Influence of redox potential (Eh) on the availability of arsenic species in soils and soils amended with biosolid

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ABSTRACT

A study was done on the influence of redox potential on the mobility and availability of the various arsenic chemical forms in a Mollisol soil from central Chile amended with biosolid. Arsenic availability was strongly dependent on the applied redox potential. As expected, under reducing conditions (-200 mV vs Hg/Hg_2Cl_2) arsenic availability increased significantly, and arsenic was found mainly as arsenite. On the contrary under oxidizing conditions (200 mV vs Hg/Hg_2Cl_2) arsenic solubility decreased markedly and was governed by the presence of arsenate. The greatest concentration of organic arsenic species was found under reducing conditions, which would indicate that methylated species may participate in the transformation of arsenate to arsenite. In biosolid-amended soils the concentrations of methylated species increased as a function of time under reducing conditions, which can be attributed to the greater microbial activity resulting from the organic matter supply from the biosolid to soil. In all the systems, a high concentration of As(V) was found under reducing conditions, indicating that the chemical kinetics for the conversion of arsenate to arsenite is slow. Along time, the content of As(V) increased in the control soils, which may be attributed to the possible dissolution of iron oxides and hydroxides under reducing conditions.

1. Introduction

Application of biosolids to soils can be a beneficial agricultural practice because they contain many essential plant nutrients and organic matter which improve the soil properties (Tsadilas et al., 1995). On the other hand, such practice might alter metal and metalloid concentration and their mobility in soils, posing serious risks of environmental contamination (Epstein, 2003).

Arsenic is a toxic element widely distributed in the earth́s crust. It occurs in nature mainly as sulfides in a great variety of minerals (Seiler et al., 1994; Francesconi and Kuehnelt, 2002). On the other hand, arsenic is a potential contaminant present in biosolids, which may limit their use to amend soils.

Soils in the northern as well as in the central zone of Chile exhibit high contents of arsenic, which is mainly associated with copper deposits. An important arsenic source in central Chile has been the copper mining processes (Narváez et al, 2007; Ascar et al., 2008).

Arsenic fate, behavior, bioavailability and toxicity vary markedly, depending on the chemical form in which this element is present. The inorganic species arsenite (As(III)) and arsenate (As(V)) are highly toxic, while the organic species monomethylarsonic acid (MMAA) and dimethylarsenic acid (DMAA) are less toxic (Kaltreider et al., 2001). However, organometallic species prevailing in sea environments (arsenocoline, arsenobetaine, arsenosugars) are essentially non-toxic (Burguera and Burguera, 1997). Compared with the other species, As(III) exhibits the highest mobility in soils, because it is present as the neutral species (H_3AsO_3). In this context, determination of total As concentration in an environmental matrix would not be a good indicator of mobility and toxicity. Consequently, determination of the different chemical species of this element is mandatory.

On the other hand, arsenic is subjected to changes among its different chemical forms as a result of variations or alterations in soil redox conditions. Thus, in a soil under aerobic conditions (100–200 mV vs Hg/Hg_2Cl_2) the predominantly stable species is As(V), which may occur as a different oxianions depending on the system pH. The pH of soils is usually from 5 to 9, thus As(V) may be found as $H_2AsO_4^-$ or as $HAsO_4^{2-}$, while the species H_3AsO_4 and AsO_4^{3-}, should not be found in the absence of very extreme pH conditions. In addition, when soil is subjected to flooding, it may reach reduced conditions, with potentials below 100 mV. In this case the predominant species should be H_3AsO_3.

Methylation is a process that theoretically does not occur in abiotic conditions even if there is a supplement of C, proteins, and other organic compounds because the C–C, C–N, and C–O bonds are more stable than the C–As bonds (Gao and Burau, 1997), therefore methylated arsenic compounds must be the result of microbial activity associated to energy transfer processes which

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would depend on the tolerance range of existing microorganisms in relation to pH and redox conditions of the different systems (Carbonell-Barrachina et al., 2000) and which might be altered as a result of amendment high in organic materials, such as the case of a biosolid.

The purpose of this study was to assess how biosolid incorporation to soils may alter both arsenic mobility and availability and how these may be altered by changes in soil redox conditions.

2. Materials and methods

2.1. Reagents

All the solutions were prepared with Milli-Q water (Millipore Corporation, USA) with $18 \, M\Omega \, cm$ conductivity. The reagents employed in soil and biosolid digestion (HNO_3, H_2O_2 and HF) were Merck Suprapur® quality.

2.2. Soil and biosolid samples

The soil sample (Mollisol order) was collected in the Chilean central zone, from a site located in Graneros (GR) in the Cachapoal valley (VI Region), which is affected by air pollution (particulate matter deposition) and water pollution (irrigation) because of its vicinity with mining copper processes.

In the selected agricultural area, soil sample was collected from the surface horizon (0–10 cm depth) by drilling and taking samples from each corner of a 100 m^2 square surface.

A sample of anaerobically stabilized sludge (or biosolid) was obtained from a monofill at a wastewater treatment plant in the metropolitan region. The soil and biosolid samples were dried at room temperature, homogenized, sieved (2 mm) and stored in plastic containers at room temperature.

2.3. Soils spiked with arsenic

In order to achieve soil samples higher in arsenic and with similar physical chemical characteristics, a solution of 120 mg L^{-1} As(V), prepared from $Na_2HAsO_4 \cdot 7H_2O$, was incorporated to GR soil to reach a concentration of 240 mg kg^{-1}. This concentration is four times higher than the soil background content, and was selected for the soil in relation to the adsorption isotherm, avoiding to ever reach saturation (Fig. 1). The resulting soil was referred to as GR + As. The As(V) solution was added to the soil in plastic containers, in a 1:2 (w/v) ratio. The mixture was stirred for 24 h and centrifuged for 30 min at 3000 rpm. Then the supernatant was removed, and the spiked soil was aged in the container for two months.
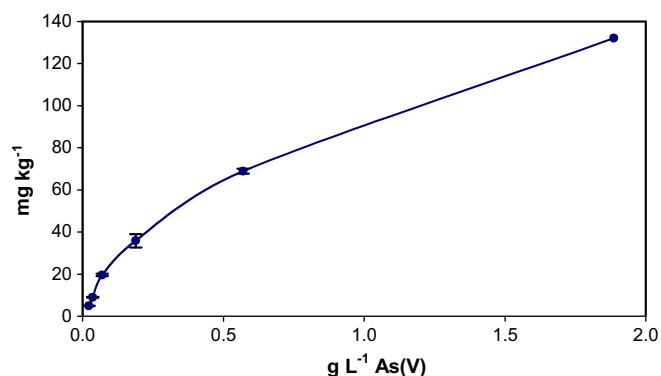

Fig. 1. As(V) adsorption isotherm for the GR soil. Error bars represents standard deviations ($n = 3$).

2.4. Biosolid incorporation

The two soil samples (control and As-spiked) were treated with the biosolid at a rate of 100 Mg ha^{-1} (corresponding to 45 g kg^{-1}), and then incubated for 45 days under controlled conditions of field capacity at a temperature of 25 °C.

After treatment, all the substrates were air dried, ground, homogenized, and stored in polyethylene containers. The resulting soils were referred to as GR + B and GR + As + B.

2.5. Characterization of soil and biosolid samples

The soils and biosolid were characterized by determination of pH, organic matter and available phosphorus. An estimate of the total arsenic content in soils was determined after digesting 200 mg soil samples with 6 mL HNO_3 and 4 mL of H_2O_2 (Krachler and Emons, 2000; Wenzel et al, 2001) in a Milestone/mls 1200 mega microwave oven. Arsenic was determined by HG-AAS, utilizing a Perkin Elmer 1100B spectrophotometer coupled to an FIAS-400 flow injection system with hydride generation. Other features of these samples have been reported previously (Ascar et al, 2008).

2.6. Redox systems

The soils were adjusted (room temperature) to three redox potentials (−200, 0, and 200 mV) within and acrylic chamber according to the systems reported by Gambell et al. (1980). In this system, the potential (Eh) was taken to reducing conditions (−200 mV) by bubbling N_2. In order to reach higher redox potentials (0 and 200 mV) air was automatically bubbled by use of a Rena 101 air pump connected to a handmade potential controller, connected in turn to a potentiometer (WTW pH 537) fitted with a platinum electrode and a calomel reference electrode. Determination of pH was done with a combined electrode. The pH meter was calibrated with WTW standard buffer of 4.0 and 7.0, at room temperature.

Soil suspensions were prepared with 200 g of soil in 1000 mL deionized water. The system was closed tightly, with constant stirring, and N_2 was bubbled to reach the lowest potential (−200 mV) for three weeks. Then, the potential was taken to 0 mV for another three weeks, and finally it was taken to oxidizing conditions (200 mV) for the same period of time. The initial pH of each system was kept constant (pH 6.7 ± 0.3) with daily adjustment by adding 1 mol L^{-1} HCl. HCl addition does no affect arsenic speciation since the sorption–desorption processes and redox reactions are not affected by variations in Cl^- concentration (Bhumbla and Keefer, 1994). Suspension aliquots were weekly taken with a syringe in order to assess the influence of both the redox potential and time on arsenic species. The samples were transferred to capped centrifuge tubes after air displacement by N_2. They were centrifuged for 30 min at 2500 rpm, and the supernatant was filtered through cellulose acetate membrane filters. Finally, determination of the arsenic species was immediately carried out to prevent possible transformations or degradations.

2.7. Arsenic speciation

Inorganic (arsenite and arsenate) and organic (MMAA and DMAA) species were determined, using hydride generation atomic absorption spectrophotometry. This method was based on the methodology described by Gao and Burau (1997) and Shraim et al. (1999, 2000) modified in order to improve speciation reproducibility. Selected experimental conditions have been described elsewhere (Ascar et al. 2008). Statistical analysis of the results was performed by applying tukeýs HSD Test.

3. Results and discussion

3.1. Characterization of soil and biosolid

Table 1 shows some characteristics of the biosolid, soils, and biosolid-amended soils. All of the systems showed a neutral pH. The highest values for OM content and available P corresponded to the biosolid, and its application to soil caused a significant increase in these parameters.

Total contents of arsenic found in the systems under study are also shown in Table 1. The content of arsenic was below the recommended values for biosolid application to soils, according to Chilean regulation (CONAMA, 2001).

3.2. Influence of redox potential

The substrate pH values were kept from 6.4 to 6.9 since these values corresponded to soil pH at the moment of carrying out the soil–water mixture. According to a redox condition of 200 mV and a pH of 6.7 applied in this study, As(V) suppose to be in the form $H_2AsO_4^-$ or $HAsO_4^{2-}$, adsorbed on the positive surface of Fe and Al oxides, whereas under reducing conditions (-200 mV), arsenic should be in the neutral form H_3AsO_3, which may be easily desorbed (Burriel et al., 2000).

Figs. 2 and 3 show the results found on application of the different redox potentials to the systems, including GR soil, GR soil enriched with As (GR + As), and both systems conditioned with biosolid at a rate of 100 Mg ha^{-1} (GR + B and GR + As + B), the greatest arsenic concentration being found in reducing conditions, and decreasing with increasing redox potential. In GR soil under reducing conditions, arsenic was predominantly in the arsenite form, with values from 54% to 63% in relation to total soluble arsenic, while the content of organic arsenic was near 5.5%. On the other hand, total soluble arsenic increased as a function of time (week 1 to week 3). As the potential was increased (0 mV), the concentration of dissolved arsenic in all its forms decreased markedly and was governed by the presence of As(V), this being the only species present under more oxidizing conditions (200 mV).

Biosolid incorporation to GR soil caused, under reducing conditions, a sharp decrease in inorganic arsenic and total soluble arsenic. Arsenic shows great affinity to sulfides in forming insoluble compounds such as realgar AsS and orpiment As$_2$S. Thus, when amending with a biosolid rich in S, an important part of the reduced arsenic may react with it, forming the above mentioned insoluble sulfides (Carbonell-Barrachina et al., 1999, 2000), which could account for the decrease in the arsenic species in the GR soil treated with biosolid. When the potential was increased (0 mV and 200 mV) the total content of soluble arsenic decreased considerably in both GR soil and Gr + B systems.

In the arsenic-enriched soils (GR + As and GR + As + B), a marked increase was found in the amount of dissolved arsenic in its different chemical species. This can be due to the fact that the arsenic spiked on this soil would be more labile and could be released more easily by the incorporation of biosolid. On the other hand, under all redox conditions, biosolid incorporation to GR + AS
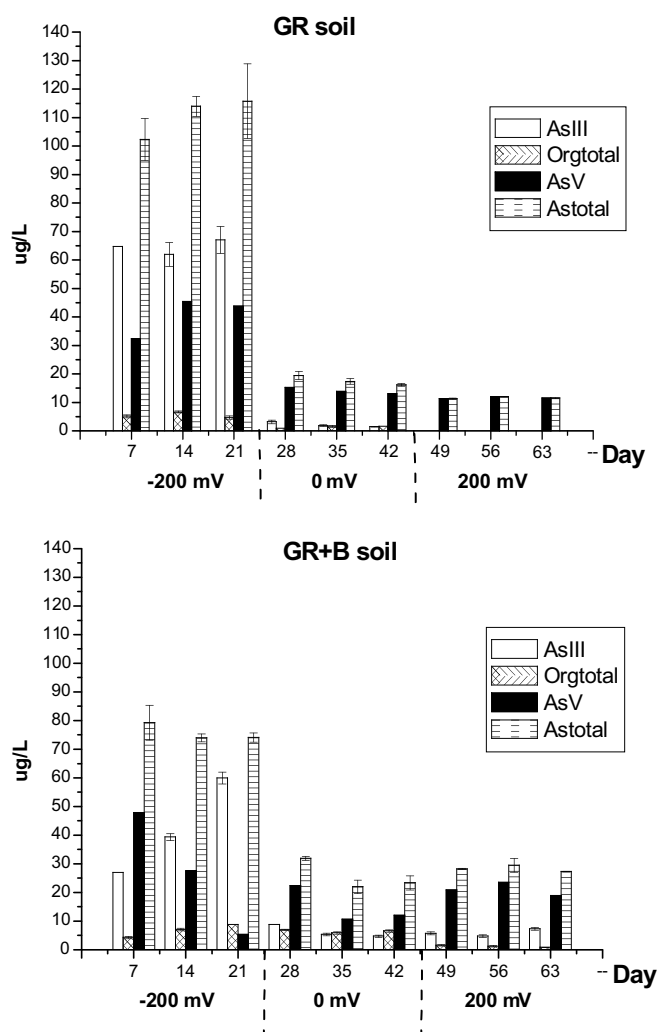

Fig. 2. Chemical speciation of arsenic in GR and GR + B soils at different redox potentials. Error bars represent standard deviations ($n = 3$).

soil caused a sharp increase in all soluble arsenic species, which can be attributed to the increase in the non-specifically adsorbed arsenic (more labile) fraction, as was previously observed (Ascar et al., 2008).

Under reducing conditions (-200 mV), a considerable amount of As(V) was found in all of the soil samples under study, indicating that chemical kinetic plays a major role in the conversion of arsenate to arsenite. Under these conditions, in the GR and GR + As soils, the content of As(V) increased along time, which would suggest that dissolution of iron oxides was faster than precipitation of arsenious sulfide and that there is no adequate microbial activity in the soils without biosolid that facilitate As(V) reduction to As(III). On the other hand, in the system containing biosolid, As(V) decreased along time, suggesting that microbial activity

Table 1
General characteristics of soil and biosolid samples

		GR	GR + B	GR + As	GR + As + B	Biosolid
pH		6.6	6.8	6.7	6.8	6.7
Organic Matter	% (SD)	3.2 (0.10)	4.2 (0.03)	3.0 (0.22)	4.3 (0.13)	41.7 (1.98)
Available P	mg kg^{-1} (SD)	18.7 (0.004)	84.4 (0.005)	30.9 (0.001)	99.9 (0.002)	591 (0.002)
As total	mg kg^{-1} (SD)	59.1 (0.10)	60.8 (7.14)	280 (0.38)	260 (3.34)	16.9 (0.90)

Mean ($n = 3$).
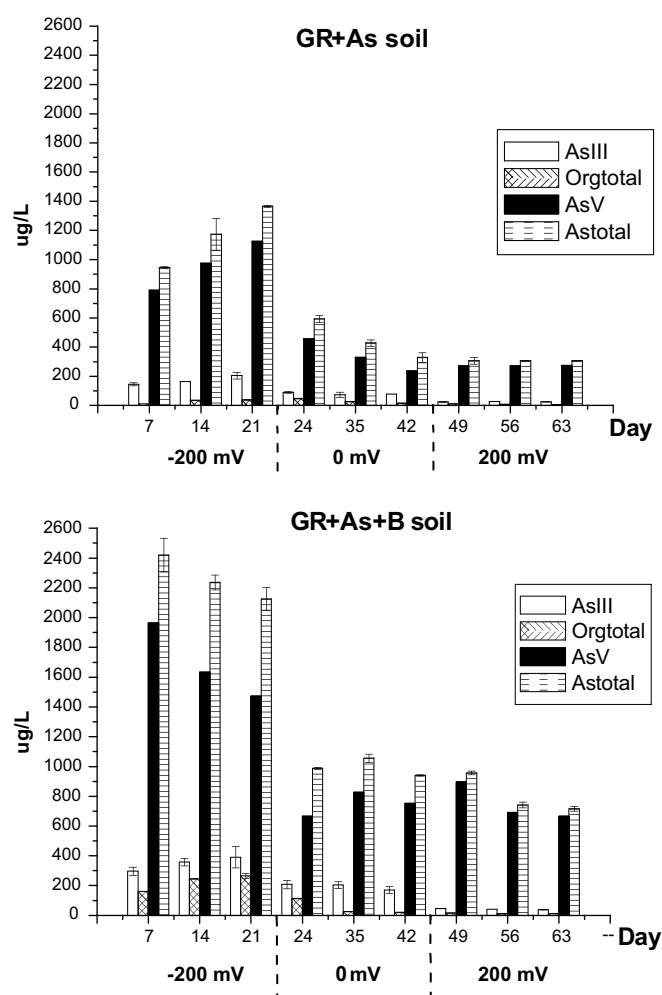SD: Standard deviation.

Fig. 3. Chemical speciation of arsenic in GR + As and GR + As + B soils at different redox potentials. Error bars represent standard deviations ($n = 3$).

was higher, possibly on account of an increase in the content of organic matter in these systems. This would indicate that As(V) would serve as an effective electron acceptor for soil microorganisms, being reduced by them to As(III) (Ahmann et al., 1994).

The highest concentrations of soluble organic arsenic were found in reducing conditions, indicating the methylation would be a path of transformation from arsenate to arsenite. Such concentrations increased from the first to the third week in biosolid-enriched soils, which may be accounted for by a greater microbial activity present in these systems. On the other hand, as the redox potential was increased, the concentration of methylated species decreased, in some cases reaching concentrations below the method detection limit.

Under oxidizing conditions (200 mV), arsenic solubility decreased markedly and was governed by the presence of As(V), with percentages ranging from 70% to 100% in relation to total soluble arsenic. This decrease would be attributed to the precipitation or adsorption of As(V) by some soil components, such as iron oxides, that have become oxidized again. Masscheleyn et al. (1991) attributed this affect to a possible co-precipitation and/or formation of iron oxides and hydroxides in sediments.

In all of the systems under study it was found that As mobilization was highly dependent on the applied redox potential, a greater concentration of arsenic in solution being found under reducing conditions (−200 mV) with significant decrease under oxidizing

conditions. These results agree with those reported by Carbonell-Barrachina et al. (2000) in water suspensions of biosolid. They found that arsenic solubility was highly dependent on the pH and redox potential of the system, and it was generally high under reducing conditions and decreased significantly as the potential was increased.

4. Conclusions

It was confirmed that in these soil-biosolid systems under study, arsenic mobility was highly dependent on the applied redox potential. Under reducing conditions (−200 mV) arsenic increased its mobility significantly, reaching the highest solubility values, and being mainly found as arsenite, while under oxidizing conditions arsenic solubility decreased and was governed by the presence of arsenate.

The greatest concentration of organic arsenic species was found under reducing conditions, suggesting that methylated species may participate in the conversion of arsenate to arsenite. In biosolid-amended soils, the concentration of such species increased as a function of time, which is attributed to the greater microbial activity, product of the increase in the organic matter content in these soils.

In all soils, As(V) concentration was high in reducing conditions, indicating that the chemical kinetic could be really important in the arsenate to arsenite conversion. In soils without biosolids incorporation, As(V) increased along time which is attributed to the possible dissolution of iron oxides and hydroxides.

Considering these results and the greater mobility associated to arsenite, it is crucial to take precautions to prevent flooding agricultural soils amended with biosolid and exhibiting high contents of this metalloid.

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