

## Experimental simulation of arsenic desorption from Quaternary aquifer sediments following sea water intrusion

Guia Morelli<sup>a,b,\*</sup>, Valentina Rimondi<sup>b</sup>, Marco Benvenuti<sup>c</sup>, Daniela Medas<sup>d</sup>, Pilario Costagliola<sup>c</sup>, Massimo Gasparon<sup>a</sup>

<sup>a</sup> School of Earth and Environmental Sciences, The University of Queensland, St Lucia, QLD 4072, Australia

<sup>b</sup> CNR - Istituto di Geoscienze e Georisorse, Via G. La Pira 4, 50121 Florence, Italy

<sup>c</sup> Dipartimento di Scienze della Terra, Università degli Studi di Firenze, Via G. La Pira 4, 50121 Firenze, Italy

<sup>d</sup> Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari, via Trentino 51, 09127, Cagliari, Italy

### ARTICLE INFO

Handling Editor: Huaming Guo

Keywords:

Arsenic

Desorption experiments

Seawater intrusion

Coastal aquifer

Quaternary sediments

Southern Tuscany

### ABSTRACT

Alluvial sediments from the coastal area in southern Tuscany (Italy) characterized by a significant As anomaly (As > 500 mg/kg) are subjected to seawater intrusion due to groundwater exploitation. Sequential extractions and kinetic experiments were carried out on Quaternary alluvial sediments to quantify the interaction between As oxianions (adsorbed on mineral surfaces) and Cl<sup>-</sup> in solutions and to establish if this mechanism may contribute to the release of As in groundwater.

The natural water-rock interaction in the aquifer was simulated in two experiments by saturating the samples with four solutions with increasing chlorinity for different time.

Firstly, a rapid change in the aquifer salinity (e.g. fast seawater intrusion, groundwater over pumping) was simulated by an interaction sediment/solution of 24 h. Solutions with Cl<sup>-</sup> ≤ 2000 mg/L extracted up to 76 µg/kg of As, while seawater (Sol 4<sub>(24)</sub>: Cl<sup>-</sup> ~ 18,500 mg/L) extracted up to 161 µg/kg of As.

In a second experiment, the ingression of water with increasing salinity in the aquifer, followed by the withdrawal of the water after progressively longer interaction times with the aquifer sediments, was simulated. The timing of the As-Cl reaction was constrained by saturating the samples with four solutions with increasing salinity (Sol1<sub>(84)</sub>: Cl<sup>-</sup> ~ 0 mg/L; Sol2<sub>(84)</sub>: Cl<sup>-</sup> = 250 mg/L; Sol3<sub>(84)</sub>: Cl<sup>-</sup> = 2000 mg/L; Sol4<sub>(84)</sub>: Cl<sup>-</sup> = 15,886 mg/L) that interacted with the sediment samples for longer saturation times (up to 21 days for each solution). After saturation with the previous three solutions up to 62 µg/kg of As were extracted by seawater, following a salinity increase from 2000 mg/L Cl to a chlorinity close to seawater, representing ~60% of the exchangeable As fraction in the sediments.

Our results constrained the timing of sediment/solution interaction of As desorption and showed that after a rapid intrusion of seawater or after a relatively long period of interaction with saline solutions an aquifer with similar geology releases in groundwater concentrations of As exceeding the 10 µg/L limit for drinking water. Also, this study estimated the potential effects caused by the ingression of seawater in lowland alluvial coastal areas induced by groundwaters exploitation or by extreme weather events. Such information is crucial for management authorities to mitigate and predict the effects of As hazard in groundwater driven by changes in the environmental aquifer conditions (e.g. seasonal fluctuations of the water table and/or changes in salinity of coastal aquifers), which are becoming increasingly frequent as consequence of climate change.

### 1. Introduction

Arsenic (As) is present in soils and groundwaters due to both natural sources and anthropogenic activities (e.g. Nicolli et al., 1989; Manning and Goldberg, 1997; Williams et al., 1998; Smedley and Kinniburgh, 2002; Scheiber et al., 2016). As described by Dixit and Hering (2003) several mechanisms (singly or in combination) explain As mobility

under different conditions which encompass inorganic and organic reactions (O'Neill, 1995; Pongratz, 1998; Smedley and Kinniburgh, 2002). In several parts of the world the presence of geogenic As anomaly in the soil is causing extensive As contamination of groundwaters used by millions of people as source of drinking water, resulting in persistent negative health effects on the local inhabitants (Yu et al., 2003; Argos et al., 2010; Joseph et al., 2015; Bhowmick et al., 2018). Concentrations

\* Corresponding author. School of Earth and Environmental Sciences, The University of Queensland, Australia.  
E-mail address: [morelliguia@gmail.com](mailto:morelliguia@gmail.com) (G. Morelli).

of As higher than 50 µg/L have been found in groundwaters around the world including Bangladesh, India, Nepal, Thailand, China, Taiwan, Vietnam, Chile, Argentina, Hungary and parts of the USA (e.g. Smedley and Kinniburgh, 2002; McArthur et al., 2004; Hossain, 2006; Bhattacharya et al., 2007; Lu et al., 2010; Bhowmick et al., 2018).

The alluvial and deltaic aquifers of Bangladesh and West Bengal represent the most serious contaminated area identified globally with million people drinking water with arsenic concentrations above 10 µg/L and up to 50 µg/L (Das et al., 2009), causing about 20% of the death in the area (Argos et al., 2010). In general, these anomalous As-rich groundwaters are found in aquifers hosted by coastal Holocene/Quaternary alluvial and deltaic environments (Kippler et al., 2016). Alluvial and deltaic plains typically have a low elevation with respect to sea level and are extremely vulnerable to a number of natural hazards such as cyclones, tidal surges, salinity intrusion, riverbank erosion, and shoreline recession frequently as a consequence of climate changes such as in the case of Bangladesh (Baten et al., 2015). All these phenomena may cause an increase in salinity in aquifers in addition to groundwater over pumping. Arsenic is considered to be efficiently adsorbed onto iron oxide in many alluvial and deltaic environments. However, the sorption behavior of As is, in principle, also dependent by the competition with other anions such as those usually present in seawater. In particular, the role of chloride ion as a competitor for As adsorption onto Fe-oxyhydroxides is highly debated. For example, Zhang et al. (2004) stated that chloride may slightly enhance the As adsorption onto a mineral mixture where hematite was predominant. On the contrary, Keon et al. (2001), in a sequential extraction experiment in soils, proved that MgCl<sub>2</sub> brings into solution the exchangeable As fraction, allowing ionic exchange between Cl<sup>-</sup> and oxyanions of As (AsO<sub>4</sub><sup>3-</sup> and AsO<sub>3</sub><sup>-</sup>). Goh and Lim (2005) have quantitatively estimated the As extracted in artificially contaminated soils by solutions made by different salts (NaCl, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>3</sub>PO<sub>4</sub>) concluding that NaCl releases into solution the highest concentration of As in the first 30 min of reaction, independently on the salt concentration. Liu et al. (2003) have correlated the high As concentrations occurring in the groundwater of the coastal areas of Taiwan to the interaction of sediment/sea water favouring ionic exchange between Cl<sup>-</sup> and As. Pansar-Kallio and Manninen (1997) stated that variations in the ionic strength and ionic exchange might induce an As mobilization.

Few studies have been published to estimate the extent of As mobilization under anion-rich or saline conditions (e.g. Wasay et al., 2000; Jackson and Miller, 2000; Alam et al., 2001; Keon et al., 2001; Cai et al., 2002; Goh and Lim, 2005; Raposo et al., 2006; Sun et al., 2015). To date there are not specific experiments that quantify the ionic exchange between As-oxyanions and Cl<sup>-</sup> and the kinetic of this reaction in the natural aquifer environment, although this aspect is of relevance in groundwaters hosted by alluvial and deltaic plains that suffer a limited amount of flushing by freshwaters (cf. Smedley and Kinniburgh, 2002).

In this work a set of experiments was designed to simulate the natural interaction between groundwater and seawater in an aquifer, by saturating aquifer sediments rich in As with solutions at increasing chlorinity for different interval of time. The aims of this study were 1) to quantify the interaction between As oxyanions (adsorbed on mineral surfaces) and Cl<sup>-</sup> in solutions, 2) to establish if this mechanism may contribute to the release of As in groundwater, and 3) to estimate the effects caused by the ingression of saline solutions in aquifers characterized by geogenic As anomaly.

The experiments were carried out on three alluvial samples from the Pecora River Valley Quaternary deposit in Southern Tuscany (Italy). This Quaternary sequence (Benvenuti et al., 2009) is characterized by a significant geogenic As anomaly (As > 1000 mg/kg; Protano et al., 1998; Costagliola et al., 2004, 2010) with an extension of about 25 km<sup>2</sup> reaching a depth of 90 m close to the coast (Rossato et al., 2011). In water wells of this Quaternary sequence, As contents may exceed the accepted drinking water standards (Rossato et al., 2011) and a

correlation between salinity and As concentration in rock wells has not yet been demonstrated. The Quaternary deposits of the Pecora River are thus a key area where to test the effects of seawater intrusion on As mobility and its release to groundwater, being coastal aquifers hosted by recent sediments one of the main cause of drinking water contamination in the world (Smedley and Kinniburgh, 2002).

## 2. Study area

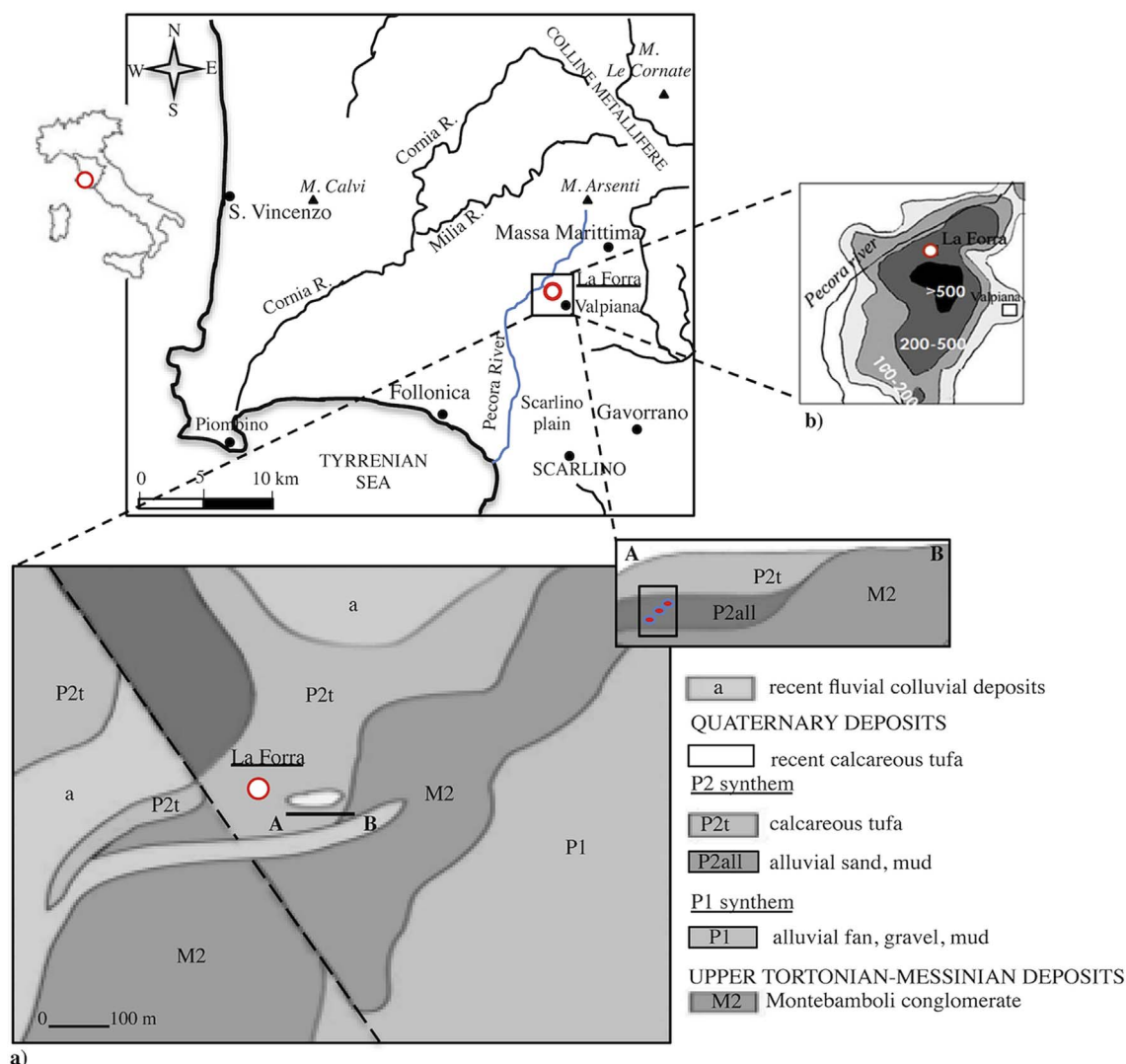
### 2.1. Geological background and sampling area

The geology of the Pecora River Valley is described in detail in Benvenuti et al. (2009) and Costagliola et al. (2008). A concise description is outlined hereafter. The geology of Tuscany is related to the Northern Apennines tectonic chain formation (Bonini and Sani, 2002). During the late Miocene and Plio-Pleistocene post-collisional phases, regional metamorphism and the emplacement of magmatic bodies (Innocenti et al., 1992; Serri et al., 2001) triggered the formation of a suite of hydrothermal ore deposits (Lattanzi et al., 1994). In Southern Tuscany, those deposits are often found in veins along the late Apenninic tectonic structures, which reach the upper crustal levels of this district, making this region one of the largest mining district of Italy, exploited since Etruscan times (c. 700 BC; Chiarantini et al., 2009; Costagliola et al., 2010). During the post-orogenic structural evolution (Late Tortonian-Upper Messinian) several continental and shallow marine basins developed and were filled with clastic sediments (Martini and Sagri, 1993) and later superimposed by Quaternary alluvial/colluvial deposits. The Pecora River Valley is an example of those Neogene/Quaternary basins (Costagliola et al., 2008; Benvenuti et al., 2009).

The Neogene/Quaternary sequence of the Pecora River Valley was selected for this experiment because it is close to the Tyrrhenian Sea and it is characterized by a large As anomaly (Fig. 1b) and flushed by a groundwater flowing from inland to the sea under a gentle westward hydraulic gradient. Concentrations of As in the sedimentary sequence are up to 1000 mg/kg (Benvenuti et al., 2009; Costagliola et al., 2008, 2010), well above the regional background value of 7 mg/kg (Protano et al., 1998) and above the range of 4–39 mg/kg found in the local pre-Neogene bedrock and in the upper Messinian fluvial gravels (Benvenuti et al., 2009; Costagliola et al., 2010). The origin of this anomaly is mainly geogenic. Following Costagliola et al. (2010), the Neogene/Quaternary sequence of the Pecora River Valley is the results of the erosion, and subsequent re-deposition, of As-bearing minerals (mainly arsenian-pyrite) hosted in veins emplaced along the late Apenninic tectonic structures that cropped out in the paleo-catchment of the river. This Quaternary alluvial/colluvial deposits, bordering the sea coast in Southern Tuscany, host aquifers that are known to be exposed to episodic sea water intrusion caused by groundwater overexploitation (Grassi and Netti, 2000). Samples were collected at La Forra, north west of the village of Valpiana from the unit identified as “P2all”, part of the Palaeo Pecora 2 synthem (P2) (Middle Pleistocene?–Holocene, Benvenuti et al., 2009) (Fig. 1).

## 3. Methods

Three samples, labelled L01, L02 and L03, were selected as the most representative of the local aquifer lithology based on previous studies (Costagliola et al., 2010). After air-drying, each sample was sieved using a 2 mm brass sieve and quartered. The passing fraction was divided in two parts using a riffle splitter. One part was used for the desorption experiments, while the other half was ground with an agate mortar and used for XRD, XRF, total digestion and sequential extraction analyses.



**Fig. 1.** a) From the top to the bottom: location of the study area and geologic map (modified from Bianchi, 2004) of the sampling site. Samples L01, L02, L03 (red dots in the AB cross section) were collected in the P2all alluvial sand deposit (Benvenuti et al., 2009; Costagliola et al., 2010); b) Distribution of As (mg/kg) represented by the contour lines around the sampling site of La Forra (from Costagliola et al., 2010). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

### 3.1. Sediment characterization

Particle size distribution was determined by wet sieving about 200 g of sample using 4.75 mm, 2.00 mm, 0.85 mm, 0.425 mm, 0.250 mm, 0.106 mm e 0.075 mm sieves. The organic carbon content was estimated based on the loss on ignition (LOI), measured by heating the three samples for 24 h at 110 °C and subsequently at 950 °C for 1 h (Ball, 1964).

Hydraulic permeability (K) was estimated using the Hazen formula ( $K = C \cdot d_{10}^2$ ) where d is the lower decile grain size diameter and C is a constant (Hazen, 1911). Electric conductivity of each aliquot of water extracted from the three samples during the 84 days experiment was measured with an electrode. The mineralogy was determined by X-ray diffraction (XRD) using a PHILIPS PW 3710 powder diffractometer, equipped with the X-PERT Philips acquisition software, in use at the Earth Science Department of the Firenze University.

X-ray fluorescence (XRF) was used for quantitative chemical analyses of major and trace elements (Al, Na, Mg, P, Si, K, Ca, Ti, Mn and Fe) using a Philips PW 1480/10 X-ray spectrometer located at Earth Science Department of the Firenze University. Concentrations of trace metals and As were determined by acid total digestion following the procedure proposed by Medved et al. (1998). An aliquot of each sample (0.5 g) was digested in a “sand bath” with aqua regia (5 mL of HNO<sub>3</sub>

and 15 mL of HCl) for 3 h. The solution was then filtered through a Whatman 42 filter before analysis. The accuracy of the method was evaluated against two international standards (NIST SRM 2710 and 2711 - Montana Soil). Arsenic recovery calculated as a percentage of the standards (both international and internal) was between 87% and 102% of the certified values. Concentrations of As obtained from the total digestion were analysed using an Atomic Absorption Spectrometer (AAS) Perkin-Elmer analyst 100 coupled with a FIAS-100 hydride system (Flow Injection Analyst System) Perkin Elmer in use at the Earth Science Department of the Firenze University.

### 3.2. Sequential extraction

Arsenic speciation was determined by sequential extraction. This is a simple and well-established method to assess trace element fractionations in different phases in soils and sediments with reagents of increasing dissolution strength. These operationally defined fractions refer to non-specifically-bound, specifically-bound, amorphous hydrous oxide-bound, crystalline hydrous oxide-bound and the residual trace element content (Tessier et al., 1979; Rauret, 1998; Wenzel et al., 2001; Smedley and Kinniburgh, 2002; Goh and Lim, 2005; Rahman et al., 2017; Wan et al., 2017). Specific protocols may have limitations for the determination of As fractionation (e.g. Wan et al., 2017) and sample

**Table 1**  
Sequential extraction procedure, modified from Wenzel et al. (2001). SSR:soil solution ratio.

Target phase	Extractant	Extraction conditions	SSR	Wash steps
A1-As non-specifically-bound	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (0.05 M)	4 h shaking	1:25	15 min centrifuge at 15,000g
A2-As specifically-bound	[(NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> (0.05 M)	16 h shaking	1:25	
A3-As bound with Carbonates	20 ml Na (CH <sub>2</sub> COONa) 1 M + 4 mL acetic acid	15 h without shaking; pH = 5	1:20; 1:4	pH:5; centrifuge
A4-As bound with amorphous Fe A1 hydrous oxide	NH <sub>4</sub> -oxalate buffer(0.2 M);	4 h shaking in the dark	1:25	10 min shaking with NH <sub>4</sub> -oxalate buffer (0.2 M); SSR 1:10
A5-As bound with crystalline Fe A1 hydrous oxide	NH <sub>4</sub> oxalate buffer (0.2 M) + ascorbic acid (0.1 M)	30 min in a water basin at 90 °C	1:15; 1:10	10 min shaking in the dark NH <sub>4</sub> -oxalate (0.2 M); SSR 1:10
A6.As in residual phases(sulfur and oxides)	Aqua regia(5 mL di HNO <sub>3</sub> + 15 mL di HCl	3 h at 50 °C in a sand bath		Solution is filtered milliRo water added

drying temperature may accelerate the aging of As in soils affecting the mobility of As (Huang et al., 2015, 2016a, 2016b). The extraction protocol used here was modified from Wenzel et al. (2001), one of the most used SEP (Sequential Extraction Procedure) in literature. Each air-dried sample (1 g) was placed in 50 mL centrifuge tubes and 25 mL of extraction reagents were added sequentially following the six steps extraction protocol described in Table 1. After each step the solid residue and the extractant were centrifuged for 15 min at 15,000 rpm. The supernatants obtained from each step were placed in a 100 mL flask. The remaining solids were washed several times using MilliQ water to recover all the extractant, and this wash solution was added to the supernatant in the 100 mL flask and acidified to 5% HNO<sub>3</sub> to prevent its chemical deterioration. The residual sediment was then used for the next extraction step. Concentrations of As were analysed by FIAS-AAS (located at the Earth Science Department of the Firenze University). The analytical quality of the sequential extraction analyses was evaluated comparing the sum of the As in the six fractions with the total As determined by a single step aqua regia leaching in each sample. The six steps sum is the 107, 112 and 107% (for sample L01, L02, and L03, respectively) of the total amount measured with the aqua regia single leaching. The variability in the recovery percentage is within the range observed in the sequential extraction method (e.g. Cuong and Obbard, 2006) and is partly attributed to sample dis-homogeneity.

### 3.3. Desorption experiments

#### 3.3.1. Single-stage 24-h desorption experiments

Single-stage desorption experiments were conducted on the < 2 mm sample fraction (un-milled) to better simulate the natural water-rock interaction in the aquifer. In this experiment four solutions with different chlorinity were added to the samples and shaken for 24 h. The solution with the highest Cl<sup>-</sup> concentration was seawater (Sol<sub>4(24)</sub>) Cl<sup>-</sup> = 18,511 mg/L) collected from the nearby coast (Follonica, Southern Tuscany). The other three solutions were diluted from seawater using MilliRo™ water to reach Cl<sup>-</sup> = 2000 mg/L (Sol<sub>3(24)</sub>), Cl<sup>-</sup> = 250 mg/L (Sol<sub>2(24)</sub>) (maximum concentration of Cl<sup>-</sup> in drinking water following the World Health Organization, 2003 recommendations) and Cl<sup>-</sup> ~ 0 mg/L (Sol<sub>1(24)</sub>). The experiments were performed using a rock to solution ratio of 1:10 following the official protocol for quantifying ionic exchange in soil (cf., US EPA METHOD 9080, 1986). An aliquot of 25 g of each sample was placed in a flask with 250 mL of

the first solution (Cl<sup>-</sup> = 0 mg/L) and shaken for 24 h. The supernatant was then decanted, filtered (0.45 µm) and acidified with 5% HNO<sub>3</sub>. This was repeated for the other three solutions, each time using a new sample aliquot. Concentrations of As were analysed by FIAS-AAS. The precision of the data analysed from FIAS-AAS evaluated by ten replicate measurements of each of the four solutions ranged between 3 and 17% RSD for sample L01 and L03.

#### 3.3.2. Sequential 84-days desorption experiments

Another set of desorption experiments was created to simulate and monitor the potential release of As from the sediment as the aquifer water became progressively more saline (gradual intrusion of sea water). In this experiment one aliquot of each un-milled sample (< 2 mm fraction) was placed in a purpose-built Perspex column and repeatedly saturated and flushed with four solutions with increasing salinity. After each saturation, water samples were collected at set time intervals during the total duration of the experiment of 84 days. The experiments were carried out in the School of Earth Sciences of The University of Queensland (Australia).

The four solutions used for saturating the samples were diluted from seawater (Sol<sub>4(84)</sub>; Cl<sup>-</sup> = 15,886 mg/L) collected in Moreton Bay (southeast Queensland, Australia). The first (Sol<sub>1(84)</sub>; Cl<sup>-</sup> ~ 0 mg/L) was made by diluting 1 mL of seawater (Sol<sub>4(84)</sub>) in 12 kg of MilliRo™ water. The other solutions were diluted from Sol<sub>4(84)</sub> to obtain the same chlorinity of the previous experiment (Sol<sub>2(84)</sub> Cl<sup>-</sup> = 250 mg/L and Sol<sub>3(84)</sub> Cl<sup>-</sup> = 2000 mg/L). Temperature, pH, conductivity and salinity of the two more saline solutions (Sol<sub>3(84)</sub> and Sol<sub>4(84)</sub>) were checked before and after the experiment to ensure that the solutions had remained reasonably stable for the duration of the experiment (Table 2).

In the 84-days long experiment, an aliquot of ~600 g of each sediment sample was placed in a purpose-built Perspex cylinder (~8 cm diameter by ~12 cm height). A brass mesh covered with a quartz filter (pore diameter ~ 5 µm) was placed at the base of the cylinder to prevent sample loss during the fluid extraction. PVC tubes were attached to the base and the top of the cylinder to allow sample saturation and collection of the solution after each experiment. In particular, the PVC tubes attached to the base of the cylinders were equipped with a valve allowing the solution to interact with the sediment for the desired time and to sample it when needed. This experimental apparatus was designed to maintain the samples completely saturated with the solution for the duration of the experiment simulating the actual sediment

**Table 2**  
84-days experiment: temperature, pH, conductivity and salinity of the solutions before and after the experiment.

	Cl- mg/L	T (°C)		pH		Conductivity (mS/cm)		Salinity (ppk)	
		before	after	before	after	before	after	before	after
Sol1(84)	0	24.7	n/a	5.5	n/a	0.02	n/a	0.008	n/a
Sol2(84)	250	n/a	n/a	n/a	n/a	0.98	n/a	0.048	n/a
Sol3(84)	2000	25.9	25.4	7.7	7.4	6.7	6.7	3.64	3.62
Sol4(84)	15886	25.7	25.4	8.0	8.1	46.5	41.1	28.3	28.7



conditions in the aquifer. At the beginning of the experiment (day0), each sample was saturated with approximately 200 mL of the first solution (Sol1<sub>(84)</sub>; Cl<sup>-</sup> ~0 mg/L). Immediately after sample saturation, four aliquots of 50 mL of the solution (total of 200 mL solution collected) were extracted from the column. In each 50 mL aliquot T, pH, electrical conductivity and salinity were measured. These solutions were filtered at 0.45 µm (using a cellulose nitrate syringe filter), acidified by adding HNO<sub>3</sub> (2% vol) and then analysed using an ICP-OES apparatus.

Soon after the extraction of the four aliquots at day 0, each sediment in the Perspex cylinder was again saturated with 200 mL of Sol1<sub>(84)</sub> which was left to interact with the sediments for 24 h. After 24 h it was sampled (day1) using the same procedure as explained above. After the solution extraction at day 1, Sol1<sub>(84)</sub> was reinjected in the cylinders and sampled after 6 days (day 7 from the beginning of the experiment) when it was collected (using the four aliquots method) and the sediment cylinders fed again with Sol1<sub>(84)</sub>. The same procedure was followed after 14 days (day 21 from the beginning of the experiment). A total amount of 16 aliquots for Sol1<sub>(84)</sub> was collected for each sediment sample.

At the end of the Sol1<sub>(84)</sub> cycle, the columns were treated with the solution with higher salinity (Sol2<sub>(84)</sub>; Cl<sup>-</sup> = 250 mg/L). More in detail, in order to flush Sol1<sub>(84)</sub> from the sample, 200 mL of Sol2<sub>(84)</sub> were initially used to purge the sediment column. This amount of Sol2<sub>(84)</sub> was immediately collected at the base of the Perspex cylinder in four aliquots of 50 mL that were analysed for T, pH, electrical conductivity, salinity and As following the procedure reported above. Then, the column was again charged with 200 mL of Sol2<sub>(84)</sub> and the same sequence of saturation/sample collection used for the Sol1<sub>(84)</sub> solution was repeated. The total amount of Sol2<sub>(84)</sub> aliquots was 20 (16 aliquots as for Sol1<sub>(84)</sub> plus 4 aliquots collected during the initial purging stage). The same procedure was applied again using the Sol3<sub>(84)</sub> and finally the Sol4<sub>(84)</sub> solution. At the end of the experiment, after 84 days a total of 76 solutions aliquots for each sediment sample were collected and analysed. The total solid:solution ratio was about 0.10 and 0.16 for the 24-h and 84-days desorption experiment, respectively. Results from each analysis are given considering the factor of dilution and reported in weight of As for 1 kg of sample.

Hydraulic conductivity was measured after each extraction using the simplified version of Darcy's law for vertical flow at constant head:

$$K = (QL)/(Aht),$$

Where K = hydraulic conductivity (cm/sec), Q = water volume (cm<sup>3</sup>), L = sample length (cm), A = sample cross-sectional area (cm<sup>2</sup>), h = hydraulic head (cm) and t = time (sec). Values of Q, L, A and h were calculated from the experimental set up and t was measured at each sample collection. Data are reported in Table 3. Due to small errors in the measurement of Q and t and small changes in h during the duration of the experiment, the error in the K values is estimated at around ± 10% of the measured values. It should be noted that the absolute K values are meaningless as they refer to the disturbed sediment samples after disaggregation and packing into the column. The data are meaningful only to monitor any changes in K as the experiments progressed.

Arsenic, major and trace elements concentrations were analysed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Perkin-Elmer Optima 3000) located in the School of Earth Sciences of The University of Queensland (Australia). Analytical quality control, guaranteed by using international standards reference materials (SLRS-4, LGC6020 river waters and SLEW-3 estuarine water), was within 10% of the certified values. In the 84-days desorption experiment, limits of quantification, calculated as three times the standard deviation of analytical blanks, were 6.2 µg/L for As and reflect the complex geometry of the extraction columns. Concentrations of As reported for the experiments are the As concentrations (µg/kg) leached from 1 kg of

**Table 3**

Hydraulic conductivity (cm/sec) measured after each 200 mL solution extractions from samples L01, L02, L03 during the 84 days experiment. Average, maximum and minimum values of the 16 measurements are also shown.

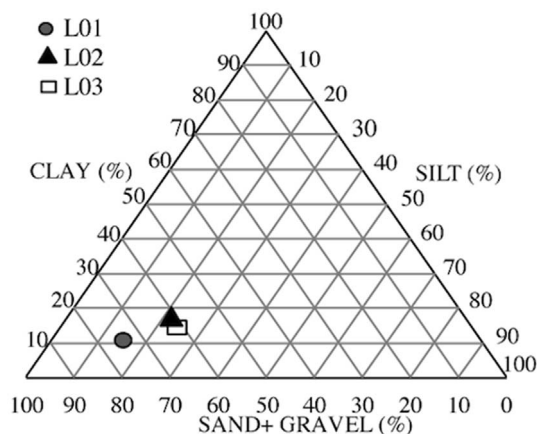
	Time	Hydraulic conductivity K (cm/sec)		
		L01	L02	L03
Sol1(84)	day 0	0.00050	0.00073	0.00021
	day 1	0.00044	0.00069	0.00028
	day 7	0.00034	0.00069	0.00030
	day 21	0.00037	0.00053	0.00033
Sol2(84)	day 0	0.00037	0.00053	0.00035
	day 1	0.00038	0.00061	0.00046
	day 7	0.00038	0.00059	0.00045
	day 21	0.00040	0.00056	0.00045
Sol3(84)	day 0	0.00040	0.00065	0.00069
	day 1	0.00039	0.00087	0.00075
	day 7	0.00049	0.00081	0.00081
	day 21	0.00048	0.00082	0.00072
Sol4(84)	day 0	0.00048	0.00098	0.00090
	day 1	0.00050	0.00111	0.00092
	day 7	0.00051	0.00111	0.00101
	day 21	0.00045	0.00086	0.00070
Average (n = 16)		0.00043	0.00076	0.00058
Standard deviation		0.00006	0.00019	0.00026
Minimum		0.00034	0.00053	0.00021
Maximum		0.00051	0.00111	0.00101

sample in 1 L of solution.

## 4. Results

### 4.1. Sediment characteristics and geochemistry

The three samples are classified as silty-clay sand (USCS classification system, Holtz and Kovacs, 1981) with gravel concentrations varying between ~10% in L02 and L03, and ~34% in L01 (Fig. 2). Diffractometric analyses on the < 2 mm fraction revealed the presence of quartz, k-feldspars, mica, phyllosilicates, and Fe(Mn)-hydroxides. In Table 4 the results of LOI, hydraulic permeability and chemical analyses of the three samples are summarized. XRF results show that the 3 samples are relatively homogeneous and are made of 60% SiO<sub>2</sub>, around 17.5% Al<sub>2</sub>O<sub>3</sub> and about 9% Fe<sub>2</sub>O<sub>3</sub>. MgO and K<sub>2</sub>O contents vary between 1.95% and 2.6%. Volatile content (expressed as LOI) is approximately 5%. Arsenic concentrations determined by acid digestion vary between 473 and 737 mg/kg and exceed the Italian guidelines (D. Lgs. 3 April 2006, n. 152) for maximum trace metal concentrations accepted in soils



**Fig. 2.** Grain size variability of sample L01, L02, L03.

**Table 4**

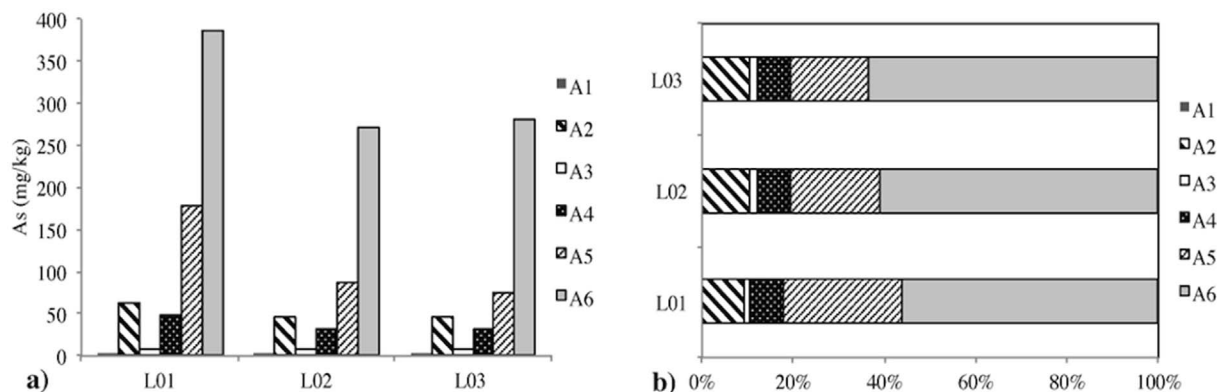
LOI (%), permeability coefficients (m/s), oxides (wt%) and trace metal concentrations (mg/kg) of samples L01, L02, L03. The maximum trace metal concentrations (mg/kg) accepted for “public, private and residential soil use” (limit a) and for “soil with commercial and industrial use” (limit b) under the Italian law D. Lgs. 3 April 2006, n. 152 are also shown. n.a.: not available.

	L01	L02	L03	Limit a	Limit b
Permeability coefficient (m/s)	0.384*10 <sup>-8</sup>	3.61*10 <sup>-8</sup>	1.96*10 <sup>-8</sup>		
LOI (%)	5.17	5.46	5.29		
Oxides (wt%)					
SiO <sub>2</sub>	61.4	60.8	60.6		
TiO <sub>2</sub>	0.70	0.76	0.76		
Al <sub>2</sub> O <sub>3</sub>	17.5	17.7	17.8		
Fe <sub>2</sub> O <sub>3</sub>	8.92	9.30	9.62		
MnO	0.41	0.4	0.45		
MgO	2.17	1.96	1.95		
CaO	0.72	0.66	0.57		
Na <sub>2</sub> O	0.43	0.40	0.36		
K <sub>2</sub> O	2.56	2.49	2.54		
P <sub>2</sub> O <sub>5</sub>	0.06	0.05	0.06		
Trace elements (mg/kg)					
As	737	506	473	20	50
V	120	128	132	90	250
Cr	236	281	301	150	800
Co	30	31	32	20	250
Ni	n.a.	35	67	120	500
Cu	n.a.	5	11	120	600
Zn	176	182	179	150	1500
Rb	161	169	166		
Sr	122	121	123		
Y	31	43	45		
Zr	124	154	159		
Nb	4	10	11		
Ba	386	378	391		
La	31	42	35		
Ce	154	136	137		
Nd	25	41	39		
Pb	44	50	40	100	1000

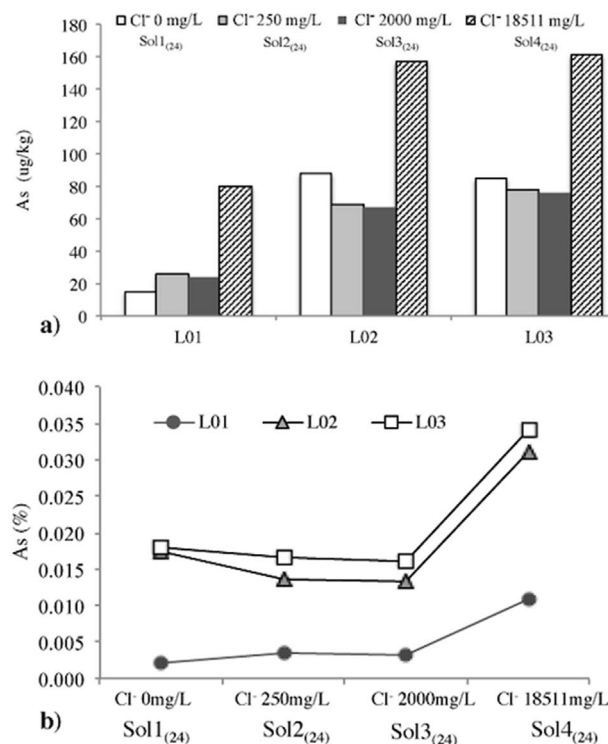
for “public, private and residential use” (As, 20 mg/kg) and in soils for “commercial and industrial use” (As, 50 mg/kg).

#### 4.2. Sequential extraction analyses

The concentration of As extracted in the different steps is shown in Fig. 3a. Arsenic non-specifically bound extracted from the first step (A1) is low in all the three samples (As < 1 mg/kg), As in the specifically bound fraction varies between 47 and 64 mg/kg (step A2), while the fraction of As associated with carbonates (A3) is around 8 mg/kg. In all samples As is mainly bound to the crystalline Fe-Al-(hydr)oxides



**Fig. 3.** a) Concentration of As (mg/kg) extracted in the different steps of sequential extraction analyses. b) Percentages (%) of As in each fraction compared to the total As concentration in the samples. The name of each steps are described in Table 1.



**Fig. 4.** a) Concentrations of As (µg/kg) extracted in each sample after shaking for 24 h with 4 solutions containing increasing concentration of Cl<sup>-</sup>. b) Percentages (%) of As extracted by each of the four solution compared to the total concentration of As in the samples.

(74–177 mg/kg, step A5) and to the residual sulphide and oxide phases (271–386 mg/kg, step A6). Sample L01A has the highest concentrations of As extracted in all the steps.

When compared to the total As concentration in the samples (Fig. 3b), the percentage of As in the potentially most mobile fraction (A1) is up to 0.07% of the total As. The fraction of As specifically adsorbed to mineral surfaces (step A2) is lower than 10%. The fraction of As associated with carbonates was less than 1.8%. The highest percentage of As is found in the residual As fraction (52–59%); the As fraction associated with Fe and Al (hydr)oxides and extractable by reduction with NH<sub>4</sub> oxalate buffer is also elevated (15–24%). In total the fraction of As non-specifically-bound and specifically-bound onto mineral surfaces (steps A1 + A2) ranged from 8.7 to 10% of the total As in the samples.

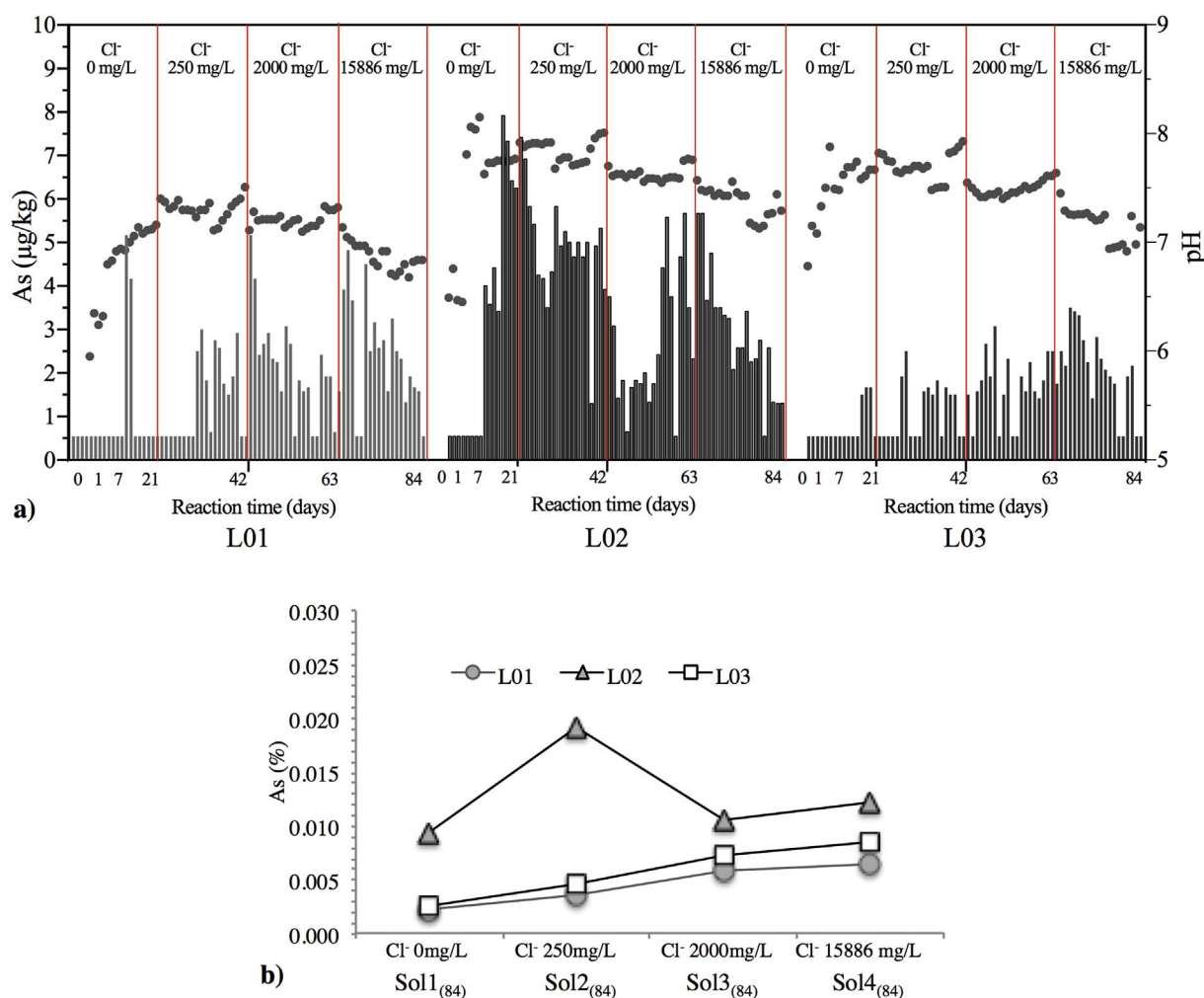


Fig. 5. a) Concentrations of As ( $\mu\text{g}/\text{kg}$ ) extracted by 4 solutions at increasing concentration of  $\text{Cl}^-$  in function of time during 84 days experiment. Bars represent measurements in every 50 mL aliquot of each solution collected. Measurements of pH (black dots) for each solution collected during the 84 days are shown in the right axis. b) Percentages (%) of the total As extracted by each of the 4 solutions compared to the total concentration of As remained in the sample considering the As extracted by the previous solutions.

#### 4.3. Single-stage 24-h desorption experiment

During the 24-h desorption experiments the highest amount of As ( $\sim 160 \mu\text{g}/\text{kg}$ ) was desorbed by seawater (Sol 4<sub>(24)</sub>) in samples L02 and L03 (Fig. 4a). Solutions Sol2<sub>(24)</sub> and Sol3<sub>(24)</sub> extracted similar concentrations of As (about 60–80  $\mu\text{g}/\text{kg}$ ) for samples L02 and L03 and about 25  $\mu\text{g}/\text{kg}$  for sample L01. Solution Sol1<sub>(24)</sub> also extracted  $\sim 80 \mu\text{g}/\text{kg}$  from samples L02 and L03 but less than 20  $\mu\text{g}/\text{kg}$  from sample L01. Overall the maximum amount of As extracted by desorption with seawater (Sol 4<sub>(24)</sub>) was 0.034% of the total As in sample L03, 0.032% in sample L02 and 0.011% in sample L01 (Fig. 4b).

#### 4.4. Sequential 84-days desorption experiments

Results of sequential desorption experiments are shown in Fig. 5 and extraction time for each aliquot of solution collected are shown in Table 5. Arsenic extracted by solution Sol1<sub>(84)</sub> ( $\text{Cl}^- \sim 0 \text{ mg}/\text{L}$ ) was mostly below 5  $\mu\text{g}/\text{kg}$  with the exception of sample L02, which released about 6–8  $\mu\text{g}/\text{kg}$  of As after 21 days saturation. The solution extracted from sample L01 was unusual as its electrical conductivity was relatively high at the beginning of the experiment (15.27 mS/cm), but decreased sharply within each batch of extractions and during the first 42 days. This trend is attributed to the dissolution of very soluble saline phases initially present in the sample. The same general trend was observed in the first 21 days in the other two samples, however their

initial electrical conductivities were much lower (at around 1 mS/cm). Solutions extracted from sample L01 were significantly more acidic than those extracted from the other two samples at the beginning of the experiments (pH  $\sim 6.3$  and  $6.8$ – $7.1$ , respectively), and remained more acidic with respect to other samples by 0.4–0.6 pH units for the duration of the experiments. The second solution Sol2<sub>(84)</sub> ( $\text{Cl}^- = 250 \text{ mg}/\text{L}$ ) extracted about 7  $\mu\text{g}/\text{kg}$  of As from L02, and less than 3  $\mu\text{g}/\text{kg}$  from L01 and L03. In all three samples at least 2  $\mu\text{g}/\text{kg}$  of As were released by Sol3<sub>(84)</sub> ( $\text{Cl}^- = 2000 \text{ mg}/\text{L}$ ) and up to about 6  $\mu\text{g}/\text{kg}$  of As from samples L01 and L02. Finally, seawater Sol 4<sub>(84)</sub> extracted up to 5  $\mu\text{g}/\text{kg}$  in L01, 6  $\mu\text{g}/\text{kg}$  in L02, and 4  $\mu\text{g}/\text{kg}$  in L03. At the end of the experiment the total As desorbed by all the solution was 134, 261 and 108  $\mu\text{g}/\text{L}$  in sample L01, L02 and L03, respectively, representing the 0.018, 0.052 and 0.026% of the total As in the three samples (Table 6). Hydraulic conductivity values were of the same order of magnitude in the three samples, and were mostly in the range  $2$ – $9 \times 10^{-4} \text{ cm}/\text{s}$  (Table 3). However the hydraulic conductivity (K) values remained relatively constant for the duration of the experiment in sample L01, while they increased slightly in samples L02 and L03 after saturation with seawater.

## 5. Discussion

The two desorption experiments showed that the introduction of increasingly more saline water in the samples has the effect of releasing

**Table 5**

Extraction time (minutes) for each solution collected during the 84 days experiment (the timing of the first set of 200 mL solution extractions when introducing a new solution in the samples were not included in the table).

Days of the experiment	Solution	Collection/saturation days	Extraction time (minutes)			Average extraction time (minutes)
			L01	L02	L03	
0	sol1(84)	day0	22	15	53	30
1		day1	25	16	39	27
7		day7	33	16	37	29
21		day21	30	22	34	29
21	sol2(84)	day0	29	19	32	27
22		day1	31	18	15	21
28		day7	29	15	25	23
42		day21	28	20	25	24
42	sol3(84)	day1	28	17	21	22
43		day1	29	13	15	19
49		day7	23	10	15	16
63		day21	24	19	16	20
63	sol4(84)	day0	22	11	12	15
64		day1	22	10	12	15
70		day7	22	10	11	14
84		day21	25	13	16	18
Total minutes of extraction			422	244	378	
Average daily extraction time			26	15	24	22
Standard deviation			3.7	3.8	12.2	

As into the solution (Table 6).

### 5.1. Influence of reaction time on arsenic desorption caused by sediment interaction with aqueous solutions at increasing salinity

It has been shown in literature that mobilization of As occurs after disturbance of the conditions of the aquifer following the introduction of recharge water not in equilibrium with the minerals constituting the aquifer host rock (Charlet et al., 2007; Lu et al., 2010; Currell et al., 2011). Our experiments showed that sediment/water interaction with low chlorinity solutions (< 2000 mg/L) releases immediately As into solution after saturation. In the case of the Pecora Valley sediments, the

**Table 6**

Summary of As concentrations (ug/kg) extracted in the three experiments from sample L01, L02, L03.

			L01			L02			L03			Average As (ug/kg) in three samples	
			ug/kg	% of the A1-total As	% of the A1-fraction	ug/kg	% of the A1-total As	% of the A1-fraction	ug/kg	% of the A1-total As	% of the A1-fraction		
Total digestion			737,000			506,000			473,000			572,000	
Exchangable A1-fraction			343,000	0.0465		354,000	0.07000		264,000	0.0559		320,333	
24-hours desorption experiment	Sol1 <sub>(24)</sub>	Cl-0 mg/L	15	0.0020	4	88	0.0174	25	85	0.0180	32	63	
	Sol2 <sub>(24)</sub>	Cl-250mg/L	26	0.0035	8	69	0.0136	19	78	0.0165	29	58	
	Sol3 <sub>(24)</sub>	Cl-2000mg/l	24	0.0033	7	67	0.0132	19	76	0.0161	29	56	
	Sol4 <sub>(24)</sub>	Cl-18511mg/L	80	0.0109	23	157	0.0310	44	161	0.0340	61	133	
84-days desorption experiment	Sol1 <sub>(84)</sub>	Cl-0 mg/L	17	0.0023	5	48	0.0094	13	12	0.0025	4	25	
	Sol2 <sub>(84)</sub>	Cl-250mg/L	27	0.0036	8	98	0.0193	28	37	0.0078	14	54	
	Sol3 <sub>(84)</sub>	Cl-2000mg/l	43	0.0058	12	54	0.0107	15	34	0.0072	13	44	
	Sol4 <sub>(84)</sub>	Cl-15886mg/L	47	0.0064	14	62	0.0123	17	40	0.0085	15	50	
	Total As extracted by all solutions after 84 days			134			261			108			168
	Average As extracted by all solutions after 84 days			33	0.0045	10	65	0.01	18	31	0.01	12	43
Total As desorpted by all solutions after 84 days				0.018	39		0.052	74		0.026	46		

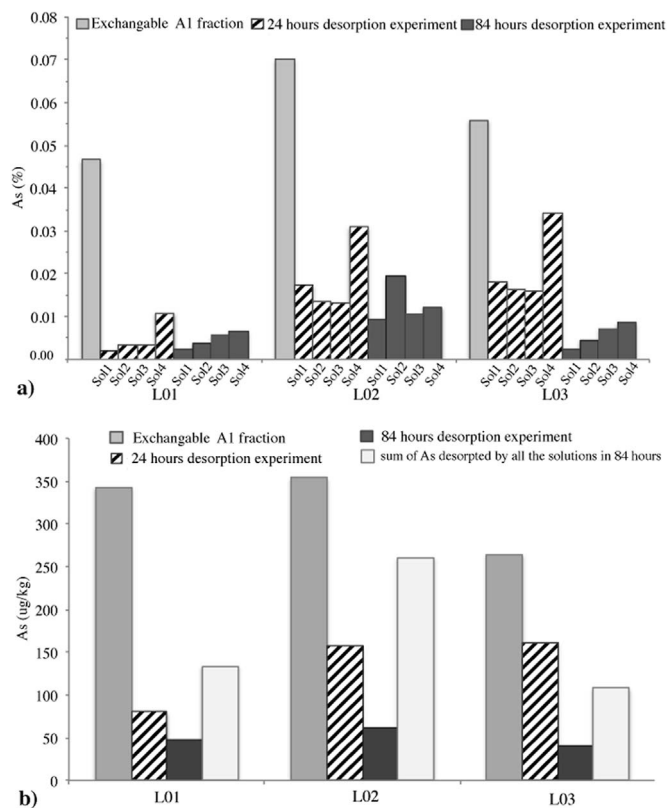
easily exchangeable fraction of As (A1 step of the sequential extraction procedure) is the pool mainly targeted by the chloride increase in solution.

The 24-h desorption experiment simulated the interaction between the Pecora Valley sediments with a low-salinity aquifer ( $\text{Cl}^- \sim 0$  mg/L, Sol1<sub>(24)</sub>) followed by a rapid ingression of three different waters with increasing salinity (Sol2<sub>(24)</sub>, Sol3<sub>(24)</sub> and Sol4<sub>(24)</sub>). Solutions with salinity  $\leq 2000$  mg/L  $\text{Cl}^-$  (Sol1<sub>(24)</sub>, Sol2<sub>(24)</sub>, Sol3<sub>(24)</sub>) desorbed similar concentrations of As ( $\sim 20$ – $80$   $\mu\text{g}/\text{kg}$ ), while seawater (Sol4<sub>(24)</sub>) extracted higher amount (or concentrations) of As ( $\sim 80$ – $160$   $\mu\text{g}/\text{kg}$ ), showing that only a dramatic increase in salinity may result in a significant, and virtually instantaneous, release of As from the three samples into the ground water. These results quantified the maximum concentrations of As potentially desorbed into groundwater after the ingression of saline water in a fresh water aquifer.

In contrast with the single-stage (24-h) desorption experiments, the 84-days desorption experiment was an attempt at simulating the As desorption following the relatively slow intrusion of increasingly more saline solutions. In these tests, the chemical exchange between sediments and saline solutions was not attained instantaneously, and the concentrations of As desorbed by the four solutions in the three samples were conceivably more influenced by variable reaction rates, sample composition or pH. It was observed that about 8  $\mu\text{g}/\text{kg}$  of As were desorbed by L02 after the contact with the Sol1<sub>(84)</sub> solution ( $\text{Cl}^- \sim 0$  mg/L; Fig. 5a) suggesting some reaction occurred soon after the interaction sediment/solution. In the first day of the experiment, during As release, pH increased up to 8.15. This rapid increase in pH might have favored As desorption. Although the initial solution had very low salinity, alkaline conditions are known to enhance desorption reactions between As phases and oxide surfaces (e.g. Dzombak and Morel, 1990). Following saturation with Sol2<sub>(84)</sub>, As levels decreased from 7.4  $\mu\text{g}/\text{kg}$  to 5.4  $\mu\text{g}/\text{kg}$  and concentrations stabilized after the first day. In summary, the first batch of each new solution was often able to “flush out” substantial amounts of As made soluble under the new conditions.

Results also highlighted how the mineralogical composition of the aquifer and how As is bound to different mineral phases control As desorption into the intruding waters with different salinity. The percentage of As extracted in all the experiments relative to the total As concentrations, and relative to the exchangeable As fraction in the samples is shown in Fig. 6a. The exchangeable fraction accounts up to





**Fig. 6.** a) Percentage (%) of As compared to the total As in the three samples extracted in: the sequential extraction (step A1) and in the two desorption experiments (by the four solutions). b) Concentrations of As (ug/kg) extracted in the sequential extraction (step A1) compared to the As extracted by seawater assuming a change in chlorinity from 2000 mg/L to 18,511 mg/L in the two desorption experiments. The sum of As (ug/kg) desorbed by all the solutions in the 84 h experiment is also shown for comparison (light grey).

0.07% of the total As in the samples, and the As desorbed by the two experiment is less than 0.034% of the total. The maximum As (0.034%) was released by seawater (Sol<sub>4(24)</sub>) in 24 h, while after 21 days of saturation with Sol<sub>4(84)</sub> in the long experiment As extracted ranged from 0.006 to 0.012% of the total As (including all the As desorbed by the previous solutions). Thus, after a rapid intrusion of marine water (24 h shaking with Sol<sub>4(24)</sub>), more As is mobilized into solution than by a change in salinity from a solution with 2000 mg/L to 15,886 mg/L of Cl<sup>-</sup> (84-days long experiment). However, after 84 days saturation with solutions at increasing salinity, the total of As extracted by all the solutions is higher than the As desorbed by an increase of salinity from 2000 mg/L Cl to a chlorinity close to seawater (Fig. 6b) highlighting that As desorption is not only influenced by the possible variations of chlorinity occurring in an aquifer, but also by the timing of sediment/solution interaction after water intrusion.

When compared to the non-specifically bound fraction (A1) at least 22% and up to 60% of the mobile As are going into solution after 24 h desorption with high NaCl extractant (Sol<sub>4(24)</sub>), while after longer saturation time (long experiment) and after an increase of salinity from 2000 mg/L Cl, seawater (Sol<sub>4(84)</sub>) desorbed up to 17% of the exchangeable As fraction A1 (Fig. 7).

Overall, the As extracted by seawater after 24 h, and similarly in the long desorption experiment, represents only < 0.04% of the total As in the samples. Those values are much lower than the potentially exchangeable As found in similar experimental works. For example in Goh and Lim (2005), As extracted by NaCl leaching is around 11% of the total As in the samples, while Charlet et al. (2007) reports that the As leached using MgCl<sub>2</sub> as an extractant varies between 6 and 20% of the total As. These high concentrations of As desorbed are possibly explainable by the higher concentration of exchangeable As fraction in

the samples used in their experiments (Goh and Lim, 2005; Charlet et al., 2007). In the Val di Pecora samples As non-specifically bound (A1) is < 1% of the total As, and As is mainly bound to Fe-hydroxides (A4, A5 fraction) and to the residual phases (A6 fraction) (Fig. 3). Actually, it must be remarked, the present results and those obtained by Goh and Lim (2005) and Charlet et al. (2007) are not fully comparable, since they performed their extractions in the < 150 μm (Goh and Lim, 2005) and < 63 μm (Charlet et al., 2007) fractions of sample. In our experiments As desorption was analysed on the < 2 mm sample fraction, in order to simulate as close as possible the water/rock interaction in a natural aquifer. The bigger grain size and the non-perfectly homogeneous samples would have contributed to low concentrations of As in the exchangeable fraction. Also, when comparing to experimental works in literature, it is important to take into account the mineralogy and the age of the samples. Since the Quaternary the Pecora River samples were exposed to weathering and other processes, which most probably changed the original speciation of As and brought into solution part of the exchangeable As originally in the samples, while Goh and Lim (2005) and Charlet et al. (2007) focussed their results to soils artificially contaminated, with a homogeneous amount of As and not exposed to any prolonged weathering processes.

Frequently, in studies where the sequential extraction method is used to evaluate the risk posed by toxic metals to the environment, only the exchangeable fraction (non-specifically bound - A1) of metals is quantified to determine the potential risk for human health. Indeed, this fraction is often used to predict the soluble As amount that can be easily re-dissolved in ground water and to assess the risk of As contamination (e.g. Panssar-Kallio and Manninen, 1997; Wenzel et al., 2001; Goh and Lim, 2005). Results in the present paper highlighted the possibility that the sequential extraction may in some cases overestimate an upper limit of the exchangeable As fraction released in to the aquifer by a solution with salinity close to seawater, thus predicting a worst case scenario for As contamination in groundwater in the event of a saline wedge intruding the sediment pile. On the other hand, the desorption experiments have shown that in aquifers where long-term contacts sediment/solution in a Cl-rich environment occur, the exchangeable fraction might be underestimated because part of the As could have already been mobilized by the intrusion of saline solutions.

## 5.2. Implications for human health and the environment

Results of desorption experiments on As rich sediments have shown that concentrations of As desorbed by saline solutions vary according to the salinity and timing of the interaction sediments/solution. Groundwater As contamination in young Quaternary alluvial plains close to the sea inhabited by large population and impacted by drought is linked to the intrusion of seawater in the aquifer sediments (e.g.; Keon et al., 2001; Smedley and Kinniburgh, 2002; Liu et al., 2003; Goh and Lim, 2005; Lu et al., 2010). In particular, accelerated flow and mixing of different waters induced by over pumping of groundwater, may change the major ions geochemistry by mineral dissolution, ion exchange, or desorption/sorption reaction that may favour As release (Currell et al., 2011).

The southern coast of Tuscany represents a perfect study case of the same processes affecting those young Quaternary alluvial plains worldwide. Here, the increasing water demand due to tourism, industry and agriculture, combined with the presence of an extended ore district (Lattanzi et al., 1994), have often led to the aquifers overexploitation. In some areas, saltwater intrusion has been responsible of the deterioration of groundwater quality and accumulation of metals (e.g. mercury or arsenic) in well waters often exceeding the law limits for drinkable water (Grassi and Netti, 2000; Protano et al., 2000; Grassi et al., 2007). For example, in the coastal sector of the Pecora River Valley, south west of the sampling site in the Scarlino Plain, the surficial aquifers around the heavily industrialized area of Scarlino are characterized by As concentrations up to 1000 μg/L, hundred times higher

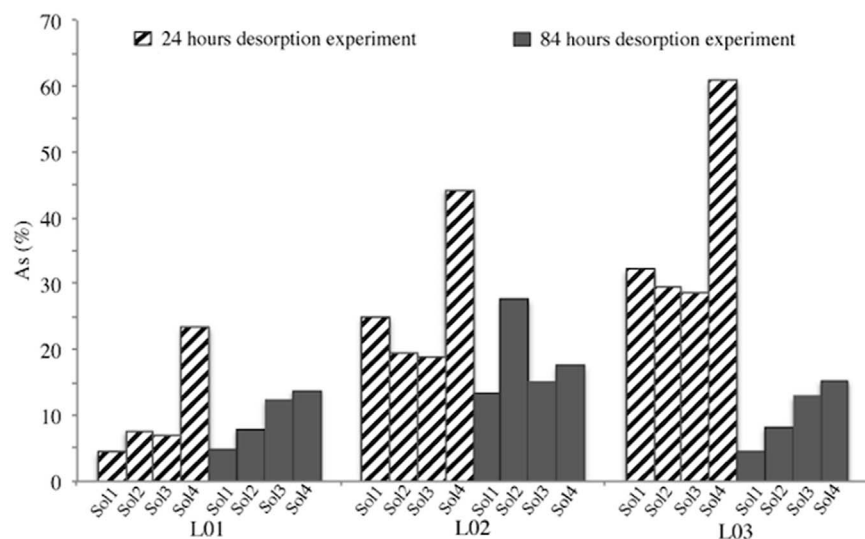


Fig. 7. Percentage (%) of As compared to the exchangeable fraction-A1 extracted by each solution in the 24 h experiment and in the 84 h experiment.

than the recommended levels for drinkable waters of 10  $\mu\text{g/L}$  (ARPAT, 2001; ARPAT-DPT/UNIFI, 2004; Rossato et al., 2011; ARPAT, 2013a; ARPAT, 2013b; ARPAT, 2014).

In the Pecora Valley, sediments hosting the local aquifer with similar lithologic composition of the three samples (P2 deposit) and characterized by high As contents, could be encountered up to a depth of about 100 m (Rossato et al., 2011). It is likely that those aquifer sediments may become in contact with the saline wedge, following intense over pumping of groundwater especially during the summer months (July to September), being the site close to the coast and to the city of Follonica.

Results from the Pecora River samples can therefore be used to give a broad estimate of the As desorbed following saline water ingress under different scenarios.

Based on the variability of salinity in groundwaters, ranging from 100 to > 2500 mg/L of Cl, typical of the studied area (Ghezzi et al., 1995; ARPAT, 2013b; ARPAT, 2014), in our experiment desorption with Solution 3 ( $\text{Cl}^- = 2000 \text{ mg/L}$ ) provides the closest simulation to the natural aquifer. In the case of a rapid change in chlorinity (24-h experiment) results have shown that a sediment with concentrations of As of  $\sim 473\text{--}737 \text{ mg/kg}$  intruded by water with  $\text{Cl}^- = 2000 \text{ mg/L}$  (Sol3<sub>(24)</sub>) will release into solution up to 56  $\mu\text{g/kg}$  of As (average among the three samples; Table 6). Assuming that an aquifer along the coast with a volume of  $1 \text{ m}^3$ , 20% porosity and  $1.9 \text{ kg/m}^3$  specific weight, is saturated by a rapid intrusion of water at that salinity, the As desorbed would produce a groundwater with 529  $\mu\text{g/L}$  of As in solution. If the ingress of water will occur with longer timing of interaction and with increasing salinity (long experiment from Sol1<sub>(84)</sub> to Sol3<sub>(84)</sub>) around  $\sim 415 \mu\text{g/L}$  of As could be dissolved into groundwater ( $\sim 44 \mu\text{g/kg}$  were released in solution from our samples). A worst-case scenario is predicted by desorption with seawater (Sol4). The three samples released about 133  $\mu\text{g/kg}$  (24-h experiment - Sol4<sub>(24)</sub>) and 50  $\mu\text{g/kg}$  (84-days experiment - from Sol3<sub>(84)</sub> to Sol4<sub>(84)</sub>) of As. Therefore, in the same aquifer, either a rapid or a slow ingress of seawater would dissolve into ground water at least 1260  $\mu\text{g/L}$  and 474  $\mu\text{g/L}$  of As respectively.

Although the obtained concentrations are simulating a hypothetical worst-case scenario in an aquifer with similar lithology and physico-chemical characteristics, the total As potentially released into solution could produce a groundwater exceeding the limit for drinking water (10  $\mu\text{g/L}$ ) accordingly to the Italian law guidelines (D. Lgs. 3 April 2006, n. 152) and the World Health Organization (WHO, 2004).

This is of particular concern in the context of global warming. In fact, the predicted risk of sea level rise could change the mechanisms of seawater inundation into coastal aquifers, extending the areas of saline

intrusion inland, as it is already occurring in many lowland coastal plains in the world, including, for example in Bangladesh (e.g. Oude Essink et al., 2010; Ferguson and Gleeson, 2012; Taylor et al., 2013).

In addition, climate change is likely to increase the frequency of intense climate extremes such as drought periods, floods, or intense storms. The consequent alteration of the hydrological cycle will induce variations in the water table and thus in the aquifers environmental conditions (e.g. Taylor et al., 2013). These changes will have an immediate effect in the studied area as well as in all those coastal areas with similar geogenic As anomaly. For example, after a long dry season, intense rain or a storm event may saturate the As rich sediments of an aquifer with water at almost no salinity (rain water can be assimilated with  $\text{Sol}_1 = \text{Cl}^- \sim 0 \text{ mg/L}$ ). Under this scenario, following an intense storm event (Sol1<sub>(24)</sub>), the 24-h experiment simulated this rapid saturation with the consequent release of up to 63  $\mu\text{g/kg}$  of As. This will correspond to up to 595  $\mu\text{g/L}$  of As potentially dissolved in groundwater in the same hypothetical aquifer described before (volume of  $1 \text{ m}^3$ , 20% porosity and  $1.9 \text{ kg/m}^3$  specific weight). On the other hand, the 84-days experiment (Sol1<sub>(84)</sub>) provided the example for an aquifer recharged and saturated for longer time (with  $\sim 25 \mu\text{g/kg}$  of As released by the samples). Thus, considering that in the area the average rainfall per year is  $\sim 400 \text{ L/m}^2$  (Follonica monitoring site - [www.sir.toscana.it](http://www.sir.toscana.it)), it will occur only half of the annual average rain water ( $\sim 200 \text{ L/m}^2$ ) to saturate the same aquifer and up to 242  $\mu\text{g/L}$  of As will potentially be dissolved in groundwater in one year for each  $1 \text{ m}^3$  of sediments. It will occur than a minimum of about 2.5 years to bring the contamination back to the limit of potability.

Although those calculations are a rough estimate based on very simple models, these simulations have provided a simulation of the possible environmental consequences that might occur in the area. In Tuscany, the decrease in precipitation over time (Grassi et al., 2007; Bartolini et al., 2017) and the reduced flow rates in the major river recorded over the last century (Dore, 2005; Grassi et al., 2007) have led to lower water recharge rates of the interconnected coastal aquifers. Consequently, following intense extraction rates, aquifer depletion and salinization could represent a critical issue especially in the coastal areas (Pranzini et al., 2002; Grassi et al., 2007; Doveri et al., 2009; Oude Essink et al., 2010; Livi et al., 2008). For example in the Cecina coastal plain (South of Livorno) the salinization front, characterized by water with  $\text{Cl}^-$  concentration  $\sim 250 \text{ mg/L}$  advanced inland by about 0.5–1 km in 4 years (1998–2002) (Grassi et al., 2007).

The experimental design applied to the samples from the Pecora River area provided an estimate under different scenarios of the concentrations of As potentially exchangeable under variable salinities.

Such information can be used to better constrain the dynamics of As contamination in groundwaters of many lowland alluvial coastal areas interested by high geogenic As anomalies (e.g. Bangladesh, China, Taiwan, Vietnam) following the over exploitation of groundwaters and the consequent ingression of seawater in aquifers.

## 6. Conclusions

Desorption experiments carried out on Quaternary alluvial sediments from southern Tuscany (Italy) have quantified the ionic interaction between As oxianions (adsorbed on mineral surfaces) and  $\text{Cl}^-$  in solutions. By saturating sediments with four solutions at increasing chlorinity for different length of time the natural water-rock interaction in fresh water aquifer was simulated and concentrations of As potentially desorbed after the ingression of saline waters quantified.

The highest concentration of As (161  $\mu\text{g}/\text{kg}$ ) were extracted by seawater ( $\text{Cl}^- = 18,511 \text{ mg}/\text{L}$ ) after 24 h contact sediment/solution, simulating a rapid change in the aquifer salinity (e.g. fast seawater intrusion, groundwater over pumping). For longer desorption periods (~21 days), conducted sequentially with four solutions at increasing salinity, about 62  $\mu\text{g}/\text{kg}$  of As were released after saturation with seawater and after an increase of salinity from 2000  $\text{mg}/\text{L}$  Cl to a salinity close to seawater ( $\text{Cl}^- = 18,511 \text{ mg}/\text{L}$ ). On the other hand, after saturation with less saline solutions ( $\text{Cl}^- \leq 2000 \text{ mg}/\text{L}$ ) the As desorbed was up to 54  $\mu\text{g}/\text{kg}$ . Our findings also showed how the amount of As desorbed from the sediments is controlled both by variations of chlorinity of the solution and by the timing of sediment/solution interaction. After a long desorption time (84 days) with solutions at increasing salinity the total As extracted by all solutions (As ~ 168  $\mu\text{g}/\text{kg}$ , average of the three samples) is higher than the As desorbed by the solution at highest salinity (As ~ 50  $\mu\text{g}/\text{kg}$ , average of the three samples), after an increase of salinity from 2000  $\text{mg}/\text{L}$  Cl to 18,511  $\text{mg}/\text{L}$  Cl.

On the basis of the experimental results, disturbances of the geochemical equilibrium driven by the ingression of the saline wedge into freshwater aquifers, hosted by sediments with high anomalous As, will desorb As in groundwaters exceeding the 10  $\mu\text{g}/\text{L}$  limit for drinking water. The aquifers in the lower part of the Pecora River basin (Scarolino Plain) are hosted by sediment deposits with similar lithology of the Pecora River samples and are often subjected by saltwater intrusion, following intense over pumping of groundwater. Results highlighted the potential risks to human health in the coastal sector of the Pecora River Valley (southern Tuscany, Italy) estimating under different scenarios the concentrations of As potentially exchangeable in an aquifer under variable groundwater salinities.

Also, this study provides a base of comparison for similar aquifer systems characterized by As geogenic anomaly in many lowland alluvial coastal areas around the world. This is especially significant in view of increasing extreme climate events (storms, floods, draught) driven by climate change for the prediction of As contamination in groundwater around overpopulated coastal areas.

## Acknowledgments

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors. The Authors would like to thank Thomas Baumgartl (UQ) for providing the equipment used for the UQ experiments and for assisting with its set up and with the sampling in the early stages of the experiment. We are grateful to Laura Livi for having provided some data published here that were obtained during her Master thesis at the Earth Science Dept. of the Firenze University. We all are PRUF (PRoud to produce some scientific product although UnderFunded).

## References

- Alam, M.G.M., Tokunaga, S., Maekawa, T., 2001. Extraction of arsenic in a synthetic arsenic-contaminated soil using phosphate. *Chemosphere* 43 (8), 1035–1041.
- Argos, M., Kalra, T., Rathouz, P.J., Chen, Y., Pierce, B., Parvex, F., Islam, T., Ahmed, A., Rakibuz-Zaman, M., Hasan, R., Sarwar, G., Slavkovich, V., van Geen, A., Graziano, J., Ahsan, H., 2010. Arsenic exposure from drinking water, and all-cause and chronic-disease mortalities in Bangladesh (HEALS): a prospective cohort study. *Lancet* 376, 252–258.
- ARPAT, 2013a. Report Arpat. Monitoraggio delle acque superficiali destinate alla produzione di acqua potabile art. 80 D.Lgs. 152/20062010–20062012. Risultati triennali 2010-2012 Proposta di classificazione. Firenze Luglio 2013.
- ARPAT, 2013b. Monitoraggio Corpi Idrici Sotterranei - Risultati 2012. Rete di Monitoraggio acque sotterranee DLgs 152/06 e DLgs 30/09 e DM 260/10.
- ARPAT, 2014. Dario Giannerini, Stefano Menichetti e Giancarlo Sbrilli. (2014). Definizione dei Valori di Fondo per alcuni parametri nelle Acque Sotterranee dei Siti in Bonifica della Pianura di Scarlino, Grosseto (2003–2012). Dipartimento provinciale ARPAT di Grosseto Direzione tecnica.
- ARPAT-DPT/UNIFI, 2001. Convenzione di ricerca su: “Studio della dispersione dell’arsenico nella piana di Scarlino-GR”.
- ARPAT-DPT/UNIFI, 2004. Convenzione di ricerca su: “Approfondimento dello studio inerente la diffusione dell’arsenico nel bacino del Fiume Pecora e zone limitrofe”.
- Ball, D.F., 1964. Loss-on ignition as an estimate of organic matter and organic carbon in non-calcareous soils. *J. Soil Sci.* 15, 84–92.
- Bartolini, G., Grifoni, D., Magno, R., Torrigiani, T., Gozzini, B., 2017. Changes in temporal distribution of precipitation in a Mediterranean area (Tuscany, Italy) 1955–2013. *Int. J. Climatol.* <http://dx.doi.org/10.1002/joc.5251>.
- Baten, M.A., Seal, L., Lisa, K.S., 2015. Salinity intrusion in Interior coast of Bangladesh: challenges to agriculture in south-Central coastal zone. *Am. J. Clim. Change* 4, 248–262.
- Benvenuti, M., Costagliola, P., Tanelli, G., 2009. Quaternary evolution of the Pecora River (southern Tuscany, Italy): paleohydrography and sediments provenance. *Boll. Della Soc. Geol. Ital.* 128, 61–72.
- Bhattacharya, P., Welch, A.H., Stollenwerk, K.G., McLaughlin, M.J., Bundschuh, J., Panaullah, G., 2007. Arsenic in the environment: biology and chemistry. *Sci. Total Environ.* 379 (2–3), 109–120.
- Bhowmick, S., Pramanik, S., Singh, P., Mondal, P., Chatterjee, D., Nriagu, J., 2018. Arsenic in groundwater of West Bengal, India: a review of human health risks and assessment of possible intervention options. *Sci. Total Environ.* 612, 148–169.
- Bianchi, S., 2004. Distribuzione dell’arsenico nei sedimenti tardo-quaternari ed in scorie archeo-metallurgiche della Media Val di Pecora (Grosseto), Tesi di laurea. Università degli Studi di Firenze, Dipartimento Scienze della Terra.
- Bonini, M., Sani, F., 2002. Extension and compression in the northern Apennines (Italy) hinterland: evidence from the late miocene-pliocene Siena-Radicofani basin and relations with basement structures. *Tectonics* 21 (3), 1–35.
- Cai, Y., Cabrera, J.C., Georgiadis, M., Jayachandran, K., 2002. Assessment of arsenic mobility in the soils of some golf courses in South Florida. *Sci. Total Environ.* 291 (1–3), 123–134.
- Charlet, L., Chakraborty, S., Appelo, C.A.J., Roman-Ross, G., Nath, B., Ansari, A.A., Lanson, M., Chatterjee, D., Mallik, S.B., 2007. Chemodynamics of an arsenic “hot-spot” in a West Bengal aquifer: a field and reactive transport modeling study. *Appl. Geochem* 22, 1273–1292.
- Chiarantini, L., Benvenuti, M., Costagliola, P., Fedi, M.E., Guideri, S., Romualdi, A., 2009. Copper production at Baratti (Populonia, southern Tuscany) in the early Etruscan period (9th–8th centuries BC). *J. Archaeol. Sci.* 36 (7), 1626–1636.
- Costagliola, P., Benvenuti, M.M., Benvenuti, M.G., Innocenti, A., Mascaro, L., Paolieri, M., Rossato, L., Tanelli, G., 2004. Arsenic distribution in the Quaternary sediments of the median valley of the Pecora stream (Grosseto, Italy). In: Donati, A., Rossi, C., Brebbia, C.A. (Eds.), *Brownfield Sites II*, pp. 201–209 Southampton: Whelan, G. ISBN:9781853127199.
- Costagliola, P., Benvenuti, M., Chiarantini, L., Bianchi, S., Benedetto, F.D., Paolieri, M., Rossato, L., 2008. Impact of ancient metal smelting on arsenic pollution in the Pecora River valley, southern Tuscany, Italy. *Appl. Geochem* 23, 1241–1259.
- Costagliola, P., Benvenuti, M.M., Benvenuti, M.G., Di Benedetto, F., Lattanzi, P., 2010. Quaternary sediment geochemistry as a proxy for toxic element source: a case study of arsenic in the Pecora Valley (southern Tuscany, Italy). *Chem. Geol.* 270, 80–89.
- Cuong, D.T., Obbard, J.P., 2006. Metal speciation in coastal marine sediments from Singapore using a modified BCR-sequential extraction procedure. *Appl. Geochem* 21 (8), 1335–1346.
- Currell, M., Cartwright, I., Raveggi, M., Han, D., 2011. Controls on elevated fluoride and arsenic concentrations in groundwater from the Yuncheng Basin, China. *Appl. Geochem* 26 (4), 540–552.
- Das, B., Rahman, M.M., Nayak, B., et al., 2009. Groundwater arsenic contamination, its health effects and approach for mitigation in West Bengal, India and Bangladesh. *Water Expo. Health* 1, 5–21.
- Dixit, S., Hering, J.G., 2003. Comparison of Arsenic(V) and arsenic(III) sorption onto iron oxide Minerals: implications for arsenic mobility. *Environ. Sci. Technol.* 37 (18), 4182–4189.
- Dore, M.H., 2005. Climate change and changes in global precipitation patterns: what do we know? *Environ. Int.* 31 (8), 1167–1181.
- Doveri, M., Gianecchini, R., Giusti, G., Butteri, M., 2009. Studio idrogeologico-geochimico dell’acquifero freatico nella zona compresa tra il Canale Burlamacca ed il Fosso della Bufalina (Viareggio, Toscana). *EngHydroEnv Geol. G. Geol. Appl.* 12, 10–117.
- Dzombak, D.A., Morel, F.M.M., 1990. Surface Complexation Modeling. *Hydrous Ferric Oxide*. John Wiley & Sons, New York.



- Ferguson, G., Gleeson, T., 2012. Vulnerability of coastal aquifers to groundwater use and climate change. *Nat. Clim. Change* 2 (5), 342–345.
- Ghezzi, G., Ghezzi, R., Muti, A., 1995. Carta idrogeologica della Pianura di Piombino, vol. Quaderni del Museo di Storia Naturale di Livorno, Suppl. n.2 al vol. 13. C.N.R., Università di Siena Provincia di Livorno, C.I.G.R.I., Parco archeo-minerario di S. Silvestro.
- Goh, K.-H., Lim, T.-T., 2005. Arsenic fractionation in a fine soil fraction and influence of various anions on its mobility in the subsurface environment. *Appl. Geochem* 20 (2), 229–239.
- Grassi, S., Netti, R., 2000. Sea water intrusion and mercury pollution of some coastal aquifers in the province of Grosseto (Southern Tuscany — Italy). *J. Hydrol.* 237 (3–4), 198–211.
- Grassi, S., Cortecchi, G., Squarci, P., 2007. Groundwater resource degradation in coastal plains: the example of the Cecina area (Tuscany—Central Italy). *Appl. Geochem* 22 (11), 2273–2289.
- Hazen, A., 1911. Discussion of Dams on sand foundations. *Trans. Am. Soc. Civ. Eng.* 73, 199–203.
- Holtz, R.D., Kovacs, W.D., 1981. The unified soil classification system (USCS). In: *An Introduction to Geotechnical Engineering*, Englewoods Cliffs, New Jersey. Prentice-Hall.
- Hossain, M.F., 2006. Arsenic contamination in Bangladesh—an overview. *Agr. Ecosyst. Environ.* 113 (1–4), 1–16.
- Huang, G.X., Chen, Z.Y., Sun, J.C., Liu, F., Wang, J., Zhang, Y., 2015. Effect of sample pretreatment on the fractionation of arsenic in anoxic soils. *Environ. Sci. Pollut. Res.* 22 (11), 8367–8374.
- Huang, G.X., Chen, Z.Y., Wang, J., Hou, Q.X., Zhang, Y., 2016a. Impact of temperature on the aging mechanisms of arsenic in soils: fractionation and bioaccessibility. *Environ. Sci. Pollut. Res.* 23, 4594–4601.
- Huang, G., Chen, Z.Y., Zhang, Y., Liu, F., Wang, J., Hou, Q.X., 2016b. Changes of arsenic fractionation and bioaccessibility in wastewater-irrigated soils as a function of aging: influence of redox condition and arsenic load. *Geoderma* 280, 1–7.
- Innocenti, F., Serri, G., Ferrara, G., Manetti, P., Tonarini, S., 1992. Genesis and classification of the rocks of the Tuscan Magmatic Province: thirty years after Marinelli's model. *Acta Vulc.* 2, 247–265.
- Jackson, B.P., Miller, W.P., 2000. Effectiveness of phosphate and hydroxide for desorption of arsenic and selenium species from iron oxides. *Soil Sci. Soc. Am. J.* 64, 1616–1622.
- Joseph, T., Dubey, B., McBeana, E.A., 2015. A critical review of arsenic exposures for Bangladeshi adults. *Sci. Total Environ.* 527–528, 540–551.
- Keon, N.E., Swartz, C.H., Brabander, D.J., Harvey, C., Hemond, H.F., 2001. Validation of an arsenic sequential extraction method for evaluating mobility in sediments. *Environ. Sci. Technol.* 35, 2778–2784.
- Kippler, M., Skróder, H., Rahman, S.M., Tofail, F., Vahter, M., 2016. Elevated childhood exposure to arsenic despite reduced drinking water concentrations — a longitudinal cohort study in rural Bangladesh. *Environ. Int.* 86, 119–125.
- Lattanzi, P., Benvenuti, M., Costagliola, P., Tanelli, G., 1994. An overview on recent research on the metallogeny of Tuscany, with special reference to the Apuane Alps. *Mem. Soc. Geol. Ital.* 48, 613–625.
- Lgs, D., 3 April 2006. n. 152. 2006. Decreto Legislativo 3 aprile 2006, n. 152. "Norme in materia ambientale", *Gazzetta Ufficiale* n. 88 del 14 aprile 2006-Supplemento Ordinario n. 96.
- Liu, C.-W., Lin, K.-H., Kuo, Y.-M., 2003. Application of factor analysis in the assessment of groundwater quality in a blackfoot disease area in Taiwan. *Sci. Total Environ.* 313 (1–3), 77–89.
- Livi, L., Benvenuti, M., Costagliola, P., Di Benedetto, F., Gasparon, M., Lattanzi, P., Vettori, S., Vaselli, O., 2008. Arsenic mobilization driven by seawater intrusion in the Pecora Valley (southern Tuscany, Italy). In: 1st SIMP-aic Joint Meeting, Sestri Levante, Italy, 7–12 September 2008.
- Lu, K.-L., Liu, C.-W., Wang, S.-W., Jang, C.-S., Lin, K.-H., Liao, V.H.-C., Liao, C.-M., Chang, F.-J., 2010. Primary sink and source of geogenic arsenic in sedimentary aquifers in the southern Choushui River alluvial fan, Taiwan. *Appl. Geochem* 25 (5), 684–695.
- Manning, B.A., Goldberg, S., 1997. Adsorption and stability of arsenic (III) at the clay mineral-water interface. *Environ. Sci. Technol.* 31, 2005–2011.
- Martini, I.P., Sagri, M., 1993. Tectono-sedimentary characteristics of late miocene-Quaternary extensional basins of the northern Apennines, Italy. *Earth-Sci. Rev.* 34, 197–233.
- McArthur, J.M., Banerjee, D.M., Hudson-Edwards, K.A., Mishra, R., Purohit, R., Ravenscroft, P., Cronin, A., Howarth, R.J., Chatterjee, A., Talukder, T., Lowry, D., Houghton, S., Chadha, D.K., 2004. Natural organic matter in sedimentary basins and its relation to arsenic in anoxic ground water: the example of West Bengal and its worldwide implications. *Appl. Geochem* 19, 1255–1293.
- Medved, J., Streško, V., Kubová, J., Polakoviová, J., 1998. Efficiency of the composition procedures for the determination of some elements in soil by atomic spectroscopic methods. *Fresenius J. Anal. Chem.* 360, 219–224.
- Nicoll, H.B., Suriano, J.M., Peral, M.A.G., Ferpozzi, L.H., Baleani, O.A., 1989. Groundwater contamination with arsenic and other trace-elements in an area of the Pampa, province of Cordoba, Argentina. *Environ. Geol. Water Sci.* 14, 3–16.
- Oude Essink, G.H.P., Van Baaren, E.S., de Louw, P.G.B., 2010. Effects of climate change on coastal groundwater systems: a modelling study in The Netherlands. *Water Resour. Res.* 46 (10), W00F04.
- O'Neill, P., 1995. Arsenic. In: Alloway, B.J. (Ed.), *Heavy Metals in Soils*, second ed. Blackie Academic & Professional, Glasgow, pp. 105–121.
- Pantzar-Kallio, M., Manninen, P.K.G., 1997. Speciation of mobile arsenic in soil samples as a function of pH. *Sci. Total Environ.* 204 (2), 193–200.
- Pongratz, R., 1998. Arsenic speciation in environmental samples of contaminated soil. *Sci. Total Environ.* 224 (1–3), 133–141.
- Pranzini, E., Aminti, P., Pelliccia, F., 2002. Evoluzione del profilo di spiaggia a seguito di un ripascimento artificiale in ghiaia su di una spiaggia altamente protetta. *Studi Costieri.* 5, 47–57 ISSN:1129–8588.
- Protano, G., Riccobono, F., Sabatini, G., 1998. La cartografia geochemica della Toscana Meridionale. Criteri di realizzazione e rilevanza ambientale attraverso gli esempi di Hg, As, Sb, Pb e Cd. *Mem. Descr. Carta Geol. d'Italia* 55, 109–140.
- Protano, G., Riccobono, F., Sabatini, G., 2000. Does salt water intrusion constitute a mercury contamination risk for coastal fresh water aquifers? *Environ. Poll.* 1001, 451–458.
- Rahman, M.S., Reichelt-Brushet, A.J., Clark, M.W., Farzana, T., Yee, L.H., 2017. Arsenic bio-accessibility and bioaccumulation in aged pesticide contaminated soils: a multi-line investigation to understand environmental risk. *Sci. Total Environ.* 581–582, 782–793.
- Raposo, J.C., Zuloaga, O., Sanz, J., Villanueva, U., Crea, P., Etxebarria, N., Olazabal, M.A., Madariaga, J.M., 2006. Analytical and thermodynamical approach to understand the mobility/retention of arsenic species from the river to the estuary. The Bilbao case study. *Mar. Chem.* 99 (1–4), 42–51.
- Rauret, G., 1998. Extraction procedures for the determination of heavy metals in contaminated soil and sediment. *Talanta* 46 449–445.
- Rossato, L., Dughetti, F., Fontani, F., Paolieri, M., Tanelli, G., 2011. Arsenic and poly-metallic anomalies in the Neogene-Quaternary sequence of La botte borehole in the Scarlino Plain (Grosseto)—southern Tuscany—Italy. *Neues Jahrb. für Mineral. - Abh.* 188 (1), 87–98.
- Scheiber, L., Ayora, C., Vázquez-Suñé, E., Cendón, D.I., Soler, A., Baquero, J.C., 2016. Origin of high ammonium, arsenic and boron concentrations in the proximity of a mine: natural vs. anthropogenic processes. *Sci. Total Environ.* 541, 655–666.
- Serri, G., Innocenti, F., Manetti, P., 2001. Magmatism from Mesozoic to Present: petrogenesis, time-space distribution and geodynamic implications. In: Vai, G.B., Martini, P.I. (Eds.), *Anatomy of an Orogen: the Apennines and Adjacent Mediterranean Basins*. Springer Netherlands, pp. 77–103.
- Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem* 17, 517–568.
- Sun, H., Alexander, J., Gove, B., Koch, M., 2015. Mobilization of arsenic, lead, and mercury under conditions of sea water intrusion and road deicing salt application. *J. Contam. Hydrol.* 180, 12–24.
- Taylor, R.G., Scanlon, B., Doll, P., Rodell, M., van Beek, R., Wada, Y., Longuevergne, L., Leblanc, M., Famiglietti, J.S., Edmunds, M., Konikow, L., Green, T.R., Chen, J., Taniguchi, M., Bierkens, M.F.P., MacDonald, A., Fan, Y., Maxwell, R.M., Yechieli, Y., Gurdak, J.J., Allen, D.M., Shamsudduha, M., Hiscock, K., Yeh, P.J.F., Holman, I., Treidel, H., 2013. Ground water and climate change. *Nat. Clim. Change* 3 (4), 322–329.
- Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* 51 (7), 844–851.
- US EPA, 1986. Test Method 9080. Cation-exchange Capacity of Soils (Ammonium Acetate). EPA, United States Environmental Protection Agency, pp. 9 September 1986.
- Wan, X., Dong, H., Feng, L., Lin, Z., Luo, Q., 2017. Comparison of three sequential extraction procedures for arsenic fractionation in highly polluted sites. *Chemosphere* 178, 402–410.
- Wasay, S.A., Parker, W., Geel, P.J.V., Barrington, S., Tokunaga, S., 2000. Arsenic pollution of a loam soil: retention form and decontamination. *J. Soil Contam.* 9 (1), 51–64.
- Wenzel, W., Kirchbaumer, N., Prohaska, T., Stüingeder, G., Lombi, E., Adriano, D.C., 2001. Arsenic fractionation in soils using an improved sequential extraction procedure. *Anal. Chim. Acta* 436, 309–323.
- Williams, A.E., Lund, L.J., Johnson, J.A., Kabala, Z.J., 1998. Natural and anthropogenic nitrate contamination of groundwater in a rural community, California. *Environ. Sci. Technol.* 32, 32–39 1998.
- World Health Organization, 2003. Chlorine in Drinking-water. Background Document for Development of WHO, Guidelines for Drinking-water Quality. World Health Organization 2003.
- World Health Organization, 2004. The World Health Report: 2004: Changing History. World Health Organization 2004.
- Yu, W.H., Harvey, C.M., Harvey, C.F., 2003. Arsenic in groundwater in Bangladesh: a geostatistical and epidemiological framework for evaluating health effects and potential remedies. *Water Resour. Res.* 39, 1146–1163.
- Zhang, W., Singh, P., Paling, E., Delides, S., 2004. Arsenic removal from contaminated water by natural iron ores. *Min. Eng.* 17 (4), 517–524.