Iron-based subsurface arsenic removal (SAR): Results of a long-term pilot-scale test in Vietnam

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Keywords: Subsurface arsenic mitigation; Mekong Delta; oxidation/adsorption; zero-waste; low-cost; groundwater contamination

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Abstract: The principle of subsurface arsenic removal (SAR) from groundwater is based on oxidation and ad-sorption reactions by infiltrating oxygen into the anoxic aquifer and the immobilization of arsenic (As) onto freshly formed iron (Fe) oxides. In this study, a pilot-scale plant for SAR has been subject to long term testing in the Mekong Delta, Vietnam. Initial concentrations of Fe (8.4 ± 1.3 mg L 1) and As (81 ± 8 µg L 1) in the exploited groundwater were successfully lowered to below the WHO guideline value limits for drinking water of 0.3 mg L 1 and 10 µg L 1 respectively. Adsorption and co-precipitation of As with iron oxides could be identified as the principal mechanism responsible for the As removal from groundwater, demonstrating the feasibility of SAR as a low-cost and zero-waste solution over a period of two years. However, naturally occurring geochemical reducing conditions and high ammoni-um levels in the groundwater delayed the removal of manganese (Mn). An additional post-treatment filtration for Mn-removal was temporarily used to comply with the Vietnamese drinking water standard until a Mn-mitigation was achieved by the SAR process. In contrast to most As-remediation tech-nologies, SAR appears to be a long-term, sustainable treatment option with the salient advantage of negligible production of toxic waste, which with ex-situ processes require additionally management costs.

***Declaration of Interest Statement**

Declaration of interests

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

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights:

- A pilot plant for subsurface arsenic removal -SAR was operated for over 2 years
- Arsenic was successfully lowered to below WHO drinking water guideline
- No remobilization of As was observed for 28 months operation
- SAR is a low-cost sustainable method with no toxic waste produced

Graphical Abstract

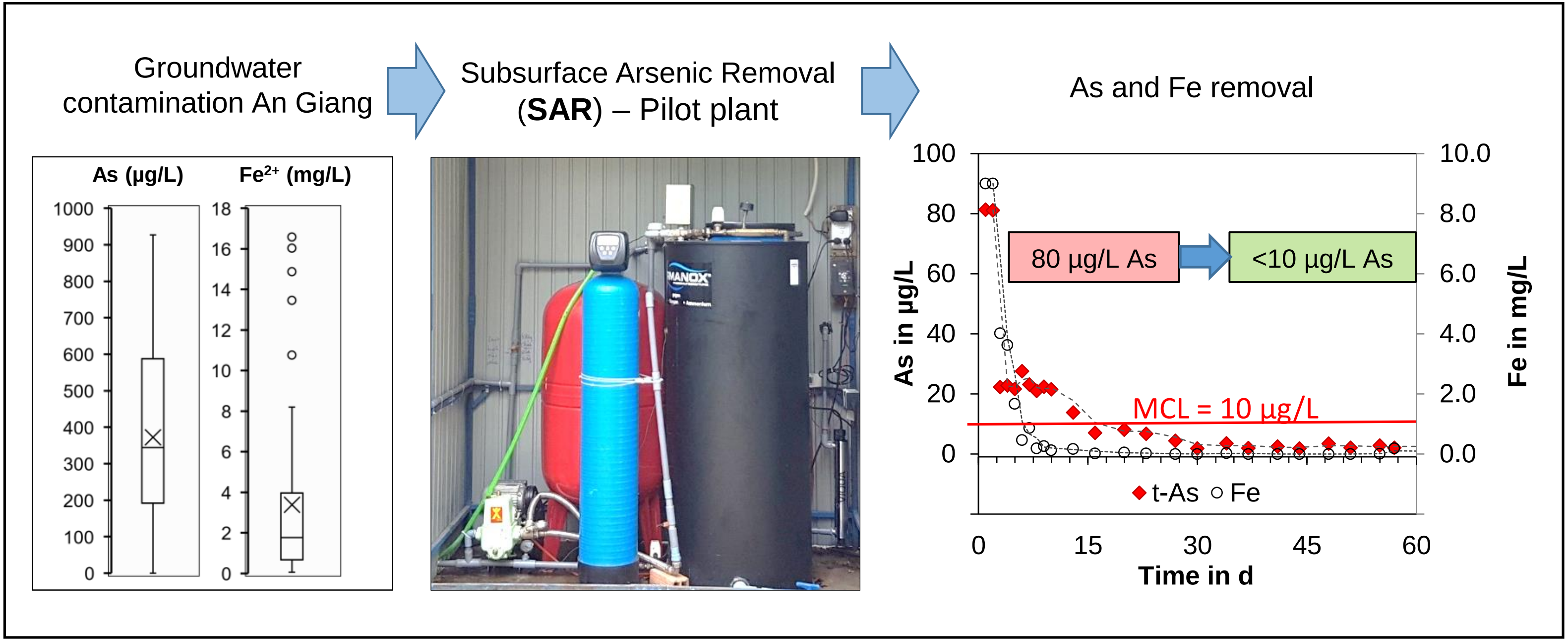


Figure 1


Storage tank
Controller
Mn filter
Pressure tank
Feed pump
Injector
Aeration tank
UV lamp
Extra tank

Figure 2

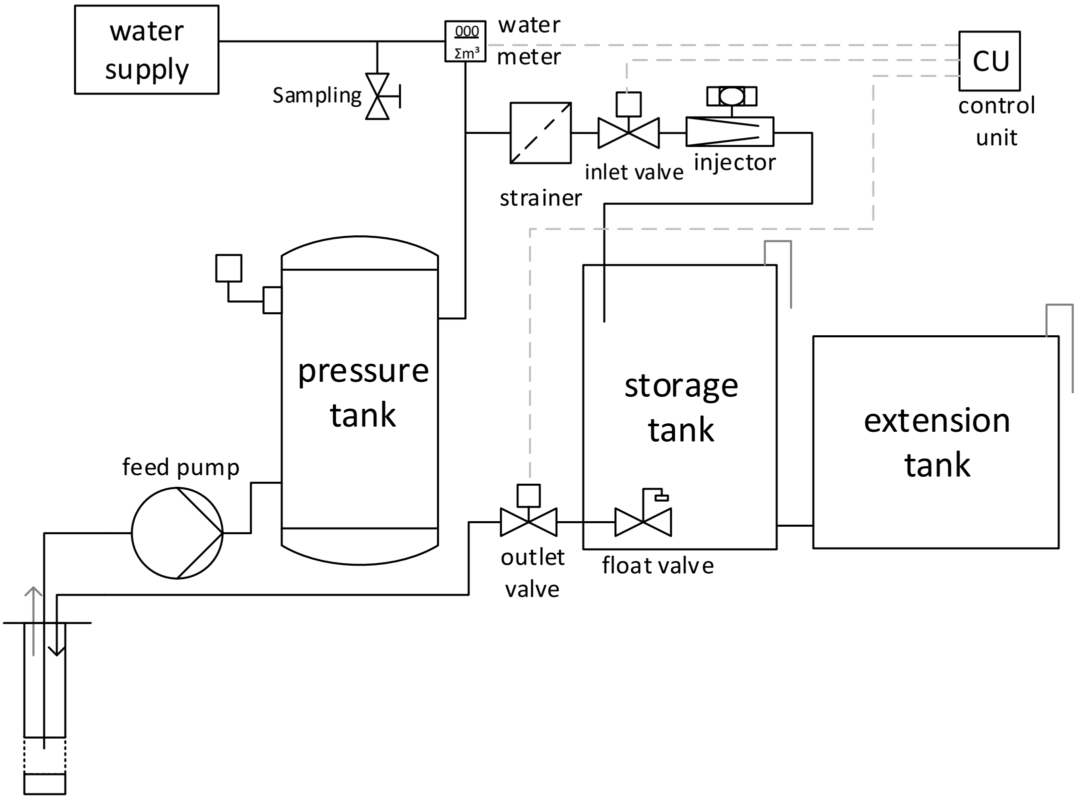

water supply
Sampling
000
Σm³
water meter
CU
control unit
strainer
inlet valve
injector
pressure tank
storage tank
extension tank
feed pump
outlet valve
float valve

Figure 3

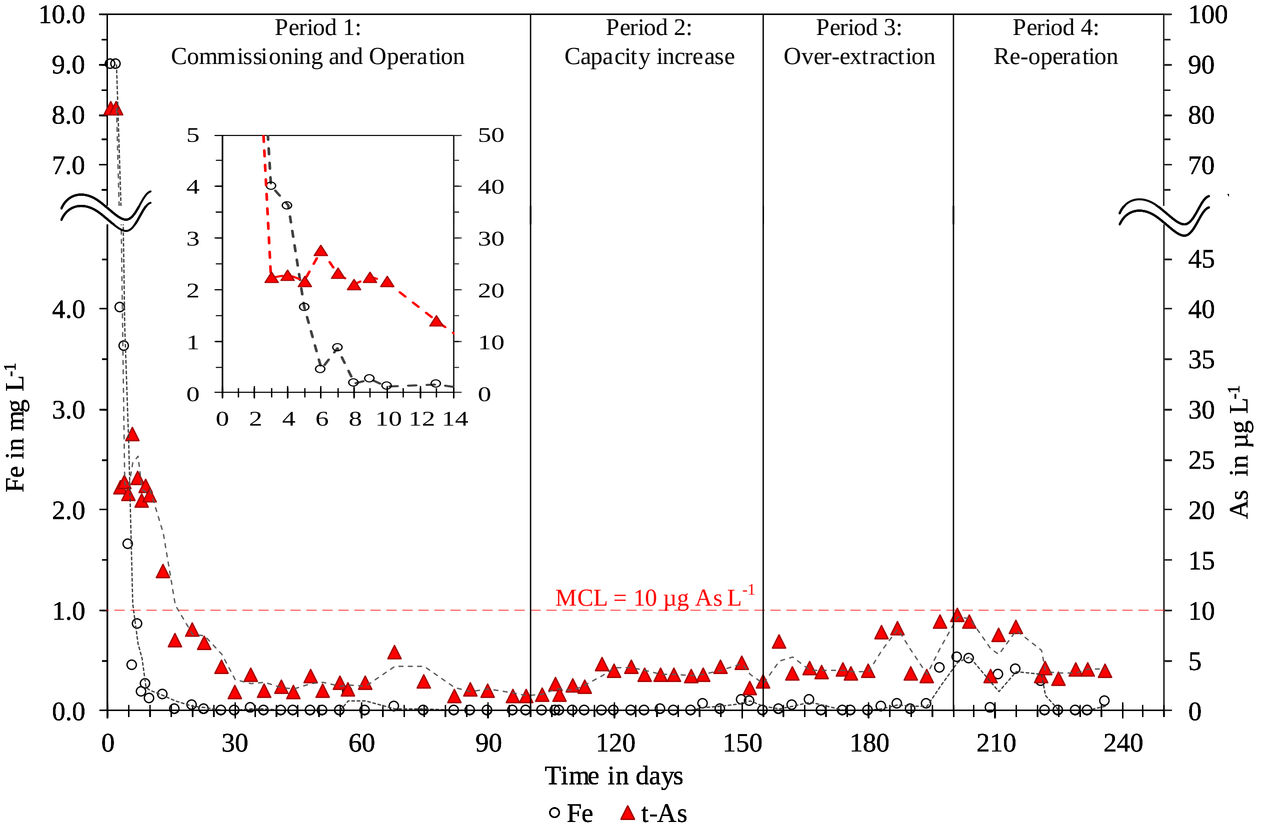
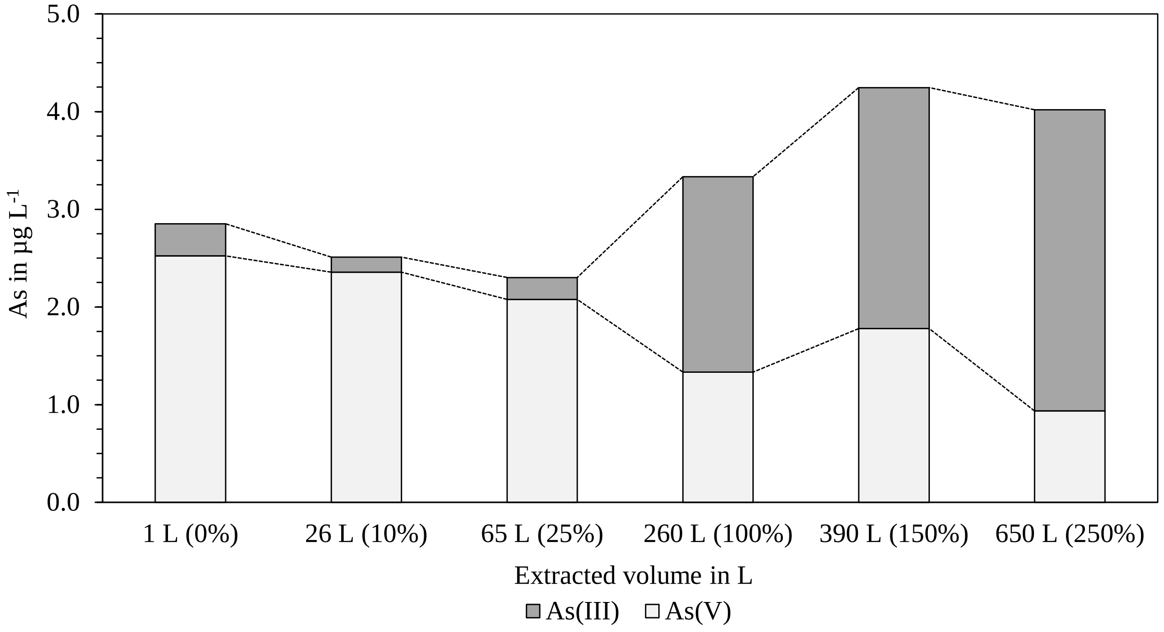

Period 1:
Commissioning and Operation
Period 2:
Capacity increase
Period 3:
Over-extraction
Period 4:
Re-operation
Fe in mg L-1
As in µg L-1
10.0
9.0
8.0
7.0
4.0
3.0
2.0
1.0
0.0
100
90
80
70
45
40
35
30
25
20
15
10
5
0
MCL = 10 µg As L-1
0
30
60
90
120
150
180
210
240
Time in days
○ Fe
▲ t-As
5
4
3
2
1
0
50
40
30
20
10
0
0 2 4 6 8 10 12 14

Figure 4



5.0
4.0
3.0
2.0
1.0
0.0
As in µg L-1
1 L (0%)
26 L (10%)
65 L (25%)
260 L (100%)
390 L (150%)
650 L (250%)
Extracted volume in L
As(III)
As(V)

Figure 6

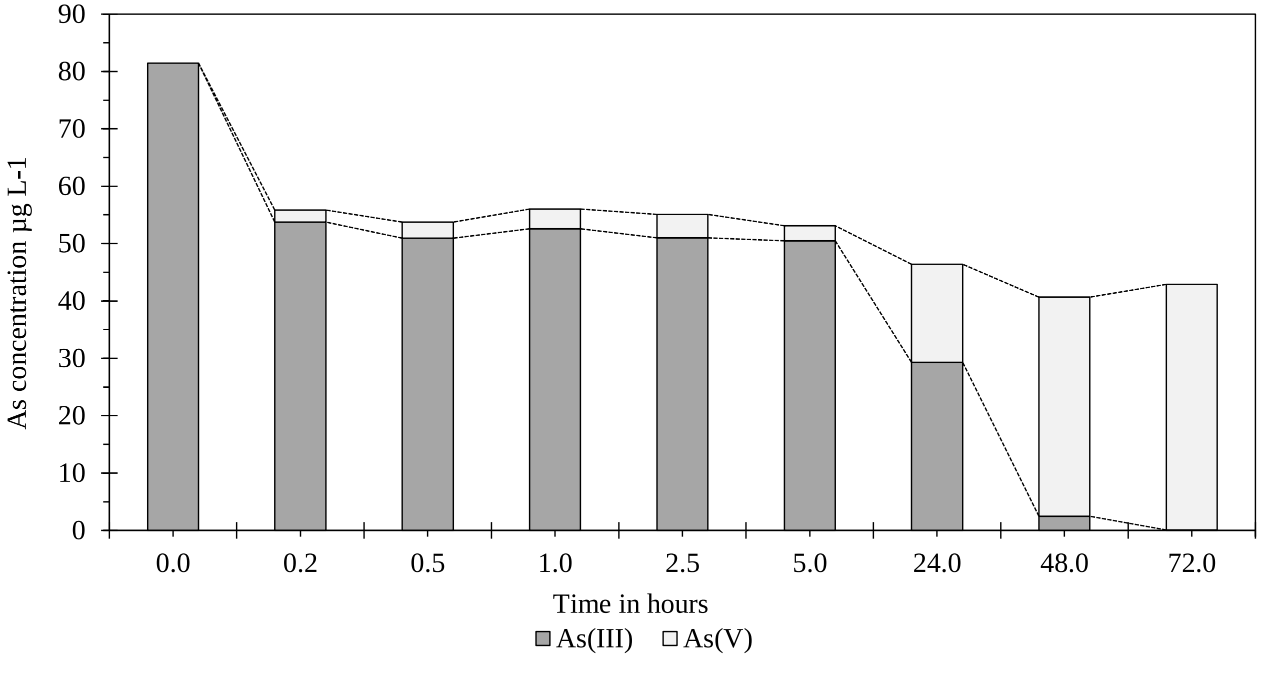
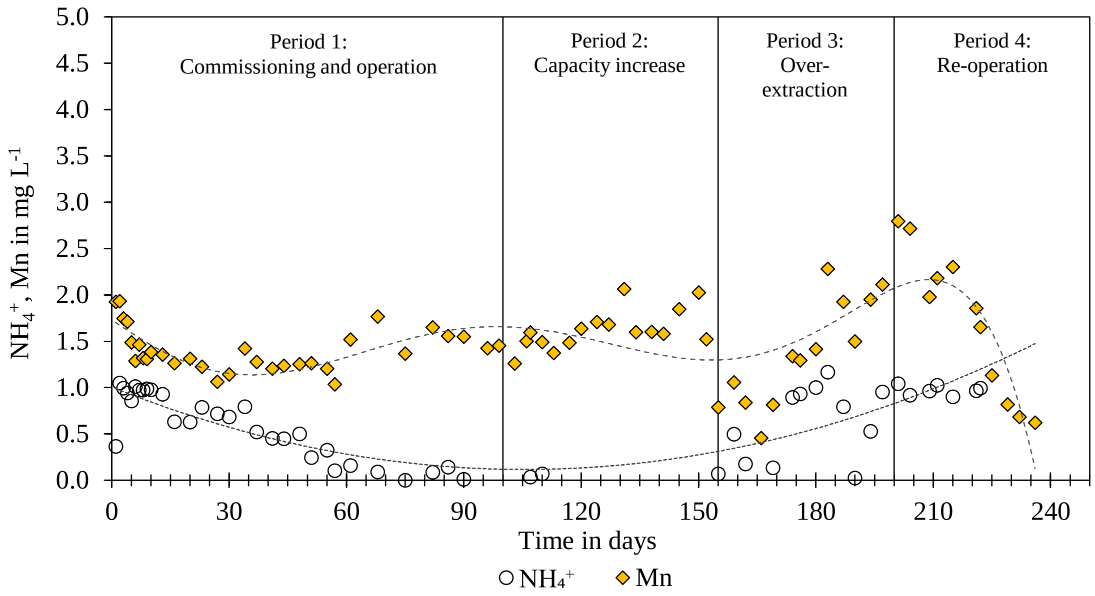

90
80
70
60
50
40
30
20
10
0
As concentration µg L-1
0.0
0.2
0.5
1.0
2.5
5.0
24.0
48.0
72.0
Time in hours
As(III)
As(V)

Figure 7


Period 1:
Commissioning and operation
Period 2:
Capacity increase
Period 3:
Over-
extraction
Period 4:
Re-operation
NH_4^+, Mn in mg L^{-1}
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
30
60
90
120
150
180
210
240
Time in days
○ NH_4^+
◆ Mn

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Reply to Editor:

The authors thank the Editor for the consideration to publish this article. Authors have carefully revised and corrected the manuscript following the reviewers' comments. Moreover, some authors have changed the working position, therefore the authors would like to update their affiliation in the revised version. Authors hope to get an acceptance to these minor changes.

A supplementary material has been attached at the end of the manuscript (and additionally uploaded as electronic supplementary material), following reviewers recommendation.

Kind regards

Prof. Dr. Jan Hoinkis

Iron-based subsurface arsenic removal (SAR): Results of a long-term pilot-scale test in Vietnam

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Abstract

The principle of subsurface arsenic removal (SAR) from groundwater is based on oxidation and adsorption reactions by infiltrating oxygen into the anoxic aquifer and the immobilization of arsenic (As) onto freshly formed iron (Fe) oxides. In this study, a pilot-scale plant for SAR has been subject to long term testing in the Mekong Delta, Vietnam. Initial concentrations of Fe (8.4 ± 1.3 mg L^{-1}) and As (81 ± 8 µg L^{-1}) in the exploited groundwater were successfully lowered to below the WHO guideline value limits for drinking water of 0.3 mg L^{-1} and 10 µg L^{-1} respectively. Adsorption and co-precipitation of As with iron oxides could be identified as the principal mechanism responsible for the As removal from groundwater, demonstrating the feasibility of SAR as a low-cost and zero-waste solution over a period of two years. However, naturally occurring geochemical reducing conditions and high ammonium levels in the groundwater delayed the removal of manganese (Mn). An additional post-treatment filtration for Mn-removal was temporarily used to comply with the Vietnamese drinking water standard until a Mn-mitigation was achieved by the SAR process. In contrast to most As-remediation technologies, SAR appears to be a long-term, sustainable treatment option with the salient advantage of negligible production of toxic waste, which with ex-situ processes require additionally management costs.

Keywords: Subsurface arsenic mitigation; Mekong Delta; oxidation/adsorption; zero-waste, low-cost; groundwater contamination

1. Introduction

1.1. Arsenic in groundwater

Arsenic (As) is considered to be one of the most serious, naturally occurring, inorganic contaminants in groundwater on a global scale (Amini et al., 2008; Sarkar and Paul, 2016; Srivastava, 2020) and it has been recognized as a significant environmental cause of cancer mortality (Khan et al., 2020; WHO, 2012). Arsenic occurrence in natural groundwater varies depending on the local geology, the hydrochemical characteristics of the aquifer and the pH and redox-dependent mechanisms for its mobilization from the solid phase into the groundwater. Arsenic is found mainly as arsenate (As(V)) and arsenite (As(III)) species in reducing and oxidizing milieus, respectively (Campbell and Nordstrom, 2014; Kumar et al., 2020; D. Zhang et al., 2017a). High concentrations of geogenic As are found in the groundwater of many world regions including Southeast Asia (Palit et al., 2019; Uppal et al., 2019), Bangladesh (Chakraborti et al., 2015; Huq et al., 2020), India (Bhowmick et al., 2018; Sankar et al., 2014), China (Li et al., 2020; L. Zhang et al., 2017), North (Janković, 2020) and Latin America (Bundschuh et al., 2012; Litter et al., 2020) as well as Australia and Europe (Medunić et al., 2020). Geogenic As in oxidizing aquifers is mostly associated to bedrock lithology and originates typically from leaching of geological materials (e.g. hard rock and sediments) (Huq et al., 2020; D. Zhang et al., 2017b), in some areas from geothermal fluids and volcanic ashes (Morales-Simfors et al., 2020a) and products from mining (e.g. tailings) and related activities (Ciminelli, 2014). Additionally, important artificial As sources can result from agricultural activities (e.g. pesticides). These sources can impact groundwater in regions as described from Latin America with its mostly oxidizing aquifers (Bundschuh et al., 2012; Litter et al., 2020; Morales-Simfors et al., 2020b). The mobilisation and release of geogenic As into the groundwater in reducing aquifers, such as in most of Southeast Asia, is a result of the reductive dissolution of both iron (Fe) and manganese (Mn) oxi(hydr)oxides from As-bearing sediments (Berg et al., 2007; Norrman et al., 2008; D. Zhang et al., 2017a). In addition, some of these regions with predominantly high levels of As also show particularly high levels of ammonium (NH_4^+) (Jia et al., 2018; Norrman et al., 2015) and Mn^{2+} (Berg et al., 2008; Datta et al., 2014).

1.2. Arsenic remediation

There are many established methods for treating As contaminated water. The most common include oxidation and filtration, adsorption, ion exchange and separation by membrane technologies, each displaying different advantages and disadvantages (Ghosh N. et al., 2019; Jadhav et al., 2015; Litter et al., 2019; Nicomel et al., 2015; Singh et al., 2015). Other emerging technologies comprise electrochemical and coagulation processes, phytoremediation and alternative adsorptive materials (Kumar et al., 2019). The main disadvantage of these "*ex-situ*" technologies is the generation of As-laden waste in the form of solids or concentrate streams, which have to be disposed of safely (Clancy et al., 2013). As a consequence, the safety and disposal costs of As-bearing wastes become an issue and alternative techniques with an economical and environmental sustainable concept approach are needed.

The *in-situ* As treatment by aeration is a technique based on subsurface iron removal (SIR), which has proven to be a technically feasible practise in Europe and the United States for decades in a variety of hydrogeochemical settings for the *in-situ* treatment of Fe, Mn and NH_4^+ in groundwater (Ahmad, 2012; Grischek et al., 2015; Hallberg and Martinell, 1976; Henning and Rott, 2003; Karakish, 2005; Rott and Friedle, 2000; Rott and Kauffmann, 2008). However, subsurface As removal (SAR) is not yet an established solution and has only been tested in a very limited number of laboratory tests and pilot trials (Kundu et al., 2018; Rahman et al., 2014; Rott et al., 1996; Sarkar and Rahman, 2001; Sen Gupta et al., 2009; van Halem et al., 2010, 2009).

The majority of studies on SAR have focused on the vulnerability of the process to diverse geochemical conditions such as pH, redox potential (Eh) and the presence of co-ions such as phosphates, sulphates, carbonates and ammonium (Luong et al., 2018) that are competing with As for adsorption sites and can have a negative influence on the As removal. In some cases, this can make it difficult to comply with the stringent guideline value for drinking water recommended by the WHO of 10 µg L^{-1} (WHO, 2017). However, the salient advantage of SAR is its low operating and maintenance costs, combined with its negligible waste production, with no waste streams containing toxic As. The major questions that arise regarding SAR are the stability of the subsurface adsorption, the possible remobilization of As and its accumulation in the aquifer (Grischek et al., 2015; Rahman et al., 2014; van Halem et al., 2011).

1.3. Principle of SAR

The basic principle of SAR is based on the adsorption and co-precipitation of As onto Fe-(hydr)oxides by periodically extracting anoxic groundwater, aerating it and infiltrating the oxygen-rich water back into the aquifer. Oxygen reacts with dissolved iron (Fe^{2+}) to form HFOs, which are poorly crystalline oxides with high porosity and large surface areas (oxidation). When water is abstracted, dissolved As adsorbs onto the freshly formed HFOs (adsorption) and groundwater with lower As concentrations can be extracted.

A given amount of groundwater with low-arsenic can be extracted after each infiltration cycle. This volume depends on the amount of oxygen that is available for the oxidation reactions (Kundu et al., 2018; Luong et al., 2018; Rott and Friedle, 2000). In order to estimate the treatment capacity of each plant and the amount of water that can be extracted after each infiltration, an important parameter of a SAR system is the injection-to-extraction ratio $Q_E = V_I/V_E$, which is the ratio of the volume of infiltrated oxygenated water (V_I) to the amount of extracted treated water (V_E). This volume-specific parameter is a design parameter principally given by the quality of the raw water and can be calculated from the stoichiometric oxygen amount required for the chemical oxidation process (Luong et al., 2018).

With a ratio of, for example, $Q_E = 0.5$, the infiltration of 1 m³ allows the extraction of 2 m³ of fresh water. However, in anoxic groundwater with high oxygen demand, for example due to high Mn^{2+} and NH_4^+ concentrations, Q_E may be higher than 1, meaning more volume must be infiltrated than the amount that can be extracted.

Since the abstracted groundwater is always infiltrated back into the aquifer, no water is lost and no waste stream is produced, which is another important feature of the process. However, the treated water quality can, in some exceptional cases (e.g. technical failure infiltration or over-extraction in daily operation), gradually decrease. This is also discussed later as a breakthrough experiment (see Section 3.2). As oxidation reactions in the aquifer are also coupled with microbial oxidation, the sorption and co-precipitation processes in the aquifer can be also influenced by given natural hydrogeological conditions and microbial activity of the aquifer. In order to ensure a safe water supply and avoid over-extraction, a maximum daily limit $V_{E,max}$ is set for each individual SAR plant (Luong et al., 2018, 2019).

1.4. Objectives

The main objective of this study is to prove the feasibility of the SAR process as a sustainable treatment option for simultaneous Fe and As removal and to evaluate the technology on a pilot-scale. For the first time, its long-term stability in terms of removal efficiency, operation stability and energy demand has been evaluated in the course of 2 years. The pilot SAR plant was installed in the Mekong Delta, Vietnam, as part of the joint research project WaKap from 2016 to 2019 (Hoinkis et al., 2016).

2. Method

2.1. SAR pilot plant and location

The SAR pilot plant (*FERMANOX®-Wasseraufbereitung type BV 45*; Figure 1) was installed in the village of Cho Vam in the Province of An Giang in the Mekong-Delta, Vietnam, next to the Cambodian border (coordinates: N 10.719308, E 105.331354). This province has previously been identified as one of the most affected by high As concentrations in the country with more than 75% of wells analysed presenting concentrations higher than 10 µg As L^{-1} (Kỳ, 2009; Thư et al., 2011).

The plant was setup for the treatment of As-laden groundwater and the water supply of a small group of people from a religious community. The existing shallow tube well (Ø = 42 cm) had a depth of 17 m and was connected to an existing storage tank used for water storage and supply for irrigation, toilet flushing and washing. Figure 1 shows the installation of the SAR pilot plant with the available storage tank and an extra aeration tank.

Figure 1: SAR pilot plant (FERMANOX®-*Wasseraufbereitung* type BV 45) in An Giang, Vietnam, incl. delivery pump, pressure tank, Mn-filter and UV-lamp for post-treatment

2.2. Raw water analysis

Before the trial tests started, 52 possible pilot sites were analysed in the province of An Giang from which the pilot test site was selected (detailed results: see Supplement 1 and Supplement 2). The presence of preferably high concentrations Fe^{2+} was important for the site selection, since a successful As-mitigation is based on the adsorption onto and the co-precipitation with the HFOs. Other important criteria considered were low Mn^{2+} and NH_4^+ as well as the total water demand of the well.

Full analysis results of the groundwater at the selected well in Cho Vam are presented in Table 1. Analyses were carried out at different times of the year in order to assess seasonal fluctuations in the groundwater quality prior to the beginning of the pilot. The high Fe:As ratio of the selected site of 106 ± 24 (w/w) was favourable for the arsenic adsorption (average ratio of study area: Fe:As = 22 ± 48 (w/w) (see Supplement 2). However, the presence of ions such as phosphate (PO_4^{3-}) and silicate (Si) competing with As for adsorption sites due to their similar adsorption mechanisms can hinder the effective removal of As. Furthermore, Mn^{2+} and NH_4^+ concentrations above the drinking water standards in the groundwater may challenge the complete treatment. For this reason, these parameters were carefully monitored during the pilot tests.

Table 1: Analysis of raw groundwater at SAR test site before trial tests (2016-2017)

Parameter	**Unit**	**Nov 16**[a]	**Feb 17** [b]	**Jun 17** [c]	**Jul 17**[c]*****	**Average**
T	°C	29.0	26.4	*N/A*	29.5	28.3 ±1.4
pH	-	7.1	7.2	*N/A*	6.8	7.0 ±0.2
E.C.	$\mu S\ cm^{-1}$	482	440	*N/A*	489	470 ±22
t-As	$\mu g\ L^{-1}$	92	78	71	82	81 ±8
Fe^{2+}	$mg\ L^{-1}$	7.0	7.4	10	9.0	8.4 ±1.3
Fe:As	-	76	95	141	111	106 ±24
Mn^{2+}	$mg\ L^{-1}$	2.3	1.4	2.1	1.9	1.9 ±0.3
Si	$mg\ L^{-1}$	16	15	11	19	15 ±3
Na^+	$mg\ L^{-1}$	28	16	18	22	21 ±5
NH_4^+	$mg\ L^{-1}$	1.1	0.89	1.2	1.1	1.1 ±0.1
K^+	$mg\ L^{-1}$	*N/A*	2.1	2.1	2.4	1.9 ±0.4
Ca^{2+}	$mg\ L^{-1}$	18	19	28	*N/A*	22 ±5
Mg^{2+}	$mg\ L^{-1}$	10	9.3	12	13	11 ±1
Cl^-	$mg\ L^{-1}$	15	8.3	*N/A*	22	15 ±5
PO_4^{3-}	$mg\ L^{-1}$	1.0	1.0	*N/A*	1.9	1.3 ±0
SO_4^{2-}	$mg\ L^{-1}$	1.2	1.0	2.7	*N/A*	1.6 ±0.7
TOC	$mg\ L^{-1}$	*N/A*	*N/A*	8.3	7.2	5.9 ±3

[a] end of rainy season in 2016; [b] dry season in 2017; [c] rainy season in 2017; *start of operation
E.C.: electrical conductivity; TOC: total organic carbon; N/A: not available/not measured

2.3. Plant operation

The pilot plant scheme is displayed in Figure 2 showing the SAR storage tank (390 L) with an air injection nozzle and air filter, the feed pump (Speck PM 15) with pressure vessel (200 L) and an automatic control unit (CU) to monitor and regulate the infiltration and extraction processes depending on the actual water demand. An extension tank (1000 L) was added in a later stage to increase the treatment capacity of the plant.

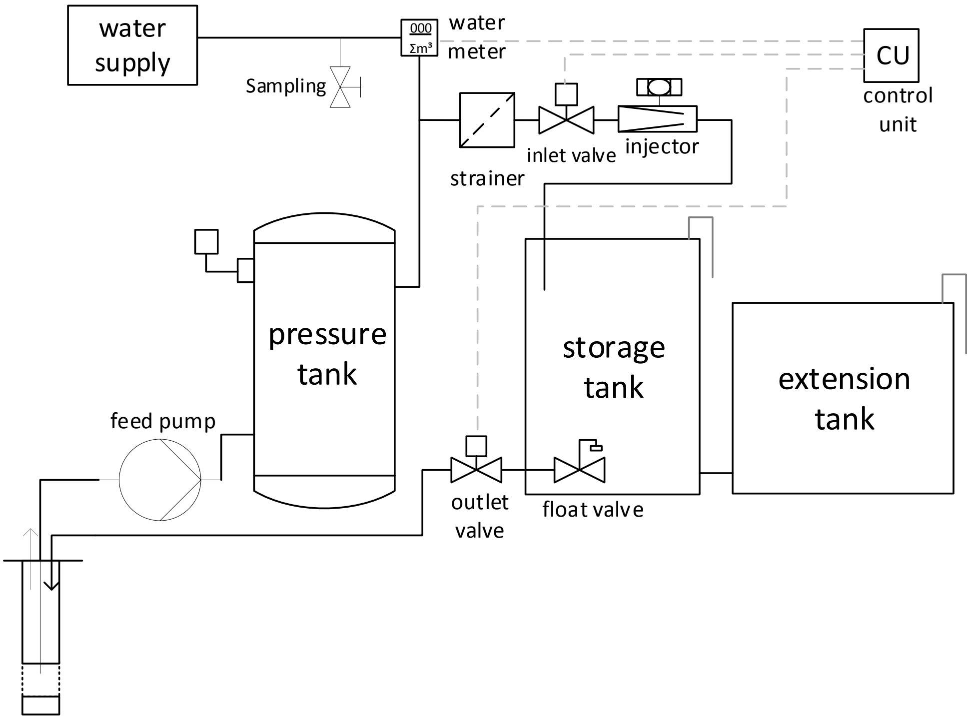

Figure 2: Scheme of SAR pilot plant for subsurface arsenic removal (SAR)

The SAR system was operated in intermittent daily cycles as manufacturer's recommendation using the following basic steps:

1. *Aeration*: Anoxic groundwater is extracted from the aquifer using the feed pump and aerated with an air injector at a pressure of $p_{min} > 0.28$ MPa. Here, a pressure tank is used which is regulated by a pressure switch ($0.28 < p < 0.35$ MPa). Each aeration cycle is controlled automatically by the CU of the system which is programmed to carry out a maximum of two cycles daily.
2. *Infiltration/adsorption*: After the groundwater is aerated, the oxygen-rich water (DO: saturation > 99%) is re-injected through the tube well into the aquifer via gravity, lifting the redox potential of the anoxic aquifer and inducing the formation of oxidation and adsorption zones around

the well. Here, Fe^{2+} is oxidized to Fe(III)-(hydr)oxides or HFOs. Then, As adsorbs onto the freshly formed HFOs and is co-precipitated within the Fe-(hydr)oxide-matrix.

3. *Abstraction:* When water is abstracted, raw groundwater flows through the oxidation/adsorption zone where As is adsorbed and more Fe(III)-(hydroxides) are formed, creating more adsorption places for the next cycle.

4. Treated water can be abstracted from the well in line with the maximum daily capacity $V_{E,max}$.

The number of *infiltration* cycles (*n*) was regulated with a control unit based on the water consumption. The maximum infiltration cycles was set to $n_{max} = 2$. If no water consumption occurred, no infiltration was needed (n = 0), however, an infiltration cycle was carried out every 2 days even without consumption in order to assure the process stability.

The pilot trials were carried out in four operational periods: during the first three months (Period 1), the plant had an infiltration capacity of $V_{I,1} = 390$ L (size of SAR tank) which corresponded to an extraction volume of $V_{E,1,max} = 470$ L with two infiltration cycles per day ($2 \cdot V_{I,1} = 780$ L) and an infiltration-to-abstraction ratio of $Q_E = 1.66$.

For the second period (Period 2), the infiltration volume was increased to $V_{I,2} = 1390$ L (SAR tank + extension tank with a capacity of 1000 L). With two infiltrations cycles per day ($2 \cdot V_{I,2} = 2780$ L), a total volume $V_{E,2,max} = 1900$ L could be extracted daily. This corresponds to an infiltration-to-abstraction ratio of $Q_E = 1.46$.

In the third and fourth period, the process stability was evaluated during over-extraction (Period 3) and after re-operation (Period 4).

In order to ensure a safe operation, an alarm was triggered when $V_{E,max}$ was exceeded. This not only prevented the breakthrough of contaminants, but also prolonged the well life by protecting the extraction area surrounding the tube well from incrustations. Furthermore, no water was extracted from the well during each infiltration cycle plus at least 15 min of subsequent rest time. This was done to avoid re-abstraction of oxygenated water after infiltration.

2.4. Sampling and analysis

Water samples were taken daily from the sample valve during the first ten days of commissioning and twice a week thereafter. Every time a sample was taken, groundwater was firstly abstracted and stored in the water supply tank until it reached the maximum extracted capacity $V_{E,max}$. The samples were acidified with nitric or hydrochloric acid for conservation before transporting them to the laboratory. Values for pH and electrical conductivity (E.C.) were measured on-site or at the laboratory (raw samples) using a portable sensor (WTW Multi-Parameter 3430). An atomic adsorption spectrometer (Analytik Jena con-trAA® 300) was used with flame technique (50 mm burner with air/acetylene gases) for the determination of Mn^{2+} and Fe^{2+}, while, hydride generation (HS 55 batch system) was used for total arsenic (t-As) determination (Analytik Jena AG, 2019). Moreover, special cartridges (Meng-cartridges, METALSOFT) were used for As(III)/As(V) separation to conduct As-speciation (Meng et al., 2001). Ion chromatography (Metrohm 883 Basic IC plus) was used to analyse cations (Metrosep C4-150/4.0 column) according to ISO 14911 and anions (Metrosep A Supp 5-150/4.0 column). The TOC was analysed with a Shimadzu TOC-L Analyzer. Measurements were repeated at least twice and samples were stored in line with the ISO 5667 3 standard.

2.5. Data gathering

This study shows the results of two years of operation including installation and commissioning of the SAR plant. Data on water samples (chemical and physical parameters), water withdrawal and energy consumption were recorded continuously for the first 8 months to evaluate the process operation and efficiency. Afterwards, the well data were periodically monitored for the complete 28 months to show the long-term stability and monitor the energy consumption.

3. Results and discussion

3.1. Iron and arsenic removal

Results in Figure 3 show how the initial Fe concentration of 9.0 ± 1 mg Fe L^{-1} dropped to below the Vietnamese drinking water standard value of 0.3 mg Fe L^{-1} within the first week of operation. This demonstrates that the oxidation of dissolved Fe^{2+} to particulate Fe^{3+} (HFO) occurs rapidly after the first infiltration cycles as it occurs in the SIR process (Braester and Martinell, 1988; Rott, 1985; Rott and Lamberth, 1993; Van Beek, 1983).

The As elimination process was evaluated by monitoring the As immobilisation onto the Fe(III)-surfaces during each of the four operational periods (see Section 2.3 Plant operation). Arsenic mitigation only started after the first infiltration cycles occurred with As concentrations decreasing from day 2 to concentrations around 20 µg L^{-1}, remaining constant for the first ten days. Compliance for As standard of 10 µg As L^{-1} was achieved after 14 days, removing more than 95% of the initial As concentration (82 ± 10 µg As L^{-1}) and with As levels dropping continuously to concentration below 2 µg L^{-1}. This shows the complete adsorption of As requires the formation of enough HFO after several cycles.

The mass balance for As and HFO (in the form of FeOOH) of the first 14 days including the extracted volumes are listed in Table 2. Results show a significant increase in the As and Fe removal from day 8 to day 9, and indicate the adsorption reaches an equilibrium with an As adsorption capacity of q_m = 8.0 ± 1 µg As mg $FeOOH^{-1}$.

Table 2: Iron and As mass balances during SAR adsorption for the first 14 days of operation with a daily injection volume V_I = 780 L (two infiltration cycles).

Day	**V_E** (L)	**$\dot{m}_{As}$** (mg day^{-1})	**$\dot{m}_{FeOOH}$** (mg day^{-1})	**q_m*** (mg As g $FeOOH^{-1}$)
1	250	14.7	1247	11.8
2	260	14.6	1342	10.9
3	260	15.5	1907	8.1
4	260	13.9	2220	6.3
5	260	15.1	2115	7.1
6	260	15.6	2292	6.8
7	260	15.3	2271	6.7
8	260	15.5	2307	6.7
9	510	34.3	4506	7.6
10	660	48.9	5926	8.3
11	465	34.0	4160	8.2
12	400	29.7	3595	8.3
13	520	39.9	4680	8.5
14	570	45.2	5130	8.8
Total	**5.2 m^3**	**0.35 g As**	**43.7 g FeOOH**	**8.0 ± 1 mg g^{-1}**

*Average adsorption capacity calculated from daily As and Fe loads.

In period 2, after the increase of the total plant capacity (day 100), concentrations of dissolved Fe and As continued to remain stable well below the drinking water standard with only small fluctuations in the concentrations being observed, which can be attributed to natural fluctuations in groundwater concentrations and increased water withdrawal depending on consumer behaviour. In period 3 (day 155) water was extracted for 12 days while no infiltration was carried out due to a technical problem with the motor of the feed pump, which led to an over-extraction ($V_E > V_{E,max}$). The over-extraction continued during period 3 for a total of 51 days due to electrical failure of the water meter and the CU. Although more water was extracted than the allowed daily limit $V_E > V_{E,max} = 1900$ L, no As breakthrough above the drinking water limit was observed and Fe remained close to the standard of 0.3 mg L^{-1} with only a small increment to a maximum of 0.51 mg L^{-1}.

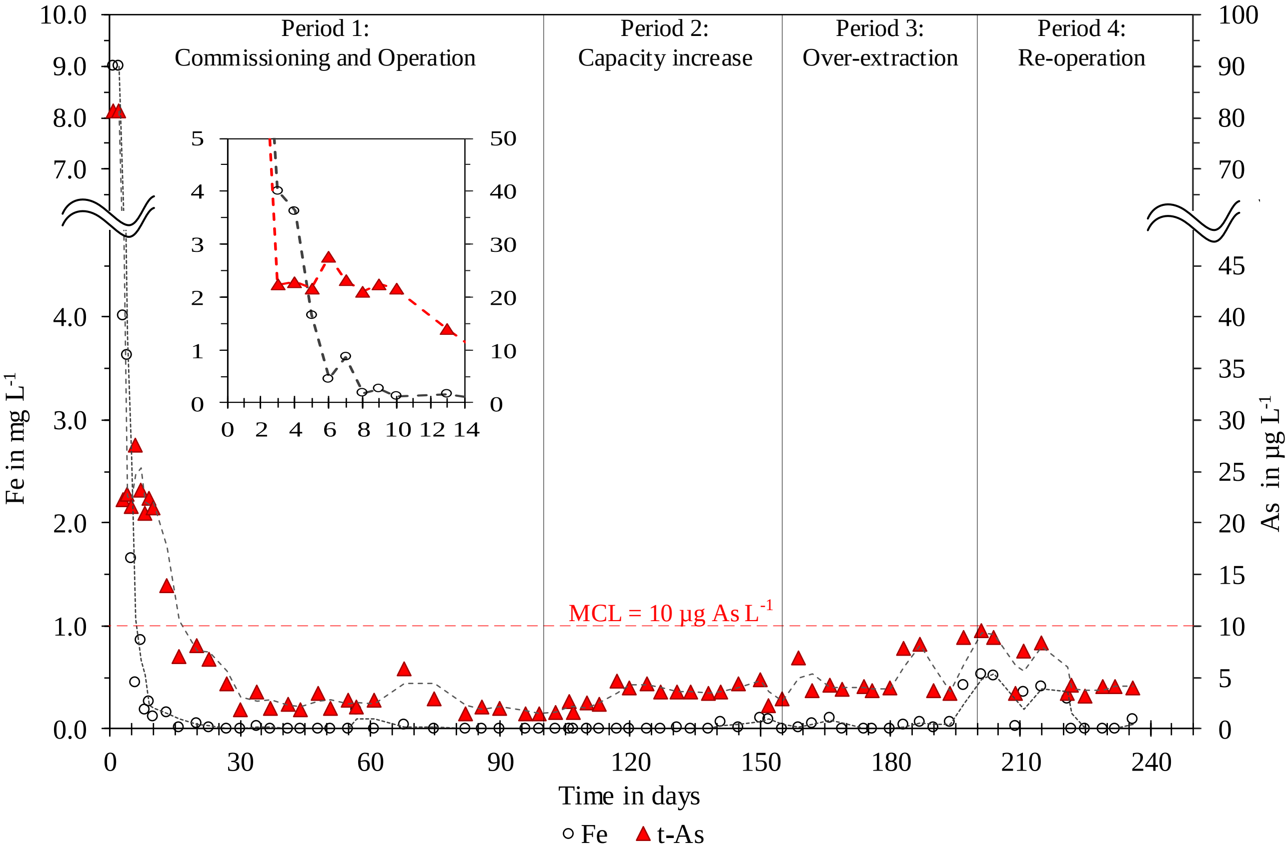

Figure 3: Iron and total arsenic concentrations after SAR treatment at pilot site location for a total of 8 months including four operational periods. Horizontal line: Arsenic drinking water guideline WHO (2017) ; MCL: Max. contaminant level.

Increases in As concentrations during periods 3 and 4 as well as the concentration spikes seen during early operation days (day 6, day 74) indicate a strong correlation to the increases in Fe concentrations, showing that As breakthrough may occur from desorption from HFO. These results also suggest that the removal of As correlated to the oxidation rate of iron, since even small fluctuations in Fe removal show change in As concentration, thus validating the proposed adsorption mechanisms of As onto the Fe(III)-(hydr)oxides. In total, As concentrations remained below the 10 µg L^{-1} limit for a total of 51 days, reaching a maximum value of 9.6 µg L^{-1}.

After regular infiltration was resumed and operation continued normally, Fe concentrations started to slowly drop to values below the drinking water limit. This shows the feasibility of the process for As removal in the long-run and its stability despite technical complications or over-extraction. However, some difficulties were observed for the elimination of Mn and NH_4^+. The detailed results are shown in Section 3.3.

By assuming a monolayer adsorption theory, the adsorption behaviour can be described with the linearized mathematical form of Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m \cdot b} \qquad \text{(Eq.1)}$$

with q_e (in mg g^{-1}) being the amount of adsorbate (in mg As) removed per weight adsorbent (in g FeOOH), C_e the As concentration at equilibrium (in mg L^{-1}), the maximum adsorption capacity q_m (in mg g^{-1}) and b the Langmuir constant (in L mg^{-1}). The isotherm parameters q_m and b can be determined from the slope and intercept of the linear regression of the isotherm by plotting C_e/q_e versus C_e. The values of $q_m = 7.9$ mg g^{-1} and $b = 0.67$ L mg^{-1} obtained are in line with the q_m value calculated from the As uptake in Table 2; however, showing lower adsorption to those found in literature for As-batch experiments (Li et al., 2015) ($q_m = 28.6$ mg g^{-1} and $b = 2.14$ L mg^{-1}). The larger the q_m value, the larger the adsorption capacity whereas b indicates a stronger adsorption bond. The low adsorption capacity calculated can be explained by the differences in real and laboratory conditions, and can be an indication of a limited adsorption due to the presence of competing ions in the raw groundwater.

3.2. Arsenic breakthrough experiments

After one month of operation, As breakthrough tests were carried out on site to evaluate the quality of the treated water over the course of one infiltration-extraction cycle. The tests were done by measuring the total arsenic (t-As) concentration and the As species distribution (arsenite As(III) and arsenate As(V)). When the SAR completed an infiltration cycle (volume $V_{I,1}$ = 390 L during period 1), treated water was pumped and samples were taken at different intervals (first sample at point ZERO) until reaching the 100% treatment target ($V_{E,max}$ = 260 L). Additionally, two more samples were examined at 150% of $V_{E,max}$ (360 L) and 250% of $V_{E,max}$ (650 L) for evaluating if any As breakthrough occurred during over-extraction. The results are presented in Figure 4.

Analyses show a slight rise in both t-As and As(III) concentrations with increasing extraction volume. It is important for the successful SAR process that sufficient HFO-surface area is provided for the effective As-adsorption. Some previous studies on the correlation of As adsorption in Fe oxidation show that Fe oxidation is influenced by the dissolved oxygen content in the infiltrated water (van Halem et al., 2010, 2009; Visoottiviseth and Ahmed, 2008). The more water is abstracted, the more Fe and As enter the treatment zone (oxidation area) and, correspondingly, the more oxygen is used for the oxidation reactions. This leads to the depletion of the oxidation zone and the decrease in the available area for further As-adsorption. Moreover, the increase of the As(III):As(V) ratio indicates both the decrease in As(III) oxidation to As(V) and the breakthrough of raw anoxic groundwater containing As(III) from the outer oxidation zone into the extraction area closer to the well. However, the increase in t-As is not substantial, indicating that the As removal persists even after 2.5 times more water is extracted than the given maximum $V_{E,max}$.

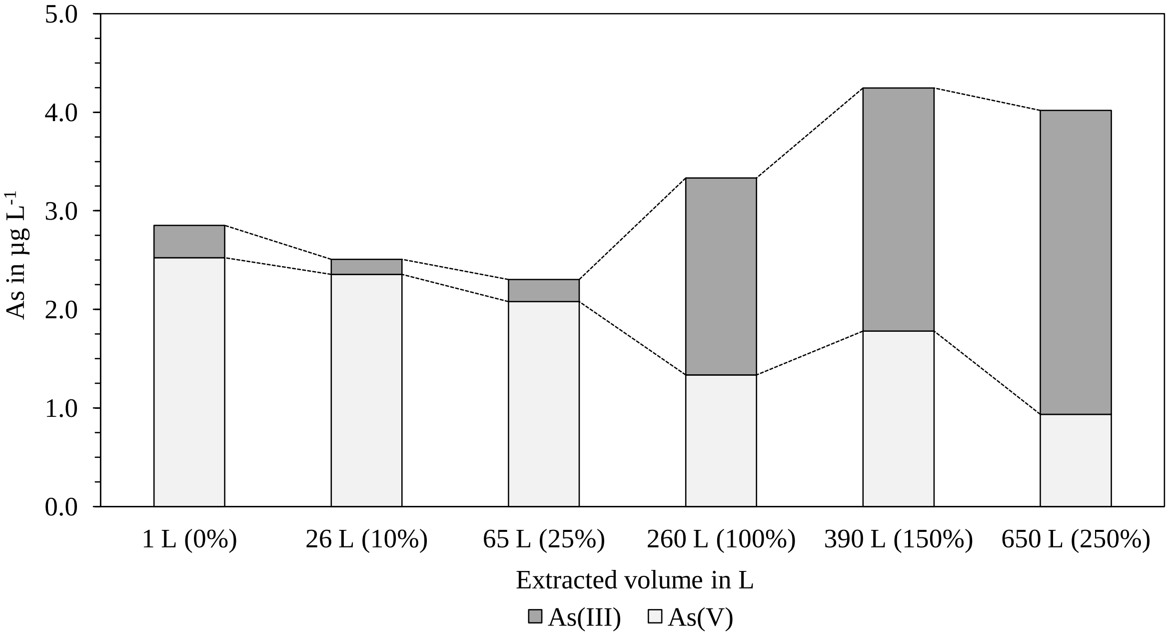

Figure 4: Total As concentration and As distribution in treated water (SAR) with increasing extracted volume at test site. Values in brackets correspond to the share of extracted volume to V_E ($V_E = 260L$); values above 100% correspond to over-extraction.

For the effective removal of As by use of oxidation/filtration processes, a minimum Fe:As ratio of 20 (w/w) is recommended in the literature (EPA, 2012). On the contrary, the experimental results show no significant correlation between the Fe:As ratio and the overall As mitigation. To evaluate this and the dependence of the adsorption to the oxygen demand and the Fe:As ratio, twelve small-scale aeration experiments were carried out with model water (N = 12) and real water on-site (N = 1). Model water containing 5 mg Fe L^{-1} and increasing As-concentrations (from 125 to 500 µg L^{-1}) was aerated using 2 L glass beakers and an air pump with stone bubbler. Additionally, two experiments with higher iron (7.2 and 9.0 mg L^{-1}) and concentrations of 60 and 81 µg As L^{-1} were carried out to also simulate higher Fe:As ratios as found in the groundwater at the pilot location. First, DI-water in the beaker glass was purged with nitrogen gas until dissolved oxygen DO < 0.5 mg L^{-1}. DO was measured using a WTW portable sensor (OXI 3210). Samples were taken at different time intervals (0, 2.5, 5, 10, 30, 60, 120 min, etc.) and filtrated immediately with a 0.45 µm syringe filter before analysing. All experiments showed a general decrease in the t-As concentration within the initial minutes until before reaching a plateau-phase. Depending on the length of each experiment (0.5 - 120 h), the As-removal was averaged from the total measurements and varied between 58% and 81%. Beyond the individual adsorption behaviour of each experiment, the average removal versus the corresponding Fe:As ratios is also of interest. The results in Figure 5 show there is no correlation between the Fe:As ratio within range 20 – 120 and a higher removal efficiency.

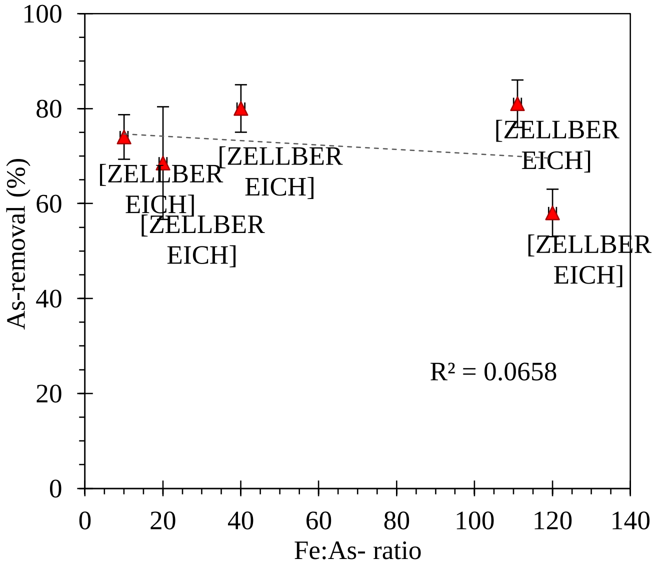

Figure 5: Arsenic removal efficiency versus Fe:As ratio of laboratory aeration experiments showing there is no correlation between both (R^2=0.0658). Number of experiments: N = 12; experimental conditions: pH = 8.4 ± 0.3; temperature = 24 ± 3°C; length t = 0.5-120 h.

In contrast to the tests with model water, the experiment in the beaker glass with real water (Figure 6) resulted in an overall lower As mitigation with a maximum removal efficiency of 49% in a 72 h aeration experiment. This may be due to the presence of competing ions such as PO_4^{3-} and Si that are naturally present in the raw water in higher concentrations than in the model water. The As(III) and As(V) ratio throughout the experiment shows an interesting trend. Initially, 100% of t-As was present as As(III), as it is in the raw groundwater. This ratio does not significantly change within the first 5 h, even though a representative part of the As-adsorption is already finalised (t-As = 53.1 µg L^{-1}). This can be explained mainly by the oxidation of As(III) to As(V) and its respective adsorption and removal from the water, however, a removal of t-As by direct adsorption of As(III) onto the Fe oxides cannot be excluded. After 72 h, the remaining amount of 42.8 µg L^{-1} of t-As in the water was present as As(V). The total mitigation of only 49% indicates an unsuccessful adsorption due to limited availability of adsorption sites as seen in the jar tests with model water.

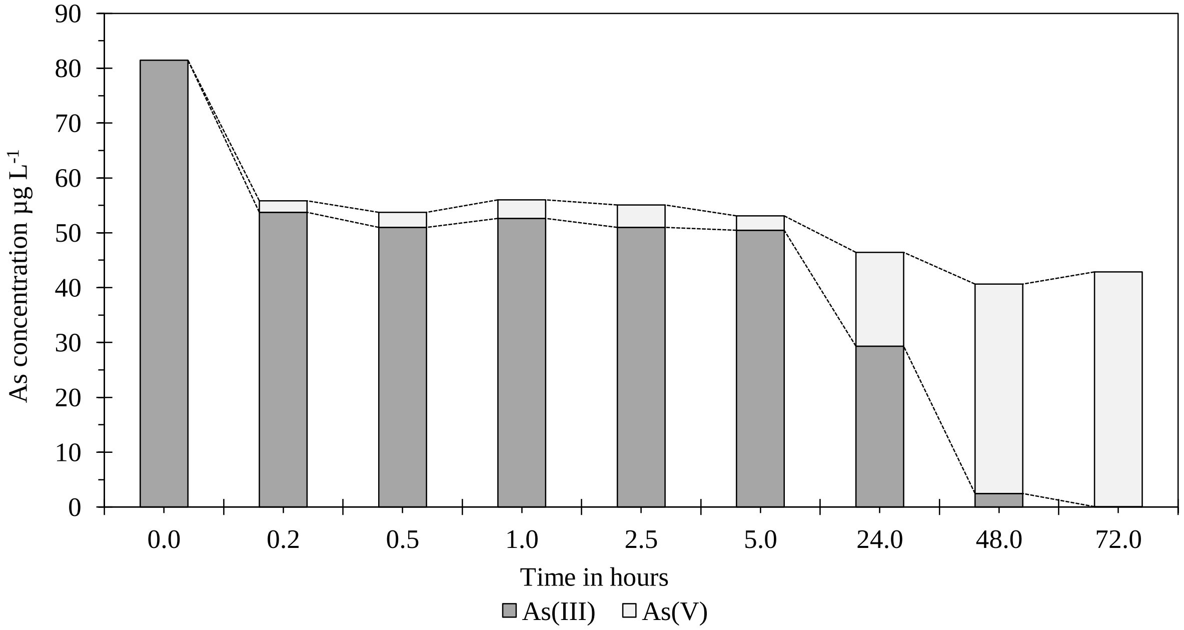

Figure 6: Total As concentration and As speciation during laboratory aeration experiment with raw water at pilot site

Other studies with column and batch experiments also demonstrated that neither the Fe:As ratio nor the amount of Fe present in the groundwater have a direct effect on the As removal capacity in SAR; they indicated, rather, that the As removal is limited by the co-adsorption of competitive ions (van Halem et al., 2009).

The results suggest that a successful SAR plant must provide both an effective oxidation zone and a sufficient adsorption volume area. This was achieved by setting a tolerance margin for the infiltration to abstraction ratio Q_E and fixing a daily target limit $V_{E,max}$. By setting this extraction limit, concentrations of As remained well below the drinking water limit at 4.25 µg L^{-1}. It could be possible to increase the margin limit for improving the capacity of the plant. However, this should be only attempted after sufficient tests have been performed.

3.3. Manganese and ammonium removal

The presence of ammonium nitrogen in groundwater is linked to reduced groundwater conditions that in general promote As release (Kurosawa et al., 2013). Ammonium mitigation through SAR is based on its oxidation to nitrate (NO_3^-), which occurs in the subsurface through both microbial and chemical oxidation processes. Results show that the NH_4^+ removal was considerably slower than the removal of As and Fe. The initial concentrations of NH_4^+ in the raw groundwater of 1.1 mg L^{-1} were below the

Vietnamese drinking water standard of 3 mg L^{-1}. These values were gradually lowered until reaching concentrations of around zero within the first 60 days of operation (see Figure 7). However, during period 3 and 4, the NH_4^+ concentrations rose back to initial raw water concentrations (max. concentration day 183: c = 1.17 mg L^{-1}) due to over-extraction.

In addition, Mn^{2+} in the groundwater remained relatively stable during period 1 and 2 following natural fluctuations (average 1.5 ± 0.2 mg L^{-1}) after a slight decrease from its initial value within the first 15 days. The effective Mn-removal only started on day 152, approx. 3 months after a NH_4^+ mitigation was achieved. The lowest Mn concentration was observed after 2 weeks linear decrease reaching a concentration of 0.46 mg L^{-1} (day 166). However, both Mn and NH_4^+ concentrations increased following the excessive extraction in period 3. While the NH_4^+ content rose to initial concentrations (c ≈ 1.1 mg L^{-1}), Mn level reached a maximum of 2.74 mg L^{-1} which was higher than the initial values. This behaviour could be linked to the microbial-mediated reductive release of Mn which causes the temporary increase in its concentration (Swain et al., 2018).

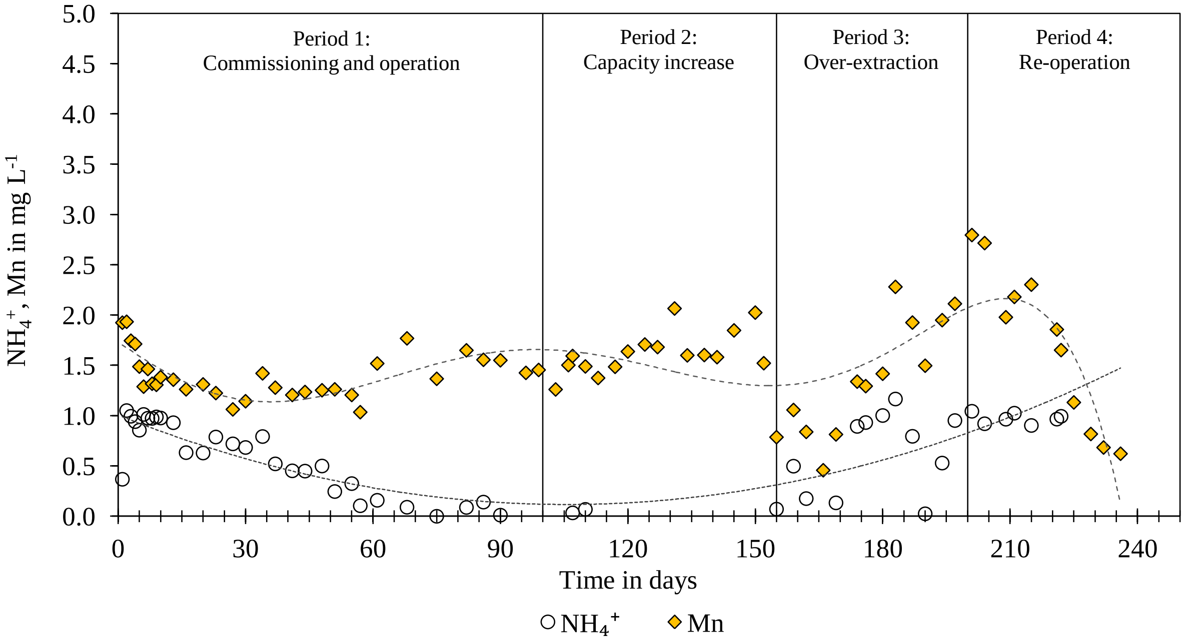

Figure 7: Ammonium and manganese removal at site location for the 4 operational periods.

Long-time experience with SIR in Europe shows that a complete removal of Mn can take long time and a mitigation of Mn with SAR is feasable (FERMANOX, 2017). In general, the biological Mn removal occurs usually simultaneous to the catalytic MnO_2 oxidation, and the required start-up period of biological filters can take several months (Farnsworth et al., 2012; Gouzinis et al., 1998a; Nitzsche et al., 2015).

The slow Mn mitigation can be associated in general to the unfavourable Eh-pH conditions given by the natural anoxic hydro-geological setting and to the high initial NH_4^+ concentrations (1.1 ± 0.1 mg NH_4^+ L^{-1}) of the groundwater. When NH_4^+ is present, the oxidation of Mn^{2+} can only take place after complete nitrification due to the necessary evolution of the redox potential (Gouzinis et al., 1998b; Luong et al., 2018).

Nevertheless, Mn levels were lowered significantly faster after normal operation was restarted in period 4. This indicates that once the removal of Mn has been established, the microorganisms responsible for the oxidation remain active and will drive the mitigation process after re-operation. In contrast to As and Fe, the rise of both Mn and NH_4^+ in period 3 was observed several days delayed to the start of the over-extraction period. This can be an indication that the oxidation mechanisms are linked to microbial activity, which will respond slower than a chemical oxidation after the oxygen feeding. Ammonium concentrations remained, thus, constant throughout the measured days in period 4 (day 240). Although NH_4^+ concentrations below the detection limit were reached again in later analyses (see Section 3.5), further research on the behaviour of the microorganisms involved is needed to critically evaluate the role of microbial oxidation during SAR.

3.4. Post-treatment for Mn-removal

As a result of the limitations on Mn removal, achieving Vietnamese drinking standard (0.3 mg Mn L^{-1}) could not be accomplished within the first 240 days of operation (Figure 7). An additional post-treatment filter (with MnO_2) for Mn-removal was temporarily used to comply with the Vietnamese drinking water standard until a Mn-mitigation was achieved by the SAR process. Concentrations of Mn before and after the oxidative granulate filter were monitored occasionally, showing that Mn concentrations below 0.3 mg L^{-1} were first achieved by use of only the SAR process (without the filter) after operation day 420. However, the lack of continuous parameter monitoring after the first 8 months of study mean a Mn mitigation could have happened earlier.

3.5. Overall SAR efficiency

After more than two years of operation, analyses show that drinking water standard was achieved for all parameters reaching stable concentrations throughout the process. The relevant results are summarized in Table 3. All parameters including coliforms and *E. coli* were analysed additionally by different certified commercial laboratories in Ho Chi Minh City.

Table 3: Chemical analysis of raw and treated groundwater.

Parameter	**Unit**	**Concentration raw water***	**Concentration treated water†**	**VN drinking water limit§**	**Removal in %**
pH	-	7.0	7.5 ± 0.4	6.5-8.5	-
Total-As	µg L^{-1}	81	5.7 ± 2.4	10	93.0%
Total-Fe	mg L^{-1}	8.4	0.042 ± 0.03	0.3	99.5%
Mn^{2+}	mg L^{-1}	1.9	0.040 ± 0.7	0.3	98.0%
NH_4^+	mg L^{-1}	1.1	BDL (0.1) -	3.0	>90.5%
Coliforms	cfu/100 mL	-	BDL (1) -	0	-
E. coli	cfu/100 mL	-	BDL (1) -	0	-

* see Table 1: Analysis of raw groundwater at SAR test site before trial tests (2016-2017)

† Values are averaged from different samples analysed by certified commercial lab analyses

§ QCVN01: Vietnamese National technical regulation on drinking water quality, VIỆT NAM, 2009 (QCVN:01, 2009)

BDL = below detection limit (detection limit of method)

3.6. Energy demand

The energy consumption of the system including the controlling unit and monitoring devices as well as the pump for both delivery and treatment, were monitored throughout the pilot. Water demand was recorded with a water meter and water consumption was logged to the controller system. An energy meter was used to measure the total energy consumption of the plant. The specific energy consumption (SEC) of the SAR plant for both treated and supplied water ranged between 0.87 and 1.07 kWh m^{-3} which leads to specific costs of 0.06 – 0.07 USD per cubic metre with average electricity prices of 0.07 – 0.12 USD kWh^{-1} (retail price for household electricity: 1678 - 2927 VND/kWh (VIETNAM ELECTRICITY, 2019)). These specific costs are remarkably below the values reported in literature, with results from different field tests varying from 0.11 to 1.11 USD m^{-3} (Shan et al., 2018) and other similar subterranean groundwater treatments reporting specific costs of about 0.5 USD m^{-3} (Sen Gupta et al., 2009).

Conclusion and recommendations

- Results show that subsurface arsenic removal (SAR) is a feasible mitigation technique for achieving safe drinking water from groundwater in regions like Vietnam and Southeast Asia, characterised by reducing aquifer conditions.
- Arsenic concentrations were lowered well below the limit of 10 µg As L^{-1} during the pilot phase of 2 years and remained stable throughout the process, even when temporary operational failures occurred causing the breakthrough of Fe.
- The salient advantages of this technique are the negligible toxic waste production, ease-of use, and the low operational and capital costs that also make the technology suitable for low-income countries such as Vietnam.
- The success of the As removal through SAR strongly depends on the infiltration to abstraction ratio of the groundwater from the aquifer. The injection - extraction dynamics should be controlled to ensure the complete and effective Fe oxidation with enough time allowed for the oxidation reactions and a sufficient adsorption area.
- In contrast to other studies and pilot plants, an appropriate aeration system must ensure oxygen saturation and the extraction to infiltration ratio Q_E must be determined to avoid over-extraction.
- Studying the SAR process under different hydrogeological settings is still needed to evaluate the feasibility and the range of applications of the technology, including the negative effect of co-ion adsorption and the removal efficiency when higher As levels (e.g. > 500 µg L^{-1}) are present.
- Hydrogeochemical conditions may affect the efficiency in obtaining drinking water standard when high NH_4^+ and Mn concentrations are present. Furthermore, the construction of informal wells in unsecured surroundings and vulnerable zones increase the risk of anthropogenic NH_4^+ contamination and should be taken into consideration when applying SAR.

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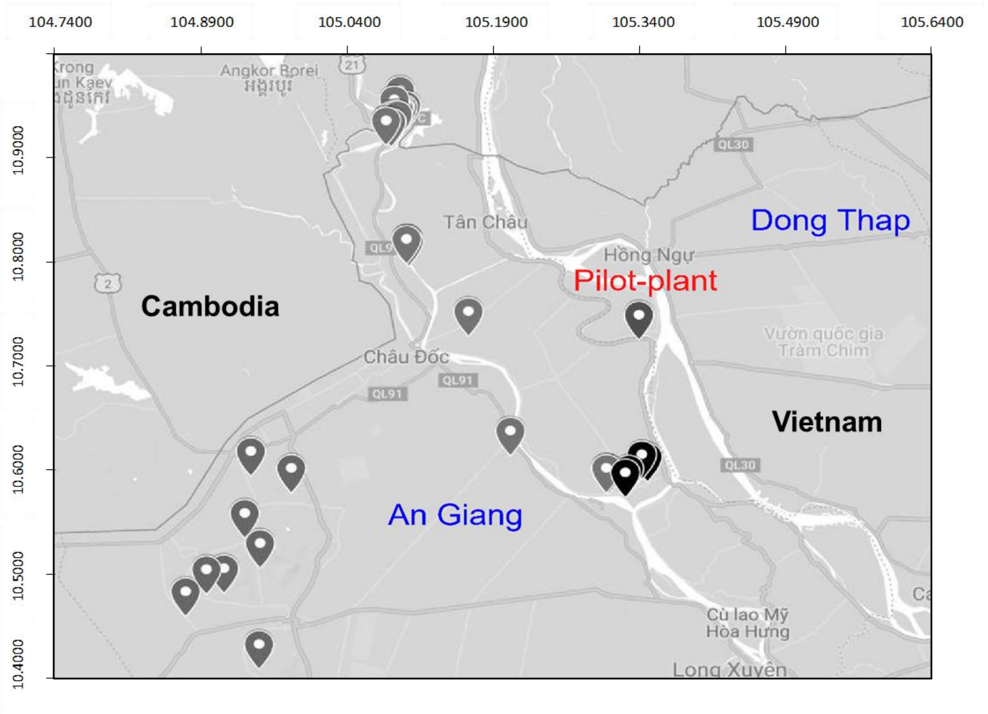
I. Supplement

i) Statistical evaluation of study area

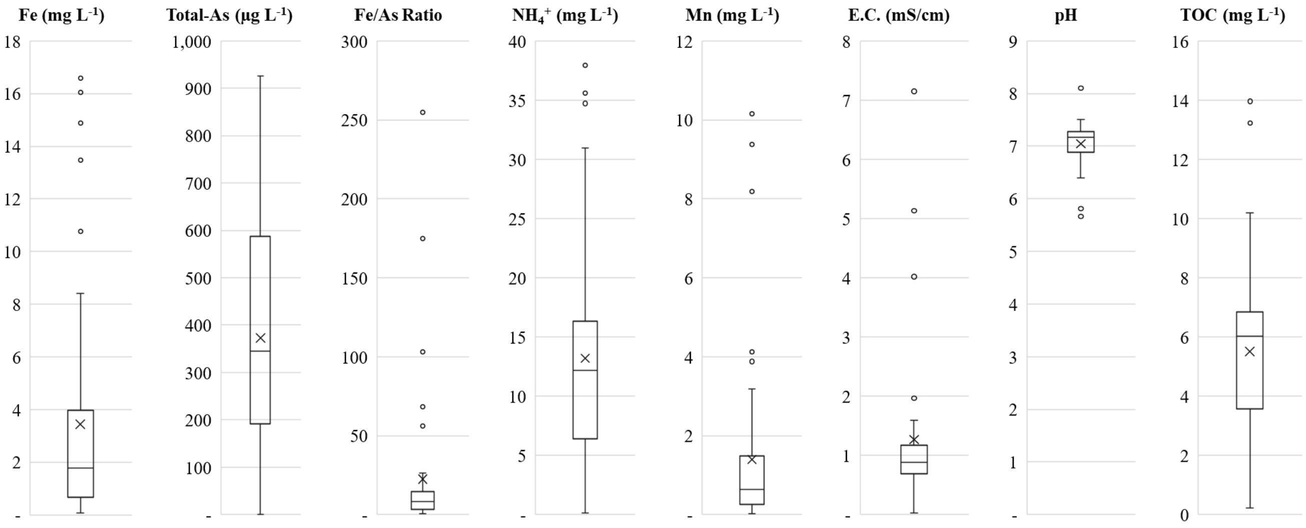
To assess the As contamination in the study area, a statistical evaluation of the physico-chemical composition and related quality of the groundwater was carried out as part of the site selection for the planned pilot trials. For this, groundwater from 52 shallow tube wells in the district of An Giang (Supplement 1) was analysed for Fe, Mn, NH_4^+, t-As and other relevant parameters. The majority of the tube wells were located in private households or were privately owned by small farmers for agriculture or aquaculture (eel farms, shrimp farms). Because of poor well management and documentation, well owners normally do not know much about the well design, which depends on local drilling practices. However, typical well design data in this province ranged between 15 – 36 m (Tran et al., 2011).



Supplement 1: Map of groundwater sampling sites in An Giang

ii) Analysis results of groundwater analyses

Results of the sampling study are summarized in the whisker-plot diagrams in showing the results of the water analysis (Supplement 2). Total Fe concentration averaged at 3.4 ± 4 mg L^{-1} with maximum values exceeding 16 mg L^{-1}. The concentration of t-As averaged at 373 ± 254 µg L^{-1}, with 41 out of the 47 tube wells tested for As exceeding the 10 µg L^{-1} limit. These results are in line with previous research on the Mekong Delta which has shown the magnitude of the As contamination in the region (c$_{(As)}$ = 207.8 - 1,522 µg L^{-1}) (Kỳ, 2009; Thư et al., 2011; Vũ, 2014). Furthermore, 75% of the tube wells (n = 47; NA = 5) showed As levels higher than 200 µg L^{-1} with the maximum value detected of 926 µg L^{-1}, exceeding the WHO guideline value by almost 100 times.



Supplement 2: Distribution of groundwater analysis of study area in An Giang. Whiskers give the highest and lowest concentrations, box the upper and lower quartiles; the horizontal line in each box marks the median.

Besides As contamination, groundwater in the region was also found to contain high NH$_4^+$ concentrations (13.2 ± 10 g L^{-1}) with more than 87% of the wells exceeding the Vietnamese standard for drinking water of 3.0 mg NH$_4^+$ L^{-1} (QCVN:01, 2009) and maximum measured values higher than 30 mg L^{-1}. This can be attributed to the reducing environment of the aquifer and various sources of nitrogen including septic effluents from household and industrial waste discharges, leaching from agricultural systems and animal manure infiltrating the groundwater due to poor well construction and area protection (Du et al., 2017; Le Luu, 2019; Lindenbaum, n.d.). The mean concentration of Mn (1.39 ± 2.2 mg L^{-1}) was about 4.5 times greater than the Vietnamese drinking water standard of 0.3 mg L^{-1}, whereas water from some wells presented concentrations above 8 mg L^{-1}, which is more than 25 times higher (QCVN:01, 2009).

Comments to Manuscript Number: WR53078
Title: Iron-based subsurface arsenic removal (SAR): 2 Results of a long-term pilot-scale testing in Vietnam
Authors: Edgardo E. Cañas Kurz, Vu T. Luong, Ulrich Hellriegel, Felix Leidinger, Tran L. Luu, Jochen Bundschuh, Jan Hoinkis*

Reply to Editor: The authors thank the Editor again for the consideration of our article. We have carefully revised the reviewers' comments and the final version of the manuscript.

COMMENTS FROM THE EDITOR AND/OR REVIEWERS

Reviewer #3:
the comments of the reviewers were addressed.
We thank this reviewer again for their revision.

Reviewer #4:

We thank this reviewer for their valuable evaluation of this manuscript. We have carefully revised their comments and the manuscript. Small additional modifications have been addressed below.

1. Fig 7 does not support the inference (line 357) that on day 190 the ammonium ion concentration fell back to the near-zero levels reached in Periods 1 and 2. The data point for day 190 appears to be an outlier, with all other results between days 185 and 225 falling in the 0.5-1.0 mg/L range.

Many thanks for this comment. We agree with the remark and we have therefore revised Section 3.3 thoroughly. In order to improve the evaluation of the results, this section has been modified including information on Mn and NH_4^+, removing some lines 354 - 359 and adding Section 3.4 for better structure. This includes comment 5 of this reviewer (lines 405-406).

2. Lines 109-110 need to be reworded. More water cannot be extracted than the volume given by QE if QE is defined as in line 99.

Lines 106 - 108 have been modified accordingly.

3. In eq 1 both terms in the denominator must have the same unit (mg/L). (b appears to be the reciprocal of the Langmuir equilibrium constant, which has units of L/mg.)

We thank this reviewer for their comment and agree there was a mistake in the definition of Langmuir equilibrium constant (as reciprocal of b). We have modified Eq. 1 to show the linearization of the isotherm (line 262 - 264) and changed the text accordingly.

4. The Fe and As concentrations given in line 308 represent a Fe:As mass ratio ranging from 10 to 40. Why does Fig 5 show points at ratios > 100?

Many thanks to the reviewer for highlighting this. Indeed, two experiments with higher Fe:As ratio were included in Figure 5. We have changed the text in lines 306 - 308 to fit this. Additionally, Fig. 5 (line 318) has been corrected (N values inversed).

5. When were Mn concentrations below 0.05 mg/L reached (line 384)?

Concentrations below detection limit of 0.05 mg/L were reached after day 240 (not shown in Figure 7). We have modified Section 3.3, therefore, this line has been removed, since it doesn’t add any information to the modified text (see comment No. 1)

Iron-based subsurface arsenic removal (SAR): Results of a long-term pilot-scale test in Vietnam

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Abstract

The principle of subsurface arsenic removal (SAR) from groundwater is based on oxidation and adsorption reactions by infiltrating oxygen into the anoxic aquifer and the immobilization of arsenic (As) onto freshly formed iron (Fe) oxides. In this study, a pilot-scale plant for SAR has been subject to long term testing in the Mekong Delta, Vietnam. Initial concentrations of Fe (8.4 ± 1.3 mg L^{-1}) and As (81 ± 8 µg L^{-1}) in the exploited groundwater were successfully lowered to below the WHO guideline value limits for drinking water of 0.3 mg L^{-1} and 10 µg L^{-1} respectively. Adsorption and co-precipitation of As with iron oxides could be identified as the principal mechanism responsible for the As removal from groundwater, demonstrating the feasibility of SAR as a low-cost and zero-waste solution over a period of two years. However, naturally occurring geochemical reducing conditions and high ammonium levels in the groundwater delayed the removal of manganese (Mn). An additional post-treatment filtration for Mn-removal was temporarily used to comply with the Vietnamese drinking water standard until a Mn-mitigation was achieved by the SAR process. In contrast to most As-remediation technologies, SAR appears to be a long-term, sustainable treatment option with the salient advantage of negligible production of toxic waste, which with ex-situ processes require additionally management costs.

Keywords: Subsurface arsenic mitigation; Mekong Delta; oxidation/adsorption; zero-waste, low-cost; groundwater contamination

1. Introduction

1.1. Arsenic in groundwater

Arsenic (As) is considered to be one of the most serious, naturally occurring, inorganic contaminants in groundwater on a global scale (Amini et al., 2008; Sarkar and Paul, 2016; Srivastava, 2020) and it has been recognized as a significant environmental cause of cancer mortality (Khan et al., 2020; WHO, 2012). Arsenic occurrence in natural groundwater varies depending on the local geology, the hydrochemical characteristics of the aquifer and the pH and redox-dependent mechanisms for its mobilization from the solid phase into the groundwater. Arsenic is found mainly as arsenate (As(V)) and arsenite (As(III)) species in reducing and oxidizing milieus, respectively (Campbell and Nordstrom, 2014;

Kumar et al., 2020; D. Zhang et al., 2017a). High concentrations of geogenic As are found in the groundwater of many world regions including Southeast Asia (Palit et al., 2019; Uppal et al., 2019), Bangladesh (Chakraborti et al., 2015; Huq et al., 2020), India (Bhowmick et al., 2018; Sankar et al., 2014), China (Li et al., 2020; L. Zhang et al., 2017), North (Janković, 2020) and Latin America (Bundschuh et al., 2012; Litter et al., 2020) as well as Australia and Europe (Medunić et al., 2020).

Geogenic As in oxidizing aquifers is mostly associated to bedrock lithology and originates typically from leaching of geological materials (e.g. hard rock and sediments) (Huq et al., 2020; D. Zhang et al., 2017b), in some areas from geothermal fluids and volcanic ashes (Morales-Simfors et al., 2020a) and products from mining (e.g. tailings) and related activities (Ciminelli, 2014). Additionally, important artificial As sources can result from agricultural activities (e.g. pesticides). These sources can impact groundwater in regions as described from Latin America with its mostly oxidizing aquifers (Bundschuh et al., 2012; Litter et al., 2020; Morales-Simfors et al., 2020b). The mobilisation and release of geogenic As into the groundwater in reducing aquifers, such as in most of Southeast Asia, is a result of the reductive dissolution of both iron (Fe) and manganese (Mn) oxi(hydr)oxides from As-bearing sediments (Berg et al., 2007; Norrman et al., 2008; D. Zhang et al., 2017a). In addition, some of these regions with predominantly high levels of As also show particularly high levels of ammonium (NH_4^+) (Jia et al., 2018; Norrman et al., 2015) and Mn^{2+} (Berg et al., 2008; Datta et al., 2014).

1.2. Arsenic remediation

There are many established methods for treating As contaminated water. The most common include oxidation and filtration, adsorption, ion exchange and separation by membrane technologies, each displaying different advantages and disadvantages (Ghosh N. et al., 2019; Jadhav et al., 2015; Litter et al., 2019; Nicomel et al., 2015; Singh et al., 2015). Other emerging technologies comprise electrochemical and coagulation processes, phytoremediation and alternative adsorptive materials (Kumar et al., 2019). The main disadvantage of these "*ex-situ*" technologies is the generation of As-laden waste in the form of solids or concentrate streams, which have to be disposed of safely (Clancy et al., 2013). As a consequence, the safety and disposal costs of As-bearing wastes become an issue and alternative techniques with an economical and environmental sustainable concept approach are needed.

The *in-situ* As treatment by aeration is a technique based on subsurface iron removal (SIR), which has proven to be a technically feasible practise in Europe and the United States for decades in a variety of hydrogeochemical settings for the *in-situ* treatment of Fe, Mn and NH_4^+ in groundwater (Ahmad, 2012; Grischek et al., 2015; Hallberg and Martinell, 1976; Henning and Rott, 2003; Karakish, 2005; Rott and Friedle, 2000; Rott and Kauffmann, 2008). However, subsurface As removal (SAR) is not yet an established solution and has only been tested in a very limited number of laboratory tests and pilot trials (Kundu et al., 2018; Rahman et al., 2014; Rott et al., 1996; Sarkar and Rahman, 2001; Sen Gupta et al., 2009; van Halem et al., 2010, 2009).

The majority of studies on SAR have focused on the vulnerability of the process to diverse geochemical conditions such as pH, redox potential (Eh) and the presence of co-ions such as phosphates, sulphates, carbonates and ammonium (Luong et al., 2018) that are competing with As for adsorption sites and can have a negative influence on the As removal. In some cases, this can make it difficult to comply with the stringent guideline value for drinking water recommended by the WHO of 10 µg L^{-1} (WHO, 2017). However, the salient advantage of SAR is its low operating and maintenance costs, combined with its negligible waste production, with no waste streams containing toxic As. The major questions that arise regarding SAR are the stability of the subsurface adsorption, the possible remobilization of As and its accumulation in the aquifer (Grischek et al., 2015; Rahman et al., 2014; van Halem et al., 2011).

1.3. Principle of SAR

The basic principle of SAR is based on the adsorption and co-precipitation of As onto Fe-(hydr)oxides by periodically extracting anoxic groundwater, aerating it and infiltrating the oxygen-rich water back into the aquifer. Oxygen reacts with dissolved iron (Fe^{2+}) to form HFOs, which are poorly crystalline oxides with high porosity and large surface areas (oxidation). When water is abstracted, dissolved As adsorbs onto the freshly formed HFOs (adsorption) and groundwater with lower As concentrations can be extracted.

A given amount of groundwater with low-arsenic can be extracted after each infiltration cycle. This volume depends on the amount of oxygen that is available for the oxidation reactions (Kundu et al., 2018; Luong et al., 2018; Rott and Friedle, 2000). In order to estimate the treatment capacity of each plant and the amount of water that can be extracted after each infiltration, an important parameter of a SAR system is the injection-to-extraction ratio $Q_E = V_I/V_E$, which is the ratio of the volume of infiltrated oxygenated water (V_I) to the amount of extracted treated water (V_E). This volume-specific parameter is a design parameter principally given by the quality of the raw water and can be calculated from the stoichiometric oxygen amount required for the chemical oxidation process (Luong et al., 2018). With a ratio of, for example, $Q_E = 0.5$, the infiltration of 1 m³ allows the extraction of 2 m³ of fresh water. However, in anoxic groundwater with high oxygen demand, for example due to high Mn^{2+} and NH_4^+ concentrations, Q_E may be higher than 1, meaning more volume must be infiltrated than the amount that can be extracted.

Since the abstracted groundwater is always infiltrated back into the aquifer, no water is lost and no waste stream is produced, which is another important feature of the process. However, the treated water quality can, in some exceptional cases (e.g. technical failure infiltration or over-extraction in daily operation), gradually decrease. This is also discussed later as a breakthrough experiment (see Section 3.2).~~However, if more water is extracted than the volume given by Q_E and the plant capacity is exceeded (over-extraction), the quality of the treated water will gradually decrease the more water is extracted.~~ As oxidation reactions in the aquifer are also coupled with microbial oxidation, the sorption and co-precipitation processes in the aquifer can be also influenced by given natural hydrogeological conditions and microbial activity of the aquifer. In order to ensure a safe water supply and avoid over-extraction, a maximum daily limit $V_{E,max}$ is set for each individual SAR plant (Luong et al., 2018, 2019).

1.4. Objectives

The main objective of this study is to prove the feasibility of the SAR process as a sustainable treatment option for simultaneous Fe and As removal and to evaluate the technology on a pilot-scale. For the first time, its long-term stability in terms of removal efficiency, operation stability and energy demand has been evaluated in the course of 2 years. The pilot SAR plant was installed in the Mekong Delta, Vietnam, as part of the joint research project WaKap from 2016 to 2019 (Hoinkis et al., 2016).

2. Method

2.1. SAR pilot plant and location

The SAR pilot plant (*FERMANOX®-Wasseraufbereitung type BV 45*; Figure 1) was installed in the village of Cho Vam in the Province of An Giang in the Mekong-Delta, Vietnam, next to the Cambodian border (coordinates: N 10.719308, E 105.331354). This province has previously been identified as one of the most affected by high As concentrations in the country with more than 75% of wells analysed presenting concentrations higher than 10 µg As L^{-1} (Kỳ, 2009; Thư et al., 2011).

The plant was setup for the treatment of As-laden groundwater and the water supply of a small group of people from a religious community. The existing shallow tube well (Ø = 42 cm) had a depth of 17 m and was connected to an existing storage tank used for water storage and supply for irrigation, toilet flushing and washing. Figure 1 shows the installation of the SAR pilot plant with the available storage tank and an extra aeration tank.

Figure 1: SAR pilot plant (FERMANOX®-*Wasseraufbereitung* type BV 45) in An Giang, Vietnam, incl. delivery pump, pressure tank, Mn-filter and UV-lamp for post-treatment

2.2. Raw water analysis

Before the trial tests started, 52 possible pilot sites were analysed in the province of An Giang from which the pilot test site was selected (detailed results: see Supplement 1 and Supplement 2). The presence of preferably high concentrations Fe^{2+} was important for the site selection, since a successful As-mitigation is based on the adsorption onto and the co-precipitation with the HFOs. Other important criteria considered were low Mn^{2+} and NH_4^+ as well as the total water demand of the well.

Full analysis results of the groundwater at the selected well in Cho Vam are presented in Table 1. Analyses were carried out at different times of the year in order to assess seasonal fluctuations in the groundwater quality prior to the beginning of the pilot. The high Fe:As ratio of the selected site of 106 ± 24 (w/w) was favourable for the arsenic adsorption (average ratio of study area: Fe:As = 22 ± 48 (w/w) (see Supplement 2). However, the presence of ions such as phosphate (PO_4^{3-}) and silicate (Si) competing with As for adsorption sites due to their similar adsorption mechanisms can hinder the effective removal of As. Furthermore, Mn^{2+} and NH_4^+ concentrations above the drinking water standards in the groundwater may challenge the complete treatment. For this reason, these parameters were carefully monitored during the pilot tests.

Table 1: Analysis of raw groundwater at SAR test site before trial tests (2016-2017)

Parameter	**Unit**	**Nov 16**[a]	**Feb 17**[b]	**Jun 17**[c]	**Jul 17**[c]*****	**Average**
T	°C	29.0	26.4	*N/A*	29.5	28.3 ±1.4
pH	-	7.1	7.2	*N/A*	6.8	7.0 ±0.2
E.C.	$\mu S\ cm^{-1}$	482	440	*N/A*	489	470 ±22
t-As	$\mu g\ L^{-1}$	92	78	71	82	81 ±8
Fe^{2+}	$mg\ L^{-1}$	7.0	7.4	10	9.0	8.4 ±1.3
Fe:As	-	76	95	141	111	106 ±24
Mn^{2+}	$mg\ L^{-1}$	2.3	1.4	2.1	1.9	1.9 ±0.3
Si	$mg\ L^{-1}$	16	15	11	19	15 ±3
Na^+	$mg\ L^{-1}$	28	16	18	22	21 ±5
NH_4^+	$mg\ L^{-1}$	1.1	0.89	1.2	1.1	1.1 ±0.1
K^+	$mg\ L^{-1}$	*N/A*	2.1	2.1	2.4	1.9 ±0.4
Ca^{2+}	$mg\ L^{-1}$	18	19	28	*N/A*	22 ±5
Mg^{2+}	$mg\ L^{-1}$	10	9.3	12	13	11 ±1
Cl^-	$mg\ L^{-1}$	15	8.3	*N/A*	22	15 ±5
PO_4^{3-}	$mg\ L^{-1}$	1.0	1.0	*N/A*	1.9	1.3 ±0
SO_4^{2-}	$mg\ L^{-1}$	1.2	1.0	2.7	*N/A*	1.6 ±0.7
TOC	$mg\ L^{-1}$	*N/A*	*N/A*	8.3	7.2	5.9 ±3

[a] end of rainy season in 2016; [b] dry season in 2017; [c] rainy season in 2017; *start of operation
E.C.: electrical conductivity; TOC: total organic carbon; N/A: not available/not measured

2.3. Plant operation

The pilot plant scheme is displayed in Figure 2 showing the SAR storage tank (390 L) with an air injection nozzle and air filter, the feed pump (Speck PM 15) with pressure vessel (200 L) and an automatic control unit (CU) to monitor and regulate the infiltration and extraction processes depending on the actual water demand. An extension tank (1000 L) was added in a later stage to increase the treatment capacity of the plant.

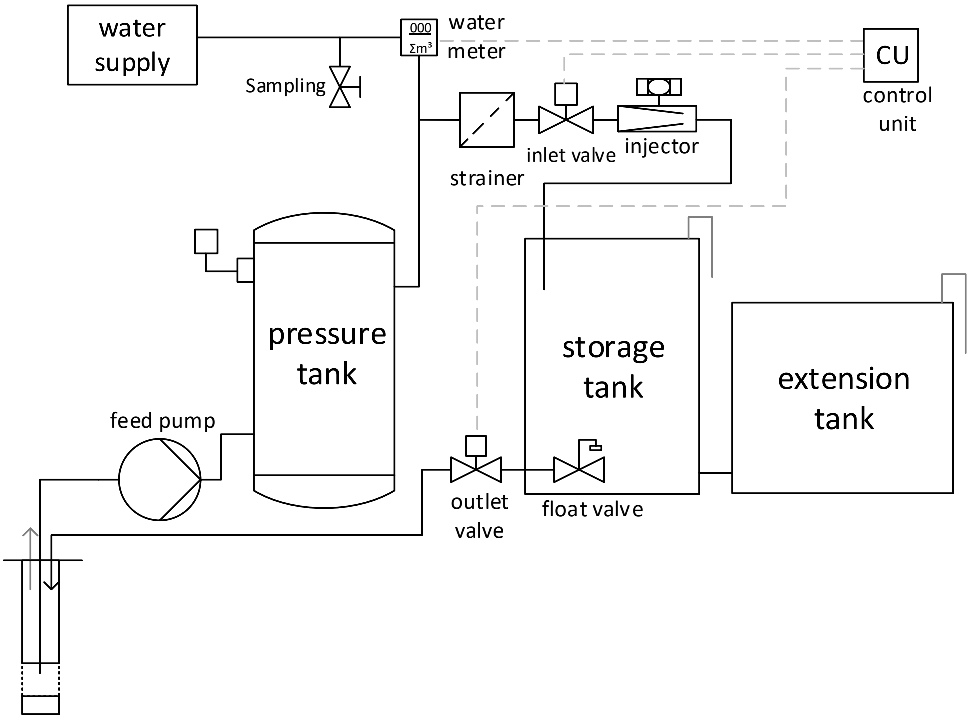

Figure 2: Scheme of SAR pilot plant for subsurface arsenic removal (SAR)

The SAR system was operated in intermittent daily cycles as manufacturer's recommendation using the following basic steps:

1. *Aeration*: Anoxic groundwater is extracted from the aquifer using the feed pump and aerated with an air injector at a pressure of $p_{min} > 0.28$ MPa. Here, a pressure tank is used which is regulated by a pressure switch ($0.28 < p < 0.35$ MPa). Each aeration cycle is controlled automatically by the CU of the system which is programmed to carry out a maximum of two cycles daily.
2. *Infiltration/adsorption*: After the groundwater is aerated, the oxygen-rich water (DO: saturation > 99%) is re-injected through the tube well into the aquifer via gravity, lifting the redox potential of the anoxic aquifer and inducing the formation of oxidation and adsorption zones around the

well. Here, Fe^{2+} is oxidized to Fe(III)-(hydr)oxides or HFOs. Then, As adsorbs onto the freshly formed HFOs and is co-precipitated within the Fe-(hydr)oxide-matrix.

3. *Abstraction:* When water is abstracted, raw groundwater flows through the oxidation/adsorption zone where As is adsorbed and more Fe(III)-(hydroxides) are formed, creating more adsorption places for the next cycle.

4. Treated water can be abstracted from the well in line with the maximum daily capacity $V_{E,max}$.

The number of *infiltration* cycles (*n*) was regulated with a control unit based on the water consumption. The maximum infiltration cycles was set to $n_{max} = 2$. If no water consumption occurred, no infiltration was needed (n = 0), however, an infiltration cycle was carried out every 2 days even without consumption in order to assure the process stability.

The pilot trials were carried out in four operational periods: during the first three months (Period 1), the plant had an infiltration capacity of $V_{I,1} = 390$ L (size of SAR tank) which corresponded to an extraction volume of $V_{E,1,max} = 470$ L with two infiltration cycles per day ($2 \cdot V_{I,1} = 780$ L) and an infiltration-to-abstraction ratio of $Q_E = 1.66$.

For the second period (Period 2), the infiltration volume was increased to $V_{I,2} = 1390$ L (SAR tank + extension tank with a capacity of 1000 L). With two infiltrations cycles per day ($2 \cdot V_{I,2} = 2780$ L), a total volume $V_{E,2,max} = 1900$ L could be extracted daily. This corresponds to an infiltration-to-abstraction ratio of $Q_E = 1.46$.

In the third and fourth period, the process stability was evaluated during over-extraction (Period 3) and after re-operation (Period 4).

In order to ensure a safe operation, an alarm was triggered when $V_{E,max}$ was exceeded. This not only prevented the breakthrough of contaminants, but also prolonged the well life by protecting the extraction area surrounding the tube well from incrustations. Furthermore, no water was extracted from the well during each infiltration cycle plus at least 15 min of subsequent rest time. This was done to avoid re-abstraction of oxygenated water after infiltration.

2.4. Sampling and analysis

Water samples were taken daily from the sample valve during the first ten days of commissioning and twice a week thereafter. Every time a sample was taken, groundwater was firstly abstracted and stored in the water supply tank until it reached the maximum extracted capacity $V_{E,max}$. The samples were acidified with nitric or hydrochloric acid for conservation before transporting them to the laboratory. Values for pH and electrical conductivity (E.C.) were measured on-site or at the laboratory (raw samples) using a portable sensor (WTW Multi-Parameter 3430). An atomic adsorption spectrometer (Analytik Jena con-trAA® 300) was used with flame technique (50 mm burner with air/acetylene gases) for the determination of Mn^{2+} and Fe^{2+}, while, hydride generation (HS 55 batch system) was used for total arsenic (t-As) determination (Analytik Jena AG, 2019). Moreover, special cartridges (Meng-cartridges, METALSOFT) were used for As(III)/As(V) separation to conduct As-speciation (Meng et al., 2001). Ion chromatography (Metrohm 883 Basic IC plus) was used to analyse cations (Metrosep C4-150/4.0 column) according to ISO 14911 and anions (Metrosep A Supp 5-150/4.0 column). The TOC was analysed with a Shimadzu TOC-L Analyzer. Measurements were repeated at least twice and samples were stored in line with the ISO 5667 3 standard.

2.5. Data gathering

This study shows the results of two years of operation including installation and commissioning of the SAR plant. Data on water samples (chemical and physical parameters), water withdrawal and energy consumption were recorded continuously for the first 8 months to evaluate the process operation and efficiency. Afterwards, the well data were periodically monitored for the complete 28 months to show the long-term stability and monitor the energy consumption.

3. Results and discussion

3.1. Iron and arsenic removal

Results in Figure 3 show how the initial Fe concentration of 9.0 ± 1 mg Fe L^{-1} dropped to below the Vietnamese drinking water standard value of 0.3 mg Fe L^{-1} within the first week of operation. This demonstrates that the oxidation of dissolved Fe^{2+} to particulate Fe^{3+} (HFO) occurs rapidly after the first infiltration cycles as it occurs in the SIR process (Braester and Martinell, 1988; Rott, 1985; Rott and Lamberth, 1993; Van Beek, 1983).

The As elimination process was evaluated by monitoring the As immobilisation onto the Fe(III)-surfaces during each of the four operational periods (see Section 2.3 Plant operation). Arsenic mitigation only started after the first infiltration cycles occurred with As concentrations decreasing from day 2 to concentrations around 20 µg L^{-1}, remaining constant for the first ten days. Compliance for As standard of 10 µg As L^{-1} was achieved after 14 days, removing more than 95% of the initial As concentration (82 ± 10 µg As L^{-1}) and with As levels dropping continuously to concentration below 2 µg L^{-1}. This shows the complete adsorption of As requires the formation of enough HFO after several cycles.

The mass balance for As and HFO (in the form of FeOOH) of the first 14 days including the extracted volumes are listed in Table 2. Results show a significant increase in the As and Fe removal from day 8 to day 9, and indicate the adsorption reaches an equilibrium with an As adsorption capacity of q_m = 8.0 ± 1 µg As mg $FeOOH^{-1}$.

Table 2: Iron and As mass balances during SAR adsorption for the first 14 days of operation with a daily injection volume V_I = 780 L (two infiltration cycles).

Day	**V_E** (L)	**$\dot{m}_{As}$** (mg day^{-1})	**$\dot{m}_{FeOOH}$** (mg day^{-1})	**q_m*** (mg As g $FeOOH^{-1}$)
1	250	14.7	1247	11.8
2	260	14.6	1342	10.9
3	260	15.5	1907	8.1
4	260	13.9	2220	6.3
5	260	15.1	2115	7.1
6	260	15.6	2292	6.8
7	260	15.3	2271	6.7
8	260	15.5	2307	6.7
9	510	34.3	4506	7.6
10	660	48.9	5926	8.3
11	465	34.0	4160	8.2
12	400	29.7	3595	8.3
13	520	39.9	4680	8.5
14	570	45.2	5130	8.8
Total	**5.2 m^3**	**0.35 g As**	**43.7 g FeOOH**	**8.0 ± 1 mg g^{-1}**

*Average adsorption capacity calculated from daily As and Fe loads.

In period 2, after the increase of the total plant capacity (day 100), concentrations of dissolved Fe and As continued to remain stable well below the drinking water standard with only small fluctuations in the concentrations being observed, which can be attributed to natural fluctuations in groundwater concentrations and increased water withdrawal depending on consumer behaviour. In period 3 (day 155) water was extracted for 12 days while no infiltration was carried out due to a technical problem with the motor of the feed pump, which led to an over-extraction ($V_E > V_{E,max}$). The over-extraction continued during period 3 for a total of 51 days due to electrical failure of the water meter and the CU. Although more water was extracted than the allowed daily limit $V_E > V_{E,max} = 1900$ L, no As breakthrough above the drinking water limit was observed and Fe remained close to the standard of 0.3 mg L^{-1} with only a small increment to a maximum of 0.51 mg L^{-1}.

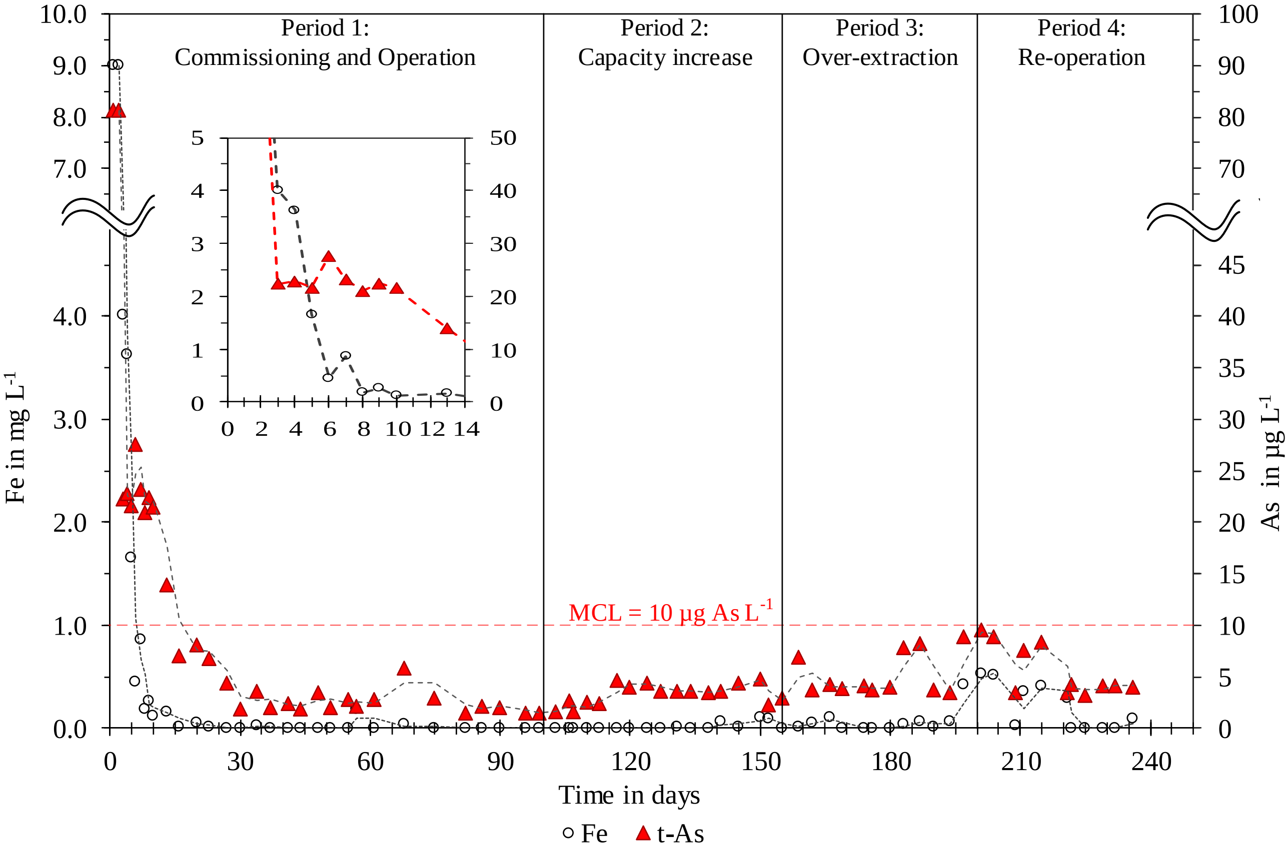

Figure 3: Iron and total arsenic concentrations after SAR treatment at pilot site location for a total of 8 months including four operational periods. Horizontal line: Arsenic drinking water guideline WHO (2017) ; MCL: Max. contaminant level.

Increases in As concentrations during periods 3 and 4 as well as the concentration spikes seen during early operation days (day 6, day 74) indicate a strong correlation to the increases in Fe concentrations, showing that As breakthrough may occur from desorption from HFO. These results also suggest that the removal of As correlated to the oxidation rate of iron, since even small fluctuations in Fe removal show change in As concentration, thus validating the proposed adsorption mechanisms of As onto the Fe(III)-

(hydr)oxides. In total, As concentrations remained below the 10 µg L^{-1} limit for a total of 51 days, reaching a maximum value of 9.6 µg L^{-1}.

After regular infiltration was resumed and operation continued normally, Fe concentrations started to slowly drop to values below the drinking water limit. This shows the feasibility of the process for As removal in the long-run and its stability despite technical complications or over-extraction. However, some difficulties were observed for the elimination of Mn and NH_4^+. The detailed results are shown in Section 3.3.

By assuming a monolayer adsorption theory, the adsorption behaviour can be described with the linearized mathematical form of Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m \cdot b} \qquad \text{(Eq.1)}$$

with q_e (in mg g^{-1}) being the amount of adsorbate (in mg As) removed per weight adsorbent (in g FeOOH), C_e the As concentration at equilibrium (in mg L^{-1}), the maximum adsorption capacity q_m (in mg g^{-1}) and b the Langmuir constant (in L mg^{-1}). The isotherm parameters q_m and b can be determined from the slope and intercept of the linear regression of the isotherm by plotting C_e/q_e versus C_e. The values of $q_m = 7.9$ mg g^{-1} and b = 0.67 L mg^{-1} obtained are ~~similar~~ in line with the q_m value calculated from the As uptake in Table 2; however, showing lower adsorption to those found in literature for As-batch experiments (Li et al., 2015) (q_m = 28.6 mg g^{-1} and b = 2.14 L mg^{-1}). The larger the q_m value, the larger the adsorption capacity whereas ~~small values of~~ b indicates a stronger adsorption bond. The low adsorption capacity calculated can be explained by the differences in real and laboratory conditions, and can be an indication of a limited adsorption due to the presence of competing ions in the raw groundwater.

3.2. Arsenic breakthrough experiments

After one month of operation, As breakthrough tests were carried out on site to evaluate the quality of the treated water over the course of one infiltration-extraction cycle. The tests were done by measuring the total arsenic (t-As) concentration and the As species distribution (arsenite As(III) and arsenate As(V)). When the SAR completed an infiltration cycle (volume $V_{I,1}$ = 390 L during period 1), treated water was pumped and samples were taken at different intervals (first sample at point ZERO) until reaching the 100% treatment target ($V_{E,max}$ = 260 L). Additionally, two more samples were examined at 150% of $V_{E,max}$ (360 L) and 250% of $V_{E,max}$ (650 L) for evaluating if any As breakthrough occurred during over-extraction. The results are presented in Figure 4.

Analyses show a slight rise in both t-As and As(III) concentrations with increasing extraction volume. It is important for the successful SAR process that sufficient HFO-surface area is provided for the effective As-adsorption. Some previous studies on the correlation of As adsorption in Fe oxidation show that Fe oxidation is influenced by the dissolved oxygen content in the infiltrated water (van Halem et al., 2010, 2009; Visoottiviseth and Ahmed, 2008). The more water is abstracted, the more Fe and As enter the treatment zone (oxidation area) and, correspondingly, the more oxygen is used for the oxidation reactions. This leads to the depletion of the oxidation zone and the decrease in the available area for further As-adsorption. Moreover, the increase of the As(III):As(V) ratio indicates both the decrease in As(III) oxidation to As(V) and the breakthrough of raw anoxic groundwater containing As(III) from the outer oxidation zone into the extraction area closer to the well. However, the increase in t-As is not substantial, indicating that the As removal persists even after 2.5 times more water is extracted than the given maximum $V_{E,max}$.

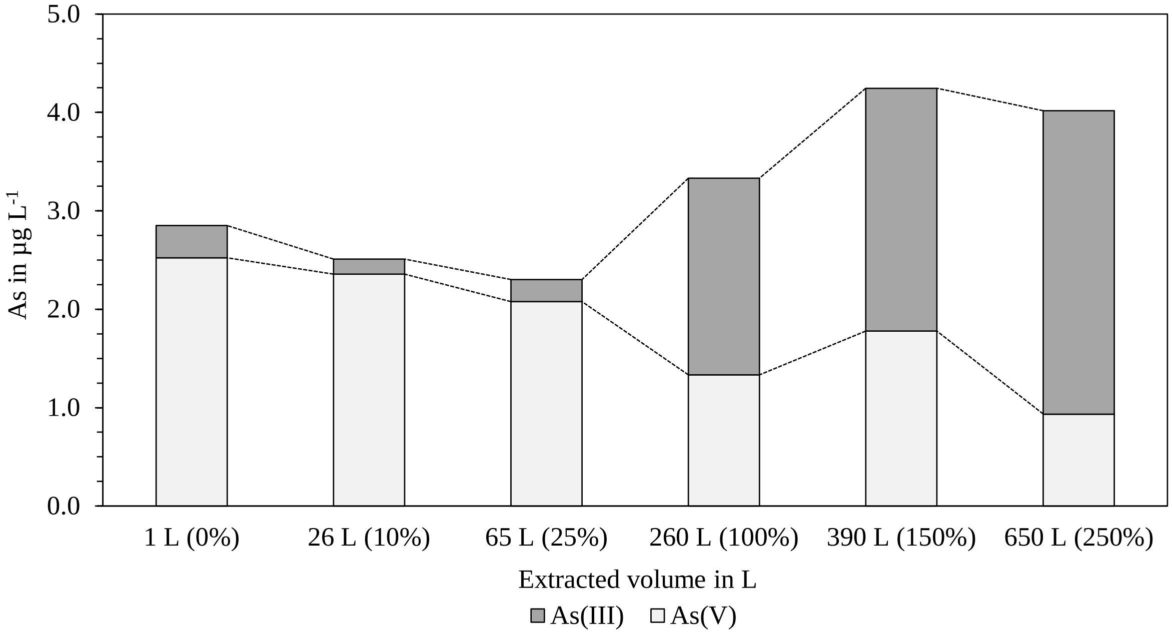

Figure 4: Total As concentration and As distribution in treated water (SAR) with increasing extracted volume at test site. Values in brackets correspond to the share of extracted volume to V_E (V_E = 260L); values above 100% correspond to over-extraction.

For the effective removal of As by use of oxidation/filtration processes, a minimum Fe:As ratio of 20 (w/w) is recommended in the literature (EPA, 2012). On the contrary, the experimental results show no significant correlation between the Fe:As ratio and the overall As mitigation. To evaluate this and the dependence of the adsorption to the oxygen demand and the Fe:As ratio, twelve small-scale aeration experiments were carried out with model water (N = 12) and real water on-site (N = 1). Model water containing 5 mg Fe L^{-1} and increasing As-concentrations (from 125 to 500 µg L^{-1}) was aerated using 2 L glass beakers and an air pump with stone bubbler. Additionally, two experiments with higher iron (7.2 and 9.0 mg L^{-1}) and concentrations of 60 and 81 µg As L^{-1} were carried out to also simulate higher Fe:As ratios as found in the groundwater at the pilot location. First, DI-water in the beaker glass was purged with nitrogen gas until dissolved oxygen DO < 0.5 mg L^{-1}. DO was measured using a WTW portable sensor (OXI 3210). Samples were taken at different time intervals (0, 2.5, 5, 10, 30, 60, 120 min, etc.) and filtrated immediately with a 0.45 µm syringe filter before analysing. All experiments showed a general decrease in the t-As concentration within the initial minutes until before reaching a plateau-phase. Depending on the length of each experiment (0.5 - 120 h), the As-removal was averaged from the total measurements and varied between 58% and 81%. Beyond the individual adsorption behaviour of each experiment, the average removal versus the corresponding Fe:As ratios is also of interest. The results in

Figure 5 show there is no correlation between the Fe:As ratio within range 20 – 120 and a higher removal efficiency.

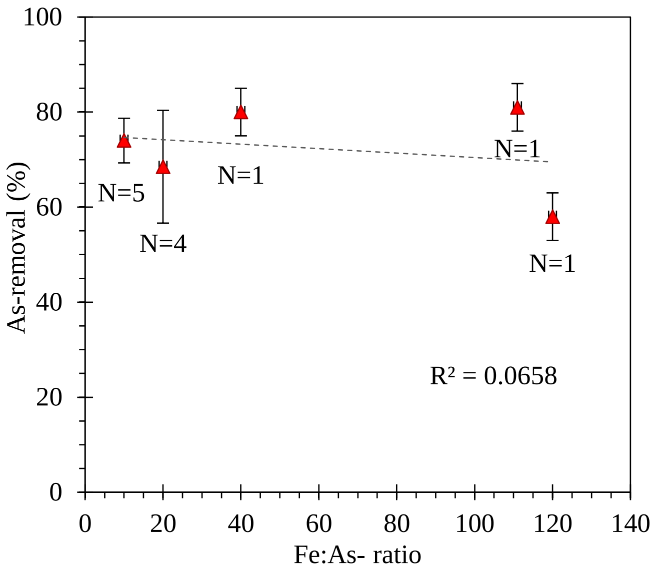

Figure 5: Arsenic removal efficiency versus Fe:As ratio of laboratory aeration experiments showing there is no correlation between both (R^2=0.0658). Number of experiments: N = 12; experimental conditions: pH = 8.4 ± 0.3; temperature = 24 ± 3°C; length t = 0.5-120 h.

In contrast to the tests with model water, the experiment in the beaker glass with real water (Figure 6) resulted in an overall lower As mitigation with a maximum removal efficiency of 49% in a 72 h aeration experiment. This may be due to the presence of competing ions such as PO_4^{3-} and Si that are naturally present in the raw water in higher concentrations than in the model water. The As(III) and As(V) ratio throughout the experiment shows an interesting trend. Initially, 100% of t-As was present as As(III), as it is in the raw groundwater. This ratio does not significantly change within the first 5 h, even though a representative part of the As-adsorption is already finalised (t-As = 53.1 µg L^{-1}). This can be explained mainly by the oxidation of As(III) to As(V) and its respective adsorption and removal from the water, however, a removal of t-As by direct adsorption of As(III) onto the Fe oxides cannot be excluded. After 72 h, the remaining amount of 42.8 µg L^{-1} of t-As in the water was present as As(V). The total mitigation of only 49% indicates an unsuccessful adsorption due to limited availability of adsorption sites as seen in the jar tests with model water.

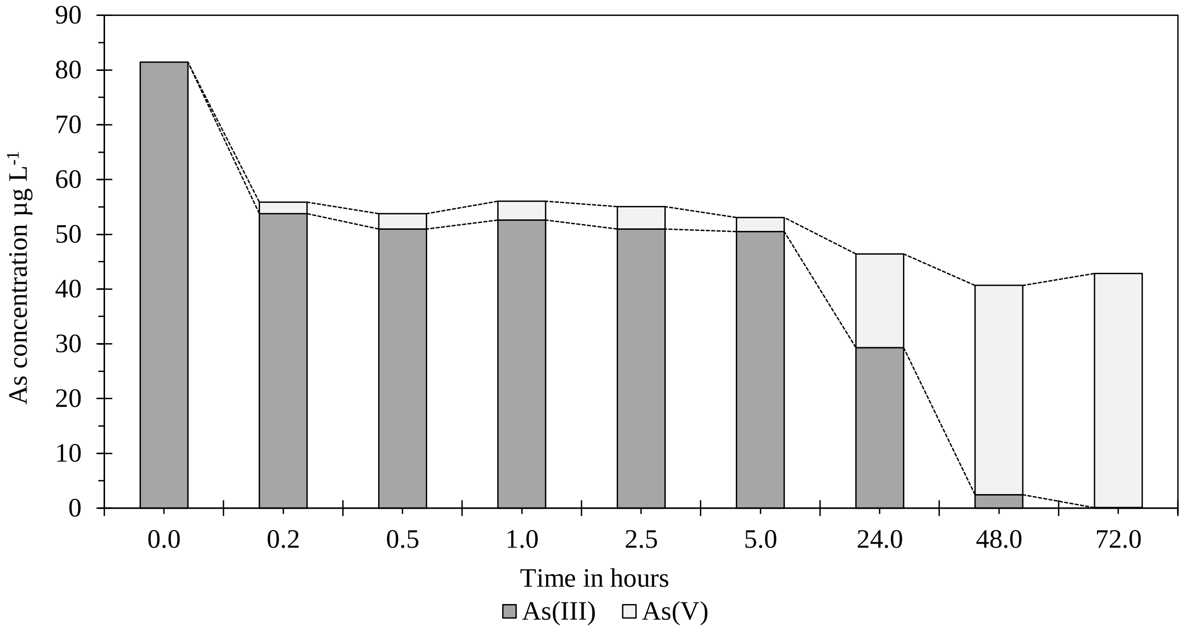

Figure 6: Total As concentration and As speciation during laboratory aeration experiment with raw water at pilot site

Other studies with column and batch experiments also demonstrated that neither the Fe:As ratio nor the amount of Fe present in the groundwater have a direct effect on the As removal capacity in SAR; they indicated, rather, that the As removal is limited by the co-adsorption of competitive ions (van Halem et al., 2009).

The results suggest that a successful SAR plant must provide both an effective oxidation zone and a sufficient adsorption volume area. This was achieved by setting a tolerance margin for the infiltration to abstraction ratio Q_E and fixing a daily target limit $V_{E,max}$. By setting this extraction limit, concentrations of As remained well below the drinking water limit at 4.25 µg L^{-1}. It could be possible to increase the margin limit for improving the capacity of the plant. However, this should be only attempted after sufficient tests have been performed.

3.3. Manganese and ammonium removal

The presence of ammonium nitrogen in groundwater is linked to reduced groundwater conditions that in general promote As release (Kurosawa et al., 2013). Ammonium mitigation ~~with the~~through SAR ~~process~~ is based on its oxidation to nitrate (NO_3^-), which occurs in the subsurface through both microbial and chemical oxidation processes. Results show that the NH_4^+ removal was considerably slower than the removal of As and Fe. The initial concentrations of NH_4^+ in the raw groundwater of 1.1 mg L^{-1}

were below the Vietnamese drinking water standard of 3 mg L^{-1}. These values were ~~steadily~~gradually lowered until reaching concentrations of around zero within the first 60 days of operation (see Figure 7). However, during period 3 and 4, the NH_4^+ concentrations rose back to initial raw water concentrations (max. concentration day 183: c = 1.17 mg L^{-1}) due to over-extraction. ~~Nevertheless, the concentrations of NH_4^+ were lowered significantly faster than in the initial phase after normal operation was restarted, taking less than 7 days to reach zero again (day 190). This indicates that once the removal of NH_4^+ has been established, the microorganisms responsible for the oxidation remain active and will accelerate the mitigation process after re-operation.~~

In addition, Mn^{2+} in the groundwater remained relatively stable during period 1 and 2 following natural fluctuations (average 1.5 ± 0.2 mg L^{-1}) after a slight decrease from its initial value within ~~during~~ the first 15 days. The effective Mn-removal only started on day 152, approx. 3 months after a NH_4^+ mitigation was achieved. The lowest Mn concentration was observed after 2 weeks linear decrease reaching a concentration of 0.46 mg L^{-1} (day 166)~~ during period 3~~. However, both Mn and NH_4^+ concentrations increased following the excessive extraction in period 3. While the NH_4^+ content rose to initial concentrations (c ≈ 1.1 mg L^{-1}), Mn level reached a~~steadily to~~ maximum of~~.~~ 2.74 mg L^{-1}~~ during the over-extraction period~~ which was higher than the initial values. This behaviour could be linked to the microbial-mediated reductive release of Mn which causes the temporary increase in its concentration (Swain et al., 2018). ~~until normal operation was resumed in period 4.~~

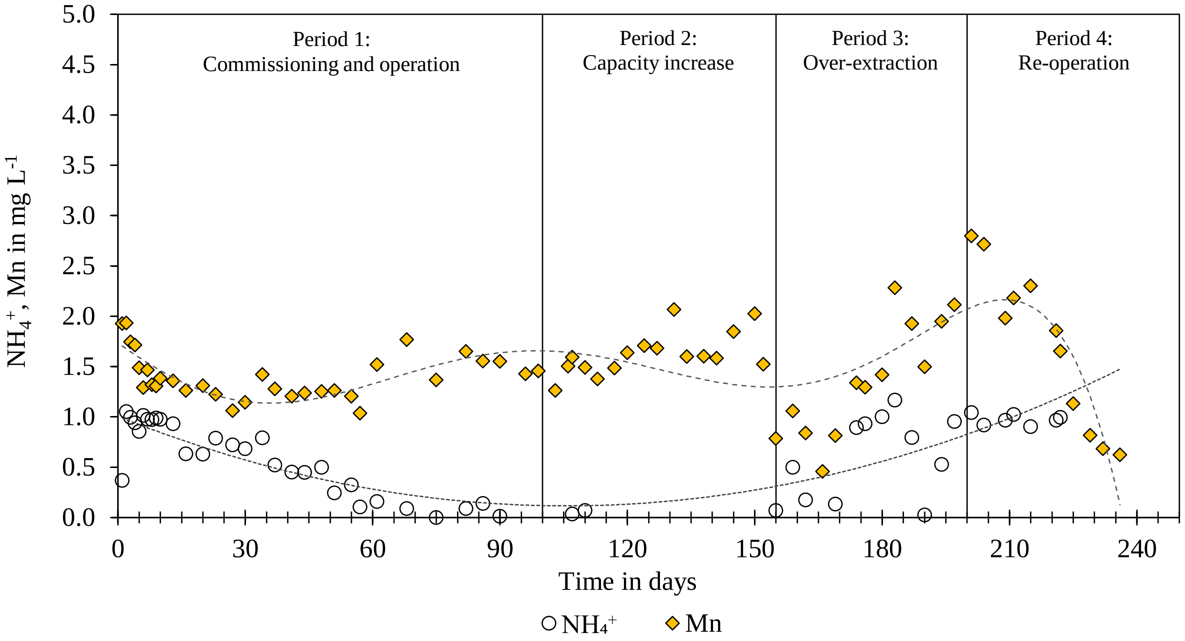

Figure 7: Ammonium and manganese removal at site location for the 4 operational periods.

Long-time experience with SIR in Europe shows that a complete removal of Mn can take ~~several~~ long ~~months~~ time and a mitigation of Mn with SAR is feasable ~~should not be excluded~~ (FERMANOX, 2017). In general, the biological Mn removal occurs usually simultaneous to the catalytic MnO_2 oxidation, and the required start-up period of biological filters can take several months (Farnsworth et al., 2012; Gouzinis et al., 1998a; Nitzsche et al., 2015).

The ~~initial results showing a~~ slow Mn mitigation can be associated in general to the unfavourable Eh-pH conditions given by the natural anoxic ~~to both the~~ hydro-geological setting and to the high initial NH_4^+ concentrations (1.1 ± 0.1 mg NH_4^+ L^{-1}) of the groundwater. When NH_4^+ is present,~~, as~~ the oxidation of Mn^{2+} ~~will~~ can only take place after complete nitrification due to the necessary evolution of the redox potential (Gouzinis et al., 1998b; Luong et al., 2018).

Nevertheless, Mn levels were lowered significantly faster after normal operation was restarted in period 4. This indicates that once the removal of Mn has been established, the microorganisms responsible for the oxidation remain active and will drive the mitigation process after re-operation. In contrast to As and Fe, the rise of both Mn and NH_4^+ in period 3 was observed several days delayed to the start of the over-extraction period. This can be an indication that the oxidation mechanisms are linked to microbial activity, which will respond slower than a chemical oxidation after the oxygen feeding. Ammonium concentrations remained, thus, constant throughout the measured days in period 4 (day 240). Although NH_4^+ concentrations below the detection limit were reached again in later analyses (see Section 3.5), further research on the behaviour of the microorganisms involved is needed to critically evaluate the role of microbial oxidation during SAR.

3.4. Post-treatment for Mn-removal

As a result of ~~T~~the limitations on Mn removal~~ can also be related to the lack of microbial activity and the unfavourable natural low redox potential, which makes the – already slow – Mn oxidation challenging. As a result~~, achieving Vietnamese drinking standard (0.3 mg Mn L^{-1}) could not be accomplished within the first 240 days of operation (Figure 7). An additional post-treatment filter ~~media~~ (with MnO_2) for Mn-removal was temporarily used to comply with the Vietnamese drinking water standard until a Mn-mitigation was achieved by the SAR process.~~An oxidative granulate for removal of Mn was installed as post-treatment for achieving drinking water quality while the Mn mitigation through the SAR process was evaluated.~~ Concentrations of Mn before and after the oxidative granulate filter were monitored occasionally, showing that ~~– until values below the drinking water standard were reached. Manganese~~Mn concentrations below 0.3 mg L^{-1} were first achieved by use of only the SAR process (without the filter) after operation day 420. However, the lack of continuous parameter monitoring after the first 8 months of study mean a Mn mitigation could have happened ~~sooner~~earlier. ~~A complete Mn removal was possible by use of SAR reaching stable concentrations below the detection limit of 0.05 mg L-1.~~

~~*3.4.*~~*3.5. Overall SAR efficiency*

After more than two years of operation, analyses show that drinking water standard was achieved for all parameters reaching stable concentrations throughout the process. The relevant results are summarized in Table 3. All parameters including coliforms and *E. coli* were analysed additionally by different certified commercial laboratories in Ho Chi Minh City.

Table 3: Chemical analysis of raw and treated groundwater.

Parameter	**Unit**	**Concentration raw water***	**Concentration treated water†**	**VN drinking water limit§**	**Removal in %**

pH	-	7.0	7.5	± 0.4	6.5-8.5	-
Total-As	µg L^{-1}	81	5.7	± 2.4	10	93.0%
Total-Fe	mg L^{-1}	8.4	0.042	± 0.03	0.3	99.5%
Mn^{2+}	mg L^{-1}	1.9	0.040	± 0.7	0.3	98.0%
NH$_4^+$	mg L^{-1}	1.1	BDL (0.1)	-	3.0	>90.5%
Coliforms	cfu/100 mL	-	BDL (1)	-	0	-
E. coli	cfu/100 mL	-	BDL (1)	-	0	-

* see Table 1: Analysis of raw groundwater at SAR test site before trial tests (2016-2017)
[†] Values are averaged from different samples analysed by certified commercial lab analyses
[§] QCVN01: Vietnamese National technical regulation on drinking water quality, VIỆT NAM, 2009 (QCVN:01, 2009)
BDL = below detection limit (detection limit of method)

~~3.5.~~3.6. *Energy demand*

The energy consumption of the system including the controlling unit and monitoring devices as well as the pump for both delivery and treatment, were monitored throughout the pilot. Water demand was recorded with a water meter and water consumption was logged to the controller system. An energy meter was used to measure the total energy consumption of the plant. The specific energy consumption (SEC) of the SAR plant for both treated and supplied water ranged between 0.87 and 1.07 kWh m^{-3} which leads to specific costs of 0.06 – 0.07 USD per cubic metre with average electricity prices of 0.07 – 0.12 USD kWh^{-1} (retail price for household electricity: 1678 - 2927 VND/kWh (VIETNAM ELECTRICITY, 2019)). These specific costs are remarkably below the values reported in literature, with results from different field tests varying from 0.11 to 1.11 USD m^{-3} (Shan et al., 2018) and other similar subterranean groundwater treatments reporting specific costs of about 0.5 USD m^{-3} (Sen Gupta et al., 2009).

Conclusion and recommendations

- Results show that subsurface arsenic removal (SAR) is a feasible mitigation technique for achieving safe drinking water from groundwater in regions like Vietnam and Southeast Asia, characterised by reducing aquifer conditions.
- Arsenic concentrations were lowered well below the limit of 10 µg As L^{-1} during the pilot phase of 2 years and remained stable throughout the process, even when temporary operational failures occurred causing the breakthrough of Fe.

- The salient advantages of this technique are the negligible toxic waste production, ease-of use, and the low operational and capital costs that also make the technology suitable for low-income countries such as Vietnam.
- The success of the As removal through SAR strongly depends on the infiltration to abstraction ratio of the groundwater from the aquifer. The injection - extraction dynamics should be controlled to ensure the complete and effective Fe oxidation with enough time allowed for the oxidation reactions and a sufficient adsorption area.
- In contrast to other studies and pilot plants, an appropriate aeration system must ensure oxygen saturation and the extraction to infiltration ratio Q_E must be determined to avoid over-extraction.
- Studying the SAR process under different hydrogeological settings is still needed to evaluate the feasibility and the range of applications of the technology, including the negative effect of co-ion adsorption and the removal efficiency when higher As levels (e.g. > 500 µg L^{-1}) are present.
- Hydrogeochemical conditions may affect the efficiency in obtaining drinking water standard when high NH_4^+ and Mn concentrations are present. Furthermore, the construction of informal wells in unsecured surroundings and vulnerable zones increase the risk of anthropogenic NH_4^+ contamination and should be taken into consideration when applying SAR.

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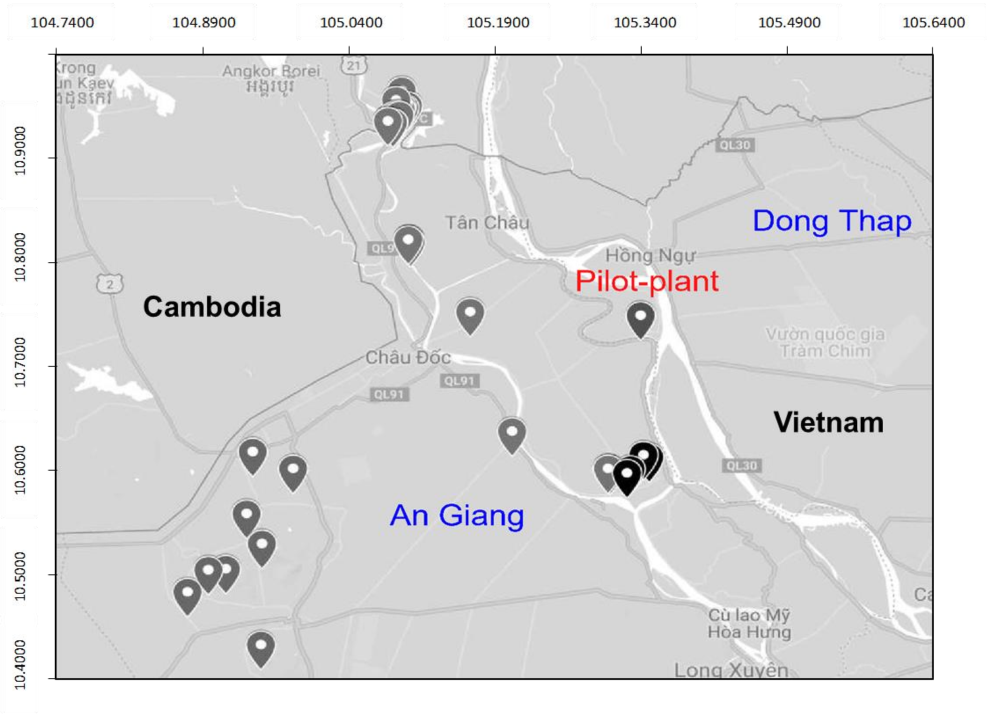
I. Supplement

i) Statistical evaluation of study area

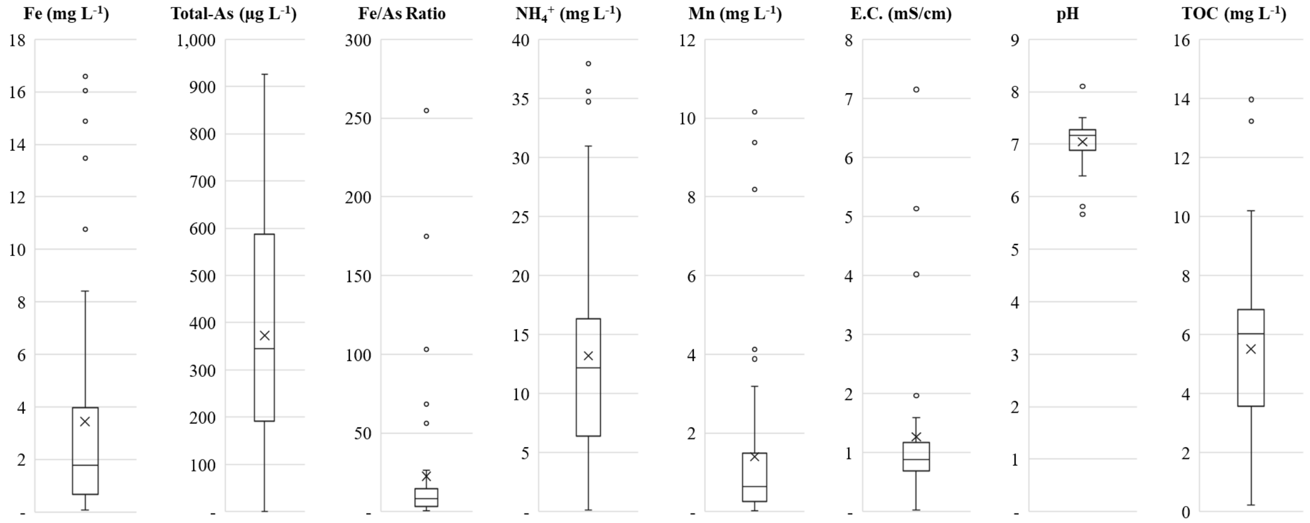
To assess the As contamination in the study area, a statistical evaluation of the physico-chemical composition and related quality of the groundwater was carried out as part of the site selection for the planned pilot trials. For this, groundwater from 52 shallow tube wells in the district of An Giang (Supplement 1) was analysed for Fe, Mn, NH_4^+, t-As and other relevant parameters. The majority of the tube wells were located in private households or were privately owned by small farmers for agriculture or aquaculture (eel farms, shrimp farms). Because of poor well management and documentation, well owners normally do not know much about the well design, which depends on local drilling practices. However, typical well design data in this province ranged between 15 – 36 m (Tran et al., 2011).



Supplement 1: Map of groundwater sampling sites in An Giang

ii) Analysis results of groundwater analyses

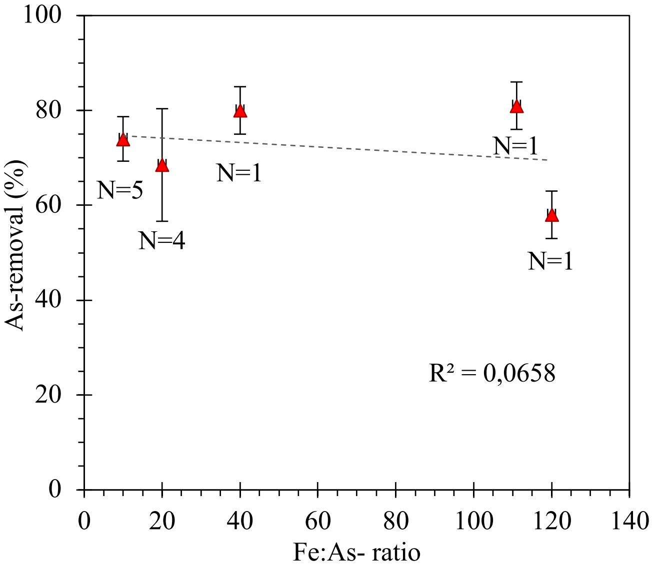
Results of the sampling study are summarized in the whisker-plot diagrams in showing the results of the water analysis (Supplement 2). Total Fe concentration averaged at 3.4 ± 4 mg L^{-1} with maximum values exceeding 16 mg L^{-1}. The concentration of t-As averaged at 373 ± 254 µg L^{-1}, with 41 out of the 47 tube wells tested for As exceeding the 10 µg L^{-1} limit. These results are in line with previous research on the Mekong Delta which has shown the magnitude of the As contamination in the region ($c_{(As)}$ = 207.8 - 1,522 µg L^{-1}) (Kỳ, 2009; Thư et al., 2011; Vũ, 2014). Furthermore, 75% of the tube wells (n = 47; NA = 5) showed As levels higher than 200 µg L^{-1} with the maximum value detected of 926 µg L^{-1}, exceeding the WHO guideline value by almost 100 times.



Supplement 2: Distribution of groundwater analysis of study area in An Giang. Whiskers give the highest and lowest concentrations, box the upper and lower quartiles; the horizontal line in each box marks the median.

Besides As contamination, groundwater in the region was also found to contain high NH_4^+ concentrations (13.2 ± 10 g L^{-1}) with more than 87% of the wells exceeding the Vietnamese standard for drinking water of 3.0 mg NH_4^+ L^{-1} (QCVN:01, 2009) and maximum measured values higher than 30 mg L^{-1}. This can be attributed to the reducing environment of the aquifer and various sources of nitrogen including septic effluents from household and industrial waste discharges, leaching from agricultural systems and animal manure infiltrating the groundwater due to poor well construction and area protection (Du et al., 2017; Le Luu, 2019; Lindenbaum, n.d.). The mean concentration of Mn (1.39 ± 2.2 mg L^{-1}) was about 4.5 times greater than the Vietnamese drinking water standard of 0.3 mg L^{-1}, whereas water from some wells presented concentrations above 8 mg L^{-1}, which is more than 25 times higher (QCVN:01, 2009).

Figure


As-removal (%)
Fe:As- ratio
0
20
40
60
80
100
0
20
40
60
80
100
120
140
N=5
N=4
N=1
N=1
N=1
R² = 0,0658