



Mobility and redox transformation of arsenic during treatment of artificially recharged groundwater for drinking water production



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ABSTRACT

In this study we investigate opportunities for reducing arsenic (As) to low levels, below 1 µg/L in produced drinking water from artificially infiltrated groundwater. We observe that rapid sand filtration is the most important treatment step for the oxidation and removal of As at water treatment plants which use artificially recharged groundwater as source. Removal of As is mainly due to As co-precipitation with Fe(III)(oxyhydr)oxides, which shows higher efficiency in rapid sand filter beds compared to aeration and supernatant storage. This is due to an accelerated oxidation of As(III) to As(V) in the filter bed which may be caused by the manganese oxides and/or As(III) oxidizing bacteria, as both are found in the coating of rapid sand filter media grains by chemical analysis and taxonomic profiling of the bacterial communities. Arsenic removal does not take place in treatment steps such as granular activated carbon filtration, ultrafiltration or slow sand filtration, due to a lack of hydrolyzing iron in their influent and a lack of adsorption affinity between As and the filtration surfaces. Further, we found that As reduction to below 1 µg/L can be effectively achieved at water treatment plants either by treating the influent of rapid sand filters by dosing potassium permanganate in combination with ferric chloride or by treating the effluent of rapid sand filters with ferric chloride dosing only. Finally, we observe that reducing the pH is an effective measure for increasing As co-precipitation with Fe(III)(oxyhydr)oxides, but only when the oxidized arsenic, As(V), is the predominant species in water.

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1. Introduction

Artificial recharge of groundwater with surface water is a widely used approach for drinking water production. Infiltration of the surface water into underground aquifers often leads to an improved chemical and/or microbiological quality (de Moel et al., 2006). After retention in the underground aquifers, the infiltrated water is recovered and further purified at water treatment plants (WTPs) to meet drinking water quality criteria before supply to consumer houses. Arsenic (As) concentrations in surface water are generally

low (Bhattacharya et al. 2002, 2007; Nriagu et al., 2007; Smedley and Kinniburgh, 2002), however, high concentrations of As can be introduced into the recharged water from aquifer matrix (Fakhreddine et al., 2015; Neil et al., 2012). The extent of As release into water is controlled by numerous geochemical mechanisms. For example, injection of oxygenated water into anoxic aquifers has been reported to mobilize As due to redox-related dissolution of As-bearing pyrite minerals (Darling, 2016; Dillon et al., 2019; Jones and Pichler, 2007; Stuyfzand, 1998). Arsenic release due to exchange with competitive ligands (e.g. phosphate) available in infiltration water has been reported (Biswas et al., 2014; Guo et al., 2008; Vanderzalm et al., 2011). Additionally, pH changes in the aquifer can also result in As desorption during artificial recharge (Aullón Alcaine et al., 2020; McNab et al., 2009; Ormachea Muñoz et al., 2013, 2016).

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In the Netherlands, trace-level release of As into the recharged water in coastal dunes has been observed which results in elevated As levels in the recovered water (Ahmad et al., 2015; Stuyfzand et al., 2008). Although the As levels in the recovered water are well below the WHO guideline of 10 µg/L, recent studies indicate that human health might be affected by As concentrations below the WHO guideline of 10 µg/L (Ahmad and Bhattacharya, 2019; Kozisek, 2017; Saint-Jacques et al., 2018; Schmidt, 2014). Therefore, as a precautionary measure, Dutch drinking water sector aims to supply drinking water with <1 µg/L As (Ahmad et al., 2020; Van der Wens et al., 2016).

The removal of As from natural anaerobic groundwater, in addition to Fe(II), Mn(II) and NH₄⁺ removal, has been extensively investigated in previous studies (Ahmad et al., 2018; Gude et al., 2016; Jessen et al., 2005; Lytle et al. 2005, 2007). The treatment of natural groundwater is generally simple, consisting of aeration followed by rapid sand filtration whereby As is mainly removed by co-precipitation with Fe(III)(oxyhydr)oxides which are formed due to oxidation of native Fe(II) and subsequent hydrolysis (Gude et al., 2016; McNeill and Edwards, 1995). The treatment of artificially recharged water, on the other hand, often requires more treatment steps than that of natural groundwater. For example, granular activated carbon (GAC) filtration is often used to remove color, improve the taste of the water and additional disinfection steps may be required to achieve microbiological stability of water (e.g. by ultrafiltration (UF) or ultraviolet (UV) treatment). A complete understanding of the fate of As at low levels during the treatment of artificially recharged dune-water is not yet fully obtained. Nevertheless, this knowledge is required to identify the water quality and operational parameters that can improve As removal at dune-water treatment plants in order to achieve very low As concentration (<1 µg/L) in drinking water. In this study, we develop a detailed understanding of As removal during dune-water treatment and investigate opportunities to reduce As levels in the recharged water to even lower levels below 1 µg/L in produced drinking water.

2. Materials and methods

2.1. Water treatment plants

Two water treatment plants (WTPs) in the Netherlands, Ouddorp (WTP 1) and Katwijk (WTP 2), which rely on artificially recharged dune-water for drinking water production were chosen for this study. For both WTPs, the treatment schemes are shown in Fig. 1. The influent and effluent quality is provided in Table 1. Design and operational details are given in Table 2.

2.2. Sampling campaigns

2.2.1. Water samples

To understand the removal of As, sampling campaigns were carried out at both WTPs which included collection of water samples before and after each treatment step and analysis of the samples for a range of water quality parameters (Table 3 and Fig. 1). Approximately 24 h before sampling, rotation of the dune-water abstraction wells was stopped and the filters were backwashed to ensure a stable water quality during the sampling campaign. For sampling, each sampling point was flushed for at least 5 min and subsequently 2 L of water was collected in an acid soaked (0.1 M oxalic acid, soaking for 20 min) and ultrapure water washed glass beaker. From that primary 2 L sample volume, 200 mL of water was directly preserved for analysis and another 200 mL was filtered through 0.45 µm filters before preservation (see section 2.6 for preservation and analysis details). The residual sample volume (1.6 L) was used for the measurements of pH, temperature and

dissolved oxygen using a potable multi-meter (HACH® HQ30D53101301). For the sampling of dune-water, care was taken to avoid aeration of the samples during collection. The pore water over the height of the rapid sand filters (RSFs) was sampled using the available sampling points (at least 10 cm apart) in the full-scale filters at an approximate flow rate of 50 mL/min.

2.2.2. Sampling of rapid sand filter material

To determine the chemical composition of the coating on the RSF media, microbial community analysis and to perform batch experiments aimed to gain insights into As adsorption, filter material from the full-scale RSFs of both WTPs were analyzed. For these purposes, approximately 5 kg of the filter material from the upper 10 cm of each filter bed was collected with a stainless steel spade directly after backwash and stored in a closed bucket.

2.3. Batch experiments

A number of batch experiments with influent, supernatant and effluent water of the RSFs (see Fig. 1 for sample points) were performed to elucidate the effect of different water quality and operational parameters on As removal. Approximately 10 min before each batch experiment, 20 L of water was collected from the relevant sample point in the full-scale WTP using a jerry can (Fig. 1). Further details about the experiments are provided in the following sections.

2.3.1. Supernatant water experiments

Arsenic removal as a function of residence time in RSF supernatant (water storage above RSF) was studied with supernatant water samples from both WTPs using a standard jar test apparatus which has been described previously (Ahmad et al., 2018). The supernatant water sample was poured in 4 jars (2 L each jar) of the jar test apparatus. This was considered t = 0, i.e. start of the experiment. Unfiltered and 0.45 µm filtered samples of the initial solution were collected and preserved for analysis (see section 2.6 for preservation and analysis details). These jars were then stirred at 100 RPM for 60 min. Unfiltered and 0.45 µm filtered samples were collected at t = 15, 30, 45 and 60 min using a sterile syringe while the jars were continuously mixed. Collection of the 60 min samples marked the end of the jar test.

2.3.2. Experiments with influent and effluent of rapid sand filters

Batch experiments were performed with the influent and effluent of RSFs to investigate options for achieving a reduction in As concentration to <1 µg/L. In the experiments with the RSF influent, the impact of 0.5–5 mg/L Fe(III) doses (achieved by FeCl₃ dosing) alone or after potassium permanganate (0.66 mg/L KMnO₄) pre-treatment was studied. The required KMnO₄ dosing was determined by preliminary experiments to achieve complete As(III) oxidation. For the RSF effluent, we investigated only the effect of different Fe(III) doses because of the absence of As(III) in RSF effluent. To investigate the effect of pH on As removal, experiments were performed at natural pH (unamended pH) (pH 7.8 for WTP 1 and pH 8.2 for WTP 2) and at an experimentally lowered pH of 7.0 (achieved by 0.1 M HCl dosing).

First, the jars were filled with the influent or the effluent of the RSFs from both WTPs. Subsequently, a predetermined aliquot of KMnO₄ and/or FeCl₃ was dosed in each jar while the solutions were mixed at 100 RPM. In the KMnO₄–FeCl₃ dosing experiments, the interval between KMnO₄ and FeCl₃ doses was kept constant at 2 min. This interval was chosen to ensure that complete oxidation of As(III) to As(V) had occurred before Fe(III) was dosed (Ahmad et al., 2018). For the pH adjustment, 0.1 M HCl or 0.1 M NaOH was used before the addition of KMnO₄ and/or FeCl₃. Finally,

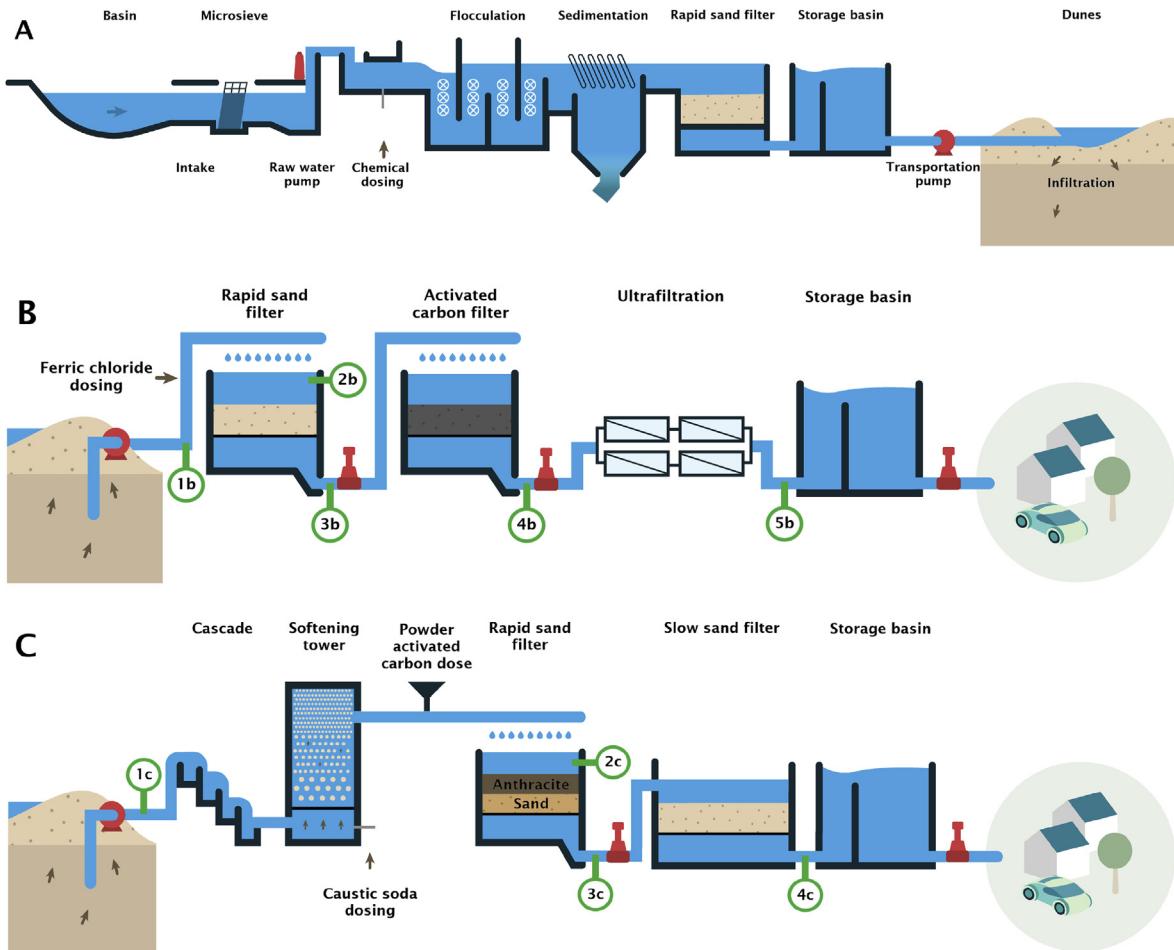


Fig. 1. Process schemes of (A) general pre-treatment of surface water before dune infiltration applicable to both WTPs. (B) Dune-water treatment at WTP 1. (C) Dune-water treatment at WTP 2. Markings 1b–5b and 1c–4c indicate sampling points at WTP 1 and WTP 2 respectively.

unfiltered and 0.45 µm filtered water samples were collected from the jars at $t = 30$ min using a sterile syringe while the jars were continuously mixed. The samples were analyzed for As and Fe concentrations (see section 2.6 for preservation and analysis details).

2.3.3. Experiments with rapid sand filter material

Adsorption and desorption of As by RSF media was studied as a function of pH (7.0–9.0), As concentration and As speciation (As(III) or As(V)). The RSF effluent of each WTP was used as the initial solution in the experiments with RSF media of that WTP. Before experiments, the filter media samples were washed at least 5 times with ultrapure water to remove loose precipitates and afterwards air dried for 24 h at room temperature. The solid-solution ratio used in the batch experiments was 250 g/L. All the suspensions were agitated by back-and-forth strokes at a rate of 120 min⁻¹. Sample aliquots of 100 mL were collected using a sterile syringe with a 30 cm Teflon tube on the tip were taken at $t = 0$, i.e. directly after solid addition and intermittently until $t = 24$ h.

2.3.4. Chemical characterization of rapid sand filter material

The RSF media grains from both WTPs were characterized for the chemical composition of the coating to investigate As(III) oxidation in RSFs. For each sample, the coating of 4.0 g of the filter material was dissolved in 50 mL ultrapure water and 6.3 mL concentrated HNO₃ (65%) followed by heating the suspension at

105 °C for 24 h. After cooling down the solution was filtered through Whatman 589/1 paper filter and analyzed for As, Ca, Fe, Mg, Mn, Si and P concentrations (see section 2.6 for preservation and analysis details).

2.4. Microbial community analysis on rapid sand filter material

To further investigate As(III) oxidation in RSFs, insights into the microbial community in RSFs were obtained by DNA extraction and 16S rRNA taxonomic profiling using next generation sequencing (NGS). To perform the analysis, 40 mL of ultrapure water (Invitrogen, ThermoFisher scientific) was added to 7.0 g of freshly collected filter material from each WTP. High energy sonication was used to release the biomass from the filter material as described previously (Magic-Knezev and van der Kooij, 2004). The suspended biomass was subsequently concentrated on polycarbonate track-etched membrane filters having a pore size of 0.2 µm (Sartorius). The PowerBiofilm Kit (Qiagen) was used for DNA extraction using the protocol described by the manufacturer. The V4 variable region of the 16S rRNA genes was amplified using the 515F-806R primer pair. Amplicons were barcoded and the size and concentration was checked on an Agilent Bioanalyser. DNA concentrations were determined using the Qubit fluorescent measurement (Fisher Scientific). Equimolar amplicon concentrations were pooled and sequenced using the MiSeq v2 (2 × 250 bp) reagents (Illumina) on an Illumina MiSeq platform. Subsequent processing of sequence

Table 1

Raw dune-water and treatment plant effluent (drinking water) quality at WTP 1 and WTP 2. Data is based on the regular water quality monitoring programs of the drinking water companies in the period 2016–2019. For comparison the drinking water quality standards in the Netherlands are also given.

Parameter	Unit	WTP 1		WTP 2		Drinking water quality standard in the Netherlands ^b
		Raw dune-water	Treatment plant effluent (drinking water)	Raw dune-water	Treatment plant effluent (drinking water)	
Temperature	°C	11.5–12.2	11.7–15.0	7.7–12.4	13.7–16.8	<25
pH	—	7.45–7.85	7.74–7.91	7.62–7.71	8.17–8.42 ^a	7.0–9.5
Dissolved Oxygen	mg/L O ₂	<0.1–2.0	9.2–10.1	1.7–3.5	9.7	>2
Electrical Conductivity	mS/m	64.5–67.5	n.m.	47–56	48.5–52.6	<125
Bicarbonate	mg/L HCO ₃	230–250	n.m.	200–210	167–184	>60
Turbidity	NTU	n.m.	<0.03	0.3–3.5	<0.03	<1
Iron	mg/L Fe	0.7–1.9	<0.01	<0.01–1.5	<0.01	<0.2
Manganese	mg/L Mn	0.08–0.11	<0.01	0.03–0.2	<0.01	<0.05
Calcium	mg/L Ca	83–88	82–87	66–72	40–46	n.r.
Magnesium	mg/L Mg	10	10	7.4–8.3	7.7–8.3	n.r.
Ammonium	mg/L NH ₄	0.25–0.33	<0.02	0.03–0.2	<0.02	<0.2
Nitrite	mg/L NO ₂	0.013–0.02	<0.007	0.05–0.10	<0.007	<0.1
Nitrate	mg/L NO ₃	<0.2–0.3	2.6–3.7	2.0–6.2	1.7–2.2	<50
Arsenic	µg/L As	6.9–12.1	2.4–3.6	3.5–4.2	3.2–3.4	<10
Ortho-phosphate	mg/L P	0.03–0.25	0.007–0.03	0.07–0.2	0.02–0.05	n.r.
Silicate	mg/L Si	3.0–4.6	3.1–4.5	n.m.	n.m.	n.r.
Total organic carbon	mg/L C	3.3–3.9	1.6–3.0	2.6–2.9	2.1	n.r.
Sulphate	mg/L SO ₄	27–50	30–52	40–46	45–51	<150
Sodium	mg/L Na	34–55	34–55	30–36	57–60	<150
Chloride	mg/L Cl	67–110	66–108	45–54	54–56	<150

n.m. Not measured.

n.r. Not regulated.

^a pH higher than the raw water because of NaOH dosing during softening.

^b Based on national guideline "Drinkwaterbesluit" in act since July 2018 which is available online at <https://wetten.overheid.nl/BWBR0030111/2018-07-01#BijlageA>.

Table 2

Process details of WTP 1 and WTP 2. Abbreviations are as follows. RSF: Rapid Sand Filter HRT: Hydraulic Residence Time. GAC: Granular Activated Carbon filter, PAC: Powdered Activated Carbon, UF: Ultrafiltration, SSF: Slow Sand Filter.

	WTP 1	WTP 2
Pre-treatment		
Surface water source	Rhine-Meuse estuary	River Meuse
Treatment before dune infiltration	Coagulation-Flocculation-Rapid sand filtration	Coagulation-Flocculation-Rapid sand filtration
Dune storage	30 days	60 days
Post-treatment		
Dune-water abstraction	4.8 Mm ³ /year	24.8 Mm ³ /year
Aeration	Spray	Cascade
Rapid sand filtration	<ul style="list-style-type: none"> Single media RSF with silica sand ($h = 1.4 \text{ m}$; $d = 2.0\text{--}3.8 \text{ mm}$) Supernatant level^a: 0.35 m HRT of supernatant: 11 min Filtration velocity: 2 m/h HRT in filter bed: 17 min Filter run time: 3–4 days 	<ul style="list-style-type: none"> Double media RSF; top layer anthracite ($h_1 = 0.5 \text{ m}$; $d_1 = 1.7\text{--}2.8 \text{ mm}$) + bottom silica sand ($h_2 = 1.0 \text{ m}$; $d_2 = 0.8\text{--}1.3 \text{ mm}$) Supernatant level^a: 1.0 m HRT of supernatant: 21 min Filtration velocity: 4 m/h HRT in filter bed: 10 min Filter run time: 7 days
Activated carbon treatment	<ul style="list-style-type: none"> GAC filter with media. Filtrasorb F300 Chemviron Carbon in Belgium ($h = 2.0 \text{ m}$; $d = 1.5\text{--}1.7 \text{ mm}$) Supernatant level^a: 0.30 m Filtration velocity: 2.5 m/h Filter run time: 10 days 	<ul style="list-style-type: none"> PAC dosing (2 mg/L) in the feed of rapid sand filters. NORIT® SA SUPER (Cabot Norit Netherlands B.V.)
Polishing filter	<ul style="list-style-type: none"> UF (pore size 20 nm). Norit X-flow S-225 Flux 55 L/m².h; Recovery>98% Operational transmembrane pressure (TMP) = 0.2 bar Hydraulic backwash after 180 min 	<ul style="list-style-type: none"> SSF with silica sand ($h = 1.0 \text{ m}$; $d = 0.3\text{--}1.2 \text{ mm}$) Supernatant level^a: 1 m Filtration velocity: 0.3 m/h Filter surface is scrapped 10 cm and replenished after every 2 years

^a Water level above a submerged granular media filter.

data was performed using the MOTHUR pipeline (Schloss et al., 2009). In short, raw paired end sequence reads were assembled, aligned against the Silva alignment database (version 132 (Quast

et al., 2013);) and potential chimeric sequences were removed. Finally, Operational Taxonomic Units (OTUs) with 97% sequence identity were predicted and taxonomic identification of the OTUs to

Table 3

Concentrations of As and other elements at various points along the treatment trains of WTP 1 and WTP 2. UNF and 0.45 µm FIL refer to unfiltered and 0.45 µm filtered samples, used to distinguish between total and dissolved elemental concentrations. The increase in supernatant Fe concentration in WTP 1 compared to raw dune-water is due to FeCl₃ dosing in the influent of RSF at WTP 1. In the supernatant of WTP 2, UNF As and Fe concentrations were slightly lower compared to the raw dune-water ($\approx 5\%$) due to removal during softening.

Water sample code	Sample point in Fig. 1	As µg/l	As(III) µg/l	As(V) µg/l	Fe mg/l	Mn mg/l	NH ₄ ⁺ mg/l	P mg/l	Si mg/l	OC mg/l	Ca mg/l	Mg mg/l	pH
WTP 1													
Raw dune-water_UNF	1b	10.3	—	—	1.20	0.11	0.30	—	—	—	80	10.1	7.5
Raw dune-water_0.45 µm FIL	1b	9.5	8.5	0.8	0.92	0.11	—	0.20	3.5	3.1	—	—	—
Supernatant RSF_UNF	2b	9.8	—	—	1.50	0.12	0.30	—	—	—	80	10.0	7.5
Supernatant RSF_0.45 µm FIL	2b	8.5	7.2	0.7	0.62	0.11	—	0.10	3.4	2.9	—	—	—
Effluent RSF_UNF	3b	2.5	—	—	<0.005	<0.005	<0.02	—	—	—	81	10.4	7.7
Effluent RSF_0.45 µm FIL	3b	2.5	<0.5	2.4	<0.005	<0.005	—	0.02	3.5	2.6	—	—	—
Effluent ACF_UNF	4b	2.5	—	—	<0.005	<0.005	<0.02	—	—	—	82	10.3	—
Effluent ACF_0.45 µm FIL	4b	2.5	<0.5	2.5	<0.005	<0.005	—	—	—	2.4	—	—	—
Effluent UF_UNF	5b	2.5	—	—	<0.005	<0.005	<0.02	—	—	—	81	9.9	7.8
Effluent UF_0.45 µm FIL	5b	2.5	<0.5	2.5	<0.005	<0.005	—	0.02	3.5	—	—	—	—
WTP 2													
Raw dune-water_UNF	1c	4.1	—	—	0.21	0.04	0.13	—	—	—	70	8.5	7.7
Raw dune-water_0.45 µm FIL	1c	3.6	1.3	2.3	0.08	0.04	—	0.10	3.7	2.9	70	8.7	—
Supernatant RSF_UNF	2c	3.8	—	—	0.19	0.04	0.13	—	—	—	48	8.5	8.3
Supernatant RSF_0.45 µm FIL	2c	3.2	1.3	1.9	<0.005	0.03	—	0.05	3.7	2.7	48	8.7	—
Effluent RSF_UNF	3c	3.2	—	—	<0.005	<0.005	<0.02	—	—	—	47	8.5	8.3
Effluent RSF_0.45 µm FIL	3c	3.2	<0.5	3.1	<0.005	<0.005	—	0.05	3.6	2.6	47	8.6	—
Effluent SSF_UNF	4c	3.2	—	—	<0.005	<0.005	<0.02	—	—	—	48	8.4	8.2
Effluent SSF_0.45 µm FIL	4c	3.2	<0.5	3.2	<0.005	<0.005	—	0.05	3.6	2.6	47	8.5	—

genus-level was performed against the Silva taxonomic database, only prokaryote OTUs were retained. PCA including the proportion of the 34 most abundant genera and a selection of water geochemical parameters (from Table 1) was carried out using the XLSTAT 2019 version 3.2.

2.5. Chemicals and other apparatus

All chemicals were reagent grade. KMnO₄ was dosed using a 0.03 M KMnO₄ (3.6 g/L MnO₄) stock solution. It was prepared by dissolving 948 mg of solid KMnO₄ (Cairox®, Carus Corporation) in 200 mL ultrapure water directly before the start of batch experiments. A FeCl₃ solution (2.0 g Fe(III)/L) was used to dose Fe(III) in water. It was prepared by dissolving 1936 mg solid FeCl₃.6H₂O (J.T. Baker®) in 200 mL ultrapure water directly before the start of the batch experiments. For As(III) and As(V) spike, certified solutions (1000 mg As(III) and As(V)/L, Inorganic ventures®) set in HCl and H₂O matrices respectively were used without any dilution. For pH control during the experiments, 0.1 M NaOH and 0.1 M HCl solutions were used. The PP/PE 50 mL sterile syringes (Sigma-Aldrich) were used for the filtration of water samples. To obtain 0.45 µm filtered samples, GE's GD/XP disposable syringe filters were used.

2.6. Preservation and analysis of water samples

All samples were analyzed at Aqualab Zuid, which is an independent accredited water analysis laboratory in the Netherlands. All samples were preserved and stored at 4 °C before analysis. The samples for the determination of arsenic (As), iron (Fe), manganese (Mn), phosphorous (P), calcium (Ca), magnesium (Mg) and silicon (Si) were preserved immediately after sampling by adding 2 mL of 50% v/v nitric acid (HNO₃) per 100 mL of water sample. The analysis of these samples was carried out by Inductively Coupled Plasma Mass Spectrometry (ICP–MS) (Thermo Fisher Scientific iCAP™ RQ), having PrepFAST 2 sc-4DX autosampler. The aerosol sample was ionized/atomized in an argon plasma and mass spectrometry using a QCell Collision/Reaction Cell for mass/charge ratio detection and optical emission spectrometry using an Echelle spectrometer equipped with two SCD detectors (combined range 165–782 nm)

were used to derive element-specific information. The samples for total organic carbon (TOC) analysis were preserved with 0.18 mL of 9.1 M H₂SO₄ (59% w/w) added in 100 mL sample. After removing inorganic carbon at pH < 2 using O₂ bubbling, the TOC measurement was carried out by high temperature combustion (680 °C) followed by non-dispersive infrared detection, according to the standard method NEN-EN 1484. The samples for As speciation were preserved with 2 mL of 125 mM EDTA added to 100 mL of the 0.45 µm filtered water sample. After separation using ion chromatography, the different As species as aerosols were ionized in an argon plasma and subsequently analyzed by a quadrupole mass-spectrometer (IC–ICP–MS). The NH₄⁺ was analyzed by a discrete analyzer spectrophotometry (Aquakem 250, Thermo Scientific). The reaction of NH₄⁺ with hypochlorite in the presence of sodium nitroprusside at pH of 12.6 provides a coloured (blue) solution. Extinction of this solution at 660 nm was used for analysis.

3. Results and discussion

3.1. Arsenic removal during dune-water treatment

Table 3 presents results of the sampling campaigns that were carried out at WTP 1 and WTP 2 to gain insights into As removal during dune-water treatment. A fraction of As and Fe concentrations in raw dune-water was removed by 0.45 µm filtration at both WTPs which shows that some portion of As and Fe is already co-precipitated in the raw dune-water at both WTPs. During treatment of dune-water, As removal is strongly correlated with Fe removal at both WTPs, attributed to further co-precipitation of As with Fe(III) (oxyhydr)oxides that are formed due to the (oxidative) hydrolysis of natural and dosed Fe in water (latter only at WTP 1, Fig. 1). At WTP 1, the effluent of RSF is treated by GAC filtration and UF (Fig. 1B) and at WTP 2 the effluent of RSF is treated by SSF to produce drinking water (Fig. 1C). We observe that the As concentrations in RSF effluent were not reduced further by any of these treatment steps (Table 3). This can be attributed to the absence of As adsorbing Fe(III)(oxyhydr)oxides in the RSF effluent at both WTPs and low adsorption affinity between As(V) (the predominant As species in RSF effluent) and the negatively charged surfaces of

activated carbon media (Newcombe et al., 1993), UF membranes (Floris et al., 2016; Li et al., 2011) and SSF media (Śmiech et al., 2018).

Complete Mn removal is observed in the RSF bed at both WTPs (Table 3). The direct oxidation of Mn(II) to form solid MnO_x with oxygen in the relevant pH range is a kinetically slow process and can explain the occurrence of dissolved Mn in the supernatant storage at both WTPs (Diem and Stumm, 1984; Knocke et al., 1991; Søgaard and Madsen, 2013; Van Benschoten et al., 1992). The Mn removal in RSFs is attributed to bacteria and surface catalysts on the filter media grains which are known to mediate the Mn(II) transformation to insoluble MnO_x (Bruins et al., 2015; Katsoyannis et al., 2008). The removal of NH_4^+ at both WTPs also occurs in the filter bed, attributed to the biological oxidation (nitrification) executed by different bacterial species in the filter bed (de Moel et al., 2006; De Vet, 2011).

Arsenic in the raw dune-water at both WTPs occurs as a combination of As(III) and As(V) (Table 1). This observation is consistent with previous studies which indicate that As mobilization in dunes could be due to reductive dissolution of Fe(III)(oxyhydr)oxides with (local) input from oxidation of As bearing pyrite minerals (Ahmad et al. 2015, 2020; Stuyfzand et al., 2008). No significant differences are observed between the concentrations of aqueous As(III) in the raw dune-water and RSF supernatant at both WTPs. This shows that aeration is not effective for As(III) oxidation to As(V). A similar slow oxidation kinetics of As(III) in oxygen systems has been reported by previous studies (Frank and Clifford, 1986; Ghurye and Clifford, 2001).

Irrespective of As speciation in the RSF influent, As(V) is the predominant species of residual As in the effluent of RSFs at both WTPs which can be attributed to oxidation of aqueous As(III) in RSFs. At WTP 1, the difference between aqueous As and Fe concentrations in the supernatant and the RSF effluent indicates an uptake of 9.7 μg As per mg of the precipitated Fe during rapid sand filtration. This is much higher than the As uptake by Fe(III) precipitates during aeration and supernatant storage (1.3 μg As per mg Fe). The higher As uptake by Fe(III) precipitates in the filter bed can be explained by the oxidation of aqueous As(III) due to either MnO_x and/or As-oxidizing bacteria which have been observed both on RSF media grains (see section 3.2, 3.3 and 3.4 for further discussion). At WTP 2, As concentration in the effluent of RSF is similar to the aqueous As in the supernatant. This can be explained by the fact that in the supernatant of WTP 2 Fe is already precipitated and therefore further Fe(III)(oxyhydr)oxide precipitation and corresponding As co-precipitation is not possible in RSF bed at WTP 2. Thus, it can be concluded that a higher As co-precipitation efficiency is achieved when a higher proportion of Fe is precipitated in RSF bed where at the same time As(III) is oxidized into As(V).

In summary, the sampling campaigns reveal that during dune-water treatment rapid sand filtration is the most important treatment step for the oxidation and removal of As. The efficiency of As co-precipitation with Fe(III)(oxyhydr)oxides is higher in RSF bed compared to aeration and supernatant storage, because of the rapid oxidation of As(III) to As(V) in the RSF bed. Therefore As removal can be increased by ensuring that more of the Fe is precipitated in the RSF bed. After the RSF no further As removal is observed due to the low affinity between As(V) and the negatively charged filtration surfaces of subsequent treatment steps.

3.2. Oxidation and removal of arsenic over filter bed height

The oxidation and removal of As during rapid sand filtration was further studied by collecting pore water samples over the RSF beds at both WTPs. The results show that removal of As, Fe, Mn and NH_4^+ predominantly occurs in the upper region (0.5 m and 0.7 m for WTP

1 and WTP 2 respectively) of the filter bed at both WTPs (Fig. 2A and Fig. 2D). Simultaneously, the oxidation of dissolved As(III) into As(V) also occurs in the upper (~0.7 m) region of RSFs (Fig. 2C and F). Nevertheless, clear differences are observed between WTP 1 and WTP 2 for As and Fe co-precipitation profiles. At WTP 1, As and Fe co-precipitation increases with filter depth until 0.5 m below the filter bed surface. Arsenic is not removed from the solution further because no Fe(III)(oxyhydr)oxides are formed below 0.5 m onto which As could adsorb (Fig. 2B). On the other hand, at WTP 2 no further As co-precipitation in the filter bed occurs (Fig. 2E) because all Fe is already oxidized and precipitated in the supernatant. Thus, though removal and oxidation of As is concentrated in the upper part of the RSFs at both WTPs, As(III) oxidation appears to be independent of Fe oxidation and precipitation.

3.3. Rapid sand filter media surface coating

The RSF media at both WTPs have been used for over a decade. To further understand the mechanism of As(III) oxidation in RSFs, the brown-black filter media coating was analyzed to determine the chemical composition (Fig. 3 and Table 4). Besides other elements such as Ca, Mg, Si, P and As, significant concentrations of Fe and Mn are found in the coating of both filter media (Table 4, Fig. S1), indicating the presence of Fe and Mn oxides in the filter material coating (Bruins et al., 2015; Gude et al., 2016, 2017; Jessen et al., 2005; Sharma, 2001). While the oxidation of As(III) by Fe(III) oxides is known to be slow (Oscarson et al., 1981), the MnO_x on the filter media grains can rapidly oxidize As(III) into As(V) (Driehaus et al., 1995; Gude et al., 2017; Lafferty et al., 2010; Moore et al., 1990; Oscarson et al., 1983) and therefore the MnO_x may be responsible for the observed rapid oxidation of As(III) in the RSFs. However, several recent studies argue that As(III) oxidation in RSFs is microbiologically mediated (Cronagle et al., 2019; Gude et al., 2018a, b). Therefore, microbial communities in RSFs of both WTPs were analyzed to investigate the presence of As-oxidizing bacteria.

3.4. Taxonomic community profiling of 16S rRNA sequences

Taxonomic profiling of the bacterial communities was performed on the filter media grains obtained from both WTPs. The overview of the relative proportions of the different bacterial taxa at family and genus level in the microbial communities shows only minor differences between the duplicate samples from each WTP. This demonstrates that representative samples were analyzed from both WTPs (Fig. 4). Family level taxonomic profiling indicates that, though much less abundant than the other genera like *Nitrospira* or *Methyloglobulus*, bacterial sequences related to *Xanthobacteraceae* and *Burkholderiaceae* are present on both the filter media. Some strains in these bacterial families carry *aioA* genes encoding for As(III) oxidase and are thus able to rapidly oxidize As(III) (Heinrich-Salmeron et al., 2011). Therefore, we hypothesize that As(III) oxidation in rapid sand filters during dune-water treatment is biologically mediated by As(III) oxidizing bacteria. The PCA of both geochemical and taxonomic data (Fig. S4) underlines the separation of two geochemical signatures. Genera associated to nitrogen and As biogeochemical cycles are associated with both water types (i.e. WTP 1 and WTP 2), however a correlation between the most abundant genus, "*Nitrospira*", and NH_4^+ concentration is observed.

3.5. Arsenic adsorption onto rapid sand filter material

The chemical characterization of filter media coating (Table 4) shows that Fe(III)(oxyhydr)oxides are present on filter media grains which may contribute to As removal in RSFs. To investigate this we performed batch experiments with RSF media and RSF effluent

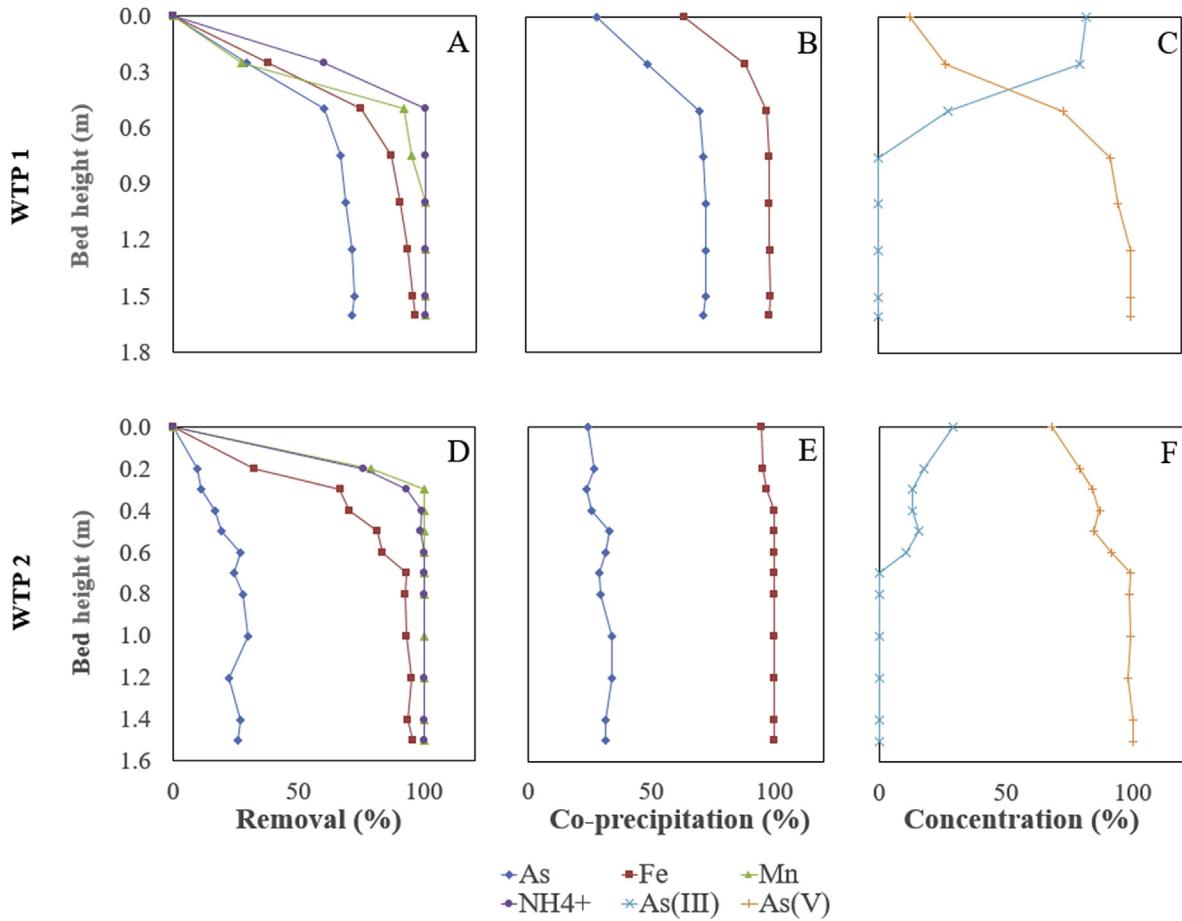


Fig. 2. Removal of total As, Fe, Mn and NH₄⁺ over rapid sand filter bed height at (A) WTP 1 and (D) WTP 2. Co-precipitated As and Fe over filter bed height at (B) WTP 1 and (E) WTP 2. Dissolved As(III) and As(V) over rapid sand filter bed height at (C) WTP 1 and (F) WTP 2. To calculate % of co-precipitated As (or Fe), we first subtracted the dissolved As (or Fe) concentration at each sampling point from the total As (or Fe) concentration in the RSF influent and then we divided this quantity by the total As (or Fe) concentration in the RSF influent.

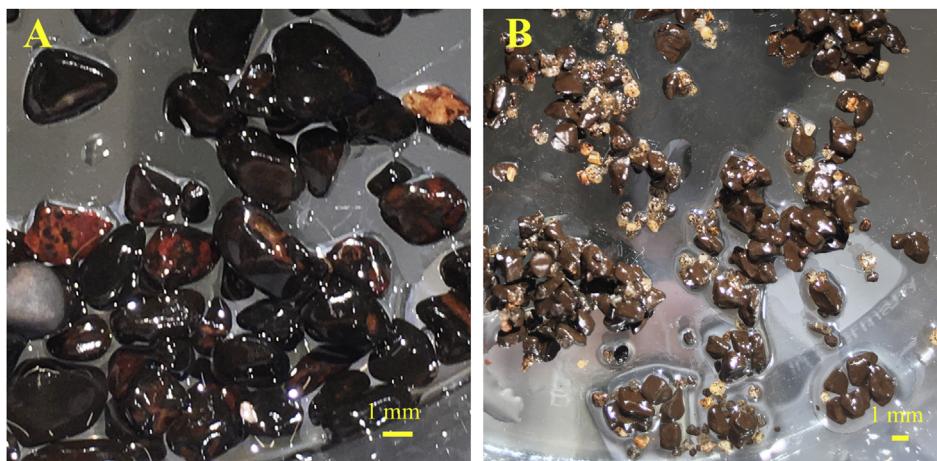


Fig. 3. Images of rapid sand filter media grains obtained from (A) WTP 1 and (B) WTP 2. Both filter media have been used for over a decade.

samples of both WTPs under different conditions of pH, initial As concentration and As speciation. The adsorption-desorption distribution coefficient (K_d) under different conditions is presented in Fig. 5 and Fig. 6. We observe that at natural pH and As concentrations, K_d value after a long equilibration time of 1440 min (24 h) is very low ($K_d \approx 0$) for both WTPs (Fig. 5A and B), indicating absence

of any adsorption of As onto RSF media coating even after a prolonged contact of 24 h (the contact time in RSFs is 17 min and 10 min for WTP 1 and WTP 2 respectively, Table 2). These results show that the adsorption sites on the Fe(III)(oxyhydr)oxides present in filter media coating are already in equilibrium with the As concentration in water and therefore no further As adsorption takes

Table 4

Elemental composition of rapid sand filter media coating in g/kg ds (ds: dry solid). The numbers in brackets represent the relative abundance in %.

Element	Filter media grains WTP 1	Filter media grains WTP 2
	g/kg ds (%)	g/kg ds (%)
Arsenic (As)	0.2 (<1)	0.004 (<1)
Calcium (Ca)	29.7 (12)	105 (84)
Iron (Fe)	109 (44)	8.0 (6)
Magnesium (Mg)	5.8 (2)	1.6 (1)
Manganese (Mn)	85.8 (34)	6.9 (6)
Silica (Si)	8.4 (3)	2.8 (2)
Phosphorous (P)	8.4 (3)	0.7 (<1)

place. Moreover, this result confirms that co-precipitation of As with freshly formed Fe(III)(oxyhydr)oxides is the main As removal mechanism at both WTPs and filter media coating does not contribute to As removal. At a pH of 7.0, a positive K_d is observed for both WTPs, indicating adsorption of As onto the RSF media coating. On the other hand, when pH is increased to 9.0, a negative K_d is observed for both WTPs, indicating desorption of As from the RSF media coating. The observed adsorption/desorption of As as a function of pH can be explained by the fact that the number of adsorption sites for As(V) (which is a deprotonated oxyanion) on Fe(III) (oxyhydr)oxides increases with a decrease in pH (Dixit and

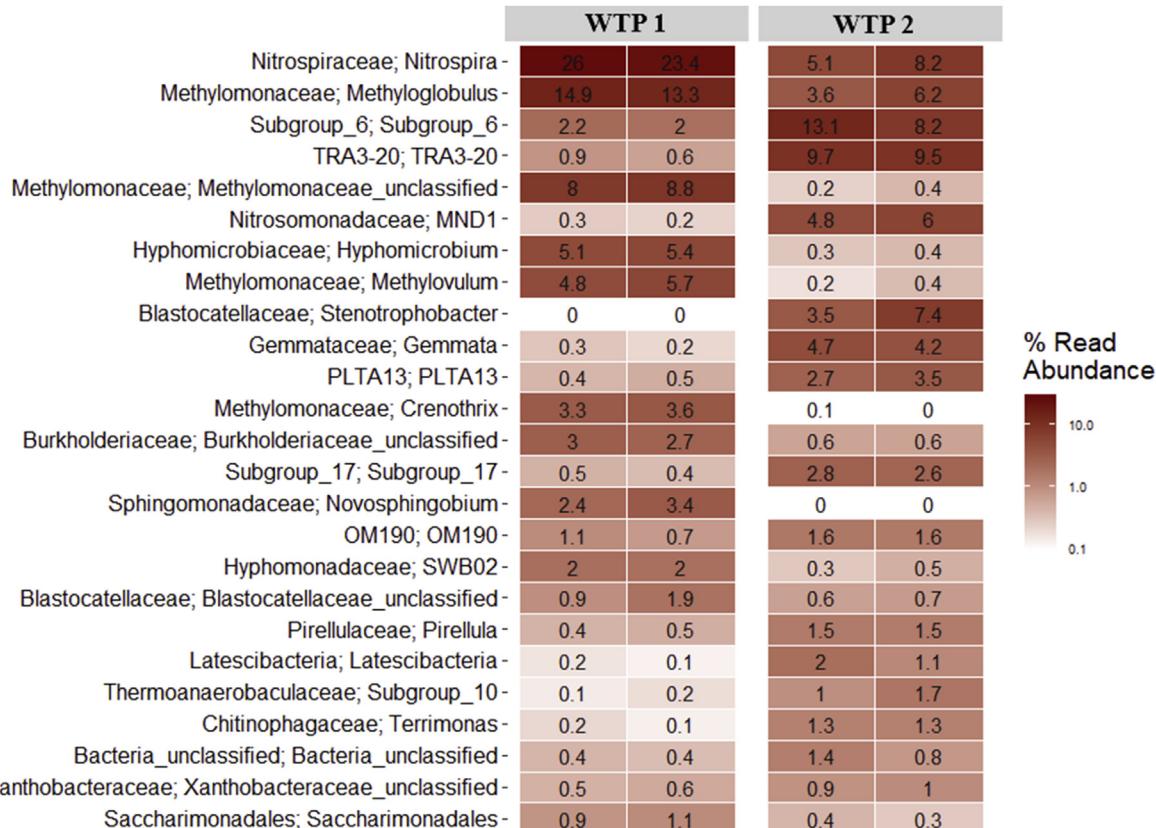


Fig. 4. Relative abundance of the 25 most abundant bacterial taxa in the microbial communities of duplicate samples from the WTP 1 and WTP 2 rapid sand filters. The names of the taxa are shown at family and genus level (from left to right separated with semi-colons).

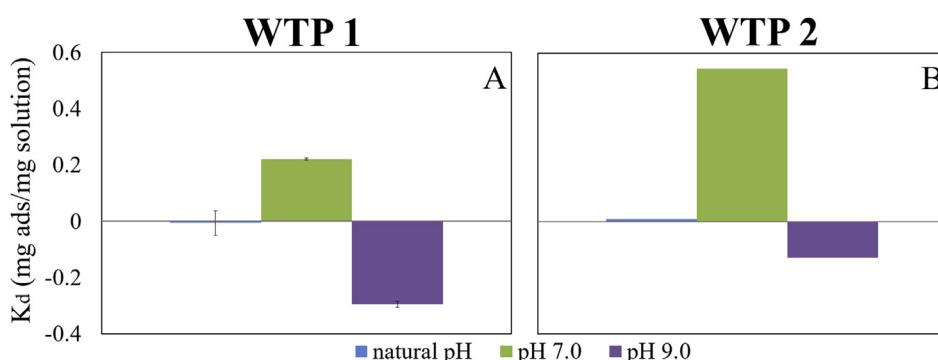


Fig. 5. Distribution coefficient (K_d) at $t = 1440$ min (24 h) for As adsorption/desorption from RSF effluent to rapid sand filter material of (A) WTP 1 and (B) WTP 2 as a function of pH. The natural pH of RSF effluent for WTP 1 and WTP 2 is 7.8 and 8.2 respectively.

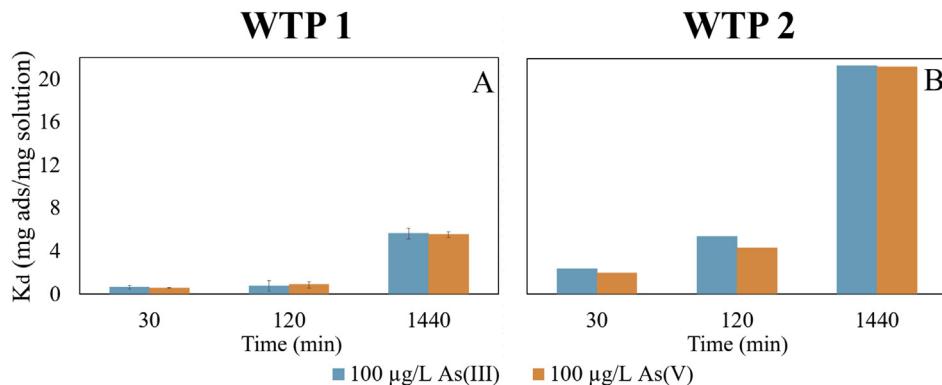


Fig. 6. Distribution coefficient (K_d) in function of time for As adsorption/desorption from RSF effluent to rapid sand filter material of (A) WTP 1 and (B) WTP 2 at initial As(III) or As(V) concentration of 100 µg/L. The natural pH of the RSF effluent from WTP 1 and WTP 2 is 7.8 and 8.2 respectively.

Hering, 2003; Kanematsu et al., 2013; Manning et al., 1998; Meng et al., 2000; Pierce and Moore, 1982). Thus, from these results it can be concluded that filter media coating does not contribute to As removal and that a reduction in pH is required to adsorb more As onto the Fe(III)(oxyhydr)oxides.

At natural pH, the adsorption of As onto filter media occurs only in the experiments with higher As concentration (100 µg/L As(III) or As(V) spike, Fig. 6A and B), which can be explained by the fact that the equilibrium loading of an adsorbent increases with an increase in adsorbate/adsorbent ratio until adsorption capacity of the adsorbent is reached (Raven et al., 1998; Wilkie and Hering, 1996). We also observe that the adsorption of As is similar when As(III) or As(V) is the initial As species (Fig. 6A and B). This can be attributed to the oxidation of aqueous As(III) to As(V) before adsorption (Fig. S2), thus again confirming the accelerating effect of filter media grains on As(III) oxidation.

3.6. Impact of extended residence time in supernatant

Jar tests were performed with the supernatant water samples from the RSFs of both WTPs to investigate whether increasing residence time of water in the supernatant storage could increase As removal. For WTP 1, As and Fe removal is $\approx 30\%$ and $\approx 70\%$ respectively at $t = 0$ (Fig. 7A, $t = 0$ refers to the occasion of supernatant sample collection which corresponds to the residence time in the supernatant (Table 2). Arsenic and Fe removal increases to 35% and 85% respectively at $t = 15$ min and 40% and 100% at $t = 30$ min (Fig. 7A). No further increase in As removal occurs after 30 min because of the absence of freshly formed additional Fe(III) precipitates. The achieved As removal efficiency in this case is much lower compared to As removal at WTP 1 (40% compared to 75%), which can be due to the fact that As(III) was not oxidized in the absence of RSF media (Fig. 7C). Thus, it can be concluded that the extended residence time in the supernatant storage is ineffective for increasing As removal during dune-water treatment. In contrast to WTP 1, no considerable increase in As removal is observed with extended residence time in jar tests with supernatant water of WTP 2 (Fig. 7B), which can be attributed to the absence of fresh formation of Fe(III) precipitates.

We also monitored removal of P and Si as a function of extended residence time in the supernatant. The results show that P is better removed than As, e.g. for WTP 1 removal of P is $\approx 60\%$ at $t = 0$ which increases to 75% and 85% at $t = 15$ min and 30 min respectively (Fig. 7A). The relatively lower removal of As compared to P can be attributed to the lower As concentration in the initial solution and the presence of a major proportion (80–85%) of aqueous As in the form of As(III) (Fig. 7C) which is generally outcompeted by

P for the adsorption sites on Fe(III) precipitates due to lower affinity of As(III) than P (Dixit and Hering, 2003; Jain and Loeppert, 2000; Stachowicz et al., 2008). The removal of Si remains low (<5%) in all the cases which can be attributed to the uncharged nature of Si species at the given pH (Kanematsu et al., 2013; Roberts et al., 2004; Swedlund and Webster, 1999).

3.7. Arsenic reduction to below 1 µg/L at dune-water treatment plants

3.7.1. $KMnO_4$ — $FeCl_3$ dosing in RSF influent

The sampling campaigns show that As removal during dune-water treatment depends on As speciation, pH and amount of freshly precipitated Fe(III)(oxyhydr)oxides in water. To explore opportunities for As reduction to very low levels (<1 µg/L), we studied As co-precipitation efficiency in RSF influent as a function of Fe(III) dosing and pH, with and without pre-treatment with $KMnO_4$. At natural pH of RSF influent, the As co-precipitation efficiency increases with Fe(III) dosing for both WTPs (Fig. 8A and Fig. 8C), attributed to the availability of a higher amount of Fe(III) precipitates in water that adsorb more As (Dixit and Hering, 2003; Hering et al., 1996; Qiao et al., 2012; Su and Puls, 2001; Wilkie and Hering, 1996; Youngran et al., 2007). We further observe that As co-precipitation efficiency corresponding to a residual As concentration of significantly lower than 1 µg/L is achieved only in case of WTP 2 (at 3 mg/L Fe(III)) and the increase in As co-precipitation is steeper for WTP 2 than WTP 1. This can be explained by the fact that in the RSF influent of WTP 2 the proportion of As(V) is higher than WTP 1 (Table 3). Interestingly, in case of WTP 1 when the pH is lowered to 7.0, the As removal efficiency remains similar to pH 7.8 (Fig. 8A). Although the amount of precipitated Fe is slightly lower at pH 7.0 compared to results obtained at pH 7.8 (due to the slower oxidation of natural Fe(II) at pH 7.0 (Vries et al., 2017)), we attribute the insignificant impact of pH on As co-precipitation to the presence of a large proportion of As in the form of As(III) at WTP 1 (Fig. S3) whose adsorption onto Fe(III)(oxyhydr)oxides is known to remain unaffected over a pH range of 4–9 (Dixit and Hering, 2003; Kanematsu et al., 2013; Stachowicz et al., 2006, 2008).

When the co-precipitation of As in RSF influent is studied with $KMnO_4$ pre-treatment (0.66 mg/L $KMnO_4$) which facilitates the oxidation of As(III) to As(V), the As removal efficiency drastically improves for both WTPs (Fig. 8B and D). For WTP 1 (Fig. 8B), the residual As concentration of ≈ 1 µg/L ($\approx 90\%$) is achieved with Fe(III) dose of only 1.5 mg/L. Similarly for WTP 2, the residual As concentration of 0.9 µg/L As ($\approx 80\%$ removal) is achieved with only 0.7 mg/L Fe(III) dose (Fig. 8D). Thus, As reduction to <1 µg/L can be achieved at a much lower Fe(III) dose if $KMnO_4$ pre-treatment is

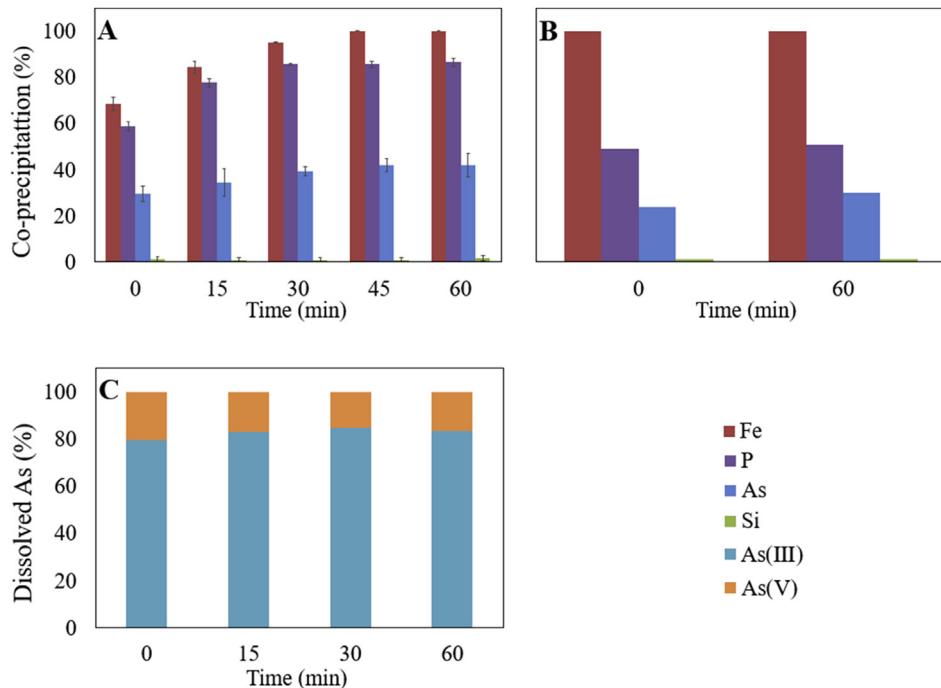


Fig. 7. Removal of As, Fe, P and Si from the supernatant water by 0.45 μm filtration in batch experiments as function of time. (A) WTP 1. (B) WTP 2. (C) the aqueous As speciation in the supernatant water of WTP 1 during the batch experiment.

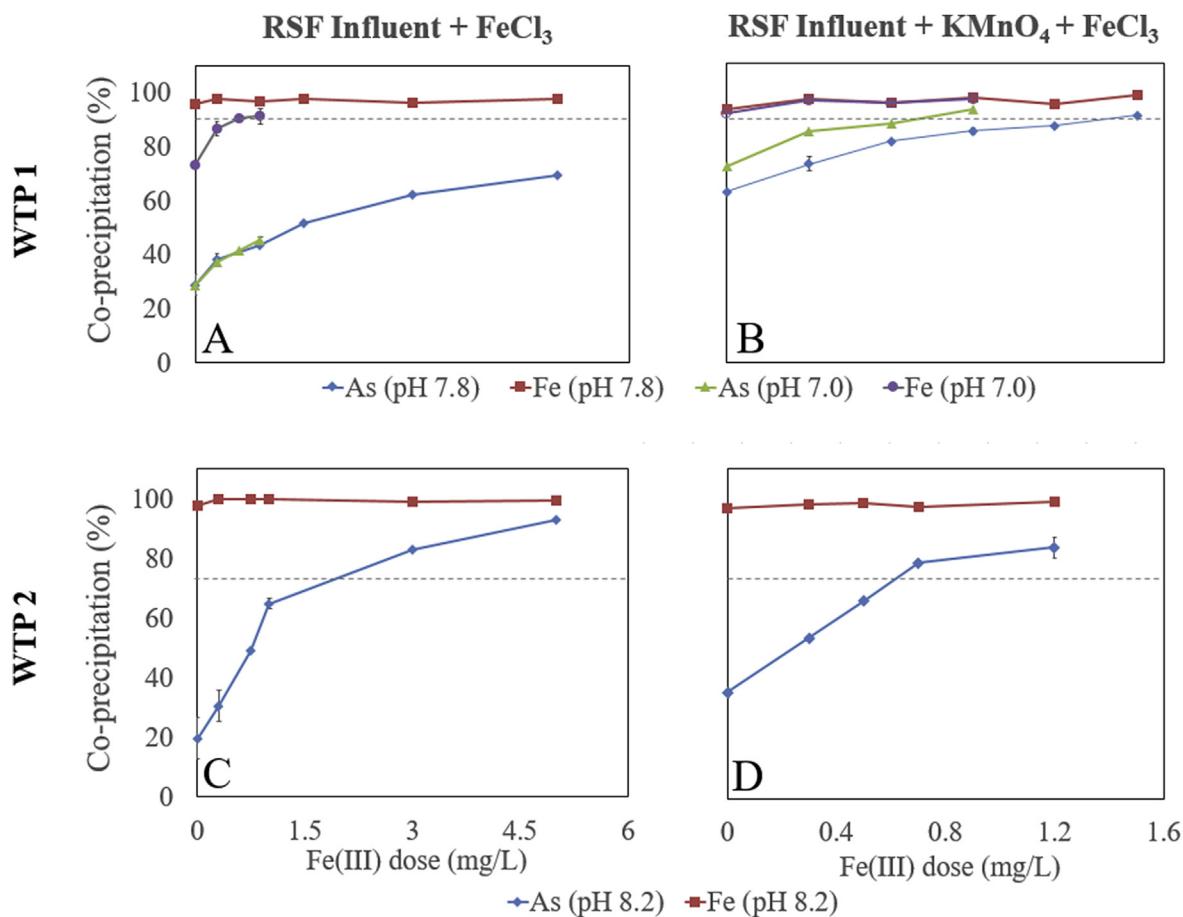


Fig. 8. Arsenic and Fe removal in batch experiments performed with the influent rapid sand filters at WTP 1 (A and B) and at WTP 2 (C and D). The rapid sand filter influent of WTP 1 and WTP 2 contained 10.8 and 4.1 $\mu\text{g/L}$ As respectively. The dashed line on each figure indicates As removal corresponding to 1 $\mu\text{g/L}$ residual As.

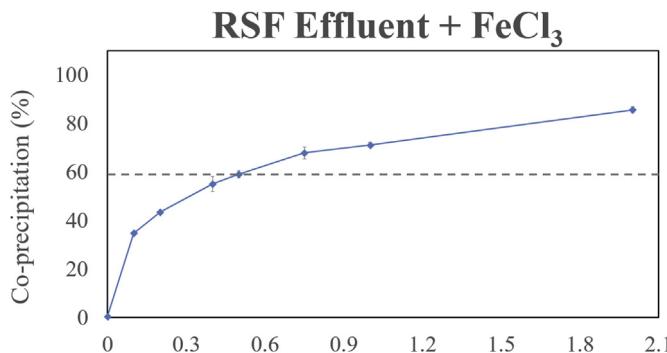


Fig. 9. Arsenic in batch experiments performed with the effluent of rapid sand filters at WTP 1. The rapid sand filter effluent of WTP 1 contained 2.3 µg/L As respectively. The dashed line indicates % As removal corresponding to 1 µg/L residual As.

applied. Oxidizing As(III) to As(V) by dosing a strong oxidant such as KMnO₄ has also been previously shown to increase As co-precipitation with Fe(III) (oxyhydr)oxides (Ahmad et al., 2018; Bissen and Frimmel, 2003; Sorlini and Gialdini, 2010) because As(V) adsorbs to Fe(III) precipitates more readily compared to As(III) (Hering et al., 1996; Hsu et al., 2008; Lakshmanan et al., 2008; Lytle et al., 2005; Qiao et al., 2012). For WTP 1, at the reduced pH 7.0 a residual As concentration of 0.8 µg/L (93% removal) with Fe(III) dose of only 0.9 mg/L is achieved which can be explained by the availability of higher number of adsorption sites for As(V) of Fe(III) precipitates at lower pH.

From these results it can be concluded that the presence of As(III) restricts the efficiency of As co-precipitation with Fe(III) (oxyhydr)oxides, even with pH adjustment to lower values. When As(III) is oxidized to As(V) by a strong oxidant (KMnO₄), not only the As uptake by Fe(III) precipitates increases but also As co-precipitation efficiency can be further increased by lowering the pH. Thus, KMnO₄–FeCl₃ dosing in the influent of RSFs is an effective approach for As reduction to <1 µg/L.

3.7.2. FeCl₃ dosing in RSF effluent

The sampling campaigns have revealed that As(III) oxidizes completely into As(V) during rapid sand filtration. We investigated if As reduction to <1 µg/L can be achieved by FeCl₃ dosing in RSF effluent of WTP 1. The results show that As removal of ≈70% is achieved (reduction from 2.3 µg/L to 0.7 µg/L) at an Fe(III) dose of 0.75 mg/L for WTP 1 (Fig. 9). Compared to the RSF influent of WTP 1, in which As reduction to <1 µg/L was not achieved even at an Fe(III) dose of 5 mg/L (Fig. 8A), the As co-precipitation efficiency with Fe(III)(oxyhydr)oxides in RSF effluent is much higher due to the fact that in RSF effluent As is predominantly present in the form of As(V) which has a higher affinity for Fe(III) precipitates than As(III). From this, we conclude that the use of KMnO₄ in dune-water treatment can be avoided by treating the RSF effluent by FeCl₃ for As(V) removal instead of treating the RSF influent for As(III) removal by KMnO₄–FeCl₃ dosing.

4. Conclusions and implications for water treatment

From this study we conclude that rapid sand filtration is the most important treatment step for oxidation and removal of As during treatment of artificially recharged groundwater. Removal of As is mainly due to As co-precipitation with Fe(III)(oxyhydr)oxides and the efficiency of As co-precipitation with Fe(III)(oxyhydr)oxides is much higher in rapid sand filter beds compared to the preceding aeration and supernatant storage steps. This is due to an accelerated oxidation of As(III) to As(V) in the filter beds which may

be caused by the manganese oxides and/or As(III) oxidizing bacteria, as both exist in the coating of rapid sand filter media grains. While more research is needed to unravel the actual As(III) oxidation mechanism, we conclude that a higher As co-precipitation efficiency can be achieved during rapid sand filtration by allowing precipitation of Fe(III)(oxyhydr)oxides to take place inside rapid sand filter bed. Arsenic removal does not take place in treatment steps such as granular activated carbon filtration, ultrafiltration or slow sand filtration, due to a lack of hydrolyzing Fe in their influent and a lack of adsorption affinity between As and the filtration surfaces.

In this study we also investigated opportunities to reduce As levels in produced drinking water. We conclude that As reduction to very low levels (<1 µg/L) at dune-water treatment plants can be achieved either by treating the influent or the effluent of rapid sand filters. Oxidizing As(III) in the rapid sand filter influent by a strong oxidant, KMnO₄, results in a significant increase in the amount of As co-precipitated with Fe and therefore leads to a reduction in the amount of Fe(III) coagulant required to reduce As to <1 µg/L. On the other hand, the occurrence of As in the form of As(V) in the RSF effluent can eliminate the need to dose KMnO₄ and As reduction to <1 µg/L can be achieved by low FeCl₃ dosing alone. Based on these results, treating the RSF effluent for As removal is expected to be more cost-effective than treating the RSF influent. For example, estimates of chemical quantity and energy requirement for full scale implementation at WTP 1 (Table S1) show that dosing of KMnO₄ and FeCl₃ in RSF influent will result in an increase of drinking water production cost by 0.017 €/m³. On the other hand, treating the RSF effluent by FeCl₃ dosing will result in an increase of drinking water production cost by only 0.005 €/m³.

We also found in this study that a slight pH reduction is an effective approach to improve As(V) co-precipitation with Fe(III)(oxyhydr)oxides, but it is relatively ineffective for As(III) co-precipitation. Therefore, we suggest pH reduction only when As(V) is the predominant As species, e.g. in rapid sand filter influent which has been pre-treated with KMnO₄ or in rapid sand filter effluent.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2020.115826>.

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