# Arsenic fractioning in natural solid matrices sampled in a deep groundwater body

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## 1. Introduction

Contamination of groundwater reservoirs by arsenic (As) has emerged as a worldwide problem and is nowadays recognized as one of the most dangerous threats for drinking water supply (e.g., Smedley and Kinniburgh, 2002; Charlet et al., 2007; Erban et al., 2013 and refer-ences therein). Evidence of hot-spot contamination patterns which are typically associated with As occurrence in deep groundwater bodies (e.g., Molinari et al., 2012; Erban et al., 2013 and references therein) drive the need to discriminate between anthropogenically and naturally induced As concentration levels.

Key information about mechanisms governing As distribution in soil–groundwater systems are inferred from laboratory scale studies, which constitute the primary focus of this work. These are usually per-formed by means of batch/incubation (Reddy and Patrick, 1974, 1976; Gao and Mucci, 2000; Frohne et al., 2011)or(flow-through) column tests (Lim et al., 2007; Nguyen et al., 2008; Razzak et al., 2009). Batch tests are commonly used to analyze the effect of temporal changes of oxidation reduction potential (ORP) (e.g., Molinari et al., 2013), which

in turn affect pH (Yu et al., 2007) and could occur in a natural aqui-fer as a consequence of variations of water table elevations and/or pumping/recharge regime which might favor mixing of waters with diverse chemical compositions.

A series of laboratory studies shows As release from the solid matrix following core flooding and the subsequent development of anaerobic conditions (e.g., Deuel and Swoboda, 1972; Hess and Blanchar, 1977; McGeehan, 1996; Frohne et al., 2011). Guo et al. (1997) attribute As release to dissolution and desorption from Fe and Mn oxides under the attainment of progressively reducing conditions. Frohne et al. (2011) perform a set of investigations based on an automated biogeochemical microcosm system. They find that dissolved As concentrations decrease significantly with increasing ORP and conclude that low ORP levels pro-mote As mobility. Batch tests are often performed by employing soil sam-ples which have been subject to anthropogenic contamination (e.g., by mining or agricultural activities) or enriched with synthetic As solutions prior to the laboratory tests (e.g., Manning and Goldberg, 1997; Smith et al., 1999; Nguyen et al., 2008) to identify the mechanisms governing As mobility under acidic conditions. Only few experiments consider real and untreated natural soils which have not been subject to anthropogenic pollution (Pfeifer et al., 2004) and only a limited set of studies (i.e., Molinari et al., 2013) document the amount of As released

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from natural solid matrices subject to redox changes consistent with ORP and pH values measured at the field scale.

While a few studies analyze the influence of organic matter (in the form of peat or humic/fulvic acids) on As adsorption on mineral phases (e.g., Grafe et al., 2002; Pfeifer et al., 2004; Wang and Mulligan, 2006; Weng et al., 2009), As release from natural deep vegetal matter in the presence of a variety of redox conditions has been documented only recently. Molinari et al. (2013) show that the occurrence of natural organic matter (NOM) within a soil sample extracted from a relatively deep groundwater body has a strong influence on solubility, mobility, bioavailability, and chemical speciation of As. This conclusion is also in line with the observations of Wang and Mulligan (2006). In this frame-work, a limited number of works have been devoted to the analysis of interactions between As and NOM and on the detailed documentation of the way NOM can influence As mobility (Redman et al., 2002; McArthur et al., 2004; Wang and Mulligan, 2006).

Information on As distribution within natural solid matrices is critical to discriminate between diverse As-bearing phases. In this context, As partitioning can be quantified through fractionation studies based on sequential extractions (Manful et al., 1994; Bombach et al., 1994; Voigt et al., 1996; Kavanagh et al., 1997; Matera et al., 2003), or speciation analysis performed by e.g., ICP-MS (e.g., Pantsar-Kallio and Manninen, 1997). Selective sequential extraction (SSE) methods are a valuable tool to distinguish trace element fractions associated with diverse solubility of the binding mineral phases (Hlavay et al., 2004) and provide critical information to characterize natural processes taking place in the soil–water environment (Bacon and Davidson, 2008).

A variety of sequential extraction procedures targeted to elements producing anionic species such as arsenic can be found in the literature (e.g., Tessier et al., 1979; Shuman, 1985; Gleyzes et al., 2001; Pagnanelli et al., 2004; Claff et al., 2010). Starting from these basic schemes, other procedures have been proposed (e.g., Tretner, 2002; Matera et al., 2003) to allow extracting specific fractions and improving characteriza-tion of As-bearing phases. Most of the approaches involving SSE of As (-Hudson-Edwards et al., 2004) have been targeted at assessing the mobility and availability of As in mine wastes (e.g., Ahn et al., 2005; van Elteren et al., 2006), contaminated sediments (e.g., Damris et al., 2005; Jay et al., 2005) and contaminated soils (e.g., Matera et al., 2003). Studies of the distribution of As in specific areas characterized by high natural concentration levels in sediments (e.g., Bhattacharyya et al., 2005), peat (González et al., 2006), and coal (Guo et al., 2004) are also available.

This work documents and compares the results of SSEs applied to four solid matrices representing natural host formations occurring in a deep groundwater reservoir which constitutes a typical example of an alluvial system. Emphasis is posed on highlighting the role of vegetal matter and silty matrix on As fractioning and dynamics. SSE results are also employed to support experimental evidences of geochemical dynamics of As release in presence of alternated redox conditions from a silty matrix representative of a typical aquitard layer. As opposed to the common practice of analyzing surface soil samples collected at depths of 5–35 cm (e.g., Masscheleyn et al., 1991; Chatain et al., 2005), our study and conclusions are based on analyses of samples collected at a depth larger than 45 m for which no (or minimal) anthropo-genic effects have been observed. Water sampled from the same ground-water system from which the solid matrix is extracted is employed in the tests, as opposed to the common laboratory practice of using distilled or deionized water (e.g., Masscheleyn et al., 1991; Burnol et al., 2007) or tap water (e.g., Nguyen et al., 2008).

## 2. Materials and methods

### 2.1. Hydrogeochemical setting of the study area

The investigated area (Fig. 1) is part of a confined multi-layer reser-voir system located near the city of Bologna (Emilia-Romagna Region, Italy) and is located in the Reno river Basin. The latter constitutes a syntectonic sedimentary wedge (Ricci Lucchi, 1984) forming the infill of the Pliocene–Pleistocene foredeep. The sedimentary evolution of the Po and Reno river basins is characterized by an overall regressive trend from Pliocene open marine facies to Quaternary marginal marine and alluvial deposits.

The aquifer system is mainly composed by coarse deposits with sub-ordinate clay and scarce sand deposits (Regione Emilia-Romagna and ENI, 1998). Based on sedimentological and hydrogeological analysis, three main hydrogeological complexes, i.e., Apennines alluvial fans, Apennine alluvial plain and alluvial and deltaic Po plain, were identified (Regione Emilia-Romagna, 2010). As a result of different deposition cycles diverse solid matrices, including organic matter, could be embed-ded within the main hydrogeological complexes identified (Amorosi et al., 1996, 2002). Previous studies (e.g., Zavatti et al., 1995; Marcaccio et al., 2005; Martinelli et al., 2005) suggested the possibility that dissolved As in the overall Po Basin portion in the Emilia-Romagna area be of natural origin (i.e., As rich sediments) and suggested a possible as-sociation between dissolved As concentrations and redox changes. Experimental results of Molinari et al. (2013) supported these hypothe-sis highlighting that redox changes can promote As release and the occur-rence of organic vegetal matter within the host porous formation can play a significant role on As dynamics.

Groundwater monitoring activities have been performed since about 20 years and indicate that an overall redox potential with a ten-dency towards slightly reducing conditions (i.e., $+50$ mV) characterizes the investigated area and that dissolved As concentrations in specific localized regions attain values which are about 10 times larger than the Italian regulation limit of 10 μg/L.

### 2.2. Previous findings

With the aim of investigating As dynamics in presence of redox chances, which has been hypothesized as a key natural driver at the basis of the observed large dissolved As concentrations within the in-vestigated area, samples of solid matrices were collected at various depths along a set of boreholes in the multi-layered aquifer. Among these boreholes, a core associated with large relative values of moni-tored dissolved As concentrations was identified. Along this borehole samples were collected at different depths (from 41.5 m to 74.5 m from the surface) in an amount required to perform sieve analysis. Samples were not pooled. Each one of them is strictly related to the sampling depth and was considered as representative of localized con-ditions. Texture data associated with the collected solid matrices are re-ported in Molinari et al. (2013) together with As and Fe content. Two of these samples, corresponding to sand and vegetal matter, both sampled at a depth of 48.25 m from ground surface, were separately subject to alternating redox conditions through a set of laboratory experiments. These experiments were performed by employing an Erlenmeyer flask hermetically sealed and filled with the tested solid matrix. Alternating redox conditions were induced through the addition of different oxidant/reducing agents to the experimental microcosm. Water samples were collected during these stages to assess As dynamics. Technical de-tails about the procedure are fully described in Molinari et al. (2013). Characterization studies performed on these two matrices highlighted that total As content in vegetal matter is one order of magnitude larger than that associated with sand. This was also confirmed from the above-mentioned tests which highlighted that As release from vegetal matter subject to redox changes is one order of magnitude larger than related to the tested sand. A distinct correspondence between temporal dynamics of aerobic/anaerobic conditions and As release was also observed for both tested matrices.

The previous work of Molinari et al. (2013) provided insights about As dynamics in the presence of alternating redox conditions from sand and vegetal matter. Arsenic partitioning from solid matrices sampled at different depths was not addressed and the behavior of silty matrix
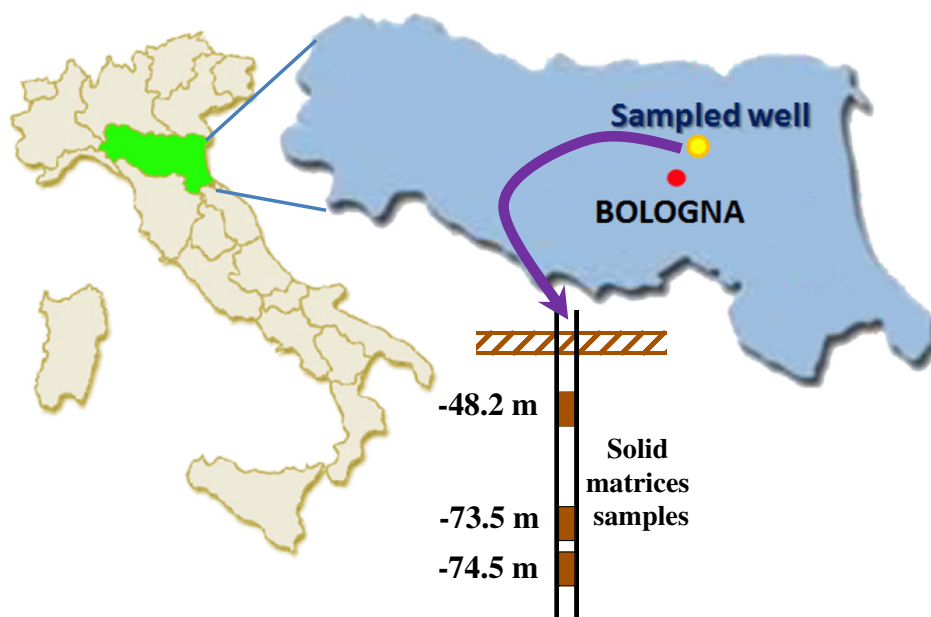
**Fig. 1.** Map of the investigated area. Full details about stratigraphic profile of the study area are reported in Molinari et al. (2012).

in terms of As dynamics in the presence of redox changes is still not investigated. These two issues are explored in this work.

### 2.3. Sampling and characteristics of solid matrices

As described in Section 2.2, several matrices were collected along a selected borehole at diverse depths ranging from 41.5 m to 74.5 m from the ground surface. Among these samples, the largest As content was documented in samples corresponding to depths of about 48.25 and 74.50 m, which are respectively related to the main aquifer and the underlying aquitard. Hence, diverse types of solid matrices have been identified at these depths and form the subject of investigation in this study. The matrix sampled at 48.25 m depth was divided into two subsamples according to particle size fractions. The first subsample is herein termed matrix A and comprises mainly sandy material. It is characterized by a granulometric fraction with particle size smaller than 2 mm and constitutes 89% of the total volume of the sample (see Table 1). The second subsample is termed matrix D and is constituted by organic matter, chiefly formed by fossil vegetal matter (see Fig. 2).

It was isolated from a section of the entire core by dry sieve analysis performed before disintegrating the sample for chemical analysis.

It is associated with a grain size fraction characterized by particle sizes larger than 2 mm and represents a volumetric fraction equal to 11% of the total sample volume (see Table 1). Samples from two addi-tional solid matrices were collected in the proximity of the bottom of the aquifer (at a depth of 73.5 m) and within the underlying aquitard (at a depth of 74.5 m) and are respectively termed as matrices B and C. Matrix B comprises mainly sandy material, while matrix C is mostly constituted by silt. Table 1 lists the key characteristics of these four solid matrices.

After sampling, the collected matrices were characterized by means of XRD analysis (Philips, Cu-anode, Type: locked coupled, Start: 3000°, End: 35.011°, Step: 0.018°, Step time: 17.6 s) for mineralogy determina-tion (this is not available for matrix D because the instrumentation employed does not enable analysis of organic matter) and selective se-quential extraction (SSE) to analyze As fractioning within each matrix. The silty material (matrix C), which is the finest among the collected matrices and is supposed to be associated with the highest potential for As release because of its high specific surface, was also subject to additional tests aimed at analyzing As dynamics, i.e., release/adsorption mechanisms, in the presence of diverse redox conditions.

**Table 1**
Total chemical element concentration detected for the tested solid matrices.

| Element (mg/kg) | Solid matrix (depth) | | | |
| --- | --- | --- | --- | --- |
| | A | B | C | D |
| Sampling depth (m) | 48.25 | 73.50 | 74.50 | 48.25 |
| Granulometric fraction type | Sand | Sand | Silt | Vegetal-rich compound |
| Al | 17,508.7 | 8834.7 | 54,493.3 | 5669.0 |
| As | 15.3 | 36.0 | 49.4 | 225.2 |
| B | 21.7 | <20 | 59.9 | 13.7 |
| Cd | <0.2 | <0.2 | 0.2 | 0.2 |
| Cr | 38.7 | 21.4 | 99.7 | 28.2 |
| Fe | 23,406.7 | 13,982.0 | 39,246.7 | 42,590.0 |
| Pb | 6.4 | 4.8 | 17.6 | 6.1 |
| K | 3533.3 | 1906.7 | 15,800.0 | 1896.7 |
| Mn | 730.5 | 849.7 | 750.3 | 203.7 |
| Ni | 28.5 | 20.4 | 86.0 | 20.0 |
| Cu | 10.4 | 6.9 | 35.0 | 18.2 |
| Na | 233.3 | 168.3 | 676.7 | 1110.0 |
| Zn | 32.8 | 36.3 | 130.6 | 22.8 |
| Ca | 69,333.3 | 60,666.7 | 40,733.3 | 63,566.7 |
| Mg | 5703.3 | 4216.7 | 9633.3 | 2473.7 |



**Fig. 2.** Fossil vegetal matter collected in the selected core.

## 2.4. Selective sequential extraction (SSE) protocol

Several protocols are available to perform SSE analysis (e.g., Coetzee et al., 1995; Kubova et al., 2004). Here, we select the protocol proposed by Torres and Auleda (2013) because it allows, with a sequence of sim-ple steps, to extract 7 fractions which can potentially bind As, a feature which is not embedded in typical protocols; it allows distinguishing crystalline from amorphous Fe–Mn oxides, the latter being highly reactive during the time span of the experiment consistent with existing literature studies (e.g., Nickson et al., 2000; Anawar et al., 2003) which highlight the important role of iron phases in the mechanisms driving As dynamics; and allows discriminating sulfide phases from organic matter.

The methodology proposed by Torres and Auleda (2013) allows characterizing the following seven fractions: (1) water soluble, (2) ex-changeable (i.e., carbonates), (3) low crystalline (i.e., Fe and Mn oxy-hydroxides), (4) crystalline (i.e., Fe and Mn oxides), (5) organic matter, (6) sulfides and (7) residual. The protocol we employ is based on seven sequential steps according to which the solid matrix is subject to different reactants allowing the progressive extraction of solid phases. The first fraction is extracted by placing the solid matrix into $O_2$-free deionized water. The second fraction is obtained from the contact with ammonium acetate while the third and fourth fractions are extracted by adding to the residual solid matrix ammonium oxalate with respectively 1 and 2 h of contact. Organic phase, constituting the fifth identified fraction, is extracted by adding NaOH to the solid residual of the previous step. $HNO_3$ is added to extract the sixth fraction and the last phase is obtained by adding $HNO_3$, HF and $HCl_4$.

## 2.5. Influence of redox conditions on As release from matrix C (silty material)

Experiments were performed by employing an Erlenmeyer flask hermetically sealed and filled with 260 g of the silty matrix C and 1550 mL of water. The target solid matrix was placed into water for about 2 days before the test to allow for rehydration of the sample. Redox and pH variations within the system were continuously monitored by oxidation reduction potential (ORP) and pH electrodes. Argon or $O_2$ gas, respectively coupled with minute amount of sodium ascorbate (i.e., 2.8 mL in 1550 mL of water) and hydrogen peroxide, were injected in the system to control redox conditions. Water samples (10 mL) were collected at selected times and analyzed by atomic absorption spectroscopy with flame (PERKIN ELMER 1100B) and in-ductively coupled plasma mass spectrometry (AGILENT 7500ce). The experimental microcosm was employed to subject the tested solid ma-trix to alternating redox conditions according to the following three phases: (1) a reducing stage, which was maintained for 24 h at an ORP of −150 mV; (2) an oxidizing stage which was kept for 24 h at an ORP of +150 mV; and (3) a final reducing stage which was sustained for 48 h with the same redox value adopted in stage 1. The slurry was continuously stirred during each stage of the test following the approach of Molinari et al. (2013) and a total of seven preliminary replicates where considered to define proper experimental conditions. The ORP was controlled during the test, while pH was left free to evolve naturally to mimic conditions occurring in the field.

## 3. Results and discussion

### 3.1. Solid matrices characterization

In the following we illustrate the results obtained from the char-acterization of the solid matrices tested through XRD analysis for mineralogy determination (this is not available for matrix D because the instrumentation employed does not enable analysis of organic matter) and the comparison of As fractioning obtained from SSE for all tested matrices.

Total concentrations of chemical elements detected within the solid matrices analyzed are listed in Table 1. Arsenic concentrations in the vegetal-reach matrix D are more than one order of magnitude larger than those detected in the other solid matrices, suggesting the occur-rence of significantly distinct features of this solid matrix, in terms of As content. Arsenic concentration in silt (solid matrix C) is larger than that observed for the two sandy matrices (i.e., A and B).

Considering the geological evolution of the study area, which consti-tutes a syntectonic sedimentary wedge, total As contents detected in matrices A and B are consistent with the findings of Ure and Berrow (1982) who observed that peaty and bog soils can be associated with a quantity of As ranging between 2 and 36 mg/kg. Arsenic content observed in matrix C is comparable to concentrations observed in Canada (Dudas, 1984; Dudas et al., 1988) or in Vietnam (Gustafsson and Tin, 1994) for acid sulfate soils. To the best of our knowledge, no data are available for As content in natural organic matter of the kind we investigate.

Comparison of As content in matrices A, B and C suggests that As content in diverse solid matrices increases with the sampling depth along the sampled borehole and tends to be largest for the smallest characteristic particle sizes. The largest As content observed for matrix C is consistent with the largest specific surface characterizing the silty particles. This latter point is also consistent with the observation that the content of most of the other elements detected in matrix C (see Table 1) is within this fine matrix.

Fig. 3 depicts XRD results for solid matrices A, B and C, highlighting the main mineralogical phases occurring in each matrix. Fig. 3a reveals that the sand in matrix A is mainly composed by quartz, calcite, gypsum, plagioclase, feldspar, mica, and chlorite. The main solid phases associated with matrix B (Fig. 3b) are quartz, calcite, feldspar, plagioclase, gypsum, chlorite and mica. The silty matrix C (Fig. 3c) is chiefly composed by quartz, gypsum, calcite, mica, plagioclase, chlorite and feldspar.

The peak observed at 2-theta = 21° for all matrices could be con-sistent with the occurrence of goethite at trace levels which, when coat-ed with quartz, could adsorb As (Smedley and Kinniburgh, 2002 and references therein). Therefore, these results appear to suggest that the significant occurrence of quartz, which exhibits low but demonstrated affinity with As(V) (Smedley and Kinniburgh, 2002; Xu et al., 1988), is consistent with As concentrations measured in the three matrices (see Table 1). Observed values for these As concentrations are in agree-ment with previous literature findings related to quartz and quartzite (e.g., Baur and Onishi, 1969; Boyle and Jonasson, 1973).

### 3.2. Arsenic partitioning within the tested solid matrices

Fig. 4 depicts the results of the SSEs for the four solid matrices ana-lyzed. For a proper interpretation of As partitioning in the tested matrices it is important to recall that structural arrangement and changes in solid phases, especially in Fe oxyhydroxides, at the atomic level can markedly affect As adsorption and desorption (Brannon and Patrick, 1987). Changes in the surface structure are likely to cause correspond-ing changes in the binding affinity of arsenate ions and protons, binding affinity being closely related to surface structure (Kinniburgh et al., 1977). For example, the conversion of ferrihydrite (which is an amor-phous structure) to goethite or to other crystalline Fe-oxide phases, which may gradually occur over time (Dzombak and Morel, 1990), can yield a decreased density of As adsorption sites (Fuller et al., 1993; Deutsch, 1997; Cornell and Schwertmann, 1996). This process can lead to desorption of adsorbed As (Hinkle and Polette, 1999). Moreover, amorphous phases, which exhibit larger specific surface area (Pfeifer et al., 2004) than crystalline structures, tend to adsorb As not only on the outer surface but also within the loose and highly hydrated struc-tures characterizing them (Bissen and Frimmel, 2003). When framed in this context, Fig. 4 enables us to observe that the amount of As bound to the crystalline fraction within each matrix is lower than the amount bound to the non-crystalline portion. This observation is relevant for
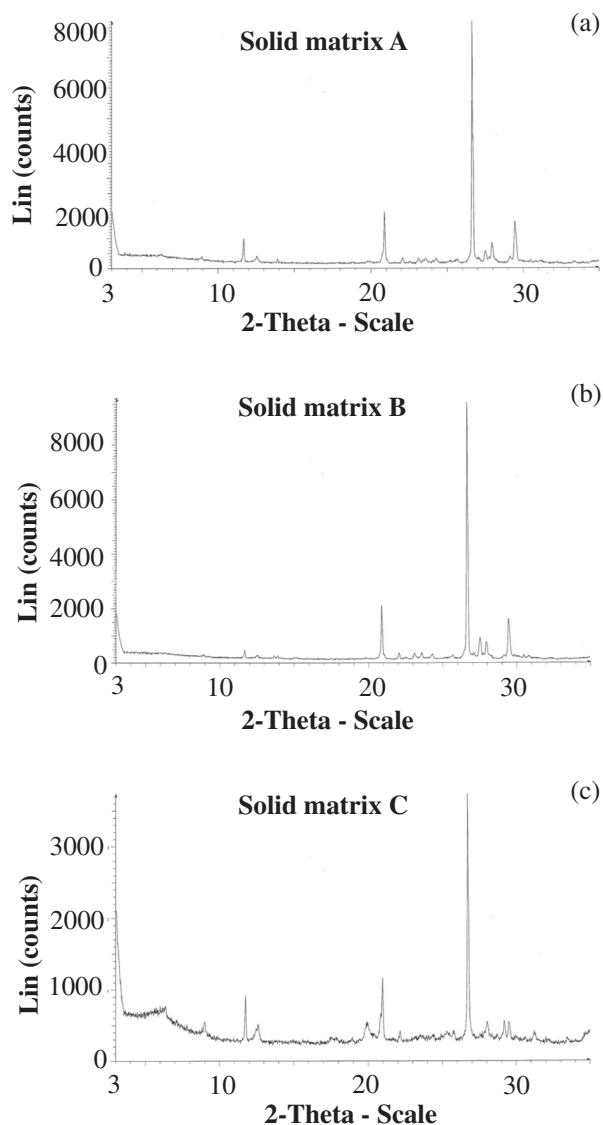
**Fig. 3.** Results of XRD analyses performed on solid matrices A (a), B (b) and C (c). Results are depicted in terms of the dependence of the measured X-ray intensity (expressed as Lin (counts)) on the X-ray angle of incidence (expressed as 2-theta-scale).



**Fig. 4.** Arsenic partitioning in solid matrices A, B, C and D.

As release assessment because the dissolution mechanisms of amor-phous and crystalline phases differ in the presence of reducing condi-tions, due to the diverse structural arrangement in solid phases at the atomic level. As a consequence, diverse As loads can be released to the resident groundwater influencing the total concentration detected in water.

Fig. 4 suggests that total As content in solid matrix D is larger (about one order of magnitude) than that observed in the other tested matri-ces. Matrix A, which was sampled at the same depth of solid matrix D (i.e., 48.25 m), is characterized by a total As concentration which is about 9 times lower than that observed for vegetal-rich matrix D. This observation suggests that the interaction between organic matter and mineral phases such as oxyhydroxides can enhance the ability of this complex system to bind arsenic as compared with the other tested ma-trices. This hypothesis is in agreement with the results of Redman et al.(2002) who found that complexation of As may occur in natural waters in the presence of natural organic matter, especially with an increase of cationic metal concentration (particularly Fe). The large As content ob-served in vegetal matrix D is consistent with the occurrence of lignin, which is a natural polymer occurring in vegetal matters of the kind we
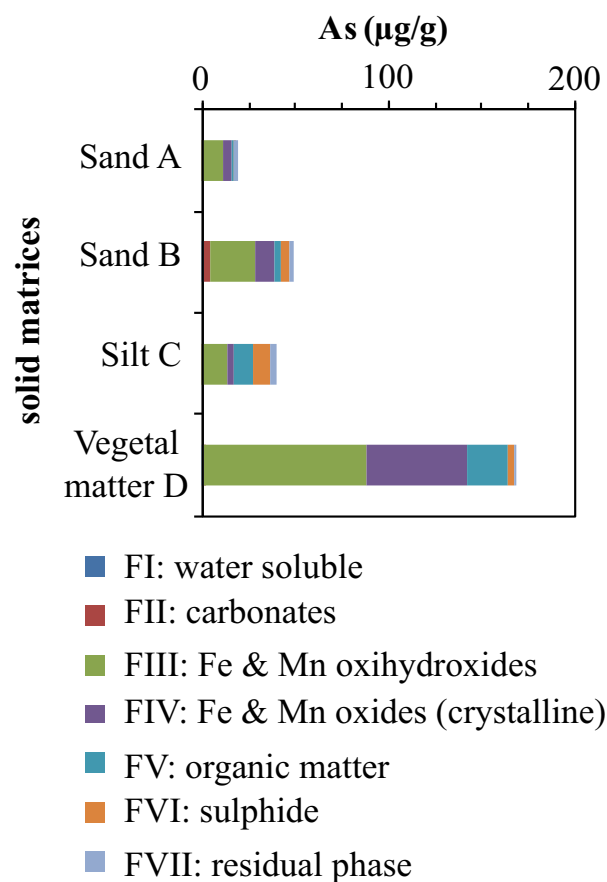
tested. Properties such as the relatively low molecular weight, the non solubility in water, and the high specific surface reveal good absorption capacities of lignin for metals (Mohanty et al., 2000). The critical role of lignin in the process of adsorption of cations such as arsenic is also highlighted by Lee and Rowell (2004) and Fallico et al. (2010).

The sand solid matrices A and B display diverse behaviors with refer-ence to total As content and As partitioning in the extracted fractions. Total As content in matrix B is more than two times larger than that in matrix A (note that matrix B has been collected close to the bottom of the aquifer).

Table 2 lists the relative proportions of As content in each of the extracted fractions and for all solid matrices analyzed. These results indi-cate that amorphous and crystalline phases constitute the most important fractions governing As partitioning in all solid matrices con-sidered. The key role of amorphous phases on As adsorption is clearly evidenced by the percentages of fraction FIII, which represents the largest component in all solid matrices (with values larger than 50%for matrices A, B and D and larger than 30% for matrix C). The amount

**Table 2**
Percentage of As content in each extracted fraction for the solid matrices analyzed.

| Solid matrix | | | | |
|---|---|---|---|---|
| A | B | C | D | Fractions |
| 0.1% | 0.4% | 0.05% | 0.2% | FI: water soluble |
| 0.1% | 7.1% | 0.1% | 0.02% | FII: carbonates |
| 56.1% | 51.0% | 33.7% | 52.0% | FIII: Fe & Mn oxyhydroxides |
| 29.9% | 21.4% | 7.4% | 32.1% | FIV: Fe & Mn oxides (crystalline) |
| 1.4% | 7.5% | 26.0% | 13.1% | FV: organic matter |
| 2.7% | 8.1% | 23.0% | 1.7% | FVI: sulfide |
| 9.7% | 4.5% | 9.8% | 0.8% | FVII: residual phase |

of As associated with Fe and Mn oxides and characterizing the crystalline fraction is also significant for all solid matrices, with the exception of the silty matrix C, where notable contents of this fraction are not evidenced.

Negligible As content was found in fraction FI, which represents the rapidly exchangeable fraction in water. This supports the idea that the simple solid–water interaction is not sufficient to trigger As release. The latter, instead, can be initiated by an abrupt change in redox condi-tions, as evidenced from the results of the batch test carried out on ma-trix C and described in Section 3.3. Arsenic association with carbonates is very poor for solid matrices A, C and D, while being only slightly sig-nificant for matrix B. Considering matrices A, B and C, one can note that increasing As concentrations were found in fractions FV (organic matter) and FVI (sulfide), consistent with the existence of dominant anaerobic conditions which take place at increasing depths along the sam-pling borehole.

Even as matrices A and D are characterized by similar percentages of As occurrence in the FIII and FIV fractions the percentage of As found in the FV fraction of matrix D is 10 times larger than that observed in matrix A. This suggests that organic matter may be characterized by As binding capacity which can be significantly larger than that related to sand and may markedly influence As biochemistry in aquifers (Redman et al., 2002; McArthur et al., 2004; Wang and Mulligan, 2006). This is a particularly critical observation when considering settings where these two matrices are in contact with paleo-waters typical of deep aquifer systems which can then become rich in dissolved As.

The observation that As content in the FVI fractions (i.e., sulfide) in-creases from matrix A to matrix C evidences that As concentrations tend to increase with increasing sampling depth along the borehole and suggests that As association with sulfide fractions increase with the de-velopment of increasingly stringent anaerobic environments and the appearance of the finest particle sizes in the texture of the host porous matrix. The latter point is also supported by the observation that As per-centages in sulfide fraction in matrix C (i.e., the silt sampled at 74.50 m) is about three times larger than As content in matrix B (i.e., sand sampled at 73.50 m). Arsenic association with sulfide minerals is also underlined by Smedley and Kinniburgh (2002) who reported that As chemistry follows closely that of S and hence highest As concentrations tend to occur in sulfide minerals, among which pyrite is usually the most abundant in groundwater systems.

The results listed in Table 2 highlight the differences observed in the behavior of the silty matrix C when compared against the other matrices tested and quantified in terms of As partitioning (resulting in significant As association with low crystallinity phases as well as with organic substrates and sulfide fractions), and fine particle size composition. Comparison between fractions of As content in matrices A and D indi-cates that, despite As contents in fractions FIII and FIV are comparable, the amount of As associated with FV fraction in matrix D is one order of magnitude larger than that in matrix A. This observation is consistent with the experimental findings of Molinari et al. (2013) who observed that As release from vegetal matter (matrix D) is one order of magni-tude larger than the corresponding amount released from sand (matrix A) sampled at the same depth. These two observations appear to sustain the hypothesis that the significant different behavior observed for As dynamics of these two samples, when subject to alternating redox con-ditions, can be due to the higher capacity of matrix D of binding As in the FV fraction. This latter point is consistent with several literature studies demonstrating the possible 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).

### 3.3. Arsenic dynamics in silty matrix C under alternating redox conditions

Among the four solid matrices sampled (see Table 1) and subject to SSE, we discuss here the results of a batch test performed on the silty

matrix C in the presence of alternating redox conditions. Matrix C is of key importance because it represents a common textural composition associated with hydrofacies distributions occurring in aquitard bodies and has the largest potential to adsorb/release As due to its high specific surface. The interpretation of As dynamics observed from this batch test is grounded on the SSE results which are key to improve our under-standing of As mechanisms in groundwater because they enable one to evaluate the relative contribution of each fraction to As release/adsorption mechanisms and support the interpretation of the behavior observed for the tested matrix when it is subject to alternating redox conditions.

Fig. 5a depicts the temporal dynamics of ORP and pH detected during the test. The reducing and oxidizing steps can be clearly identified. The solution displays limited pH variations within the range of 7.0–8.4.

Fig. 5b depicts measured dissolved As and Fe concentrations as a function of sampling time together with the corresponding ORP. A good correspondence between the temporal dynamics of As and Fe con-centrations is noted during the three stages of the test, consistent with the results of Nickson et al. (2000) and Anawar et al. (2003). This obser-vation is also consistent with the likely occurrence of Fe-hydroxides and goethite within matrix C, which is evidenced by XRD analysis (see Fig. 3c). The key role of Fe mineral phases, especially of amorphous phases, on As mobility displayed under both reducing and oxidizing conditions is supported by the results of SSE which reveal that the largest percentage of As was observed in the FIII fraction, i.e., Fe & Mn oxyhydroxides (see Table 2). Arsenic release from As-bearing minerals was facilitated by sharp changes from oxidizing to reducing conditions and by the occurrence of a sustained reducing environment (48 h in the last stage of the test). These mechanisms are mainly driven by amorphous phases (i.e., FIII fraction), as evidenced by SSE results according to which the largest As percentages were found in association with oxyhydroxides (Table 2).

In agreement with other literature studies (e.g., Islam et al., 2004) we noted that As release displayed distinct behaviors when considering the transition from oxidizing to reducing conditions and the temporal window within which steady and strong reducing conditions are
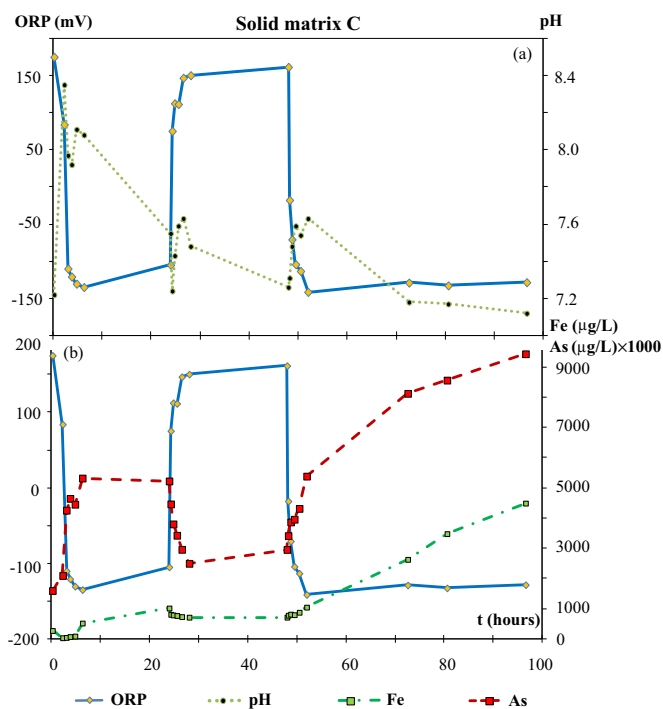


**Fig. 5.** (a) Temporal variations of ORP and pH during the test performed on solid matrix C (silt); (b) ORP, Fe and As (×1000) concentrations. Solid and dashed curves are drawn for visual aid.

attained within the system. During the transition at times of about $t = 4$ and 48 h we noted that dissolved As concentrations increased with an approximately linear rate and with a steep slope, as opposed to the be-havior detected under oxidizing conditions before the transition. Other-wise, when steady and highly reducing conditions are achieved within the microcosm, dissolved As concentrations exhibit a significant in-crease (note the sampled points at the end of the third experimental stage in Fig. 5b). The behavior observed during the transition phase is consistent with other literature findings (e.g., Masscheleyn et al., 1991; Smedley and Kinniburgh, 2002) according to which As solubility tends to increase as reducing conditions become more stringent. For instance, Masscheleyn et al. (1991) found that As solubility at a redox potential of $-200$ mV increased by a factor of 13 as compared to the sol-ubility of As at a redox potential of $+500$ mV due to the formation of As(III) which becomes the major compound in solution. At the same time Carbonell-Barrachina et al. (2000) found that the mobility of As decreases at a redox potential of $-250$ mV due to the formation of sul-fides. These observations seem to suggest a possible non-linear behavior of dissolved As concentrations at long times after the sharp change in redox conditions, most likely due to the possible formation within the slurry of secondary sulfides such as orpiment $As_2S_3$, and/or As rich pyrite which can cause the precipitation of a part of the dissolved As (Belzile and Tessier, 1990). Moreover, these two observed distinct trends appear to be consistent with SSE findings and with the phenom-enological picture according to which naturally occurring As that is sorbed to Fe oxy-hydroxides (i.e., FIII and FIV fractions) is released when reducing conditions take place (Bhattacharya et al., 1997; McArthur et al., 2001; Nickson et al., 1998, 2000). On the other hand, As is released less rapidly from crystalline phases (i.e., FIV fractions) in the presence of highly persistent reducing conditions as dissolution of these phase, and hence release of the restrained As, occurs at a slower rate under such conditions. The largest As concentrations detected at the end of the test, when concentrations still do not reach steady-state, are consistent with the observation that the other two relevant As restraining fractions occurring within C matrix (i.e., organic mat-ter–FV fraction, and sulfide–FVI fraction; Table 2) might have started to contribute to As release at such long times after the sharp change in redox conditions. This suggests that the late time non-linear behavior observed in the test might be caused by the joint effect of these two phases which is juxtaposed to the contribution associated with the dissolution of fractions FIII and FIV.

Consistent with the high adsorption capacity of the Fe oxides (FIV fractions) occurring in matrix C, which is then favored by the induced oxidizing environment, dissolved As concentrations detect-ed during the oxidizing stage exhibit a sharp decrease. The slight increase observed in Fig. 5 during the period of free ORP evolution lies within the range of measurement error and can then be consid-ered as negligible.

The release/adsorption dynamics observed in Fig. 5 for As are in a good qualitative agreement with release/adsorption processes ob-served for Fe. The latter exhibits a decreasing trend when the system is switched from reducing to oxidizing conditions, and an increasing trend when switching from oxidizing to reducing environments. These observations are consistent with literature findings (e.g., Nickson et al., 2000; Anawar et al., 2003) suggesting that mechanisms of As release and adsorption are respectively the reductive dissolution of the solid ma-trix bound to Fe(III) oxy-hydroxides (i.e., FIII fractions of SSE) and the pre-cipitation of minerals (such as ferrihydrite or pyrolusite) which could bind As in an oxidizing environment. The persisting increase in Fe concen-tration observed in Fig. 5 during the third experimental stage is consistent with the effect of the mechanisms evidenced for As release and the reduc-tive dissolution of Fe oxy-hydroxides minerals (e.g., Bhattacharya et al., 1997; McArthur et al., 2001) such as goethite, the occurrence of which was evidenced in our samples by XRD analysis (Fig. 3c). This aspect is also extensively discussed in the context of estuarine, lake, river particles and sediments (Davison, 1993; Lovley and Chapelle, 1995). We note that

As and Fe temporal trends documented during this test are comparable to those observed in a corresponding experiment performed by Molinari et al. (2013) on matrix A, which is characterized by different features (e.g., characteristic particle sizes) when compared to matrix C. The key mechanism triggering As release/adsorption for both matrices appears to be the abrupt and rapid change in redox conditions. This is consistent with observations from other worldwide investigations (e.g., West Bengal, Taiwan or Bangladesh) where As mobilization might occur by a complex combination of redox changes brought on by rapid burial of allu-vial and deltaic sediments, including the reduction of As solid-phase to As(III), desorption of As from Fe oxides, reductive dissolution of the oxides and likely changes in Fe-oxide structure and surface properties following the onset of reducing conditions (BGS and DPHE, 2001). These observa-tions allow identifying that the two types of tested matrices are character-ized by the same qualitative dynamic behavior. However, we note that significant quantitative differences between the amounts of dissolved As detected in the tests performed on these two solid matrices are observed, consistent with the different total As content associated with each matrix (see Table 1). Arsenic concentrations released from solid matrix C are larger (about an order of magnitude) than those released from solid ma-trix A as reported by Molinari et al. (2013), despite the amount of solid matrix employed in the test performed on matrix C is lower than that re-lated to the test carried out on matrix A. This result is consistent with the large total As content of solid matrix C (see Table 1), which is more than three times larger than the value detected in matrix A, in agreement with the high concentrations (up to 41 mg/kg) found in acid sulfate soils from the Mekong delta of Vietnam (Gustafsson and Tin, 1994). The important contribution of sulfide fractions to As release from matrix C is also highlighted by SSEs (see Table 2) which reveal the larger occurrence of As in the FV (organic matter) and FVI (sulfides) fractions in matrix C than in matrix A. This observation is consistent with a previous study which highlighted that argillaceous deposits can exhibit higher average As concentrations than sandstones due to the larger proportion of sulfide minerals, oxides, organic matter and clays (Ure and Berrow, 1982). These observations suggest a potentially significant As adsorption/ desorption capacity characterizing the silty solid matrix, which is mainly linked to the observation that silty matrices (i.e., matrix C) are associated with a larger specific surface than sands (i.e., matrix A) due to particle size and mineral composition. This aspect is also highlighted by Scott and Morgan (1995) who showed that the rate of As adsorption/desorption is controlled by the surface reaction.

The amount of As released at the end of the test performed on matrix C is significantly high and close to the limiting value indicated by the Italian regulation (10 μg/L), even as the duration of the reducing stages employed in this experiment is shorter than that related to the test per-formed by Molinari et al. (2013) on solid matrix A. This finding indicates that the occurrence of a fine solid matrix (such as matrix C) within an aquifer body could play a remarkable role in the occurrence of localized large As concentrations of the kind which are associated with observed hot spot patterns in natural aquifers. This observation is in agreement with the high-As concentrations in groundwater detected in the Chaco-Pampean Plain of central Argentina where the occurrence of Quaternary deposits of loess (mainly silt) with intermixed rhyolitic or dacitic volcanic ash have been identified as one of the possible natural factors causing the large As values (range 6–11,500 μg/L, with median 255 μg/L) detected in groundwater (Nicolli et al., 1989).

We finally note that As dynamics observed in matrix C (silt) under alternating redox conditions exhibit trends which are comparable to those observed by Molinari et al. (2013) for matrix D (vegetal matter). The quantitative difference observed between these cases appears to be consistent with the observation that both matrices exhibit a relative-ly large percentage of As content in the FV fraction (i.e., larger than 10%, as evidenced in Table 2).

Close inspection of As dynamics observed in these two matrices appear to evidence the same pseudo-logarithmic trend of As concentrations released during the third reducing stage. This result suggests

that fine and vegetal matrices, which are characterized by large specific surface and large number of available adsorption sites, can release As with similar mechanisms in the presence of sustained reducing conditions.

## 4. Conclusions

Our work leads to the following major conclusions:

1. Arsenic content associated with vegetal-rich compounds was found to be one order of magnitude larger than that observed in sandy or silty solid matrices occurring in the investigated alluvial system. Host porous media characterized by the occurrence of lignin, in the form of vegetal-rich compounds or non-decomposed peats, can adsorb significant amount of cations such as arsenic to a larger extent than what can be observed for sands sampled at the same depth. Otherwise, significant As release could be expected in groundwater bodies characterized by the occurrence of vegetal-rich compounds in contact with paleo-waters. These findings suggest the need to quantify the actual contribution of organic matter to concentration values detected in groundwater bodies for the characterization of the potential origin (either natural or anthropogenic) of dissolved As.

2. Among the fractions extracted from the sampled solid matrices, amorphous and crystalline phases are key to control As partitioning, the amorphous phase being the fraction exhibiting the largest As content. Accurate quantification of the occurrence of all these fractions is critical for the assessment of As release from a natural solid matrix because the dissolution mechanisms of amorphous and crystalline phases may be different in the presence of reducing conditions, thus providing different loads of As which can impact the natural quality of a groundwater body.

3. Arsenic content and its association with sulfide fractions tend to increase with the development of increasingly stringent anaerobic conditions, and the occurrence of fine particle size in the textural composition of the host porous matrix.

4. Arsenic can be mobilized by abrupt and rapid changes in redox conditions, the largest released concentrations being exhibited in the presence of a sustained reducing conditions, up to about $-150$ mV. Fine grained and vegetal-rich matrices, which are respectively characterized by a significant specific surface and a large number of available adsorption sites, can release As with similar mechanisms in presence of persistent reducing conditions.

5. The combination of the findings stemming from SSE and batch experiments can be of potential use for groundwater preservation strategies, as they provide critical elements to identify the type of solid fractions onto which As is chiefly adsorbed and the conditions under which As can be mobilized to groundwater.

6. The environmentally critical As concentrations detected within alluvial aquifer in the Emilia-Romagna Region, Italy, from which the tested solid matrices are extracted, was found to be consistent with the occurrence of localized high natural As content associated with vegetal matter and the potentially significant role of the silty matrix in driving As dynamics.

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