



# Arsenic removal with zero-valent iron filters in Burkina Faso: Field and laboratory insights

Anja Bretzler<sup>a,\*</sup>, Julien Nikiema<sup>b</sup>, Franck Lalanne<sup>c</sup>, Lisa Hoffmann<sup>a,d</sup>, Jagannath Biswakarma<sup>a,e</sup>, Luc Siebenaller<sup>f</sup>, David Demange<sup>f</sup>, Mario Schirmer<sup>a,g</sup>, Stephan J. Hug<sup>a</sup>

<sup>a</sup> Eawag, Swiss Federal Institute of Aquatic Science and Technology, CH-8600 Dübendorf, Switzerland

<sup>b</sup> Université Ouaga 1 Pr. Joseph Ki-Zerbo, Ouagadougou, Burkina Faso

<sup>c</sup> Institut International d'Ingénierie de l'Eau et de l'Environnement (2iE), Ouagadougou, Burkina Faso

<sup>d</sup> Institute of Groundwater Management, Technische Universität Dresden, Germany

<sup>e</sup> Swiss Federal Institute of Technology (ETH) Zurich, IBP, CH-8092 Zürich, Switzerland

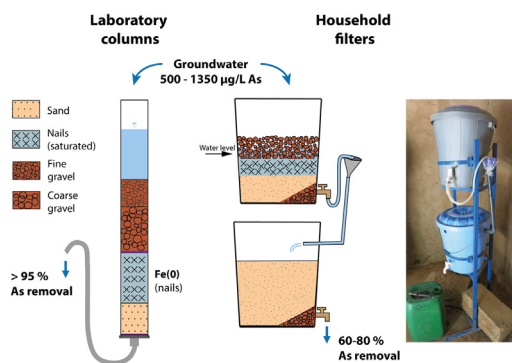
<sup>f</sup> ONG-D "Le Soleil dans la Main" a.s.b.l., Winseler, Luxembourg

<sup>g</sup> Centre d'Hydrogéologie et de Géothermie (CHYN), Université de Neuchâtel, Switzerland

## HIGHLIGHTS

- Low-cost filters with nails as the active ZVI layer tested in field and laboratory.
- Filters and columns operated with groundwater containing 500–1350 µg As/L.
- Ensure permanently saturated nail bed to increase water/nail contact time.
- Transformation of amorphous Fe-(hydr)oxides to stable magnetite with incorporated As(V)
- Field filters achieved 60–80% As removal, lab columns >95%.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 9 January 2020

Received in revised form 1 May 2020

Accepted 13 May 2020

Available online 16 May 2020

Editor: Ching-Hua Huang

### Keywords:

Arsenic  
Drinking water treatment  
Zero-valent iron  
Burkina Faso  
Filtration  
Groundwater

## ABSTRACT

Groundwater contaminated with geogenic arsenic (As) is frequently used as drinking water in Burkina Faso, despite adverse health effects. This study focused on testing low-cost filter systems based on zero-valent iron (ZVI), which have not yet been explored in West Africa for As removal. The active ZVI bed was constructed using small-sized iron nails, embedded between sand layers. Household filters were tested for nine months in a remote village relying on tube well water with As concentrations of 400–1350 µg/L. Daily filtered volumes were 40–60 L, with flow rates of ~10 L/h. In parallel, downscaled laboratory filter columns were run to find the best set-up for optimal As removal, with special attention given to the influence of input pH, flow rate and water/nail contact time. Arsenic removal efficiencies in the field were 60–80% in the first six months of operation. The laboratory experiments revealed that trapped air in the nail layer greatly lowered As removal due to preferential flow and decreased water/nail contact time. Measures taken to avoid trapped air led to a partial improvement in the field filters, but effluent As remained >50 µg/L. Similar structural modifications were however very successful in the laboratory columns, where As removal efficiencies were consistently >95% and effluent concentrations frequently <10 µg/L, despite inflow As >1000 µg/L. A constantly saturated nail bed and careful flow control is necessary for optimal As removal. Slow flow and longer pauses between filtrations are important for sufficient contact

\* Corresponding author.

E-mail address: [anja.bretzler@eawag.ch](mailto:anja.bretzler@eawag.ch) (A. Bretzler).

times and for transformation of brown amorphous Fe-hydroxides to dense magnetite with incorporated As(V). This preliminary study has shown that nail-based filters have the potential to achieve As removal >90% in a field context if conditions (filter bed saturation, flow rate, pauses between filtrations) are well controlled.

© 2020 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Groundwater contaminated with geogenic Arsenic (As) is widely used as drinking water in West African countries. In Burkina Faso, ~560,000 people in rural communities are estimated to rely on water from As-contaminated tube wells (Bretzler et al., 2017). Well-switching to uncontaminated sources has proven to be an effective As mitigation measure in other countries, e.g. Bangladesh (Inauen et al., 2013). However, due to the different climatic and geological conditions in Burkina Faso (semi-arid climate, lower water tables, fractured crystalline bedrock aquifers) and resulting elevated cost of drilling, villages may only be supplied by one or a few community tube wells. As a result, switching to uncontaminated wells is frequently not possible. Therefore, water treatment by removing As is often the only option to supply drinking water adhering to the WHO (and Burkinabè national) guideline value of 10 µg/L.

Considerable research has been undertaken in the last decades in finding effective As removal technologies with inexpensive and generally available materials for low- and middle-income regions, spurred by the “As crises” in Asia and Latin America (Bundschuh et al., 2010; Litter et al., 2012; Mohan and Pittman, 2007; Mondal et al., 2013; Singh et al., 2014). Due to the affinity of As to bind to Fe-oxides, filtration of water with Fe-based materials has been amongst the most successful and widespread solutions. In industrial countries, As is removed by oxidation of As(III) (arsenite) to As(V) (arsenate), followed by addition of Fe(II) or Fe(III) for controlled coagulation and precipitation, or by adsorption on commercial adsorbents (Hering et al., 2017). Adsorbents such as granular ferric hydroxide (German: granuliertes Eisenhydroxid, GEH®) (Driehaus et al., 1998; Usman et al., 2018) or Bayoxide® (Kanematsu et al., 2010; Katsoyiannis et al., 2015) are widely used and very effective in removing As(V). However, the comparatively high cost and limited availability of these materials restrict their application in low-income rural communities. Technologies based on low-cost and generally available metallic iron, mostly referred to as Fe(0) or zero-valent iron (ZVI), in the form of iron filings, scrap iron or iron nails, have been developed and shown to be promising (Bang et al., 2005; Fu et al., 2014; Katsoyiannis et al., 2015; Katsoyiannis et al., 2008; Lackovic et al., 2000; Lien and Wilkin, 2005; Mwakabona et al., 2017; Su and Puls, 2008; Sun et al., 2006). The corrosion of ZVI leads to the formation of dissolved Fe(II) and various mixed Fe(II)/Fe(III) and Fe(III) phases that act as sorbents for both As(III) and As(V) (Leupin and Hug, 2005). In addition, reactions of ZVI with dissolved oxygen in aerated waters form oxidants that can oxidize As(III) to As(V) (Hug and Leupin, 2003; Katsoyiannis et al., 2008; Leupin and Hug, 2005). The most widely used and successful ZVI-based filter so far is the SONO filter employing a composite iron matrix (CIM) of sub-millimetre to millimetre sized scrap iron particles embedded between sand layers (Hussam and Munir, 2007; Neumann et al., 2013). Over 270,000 SONO-filters were produced and deployed in Bangladesh by 2014 (Kundu et al., 2016). Another widely used ZVI-filter is the Kanchan filter developed in Nepal, employing iron nails (Ngai et al., 2007). However, it has been reported that the contact times in the Kanchan filter are often too short for sufficient As-removal (Chiew et al., 2009; Singh et al., 2014; Smith et al., 2017). Other ZVI filters for As-removal have been developed and tested at both the household and community level (Banerji and Chaudhari, 2017; Smith et al., 2017). The design and efficiency of the different systems can vary considerably. The community-scale system developed by the Indian Institute of Technology Bombay (IITB) utilises a similar concept as Kanchan filters, but is more effective as water/

nail contact time is increased (Banerji and Chaudhari, 2017). Also NIS (“nails-in-sand”) filters developed in China have attempted to increase water/nail contact time and yielded promising results (Smith et al., 2017).

Arsenic removal is dependent on various factors and no technology performs consistently well for all water types. The presence of high P (phosphate) concentrations competing with As for adsorption sites can considerably reduce As uptake, and to a lesser extent also Si (silicate) (Leupin and Hug, 2005; Leupin et al., 2005; Roberts et al., 2004; Tyrovolas et al., 2006; Wenk et al., 2014; Sun et al., 2006). As(V) sorbs preferentially over As(III) to Fe oxides in the prevailing pH conditions of natural waters (Dixit and Hering, 2003), and groundwater containing mainly As(III) may have to undergo pre-oxidation before the main As removal step. Technologies therefore have to be chosen and/or adapted to suit local groundwater composition, pH and redox state (Hug et al., 2008). In contrary to the often reducing groundwater systems in low-land Asia dominated by As(III), geogenic As in Burkina Faso stems from the oxidation of sulphide minerals (e.g. arsenian pyrite, arsenopyrite) often associated to gold mineralisations and occurs as As(V) under oxic conditions (Bretzler et al., 2017; Smedley et al., 2007). Together with low P concentrations (< 0.05 mg/L) and circum-neutral pH, conditions are relatively favourable for As(V) adsorption onto iron oxide phases (Dixit and Hering, 2003; Leupin and Hug, 2005; Leupin et al., 2005; Roberts et al., 2004; Sun et al., 2006; Tyrovolas et al., 2006; Wenk et al., 2014). Dissolved Fe concentrations, on the other hand, are generally very low (< 100 µg/L) and not sufficient for As removal without additional Fe sources (Berg et al., 2006).

Despite the widespread occurrence of As-contaminated wells in this region (Ahoule et al., 2015; Bretzler et al., 2017), As mitigation activities are still almost non-existent compared to Asian or South-American countries. Tube wells identified as As-affected are usually closed by the authorities without replacement. Due to the extreme poverty and very low purchasing power of rural communities in Burkina Faso, utilising a low-cost, As removal method exclusively sourced from locally available materials was a priority of this study. We chose the SONO technology as the basis for filter materials and filter design for Burkina Faso, as SONO filters are well studied, need little maintenance and can be operated for years without exchanging the Fe matrix (Hussam and Munir, 2007; Neumann et al., 2013).

The challenge for reproducing SONO was finding a ZVI material to replicate the function of the CIM, which is exclusively produced in Bangladesh. For this study, it was not possible to find or produce similar lubricant-free iron filings in Burkina, at least not in a quantity necessary for multiple filters. Countless small street-side workshops working with steel produce small quantities of iron scrap that falls onto unpaved ground, where it mixes with other detritus and dust. Larger workshops and enterprises produce larger amounts of Fe shavings and scrap, but the iron is usually contaminated with machine oils, rendering it unsuitable for drinking water treatment. Nails were chosen as an Fe-source as they are inexpensive (USD 400–1000/ton), globally widely available, also in rural Burkina Faso, and do not need elaborate cleaning. Although they have a lower specific surface area than Fe shavings/turnings used in SONO filters, small iron nails are the cleanest and least expensive source of suitable Fe(0) for As removal in Burkina Faso.

The purpose of this study was to develop and test filters that use the same design as SONO filters, but built with locally and generally available iron nails instead of the finer iron turnings and filings used in the CIM, and to determine the filter performance under different operating conditions. Iron nails were the most easily available form of small sized

iron. Due to time constraints, we did not investigate other options such as steel wool or wire, which would be interesting for future studies. As a reference, we also conducted field tests at the same location with filters of the same design, but with GEH as the active layer. The removal mechanism of GEH being different to that of ZVI, this part of the study did not aim to scientifically compare the two materials. Rather, we wanted to test the efficiency of a proven and well-studied, industrial material under similar conditions, also to show alternatives to ZVI to local communities.

In parallel to field testing of filters, laboratory experiments with different filter column designs were carried out to find the ZVI set-up with optimal As removal. The influence of flow rate and water/nail contact time on As removal could be addressed in detail in the laboratory. The field filters and laboratory columns were monitored over twelve and eight months, respectively, to evaluate filter performance, Fe(0) corrosion and As removal efficiency over longer time scales.

## 2. Materials and methods

### 2.1. Field experiments

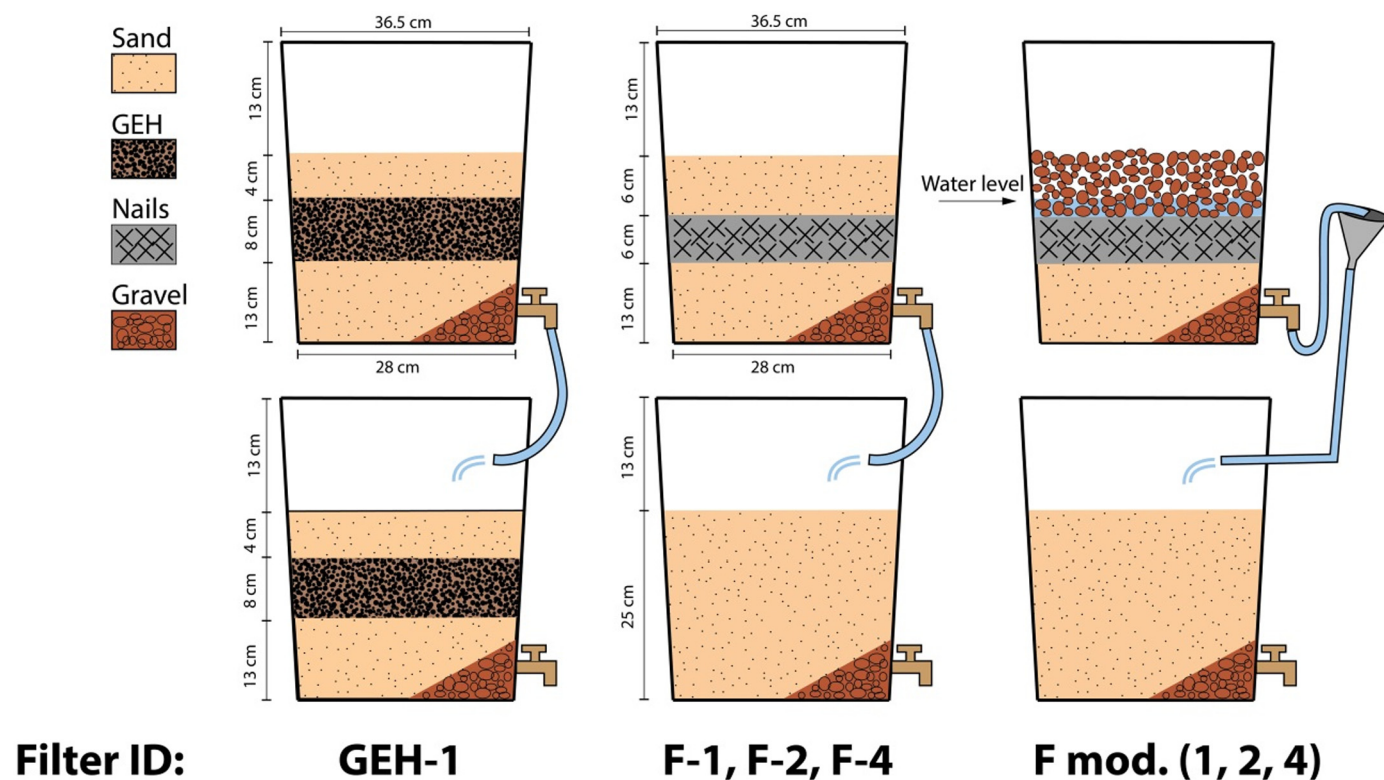
The field experiments were conducted in the village of Souriyala in northern Burkina Faso (Province de Bam). The village was already a focus site of the partner NGO “Le soleil dans la main” and villagers were familiar with previous NGO activity and interventions. Two tube wells with highly elevated As concentrations ( $\sim 450$  and  $\sim 1000$   $\mu\text{g/L}$ ) had previously been identified.

#### 2.1.1. Filter construction and set-up

Filters for filtration of 3 times 20 L water per day were constructed based on the design of the SONO filters (Fig. 1). The upper plastic buckets (280–365 mm diameter, 380 mm height) contained an upper layer of sand, a central active layer of 8 kg iron nails, and

a lower layer of sand and gravel. The average diameter of the nail layer was 320 mm and its height 60 mm. The lower buckets contained sand and gravel to remove remaining suspended iron oxide particles. Altogether four household As removal filters were constructed, three using iron nails and one using commercial GEH® (Fig. 1, Table 1). GEH is a granular form of akagenite ( $\beta\text{-FeOOH}$ ) (grain sizes 0.2–2 mm) with an iron content of 610 g/kg and a specific surface area of 300  $\text{m}^2/\text{g}$  (GEH Wasserchemie, 2013). The GEH filter was constructed as a kind of “benchmark”, to compare the As removal efficiency of the nail-based filters with an established and well-studied sorbent, which is nevertheless more expensive and needs to be imported. In the nail filters, two different nail sizes were used, 20 mm  $\times$  1 mm (Filter F-1 and F-2) and 12 mm  $\times$  1 mm (Filter F-4). Non-galvanized steel nails were purchased in Burkina Faso. Steel nails are globally produced in large quantities from low-carbon unalloyed steel wire and have a fairly uniform composition, as described previously (Wenk et al., 2014) and in more detail in the Supplementary Material. The nails (8 kg per filter) underwent some pre-treatment for cleaning and to start the corrosion processes (several 12–24 h cycles of soaking in water or diluted vinegar, followed by drying), as described in Hussam and Munir (2007) and Smith et al. (2017) for the iron filings used in SONO filters. The sand layers consisted of fine quartz sand with grain sizes of 0.4–0.8 mm. The sand, nail and gravel layers in the filter were separated by a double layer of fine polyethylene mosquito netting. In order to reduce the flow velocity and increase water/nail contact times in filters F-1, F-2 and F-4, the tap of the top bucket was adjusted and fixed with tape so that water left the bucket at a flow rate of about 8–12 L/h. The tap of the GEH filter was left unchanged, with flow rates exceeding 20 L/h.

Due to an unsatisfactory As removal efficiency after six months of filter operation (see Results, Section 3.1), and following new insights attained during the laboratory experiments, the nail-based filters were



**Fig. 1.** Overview of the different filter designs used in the field experiments. While the filter GEH-1 remained unchanged throughout the experimental period, the three filters containing nails (F-1, F-2, F-4) were all modified to the setup on the far right (F mod.) in October 2017 as a result of insights attained during the laboratory experiments.

**Table 1**  
Characteristics of field filters (F-1, F-2, F-4, GEH-1) and laboratory filter columns (L1 to L5).

Filter/Column	Operation period	[As] <sub>input</sub> (µg/L)	Iron source (Nail length, diameter) (mm)	Direction of flow and flow rate	Empty bed flow velocity (cm/h)	Empty bed contact time (min)	*Contact time × ZVI surface area/L (s m <sup>2</sup> /L)	Specific characteristics
F-1	Mar 2017 – Mar 2018	600–1350	8 kg nails (20, 1.0)	Downflow 8–12 L/h	10–15	24–36	1250–1875	
F-2	Mar 2017 – Mar 2018	400–600	8 kg nails (20, 1.0)	Downflow 8–12 L/h	10–15	24–36	1250–1875	
F-4	Mar 2017 – Mar 2018	400–600	8 kg nails (12, 1.0)	Downflow 8–12 L/h	10–15	24–36	1270–1905	
GEH-1	Mar 2017 – Mar 2018	600–1350	14 kg GEH	Downflow 20–40 L/h	25–50	19–39	(3.8–7.6) · 10 <sup>8</sup>	
L-1A / L-1B	Jul 2017 – Mar 2018	500–1200	85 g nails (12, 1.0)	Downflow 80–120 mL/h	10–15	24–36	1350–2025	Water-saturated nail layer
L-2A / L-2B	Jul – Aug 2017	500–1200	85 g nails (12, 1.0)	Downflow 80–120 mL/h	10–15	24–36	1350–2025	Same design as F-1, F-2 and F-4. Temporarily unsaturated nail layer
L-3A / L-3B	Jul – Aug 2017	500–1200	85 g nails (12, 1.0)	Upflow (peristaltic pump), 100 mL/h	12.5	29	1620	Closed column, no headspace, constantly saturated filter bed
L-4	Sept 2017 – Apr 2018	500–1200	85 g nails (23, 1.5)	Downflow 80–160 mL/h	10–20	18–36	670–1340	Constantly saturated nail layer (raised outlet)
L-5	Sept 2017 – Apr 2018	500–1200	85 g nails (23, 1.5)	Downflow 80–160 mL/h	10–20	18–36	670–1340	Constantly saturated nail layer (raised outlet), Gravel
					F1, F2, F4		L1–L5	
Diameter / length of active layer (mm)					320 / 60		32 / 60	
Empty bed volumes of active ZVI layers					4825 mL		48.3 mL	
Pore volume of active ZVI layers					3808 mL		37.4 mL	
Pore volume / Empty bed volume					0.79		0.78	
Filtered volume in each filtration					20,000 mL		113 mL	
Remaining volume in ZVI and lower sand layer					7484 mL		50.3 mL	
Remaining volume / Volume of filtered water					0.374		0.445	

\*Contact times × ZVI surface area/per L of pore volume are based on effective contact times with ZVI in the pore volume of the active ZVI layer during flow. For comparison, estimated contact times × ZVI surface area/L for SONO filter columns with similar flow rates were 6840 s m<sup>2</sup>/L, 4–12 times larger due to the smaller size of the used iron particles. Estimated specific surface areas of iron filings in SONO filters are 1.6 · 10<sup>3</sup> m<sup>2</sup>/g and 3.5–5.3 · 10<sup>4</sup> m<sup>2</sup>/g in iron nails. Granular ferric hydroxide (GEH) has contact times per surface area and volume that are orders of magnitude larger. GEH characteristics: 1150 kg/m<sup>3</sup>, intra-particle porosity 0.7–0.8, specific surface area (BET) 250–300 m<sup>2</sup>/g (Westerhoff et al., 2005). Recommended filtration velocities can be 20 m/h (100-fold higher than in nail filters).

structurally modified in October 2017. The outlet tube of the first bucket was raised to ensure that the water level stayed above the nail layer, which consequently remained permanently saturated. The top fine sand layer was replaced by gravel (mixed grain sizes of 2–20 mm) to allow trapped air in the nail layer to escape more easily (Fig. 1).

### 2.1.2. Operation and use of the field filters

Initial meetings with village elders and decision makers were held in February 2017 to present the project and discuss filter implementation. The filters were installed in households recommended by village heads as being reliable and willing to participate. Villagers were instructed to filter three 20 L jerrycans of groundwater per day (morning, midday and evening). Considering the very hot climate and large families (5.4 live births per woman (United Nations, 2017)), 60 L is a realistic daily need in drinking and cooking water of a rural family. During the rainy season (July–September), only two jerrycans were filtered daily (40 L), as villagers often spent the whole day on the fields tending their crops. Sampling of raw and filtered water was performed weekly in the first two months after filter installation, then twice per month by an employee of the NGO. Due to accessibility problems to the village during the rainy season, sampling was more sporadic from August to October. Samples (4–5 mL) were collected unfiltered in 5 mL pre-acidified vials (150 µL 1 M HNO<sub>3</sub> suprapure) and shipped to Eawag, Switzerland, for analysis using ICP-MS (Agilent 7500cx). In addition, filtered samples (0.2 µm) were taken on a monthly basis and As speciation investigated using silicate filter cartridges that pass As(III) and retain As(V) (Meng and Wang, 1998).

## 2.2. Laboratory experiments

### 2.2.1. Laboratory filter construction and set-up

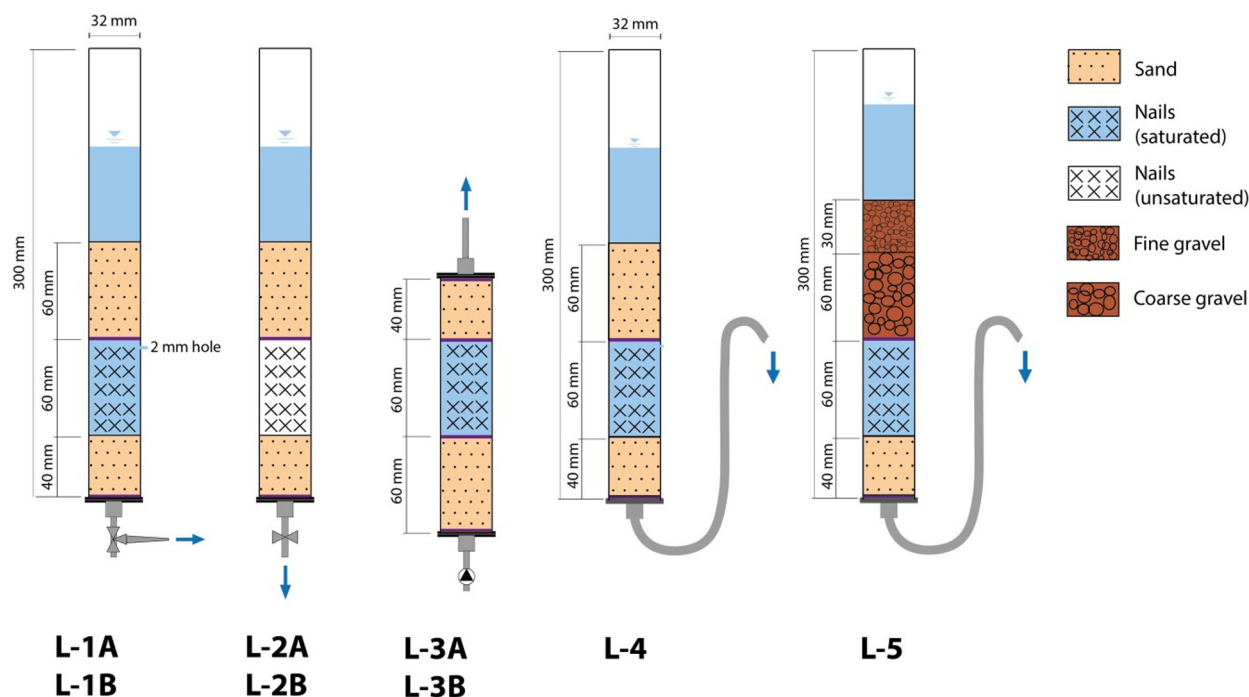
Downscaled laboratory filters for filtration of 3–8 times 113 mL water per day were constructed from acrylic glass tubes with an inner diameter of 32 mm and a height of 300 mm. The vertical dimensions of the active nail layer (consisting of 80–100 g iron nails) were the same as in the field filters (60 mm). The reduction of the diameter by a factor of 10 allowed for a reduction of the flow by a factor of 100, while maintaining the same range of vertical flow velocities and contact times as in the field filters. The equivalent volume of water per filtration of 200 mL was reduced to 113 mL to achieve similar average As loads per filtration as in the field (As concentrations in the laboratory were by a factor 1.5–1.8 higher than in the field).

Initially, three different filter column variations were tested in duplicate (L-1A/L-1B, L-2A/L-2B, L-3A/L-3B), with L-2A/L-2B being identical in their set-up to filters F-1, F-2 and F-4 tested in Burkina Faso (Fig. 2, Table 1, Table SI-1). As opposed to field filters, nails were not pre-treated with vinegar to enhance initial corrosion. Laboratory experiments showed that treatment with vinegar or other acids was not necessary to start corrosion. As observed through the transparent columns, corrosion started within 1–2 days after the experiment was started.

### 2.2.2. Influent water composition in laboratory experiments

Natural groundwater was used as influent water for the columns, with some adjustments to the water composition to mimic groundwater chemistry in Burkina Faso. Freshly pumped groundwater from a





**Fig. 2.** Diagram showing the set-up of the five different filter columns. Columns L-2A and L-2B represent the same set-up as filters F-1, F-2 and F-4 installed in Burkina Faso. Columns L-1A and L-1B were operated with a constantly water-saturated nail layer, as were the up-flow columns L-3A and L-3B. Columns L-4 and L-5 were constructed after the de-commissioning of columns L-2A/L-2B and L-3A/L-3B in September 2017. Column L-5 represents the same set-up as the modified field filters (F mod. 1, 2, 4). The raised outflow ensures that the water level always remains above the nail layer. Vertical dimensions of the iron layers were the same as in field filters, while the diameter (at the height of the ZVI-layers) was 10-times reduced. Flow rates were thus by a factor of 100 smaller than in the field filters (80–120 mL/h), but the vertical flow velocity and contact time with ZVI was in the same range (Table SI-1).

groundwater well on the Eawag campus (Switzerland) was diluted 1:1 with deionised water and Si concentration raised to 10–15 mg/L by adding  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ . As(V) or As(III) were spiked to attain the desired As concentration (500  $\mu\text{g/L}$  or 1000  $\mu\text{g/L}$ ). A comparison of the water composition of the two tube wells in Burkina Faso with the Swiss groundwater adjusted in the laboratory is presented in Table 2. Small

differences in water composition remained, with adjusted groundwater having higher  $\text{Cl}^-$  and lower Mg concentrations than the groundwater in Burkina Faso. Higher concentrations of  $\text{Cl}^-$  may enhance ZVI corrosion, but the effect of the low  $\text{Cl}^-$  concentration (0.70 mM) in our prepared groundwater can be expected to be minor. Increasing rates of corrosion reactions with increasing  $\text{Cl}^-$  are observed at higher concentrations, e.g. from 20 to 1000 mM (Caceres et al., 2007). Divalent cations such as  $\text{Mg}^{2+}$  may also lead to faster corrosion through depassivation of the ZVI surface by freeing the ZVI sites from Fe(III) oxides (Liu et al., 2014; Zhang et al., 2019). Considering that enhanced corrosion should have a positive effect on As removal (due to higher  $\text{Cl}^-$  in adjusted groundwater and higher  $\text{Mg}^{2+}$  in field groundwater), the differences in water composition should not be relevant for comparability of laboratory and field results. The pH-values of the synthetic groundwater (stored in a 20 L PE-reservoir) was adjusted to pH values from 6.2–7.8 by addition of  $\text{CO}_2$  to investigate the influence of pH on As-removal. For some periods, the pH was allowed to increase to 8.5.

**Table 2**

Chemical composition of influent groundwater in Burkina Faso and adjusted groundwater used for the laboratory column experiments.

Location	Souriyala Hollé (BF) old well	Souriyala Hollé (BF) new well	Eawag (CH) groundwater	Eawag adjusted groundwater
Filter IDs	F-2, F-4	F-1, GEH-1		All columns
pH	7.0	6.4	8.3	6.5–7.5
EC $\mu\text{S/cm}$	666	352	674	365
DO $\text{mg/L}$	1.31 <sup>a</sup>	2.65 <sup>a</sup>	1.8	8–9
Temp $^\circ\text{C}$	31.3	30.6	4–12	22–24
Redox $\text{mV}$	361	398		
DOC $\text{mg C/L}$	1.2	1	1.3	0.8
Alkalinity $\text{mmol/L}$	7.7	4	5.8	3.1
Cl $\text{mg/L}$	2.2	0.7	48.3	24.6
$\text{NO}_3^-$ -N $\text{mg NO}_3^-/\text{N/L}$	<0.25	<0.25	2.7	1.3
$\text{SO}_4$ $\text{mg/L}$	12.6	5.9	29	14
Na $\text{mg/L}$	41	14	31	18
Mg $\text{mg/L}$	39	30	16	8.0
Ca $\text{mg/L}$	61	20	103	51
K $\text{mg/L}$	1.5	0.8	4.6	2.7
P $\text{mg/L}$	< 0.01	< 0.01	< 0.01	< 0.01
Si $\text{mg/L}$	20.3	7.8	4.5	10–15
Fe $\mu\text{g/L}$	60	68	< 10	< 10
As $\mu\text{g/L}$	419	1000	< 0.1	500–1000

<sup>a</sup> The oxygen concentration after contact with air in the jerrycans and in the top of the filters was close to saturation before the water entered the filters (8.2–8.8 mg/L for laboratory columns operated at 22–24  $^\circ\text{C}$  and 7.2–7.6 mg/L for field filters operated at 30–35  $^\circ\text{C}$ ).

### 2.2.3. Operation of the laboratory columns and adjustments

An influent water volume of 113 mL was pumped into the columns three times daily. All columns were operated in gravity driven down-flow mode (to reflect conditions in the field filters) except L-3A and L-3B, which were operated in reversed up-flow to maintain a constantly saturated nail layer. The approximate flow rate of 10 L/h used in the field was downscaled to an ideal rate of 106 mL/h (1.77 mL/min) for the columns (Table 1). This flow rate could only be maintained constant for columns L-3A and L-3B (up-flow controlled by a peristaltic pump), whereas the gravity-filtered columns experienced variations in flow rate during each filtration due to the changes in water level and hydrostatic pressure. This effect cannot be avoided and also occurs in the field filters. The flow rate of columns L-1A and L-1B was regulated by flow restrictors (fine pipette tips) at the outlets of the columns (Fig. 2). The columns were filmed with a time lapse camera (30 s resolution), to

record the duration of each filtration. Together with the volume of the collected water, an average flow rate could be calculated for each filtration.

In the filters with outflows located below the columns, air was drawn into the ZVI layer between filtrations. The trapped air could subsequently not escape due to the closed pore space of the moist sand above. To allow trapped air to escape, a small hole ( $\varnothing$  2 mm) was drilled into columns L-1A and L-1B above the nail layer and was opened when needed. Measures to remove trapped air were not taken for columns L-2A and L-2B.

The laboratory columns L-1A, L-1B, L-2A, L-2B, L-3A and L-3B were operated for six weeks in July/August 2017. At the end of this period, columns L-2A and L-2B were de-installed, as results had shown that trapped air accumulated in the nail layers resulted in insufficient As removal. The up-flow columns L-3A and L-3B were also discontinued, as they yielded similar results as the down-flow columns L-1A and L-1B, with the latter better representing the conditions in the gravity driven field filters. As a replacement, two additional columns with an improved design were constructed (column L-4 and L-5). In these columns, the development of trapped air was avoided and the nail layer constantly kept saturated by raising the outlet to 1–5 mm above the upper limit of the nail layer (Fig. 2, Table 1). In column L-5, the top sand layer was additionally replaced by gravel, to enable any trapped air to move into the large pore spaces provided by the gravel. In March 2018, seven months after the start of the experiment, columns L-1A and L-1B were discontinued. The remaining columns, L-4 and L-5, were then operated in series for four weeks. This means that inflowing water first went through column L-4 before directly flowing into column L-5. The reason for this change was to observe whether As concentrations in the outflow could be further reduced with this set-up, especially when higher flow rates and larger inflow volumes were applied. The number of filtration cycles per day was increased from three to eight in the in-series

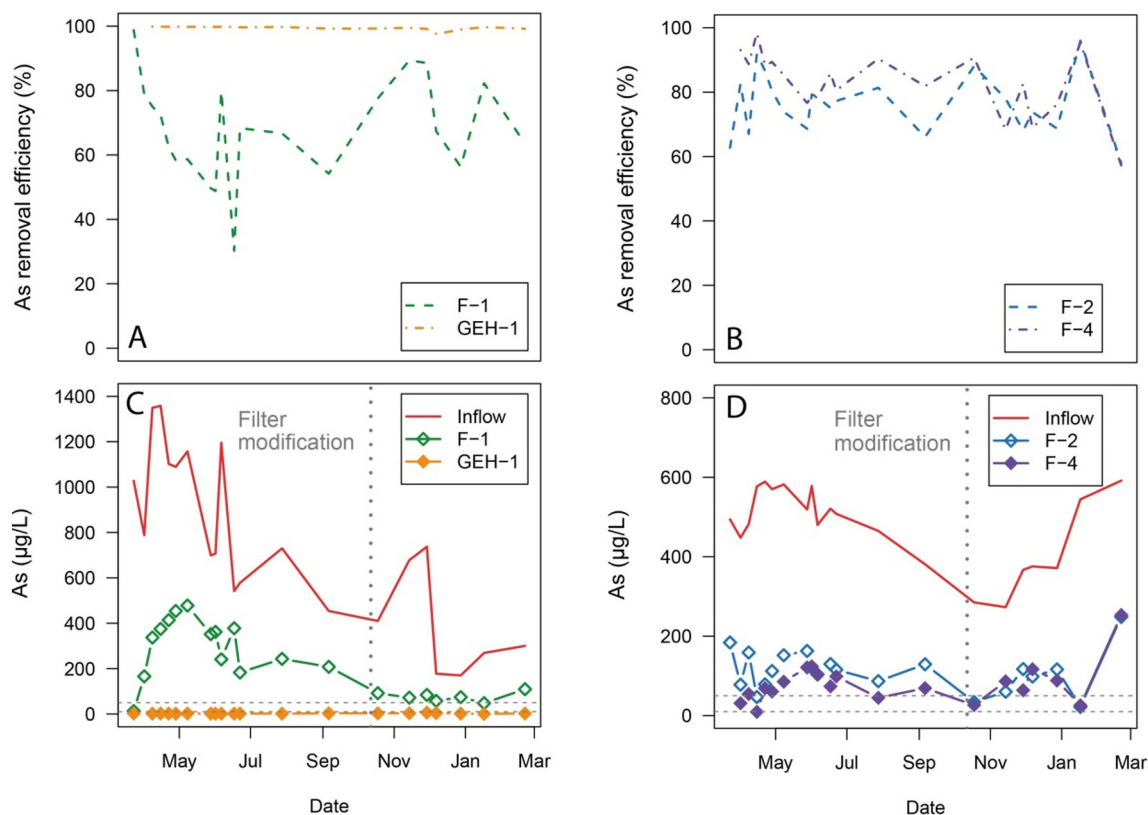
experiment. Additionally, in order to investigate whether arsenic is easily leached from the iron nails, the columns were operated with inflowing groundwater containing no arsenic for two weeks.

#### 2.2.4. Aqueous sampling and analysis

In the first two weeks after installation, effluent water was sampled after each filtration (three times daily). This was then reduced to daily sampling (mixed samples of three filtrations) and later three times a week (mixed samples of seven filtrations). When inflow pH was low ( $< 7$ ) and the column effluent contained visible Fe solids, filtered samples ( $0.2 \mu\text{m}$ ) were additionally taken. Every time new influent groundwater was mixed, a sample was taken for analysis. The pH and dissolved  $\text{O}_2$  values of the influent water were measured three times per week. All water samples (influent and effluent) were acidified with  $\text{HNO}_3$  suprapure and analysed for total concentrations of As, Ca, Mg, K, P, Si, Mn and Fe using ICP-MS (Agilent 7500cx).

#### 2.2.5. Solid sampling and analysis

The solid phases that developed on the surface of the nails were investigated using X-ray diffraction (XRD). Some nails and water of column L-3A were removed from the column under exclusion of air and shaken overnight to dislodge the coating of the nails. The slurry with suspended solids was removed from the nails and then centrifuged. The concentrated black residue was spread on a silicon wafer, dried under an  $\text{N}_2$  atmosphere and analysed with X-ray diffraction (Panalytical Expert<sup>3</sup> Powder with Co source) twice for 60 min. Between the two measurements, the sample was exposed to air to allow for oxidation of the unstable reduced Fe phases. Solid phase analysis of iron products from the field filters was not carried out, as an anoxic transport of nails from Burkina Faso to the laboratory at Eawag in Switzerland was not possible.



**Fig. 3.** Diagram showing the performance of the four filters installed in the village of Souriyala. The bottom diagrams (C, D) depict the inflow and outflow As concentrations of filters F-1, F-2 and F-4 (nail-based), as well as of the GEH filter (GEH-1). Corresponding As removal efficiencies are plotted on the top diagrams (A, B). The horizontal dashed grey lines indicate the 10 µg/L and 50 µg/L guideline values and the vertical dashed line marks the date of the filter modification.

### 3. Results

#### 3.1. Field experiment

The field filters F-1, F-2, F-4 and GEH-1 were monitored over a period of twelve months (Fig. 3). Filter F-1 and GEH-1 received water from the same tube well, with very high inflow As concentrations fluctuating between ~500 and ~1350 µg/L. Filters F-2 and F-4 were operated with water from the slightly less contaminated well (~350 – ~600 µg/L). The lowest inflow groundwater As concentrations were observed during the months of the rainy season (Jul – Oct) (Fig. 3).

The capacity of the nail-based filters to remove As varied considerably over the 12 month monitoring period (Fig. 3). From March to September, filter F-1 showed an average As removal efficiency of 65%, filter F-2 77% and filter F-4, which contained the smaller sized nails, 86%. None of these filters removed As consistently to <50 µg/L, with filter F-4 overall showing the most promising results. Only the GEH-based filter (GEH-1) always yielded effluent As concentrations of <10 µg/L and an As removal efficiency of 99%.

After the structural modification of the nail-based filters in October 2017 (see Fig. 1 for details of the set-up), the mean As removal efficiency of filter F-1 improved markedly to 85%, though the outflow As concentrations were still slightly above 50 µg/L due to the very high As inflow (Fig. 3). An even clearer improvement was achieved in Filters F-2 and F-4 in the week after the modification, with As concentrations in filtered water dropping to below 50 µg/L and removal efficiency rising to 90%. Unfortunately, both filter's performance then decreased, with effluent concentrations of 60–100 µg/L. A possible reason could be insufficient control of flow conditions and the positions of the outlets by the users,

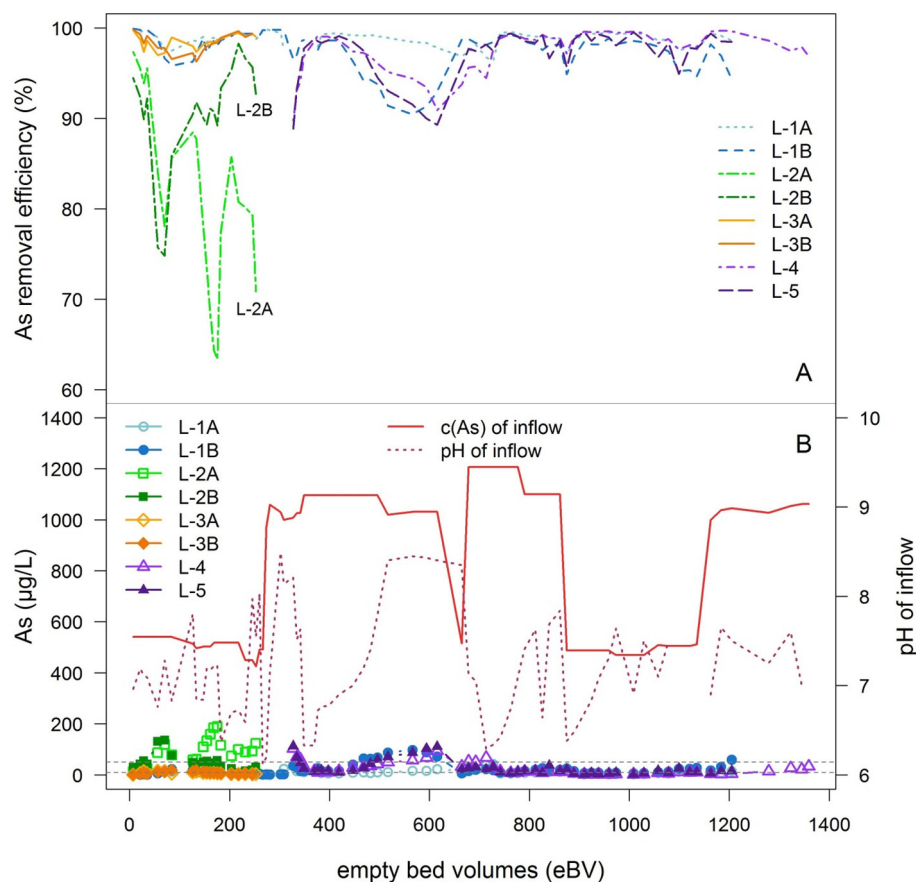
leading to fast flow or a drop in water level, exposing the nails to air. In general, filter F-4 performed consistently better than F-2 over most of the operation period, most likely due to the smaller nail size used in F-4 and correspondingly higher specific surface area and Fe-oxide production.

The Fe concentrations in the filtered water of F-1, F-2 and F-4 were always below 150 µg/L, showing that the sand filter in the bottom bucket is sufficient to remove the Fe-oxides and remaining Fe(II) in the water after passing the nail layer.

#### 3.2. Laboratory experiments

##### 3.2.1. Arsenic removal

The performance of all columns over the total operation period of eight months is illustrated in Fig. 4. The filter columns L-1A/L-1B, L-2A/L-2B and L-3A/L-3B were continuously run for six weeks (Jul-Aug 2017) with three filtrations daily. Arsenic concentrations in the outflow of columns L-1A/L-1B and L-3A/L-3B (with a constantly saturated nail layer) always remained below 25 µg/L, and below 10 µg/L in 82% (L-1A/L-1B) and 70% (L-3A/L-3B) of samples. The mean As removal efficiency for columns L-1A/L-1B and L-3A/L-3B was 98.5% during this period. Columns L-2A/L-2B, with the same set-up as the filters in the field initially had, performed less well. Arsenic concentrations in these columns were always above 10 µg/L and frequently above 100 µg/L, with mean As removal efficiencies of 80% (L-2A) and 90% (L-2B). In contrast to columns L-1A/L-1B and L-3A/L-3B, a gas phase that was easily visible by eye through the transparent columns developed in the nail layer of columns L-2A and L-2B and water therefore trickled over only limited sections of the nail layer in preferential flow paths. The



**Fig. 4.** Arsenic removal efficiency (top diagram, A) and influent/effluent As concentrations (bottom diagram, B) of the column experiments as a function of filtered bed volumes. Columns L-2A/L-2B and L-3A/L-3B were dismantled after six weeks of operation (~250 eBV) and the new columns L-4 and L-5 subsequently started. The dashed grey horizontal lines indicate the 10 µg/L and 50 µg/L guideline values. Flow rates varied from 80 to 160 mL/h, resulting in down-flow velocities of 10–20 cm/h. The major influence on As-removal was the pH and entrapped air in columns L-2A/L-2B.

insufficient As-removal can thus be attributed to insufficient contact areas and times due to preferential flow. The improvement of the performance of column L-2B after 100 bed volumes (three weeks of operation) in comparison to L-2A (Fig. 4) can be attributed to the development of a 1.5 cm thick water-saturated layer at the bottom of the nail layer.

Columns L-1A/L-1B were kept operational after the deactivation of columns L-2A/L-2B and L-3A/L-3B and showed continuously good As removal, with the exception of a period of three weeks between bed volumes 500–700 when the input pH was very high at 8.5 (Fig. 4). New columns (L-4 and L-5) constructed in September 2017 (after 350 bed volumes) with a raised outflow (to keep the nail layer saturated), displayed very good As removal, despite the larger nails used in these columns (Fig. 4). With the exception of the first days after column construction when the nails were not yet sufficiently corroded and of the high-pH period, As concentrations in columns L-4 and L-5 remained below 50 µg/L in 95% and below 10 µg/L in 36% of samples. The mean As removal efficiency for both columns was 97%.

After 1400 bed volumes, columns L4 and L5 were operated in a vertical arrangement in series. In Fig. 5, S4 denotes the outlet of the upper column L4, S5 denotes the outlet of lower column L5. With this arrangement, higher flow rates and a higher number of filtrations per day still resulted in satisfactory As removal (< 20 µg/L) at the outflow of the second column (S5) even with an inflow concentration of 1000 µg/L (Fig. 5). When the inflow contained no As (eBV 200–380), effluent concentrations dropped to below 8 µg/L, indicating that As is not leached from the nails but rather tightly bound to the formed Fe(II, III)-oxides.

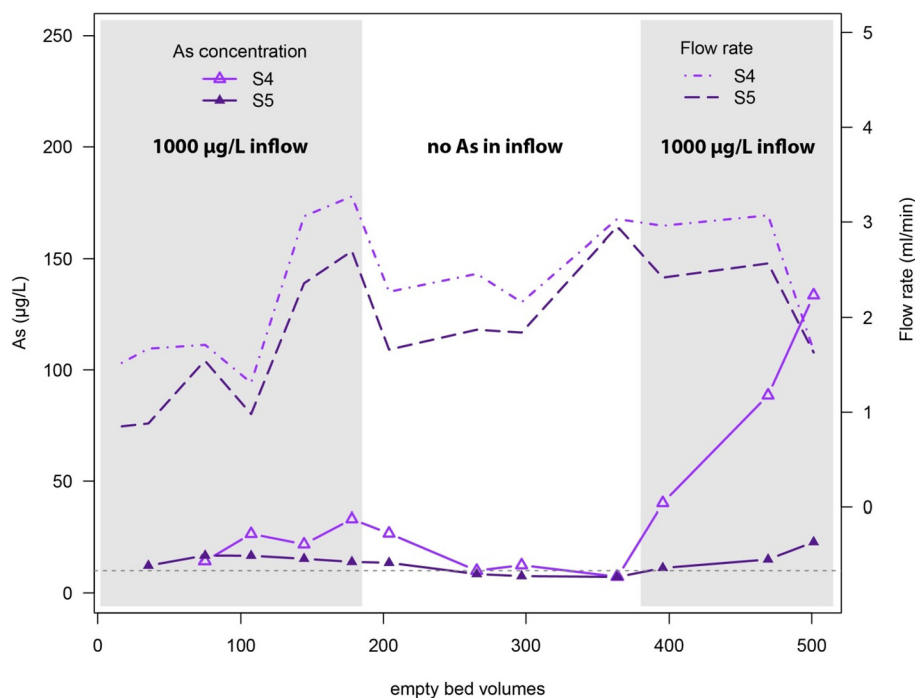
### 3.2.2. Fe and Ca concentrations

The pH-value of the influent water was observed to be highly influential on the Fe corrosion rate, Fe(II) production and the rate of Fe(II) oxidation (Fig. 6). At an influent pH < 6.5, Fe concentrations in the column effluent rose markedly due to the increased corrosion and the decreased oxidation rate for Fe(II). The collected effluent water was orange-coloured from suspended Fe(III) precipitates. A comparison between As concentrations of filtered and unfiltered samples during this

period showed that As leaving the columns sorbed to these Fe(III)-oxides, with aqueous As concentrations generally lower in filtered than in unfiltered samples (Fig. SI-1). In contrast, virtually no Fe was present in the effluents during a period of high pH-values (> 8.0) between empty bed volume 500–700, with effluent Fe concentrations below 0.02 mg/L in all columns (Fig. 6), due to decreased corrosion rates at higher pH. This also had a clear effect on As removal, with outflow As concentrations rising due to a lack of freshly produced Fe(III)-oxides for co-precipitation (Fig. 6). In the most relevant pH-range from 6.5–7.5, Fe(II) production rates seem to be sufficient for effective As removal. Effluent Ca concentrations show a similar pattern as Fe (Fig. 6) and rose above influent levels during the low-pH phases, possibly due to the dissolution of CaCO<sub>3</sub> that accumulated on the nail surfaces when the pH was >7.5 (Wenk et al., 2014). Influent Ca concentrations were higher for the first three datapoints shown in Fig. 6 as undiluted groundwater was mistakenly used, but this had no long-term effect.

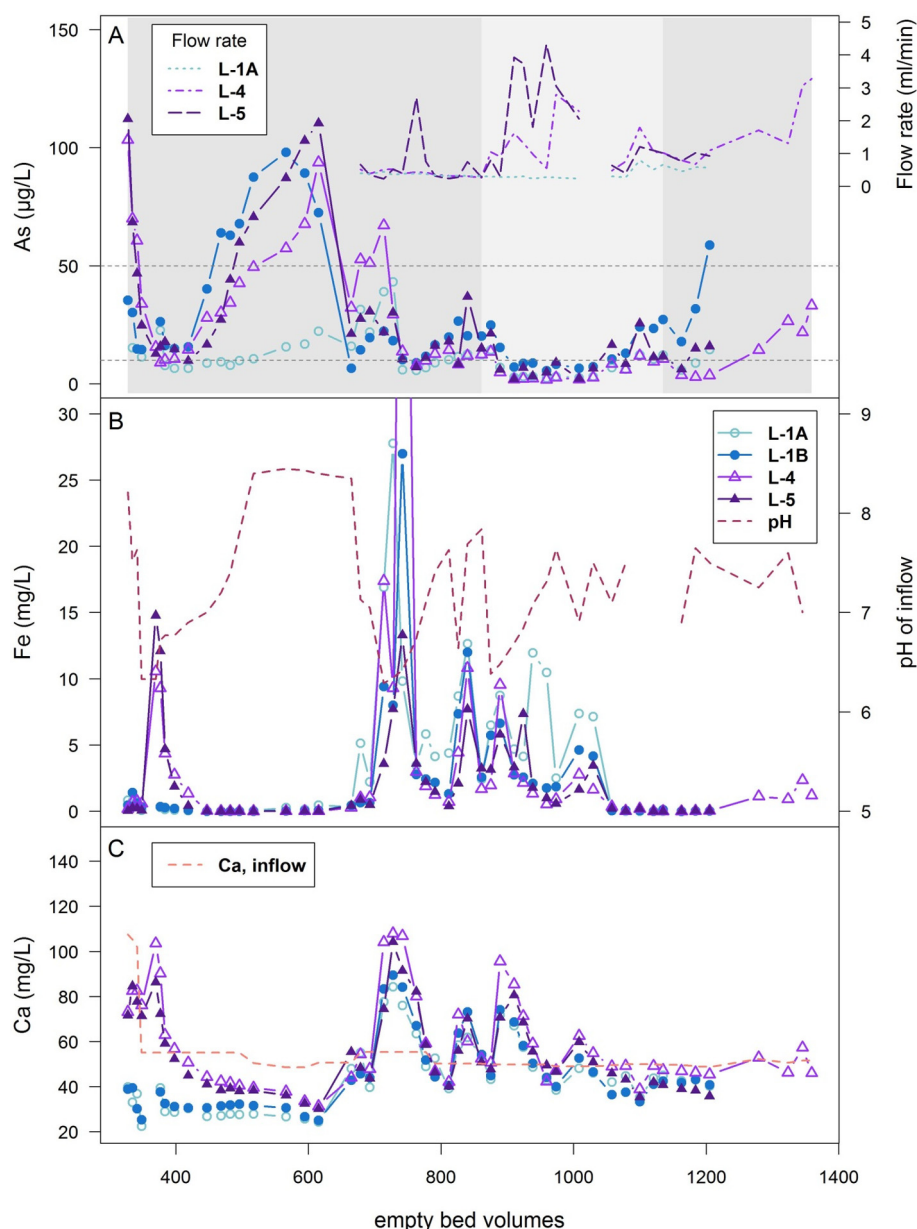
### 3.2.3. Influence of flow rate on As removal

The rate at which the inflow water flowed through the filter bed was expected to have an influence on the effectiveness of As removal, with higher flow rates leading to decreased As removal due to decreasing water-to-nail contact time. Fig. 6 (top graph) shows that within the range of tested flows, this was only partly the case. Despite a large difference and fluctuations in flow rates between columns L-1A and L4/L5 (e.g. bed volume 700–1000), As removal in all three columns was very similar during this period. On the other hand, from bed volume 1200 onward, some apparent correlation between flow rate and As removal can be observed for column L4. In this period, not only the flow rate, but also the frequency of filtrations was increased (from 3 times daily to 8 times daily). This means that pauses between filtrations were significantly reduced, diminishing the contact time of the standing water with the nails in-between filtration cycles. We hypothesise that this effect is partly responsible for the reduction in As removal and less so the actual flow rate of each individual filtration.



**Fig. 5.** Results of the in-series column experiment, where inflowing water first flowed through column L4 (outlet S4) and then directly into L5 (outlet S5). Arsenic concentrations are plotted on the left y-axis and flow rates on the right y-axis. The grey background indicates an As concentration of 1000 µg/L in the inflow, the white background an inflow with no As. The grey dashed horizontal line represents the 10 µg/L guideline value. Instead of three filtrations per day as in all preceding experiments, eight daily filtration cycles of still 113 mL each were performed.





**Fig. 6.** Arsenic (panel A), Fe (panel B) and Ca (panel C) concentrations in columns L-1A/L-1B, L-4 and L-5. The flow rates (A) and pH (B) are plotted on the second y-axes. The flow rate data series only starts at eBV ~650, as measurement of flow rates was not continuous before. Dark grey background shading in panel A corresponds to an As inflow concentration of ~1000 µg/L, light grey to ~500 µg/L. The dashed grey horizontal lines in the top diagram indicate the 10 µg/L and 50 µg/L values. Arsenic concentrations from empty bed volume 750 onward are those measured in filtered samples (0.2 µm). The pH was the major influence on fluctuating Fe and Ca concentrations.

### 3.2.4. Arsenic removal with As(III) inflow

In order to test the As removal efficiency of the columns when As occurs in its reduced form, As(III), columns L-1A/L-1B were run with As (III) in the inflow water (instead of As(V)) for a period of two weeks. Arsenic concentrations in the outflow water did not change significantly after the switch to As(III), staying mostly below 10 µg/L (Fig. SI-2). This suggests that As(III) is sufficiently oxidised to As(V) in the columns, as As(V) is the better sorbent to Fe oxides.

### 3.2.5. X-ray diffraction (XRD) of nail surfaces

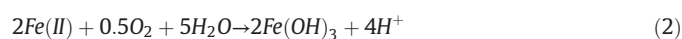
The most dominant phase identified in the X-ray diffractogram was magnetite (Fig. SI-3). The other detected Fe phase was carbonate green rust. After the sample had been exposed to air, the peak intensity of the unstable green rust had clearly decreased due to oxidation, while all other identified phases remained stable. The

presence of calcium carbonate and quartz was also indicated in the diffractogram, the latter possibly resulting from contamination by the sand used in the columns.

## 4. Discussion

### 4.1. Reactions

The oxidation of Fe(0) to Fe(II) and Fe(III) in oxygen-containing water is the main chemical reaction occurring in the nail layer of the columns and filters and can be summarised in the following equations:



Eq. (1) is an overall reaction equation that does not reflect the full complexities of corrosion reactions. In addition to reaction with Fe(0), O<sub>2</sub> can be reduced at cathodic sites consisting of Fe(II)-containing rust phases, while Fe<sup>2+</sup> is formed at anodic sites of exposed Fe(0). At circumneutral pH and under oxic conditions, O<sub>2</sub> is the main electron acceptor, while under anoxic conditions, H<sup>+</sup> reduction can occur at a slower rate (Furukawa et al., 2002; Matheson and Tratnyek, 1994; Noubactep, 2008; Sherar et al., 2011). Fe(OH)<sub>3</sub> in Eq. (2) represents Fe(III)(oxy)(hydr)oxide phases such as FeOOH, ferrihydrite or poorly crystalline lepidocrocite and other Fe phases (Neumann et al., 2013; Senn et al., 2015). If As is present in solution, it can sorb to and co-precipitate with the Fe phases formed during Fe corrosion:



As(V) generally sorbs better to Fe phases than As(III), but even if As occurs as As(III), the formation of reactive intermediates (H<sub>2</sub>O<sub>2</sub>, Fe(II, III, IV)) during the oxidation of Fe(0) and Fe(II) by O<sub>2</sub> can lead to the oxidation of As(III) to As(V) (Katsoyiannis et al., 2008). This explains the still good As removal observed in the filter columns when they were operated with As(III) instead of As(V) (Fig. SI-2). With increasing filter/column age, the generally amorphous Fe(II, III) phases can undergo structural transformation to more crystalline and stable compounds such as magnetite (Fe<sub>3</sub>O<sub>4</sub>) (Neumann et al., 2013). The formation of green rust and magnetite with incorporated As(V) (Neumann et al., 2013; van Genuchten et al., 2020; Zhang et al., 2019) occurs during paused flow due to the depletion of dissolved oxygen in the ZVI layer, formation of Fe(II) and rising pH. Magnetite and green rust were observed on the six week old surface of the nails (XRD data, Fig. SI-3). Magnetite formation is thought to have a positive effect on filter performance as it is less voluminous than brown amorphous Fe oxides, preventing filter clogging (Neumann et al., 2013). In addition, As is tightly bound in the crystal lattice of magnetite (Coker et al., 2006; Van Genuchten et al., 2019; van Genuchten et al., 2020) and should not be remobilised from the nails when the filter is not used or no longer needed (Hussam and Munir, 2007; Neumann et al., 2013). An indication of this was given in the in-series experiment, where As did not leach out of the column when the influent water contained no As (Fig. 5).

#### 4.2. Flow conditions

One of the main problems limiting As removal efficiency that was identified during the laboratory study was the presence of trapped air in the nail layer (columns L-2A/L-2B). Trapped air results in preferential flow, limiting the contact times with ZVI in preferential paths to only a few seconds and leading to decreased Fe(II) and Fe(III) production. Formation of trapped air probably also occurred in the filters in the field during the first six months of operation, explaining their less-than-expected As removal. The presence of air in the ZVI layer had not been expected, as SONO filters (similarly constructed), are not reported to experience this problem. Most likely, the higher surface area of SONO's Composite Iron Matrix (CIM), smaller pore size and higher capillary forces in comparison to nails retains water in the CIM instead of allowing it to drain out. Raising the water level permanently above the nail layer (columns L-4 and L-5) increased nail/water contact time and greatly improved As removal in the laboratory columns. The only partial success seen in the modified field filters at the time of writing is difficult to explain. It is possible that the raised outflow tube of filters F-2 and F-4 was pushed too far down into the recipient funnel by household users, lowering the water level again below the nail layer.

In the laboratory, As removal was still effective even when flow rates greatly exceeded 1.77 mL/min (equivalent to 10 L/h in the field). In the columns with saturated nail layers, 35–45% of the filtered water of each new filtration cycle is standing water from the previous filtration, that has been in contact with Fe oxides in the column for hours (depending on the frequency of filtration). The effect of flow rate is thus partly

buffered by water remaining in the filters between filtrations, but 55–65% of the effluent is still newly filtered water. This also reflects the real situation in households in Burkina Faso, where water is filtered 2–3 times daily. When the number of filtration cycles per day was increased from three to eight in the laboratory (in-series experiment), lowering the overall contact time of water to nails over the course of the day, As removal efficiency in the first column (L4, outlet S4) decreased clearly (Fig. 5). Besides contact time, other important factors influencing As removal in the conducted experiments were the pH of the inflow water and the specific surface area of the nails. At pH > 8, corrosion is slow and Fe(II) is very short-lived (few minutes to seconds (Millero et al., 1987)), oxidising and precipitating quickly as Fe(III)(oxy)(hydr)oxides on surfaces. Arsenic in the water then has less contact to the Fe(0) surface, where Fe(II) and Fe(III) are formed and As is removed via co-precipitation with Fe(III) (Katsoyiannis et al., 2008; Wenk et al., 2014). This is illustrated in the clear drop in As removal efficiency when inflow water had a pH of ~8.5 (Fig. 4, Fig. 6). Important are also longer pauses between filtration cycles that provide time for Fe(0) oxidation, depletion of oxygen, and formation of higher Fe(II) concentrations leading to solid phase transformations and As incorporation.

#### 4.3. Specific surface area and contact times

The specific surface area of a filter material is an important parameter as it determines the number of adsorption sites and the accessibility of the contaminant to the adsorbent (Crittenden et al., 2012). In the case of the nails, the higher the specific surface area, the higher Fe corrosion and the more Fe(II) and Fe(III) is produced for As sorption. In a direct comparison, filter F-4 generally outperformed F-2, the former using smaller nails with a slightly higher specific surface area (Fig. 3). The very effective As removal of the GEH filter in comparison to the nail filters is not surprising, considering that the specific surface area of GEH is six orders of magnitude larger than that of the nails (Table SI-1). In addition, GEH is composed of stable, oxidised Fe(III) phases and does not need to undergo the oxidation steps of Fe(0).

Even though As removal efficiency was high in the modified filters F-1, F-2 and F-4 (70–90%), they did not remove As to levels below 50 µg/L. This is certainly connected to the very high As concentrations (up to 1350 µg/L) of the two tube wells and the large volumes of water filtered per day (40–60 L), conditions that are at the extreme end for nail-based filters.

#### 4.4. Comparison with other filters

Other studies employing nail-based filters mostly worked with As input concentrations <400 µg/L (Banerji and Chaudhari, 2017; Chiew et al., 2009; Ngai et al., 2007; Singh et al., 2014; Smith et al., 2017). Two newer studies tested filters with nails or iron filings mixed with sand. The Chinese NIS ("nails-in-sand") filter tested by Smith et al. (2017) used a relatively thin layer (3–4 cm) of 5 kg nails mixed with sand, positioned between an 8 cm upper and a 30 cm lower layer of sand in an 80 L bucket. This filter removed As to <50 µg/L for six months, but the As inflow concentrations were lower (150–350 µg/L) and less water was filtered per day (~20 L), limiting comparability with the filters in Burkina Faso. Smiech et al. (2018) tested filter columns (25 cm diameter, 150 cm length) with a 25 cm active layer of 600 g iron filings mixed with 12 L dry sand at the top of the column (iron filings with a diameter 0.3–1.25 mm were produced by a metal sawing machine). The columns were operated for 230 days in continuous down-flow (6 L/h) with As(III) input concentrations of 70 µg/L with occasional peaks up to 230 µg/L. Median outflow concentrations were 9.9 µg/L, but started to rise after 200 days, which was attributed to the depletion of the iron layer. Due to the different designs and operation, it is difficult to directly compare the different filters, but the following recommendations can be made.

#### 4.5. Design and operation of filters

For the treatment of water with high concentrations of As(III) and As(V), iron filters without sand in the ZVI-layer and operated with longer pauses between filtrations have the following advantages: (1) While continuous flow of aerated water results in the formation of brown iron(hydr)oxides consisting of mainly ferrihydrite, goethite and lepidocrocite (Smiech et al., 2018), intermittent operation results in formation of green rust and magnetite (Neumann et al., 2013). Since magnetite is much denser than iron(hydr)oxides, clogging is less likely. (2) Loosely packed ZVI layers have a higher porosity (0.63–0.79) than sand (0.4), resulting in longer contact times and in better access of water to the corroding iron surfaces. For the formation of green rust and magnetite, the iron layers need to remain saturated between filtrations, which can be achieved with outlets raised above the top of the iron layer. Future designs should raise the water level at least 5–10 cm above the nail layer and make sure that the raised outlet cannot be tampered with. Replacing the CIM of SONO-filters with nails results in a smaller specific Fe(0)-surface area, which makes slow and controlled flow more important. Users of the filters have to regularly observe, clean and adjust the flow at the outlet taps and ensure that the flow velocity in the filter does not exceed 20 cm/h (16 L/h in filters with a diameter of 320 mm). As this can be challenging in day-to-day operation, installing simple flow-regulating valves might be an adept measure to facilitate flow control.

#### 5. Significance and implications

To our knowledge, zero-valent iron-based household filters were field-tested for the first time in As-affected areas of West Africa. With influent concentrations of 400–1300 µg/L, As was reduced by an average of ~70% and for 300–600 µg/L by an average of ~80%. The filters did not undergo any maintenance during the trial period of twelve months, nor did users report any clogging. However, the combined effects of very high As input concentrations and filtered volumes of 40–60 L/d, with not well-controlled flows resulted in effluent As concentrations above the older limits of 50 µg/L and the new limit of 10 µg/L. The efficiency thus needs to be improved, either by employing a ZVI material with a higher surface area (iron filings, steel wool), by adding another nail bed, or ultimately by an adapted design and operation of the described filter. The parallel experiments with the downsized laboratory filters have shown that the filters can reach the limit of 50 µg/L, if flow conditions are controlled and preferential flow and inclusion of air is avoided. Careful construction of the filters in the field with a homogeneous nail-bed and a raised outflow position ensuring constant immersion of the nails should achieve the same laminar flow of water during filtrations as in the laboratory columns. Controlling the proper fabrication and operation of filters is currently a challenge in the villages where As removal is most urgent, even though these filters could, in the future, also provide opportunities for local entrepreneurs or social businesses.

Due to lack of other water sources, alternatives to As removal may not be available. Even with optimized nail filters, effluent concentrations below 10 µg/L are unlikely to be achieved, but the less stringent older limit of 50 µg/L, which is still valid in Bangladesh and other countries, can be reached, even with high input concentrations. In India, for example, the permissible limit for As in the absence of an alternate source of water is 50 µg/L (BIS, 2012). Since visible signs of arsenicosis are rarely observed with 50 µg/L and cancer risks are assumed to be linear with As concentration (Schmidt, 2014), a reduction of As concentrations from 400 to 1000 µg/L down to below 50 µg/L results in large health benefits (WHO, 2018).

For less contaminated wells where As is between 10 and 100 µg/L, the simple nail filter is likely to lead to outflow concentrations of <10 µg/L, although further field trials would be needed to confirm this hypothesis. 80–90% of As-affected tube wells in Burkina Faso have

concentrations between 10 and 100 µg/L (Bretzler et al., 2017). Nevertheless, the high-As tube wells (concentrations >100 µg/L) remain of largest health concern for the population, with the cancer risk rising greatly at these exposure levels (Argos et al., 2010; Soheli et al., 2009). Although the longer-term goal has to be compliance with the 10 µg/L guideline, implementation of technologies that can reach the 50 µg/L are preferable as an intermediate solution to no action at all. Additionally, a focus should lie on finding or producing suitable scrap iron filings and turnings with a high specific surface area to use in a SONO-style composite iron matrix. Steel wool could also be a promising material due to its high surface area and reactivity (Lufingo et al., 2019; Tepong-Tsinde et al., 2019). If nails are used, then a constant saturation of the nail bed and several hours of pause between filtrations need to be guaranteed in order to maximise As removal efficiency.

#### CRedit authorship contribution statement

**Anja Bretzler:** Conceptualization, Formal analysis, Investigation, Writing - original draft, Writing - review & editing, Visualization. **Julien Nikiema:** Conceptualization, Investigation, Resources. **Franck Lalanne:** Conceptualization, Resources. **Lisa Hoffmann:** Methodology, Investigation. **Jagannath Biswakarma:** Investigation. **Luc Siebenaller:** Resources, Project administration. **David Demange:** Resources, Project administration. **Mario Schirmer:** Supervision, Project administration. **Stephan J. Hug:** Conceptualization, Supervision, Methodology, Resources, Writing - review & editing.

#### Declaration of competing interest

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

#### Acknowledgements

Many thanks to the team of the NGO “Le Soleil dans la Main”, especially Adèle Ouédraogo and Didier Kienou for the organization and support of the field trials. Thank you to Moustapha Ouédraogo (2iE) for assembling the filter buckets and to the villagers of Souriyala for their collaboration and cooperation. We are grateful to Thomas Rüttimann (Eawag) for ICP-MS analysis and technical support. We gratefully acknowledge Carsten Bahr of GEH Wasserchemie GmbH & Co. KG in Osnabrück for supplying GEH free of charge for research purposes. Thanks also to Guillaume Clair (Eawag) for helpful discussions and to all people that transported water samples from Ouagadougou to Switzerland. Funding for this study was provided by the Swiss Agency for Development and Cooperation (SDC) through the “Programme 3E” (contract no. 81016359) and the Information Management System on Geogenic Contaminants, GAP (contract no. 81025383).

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2020.139466>.

#### References

- Ahouél, D., Lalanne, F., Mendret, J., Brosillon, S., Maïga, A., 2015. Arsenic in African waters: a review. *Water Air Soil Pollut.* 226 (9), 1–13. <https://doi.org/10.1007/s11270-015-2558-4>.
- Argos, M., Kalra, T., Rathouz, P.J., Chen, Y., Pierce, B., Parvez, F., Islam, T., Ahmed, A., Rakibuz-Zaman, M., Hasan, R., Sarwar, G., Slavkovich, V., Van Geen, A., Graziano, J., Ahsan, H., 2010. Arsenic exposure from drinking water, and all-cause and chronic-disease mortalities in Bangladesh (HEALS): a prospective cohort study. *Lancet* 376 (9737), 252–258.



- Banerji, T., Chaudhari, S., 2017. A Cost-Effective Technology for Arsenic Removal: Case Study of Zerovalent Iron-Based IIT Bombay Arsenic Filter in West Bengal Water and Sanitation in the New Millennium. Springer, pp. 127–137.
- Bang, S., Korfiatis, G.P., Meng, X., 2005. Removal of arsenic from water by zero-valent iron. *J. Hazard. Mater.* 121 (1–3), 61–67. <https://doi.org/10.1016/j.jhazmat.2005.01.030>.
- Berg, M., Luzzi, S., Trang, P.T.K., Viet, P.H., Giger, W., Stüben, D., 2006. Arsenic removal from groundwater by household sand filters: comparative field study, model calculations, and health benefits. *Environ. Sci. Technol.* 40 (17), 5567–5573. <https://doi.org/10.1021/es060144z>.
- BIS, 2012. Indian Standard Drinking Water Specification (Second Revision). Bureau of Indian Standards, New Delhi.
- Bretzler, A., Lalanne, F., Nikiema, J., Podgorski, J., Pfenninger, N., Berg, M., Schirmer, M., 2017. Groundwater arsenic contamination in Burkina Faso, West Africa: predicting and verifying regions at risk. *Sci. Total Environ.* 584–585, 958–970. <https://doi.org/10.1016/j.scitotenv.2017.01.147>.
- Bundschuh, J., Litter, M., Ciminelli, V.S.T., Morgada, M.E., Cornejo, L., Hoyos, S.G., Hoinkis, J., Alarcón-Herrera, M.T., Armienta, M.A., Bhattacharya, P., 2010. Emerging mitigation needs and sustainable options for solving the arsenic problems of rural and isolated urban areas in Latin America – a critical analysis. *Water Res.* 44 (19), 5828–5845. <https://doi.org/10.1016/j.watres.2010.04.001>.
- Caceres, L., Vargas, T., Herrera, L., 2007. Determination of electrochemical parameters and corrosion rate for carbon steel in un-buffered sodium chloride solutions using a superposition model. *Corros. Sci.* 49 (8), 3168–3184. <https://doi.org/10.1016/j.corsci.2007.03.003>.
- Chiew, H., Sampson, M.L., Huch, S., Ken, S., Bostick, B.C., 2009. Effect of groundwater iron and phosphate on the efficacy of arsenic removal by iron-amended bios and filters. *Environ. Sci. Technol.* 43 (16), 6295–6300. <https://doi.org/10.1021/es803444t>.
- Coker, V.S., Gault, A.G., Pearce, C.L., Van Der Laan, G., Telling, N.D., Charnock, J.M., Polya, D.A., Lloyd, J.R., 2006. XAS and XMCD evidence for species-dependent partitioning of arsenic during microbial reduction of ferrihydrite to magnetite. *Environ. Sci. Technol.* 40 (24), 7745–7750. <https://doi.org/10.1021/es060990+>.
- Crittenden, J.C., Trussell, R.R., Hand, D.W., Howe, K.J., Tchobanoglous, G., 2012. *MWH's Water Treatment: Principles and Design*. John Wiley & Sons.
- Dixit, S., Hering, J.G., 2003. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: implications for arsenic mobility. *Environ. Sci. Technol.* 37 (18), 4182–4189.
- Driehaus, W., Jekel, M., Hildebrandt, U., 1998. Granular ferric hydroxide – a new adsorbent for the removal of arsenic from natural water. *J. Water Serv Res Tec* 47 (1), 30–35.
- Fu, F., Dionysiou, D.D., Liu, H., 2014. The use of zero-valent iron for groundwater remediation and wastewater treatment: a review. *J. Hazard. Mater.* 267, 194–205. <https://doi.org/10.1016/j.jhazmat.2013.12.062>.
- Furukawa, Y., Kim, J.W., Watkins, J., Wilkin, R.T., 2002. Formation of ferrihydrite and associated iron corrosion products in permeable reactive barriers of zero-valent iron. *Environ. Sci. Technol.* 36 (24), 5469–5475. <https://doi.org/10.1021/es025533h>.
- GEH Wasserchemie, 2013. *GEH 102: Granular Ferric Hydroxide for Arsenic Removal from Drinking Water*. GEH Wasserchemie GmbH & Co. KG, Osnabrück, Germany.
- van Genuchten, C.M., Behrends, T., Stipp, S.L.S., Dideriksen, K., 2020. Achieving arsenic concentrations of <1 µg/L by Fe(0) electrolysis: the exceptional performance of magnetite. *Water Res.* 168. <https://doi.org/10.1016/j.watres.2019.115170>.
- Van Genuchten, C.M., Behrends, T., Dideriksen, K., 2019. Emerging investigator series: interdependency of green rust transformation and the partitioning and binding mode of arsenic. *Environ. Sci. Process Impacts* 21 (9), 1459–1476. <https://doi.org/10.1039/c9em00267g>.
- Hering, J.G., Katsoyiannis, I.A., Theodulou, G.A., Berg, M., Hug, S.J., 2017. Arsenic removal from drinking water: experiences with technologies and constraints in practice. *Journal of Environmental Engineering (United States)* 143 (5). [https://doi.org/10.1061/\(ASCE\)EE.1943-7870.0001225](https://doi.org/10.1061/(ASCE)EE.1943-7870.0001225).
- Hug, S.J., Leupin, O., 2003. Iron-catalyzed oxidation of arsenic(III) by oxygen and by hydrogen peroxide: pH-dependent formation of oxidants in the Fenton reaction. *Environ. Sci. Technol.* 37 (12), 2734–2742. <https://doi.org/10.1021/es026208x>.
- Hug, S.J., Leupin, O.X., Berg, M., 2008. Bangladesh and Vietnam: different groundwater compositions require different approaches to arsenic mitigation. *Environ. Sci. Technol.* 42 (17), 6318–6323. <https://doi.org/10.1021/es7028284>.
- Hussam, A., Munir, A.K.M., 2007. A simple and effective arsenic filter based on composite iron matrix: development and deployment studies for groundwater of Bangladesh. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering* 42 (12), 1869–1878. <https://doi.org/10.1080/10934520701567122>.
- Inauen, J., Hossain, M.M., Johnston, R.B., Mosler, H.J., 2013. Acceptance and use of eight arsenic-safe drinking water options in Bangladesh. *PLoS One* 8 (1). <https://doi.org/10.1371/journal.pone.0053640>.
- Kanematsu, M., Young, T.M., Fukushi, K., Green, P.G., Darby, J.L., 2010. Extended triple layer modeling of arsenate and phosphate adsorption on a goethite-based granular porous adsorbent. *Environ. Sci. Technol.* 44 (9), 3388–3394. <https://doi.org/10.1021/es903658h>.
- Katsoyiannis, I.A., Zikoudi, A., Hug, S.J., 2008. Arsenic removal from groundwaters containing iron, ammonium, manganese and phosphate: a case study from a treatment unit in northern Greece. *Desalination* 224 (1–3), 330–339. <https://doi.org/10.1016/j.desal.2007.06.014>.
- Katsoyiannis, I.A., Mitrakas, M., Zouboulis, A.I., 2015. Arsenic occurrence in Europe: emphasis in Greece and description of the applied full-scale treatment plants. *Desalin. Water Treat.* 54 (8), 2100–2107. <https://doi.org/10.1080/19443994.2014.933630>.
- Kundu, D.K., Mol, A.P.J., Gupta, A., 2016. Failing arsenic mitigation technology in rural Bangladesh: explaining stagnation in niche formation of the Sono filter. *Water Policy* 18 (6), 1490–1507. <https://doi.org/10.2166/wp.2016.014>.
- Lackovic, J.A., Nikolaidis, N.P., Dobbs, G.M., 2000. Inorganic arsenic removal by zero-valent iron. *Environ. Eng. Sci.* 17 (1), 29–39. <https://doi.org/10.1089/ees.2000.17.29>.
- Leupin, O.X., Hug, S.J., 2005. Oxidation and removal of arsenic (III) from aerated groundwater by filtration through sand and zero-valent iron. *Water Res.* 39 (9), 1729–1740. <https://doi.org/10.1016/j.watres.2005.02.012>.
- Leupin, O.X., Hug, S.J., Badruzzaman, A.B.M., 2005. Arsenic removal from Bangladesh tube well water with filter columns containing zerovalent iron filings and sand. *Environ. Sci. Technol.* 39 (20), 8032–8037. <https://doi.org/10.1021/es050205d>.
- Lien, H.L., Wilkin, R.T., 2005. High-level arsenite removal from groundwater by zero-valent iron. *Chemosphere* 59 (3), 377–386. <https://doi.org/10.1016/j.chemosphere.2004.10.055>.
- Litter, M.I., Alarcón-Herrera, M.T., Arenas, M.J., Armienta, M.A., Avilés, M., Cáceres, R.E., Cipriani, H.N., Cornejo, L., Dias, L.E., Cirelli, A.F., Farfán, E.M., Garrido, S., Lorenzo, L., Morgada, M.E., Olmos-Márquez, M.A., Pérez-Carrera, A., 2012. Small-scale and household methods to remove arsenic from water for drinking purposes in Latin America. *Sci. Total Environ.* 429, 107–122.
- Liu, T.X., Li, X.M., Waite, T.D., 2014. Depassivation of aged Fe-0 by divalent cations: correlation between contaminant degradation and surface Complexation constants. *Environ. Sci. Technol.* 48 (24), 14564–14571. <https://doi.org/10.1021/es503777a>.
- Lufingo, M., Nde-Tchoupe, A.I., Hu, R., Njau, K.N., Noubactep, C., 2019. A novel and facile method to characterize the suitability of metallic iron for water treatment. *Water-Sui* 11 (12). <https://doi.org/10.3390/w11122465>.
- Matheson, L.J., Tratnyek, P.G., 1994. Reductive dehalogenation of chlorinated methanes by iron metal. *Environ. Sci. Technol.* 28 (12), 2045–2053. <https://doi.org/10.1021/es00061a012>.
- Meng, X., Wang, W., 1998. Arsenic speciation with disposable cartridges. Paper Presented at the Third International Conference on Arsenic Exposure and Health Effects, San Diego, California, July 12–15, 1998.
- Millero, F.J., Sotolongo, S., Izaguirre, M., 1987. The oxidation kinetics of Fe (II) in seawater. *Geochim. Cosmochim. Acta* 51 (4), 793–801.
- Mohan, D., Pittman, C.U., 2007. Arsenic removal from water/wastewater using adsorbents – a critical review. *J. Hazard. Mater.* 142 (1), 1–53.
- Mondal, P., Bhowmick, S., Chatterjee, D., Figoli, A., Van der Bruggen, B., 2013. Remediation of inorganic arsenic in groundwater for safe water supply: a critical assessment of technological solutions. *Chemosphere* 92 (2), 157–170. <https://doi.org/10.1016/j.chemosphere.2013.01.097>.
- Mwakabona, H.T., Nde-Tchoupe, A.I., Njau, K.N., Noubactep, C., Wydra, K.D., 2017. Metallic iron for safe drinking water provision: considering a lost knowledge. *Water Res.* 117, 127–142. <https://doi.org/10.1016/j.watres.2017.03.001>.
- Neumann, A., Kaegi, R., Voegelin, A., Hussam, A., Munir, A.K.M., Hug, S.J., 2013. Arsenic removal with composite iron matrix filters in Bangladesh: a field and laboratory study. *Environ. Sci. Technol.* 47 (9), 4544–4554. <https://doi.org/10.1021/es305176x>.
- Ngai, T.K.K., Shrestha, R.R., Dangol, B., Maharjan, M., Murcott, S.E., 2007. Design for sustainable development – household drinking water filter for arsenic and pathogen treatment in Nepal. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering* 42 (12), 1879–1888. <https://doi.org/10.1080/10934520701567148>.
- Noubactep, C., 2008. A critical review on the process of contaminant removal in Fe-0-H<sub>2</sub>O systems. *Environ. Technol.* 29 (8), 909–920. <https://doi.org/10.1080/09593330802131602>.
- Roberts, L.C., Hug, S.J., Ruettimann, T., Billah, M., Khan, A.W., Rahman, M.T., 2004. Arsenic removal with Iron(II) and iron(III) in waters with high silicate and phosphate concentrations. *Environ. Sci. Technol.* 38 (1), 307–315. <https://doi.org/10.1021/es0343205>.
- Schmidt, C.W., 2014. Low-dose arsenic in search of a risk threshold. *Environ. Health Perspect.* 122 (5), A130–A134. <https://doi.org/10.1289/ehp.122-A130>.
- Senn, A.C., Kaegi, R., Hug, S.J., Hering, J.G., Mangold, S., Voegelin, A., 2015. Composition and structure of Fe(III)-precipitates formed by Fe(II) oxidation in water at near-neutral pH: interdependent effects of phosphate, silicate and Ca. *Geochim. Cosmochim. Acta* 162, 220–246. <https://doi.org/10.1016/j.gca.2015.04.032>.
- Sherar, B.W.A., Keech, P.G., Shoesmith, D.W., 2011. Carbon steel corrosion under anaerobic-aerobic cycling conditions in near-neutral pH saline solutions. Part 2: corrosion mechanism. *Corros. Sci.* 53 (11), 3643–3650. <https://doi.org/10.1016/j.corsci.2011.07.008>.
- Singh, A., Smith, L.S., Shrestha, S., Maden, N., 2014. Efficacy of arsenic filtration by Kanchan arsenic filter in Nepal. *J. Water Health* 12 (3), 596–599. <https://doi.org/10.2166/wh.2014.148>.
- Smedley, P.L., Knudsen, J., Maiga, D., 2007. Arsenic in groundwater from mineralised Proterozoic basement rocks of Burkina Faso. *Appl. Geochem.* 22 (5), 1074–1092.
- Smiech, K.M., Tolsma, A., Kovacs, T., Dalbosco, V., Yasadi, K., Groendijk, L., Agostinho, L.L.F., 2018. Comparing mixed-media and conventional slow-sand filters for arsenic removal from groundwater. *Water-Sui* 10 (2). <https://doi.org/10.3390/w10020119>.
- Smith, K., Li, Z., Chen, B., Liang, H., Zhang, X., Xu, R., Li, Z., Dai, H., Wei, C., Liu, S., 2017. Comparison of sand-based water filters for point-of-use arsenic removal in China. *Chemosphere* 168, 155–162. <https://doi.org/10.1016/j.chemosphere.2016.10.021>.
- Sohel, N., Persson, L.A., Rahman, M., Streetfield, P.K., Yunus, M., Ekström, E.C., Vahter, M., 2009. Arsenic in drinking water and adult mortality: a population-based cohort study in rural Bangladesh. *Epidemiology* 20 (6), 824–830.
- Su, C., Puls, R.W., 2008. Arsenate and arsenite sorption on magnetite: relations to groundwater arsenic treatment using zerovalent iron and natural attenuation. *Water Air Soil Pollut.* 193 (1–4), 65–78. <https://doi.org/10.1007/s11270-008-9668-1>.
- Sun, H., Wang, L., Zhang, R., Sui, J., Xu, G., 2006. Treatment of groundwater polluted by arsenic compounds by zero valent iron. *J. Hazard. Mater.* 129 (1–3), 297–303. <https://doi.org/10.1016/j.jhazmat.2005.08.026>.
- Tepong-Tsinde, R., Nde-Tchoupe, A.I., Noubactep, C., Nassi, A., Ruppert, H., 2019. Characterizing a newly designed steel-wool-based household filter for safe drinking water



- provision: hydraulic conductivity and efficiency for pathogen removal. *Processes* 7 (12). <https://doi.org/10.3390/pr7120966>.
- Tyrovola, K., Nikolaidis, N.P., Veranis, N., Kallithrakas-Kontos, N., Koulouridakis, P.E., 2006. Arsenic removal from geothermal waters with zero-valent iron-effect of temperature, phosphate and nitrate. *Water Res.* 40 (12), 2375–2386. <https://doi.org/10.1016/j.watres.2006.04.006>.
- United Nations, 2017. *World Population Prospects: The 2017 Revision, Data Booklet. Department of Economic and Social Affairs, Population Division, New York*.
- Usman, M., Katsoyiannis, I., Mitrakas, M., Zouboulis, A., Ernst, M., 2018. Performance evaluation of small sized powdered ferric hydroxide as arsenic adsorbent. *Water-Sui* 10 (7). <https://doi.org/10.3390/w10070957>.
- Wenk, C.B., Kaegi, R., Hug, S.J., 2014. Factors affecting arsenic and uranium removal with zero-valent iron: laboratory tests with Kanchan-type iron nail filter columns with different groundwaters. *Environ. Chem.* 11 (5), 547–557. <https://doi.org/10.1071/EN14020>.
- Westerhoff, P., Highfield, D., Badruzzaman, M., Yoon, Y., 2005. Rapid small-scale column tests for arsenate removal in iron oxide packed bed columns. *J Environ Eng-Asce* 131 (2), 262–271. [https://doi.org/10.1061/\(ASCE\)0733-9372\(2005\)131:2\(262\)](https://doi.org/10.1061/(ASCE)0733-9372(2005)131:2(262)).
- WHO, 2018. *Factsheet on Arsenic*. World Health Organisation.
- Zhang, W., Oswal, H., Renew, J., Ellison, K., Huang, C.H., 2019. Removal of heavy metals by aged zero-valent iron from flue-gas-desulfurization brine under high salt and temperature conditions. *J. Hazard. Mater.* 373, 572–579. <https://doi.org/10.1016/j.jhazmat.2019.03.117>.