Effect of biosolid incorporation on arsenic distribution in Mollisol soils in central Chile

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Abstract

The effect of biosolid incorporation on arsenic distribution in Mollisol soils in central Chile was studied. Two soils were sequentially extracted for arsenic with a five-step method that accounts for the following arsenic forms: non-specifically adsorbed (F1), specifically adsorbed (F2), amorphous and poorly crystallized Fe and Al oxides (F3), well-crystallized Fe and Al oxides (F4) and residual (F5). The arsenic residual fraction was predominant in Pintué soil, whereas in Graneros soil, arsenic was mostly associated to amorphous Fe and Al oxides.

Graneros soil exhibited a higher As(V) adsorbing capacity than Pintué soil, which relates to the higher clay and iron and aluminum oxides contents, confirming that these components participation is essential for the adsorption of this metalloid.

Biosolid application at a rate of 100 Mg ha^{-1} caused an increase in arsenic bound to amorphous Fe and Al oxides and in the residual fraction, in Pintué soil. When Pintué soil was spiked with arsenic, aged for two months, and treated with biosolid (100 Mg ha^{-1}), the content of arsenic in the most labile fractions decreased, thus showing a favorable effect in its application to soils with few specific sites for arsenic adsorption.

Arsenic speciation was carried out in the first two fractions of the sequential extraction procedure. As(V) was the main form in both fractions. Biosolid incorporation at a rate of 100 Mg ha^{-1} caused a significant increase in organic arsenic forms.

Keywords: Arsenic; Soil; Biosolid; Fractionation

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1. Introduction

Biosolid application in soils has undergone a strong development in the last years on account of its high nutrient (N and P) and organic matter content, which may improve both the chemical and physical properties of soil (Tsadilas et al., 1995). On the other hand, such incorporation might alter metal and metalloid concentration, and mobility in soils, the latter with serious environmental contamination risks.

Arsenic is a potentially toxic element, which is widely distributed in the Earth's crust. Arsenic is found in nature mainly as sulfides, in a great variety of minerals. It is contained copper, lead, iron, nickel, cobalt, and other minerals (Seiler et al., 1994; Francesconi and Kuehnelt, 2002).

Soils both in the northern and the central zone of Chile, exhibit high contents of arsenic, which is mainly associated to copper deposits. An important arsenic source in central Chile is the Caletones smelter and other mining processes carried out in the VI Region, about 150 km from Santiago (Capital City).

Since arsenic exists mainly in anionic form in soils, and also because of its similitude to phosphorus, sequential extraction from soils and sediments has been carried out with the same chemical extractant method developed for phosphorus (Gruebel et al., 1988; McLaren et al., 1998). Wenzel et al. (2001) developed a specific sequential extraction procedure for arsenic in soils. This method takes into

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account the following arsenic fractions: (1) non-specifically adsorbed; (2) specifically adsorbed; (3) amorphous and poorly-crystalline Fe and Al oxides; (4) well-crystallized Fe and Al oxides; and (5) residuals. The findings reported that arsenic was mostly associated to amorphous Fe and Al oxides and crystalline fraction in synthetic Fe and Al oxides, as well as in Austrian arsenic-contaminated soils. Other authors found similar results in Austrian and USA arsenic-contaminated soils (Lombi et al., 2000; Rodriguez et al., 2003).

Arsenic fate, behavior, bioavailability and toxicity vary markedly, depending on the chemical form in which this element is present. The inorganic arsenite (As(III)) and arsenate (As(V)) species are highly toxic, while the organic monomethylarsonic acid (MMAA) and dimethylarsenic acid (DMAA) species are less toxic (Kaltreider et al., 2001). On the other hand, As(III) exhibits the highest mobility in soils, compared to the other species, because it is present as the neutral species (H_3AsO_3). In this context, the determination of total arsenic 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.

The purpose of this study was to evaluate the effect of biosolid application in soils with different contents of this metalloid and to determine the content of inorganic [As(V) and As(III)] and organic (MMAA and DMMA) arsenic species in the first two steps of Wenzel fractionation, corresponding to non-specifically adsorbed arsenic (F1) and specifically adsorbed arsenic (F2). Speciation, from the third to fifth Wenzel arsenic fractions was not considered because the redox character of the extraction media modifies species concentration.

2. Materials and methods

2.1. Reagents

All the solutions were prepared with Milli-Q water (Millipore Corporation, USA) with an 18 MΩ cm conductivity. The standard for arsenic was obtained from Titrisol®, Merck standard solution. The reagents employed in soil and biosolid digestion (HNO_3 and H_2O_2) were Merck Suprapur® quality. Analytical grade Merck reagents were used for sequential extraction.

2.2. Soils and biosolid samples

Two agricultural soils were selected from Chilean central zone (Fig. 1), both of them belong to the Mollisol order. One of them, Pintué soil (PT) is located in the Metropolitan Region, far from mining zones. The other, Graneros soil (GR) is located in the Cachapoal valley (VI Region), which is affected by air pollution (particulate matter deposition) and water pollution (irrigation) because of its vicinity to mining copper processes.

In the selected agricultural areas, soil samples were collected from the surface horizon (0–10 cm depth) by drilling, and taking samples in each corner of a 100 m^2 square surface. The samples were air dried on plastic surfaces, ground, sieved through a plastic 2 mm sieve, mixed, homogenized and stored in plastic containers for further use.

A sample of anaerobically stabilized sludge (or biosolid) was obtained from a monofill at a wastewater treatment plant of the Metropolitan Region. The biosolid sample was dried at room temperature, homogenized, sieved

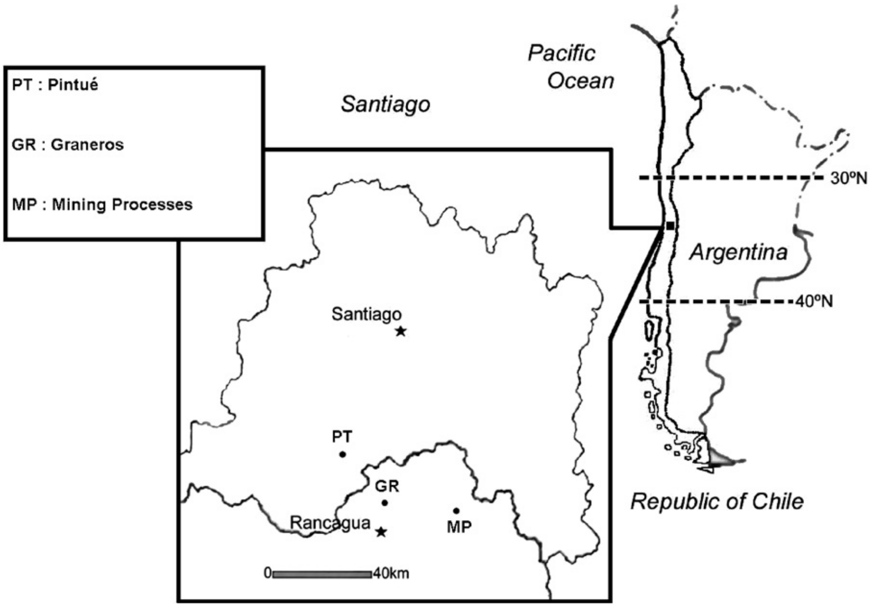

Fig. 1. Map of the sampling zone.

(2 mm) and stored in plastic containers at room temperature.

2.3. Soils spiked with arsenic

In order to achieve higher As content soil samples with similar physico-chemical characteristics, solutions of 40 and 120 mg l^{-1} As (V) were respectively incorporated to PT and GR soils to reach concentrations of 80 and 240 mg kg^{-1}, respectively. These concentrations are four times higher than their background content, and were selected from each soil respective adsorption isotherm, avoiding saturation. The resulting soils were referred to as PT + 40As and GR + 120As. The respective As(V) solutions were added to the soils in plastic containers, in a 1:2 (w/v) ratio. The mixtures were stirred for 24 h and centrifuged for 30 min at 3000 rpm. Then the supernatant was removed, and the spiked soils were aged in the containers for two months.

2.4. Biosolid incorporation

The four soils samples (controls and arsenic-spiked) were treated with the biosolid at three rates (0, 15 and 100 Mg ha^{-1}), and then incubated for 45 days under controlled conditions of field capacity at a temperature of 25 °C.

After each treatment, all the substrates were air dried, ground, sieved through a 2 mm plastic sieve, and stored in polyethylene containers.

2.5. Characterization of soils and biosolid samples

Determination of pH was done in the supernatant of a soil–water suspension, at a 1:2.5 (w/v) ratio (Mc Lean, 1982). Organic matter content was determined by the Metson method using spectrophotometry at 600 nm (Blakemore et al., 1987). Cation exchange capacity (CEC) was determined by the sodium acetate method (pH 8.2) (Rhoades, 1982). Iron crystalline oxides were extracted with citrate-bicarbonate buffer and dithionite (Mehra and Jackson, 1960), and the corresponding amorphous oxides were extracted with ammonium oxalate (pH 3) (Olson and Roscoe, 1982). The available phosphorus was extracted by the Olsen method (Olsen and Sommers, 1982) followed by spectrophotometry at 880 nm. Soil texture was determined by the hydrometer method (Day, 1965).

Total arsenic content in soils was determined after digesting 200 mg soil samples with 6 ml HNO_3 and 4 ml de H_2O_2 (Krachler and Emons, 2000) in a Milestone/mls 1200 mega microwave oven. Before quantification, both samples and standards were pre-reduced using 5% w/v KI and 5% w/v ascorbic acid, in 10% v/v HCl medium, then they were allowed to stand for 45 min, and finally the same acid was added to reach 10 ml. Arsenic was determined by HG-AAS, utilizing a Perkin Elmer 1100B spectrophotometer coupled to an FIAS-400 flow injection system with hydride generation, using a 10% v/v HCl carrier solution, and a 0.2% w/v $NaBH_4$ in 0.05% w/v NaOH solution as a reducing agent. The accuracy of the method utilized in this study for arsenic determination was assessed through a certified reference material, SRM 2710 (Montana Soil), which contains 626.0 ± 38 mg As kg^{-1} soil. A total of four replicates gave 636.9 ± 5.7 mg of As kg^{-1} soil.

2.6. Sequential extraction procedure

Sequential extraction was carried out according to the method described by Wenzel et al. (2001). This procedure allows the sequential extraction of five arsenic fractions: non-specifically-adsorbed (F1), specifically-adsorbed (F2), amorphous and poorly-crystalline Fe and Al oxides (F3), well-crystallized Fe and Al oxides (F4), and residual (F5). Extraction conditions are described in Table 1.

Every extraction step was followed by 30 min centrifugation at 3000 rpm, filtration of the supernatant, and treatment of the previously weighed solid residue with the extractant that corresponded to the following step. Step 4 residue was dried at 30 °C, then 200 mg were weighed and digested as for total arsenic determination. By using a second portion of the residue, moisture was determined to make the necessary corrections.

Quantifications of total arsenic content in each step were carried out in a Perkin Elmer 1100 B spectrophotometer coupled to a FIAS-400 flow injection system with hydride generator.

2.7. Arsenic speciation in the first fractions of the sequential extraction method

Inorganic (arsenite and arsenate) and organic (MMAA and DMAA) species were determined, using hydride

Table 1
Experimental conditions for sequential extraction of arsenic in the systems under study

Step	Extractant	Conditions	Soil-extractant ratio (g/ml)
1	0.05 M $(NH_4)_2SO_4$	4 h shaking, 20 °C	1:25
2	0.5 M $(NH_4)H_2PO_4$	16 h shaking, 20 °C	1:25
3	0.2 M NH_4 buffer oxalate pH 3.25	4 h shaking in the dark, 20 °C	1:25
4	0.2 M NH_4 buffer oxalate + 0.1 M ascorbic acid, pH 3.25	30 min at 96 °C	1:25
5	HNO_3 and H_2O_2	Digestion	0.2 :10

Table 2
Experimental conditions for arsenic chemical speciation

Species	HCl ($mg\ l^{-1}$)	L-cysteine (%)	NaBH4 (%)	Contact time (h)
As(III)	4.0	0	0.05	0
Organic As	4.0	0.4	0.01	1
Total As	0.01	4.0	1.00	1

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 are described in Table 2. The content of As(V) was determined by the difference between total As and (As(III) + organic As). Chemical speciation was performed on the extracts from the first two fractions obtained in the sequential extraction carried out in soils. Statistical analysis of the results was performed by applying Tukey's HSD Test.

3. Results and discussion

3.1. Characterization of soil and biosolid

Texture determination revealed that PT soil contains the following percentages of clay, silt and sand: 73.5%, 12.7% and 13.8%, respectively. In GR soil the percentages were: 55.0%, 22.0% and 23.0%, respectively.

Table 3 shows some characteristics of the biosolid, soils, and biosolid-amended soils. All of the systems showed neutral pH. PT soil showed a greater content of organic matter (OM) and available P. On the other hand, GR soil showed a higher content of iron oxides compared with PT soil, which may account for its greater As(V) adsorbing capacity. The highest values for OM content, CEC, and available P corresponded to the biosolid, and its application to soils caused a significant increase in these parameters, which demonstrated a possible positive effect when the biosolid was used to amend the systems under study. The total content of arsenic in biosolids was below the recommended value for biosolid application to soil, according to Chilean regulations (CONAMA, 2001).

Table 3 also shows total arsenic concentration in both systems. Higher arsenic concentration is observed in GR soil, which is consistent with its closer vicinity to mining copper processes.

3.2. Sequential extraction of As from soils and biosolid-amended soils

Arsenic concentration obtained in each fraction of the sequential extraction procedure is lower in PT soil than in GR soil, which is consistent with the lower total arsenic concentration observed in PT soil (Table 3). On the other hand, although PT soil has a smaller total arsenic content than GR soil, the arsenic percentage in the first two most labile fractions was higher in PT soil than in GR soil (Table 4), thus corroborating the need to carry out sequential extraction studies when making environmental decisions on soils. The predominant fraction for PT soil was the residual one (F5), followed by the arsenic fraction associated to amorphous Fe and Al oxides (F3), while in GR soils the predominant fraction was the arsenic associated to amorphous Fe and Al oxides (F3), followed by the residual fraction (F5), which is coincident with the high content Fe oxides present in this soil. In both cases the most labile arsenic fraction (F1) was found in the small amount. Results obtained in GR soil are consistent with previous reports by other authors (Lombi et al., 2000; Shiowatana et al., 2001; Wenzel et al., 2001; Rodriguez et al., 2003)

Table 3
General characteristics of soil and biosolid samples

Soil	pH	OM (%)	CEC ($cmol\ kg^{-1}$)	Fed ($g\ kg^{-1}$)	Feox ($g\ kg^{-1}$)	P ($mg\ kg^{-1}$)	As ($mg\ kg^{-1}$)
PT	7.7	4.8a*	29.0	7.7a	2.6a	34.2	10.4a
PT + 15B	7.6	4.7a	30.1	7.6a	3.1ab	43.2	10.7a
PT + 100B	7.3	5.9b	33.7	8.1a	3.7b	86.6	11.2a
PT + 40As	7.8	4.3a	34.0	6.5b	3.8b	47.7	73.0b
PT + 40As + 15B	7.7	4.5a	29.9	7.5a	3.5ab	52.7	73.9b
PT + 40As + 100B	7.2	5.6b	32.7	7.8a	5.0c	102	69.6b
GR	6.6	3.2c	29.9	24.3c	8.7d	18.7	59.1b
GR + 15B	6.9	3.5c	31.6	23.1d	8.9d	37.2	61.9b
GR + 100B	6.8	4.2d	33.0	21.8e	8.4de	84.4	60.8b
GR + 120As	6.7	3.0c	30.7	22.2e	8.0e	30.9	280c
GR + 120As + 15B	6.9	3.2c	32.2	22.4de	8.6de	53.2	266c
GR + 120As + 100B	6.8	4.3d	33.9	22.2e	8.5de	99.9	260c
Biosolid	6.7	41.7e	50.9	15.3f	12.1f	591	16.9a

Mean ($n = 3$).
OM: organic matter.
CEC: cation exchange capacity.
Fed: Fe extracted by dithionate.
Feox: Fe extracted by oxalate.
* Values followed by the same letter in each column for the same soil show no significant differences for $P < 0.05$, according to Tukey HSD.

Table 4
Sequential extraction of arsenic in soils and biosolid-amended soils

Soil	F1		F2		F3		F4		F5	
	mg kg^{-1}	RSD	mg kg^{-1}	RSD	mg kg^{-1}	RSD	mg kg^{-1}	RSD	mg kg^{-1}	RSD
PT	0.34a[*]	4.5	1.3a	2.6	2.0a	4.0	1.1a	2.9	3.7a	12
PT + 15B	0.37a	4.9	1.3a	8.7	2.0a	3.7	1.1a	1.2	4.7b	13
PT + 100B	0.45b	4.7	1.3a	2.1	2.3b	2.5	0.94b	7.8	4.3ab	8.5
PT + 40As	19a	0.8	39a	6.6	16a	4.7	3.0a	5.3	4.2a	6.2
PT + 40As + 15B	18a	5.2	38ab	3.6	18b	6.6	2.9a	6.4	5.4b	11
PT + 40As + 100B	16b	4.2	35b	1.0	20c	2.6	2.8a	2.6	5.8b	13
GR	0.15a	1.2	4.0a	0.7	25a	2.4	11a	4.8	16a	8.4
GR + 15B	0.27b	7.4	4.5b	0.8	24a	0.6	11a	4.7	17a	11
GR + 100B	0.47c	0.6	3.7c	3.3	24a	1.3	11a	6.8	17a	8.1
GR + 120As	10a	8.5	100a	5.7	122a	5.3	20a	5.4	23a	8.3
GR + 120As + 15B	14b	8.9	109a	6.3	128a	8.2	20a	11.4	24a	1.7
GR + 120As + 100B	18c	1.5	100a	2.8	129a	5.4	19a	3.5	24a	7.4

Mean ($n = 3$).

F1: non-specifically adsorbed, F2: specifically adsorbed, F3: amorphous and poorly crystallized Fe and Al oxides, F4: well-crystallized Fe and Al oxides and F5: residual. RSD: relative standard deviation.

[*] Values followed by the same letter in each column for the same soil show no significant differences for $P < 0.05$, according to Tukey HSD.

who have found a high amount of arsenic, extractable with ammonium oxalate, hydroxylamine chlorohydrate, or NaOH, indicating a close association of arsenic to iron oxides in soils abounding in the latter, a situation that is favored in clay soils since these present a greater adsorbent surface. According to Fendorf et al. (1997), Grossl et al. (1997) and Grafe et al. (2001), arsenic is bound to Fe oxides mainly through the formation of mono- and bidentate complexes, thus becoming one of the main active sites of these oxyanions in soils.

3.3. Effect of biosolid incorporation on As distribution in soils

Generally, the 15 Mg ha^{-1} biosolid rate application did not have a statistically relevant effect on the different fractions of the studied soils.

The most labile fraction, corresponding to non-specifically adsorbed arsenic (F1) (Table 4) increased with incorporation of the higher biosolid rate in both PT and GR soil, indicating that the arsenic contributed by the biosolid became part of the most soluble fraction. Biosolid incorporation to PT soil also caused an increase in arsenic associated to amorphous Fe and Al oxides (F3), and in the residual fraction (F5).

Incorporation of arsenic to the soils under study (Table 4) becomes distributed mostly in the first three fractions. In PT soil, the specifically adsorbed arsenic (F2) had the highest increase level, followed by non-specifically adsorbed arsenic (F1), and by arsenic bound to amorphous Fe and Al oxides (F3), whereas in GR soil arsenic bound to amorphous Fe and Al oxides (F3) had the highest increase level, followed by specifically adsorbed arsenic (F2) and by non-specifically adsorbed arsenic (F1). It should be noted that although the amount of arsenic incorporated to GR soil was three times higher, it was found that PT soil had a higher amount of non-specifically adsorbed arsenic, which indicated that this soil does not have enough arsenic retention sites, this is possibly related to the smaller content of Fe oxides and clay. Nevertheless, others additional factors, such as the aging time of arsenic on sorbents, the nature of the sorbents, and the presence of foreign ligands (e.g. phosphate) may influence the mobility of arsenic (Pigna et al., 2006; Lin and Puls, 1999).

Biosolid incorporation to arsenic-spiked GR soil (Table 4) caused a statistically significant arsenic increase in the most available fraction, while in the PT + 40 As soil, biosolid application caused a decrease in the first two arsenic fractions, and an increase in the arsenic fractions extracted in F3 and F5, arsenic thus becoming less available.

For all the systems under study, recovery in relation to total Arsenic content by the sequential extraction procedure was from 81% to 115%, which is consistent with studies carried out by Wenzel et al. (2001).

3.4. Chemical speciation of As in the first two fractions of the sequential extraction procedure in soils and biosolid-amended soils

In the first two fractions of the sequential extraction procedure (Table 5), over 91% arsenic was present as As(V).

As observed in Table 5, biosolid application caused a significant increase in As(V) and organic arsenic, while As(III) decreased, indicating that organic matter incorporation to the systems may favor biological processes that transform As(III) into other species.

In the first fraction (Table 5) both of the soils that were not spiked with arsenic showed As(III) levels that were lower than the method detection limit. However, the same soils spiked with arsenic showed quantifiable amounts, which decreased with an increasing biosolid rate.

Biosolid incorporation to PT, GR, and GR + 120 As soils caused an increase in the content of non-specifically

Table 5
Arsenic speciation of first and second fraction of sequential extraction procedure, as mg/kg soil

Soil	As(III)	%	T org	%	As(V)	%	T As
Non-specifically adsorbed As species							
PT	nd		0.019a	5.5	0.323a	95	0.342a
PT + 15B	nd		0.018a	5.0	0.348a	95	0.367a
PT + 100B	nd		0.024b	5.4	0.427b	95	0.451b
PT + 40As	0.239a[*]	1.3	0.635a	3.4	18.0a	95	18.9a
PT + 40As + 15B	0.214b	1.2	0.585 b	3.2	17.3a	95	18.1a
PT + 40As + 100B	0.200b	1.2	0.483 c	3.0	15.4b	96	16.1b
GR	nd		nd		0.148a	100	0.148a
GR + 15B	nd		0.014 a	5.3	0.252b	95	0.266b
GR + 100B	nd		0.029 b	6.1	0.445c	94	0.473c
GR + 120As	0.481a	4.6	0.341a	3.3	9.6a	92	10.4a
GR + 120As + 15B	0.229b	1.7	0.443b	3.2	13.0b	95	13.7b
GR + 120As + 100B	0.316c	1.7	0.626c	3.4	17.4c	95	18.4c
Specifically adsorbed As species							
PT	0.024a[*]	1.8	0.086a	6.7	1.17a	91	1.28a
PT + 15B	0.021a	1.7	0.086a	6.9	1.14a	91	1.25a
PT + 100B	0.021a	1.7	0.081a	6.6	1.13a	92	1.23a
PT + 40As	0.553a	1.4	1.30a	3.4	36.5a	95	38.3a
PT + 40As + 15B	0.460b	1.3	1.27a	3.5	34.9ab	95	36.6ab
PT + 40As + 100B	0.427b	1.3	1.14 b	3.3	32.4b	95	34.0b
GR	0.054a	1.4	0.142a	3.6	3.73a	95	3.93a
GR + 15B	0.060a	1.4	0.163b	3.7	4.14b	95	4.37b
GR + 100B	0.049a	1.4	0145a	4.0	3.43c	95	3.63c
GR + 120As	1.21a	1.2	2.78a	2.8	93.8a	96	97.8a
GR + 120As + 15B	1.37a	1.3	2.99a	2.8	102a	96	106a
GR + 120As + 100B	1.20a	1.2	2.71a	2.8	93.1a	96	97.0a

nd: no detected.
Mean ($n = 3$).
[*] Values followed by the same letter in each column for the same soil show no significant differences for $P < 0.05$, according to Tukey HSD.

adsorbed organic arsenic, which could be the result of an increase in biological activity in these systems.

Arsenic incorporation to soils caused an increase in all of the arsenic chemical forms under study, PT soil showing an increase in organic arsenic about twice higher than GR soil.

In the specifically adsorbed arsenic fraction (Table 5), As(V) was also the predominant species in every soil. However, both As(III) and organic arsenic concentrations were higher than those found in the first soil fraction.

In general, biosolid incorporation showed no effect on the distribution of the various arsenic chemical species in step 2 of the sequential extraction procedure, corresponding to specifically adsorbed arsenic, except for the case of PT + 40 As soil, where a decrease was found in the content of all of the arsenic species under study. These results confirm the idea that biosolid application to soils low in iron oxides could have a beneficial effect by strongly retaining arsenic.

4. Conclusions

GR soil exhibited higher As(V) adsorbing capacity than PT soil, which correlates with the higher contents of clay and crystalline as well as amorphous iron and aluminum oxides, confirming that the participation of these components is essential to the adsorption of this metalloid.

Results of physico-chemical analyses performed on the substrates confirmed that GR soil has greater arsenic content than PT soil, which could be accounted for by the closer vicinity of GR soil to mining copper processes.

Arsenic in both soils under study was found mainly associated to amorphous Fe and Al oxides, and in the residual fraction, while a very small amount was found in the most available form.

Arsenic incorporated to the soils under study showed different distribution, with a remarkable increase in third fraction of arsenic in GR soil, which is consistent with the greater content of amorphous Fe oxides present in this soil, resulting in less available arsenic in case of arsenic contamination.

In both PT and arsenic-spiked PT soils, biosolid application at a rate of $100\ \mathrm{Mg\ ha^{-1}}$ caused an increase statistically significant according to Tuckey's HSD Test in arsenic bound to amorphous Fe and Al oxides, and in the residual fraction. Arsenic spiked PT soil had a decrease in arsenic content in the most labile fractions of the sequential extraction procedure, thus showing a favorable effect in its application to soils with few specific sites for arsenic adsorption.

Arsenic speciation in the first two fractions of the sequential extraction procedure revealed over 91% of arsenic as As(V), corresponding to the least mobile and least toxic inorganic arsenic species.

Overall, biosolid application to soils increased the content of non-specifically adsorbed organic arsenic, possibly due to greater biological activity caused by the increase in the content of organic matter in the systems.

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