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An approach for arsenic in a contaminated soil: speciation, fractionation, extraction and effluent decontamination

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Abstract

The fractionation and speciation of As in a contaminated soil were investigated, and a remediation strategy was tested. Regarding speciation, we found that As(V) prevails over As(III) whereas more than 40 % of total arsenic is in organic form. The fractionation of As was investigated with two sequential extraction methods: a low mobility was found. Then we tested the possibility of using phosphoric acid to extract As from the soil and cleaning the washing effluents by sorption onto montmorillonite. The efficiency of the extraction and of the adsorption on the clay were also investigated for Cr, Cu, Fe, Mn, Ni, Pb and Zn, whose total concentrations and fractionation in the soil are reported here. The extraction percentages for As and metals ranged from 30 to 65%; the residual proportions in the soil are presumably in very unreactive forms. Montmorillonite showed a good uptake capacity towards the investigated pollutants.

Keywords: arsenic; speciation; fractionation; soil washing; montmorillonite

Capsule: *Arsenic in a contaminated soil was present in different forms and it was extracted by soil washing followed by effluent treatment by sorption onto a natural clay*

1. Introduction

Pollution by arsenic is a potentially serious problem throughout the world. Inorganic arsenic is classified as the number one toxin in the US Environmental Protection Agency (EPA) list of prioritized pollutants. This element can be found in surface and subsurface water bodies, many foods, and soils. Primary As anthropogenic sources include copper smelting, coal combustion, herbicide, pesticide and rodenticide use, as well as waste incineration, steel/glass production, and pressurized wood production (Matschullat, 2000). Naturally occurring As in soils originates from the weathering of primary and secondary As-bearing minerals (Datta et al., 2007). Arsenic-containing compounds vary in toxicity to mammals according to valence state, form (inorganic or organic), physical state (gas, solution or powder) and factors such as solubility, particle size, rates of absorption and elimination, and presence of impurities which may facilitate the intake of this element into organisms. Recent research suggests that arsenic in drinking water may be more dangerous than previously believed (Kim and Nriagu, 2000). In 2001, the US limit of 50 ppb for arsenic in drinking waters was lowered to 10 ppb (~ 130 nM), while recently the EU limit was further lowered from 10 to 5 ppb. Chronic exposure to arsenic, particularly inorganic arsenite (As(III)) and arsenate (As(V)), has been implicated in many physiological disorders and various types of cancers.

Arsenic is present in the terrestrial and aquatic environments as inorganic As(III) and As(V) compounds (H_3AsO_3, $HAsO_4^{2-}$, $H_2AsO_4^-$) and in organic form (monomethylersonic acid, MMA, dimethylarsonic acid, DMA) (Ko et al., 2004). In soil

environment, the proportions of As(III) and As(V) vary as function of redox conditions and pH (Haswell et al., 1985; Masscheleyn et al., 1991; McGreehan and Naylor, 1994). In the typical pH range of soils, arsenate exists as mono- or bivalent anions, while arsenite is uncharged unless the pH is strongly alkaline. Biomethylation can lead to organic As species such as MMA (pKa_1: 8.2, pKa_2: 3.6) and DMA (pK_a: 6.2). The inorganic species of arsenic are more toxic than the organic species, with arsenite being more toxic than arsenate (Le et al., 2000).

As reported above the toxicity of arsenic depends on its chemical form: the inorganic species are more toxic than the organic species, with arsenite being more toxic than arsenate (Le et al., 2000). For this reason both the quantitative determination and speciation of this element are essential (Mir et al., 2007). Furthermore it is now well established that, in addition to total concentrations, the mobility and availability of arsenic and other potentially toxic elements must be assessed in order to elucidate their behaviour in soils and prevent possible toxic hazards (Banat et al., 2005). The availability of inorganic pollutants (such as As, Zn, Pb and Cd) depends on physical, chemical and biological parameters, including pH, soil texture, microbial activities and presence of cultivars (Deneux-Mustin et al., 2003; Pueyo et al., 2003). It is usually investigated by extraction with suitable reagents. As to metals, single extractions with water, diluted acetic acid, neutral salts and ethylenediaminetetraacetic acid (EDTA) (Ministerial Decree, 1999) are generally performed in order to evaluate the proportion of metals weakly bound to the matrix, as preliminary indication on the possible release of pollutants into the environment or their uptake by plants. In addition, sequential extractions are carried out with reagents of different chemical properties, in order to identify fractions of elements with different labilities. Several sequential extractions

schemes for metals (Tessier et al., 1979; Meguellati et al., 1983; Quevauviller et al., 1994) have been developed; in particular Tessier's scheme (Tessier et al, 1979) is one of the most widely used and it has been extensively applied to aquatic sediments (Pagnanelli et al., 2004), soils (Karathanasis and Pils, 2005) and sludges (Barajas-Aceves et al., 2007).

While there is a large number of sequential extraction procedures available for cations, only limited work has been done on oxyanions such As (Adriano, 2001). Some extraction schemes recognize the anionic behaviour of As in soils and sediments, and are mainly based on extraction procedure for P (Hudson-Edwards et al., 2004).

To protect animal and human health, remediation of the As-contaminated sites has become an important issue (Jankong et al., 2007). Occasionally, arsenic-contaminated soils have been excavated and disposed to controlled-type landfill sites as hazardous materials. Alternately, contaminated soils have been treated by containment (Mulligan et al., 2001), capping (USEPA, 2002a), and solidification/stabilization (Paria and Yuet, 2006). However, these methods do not sufficiently reduce environmental risks, because of possible leaching of arsenic from treated soils (Alam et al., 2007). One permanent solution to such soil contamination problems is to remove the bulk of arsenic from soils so that environmental risk can be drastically reduced (Legiec et al, 1997; Wasay et al., 1998). Soil washing has the potential to remove As from contaminated soils by using inorganic salts (potassium phosphate, potassium chloride, potassium nitrate, potassium sulphate or sodium perchlorate), inorganic acids (sulphuric acid, nitric acid, phosphoric acid, hydrochloric acid or mixed acid), organic acids (citric or acetic acids) or alkaline agent (e.g., sodium hydroxide) (Alam et al., 2001; Jackson and Miller, 2000; Tokunaga and Hakuta, 2002; Jang et al., 2005). There is no comprehensive precise report available

for the widely acceptance of technology for the removal of arsenic from contaminated soils and also the effect of chemical extraction on As species (Alam and Tokunaga, 2006).

In a previous work, we studied the availability and removal of metals from an industrially-polluted soil close to the small town of Cengio, Italy (Abollino et al., 2007). In this work we have focused our attention on arsenic: we studied its availability and speciation in such soil and tested a procedure for its removal by soil washing and for the cleaning of the soil extracts. The efficiency of such procedure was also evaluated for some metals present in the soil.

First of all, we determined the arsenic forms present in the considered soil using Chappell's method (Chappell et al., 1995), in which arsenic is extracted from the soil with concentrated hydrochloric acid and is speciated using solvent extraction. Then we evaluated the mobility of As and metals using the simple sequential extraction procedure proposed by Cai (Cai et al., 2002) which enables to distinguish among mobile, mobilizable, and residual fractions.

We subsequently tested a procedure for the removal of arsenic by soil washing using phosphoric acid, since it was reported as the most efficient releasing agent for arsenic (Tokunaga and Hakuta, 2002).

We finally addressed the fate of washing effluents. Clay linings have been used as barriers in landfills to prevent contamination of groundwater and subsoil by leachates containing metals. Generally, these linings are constituted of bentonite and, in particular, montmorillonite (Bayley et al, 1999). We chose montmorillonite as a sorbent for the development a procedure for the decontamination of the soil extracts. The sorption efficiency of montmorillonite was studied using a continuous flow system.

We also evaluated the fractionation pattern and the efficiency of extraction and effluent decontamination for some metals present in the soil at high concentration, namely Cr, Cu, Fe, Mn, Ni, Pb and Zn.

2. Materials and methods

2.1 Site description and sampling

The industrial soil of Cengio (Province of Savona, Northern Italy) is extremely polluted by metals, arsenic, polycyclic aromatic compounds, chlorinated aliphatic solvents and has been classified as dangerous waste. The main sources of pollution were the activities of a local factory, A.C.N.A. (Aziende Chimiche Nazionali Associate), which has now been closed. The site has been included in the list of national priorities for environmental reclamation since 1999. Other details can be found elsewhere (Abollino et al., 2007).

The investigated soil was sampled in the A.C.N.A. site in the tanks for the waste disposal. Soil sample was air – dried, passed through a 2 mm stainless steel sieve and ground in a centrifugal ball mill in order to homogenise it.

2.2. Apparatus and reagents

Sample dissolution for the determination of total metal concentrations was performed in PTFE bombs, with a Milestone MLS-1200 Mega (Milestone, Sorisole, Italy) microwave laboratory unit.

Analytes were determined with a Varian Liberty 100 model (Varian Australia, Mullgrave, Australia) inductively coupled plasma-atomic emission spectrometer (ICP-

AES) or with a Perkin Elmer Analyst 600 (Perkin Elmer, Norwalk, Connecticut, USA) electrothermal atomic absorption spectrometer equipped with Zeeman-effect background spectrometer and graphite furnace (GF-AAS).

Analytical grade reagents were used throughout. Standard metal solutions were prepared from concentrated Merck Titrisol stock solutions (Merck, Darmstadt, Germany).

High-purity water (HPW) with a specific resistivity of 18 MΩ cm, produced with a Millipore water purifier system, was used for the preparation of sample and standard solutions.

Polypropylene columns (Bio-Rad), 4 cm high and 5 mm i.d., were slurry-packed with 0.7 g of Na-montmorillonite (Aldrich). At the bottom of the columns, on the porous polymer bed support, a 0.45 μm cellulose acetate filter (Millipore) was placed.

A Gilson Minipuls 4 multichannel peristaltic pump was used to drive the sample solutions into the columns with a constant and reproducible flow rate (0.19 ml/min). This pump was connected to the columns by polypropylene low-pressure fittings and PVC tubes.

2.3. Procedures

Three replicates of the following experiments were performed and blanks were simultaneously run. For each experiment, standard solutions for instrument calibration were prepared in the corresponding matrix.

Metals determinations were performed by ICP-AES. Arsenic, present below the ICP-AES detection limits, was determined by GF-AAS.

2.3.1. Sample digestion for total metal determination

Aqua regia (5 ml) and HF (2 ml) were added to 0.1 g of sample in PTFE bombs and heated in a microwave oven following the sequence: three steps of 5 min each (at a power of 250, 400, 500 W, respectively) followed by a final 3 min step at 600 W. Then 0.7 g of H_3BO_3 were added and the bombs were further heated for 10 min at 250 W. Finally, the samples were filtered and diluted to 100 ml (Abollino et al., 2002).

2.3.2. Speciation of arsenic by solvent extraction

This method consists of three steps:

1) Extraction of arsenic from the soil. A 5 g aliquot of soil was weighed into a centrifuge tube and 20 ml of 10 M HCl were added. The extraction was assisted by shaking vigorously for about 30 min. The resulting slurry was centrifuged at 3000 rpm for 5 min and the supernatant was gravity-filtered into a 100 ml volumetric flask. This procedure was repeated two more times on the same portion of soil. Then the soil was washed into the filter paper with water and the solution diluted.
2) Determination of trivalent arsenic. A 10 ml aliquot of the extract was transferred to a 100 ml separating funnel and 80 ml of 10 M HCl were added, adjusting the acid concentration to higher than 9 M. This was followed by extraction of As(III) into $CHCl_3$ with 4 × 10 ml washings. At this stage the strongly acidic aqueous phase was discarded. Arsenic was then back-extracted from the organic phase into 2 × 20 ml aliquots of water and diluted to 100 ml.
3) Determination of total inorganic arsenic. A separate 10 ml aliquot of the extract was transferred to a large test tube and 10 ml of 50 % w/v KI solution were

added. The tube was covered and immersed into a water bath at 60° C for about 30 min. After the solution had cooled, it was diluted to 50 ml, 10 ml of which were transferred into a 100 ml separating funnel. The extraction for total inorganic arsenic was then performed as for As(III).

2.3.4. Sequential extraction procedures

2.3.4.1. Tessier's extraction

This method yields five different fractions: exchangeable (1 M $MgCl_2$, pH 7); bound to carbonates or specifically adsorbed (1 M NaOAc/HOAc, pH 5); bound to Fe-Mn oxides (0.04 M $NH_2OH{\cdot}HCl$ in 25 % HOAc); bound to organic matter and sulphides (0.02 M HNO_3 in 30 % H_2O_2, pH 2; 3.2 M NH_4OAc in 20 % HNO_3) and residual (*aqua regia* and HF). The procedure was applied to 1 g of soil. After each extraction, the suspension was centrifuged, and the supernatant removed for analysis. The residue was then rinsed with HPW and the washing solution, after centrifugation, was added to the supernatant. The residue of the fourth extraction was digested with HNO_3, HCl and HF according to the procedure described for the total metal analysis. Further details are reported in our previous paper (Abollino et al., 2007).

2.3.4.2. Cai's extraction

The mobile and mobilizable fractions were estimated by using 0.1 M $NaNO_3$ and 0.1 M KH_2PO_4, respectively. 25 ml of 0.1 M $NaNO_3$ were added to 0.5 g of soil and shaken for 24 h; the suspension was centrifuged and the supernatant removed to determine mobile fraction. 25 ml of 0.1 M KH_2PO_4 were added to the residue for the determination of the mobilizable fraction. The final residue was subjected to acid digestion with the same

procedure described in section 2.3.

2.3.5. Soil washing

25 ml of 1.6 M phosphoric acid were prepared in centrifuge tubes by diluting concentrated H_3PO_4. 0.5 g of contaminated soil were added to three tubes and shaken for 6 h at room temperature. The suspension was centrifuged and filtered. The filtrate was analysed not only for arsenic, but also for Cr, Cu, Fe, Mn, Ni, Pb and Zn.

2.3.6. Clean-up of extracts and total capacity of montmorillonite

The solutions deriving from the soil washing treatment with phosphoric acid were driven through the columns packed with montmorillonite with the aid of a peristaltic pump.

The effluent solutions were analysed for As, Cr, Cu, Fe, Mn, Ni, Pb and Zn. The percentage of each element adsorbed on to the clay was calculated from the difference between the content of metal in influent solution and that one in effluent solution, corrected with the blank.

The total capacity of montmorillonite towards As(III) and As(V) was evaluated with the breakthrough technique generally used in chromatography to measure the highest degree of column utilisation in a given process (Abollino et al., 2003). 0.01 M NaAc/HAc solutions containing $1x10^{-3}$ M As were driven, with pH controlled at 5, through the columns packed with the clay previously conditioned at pH 5 with 10 ml of 0.1 M NaAc/HAc, and successive aliquots of 25 ml of the effluent were collected and analysed.

3. Results and discussion

3.1. Total element content

Table 1 reports the total contents of As and of Cr, Cu, Fe, Mn, Ni, Pb, and Zn in the investigated soil and, for comparison, the typical ranges and common values present in unpolluted soils and the average abundance in the earth's crust (Alloway, 1990). The concentrations of all elements are higher than the common values and (with the exception of Cr, Mn, Ni and Zn) are above the typical ranges. These data were widely discussed in another paper (Abollino et al., 2007).

The main activities of the A.C.N.A. farm were the production of sulphuric acid using Herreschoff's furnaces for the roasting of pyrites and the experimentation of colouring agents for dying. Pyrites are the first matter in the sulphuric acid production and they contain large amounts of copper and arsenic and traces of nichel and cobalt. During the roasting As is transferred to the gas phase (as As_4O_6 present as impurity of SO_2), and also the ashes and the slag contain arsenic. So a lot of arsenic was emitted into the surrounding area during the production of sulphuric acid and gave rise to pollution.

A part of the arsenic present in the soil may have a natural origin; in particular, it is commonly present in geologic strata as arsenides (e.g. Cu_3As) and sulfides (e.g. arsenopyrite, FeAsS).

Dye manufacturing was another source of copper pollution, since many colouring agents contain copper; the high concentrations of iron found in the soil are due to the continuous disposal of ferrous wastes, also taking into account that the first activity in the area was the production of explosives.

These results clearly show that the soil is heavily contaminated by metals and arsenic

and therefore needs remediation.

3.2. Speciation of arsenic

The concentrations of As(III), As(V) and organic arsenic were determined.

Arsenic was extracted from the soil with concentrated HCl, according to Chappell's method (Chappell et al., 1995). The efficiency of extraction rises sharply with increasing acid concentration, yielding a 100% extraction at acid concentrations of 9 M of greater (Holak et al., 1991). Based on the observation that arsenite and arsenate are more than 99.9% soluble in HCl at the concentrations encountered in the method, it is assumed that As(III) and As(V) are extracted from the soil with equal efficiency (Chappell et al., 1995). Arsenic trichloride is a covalent molecule while arsenic pentachloride probably exists as complex ion, $[AsCl_4]^+[AsCl_6]^-$. The organic arsenic remains as MMA and DMA.

In the next step As(III) can be selectively extracted into an organic phase such as $CHCl_3$, while arsenic pentachloride is excluded owing to its ionic properties. As(III) can then be back-extracted into water for analysis. In fact As(III) is most stable in solution in its hydrolysed form, therefore when it comes into contact with water, hydrolysis occurs, excluding the arsenic from the organic phase.

In the third step of the speciation procedure, KI is added as reductant and all As(V) present in solution is reduced to As(III). The same procedure described before is used to determine the total arsenic as As(III), and the amount of As(V) is calculated by difference between total inorganic arsenic and the result for As(III).

During reduction with potassium iodide, it is possible that MMA and DMA are reduced to CH_3AsI_2 and $(CH_3)_2AsI$ respectively. If these compounds are formed and can be

extracted into chloroform, then the results for total inorganic arsenic and hence for inorganic As(V) will be erroneous. However, it seems that the reduction of DMA to $(CH_3)AsI_2$ is very slow and does not occur to any significant level during the time scale of the experiment. The reduction of MMA to $(CH_3)_2AsI$ is much faster but the organic arsenic (III) product is not likely to be soluble in chloroform to any appreciable extent. Therefore, it was concluded that only inorganic As(III) would be extracted into $CHCl_3$. The concentration of organic arsenic was determined by difference between the total concentration of arsenic determined by acid digestion and total inorganic arsenic.

The results obtained are reported in Table 2 and show that As(V) slightly prevails over As(III) whereas more than 40 % of total arsenic is in organic form. Generally the organic forms of arsenic can be changed in inorganic forms depending on the environmental conditions (pH and redox potential). The percentage of organic matter in the soil, determined in a previous work, is 7.6 % (Abollino et al., 2007): this percentage reflects the presence of organic pollutants, like polycyclic aromatic compounds, due to the past industrial activities, in addition to the organic matter originally present in the soil. The high percentage of organic arsenic is probably favoured by the large amount of organic matter in the soil.

Inorganic arsenic is generally more toxic than organic arsenic (Alam et al., 2007). Generally, the organoarsenic compounds are considered to be scarcely adsorbed by mammals and they are eliminated through the urine. However, animal studies have recently shown that methyl- and phenyl- arsenates can produce health effects similar to those produced by inorganic arsenic (Mandal and Suzuky, 2002). The toxicity of As(III) is several times greater than that of As(V), due to greater cellular uptake; in fact it can remain in the organisms for longer times because it binds to the sulphydril groups of

proteins, enzymes, coenzyme A and reduced glutathione. At equivalent intracellular levels, As(III) and As(V) compounds are equipotent. As(V) inhibits the enzymatic systems. Its toxicity is explained in terms of molecular imitation, because arsenate imitates phosphate and it is transported through the cellular membrane by carriers of phosphorus (Clarkson, 1993).

3.3. Sequential extraction procedures

3.3.1. Tessier's procedure

Although it is undoubtedly important to know the total content of As and metals in the soils, their concentrations do not give any information about the potential mobility of the elements within the soils.

The results obtained for the heavy metals by Tessier's sequential extraction procedure were widely reported in another paper (Abollino et al., 2007). For the sake of clearness, the percentages of metals in each fraction of Tessier's procedure are however shown in Table 3.

Briefly, the first solution (1 M $MgCl_2$) is a very weak extractant and it only extracts the metals weakly bound to the matrix. Only As, Fe and Mn were extracted in concentrations higher than the detection limits of the ICP-AES and GF-AAS, but among these only Mn was released in a significant percentage. The second solution is weakly acid and extracts those element that could be released after a change of the environmental conditions (e.g. acid rain). The first two Tessier's fractions give us an idea of the metals that could be readily transferred to other environmental compartments, such as water and plants; high extractability in these fractions suggests

the presence of metals with anthropogenic origin (Zhai et al., 2003). In particular the amounts of Cr, Cu, Mn, Ni and Pb present in the second fraction are higher than those found in clean soils (Abollino et al., 2007). This shows that the easily available fraction is large and confirms the effective pollution of the soil in this area caused by the A.C.N.A. plant. On the other hand, even if the total content of iron is elevated, its mobility is very low (5.6 % of the total amount in the first four fractions). The reagent used in the third fraction is a strong reductant, and causes greater percentages of release than in the previous ones for all considered metals and in particular for lead. Likewise, the percentages extracted in the fourth fraction due to the addition of oxidants are substantial for all metals. In particular a large proportion of Cu is extracted in the mixture of nitric acid and hydrogen peroxide, in agreement with the well known affinity of copper for soil organic matter (Mesquita et al., 2004). In the fifth fraction we find the amount of metals strongly bound to the structure of the soil.

In this work we concentrated our attention on the behaviour of arsenic. Arsenic is released only at very low percentages from the soil in the first four fractions (obtained by application of Tessier's procedure), even if it is a principal pollutant in this soil. It is important to underline that this element is present in soil in anionic or neutral form while the other considered elements are present in cationic form. For this reason its behaviour is very different. Tessier's procedure is suitable for the elements present as cations in the soil and so, the low leachability observed for arsenic is not significant about its real mobility. A specific extraction procedure is requested in order to assess its lability and therefore estimate the hazards associated to its release. Presently, there is no universally agreed standard method based on single or sequential extraction that allows to understand and predict its behaviour in soils and sediments. However, some

researchers developed procedures specific for arsenic, which exploit its similarities with phosphorus. In particular, we adopted Cai's procedure, as described below.

3.3.2. Cai's procedure

In Cai's procedure, the mobile and mobilizable fractions are estimated by using $NaNO_3$ and KH_2PO_4 respectively (Cai et al., 2002).

Sodium nitrate permits to extract water-soluble arsenic and the non specifically adsorbed fraction, which can be replaced by nitrate ions through anion exchange and mass action. The $NaNO_3$-extracted fraction is considered to be the most available to biota and most easily leached to groundwater.

Because arsenate and phosphate are chemically similar, KH_2PO_4 should be an effective extractant to replace arsenate specifically adsorbed on soils. A ligand exchange mechanism is believed to occur. Through this mechanism, the arsenites and arsenates that form inner-sphere As-Fe surface complexes are replaced by PO_4^{3-}.

Cai's method was designed for As and it can help us to understand and predict the extent of availability and mobilization of arsenic in response to the dynamic changes in the environment, which in turn will provide useful information for an appropriate risk management program.

The results obtained with this procedure are reported in Table 4.

The percentages of extraction of the mobile and mobilizable fraction are low (0.43 % and 2.12 % respectively), while the proportion of arsenic present in the residual fraction probably derives, at least in part, from debris containing arsenopyrite. Lumsdon et al. (2001) studied the theoretical behaviour of arsenic in soil and calculated that arsenopyrite can be gradually dissolved in well areated soils, when the redox potential

will be close to equilibrium with atmospheric O_2. We cannot assess whether this phenomenon takes place in the A.C.N.A. soil, however we can hypothesize that the extent and the rate of dissolution, if any, would be minimal since the soil was stored in the tank for more than twenty years and the percentages of mobile forms (which would include also As derived from the dissolution of arsenopyrite) are very low.

The concentrations of the other considered inorganic pollutants were also measured in the extracts. Only low percentages of Fe and Mn were found in the mobile fraction (0.013% and 0.33% respectively). The metal most extensively extracted in the mobilizable fraction was Mn, 4.94%, while Cu and Fe were extracted in a lesser extent (0.79 and 0.021% respectively). With Cai's procedure most of the metals remains in the residual fraction, because the extractants are weaker than those used in Tessier's scheme.

3.4. Soil washing

In a previous study (Abollino et al., 2007) we tested the possibility to use the reagents employed in the third fraction of Tessier's procedure (0.04 M $NH_2OH{\cdot}HCl$ in 25% CH_3COOH) as soil washing reagents, because the percentages of extraction of most of the metals were higher than those observed with the reagents used in other fractions. The use of the extractants of the fourth fraction (0.02 M HNO_3, 30% H_2O_2, 3.2 M CH_3COONH_4), that permitted to obtain high percentages of metal removal, was ruled out, because the addition of nitric acid and hydrogen peroxide caused a violent reaction, involving the organic contaminants present in the soil, with the formation of foam and possible spilling upon heating. 0.04 M $NH_2OH{\cdot}HCl$ in 25% CH_3COOH permitted to extract the considered elements with relatively low percentages (see Table 5).

In this work, we tested phosphoric acid as extractant owing to its well known high affinity for As. Some authors (Alam et al., 2007; Tokunaka and Hakuta, 2002) compared the efficiency of H_3PO_4 with that of other mineral acids like hydrogen chloride, hydrogen bromide, sulfuric acid: they found that phosphoric acid permitted to obtain much higher extraction efficiency for both As(III) and As(V). As and P belong to the same chemical group, have similar chemical properties (tetrahedral geometry, atomic radii, bonding radii, ionization potentials, electronegativities…), comparable dissociation constants for their acids and solubility products for their salts, and show similar geochemical behaviour in the soil. The effectiveness of phosphoric acid for the removal of arsenic can be attributed to its synergic function as a donor of phosphate ions. Ligand exchange has been considered by Tokunaga and Hakuta (2002) as one of the major mechanisms that removed As(V) during soil washing with H_3PO_4. Persson et al. (Persson et al., 1996) found that PO_4^{3-} was able to compete with the As(V) oxyanion for oxide surface sites because phosphate ions, like As(V) oxyanions, could be also adsorbed as an inner-sphere complex on both amorphous Al and Fe oxides. Under oxidizing conditions, As is predominantly retained by adsorption at Fe and Mn oxides surface and can be desorbed by exchange with ligands (PO_4^{3-} ions) that are held more tightly than As.

Initially, a comparison of the efficiency of extraction with 0.04 M $NH_2OH{\cdot}HCl$ in 25% CH_3COOH and with 1.6 M H_3PO_4 on the same amount (1 g) of soil was performed: the percentages of arsenic extracted were 12% and 23% respectively.

We tried to increase the percentage of As extracted by modifying some parameters used in the original procedure, i.e. varying the amounts of sample (0.1, 0.25, 0.5, 0.75, 1 g), the concentration of phosphoric acid (1, 1.6, 2, 3 M) and the contact time between the

soil and the solution (6, 8, 16, 24 h). The variation of acid concentration and of the contact time did not cause a significant increase in the percentage of extraction of the element, whereas the change of the soil weight permitted to obtain better results. This improvement is not due to the increase of the molar ratio between arsenic and phosphoric acid, but to a more efficient contact between the soil particles and the solution. Therefore we decided to use 0.5 g of soil instead of 1 g, while maintaining the original H_3PO_4 concentration (1.6 M) and contact time (6 h). With these conditions the percentage of As extracted from the investigated soil was about 48%, as reported in Table 5, instead of 23% extracted using the conditions described in the original procedure.

Other authors obtained percentages of extraction greater than 97 % with phosphoric acid in different arsenic contaminated soils (Alam et al., 2007; Tokunaga and Hakuta, 2002). The lower release observed in our work is probably caused by the fact that As is present in very unreactive form, as demonstrated by the results of Cai's fractionation scheme (section 3.3.2).

Generally, the extraction efficiency of an element depends on the form in which it is present in the soil and on its binding behaviour with the soil phases. The amount of arsenic that remains in the soil after the release with phosphoric acid can be assumed not to be involved in environmental processes.

The efficiency of the optimised extraction procedure was evaluated also for Cr, Cu, Fe, Mn, Ni, Pb and Zn. As Table 5 shows, all metals were extracted with percentages greater than those obtained with $NH_2OH{\cdot}HCl$ in CH_3COOH. The use of acids for the removal of metals from soils is well known; the solubilization of metals occurs as a consequence of the protonation of the surface groups of soil, to which metals are

electrostatically adsorbed, and to the dissociation of their complexes with humic acids and other organic substances. Recently Maturi and Reddy (2008) investigated phosphoric acid and six organic acids to determine the feasibility of using these acids for the removal of phenanthrene and heavy metals from different soils. They found that phosphoric acid was effective for the removal of metals from all the soils in single step extraction.

As pointed out for As, the proportions of metals left in the soil after extraction with H_3PO_4 are presumably strongly bound to the soil matrix or are present as mineral phases and therefore are expected not to be harmful for the environment and human health.

Tokunaga and Hakuta (2002) observed that the acid-washed soils showed strong acidity due to residual acid adhering to the soil surface, and proposed a chemical stabilization of the soil by neutralization with sodium hydroxide or by the addition of chlorides, hydroxides, or oxides of lanthanum, cerium, iron(III), or calcium. Moreover, lanthanum, cerium (III) and iron (III) chlorides successfully immobilized residual arsenic in the soil.

Even if the extent of the release of As and metals from A.C.N.A. soil was relatively low, ranging from 30 to 65 %, the extracts contain high concentrations of pollutants and their disposal is troublesome, unless a decontamination is performed.

3.5. Treatment of soil washing effluents

We tested the suitability of a natural clay, namely montmorillonite, as a sorbent for arsenic and metals extracted with phosphoric acid.

The sorption efficiency of montmorillonite was studied using a flow system. This system appears as the most appropriate because it allows to perform the global

purification process by a single step while batch methods need several stages (shaking, settling and/or filtration), requiring, therefore, more time and space (Abollino et al., 2003; Abollino et al., 2007).

The total capacity of montmorillonite towards As, determined with the continuous column method, was found to be 3.39 mg/g_{clay} for As(III) and 0.15 mg/g_{clay} for As(V). These values are very high if compared to those obtained by the same procedure using vermiculite (0.033 mg/g_{clay} for As(III) and 0.012 mg/g_{clay} for As(V)). The total capacity of montmorillonite toward heavy metals (Cr, Cu, Mn, Ni, Pb and Zn) had been studied previously (Abollino et al., 2003).

Montmorillonite and vermiculite have a high cation exchange capacity and this explains their high tendency to adsorb the cations present in solution. These clays can adsorb also anionic and neutral species. Dissolved anionic species of heavy metals and metalloids are attracted to positively charged sites by coulombic forces but are subsequently fixed to these sites by partly covalent coordinate bonds and the sharing of oxygenic ligands with structural cations of the mineral. Anion exchange sites are points of temporary positive charge formed on the mineral surfaces by reversible pH-controlled association of H^+ ions with amphoteric OH groups and O atoms, or by displacement of OH^- groups, on the mineral surfaces (Evangelou, 1998). In the specific sorption of metal and metalloid anions, ligand exchange reactions probably occur, and oxygenic ligands (OH groups and O atoms) act as bridges linking structural cations of oxides and edges of clay crystals to the metal or metalloid of the anion, forming a binary coordination complex at the mineral surface, which can be regarded, in effect, as an extension of the mineral. Uncharged species, like H_3AsO_4, may be sorbed to uncharged sites of mineral colloids by H-bonding and by Van der Waals bonds and

other dipole interactions (Parker and Rae, 1998). The greater capacity towards As at pH 5 found for montmorillonite than for vermiculite reflects the greater number of positively charged sites on the former compared with those on the latter. In fact, in vermiculite the substitutions of coordination cations take place in tetrahedral sheet, so there are many negative charges on the interlayer spacing that contrast the diffusion of the anionic species. In montmorillonite some substitutions take place in more internal octahedral sheets, so the negative charges are more effectively screened by the tetrahedral sheets and they do not influence the charges on the interlayer spacing and the diffusion of the anionic species. For this reason montmorillonite has a greater tendency to form positively charged sites suitable to adsorb $H_2AsO_4^-$ (predominating in the pH range 2-6) and $HAsO_4^{2-}$(predominating in the pH range 6-11), while vermiculite, having a greater number of negative charges, has a lower affinity for anionic species. Therefore the use of montmorillonite for the clean-up of the soil washing effluents was investigated. The pH value of the extract obtained by the treatment with phosphoric acid was about 1.5. The extract was driven through the column packed with montmorillonite conditioned at pH 5. We performed the conditioning at this pH because it allowed us to obtain high uptake of As during the breakthrough study. The percentage of As adsorbed by montmorillonite was 9.42%. This percentage was very low if compared with the results obtained in breakthrough studies, probably because the metal solutions used in the latter were at pH 5.0. At this pH arsenic is present in solution predominantly in anionic form, for example As(V) is present as H_3AsO_4 (2%) and as $H_2AsO_4^-$ (98%). In these conditions the anionic form of arsenic is easily adsorbed on the positive surface sites of the clay. At the pH of the soil extract As(V) is present as H_3AsO_4 (86%) and as $H_2AsO_4^-$ (14%), that is the neutral form is predominant and it is more difficulty

adsorbed on the clay. Moreover the phosphate ions present in the solution may compete with arsenic for the adsorption sites of the clay.

To evaluate the effect of the solution pH on the uptake of As on the clay, the soil extract was brought to pH 5.0 ± 0.2 by addition of 6 M NaOH and the solution was driven through the column packed with montmorillonite conditioned to pH 5**.** In these conditions the percentage of As adsorbed on the clay was 95.5%, confirming the good results obtained with montmorillonite in the breakthrough experiments. Therefore phosphate does not interfere with the adsorption of arsenic.

The efficiency of the system was evaluated also for Cr, Cu, Fe, Mn, Ni, Pb and Zn and the results obtained are shown in Table 6. It is evident that the uptake capacity of the system towards the investigated pollutants was good. The high percentages of adsorption obtained for the metals present as cations in solution confirm the observations on the efficiency of montmorillonite as sorbent reported in a previous work (Abollino et al., 2003). Therefore, sorption onto this clay can be a good method for the decontamination of soil washing extracts. Montmorillonite has the advantage of being a natural, inexpensive material, if compared to synthetic sorbents.

In our previous studies on vermiculite we verified that the adsorbed contaminants can be eluted from the clay and the same aliquot of sorbent can be reused for further decontamination steps (Abollino et al., 2007); we can hypothesize that also montmorillonite will show a similar behaviour.

After retention of the contaminants, the clay can be directly disposed of in a landfill suitable for hazardous wastes. The advantages over the disposal of the contaminated soil are that the pollutants are concentrated in a much smaller volume of solid, due to the good retention capacity of the clay, and that they are strongly bound to it, so that they

would be mobilized into other environmental compartments only after a drastic treatment, e.g. with an acid.

In alternative, the sorbed elements can be eluted into a small volume of a proper stripping agent (e.g. an acid or, in the case of metal ions, a ligand) and the clay can be reused for the treatment of further aliquots of soil washing fluids. Arsenic present in the final eluate, as well as metals such as lead, copper and zinc, can be recovered by controlled potential electrolysis, or the eluate can be disposed of as hazardous waste. The advantage of the whole procedure is that the pollutants will be concentrated in a small volume of liquid, instead of being dispersed in a larger volume of soil washing effluent.

4. Conclusions

Based on the present investigation, it can be concluded that:

1) The A.C.N.A. soil contains high concentrations of arsenic and of the considered metals (Cr, Cu, Fe, Mn, Ni, Pb and Zn), as a consequence of the former industrial activities in the site.

2) The results of the speciation scheme showed that As(V) slightly prevails over As(III) whereas more than 40 % of total arsenic is in organic form, probably because the soil is heavily polluted by organic substances.

3) With Tessier's fractionation scheme, Cr, Cu, Ni, Mn and Zn are extracted at significant percentages into the first two fractions, so they have a high availability and can be transferred to other environmental compartments. Using this procedure, As was extracted at very low extent, but this result is not significant about its real availability,

because Tessier's procedure is suitable for the elements present in the soil as cations.

4) Using Cai's extraction procedure, which was designed for arsenic, the percentages found in the mobile and mobilizable fractions are low The residual fraction of arsenic is probably composed, at least in part, of arsenopyirite.

5) Phosphoric acid permitted to extract nearly half of the arsenic and variable percentages (from 30 to 65 %) of the metals present in the investigated soil. The fraction of elements remaining in the soil is composed of unreactive forms, (i.e. strongly bound to the soil matrix or present as mineral phases) which can be expected not to be involved in environmental processes.

We presume that a higher extraction efficiency would be obtained with phosphoric acid from a soil containing higher proportions of available arsenic or metals.

6) The retention of the pollutants onto an inexpensive, natural sorbent like montmorillonite was nearly quantitative; this treatments permits to decontaminate the effluents deriving from soil washing with phosporic acid and to immobilize arsenic and metals in view of their subsequent safe disposal or recovery.

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Table 1

Total As and metal concentrations in the considered soil, typical ranges and common values present in unpolluted soils and the average abundance in the earth's crust (mg/kg)

Element	Concentration	Range	Common values	Earth's crust
As	**292**	**0.1-50**	**1-20**	**40**
Cr	306	5-1500	70-100	200
Cu	657	2-250	20-30	70
Fe	234000	7000-42000	-	50000
Mn	1 480	20-10000	1000	1000
Ni	351	2-1000	50	80
Pb	750	2-300	10-100	16
Zn	159	10-300	50	132

Table 2
The concentrations (mg/kg) and the percentages of As(III), As(V) and organic As forms in the considered soil determined by the speciation procedure

As species	**Concentration**	**Percentage**
As(III)	76.2	26.1
As(V)	94.3	32.3
As_{org}	121	41.5

Table 3
The percentages of As and metals extracted in the fractions of Tessier's scheme

Element	% of extraction				
	Fraction 1	**Fraction 2**	**Fraction 3**	**Fraction 4**	**Fraction 5**
As	0.06	0.06	0.33	1.01	74.5
Cr	≤0.03	0.93	27.4	13.0	55.0
Cu	≤0.01	5.34	5.35	75.5	13.2
Fe	0.02	0.02	4.64	0.90	81.6
Mn	1.14	10.1	19.8	5.58	61.8
Ni	≤0.04	1.86	12.0	5.29	76.7
Pb	≤0.05	2.87	42.7	22.2	22.1
Zn	≤0.01	≤0.02	≤0.04	13.3	68.1

Table 4
The percentages of As and metals in the fractions of Cai's procedure

Element	Mobile fraction	Mobilizable fraction	Residual fraction
As	0.43	2.12	70.5
Cr	≤0.06	≤0.06	85.7
Cu	≤0.02	0.79	78.9
Fe	0.01	0.02	82.4
Mn	0.33	4.94	87.5
Ni	≤0.08	≤0.08	113
Pb	≤0.10	≤0.10	98.8
Zn	≤0.02	≤0.02-	60.2

Table 5
The percentages of As and metals extracted with $NH_2OH{\cdot}HCl$ in CH_3COOH and H_3PO_4

Element	**% extracted with $NH_2OH{\cdot}HCl$**	**% extracted with H_3PO_4**
As	12.2	47.9
Cr	27.7	41.9
Cu	4.26	30.2
Fe	3.45	48.5
Mn	41.8	56.2
Ni	13.4	43.3
Pb	34.1	64.8
Zn	27.2	63.7

Table 6
The percentages of As and metals adsorbed by montmorillonite at the natural pH of the soil extract (pH = 1.5) and at pH = 5.0

Element	**% of adsorption $pH_{extract}$ = 1.5**	**% of adsorption $pH_{extract}$ = 5**
As	9.4	95
Cr	76	100
Cu	27	100
Fe	n.d.	100
Mn	n.d.	93
Ni	69	75
Pb	70	100
Zn	81	100

n.d.= not determined