Arsenic removal from groundwaters containing iron, ammonium, manganese and phosphate: A case study from a treatment unit in northern Greece

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Abstract

The city of Malgara in the municipality of Aksios, in northern Greece, relies on local groundwater for the municipal water supply. The groundwater has pH 7.9 and contains elevated concentrations of arsenic (20 µg/L), phosphate (550 µg/L), manganese (235 µg/L) and ammonium (1.2 mg/L), whereas the iron concentration (165 µg/L) is relatively low. Arsenic, manganese and ammonium exceed the parametric values, according to the EC directive 98/83. This directive has been adopted as national law since the beginning of 2003 and a groundwater treatment plant is in operation since the beginning of 2005. The treatment plant consists of aeration, up-flow filtration for the biological oxidation of ammonium, manganese and arsenic, followed by coagulation with FeCl\textsubscript{3}SO\textsubscript{4} at a concentration of 2.3 mg Fe/L, and final down-flow filtration for the removal of arsenic and the additional iron. In a final stage, the water is disinfected with NaOCl before the distribution to the consumers. During aeration, Fe(II) is oxidized and some phosphate is sorbed on the formed iron oxides but remains in suspension until it is removed during the subsequent biological filtration stage. Mn(II) is oxidized by biological oxidation and the produced insoluble manganese oxides are removed by filtration. NH\textsubscript{4}\textsuperscript{+} is biologically oxidized and removed from the water via nitrification and formation of nitrates. As(III) is oxidized but not removed during the subsequent biological filtration stage. Arsenic is removed to below 10 µg/L during the subsequent coagulation and filtration treatment stage. Similarly, the final concentrations of Fe(tot), Mn(tot) and NH\textsubscript{4}\textsuperscript{+} are below the EC parametric values of 200, 50 and 500 µg/L respectively.

\textbf{Keywords:} Arsenic; Phosphate; Biological oxidation; Manganese oxides; Ammonium; Nitrification

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1. Introduction

Groundwater is used for drinking water supply almost everywhere in the world and usually constitutes water of higher quality than the surface water, since it is typically free from disease causing microorganisms. However, groundwater contamination by organic or inorganic micropollutants is a major public concern in many regions across the world [1].

In particular, iron and manganese are typical unwanted constituents in drinking water causing aesthetic problems, but manganese is also toxic and is regulated in most countries (WHO health based guideline value of 0.4 mg/L [2]). The presence of ammonium is undesirable because it causes taste and odour problems as well as reduced disinfection efficiency if the drinking water is to be disinfected with chlorine [3]. Arsenic, which is also a common groundwater contaminant, is a highly toxic element and chronic arsenic consumption can lead to carcinogenesis. [4]. These constituents are frequently present in anaerobic groundwaters. After oxygen is consumed, manganese oxides, nitrate and iron oxides are used as electron acceptors by the microorganisms and the outcome of these reactions is the release of dissolved Fe(II), Mn(II) and NH$_4^+$ in the reducing groundwater (i.e, anaerobic groundwater where reducing conditions prevail) [5]. In addition, iron exerts a strong influence on arsenic concentrations in anaerobic groundwaters, because one possible mechanism promoting the mobility of arsenic in groundwater is the reductive dissolution of iron oxides with sorbed arsenic [6].

In Greece, the presence of these compounds in drinking water is regulated by the Drinking Water Directive of the European Council (98/83/EC) on the quality of water intended for human consumption. According to this directive, the parametric values (previously, the term was Maximum Admissible Concentration) for these constituents are: 200 µg/L for Fe, 50 µg/L for Mn, 500 µg/L for NH$_4^+$ and 10 µg/L for As.

The removal of iron and manganese is generally accomplished by chemical or biological oxidation [7]. The removal of ammonium can be accomplished by biological oxidation and conversion to nitrate [8]. Several methods exist also for the removal of arsenic, such as coagulation and filtration, adsorption on activated alumina or granular ferric hydroxide, removal during Fe-Mn oxidation, membrane filtration, biological oxidation of Fe(II) and Mn(II) and the use of zero valent iron [9,10].

It is well established that in reducing groundwaters at circumneutral pH values, arsenic is mainly present in its trivalent form of arsenite as undissociated arsenious acid (H$_3$AsO$_3$, pK$_a$:9.22) [11]. Oxidation of arsenite to arsenate (i.e., HAsO$_4^{2-}$) is generally a prerequisite for efficient arsenic removal. Therefore, in the case of reducing groundwaters, arsenic oxidation should be taken under consideration in the design of a treatment method [9].

The objective of the present paper is to present the application of a treatment method for the removal of iron, manganese, ammonium and arsenic from groundwater, which is intended for human consumption. It represents a case study, applying the biological oxidation of NH$_4^+$ and Mn(II) for the simultaneous As(III) oxidation and subsequent As(V) removal by coagulation from groundwaters. To the best of our knowledge, this is the first paper presenting this type of application in real groundwaters in full-scale operation. Furthermore, the investigation of the chemical, physical and biological processes taking place during the several treatment stages shed light on the mechanism of arsenic removal from iron and manganese containing groundwaters, in the presence of relatively high concentrations of phosphate. The location of the treatment unit is in Northern Greece in the city of Malgara, which is an arsenic affected area of the European Union and where As(III) comprises the main arsenic species in the groundwater. Uranium concentrations were relatively low (below 1 µg/L) in the
specific groundwaters because the prominent reducing conditions diminish its mobility [12].

2. Experimental

2.1. Description of the treatment unit

The applied method is based on the oxidation of Fe(II) by aeration, followed by biological oxidation of Mn(II), ammonium and As(III) in upflow filters, and subsequent coagulation-direct filtration in down flow filters. The treatment plant comprised initially only the coagulation unit and it was designed to remove manganese from groundwater, since arsenic was below the maximum admissible concentration of 50 µg/L, according to the previous European drinking water directive 80/778/EEC. After the revision of the limit, the treatment unit was improved to remove also the arsenic to below 10 µg/L. The improved treatment unit is in operation since the beginning of 2005 and it consists of five treatment stages, as shown in Fig. 1: (a) aeration, (b) up-flow filtration-biological oxidation, (c) coagulation (d) down-flow filtration and (e) disinfection using NaOCl.

(a) Firstly the groundwater is subjected to aeration, directly after pumping. The water flows through the aeration tank \((V = 30 \, \text{m}^3)\) to achieve complete saturation with oxygen (i.e., 8.2 mg O\(_2\)/L), as measured systematically in the field. Oxygenation takes place through air dispersers and the water stays in contact with air for 7 min.

(b) The second stage is an up-flow filtration unit based on three open columns operating in parallel and filled with sand and anthracite of total height 1 m and inner diameter of 2.4 m. The first (lower) layer consists of sand and is of 0.4 m in height. The sand grains diameter is 0.4–0.8 mm and the porosity is 42%. The second (upper) layer (0.6 m in height) consists of anthracite (0.8–1.6 mm grain diameter) and a porosity of 49%. The filters operate in up flow mode at a linear velocity of 10 m/h. Backwashing in these filters takes place once per day in one filter, while the operation in the other two filters continues. In this way, every filter is backwashed every three days. The backwashing is operated at 30–50 m/h velocity at a flowrate of 113 m\(^3\)/h for 4 min. In the filter columns filtration and biological oxidation take place, which lead to removal of previously oxidized Fe(II), oxidation and removal of remaining Fe(II), Mn(II) and NH\(_4^+\) and to oxidation of As(III). The biological oxidation takes place through the growth of iron and manganese oxidizing bacteria, which are indigenous in groundwaters. The aeration in the previous step helps the microorganisms to oxidize iron and manganese. The bacteria derive energy required for their growth by reactions in which Fe(II), Mn(II) and NH\(_4^+\) are oxidized and removed from the water [7,8]. It has to be mentioned that in the absence of bacteria, manganese oxidation is very slow and actually takes place only at pH values above 9. This observation and data from previously published papers [7,8] supported the fact that the oxidation processes taking place are catalyzed by bacteria.

(c) In the third treatment stage, the treated water is subjected to coagulation for the removal of arsenic. The coagulation is carried out by spiking FeCl(SO\(_4\))\(_2\) (13 ml/m\(^3\)) from a stock solution of 180g Fe/L in a coagulation tank with a cross section of 4.7 m\(^2\) and 5 m\(^3\) total volume.

(d) The water after coagulation enters the final closed filters, which operate in down flow mode. In this final stage, arsenic is removed by filtration of the insoluble products. These filters consist also of an upper layer of anthracite and a lower layer of sand. At the very bottom there are two thin layers of sand of higher grain diameter, firstly of sand with 1–3 mm grain size (150 mm deep) followed by another 150 mm deep layer of sand with grains of 3–6 mm diameter. The backwashing takes place every 18 h and is performed in up-flow mode, firstly with air injection followed by treated groundwater. The air flow rate is 180 m\(^3\)/h and it lasts 3–5 min. Subsequently,
treated water flows at a linear velocity of 30–50 m/h (3–5 times higher flow rate than in normal operation) for 10 min. After the filters are set back into operation, the water treated in the following 7 min is not distributed to consumption.

(e) Finally, in the last stage the water is disinfected with NaOCl (at a rate of 1.17 L 12% NaOCl/h). The use of hypochlorite is necessary because the water pipe distribution system is old and the water must have residual disinfection activity, to avoid microbiological contamination during the water supply. The total water supply rate is 70 m$^3$/h.

2.2. Sampling and analysis

Water samples were collected regularly from five sampling points: (1) at the inlet (corresponding to the groundwater); (2) after the aeration stage; (3) after the up-flow filtration stage; (4) after the coagulation tank; and finally (5) after the down-flow filtration, which corresponds to the water going to distribution before the disinfection stage (Fig. 1). Unfiltered, not acidified samples were collected for the measurement of alkalinity, sulfate, TOC and nitrate. For the determination of cations, total arsenic and boron unfiltered and filtered (0.2 µm nylon filters) samples were collected and acidified on site with 2M HCl to 25 mM final HCl concentration.

Additional samples were collected for arsenic speciation, performed on site, using the technique of Meng and Wang [13]. Briefly, 50 ml of groundwater sample were filtered through a disposable cartridge packed with 2.5 g of selective aluminosilicate adsorbent for As(V). As(III) remained in the filtrate. The filtrate was acidified and later analyzed for total arsenic. Meng and Wang reported that the average recovery of As(III) in the filtrate was 98% for total arsenic concentrations below 500 µg/L, which we have verified in the laboratory for lower concentrations (i.e., 50 µg/L).

2.3. Analytical determinations

Total arsenic concentrations were determined with a hydride generation atomic fluorescence spectrometer (PS Analytical Ltd., Kent, UK) and with ICP-MS (Thermo Finnigan Element 2).

Major elements such as Fe, Mn, P, B, Na, K, Ca, Mg, P, S were determined by ICP-OES
(Spectro Ciros CCD). Alkalinity and total hardness were measured by titration (Metrohm 809, Titrand). Ammonium and nitrate were measured immediately after sampling using test kits from Merck with detection limits of 0.01 mg/L for \( \text{NH}_4^-\text{N} \) and 0.1 mg/L for \( \text{NO}_3^-\text{N} \). The methods are analogous to ISO 7150/1 and ISO 7890/1 respectively. We validated the field measurements with laboratory measurements, i.e., by comparing the sum of \([\text{NO}_3^-]\) and \([\text{NH}_4^+]\) concentrations by the total-N concentration, measured in the laboratory with a TOC-analyzer (Shimatzu 5000). The results from test kits and laboratory measurements did not differ by more than 10%.

3. Results and discussion

3.1. Groundwater characterization and reasoning for the decision on the treatment method

The chemical composition of the groundwater is presented in Table 1, together with the water composition after the treatment and the respective parametric value imposed by the drinking water directive 98/83/EC, for several contaminants.

The groundwater, directly after pumping, has a pH of 7.9, is relatively anoxic (DO <2 mg/L) and has a redox potential slightly over 0 mV, indicating that reduced conditions prevail. The presence of Fe(II), Mn(II) and \( \text{NH}_4^+ \) are typical of reducing conditions. Manganese and ammonium concentrations (0.235 and 1.2 mg/L respectively) were over the EC parametric values (0.05 and 0.5 mg/L respectively), whereas Fe(II) concentration (165 \( \mu \text{g/L} \)) was below the current EC parametric value.

The total arsenic concentration of 20 \( \mu \text{g/L} \) is higher than the EC parametric value of 10 \( \mu \text{g/L} \) and requires remedial action. Arsenic is mostly present in its trivalent form \((\text{As(III)}/\text{As(tot)} = 70\%)\), in consistency with the observed groundwater reducing conditions. Arsenic speciation can be used as a redox indicator of groundwaters [14] and is also of great importance in the decision of treatment. \text{As(III)} is generally less efficiently removed by the conventional methods and therefore, for efficient As(III) removal oxidation to As(V) is necessary [9].

While the concentration of phosphate at 550 \( \mu \text{g/L} \) does not constitute a problem for the drinking water quality, it can adversely affect arsenic removal efficiency, since phosphate competes with arsenic for the available sorption sites on iron and manganese oxides [15].

The above factors are important in the decision of the treatment method. Arsenic, manganese and ammonium must be removed from the water before it will be distributed for consumption. Iron and manganese could be removed by chemical oxidation. However the use of chemical reagents increases the overall cost of the treatment method and reduces its sustainability. Alternatively, biological oxidation of iron and manganese can

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Groundwater (filtered samples)</th>
<th>Treated water (filtered samples)</th>
<th>EC limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(tot) (( \mu \text{g/L} ))</td>
<td>20 (0.27 ( \mu \text{M} ))</td>
<td>4 (0.05 ( \mu \text{M} ))</td>
<td>10</td>
</tr>
<tr>
<td>As(III) (( \mu \text{g/L} ))</td>
<td>14 (0.19 ( \mu \text{M} ))</td>
<td>1.4 (0.02 ( \mu \text{M} ))</td>
<td>—</td>
</tr>
<tr>
<td>Fe (( \mu \text{g/L} ))</td>
<td>165 (2.95 ( \mu \text{M} ))</td>
<td>5 (0.09 ( \mu \text{M} ))</td>
<td>200</td>
</tr>
<tr>
<td>Mn (( \mu \text{g/L} ))</td>
<td>235 (4.3 ( \mu \text{M} ))</td>
<td>5 (0.09 ( \mu \text{M} ))</td>
<td>50</td>
</tr>
<tr>
<td>B (mg/L)</td>
<td>0.24 (24 ( \mu \text{M} ))</td>
<td>0.24 (24 ( \mu \text{M} ))</td>
<td>1</td>
</tr>
<tr>
<td>NO3 (mg/L)</td>
<td>0.25 (4 ( \mu \text{M} ))</td>
<td>4.3 (69 ( \mu \text{M} ))</td>
<td>50</td>
</tr>
<tr>
<td>NH4 (mg/L)</td>
<td>1.2 (67 ( \mu \text{M} ))</td>
<td>0.05 (2.7 ( \mu \text{M} ))</td>
<td>0.5</td>
</tr>
<tr>
<td>PO4 (( \mu \text{g/L} ))</td>
<td>550 (5.8 ( \mu \text{M} ))</td>
<td>30 (0.3 ( \mu \text{M} ))</td>
<td>—</td>
</tr>
<tr>
<td>SO4 (mg/L)</td>
<td>0.49 (5 ( \mu \text{M} ))</td>
<td>3.4 (35 ( \mu \text{M} ))</td>
<td>250</td>
</tr>
</tbody>
</table>
be applied, based on the iron and manganese oxidation by the iron and manganese oxidizing bacteria, which are indigenous in groundwaters [7,16]. In addition, it is also well established that ammonium can be removed by biological oxidation by indigenous nitrobacteria, and the end product will be nitrate through the process of nitrification [8].

The application of biological oxidation can also lead to As(III) oxidation, according to recent publications describing the oxidation of As(III) during the biologically mediated oxidation of Fe(II) and Mn(II) [16,17]. However, because the concentration of iron and manganese are not sufficiently high to produce excessive iron and manganese oxides, it is expected that phosphate will out-compete arsenic sorption and hinder its removal. For these reasons the subsequent coagulation and filtration step is applied.

3.2. Fe, NH$_4^+$, Mn and PO$_4^{3-}$ removal

The concentrations of iron and manganese in the different treatment stages are shown in Fig. 2. During the first treatment stage of aeration, which is essential for the subsequent biological oxidation (the bacteria require oxygen to mediate the reactions), it can be noticed that only the concentration of dissolved iron in the filtered samples changes. This is expected since the kinetics of iron oxidation at pH 7.9 are very fast ($t_{1/2}$: roughly 2–3 min) [5] and therefore, by simple aeration, Fe(II) is oxidized to Fe(III), which at pH 7.9 forms hydrous ferric oxides (HFO). Therefore, the Fe(II) concentration in the filtered samples after aeration was negligible. On the other hand (Fig. 2b), the oxidation of Mn(II) by dissolved oxygen results only in a low decrease (i.e., 5–10%) of the dissolved manganese concentration, attributable to the fact that Mn(II) oxidation by dissolved oxygen does not take place significantly at pH values below 9 [5]. Ammonium concentration remained practically constant as well (data not shown).

A significant decrease in dissolved phosphate concentration (27% or 1.6 µM) occurs during the stage of aeration. This can be attributed to phosphate sorption onto the particulate iron oxides which are formed during Fe(II) oxidation. Indeed, during aeration, we observed 2.7 µM of Fe(II) oxidation. Considering that one mole of phosphate can formally react with 1 mole of Fe(III) to form FePO$_4$ and in practice Fe/P ratios of 1.5–2.0 are needed to precipitate phosphate [15], the formation of 2.7 µM Fe(III) resulted in the expected sorption of phosphate (1.6 µM) and removal in the filters.

Manganese and ammonium are removed during the next treatment stage, which involves the up flow filtration and biological oxidation. Ammonium oxidation leads to its conversion to nitrate through the process of nitrification, which is confirmed by the increase in the nitrate concentration during treatment (Table 1). From 1.2 mg/L of ammonium the residual concentration is <0.05 mg/L, which means that roughly 64 µM of ammonium are converted to nitrate during the biological treatment stage. Indeed, the nitrate concentration increases from 0.25 to 4.3 mg/L during biological oxidation, which corresponds to the formation of approximately 65 µM of nitrate implying, an 1:1 ammonium conversion to nitrate.

Mn(II) is efficiently oxidized and removed (Fig. 2b) in the second stage, due to the presence of manganese oxidizing bacteria and contact with manganese oxide surfaces, which accumulate in the filter during the filtration of manganese oxides on the sand and anthracite, as also reported in the literature [7]. Iron removal occurs mainly by filtration of the HFO formed in the first (aeration) stage. During biological filtration and oxidation, we observed also roughly 68% phosphate removal (4 µM removal), which is most likely attributable to the retention of phosphate sorbed on the HFO formed during aeration and additional sorption on biogenic manganese oxides formed in the filter (Fig. 3).
Additional phosphate removal was recorded during the coagulation-direct filtration step. The use of FeClSO₄ as a coagulant adsorbed the rest of phosphate, which was removed during the subsequent filtration step.

3.3. As(III) oxidation and As removal

The concentration of As(III) and of As(tot) in unfiltered and filtered samples in the different treatment stages is illustrated in Fig. 4. In the first treatment stage, aeration of the groundwater to saturation takes place. As already discussed, this process promoted the oxidation of ferrous iron but not of manganese. Similarly to manganese, As(III) oxidation was insignificant. The As(III) concentration was reduced by roughly 10%, while the total arsenic concentration decreased by 3%. This is attributable to the fact that abiotic oxidation of As(III) by dissolved oxygen is very slow (t₁/₂ 2–5 days), depending on the concentrations of dissolved ferrous iron [18]. Recently
Hug and Leupin [19] have shown also that As(III) oxidation by dissolved oxygen was not measurable in the absence of Fe(II) and took place only in the presence of 20 µM or higher of Fe(II). In the present case study, the concentration of dissolved ferrous iron is relatively low (roughly 3 µM) and although the water was air saturated, oxidation of As(III) on the time scale of minutes was negligible.

However, As(III) was almost completely oxidized in the following treatment stage, in which manganese and ammonium were oxidized as
well. These results are in very good agreement with previously published work, which reported As(III) oxidation in parallel to biological Fe(II) and Mn(II) oxidation in groundwater treatment [17,20]. However, the removal of As(tot) in this stage was low (roughly 22% in the filtered samples) and therefore, after this treatment stage the arsenic concentration was still higher than 10 µg/L.

According to previously published papers [17,20], higher removal of As(tot) would be expected to take place by sorption onto the bacteriogenic iron and manganese oxides that accumulate in the filtration column, during their filtration and removal from water.

In the present case, low Fe(II) and Mn(II) concentrations in addition to the relatively high phosphate concentration are the reasons for the ineffectiveness of As(tot) removal in this treatment stage. The low concentrations of Fe(II) and Mn(II) result in only low amounts of oxides acting as adsorbents for arsenic removal. The limited adsorption sites on the iron and manganese oxides are occupied by phosphate, since roughly 68% phosphate removal was recorded. These results are in agreement with previous studies, where As(III) removal was examined in Fe(II) (150 µg/L) and Mn(II) (600 µg/L) containing groundwaters in the presence of phosphate in the range of 0.6–1 mg/L. In that study it was shown that, although arsenic removal was adversely affected by the presence of phosphates, As(III) oxidation was very efficient and practically unaffected [20].

The removal of arsenic takes place in the next stages of coagulation and the following down flow filtration. The water, after biological oxidation, is treated with the coagulant (FeClSO₄). As(V) is sorbed on the HFO colloids formed by hydrolysis of the added Fe(III), which stay in suspension in the coagulant tank until they are removed in the next stage of down flow filtration [21]. This is clearly shown in Fig. 4 where the As(tot) unfiltered concentration was still over 12 µg/L, while the As(tot) filtered concentration was below 4 µg/L and did not change significantly in the last filtration stage.

4. Conclusions

The decision on a remedial action for the removal of arsenic from groundwater depends strongly on the local groundwater composition. In the present case study, the following factors were important for the design of the treatment method: (a) As(III) constituted roughly 70% of the total arsenic content (b) manganese and ammonium concentrations were higher than the EU parametric values and (c) the phosphate concentration was sufficient to out-compete arsenic sorption on the bacteriogenic iron and manganese oxides.

The biological oxidation of manganese and ammonium promoted As(III) oxidation as well, which was essential to achieve efficient arsenic removal. However, due to the presence of phosphate and low natural Fe(II) concentration, an additional treatment stage was necessary to produce drinking water with arsenic concentrations below 10 µg/L. In an added coagulation step with addition of FeClSO₄, HFO colloids with sorbed arsenic were formed and subsequently removed by filtration. The final treated water complies with the EC directive 98/83 of water intended for human consumption. This method presents several advantages over conventional treatment methods, such as low operational costs due to the circumvention of added oxidants and high reaction rates due to biological oxidation. It is a combined groundwater treatment approach, i.e, bioremediation combined with physicochemical treatment and can find broader application in other cases, such as in arsenic affected regions in southeastern Europe (Romania, Hungary, and Croatia).

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