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# Arsenic in drinking water wells on the Bolivian high plain: Field monitoring and effect of salinity on removal efficiency of iron-oxides containing filters

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#### ABSTRACT

In the rural areas around Oruro (Bolivia), untreated groundwater is used directly as drinking water. This research aimed to evaluate the general drinking water quality, with focus on arsenic (As) concentrations, based on analysis of 67 samples from about 16 communities of the Oruro district. Subsequently a filter using Iron Oxide Coated Sand (IOCS) and a filter using a Composite Iron Matrix (CIM) were tested for their arsenic removal capacity using synthetic water mimicking real groundwater. Heavy metal concentrations in the sampled drinking water barely exceeded WHO guidelines. Arsenic concentrations reached values up to 964  $\mu$ g L<sup>-1</sup> and exceeded the current WHO provisional guideline value of 10  $\mu$ g L<sup>-1</sup> in more than 50 % of the sampled wells. The WHO guideline of 250 mg  $L^{-1}$  for chloride and sulphate was also exceeded in more than a third of the samples, indicating high salinity in the drinking waters. Synthetic drinking water could be treated effectively by the IOCS and CIM based filters reducing As to concentrations lower than 10 µg L<sup>-1</sup>. High levels of chloride and sulphate did not influence As removal efficiency. However, phosphate concentrations in the range from 4 to 24 mg  $L^{-1}$  drastically decreased removal efficiency of the IOCS based filter but had no effects on removal efficiency of the CIM based filter. Results of this study can be used as a base for further testing and practical implementation of drinking water purification in the Oruro region.

#### **INTRODUCTION**

In various parts of the world, high arsenic (As) concentrations are present in groundwater, e.g. up to 2000  $\mu$ g L<sup>-1</sup> in Bangladesh<sup>[1]</sup>, 3400  $\mu$ g L<sup>-1</sup> in West Bengal<sup>[2]</sup>

and 262.9  $\mu$ g L<sup>-1</sup> in Mexico.<sup>[3]</sup> It is assumed that As is naturally present in minerals and is released to groundwater, either through oxidation of pyrite, or release from iron oxides<sup>[4]</sup>. The oxidation of pyrite is often caused by a decline of the groundwater level due to extensive evaporation or water-demanding mining activities. The release from iron oxides is mostly associated with increasing pH and/or reduction due to oxygen shortage when groundwater levels increase. <sup>[4]</sup> There are indications that groundwater on the Bolivian altiplano (high plain) also contains elevated As concentrations.<sup>[5, 6]</sup> Due to a lack of clean water resources some of this water is being used as drinking water especially in rural – less developed – areas.

Much previous arsenic-related research focused on health issues related to the consumption of such arsenic contaminated drinking water. Ratnaike <sup>[7]</sup> and others <sup>[8,9]</sup> state that ingestion of low As concentrations over a long-term period can result in multisystem diseases and different types of cancer, of which skin and bladder cancer are most common. Therefore, the World Health Organization (WHO) in 1993 established a provisional guideline value of 10 µg L<sup>-1</sup> as upper limit for drinking water. When high As concentrations are observed in drinking water, immediate action should focus on finding a safe alternative source of drinking water. However, the Bolivian high plain is known for its semi-arid climate characterised by low levels of rainfall, high evapotranspiration rates and soils with low water retention capacities. <sup>[10, 11]</sup> There is a general shortage of water. In combination with an extensive water demand and pollution of ground- and surface waters by mining activities, safe water resources are scarce. Accordingly, removal of As from the contaminated drinking water sources should be considered.

Numerous methods have been developed for the removal of As from drinking water. These include co-precipitation, adsorption, ion-exchange or membrane processes. <sup>[12]</sup> Because As related health issues often occur in less populated areas, methods designed to be technically and economically feasible for use in rural communities have been developed. Adsorption technology using iron oxides is one of these methods proven to be cheap and very efficient in large scale water utilities<sup>[13]</sup>, as well as in small scale water utilities.<sup>[14]</sup> In most cases, iron is easily available. Methods using iron oxides can also be considered as clean and easy to understand for the rural communities in developing countries. However, problems could occur related to filter regeneration and microbial contamination. Chemical methods, such as lime softening or co-precipitation, require certain skills that most people in the rural communities do not have. Membrane and ion-exchange based methods and distillation units are very good alternatives for iron oxides, but in most cases they are too expensive. Therefore, preference is given to adsorption technologies using iron oxides.

The adsorption of As by iron oxides has been well studied by various researchers<sup>[15]</sup>. Both arsenate and arsenite can be present in the groundwater. When working in a normal pH range of drinking water (6.5 - 8), arsenate is expected to be present as an anion, but arsenite is not. Since iron oxides have a positive surface charge in this pH range, arsenate will be more easily adsorbed than arsenite. <sup>[16]</sup> Therefore, several treatment procedures include an oxidation step to oxidize arsenite into arsenate prior to adsorption on iron oxides<sup>[14]</sup>. Due to the earlier mentioned high levels of evapotranspiration and the abundance of igneous rocks, salinity of water on the Bolivian high plain can be very high in comparison to other world regions. It has been

reported that efficiencies of methods to remove As could be affected by salinity due to competition of anionic ligands for adsorption to the filter medium.<sup>[15-17]</sup>

This study aimed to characterise the composition of drinking water sampled from wells of rural areas in the Bolivian Oruro district. Subsequently, two filters based on use of iron-oxide coated sand (IOCS) and a composite iron matrix (CIM) were tested for removal of As from a synthetic drinking water solution mimicking the real groundwater, with emphasis on the effects of presence of anions (chloride, phosphate and sulphate) on As removal efficiency and capacity of the filter.

#### **MATERIAL AND METHODS**

#### **Study Area**

The Oruro district is situated around the city of Oruro on the Altiplano in the northwest of Bolivia. The city is located at an altitude of 3709 m above sea level and characterised by a semi-arid climate. Yearly precipitation is low, ranging from 131 mm to 384 mm.<sup>[6]</sup> Evaporation is high, reaching values up to 1648 mm year<sup>-1</sup>. This is reflected in the various salt plains and scarce water resources.<sup>[18]</sup> The entire region is characterised by the presence of glacial, eolic, fluvial and alluvial sediments and salt flats, such as Salar de Uyuni and Coipasa.<sup>[18]</sup> Most sediments are volcanic and rich in minerals. Weathering of these minerals and mining activities induce high salinities and presence of heavy metals in the ground- and surface water.<sup>[11]</sup>

### **Field Sampling**

Drinking water quality was assessed in sixteen communities in the rural area of Oruro (Fig. 1).

## Figure 1

The number of samples taken in each community depended on community size and accessibility of its drinking water resources. In total, 67 drinking water wells were sampled. Depending on the type of well, samples were taken with a bucket or pump. Buckets were rinsed with well water before a sample was taken. When a pump was present, water was collected after a minute of pumping. Samples were always taken in duplicate. When a bucket was used, two samples were taken out of the same bucket. The first sample was prepared in the field for subsequent As speciation analysis in the laboratory (arsenite and arsenate). Sample preparation and conservation was aimed to prevent conversions between arsenite and arsenate. <sup>[19]</sup> Preparation involved filtering over a 0.45  $\mu$ m filter, and adding 1 mL of a 7.5 mg L<sup>-1</sup> Na<sub>2</sub>EDTA solution to 19 mL of filtered sample. This sample was stored in a dark bottle. The other sample was not filtered. Both samples were stored at -5°C awaiting their shipment to the laboratory in Belgium. Redox potential (Hanna Instruments HI 98120, Rhode Island (USA)), pH, temperature and electrical conductivity (Hanna Instruments HI98130, Rhode Island (USA)) were measured *in situ*.

The samples were thawed in the laboratory. Dissolved organic carbon (DOC, TOC-5000 Shimadzu),  $Cl^{-}$ ,  $SO_4^{2-}$  (Metrohm-761 Compact IC, Zofingen, Switzerland) were analyzed in all samples after 0.45  $\mu$ m filtration. Total As, Fe, Zn, Pb, Ni, Cd, Mn and Cu concentrations were analyzed after treating 25 mL of unfiltered sample with 3 mL of H<sub>2</sub>O<sub>3</sub> and 1 mL of H<sub>2</sub>O<sub>2</sub>, heating this mixture at 150°C in 3 cycles of 20 minutes. This solution was subsequently diluted to 50 mL. Concentrations in these solutions were analysed using ICP-MS (Perkin Elmer SCIEX, Elan DRC-e, Massachusetts, USA). Detection limits were 1, 3, 10, 10, 5, 3, 0.5, 10, 20, and 1  $\mu$ g L<sup>-1</sup>, for As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, respectively. Thirty-seven samples were subjected to speciation analysis. Analysis of arsenite and arsenate was performed using HPLC-ICP-MS (PerkinElmer Series 200 HPLC + Elan DRC-e ICP-MS, Massachusetts, USA) with a Hamilton PRP-X100 anion exchange column and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> in 2 % methanol as mobile phase. <sup>[20]</sup>

#### **Filtration Experiment**

Glass tubes of 38 cm length and 2 cm diameter were filled for about 75% with filter material (bed volume = about 100 mL). The Composite Iron Matrix filter (CIM) was constructed with 25 g of iron nails (1.2x20 mm) which had been kept for 2 weeks in a nitric acid solution (pH 3) to cause formation of iron (hydr)oxides. These are expected to retain As according to the following reactions:<sup>[21]</sup>

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$$= FeOH + H_2AsO_4^{-} \leftrightarrow = FeHAsO_4^{-} + H_2O (K = 10^{24})$$
$$= FeOH + HAsO_4^{2-} \leftrightarrow = FeAsO_4^{2-} + H_2O (K = 10^{29})$$

The other filter, i.e. the iron oxide coated sand filter (IOCS), contained a layer of 10 g fine sand (< 1 mm) which was coated with iron oxides at a high temperature. To

prepare this filter material, 160 mL 2.5 M FeCl<sub>3</sub> and 2 mL 10 M NaOH were poured over 400 grams of sand. This mixture was heated during 4 h at 110°C and during 3 h at 550°C. To make a second coating layer, this material was again treated with 80 mL 2.5 M FeCl<sub>3</sub> and 1 mL 10 M NaOH, and heated at 110°C during 20 h. Afterwards, it was mechanically broken into individual grains and sieved to 1 mm mesh size. <sup>[22]</sup> To avoid loss of the coating in alkaline conditions, a heating cycle of 110°C during 4 h followed by storage at room temperature during 20 h was repeated 5 times. Subsequently, the cooled sand was washed with deionised water until the dark color disappeared. Initially, the sand contained 1.98 mg Fe g<sup>-1</sup> sand. After coating, it contained 40.8 mg Fe g<sup>-1</sup> sand. In both filters, about thirty grams of fine sand (< 1 mm) were put below the active iron oxide layer. Finally, about 30 grams of gravel (> 4 mm) were put on top and at the bottom of the filter providing mechanical stability, stream stabilization and filter capacity for organic and particulate material. The sand and gravel were soaked 6 times during 6 h in freshly prepared nitric acid solution (pH 1), subsequently rinsed 5 times with deionised water and dried.

The filters were percolated with synthetic drinking water solutions of different salinities and As concentrations at a speed of about 1 bed volume per hour. Synthetic drinking water solutions were prepared to mimic a typical composition of drinking water in the studied region. Instead of using the average As concentration of all the samples, the composition of a drinking water sample with an As concentration in the third quartile was selected as template composition for the synthetic drinking water solution. Most other components, such as  $SO_4^{2-}$ , Cl<sup>-</sup>, Na<sup>+</sup> and Ca<sup>2+</sup>, were present in more or less average concentrations. Solution A contained 180 µg L<sup>-1</sup> As (added as NaH<sub>2</sub>AsO<sub>4</sub>), 755 mg L<sup>-1</sup> Cl<sup>-</sup> (added as NaCl), 170 mg L<sup>-1</sup>  $SO_4^{2-}$  (added as CaSO<sub>4</sub><sup>2-</sup>)

and 4 mg  $L^{-1}$  PO<sub>4</sub><sup>3-</sup> (added as NaH<sub>2</sub>PO<sub>4</sub>.2H<sub>2</sub>O). Because phosphate concentrations could not be measured on all field samples due to a lack of sample volume, the phosphate concentration of the synthetic solution was based on analysis of only the field sample which contained 180  $\mu$ g L<sup>-1</sup> As. It should be noted that this selected phosphate concentration is likely to be located in the upper range of phosphate concentrations in field drinking water samples of the Oruro district (University of Oruro, oral communication). The concentrations in the other solutions were the same as in solution A except for the concentration of one anion which was varied. The concentrations of the individual anions in the different solutions were 341 (solution S1) and 511 (solution S2) mg  $L^{-1}$  for SO<sub>4</sub><sup>2-</sup>, 1511 (solution C1) and 2266 (solution C2) mg  $L^{-1}$  for Cl<sup>-</sup>, and 12 (solution P1) and 24 (solution P2) mg  $L^{-1}$  for PO<sub>4</sub><sup>3-</sup> to study the effect of these anions on the As removal capacity of the filters. Arsenic and Fe concentrations were measured in the percolates after elution of different bed volumes, using ICP-MS (Perkin Elmer SCIEX, Elan DRC-e, Massachusets (USA)) and ICP-OES (Varian Vista MPX, Palo Alto (USA)), respectively. This was done after acidification to pH<1 with HNO<sub>3</sub>.

#### **Statistical Analysis**

To link the presence and concentration of As in the different communities to the presence of other elements such as iron, sulphate, manganese and TOC a correlation analysis was conducted using PASW statistics 18.<sup>[23]</sup>

To detect significant effects of the competing anions and possible interactions between the competing anions and the number of treated bed volumes on measured effluent As concentration, analysis of variance (ANOVA) was conducted using PASW statistics 18<sup>[23]</sup>. Tukey post-hoc tests were conducted to determine homogenous subsets at 0.05 significance level.

#### **RESULTS AND DISCUSSION**

#### **Total Arsenic And Arsenic Speciation In Drinking Water From The Wells**

Summary statistics reflecting the composition of the drinking water sampled from the wells are presented in Table 1.

#### Table 1

Arsenic reached concentrations up to 964  $\mu$ g L<sup>-1</sup>. Concentrations exceeding the WHO drinking water quality guideline of 10  $\mu$ g L<sup>-1</sup> were found in more than half of the 67 sampled wells.

Of the 37 samples which were subjected to speciation analysis, only 3 samples contained amounts of arsenite between 10 and 30 % of total As (data not shown). All others only contained less than 3 % arsenite. This finding corresponds with expectations from speciation modeling at the observed high pH and ORP values. <sup>[24]</sup> It confirms that a preliminary oxidation step to transform arsenite into arsenate for optimal removal is not needed in most wells of this Bolivian region . However, such preliminary oxidation step may be needed when treating water from the arsenite-containing wells.

The WHO guidelines for Cr, Zn and Cu were never exceeded (Table 1). The WHO guideline for Pb was exceeded in less than 10 % of the drinking water wells. Up to 25 % of the wells contained Fe in concentrations above its WHO guideline, making it the most abundant heavy metal in the sampled drinking waters. In one drinking water well located near the mine of Huanuni, Ni and Cd concentrations exceeded the WHO guideline. Contact between acid mine drainage and groundwater probably caused this contamination. The WHO guideline of 250 mg  $L^{-1}$  for sulphates and chlorides was also exceeded in more than 35 % of the wells. Conductivities up to 12.8 mS cm<sup>-1</sup> were measured.

Although high metal concentrations were observed in drinking water near the Huanuni mine, no elevated As concentrations were observed. Moreover, the highest As concentrations were measured in drinking wells which are located relatively far away from mining sites. This suggests that no relationship can be inferred between the mining activities and the elevated As concentrations in the drinking water in the investigated area. Relations between the presence of As, sulphate, Fe, Mn, Total Organic Carbon and pH were examined trying to explain the presence of the high As concentrations in the groundwater. Correlation analysis did not reveal direct relations between the different variables. However, the only variable that seemed moderately related to As concentrations was pH. Figure 2 illustrates that higher As concentrations are associated with higher pH values. This is consistent with the general observation that anions tend to be less sorbed, and are more mobile at higher pH values. <sup>[25]</sup> Alkaline conditions (pH > 8) were present in more than 30 % of the drinking water wells. Due to the alkaline conditions, arsenate desorption from Fe oxides is expected to occur, inducing release of As to the groundwater<sup>[26]</sup>. Competition of arsenate with

other anions such as phosphate and sulphate for sorption on the Fe oxides could further have induced release of As. <sup>[24]</sup> Although desorption due to the presence of anions is expected to contribute to As release, pyrite oxidation cannot be excluded as a source of As due to the presence of As-containing sulphide minerals and decreasing groundwater levels. The latter can be attributed to increased water demand by mining activities and evapotranspiration in the study area.

## Figure 2

#### **Filtration Experiment**

For the IOCS filter, the WHO guideline of 10  $\mu$ g L<sup>-1</sup> was exceeded after treating more than 45 bed volumes of the synthetic solution A and approximately 640  $\mu$ g As was adsorbed by 10 g IOCS before breakthrough. Analysis of random effluent samples collected during the filtration experiment showed an average iron concentration of 0.1 mg L<sup>-1</sup> indicating no or very little loss of iron from the filter material.

An arsenic removal capacity was calculated by the difference between the applied arsenic loading and the amount removed by IOCS, divided by the mass of IOCS involved. When treating solution A the arsenic removal capacity before reaching an As concentration of 5 and 10  $\mu$ g L<sup>-1</sup> in the effluent was respectively 0.32 mg g<sup>-1</sup> IOCS and 0.64 mg g<sup>-1</sup> IOCS. These results indicate little difference compared to the results obtained by Thirunavukkarasu et al.<sup>[26]</sup> who achieved a value of 0.41 mg g<sup>-1</sup> IOCS. In the experiments conducted by Thirunavukkarasu et al.<sup>[22]</sup> no fine sand nor gravel layer were used. This indicates that the sand and gravel have only a limited effect on the removal capacity of IOCS. However, they can have a function in removing natural

organic material and other particulate material. Furthermore, Thirunavukkarasu *et al.* <sup>[22]</sup> used lower salinity water for their experiments (containing 12 mg L<sup>-1</sup> of chloride). This may be a first indication that the high salinity of the Bolivian water, about 400 times higher than in the experiment of Thirunavukkarasu et al. <sup>[22]</sup>, has little effect on the As removal capacity of IOCS.

Subsequently the effect of competing anions was tested with the synthetic water solutions. In Figure 3 the arsenic removal efficiency using different concentrations of sulphate, phosphate and chloride is shown. The arsenic removal efficiency is calculated by the difference of influent arsenic and effluent arsenic divided by influent arsenic. For each anion three different concentrations were used in triplicate. Increasing the concentration of sulphate and chloride had little effect on the removal efficiency. Variance analysis showed no significant (p<0.01) differences between the removal efficiencies using the synthetic solutions A, S1 and S2 or solutions A, C1 and C2. The overall absence of an effect of sulphate is in correspondence with findings of Hsu et al.<sup>[17]</sup> In the study of Sun et al.<sup>[27]</sup> arsenic removal was found to improve slightly in the presence of very high concentrations (1200 mg L<sup>-1</sup>) of sulphate<sup>[27]</sup>. Sun *et al.*<sup>[27]</sup> mentioned the formation of FeAsS under reducing conditions as possible removal mechanism in their experiment:<sup>[27]</sup>

$$14Fe^{2+} + SO_4^{2-} + AsO_3^{-} + 14H^+ \rightarrow FeAsS + 13Fe^{3+} + 7H_2O$$
.

However, our results did not demonstrate any difference in As removal efficiency when increasing the sulphate concentration. This might be due to the shorter contact time and less reducing conditions in our column experiment as opposed to the batch setup used by Sun et al.<sup>[27]</sup>

Previous research on the effect of chloride on As removal by Vaishya & Gupta <sup>[28]</sup> and Hsu et al. <sup>[17]</sup> showed that chloride concentrations up to 1000 mg L<sup>-1</sup> had no significant effect on As removal efficiencies. However these concentrations were frequently exceeded on the Bolivian high plain. In our study, also no significant effects (p<0.01) of chloride on As removal efficiencies were found in a range of 755 to 2266 mg L<sup>-1</sup> Cl<sup>-</sup>.

## Figure 3

A significant effect on As removal was observed for phosphate (Fig. 3c). This is in correspondence with Hsu et al. <sup>[17]</sup> and Mahin et al.<sup>[29]</sup> amongst others. With the highest phosphate concentration tested (24 mg L<sup>-1</sup>), only 10 bed volumes could be filtered before breakthrough occurred. Phosphate competes with As(V) for available adsorption sites on the IOCS. <sup>[17]</sup> For most effluent samples, As removal efficiencies could be classified in three homogenous groups using the Post Hoc Tukey test. The first group contained the As removal efficiencies when treating solution A, the second group the As removal efficiencies when treating solution P1 and the third group the As removal efficiencies when treating solution P2. Such results agree with the findings of Zhang et al.<sup>[30]</sup> who stated that an increase of the molar ratio of phosphate to As results in a significant decrease in As(V) adsorption capacity of iron oxides, indicating competition between arsenate and phosphate for binding sites of the adsorbent. Interference of phosphate with As removal is plausible around pH 7.5 since As adsorption is mostly based on electrostatic attraction of the opposite charges of As(V) and the iron oxide surface. Because phosphate is present in much larger

concentrations than As, it is able to interfere and block a large part of the adsorption sites.

Variability of phosphate concentrations in the drinking waters of the sampled area was previously reported to be quite low (University of Oruro, oral communication). The highest phosphate concentrations used in the synthetic drinking water were not representative for field samples, but chosen in the laboratory experiments to study potential effects of phosphate on As removal. As was already mentioned in the materials and methods section, the phosphate concentration in the synthetic solution A was more likely to be situated in the upper range of the field drinking water samples. Using batch studies, Hsu et al. <sup>[17]</sup> illustrated that an augmentation from 0 to 5 mg L<sup>-1</sup> phosphate causes arsenic removal to decrease by more than 50 %. This implies that lower phosphate concentrations in the field can be expected to result in higher removal efficiencies and treatment capacities of the IOCS filter compared to what can be predicted from our laboratory experiments.

Also when the CIM filter was used to treat synthetic solution A, initial removal efficiencies were high. Arsenic was removed for more than 98 % during treatment of more than 20 bed volumes (Fig. 4). The WHO guideline of 10  $\mu$ g L<sup>-1</sup> was exceeded after treatment of 35 to 50 bed volumes of solution A. The As removal capacity of the 25 g of rusted iron nails varied between 11 and 21  $\mu$ g As g<sup>-1</sup> CIM. This was much lower than that of the IOCS filter, but markedly higher than the biosand filter containing iron nails used by Chiew et al.<sup>[31]</sup> In their filter, As was never removed to concentrations lower than 74  $\mu$ g L<sup>-1</sup>. The limited contact time of the nails with the water is given as the main reason for this low As removal capacity. Most likely the layers of fine sand in our CIM filter resulted in a longer contact time, causing a higher

removal capacity. Other experiments with rusted iron material in the SONO filter used by Hussam & Munir <sup>[21]</sup> resulted in a higher removal capacity than the CIM filter of our experiment and the biosand filter used by Chiew et al.<sup>[31]</sup> The SONO filter was able to filter more than 25000 L water with an As concentration between 1139 and 1600  $\mu$ g L<sup>-1</sup> to a concentration lower than 10  $\mu$ g L<sup>-1</sup> using 5-10 kg of rusted iron material. The arsenic removal capacity that was reached can be roughly estimated to be above 4000  $\mu$ g As g<sup>-1</sup> rusted iron material, which is about 100 times higher than the As removal capacity of our IOCS filter. However, this difference can be explained by the main part of IOCS being fine sand while the Composite Iron Matrices of the SONO, CIM and biosand filter consist mainly of iron. This results in the presence of more iron (hydr)oxides and thus in a much higher removal capacity.

The lower breakthrough volume of the CIM filters in comparison to the IOCS and the SONO filters <sup>[21]</sup> can be attributed to the continuous saturation of the filter when water is being poured over the filter. This probably results in the occurrence of Fe oxide reduction processes and concurrent release of Fe and As from the filter material. Indeed, iron concentrations increased above the WHO guideline of 0.2 mg L<sup>-1</sup> after treatment of only 5 bed volumes, suggesting dissolution of iron through reduction. These reduction processes may be prevented by physically separating the CIM containing unit from its preceding unit (gravel and sand) and subjecting the CIM unit to lower loading rates.

#### Figure 4

The effect of competing anions was also investigated with synthetic solution when using the CIM-filter. Figure 4 illustrates that increasing sulphate and chloride concentration had no considerable effect on the As removal efficiency as was also observed when using the IOCS filter. Variance analysis did not reveal significant differences in treating synthetic solutions A, S1 and S2 or solutions A, C1 and C2. Figure 4c illustrates that increasing phosphate concentrations also did not result in a decrease of the As removal efficiency. This does not coincide with results obtained for the IOCS filter, where a clear difference was noticeable after only 5 treated bed volumes. This was confirmed by the variance analysis: phosphate concentrations do not have a significant (p > 0.05) influence on the As removal efficiency in the CIM filter. The lower effect of phosphate on the residual As concentrations when using the CIM-filter as compared to the IOCS filter is probably related to the greater abundance of iron hydroxides.

Finally, removal efficiencies of both filters were assessed for well water collected in the field. As insufficient sample volumes were available, only 5 bed volumes could be treated and breakthrough volumes using the different filters could not be compared. It was also not possible to compare filter performance when using synthetic water with filter performance when using the real well water. However, during the treatment of the 5 bed volumes, removal efficiencies were not significantly different between the well water collected in the field and the synthetic solution A. This suggests that additional compounds present in samples collected in the field (e.g., some dissolved organic carbon) did not primarily affect As removal.

#### CONCLUSIONS

Arsenic concentrations in drinking water of the Oruro district in Bolivia significantly exceed WHO guidelines, while heavy metals are barely present. High salinity values were found throughout the entire study area. The sampled drinking water contained high concentrations of sulphates and chlorides often exceeding WHO guidelines. Filter experiments indicate that the drinking water could be treated effectively using iron-oxide coated sand (IOCS) and CIM (composite iron matrix) based filters. The treatment efficiency is not affected by chlorides and sulphates. However, phosphate concentrations in the range from 4 to 24 mg  $L^{-1}$  drastically decreased removal efficiency of the IOCS based filter but had no effects on removal efficiency of the CIM based filter. Results of this study can be used for further development of drinking water purification techniques in As-rich regions with high and variable salinities, such as the Bolivian altiplano. Further studies involving the role of organic matter and using lower phosphate concentrations should be performed. Moreover, large scale tests with real well water instead of only synthetic drinking water solutions are essential before the filters can be taken in use. Furthermore, since salinity is also a major concern in the study area, costs and benefits of the selected treatment methods should be compared with those of more expensive techniques that also reduce salinity, e.g. techniques based on reverse osmosis and distillation units.

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#### LIST OF FIGURE CAPTIONS

Fig. 1: The study area with sampled communities indicated by white dots.

**Fig. 2**: Scatterplots of measured As concentrations as a function of pH in the sampled wells.

**Fig. 3**: Average As removal efficiencies when using the IOCS filter for a) increasing sulphate concentrations (A=170 mg L<sup>-1</sup>, S1=341 mg L<sup>-1</sup> and S2=511 mg L<sup>-1</sup>), b) increasing chloride concentrations (A=755 mg L<sup>-1</sup>, C1=1511 mg L<sup>-1</sup> and C2=2266 mg L<sup>-1</sup>) and c) increasing phosphate concentrations (A=4 mg L<sup>-1</sup>, P1=12 mg L<sup>-1</sup> and P2=24 mg L<sup>-1</sup>) (\*: difference with As removal efficiency of solution A significant at p<0,05 and \*\*: difference with As removal efficiency of solution A significant at p<0,01; n=3).

**Fig. 4**: Average As removal efficiencies when using the CIM filter for a) increasing sulphate concentrations (A=170 mg L<sup>-1</sup>, S1=341 mg L<sup>-1</sup> and S2=511 mg L<sup>-1</sup>), b) increasing chloride concentrations (A=755 mg L<sup>-1</sup>, C1=1511 mg L<sup>-1</sup> and C2=2266 mg L<sup>-1</sup>) and c) increasing phosphate concentrations (A=4 mg L<sup>-1</sup>, P1=12 mg L<sup>-1</sup> and P2=24 mg L<sup>-1</sup>) (\*: difference with As removal efficiency of solution A significant at p<0,05 and \*\*: difference with As removal efficiency of solution A significant at p<0,01; n=3).



Fig. 1





→24 mg L<sup>-1</sup> PO4 (Solution P2)

10

20 30 Bed Volume 40

50

40

30

0



Fig. 3





## TABLES

**Table 1:** Summary of drinking water properties (n = 67) and their WHO guideline values.

	Minimu	Averag	Media	Maximu	WHO
_	m	e	n	m	guideline
Chloride (mg L <sup>-1</sup> )	1.24	237	80.4	2683	250
Nitrate (mg L <sup>-1</sup> )	< 0.1	9.64	4.9	76.4	50
Sulphate (mg L <sup>-1</sup> )	< 0.3	252	121	1838	250
рН	3.87	7.6	7.67	8.69	6.5-9.5
T (°C)	7.69	13	13	19	-
EC (mS cm <sup>-1</sup> )	0.11	1.84	1.31	12.8	0-0.8
ORP (mV)	207	345	353	551	-
Cd (µg L <sup>-1</sup> )	< 3	4.15	< 3	235	3
Co (µg L <sup>-1</sup> )	< 10	< 10	< 10	45.9	-
Cr (µg L <sup>-1</sup> )	< 10	10.7	9.34	37.2	50
Cu (µg L <sup>-1</sup> )	< 5	10.41	4.79	219	2000
Fe (µg L <sup>-1</sup> )	< 3	233	90.7	2691	200
<b>Mn (μg L<sup>-1</sup>)</b>	< 0.5	36.7	9.68	466	400
Ni (μg L <sup>-1</sup> )	< 10	< 10	< 10	183	70
Pb (μg L <sup>-1</sup> )	< 20	< 20	< 20	58.5	10
Zn (µg L <sup>-1</sup> )	< 1	106	30.3	2330	5000
As (µg L <sup>-1</sup> )	< 1	63.6	10.22	964	10
TOC (mg $L^{-1}$ )	0.25	7.57	3.87	39	-