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Influence of HPO_4^{2-}, H_4SiO_4, Ca^{2+}, Mg^{2+} on Fe floc growth and As(III) removal in aerated, natural groundwater

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ABSTRACT

Our aim was to systematically investigate the influence of anions (HPO_4^{2-}), cations (Ca^{2+}, Mg^{2+}) and neutral H_4SiO_4 on Fe flocculation and As(III) removal in the complex natural water matrix. For this purpose, three different anaerobic groundwaters were selected and manipulated by dosing of Ca^{2+}, Mg^{2+}, HPO_4^{2-}, or by their removal by cation – and anion exchange. The change in Fe floc volume and of dissolved Fe and As were followed in aerated jar experiments. Fe floc growth was improved by addition of Ca^{2+} or Mg^{2+}, and hindered by their removal. This hindered floc growth was more severe for groundwaters with higher P:Fe ratios, where Fe flocs carry a larger net negative surface charge, and rely stronger on Ca^{2+} or Mg^{2+} for charge neutralisation. When expressing the charge balance of the different groundwaters as the molar ratio (Ca^{2+} + Mg^{2+})/P, a linear relationship was found with the cumulative Fe floc volume, with a plateau at molar ratios > 500. At environmentally relevant concentrations, H_4SiO_4 was found more likely to compete with As(III) for adsorption capacity than HPO_4^{2-}. As(III) removal was strongly related to Fe removal - independent of Ca^{2+} or Mg^{2+} presence - indicating that As(III) is primarily adsorbed at an early stage in the flocculation process.

1. Introduction

The removal of iron, as Fe^{2+}, from groundwater is one of the traditional treatment goals and is often achieved by aeration and sand filtration. Introduction of dissolved oxygen to the anaerobic groundwater allows Fe^{2+} to oxidize to Fe^{3+} and form solid Fe flocs, followed by Fe floc removal by rapid sand filtration. At PS Eindhoven (Brabant Water), groundwater is collected from various wells with considerable differences in groundwater composition. Although the concentrations of Fe in the treated water were within company specifications (< 15 µg Fe/L) at all times, it was found that retention of iron flocs in the rapid sand filters was affected by the selection of wells that were in use. It is hypothesised that differences in water quality, especially the (ratio of) concentrations phosphate (HPO_4^{2-}), silicate (H_4SiO_4), calcium (Ca^{2+}) and magnesium (Mg^{2+}) control Fe floc growth. As a consequence, removal of the Fe flocs in the rapid sand filter is expected to improve when larger Fe flocs are formed. It is therefore the aim of this study to gain understanding of the effect of water composition on Fe floc growth. In addition, arsenic (as As(III), H_3AsO_3 at groundwater relevant pH) is of increasing concern for water supply companies in the Netherlands, particularly in the lower concentration ranges (< 20 µg/L). Therefore, co-removal of As(III) with Fe in existing aeration-filtration systems is included in this research by investigating how As(III) adsorption is affected by differences in Fe floc growth. Fe flocs are a well-known adsorbent for As(III), with the unique property that this adsorbent is being assembled while adsorption is occurring. Changes in floc growth could potentially affect the accessibility of adsorption sites for As(III).

The rate of Fe oxidation and flocculation are affected by the design of the treatment plant (e.g. intensity of aeration, use of chemical oxidants) and groundwater characteristics [1]. The oxidation rate of Fe^{2+} strongly depends on pH, and increases at higher pH values in the pH range 5–8 [2]. Besides the oxidation rate of Fe^{2+}, the floc formation of the oxidized Fe^{3+} is dependent on pH as well. Fe^{3+} hydrolyses into $Fe(OH)^{2+}$, $Fe(OH)_2^{+}$, $Fe(OH)_3$ or $Fe(OH)_4^{-}$ (ordered from low to high pH) [3,4]. When Fe^{3+} species are strongly charged both at high and low pH, flocculation is hindered, while a net zero charge is reached within a range of 7–8 [5].

Binding of anions such as HPO_4^{2-} and H_4SiO_4 with Fe oxides can result in a net negative charge of the floc and hinder flocculation [6,7]. Inclusion of HPO_4^{2-} within an Fe floc changes the floc structure, shifting from a lepidocrocite structure to an amorphous Fe(III)-

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HPO_4^{2-}structure at dissolved P:Fe ratios over 0.55 [8]. Guan et al. [7] found that at pH < 6, the addition of 1 mg/L P had limited influence on Fe removal, but Fe removal was reduced to only 5–8% at pH > 7. This can be related to a larger net negative charge at pH 7, since HPO_4^{2-} and neutral Fe species are prominent at pH 7, while H_2PO_4- and positively charged Fe species are prominent at pH 6. Neutral silicic acid starts to dissociate to the Si anion only at high pH values, with a pKa of 9.8 [9]. Several authors found that Fe removal in the presence of Si decreased at pH > 8, but was relatively unaffected at lower pH values [10–12], which could support that H_4SiO_4 mainly hinders Fe flocculation when it can induce charge repulsion.

The adsorptive removal of As during Fe flocculation is known to be hindered by the presence of HPO_4^{2-}, and H_4SiO_4, either due to adsorption competition and/or due to hindered Fe flocculation. Evidence of adsorption competition with arsenic follows from studies where preformed Fe oxides were used, for example, HPO_4^{2-} competes with As(V) and As (III) for adsorption on goethite over a wide pH range [13–16]. When H_4SiO_4 is dosed as sodium silicate or meta-silicic acid, it mainly seems to hinder the adsorption of As(V) at pH > 7, while the adsorption of As(III) is hindered over the entire pH range [10,16,17]. This could indicate that As(V) adsorption is mainly hindered by charge repulsion, while As(III) is hindered by competition for adsorption sites. Addition of Ca^{2+} improved As adsorption and Fe flocculation in the presence of HPO_4^{2-}, H_4SiO_4 [12,15,18,19] or at high pH values when Fe species carry a negative surface charge [20–22]. Besides charge neutralisation, Ca^{2+} can also remove HPO_4^{2-} by precipitating as hydroxyapatite ($Ca_5(PO_4)_3(OH)$) [23], although this reaction is considered to be slow, especially in the presence of Mg^{2+} [23–25]. Simultaneous presence of Ca^{2+}, H_4SiO_4, HPO_4^{2-} and Fe has been found to result in formation of different Fe floc structures, depending on the ratio P:Fe and Si:Fe [25].

In the presented study, experiments were conducted on-site, with natural groundwater. The use of natural groundwater was preferred over using synthetic water since it closer represents the full scale process. Three groundwaters were selected with different initial water composition. To enable comparison of Fe floc growth and As(III) adsorption between the different groundwaters, Fe^{2+} and As(III) were dosed to the raw groundwater. The aerated jar test experiments were conducted with (a) raw groundwater, (b) after increasing the concentrations of HPO_4^{2-}, Ca^{2+}, Mg^{2+}, or (c) after decreasing the concentrations with either anion or cation exchange resin.

2. Materials and methods

2.1. Chemicals and stock solutions

$Fe_2SO_4{*}7H_2O$, $NaHCO_3$, $CaCl_2{*}2H_2O$, $MgCl_2$, $NaAsO_2$, Na_2HPO_4 were obtained from Sigma Aldrich. All stock solutions were prepared in demineralized water. The stock solution for Fe^{2+} was acidified to pH 2. NaOH and HCl were used for pH correction.

2.2. Water analyses

Particle size/quantity analysis was carried out with a particle counter based on laser obscuration (HIAC Royco model 9703, Pacific Scientific). For this analysis, 50 mL of solution was poured in a beaker and measured undiluted. Mixing rates in the particle counter were set to approach the mixing rate during the jar test. The particle counter measured the number of particles for specific particle diameters. The lower analysis limit of the particle counter was 2 μm, and data was used untill a particle diameter of 50 μm. Water samples were acidified with 1% (v/v) nitric acid and As, Fe, Ca, Mg, Si, P, S were analysed by ICP-MS (PlasmaQuant, Analytik Jena). In the analysis method, an Ar flow of 7.5 L/min was used for the plasma, with an auxillary flow of 1.1 L/min and nebulizer flow of 1.05 L/min. The R/F was set to 1.3 kW. As and Fe were measured with an additional dose of 80 ml/min H_2, while Mg was measured with an additional dose of 120 mL/min He. Before aeration, HCO_3^- was determined by titration (702 SM Titrino, Metrohm) using 0.01 M HCl until an endpoint of pH 4.3 was reached. DOC analyses were carried out by Aqualab Zuid.

2.3. Jar tests

Jar tests were executed on a JLT6 flocculation tester (Velp scientifica), using 1 L of solution in baffled jars. A mixing rate of 80 rpm was maintained, and experiments were carried out at 15–16 °C.

All experiments were performed in duplicate. The chemical additions were done in anaerobic groundwater, and in the first 30 s of the jar test, the samples were aerated intensively, where an O_2 concentration of 9.7 mg/L was reached. Water samples were collected before aeration, and after 1, 5, 15, 30 and 60 min for elemental analysis. DOC was measured before aeration and after 60 min, and particle size/quantity analysis was done only after 60 min.

2.4. Groundwater preparation

For this study, natural groundwater was collected at PS Eindhoven (Brabant Water, the Netherlands) from three different wellfields; “Aalsterweg Middeldiep” (AMD), “Aalsterweg” (AP) and “Klotputten” (KG). These wellfields were selected for the considerable differences in groundwater composition (Table 1). In order to facilitate the comparison of As removal and Fe flocculation between these groundwaters, the Fe concentration was increased to 5 mg/L (as Fe^{2+}) and the As concentration to 20–25 μg/L (as As^{3+}). Groundwater was sampled in 2 L sampling bottles. The bottles were completely filled and allowed to overflow during sampling to collect anaerobic samples. The experiment was conducted on the same day as sampling. Besides Fe and As, further additions were either 40 mg/L (1 mmol/L) Ca^{2+}, 24.3 mg/L (1 mmol/L) Mg^{2+}, 1 mg/L HPO_4^{2-}, 10 mg/L HPO_4^{2-}. $Ca^{2+}$and Mg^{2+} were dosed in equimolar concentrations. Groundwaters were also pre-treated by anIEX resin (Amberlite IRA 400 (Cl-), Sigma Aldrich) or catIEX resin (Amberlite IR120 (Na^+), Sigma Aldrich), by adding 70 g resin to a completely filled 2 L sampling bottle and stirring anaerobically for 30 min. After catIEX treatment, groundwater was used directly. After anIEX treatment, 150 mg/L HCO_3- was added as buffer and the pH was adjusted to 7. An overview of the experimental conditions is shown in Fig. 1, and the corresponding initial water quality data can be found in Appendix A in supplementary data.

Table 1

Original water quality of groundwaters AMD, AP, KG. Concentration of Fe and As after addition is shown in brackets. Fe, As, Ca, Mg, Si, P and S were analysed as elements with ICP-MS.

	Fe (mg/L)	As (μg/L)	Ca (mg/L)	Mg (mg/L)	Si (mg/L)	P (mg/L)	S (mg/L)	HCO_3^- (mg/L)	DOC (mg/L C)	pH
AMD	6.9 (6.9)	0.33 (23.0)	43.5	4.1	11.9	0.18	5.8	146	3.0	7.01
AP	4.3 (4.9)	1.9 (21.8)	20.9	2.5	7.5	0.34	0	103	3.0	6.83
KG	1.7 (4.8)	25.8 (25.8)	28.4	11.5	5.9	0.26	1.6	196	2.9	7.31

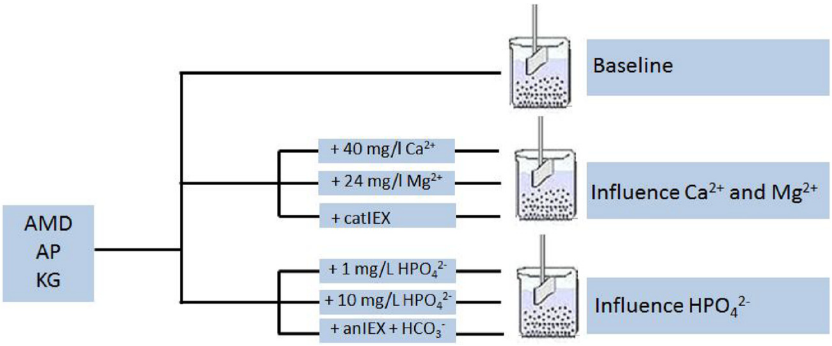

Fig. 1. Overview of the experimental conditions. Initial concentrations of H_4SiO_4, Ca^{2+}, Mg^{2+}, HPO_4^{2-} varied between the three different groundwaters AMD, AP and KG.

3. Results and discussion

3.1. Baseline

Baseline experiments were carried out with the original, raw groundwaters, after Fe and As addition (Table 1). The development of Fe flocs was followed by periodically taking samples from the jar and determining the amount of Fe removed after 0.45 µm filtration (Fig. 2, left). Additionally, particle size and quantities were measured at the end of the 60 min jar test, and are shown in Fig. 2 (right).

The initial rate of Fe removal is highest in KG water, followed by AMD and AP water (Fig. 2, left graph). This can be related to the pH values of these natural groundwaters, which is 7.31, 7.01 and 6.83 for KG, AMD and AP water, respectively. Higher pH values increase the oxidation rate of Fe^{2+}. After 60 min, Fe removal after 0.45 µm filtrationfor both KG and AP is similar, and higher for AMD since this groundwater had a higher initial Fe concentration. Nevertheless, the particle size distribution and quantities are rather similar for AMD and KG water (Fig. 2, right). This could indicate that denser Fe flocs were formed in AMD water, and/or that a part of the Fe flocs in AMD water have not grown to a size > 2 µm, which is the lower analysis limit of the particle counter. While findings of Kaegi et al. [18] suggest that the higher H_4SiO_4 concentration of AMD water can contribute to formation of smaller particles, this seems to contradict that H_4SiO_4 only started to affect Fe flocculation at higher pH [10–12]. Possibly, the slower oxidation rate of Fe^{2+} in AMD water prevented part of the Fe flocs to grow beyond 2 µm. This effect is even more pronounced for AP water, where the floc quantities are much lower as compared to KG and AMD after 60 min.

As removal after 0.45 µm filtration generally follows the same trend as Fe removal (Fig. 3). As removal in AMD water is relatively limited given the higher amount of Fe removed in this water as compared to KG water. This could indicate that arsenic suffers from stronger adsorption competition. While HPO_4^{2-} is a known competitor, its concentration is lowest for AMD water. It is more likely that H_4SiO_4 is responsible for the decreased arsenic adsorption in AMD water. Laky and Licsko [26] reach a similar conclusion, when investigating the influence of $HPO_4^{2-}$and H_4SiO_4 on arsenic removal, where all solutes were dosed at environmentally relevant concentration levels.

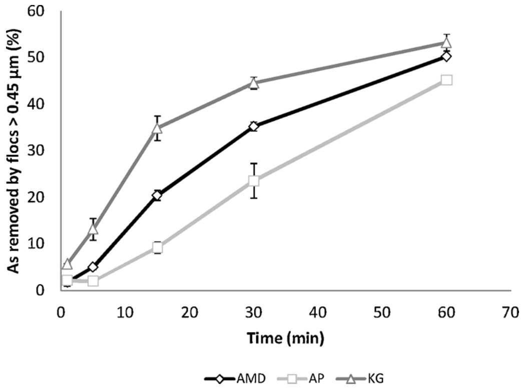

Fig. 3. Removal of As during 60 min for groundwaters AMD, AP and KG.

3.2. Influence Ca^{2+} and Mg^{2+}

The influence of the presence of major cations, Ca^{2+} and Mg^{2+}, on Fe floc formation is shown in Fig. 4, where the particle size distribution and quantities after 60 min are depicted after addition of 40 mg/L (1 mmol/L) Ca^{2+} or 24 mg/L (1 mmol/L) Mg^{2+} or after removal of cations with IEX. The measured concentrations of Fe, As, Ca, Mg, Si, P, S, HCO_3^-, the pH and the calculated ionic strength at the start of these

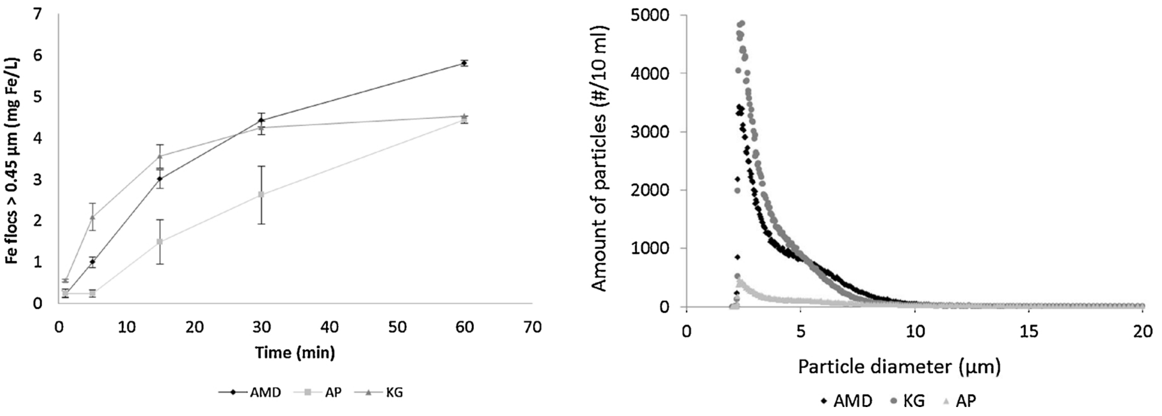

Fig. 2. Removal of Fe during 60 min, and particle counts after 60 min for groundwaters AMD, AP and KG.

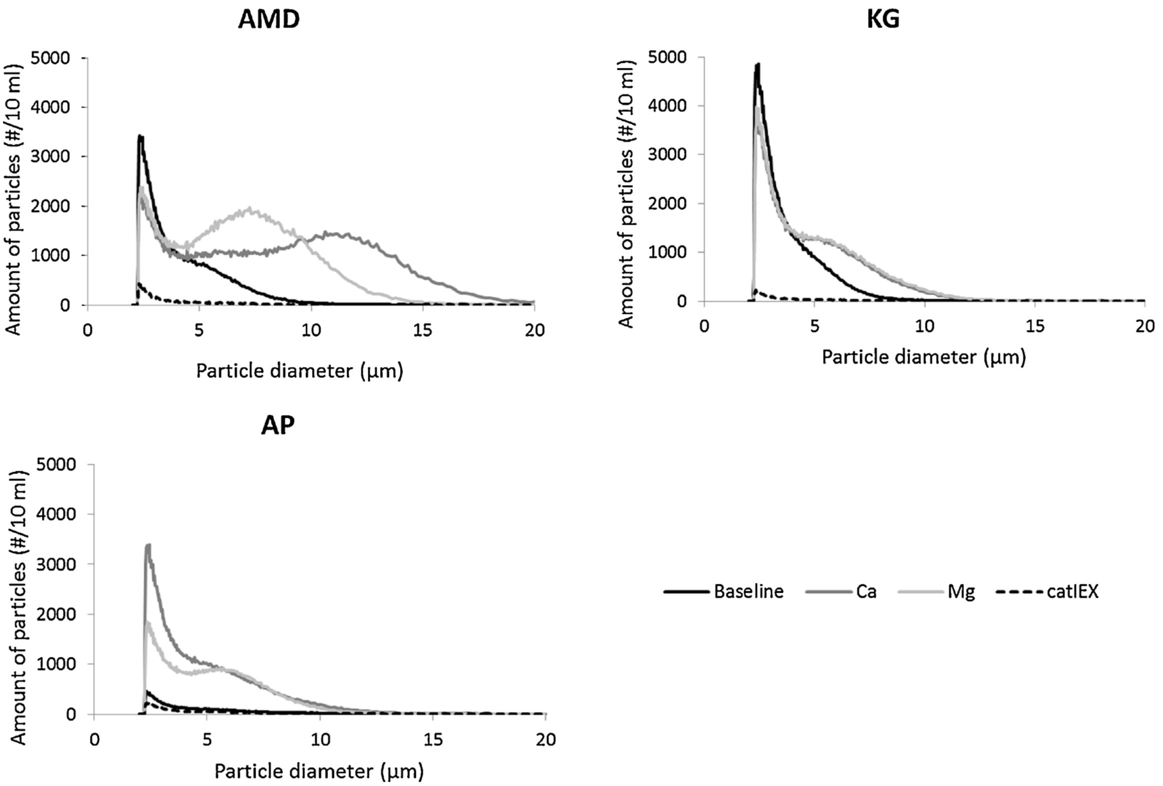

Fig. 4. Influence of dosing Ca^{2+} (40 mg/L; 1 mmol/L), Mg^{2+} (24 mg/L; 1 mmol/L) or cation exchange on Fe floc size and quantity after 60 min jar experiment in aerated groundwaters AMD, KG and AP.

experiments are reported in Appendix A in supplementary data.

Addition of Ca^{2+} or Mg^{2+} led to larger Fe flocs in all groundwaters. In KG and AP water, both Ca^{2+} and Mg^{2+} increased the floc sizes to a similar extend, indicating that both cations can be equally effective for charge neutralisation. In AP water, floc growth was stimulated considerably by addition of Ca^{2+} or Mg^{2+} when compared to the baseline, while this was less pronounced in KG water. AP water has a lower initial concentration of Ca^{2+} and Mg^{2+}, and a higher concentration of $HPO_4{}^{2-}$ than KG water (Table 1). As a consequence, it is expected that iron flocs in AP water have a larger negative charge than in KG water, and benefit more from charge neutralisation.

In AMD water, dosing Ca^{2+} and Mg^{2+} not only led to the formation of a larger Fe flocs as compared to AP and KG water, but also considerable larger flocs were formed in the presence of Ca^{2+} as compared to Mg^{2+}. Possibly, the addition of Ca^{2+} in AMD water led to precipitation of hydroxyapatite. Theoretically, hydroxyapatite could precipitate, since it is slightly supersaturated (saturation index +0.68, Appendix B in supplementary data). While the saturation index is higher in KG water (+0.84, Appendix B in supplementary data), the concentration of Mg^{2+} - which can hinder hydroxyapatite precipitation – is higher in KG water as well.

After cation exchange, floc growth is severely limited in all groundwaters. In AMD water, Fe removal after 0.45 µm filtrationwas still similar to the baseline study, but it decreased to 40% for KG water and only 13% for AP water (Appendix C in supplementary data). This is inversely proportional to their P:Fe ratios (0.04, 0.07 and 0.12 for AMD, KG and AP, respectively). Flocs with higher P:Fe ratio may carry a higher negative charge, and would rely more on the bivalent cations to neutralize this charge.

As(III) removal after cation exchange is highest for AMD water, followed by KG and AP water (Fig. 5), which matches the Fe removal. Despite the increase in floc growth after dosing Ca^{2+} or Mg^{2+} in AMD and KG waters, no considerable change is observed in As removal. This could indicate that the adsorption sites for As are still readily accessible in the larger flocs that are formed after Ca^{2+} or Mg^{2+} dosing, or alternatively, that adsorption occurs in an early stage of flocculation. In AP water, however, adsorption of As slightly decreased after dosing Ca^{2+} or Mg^{2+}.

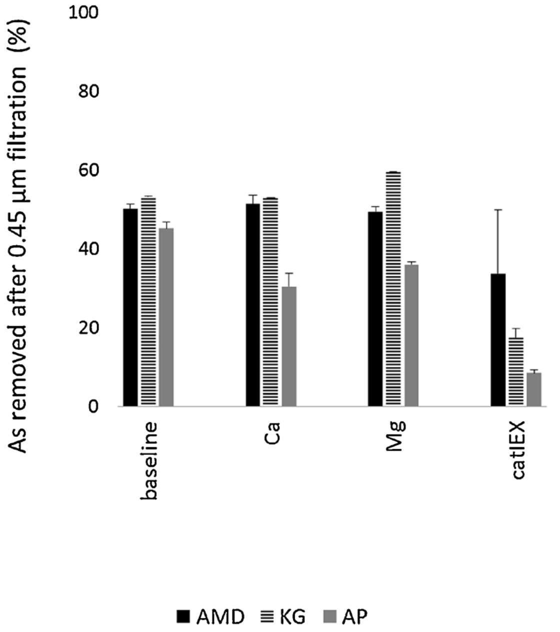

Fig. 5. Influence of dosing Ca^{2+} (40 mg/L; 1 mmol/L), Mg^{2+} (24 mg/L; 1 mmol/L) or cation exchange on As(III) removal after 60 min jar experiment in aerated groundwaters AMD, KG and AP.

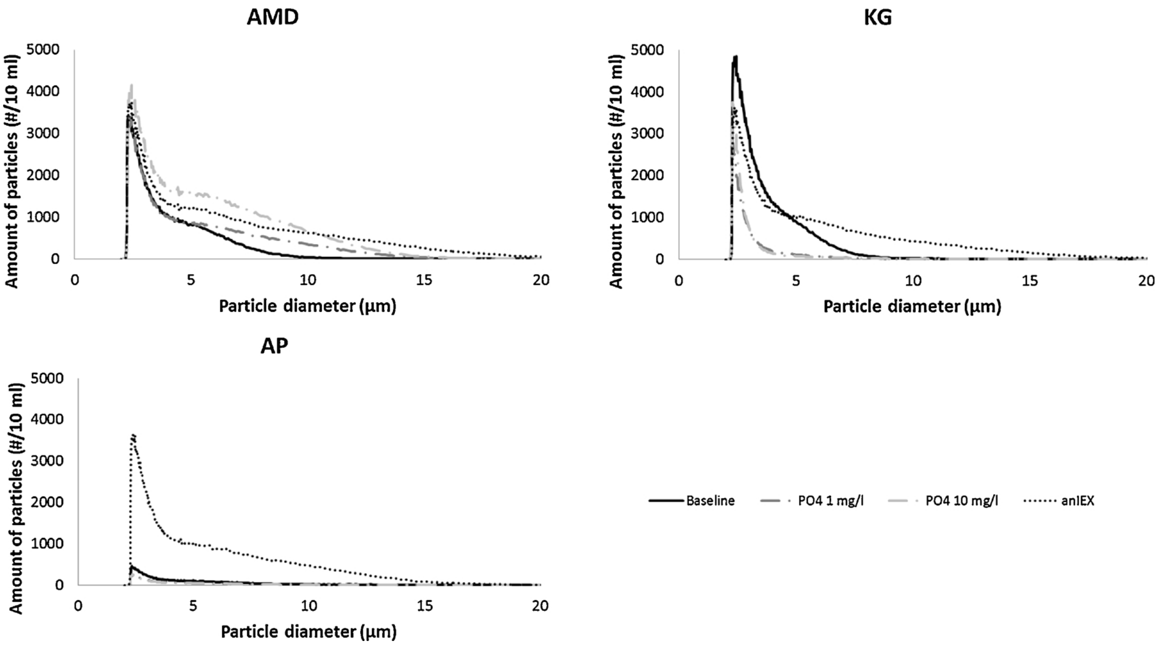

Fig. 6. Influence of dosing 1 or 10 mg/L HPO_4^{2-}, or anion exchange (anIEX) on Fe floc size and quantity after 60 min jar experiment.

3.3. Influence HPO_4^{2-}

To investigate the influence of HPO_4^{2-}, either 1 mg/L or 10 mg/L HPO_4^{2-} was dosed and anion exchange was applied to remove, amongst others anions, HPO_4^{2-}. Since anion exchange also removed HCO_3- buffer, 150 mg/L HCO_3- was dosed after anion exchange and the pH was corrected to 7. The measured concentrations of Fe, As, Ca, Mg, Si, P, S, HCO_3-, the pH and the calculated ionic strength at the start of these experiments are reported in Appendix A in supplementary data. H_4SiO_4 was not removed during anion exchange, indicating that it was uncharged during our experiments.

When HPO_4^{2-} was dosed to the baseline, it decreased the Fe floc sizes for KG and AP waters (Fig. 6). For AMD water, the opposite was observed, and a considerable increase in floc size was measured for increasing concentrations of HPO_4^{2-}. Similar to the discussion in §3.2, precipitation of hydroxyapatite could be more prominent in the Ca-rich and Mg-poor AMD water as compared to KG and AP water (see Appendix B in supplementary data for saturation indices).

After anion exchange, floc sizes increased in all groundwaters. This can be the combined effect of lower charge repulsion due to the removal of HPO_4^{2-}, and increased charge shielding, since the additional dosing of HCO_3- increased the ionic strength. For AMD water, this implies that both removal and addition of HPO_4^{2-} stimulated floc growth. This may indicate that different flocculation mechanisms possibly occur. In the *presence* of HPO_4^{2-}, the polymerisation of Fe is hindered and only small oligomers exist, but in the presence of (sufficient) Ca^{2+}, these can aggregate via Ca-O-P links [27]. In the *absence* of HPO_4^{2-}, the polymerisation of Fe is not hindered, and can be the main mechanism for aggregation.

While addition of HPO_4^{2-} decreased floc sizes in KG and AP water, there was still > 80% removal of Fe after 0.45 µm filtration (Appendix D in supplementary data). The adsorption of As(III), however, decreases to < 10% in all groundwater after dosing 10 mg/L HPO_4^{2-} (Fig. 7). This would indicates that HPO_4^{2-} hinders As(III) removal mainly directly via adsorption competition, rather than indirectly via hindered Fe flocculation.

3.4. Integrated influence on floc growth

Since charge repulsion and –neutralisation are widely considered to be important processes that explain Fe flocculation, it was investigated if the molar ratio of $(Ca^{2+} + Mg^{2+})/P$ can predict floc size. A higher $(Ca^{2+} + Mg^{2+})/P$ ratio implies that a negative surface charge imposed by the HPO_4^{2-} anion can be more readily compensated by bivalent cations Ca^{2+} and Mg^{2+}. H_4SiO_4 was excluded from this ratio, since it would have been neutral at the pH values in the experiments. Floc size is represented as the cumulative floc volume inbetween 2–50 µm, and normalized for the Fe concentration. The data of all experiments is included in Fig. 8.

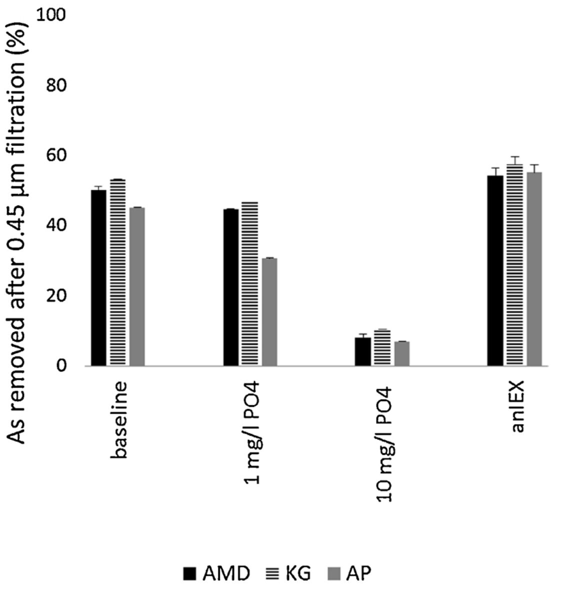

Fig. 7. Influence of dosing 1 or 10 mg/L HPO_4^{2-}, or anion exchange (anIEX) on As(III) removal after 60 min jar experiment.

A reasonably linear trend is found between the $(Ca^{2+} + Mg^{2+})/P$ ratio and the cumulative floc volume after 60 min, with a close overlap of the trends found for KG and AP waters. Outliers were found for AMD water, where the observed floc volume was higher than expected based on the $(Ca^{2+} + Mg^{2+})/P$ ratio. This can possibly be explained by formation of more voluminous Fe flocs and/or hydroxyapatite precipitation

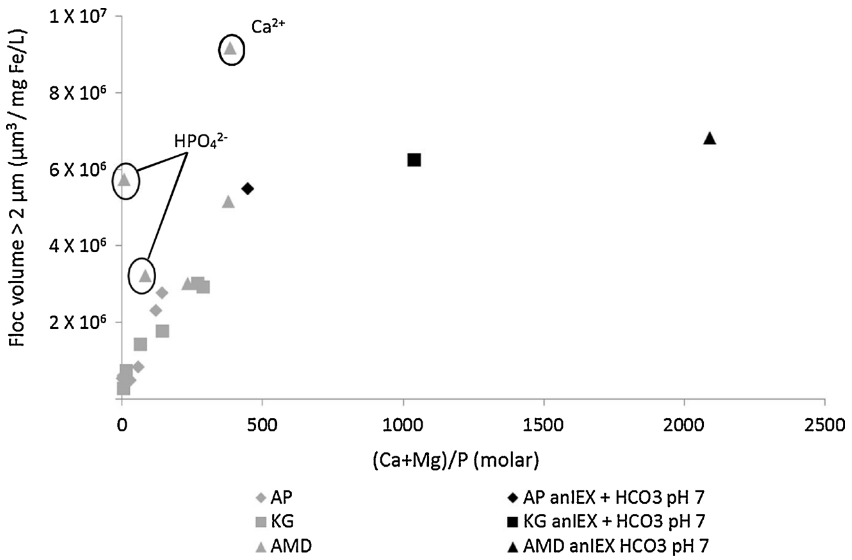

Fig. 8. Cumulative floc volume of particle diameters 2–50 µm versus ($Ca^{2+} + Mg^{2+}$)/P ratio after 60 min jar experiment. The cumulative floc volume is normalized for the initial Fe concentration.

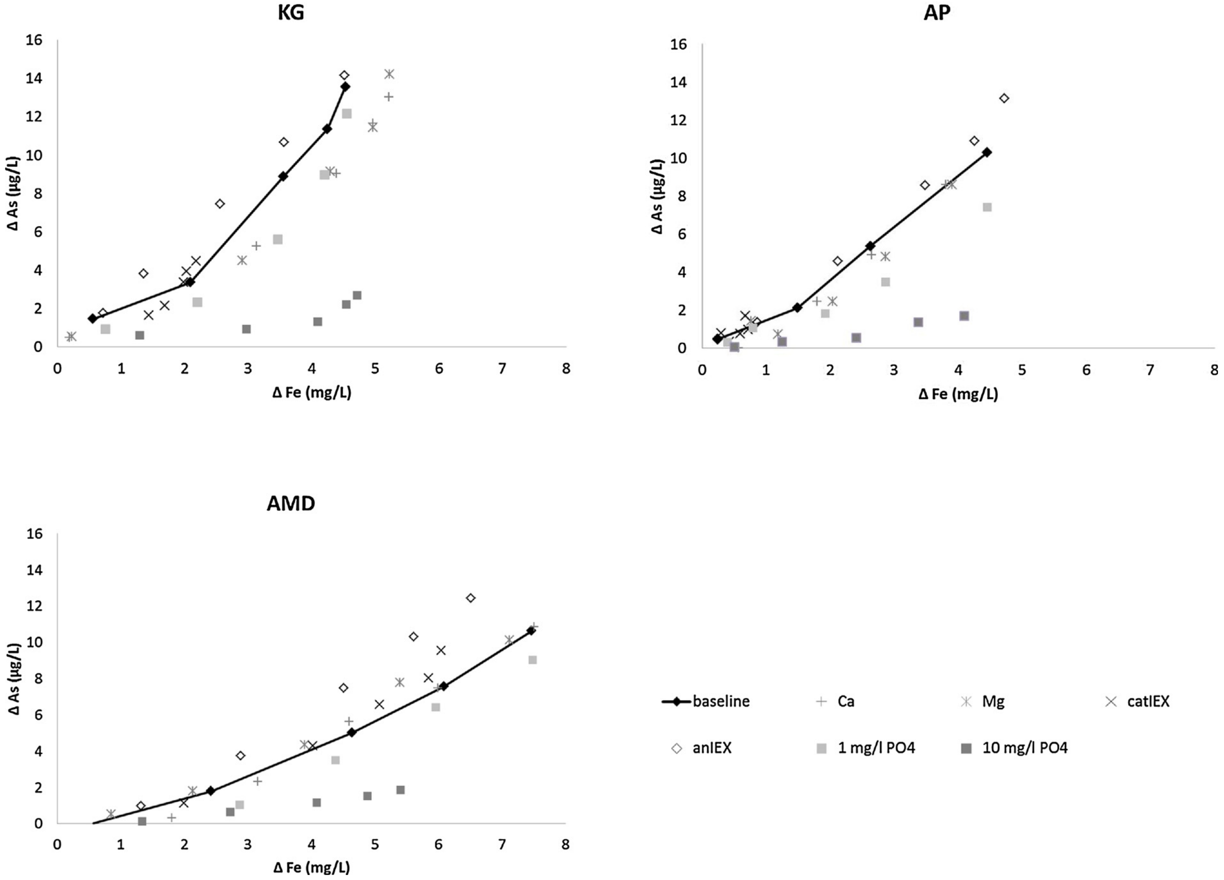

Fig. 9. Relationship between Fe removal and As(III) removal, shown specified per experiment for AMD, AP, KG. Initial concentration were 20.8–26.0 µg/L for As(III) and 5 mg/L (AP, KG) or 6–8 mg/L (AMD) for Fe^{2+}.

at the relatively high concentrations of Ca^{2+} and H_4SiO_4 in AMD water. A plateau seems to have been reached at a (Ca^{2+} + Mg^{2+})/P ratio of 500. Possible explanations for a plateau value can be that (i) all available Fe has been flocculated to particles > 2 µm, and the maximum floc volume is reached, and/or (ii) the quantity of Ca^{2+} and Mg^{2+} is sufficient to completely neutralize the influence of $HPO_4{}^{2-}$.

3.5. *Adsorption competition versus hindered floc growth*

In order to separate the influence of adsorption competition from the influence of reduced Fe flocculation on As(III) removal, a comparison is made between the *removal* of Fe and the *removal* of As, both after 0.45 µm filtration (Fig. 9). The data of the different time intervals during the jar test was included.

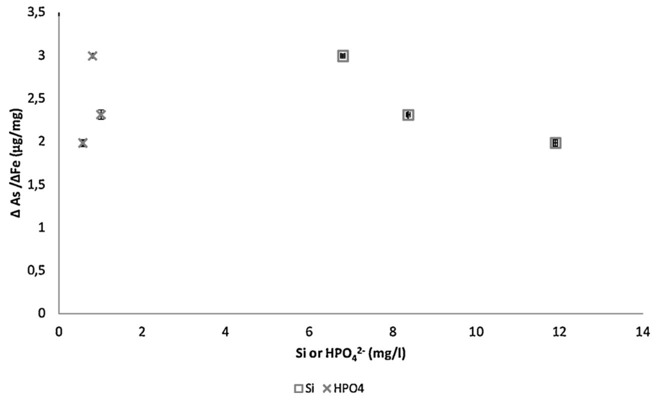

Fig. 10. Relationship between initial Si or HPO_4^{2-} concentration and ΔAs/ΔFe of the baseline experiments of AMD, AP and KG groundwater after 60 min jar experiment.

In general, it was observed that As removal and Fe removal were closely related, and that the capacity for Fe to adsorb As, i.e. ΔAs/ΔFe, seems relatively independent of the water quality. Adsorption competition was only evident after dosing 10 mg/L HPO_4^{2-}, it reduced As removal to below 3 µg/L for all groundwaters. When 1 mg/L HPO_4^{2-} was dosed, the adsorption capacity was relatively similar to that of the baseline, although consistently lower. When the baselines of AMD, KG and AP waters are compared, it is observed that the adsorption capacity (ΔAs/ΔFe) for As is systematically about factor 2 lower for AMD water. As discussed in §3.1, it is likely that H_4SiO_4 is competing with As for adsorption onto the Fe oxide as the H_4SiO_4 concentrations in AMD water are roughly factor 2 higher than in KG and AP water (Table 1). When comparing adsorption capacities (ΔAs/ΔFe) of iron flocs in these different groundwaters against the native H_4SiO_4 and HPO_4^{2-} concentration, an inverse correlation between the adsorption capacity and the H_4SiO_4 concentration is found, but this is not observed for HPO_4^{2-} (Fig. 10). At environmentally relevant concentration levels, our data suggests that H_4SiO_4 would be a stronger competitor for arsenic adsorption onto Fe flocs than HPO_4^{2-}.

4. Conclusions

In aerated grondwaters, As(III) removal can be affected both indirectly by hindered Fe floc formation, as directly by adsorption competition with HPO_4^{2-} and H_4SiO_4. As(III) removal was closely related to Fe^{2+} removal and relatively independent of the differences in water matrix. This indicates that As adsorbs onto Fe particles at an early stage in the flocculation process. At the natural groundwater concentrations, H_4SiO_4 is more likely to be responsible for adsorption competition than HPO_4^{2-} as the adsorption capacity of Fe for arsenic (ΔAs/ΔFe) was inversely related to the H_4SiO_4 concentration, while this was not observed for HPO_4^{2-}. Addition of Ca^{2+} or Mg^{2+} improved Fe floc growth, as expressed by an increase in the total Fe volume > 2 µm and an increase in the amount of larger particles. Removal of Ca^{2+} and Mg^{2+} by cation exchange hindered floc growth. This was more severe for aerated groundwaters with higher P:Fe ratios, where Fe flocs carry a larger net negative surface charge, and rely stronger on Ca^{2+} or Mg^{2+} for charge neutralisation. When expressing the charge balance of the different aerated groundwaters as the molar ratio $(Ca^{2+}+Mg^{2+})/P$, a linear relationship was found with the cumulative Fe floc volume > 2 µm, indicating the importance of Ca^{2+} and Mg^{2+} for charge neutralisation, although deviations from this trend were observed.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jwpe.2018.07.004.

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