Arsenic release from deep natural solid matrices under experimentally controlled redox conditions

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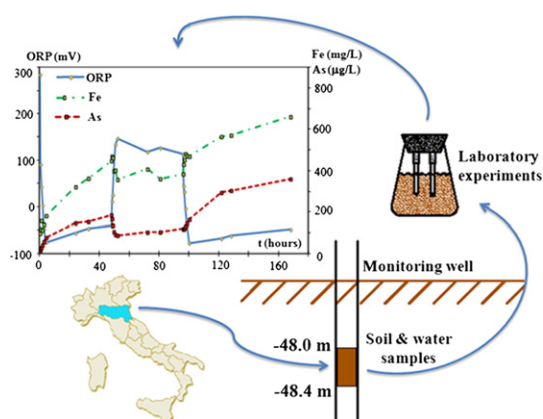[c] Università della Calabria, Dipartimento di Difesa dal Suolo, via P Bucci 42B, 87036 Rende (CS), Italy
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HIGHLIGHTS

► As release from two solid matrices was explored under different redox conditions.
► As content in vegetal matter is one order of magnitude larger than in sand.
► High correlation between redox conditions and As release was evidenced from the tests.
► Vegetal matter has large binding capacity and can enhance As release to groundwater.
► As concentration in groundwater depends on release from different solid matrices.

GRAPHICAL ABSTRACT

ABSTRACT

We investigated the role of iron (Fe) on arsenic (As) release from two samples of a natural deep soil collected in an aquifer body in the Emilia-Romagna Region, Italy. Each sample is representative of a different solid matrix, i.e., sand and vegetal matter. Batch experiments were performed by applying alternating aerobic/anaerobic conditions to the samples under a range of redox and pH conditions, consistent with the corresponding values measured in the field. Arsenic mobilization was triggered by abrupt and rapid changes in redox conditions and displayed a clear correlation with oxidation/reduction potential for both solid matrices. Vegetal matter showed high binding capacity and large As concentration release. Arsenic release was also correlated with Fe released from the solid matrices. Our results suggest that the environmentally critical As concentrations detected in some aquifers in the Emilia-Romagna Region are consistent with (a) the occurrence of high natural As content in the component of the host porous medium associated with vegetal matter and (b) the effect of possible sharp localized (and temporally oscillating) variations in redox conditions.

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1. Introduction

Most environmental problems related to Arsenic (As) occurrence in groundwater are the result of mobilization processes from sediments or rocks under natural conditions (Smedley and Kinniburgh, 2002). Anthropogenic activities can also play a significant role to increase As concentration in groundwater through mining activities, combustion of fossil fuels, the use of arsenical pesticides, herbicides and crop desiccants, and additives to livestock food (e.g., Harvey et al., 2002; Wang and Mulligan, 2006). An additional potential driver of dissolved As concentrations is related to anthropogenically-induced chemical changes to natural systems leading to enhanced releases from the host porous matrix (e.g., Yaron et al., 2012 and references therein).

The occurrence of high concentrations of As in groundwater is a globally recognized problem (Smedley and Kinniburgh, 2002 and references therein). Arsenic is highly toxic and its limit value in drinking waters was set to 10 μg/L (WHO, 1993). Arsenic concentrations above 50 μg/L have been documented in different aquifers worldwide, including Argentina, Bangladesh, Chile, China, Hungary, India (West Bengal), Mexico, Romania, Taiwan, Vietnam and south-west USA. Moreover, occurrence of As in natural springs associated with geothermal waters has been reported in Japan, New Zealand, Russia (Kamchatka region), Iceland, France, Dominica and USA (Smedley and Kinniburgh, 2002 and references therein). High natural As concentrations in sediments are also common in volcanic matrices. For example, Baiocchi et al. (2011) reported a map of volcanic aquifers in central and southern Italy where As concentrations frequently exceed 50 μg/L.

Significant As concentrations have been recorded at a number of locations in Italy, including Sardinia (Frau et al., 2008), the Brenta Plain in northeastern Italy (Ungaro et al., 2008), southern Tuscany (Baroni et al, 2004), Ischia Island (Daniele, 2004) and Central Italy (Preziosi et al., 2010).

The Emilia-Romagna Region in Italy displays a typical signature of an As hot-spot. The regional aquifer system has been monitored for the past 20 years through an extensive network of observation wells managed by ARPA — Regional Agency for Environmental Protection. Observed As concentrations in groundwater locally showed consistently large values, often exceeding 50 μg/L (e.g., Molinari et al., 2012 and references therein). Zavatti et al. (1995) hypothesized these large values to be associated with natural release processes from the geomaterial filling the Po Basin. Martinelli et al. (2005) and Marcaccio et al. (2005) proposed a different explanation based on local dynamics of redox potential according to which changes in groundwater levels as a result of water withdrawals could lead to the enhanced dissolution of As-bearing Fe oxides/hydroxides (Postma et al., 2007; Berg et al., 2007). This idea is consistent with other studies performed in phreatic water bodies (e.g., Harvey et al., 2002; Du Laing et al., 2009).

Several studies (e.g., Sadiq, 1997; Smith et al., 1998; Sracek et al., 2004) documented adsorption of As on clay, Fe(III), Mn(III/IV), and Al(III) oxides, calcium carbonates, and humic substances. There is an overall consensus that Fe oxides/hydroxides are the most important adsorbents for As in sandy aquifers in both acidic and alkaline soils (Sadiq, 1997; Manning et al., 1998; Lin and Puls, 2000; Dixit and Hering, 2003). The reductive dissolution of Fe oxides, promoted by burial, flooding, transport of organic material or other reducing agents is considered as a key mechanism of As release in groundwater (e.g., Korte, 1991; Stumm and Sulzberger, 1992; Nickson et al., 2000; Anawar et al., 2003).

In aqueous environments As mostly occurs in inorganic forms, as oxyanions of arsenite, As(III), or as arsenate, As(V) (Adriano, 2001). The adsorption properties of these two species are influenced by the presence of competing ions, most notably PO_4^{3-} and HCO_3^- (Livesey and Huang, 1981; Manning and Goldberg, 1996; Appelo et al., 2002). An additional relevant factor governing As mobility is pH (e.g., Pierce and Moore, 1982; Dzombak and Morel, 1990; Stumm and Morgan, 1996). Variations in pH and oxidation/reduction potential (ORP) can

be related to changes between aerobic/anaerobic conditions occurring in the subsoil and affect As speciation and its mobility (Smedley and Kinniburgh, 2002). Arsenic mobilization is difficult for high values of ORP (Oscarson et al., 1983; Gulens et al., 1979; Masscheleyn et al., 1991). On the other hand, Fe(III) and Mn(III/IV) are respectively reduced to Fe(II) and Mn(II) under neutral and acidic conditions and for ORP< +200 mV, thus causing mobilization of As bound to Fe and Mn oxides/hydroxides.

Natural organic matter (NOM) occurring in the solid matrix strongly influences solubility, mobility, bioavailability, and chemical speciation of elements such as As (Wang and Mulligan, 2006). Interactions between NOM and As include (a) the competition of As and phosphate for available sorption sites (Fontes et al., 1992; Geelhoed et al., 1998; Eick et al., 1999), (b) the formation of aqueous complexes due to the binding capacity of organic matter and changes in the redox potential of the site surfaces (Welch and Lico, 1998; Bradley et al., 1998; McArthur et al., 2001, 2004), and (c) the release of adsorbed As following the reduction of Fe and Mn oxides (Stone et al., 1994; McArthur et al., 2001). Wang and Mulligan (2006) observed that most investigations on As release considered pure minerals under laboratory conditions whereas little research has been devoted to the analysis of interactions with NOM. Redman et al. (2002) concluded that the presence of NOM may explain enhanced mobility of As(III) in sediments.

Process understanding of As release relies typically on laboratory scale experiments, either batch/incubation tests (Reddy and Patrick, 1976; Gao and Mucci, 2000; Frohne et al., 2011 and references therein) or column tests (Lim et al., 2007; Nguyen et al., 2008; Razzak et al., 2009). Considerable evidence from laboratory studies showed that As is released from sediments following flooding and the subsequent development of anaerobic conditions (e.g., Deuel and Swoboda, 1972; Hess and Blanchar, 1977; McGeehan, 1996). Guo et al. (1997) attributed the rate of As release predominantly to the dissolution of Fe and Mn oxides. Batch tests have also been employed to evaluate As adsorption and/or dissolution kinetics associated with several mineral phases (e.g., Matis et al., 1997; Jönsson and Sherman, 2008). Frohne et al. (2011) performed a set of batch experiments during which stepwise ORP variations were imposed and concluded that low ORP promotes As mobility.

Batch tests performed to assess key mechanisms governing As release have often been based on soil samples which were artificially enriched in As (e.g., Manning and Goldberg, 1997; Smith et al., 1999; Nguyen et al., 2008). Most of the documented tests typically employed distilled or deionized water (e.g., Masscheleyn et al., 1991; Burnol et al., 2007) or tap water (e.g., Nguyen et al., 2008). Only a limited set of experiments considered real untreated natural sediments (Pfeifer et al., 2004; Frohne et al., 2011) and, to the best of our knowledge, the amount of As released from natural solid matrices subject to redox changes consistent with ORP and pH values measured at field scale is still poorly documented. While a few studies analyzed the influence of organic matter (i.e., peat or humic/fulvic acids) on As adsorption on several mineral phases (e.g., Grafe et al., 2002; Pfeifer et al., 2004; Weng et al., 2009), no studies documented As release from deeply buried vegetal matter.

This work is part of a comprehensive effort aimed at investigating the natural background levels of As concentrations detected in a groundwater body located in the Emilia-Romagna Region, Italy. We present the results of a set of laboratory tests on As mobilization triggered by changes in redox conditions performed on two solid matrices, i.e., sand and vegetal matter, representative of the natural host aquifer.

2. Materials and methods

2.1. Study area, water and solid matrix sampling and preparation

Water and solid matrices samples were collected from a confined groundwater body located near Bologna (Emilia-Romagna Region,

Italy). The sedimentary dynamics of the basin are associated with an overall regressive trend from Pliocene open marine facies to Quaternary marginal marine and alluvial deposits (Ricci Lucchi et al., 1982). These form large aquifer systems composed of coarse deposits with subordinate clay, and scarce sand deposits (Regione Emilia–Romagna, 2010).

Oxidation/reduction potential (ORP) in the aquifer was continuously monitored in 1987–98 and showed the occurrence of relatively stable and slightly reducing conditions. This is consistent with (a) the presence of paleo-peats (Amorosi et al., 1996; Cremonini et al., 2008) and vegetal matter observed in the cores sampled, and (b) the detection of the reduced form of nitrogen (NH_4) in water.

Our experiments employed groundwater collected at the site in a borehole located close to the solid matrices sampling location. All As concentrations, reported during the above referenced 20 year period, were below detection limit. Other anthropogenic indicator parameters (chloride < 30 mg/L, nitrate < 1 mg/L, sulfate < 1 mg/L) showed no significant anthropogenic influence on this monitoring location.

Solid matrices collected at a relatively deep location (about 48 m), where monitored As concentrations in water were relatively large and for which no significant anthropogenic effects have been observed, were employed in the experiments, as opposed to the common practice of analyzing near surface soils (collected at a few cm depth) (e.g., Masscheleyn et al., 1991; Chatain et al., 2005). Data on the chemical composition of groundwater at this specific borehole are available from 2008. Table 1 reports grain size distribution of the solid matrix at different depths together with As and Fe contents along the selected core.

Occurrence of a sand fraction exceeding 75% was indicative of samples belonging to the target aquifer. Only these samples were selected for the total chemical determination of As and Fe contents. The deepest sample (i.e., 74.5 m) was excluded from the chemical analyses because it was identified as pertaining to the underlying aquitard. The 48.25 m deep sample was then selected for the experiments. It was noted that significant differences in As and Fe contents detected in the solid matrices collected at 48.25 and 48.30 m depth are consistent with the observation that vegetal matter is abundant in the former sample and poorly present in the latter.

The selected gravel-free solid matrix sample was then divided into two subsamples. The first one (89% of the total sample) was termed matrix A and comprised mainly sandy material with particle size less than 2 mm. The second subsample (11% of the sample) was termed matrix D and was constituted by vegetal matter which is likely the result of fossil deposition and is associated with a granulometric fraction larger than 2 mm.

2.2. Reagents used for the test

Anaerobic conditions were attained by injection of pure argon (Ar) which is chemically inert and does not produce secondary compounds during replacement of oxygen. The large atomic weight of Ar (39.948 g/mol) facilitates replacement of oxygen (15.999 g/mol) (e.g., Reddy and Patrick, 1976) and the corresponding efficient decrease of ORP to induce reducing conditions.

To drive the system towards a strongly reducing environment, we supplied a small amount of sodium ascorbate ($C_6H_7O_6Na$), which has been reported to increase the solubility of As and Fe without significantly altering the pH (Chatain et al., 2005). Reverting the system to oxidizing conditions is accomplished by supplying O_2 gas (50% in volume) with a 15% diluted solution of H_2O_2 (e.g., Voegelin and Hug, 2003). All analytical reagents employed were of high-grade purity. All analytical procedures have been validated using certified and/or internal reference materials.

2.3. Chemical analyses on solid matrices

The mineralogy of solid matrix A was determined by XRD analysis (Philips, Cu-anode). Table 2 reports the chemical concentrations of the different species detected in the two subsamples. Values of As concentrations in matrix D exceeded those detected in matrix A by more than an order of magnitude. There was also a notable difference in the Fe content between the two matrices. Values reported in Table 2 differ from those observed in the borehole at the two depths of 48.25 m and 48.30 m (see Table 1). This is due to the heterogeneous structure of the solid matrices and the possible mixing and subsequent homogenization of the different matrices which might have occurred during sampling operations.

2.4. Experimental setup

The experimental apparatus (Fig. 1) comprised a 2 L glass vessel conical flask which was hermetically sealed with an air-tight lid and filled with the solid matrix and water. Redox and pH variations in the system were continuously monitored by ORP and pH electrodes. Data transfer to a computer was performed via two data loggers. This system allowed obtaining fast and accurate modifications in redox conditions to attain the desired target values.

The experimental device is equipped with a magnetic stirrer, a combined ORP platinum electrode with a silver–silver chloride (Ag/AgCl) reference (Intelligent ORP Electrode HI 3620D, Hanna Instruments), and a pH electrode with an Ag/AgCl reference (Intelligent pH Electrode HI 1618D, Hanna Instruments) integrated with a temperature sensor. All sensors were connected to two data loggers (HI 98150N, Hanna Instruments) allowing measurements to be taken with high temporal

Table 1
Particle size distribution and As and Fe content in samples extracted at different depths within the selected core.

Depth from ground surface (m)	Sand (2000–50 μm) %	Silt (50–20 μm) %	Silt (20–2 μm) %	Clay (<2 μm) %	As (mg/kg)	Fe (mg/kg)
41.50	80.9	7.8	4.3	7.0	1.9	19,450
44.40	91.2	2.3	2.5	4.0	7.9	16,950
48.25	84.2	6.0	5.3	4.5	62.5	61,000
48.30	87.6	3.8	2.8	5.8	8.6	20,800
52.30	91.2	1.0	2.8	5.0	4.2	17,550
57.90	78.2	7.5	5.3	9.0	7.3	24,350
70.30	80.4	6.3	7.3	6.0	3.6	17,750
72.50	92.9	1.8	1.0	4.3	3.8	12,200
74.50	45.8	16.8	32.1	5.3	–	–

Table 2
Concentrations of elements measured in solid matrices A and D adopted in the experiments. Total element concentrations in the solid matrix were determined following the UNI EN 13346 (2002) methodology.

Element	Solid matrix	
	Sand (matrix A) mg/kg	Vegetal matter (matrix D) mg/kg
Al	17,508.7	5669.0
Ca	69,333.3	63,566.7
Mg	5703.3	2473.7
K	3533.3	1896.7
Na	233.3	1110.0
Fe	23,406.7	42,590.0
Mn	730.5	203.7
As	15.3	225.2
Cd	<0.2	0.2
Cr	38.7	28.2
Cu	10.4	18.2
Ni	28.5	20.0
Pb	6.4	6.1
Zn	32.8	22.8
B	21.7	13.7

1 non-return gas exit valve

2 gas inlet tube

3 sampling/ORP regulation tube

4 on/off valve

5 syringe for sampling and reagent inlet

6 airtight lid

7 thermostat

8 magnetic stirrer bar

9 cylindrical membrane for gas diffusion

10 pH electrode

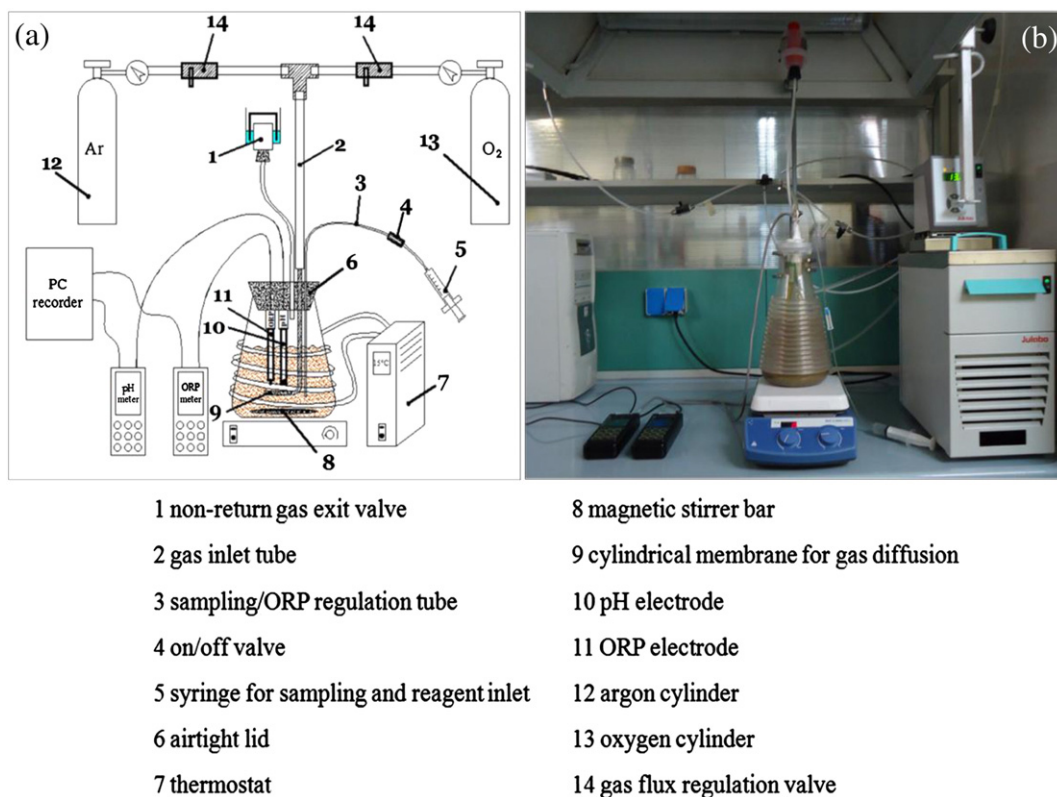11 ORP electrode

12 argon cylinder

13 oxygen cylinder

14 gas flux regulation valve

Fig. 1. Schematic design and picture of the experimental setup.

resolution (every 30 s). Ar or O_2 gases entered the system by an inlet gas tube equipped with a cylindrical membrane at the end to improve gas diffusion. A sampling tube with an on/off valve allowed collecting water samples for analysis at selected times.

Sampling was performed by means of a syringe. A syringe was also employed to inject reagents (H_2O_2 or $C_6H_7O_6Na$) into the system. The vessel was wrapped with a tygon tube which was linked to a thermostat to allow water circulation and to maintain a constant temperature of 15 °C during the test.

2.5. Laboratory tests

The experiments were performed under alternating redox conditions according to the following three phases: (1) a reducing stage which was maintained for 48 h (at −150 mV for solid matrix A and −60 mV for solid matrix D); (2) an oxidizing stage which was kept for 48 h (at +150 mV for both solid matrices); and (3) a final reducing stage sustained for 72 h (with the same redox values considered in stage 1). Differences in ORP adopted for the two matrices during the reducing stages were related to the individual solid matrices characteristics. Sandy matrix A resulted in a slightly alkaline slurry, and strong reducing conditions were attained without overstressing the system. This could not be achieved for the vegetal matter (matrix D), since it resulted in acidic slurry (associated with pH variations from 5.2 to 3.9).

We used 350 g of sand placed in 1800 mL of water for the test on solid matrix A. The test performed on solid matrix D was based on 100 g of vegetal matter placed in 880 mL of water. In both cases, the solid matrix was placed in water for 2 days before the test to allow rehydration. The vessel was then sealed to obtain a closed microcosm and the slurry was stirred to homogenize the mixture. ORP, pH, and temperature were then automatically recorded and stored during the tests.

Preliminary tests were performed to assess the optimal amount of reagent and the duration of each test phase. The first water sample was

collected after 30 min of stirring and was considered as representative of the initial conditions of the system. Argon flux at 0.9 bar was supplied to remove the free dissolved oxygen in water and bring the system to +50 mV. Once this slightly reducing condition was attained, a second sample was collected and 1 mL of sodium ascorbate 1 M was added to reach the target strongly reducing conditions. Each 10 mL solution sample was passed through a 0.45 μm hydrophilic syringe filter (Minisart, Germany) to analyze the soluble fraction.

For the first reducing and oxidizing stages (phases (1) and (2)), water samples were collected after 0.25, 0.75, 1.5, 2.5, 4.0, 24.0, 32.5, and 47.5 h. For the final reducing stage (phase (3)), samples were collected after 0.25, 0.75, 1.5, 2.5, 4.0, 24.0, 32.5, and 72.5 h.

2.6. Analytical methods for solution samples

Each 10 mL solution sample was treated before analysis with 0.3 mL of HNO_3 65%. Fe and As concentrations were determined by using atomic absorption spectroscopy with flame (PERKIN ELMER 1100B) and inductively coupled plasma mass spectrometry (AGILENT 7500ce) respectively.

Assessment of repeatability, method precision and accuracy were investigated according to UNI CEI ENV 13005 (2000) and ISO ENV 13005 (1999) protocols. The relative standard deviation values for repeatability and intermediate precision were 4% and 6%, respectively for As and Fe. All concentrations were corrected for volume changes due to aliquots of removed samples and reagent injections according to the formulation of Frau et al. (2008).

3. Results and discussion

Here, we present the results of the tests performed on solid matrices A and D. ORP was controlled during the first 5 h of each stage and was then allowed to evolve freely; pH was left free to evolve naturally during the whole test to mimic conditions occurring in the field. The mechanism triggering As release/adsorption was the abrupt and rapid

change in redox conditions. The largest concentrations of dissolved As were detected for persistent reducing conditions. This is particularly evident for the test performed on solid matrix D, as detailed in the following.

3.1. Solid matrix A (sand)

Interpretation of XRD pattern (Fig. 2) for solid matrix A reveals that the sand sample is composed by quartz (46%), calcite (18%), gypsum (11%), plagioclase (10%), feldspar (6%), mica (4%), and chlorite (5%). The peak observed at 2-Theta = 21° could be consistent with the presence of goethite at trace levels. Goethite and quartz are known to adsorb As (Smedley and Kinniburgh, 2002 and references therein). Therefore, the significant occurrence of quartz in matrix A is consistent with As concentration measured in the solid matrix (see Table 2).

Fig. 3a depicts the temporal dynamics of ORP and pH measured during the test. The reducing and oxidizing steps can be clearly identified. The solution displayed a small pH variation which is contained within the range 6.9–7.7. Once the target ORP value was achieved (± 150 mV, positive or negative depending on the stage), the system was left free to evolve naturally and the ensuing ORP and pH trends can be considered as the result of naturally occurring processes.

The As and Fe concentrations observed during the experiment are depicted in Fig. 3b. Arsenic release from the crystalline structure of As-bearing minerals was facilitated by sharp changes from oxidizing to reducing conditions and by the presence of a persistent reducing environment (more than 72 h in our tests). Data revealed a good correlation between As and Fe, consistently with the results of Nickson et al. (2000) and Anawar et al. (2003). This supports the key role of Fe mineral phases on As mobility in both reducing and oxidizing conditions. It also reveals that, despite the occurrence of other minerals which are basically constituted by other geogenic elements, Fe phases appear to display the highest affinity to adsorption of dissolved As and play a prominent role in driving As mobility.

Arsenic release displayed a distinct behavior when the solution was brought to reducing conditions: (a) As concentration increased at an approximately linear rate and with a steep slope during the initial rapid change from oxidizing to reducing conditions; (b) As concentration continued rising, albeit at a lower rate, during both reducing stages while ORP was evolving freely; and (c) dissolved As concentration increased significantly under persistent and strongly reducing conditions (note the last sampled point in Fig. 3b) highlighting a possible non-linear behavior of As concentrations for long times after the sharp change in redox conditions.

The documented As and pH behaviors were consistent with the observations of Stumm and Morgan (1996) who showed that arsenate

adsorption on Fe-oxide surfaces increases when Fe-oxide net surface charge changes from positive to negative. This happens when the pH reaches (or exceeds) the zero-charge point, which is about 7.7 for goethite (crystalline Fe oxide) (Stumm and Morgan, 1996). The observed decrease in As concentrations is also consistent with the studies of Fuller et al. (1993) who highlighted an initial rapid adsorption uptake (less than 5 min) followed by continuous uptake for at least 8 days because of As diffusion to adsorption sites on $Fe(OH)_3$ surfaces. Considering the rate at which As adsorption could occur, 90% of adsorption might have been reached within a few hours (Sadiq, 1997).

Arsenic concentration in water was then expected to decrease during the successive oxidizing phase, under free ORP evolution, as a consequence of the high adsorption capacity of Fe oxides favored by the induced oxidizing environment. A slight reduction of the ORP occurred during the oxidizing phase due to possible reducing processes which might have occurred in the system, even in the presence of global oxidizing conditions. This explains the slight increase of dissolved As detected during this experimental setup (Fig. 3b).

A recognized mechanism of As release is the reductive dissolution of the solid matrix bound to Fe(III) oxy-hydroxides (Nickson et al., 2000; Anawar et al., 2003). Fig. 3b shows that a sudden, albeit small, release of Fe took place during the first day of reducing conditions, representing the release of the rapid exchangeable fraction. A seemingly linear temporal variation of Fe concentration was observed during the reducing conditions after this first release. No significant Fe release was noted during the oxidizing stage, consistent with the mechanisms already explained. A persisting increase in Fe concentration was again observed during the transition to the third experimental phase, after switching again to reducing conditions.

3.2. Solid matrix D (vegetal matter)

Fig. 4a displays the ORP and pH temporal variation observed during the test performed on soil matrix D. The two reducing stages (ORP about -60 mV) and the oxidizing step (ORP about $+150$ mV) can be clearly identified. The test was performed under acidic conditions (pH variations in the range 3.9–5.1), consistent with the possible occurrence of humic acids bound to the vegetal matter constituting solid matrix D. The dominant occurrence of vegetal matter implies that dissolution/precipitation of minerals should not influence significantly the composition of the resulting slurry. Redox equilibrium conditions were attained more rapidly than in the experiment associated with solid matrix A (only limited variations of ORP and pH occurred within each experimental stage).

Fig. 4b depicts Fe and As concentrations measured in solution as a function of time. Observed trends were similar to those observed in
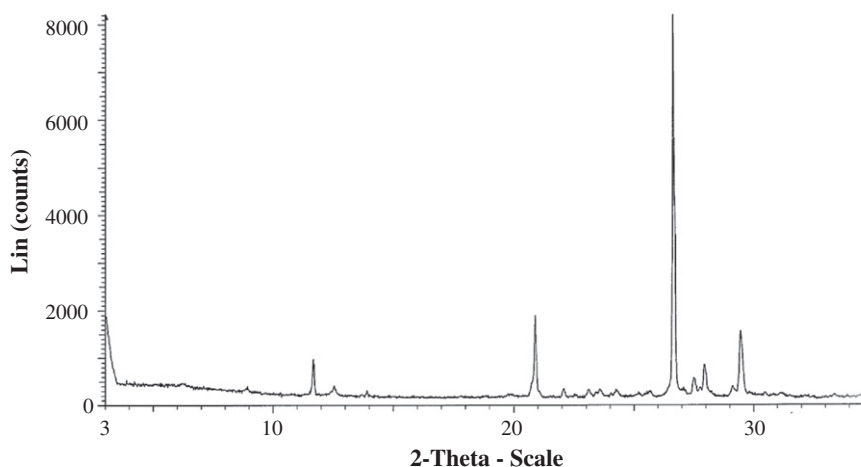

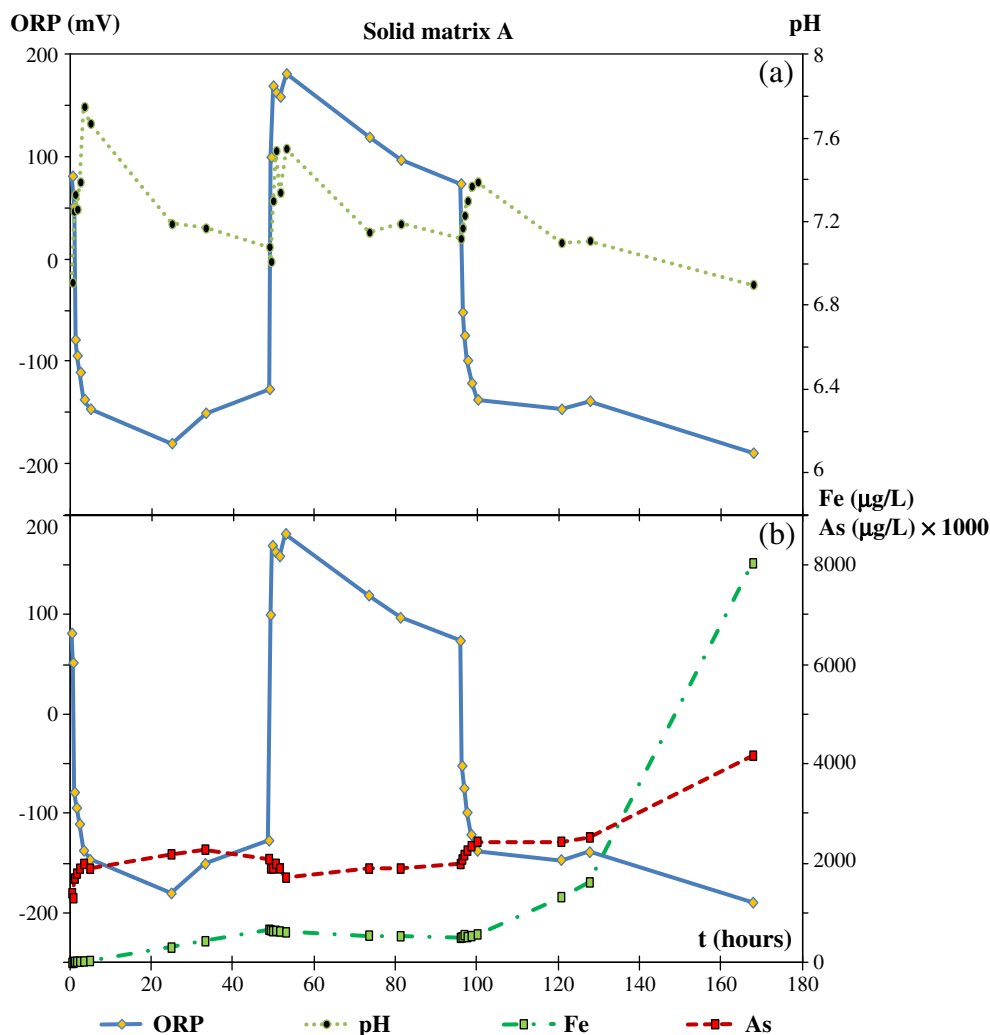**Fig. 2.** Results of the XRD analysis performed on solid matrix A (sand).

Fig. 3. (a) Temporal variations of ORP and pH during the test on solid matrix A (sand) and (b) ORP, Fe and As concentrations. Solid and dashed lines are drawn for visual aid.

the experiment performed on matrix A. The actual measured values are consistent with (a) the larger As content characterizing solid matrix D (see Table 2) and (b) the catalytic role played by organic matter for both oxidation and reduction reactions (Senesi and Steelink, 1989; Perlinger et al., 1996). Note that Fe concentrations in Fig. 4b were much larger than those reported in Fig. 3b emphasizing the significance of Fe release in this test. This is consistent with the properties of the NOM which interacts with metals and surface sites acting as an electron shuttle between inert redox species or microorganisms and ionic species (Scott et al., 1998).

The relatively high concentrations detected at the end of each reducing stage were consistent with organic matter decomposition, induced by the reduction of dissolved O_2 concentration. This resulted in increased dissolved CO_2, enhancing denitrification. Under reducing conditions Fe and As appear in their soluble forms, Fe(II) and As(III). The increase in dissolved As concentration is consistent with the replacement of As from adsorption sites by competing anions (e.g., HCO_3^-).

Dissolved As concentrations during the test were very large, highlighting the significance of As release from the natural organic solid matrix. These concentrations decreased rapidly after the sudden change from reducing to oxidizing conditions, but later displayed a slightly increasing trend during the oxidizing stage. This observation is consistent with the occurrence of As adsorption onto Fe (oxy-)hydroxides and the possible formation of aqueous complexes promoted by the binding capacity of organic matter.

Fast release of Fe, representing the rapid exchangeable fraction bound to vegetal matter, was observed during the first day of induced anaerobic conditions. Anaerobic degradation, which started after 24 h of imposed reducing conditions, caused the dissolution of Fe minerals occurring in trace amounts, and the breaking of bonds linking Fe complexes to vegetal matter. Consistent with these two mechanisms, a notable increase in Fe concentration was then observed from about 200 mg/L to about 450 mg/L at the end of the first reducing stage.

We then observed a fast decrease of Fe concentration during the transition to oxidizing conditions (Fig. 4b, after about 50 h from the beginning of the experiment), consistent with Fe oxidation and binding processes to organic matter. This was followed by Fe concentration values fluctuating around 380 mg/L during stage 2. This observed behavior is consistent with the possible occurrence of precipitation of Fe-hydroxide transferred in solution by aerobic oxidation of the organic substance.

Iron concentration increased sharply during the transition to the third (reducing) stage, and continued to increase approximately linearly when reducing conditions were stable and persist for a long time. This behavior is consistent with different processes: (a) Fe oxides redissolution; (b) release of aqueous complexes bound to organic matter during the prior oxidizing stage; and (c) release of aqueous complexes from anaerobic degradation of organic matter.

A good correlation between As and Fe concentrations was also found for solid matrix D. This supported the idea that As mobility strongly
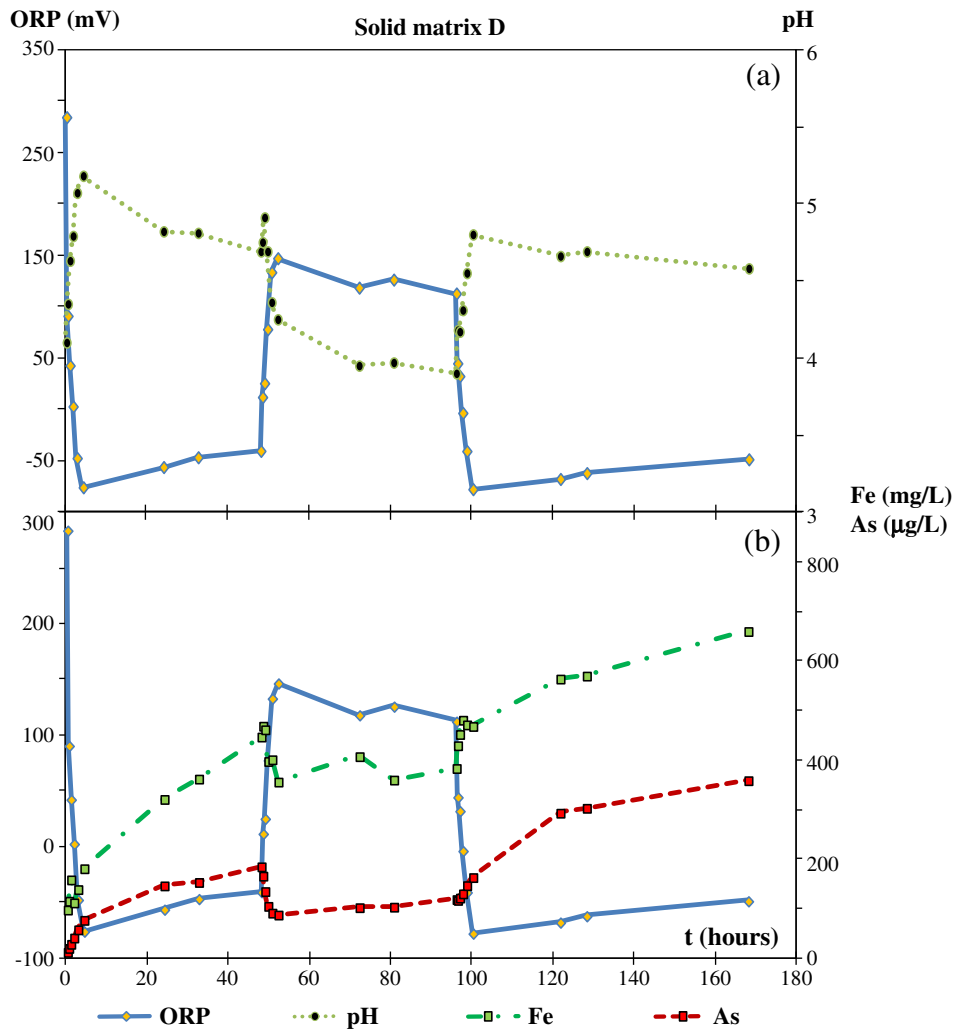
Fig. 4. (a) Temporal variations of ORP and pH during the test on solid matrix D (vegetal matter) and (b) ORP, Fe and As concentrations. Solid and dashed lines are drawn for visual aid.

depends on Fe dynamics also in the presence of organic matter, in agreement with Redman et al. (2002). This behavior could be related to a large availability of adsorption sites for As under oxidizing conditions that could be remobilized in a reducing environment.

Occurrence of dissolved As species at the field scale might then be related to processes that could have occurred in the aquifer according to different mechanisms, such as dissolution or desorption. Dissolved As concentration can then be fixated onto vegetal matter. A further change in the local groundwater redox state to reducing conditions induced by natural causes or anthropogenic activities could then remobilize As, increasing resident concentrations.

It should also be noted that As concentrations observed in solution during the third experimental stage were larger than those associated with the first reducing stage despite similar reducing conditions were attained. Our experiments highlighted that this mechanism could depend on the duration and strength of the transition between different redox stages.

3.3. Comparative analysis of experimental results

Comparison of Figs. 3 and 4 reveals that very different amounts of As were released from the two solid matrices. This is consistent with the As content in solid matrix D being 15 times larger than that in solid matrix A (Table 2). Such differences highlight the significant role of vegetal matter in the large As concentrations observed in the groundwater in the study area. Vegetal matter shows high As binding

capacity during the transition to the oxidizing stage when As concentrations in water decreases by about 100 µg/L (Fig. 4).

Fig. 5 juxtaposes the dynamics of As released concentrations which were monitored during the various stages of the tests associated with the two different solid matrices. Qualitatively similar trends can be recognized for both cases. Note that matrix A contains a small amount of vegetal matter, which is associated with the particle size fraction smaller than 2 mm. This could result in an amplification of the mechanisms that govern As mobility relative to sandy aquifers. Considering that most aquifers comprise sand with a little amount of organic matter, these findings are relevant in the framework of groundwater quality management because the detection of a significant amount of vegetal matter in a given aquifer area could be consistent with high As concentrations detected in groundwater. From the perspective of a field scale scenario, induced non-uniform flows caused by pumping could also contribute to redox variations with time and subsequent increase of dissolved As concentrations.

Solid matrices A and D have been collected from the excavation of a monitoring well pertaining to the ARPA groundwater monitoring network. Arsenic concentrations at this well location are available from 2008 to 2011 and can be compared with the aqueous concentrations measured during the tests. Dissolved As concentrations detected in the borehole vary from 2 to 74 µg/L and range between 1.3–4.2 µg/L and 12.6–360 µg/L during the tests respectively performed on solid matrices A and D. Measured dissolved concentrations depend on the solid–liquid ratio adopted during the tests which was different from that observed in
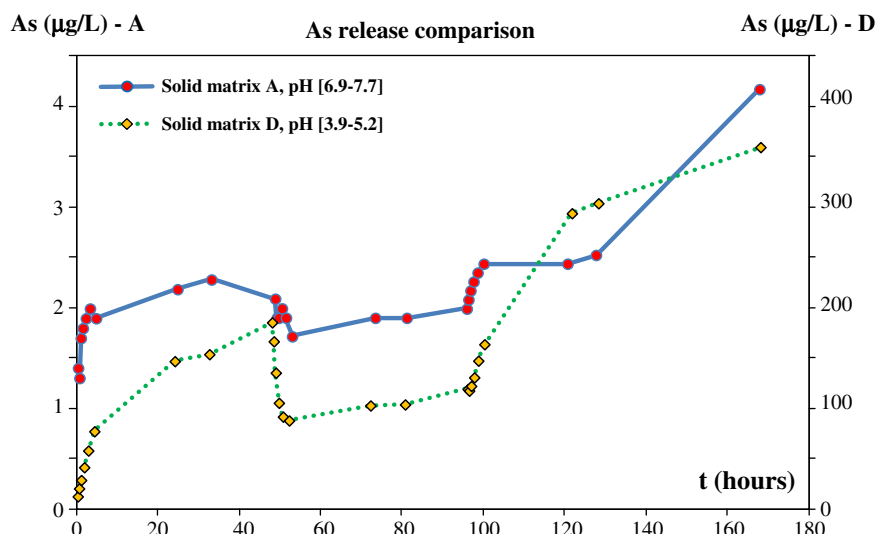
Fig. 5. Comparison between As release observed during the tests on solid matrices A and D (note the different vertical axes).

the field. The possible occurrence of other processes at the field-scale did not allow to directly transfer the observed laboratory scale concentration levels to the observed field values. However, our findings suggest that field-scale concentrations could be considered as a weighted contribution from the two solid matrices A and D. The relative weights associated with the two matrix components are proportional to the local volumetric fraction of each matrix in the porous medium, consistent with the hypothesis that the occurrence of vegetal matter can amplify As concentrations released from a sandy matrix.

Values of pH measured in the field range between 7.3 and 8.3. In our experiments we observed pH variations between 6.9–7.7 and 3.9–5.2, respectively for solid matrices A and D. Our measured pH values can be considered as representative of natural pH conditions occurring in the field under the assumption that the aquifer is mainly constituted by the analyzed solid matrix. In this sense, we observed that solid matrix D plays only a limited role to lower the total observed pH due to its intrinsic acidic features. This mechanism is consistent with the observation that, while there might be additional reactions which can affect pH, the range observed in the field under redox conditions similar to those associated with our laboratory experiments is very close to that of solid matrix A where only a minute amount of vegetal matter was found.

4. Conclusions

Our work aimed at investigating whether the high As concentrations detected at some sites within the Emilia-Romagna aquifers can be related to real field redox dynamics. We explored the trend and magnitude of As release from two natural solid matrices by a set of batch experiments under alternating redox conditions. Our work leads to the following major conclusions:

1. Laboratory scale experiments showed a distinct correlation between temporal dynamics of aerobic/anaerobic conditions and As release. Iron was associated with release trends from the tested solid matrices, similar to those of As. These trends were driven by sudden changes of redox scenarios and by temporally sustained redox conditions.
2. The high As content observed in the vegetal matter tested, as compared to values characterizing sand at the same depth, highlighted the large binding capacity of organic matter. As a consequence, the occurrence of vegetal matter in an aquifer can enhance the release of As in groundwater. This evidence suggested the need to quantify

the actual contribution of organic matter on real concentrations detected in groundwater bodies for the characterization of areas with potential high As content.
3. Arsenic was released faster from organic matter than from As-bearing minerals. This suggested that a significant occurrence of organic matter in groundwater could lead to different behaviors of aquifers in terms of temporal dynamics of dissolved species concentrations in presence of time-varying redox conditions.
4. Total observed As concentrations at the field scale in the target aquifer system could be mainly driven by (a) the amount of adsorbed As on the different solid matrices and (b) the relative fraction of each matrix occurring in the system.
5. To obtain results close to natural concentrations measured in a given groundwater body, experiments should be performed employing solid matrices and water collected at depths which are consistent with those of the target water body and relying on observation boreholes which are not influenced by anthropogenic activities.
6. High As concentrations detected in Emilia-Romagna could be consistent with the high natural content of this metalloid which is prevalently adsorbed on vegetal matter and mobilized by variations in redox conditions.

Acknowledgments

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