filter bed can

be determined by measuring the As(III) decrease over the filter bed. Figure 2.8 depicts the oxidation of As(III) and the formation of As(V) in the filter bed at WTP2 and WTP3, related to residence time in the filter bed.



**Figure 2.8** As(III) oxidation and As(V) production at WTP2 (left) and WTP3 (right) over residence time in the filter bed.

The As(III) concentrations of WTP2 and WTP3 were  $11.0 \mu\text{g/l}$  and  $13.2 \mu\text{g/l}$ , respectively, when entering the filter bed. Upon contact with the filter grains, rapid As(III) oxidation occurred and As(V) was formed and partly removed. Assuming that the sand grain coating (containing bacteria, Fe and Mn oxides) played a key role in the oxidation process, three principal As(III) oxidation mechanisms can be identified in the filter bed: (1) Fe(II) catalytic oxidation on Fe oxides (Amstaetter et al., 2010; Wang et al., 2015), (2) biotic oxidation of As(III) (Lytle et al., 2007) and (3) direct oxidation by Mn oxides (Driehaus et al., 1995; Lafferty et al., 2010; Manning et al., 2002). Complete As(III) oxidation on the Fe mineral surface has not been demonstrated (Amstaetter et al., 2010; Wang et al., 2015), so it is recommended to further investigate the (combined) mechanisms of biotic oxidation and direct oxidation by Mn oxides in rapid groundwater filters.

## 2.4 Conclusions

The aim of this study was to investigate the As removal capacity at three groundwater treatment plants ( $10\text{-}26 \mu\text{g As/L}$ ) in order to identify operational parameters that can contribute to lowering the filtrate As concentration to  $<1 \mu\text{g/L}$ . Results showed that

As(III) was not efficiently removed in the supernatant water after aeration. Also, after extending residence times during supernatant water experiments, all Fe(II) was precipitated into filterable HFO flocs but most As(III) remained mobile. However, when adding As(V) during these experiments, As(V) was readily adsorbed.

In the rapid filter, an instant acceleration of As(III) removal was observed compared to the aerated supernatant water, also after 60 minutes residence time. This was in contrast to PO<sub>4</sub> where such increase in removal efficiency was not observed. Mn was barely found in the backwash water, but abundantly on the filter grains, and must therefore mostly be accumulated on the filter grains as Mn oxides. These Mn oxides are able to oxidise As(III), and potentially explain the accelerated As(III) oxidation and subsequent adsorption to the formed HFO in the top layer of the filter bed. These HFO flocs did not have any residual capacity for As(V), however, adjusting the pH of the filtrate resulted in release (higher pH) and uptake (lower pH) of As. A similar mechanism was observed for coated filter grains, where an increased pH mobilised As.

The overall conclusion is that not aeration and supernatant storage, but the filter bed is the crucial treatment step for rapid As(III) removal, indicating the importance to control the oxidation sequence of Fe and As for achieving improved As removal efficiencies.

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### 3. As(III) oxidation by MnO<sub>2</sub> during groundwater treatment

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#### Abstract

The top layer of natural rapid sand filtration was found to effectively oxidise arsenite (As(III)) in groundwater treatment. However, the oxidation pathway has not yet been identified. The aim of this study was to investigate whether naturally formed manganese oxide (MnO<sub>2</sub>), present on filter grains, could abiotically be responsible for As(III) oxidation in the top of a rapid sand filter. For this purpose As(III) oxidation with two MnO<sub>2</sub> containing powders was investigated in aerobic water containing manganese(II) (Mn(II)), iron(II) (Fe(II)) and/or iron(III) (Fe(III)). The first MnO<sub>2</sub> powder was a very pure - commercially available - natural MnO<sub>2</sub> powder. The second originated from a filter sand coating, produced over 22 years in a rapid filter during aeration and filtration. Jar test experiments showed that both powders oxidised As(III). However, when applying the MnO<sub>2</sub> in aerated, raw groundwater, As(III) removal was not enhanced compared to aeration alone. It was found that the presence of Fe(II) and Mn(II) inhibited As(III) oxidation, as Fe(II) and Mn(II) adsorption and oxidation were preferred over As(III) on the MnO<sub>2</sub> surface (at pH 7). Therefore it is concluded that just because MnO<sub>2</sub> is present in a filter bed, it does not necessarily mean that MnO<sub>2</sub> will be available to oxidise As(III). However, unlike Fe(II), the addition of Fe(III) did not hinder As(III) oxidation on the MnO<sub>2</sub> surface; resulting in subsequent effective As(V) removal by the flocculating hydrous ferric oxides.

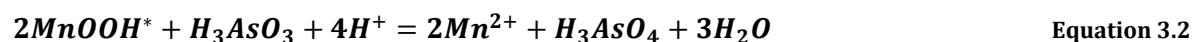
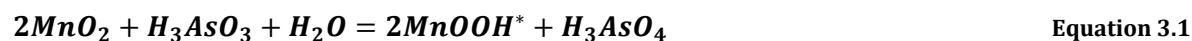
#### 3.1 Introduction

Conventional groundwater treatment plants consisting of aeration and rapid sand filtration, are merely designed and optimised for iron (Fe), manganese (Mn) and ammonium (NH<sub>4</sub><sup>+</sup>) removal (Moel et al., 2006). However, due to ever decreasing detection limits and more insight into the toxicity of other inorganic parameters such as arsenic

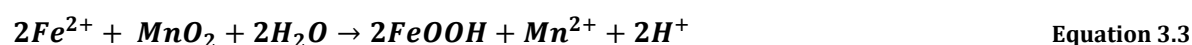
(As), chromium and nickel (van Halem et al., 2009; WHO, 2011), drinking water companies in the Netherlands are considering to bring the current national As standard of 10  $\mu\text{g/L}$  down to a new guideline of 1  $\mu\text{g/L}$ . The benefits of aeration and rapid filtration, apart from being economically attractive, are that (i) no chemicals are required, (ii) dense, possibly valuable, iron (Fe) rich waste streams are generated and (iii) biologically stable drinking water is produced. The latter is crucial for the Netherlands, as (post) chlorination is not applied and biologically stable drinking water (low in nutrients) is required to assure the microbial safety in the distribution network (Smeets et al., 2009).

The filter bed plays a crucial role in efficient As removal (Gude et al., 2016) due to the rapid oxidation of As(III) to As(V). In the filter bed, Fe(II) is removed by homogeneous, heterogeneous and biological oxidation (van Beek et al., 2015; de Vet et al., 2011). The accumulated Fe in the filter bed is easily removed from the filter during the periodic backwash procedure, and only a small part is retained in a filter coating as hydrous ferric oxides (HFO). Mn, on the other hand, is not oxidised in absence of bacteria and surface catalysts (Diem and Stumm, 1984) and has therefore mainly been found to be retained in the filter coating (Gude et al., 2016), predominantly as poorly crystalline  $\text{MnO}_2$  identified as Birnessite (Bruins et al., 2014).  $\text{NH}_4^+$  is removed in the rapid sand filter bed by biotic oxidation in a two-step oxidation process from  $\text{NO}_2^-$  to  $\text{NO}_3^-$  (Katsoyiannis et al., 2008; Lee et al., 2014). The fate of As(III) in the rapid sand filter bed is still unrevealed. Oscarson et al. (1981) found that As(III) oxidises on a  $\text{MnO}_2$  surface, but HFO was inactive with regard to As(III) oxidation. Therefore, Gude et al. (2016) suggested that the cause of accelerated As oxidation in the filter bed was either biotic or by, the highly reactive, biogenic  $\text{MnO}_2$  (Spiro et al., 2010) present on the filter grains.

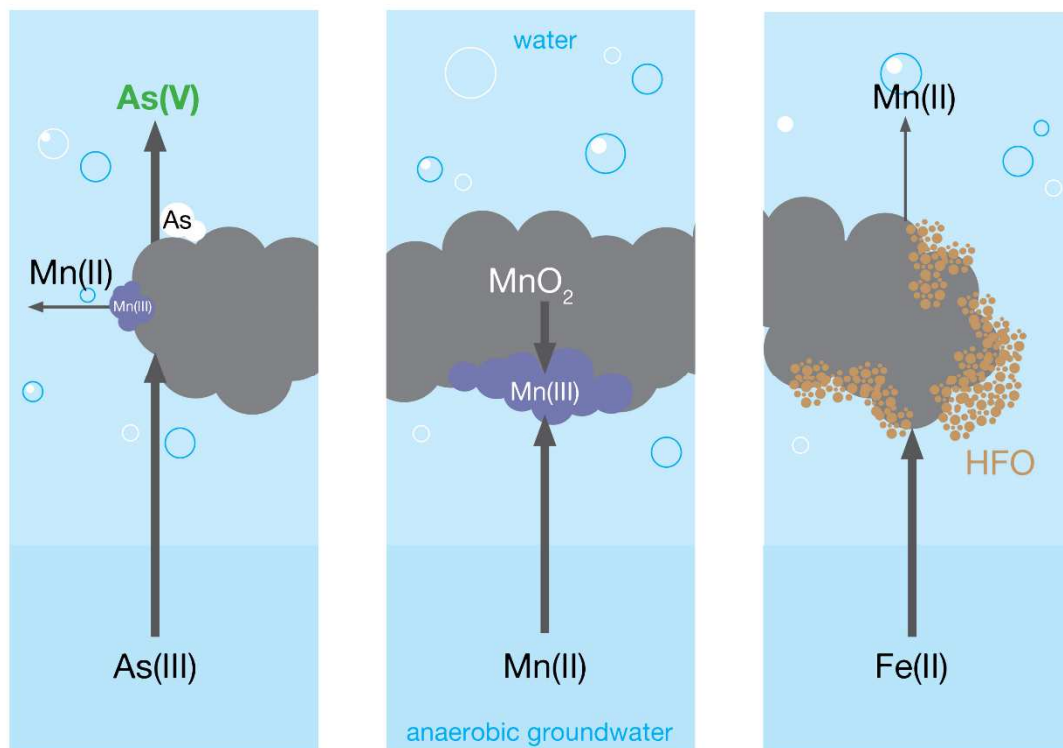
In this reaction,  $\text{MnO}_2$  is the electron acceptor for As(III) oxidation, resulting in the reduction of  $\text{MnO}_2$  to Mn(II). The reduction of  $\text{MnO}_2$  by As(III) entails a two-step reaction where both the initial  $\text{MnO}_2$  and the intermediate product,  $\text{MnOOH}$ , can oxidise As(III) (Manning et al., 2002; Nesbitt et al., 1998):



During this oxidation process, depending on pH, As can either adsorb onto MnO<sub>2</sub> surface (Manning et al., 2002) or remain in solution. Apart from As(III), Fe(II) can also react on the MnO<sub>2</sub> mineral surface, resulting in formation of HFO and mobilization of Mn(II) (Postma, 1985; Postma and Appelo, 2000).



Wu et al. (2015) studied the redox and sorption interactions between MnO<sub>2</sub>, As(III) and Fe(II) in anaerobic water. Similar to the reactions described by Nesbitt et al. (1998), the As(III) oxidation showed a two-phase trend with a fast initial oxidation followed by a decreased oxidation rate. Furthermore, observations concerning Fe(II) addition were analogue to Equation 3.3. The Fe(II) was oxidised at the MnO<sub>2</sub> surface, mobilising Mn(II), and thereby inhibiting As(III) oxidation, but overall increasing As removal by adsorbing As on the formed HFO. Also Mn(II) was found to be able to inhibit As(III) oxidation and pacify a MnO<sub>2</sub> surface. Using X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) among other techniques, Lafferty et al. (2010) showed increased Mn(III) content in a MnO<sub>2</sub> mineral as a results of Mn(II) sorption. The interactions of As(III), Fe(II) and Mn(II) individually on MnO<sub>2</sub> are schematically depicted in Figure 3.1.



**Figure 3.1** Schematics of As(III), Fe(II) and Mn(II) interaction with  $\text{MnO}_2$  derived from literature (Lafferty et al., 2010; Manning et al., 2002; Postma, 1985).

As(III) and As(V) adsorption onto HFO has been thoroughly investigated. Adsorption of As(III), the reduced uncharged As state, is stable at the neutral pH range of 7 to 8 (Dixit and Hering, 2003). As(V), being the oxidised and negatively charged state form, shows a decrease in sorption onto HFO with increasing pH (Dixit and Hering, 2003; Manning et al., 1998). At low As to Fe molar ratios ( $\approx 0.01$ ) and limited contact times, As(V) is easier to remove by adsorption on HFO than As(III) (Bissen and Frimmel, 2003a). However in aerobic Fe(II) and As(III) systems; As(III) has been shown to catalytically oxidise by intermediate Fe(IV) species, either during homogeneous Fe(II) oxidation (Hug and Du, 2003; Johnston and Singer, 2007), but also during heterogeneous oxidation, where Fe(II) oxidises on a Fe oxide (Amstaetter et al., 2010; Wang et al., 2015). Therefore, a beneficial effect concerning As(III) removal can be expected from HFO originating from Fe(II) at near neutral pH. This beneficial effect is reported by Roberts et al. (2004) by using Fe(II) and Fe(III) for the removal of high As(III) concentrations in simulated groundwater.

Rapid As(III) oxidation has been found to occur in the top layer of natural groundwater filters (Gude et al., 2016). In addition, MnO<sub>2</sub> has been found to accumulate on the sand grain surface in these filters. Although it is known that MnO<sub>2</sub> is capable of oxidising As(III), it is unknown whether naturally grown MnO<sub>2</sub> on filter sand grains are able to oxidise As(III). Additionally, it is unclear whether MnO<sub>2</sub> in a sand filter remains capable to oxidise As(III) in competition with other reduced constituents in natural groundwater like commonly co-occurring Fe(II) and Mn(II). Basically, the effect of MnO<sub>2</sub> on As(III) in the complexity of the natural groundwater matrix remains a knowledge gap. Therefore, it was the aim of this study to investigate whether MnO<sub>2</sub> – in the absence of bacteria – could be responsible for the observed As(III) oxidation in the top layer of natural rapid sand filters. For this purpose, abiotic oxidation of low As(III) concentrations (20 µg/L) by MnO<sub>2</sub>, obtained from both a commercial supplier and from a filter sand coating, was studied in oxygenated, buffered, demineralised water at pH 7. Additionally, As(III) and MnO<sub>2</sub> interactions were investigated in the presence of Mn(II) and Fe(II) both in demineralised water and natural aerated groundwater.

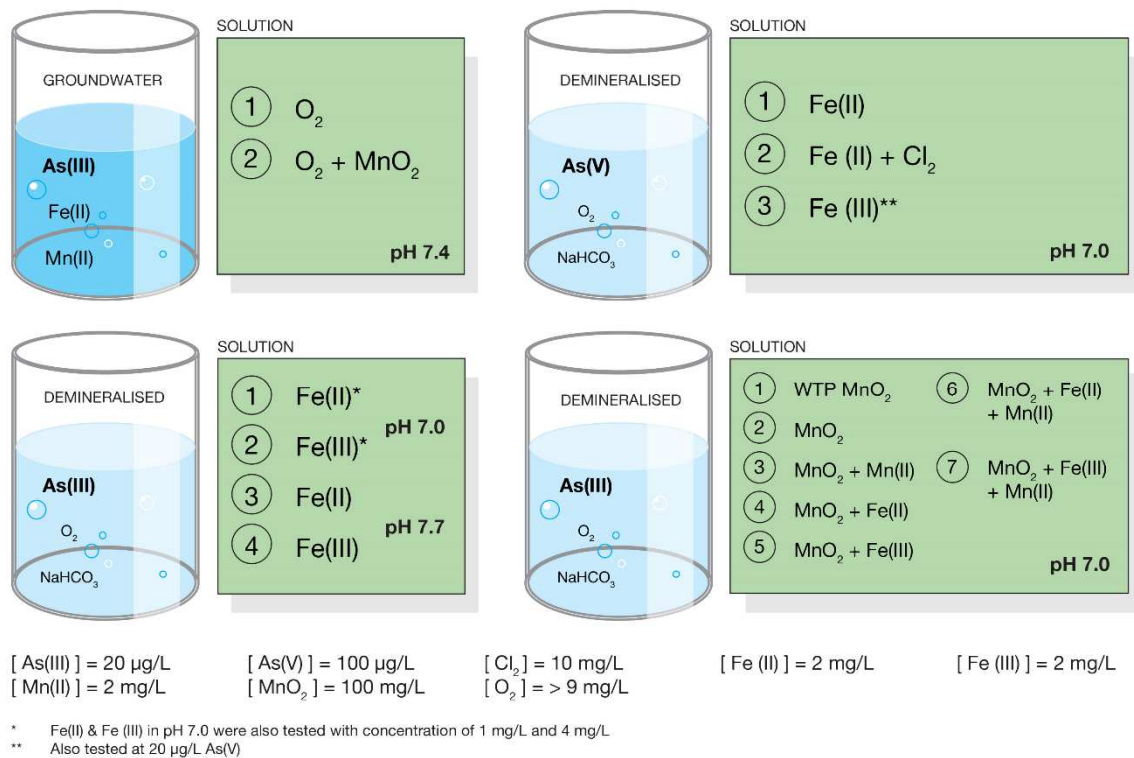
## 3.2 Materials and methods

### 3.2.1 Jar test procedure

Jar test experiments were executed to simulate As(III) oxidation and removal in the presence of MnO<sub>2</sub>, Fe(II), Fe(III) and/or Mn(II). Additionally, As(III) adsorption experiments with HFO, originating from either Fe(II) or Fe(III), were executed to differentiate between the effect of HFO alone and the added effect of MnO<sub>2</sub>. The origin of the HFO and its influence on As(V) adsorption was further scrutinised by a comparison between HFO originating from Fe(II) + O<sub>2</sub>, Fe(II) + Cl<sub>2</sub> and Fe(III).

The general procedure for the jar tests with synthetic water was: 20 µg/L As(III) or 100 µg/L As(V) and 2 mM NaHCO<sub>3</sub>, acting as a pH buffer, were added to 1.8 L demineralised water. The solution was fully saturated with O<sub>2</sub> and brought to pH 7 or to 7.7 by addition of HNO<sub>3</sub>. Figure 3.2 depicts the experimental settings schematically.





**Figure 3.2 Schematic overview of experimental settings. Experiments were performed in duplicate.**

To start the experiment using As and demineralised water, 0.1 g/L MnO<sub>2</sub> powder, 2 mg/L Fe(II,III) and/or 2 mg/L Mn(II) were added to the jar. Independent of the used chemicals, the dosing sequence remained the same. The chemicals sequence was: NaHCO<sub>3</sub>, As(III)/As(V), Cl<sub>2</sub> (only used in combination with As(V)), Mn(II), Fe(II,III) and MnO<sub>2</sub> as the final additive. For the natural groundwater tests 0.28 g/L MnO<sub>2</sub> powder was used because more Fe(II) and competing ions were present. Before addition to the natural groundwater and the demineralised water, the MnO<sub>2</sub> powder was brought into suspension using 20 mL demi water; 1.8 mL NaOH 10 mM was added to the MnO<sub>2</sub> suspension when used with Fe(II) and Fe(III) to compensate for the pH drop. For all experiments, fresh, dry MnO<sub>2</sub> was used and reaction time was kept under 2 h to exclude the effect of homogeneous As(III) oxidation and the role of manganese oxidising bacteria. The sample intervals for the natural groundwater experiments were 10, 20 and 60 min. The experiment was done in duplicate and the samples were taken from the same jar over time. The sample intervals for the experiments using demineralised water were 2, 5, 10, 20, 30, 60 and 120 min and were also performed in duplicate. For each measurement 120 mL sample water was taken

from the same jar, leaving approximately 1.0 L of test water at the end of each run. The reaction was stopped by directly filtering the sample over 0.45 µm and acidifying to pH 5 by adding HNO<sub>3</sub> to prevent further Fe(II) oxidation during As speciation. 50 mL was used for analysis of total As, Fe and Mn, and 70 mL was used for As speciation. The jars were stirred by a magnetic stirrer (Labinco model LD-746) at 40% power, maintaining the MnO<sub>2</sub> powder in suspension. The jars were continuously analysed for pH and temperature. At the start of the demineralised water experiments, the pH drop, caused by Fe(II) and Fe(III) addition, was compensated within 1 min to the initial pH using NaOH. During the 120 min experiment, the solution pH was kept constant by adding diluted HNO<sub>3</sub> intermittently.

### 3.2.2 Chemicals and preparation

As(III), NaAsO<sub>2</sub>, 0.05M, Company (Fluka Analytical) and As(V) HAsNa<sub>2</sub>O<sub>4</sub>·7H<sub>2</sub>O, ≥98%, (Sigma-Aldrich) were prepared into a stock solution of 1 mg/L on a daily basis. To stabilise pH during the experiment, 2 mM NaHCO<sub>3</sub> (J.T. Baker) was used, which is a common concentration in Dutch groundwater. For Fe(II), Fe(III) and Mn(II), stock solutions were prepared with Cl<sub>2</sub>Fe·4H<sub>2</sub>O (99.99%, Sigma-Aldrich), Cl<sub>3</sub>Fe·8H<sub>2</sub>O (≥98%, Sigma-Aldrich) and Cl<sub>2</sub>Mn·4H<sub>2</sub>O (99.99%, Sigma-Aldrich), respectively. The chemicals were dissolved in demineralised water to 2 g/L and acidified with HCl; the same stock solutions were used for all experiments. The Cl<sub>2</sub> used for instantaneous oxidation of Fe(II) was diluted from a stock solution of 15% Cl (Brenntag) sodium hypochlorite to 20 mg/L Cl<sub>2</sub> in the test water. At the start of an experiment, the stock solutions were dosed to the ambient air saturated (> 9 mg/L O<sub>2</sub>) demineralised water (21-23°C) with a calibrated ThermoFisher Finnpiquette F1 (0.5 – 5.0 ml).

### 3.2.3 Natural aerated groundwater

On-site experiments were executed at a water treatment plant in Loosdrecht (Vitens Water Supply). The groundwater composition at this plant was: temperature 11 °C, pH 7.39; HCO<sub>3</sub> 115 mg/L, electrical conductivity (EC) 250 µS/cm, oxidation reduction potential (ORP) -139 mV, As 26.1 µg/L, As(III) 22.4 µg/L, Fe 4.33 mg/L, Mn 0.178 mg/L,

$\text{NH}_4^+$  0.29 mg/L-N, phosphate ( $\text{PO}_4$ ) 0.19  $\mu\text{g}$  /L-P, total organic carbon 2.56 mg/L and sulphate 7.72 mg/L.

### 3.2.4 $\text{MnO}_2$ grains

Two types of  $\text{MnO}_2$  powders were used. The first was the commercially available Mangalox-K-45 (Sibelco;  $d_{10}$  2.2  $\mu\text{m}$ ,  $d_{50}$  9.4  $\mu\text{m}$ ,  $d_{90}$  36.1  $\mu\text{m}$ ), hereafter ' $\text{MnO}_2$ '. The second originated from a filter coating produced in 22 years during a filtration process in the Netherlands (WTP 1 in Gude et al. (2016)), hereafter 'WTP  $\text{MnO}_2$ '. The coating was easily, manually peeled off the extracted filter sand grains (coating thickness was approximately 2 mm) and dried at 80 °C for 24 h. The dried filter sand coating was ground into a fine powder.

For analytic purposes, the powdered  $\text{MnO}_2$  was dissolved in a solution of 0.05 M sulphuric acid and 0.04 M oxalic acid (Artamonova et al., 2013). For the solution, 278  $\mu\text{l}$  of  $w(\text{H}_2\text{SO}_4)=96\%$  and 0.36 g  $\text{H}_2\text{C}_2\text{O}_4$  in powder were added to sample containers with 100 mL demineralised water. 0.1g of the two  $\text{MnO}_2$  powders remained in the containers for at least 11 d before ICP-MS analysis. X-ray diffraction (XRD) was performed in a Bruker D8 Advance diffractometer for both powders, X-ray fluorescence (XRF) was performed in a Panalytical Axios Max WD-XRF spectrometer and particle sizes of the  $\text{MnO}_2$  powder were measured with a Malvern Mastersizer 2000. The relevant properties of both  $\text{MnO}_2$  powders are summarised in Table 3.1.

**Table 3.1 Properties of  $\text{MnO}_2$  and WTP  $\text{MnO}_2$**

Parameter	Unit	$\text{MnO}_2$	WTP $\text{MnO}_2$
<b>Mn</b>	mg/g	548	301
<b>Fe</b>	mg/g	20	126
<b>Ca</b>	mg/g	2	38
<b>XRD<sup>1</sup></b>	compound	Vernadite ( $\text{Mn}(\text{OH})_4$ ) Ramsdellite ( $\text{MnO}_2$ ) Bixbyite ( $\text{MnFeO}_3$ ) Pyrochroite ( $\text{Mn}(\text{OH})_2$ )	Birnessite $(\text{MnO}_2)(\text{H}_2\text{O})_{1.784}$ Quartz ( $\text{SiO}_2$ )

		Quartz (SiO <sub>2</sub> )	
<b>XRF</b>	compound	MnO <sub>2</sub> (82%)	MnO <sub>2</sub> (63%)
		Al <sub>2</sub> O <sub>3</sub> (6%)	Fe <sub>2</sub> O <sub>3</sub> (24%)
		SiO <sub>2</sub> (5%)	CaO (8%)
		Fe <sub>2</sub> O <sub>3</sub> (4%)	SiO <sub>2</sub> (4%)
		Rest (<3%)	Rest (<1%)

<sup>1</sup>Not all peaks were identified

### 3.2.5 Analyses

pH, EC, ORP, O<sub>2</sub> and temperature were measured with WTW electrodes (SenTix940, SenTix ORP 900, TerraCon 925 and FDO925). During the on-site groundwater experiments, water samples of 50 mL were analysed for Fe, As, Mn, P, both unfiltered and filtered over a polyethersulfone 0.45 µm filter (25 mm, VWR). For the demineralised water experiments, a cellulose acetate 0.45 µm membrane 47mm (Whatman) with a vacuum system was used. Both filtered and unfiltered samples were acidified with 0.6 mL 5M HNO<sub>3</sub> and analysed with Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

### 3.2.6 As speciation

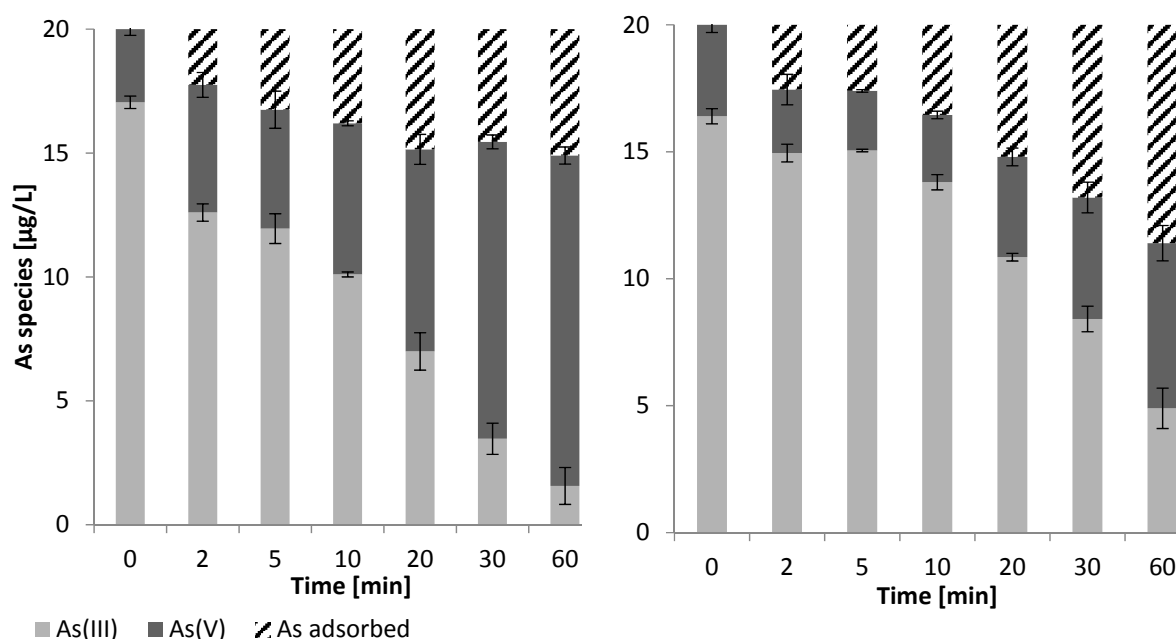
As(III) was measured by filtering 70 mL of water through a syringe of 60 mL filled with 40 mL Amberlite® IRA-400 chlorite form anion ion-exchange resin. The first 20 mL was discarded, and the last 50 mL was collected and analysed for As by ICP-MS. The measured As after contact with the resin was considered to be the uncharged As(III) (Clifford et al., 2005). As(V) was calculated by subtracting As(III) from the concentration of total As. However, the resin was found to retain 15.1%, just after preparation of test water, and 14.8 % As(III), after 120 min aeration of the test water (n=6). Indicating that (1) no measurable As(III) oxidation occurred within the 2 h experiment and (2) some unwanted As(III) removal by the resin cannot be excluded with this method. An additional check was performed by exposing 100 µg/L As(III) to aerated drinking water for 24 h. It was found that only 6% of the As(III) was oxidised, thereby excluding homogeneous

As(III) oxidation by  $O_2$  as an oxidation pathway within the timeframe of our experiments (max. 120 min).

### 3.3 Results and discussion

#### 3.3.1 As(III) oxidation by $MnO_2$ containing powder

As(III) was put into contact with  $MnO_2$  powder and WTP  $MnO_2$  powder in demineralised water at pH 7. The oxidation of As(III) and formation of As(V) over time on both  $MnO_2$  powders in oxygenated, buffered, demineralised water is depicted in Figure 3.3.



**Figure 3.3** Oxidation of As(III) in 60 min by  $MnO_2$  (left) and WTP  $MnO_2$  (right); oxygenated, buffered demineralised water with 20  $\mu\text{g/L}$  As(III) and 0.1  $\text{g/L}$   $MnO_2$  containing powder at pH 7.

Addition of both  $MnO_2$  powders resulted in As(III) oxidation, as As(III) concentrations decreased and As(V) concentrations increased over time. At the end of the 60 min experiment, the jars containing  $MnO_2$  powder contained 2  $\mu\text{g/L}$  As(III) and 13  $\mu\text{g/L}$  As(V), 5  $\mu\text{g/L}$  of the initial As(III) was adsorbed. The jars containing WTP  $MnO_2$  powder resulted in 5  $\mu\text{g/L}$  As(III), 7  $\mu\text{g/L}$  As(V) and adsorbing 9  $\mu\text{g/L}$  of the initial As(III). The  $MnO_2$  powder, containing mainly  $MnO_2$ , decreased the concentration of mobile As(III) more effectively, whereas the WTP  $MnO_2$  powder, also containing HFO (12%w Fe), resulted in a lower total As concentration. Therefore it is concluded that the As(III) was oxidised by the  $MnO_2$  present in the powder, and the HFO, mainly present in the WTP  $MnO_2$ , resulted

in adsorbing As. This is in line with Oscarson et al. (1981) who found MnO<sub>2</sub> to oxidise As(III) and Fe oxides do not. Furthermore, limited As adsorption can be expected on the MnO<sub>2</sub> (Manning et al., 2002) where on the other hand As is effectively adsorbed to HFO at pH 7 (Dixit and Hering, 2003). The production of As(V) over time by WTP MnO<sub>2</sub> shows that the MnO<sub>2</sub> present in rapid sand filters can potentially oxidise As(III), also in absence of bacteria.

### 3.3.2 MnO<sub>2</sub> addition to natural aerated groundwater

It is generally accepted that for efficient As(III) removal with HFO, an oxidation step to As(V) is imperative (Bissen and Frimmel, 2003b; Gude et al., 2016). Since MnO<sub>2</sub> rapidly oxidises As(III) (Figure 3.3), it may be expected that the HFO-MnO<sub>2</sub> system removes As(III) more efficiently than HFO alone. Therefore, the MnO<sub>2</sub> powder was brought into contact with aerated groundwater containing As(III) as well as other typical groundwater constituents such as Fe, Mn, PO<sub>4</sub> and NH<sub>4</sub><sup>+</sup> at a drinking water treatment plant. Table 3.2 shows the results after 60 min of aeration, both with and without addition of MnO<sub>2</sub> powder.

**Table 3.2 Comparison of As(III), Fe, Mn and PO<sub>4</sub> during aeration of natural groundwater, with and without addition of 0.28 g/L MnO<sub>2</sub> powder at pH 7.4, O<sub>2</sub> 9.6 mg/L and 11 °C. ORP (t=60) aeration and aeration + MnO<sub>2</sub> - 41 mV and 216 mV respectively. Results shown are averaged from duplicates.**

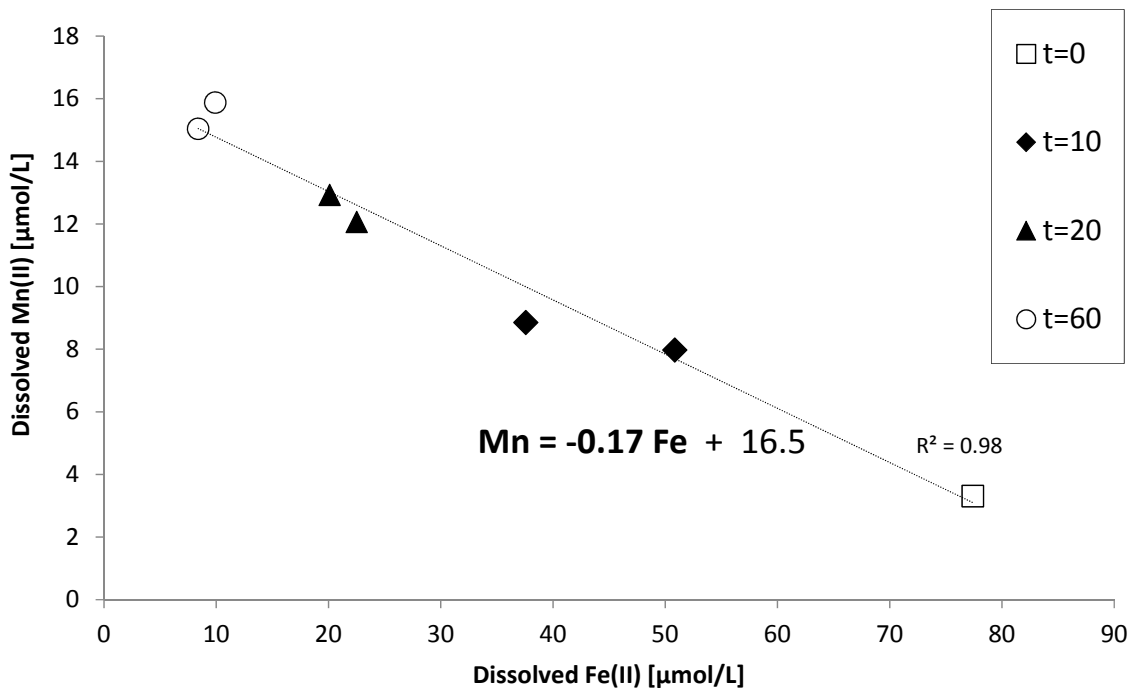
	Time	As <sup>1</sup>		Fe		Mn		PO <sub>4</sub>	
		µg/L	Rem.	mg/L	Rem.	mg/L	Rem.	mg/L	Rem.
<b>Groundwater</b>	t=0	26.1		4.3		0.18		0.18	
<b>Aeration</b>	t=60	17.3	34%	1.2	72%	0.19	-3%	0.03	84%
<b>Aeration + MnO<sub>2</sub></b>	t=60	17.3	34%	0.5	88%	0.85	-68%	0.07	60%

<sup>1</sup>As≈As(III), all mobile As was analysed to be As(III) within 60 min.

Aeration alone and aeration aided by an addition of 0.28 g/L MnO<sub>2</sub> powder resulted both in 34% As removal from the natural groundwater and, additionally, it was measured that, after the 60 min experiment, the remaining mobile As of both experiments was in the reduced As(III) form. Hence it was concluded that adding 0.28 g/L MnO<sub>2</sub> powder in

aerated groundwater, did not increase the As(III) removal efficiency compared to aeration alone, so less As(III) was oxidised in natural groundwater – containing Fe(II) and Mn(II) – than in demineralised water. Although the As(III) removal was not enhanced, the MnO<sub>2</sub> addition resulted in an increased Fe(II) removal of 0.7 mg/L Fe as compared to aeration alone.

Soluble Fe concentrations decreased over time, as expected, since the HFO formed by Fe(II) oxidation are retained by 0.45 µm filters. On the other hand, mobile Mn concentrations increased during the experiment after filtration over 0.45 µm. The increased Mn concentrations were most likely the result of Fe oxidation on the MnO<sub>2</sub> surface, thereby reducing the MnO<sub>2</sub> (and MnOOH) to soluble Mn(II) (equation 3). The Mn concentration quadrupled during the 60 min experiment and increased over all measured time intervals while Fe(II) decreased. Figure 3.4 depicts the Fe and Mn concentrations at intervals 0, 10, 20 and 60 min contact time.



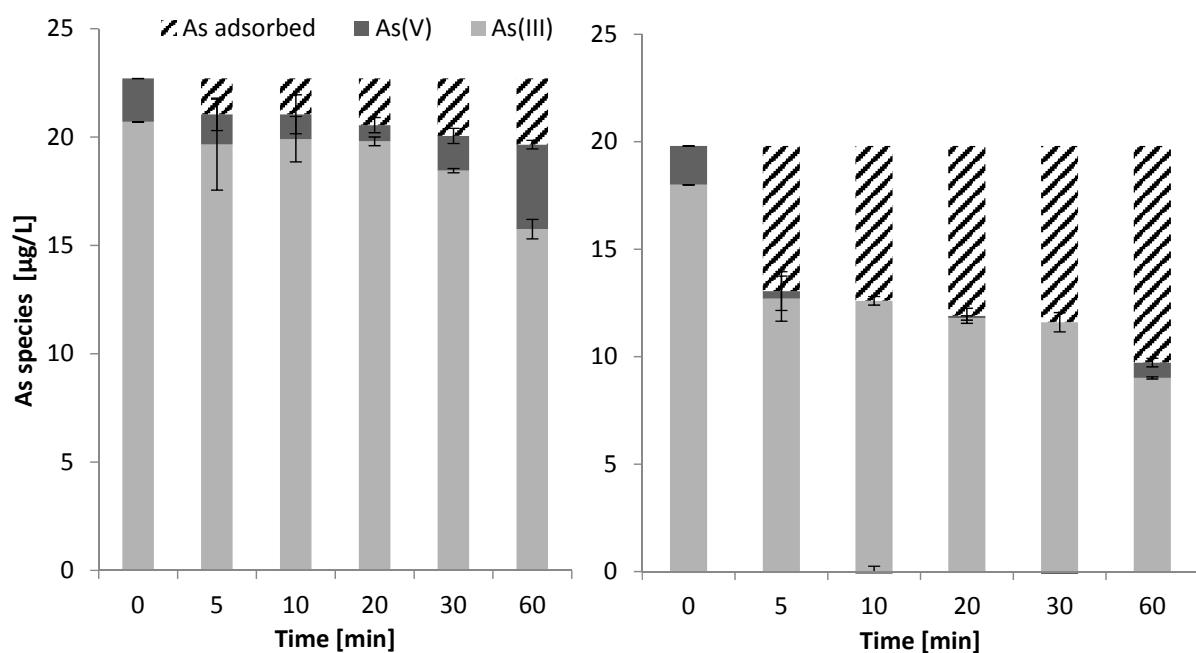
**Figure 3.4** Concentrations of Fe(II) and Mn(II) in µmol/L in the same time interval as a result of adding 0.28 g/L MnO<sub>2</sub> powder to aerating groundwater at pH 7.4.

From the mobilisation of Mn(II) and the decreased concentration of Fe(II), it is concluded that the Fe oxidation is enhanced by the added MnO<sub>2</sub> powder. The total oxidised Fe(II) concentration was 68 µM, and this mobilised 12.5 µM Mn, which corresponds to a molar ratio of 0.17 Mn/Fe. According to Equation 3, Fe(II) reacts to mobilise Mn(II) at a ratio of

0.5 Mn/Fe. The difference between the theoretical and actual Mn/Fe ratio indicates that Fe(II) had also oxidation pathways other than MnO<sub>2</sub>, e.g. through homogenous oxidation with O<sub>2</sub> in the aerated water (Stumm and Lee, 1961). An additional explanation is that soluble Mn and/or Fe concentrations were affected by co-occurring adsorption processes during the experiment, i.e. Fe and/or Mn adsorption and oxidation onto HFO or MnO<sub>2</sub> (Lafferty et al., 2010; Postma, 1985). Either way, a considerable proportion of Fe(II) was oxidised by MnO<sub>2</sub> and may have been responsible for inhibiting As(III) oxidation. Apparently the HFO precipitated in the presence of MnO<sub>2</sub> removed less PO<sub>4</sub> than the HFO in absence of MnO<sub>2</sub>, even though more HFO was formed (Table 3.2). It is therefore suggested that the HFO formation on MnO<sub>2</sub> reduced formation of Fe-PO<sub>4</sub> precipitates as described by Voegelin et al. (2010).

### 3.3.3 Inhibition by Mn(II) and Fe(II)

In order to differentiate between the effect of Mn(II) and Fe(II) on As(III) oxidation by MnO<sub>2</sub>, jar tests were executed, adding these constituents to demineralised water. Figure 3.5 depicts As speciation during the 60 min experiments in the presence of either 2 mg/L Mn(II) (left) or 2 mg/L Fe(II) (right).





**Figure 3.5 Effect of 2 mg/L Mn(II) (left) and 2 mg/L Fe(II) (right) on As(III) oxidation by 0.1 g/L MnO<sub>2</sub> powder at pH 7.**

After Mn(II) addition to the As(III)-MnO<sub>2</sub> system, mobile As(V) remained <2 µg/L throughout the first 30 min and increased to 4 µg/L (17%) in the second half of the experiment, leaving 16 µg/L As(III) mobile. This in contrast with the As(III)-MnO<sub>2</sub> system without Mn(II) dosing (Figure 3.3), where only 2 µg/l As(III) remained mobile after 60 min and the mobile As(V) concentration increased to 13 µg/l. Therefore, the resulting conclusion is that the added Mn(II) inhibited the As(III) oxidation by MnO<sub>2</sub>. In addition, less As was adsorbed to the MnO<sub>2</sub> in the presence of Mn(II): MnO<sub>2</sub> adsorbed 5 µg/L As without addition of Mn(II) (either directly, or after oxidation), and by addition of Mn(II) only to 3 µg/L As was adsorbed to the MnO<sub>2</sub> powder.

In the experiment where Fe(II) was dosed to the demineralised water containing As(III) and MnO<sub>2</sub> (Figure 3.5 right), the mobile As(III) concentration decreased to 9 µg/L while the concentration of mobile As(V) remained negligible and <1 µg/L. The added Fe(II) reacted to form HFO, which subsequently has a strong affinity for As adsorption (Dixit and Hering, 2003). This can be observed by the higher total As removal when adding Fe(II) to MnO<sub>2</sub> (50% As removal) compared to the Mn(II) addition to MnO<sub>2</sub> (13% As removal). In the HFO-MnO<sub>2</sub> system, As may be directly adsorbed as As(III) or indirectly after oxidation to As(V). Still, the As(III) concentration decreased less than in the As(III)-MnO<sub>2</sub> system alone (Figure 3.3). Indicating that both Mn(II) and Fe(II) inhibited As(III) oxidation. In order to assess whether Mn(II) and Fe(II) reacted with the MnO<sub>2</sub> surface, the mobilisation of Mn(II) during the experiments is depicted in Figure 3.6. As a reference, Fe(III) addition to the As(III)-MnO<sub>2</sub> is included as well.

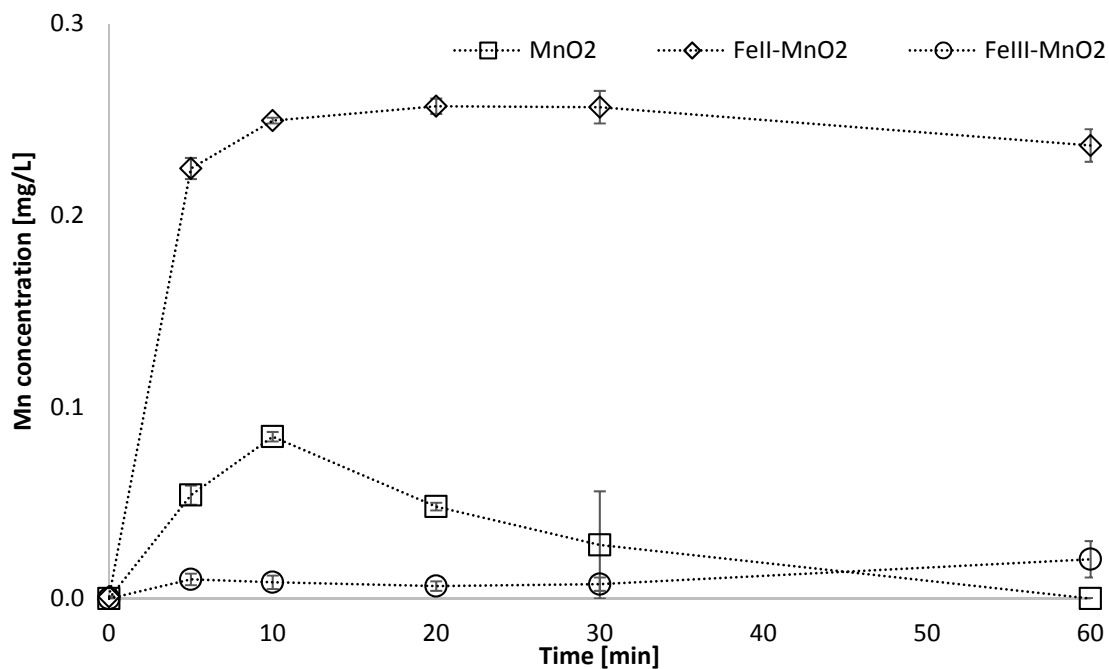


Figure 3.6 Mobilisation of Mn(II) from 100 mg/L MnO<sub>2</sub> powder; without Fe dosage (As(III)-MnO<sub>2</sub>), with 2 mg/L Fe(II) dosage (As(III)-FeII-MnO<sub>2</sub>) and with 2 mg/L Fe(III) dosage (As(III)-FeIII-MnO<sub>2</sub>).

MnO<sub>2</sub> powder added to a 20 µg/L As(III) solution increased mobile Mn(II) concentrations to approximately 0.09 mg/L. However, based on Equations 1 and 2, As(III) oxidation by MnO<sub>2</sub> should only release 0.03 mg/L. It is therefore suggested that during the experiment, also some Mn(II) leached from the mineral surface. However, when adding Fe(II) to the jar, mobile Mn(II) concentrations increased up to 0.26 mg/L, which subsequently cannot be explained by leaching alone. From Equation 3 it can be concluded that at least 0.3 mg/L Fe(II) must have been oxidised by MnO<sub>2</sub> to account for the Mn(II) release, whereas the remaining Fe(II) may have been oxidised at the mineral surface, but did not result in mobile Mn(II) or was homogeneously oxidised by dissolved O<sub>2</sub> in the water (Stumm and Lee, 1961). Altogether, the results show that Fe(II) was active on the MnO<sub>2</sub> surface and therefore inhibited As(III) oxidation. The reference graph with Fe(III) addition to MnO<sub>2</sub> powder does not show such reactivity, as Mn(II) was hardly mobilised. This indicates that either Fe(III) prevented the MnO<sub>2</sub> surface from mobilising Mn(II) or that the mobilised Mn(II) was adsorbed to HFO originating from Fe(III).

### 3.3.4 As adsorption onto HFO

The previous experiments illustrate that Fe and Mn played a vital role in both the oxidation and removal of As(III) from natural groundwater in the presence of MnO<sub>2</sub>. In order to differentiate between the added effect of MnO<sub>2</sub> on As(III) adsorption on HFO, experiments were executed in the presence of Fe but in absence of MnO<sub>2</sub>. Table 3.3 depicts the removal of either As(III) or As(V) in contact with 2 mg/L Fe(III). The comparison of As(III) and As(V) at low concentrations (+/- 20 µg/L) and the resulting adsorption to HFO originating from Fe(III) show that the 23 µg/L As(V) is already lowered to <1 µg/L at the first measuring interval (2 min). Under identical settings, 23 µg/L As(III) was lowered to 16.9 µg/L (only 26% removal) in 2 min and was further lowered to 10.2 µg/L (55% removal) after 60 min contact time.

**Table 3.3 Adsorption of As(III) and As(V) onto HFO originating from addition of Fe(III) at pH 7. Experiments are averaged from duplicates.**

<b>Time</b>	<b>As(III)</b>	<b>As(V)</b>
[min]	[µg/L]	[µg/L]
0	23.0	23.5
2	16.9	0.9
5	15.4	<0.5
10	13.9	<0.5
30	11.9	-
60	10.2	-

This illustrates that for rapid As(III) removal with Fe(III), it is crucial to oxidise to As(V) first. To confirm this observation, the experiment was repeated for higher As(V) concentrations in the presence of HFO originating from different sources: (a) Fe(III), (b) Fe(II), hypochlorite (Cl<sub>2</sub>) and O<sub>2</sub> and (c) Fe(II) and O<sub>2</sub>. Table 3.4 provides an overview of the As(V) and filterable Fe (0.45µm) during these 60 min experiments.

**Table 3.4 Adsorption of As(III) and As(V) onto HFO originating from Fe(III), Fe(II)+O<sub>2</sub>+Cl<sub>2</sub> and Fe(II)+O<sub>2</sub> at pH 7. Experiments were executed in duplicate and averaged.**

Time [min]	Fe(III)		Fe(II)+O <sub>2</sub> +Cl <sub>2</sub>		Fe(II)+O <sub>2</sub>	
	As(V) [µg/L]	Fe [mg/L]	As(V) [µg/L]	Fe [mg/L]	As(V) [µg/L]	Fe [mg/L]
0	84.4	1.9	85.6	2.0	86.0	1.9
2	1.2	0.01	1.4	<0.01	58.1	1.5
5	1.0	<0.01	1.1	<0.01	31.5	1.0
10	1.0	<0.01	1.0	<0.01	18.2	0.8
30	0.8	<0.01	0.7	<0.01	6.7	0.3
60	0.6	<0.01	0.6	<0.01	4.9	0.1

Even with four times higher As(V) concentrations than the former experiment, As concentrations dropped to <1.0 µg/L within 5 min contact time when adding Fe(III). Both Fe(III) and Fe(II)+O<sub>2</sub>+Cl<sub>2</sub> removed As(V) identically; within 2 min, the bulk of the As was removed, and simultaneously the soluble Fe dropped to <10 µg/L. For HFO originating from homogeneous Fe(II) oxidation by O<sub>2</sub>, the As(V) removal was less efficient. After 60 min contact time, most Fe(II) was oxidised, however the As(V) concentration remained 4.9 µg/L. This finding, in combination with the similarity in As(V) removal between Fe(III) and Fe(II)+Cl<sub>2</sub>+O<sub>2</sub>, leads to the conclusion that the mode of oxidation-precipitation, and not the source of Fe (as Fe(II) or Fe(III)), determined As(V) removal. Figure 3.7 depicts the HFO colour at the end of the three experiments, which illustrates that instantly oxidised Fe(II) by Cl<sub>2</sub> is similar in colour to Fe(III) than to Fe(II) oxidised by O<sub>2</sub>. Different colours of HFO could hint to a different HFO structure. Jeon et al. (2003) reported a brown HFO suspension to make a colour shift to yellow by addition of Fe(II). Dixit and Hering (2003) showed different Fe minerals, such as Ferrihydrite, Goethite and Magnetite, have different site densities. Therefore, it is hypothesised that the precipitated HFO in the homogeneous Fe(II) oxidation process, adsorbed Fe(II) as described by Silvester et al. (2005) which resulted in a denser Fe framework and a lower sorption site density than HFO originating from Fe(III).

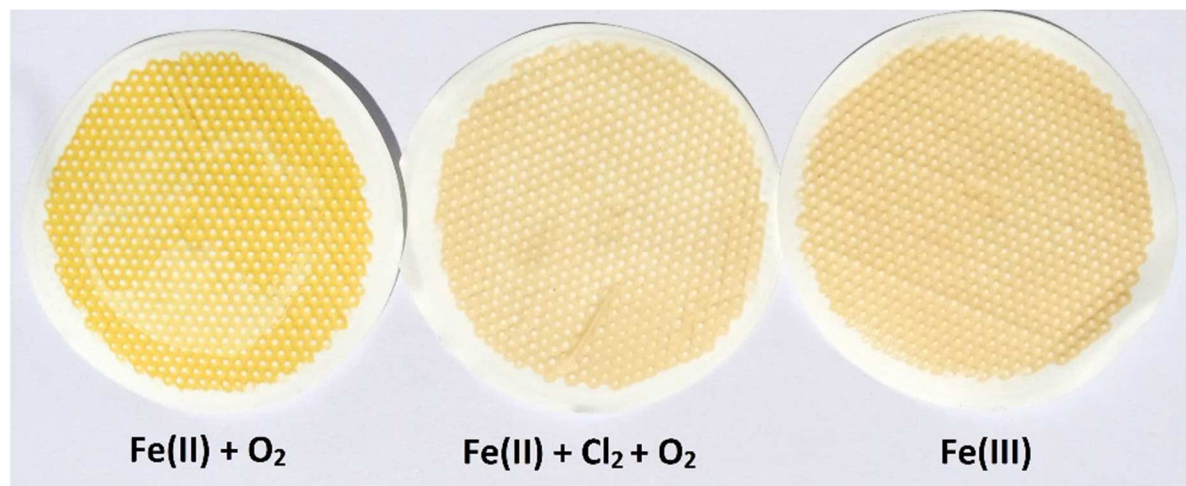


Figure 3.7 The colour of HFO originating from Fe(II)+O<sub>2</sub>, Fe(II)+Cl<sub>2</sub>+O<sub>2</sub> and Fe(III).

In the presence of O<sub>2</sub>, As(V) removal by Fe(II) lagged behind compared to As(V) removal by Fe(III), therefore a series of experiments were performed to also investigate this for As(III). Results of As(III) removal after 60 and 120 min for 1, 2 and 4 mg/L Fe(II) or Fe(III) are depicted in Figure 3.8.

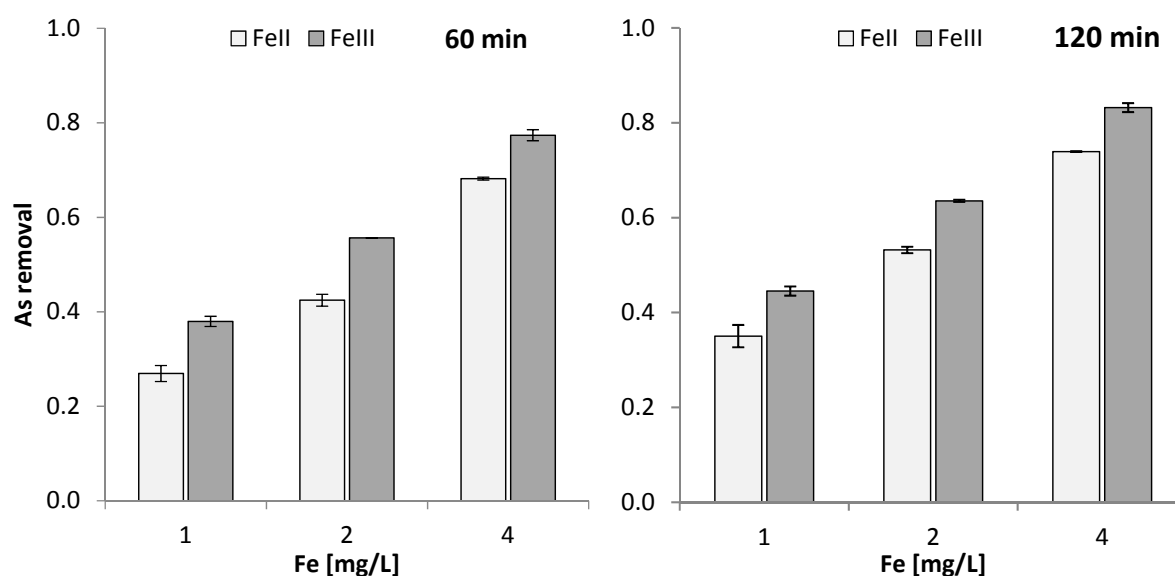
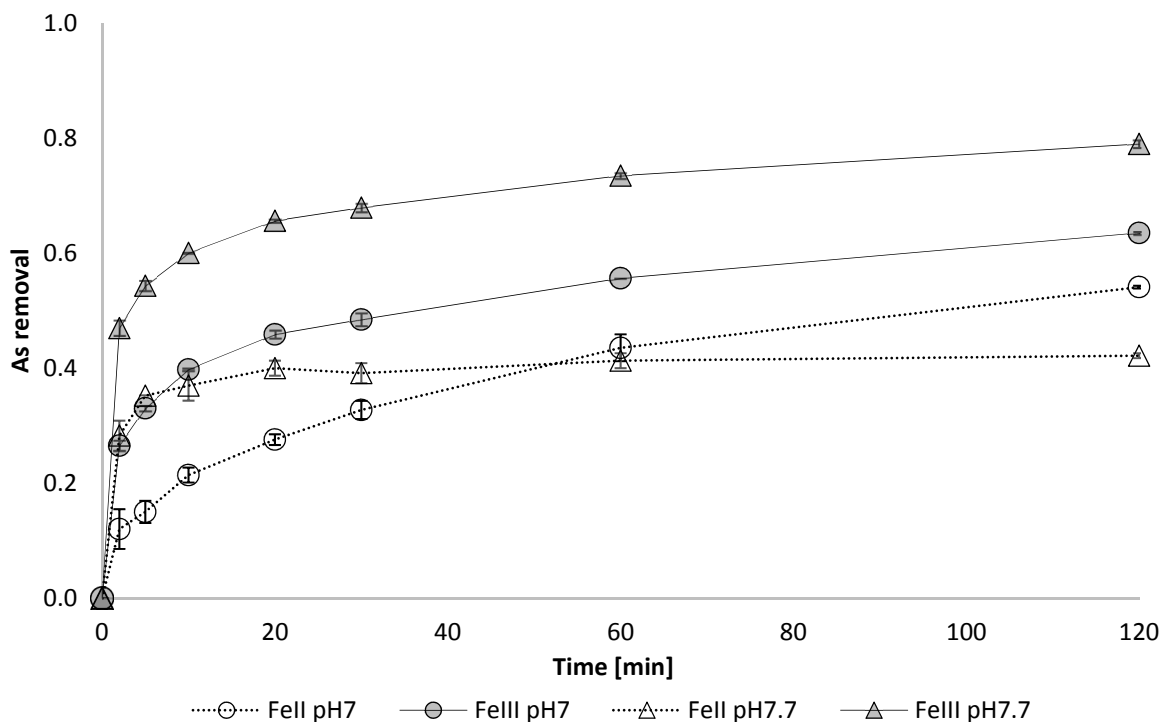


Figure 3.8 As(III) removal by Fe(II) and Fe(III) after 60 min (left) and 120 min (right) contact time. Fe concentration range 1, 2 and 4 mg/L and 20 µg/L As(III) at pH 7.

HFO, either originating from Fe(II) or Fe(III), partly adsorbed the As(III) in all cases. For both Fe(II) and Fe(III), As(III) removal was increased at a higher Fe/As ratio. This is consistent with findings of Qiao et al. (2012), since higher Fe concentrations increase the amount of adsorption sites available for As(III) adsorption. Figure 3.8 also shows that after 60 and 120 min contact time, the HFO, originating from Fe(III), consistently removed

more As(III) than Fe(II). Even after 120 min, Fe(II) removed less As(III) than Fe(III) after 60 min. The removal efficiencies were: 35%, 53%, 74% for Fe(II) at 120 min versus 38%, 56% and 77% for Fe(III) at 60 min for 1, 2 and 4 mg/L, respectively.

The higher As(III) removal by Fe(III) is inconsistent with the general finding of Roberts et al. (2004), who found that addition of Fe(II), even though Fe(III) resulted in more sorption sites, resulted in increased As(III) removal due to the co-oxidative effect of Fe(II) oxidation described by Hug and Du (2003). However, for their experiments 4 h reaction time was chosen and As, Fe and high concentrations of co-occurring ions were used. So either the co-oxidation effect did not occur, or it was of less importance than other processes, like the co-occurring ions or the mode of oxidation-precipitation of the HFO. For this reason the pH effect on possible As(III) co-oxidation by Fe(II) and adsorption onto HFO originating from Fe(II) or Fe(III) was investigated in a 2 h kinetics experiment, the results of which are depicted in Figure 3.9.



**Figure 3.9** As(III) removal by HFO originating from Fe(II) and Fe(III) over time. 2 mg/L Fe and 20 µg/L As(III) at pH 7 and 7.7.

HFO originating from Fe(III) at pH 7.7 achieved a higher As(III) removal than at pH 7, 64% versus 79%, after 120 min. The majority of the removal difference was achieved by the first sample interval at 2 min contact time. The concentration of HFO during the Fe(III)

was considered to be constant and no beneficial effects may be expected for As(III) adsorption to HFO at pH 7.7 compared to pH 7, because the adsorption efficiency difference of As(III) to HFO is very limited at these pH values and becomes even less pronounced at low As/Fe ratios (Dixit and Hering, 2003; Goldberg and Johnston, 2001). Therefore, the 30% higher As(III) removal efficiency by the HFO originating from Fe(III) at pH 7.7 is ascribed to a beneficial precipitation-flocculation process since the point of zero charge of HFO in demineralised water  $\approx 0$  at pH 7.7 (Du et al., 2014).

For Fe(II), pH plays an important role in a kinetics experiment since it largely affected the Fe oxidation rate (Morgan and Lahav, 2007). In Figure 3.9, at pH 7.7, within 2 min, 99% of the Fe(II) was oxidised into HFO compared to only 87% after 30 min at pH 7. The amount of HFO greatly affected the As(III) adsorption efficiency as seen in Figure 3.8. Therefore, the increased As(III) adsorption until 60 min at pH 7.7 can be mainly ascribed to the higher HFO concentration. However, the slower oxidation of Fe(II) at pH 7 resulted in an overall higher As(III) removal during the 120 min experiment. The general conclusion of the experiment is that Fe(III) and Fe(II) showed different effects with pH alteration on As(III) removal. For Fe(III), As(III) adsorption was mainly affected at the start of the experiment and was suggested to be ascribed to the initial flocculation speed. Fe(II) on the other hand was largely affected by oxidation speed at different pH; at pH 7 a slower Fe(II) precipitation rate and therefore a prolonged new HFO formation over time may have led to the increased overall As(III) removal. This is in line with experiments of Roberts et al. (2004) where multiple additions of Fe(II) led to an increased As(III) removal compared to the same Fe(II) concentration in a single addition. These experiments suggest that HFO formation plays a key role in As(III) adsorption for both HFO originating from Fe(III) and Fe(II).

### **3.3.5 Influence of Fe(II) versus Fe(III) on As(III)-MnO<sub>2</sub> system**

In the previous sections, we determined that both Mn(II) and Fe(II) were active on the MnO<sub>2</sub> surface, thereby inhibiting As(III) oxidation and subsequently lowering As(III) removal efficiency. Additionally it was shown that HFO originating from either Fe(II) and Fe(III) was of a different structure. Therefore, the combined effect of As(III) oxidation and removal in the presence of MnO<sub>2</sub>, Fe(III), Fe(II) and/or Mn(II) was investigated, and the

results are depicted in Figure 3.10. The setups of the experiments presented in Figure 3.10 were identical except for the oxidation state of the added Fe. The left graph depicts the results of Fe(II) and the right graph of Fe(III) addition.

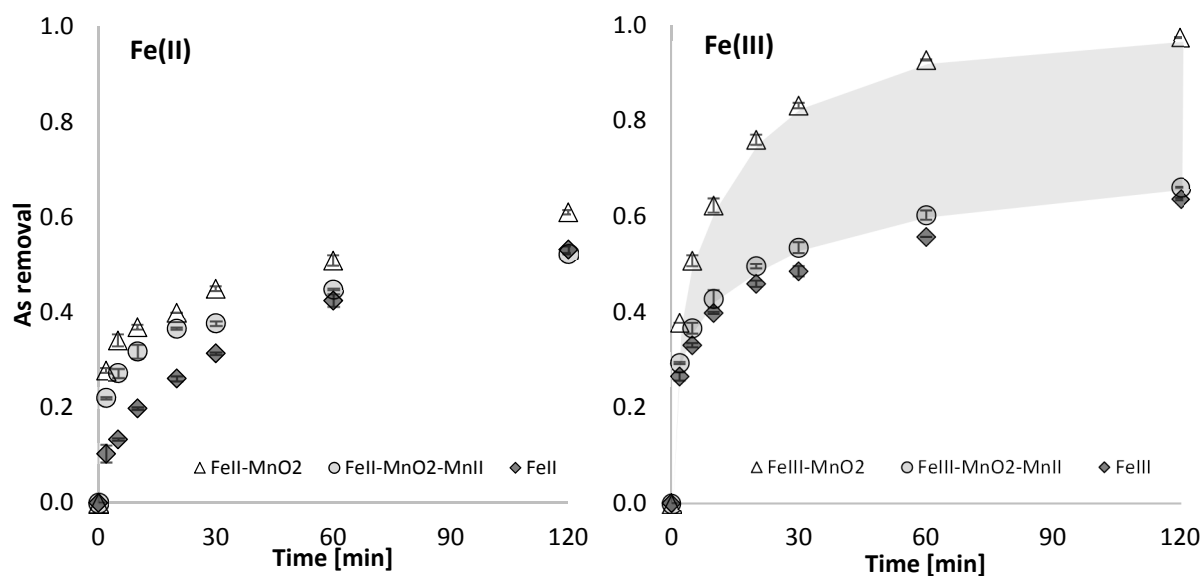


Figure 3.10 As(III) removal by Fe(II) and Fe(III) in presence and absence of MnO<sub>2</sub> and Mn(II) at pH 7 over 120 min. Concentrations were 20 μg/L As(III), 2 mg/L Fe, 2 mg/L Mn and 100 mg/L MnO<sub>2</sub> powder. Left Figure is As(III) removal by Fe(II) and right Figure Fe(III).

The data for HFO originating from Fe(III) and Fe(II) are the same as in Figure 3.9 and set a reference for As(III) adsorption to HFO (diamonds) without MnO<sub>2</sub> addition. The triangles in Figure 3.10 show the added effect of MnO<sub>2</sub> powder to As(III) adsorption on HFO originating from Fe(II) and Fe(III). MnO<sub>2</sub> addition to the As(III)-Fe(II) system resulted in a limited (16%) increased As removal, whereas the addition of MnO<sub>2</sub> to As(III)-Fe(III) caused a 52% improved removal; the combination Fe(III) and MnO<sub>2</sub> resulted in a As(III) concentration decrease from 20 μg/L As(III) to < 1 μg/L. In order to identify why Fe(III) and MnO<sub>2</sub> were better capable of removing As(III) than Fe(II) and MnO<sub>2</sub>, a set of experiments were conducted with an extra addition of Mn(II) to both systems, results are depicted by the circles in Figure 3.10. As concluded earlier, Mn(II) inhibits As(III) oxidation by MnO<sub>2</sub>. Therefore, this experiment was considered an indicator for As(III) removal in the presence of MnO<sub>2</sub> *without* its oxidising capabilities. In the case of Fe(III), it was concluded that 66% of As(III) was adsorbed onto the HFO or MnO<sub>2</sub> surface (circles; right) thereby removing only 2% more As(III) than HFO alone. For Fe(II), it was concluded



that the addition of Mn(II) did not inhibit the oxidation of Fe(II) by MnO<sub>2</sub> and subsequently did not influence As removal much, since Fe(II) already inhibited As(III) oxidation. This is illustrated by the limited decreased As removal in the Fe(II)-MnO<sub>2</sub>-Mn(II) system (circles; left) compared to Fe(II) and MnO<sub>2</sub> alone (triangles; left), but increased removal in the beginning over Fe(II) alone (diamonds; left).

As a result of dosing of Fe(III) and MnO<sub>2</sub> together, As(III) was oxidised to As(V), and subsequently adsorbed onto the precipitating HFO resulting in a near complete As(III) removal (triangles; right/grey area). However, in the case of Fe(II), the oxidation process of As(III) by MnO<sub>2</sub> was inhibited by Fe(II), as shown in Figure 3.4, therefore limiting As(V) production (triangles; left). This explains the removal difference between Fe(II) and Fe(III) in Figure 3.10, since the oxidation of As(III) to As(V), which is required for efficient removal by HFO, was only achieved in the presence of Fe(III).

Soluble Fe and Mn concentrations during these experiments are plotted in Figure 3.11 in order to confirm that Fe(II) and Mn(II) reacted with the MnO<sub>2</sub> surface. It shows that Fe(II) concentrations decreased faster in the presence of MnO<sub>2</sub>, either in the presence or absence of Mn(II). This confirms that Fe(II) oxidation took place on the MnO<sub>2</sub> surface and was not subject to interference by the presence of Mn(II). In Figure 3.11 (right), the Mn(II) concentrations illustrate that the added 2 mg/L Mn(II) was partially removed over time by the Fe(III)-MnO<sub>2</sub> system or by MnO<sub>2</sub> alone. Fe(III), without MnO<sub>2</sub>, did not considerably remove Mn(II), so this suggests that Mn(II) was only adsorbed onto MnO<sub>2</sub>. The presence of Fe(II) resulted in an increased Mn(II) concentration of 0.10 mg/L. The mobilisation of Mn(II) from the MnO<sub>2</sub>, even in the presence of 2 mg/L Mn(II), is a clear indication that Fe(II), independent of Mn(II) concentrations, was active on the MnO<sub>2</sub> surface and was the preferred ion by the MnO<sub>2</sub> mineral surface.

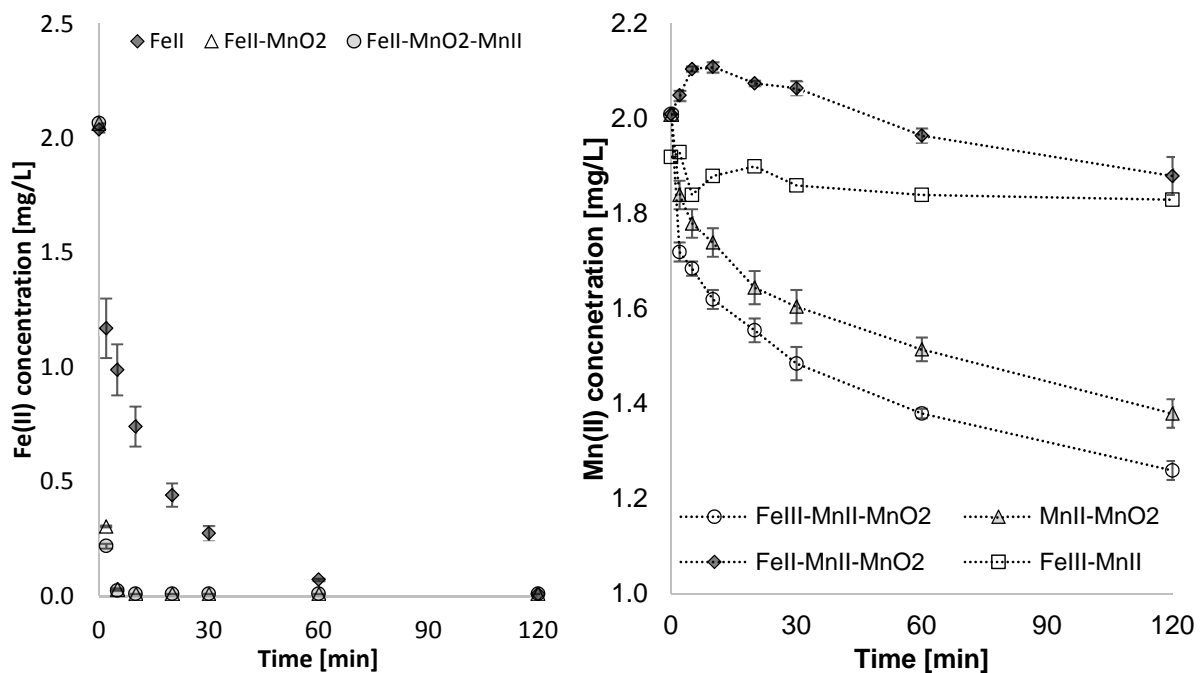


Figure 3.11 Fe(II) concentrations (left) and Mn(II) concentrations (right) at pH 7 over time. 2 mg/L Fe, 2 mg/L Mn(II) and 0.1 g/L MnO<sub>2</sub> powder.

The Fe and Mn concentrations in Figure 3.11 confirm that Fe(III) did not pacify the MnO<sub>2</sub> surface and thereby did not inhibit the As(III) oxidation on MnO<sub>2</sub>. On the other hand, Fe(II) reacted on MnO<sub>2</sub> and thereby inhibited As(III) oxidation. For Mn(II) addition to the MnO<sub>2</sub>, a similar explanation as for Fe(II) is justified since Mn(II) does not oxidise homogenously in aerated water at pH 7 (Diem and Stumm, 1984) and the observed loss in dissolved Mn(II) was 30%. Therefore, the Mn(II) must have been retained on the MnO<sub>2</sub> surface, which could have led to similar surface passivation of the MnO<sub>2</sub> as Fe(II). Leading to the overall conclusion that, in the presence of Fe(II) and Mn(II), MnO<sub>2</sub> cannot durably contribute to efficient As(III) removal by HFO.

### 3.4 Conclusions

In this study, it was investigated whether MnO<sub>2</sub> could be responsible for the observed As(III) oxidation in the top layer of rapid sand filters treating aerated groundwater. Although it is known that MnO<sub>2</sub> is capable of oxidising As(III), it is unknown whether naturally grown MnO<sub>2</sub> on filter sand grains are oxidising As(III) in competition with other reduced constituents (Fe(II), Mn(II)). In a series of jar test experiments it was found that both commercial and 22-year old filter grain MnO<sub>2</sub> were capable of rapidly oxidising

As(III) by reduction to Mn(II). However, this process was inhibited in the presence of Fe(II) and Mn(II), as Fe(II) and Mn(II) adsorption and oxidation were preferred over As(III) on the MnO<sub>2</sub> surface (at pH 7). Under these conditions, the unavailability of the MnO<sub>2</sub> surface for As(III) oxidation limited subsequent removal of As(V) by the precipitating HFO. Therefore it is concluded that just because MnO<sub>2</sub> is present in a filter bed, it does not necessarily mean that MnO<sub>2</sub> will be available to oxidise As(III). However, unlike Fe(II), the addition of Fe(III) did not hinder As(III) oxidation on the MnO<sub>2</sub> surface; resulting in subsequent effective As(V) removal by the flocculating HFO.

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## 4. Biological As(III) oxidation in rapid sand filters

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### Abstract

The objective of this study was to investigate whether arsenic-oxidising bacteria (AsOB) will grow and survive in rapid sand filters. Additionally, the interdependence of other groundwater constituents (Fe(II), Mn(II), NH<sub>4</sub>) with biological As(III) oxidation was investigated. For this purpose As(III) oxidation was monitored in pilot-scale filter sand columns fed with raw groundwater, as well as treated groundwater (drinking water) with spikes of either As(III), Mn(II) or NH<sub>4</sub>.

It was concluded that biological As(III) oxidation rapidly developed in the rapid sand filter columns. With a typical lag and log phase, decreasing As(III) and increasing As(V) concentrations in the effluent of the sand columns were observed in a timeframe of weeks. The growth of biomass in the sand columns was confirmed with ATP analysis. ATP concentrations on the sand grains increased from 0.7 ng/g to 16, 8 and 2 ng/g filter sand stratified from the top of the sand filter to the bottom, respectively. Additionally, a microbial community analysis (16S rRNA) showed a high relative abundance of  $\alpha$ - and  $\beta$ -Proteobacteria; the same classes where most AsOB are phylogenetically placed.

This study establishes that AsOB are able to grow and maintain their population on low As(III) concentrations, either in presence, or absence, of other common groundwater bacteria and mineral precipitates, directly leading to an increased As removal in the filter bed.

### 4.1 Introduction

Conventional groundwater treatment plants for drinking water production, consisting of aeration and rapid sand filtration, are primarily designed for removal of dissolved iron (Fe), manganese (Mn) and ammonium (NH<sub>4</sub>). However, when present, arsenic (As) is often only partially removed by this technology, potentially affecting drinking water



safety. Therefore, drinking water companies in the Netherlands are currently considering a new target of 1 µg/L. To prevent costly modifications to an otherwise simple treatment set-up, better understanding of As removal mechanisms in rapid sand filters needs to be gained.

Prior to rapid sand filtration, anaerobic groundwater is aerated with spray or cascade aeration, equilibrating the water with oxygen (O<sub>2</sub>), and removing (part of the) carbon dioxide (CO<sub>2</sub>), hydrogen sulphite (H<sub>2</sub>S) and methane (CH<sub>4</sub>). O<sub>2</sub> facilitates the oxidative removal of Fe, Mn and NH<sub>4</sub> in the subsequent filter bed. The aerated water is supplied to the supernatant water of a rapid sand filter, that typically consists of a sand bed with a height of 1.5 – 2.5 m, and is operated with a downward filtration velocity of 3-8 m/h. Pressure drop or effluent water quality trigger a periodical backwash procedure to remove the retained solids (Moel et al., 2006).

In the filter bed, Fe(II) can be removed via homogeneous, heterogeneous and biological oxidation, depending on operational parameters such as, supernatant water level, filtration velocity, pH and O<sub>2</sub> concentration (van Beek et al., 2015). The backwashed solids mainly consist of hydrous ferric oxides (HFO) and its adsorbed substances (Gude et al., 2016). Homogeneous Mn(II) oxidation is slow (Diem and Stumm, 1984) and therefore removal of Mn (mainly) occurs in the filter bed via a biological oxidation pathway to Mn oxides (MnO<sub>2</sub>) (Abu Hasan et al., 2012; Bruins et al., 2015; Katsoyiannis and Zouboulis, 2006). NH<sub>4</sub> is also biologically oxidised in the filter bed (Lee et al., 2014), in a two-step process, executed by bacteria and archaea, via nitrite (NO<sub>2</sub>) to nitrate (NO<sub>3</sub>) (Niu et al., 2013).

As, when dissolved in anaerobic groundwater, is at neutral pH and slightly acidic water typically present as H<sub>3</sub>AsO<sub>3</sub><sup>\*</sup>, the reduced, uncharged, trivalent form (Smedley and Kinniburgh, 2002; Stuyfzand et al., 2006). While, after filtration, the remaining As is present as H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> (Gude et al., 2016). This is the oxidised, charged, pentavalent form. At neutral pH, As(V) is, in contrast to As(III), negatively charged and is therefore more efficiently removed via adsorption to HFO (Bissen and Frimmel, 2003; Gude et al., 2017). Measurements over the height of the filter bed pointed out that As(III) oxidises rapidly in the top layer of a rapid sand filter (Gude et al., 2016). Since homogeneous As(III) oxidation occurs on a time scale of days (Bissen and Frimmel, 2003; Kim and Nriagu, 2000), the observed rapid oxidation was hypothesised to be either biological, by MnO<sub>2</sub> present on

the filter grains, or a combination of the two. However, although  $\text{MnO}_2$  is capable of oxidising As(III) (Manning et al., 2002), it can be inhibited in presence of Fe(II) and Mn(II) (Gude et al., 2017; Lafferty et al., 2010; Wu et al., 2015). The alternative explanation for the accelerated As(III) oxidation during rapid sand filtration, is the presence of As(III) oxidising bacteria (AsOB). At least 50 phylogenetically diverse As(III)-oxidising strains, distributed over 25 genera, have been isolated from various environments (Quéméneur et al., 2008), and aerobic AsOB have been found in groundwater aquifers (Dey et al., 2016; Liao et al., 2011) and groundwater treatment filters (Cavalca et al., 2013a).

AsOB can be subdivided into: heterotrophic bacteria (Ike et al., 2008; Muller et al., 2003; Wan et al., 2010) and chemolithoautotrophic bacteria (Battaglia-Brunet et al., 2002; Rhine et al., 2005; Wan et al., 2010). Heterotrophic bacteria oxidise As(III) as a detoxification mechanism (Huang, 2014; Tsai et al., 2009; Vanden Hoven and Santini, 2004) and require organic matter for growth and As(III) oxidation. Chemolithoautotrophic bacteria, on the other hand, can use As(III) as the principal electron donor in catabolism, and use inorganic carbon as their carbon source (Santini et al., 2000). Phylogenetic studies classified most AsOB in the Proteobacteria phylum. Within this phylum they can be subdivided as follows: most AsOB in the  $\alpha$ -Proteobacteria class are chemolithoautotrophic, most in the  $\beta$ -Proteobacteria class are heterotrophic and all AsOB in the  $\gamma$ -Proteobacteria class are heterotrophic (Cavalca et al., 2013b; Oremland and Stolz, 2003).

So far As(III) oxidation in rapid sand filters has only been studied in the relation to other biological processes, whereby As(III) oxidation was regarded to rely on co-occurring (bio-)chemical processes, including oxidation with Fe (Katsoyiannis and Zouboulis, 2004), Mn (Driehaus et al., 1995; Katsoyiannis et al., 2004),  $\text{NH}_4$  (Lytle et al., 2007) or in combination with biogenic  $\text{MnO}_2$  (Yang et al., 2014). Other studies have focussed on using various inoculates to invoke biological As(III) oxidation (Jones et al., 2012; Yang et al., 2014). Although AsOB are found in rapid sand filters (Cavalca et al., 2013a), it is however, far less researched whether these bacteria are responsible for As(III) oxidation independent of co-occurring chemical and biological processes, as a result of Fe, Mn and  $\text{NH}_4$  removal. The oxidation of As(III) by AsOB is of great interest for As(III) removal, because the resulting As(V) formation is imperative for subsequent adsorption onto HFO in filters (Bissen and Frimmel, 2003; Gude et al., 2017).

Therefore, the objective of this study was firstly to investigate whether AsOB will grow on As(III) substrate in rapid sand filters, in absence of other biological (ammonium, manganese and ferrous oxidising bacteria) and chemical (HFO,  $\text{MnO}_2$ ) processes. And secondly, it was the aim to assess whether a mature AsOB population can survive in rapid sand filters with low As(III) concentrations ( $<10 \mu\text{g/L}$ ) amidst the other major groundwater constituents (Fe(II), Mn(II),  $\text{NH}_4$ ). For this purpose As(III) oxidation was investigated in pilot-scale sand filter columns fed with raw groundwater, as well as treated groundwater (drinking water) with spikes of either As(III), Mn(II) or  $\text{NH}_4$ .

## 4.2 Materials and methods

### 4.2.1 Experimental procedure

For the purpose of accumulating different biomasses that were tested on their ability to oxidise As(III), multiple experiments were executed by preloading sand columns with different feed water qualities, i.e., preloading consisted of gently flowing a specific water quality through the columns to establish a biomass in the column. As(III) oxidation was tested with five different water quality settings of which the first two can be considered as control settings: (1) “virgin sand” (no preloading), (2) “blank” (sand preloaded with drinking water), (3) “As(III)” (sand preloaded with drinking water and added As(III)), (4) “ $\text{NH}_4$ ” (sand preloaded with drinking water and added  $\text{NH}_4$ ), and (5) “Mn” (sand preloaded with drinking water and added Mn(II)). Additionally an experiment with naturally As(III)-containing groundwater was done to find the influence of the natural groundwater matrix on the AsOB. Here, the filtrate of sand filters was compared for 50 days by using virgin sand (no preloading) and sand with an As(III) oxidising biomass (preloaded by drinking water spiked with As(III)). All experiments were executed as triplicates.

### 4.2.2 Experimental column set-up

The experimental set-up consisted of 12 identical columns, therefore 4 settings could run simultaneously in triplicates (Figure 4.1). Each column has a diameter of 90 mm and a height of 1m. The columns were filled with 0.5m (+/- 2%) quartz sand (0.4 - 0.8 mm)

obtained from 'Aqua Techniek', which is typically used for rapid sand filtration. Before starting the experiment the columns were extensively backwashed with drinking water until the supernatant was visually clear. The flowrate used for all experiments was set to 105 ml/min per column, resulting in a filtration velocity of 1 m/h (+/- 10%). Supernatant water level in the columns was kept at 10 cm during the drinking water experiments for the purpose of sufficient chemical mixing. Chemicals, when used, were directly dosed in the supernatant water, using peristaltic dosing pumps (Cole-Parmer Masterflex L/S) at a continuous flow of 1 ml/min. For the aerated groundwater experiments the supernatant water level was lowered to an initial height of 2 cm, which, as a result of filter clogging, rose to 15 cm just before backwashing. Backwashing procedure was executed with drinking water and consisted of expanding the filter bed by 20% until the supernatant water was visually clear. The anaerobic groundwater was aerated by cascading the groundwater directly into the supernatant water. No chemicals were dosed in the natural groundwater. Throughout the experiment, the sand columns were continuously fed with (spiked) drinking water or groundwater and covered to prevent direct (sun)light influencing the results.

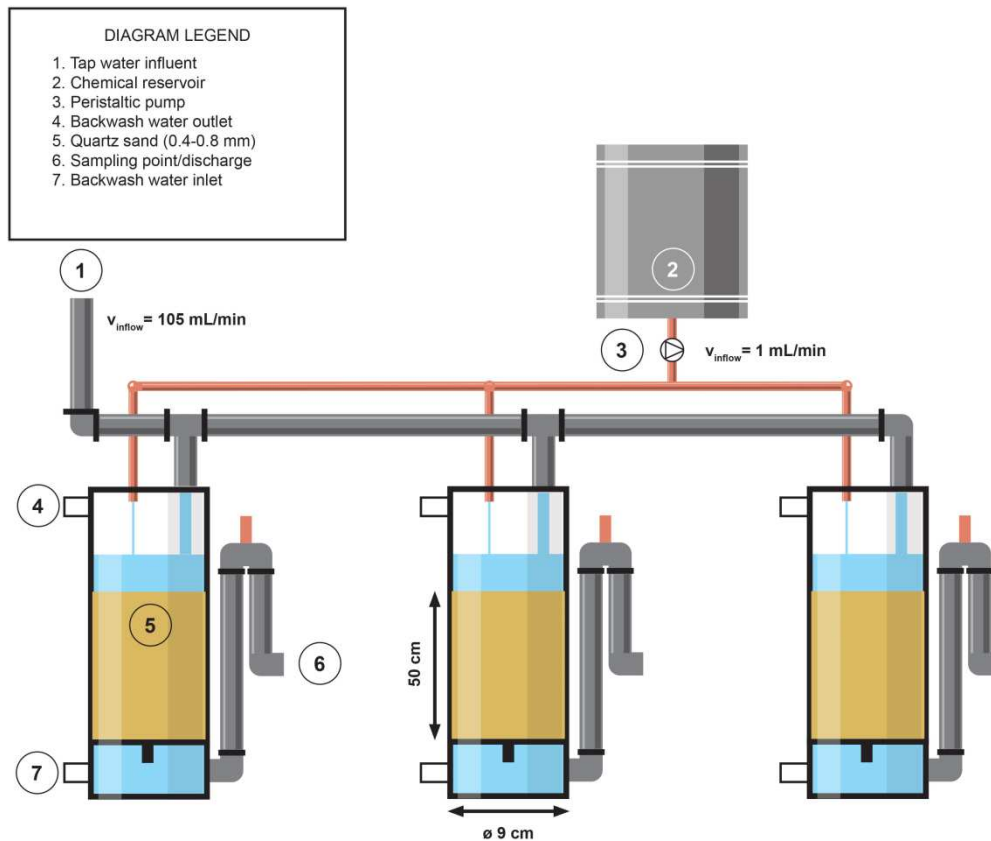


Figure 4.1 Schematic overview of sand filter set-up as triplicates (valves not shown).

#### 4.2.2 Water quality

The column experiments were performed at water treatment plant Dorst (Brabant Water). Natural groundwater was used to perform the experiments in the presence of Fe, Mn and  $\text{NH}_4$ . Preloading was executed with drinking water produced at this production location spiked with the prior mentioned desired components. Both the quality of the groundwater and the drinking water are shown in Table 4.1. The groundwater is anaerobic and abstracted from 140 m depth. Drinking water is produced by aeration and rapid sand filtration, including the dosage of 2 mg/L  $\text{NaMnO}_4$  and 2 mg/L  $\text{FeCl}_3$  to stimulate As removal.

Table 4.1 Drinking water and groundwater quality used in column experiments.

Water quality parameters	Units	Raw groundwater	Drinking water
pH	[-]	7.54 <sup>1</sup>	7.69
Temperature	°C	15.5	16.5
O <sub>2</sub>	mg/L	< 0.01 <sup>1</sup>	9.07
HCO <sub>3</sub>	mg/L	259	238
Conductivity	mS/m	40.9	39.1
As(tot)	µg/L	13.2	< 1.0
As(III)	µg/L	12.7	< 1.0
Fe	mg/L	1.4	< 0.01
Mn	mg/L	0.04	< 0.01
NH <sub>4</sub>	mg/L	0.62	<0.03
NO <sub>3</sub>	mg/L	< 0.03	1.86
PO <sub>4</sub>	mg/L	0.45	0.078
TOC	mg/L	2.1	2.1
SO <sub>4</sub>	mg/L	< 0.1	0.37
ATP	ng/L	1.1	3.2

<sup>1</sup>The pH and O<sub>2</sub> in the supernatant level of the pilot columns was, depending on the supernatant level, between 7.6 - 7.7 and 4 - 4.5 mg/L respectively.

#### 4.2.3 Chemicals, addition and concentrations

The As(III), Mn(II) and NH<sub>4</sub> dosing solutions were prepared from the following reagent grade chemicals: As(III)Cl<sub>3</sub> (Aldrich chemistry, 99.99% trace metals basis), Mn(II)Cl<sub>2</sub>, (Aldrich chemistry, 98% beads) and NH<sub>4</sub>Cl (Emsure, 99.8%). The chemicals were diluted in drinking water to 10.6, 212 and 106 mg/L, respectively. To prevent oxidation in the dosing vessels (25L), the vessels containing As(III) and Mn(II) were acidified to pH 3-4 by adding 8-12 ml 5M HNO<sub>3</sub>. The chemicals were continuously pumped into the supernatant

water, with a flow rate of 1 ml/min, targeting an influent concentration of approximately 100 µg/L As(III), 1 mg/L NH<sub>4</sub> and 2 mg/L Mn(II).

#### 4.2.4 Sampling and analytical methods

Samples from supernatant water were collected with a syringe from the lowest part of the supernatant water. Filtrate was obtained from the discharge tube after the overflow to prevent changing the filtration rate. pH, electrical conductivity (EC) and O<sub>2</sub> were measured with WTW electrodes (SenTix 940, TerraCon 925 and FDO925). As, Fe and Mn were analysed with Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Thermo X2-series), NH<sub>4</sub>, NO<sub>2</sub>, NO<sub>3</sub> and PO<sub>4</sub> were analysed by a discrete analyser spectrophotometry (Aquakem 250, Thermo Scientific). As speciation was done according the Clifford (2006) method. Here, 150 mL sample is passed through an anionic resin (80 mL Amberlite® IRA-400 chlorite form resin in a 100-mL syringe) that retains only the charged As(V) species. The filtrate from the resin is considered to be As(III) only. As(V) is then calculated by subtracting As(III) from the measured total As concentration. The first 50 mL was always discarded, the remaining 100 mL was collected and analysed using ICP-MS. The Clifford method is a robust method, however it was found that unavoidably the resin retained 14% of As(III), min=7%, max=23%; n=24.

#### 4.2.5 Biomass characterization and profiling

The biomass accumulation stages were finalised by removing the filter sand from the columns and analysed on adenine triphosphate (ATP), which serves as an indicator of active biomass (Hammes et al., 2010; Magic-Knezev and van der Kooij, 2004), for the purpose of quantifying the biomass after the different experiments. From a completely filled sampling bottle (100 ml) 1 gram of sand was weighted and 9 ml of ATP free water was added. This sample was shaken shortly where after it was ultrasonically vibrated for 10 min in an ultrasonic bath (Bransson). Subsequently, the sample was rested for 5 min before ATP measurement. Samples were processed by the ATP meter “Centro XS3 LB960” (Berthold) using a chemical kit from BioTHema. In addition to the ATP analysis, a microbial community analysis was performed for all columns experiments. 100 mL filter sand was harvested and stored at -80 °C. Of these samples around 0.5 gram was used for

DNA extraction with the DNeasy UltraClean microbial kit (Qiagen). The DNA was subjected to quality checks that consisted of agarose-gel electrophoresis aiming to verify DNA integrity and a QuBit fluorometer and the ds DNA HS assay (Life technologies) analysis to determine the concentration of DNA that was obtained from the sand samples. The BioAnalyzer (Agilent) was used to perform an additional integrity and concentration check after which bacterial (V3-V4) 16S rRNA genes were amplified and subjected to high throughput sequencing using the MiSeq platform (from Illumina and at BaseClear, Leiden, the Netherlands). Reads were generated using the Illumina Casava pipeline (version 1.8.3), checked using Illumina Chastity filtering plus an in-house protocol (Baseclear) and final assessment was made using the FASTQC quality control tool (version 0.10.0). QIIME workflows were used to generate taxonomic summaries (Caporaso et al., 2010).

### **4.3 Results and discussion**

#### **4.3.1 As(III) oxidation in various preloaded sand columns**

Sand columns were preloaded with drinking water (“blank”), drinking water with added  $\text{NH}_4$  (“ $\text{NH}_4$ ”), drinking water with added Mn(II) (“Mn”) and drinking water with added As(III) (“As”). During preloading the water quality was monitored to determine if bacteria had grown to convert  $\text{NH}_4$ , Mn and As in the columns, the moment of conversion determined the minimum duration of pre-loading. Table 4.2 summarises the in- and effluent water quality at the end of preloading, as well as the duration of preloading per column.



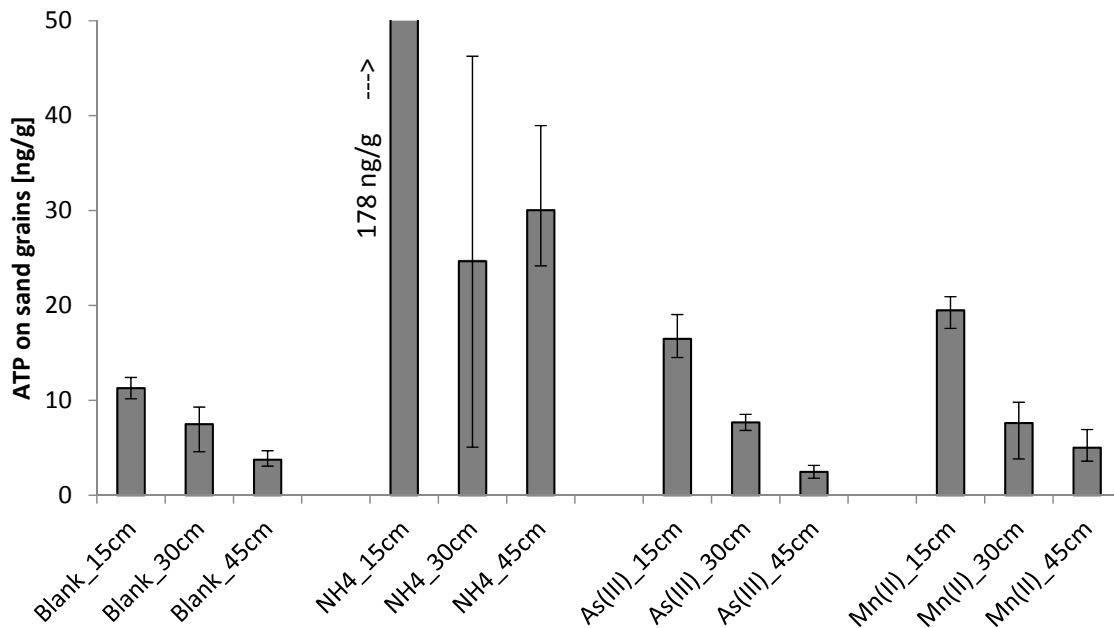
Table 4.2 Water quality parameters before and after preloading.

Parameter	unit	Supernatant / Influent while preloading				Filtrate / Effluent after preloading per column			
		n	Average	min	max	Drinking water	+NH <sub>4</sub>	+Mn	+As
Duration preloading	[days]					80	80	80	38
Water temperature	[°C]	12	16.7	15.9	18.2				
O <sub>2</sub>	[mg/L]	12	9.03	8.89	9.25	9.1	8.07	9.08	9.1
pH		12	7.81	7.76	7.87	7.91	7.73	7.88	7.8
NH <sub>4</sub>	[mg/L]	12	0.95	0.87	1.07		0.01		
Mn	[mg/L]	8	1.61	1.47	1.8			1.61	
As	[µg/L]	42	111.3	93.9	135.3				106

The water quality parameters in Table 4.2 primarily shows an effect from preloading in the NH<sub>4</sub> columns, preloading did not affect the water quality over time in the other columns. Initially part of the As was adsorbed to the filter sand, however over the course of the experiment As adsorption decreased, resulting in an average removal of 4.5% during preloading. The preloading with NH<sub>4</sub> resulted in measureable changes in O<sub>2</sub> and pH caused by its oxidation. After the preloading period, the effluent of the columns no longer contained NH<sub>4</sub> nor NO<sub>2</sub>, so nitrification to NO<sub>3</sub> was found to be complete. Surprisingly, Mn oxidising bacteria, did not seem to have grown in the Mn(II) preloaded columns, because Mn(II) removal as MnO<sub>2</sub> was not observed, additionally Mn(II) oxidation would have resulted in changing O<sub>2</sub> and pH values during the experiment and this was not observed.

The column preloaded with drinking water, did not show apparent water quality changes, however, the post-experiment analyses of ATP on the filter sand showed that indeed drinking water native bacteria had grown in the column (Figure 4.2). Note that the ATP value on the virgin filter sand was only 0.71 ng/g prior to preloading.

The drinking water used for these experiments contained 3.7 ng/L ATP. The ATP values in the columns preloaded with drinking water-containing Mn or As, showed similar values and, although modest, showed more bacterial activity in the top layer than the blank columns, with 73% and 45% higher ATP concentrations respectively. The largest ATP concentrations on sand were achieved by preloading with drinking water and  $\text{NH}_4$ . In the top of the sand bed this led to more than 15 times higher ATP concentrations than the preloaded columns with drinking water only. Additionally it was observed that the biomass was stratified over the filter, from the highest concentration of biomass in the top of the sand filter to the lowest biomass concentration at the bottom. This is in line with findings of Lee et al. (2014), where  $\text{NH}_4$  oxidising bacteria in a sand filter showed a similar vertical distribution.



**Figure 4.2** ATP concentration on the filter sand at 15, 30 and 45 cm from top of the filter after preloading with drinking water (blank),  $\text{NH}_4$ , As(III) or Mn(II). Two outliers removed with 95% certainty interval with Dixon's Q-test.

After the preloading stage, all columns were loaded with 20  $\mu\text{g/L}$  As(III) for 24h to investigate whether the bacteria in the various columns were capable of oxidising As(III) to As(V). About 10% of the dosed As was retained in the sand columns, therefore the percentage of oxidised As in the filtrate is depicted in Figure 4.3.

During the first 6 hours no As(III) was oxidised in the columns preloaded with  $\text{NH}_4$ , Mn(II) or drinking water alone. Thereby establishing that no significant abiotic As(III) oxidation

occurred in the sand columns and the biomasses that had not, in advance, been exposed to As(III) could not instantly oxidise the dosed As(III). This was in contrast to the columns preloaded with 100 µg/L As(III), the filtrate of these columns contained solely oxidised As. Apparently, within 38 days, AsOB had grown in these columns during preloading. After 24 hours, it seems that oxidation of As(III) started to occur in all columns, particularly in the NH<sub>4</sub> preloaded column, where 40% of the As in the filtrate was As(V). Apparently an adaptation phase of the well-developed biofilm started and resulted in the oxidation of 9 µg/L As(III).

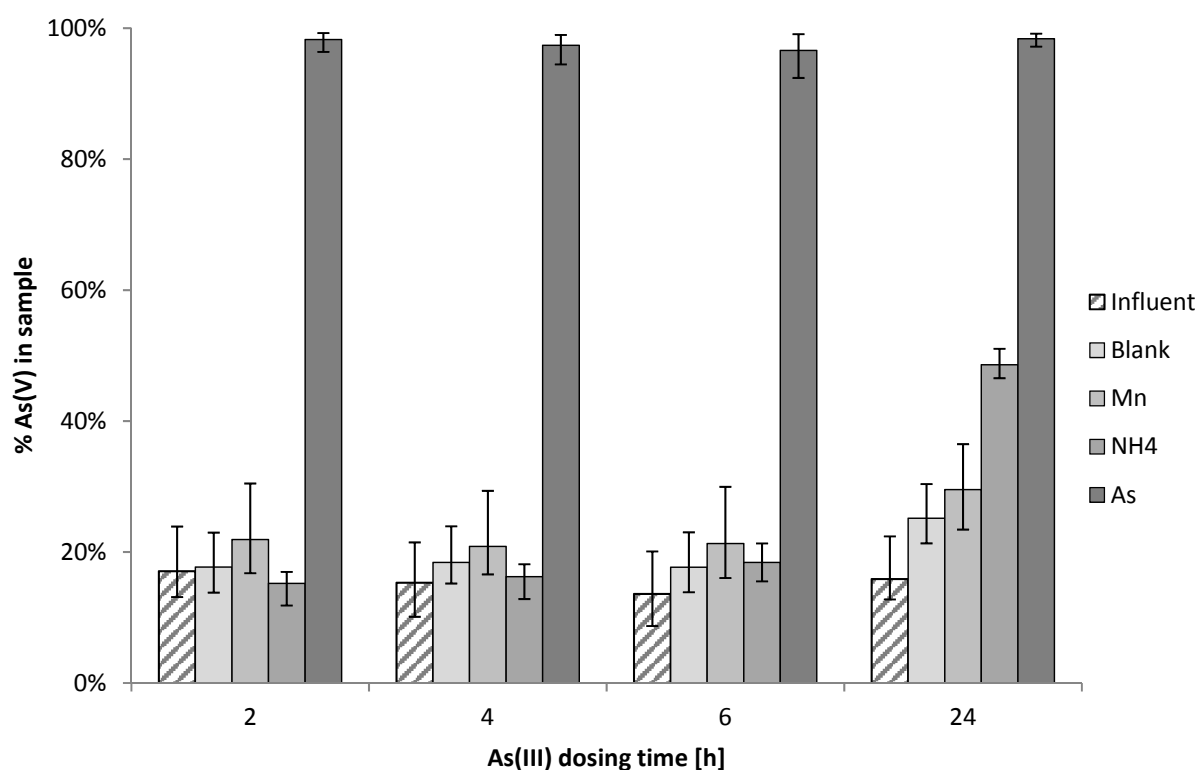
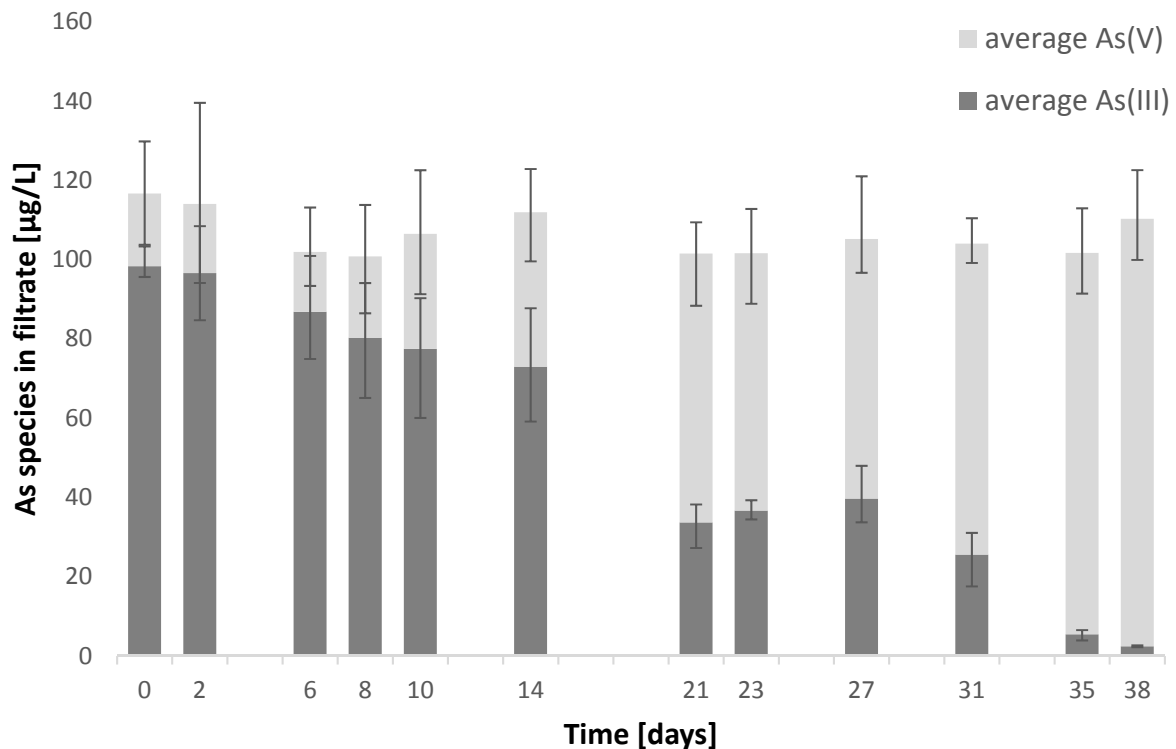


Figure 4.3 Percentage of As(V) of total As in water sample during 24 h in the preloaded sand columns. Samples obtained from influent and filtrate of the filter sand columns after preloading with drinking water, NH<sub>4</sub>, As(III) or Mn(II).

#### 4.3.2 Bacterial growth profile of As(III) oxidation on virgin filter sand

As(III) and As(V) in the filtrate during this 38 days of pre-loading with As(III)-spiked drinking water are depicted in Figure 4.4. During the entire experiment, the average As(III) concentration in the supernatant water was 116 µg/L (min 98, max 135 µg/L), but

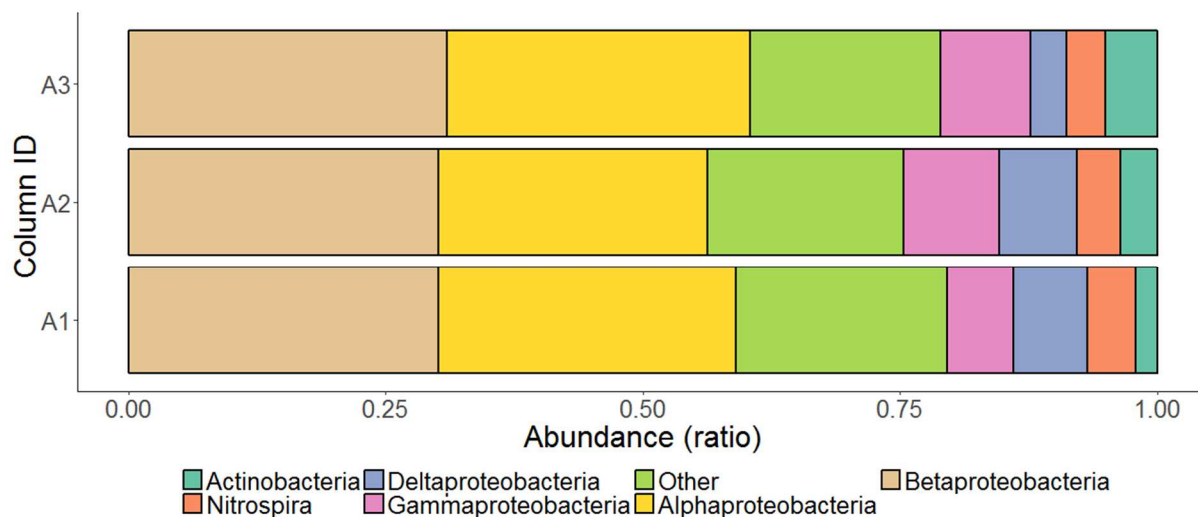
due to (slow) homogeneous oxidation in the dosing vessel the As(III) concentration at the end of the experiment decreased to 95  $\mu\text{g/L}$ .



**Figure 4.4** As(III) and As(V) species in the filtrate of sand columns over time (38 days) by feeding drinking water added with approximately 100  $\mu\text{g/L}$  As(III).

The results in Figure 4.4 show that initially the sand columns did not oxidise As(III), but with a daily influx of 150 L As(III)-containing drinking water, the columns gradually started oxidising As(III). After 38 days, 98% of As(III) was oxidised to As(V) in the sand columns. The process started after approximately one week, however, the oxidation rate accelerated after 14 days. This is typical for a bacterial process, where after a lag phase of limited bacterial growth a log phase follows of rapid bacterial growth (Brown, 2015). Additionally, the ATP concentration of the filter sand increased from 0.71 ng/g to 16 ng/g (in the top of the sand filter) indicating an increased bacterial activity within the 38 days experiment (Hammes et al., 2010). Therefore it may be concluded that the gradual As(III) oxidation observed in the columns was caused by AsOB. Given that the experiment with drinking water without As(III) or Mn(II) and  $\text{NH}_4$  initially showed no As(III) oxidation (Figure 4.3), it is suggested that a specific AsOB population was grown by preloading filter sand with As(III) substrate. Additionally, microbial community profiling of the biomass

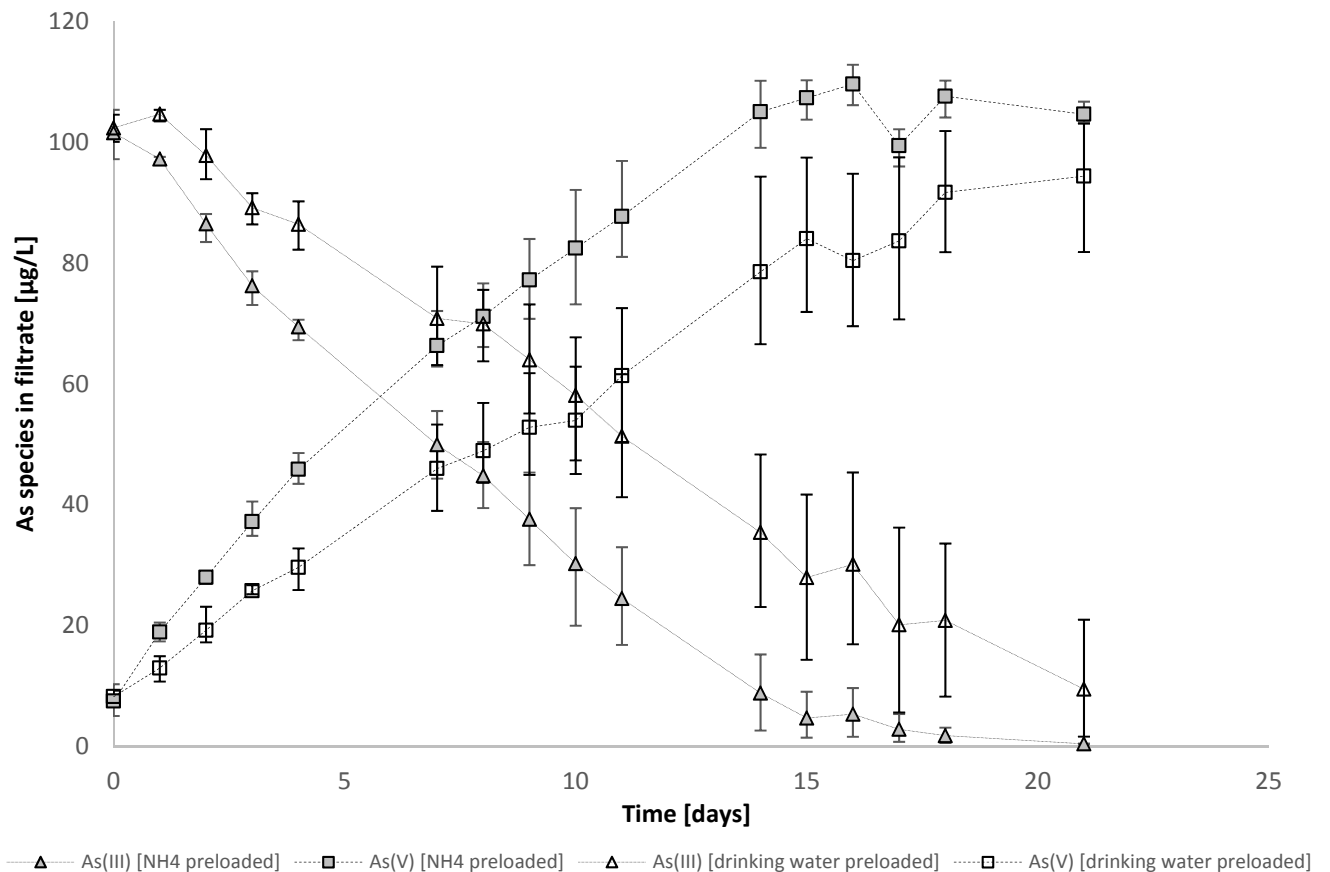
on the filter sand after preloading with As(III), showed a biomass with a high relative abundance of  $\alpha$ - and  $\beta$ -Proteobacteria (Figure 4.5). Within these two classes of Proteobacteria most AsOB are phylogenetically placed (Cavalca et al., 2013b; Oremland and Stolz, 2003).



**Figure 4.5** Results of microbial community analysis after feeding drinking water with 100  $\mu\text{g/L}$  added As(III) for 38 days. Relative abundance of bacteria is shown at the taxonomic rank Class (L3) of the filter sand columns ID's A1, A2 and A3 (triplicates).

#### 4.3.3 As(III) oxidising biomass growth in existing biomass

To investigate whether AsOB would grow in an already accumulated biomass, 100  $\mu\text{g/L}$  As(III) was dosed to preloaded columns for 22 days. Prior to As(III) dosage the columns were loaded with drinking water and drinking water with additional  $\text{NH}_4$  for 50 days. The experiment started when the latter biomass was capable of completely converting 1 mg/L  $\text{NH}_4$  to  $\text{NO}_3$ . The resulting As(III) and As(V) concentrations in the filtrate are depicted in Figure 4.6.



**Figure 4.6 As(III) and As(V) in the filtrate of drinking water pre-loaded columns spiked with and without 0.79 mg/L-N NH<sub>4</sub>. Influent As(III) concentration was 98 µg/L min 83 max 118 (n=16) As(III) spiked in drinking water.**

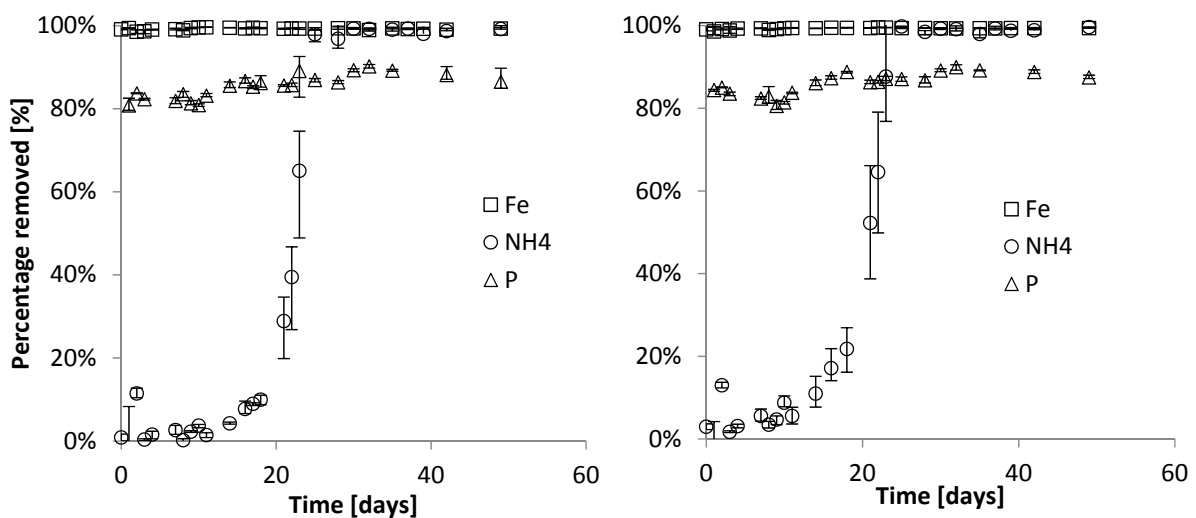
Results show that independent of the type of preloading, both columns successfully oxidised the added As(III) within three weeks and, in addition, compared to the As(III) oxidation experiment on virgin sand (Figure 4.4), both columns already containing a biomass reached complete oxidation in a shorter time. In the NH<sub>4</sub> preloaded sand columns As(III) was completely oxidised within 21 days without retarding or inhibiting nitrification. The experiment without NH<sub>4</sub> addition, using the same drinking water, showed a similar As(III) oxidation pattern, only initially deviating from the oxidation pattern in the NH<sub>4</sub> preloaded columns. Starting with a more gentle slope than the NH<sub>4</sub> preloaded columns in the first week, after 7 days and onwards these columns followed the same As(III) concentration gradient.

The above suggests that established biological processes prior to As(III) exposure do not retard or prevent biological As(III) oxidation but accelerate them. A comparable study

performed by Lami et al. (2013) showed that when As(III) was dosed to a mixed biomass soil culture, analogue to Figure 4.6, alteration and adaptation of the biomass was observed within weeks, whereby some As(III)-oxidising bacterial groups had increased up to 20-fold compared to a control experiment. The overall conclusion here is that  $\text{NH}_4$  oxidising biomass (nitrification) had no detrimental effect on the development of biological As(III) oxidation in groundwater filters, but the additional  $\text{NH}_4$  or  $\text{NO}_3$  (nutrients) rather stimulated the AsOB accumulation.

#### 4.3.4 Biological As(III) oxidation in natural, aerated groundwater

In natural groundwater, apart from  $\text{NH}_4$  and  $\text{Mn(II)}$ , also other constituents, such as  $\text{Fe(II)}$ ,  $\text{PO}_4$ ,  $\text{CH}_4$  and  $\text{H}_2\text{S}$  may enter the filter bed together with As(III). Therefore, the sand column experiments were repeated with natural, aerated groundwater with virgin sand columns and As(III) preloaded (35 days) sand columns capable of oxidising  $100 \mu\text{g/L}$  As(III). In contrast to prior experiments, oxidising  $\text{Fe(II)}$  caused the filter bed to clog with HFO and a 2-3 day backwash cycle had to be applied. The run time of this experiment was 50 days and during this period the supernatant water level, pH and  $\text{O}_2$  were 2 - 15 cm, 7.47 - 7.78 and 3.56 - 4.58 mg/L, respectively. Figure 4.7 depicts removal percentages for Fe,  $\text{NH}_4$  and  $\text{PO}_4$  over the run time of the virgin sand columns (left) and the columns preloaded with As(III) (right).



**Figure 4.7** Removal percentage of Fe,  $\text{NH}_4$  and P over time in virgin sand columns (Left) and As(III) preloaded sand columns (Right). Filtration velocity 1 m/h; bed height 0.5 m. Initial concentration of the groundwater: Fe

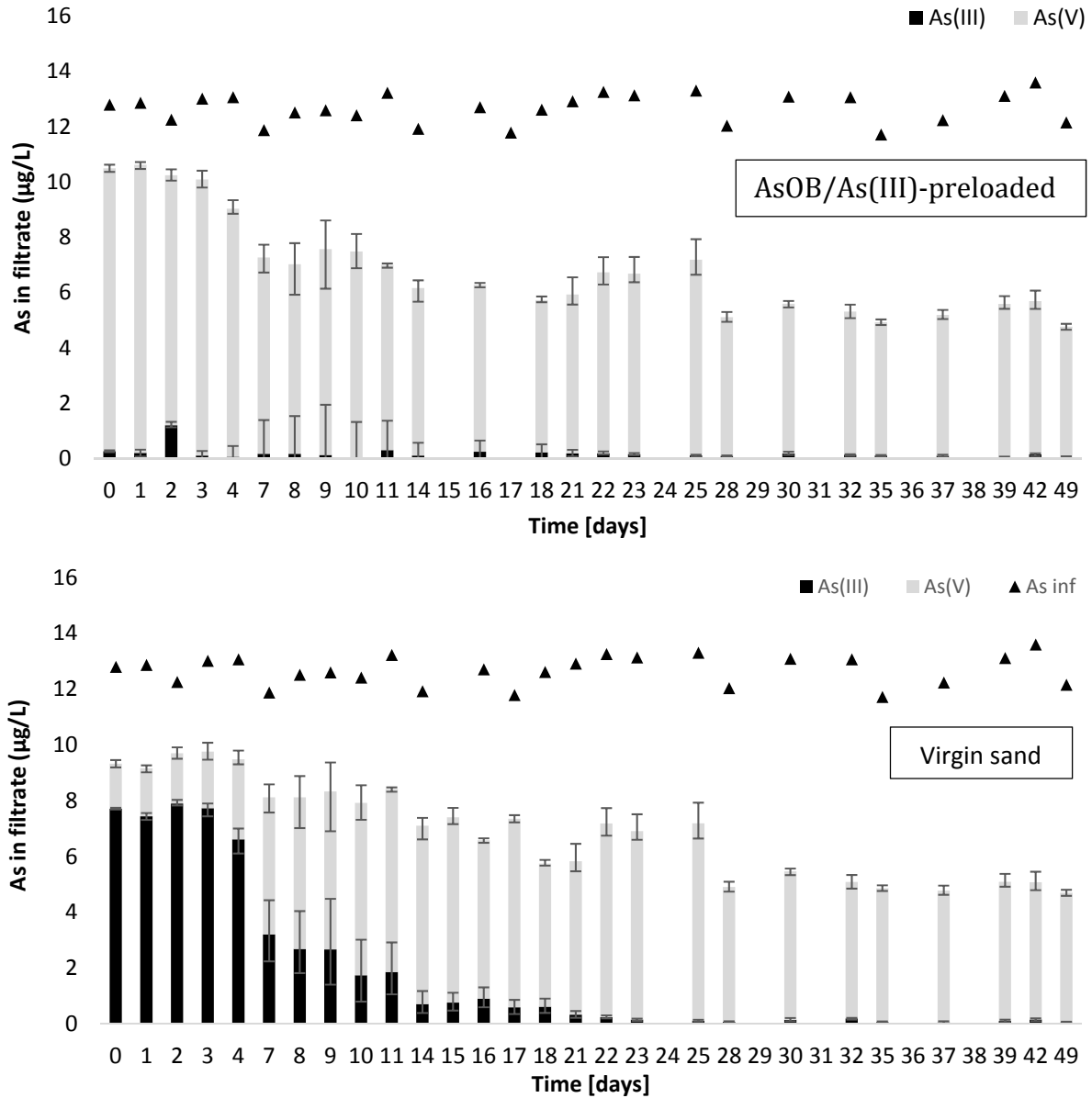
**1.4 mg/L; As 13 µg/L (as As(III)); PO<sub>4</sub> 0.45 mg/L; Mn 0.04 mg/L; NH<sub>4</sub> 0.62 mg/L; pH 7.54; Water temperature 14 - 18 °C. After aeration/supernatant level: O<sub>2</sub> 4.4 mg/L; pH 7.65**

Fe was instantly and completely removed in all columns. It is expected that initially the removal process was due to abiotic, homogeneous and heterogeneous oxidation (van Beek et al., 2015). It is possible that during the experimental period this shifted to a partially biological Fe oxidation process (de Vet et al., 2011; Katsoyiannis and Zouboulis, 2006). The 150 µg/L PO<sub>4</sub> was consistently removed between 80 and 90% in both columns, presumably by (co-)precipitation with oxidised Fe(II) and adsorption to HFO (Voegelin et al., 2013). The increased PO<sub>4</sub> removal (+/-10 µg/L) after the lag and log phase of the ammonium removal process could indicate the utilisation of PO<sub>4</sub> for the growth of biomass responsible for nitrification (Momba and Cloete, 1996). The difference in ripening time between the column types was about 2 days which is consistent with the previous findings where it was observed that preloading had a generic accelerating effect on biological processes (Figure 4.6). However both column types consistently converted the major part of the NH<sub>4</sub> within 30 days. Mn removal did not start within this 50 day experiment, both in the virgin sand columns and in the preloaded columns. At the end of the experiment, the various oxidation processes in both the virgin sand and As(III) preloaded columns consumed about 1.6 mg/L O<sub>2</sub>.

From the results depicted in Figure 4.7 it can thus be concluded that preloading sand columns with As(III)-containing drinking water did not influence Fe, Mn, and PO<sub>4</sub> removal, and only mildly accelerated start-up of NH<sub>4</sub> removal. This suggests that the As(III) oxidising biomass did not accelerate NH<sub>4</sub> and Mn(II) removal.

Figure 4.8 depicts the As concentration in the raw groundwater, more than 90% present as As(III), and in the filtrate for both the As(III) preloaded sand columns (top) and virgin sand columns (bottom) over time. As concentration in filtrate is depicted as the sum of the As(III) and As(V) species.





**Figure 4.8** As(III) and As(V) in the filtrate of As(III) preloaded (top) and virgin sand columns (bottom) over time. Filtration velocity 1 m/h and bed height 0.5 m. Initial concentration of the groundwater: Fe 1.4 mg/L; As 13 µg/L (as As(III)) also depicted <•>; PO<sub>4</sub> 0.45 mg/L; Mn 0.04 mg/L; NH<sub>4</sub> 0.62 mg/L. As concentration in the filtrate is depicted as the sum of the As(III) and As(V) species.

The sand columns that were preloaded with As(III), oxidised the 13 µg/L As(III) in the groundwater immediately and consistently during the 50 days experiment. The increased biological activity caused by conversion of other groundwater compounds during the course of the experiment did not hinder the As(III) oxidation in the 0.5 m sand bed (Figure 4.8). The virgin sand columns, which did not contain an As(III) oxidising biomass at the start of the experiment, initially did not show As(III) oxidation. However, complete

oxidation of the 13 µg/L As(III) developed within 23 days (Figure 4.8), suggesting that, even though As(III) concentrations were low compared to the other groundwater constituents, the AsOB were able to maintain their population on the filter sand and oxidise the As(III) in the natural groundwater.

Concerning the actual As removal, three separate stages can be differentiated for both the virgin sand columns and the As(III) preloaded sand columns. The first five days of filtration As(III) oxidation in the virgin sand columns was low and the removal efficiency of As was steady at around 30%. Although complete oxidation in the As(III) preloaded sand columns was achieved throughout the experiment, initially slightly less As was removed compared to the virgin sand columns; potentially caused by As(III) saturation of the sand grain surface during preloading and desorbing the first days of feeding aerated groundwater. From day 5 until 28, biological As(III) oxidation was developed in the virgin sand columns and subsequently increased the As removal efficiency from 30% to 60%, because the produced As(V) has a higher affinity to HFO than As(III) (Bissen and Frimmel, 2003; Gude et al., 2017). After 28 days the As removal became stable at 60% for both columns until the end of the experiment. The similarity of both the As(III) preloaded sand columns and the virgin sand after this period suggests that the biological oxidation potential was fully utilised and a higher As removal, due to adsorption on HFO, could not be expected in the current column design and operation. It is concluded that preloading of As(III) to establish an As(III) oxidising biomass provided only a beneficial effect in the initial weeks of operation, as this positive effect got neutralised by the growth of AsOB on the sand grains in columns without any preloading. Additionally, regarding the gradually increasing removal efficiency after complete oxidation was achieved in the filtrate of virgin sand columns, it is hypothesised that as a consequence, the As(III) concentration profile over the height of the column moved upward to the Fe removal zone in the top of the filter bed, subsequently resulting in a higher As removal.

#### 4.4 Conclusions

It was observed in this study that biological As(III) oxidation quickly developed in rapid sand filter columns fed by drinking water spiked with As(III). With a typical lag and log phase, decreasing As(III) and increasing As(V) concentrations in the effluent of the sand

columns were measured in a timeframe of weeks. The growth of biomass in the sand columns was confirmed with ATP analysis. ATP concentrations on the sand grains increased from 0.7 ng/g to 16, 8 and 2 ng/g filter sand stratified from the top of the sand filter to the bottom, respectively. Therefore it was concluded that AsOB can develop on filter sand in absence of other chemical and biological oxidation processes (e.g. as a results of Fe, NH<sub>4</sub> and Mn presence).

Other experiments, performed with natural groundwater, showed that AsOB were able to grow and survive amidst Fe(II) and NH<sub>4</sub> oxidising processes in filters and prior to Mn(II) removal; complete As(III) oxidation was achieved within 22 days on virgin sand. Additionally, AsOB accumulated in filters by preloading with As(III)-containing drinking water were instantly and consistently capable of oxidising As(III) present in natural groundwater. The overall conclusion of this study is that AsOB are able to grow and maintain their population in rapid sand filters at low As(III) concentrations, either in presence or absence, of other common groundwater bacteria and naturally formed mineral precipitates (e.g. HFO and MnO<sub>2</sub>).

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## 5. As(III) removal in rapid filters: effect of pH, Fe(II)/Fe(III), filtration velocity and media size

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### Abstract

In the top layer of aerated rapid sand filtration systems, uncharged As(III) is biologically converted to charged As(V). Subsequently, the main removal mechanism for As(V) is adsorption onto oxidised, flocculated Fe(III) (hydrous ferric hydroxides; HFO). The aim of this research was to understand the interactions between As and Fe in biologically active rapid filter columns and investigate the effect of different operational modes on Fe removal to subsequently promote As removal. For this purpose, different filter media column experiments were performed using natural, aerated groundwater containing 3.4 µg/l As(III). Results show that independent of the filter media size, complete (biological) conversion of As(III), manganese, ammonium and nitrite was achieved in approximately 70 days. After ripening, enhanced As removal was achieved with a top layer of coarse media or by dosing additional Fe(III). Addition of Fe(II) did not have the same effect on As removal, potentially due to heterogeneous Fe(II) oxidation in the upper layer of the filter, attaching rapidly to the filter grain surface and thereby preventing HFO flocs to penetrate deeper into the bed. Increasing the flow rate from 1 to 4 m/h did not improve As removal and lowering the pH from 8 to 7.4, resulted in an 55% increased removal of dissolved As. Altogether it is concluded that As removal in biologically active rapid sand filters can be improved by applying coarser filter media on top, in combination with dosing Fe(III) and/or pH correction.

### 5.1 Introduction

Arsenic (As) removal is increasingly important when treating groundwater for drinking water production. The World Health Organization (WHO) put in effect a provisional guideline of <10 µg/L on As since 1993, however, As is toxic and can cause adverse health

effects even at concentrations below 10 µg/L (Roh et al., 2017; van Halem et al., 2009; WHO, 2011). Hence, drinking water companies in the Netherlands have decided to investigate the practical implications of distributing drinking water with As concentrations < 1.0 µg/L. In practice, requiring a reduction in the range of 1 - 4 µg/L to below 1 µg/L (Vitens, 2014) in commonly applied aeration - rapid sand filtration systems. At these low concentrations, the challenge for effective As removal is rapid oxidation of As(III) to As(V) before iron (Fe) removal occurs, since As(V) is more effectively adsorbed onto flocculating hydrous ferric oxides (HFO) than As(III) (Bissen and Frimmel, 2003; Gude et al., 2018, 2017, 2016). Both reduced As(III) and Fe(II), react with O<sub>2</sub> to As(V) and Fe(III), respectively. These are the species present at thermodynamic equilibrium in an oxic environment at alkaline pH (Stumm and Morgan, 1996). Unlike Fe(II) oxidation, homogeneous As(III) oxidation by oxygen (O<sub>2</sub>) is sluggish (Driehaus et al., 1995). Kim and Nriagu (2000) observed that in 5 days only 54% of 48 µg/L As(III) in groundwater (pH between 7.6 – 8.5) was oxidised when exposed to air. This oxidation pathway is therefore not relevant for centralised groundwater treatment plants with limited residence times (Gude et al., 2016). Strong oxidants like chlorine, permanganate and ozone gas can instantly oxidise As(III) together with most other reduced constituents in groundwater (Ghurye and Clifford, 2004). However, as an alternative, also biological oxidation of As(III) can be employed. The existence of bacteria that are capable of oxidising As(III) with oxygen (O<sub>2</sub>) has been well documented (Cavalca et al., 2013; Huang, 2014; Oremland and Stolz, 2003; Quéméneur et al., 2008), and their presence in rapid sand filters has been observed (Bai et al., 2016; Corsini et al., 2015; Gude et al., 2018). Despite their usefulness, no extensive research is available on how these As(III) oxidising bacteria in rapid sand filters can be optimally exploited for enhanced As removal.

For Fe(II) oxidation with O<sub>2</sub> in aeration-filtration systems a subdivision is generally made between homogeneous, heterogeneous and biological oxidation (van Beek et al., 2015; Vries et al., 2017). Homogeneous oxidation rate is mainly influenced by pH and O<sub>2</sub> concentration (Stumm and Lee, 1961) and occurs predominantly during aeration and supernatant water storage. Heterogeneous and biological Fe(II) oxidation occur on the surface of filter media in the rapid filter. During heterogeneous Fe(II) oxidation, Fe(II) is adsorbed to Fe oxides (such as HFO) prior to oxidation (Sharma et al., 1999; Wolthoorn et al., 2004). This oxidation rate is similarly governed by pH and O<sub>2</sub> but much faster, since

it is catalysed by Fe oxides (Jones et al., 2014; Tamura et al., 1976). Additionally biological oxidation can occur in the filter bed, becoming more predominant when homogeneous and heterogeneous oxidation are hampered (de Vet et al., 2011; I. A. Katsoyiannis and Zouboulis, 2004).

The aim of this research was to understand the interactions between As and Fe in biologically active rapid filter columns and investigate the effect of different modes of Fe removal to subsequently promote As removal. Filter media size, filtration velocity, supernatant level and pH can greatly affect Fe(II) and HFO removal pathways in rapid sand filters e.g. Sharma et al. (2001) and van Beek et al. (2015), however, to the best of our knowledge, the influence of these design and operational conditions on As removal has not been investigated yet. As(III) in the native groundwater is oxidised in the top layer of biologically active filters (Gude et al., 2016), so As(V) is mainly present in the deeper layers of the filter bed. It is therefore hypothesised that stimulating HFO penetration deeper into the filter bed, with applicable operational and design conditions, will result in more effective As adsorption in filters. Therefore experiments were performed to compare various filter media sizes, Fe(II) and Fe(III) additions, filtration velocity and pH in natural groundwater containing, on average, 3.4 µg/l As(III).

## **5.2 Materials and methods**

### **5.2.1 Groundwater quality**

The research was performed at drinking water production plant Wageningseberg (Vitens N.V.). The tested water has a relative high pH (pH 8.0), contains low concentrations of As (3.4 µg/L), Fe (0.31 mg/L) and ammonium (NH<sub>4</sub><sup>+</sup>) (0.04 mg/L). The manganese (Mn) concentrations were 0.14 mg/L. The groundwater, used for these experiments, was the same as used for regular drinking water production. Therefore, depending on production demand, the number of groundwater wells in operation varied multiple times per day, leading to minor water quality changes as depicted in Table 5.1.

Table 5.1 Groundwater quality water production plant Wageningseberg (Vitens N.V.).

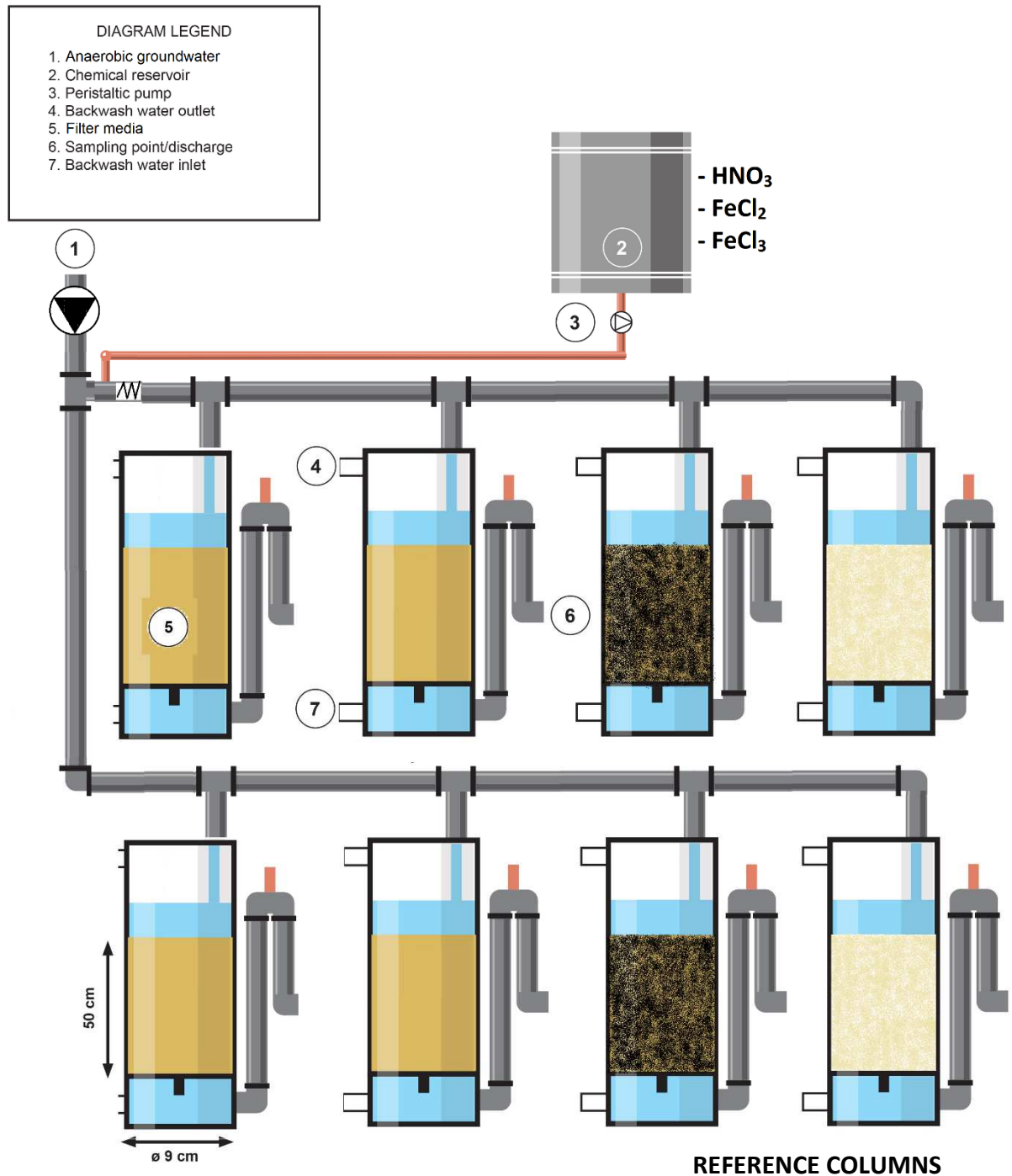
Water quality parameters	Units	average	min	max
Temperature	°C	10.7	10.7	10.7
O <sub>2</sub>	mg/L	0.02	0.01	0.02
ORP	mV	-172	-180	-165
Conductivity	µS/cm	185	185	185
pH	[-]	8.01	7.82	8.08
HCO <sub>3</sub> <sup>-</sup>	mg/L	94.5	85.8	99.7
As	µg/L	3.43	3.08	3.78
Fe	mg/L	0.31	0.25	0.34
Mn	mg/L	0.14	0.13	0.15
Ca	mg/L	29.4	27.5	31.0
Mg	mg/L	2.28	1.89	2.45
NH <sub>4</sub> <sup>+</sup>	mg/L	0.04	0.03	0.06
NO <sub>2</sub> <sup>-</sup>	mg/L	<0.01	<0.01	<0.01
PO <sub>4</sub> <sup>3+</sup>	mg/L	0.13	0.12	0.14
SiO <sub>2</sub>	mg Si /L	5.93	5.56	8.81

### 5.2.2 Experimental column set-up

The experimental set-up consisted of eight columns, with a diameter of 90 mm and a height of 1 m. Four pairs were made by filling duplicate columns with either fine sand, coarse sand, anthracite or pumice at a filter bed height of 50 cm, mainly simulating the upper part of a rapid filter. All variable settings were tested on one of the duplicate columns, whereas the other acted as the reference (Figure 5.1). A fixed pressure of 6 m was obtained by a feed pump in the raw water (Wilo, Yonos PARA 3 - 45W). To ensure a constant, steady flow throughout the experiment the pressure was reduced just before

the individual columns. Before starting the experiment, the columns were >30 min backwashed at  $\pm 30\%$  expansion (15 cm). Backwashing was done with tap water without air scouring.

Aeration of the anaerobic groundwater was achieved by application of a small spray aeration device and cascading the water from 30 cm directly into the supernatant water; resulting in an  $O_2$  concentration of 5 to 6 mg/L. This is half of the  $O_2$  equilibrium concentration at  $10^\circ\text{C}$  ( $\pm 11.8$  mg/L  $O_2$ ), however, the cumulative  $O_2$  demand of the oxidation reactions of As(III), Fe(II), Mn(II) and  $NH_4^+$  is below 0.5 mg/l  $O_2$ . The supernatant water height was set at 1 cm by adjusting the height of the filtrate overflow, directly after backwashing. The default filtration velocity was 1 m/h (6.4 L/h per column). Due to filter clogging the supernatant water in the fine sand columns rose to  $\pm 10$  cm in three to four days; for the other columns no rise in supernatant level was observed in this timeframe. After clogging of the fine sand columns, all columns were backwashed. Throughout the nine months of experiments, the columns were continuously fed with aerated groundwater and were situated at a location deprived from sun and artificial light.



**Figure 5.1** Schematic overview of the filter column set-up, with duplicate columns for fine sand, coarse sand, anthracite and pumice.

### 5.2.3 Experimental settings

All collected data contributed to the assessment of five experiments: (1) biological filter ripening, (2) influence of filter media on Fe and As removal, (3) Fe(II) or Fe(III) addition

in the supernatant water, (4) influence of filtration velocity on Fe and As removal and (5) adjusting the pH in the range of 7.4 to 8.0 thereby varying the time to homogeneously oxidise 90% of the Fe(II) from  $\pm 20$  min to  $\pm 1.5$  min (calculated in PHREEQC with wateq4f.dat), so greatly affecting the mode of Fe removal within the practical pH-range of groundwater treatment. In experiment 1, the column pairs were operated in the same manner and therefore acted as real duplicates. In experiments 3-5, the duplicate filter media columns were operated as single columns. One was used to impose the various settings, while the other column acted as reference to account for the small water quality changes in the raw water. In this set-up, the reference column and the setting column were measured twice in the time span of 3h and averaged. The results could therefore be subjected to the paired t-test for statistical analysis to evaluate whether a significant difference was measured between the reference and the setting columns. Experiment 1, the biological ripening phase, was performed to observe the changing water quality as a result of the accumulation of biomass. As(III),  $\text{NH}_4^+$  and Mn(II) were analysed in the filtrate twice a week at a filtration rate of 1 m/h ( $\pm 10\%$ ). After the ripening period (72 days) and an additional 70 days stable operation was observed in all filter columns. Mn,  $\text{NH}_4^+$  and nitrite ( $\text{NO}_2^-$ ) were converted or removed completely. At this point the other experiments (2-5) were performed. For experiment 2, the influence of filter media on As removal, all measurements of the reference filters were used. 18 measurements over 4 months with the same settings were averaged ( $n=18$ ). When running the other experimental settings (3-5), a stabilisation period of at least two days per setting was used before taking samples (Gude et al., 2016; Jessen et al., 2005), and before every setting the columns were backwashed. After 48 hours runtime, the filtrate of all columns was sampled and analysed.

For experiment 3, on top of the naturally occurring 0.3 mg/L Fe(II), 0.3 and 0.6 mg/L Fe(II) or Fe(III) was added to the feed water of the four columns containing fine sand, coarse sand, anthracite and pumice. In experiment 4, different pH values, between 7.4 and 8.0, were tested by acidifying the raw groundwater with  $\text{HNO}_3$ . Finally, for experiment 5, the filtration velocity was increased to 4 m/h and compared to their reference filters that were kept at a velocity of 1 m/h. To ensure that the biomass was adjusted to the higher flow rate, the filter columns were ripened for an additional 32 days. Duplicates for all settings were obtained by sampling all columns twice within a period of two hours



### 5.2.4 Filter media

Four types of filter media were compared on their ability to remove As; the filter media and their properties are depicted Table 5.2.

**Table 5.2 Properties of filter material used in the column experiments: fine sand, coarse sand, anthracite and pumice. Data obtained from product sheets supplier: Aqua-Techniek B.V.**

	<b>Size</b>	<b>Effective size (d<sub>10</sub>)</b>	<b>Hydraulic size</b>	<b>Mass Density</b>	<b>Porosity</b>
	mm	mm	mm	Kg / m <sup>3</sup>	[-]
<b>Fine sand</b>	0.4 – 0.8	0.47	0.59	2.57	0.35
<b>Coarse sand</b>	1.4 – 2.0	1.51	1.66	2.58	0.39
<b>Anthracite</b>	2.0 – 4.0	2.4	2.8	1.36	0.46
<b>Pumice</b>	2.3 – 3.4	2.51	2.83	2.40	0.80

Filter media were obtained from Aqua-techniek B.V., fine and coarse sand were of 100% natural silica and type 1 according to EN 12904. Anthracite was type III and the pumice was Aqua-Volcano according to EN 12906. Sand and anthracite are non-porous, pumice is (initially) porous (Technical datasheet).

### 5.2.5 Chemicals, Sampling and analytical methods

Fe was obtained from Sigma Aldrich: FeCl<sub>2</sub> • 4H<sub>2</sub>O (99.99%) and FeCl<sub>3</sub> • 6H<sub>2</sub>O (99%). Reagents grade 5M HNO<sub>3</sub> was used to adjust the pH of the columns and to stabilize the Fe(II) and Fe(III) dosing solutions by decreasing the pH to 3. The chemical concentration was adjusted in the reservoir, see Figure 5.1, to obtain the various desired concentrations; the peristaltic pump continuously pumped the chemicals into the supernatant water at a flow rate of 0.9 ml/min (only pH 7.7 was achieved by increasing the pump speed to 1.8 ml/min).

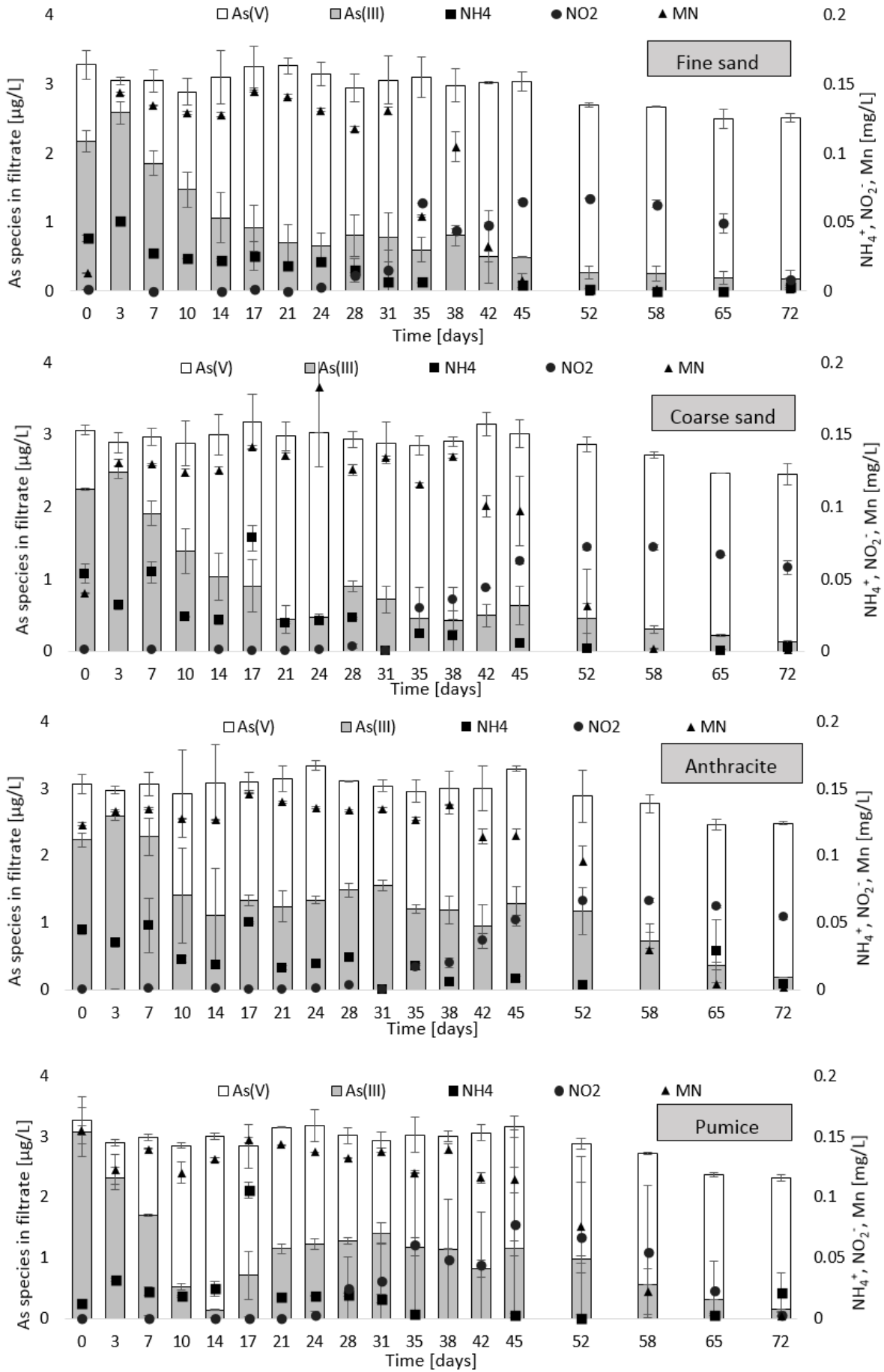
Filtrate was collected in 2L jars that were continuously fed after the overflow to prevent changing the filtration rate while sampling. From these jars, filtered samples (0.45 µm), and unfiltered samples were taken and analysed. After 0.45 µm filtration total Fe concentrations in all samples were < 0.02 mg/L, so the As in these samples can be considered as dissolved As. pH, electrical conductivity (EC) and O<sub>2</sub> were measured with

WTW electrodes (SenTix 940, TerraCon 925 and FDO925, respectively). As, Fe and Mn were analysed with Inductively Coupled Plasma Mass Spectrometry conform NEN-EN-ISO 17294-2. (ICP-MS; Thermo X2-series),  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$  were analysed by a spectrophotometer (Aquakem 250, company: Thermo Scientific). As speciation was done according the Clifford (2006) method. Here, 150 mL sample was passed through an anionic resin (80 mL Amberlite® IRA-400,  $\text{Cl}^-$ ) in a 100-mL syringe. The first 50 mL was always discarded, the remaining 100 mL was collected and analysed using ICP-MS. The charged As(V) species are retained by the resin, and the filtrate from the resin is considered to be only As(III). An additional measurement, without using resin, was done to determine the total As concentration, and the As(V) concentration was determined by subtracting the As(III) concentration from the total As concentration. However, at neutral pH the resin unavoidably retains on average 14% of As(III) (min=7%, max=23%; n=24) (Gude et al., 2018).

## 5.3 Results and discussion

### 5.3.1 Ripening of the filters

In rapid sand filters that treat aerated groundwater without application of strong oxidants like permanganate and chlorine, As(III) is biologically oxidised (Gude et al., 2018; Katsoyiannis and Zouboulis, 2004; Oremland and Stolz, 2003), Mn(II) starts biologically (Bruins et al., 2015) and  $\text{NH}_4^+$  oxidation is solely a biological process (Lee et al., 2014). The processes start to become effective when sufficient biomass has accumulated on the filter media grains during a period of several weeks. Previous work showed that biological As(III) oxidation develops first, followed by  $\text{NH}_4^+$  and Mn(II) (Gude et al., 2018). In the current study, the ripening of the different filter media was monitored for a period of 72 days. The filtrate concentrations of dissolved As(III), As(V),  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  and Mn are depicted in Figure 5.2 for each of the filter media.



**Figure 5.2 As(III) oxidation,  $\text{NH}_4^+$  and Mn removal over time on quartz sand 0.4 -0.8 mm; quartz sand 1.4 - 2.0 mm; anthracite 2.0 - 4.0 mm (Type N/III); pumice 2.3 - 3.4 mm. Filtration velocity of 1 m/h and water temperature was 10.7°C. Error bars represent min and max values of duplicates.**

The biological oxidation processes of As(III),  $\text{NH}_4^+$  and Mn(II) developed sequentially over time. In all columns As(III) oxidation developed first, followed by  $\text{NH}_4^+$  oxidation and thereafter Mn(II) oxidation. Nevertheless, a differentiation between the various filter media can be made on the rate of start-up of the various processes. The biological ripening time was shortest for the fine sand columns and after 72 days all As(III),  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  and Mn was completely converted or removed. On the coarse sand and anthracite, which have a larger grain size and therefore a smaller specific surface area than fine sand, Mn oxidation and removal started about 1-3 weeks later, while nitrification (i.e.  $\text{NO}_2^-$  production) started about 2 weeks later. Measurements (not shown in Figure 5.2) indicated that all columns completely removed and converted all As(III),  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  and Mn after 86 days.

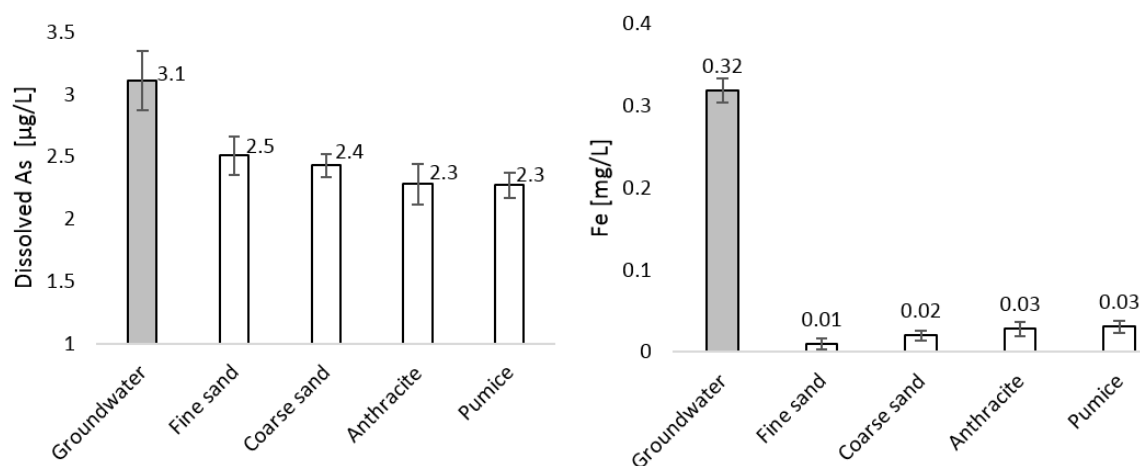
Pumice, with the largest grain size, but with a very high internal porosity, was quickest to establish a biomass to convert As(III) to As(V). However, after 14 days, the steep decline in As(III) concentration was reversed and As(III) concentrations in the filtrate increased again. We visually observed, using a microscope, that in time, pumice becomes covered with mineral deposits, possibly hindering the transport of As(III) to the internal biomass. While not shown in Figure 2, the Fe removal (initial concentration 0.3 mg/L) was instantaneous in all columns and Fe oxides may thus well be responsible for blockage of the internal pores of pumice.

Overall, the filter media with their different sizes, surface areas and shapes had a minor impact on the start-up time of As(III),  $\text{NH}_4^+$  and Mn oxidation. This may be related to the relatively low concentrations of Mn,  $\text{NH}_4^+$  and As(III) in the groundwater, for which only a limited amount of surface would suffice to accommodate the required biomass. This is confirmed by Lee et al. (2014) in Denmark, where Fe, Mn, and  $\text{NH}_4^+$  at similar concentrations were completely removed in the first 50 cm of a sand filter in a pilot experiment. It is expected that when the filter loading increases more surface area is required for the biomass. In addition, the accompanying effect due to frequent

backwashing to remove the higher (Fe) solids load can disrupt immature biofilms and flush loosely attached biomass out of the system (Liu et al., 2012).

### 5.3.2 Influence of ripened filter media on As removal

The major part of removed As in a rapid sand filter is achieved by adsorption of As(V) to HFO (Gude et al., 2016). The HFO originates from naturally present Fe(II) by either homogeneous oxidation in the supernatant or in the pore volume of the filter material, or heterogeneous/ biological oxidation on the surface of the filter grains. The homogeneously formed HFO flocs are subsequently retained in the filter, while, at least part of, the heterogeneous oxidised Fe(II) attaches itself to the filter media grains (de Vet et al., 2011; van Beek et al., 2015; Vries et al., 2017). In this respect, it was hypothesised that different (ripened) filter media sizes (i.e. different surface area and hydraulic pore channel size) perform differently concerning Fe removal and the accompanied As adsorption. Both dissolved As (left) and total Fe (right) concentrations in the filtrate of the columns are depicted in Figure 5.3. The variations per filter media, which are depicted by the error bars, were mostly due to water quality changes during the measuring period of four months.



**Figure 5.3** Average dissolved As (left) and total Fe (right) concentration in the groundwater influent and filtrate of the various ripened filter media in filtration mode. Filtration velocity of 1 m/h, water temperature was 10.7°C and samples taken after  $\pm 48\text{h}$  runtime. Error bars represent standard deviation ( $n=18$ ). Using the paired

**t-test on the As values, chances of being in the same group are  $p < 0.025$  (being significantly different), with exception of comparing anthracite and pumice, they score  $p = 0.85$  (being very similar).**

The removal of Mn,  $\text{NH}_4^+$  and  $\text{NO}_2^-$  was, after ripening, complete and consistent in all columns, As on the other hand varied as a result of the applied filter media. The removal of As was highest for the filter materials with the largest grain sizes. 27%, 27%, 22% and 19% As removal for pumice, anthracite, coarse sand and fine sand respectively. For Fe the opposite was observed, Fe removal was less effective in the columns with larger size filter media grains. The remaining Fe in the filtrate for pumice, anthracite, coarse sand and fine sand was 31, 28, 20 and 10  $\mu\text{g/L}$ , respectively. Consequently less HFO was present in the coarser filter media, however an increased As adsorption was observed. In Table 5.3 the accumulated As and the accumulated Fe present in the filter bed at the moment of sampling are depicted.

**Table 5.3 Accumulated As and Fe after 48h runtime in the fine sand, coarse sand, anthracite and pumice columns (n=18). Filtration velocity 1 m/h, pH 8 and water temperature of 10.7°C.**

	<b>As</b>	<b>Fe</b>	<b>As/Fe</b>
	[mg]	[mg]	[-]
<b>Fine sand</b>	0.190	94.7	2.01E-03
<b>Coarse sand</b>	0.190	91.6	2.08E-03
<b>Anthracite</b>	0.252	89.2	2.82E-03
<b>Pumice</b>	0.249	88.2	2.82E-03

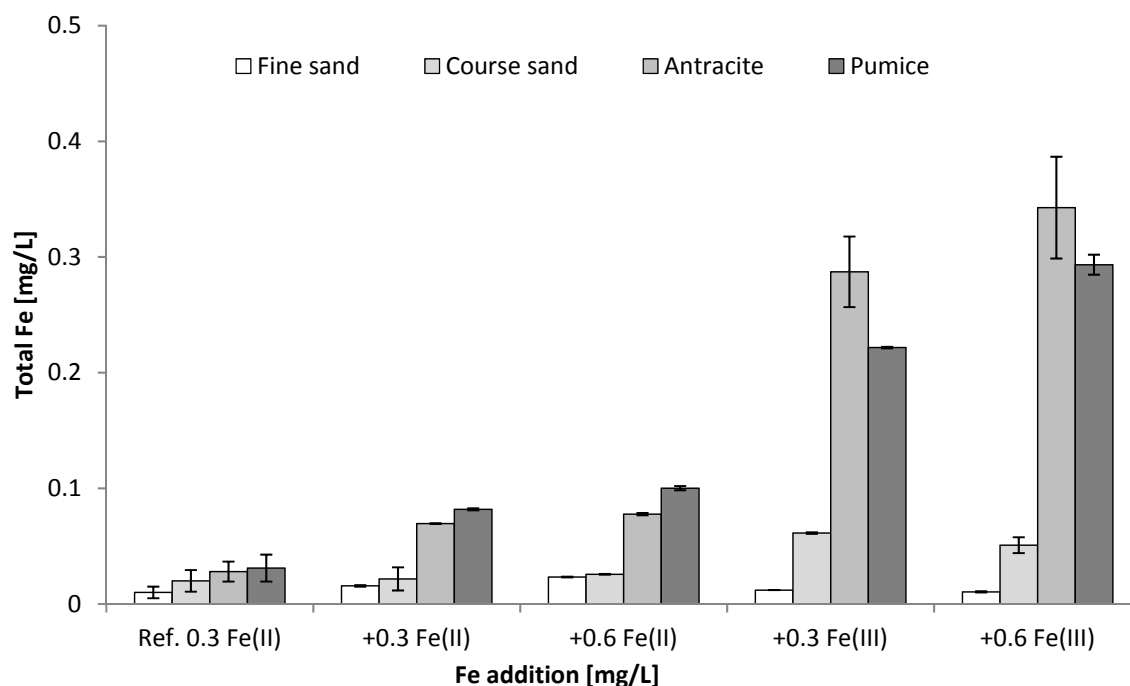
Not only the dissolved As concentrations are lower in the filtrate of the anthracite and pumice columns also the total As is lower. In 48h the accumulated As is highest in the anthracite and pumice columns while least HFO is retained. Hence it is concluded that not only the amount of HFO is important in rapid filtration, the location where the HFO is retained in the filter bed, i.e., height over the filter, is of importance for effective As removal.

The application of different size filter media influences As and Fe removal. A smaller grain diameter results in high available surface area for chemical and biological processes, while a larger diameter results in more deep-bed filtration and subsequently a less

effective particle retention (Moel et al., 2006). Apparently, the positive effect on biological activity by an increased surface area in the fine sand columns is out-competed by the positive effect of deep-bed filtration of Fe in the coarser media columns. The proposed mechanism that larger grain sizes resulted in more effective As removal is that they permit less effective sieving/filtering of formed HFO and the larger hydraulic pore channels of the coarse filter media allows more homogeneous HFO production. Since homogeneous Fe(II) oxidation it is not surface related, it is assumed that the subsequently formed HFO can penetrate deeper in the filter bed.

### 5.3.3 Effect oxidation state of Fe entering the filter bed on As removal

It was shown that by applying filter media with larger grains, more Fe ended up in the filtrate, indicating that HFO penetrated deeper into the filter bed and subsequently adsorbed more As. This positive effect was hypothesised to be related to a higher ratio homogeneous Fe oxidation and flocculation, compared to heterogeneous (surface-related) oxidation within the larger hydraulic pore channels of the coarser material. To investigate the role of Fe oxidation state in the filter bed, different Fe(II) and Fe(III) concentrations were dosed to the influent. Total Fe concentrations in the filtrate of the fine sand, coarse sand, anthracite and pumice columns, after dosing additional Fe, are depicted in Figure 5.4, for 0.3 and 0.6 mg/l Fe(II) and 0.3 and 0.6 mg/L Fe(III) additions.

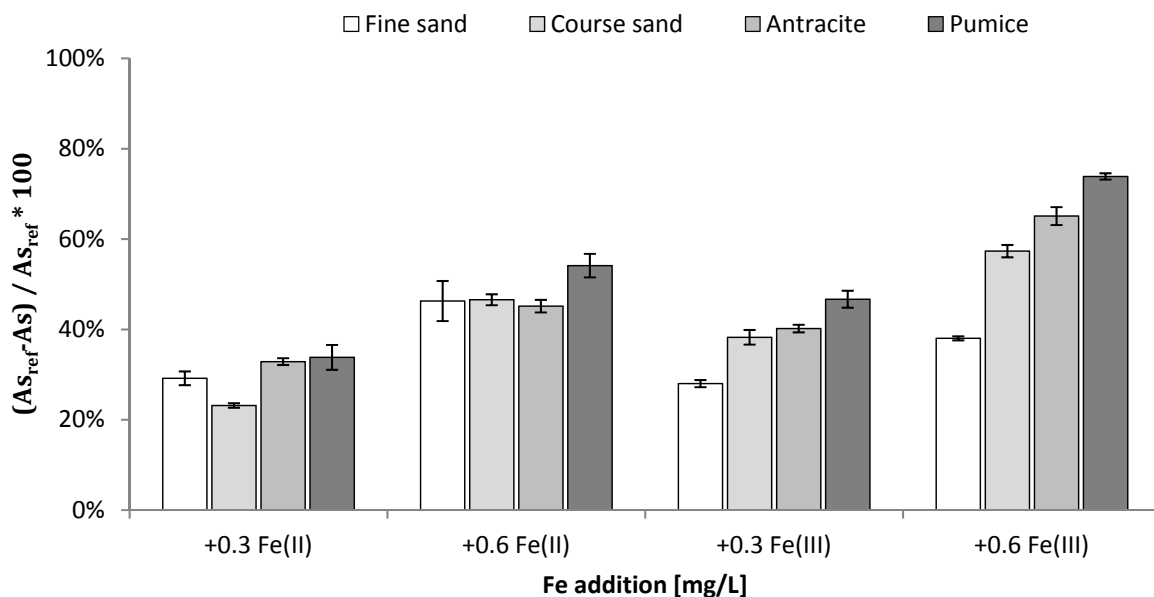


**Figure 5.4 Fe concentrations in filtrate [mg/L] as a result of Fe(II) and Fe(III) additions on top of 0.3 mg/L Fe(II) naturally present in the groundwater. Filtration velocity of 1 m/h, water temperature was 10.7°C and samples taken after ±48h runtime. Error bars represent min and max values of duplicates.**

Addition of either Fe(II) or Fe(III) at the same concentrations resulted in different Fe concentrations in the filtrate. Fe(II) was more effectively retained than Fe(III) in the coarse sand, anthracite and pumice filter columns. Fine sand, on the other hand, removed the additional Fe(III) slightly more effectively than Fe(II). The dosing of 0.3 and 0.6 mg/L Fe(II) resulted in filtrate concentrations of 16 and 23 µg/L versus 12 and 11 µg/L for Fe(III). Apparently, confirmed by the strongest increase in pressure drop, the Fe(III) blocked the pores in the top layer of the fine sand column, increasing Fe(III) removal efficiency also observed by Sharma et al. (2001) where 4 times more head loss was occurred in fine media compared to coarse media during Fe floc filtration. The other media did not remove Fe(III) better than Fe(II). Clearly the larger hydraulic pore channels in the coarse filter media retained less HFO flocs (originating from the Fe(III)), ending up deeper in the filter bed and ultimately in the filtrate. Similarly for Fe(II), the grain size determined the Fe removal efficiency, however, the removal efficiencies were more in the same range. Apparently Fe(II) is more efficiency removed in coarse filters than Fe(III), probably due to the surface related heterogeneous Fe(II) oxidation which does not occur when Fe(III) is dosed. Sharma et al. (2001) also observed decreased Fe concentrations in the filtrate when comparing adsorptive Fe(II) removal compared to floc filtration. Altogether is concluded that heterogeneously oxidised Fe(II), especially in media with larger grain size, was more effectively removed than homogeneous Fe(II) oxidation prior to filtration (simulated by Fe(III) addition in the feed water).

Figure 5.5 depicts the decrease of dissolved As in the filtrate as a result of Fe(II) and Fe(III) additions; this decrease was calculated by using the dissolved As values:  $(As_{ref} - As) / As_{ref} * 100$ .





**Figure 5.5** Effect of 0.3 and 0.6 mg/L Fe(II) and Fe(III) additions on dissolved As concentration in filtrate. Results depicted as percentage of additional dissolved As removal with respect to their reference column. Filtration velocity of 1 m/h, water temperature was 10.7°C and samples taken after  $\pm 48$ h runtime. Error bars represent min and max values of duplicates.

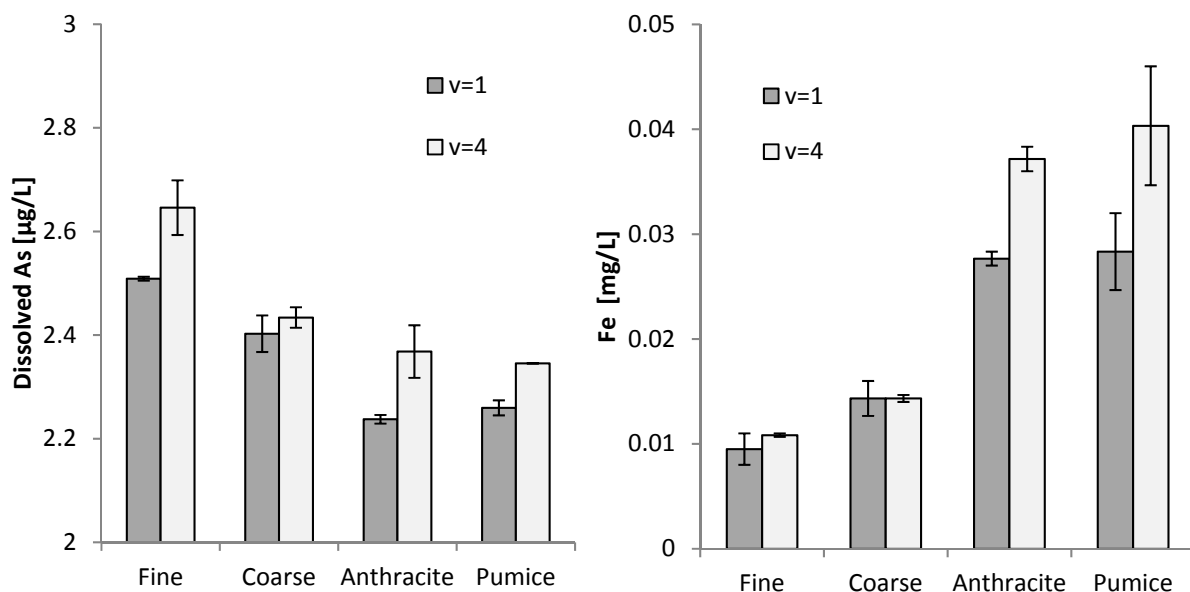
As a result of adding 0.3 mg/L Fe(III), dissolved As was decreased by 28% 38% 40% and 46% for fine sand, coarse sand, anthracite and pumice respectively. Addition of 0.6 mg/L Fe(III) resulted even in higher adsorption of dissolved As: 28%, 57%, 65% and 74% also fine sand, coarse sand, anthracite and pumice respectively. For Fe(II), dissolved As adsorption was lower: 29%, 23%, 33% and 34% for fine sand, coarse sand, anthracite and pumice respectively, when adding 0.3 mg/L Fe(II) and 46%, 47%, 45% and 54% when adding 0.6 Fe(II). For all filter media, except fine sand, the addition of Fe(III) thus resulted in a larger decrease in dissolved As than the addition of Fe(II). Confirming the hypothesis that more As is adsorbed in rapid filters when Fe(II) is oxidised prior to filtration or in the pore channels. In addition, the better retention of Fe(II) - compared to Fe(III) resulted in more HFO accumulation during a filter run, however, this did not attribute to increased As removal. Calculating the As/HFO ratio that was retained in the filter during the run time it was found that both the Fe(II) and Fe(III) additions, the As/Fe ratio in the filter bed increased with the filter media size (fine sand < course sand < anthracite < pumice). Indicating that the filter media that retained the least amount of HFO, most effectively

adsorbed As. The data suggest that application of a dual layer filter with coarse media in the top to effectively adsorb As to HFO and fine media in the bottom to retain the As-HFO flocs would result in maximum As removal.

Possible explanations for the lower effectivity of reducing the dissolved As concentrations by Fe(II) compared to Fe(III) are, (1) Fe(II) oxidises (partly) on the grain surface and is removed rapidly in the top layer of the filter bed (Mettler et al., 2009; Tamura et al., 1976; Vries et al., 2017), preventing it to reach deeper layers for As(V) adsorption (Sharma et al., 2001; van Beek et al., 2015), and/or (2) heterogeneous oxidation results in less available sites for surface complexation, lowering the adsorption capacity of the HFO – comparable to HFO formed through Fe(II) oxidation by MnO<sub>2</sub> (Gude et al. 2017) and/or (3) that the Fe minerals form a mineral layer on top of As-oxidising biofilm or taking available surface, hindering As(III) oxidation.

### 5.3.4 Influence of filtration velocity on As removal

Increasing the filtration velocity can be an alternative method to force HFO deeper into the filter bed, as it, among other mechanisms, increases the hydraulic shear forces within the pore channels. On the other hand biological As(III) oxidation may occur deeper in the filter bed as well. Figure 5.6 depicts the total Fe and dissolved As concentration in the filtrate of the fine sand, coarse sand, anthracite and pumice columns at 1 m/h and 4 m/h.



**Figure 5.6 Average dissolved As concentrations in the filtrate after 0.45  $\mu\text{m}$  filtration (left) and total Fe concentration in the filtrate (right) at 1 m/h and 4 m/h in the fine sand, coarse sand, anthracite and pumice columns. Water temperature was 10.7°C and samples taken after  $\pm 48\text{h}$  runtime. Error bars represent min and max values of duplicates. The paired t-test results ranging from  $0.1 > p > 0.3$  indicating no significant change ( $p > 0.05$ ) in As concentrations for the two filtration velocities**

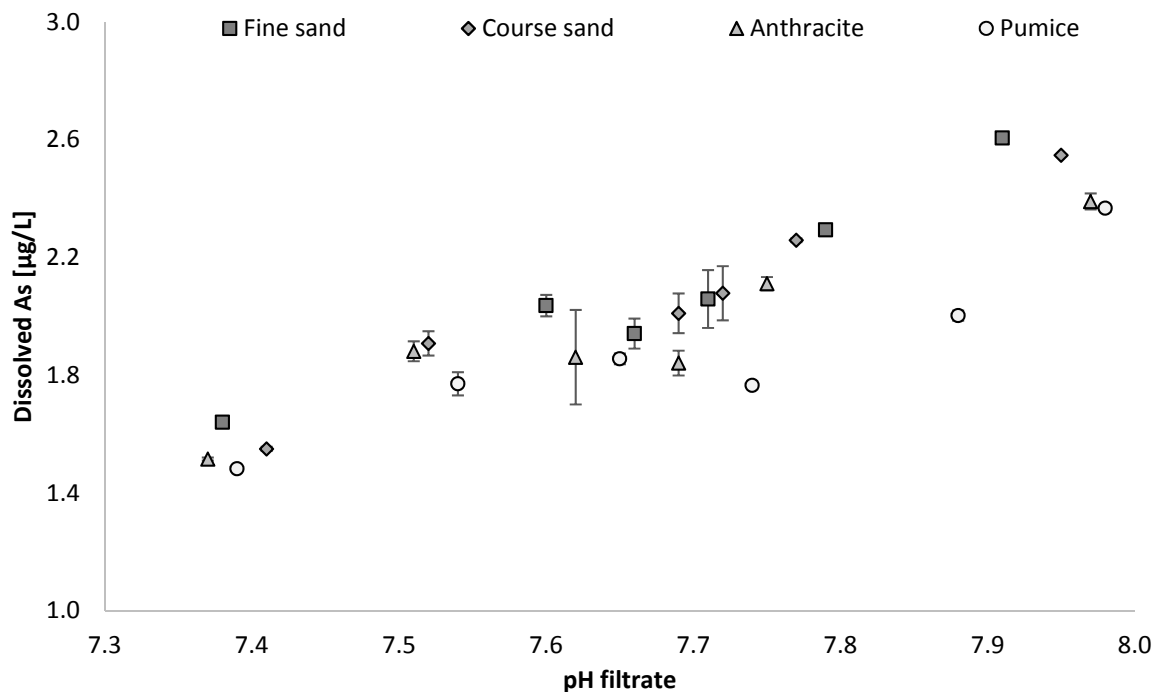
There were basically no changes in Fe concentrations in the filtrate of the fine and coarse sand filters, when increasing the filtration velocity from 1 m/h to 4 m/h. Only in the anthracite and pumice columns an increase of 10  $\mu\text{g/L}$  Fe was observed in the filtrate, and instead of improving the As removal, the concentration in the filtrate went up. Modestly however, with 5%, 1%, 6% and 4% for fine sand, coarse sand, anthracite and pumice respectively. These results show that by increasing filtration velocity, As adsorption to HFO is slightly decreased. However, the removal was not significantly reduced in the columns with increased filtration velocity (t-test  $p > 0.05$ ).

It seems that the strictly surface-related biological As(III) oxidation is differently affected by increased filtration velocity than HFO formation. Together this resulted in a negative effect on As removal, which is in line with the general finding that Fe(II) oxidation prior to filtration is beneficial for As removal. At increased filter loading, the residence time in the supernatant level is shortened which should result in increased Fe(II) in the filter bed and a subsequent negative effect on As removal. Additionally, the increased filtration velocity results in a factor 4 higher Reynold numbers (e.g. pumice from 1.2 to 4.7; Tchobanoglous et al., 2003). More turbulence within the hydraulic pore channels may have accelerated the transport of Fe(II) to the grain surface and increased the chance for heterogeneous oxidation at the grain surface. In addition, the surface related mineral formation may have competed with biological As(III) oxidation for the available surface. Building on observations concerning  $\text{NH}_4^+$  by (Lee et al., (2014) where increased loading of a rapid sand filter did not result in additional oxidation of  $\text{NH}_4^+$ .

The complexity and amount of processes involved make it difficult to draw a general conclusion on the observations shown in Figure 6. However, it is clear that by simply increasing the filtration velocity to bring HFO deeper in the filter bed the As removal will not be enhanced. The complexity and amount of processes involved make it difficult to draw a general conclusion on the observations shown in Figure 6. However, it is clear that simply increasing the filtration velocity to bring HFO deeper in the filter bed increasing As removal is not true.

### 5.3.5 Influence of pH on As removal

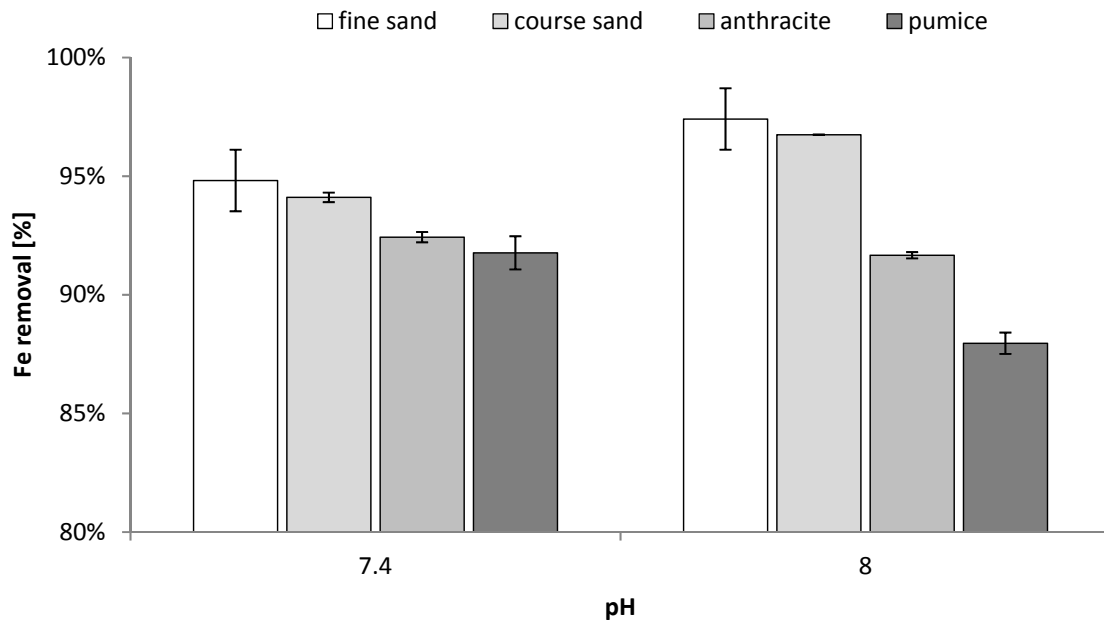
Lowering the pH decreases the rate of Fe(II) oxidation, both homogeneous (Stumm and Lee, 1961) and heterogeneous (Tamura et al., 1976), and could potentially cause Fe to penetrate deeper in the filter bed. Additionally, HFO has a higher adsorption capacity for As(V) at lower pH (Dixit and Hering, 2003; Dzombak and Morel, 1990; Gude et al., 2016), suggesting that As(V) adsorption can be increased at lower pH values after As(III) is oxidised. Influence of pH was investigated at a pH range of 7.4 to 8.0 which is not an uncommon pH for groundwater treatment. The dissolved As concentration in the filtrate as a function of pH for the investigated filter media is depicted in Figure 5.7.



**Figure 5.7** Effect of pH on dissolved As in the filtrate of fine sand, coarse sand, anthracite and pumice columns. Filtration velocity of 1 m/h, water temperature 10.7°C and samples taken after ±48h runtime. Error bars represent min and max values of duplicates.

The results show that in the investigated pH range, the dissolved As in the filtrate decreased as the pH decreased for all filter media. Dissolved As concentrations decreased from 2.40 – 2.60 µg/L at pH 8.0 to 1.50 – 1.65 µg/L at pH 7.4, respectively. This corresponds to a decrease in dissolved As of 15% to 55%. Pumice exceptional As removal performance at the measurement intervals >pH 7.7 is probably caused by a greater ‘pool’ of retained HFO in the filter bed from previous runs, which provide (temporarily) additional sorption sites while lowering the pH, analogue to observations in Gude et al.

(2016) where HFO showed increased sorption capacity at lower pH. Figure 5.8 depicts the corresponding Fe removal percentage in the fine sand, coarse sand, anthracite and pumice for pH 7.4 and 8.0.



**Figure 5.8** Fe removal efficiency shown for pH 7.4 and 8 in fine sand, coarse sand, anthracite and pumice filtrate. Filtration velocity 1m/h. Error bars represent min and max values of duplicates.

Anthracite and pumice, the coarsest filter media, showed improved Fe removal: from 91% and 88% at pH 8 to 93% to 92% at pH 7.4, respectively. While for the fine and coarse sand filters, Fe removal efficiency dropped from about 97 to 94%. Given that floc filtration is not so effective while using large grain sizes the increased removal can perhaps be explained by a switch to adsorptive removal which was also observed by (Sharma et al., 2001). In itself, this shift to surface-related, heterogeneous oxidation was observed not be beneficiary for As removal – as observed in the prior experiments with Fe(II) additions – however, when reducing the pH also heterogeneous Fe oxidation rate is reduced (Jones et al., 2014; Tamura et al., 1980). Additionally, substantial increase in adsorption capacity of HFO for As(V) was found at lower pH (Dixit and Hering, 2003; Gude et al., 2016; Mercer and Tobiason, 2008; Qiao et al., 2012). Hence, HFO formation may have occurred deeper in the filter bed where biological As(III) oxidation was complete and the adsorption capacity would have been increased due to favourable charge conditions.

## 5.4 Conclusions

The research aimed at promoting As removal by understanding its interaction with Fe(II) and HFO in the filter bed. For this purpose the effect of filter media size, pH, Fe(II) and Fe(III) additions and filtration velocity were investigated in natural groundwater filter columns. Based on the presented research it may be concluded that biological As(III) oxidation developed in filter columns, independent of the applied filter media (fine sand, coarse sand, anthracite or pumice), with a slightly faster ripening for media with a finer grain size or larger internal porosity (pumice). After ripening, enhanced As removal was achieved with a layer of coarser media or by dosing additional Fe(III), promoting HFO flocs to penetrate deeper into the bed, which was observed by higher Fe concentrations in the filtrate. Apparently, Fe(II) oxidation prior to rapid filtration is beneficial to As(III) removal. This was confirmed by increasing the flow rate from 1 to 4 m/h, where As removal was not improved, although HFO flocs were 'pushed' deeper in the filter bed. Lowering the pH in the range of 7.4 – 8.0 resulted in a positive effect on As removal. Possibly due to slowing the Fe removal rate and the advantageous adsorption capacity of HFO at lower pH. Altogether it is concluded that As removal in biologically active rapid sand filters can be improved by applying coarser filter media, in the top of the filter bed, in combination with dosing of Fe(III) and/or pH correction.

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## 6. Effect of supernatant water level on As removal in biological rapid sand filters

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### Abstract

Current groundwater treatment facilities, mostly relying on aeration-filtration configurations, aim at the removal of iron (Fe), ammonia (NH<sub>4</sub>) and manganese (Mn). However, recently water companies expressed the ambition to also reduce arsenic (As) concentrations in these rapid sand filters. The aim of this study was to investigate the effect of the Fe oxidation state entering a biological filter bed on As removal. By varying supernatant water level, either Fe(II) or Fe(III) in the form of hydrous ferric oxides (HFO) could be stimulated to enter the filter bed at alkaline groundwater pH (7.6). The experimental pilot column filters showed that once the As(III) oxidation stabilised in the top layer of the filter sand, As removal reached its maximum ( $\pm 75\%$  at 120 cm supernatant level and 1.5 m/h filtration velocity). The increase in supernatant level from 5 to 120 cm resulted in additional HFO production prior to rapid filtration (1.5, 5 and 10 m/h), i.e. homogeneous Fe(II) oxidation and flocculation, and subsequently, HFO ending up deeper into the filter bed (120 cm filter depth). At a low supernatant water level of 5 cm, Fe(II) oxidised heterogeneously and was removed within the top 20 cm of the filter bed. Consequently, filters with high supernatant levels removed As to lower levels (by 20%) than in filters with low supernatant water levels. The benefits of Fe(II) oxidation prior to filtration for As removal was confirmed by comparing Fe(III) to Fe(II) additions in the supernatant water or in the filter bed. Overall it is concluded that in biological groundwater filters, the combination of a higher supernatant level and/or Fe(III) addition with biological As(III) oxidation in the top of the filter bed promotes As removal.

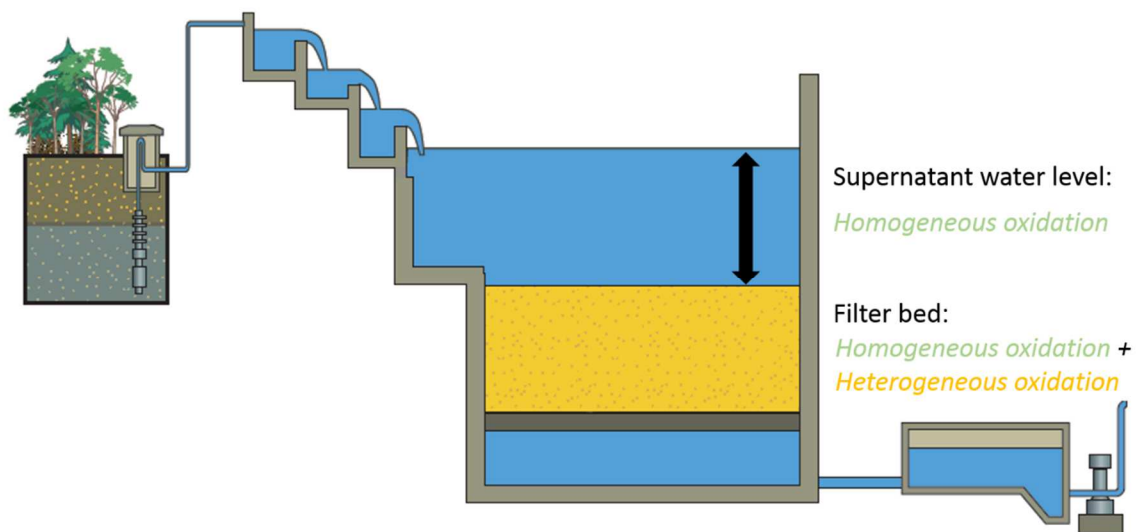
### 6.1 Introduction

Current groundwater treatment facilities, mostly relying on aeration-filtration configurations, aim at the removal of iron (Fe), ammonia (NH<sub>4</sub>) and manganese (Mn).

However, recently water companies have expressed the ambition to reduce arsenic (As) concentrations to below 1 µg/L, to exclude potential undesired health effects (Middleton et al., 2016; van Halem et al., 2009; WHO, 2011). In Belgium and the Netherlands As levels in groundwater are generally low (<10 µg/L), though at some pumping stations concentrations as high as ±70 µg/L are observed. As a consequence, the existing drinking water treatment infrastructure, frequently in good condition, needs upgrading for the removal of several µg As/L. For water companies, optimisation of existing treatment processes for As removal is preferred over implementation of new treatment steps (e.g., adsorbents, membrane filtration) or introduction of invasive chemicals (e.g., strong oxidants).

In groundwater filters, rapid oxidation of As(III) to As(V) is crucial for efficient As removal. Previous research has found As(III) oxidation to occur in the top of the filter bed (Bissen and Frimmel, 2003; Gude et al., 2016), facilitated by bacteria (Gude et al., 2018a; Katsoyiannis et al., 2004). The oxidised As(V) is subsequently removed by adsorption onto hydrous ferric oxides (HFO) that originate from oxidised and subsequently flocculated or adsorbed Fe(II) (Dixit and Hering, 2003; Gude et al., 2017; Sharma et al., 2001; van Beek et al., 2015). HFO is either produced in the supernatant water or in the filter bed which is determined to a large extent by the supernatant water level (SWL), but also on water quality (e.g., pH), filter design (e.g., filter material) and operational conditions (e.g., flow rate) (Stumm and Lee, 1961; Vries et al., 2017). Therefore, the aim of this study was to investigate the effect of the Fe oxidation state, entering the biological filter bed, on As removal. The Fe oxidation state, entering the filter bed, can be controlled by adjusting the SWL. The supernatant water can be regarded as a completely stirred tank reactor (Vries et al., 2017), therefore the major difference between high and low SWL is residence time of the aerated groundwater. Mn(II), NH<sub>4</sub> and As(III) do not homogeneously oxidise in the timespan of one hour (Diem and Stumm, 1984; Kim and Nriagu, 2000; Tatari et al., 2016), which can be considered the practical maximum residence time, however, depending on O<sub>2</sub> concentrations and pH part of the Fe(II) will homogeneously oxidise and form HFO flocs (de Ridder and van Halem, 2017; Sharma et al., 2001; Stumm and Lee, 1961). The produced HFO typically adsorbs about 20-40% As(III) depending on, among other parameters, As/Fe ratio and residence time (Dixit and Hering, 2003; Gude et al., 2017, 2016; Qiao et al., 2012). The Fe(II) that reaches the filter bed can heterogeneously

(or at pH <7.5 partly biologically (de Vet et al., 2011)) oxidise on the filter grains. Kinetics of heterogeneous Fe(II) oxidation are faster than homogenous (Tamura et al., 1980), the HFO formed is less voluminous and causes less filter resistance than HFO floc-filtration (Sharma et al., 2001) and could have a lower sorption site density, as was observed by Dixit and Hering (2003) for different Fe oxides minerals (HFO, Goethite and Magnetite), where the site density on the mineral surface increased as the density of the mineral decreased. Analogous to observations by Senn et al. (2018) where aging HFO at 40°C caused a release of As(V).



**Figure 6.1** Groundwater treatment: abstraction, followed by aeration and rapid filtration. Increasing the supernatant level, increases the amount of HFO entering the filter bed by lengthening residence time in the SWL.

Impact of SWL on the oxidation can only be expected at alkaline groundwater pH which guarantee a sufficiently high homogeneous Fe(II) oxidation rate. To test the effect of SWL, and thus the Fe oxidation state, on the removal of As during rapid sand filtration, two pilot scale sand columns with a filter bed height of 1.4 m were operated for a period of nine months. The filter columns were fed with aerated, natural alkaline ( $\pm$ pH 7.6) groundwater, containing 13  $\mu\text{g/L}$  As(III), 2 mg/L Fe(II), 0.6 mg/L  $\text{NH}_4$  and 20  $\mu\text{g/L}$  Mn(II). One column was operated with high (>1 m) SWL while the other was operated with low SWL (<0.05 m). In addition, to have a direct comparison on the influence of either Fe(III) or Fe(II) entering the filter bed on the removal of As(III), an experiment was included by dosing 1 mg/L Fe(II) or Fe(III) at equal SWL. To observe As(III) oxidation and Fe/HFO

mobility in the filter bed, water samples were measured over the height of the filter bed, during start-up of the sand filters (i.e. ripening) as well as during stable operation.

## 6.2 Materials and methods

### 6.2.1 Groundwater quality

The pilot experiments were performed at drinking water production plant Hoogstraten in Belgium (Pidpa). The groundwater quality is depicted in Table 6.1.

Table 6.1 Groundwater quality Hoogstraten and feed water of the column experiment.

Water quality parameters	Units	Avr.	Min.	Max.
Temperature	°C	11.7	10.5	12.8
O <sub>2</sub>	mg/L	<0.01	<0.01	<0.01
ORP	mV	-129	-188	-61
EC	µS/cm	406	386	432
pH	[-]	7.56	7.45	7.70
HCO <sub>3</sub>	mg/L	225	214	229
As	µg/L	12.5	8.3	15.0
Fe	mg/L	1.97	0.89	2.27
Mn	µg/L	17.7	11.9	25.9
Ca	mg/L	69.3	65.6	75.3
Mg	mg/L	5.2	4.6	5.8
NH <sub>4</sub>	mg/L	0.68	0.62	0.74
PO <sub>4</sub>	µg/L P	257	248	283
SiO <sub>2</sub>	mg/L	23.0	22.1	23.9

### 6.2.2 Experimental column set-up

The experimental set-up consisted of two columns with a diameter of 300 mm (Figure 6.2). Both columns were filled with sand to 140 cm bed height, where one column was 2 m in height and one column was 3 m in height to allow for a high SWL. For equal flow

distribution and spray aeration, raw groundwater was increased in pressure with a centrifugal pump at the intake and manually set (reduced in pressure) to the desired flow just before the columns. Aeration was achieved by spraying in the columns with a fall height of 30 cm into the supernatant water, resulting in an average dissolved oxygen (DO) concentration of 6.6 mg/L with a standard deviation of 1.1 mg/L. The calculated DO demand of the Fe(II), Mn(II),  $\text{NH}_4^+$  and As(III) combined is 2.78 mg/L  $\text{O}_2$ . The additional 1 mg/L Fe(II) adds 0.14 mg/L, making the total DO demand 2.92 mg/L  $\text{O}_2$ . The applied aeration sufficed to ensure oxic conditions in the filter bed. The SWL was maintained constant throughout the runtime with a control valve compensating for the increased pressure drop due to clogging of the filter bed. The columns were filled with 1.4 m quartz filter sand of size 0.70 – 1.25 mm. Before starting the experiment the columns were intensively backwashed with tap water to remove all fines. Over the course of the experiment the filtrate of the columns was collected and used as backwash water. Throughout the seven months experiment, the columns were continuously fed with aerated groundwater and were situated in a location deprived of (sun)light.

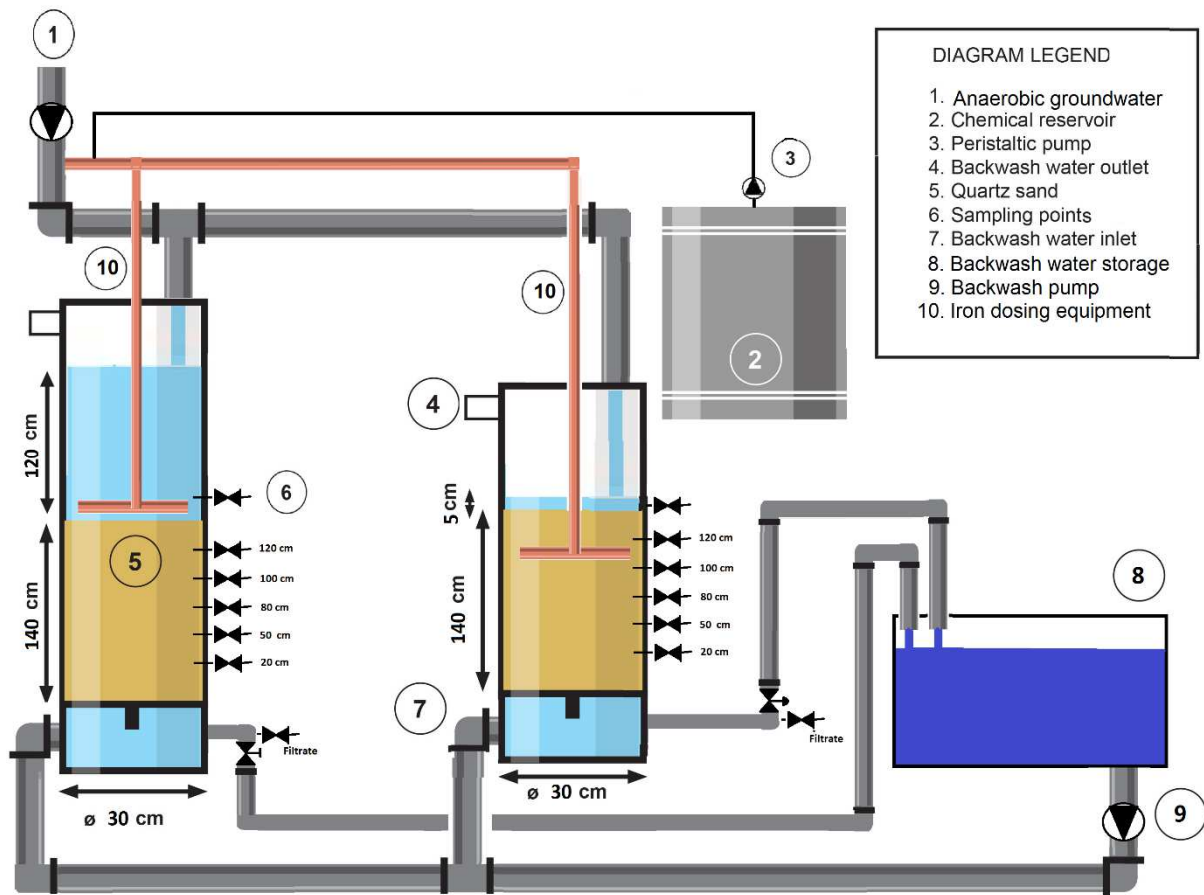




Figure 6.2 Schematic overview of the filter column set-up including sample points over the height of the filter bed. Fe(II)/Fe(III) dosing equipment was installed only for specific experiments.

### 6.2.3 Experimental conditions

Table 6.2 Experimental overview

Period	Filtration velocity	SWL column 1	SWL column 2	Experiment
[week]	[m/h]	[m]	[m]	
1-9	1.5	0.05	1.20	Biological ripening
10-13	5	0.05	1.20	Flowrate increase to 5 m/h
14-19	10	0.05	1.20	Flowrate increase to 10 m/h
20	5	0.05	1.20	Flowrate return to 5 m/h
21	1.5	0.05	1.20	Flowrate reduction to 1.5 m/h
22	5	0.5	0.5	Stable operation at equal SWL
26	5	0.5	0.5	1 mg/L Fe(II) addition in filter bed (column 1) and supernatant (column 2)
27	5	0.5	0.5	1 mg/L Fe(III) addition in filter bed (column 1) and supernatant (column 2)
30	5	0.5	0.5	Disinfection with Cl <sub>2</sub>

The experiment started with virgin sand, which was ripened with aerated groundwater for nine weeks at a velocity of 1.5 m/h with 5 cm SWL and 120 cm SWL for column 1 and 2, respectively. Once the biological processes sufficiently progressed (only Mn was not completely removed), the filtration velocity was increased. The first three weeks to 5 m/h and the subsequent four weeks it was increased to 10 m/h. Afterwards the filtration velocity was set back to 5 m/h and subsequently reduced to 1.5 m/h. For a complete overview of the experimental conditions is referred to Table 6.2. In week 22, the SWL was set to 50 cm in both columns for a period of three weeks to stabilise conditions in both

columns. At this point two identical PVC Fe(II)/Fe(III) dosing unit were installed. The outlet of the first was installed in the top of the filter bed of column 1, at a depth of 30 cm (Figure 2) and the second in the SWL of column 2. 10% of the anaerobic groundwater was pumped through the dosing units, right before the centrifugal pump the FeCl was dosed with a peristaltic pump (Watson marlow U120) to ensure proper mixing. Successively, 1 mg/L Fe(II) was dosed in the filter bed in column 1 and 1 mg/L Fe(II) in the SWL of column 2. Samples throughout the complete installation were taken at 3 and 7 days of chemical injection and were averaged. The same experiment was repeated for Fe(III) dosing. Finally the columns were disinfected to confirm the biological nature of the processes by pumping chlorinated water of 1.5 times the reactor volume into the columns and allowed a reaction time of 24 h. After 24 h, the columns were backwashed and operated as before.

#### 6.2.4 Chemicals, sampling and analytical methods

Fe was obtained from Sigma Aldrich: FeCl<sub>2</sub> • 4H<sub>2</sub>O, mw 198.81 g/mol (99.99%) and FeCl<sub>3</sub> • 6H<sub>2</sub>O mw 270.30 g/mol (99%). 15% stock solution NaOCl was diluted to 150 mg/L with drinking water. 10% of the anoxic main flow was diverted and injected with the undiluted FeCl<sub>2</sub>/FeCl<sub>3</sub>. The chemicals were continuously pumped into a PVC dosing unit placed just above the filter bed in the supernatant water and at 30 cm depth (from the top) in the sand bed. The dosing unit consisted of a cross with 5 small holes per arm to enhance the mixing of the Fe. The default sample frequency was once per week and while sampling the sample-water flow remained always below 10% of the main flow to prevent large changes in filtration velocity. Samples were processed via three methods: (1) untreated, (2) filtered over 0.45 µm, and (3) filtered over 0.45 µm and anionic resin for the purpose of As speciation.

As speciation was done according the method proposed by Clifford (2006). Here, 150 mL sample is passed through an anionic resin (80 mL Amberlite® IRA-400 chlorite form resin in a 100-mL syringe) that retains only the charged As(V) species. The filtrate from the resin is considered to be As(III). As(V) is then calculated by subtracting As(III) from the measured total As concentration. The first 50 mL was always discarded, the remaining 100 mL was collected and analysed using Inductively Coupled Plasma Mass Spectrometry

(ICP-MS). This is considered to be a robust method, however, at neutral pH the resin unavoidably retains 14% of As(III) (min=7%, max=23%; n=24) (Gude et al., 2018a), which was not compensated for in the Figures. pH, electrical conductivity (EC) and O<sub>2</sub> were measured with WTW electrodes (SenTix 940, TerraCon 925 and FDO925).

Determination of total iron concentration was performed spectrophotometrically by the phenanthroline method (American Public Health Association 1985). As, Mn and P were analysed with ICP-MS (type XSeries2 van Thermo Scientific), while NH<sub>4</sub>, NO<sub>2</sub>, NO<sub>3</sub> were analysed by a discrete analyser spectrophotometry (Aquakem 250, company: Thermo Scientific).

## **6.3 Results and discussion**

### **6.3.1 Biological ripening of As(III), Mn(II) and NH<sub>4</sub>**

In Figure 6.3, the speciation of the dissolved As in the two filter columns with different SWL is depicted in the supernatant water and over the height of the filter bed at day 1, 8, 15 and 36.

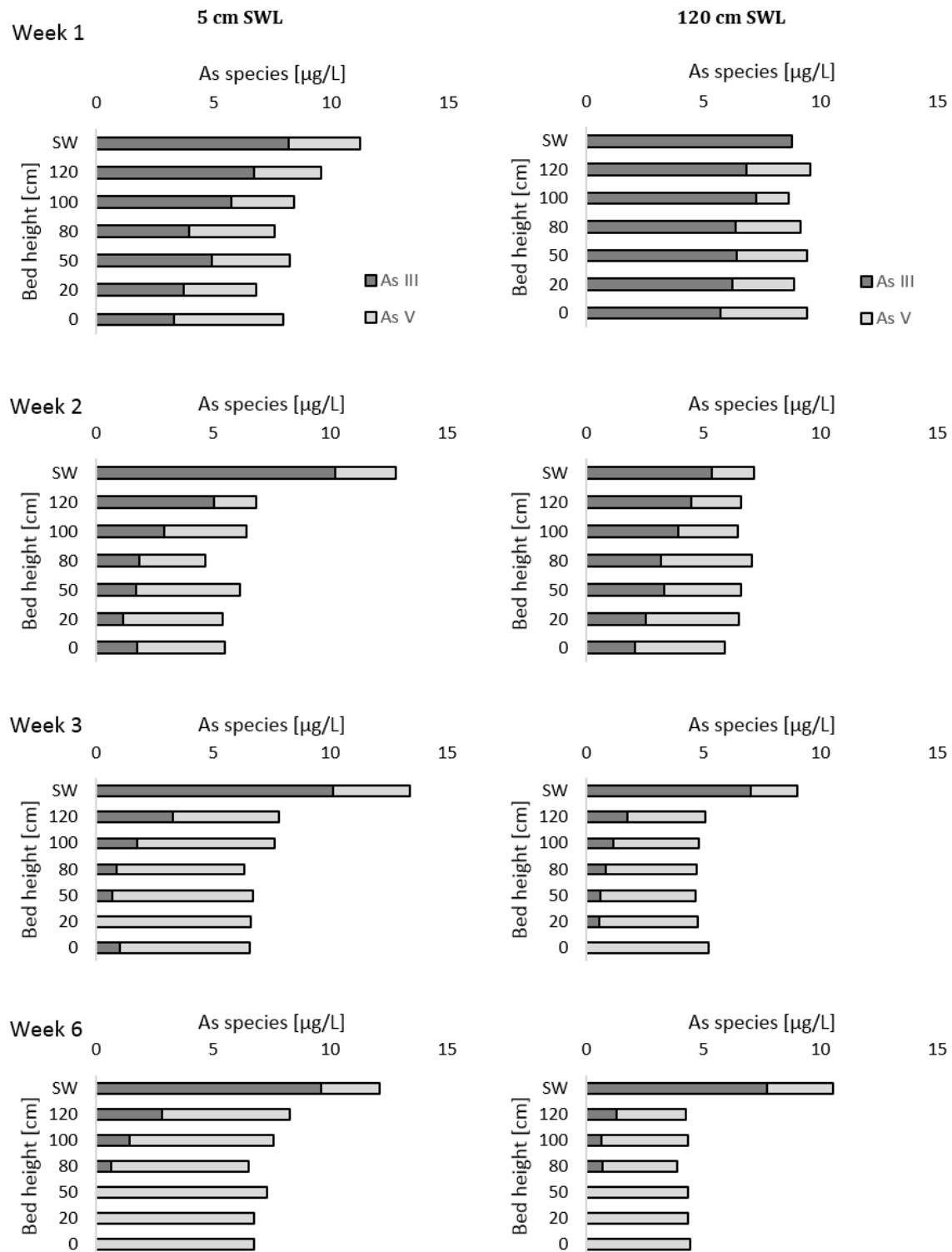


Figure 6.3 As(III) and As(V) speciation of dissolved As over the filter bed height for 5cm SWL (left) and 120cm SWL (right) with filtration velocity of 1.5 [m/h] for day 1, 8, 15, 36

The gradually increased As(V) concentrations over the filter bed profile illustrates the onset of biological As(III) oxidation. After 36 days, before  $\text{NH}_4^+$  and Mn started (Figure 4), As in the filtrate was completely in the As(V) form, both in the 5 and 120cm SWL columns.

Over the first 5 weeks, the As(III) conversion gradually moved upwards in the filter bed, as a result of filter ripening. This process only slowed down until the major part was oxidised in the top 20 cm of the filter bed. While As(III) oxidation occurred higher in the filter bed, total As removal efficiencies increased in the filtrate. It was observed that even though within 2-3 weeks complete oxidation was achieved in the filtrate, the removal efficiency in the 120 cm SWL column gradually increased until week 5-6. Apparently, the biological As(III) oxidation occurring in the top of the filter bed contributes to increased As removal.

Apart from As(III) conversion, other biological processes also started in the ripening stage of groundwater filters. The  $\text{NH}_4$  and Mn concentration profile over the filter bed are depicted in Figure 6.4 during the first 63 days of operation.

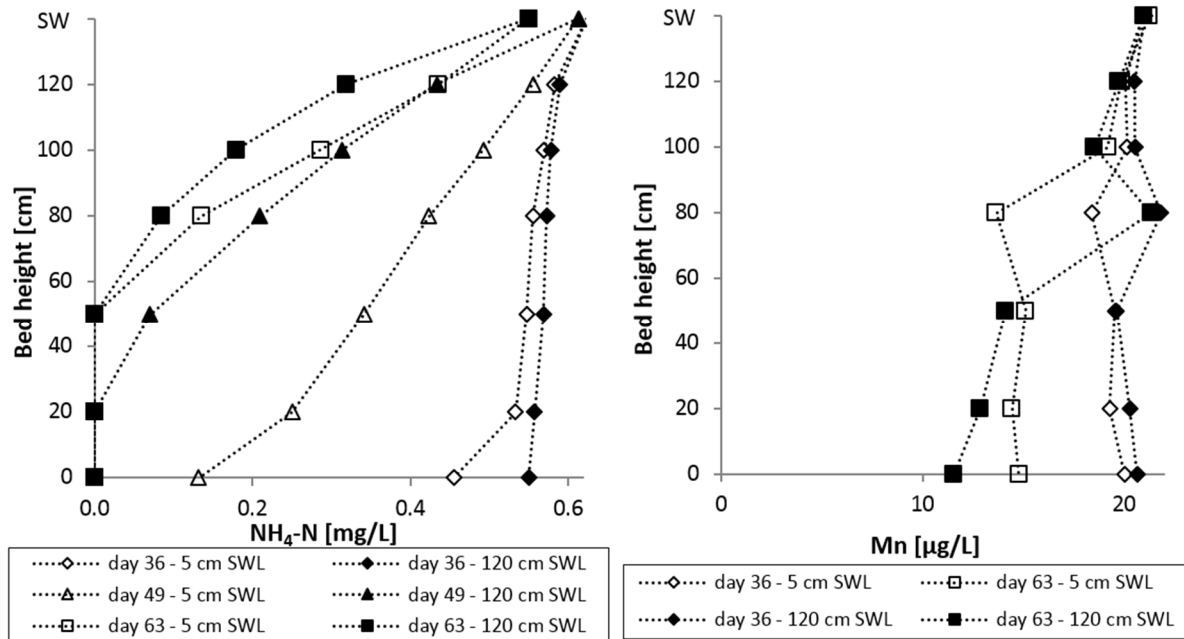
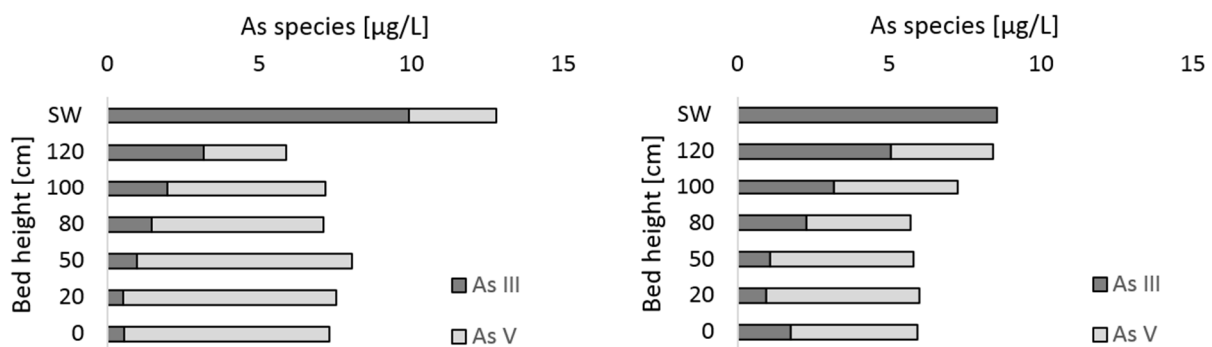


Figure 6.4  $\text{NH}_4$  (left) and Mn (right) concentrations over the height of the filter bed after 36, 49 and 63 days, for 5 cm (open) and 120 cm (closed) SWL

$\text{NH}_4^+$  oxidation commenced and was (almost) complete in the filtrate at day 49 and, like As(III), climbed to the top of the filter bed at least until day 63. Although  $\text{NH}_4^+$  oxidation started at day 36 for both 5 and 120 cm SWL, by day 49 and 63 more was oxidised in the 120 cm SWL column, and oxidation occurred higher in the filter bed. Mn(II) removal did not fully develop during the ripening stage, as only 29% and 45% was removed in the 5 and 120 cm SWL columns, respectively. However, similar to both  $\text{NH}_4^+$  and As(III), the 120 cm SWL column removed more Mn than the 5 cm SWL column at day 63, which

suggests that biological processes benefit from Fe(II) oxidation prior to filtration. The development of biomass for As(III) conversion was fastest, followed by  $\text{NH}_4^+$  and subsequently Mn, which is in-line with results from ripening experiments with other natural groundwaters containing, As(III), Mn(II) and  $\text{NH}_4^+$  (Gude et al., 2018a, 2018b). The results in Figure 4 suggest that specific As(III) oxidising bacteria were accumulated in sand filters since As(III) oxidation developed prior to  $\text{NH}_4^+$  and Mn(II) oxidation. This is in line with observations in Gude et al., (2018b) showed that As(III) oxidising bacteria accumulated rapidly on As(III)-substrate in an environment of  $\text{NH}_4^+$  without  $\text{NO}_3^-$  and vice versa, in both these systems no  $\text{MnO}_2$  minerals were present on the filter sand. The results of increasing the filter loading (e.g. filtration velocity) are depicted in Figure 6.5. Here As(III) and As(V) concentration profiles are shown after 1 week of increasing the flow from 1.5 m/h to 5 m/h.



**Figure 6.5** loading increase and measurements after 1 week 1.5 to 5 m/h As(III) and As(V) profile over the height of the filter bed at 5 cm SWL (left) and 120 cm SWL (right)

As(III) concentrations throughout both columns increased as a result of an increased loading. Apparently the biological oxidation was in equilibrium with the loading of 1.5 m/h and the columns could not directly cope with the, more than tripling, of As(III) loading at 5 m/h. The elevated As(III) concentrations were accompanied by a decrease in As removal efficiency. To confirm that As(III) conversion was a biological process in the columns, the columns were disinfected with  $\text{Cl}_2$  at the end of seven months of experiments. Figure 6.6 depicts the As speciation in the columns after returning to regular operational mode (at 5 m/h) for a period of 24 hours.

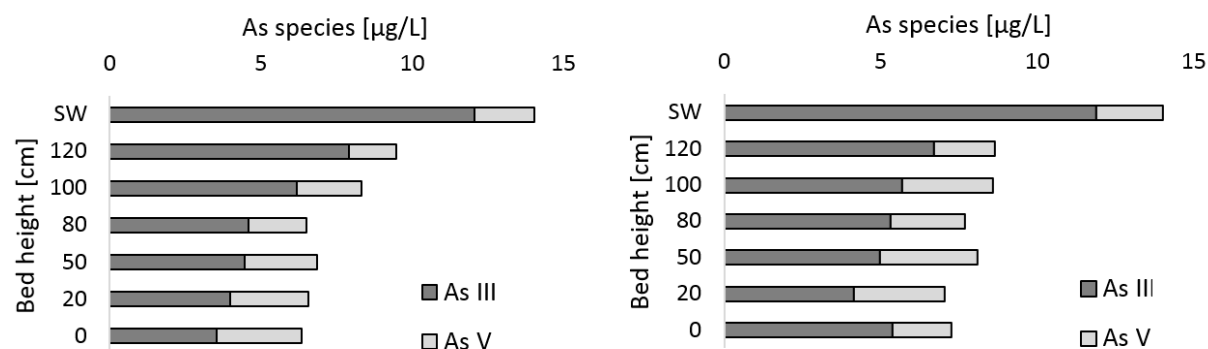


Figure 6.6 As(III) and As(V) profile through the filter bed after disinfection with Cl<sub>2</sub>

After disinfection, the As(III)/As(V) profile over the filter bed closely resembled the profile of the first measurement at day 1. Hence, As(III) oxidation stopped almost completely after disinfection. This confirms that the As(III) oxidation during these experiments was of biological nature. Although not measured over the height of the filter bed, NH<sub>4</sub><sup>+</sup> concentrations in the filtrate (0.60 mg/L) remained identical to the influent concentrations (0.61 mg/L), indicating that the disinfection inactivated the nitrifiers as well, also observed by Gagnon et al. (2005). On the other hand, Fe removal was just as effective after chlorination as before chlorination, with Fe concentrations in both columns below 0.01 mg/L. Therefore, although biological Fe(II) oxidation in the filter bed could have occurred (de Vet et al., 2011; van Beek et al., 2015), it is demonstrated that for these columns with alkaline groundwater homogeneous and heterogeneous Fe(II) oxidation sufficed for Fe removal. However, it is clear that the nature of As(III) oxidation was predominantly biological, as after disinfection the majority of the As in the filtrate was in the As(III) form. Minerals, present on the filter sand, potentially potent for As(III) oxidation, like MnO<sub>2</sub> (Gude et al., 2017; Jones et al., 2012), apparently did not oxidise As(III) while the bacteria were inactivated.

### 6.3.2 SWL and As removal

Extending residence times in the supernatant water results in increased homogeneous HFO production, and reduces the contribution of heterogeneous Fe(II) oxidation in the filter bed. Fe removal over the filter bed height, both total Fe and 0.45 µm filtered Fe, are depicted in Figure 6.7 together with dissolved and adsorbed As.

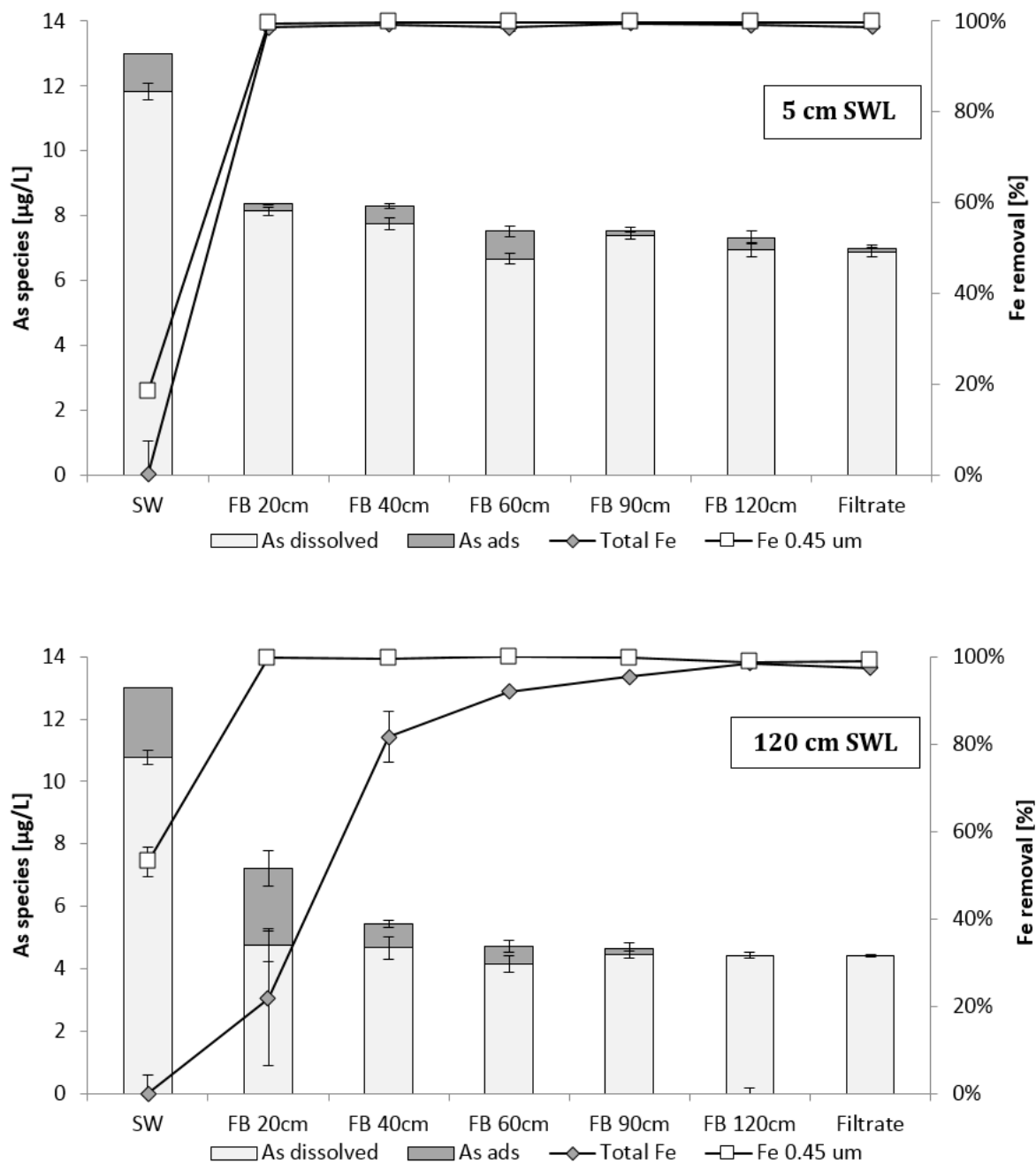


Figure 6.7 Dissolved As and adsorbed As to mobile HFO (yet to be retained by the sand filter) in µg/L. On secondary axis Fe removal both over the filter bed depth (FB) at 5 cm SWL (top) and 120 cm SWL (bottom). Filtration velocity 1.5 m/h. Data shown are averaged values of week 6 and 7 of operation. Error bars represent min. and max. values.

The profiles of the columns with 5 and 120 cm SWL were distinctly different for As and Fe. At 5 cm SWL, Fe removal was rapid and efficient since 98.6% was removed in the first measuring interval at 20 cm from the top of the filter bed. In this system, the majority of the Fe enters the filter bed as Fe(II) (82% was not retained by a 0.45 µm filter) and



apparently this was efficiently removed. The rapid Fe removal resulted in a low level of As adsorption throughout the filter bed. 5 µg/L As (total) was removed in the first 20 cm of the filter bed, whereas in the rest of the 120 cm sand filter only 1 µg/L As was removed. In the 120 cm SWL column, the Fe(II) was allowed to be homogeneously oxidised for 45 min at 5 mg/L O<sub>2</sub> and pH 7.6. The retention time caused 53% of the 1.93 mg/L Fe(II) to be retained by a 0.45 µm filter, apparently being oxidised and flocculated into HFO flocs. These flocs were observed throughout the filter bed and were only completely removed after 120 cm of sand filtration (deep-bed filtration). Apparently homogeneously formed HFO in the supernatant water was more mobile in sand filters than dissolved Fe(II) as was also observed by Sharma et al. (2001). This deep-bed filtration of HFO changed the As profile compared to the profile in the 5 cm SWL column. In terms of As removal the 120 cm SWL column outperformed the 5 cm SWL column. In the first 20 cm of the filter bed, an additional decrease of 2 µg/L dissolved As and an additional 2.5 µg/L adsorbed As was observed. The adsorbed As to the (mobile) HFO was subsequently removed in the filter bed. This observation is in-line with an As removal profile in a full-scale rapid filter which was operated with a high supernatant level and a NaOH injection (Gude et al., 2016). An additional observation is that after 20 cm of the sand filter, the dissolved As remained steady for the rest of the filter bed. Probably, the HFO deeper in the filter bed had already reached equilibrium sorption and/or further flocculation of the HFO prevented additional adsorption of the produced As(V). Overall, increased SWL, at a pH high enough for homogeneous Fe(II) oxidation to occur, resulted in increased HFO production prior to filtration which was beneficial to As adsorption onto HFO and subsequent removal in the filter bed.

### 6.3.3 Supernatant level and filtration velocity

Increasing the filtration velocity reduces the homogeneous oxidation time in the supernatant water and therefore the HFO production. To observe whether the positive effect of a high SWL is maintained at higher filtration velocities, the results of the As removal at different velocities are depicted in Figure 6.8 (1.5, 5 and 10 m/h).

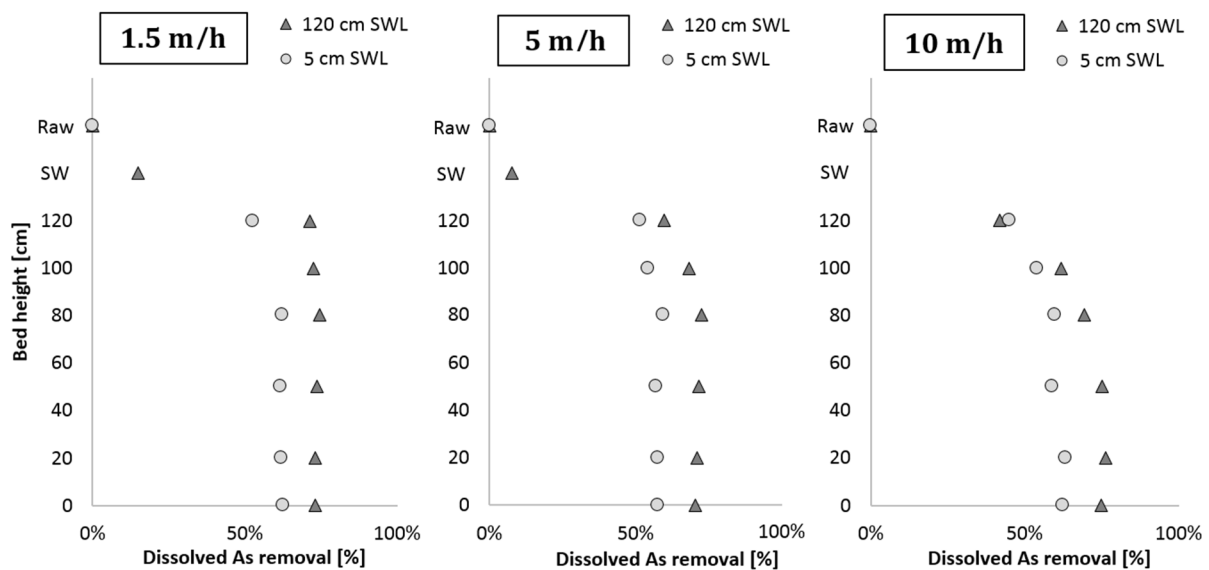
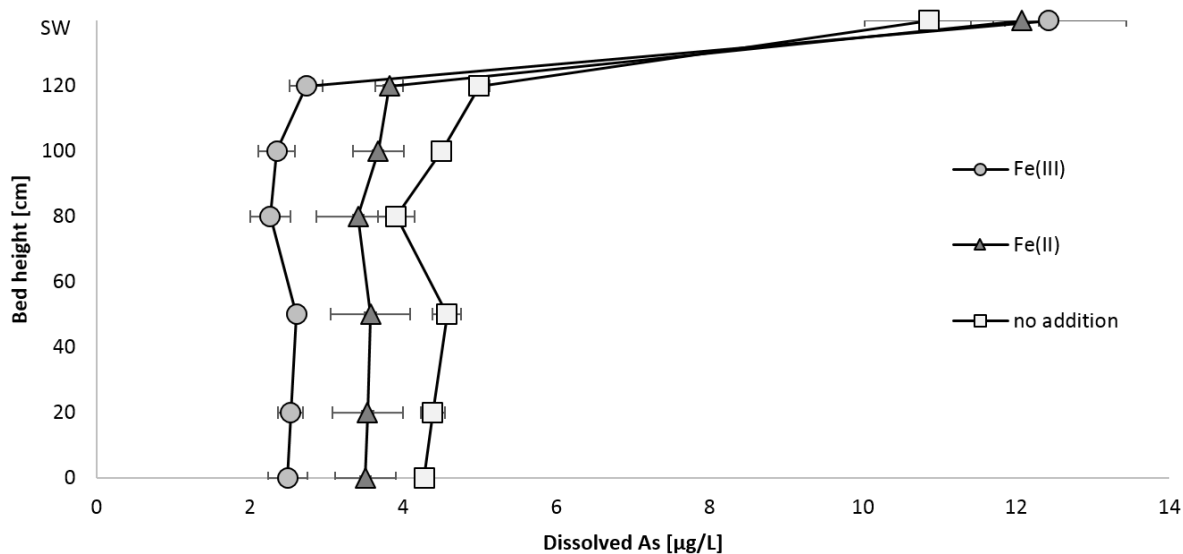


Figure 6.8 Dissolved As removal from raw water to supernatant and throughout the filter bed at 1.5 m/h left (day 120), 5 m/h middle (day 148) and 10 m/h right (day 155).

Independent of the filtration velocity, 120 cm SWL resulted in an increased As removal compared to 5 cm SWL throughout the filter bed. The increase in As removal in the filtrate was 10%, 12% and 12% respectively for 1.5, 5 and 10 m/h. The minor differences are more likely to be explained by the variations in water quality than in process conditions. At an increased filtration velocity, As removal moved deeper into the filter bed. At 1.5 m/h, As removal occurred in the upper layer of the filter bed and no additional removal was observed further in the filter bed, while at 5 m/h and even more pronounced at 10 m/h As removal was occurring deeper in the filter bed. Apparently the increased filter loading and/or the decreased contact time caused the process to acquire additional surface area at higher filtration rates. In this experiment however, although the removal occurred deeper in the filter bed, no effect on the total As removal in the complete filter bed was observed.

#### 6.3.4 Fe(II)/Fe(III) addition in supernatant water

To have a direct comparison of the influence of either Fe(III) or Fe(II) entering the filter bed on the removal of As, an experiment was included adding 1 mg/L Fe(II) or Fe(III). Figure 6.9 depicts either Fe(II) or Fe(III) additions, as well as the natural groundwater composition with process conditions of 50 cm SWL and 5 m/h filtration velocity.



**Figure 6.9** Dissolved As concentrations over the bed filter bed height for addition of 1 mg/L Fe(II) or Fe(III) to supernatant water with 50 cm SWL. Native Fe concentration was 2 mg/L (as Fe(II)) and filtration velocity 5 m/h.

Both Fe(II) and Fe(III) additions resulted in a more effective removal of As than was the case for natural groundwater without addition, indicating that additional formation of HFO resulted in increased As removal, as also previously observed by Qiao et al. (2012) where As(V) removal percentages increased at lower As(V)/Fe(III) ratios. Chiew et al. (2009) observed more As removal in filters where more Fe was present. However, Fe(III) addition in the supernatant water was more effective in decreasing As compared to Fe(II) addition. Evidently, Fe(III) entering the filter bed is more effective at removing As than Fe(II), which is in-line with the SWL experiments presented earlier. The  $\pm 1$   $\mu\text{g/L}$  increase in removal was obtained in the upper layer of the filter bed and remained more or less stable further throughout the filter bed. The mechanism involved here is that the HFO flocs formed by Fe(III) are not accumulating on the surface of the top of the filter bed where the As(III) is oxidised (observed at 120 cm SWL in Figure 6.7 and by Sharma et al. (2001)), but in majority passing them in the pore volume of the filter bed and subsequently absorbed the produced As(V) more effectively.

### 6.3.5 Fe(II)/Fe(III) addition in filter bed

To obtain HFO in the zone of the filter bed where As(V) is present, in order to better adsorb As in rapid filters, also Fe(II) and Fe(III) were dosed in the filter bed at 30 cm under

the top of the filter bed and compared to an equal Fe addition in the supernatant water. The results for dissolved As and Fe are depicted in Figure 6.10.

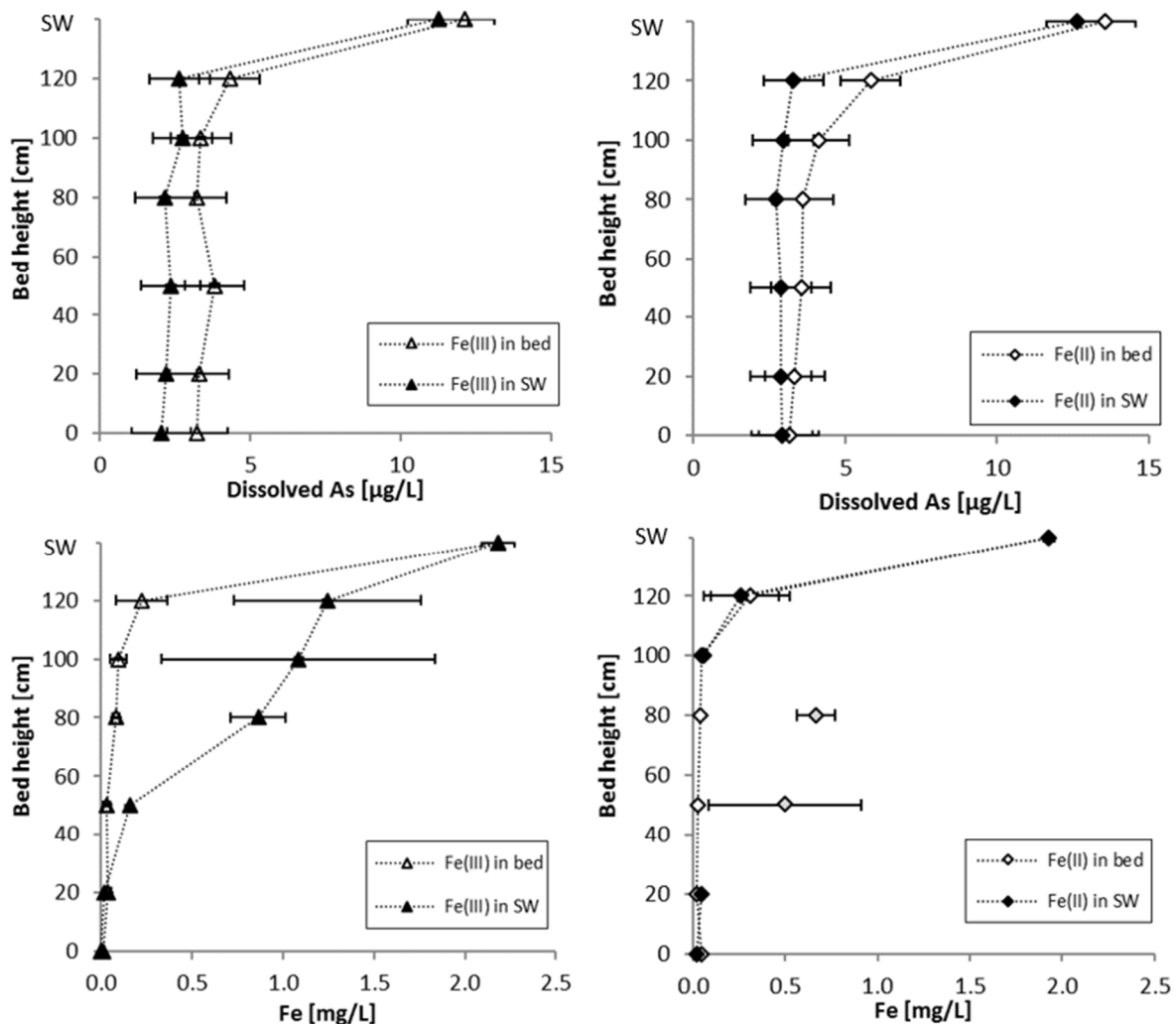


Figure 6.10 Fe(III) (left) and Fe(II) (right) addition of 1 mg/L in supernatant water and filter bed at 110 cm bed height. All experiments were performed with 50 cm SWL and filtration velocity of 5 m/h.

As removal as a result of Fe addition in the supernatant causes the majority of the As removal to take place in the upper layer of the filter bed. This in contrast to the Fe addition at 30 cm in the filter bed. Here the removal was achieved over a larger filter bed height and remained constant after 60 cm of sand filtration. The Fe addition in the supernatant water caused the overall As removal to be more effective than Fe addition in the filter bed. For Fe(III) addition in the supernatant, 1.2  $\mu\text{g/L}$  additional As was removed. In the filter bed where the Fe was dosed a drop of 1.0  $\mu\text{g/L}$  is observed. However, this did not result

in the desired effect since the dissolved As concentration remained higher than in the same sampling point while dosing in the supernatant water. For Fe(II), a similar trend is observed. Fe(II) dosed in the filter bed caused some additional removal compared to highest sampling point in the filter bed. However it did not result in increased removal compared to the Fe(II) added in the supernatant water.

The Fe profile as a result of Fe(III) additions was clearly different for dosing in the supernatant and dosing in the filter bed. Additions in the supernatant water effectively caused (a maximum  $\pm 1$  mg/L) increased Fe concentrations over the first 90cm of the filter bed. On the other hand, while adding the same concentration Fe in the filter bed almost no additional Fe was observed in the filter bed. Apparently adding in the filter bed, the flocs were more effectively locally retained due to improper mixing and direct availability of sand surfaces, potentially explaining the reduced As removal compared to the well-mixed dosing in the supernatant water similar to observations of Sharma et al. (2001), here Fe(III) entering the filter bed resulted in 2.5 times high filter resistance (rapidly clogging a filter bed by voluminous flocs). The Fe profile for Fe(II) addition in the filter bed and in the supernatant was similar, apart from 2 outliers; which was, in both experiments, dominated by rapid heterogeneous oxidation (Hiemstra and van Riemsdijk, 2007; Tamura et al., 1980) and thus, similarly to previous experiments, not resulting in better As removal than when adding Fe(III).

#### 6.4 Conclusions

The research aimed at establishing an As(III) oxidising biomass in the top of the filter bed and investigating the role of Fe oxidation state prior to rapid filtration. For this purpose the SWL was varied and Fe(II) and Fe(III) additions were compared in a pilot plant using alkaline groundwater (pH 7.6) with naturally containing As(III). From the experiments it may be concluded that As(III) oxidation gradually moved upward in the filter columns during ripening of biological sand filters, similar to  $\text{NH}_4$  but more rapidly. Once the biomass established itself in the top of the filter bed, As removal efficiency stabilised at its maximum. Disinfection by chlorine caused the As(III)/As(V) profile to return to its initial values, confirming the biological nature of this process. As removal greatly benefitted from increasing the SWL from 5 cm to 120 cm, for all tested filtration velocities (1.5, 5 and

10 m/h). A closer look in the filter bed revealed that HFO penetrated the filter bed further and seemed to be more efficiently used as an adsorbent at a higher SWL. The beneficial properties of HFO formed prior to rapid filtration were confirmed by the increased As adsorption by Fe(III) addition in the supernatant water compared to Fe(II) addition and/or Fe injection into the filter bed.

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## 7. Conclusions and recommendations

### 7.1 Conclusions

#### 7.1.1 Overall conclusion

The results presented in this thesis demonstrate that arsenic (As) and iron (Fe) speciation determine the removability of As to a large extent and biological As(III) oxidation can be achieved in the top layer of the filter bed. In addition, the formed As(V) should be removed by formed hydrous ferric oxides (HFO) accumulated deeper in the bed. Based on these insights, the practical conclusion can be drawn that, at low influent As concentrations, As removal efficiency in rapid filters can be improved by the adjusting supernatant level and filter media size and configuration. These improvements can be implemented at low costs and in most of the existing groundwater treatment plants. In case higher influent As concentration occur, addition of CO<sub>2</sub>-gas and FeCl<sub>3</sub> can be considered to adjust pH and promote As(V) adsorption, respectively, which are - compared to currently applied NaMnO<sub>4</sub> - non-invasive chemicals in terms of costs, water quality and handling.

#### 7.1.2 Need for As(III) oxidation

A large contributor to efficient As(III) removal is oxidation towards As(V). It was found that for efficient As(V) removal by hydrous ferric oxides (HFO), originating from precipitating Fe(II), rapid As(III) oxidation was thus imperative. In full-scale filters, chapter 2 of this thesis, it was found that As(III) oxidation occurred rapidly in the top of the three investigated filter beds. While in case of only aeration, As largely remained dissolved in the supernatant water in the As(III) form. Even after 60 min contact time, only 20-48% of the As was adsorbed, although >96% of the initial Fe(II) was oxidised in HFO and available for adsorption. In the filter bed however, the As(III) completely oxidised within 2 min of residence time. The oxidation contributed to As removal efficiencies of 48-90% to similar qualities of HFO because in the rapid filter, the As(V) was readily adsorbed to the formed HFO flocs in contrast to As(III) in the supernatant level. The need for oxidation of As(III) for As removal was again illustrated by the experiment (Chapter 3) comparing adsorption efficiency of As(III) and As(V) to HFO originating from Fe(III) at pH 7. Here, a concentration of 23 µg/L of dissolved As(V) was lowered to <1

$\mu\text{g/L}$  at the first measuring interval of 2 min, whereas, under identical settings, the concentration of  $23 \mu\text{g/L}$  As(III) was only lowered to  $16.9 \mu\text{g/L}$  (only 26% removal). Only 55% of the As(III) was adsorbed after 60 min residence time.

### 7.1.3 The mechanism of As(III) oxidation

Accelerated As(III) oxidation in the filter bed could have various causes, including mineral surface ( $\text{MnO}_2$ ) or microbial conversion. Although it was found that  $\text{MnO}_2$  is able to oxidise As(III) under ideal conditions, in the presence of Fe(II) and Mn(II), As(III) oxidation by  $\text{MnO}_2$  was demonstrated to be inhibited (chapter 3). Therefore it is concluded that, although  $\text{MnO}_2$  is present in a filter bed, it does not necessarily mean that  $\text{MnO}_2$  will be available to oxidise As(III).

Instead, we observed that bacteria were responsible for As(III) oxidation (chapter 4). Biological As(III) oxidation quickly developed in sand columns fed with drinking water with added As(III). With a typical lag and log phase, decreasing As(III) and increasing As(V) concentrations in the effluent of the sand columns were measured in a timeframe of weeks. The growth of biomass in the sand columns had resulted in increased ATP concentrations on the sand. Further confirmation was obtained by disinfection: a thriving As(III) oxidising biomass was disrupted towards a limited initial oxidation capacity after 24 h exposure to chlorine (chapter 6).

During groundwater filtration, in the midst of other typical biological conversion processes such as  $\text{NH}_4$  and Mn(II) oxidation, As(III) was found to be the first component to be fully oxidised and the As oxidising bacteria (AsOB) gradually moved towards the top of the filter bed as filtration proceeded (chapter 6). The  $\text{NH}_4$  oxidising biomass (nitrification) had no detrimental effect on the development of biological As(III) oxidation in groundwater filters, but the additional of nutrients ( $\text{NH}_4$  or  $\text{NO}_3$ ) rather stimulated the AsOB accumulation (chapter 4).

### 7.1.4 Optimising As removal in rapid filters

Efficient exploitation of these naturally occurring As(III) oxidising bacteria can increase As removal, but in order to achieve As removal, it is crucial to understand the interaction between the different species of As and the adsorption onto HFO originating from the

different species of Fe (Fe(II) and Fe(III)) and their transport in the filter bed. Fe(II) oxidation, HFO floc formation and subsequent As(V)/As(III) adsorption onto these flocs is a complex system, which was investigated in this thesis by adjusting critical operational parameters (chapter 5). By increasing the supernatant level above a rapid filter, the homogeneous Fe(II) oxidation and HFO floc formation was stimulated, resulting in a 20% increase in As removal. Consequently, As removal (8%) was also enhanced by the use of double media filtration comprising of a coarse top layer and a fine supporting layer, allowing for deeper penetration of HFO flocs into the bed. Hypothetically offering As sorption sites further into the filter by limiting efficient Fe(II) removal on the filter media surface while still providing surface area for rapid biological oxidation. Moreover, As removal was stimulated (55%) by decreasing the pH from 8 to 7.4 (chapter 5), which is most likely caused by the stronger affinity of As(V) to HFO and reduced Fe(II) removal kinetics at lower pH. Finally, dosing of FeCl<sub>3</sub> showed that Fe(III) addition, penetrating the filter bed deeper and less efficiently removed than FeCl<sub>2</sub> (Fe(II)), also resulted in more As removal.

The common mechanisms behind the proposed process enhancements are related to Fe(II) oxidation and removal and the adsorption capacity of HFO. Using a high supernatant level for enhanced As removal, forming Fe(III) before entering the filter bed, shows that Fe(II) entering the filter bed is not the beneficial way to produce HFO concerning efficient As adsorption. Therefore, we propose that heterogeneous Fe(II) oxidation, which results in efficient Fe removal in the top layer of the filter bed, reduces the As adsorption capacity. In addition, coarse filter media in the top layer of the filter bed is proposed to perform better than fine sand, because a lower surface area and fewer but larger pore channels which result in increased homogeneous oxidation of Fe. It was shown in Chapter 3 that Fe(II) oxidised on MnO<sub>2</sub> surface, which could be comparable to heterogeneous oxidation to filter media surface, resulted in fewer surface complexation sites for As and PO<sub>4</sub>. Resulting in the conclusion that heterogeneous oxidation in the filter bed should be avoided.

The decreased pH is probably for the major part beneficial because of an increased adsorption capacity of HFO, since positively charged HFO at lower pH has an increased charge affinity to the negatively charged As(V) (chapter 2). Slower heterogeneous Fe(II)

oxidation at lower pH can also result in HFO formation further in the filter bed where As(V) can adsorb onto the HFO.

Although the exact mechanisms behind this were not conclusive, As removal in the filter bed benefits from Fe(II) oxidation prior to rapid filtration. Additional adsorption was achieved by decreasing the pH.

## 7.2 Recommendations

### 7.2.1 Future research

Although we successfully present a toolbox to increase As removal in aeration and rapid filtration presented in 8.1.4. This thesis leaves open a more fundamental and mechanistic study of homogeneous, heterogeneous Fe(II) oxidation and its effect on the resulting HFO properties, especially with focus on As(III) and As(V) adsorption. Additionally the mapping and quantification of all mechanisms affecting As removal when adjusting filtration velocity and filter media type and size remain a knowledge gap. We are convinced this can be measured when smaller intervals are taken in the filter bed as we expect this process, depending on conditions like filtration velocity, filter media size and water quality, to take place in the top 10 cm of the filter bed.

On the account of biological As(III) oxidation we could conclude that AsOB were widely available and rapidly accumulating, however, apart from a minor increase by nitrification (chapter 4) we did not yet find ways to stimulate them. With more knowledge on their exact metabolism, it is likely that if the As(III) oxidation performance can be boosted in respect to other processes, As removal can be optimised along the way.

A successful and promising begin was made on a predictive water quality model (in excel with a pHreeqc plug-in). Phreeqc, with Wateq4F database, is an excellent tool to calculate the mass balances of all involved elements with resulting pH change and O<sub>2</sub> demand in the supernatant level and through the filter bed. Kinetics induce As(III), Fe(II), NH<sub>4</sub> and Mn(II) oxidation with separate rates in the supernatant level and the filter bed. The calculated Fe(III) is then equilibrated with HFO and allocated with surface complexation sites. With the incorporated constants from the WateQ4F database sorption of cations and anions with the particular interest of As(V) can be calculated. The kinetics of Fe(II), As(III), NH<sub>4</sub> and Mn(II), transport and hydraulics of HFO through the filter and mineral

and biological deposits on the filter media must be better understood in order to improve the model and be able to fully incorporate the complex behaviour of As and other compounds through a rapid filter.

### **7.2.2 For practice**

Not only centralised treatment facilities can benefit from the findings in this thesis. The presented results pave the way for the design of efficient decentralised or small scale As removal units too. For this purpose, tests were done in Bangladesh to utilise biological As(III) oxidation and the natural removing capacity of Fe present in the groundwater and zero-valent-iron with high As(III) concentrations. It appeared that the As(III) oxidising biomass rapidly accumulated in the top of the sand filter and contributed to 80% removal within weeks of operation. Building on this work, a proposal was submitted for the Horizon2020 EU-India call. Here we proposed to develop a separate As(III) oxidation reactor that is before a subsequently placed rapid sand filter to produce As-free drinking water for 1000 people in an As affected area in West-Bengal India. The advantage of the proposed technology is that it can be constructed at very low cost and low technology level and therefore easy to operate.



## 8. Summary

Arsenic (As) mobility in water is worldwide studied since its toxicity was proven in 1888. Intake of As can lead to skin disease, cancer, kidney and heart failure, diabetes and paralysis. In the Netherlands, groundwater used for drinking water production contains As in the range from 0 – 70 µg/L. Currently, all groundwater treatment plants reduce As in drinking water below the WHO standard of 10 µg/L. However, to ensure no adverse health effects occur by the intake of drinking water, Dutch drinking water companies investigate implications of distributing water with As concentrations below 1 µg/L. The new *target* value causes 58% of the treatment plants with measurable As in the raw water (19% of all total groundwater treatment plants) to need some sort of adjustment to their treatment scheme to comply with the new As target value.

Groundwater treatment commonly consists of aeration, with subsequent sand filtration without using chemical oxidants like chlorine. In this process, spontaneous and unintentional As removal occurs, ranging from 15% - 95%. Given that the removal percentages vary greatly and the level of As removal that is required is low, more knowledge on As removal mechanisms in rapid sand filters could result in improved removal performance by better operation of these filters, saving water companies from expensive, undesirable, additional water treatment processes. Therefore this thesis aims to discern the relevant As removal processes that occur during aeration and rapid filtration and to establish a 'toolbox' to increase the removal capacity of the aeration – rapid filtration process.

The research methodology consisted of 3 components: (1) extensive measurements at full scale groundwater treatment plants, (2) jar tests, with As containing demineralised water and natural groundwater and (3) pilot-scale rapid filters (6-12 months) with natural groundwater at three different locations. Measurements typically included As, Fe, Mn, NH<sub>4</sub>, PO<sub>4</sub> with emphasis on As speciation and dissolved and particulate Fe and As.

For the measurements at full scale treatment plants, partially removing As, three groundwater treatment plants (10-26 µg As/L) were selected to identify operational parameters that contribute to lowering the filtrate As concentration to <1 µg/L. Results showed that after aeration, arsenic largely remained mobile in the supernatant water; even during extended residence times only 20 - 48% removal was achieved (with 1.4 –



4.2 mg/L precipitated Fe(II)). Speciation showed that the mobile As was in the reduced As(III) form, whereas, As(V) was readily adsorbed to the formed HFO flocs. In the filter bed, the remaining As(III) completely oxidised within 2 min of residence time and As removal efficiencies increased to 48 - 90%. Filter grain coating analysis showed the presence of Mn at all three treatment plants. In addition, pH adjustment from 7.8 to 7.0 was found to improve the capacity for As(V) uptake by the hydrous ferric oxide (HFO) flocs in the filter bed.

By performing elaborate jar tests, it was investigated whether Mn oxide ( $\text{MnO}_2$ ), present on filter grains, could abiotically be responsible for As(III) oxidation in the top of a rapid sand filter. Two  $\text{MnO}_2$  containing powders were selected and brought in contact with As(III) in aerobic water containing Mn(II), Fe(II) and/or Fe(III). Jar test experiments showed that both powders oxidised As(III). However, when applying the  $\text{MnO}_2$  in aerated, raw groundwater, As(III) removal was not enhanced compared to aeration alone. It was found that the presence of Fe(II) and Mn(II) inhibited As(III) oxidation, as Fe(II) and Mn(II) adsorption and oxidation were preferred over As(III) on the  $\text{MnO}_2$  surface (at pH 7).

Consequently it was hypothesised that biological As(III) oxidation occurs in the top of rapid filters. Therefore it was investigated whether arsenic-oxidising bacteria (AsOB) grow and survive in rapid sand filters. Additionally, the interdependence of other groundwater constituents (Fe(II), Mn(II),  $\text{NH}_4$ ) with biological As(III) oxidation was investigated. For this purpose As(III) oxidation was monitored in pilot-scale filter sand columns fed with raw groundwater, as well as treated groundwater (drinking water) with spikes of either As(III), Mn(II) or  $\text{NH}_4$ . It was concluded that biological As(III) oxidation rapidly developed in the rapid sand filter columns. With a typical lag and log phase, decreasing As(III) and increasing As(V) concentrations in the effluent of the sand columns were observed in a timeframe of weeks. The growth of biomass in the sand columns was confirmed with ATP analysis. Additionally, a microbial community analysis (16S rRNA) showed a high relative abundance of  $\alpha$ - and  $\beta$ -Proteobacteria; the same classes where most AsOB are phylogenetically placed.

In the top layer of aerated rapid sand filtration systems, uncharged As(III) is biologically converted to negatively-charged As(V). Subsequently, the main removal mechanism for As(V) is adsorption onto oxidised, flocculated Fe(III) (HFO). Pilot plant research was

executed to establish a As(III) oxidising biomass and subsequently promote As removal by understanding its interaction with Fe(II) and HFO in the filter bed. For this purpose, different filter media column experiments were performed using natural, aerated groundwater containing 3.4 µg/l As(III). Results show that independent of the filter media size, complete (biological) conversion of As(III), Mn(II) and NH<sub>4</sub> and NO<sub>2</sub> was achieved in approximately 70 days. After ripening, enhanced As removal was achieved with a top layer of coarse media or by dosing additional Fe(III). Addition of Fe(II) did not have the same effect on As removal, potentially due to heterogeneous Fe(II) oxidation in the upper layer of the filter, attaching rapidly to the filter grain surface and thereby preventing HFO flocs to penetrate deeper into the bed. Increasing the flow rate from 1 to 4 m/h did not improve As removal and lowering the pH from 8 to 7.4, resulted in an 55% increased removal of dissolved As.

In extension to this, the effect of the Fe oxidation state entering the biological filter bed on As removal was investigated by varying supernatant water level. By varying supernatant water level, either Fe(II) or Fe(III)/HFO are stimulated to enter the filter bed, i.e., allowing for either hetero- or homogeneous Fe(II) oxidation. The As(III), NH<sub>4</sub> and Mn(II) in the native groundwater caused biological processes to start over the course of weeks, whereby As(III) oxidation developed first. It was observed that once the As(III) oxidation stabilised in the top layer of the filter sand As removal reached its maximum. The increase of supernatant level resulted in additional HFO production prior to filtration, i.e. homogeneous Fe(II) oxidation and flocculation, with HFO ending up deeper into the filter bed (120 cm depth) compared to the Fe(II) that oxidised heterogeneously at low supernatant water level (20 cm depth). In filters with high supernatant level (1.2m) As was removed to lower levels (by 20%) than in filters with low supernatant water level (0.05m). The benefits of Fe(II) oxidation prior to filtration for As removal, particularly in the top layer of the filter bed, was confirmed by comparing Fe(III) and Fe(II) addition in the supernatant water.

The results presented in this thesis demonstrate that As and Fe speciation determine the removability of As to a large extent and biological As(III) oxidation can be achieved in the top layer of the filter bed. In addition, the formed As(V) should be removed by HFO accumulated deeper in the bed. Based on these insights, the practical conclusion can be drawn that, at low influent As concentrations, As removal efficiency in rapid filters can be

improved by the adjusting supernatant level and filter media size. These improvements can be implemented at low costs and in most of the existing groundwater treatment plants. In case higher influent As concentration occur, addition of CO<sub>2</sub>-gas and FeCl<sub>3</sub> can be considered to adjust pH and promote As(V) adsorption, respectively, which are - compared to currently applied NaMnO<sub>4</sub> - non-invasive chemicals in terms of costs, water quality and handling.

## 9. Samenvatting

Arseen (As) mobiliteit in water wordt wereldwijd bestudeerd sinds de toxiciteit ervan werd bewezen in 1888. Inname van (veel) As kan leiden tot huid- en vaatziekten, kanker, nier- en hartfalen, diabetes en verlamming. Grondwater gebruikt voor de productie van drinkwater in Nederland bevat As-concentraties van 0 tot 70 µg/L. Alle grondwaterzuiveringen produceren drinkwater met As-concentraties onder de WHO-norm van 10 µg/L, maar om er zeker van te zijn dat er geen nadelige gezondheidseffecten optreden door de inname van drinkwater, onderzoeken Nederlandse drinkwaterbedrijven de mogelijkheden om water met As concentraties lager dan 1 µg/L te distribueren. Het gevolg van deze nieuwe streefwaarde is dat 19% van de grondwaterzuiveringen aangepast zal moeten worden.

Grondwaterzuiveringen in Nederland bestaan voor het grootste deel uit beluchting en aansluitende zandfiltratie, zonder chemische oxidatiemiddelen zoals bijvoorbeeld chloor. Uit nader onderzoek blijkt dat de huidige grondwaterzuiveringen grote variaties kennen op het gebied van As-verwijdering (15% - 95%). Deze sterke variatie duidt erop dat bij bepaalde installaties en grondwatertypen, As effectief verwijderd wordt. De verwachting is dat meer kennis over As-verwijderingsmechanismen in zandfilters zal resulteren in concrete voorstellen voor verbetering van grondwaterzuiveringen op het gebied van As-verwijdering. Optimalisatie van de huidige installaties zouden waterleidingbedrijven kunnen behoeden voor het toepassen van sterke oxidatoren (b.v. kalium-permanganaat, chloor of ozon) of na-geschakelde filters gevuld met dure adsorbents. In dit proefschrift worden de relevante As-verwijderingsprocessen in beluchting en zandfiltratie onderzocht, om een instrumentarium te ontwikkelen waarmee de natuurlijke As-verwijderingscapaciteit van grondwaterzuiveringen gemaximaliseerd kan worden.

De onderzoeksmethode bestond uit 3 componenten: (1) uitgebreide metingen bij grondwaterzuiveringen (2) bekersglasproeven met As in gedemineraliseerd water en natuurlijk grondwater en (3) kolomexperimenten (6-12 maanden) met natuurlijk grondwater op drie verschillende locaties. Gemeten waterkwaliteit-parameters waren voornamelijk As, ijzer (Fe), mangaan (Mn), ammonium (NH<sub>4</sub><sup>+</sup>) en fosfaat (PO<sub>4</sub><sup>3+</sup>), met speciale nadruk bij alle proeven op As-speciatie en colloïdaal of opgelost Fe en As.

Voor de metingen bij grondwaterzuiveringen zijn drie locaties gekozen met arseenconcentraties tussen de 10 - 26  $\mu\text{g As/L}$ . Op deze waterzuiveringen is onderzocht welke mechanismen bijdragen aan het verlagen van de arseenconcentratie in het filtraat. De resultaten toonden aan dat na beluchting het As grotendeels mobiel bleef in het water boven de zandfilters; zelfs bij lange verblijftijden werd slechts 20 - 48% verwijdering behaald. Speciatiemetingen wezen uit dat zelfs na 60 min verblijftijd het mobiele As in de gereduceerde As(III) vorm bleef. Dit in tegenstelling tot in het filterbed. Het overgebleven As(III) werd daar volledig geoxideerd binnen 2 min verblijftijd, waarbij de As-verwijderingsrendementen omhoog gingen tot 48-90%. Op de filterzandkorrels zijn allerlei mineralen (o.a. ijzer- en mangaanafzettingen) en bacteriën aanwezig. Contact van mobiel As(III) met deze korrels resulteerde in snelle oxidatie en verhoging van As-verwijderingsrendementen.

Met uitgebreide bekerglasproeven is onderzocht of Mangaanoxide ( $\text{MnO}_2$ ), aanwezig op de filterkorrels As(III) kan oxideren in de bovenlaag van zandfilters. Hiervoor zijn twee  $\text{MnO}_2$  bevattende poeders geselecteerd en in contact gebracht met As(III) in zuurstofrijk water met afgewisseld Mn(II), Fe(II) en/of Fe(III) daaraan toegevoegd. De resultaten toonden aan dat beide poeders As(III) konden oxideren, maar dat verrassend genoeg de  $\text{MnO}_2$  toegevoegd aan grondwater de As-verwijdering niet stimuleerde. Het bleek dat de aanwezigheid van Fe(II) en Mn(II) de As(III)-oxidatie op het oppervlak van de  $\text{MnO}_2$  poeders remde en zo ook de As-verwijderingseffectiviteit niet verhoogde.

Doordat het onwaarschijnlijk is dat  $\text{MnO}_2$  bovenin in het filterbed As(III) kan oxideren omdat daar vaak nog Fe(II) en Mn(II) aanwezig zijn, werd onderzocht of er arseen-oxiderende bacteriën (AsOB) groeien en aanwezig kunnen zijn in zandfilters. In proefkolommen met filterzand werd As(III) in leidingwater en grondwater toegevoegd voor meerdere weken. Na enkele dagen werd er geoxideerd As(V) gevonden in het filtraat en na enkele weken werd 100  $\mu\text{g/L As(III)}$  volledig omgezet in As(V). Het bleek dat er, met een typische lag- en log-fase, biologische As(III)-oxidatie was opgetreden. De groei van biomassa in de zandkolommen werd bevestigd met ATP-analyses. Bovendien kon met een microbiële gemeenschapsanalyse (16S rRNA) een hoge relatieve abundantie van  $\alpha$ - en  $\beta$ -Proteobacteria worden gevonden. In deze bacterieklassen zitten fylogenetisch de meeste AsOB.

Proefinstallatieonderzoek met natuurlijk grondwater is uitgevoerd om te begrijpen uit welke interactie As met Fe(II) en Fe(III) in een biologisch actief filterbed bestaat. Resultaten toonden aan dat onafhankelijk van het filtermediaformaat, volledige (biologische) omzetting van As(III), Mn(II) en  $\text{NH}_4^+$  en  $\text{NO}_2^-$  werd bereikt na ongeveer 70 dagen. Na filterrijping, bleek dat toepassing van een grove filter-toplaag extra As verwijderde. Ook bleek dat het doseren van Fe(III) dieper in het filterbed doordrong dan Fe(II) en daarbij meer As-verwijdering tot gevolg had. Verhoging van het debiet van 1 tot 4 m/h verbeterde de As-verwijdering niet, maar het verlagen van de pH van 8 tot 7,4 resulteerde in een 55% extra verwijdering van opgeloste As.

In het verlengde hiervan werd nog een experiment uitgevoerd, om het effect van de Fe-oxidatietoestand voor het biologisch filterbed op As-verwijdering te onderzoeken. Door het variëren van het waterniveau van de bovenwaterstand van een snelfilter, kan de verhouding Fe(II)/Fe(III) worden beïnvloed. De resultaten gaven aan dat wederom de As(III),  $\text{NH}_4^+$  en Mn(II) in het grondwater in de loop van weken biologisch werden omgezet, waarbij As(III)-oxidatie als eerste ontwikkelde. Zodra de As(III)-oxidatie in de toplaag gestabiliseerd was, bereikte de As-verwijdering het maximum. Het effect van de bovenwaterstand kwam duidelijk naar voren in de experimenten, hogere bovenwaterstand (120 cm t.o.v. 5 cm) resulteerde in extra Fe-oxidatie voorafgaande aan filtratie en de gevormde vlokken drongen dieper in het filterbed. Dit verschil resulteerde in 20% extra As-verwijdering voor de kolommen met de hogere bovenwaterstand. De voordelen van Fe(II)-oxidatie voorafgaand aan filtratie werd verder bevestigd door toevoeging van Fe(II) en Fe(III), waarbij dezelfde hoeveelheid Fe(III) meer As-verwijderde dan Fe(II).

De resultaten in dit proefschrift demonstreren dat As- en Fe-speciatie het verwijderingsrendement van As in grote mate bepalen, en dat As(III) biologisch geoxideerd kan worden in de toplaag van een snelfilter. Het geoxideerde As(V) kan dan dieper in het filterbed adsorberen aan Fe(III)-vlokken. Op basis van deze inzichten kan de praktische conclusie worden getrokken dat de As-verwijderingsefficiëntie in snelfilter kan worden verbeterd door de bovenwaterstand en de grootte van het filtermateriaal aan te passen. Deze verbeteringen kunnen worden uitgevoerd tegen lage kosten en in de meeste van de bestaande grondwaterzuiveringen. Indien daarbovenop nog meer As-verwijdering gewenst is, kunnen toepassing van  $\text{CO}_2$ -gas en  $\text{FeCl}_3$  worden overwogen.



## 10. Curriculum vitae

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Date of birth	August 1, 1983		
Nationality	Dutch		
Education	2014 - 2018	PhD at Delft University of Technology	
	2006 - 2010	MSc Watermanagement at Delft University of Technology	
	2001 - 2006	BSc Civil engineering at "Hogeschool van Amsterdam"	
Job history	2014 - 2018	PhD researcher	Delft University of Technology
	2012 - 2014	Drinking water engineer	Brabant Water 's-Hertogenbosch
	2011	Drinking water engineer	Witteveen+Bos Deventer
	2009	Calculator	DHV Amersfoort
	2008	Process engineer	PWN Heemskerk
	2006 - 2007	Researcher	Waternet Amsterdam
Publications	M.J. Oosterkamp, J.C.J. Gude, D. van Halem. Identification of As(III) oxidising bacteria and the aioA functional gene in groundwater filters. In preparation.		
	J.C.J. Gude, K. Joris, K. Huysman, L.C. Rietveld and D. van Halem, 2018. Effect of supernatant water level on As removal in biological rapid sand filters. Accepted in Water Research on 22 October 2018, minor revisions		
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