

# Solubility of arsenic in untreated and ZVI-treated contaminated aquifer material

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# Solubility of arsenic in untreated and ZVI-treated contaminated aquifer material

Löslighet av arsenik I obehandlat och ZVI behandlat kontaminerat material från en akvifär

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#### Abstract

Arsenic (As) is a toxic element to all life and exists in nature both naturally and anthropogenically. Naturally As contaminated soils are formed due to high geogenic background As concentrations which is released when bedrock is eroded. Asia is a continent with a high amount of naturally As contaminated soils and groundwater. Anthropogenically As contaminated soils can originate from several sources such as industry, agriculture, burning of As containing fossil fuels etc. The main issue with As contaminated soils is that it ends up in the groundwater contaminating it and possibly in turn local drinking water. In nature, As exists predominantly as either As(III) in anoxic conditions or as As(V) in oxic conditions. As(III) is more soluble than As(V) leading to As being more soluble in anoxic conditions.

The use of ZVI to immobilize As in the ground is a remediation technique that has become a more common the past decades. It is a technique that is favoured because of several factors, some being its efficiency, economical cost, and simplicity to use. ZVI also has the ability of effectively immobilizing As in oxic and anoxic conditions.

In this report the As solubility in untreated and ZVI (mZVI and nZVI) -treated samples was analysed. The samples were collected in an anoxic aquifer within a CCA (Chromated copper arsenate) -contaminated area in Hjältevad. First, experiments were carried out to determine if phosphate and oxalate extractions are a good method in determining how As is bound in untreated and ZVI-treated sediment samples. Second, batch experiments were carried out to first determine the reaction kinetics of the experiment. Then, a pH-dependent As solubility experiment with different amounts of added As was carried out. Results from the extraction experiment and batch experiment were then used as input parameters in the chemical equilibrium software Visual MINTEQ. The purpose of this was to see if it was possible to find a model that fit the measured results by adjusting the available As for reaction and the amount of active ferrihydrite for the As to bind to.

The results from the phosphate extraction were unexpected and showed an increase of As for ZVI-treated samples over time. This increase was also observed for Fe. This released Fe was most likely amorphous Fe that also had As bound to it, which lead to an increase of As over time. The reason for the amorphous Fe to be released into solution is not fully understood but the high concentration of  $PO_4^{3-}$  (0.5 M) in the solution could over time perhaps interrupt the structure of the amorphous Fe.

The geochemical modelling proved to be a challenge and no model was able to be made that fit the measured values with a great degree. The results did indicate that all the oxalate-extractable As was taking part in the equilibrium reactions. However, since the models did not fit perfectly it is difficult to determine if this is the actual case. The best fit model indicated that about 54% of the oxalate-extractable ferrihydrite is active and takes part in the reactions.

*Keywords:* Hjältevad, zerovalent iron, phosphate extraction, Oxalate extraction, Visual MINTEQ, geochemical modelling

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# Abbreviations

AGW	Artificial ground water
ARD	Aqua regia digestion
As	Arsenic
As(III)	Arsenic in oxidation state III
As(V)	Arsenic in oxidation state V
Fe	Iron
Fe(0)	Iron in oxidation state 0
Fh	Ferrihydrite
kDa	Kilo Dalton (1000 Dalton)
L:S	Liquid to solid
mZVI	Micro Zerovalent Iron
nZVI	Nano Zerovalent Iron
OE	Oxalate extracted
Р	Phosphorus
PE	Phosphate extracted
RMSE	Root mean Square Error
ZVI	Zerovalent Iron

# 1. Introduction and Aims

Arsenic (As) is the 20<sup>th</sup> most abundant element in the crust of the earth and is potentially toxic to all life. Studies have shown that even in lower concentrations As is carcinogenic (Centeno et al., 2002; Chen and Ahsan, 2004). Humans ingest As mainly through drinking water. Under reducing conditions As becomes less stable in sediments and soils, which increases leaching into groundwater. High levels of As in soil and groundwater can be attributed to both anthropogenic activities and naturally high background concentrations. As has throughout human history been used for several purposes, for example within medicine, agriculture, livestock, electronics, industry, and metallurgy. Since the revelation of As toxicity to human life its utilization has been reduced.

As contaminated groundwater is a worldwide issue and depending on which continent you are, As contamination can be mainly due to anthropogenic activities, natural background concentrations or a combination (Bhattacharya et al, 2007). In Asia natural background levels of As can be extremely high, especially in the Bangal Basin in Bangladesh and western India (Bhattacharya et al, 1997).

In Sweden the most heavily As contaminated areas are due to industrial activities such as wood impregnation, sawmills, glasswork and sulphate and metal industries (Forslund et al., 2010).

From 1949-1985 a wood impregnation site in Hjältevad, Sweden, was in use and used the chemical CCA (Chromated copper arsenate) for most of the operation time to impregnate telephone poles. During the time of the operation high amounts of CCA was released into the soil both by leaking tanks and daily operation (SWECO, 2019). This has led to contamination of soils and groundwater within the area, and the main issue in the area is the As contamination which if left unattended could lead to contamination of local water bodies. Previous remediation has included soil washing and "pump-and-treat" (pumping up and cleaning groundwater). Since the last remediation effort in 1997 As concentrations have slowly been increasing with concentrations in 2019 exceeding 500  $\mu$ g/l. The next remediation plan is to inject ZVI (Zerovalent iron) into the ground that would bind the As and immobilise it in the ground (SWECO, 2019). Before this operation is carried out it is important to know how the ZVI might act in the soil and how effective it will be. Because of this several surveys of the soil and groundwater, and how they react with ZVI have been conducted in the area.

In a previous study an attempt was made to characterize the solid-phase pool of As in ZVI-treated and untreated soils (Leicht, 2021). In this attempt the fraction of As bound to ferrihydrite that was also extractable by phosphate extraction was unexpectedly low. Therefore, in the current project the phosphate extractions will be run for a longer time to detect if the fraction phosphate-extractable As might be higher than previously proven.

The second part of this report will investigate the pH and initial As concentration dependent solubility of As in the sediment. An initial kinetic experiment was run to determine how long it takes for different types of treated and untreated sediments to reach equilibrium with and without added As to a solution. With the results given in this experiment, an experiment investigating the pH-dependent As solubility could be set up and run. The results of the experiment were evaluated when using the chemical equilibrium software Visual MINTEQ. By adjusting the available ferrihydrite (Fh) and As to make the model fit the measured results the amount of Fh and As that takes part in the reactions can be determined.

One hypothesis of this project is that by increasing the duration of the phosphate extraction an increase in the As pool bound to ferrihydrite extractable by phosphate will be seen. By increasing the time, the kinetics of reaching equilibrium will also be able to be determined. Another hypothesis is that when the calibration is complete in Visual MINTEQ the amount of available As used to generate the best fitting model will be similar to the fraction of As extracted by phosphate.

The overall aim of this study was to investigate the solubility of As in untreated and ZVI-treated contaminated sediment samples under oxic conditions.

The specific aims were to:

- Investigate the ability of phosphate and oxalate extractants to assess the "geochemically active" pool of As.
- To evaluate the performance of the geochemical equilibrium model Visual MINTEQ in predicting the solubility of As in a contaminated sediment sample with and without added As(V).

# 2. Background

### 2.1 Chemistry of Arsenic

Arsenic (As) is the 20<sup>th</sup> most abundant element in the earth's crust and is particularly abundant in sulfidic rocks (Cullen & Reimer, 1989). As exists predominantly in four different oxidation states, they are As(V), As(III), As(0) and As(-III) (Singh et al., 2015). Depending on the oxidation state different species can form, As(V) forms arsenate, As(III) forms arsenite, As(0) forms arsenic and As(-III) forms arsine. The most prevalent forms naturally in groundwaters are arsenite and arsenate (Bowell et al., 2014). For arsenate the most important species are the oxyanions H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> and HAsO<sub>4</sub><sup>2-</sup>, (at pH 2-12) while arsenite exists in an undissociated state as H<sub>3</sub>AsO<sub>3</sub><sup>0</sup> (at pH <9.2; Figure 1) (Ramos et al., 2009; Kanel et al., 2005). Arsenite is more common at lower pH and under anoxic conditions, whilst arsenate is more common at higher pH levels and oxic conditions (Figure 1). Like other oxyanion-forming metalloids As is mobile in pH ranges common in groundwater under both oxic and anoxic conditions, which can make it a very mobile element when released into groundwater (Bowell et al., 2014). Arsenite is especially mobile partly because it can exist in its neutral form H<sub>3</sub>AsO<sub>3</sub><sup>0</sup> (Kanel et al., 2005). Because of this As becomes more soluble in reducing conditions where As(III) becomes the more dominant form (Kanel et al., 2005; Manning et al., 2002).

Arsenic mobility in soils is dependent on sorption onto soil components or coprecipitation with metal ions (Zhu et al., 2011; Raven et al., 1998). As has a strong affinity to sorb to metal hydroxides and As (III) and As(V) has especially high affinity to sorb to Fe hydroxides, such as ferrihydrite (Zhu et al., 2011; Dixit & Hering, 2003).

As is released to the environment both naturally and anthropogenically (Cullen and Reimer, 1989). It is released naturally by weathering of bedrock, biological activities, and volcanic emissions (Bowell et al., 2014). Anthropogenic sources of As in the environment comes from a wide variety of uses. Through history As has



been used in agriculture, insecticides/herbicides, wood preservatives, feed additives and drugs. It can also be found in fossil fuels and is released into the atmosphere during incineration (Mandal and Suzuki, 2002).

Figure 1. Eh-pH diagram of aqueous As species, represented in the system  $As-O_2-H_2O$  at 25 °C 1 bar pressure and ionic strength of about 0.01 M (adapted from Smedley and Kinniburgh, 2002 pp. 521).

### 2.2 Zerovalent iron and arsenic

Stabilisation and immobilisation as a remediation technique for contaminated soils has been a practice used for quite some time (Kumpiene et al., 2008). ZVI has been established as one of the most effective remediation techniques for immobilizing As (Kanel et al., 2005; Manning et al., 2002). Some of the main advantages to using ZVI as a remediation substance is that it is cheap, simple to handle and its capability to form strong sorption complexes with both As(III) and As(V) (Manning et al., 2002). There are different types of ZVI on the market, two of the most common types being microparticulate ZVI (mZVI) and nanoparticulate ZVI (nZVI). One factor that determines the ZVIs efficiency is its surface area to mass ratio, this makes nZVI more effective than mZVI (Singh and Bose, 2016).

The ZVI core (Fe<sup>0</sup>) is very reactive and will corrode in both oxic and anoxic conditions. In oxic conditions redox between ZVI and oxygen takes place (Eq. 1) whilst in anoxic conditions redox with water becomes more common (Eq. 2) (Zhu L. et al., 2014 and Ponder et al., 2000):

$$2 \text{ Fe}^{0}_{(s)} + 0_{2(g)} + 2 \text{ H}_{2}0 \rightarrow 2 \text{ Fe}^{2+} + 4 \text{ OH}^{-}$$
 Equation 1

$$\operatorname{Fe}^{0}_{(s)} + 2 \operatorname{H}_{2} O \longrightarrow \operatorname{Fe}^{2+} + \operatorname{H}_{2(g)} + 2 \operatorname{OH}^{-}$$
 Equation 2

The  $Fe^{2+}$  can then continue in a set of redox reactions and form a poorly crystalline Fe hydroxide shell surrounding the  $Fe^{0}$  core (Leupin and Hug, 2005).

There are several ways for As in the soil to react and stabilize as a reaction to ZVI being injected into the soil. ZVI can immobilize As by adsorption, coprecipitation and redox reactions (Calo et al., 2012; Lackovic et al., 2000; Melitas et al., 2002). The adsorption mainly takes place in the corroded shell of Fe hydroxides (Bang et al., 2005). Adsorption into the Fe hydroxide shell is more common and forms stronger complexes with As(V) than As(III) (Sasaki et al., 2009). Therefore, adsorption is during oxic conditions the predominant immobilization effect. As can coprecipitate with Fe<sup>0</sup> corrosion products, these coprecipitates can age and form stable minerals such as FeAsO<sub>4</sub> (Farrell et al., 2001). Reduction of As(V) and As(III) to As(0) by Fe<sup>0</sup> is thermodynamically favourable which is why redox reactions is a predominant part of immobilizing As



in soil with ZVI (Wang et al., 2021). Figure 2 illustrates a combination of ways for As to react with ZVI. A more extensive explanation of how ZVI might immobilize As has been produced by Leicht (2021) and Wang et al. (2021).

*Figure 2. Possible immobilization of As by adsorption, coprecipitation and redox reactions by ZVI (Yan et al., 2012).* 

# 3. Study site (Hjältevad)

All the information regarding the study site was taken from (SWECO 2019).

#### 3.1.1 Overview

The contaminated site is located in Hjältevad which is in Eksjö municipality in southern Sweden. The contaminated site was used by Televerket (today "Telia Sverige Net Fastigheter AB") as a wood impregnation plant (Figure 3). The plant was in operation between 1949-1985 and the main wood impregnation solution used was CCA (Chromated copper arsenate). Both shallow sediments and sediments lying under the groundwater table were contaminated in the 5.4 ha area of operation. In 1968 it was discovered that an underground steel tank containing CCA was leaking into the groundwater. At the time it was thought that the tank had recently started leaking but the discovery of zinc in the groundwater indicated that this leak had probably existed since at least 1952 which was the last time a solution containing zinc was last used. The amount of As found in the groundwater was also a lot higher than expected, also an indication that the leak had been existing for a longer time than first thought. During the entire time of operation solution was also spilled from equipment and dripped from wood during coating. This contaminated the topsoil in the area of operation.



Figure 3. Area of the previous wood impregnation plant.

### 3.1.2 Previous remediation efforts

The contaminated area has undergone remediation on a few occasions previously. When the leakage into the groundwater from the steel tank was discovered in 1968, groundwater was pumped up, treated, and then dumped in the forest about 2 km west of Hjältevad.

In 1984 the groundwater started to be pumped up and oxidized, acidified and placed in infiltration beds. This was to precipitate the contaminants. This was done successfully, and the operation was upgraded several times between 1984 and 1991. In total about 296,000 m<sup>3</sup> of water was treated this way between 1984 and 1993 and removed about 150 kg of As.

In 1997 remediation efforts based on soil washing was undertaken. Within the contaminated area soil layers were removed and cleaned in 0.1 m depth parts, if the following 0.1 m soil layer had >40 mg/kg of As it was also removed and cleaned. In an area of 800 m<sup>2</sup> which was the most heavily contaminated area, where the steel tank previously was placed, the soil was removed to a depth of 10 m (7 m below the groundwater table) (Figure 4). In this operation a total of 26,600 tonnes of soil was washed. 3,500 tonnes of soil that was too contaminated to be washed was removed and placed on a landfill. The operation removed about 4,600 kg of As which was assessed to be equivalent to about 2/3 of the total amount of As that was in the ground before decontamination.



Figure 4. Image over the area of soil that went through soil wash because As concentrations were above 40 mg/kg. Also shows the area of deep soil removal and cleaning.

### 3.1.3 Current contamination situation

After the treatment in 1997 three new wells (9701, 9702 and 9703) and one previously existing well (TB8) were used to take groundwater samples to check that the As, copper and chromium levels had not increased (Figure 4). However, between 1997 and 2019, concentrations of As increased in TB8 from about  $40 \mu g/L$  to over 500  $\mu g/L$ . In 2014 samples were collected in an area surrounding TB8, which showed that the increase of As was not local to TB8. More thorough sampling followed this in 2016 and 2017 to measure the groundwater flow, groundwater table level, As concentrations and how As in the area reacts to pH and redox levels. Using data from analysis and interpolation maps of the spread of As through the area was created the weighted average concentration for each sample location (Figure 5).



*Figure 5. Weighted average of As from each sample location. Map showing the distance of plume from the placement of the leaking tank.* 

# 4. Method

# 4.1 Sampling and treatment of sediment samples preceding use in current project

### 4.1.1 Sampling of sediment

Sediments used in all experiments were sampled in Hjältevad in 2019 at sampling point 1904 (Figure 4), at a depth of 16-18 m below soil level. The sampling was executed using a Sonic Geo Drill and during sampling it was made sure that as little O<sub>2</sub> came in contact with the core as possible to keep it anoxic. This was also ensured during transport of the core and while stored at SLU. The core was divided into several subsamples in a glovebox that kept O<sub>2</sub> levels under 20 ppm during operation and under 5 ppm when not used (Leicht 2021).

#### 4.1.2 Treatment of sediment samples

Before the samples were used in this project, they had undergone a variety of treatments. Some of the subsamples extracted from the drill core were divided into Control, mZVI, nZVI and REF sample types (Table 1).

In order to investigate the ability of nZVI and mZVI reagents to immobilize As at anoxic conditions a batch experiment was made in a glovebox (anoxic conditions). In addition to the nZVI and mZVI-treated sediment samples a control sample, with no added ZVI, was included (Control). In the batch experiment, the samples were equilibrated in an end over end shaker with AGW (artificial groundwater) representing the conditions of the groundwater in the field (Leicht 2021). Micro sized ZVI (mZVI) and nanosized ZVI (nZVI) were mixed into individual subsamples at a dose of 0.2% and 1% (per weight) for the nZVI and mZVI sorbents, respectively (Table 2). Since the nZVI was expected to be more effective compared to mZVI, due to its larger surface area, five times more mZVI was used when treating the samples compared to the nZVI. The three samples obtained from the experiment in the glovebox (Control, mZVI and nZVI) were divided into subsamples and given individual Samples IDs (Table 1). After equilibration the solids were flash frozen at -47 °C and either freeze dried or air

dried (in the glovebox) and stored in -18 °C until used in this project. A reference subsample (REF), not treated in the glovebox, was sieved, air dried and stored in an oxic environment. All experiments in this report were conducted under oxic conditions and therefore all sediments used were opened and exposed to oxygen in normal atmospheric conditions, for at least a week, before any analyses were performed.

Sample type		Control	l	mZVI				REF		
Sample ID	521	522	523	60	501	502	138	531	532	1, 2 & 3
AGW equilibration time (d)	33	34	40	30	33	33	23	33	33	X
Fe lost during AGW equilibration (mg/kg)	6.3	7.4	6.1	0.01	0.08	0.11	0.08	0.45	0.18	X
As lost during AGW equilibration (mg/kg)	7.7	8.8	7.7	0.06	0.05	0.06	0.11	0.78	0.22	X
Freeze dried or Air dried	FD	FD	AD	FD	FD	FD	FD	FD	FD	AD
Amount of sample (g)	13	14.9	14.9	3.4	13.5	15.3	4.5	13	15.3	>300

Table 1 - Sample IDs, equilibration time, type of drying used and amount of sample available.

Table 2. ZVI reagents used and target dose.

Reagent	Composition	Commercial name	Company	Target dose (kg reagent/kg soil)
mZVI	Solid, 95% Fe(0)	Ferox Target	Hepur Technologies	0.01
nZVI	Suspension, 20% Fe(0)	NANOFER 25	NANO IRON	0.002

# 4.2 Filtration methods

In this report two filtration methods were used. All samples that were analysed with an ICP-MS were filtered through a 0.45  $\mu$ m filter. Using this size of a filter removes any non-dissolved particles from solution (Powell et al., 1996). Within the <0.45  $\mu$ m fraction however there is a fraction in solution and one colloidal fraction. By using ultrafiltration with a membrane, the colloidal fraction can be filtered away leaving only the substances in solution. Depending on the size of the colloids a membrane filter between 1-10 kDa (1000-10,000 Dalton) can be used (Powell et al., 1996). In this study the main use of the ultrafiltration will be to determine the colloidal fraction of Fe in the solutes. Colloidal Fe has shown to be >10 kDa (Powell et al., 1996) which is why a 10 kDa membrane will be used in this study.

### 4.3 Extractions

Extractions were performed on the soils to be able to determine how As is bound in the soil. The purpose of performing the phosphate extractions is to determine the geochemical active pool of As that takes part of reactions in the soil. Phosphate works well to extract As because of its chemical similarities. The phosphates size is smaller and charge density higher than As which leads to it outcompeting As at the adsorption sites at high added concentrations (Manning & Goldberg, 1969). Phosphate extractions are particularly good at extracting As without affecting the adsorption sites the As is bound to (Cai et al., 2002). If enough phosphate is in solution with an As contaminated soil all the available adoption sites that As is bound to should be swapped out to phosphate and the As will end up in the solution.

Phosphate extractions were previously performed in 2021 on a batch of samples from sampling point 1904 (Leicht 2021). The duration (16 h) and P concentration used then (0.5 M) was based on literature review and geochemical modelling (Leicht 2021), however the results showed a lower fraction of As being extracted by phosphate than expected. Therefore, new phosphate extractions were carried out for durations of 4, 16, 72 and 240 h. This was to investigate if the phosphate would extract more As over time or if equilibrium had already been reached after 16 h.

Oxalate extractions were performed on the same samples to determine the total amount of amorphous Fe and the amount of As bound to it (Lee et al., 2016). Aqua regia digestion and analysis of samples were performed to determine the total As and Fe concentrations in the soils.

Samples from four different types of treated and untreated sediments were taken for phosphate and oxalate extractions. The sediment samples that extraction samples were collected from can be found in Table 1. From each sample ID (Table 1) five 0.5 g samples were weighed into 50 ml centrifugal tubes, 4 for the phosphate extractions (4 h, 16 h, 72 h and 240 h) and one for the oxalate extractions.

The day before experiments were carried out all glassware used were acid washed over night in 1% HNO<sub>3</sub>. After the acid wash all utensils were rinsed 3 times in deionised water and once in ultrapure water.

#### 4.3.1 Aqua regia digestion

Aqua regia digestion was performed on samples to determine the total concentration of As and Fe in the samples. To generate enough material for the analysis subsamples (Sample ID Table 1) from each treatment type (control, mZVI and nZVI) were pooled together using same amount of material from each sample. This was not carried out for REF sample since it consists of enough material. A total of six samples were analysed, one of each pooled treatment type and three REF samples. Samples were sent to ALS for aqua regia digestion and ICP-MS analysis.

#### 4.3.2 Oxalate extractions

For the oxalate extraction a 0.2 M oxalate solution (pH 3.0) was prepared using 0.2 M di-ammonium oxalate ((NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) and 0.2 M oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>). Solutions were mixed at a ratio of 25:19 ((NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>:H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) and adjusted to the amount needed for 12 samples (600 ml). When solutions were mixed if pH >3.0 then 0.2 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> was added until pH 3.0  $\pm$ 0.05 was reached, and if pH <3.0 then 0.2 M (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> was added until pH 3.0  $\pm$ 0.05 was reached. The oxalate solution was then stored for up to 3 d until used in the dark, as to avoid photochemical reactions to take place with the Fe.

For each 0.5 g  $\pm$ 0.01 g 50 ml of the 0.2 M oxalate solution was added, generating a liquid to solid ratio of 100:1 and shaken with an end-over-end shaker for 4 h. After the shaking the samples were centrifuged for 15 min at 4000 RPM (Allegra X15R Beckman Coulter Centrifuge with a rotor length of 207.8 mm). The supernatant was then transferred to a new 50 ml tube, leaving the sediment in the other tube. A 20 ml aliquot was filtered through a 0.45 µm filter and stored in dark place at +4°C until it was sent to ALS for ICP-MS analysis of As and Fe.

#### 4.3.3 Phosphate extractions

For the phosphate extractions a 0.5 M phosphate solution (pH 8.0) was mixed using Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub>. By combining literature methods (Wenzel et al., 2001; Larios et al., 2013), which used a phosphate solution with pH 8.0, with modelling in Visual MINTEQ and setting PO<sub>4</sub><sup>3-</sup> to 0.5 M and adjusting the [Na<sup>+</sup>] to 0.986 M pH 8.0 is reached, the ratio needed of each chemical could be calculated. When solutions were mixed if pH >8.0 then 0.5 M NaH<sub>2</sub>PO<sub>4</sub> was added until pH 8.0 ( $\pm$ 0.05) was reached, and if pH <8.0 then 0.5 M Na<sub>2</sub>HPO<sub>4</sub> was added until pH 8.0 ( $\pm$ 0.05) was reached.

For each sample 50 ml of phosphate solution was added, which generates a liquid to solid ratio of 100:1. The samples were then shaken for 4 h, 16 h, 72 h and 240 h. After the shaking process was complete each sample was centrifuged for 15 m at 2500 RPM (Allegra X15R Beckman Coulter Centrifuge, rotor length: 207.8 mm), and a 20 ml aliquot was collected and filtered through a 0.45  $\mu$ m filter and was acidified to 4% HNO<sub>3</sub>. The samples were then stored in the dark at +4 °C until it was sent to ALS for ICP-MS analysis of Fe and As.

From the 240 h phosphate samples an aliquot of 20 ml was also collected after centrifuging process and filtered through a 0.45 µm filter into a 10 kDa ultrafilter. The 10 kDa filter was then run in the centrifuge for 20 min at RPM 2500 (Allegra X15R Beckman Coulter Centrifuge with a rotor length of 207.8 mm). Before using the 10 kDa filters they were centrifuged 4 times for 15 min at 2500 RPM (Allegra X15R Beckman Coulter Centrifuge with a rotor length of 207.8 mm) Once with a 1 mM HNO<sub>3</sub> solution and three times with MQ water. The aliquot was acidified to 4% HNO<sub>3</sub> before being sent to ALS for ICP-MS analysis.

# 4.4 Fractionation of As

Using the results of the oxalate extraction, aqua regia digestion and losses during shaking with AGW (Table 1) As and Fe concentrations could be divided into different fractions. Because of inconclusive results from the phosphate extractions, this fraction was left out. These fractions consist of:

• **F**<sub>leached</sub> – Fraction lost when samples were equilibrated with AGW (F<sub>AGW</sub>). This fraction consists of Fe and As that is weakly bound by ionic bonding in the sediment (Eq. 1).

$$F_{leached} = F_{AGW}$$
 Equation 1

F<sub>oxalate</sub> – Fraction extracted by OE (F<sub>OE</sub>).
 This fraction consists of the As bound to amorphous Fe (Eq. 2). The Fe in this fraction consists of the amorphous Fe within the sediment.

$$F_{oxalate} = F_{OE}$$
 Equation 2

• **F**<sub>residual</sub> – Residual Fe and As. This fraction consists of the Fe and As that is left after OE. This consists of crystalline Fe and As bound within it (Eq. 3).

$$F_{residual} = F_{tot} - F_{leached} - F_{oxalate}$$
 Equation 3

• **Total** – This consists of the total amount of Fe and As in the sediment, generated by adding the results from aqua regia digestion (F<sub>ARD</sub>) and F<sub>AGW</sub> (Eq. 4).

$$F_{tot} = F_{ARD} + F_{AGW}$$
 Equation 4

# 4.5 Batch experiments

In this part an experiment was set up to determine the solubility of As, in an As contaminated sediment, within a pH range of 4.5-7.9 and with a varying initial As concentration in the solution (0, 1 and 2 mg/l). The results from this experiment were later used in a chemical equilibrium modelling software. For the modelling to work it is important that the samples have reached equilibrium when the experiment is ended. To perform the analysis at different pH levels and varying As concentrations the kinetics to reach equilibrium first needed to be determined. Therefore, a reaction kinetics experiment was first run.

### 4.5.1 Reaction kinetics

Untreated and ZVI-treated samples (Control, REF, mZVI, nZVI) with and without added As were shaken for 1, 5 and 20 days, using an end-over-end shaker, in a 10

mM NaNO<sub>3</sub> solution. In the samples with added As Na<sub>2</sub>HAsO<sub>4</sub> equivalent to 1 mg/l of As(V) was added to the 10 mM NaNO<sub>3</sub> solution. To be able to produce enough material for the experiment some samples with different IDs (Table 1) but with the same treatment method were pooled together (501 & 502, 521 & 522, 531 & 532). Samples were mixed in the solution at a L:S (liquid to solid) ratio of 10. Samples were removed from the shaker after 1, 5 and 20 days. On each occasion the samples were centrifuged for 15 min at 2500 RPM (Allegra X15R Beckman Coulter Centrifuge with a rotor length of 207.8 mm). An aliquot of the solution was filtered through a 0.45  $\mu$ m filter, acidified to 1% HNO<sub>3</sub> and stored at 4 °C for a maximum of 20 days until it was sent to ALS for ICP-MS analysis. Another aliquot was used to measure pH of the samples and the remaining solution was stored at 4 °C.

Results from the reaction kinetics experiment showed an increase of iron, which was concomitant with an increase of pH over time. With the higher pH levels this was thought to be colloidal Fe(OH)<sub>3</sub> rather than Fe(OH)<sub>3</sub> reducing to Fe<sup>2+</sup>. If this was the case equilibrium might be reached earlier than the results showed. To be certain of this, leftover solution of each sample was filtered through a 10 kDa ultrafilter and sent to ALS for analysis. Before using the 10 kDa filters they were rinsed using a centrifuge 4 times for 15 min at 2500 RPM (Allegra X15R Beckman Coulter Centrifuge with a rotor length of 207.8 mm). Once with a 1 mM HNO<sub>3</sub> solution and three times with MQ water.

Results from equilibrium kinetics analysis (4.3.1) resulted in the pH-dependent experiment to be run for 10 days. Results from this analysis could then be added to the equilibrium kinetics analysis, to determine if equilibrium was reached after 10 days. Since the pH-dependent analysis only used the REF sample this was only possible for the REF sample.

### 4.5.2 pH-dependent As/Fe solubility

The pH-dependent solubility of As(V), at equilibrium conditions, was investigated in the untreated REF sample. In this analysis the samples were first divided into three series of samples. For each series a specific amount of As(V) was added into the solution. This was without added As(V), with 1 mg/L added As(V) and with 2 mg/L added As(V). The As(V) was added using a Na<sub>2</sub>HAsO<sub>4</sub> stock solution. Each series of samples were divided into a range of 8 different pH levels. The different pH levels were generated adding either a solution with NaOH or HNO<sub>3</sub> (Appendix 5). 10 mM of NaNO<sub>3</sub> was added to every sample. For a complete recipe for each sample see Appendix 5. 4  $\pm$ 0.01 g of sediment (REF sample) was weighed in for each sample point and mixed in a L:S ratio of 10, generating 40 ml of solution for each sample. The sample tubes were then shaken for 10 days using an end-overend shaker. After equilibration 25 ml of solute was filtered using a 0.45 µm filter. A 15 ml aliquot of the filtrate was used to produce 10 ml of 10 kDa ultrafiltered solution. This produced 10 ml of 0.45 µm filtered solution and 10 ml of ultrafiltered solution for each sample. Each solute was acidified with 1% HNO<sub>3</sub> before being sent to ALS for ICP-MS analysis. The rest of the unfiltered solute was used to measure pH for each sample.

### 4.6 Geochemical modelling

Geochemical modelling was performed using the software Visual MINTEQ V3.1. The purpose of the modelling was to analyse if all oxalate-extractable Fh and As takes part in equilibrium reactions within the soil. To calibrate the model results from the pH-dependent solubility of As experiment and data from the extractions were used. The input parameters in the model can be found in appendix 6. All major cations and anions from the pH-dependent solubility experiment were added and fixed as "total dissolved" in VM. The ICP-MS analysis only gives the total phosphorus concentration and not the concentration of  $PO_4^{3-}$ , however, since only the ultrafiltered samples are used this means the phosphorus analysed should be in solution and was therefore assumed to be  $PO_4^{3-}$ .

The first step was to estimate the total amount of ferrihydrite in the soil and the amount of As available for reaction based on oxalate-extractable concentrations of As and Fe (3.2.2). Since the results from the oxalate extractions generated the concentration of Fe and not Fh the concentration of Fh was calculated using a molar weight of Fh of 89 g/mol (Dzombak & Morel, 1990; Hiemstra & Riemsdijk, 2009) (equation 7).

$$\frac{Fe\frac{g}{mol}}{Fh\frac{g}{mol}} \times Fe\frac{g}{l} = Fh\frac{g}{l}$$
Equation 7

Since the total amount of Fh available might not be active, using the oxalateextractable amount in the model might overestimate the actual available spots for As to sorb to. The initial calibration was performed by visual comparison between the modelled and measured As concentrations. The Fh concentrations in the model was adjusted until the best fitting graph could be found. This was first performed on the samples without added As and when a match was found they were added to the inputs.

The next step in the calibration after the best match was found by lowering Fh concentration was to lower the available As concentration. It is not clear if all the oxalate-extractable As takes part in the reactions in which case the oxalate-extractable As concentration might be an overestimation in the model.

To be able to determine the best model statistically, RMSE (Root Mean Square Error) was used (equation 8). RMSE can be used to measure the difference between a modelled datapoint and a measured datapoint. The lower the RMSE value is the closer the model is to the measured value.

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N} (y_i - \hat{y}_i)^2}{N}}$$
 Equation 8

Where i = the variable N = number of datapoints  $y_i$  = measured datapoints  $\hat{y}_i$  = modelled datapoints

Even though the visually best model fit had been determined a sweep method calculating RMSE was run. The sweep method calculated the RMSE value first using 100% OE As with 100%, 90%, 80%...and 20% OE Fh. The model was then run similar way but with 90% OE As. This method was used for samples with and without added As (Appendix 7). The reason for the sweep method was to see if a possible combination of OE As and Fh could generate a good match that was missed using the visual method. The lowest generated RMSE value either from visual method or sweep method was then used in the final calibration step. In this step the OE Fh concentration was lower or increased in incremental steps to see if a lower RMSE value could be found. When the lowest possible RMSE was found the OE As concentration was increased and lowered using the same method until the lowest possible RMSE value was found. The lowest RMSE was calculated first individually for samples without added As, with 1 mg/l added As and 2 mg/l As. After these RMSE values had been determined the lowest RMSE value for the combined samples was calculated.

# 5. Results

# 5.1 Extractable As and Fe

### 5.1.1 Aqua regia and oxalate

Aqua regia digestion results are presented in Table 3. The REF sample shows a higher As content, which was to be expected since this sample has not undergone any AGW equilibration. The REF sample does show a lower total amount of Fe compared to Control sample which was unexpected. mZVI and nZVI samples were expected to contain more As than the Control sample, because an insubstantial amount of As was released during the AGW equilibration. ZVI-treated samples were also expected to contain higher amounts of Fe than the control sample because of their treatment. This was the case for mZVI sample but not the nZVI sample which was unexpected.

	Control	mZVI	nZVI	REF
ARD As mg/kg	38.9	41.5	47.8	60.3
ARD Fe g/kg	7.62	16.9	7.63	6.83

Table 3. Aqua regia digestion results.

Oxalate extracted As and Fe is presented in Table 4. Oxalate extracted As and Fe is higher in REF samples compared to control, which was to be expected since control samples have lost some As and Fe when shaken with AGW.

Table 4. Oxalale extracted As and $\Gamma$	Table 4.	Oxalate	extracted	As	and	Fe.
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		Control			mZVI			nZVI			REF	
Sample	521	522	523	60	501	502	138	531	532	REF1	REF2	REF3
OE As (mg/kg)	25.8	21.6	19.6	27.8	32.7	31.4	34.4	30.0	34.0	37.7	37.6	39.4
OE Fe (g/kg)	0.85	0.81	0.84	7.39	8.49	9.62	3.08	2.88	2.91	0.63	0.66	0.46

The As fractionation results are presented in Table 5. All datapoints have been converted to mg/kg of As taking L:S ratios into account. Note that REF sample did not undergo AGW equilibration which generates a higher oxalate-extractable value

compared to control (Table 5). Data used to calculate average values and standard error of the mean can be found in Appendix 2.

Even though all samples should originate from a similar point in the soil the total concentrations do vary a bit, with REF sample showing a higher total concentration than the other samples (60.3 mg/kg).

Table 5. As divided into fraction Leached, oxalate and residual. Results are presented as the average from three samples of each type and is given in mg/kg with standard error of the mean. Percentage is based off total As in soil.

As	Leache	ed	Oxala	te	Residu	al	Total		
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	
Control	8.06 ± 0.364	17.2	22.3 ± 1.82	47.6	16.6 ± 1.83	35.3	47.0 ± 0.36	100	
mZVI	0.06 ± 0.003	0.14	30.6 ± 1.46	73.7	10.9 ± 1.46	26.1	41.6 ± 0.003	100	
nZVI	0.37 ± 0.21	0.77	32.8 ± 1.41	68.1	15.0 ± 1.41	31.1	48.2 ± 0.21	100	
REF	0 ± 0	0	38.2 ± 0.58	63.4	22.0 ± 0.58	36.6	60.3 ± 1.90	100	

Table 6. Fe divided into fraction Leached, oxalate and residual. Results are presented as the average from three samples of each type and is given in mg/kg with standard error of the mean. Percentage is based off total As in soil.

Fe	Leach	ed	Oxalat	е	Residu	al	Total		
	mg/kg	mg/kg %		%	mg/kg	%	mg/kg	%	
Control	6.6 ± 0.41	0.086	831 ± 13.5	11	6789 ± 13.5	89	7627 ± 0.41	100	
mZVI	0.066 ± 0.031	0.0004	8500 ± 644	50	8400 ± 644	50	16900 ± 0.031	100	
nZVI	$0.24 \pm 0.11$	0.0031	2957 ± 62.3	39	4673 ± 62.3	61	7630 ± 0.11	100	
REF	0 ± 0	0	585 ± 62.7	9	6241 ± 62.7	91	6827 ± 0	100	

#### 5.1.2 Phosphate

Results from the phosphate extractions showed an increase in extracted As over time, especially for the ZVI-treated samples (Figure 6). During phosphate extractions a clear trend of Fe being released into solution could also be seen for the ZVI-treated samples but not at all for control and REF samples (Figure 6). Ultrafiltered samples after 240h showed an increase in As and Fe concentrations, which was unexpected. The phosphate-extractable As in the ZVI samples at 240h were about 45% of the amount of oxalate-extractable As. The trend from diagram A (Figure 6) also shows if shaken for longer more As could have been extracted. The continuous trend of increased extractable As over time for the ZVI-treated



samples could correlate to the high amount of Fe being released into solution during phosphate extractions.

Figure 6. Results from phosphate extractions. The average concentrations from each treatment type were plotted over time in a scatter plot. Standard error of the mean for each plot was added. The plots include the results of the ultrafiltered sample from 240h. It is plotted at 245h to be able to distinguish from the 240h 0.45um filtered sample. Diagram A shows the phosphate extracted As over time. Diagram B shows the phosphate extracted Fe over time.

### 5.2 Batch experiments

Results from the reaction kinetics analysis were analysed to determine for how long the pH-dependent analysis will be run for. Results from the pH-dependent analysis are presented in graphs.

#### 5.2.1 Reaction kinetics

To be able to determine how long it takes for the reaction to reach equilibrium the results were plotted in a time series for each treatment type. Since the next analysis will be run with the REF sediment, the equilibrium results for this data will determine for how long the pH-dependent analysis will be run for.

Data from the equilibrium kinetics experiment are presented in Figures 7 (As), 8 (Fe) and 9 (pH). For REF samples results from the pH-dependent experiment were added later to check if the selected amount of time needed to reach equilibrium was correct. These datapoints were only plotted as points.

When plotting the results from REF sample in the kinetics analysis it was not completely clear when equilibrium was reached looking at the 0.45  $\mu$ m filtered solution (Figure 7 B). Looking at the ultrafiltered solution it becomes clearer when the solution reached equilibrium. The ultrafilter results for As concentrations (Figure 6 B) without added As indicates that the solution reaches equilibrium within 5 days. When adding 1 mg/l of As it takes a bit longer. It is difficult to say exactly after how many days equilibrium is reached, but from inspecting the time series equilibrium should be reached at about day 8 or 9. The ZVI-treated samples do not show a great increase in As when 1mg/l of As(V) is added to the solution compared

to the untreated samples. The ZVI-treated samples also have a much lower concentration of As in the ultrafiltered samples compared to the 0.45  $\mu$ m filtered sample, indicating a high fraction of colloidal As in the solution.

The 10-day results added from the pH-dependent analysis for the REF sample shows that the samples had reached or were close to reach equilibrium after 10 days when looking at the ultrafiltered samples. The 0.45  $\mu$ m filtered samples however showed much lower concentrations than expected and did not follow the trend from the equilibrium kinetics analysis. The reason for this is addressed in discussion (6.2).



Figure 7. Time series showing the As concentration in the solution after 1, 5 and 20 days of shaking. As concentrations have been plotted with and without added As in the beginning of experiment. Plots include solution that has been filtered through a 0.45um filter and solution filtered through an ultrafilter. Each datapoint have been plotted (dots) with a "scatter with straight lines" plot following the average of the duplicates. Diagram A shows the results from control sample, diagram B shows REF sample, diagram C shows mZVI sample and diagram D shows nZVI sample.

Fe concentrations vary over time but seem to reach equilibrium after about 5 days for most samples (Figure 8). The same issue of the 0.45  $\mu$ m filtered 10-day REF samples can be seen here. If these specific values are ignored it seems the REF samples are in equilibrium at day 5. The control sample does however seem to show a continuing increase even at day 20 (Figure 8A). Most of the data for the ultrafiltered Fe concentrations were below the detection limit (<0.002 mg/L). If data would have been over detection limit the ultrafiltered control samples might show that in solution equilibrium was reached earlier.



Figure 8. Time series showing the Fe concentration in the solution after 1, 5 and 20 days of shaking. Fe concentrations have been plotted with and without added As in the beginning of experiment. Plots include solution that has been filtered through a 0.45um filter and solution filtered through an ultrafilter. Each datapoint have been plotted (dots) with a "scatter with straight lines" plot following the average of the duplicates. Diagram A presents the results from control sample, diagram B presents REF sample, diagram C presents mZVI sample and diagram D presents nZVI sample. Note that x axis in diagram A is not in logarithmic scale, compared to diagram B, C and D.

There is a trend of an increasing pH over time for all samples (Figure 9). The pH values for all samples does not seem to have fully reached equilibrium after 20 days (Figure 9). The total increase in pH over 20 days is less than 1 pH unit in all samples, and there seems to be a trend of stagnation of the increase in pH for all samples. 10-day pH value for REF sample does not seem to follow the trend just like the other 10-day samples for As and Fe concentrations.

To be sure that the solution reaches equilibrium when taken out of the end-overend shaker in the second part of the experiment it was decided that it should be run for 10 days. Even though the pH does not seem to have reached equilibrium yet, it is thought that this will not affect the solubility of As too much.



Figure 9. Time series showing the pH in the solution after 1, 5 and 20 days of shaking. pH values have been plotted with and without added As in the beginning of experiment. Each datapoint have been plotted (dots) with a "scatter with straight lines" plot following the average of the duplicates. Diagram A shows the results from control sample, diagram B shows REF sample, diagram C shows mZVI sample and diagram D shows nZVI sample. Kinetics with added As and pH variation

### 5.2.2 pH-dependent As/Fe solubility

Results of the pH-dependent As solubility at different initial As concentration in the solution, of the untreated REF sample, were plotted in Figure 10. The results show an increase in As solubility with increasing pH (Figure 10A). The Fe concentration increases at low pH with Fe concentrations in ultrafiltered samples being as high as the 0.45  $\mu$ m filtered samples. At higher pH the Fe concentrations are also increased but are filtered away with the ultrafilter. There is one exception for this trend with "2 mg/L As UF" (Figure 10B) at pH 7.1, the reason for this is addressed in discussion.

In diagram A figure 10 there is an outlier for sample without added As at pH 6.1. In this outlier the datapoint filtered using a 0.45  $\mu$ m filter is significantly lower than the ultrafiltered sample which should not be possible. This is the same datapoint that was also used as the 10-day datapoint for REF samples in diagram B in figures 7, 8 and 9.



Figure 10. Diagrams showing the As and Fe solubility at different pH and different initially added  $A_{S}(V)$ . Diagram A presents As concentrations in solution and diagram B shows the Fe concentrations in solution.

# 5.3 Geochemical modelling

Initial modelling results when only considering the data series without added As(V) and varying the OE Fh to give a general idea of how this factor might affect the model is presented in Figure 11. The pH-dependent solubility of As is never as high in the models as in the measured values and with lower amounts of available Fh the pH dependency is lowered even further (Figure 11).



*Figure 11. Graph presenting modelled As pH-dependent solubility at varying amounts of OE Fh. Data is based on series without added As(V).* 

The best RMSE values generated for each sample type and the lowest combined RMSE generated are presented in Table 7. Model 3 generated the lowest combined RMSE value for all samples using 100% OE As and 54% OE Fh. For all samples the lowest RMSE value was generated using 100% OE As. When conducting the sweep method, a lower RMSE value was generated for samples with 2 mg/l added As using 90% OE As and 50% OE Fh (Appendix 7). However, when pinpoint the

lowest possible RMSE starting at those values and changing OE Fh and As in incremental steps it still ended up using 100% OE As and 55% OE Fh.

	Model 1	Model 2	Model 3
Oxalate-extractable As	100%	100%	100%
<b>Oxalate-extractable Fh</b>	51%	55%	54%
<b>RMSE</b> Without added As	91	97	94
RMSE 1 mg/l added As	306	317	311
RMSE 2 mg/l added As	500	475	476
<b>RMSE</b> all combined	342	334	333

Table 7. Lowest RMSE values generated after calibration. Green coloured boxes are the lowest RMSE values.

Model 3 from Table 7 which generated the lowest combined RMSE value and the measured values were plotted against pH to visually see the best model fit (Figure 12). The models generate and visually fit best for samples without added As and diverge when As is added to sample. The main issue seems to be that the models are less pH-dependent than the measured values.



Figure 12. Graph to visually compare the measured values with modelled values for samples with and without added As.

# 6. Discussion

### 6.1 Extractions

The aqua regia digestion results did act as expected to some degree with REF sample having the highest amount of As. This was expected since it is the only sample that has not undergone AGW equilibration and did therefore not lose any As in that process. The ZVI-treated samples, however, did not lose much As during the AGW equilibration (<0.78 mg/l; Table 1) and should then have about the same amount of total As left in the soil as the REF sample, which was not the case (Table 3). This could have to do with variation between the samples. Even if the samples are taken from the same part of the drill core there could be local heterogeneity within the sediment. The aqua regia extractable Fe for the nZVI-treated sample was very similar to the Control sample, which was unexpected. Since Fe has been added to the nZVI-treated sample the Fe content was expected to be higher. This could also be attributed to variations between the samples, if for example the nZVI sample had a lower amount of Fe before the treatment, the treatment might have increased the Fe content to match the control sample. The REF sample had about 10% less Fe than the Control sample, indicating at a natural variation between the samples. The mZVI-treated sample has a much higher Fe content than the other samples, but it was also treated with 5 times the amount of ZVI compared to the nZVI (Leicht, 2021).

The oxalate extraction results were as expected with REF sample again showing a bit higher oxalate-extractable As than the other samples. This follows the trend given by the aqua regia digestion. The control sample had a bit lower oxalateextractable As fraction which was also to be expected since about 8 mg/kg of As was lost during AGW equilibration (Table 1).

Because the phosphate-extractable fraction of As was difficult to determine (5.1.2) this fraction was excluded from the fractionation of As. Without this data the oxalate fraction simply consists of all oxalate-extractable As. With the phosphate-extractable fraction available the oxalate-extractable fraction could have been divided into As bound to ferrihydrite available for extraction and As bound to ferrihydrite not available for phosphate extraction.

The results of the phosphate extraction were unexpected. It was thought that the phosphate-extractable fraction determined previously were a bit low (Leicht, 2021). The results when increasing the phosphate extraction time to 240 h are surprisingly large, especially for the ZVI-treated samples (Figure 6A). These results do not correlate with other studies analysing extraction time of As using a phosphate solution. In other studies, a stagnation of the extractable As is reached after about 8-11 h (Wenzel et al., 2001; Larios et al., 2013).

The increase of phosphate-extractable As even after 240 h is unexpected. The ZVI-treated samples specifically show a heavy increase of extracted As over time and even passes the control and REF sample after about 20 h. This could perhaps be explained by the high amounts of Fe that is released from the ZVI-treated samples during the phosphate extractions (Figure 6B). The reason for the high release of Fe is not fully understood but could be attributed to the ZVI-treated samples containing higher amounts of amorphous Fe, as seen by the oxalate extraction (Table 4). When compared to the untreated samples, which also do contain some but not as much oxalate-extractable Fe the untreated samples showed no increased release of Fe over time in the phosphate extractions (Figure 6B). This could be interpreted that some of the amorphous Fe in the ZVI-treated samples, although in higher concentration, is not as strongly bound together as the amorphous Fe in the untreated samples. This could lead to a small colloidal fraction, <10 kDa, of Fe hydroxides that are mobilised by the phosphate. Since the phosphate is in a quite high concentration, they can bind to the Fe hydroxides in high amounts which could make them negatively charge, this in turn could lead to the mobilization. Dispersion of Fe by phosphate have been seen to some degree in other studies (Jackson and Miller, 2000). As bound to these sites and within the Fe hydroxides are then mobilised together with the Fe. This could also explain why the ultrafiltered ZVI-treated samples did not show a colloidal fraction of Fe hydroxides (Figure 6B). Because of the oxidizing conditions and pH range that these samples are analysed at the Fe should not be able to exist predominantly as Fe(II) but rather as Fe(III) (Figure 13). Another theory could simply be that the ultrafilter malfunctioned, and solution passed through without infiltrating the membrane.

The untreated samples that did not show the mobilisation of Fe also had a lower mobilisation of As. Even though these samples did not seem to have fully reached equilibrium at 240h, it seems that the increase of As was stagnating (Figure 6A), especially the Control sample. The reason for these samples not reaching equilibrium therefore seems to be of a kinetics related problem. Why the phosphate-extractable As was not extracted within 240 h compared to 8-11 h as was seen in the literature review is not fully understood.



Figure 13. "Replicated Pourbaix diagram for the iron-water system,  $\alpha_{Fe2+}$  / $_{t=0}$ = 10–6 M. Bold solid lines show boundaries between two solid species, thin solid lines show boundaries between one solid and one aqueous species and dotted lines show boundaries between two aqueous species. The two dashed lines show the boundaries for the oxidation and reduction of water." (Perry et al., 2019).

Results from the ultrafiltered samples also showed a slight increase in concentrations at 240 h compared to the 0.45  $\mu$ m filter (Figure 6). This should not be the case since it is the same samples that has simply gone through an extra filter, so an increase in concentrations should not be possible. This could be explained by an issue that occurred when samples were sent for analysis at ALS. The first results received from ALS had undergone such high dilution that the detection limit of the As was not reached in any of the samples run for less than 240 h. Because of this ALS were asked to run the samples again but with less dilution. When they did this, they had to use a different ICP-MS instrument. This was only done for the 0.45  $\mu$ m filtered samples and therefore the results in Figure 6 are a mix from two separate analysis using different instruments. This could explain why the ultrafiltered results show a higher concentration than the 0.45  $\mu$ m results.

### 6.2 Batch experiments

#### 6.2.1 Reaction kinetics

The reaction kinetics experiment showed quite clearly that the solutions reach equilibrium within 10 days for the REF sample. This follows trends seen in previous studies (Zhang and Selim, 2005; Rahman et al., 2019). The samples were expected to show an increase in As over time when As was not added, until equilibrium was reached and a decrease of As in solution over time, until equilibrium was reached, when 1 mg/l of As(V) was added. This proved to be the case for the untreated samples, however, the ZVI-treated samples showed an increase of As over time in both cases. It seems that the ZVI-treated samples with 1 mg/l added As binds the added As within the first day and then starts to release it back into the solution over

time, until equilibrium is reached. The mechanics of the As first binding and later being released into solution is not fully understood.

Fe concentrations seem to reach equilibrium earlier than As with small variations in concentrations when comparing 1-day datapoints with 20-day datapoints. The pH values do not seem to have reached equilibrium within 10 days. The pH range over the time of the experiment does not vary by much in any samples. The continuous increase of pH over time could be attributed to other factors, such as of weathering of primary minerals, although with the soil composition in the samples this seems unlikely.

When adding the 10-day data point in the REF sample from the pH-dependent As solubility analysis the 0.45  $\mu$ m datapoints did not match the trend set by the 1-, 5- and 20-day datapoints. The ultrafiltered datapoints did however match the trend quite well. This is most likely due to an error occurring either during lab work or during ICP-MS analysis at ALS with the 10-day REF 0.45  $\mu$ m filtered samples. In figure 10A the datapoint for 0.45  $\mu$ m filtered sample without added As at pH 6.1 is lower than the ultrafiltered sample. This is the datapoint without added NaOH or HNO<sub>3</sub> and is the same datapoint used in Figures 7B and 8B. Therefore, the 10 day 0.45  $\mu$ m datapoints in figures 7B and 8B are assumed to be incorrect and were ignored.

The 10-day pH datapoint (Figure 9B) also does not follow the trend set by the previous datapoints. The reason for this could be of the same origin as the As and Fe concentrations.

#### 6.2.2 pH-dependent As/Fe solubility

The As solubility results were as expected, with an increase of As concentration at higher pH levels (Al-Abed et al., 2007; Gersztyn et al., 2013). The ultrafiltered samples showed that nearly all As in the solution were not colloidal. The pH-dependent solubility of As was evident in all three series run, although it was slightly lower dependent on how much As was added (Figure 10). This makes sense since there is a limit to the number of spaces for the As to bind to and when more As is added to the solution the ratio of As to binding spots becomes higher and a higher ratio of As will then always be in solution independent on the pH levels.

As mentioned previously (6.2) there was one datapoint (0.45  $\mu$ m filtered sample without added As at pH 6.1) which did not follow the trend and had a lower value than the corresponding ultrafiltered sample. Since the ultrafiltered sample does follow the trend, it is thought that the sample may have been contaminated at some point after the original sample was divided into 0.45  $\mu$ m filtered sample and ultrafiltered sample.

In the pH-dependent Fe solubility graph (Figure 10B) the Fe does act as expected at the higher pH range (pH 6-8). At higher pH (6-8) the ultrafiltered samples show a decrease in Fe, which is expected since the Fe should exist predominantly as Fe(III). At the lower pH range (4.5-6) the Fe in the ultrafiltered samples is just as high as the 0.45  $\mu$ m filtered samples. This could indicate that the Fe is either in solution or that colloids smaller than 10 kDa are formed in this pH range. Because of the oxic environment in which these experiments are run in, it is most likely that a small colloidal fraction (<10 kDa) of Fe hydroxides is formed in the solute at the lower pH values. Similar situation was detected in Fe concentrations after ultrafilter during the phosphate extractions. It is difficult to say exactly why the small Fe hydroxide colloids are formed in the lower pH range.

### 6.3 Geochemical modelling

The geochemical modelling results were not optimal in this scenario since no model with a great fit to the measured values was generated. As seen in figure 11 none of the modelled lines follow the measured values very closely. Especially for the samples with added As, which can also be seen in the RMSE values which rise when As is added to the samples. This problem seems to mainly stem in the models not being as pH-dependent as the measured values. Even though they do follow the same trend of increasing As in solution when pH is increased the pH dependency is not as high.

When adding the ICP-MS measured phosphorous in the input as PO<sub>4</sub><sup>3-</sup> it was assumed that all ultrafiltered phosphorous was in the form of PO<sub>4</sub><sup>3-</sup>. This was based on results in previous experiments showing that total P concentrations in the solutions were similar to PO<sub>4</sub><sup>3-</sup> concentrations in the groundwater, indicating that total P in the solution was in the form of  $PO_4^{3-}$ . The concentrations measured in the ICP-MS were also added into the model as "total dissolved" concentrations. When this option is chosen VM will calculate the amount of  $PO_4^{3-}$  adsorbed to the soil at equilibrium with the dissolved phase. However, in the solutions there was an increase in total P at lower pH levels (Appendix 6). If the total P consisted of  $PO_4^{3-1}$ then it should act in a similar way as the As in the solution, which does not increase at lower pH. This could indicate that phosphorous being leached into the solution at lower pH is not primarily in the form of free  $PO_4^{3-}$ . Therefore, assuming that all P in solution at lower pH is  $PO_4^{3-}$  is probably incorrect. A new model was run instead where the available P was estimated as the dissolved + adsorbed P in the model from the sample without added  $A_{S}(V)$  at the highest pH (7.7). This available P was used as PO<sub>4</sub><sup>3-</sup> for all simulations and instead of selecting it as "total dissolved" it was set as the total concentration of  $PO_4^{3-}$  in the model. This did lower the As concentrations at lower pH resulting in a lower RMSE value but did not affect the concentrations at higher pH (Figure 14). Even though the exact phosphate concentrations are not known in the samples it is important to keep the phosphate in the input of the model because of its strong affinity to mobilise arsenic (Tiberg et al., 2016).



*Figure 14. Graph including model 2, which sets*  $PO_4^{3-}$  *as a constant total concentration.* 

The results of the modelling performed in this report indicate that 100% of the OE As was taking part in equilibrium reactions. However, since the models didn't fit the measured value to a great degree, it is difficult to say if this is the actual case. Results from the sweep method (Appendix 7) shows that there is a ratio of OE As and Fh that generates lower RMSE values. When the percentage of OE As is lowered the best fitting models are generated when a lower percentage of OE Fh is modelled together. For example, in the sweep method the lowest generated RMSE value was with the input 90% OE As and 50% OE Fh. If a better fitting model could be found by adding features into the model which are not part of it now, this model might show a lower percentage of OE As taking part in the reaction.

# Future work

Since some of the results in this study were inconclusive, this part aims to summarise how parts of the methods and results could be improved by future research. Some suggestions of future research based on this study are:

- Phosphate extractions could be used to determine active fraction of As in untreated samples if given enough time to reach equilibrium. By using same method as in this report but increasing the phosphate extraction time to up to a month a more precise measure of the active fraction of As in the samples could be determined.
- To determine the active fraction of As in the treated samples however, the method would have to be changed. A suggestion could be to perform a literature study to find either completely other methods of extracting As or to find another method of using phosphate to extract the As without mobilising any of the Fe.
- To improve the model in Visual MINTEQ a good method would be to go through each input parameter and evaluate if this input is correct or if it perhaps could be improved. Similar to what was done with the phosphate concentrations in the input of the model.

# Conclusions

- Aqua regia digestion work well to determine the total amount of As and Fe in the soil samples. Oxalate extraction method works well to determine the amorphous Fe and As bound to it.
- Phosphate extraction method used to determine the reactive fraction of As bound to the amorphous Fe needs to be modified.
- To determine the colloidal fraction in these experiments a smaller ultrafilter membrane should be used.
- Visual MINTEQ works to some degree for modelling the pH-dependent As solubility. But more factors probably need to be included in the model than used in this report.

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# Popular science summary

Arsenic (As) is a toxic element to all life and exists in nature both naturally and anthropogenically. Naturally As contaminated soils are formed due to high geogenic background As concentrations which is released when bedrock is weathered. Asia is a continent with a high amount of naturally As contaminated soils and groundwater. Soils contaminated with As by human activity can originate from several sources such as industry, agriculture, burning of As containing fossil fuels and more. The main issue with As contaminated soils is that it ends up in the groundwater contaminating it and possibly in turn local drinking water. As exists predominantly in nature in the oxidations state As(III) in anoxic conditions (low oxygen access) or in the oxidations state As(V) in oxic conditions (high oxygen access). As(III) is more soluble than As(V) leading to As being more soluble in anoxic conditions.

The use of ZVI (zerovalent iron) to immobilize As in the ground is a remediation technique that has become a more common the past decades. ZVI is Fe in oxidation state Fe(0) and is very reactive. It has a strong affinity to reduce other elements and can in this way immobilize them in the soil stopping them from contaminating the groundwater. It is a technique that is favoured because of several factors, some being its efficiency, economical cost, and simplicity to use. ZVI also has the ability of effectively immobilizing As in oxic and anoxic conditions.

In this report the As solubility in untreated and ZVI (mZVI and nZVI) treated samples were analysed. The samples were collected in an anoxic aquifer within a CCA (Chromated copper arsenate) contaminated area in Hjältevad. CCA is a wood preservative that was used a lot in the mid to late 1900s. First experiments were carried out to determine if phosphate and oxalate extractions are a good method in determining how As is bound in untreated and ZVI-treated sediment samples. Secondly batch experiments were carried out to determine first the reaction kinetics of the experiment. Secondly to use those values to carry out a pH-dependent As solubility experiment with different amounts of added As. Results from the extraction experiment and batch experiment were then used as input parameters in the chemical equilibrium calculator software Visual MINTEQ. The purpose of this was to see if it was possible to find a model that fit the measured results by adjusting the available As for reaction and the amount of active ferrihydrite for the As to bind to.

The results from the phosphate extraction were unexpected and showed an increase of As for ZVI-treated samples over time. This increase was also observed for Fe. This released Fe was most likely amorphous Fe that also had As bound to it, which lead to an increase of As over time. The reason for the amorphous Fe to be released into solution is not fully understood but the high concentration of  $PO_4^{3-}$  (0.5 M) in the solution could over time perhaps interrupt the bindings of the amorphous Fe.

The geochemical modelling proved to be a challenge and no model was able to be made that fit the measured values with a great degree. The results did indicate that all the oxalate-extractable As was taking part in the equilibrium reactions. However, since the models did not fit perfectly it is difficult to determine if this is the actual case. The best fit model indicated that about 54% of the oxalateextractable ferrihydrite is active and takes part in the reactions.

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As		Oxalate	Phosph	ate			UF
		4h	4h	16h	72h	240h	240h
Control	521	25.8	2.1	2.7	3.8	5.4	
	522	21.6	1.6	2.4	3.6	4.6	
	523	19.6	1.2	1.9	2.9	4.2	
Average		22.3	1.7	2.3	3.5	4.8	
SEM		1.8	0.3	0.2	0.3	0.3	
mZVI	60	27.8	1.6	2.5	5.4	9.7	12.4
	501	32.7	2.1	3.0	7.0	13.0	11.3
	502	31.4	2.0	3.4	7.7	13.2	
Average		30.6	1.9	3.0	6.7	12.0	11.9
SEM		1.5	0.1	0.3	0.7	1.1	0.6
nZVI	138	34.4	1.8	2.6	5.4	10.2	11.7
	531	30.0	2.8	4.7	9.4	14.4	18.2
	532	34.0	2.9	4.5	10.8	16.4	22.6
Average		32.8	2.5	4.0	8.5	13.7	17.5
SEM		1.4	0.4	0.7	1.6	1.8	3.2
REF	REF1	37.7	2.9	4.0	6.3	9.3	10.7
	REF2	37.6	2.7	4.0	6.0	9.1	10.2
	REF3	39.4	2.8	3.8	6.5	9.0	
Average		38.2	2.8	3.9	6.2	9.1	10.5
SEM		0.6	0.0	0.1	0.2	0.1	0.3

Table A1a. Table showing As concentrations in mg/kg from extractions.

Fe		Oxalate	Phosp	hate			UF
		4h Oxalate	4	16	72	240	243
Control	521	0.850	0.129	0.082	0.106	0.112	0.132
	522	0.805			0.106	0.116	0.089
	523	0.838		0.089		0.111	0.149
Average		0.831	0.129	0.086	0.106	0.113	0.123
SEM		0.013		0.003	0.000	0.002	0.018
mZVI	60	7.390	0.115	0.253	0.590	1.060	1.210
	501	8.490	0.222	0.314	0.938	1.400	1.530
	502	9.620	0.245	0.396	0.988	1.580	1.480
Average		8.500	0.194	0.321	0.839	1.347	1.407
SEM		0.644	0.040	0.041	0.125	0.152	0.099
nZVI	138	3.080	0.131	0.211	0.460	0.883	0.926
	531	2.880	0.254	0.365	0.968	1.340	1.560
	532	2.910	0.246	0.374		1.360	1.500
Average		2.957	0.210	0.317	0.714	1.194	1.329
SEM		0.062	0.040	0.053	0.254	0.156	0.202
REF	REF1	0.634			0.083	0.125	0.158
	REF2	0.661		0.096	0.083	0.111	0.113
	REF3	0.461	0.082			0.133	0.140
Average		0.585	0.082	0.096	0.083	0.123	0.137
SEM		0.063			0.000	0.006	0.013

Table A1b. Table showing Fe concentrations in g/kg from extractions.

		Leac	ned	Oxal	ate	Resid	ual	Tot	al
		mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
Control	521	7.7	17	26	55	13	28	47	100
	522	8.8	18	22	45	17	36	48	100
	523	7.7	16	20	42	19	41	47	100
Average		8.1	17	22	48	17	35	47	100
SEM		0.364	0.638	1.827	3.989	1.827	3.886	0.364	0.000
mZVI	60	0.1	0.1	28	67	14	33	42	100
	501	0.1	0.1	33	79	9	21	42	100
	502	0.1	0.1	31	76	10	24	42	100
Average		0.1	0.1	31	74	11	26	42	100
SEM		0.003	0.006	1.466	3.531	1.466	3.525	0.003	0.000
nZVI	138	0.1	0.2	34	72	13	28	48	100
	531	0.8	1.6	30	62	18	37	49	100
	532	0.2	0.5	34	71	14	29	48	100
Average		0	1	33	68	15	31	48	100
SEM		0.208	0.427	1.405	3.196	1.405	2.771	0.208	0.000
REF	REF 1	0.0	0.0	38	67	19	33	57	100
	REF 2	0.0	0.0	38	61	24	39	62	100
	REF 3	0.0	0.0	39	63	23.2000	37	63	100
Average		0	0	38	64	22	36	60.3	100
SEM		0.000	0.000	0.584	1.697	1.637	1.697	1.901	0.000

Table A2a. Data of fractionation of As used to create Table 4.

Fe		Lea	ched	Oxala	te	Residu	ual	Total	
		mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
Control	521	6.3	0.08	850	11.1	6770	88.8	7626.3	100
	522	7.4	0.10	805	10.6	6815	89.4	7627.4	100
	523	6.1	0.08	838	11.0	6782	89.0	7626.1	100
Average		6.6	0.086	831	11	6789	89	7627	100
SEM		0.41	0.0053	13.5	0.18	13.5	0.18	0.41	0
mZVI	60	0.01	0.00003	7390	43.7	9510	56.3	16900.0	100
	501	0.08	0.00047	8490	50.2	8410	49.8	16900.1	100
	502	0.11	0.00066	9620	56.9	7280	43.1	16900.1	100
Average		0.066	0.00039	8500	50	8400	50	16900	100
SEM		0.031	0.00019	644	3.81	644	3.81	0.031	0
nZVI	138	0.08	0.0011	3080	40.4	4550	59.6	7630.1	100
	531	0.45	0.0059	2880	37.7	4750	62.3	7630.4	100
	532	0.18	0.0024	2910	38.1	4720	61.9	7630.2	100
Average		0.24	0.0031	2957	39	4673	61	7630	100
SEM		0.11	0.0014	62.3	0.82	62.3	0.8	0.11	0
REF	REF 1	0	0.0	634	9.29	6193	90.7	6826.7	100
	REF 2	0	0.0	661	9.68	6166	90.3	6826.7	100
	REF 3	0	0.0	461	6.75	6366	93.2	6826.7	100
Average		0.0	0	585	9	6241	91	6827	100
SEM		0.0	0.0	62.7	0.9	62.7	0.9	0.000	0

Table A2b. Data of fractionation of Fe used to create Table 5.

C	Column 2		Control	Control	Control	Control	Control	Control	mZVI	mZVI	mZVI	mZVI	mZVI	mZVI	nZVI	nZVI	nZVI	nZVI	nZVI	nZVI	REF	REF	REF	REF	REF	REF +As
	filtor	Colur	1 10		200	+As 10	+As 50	+As Zud	10	50	200	+AS 10	+As 5a	+As 20a	10	50	200	+As 10	+As 5a	+As 200	10	50	200	+AS 10	+As 5a	200
0.45um	mer	Unit	1	5	20	1	5	20	1	5	20	1	5	20	1	5	20	1	5	20	1	5	20	1	5	20
As	Duplicate 1	µg/L	70	105	147	650	480	468	40.2	34.6	95.4	26.6	57.6	144	96.8	274	318	208	422	798	117	172	156	543	451	327
	Duplicate 2	μg/L	63	114	188	614	504	536	36.4	48.8	90.4	41	107	292	98.8	228	160	226	486	512	107	152	161	530	447	327
	Average	μg/L	66.5	110	167	632	492	502	38.3	41.7	92.9	33.8	82.2	218	97.8	251	239	217	454	655	112	162	159	537	449	327
Fe	Duplicate 1	mg/L	0.28	0.75	1.06	0.30	0.89	0.86	7.72	6.52	21.8	3.08	8.02	24.8	6.52	17.9	19.4	5.62	15.9	32.8	1.16	1.6	1.77	1.08	3.16	1.81
	Duplicate 2	mg/L	0.22	0.85	1.54	0.23	0.82	1.64	7.26	10.0	19.4	5.04	14.5	47.2	7.18	15.1	9.3	6.64	19.1	21.2	1.06	2.18	2.52	1.4	3.71	1.49
	Average	mg/L	0.25	0.80	1.30	0.26	0.85	1.25	7.49	8.28	20.6	4.06	11.2	36	6.85	16.5	14.3	6.13	17.5	27	1.11	1.89	2.15	1.24	3.44	1.65
UF																										
As	Duplicate 1	μg/L	47.8	66.2	87.5	577	342	322	х	1.2	1.9	0.9	1.8	2.1	5.1	13.4	16.5	7.9	14.0	21.6	31.8	55.1	53.1	366	233	179
	Duplicate 2	μg/L	44.9	67.4	86.7	536	355	340	x	1.1	1.8	0.9	1.9	2.6	4.5	12.2	15.0	7.1	13.8	29.6	30.8	52.3	52.3	386	233	177
	Average	μg/L	46	67	87	556	349	331	x	1.2	1.8	0.9	1.8	2.3	5	13	16	8	14	26	31	54	53	376	233	178
Fe	Duplicate 1	mg/L	0.006	x	x	x	x	x	x	x	0.011	x	x	0.010	x	x	0.009	x	x	0.017	0.010	0.008	0.005	0.010	0.008	0.005
	Duplicate 2	mg/L	x	x	x	x	x	х	х	х	0.014	x	х	0.011	х	0.007	0.026	x	x	0.100	0.009	0.007	0.035	0.013	0.006	0.036
	Average	mg/L	0.006	×	x	x	x	x	x	x	0.013	x	х	0.010	х	0.007	0.017	х	х	0.058	0.009	0.007	0.020	0.011	0.007	0.018
0.45um	-UF (colloid	dal c	oncent	tratior	ı)																					
As		μg/L	20	43	80	76	143	171	х	41	91	33	80	216	93	238	223	209	440	629	81	108	106	161	216	149
Fe		mg/L	0.25	x	x	x	x	x	x	x	20.6	x	x	36.0	x	16.5	14.3	x	x	26.9	1.10	1.88	2.12	1.23	3.43	1.63
рН	Duplicate 1		6.7	6.8	7.6	6.5	6.9	7.4	7.0	7.3	7.8	7.2	7.5	7.8	7.1	7.1	7.7	7.0	7.2	7.5	6.1	6.5	7.1	6.1	6.4	7.1
	Duplicate 2		6.8	7.0	7.7	6.8	7.0	7.5	7.0	7.4	7.8	7.1	7.5	7.8	6.9	7.1	7.7	7.0	7.2	7.6	6.2	6.5	7.0	6.1	6.4	7.1
	Average		6.7	6.9	7.6	6.6	6.9	7.4	7.0	7.4	7.8	7.2	7.5	7.8	7.0	7.1	7.7	7.0	7.2	7.6	6.2	6.5	7.0	6.1	6.4	7.1

#### Table A3. Data from equilibrium kinetics study.

	As			As UF						
NaOH/HNO3	Without	1 mg/L	2 mg/L	NaOH/HNO3	Without	1 mg/L	2 mg/L			
(+/-)	As	As	As	(+/-)	As UF	As UF	As UF			
0.5	620	1390	2230	0.5	542	1260	2090			
0.25	225	584	1410	0.25	178	510	1340			
0	21.0	193	562	0	38.5	184	573			
-0.25	28.6	95.9	256	-0.25	28.6	103	254			
-0.5	26.1	68.6	196	-0.5	23.6	74.9	163			
-0.75	22.5	61.4	126	-0.75	21.8	58.2	121			
-1	24.5	50.3	85.6	-1	19.9	47.2	83.4			
-1.5	35.9	85.1	125	-1.5	37.1	87.5	130			
	Fe				Fe UF					
NaOH/HNO3	Without	1 mg/L	2 mg/L	NaOH/HNO3	Without	1 mg/L	2 mg/L			
(+/-)	As	As	As	(+/-)	As	As	As			
0.5	1.51	1.2	2.02	0.5	0.111	0.0235	0.0512			
0.25	0.805	0.63	0.859	0.25	0.0278	0.0298	0.959			
0	0.0152	0.0577	0.149	0	0.0159	0.0109	0.0138			
-0.25	0.0508	0.05	0.0477	-0.25	0.0472	0.0507	0.0927			
-0.5	0.438	0.452	0.545	-0.5	0.373	0.433	0.407			
-0.75	1.34	1.45	1.36	-0.75	1.34	1.35	1.29			
-1	2.79	2.7	2.7	-1	2.37	2.56	2.63			
-1.5	5.75	5.92	5.48	-1.5	5.75	5.91	5.42			
	рН									
NaOH/HNO3 (+/-)	Without As	1 mg/L As	2 mg/L As							
0.5	7.7	7.5	7.9							
0.25	7.0	7.0	7.1							
0	6.1	6.3	6.4							
-0.25	5.6	5.6	5.7							
-0.5	5.2	5.2	5.1							
-0.75	5.0	5.0	4.9							
-1	4.8	4.8	4.8							
-1.5	4.6	4.5	4.6							

Table A4. Datapoints used to produce diagrams in figure 10.

NaOH/HNO3 (+/-)	Without added As	1 mg/L added As	2 mg/L added As
0.5 mM	0.5 NaOH	0.5 NaOH +1As	0.5 NaOH +2As
0.25 mM	0.25 NaOH	0.25 NaOH +1As	0.25 NaOH +2As
0	0 + 0 - 1	0 + 1As - 1	0 +2As
-0.25 mM	0.25 HNO3	0.25 HNO3 +1As	0.25 HNO3 +2As
-0.5 mM	0.5 HNO3	0.5 HNO3 +1As	0.5 HNO3 +2As
-0.75 mM	0.75 HNO3	0.75 HNO3 +1As	0.75 HNO3 +2As
-1 mM	1 HNO3	1 HNO3 +1As	1 HNO3 +2As
-1.5 mM	1.5 HNO3	1.5 HNO3 +1As	1.5 HNO3 +2As

Table A5. Configuration of sample run in pH-dependent experiment. To each sample 10 mM of NaNO3 was added. Table shows the labelling of each sample.

	рН	Са	К	Mg	Mn	Na	NO3	Р	Si
SAMPLE		Molal	Molal	Molal	Molal	Molal	Molal	Molal	Molal
0.5 NaOH UF	7.71	2.97E-05	3.99E-05	8.06E-06	1.93E-07	0.01	0.01	1.31E-06	9.01E-05
0.25 NaOH UF	6.99	5.04E-05	4.25E-05	1.63E-05	8.32E-07	0.01	0.01	4.84E-07	9.83E-05
0+0-1 UF	6.10	1.07E-04	5.09E-05	2.70E-05	4.19E-06	0.01	0.01	1.61E-07	1.18E-04
0.25 HNO3 UF	5.62	1.33E-04	5.91E-05	3.18E-05	5.19E-06	0.01	0.01	2.85E-07	1.37E-04
0.5 HNO3 UF	5.19	1.89E-04	6.32E-05	3.93E-05	6.88E-06	0.01	0.01	3.65E-07	1.64E-04
0.75 HNO3 UF	4.96	2.38E-04	6.91E-05	4.81E-05	7.63E-06	0.01	0.01	6.39E-07	1.83E-04
1 HNO3 UF	4.85	3.09E-04	8.31E-05	6.17E-05	8.77E-06	0.01	0.01	7.39E-07	2.36E-04
1.5 HNO3 UF	4.56	4.07E-04	9.80E-05	7.90E-05	1.19E-05	0.01	0.01	1.78E-06	2.84E-04
0.5 NaOH + 1As UF	6.98	2.89E-05	3.99E-05	7.45E-06	9.59E-08	0.01	0.01	1.32E-06	8.83E-05
0.25 NaOH + 1As UF	7.50	5.54E-05	4.63E-05	1.75E-05	9.59E-07	0.01	0.01	3.12E-07	1.10E-04
0+1As-1 UF	6.27	8.13E-05	5.17E-05	2.51E-05	3.22E-06	0.01	0.01	2.03E-07	1.15E-04
0.25 HNO3 + 1As UF	5.64	1.27E-04	5.45E-05	3.11E-05	5.52E-06	0.01	0.01	2.94E-07	1.33E-04
0.5 HNO3 + 1As UF	5.16	1.81E-04	6.19E-05	3.94E-05	6.64E-06	0.01	0.01	5.97E-07	1.60E-04
0.75 HNO3 + 1As UF	4.95	2.34E-04	7.03E-05	4.85E-05	7.55E-06	0.01	0.01	6.97E-07	1.93E-04
1 HNO3 + 1As UF	4.82	2.92E-04	8.01E-05	6.13E-05	8.92E-06	0.01	0.01	8.75E-07	2.25E-04
1.5 HNO3 + 1As UF	4.51	3.94E-04	9.59E-05	7.82E-05	1.13E-05	0.01	0.01	2.12E-06	2.67E-04
0.5 NaOH + 2As UF	7.86	2.92E-05	4.09E-05	8.23E-06	1.13E-07	0.01	0.01	1.51E-06	9.36E-05
0.25 NaOH + 2As UF	7.15	5.11E-05	4.86E-05	1.82E-05	9.21E-07	0.01	0.01	1.09E-06	1.43E-04
0+2As UF	6.38	7.11E-05	4.99E-05	2.31E-05	2.88E-06	0.01	0.01	3.68E-07	1.17E-04
0.25 HNO3 + 2As UF	5.67	1.19E-04	5.68E-05	3.20E-05	5.06E-06	0.01	0.01	2.13E-07	1.48E-04
0.5 HNO3 + 2As UF	5.12	1.73E-04	6.39E-05	4.01E-05	6.02E-06	0.01	0.01	5.42E-07	1.69E-04
0.75 HNO3 + 2As UF	4.92	2.28E-04	7.29E-05	5.06E-05	8.01E-06	0.01	0.01	8.40E-07	1.94E-04
1 HNO3 + 2As UF	4.82	2.84E-04	8.24E-05	6.09E-05	9.30E-06	0.01	0.01	1.17E-06	2.35E-04
1.5 HNO3 + 2As UF	4.57	3.89E-04	9.74E-05	7.94E-05	1.08E-05	0.01	0.01	1.92E-06	2.88E-04

#### Table A6. Inputs in Visual MINTEQ model.

		OE As (%)											
OE Fh (%)	100%	90%	80%	70%	60%	50%	40%	30%					
100.00	168	174	179	184	188	191	194	197					
90.00	161	168	175	180	185	189	193	196					
80.00	151	160	169	176	182	187	191	195					
70.00	135	148	159	169	177	183	189	193					
60.00	111	129	145	158	169	178	185	191					
50.00	92	100	120	140	156	170	180	188					
40.00	118	130	96	109	133	154	170	182					
30.00	697	460	270	143	101	122	150	171					
20.00	1529	1199	884	594	345	166	110	142					

Table A7a. RMSE values from sweep method for samples without added As.

Table A7b. RMSE values from sweep method for samples with 1 mg/l added As.

	OE As (%)									
OE Fh (%)	100%	90%	80%	70%	60%	50%	40%	30%		
100.00	442	451	458	465	470	475	478	482		
90.00	429	442	452	460	467	472	477	481		
80.00	411	428	442	453	462	469	475	479		
70.00	379	406	427	442	455	464	472	477		
60.00	326	367	399	424	443	457	467	475		
50.00	285	303	349	390	421	443	459	470		
40.00	570	365	293	324	376	417	444	463		
30.00	1297	925	603	373	305	353	409	446		
20.00	442	451	458	465	470	475	478	482		

Table A7c. RMSE values from sweep method for samples with 2 mg/l added As.

	OE As (%)									
OE Fh (%)	100%	90%	80%	70%	60%	50%	40%	30%		
100.00	800	823	842	858	870	880	888	895		
90.00	769	801	826	846	862	875	885	893		
80.00	720	766	802	830	851	868	880	890		
70.00	638	709	763	804	834	857	874	887		
60.00	517	611	695	759	806	839	863	881		
50.00	526	491	576	676	754	809	846	871		
40.00	1046	703	518	540	649	746	812	855		
30.00	1917	1436	1001	665	534	613	733	817		
20.00	2955	2419	1898	1402	959	641	582	712		

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