

## Disposal of domestic sludge and sludge ash on volcanic soils

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### Abstract

Column leaching experiments were conducted to test the ability of Chilean volcanic soils in retaining the mineral constituents and metals in sewage sludge and sludge ash that were incorporated into the soils. Small or negligible amounts of the total content of Pb, Fe, Cr, Mn, Cd, and Zn (0 to <2%), and more significant amounts of mineral constituents such as Na (7–9%), Ca (7–13%), PO<sub>4</sub> (4–10%), and SO<sub>4</sub> (39–46%) in the sludge and sludge ash were readily soluble. When they were incorporated on the surface layer of the soils and leached with 12 pore volumes of water over a 3 month period of time, less than 0.1% of the total amount of heavy metals and PO<sub>4</sub> in the sludge and sludge ash were collected in the drainage water. Cation exchange selectivity, specific anion adsorption and solubility are the processes that cause the reduction of leaching. The volcanic soils were capable of retaining the mineral constituents, P, and metals in applied sewage sludge and sludge ash and gradually released them as nutrients for plant growth.

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### 1. Introduction

Sewage sludge is the inevitable end product of municipal wastewater treatment processes worldwide. As the wastewater is being purified, the impurities removed from the water stream are being concentrated. The sludge stream thus contains many chemical and microbiological constituents usually in concentrated forms that may become potential sources of pollutants when the material is released. No matter how many treatment steps it undergoes, at the end, the sludge and/or its derivatives (such as sludge ash), require the ultimate disposal. For disposal, the sewage sludge may be land applied, land filled, incinerated, or ocean dumped. There is not an entirely satisfactory solution and all of the currently employed disposal options have serious draw backs. Land application however is by far the most commonly used method around the world. Approximately six million dry tons of sewage sludge is produced annually in the United States [1]. Recent report showed that the annual production of sewage sludge in member countries of the European Union may

reach as much as  $8 \times 10^6$  tons [2]. Significant amounts of sewage sludge produced in the United States and the western European nations have been applied on land. Dependent on the regions, 24–89% of the sludge produced in the US has been applied on land [1]. Bonnin [2] reported that 65% of the sewage sludge in France was land applied; the situations in other parts of the world are expected to be similar. Recently, European countries are studying more restrictive directives to sewage sludge applications on land.

As the residue of municipal wastewater treatment, sewage sludge represents the aggregation of organic matter, pathogens, trace elements, toxic organic chemicals, essential plant nutrients, and dissolved minerals originally dispersed in the wastewater and are captured and transformed by the wastewater treatment processes. Properly managed, the potential pollutants are assimilated via the biochemical cycling processes of the receiving soils in the land application. The practice provides soils with organic materials and offers the possibility of recycling plant nutrients, which in turn, improve the fertility [3] and physico-chemical properties of agricultural soils [4]. If not appropriately controlled, the potential pollutants released through the land application may degrade the quality of downstream water bodies, be transferred through the food chain to harm the consumers of har-

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vests, and drastically alter the physical and chemical properties of the receiving soils. It is imperative that mass input provides adequate amounts of substances that are useful to plant development and the pollutant inputs are controlled to avert detrimental public health and environmental effects. Major countries such as the US, the European Union [5] and China [6] have enacted regulations or issued guidelines that limited the disposal options for a variety of reasons.

In Chile, the treatment works are gradually being brought online in recent years, before the collected wastewater was directly discharged and sewage sludge did not exist. With the commencement of wastewater treatment, sewage sludge and ash of the incinerated sewage sludge are accumulating in the metropolitan areas awaiting final disposals. In the sewage sludge used, the levels of heavy metals follow the sequence  $Zn > Mn > Cu > Cr > Pb > Ni > Mo > Cd$  (from 1780 mg/kg for Zn down to 5 mg/kg for Cd), being land application one of the primary options under consideration at this time.

The agricultural soils in Central Chile where most of the country's population centers are situated are derived from parent material of volcanic origin, and account for approximately 69% of nation's arable land. The predominant minerals of these soils are allophane and ferrihydrite in the Andisols and kaolinite, halloysite and iron oxides in Ultisols. These soils are rich in iron oxides and organic matter contents, possess pH-dependent variable surface charge and high  $PO_4$  accumulation. However, the soils have poor fertility; at the original acidic pH range of 4.5–5.5, they have low capacity for exchangeable cations (CEC) and a strong selectivity for K and Ca over Mg [7]. Phosphorus is strongly fixed by the minerals, thus is not readily available for plant absorption in these soils. To be productive, they require frequent adjustments of soil pH, replenishment of exchangeable Mg, and heavy  $PO_4$  applications. When soil pH increases the CEC increases, P fixation decreases and K selectivity is reduced. On the other hand, when the soil organic matter increases, the K selectivity is also reduced [7]. Municipal sewage sludge and ash of the incinerated sewage sludge appear to possess the essential plant nutrients and dissolved minerals and the buffering capacity [8–11]. When land applied, they may replenish the depleting nutrient reservoirs in these soils under cultivations. If the added constituents are retained in the soils and absorbed by plants, the risk of contaminating the downstream water bodies may be minimized. In this study, the capacity of volcanic soils to retain chemical constituents in the land applied sewage and sewage sludge ash was investigated.

## 2. Materials and methods

### 2.1. Soils

The surface 0–25 cm depth layers of five volcanic soils located in the agricultural regions of the Southern Central Chile were collected. Namely, they were Collipulli, Diguillin, Nueva Braunau, Metrenco, and Ralún reflecting the localities from where soils were extracted. The samples were obtained from well drained and regularly cultivated fields. Collipulli and Metrenco are classified as Ultisols and Ralún, Diguillin, and

Nueva Braunau as Andisols. General information on the climate and geography of the soils may be found in Escudey et al. [12]. Soil samples were screened in the field to pass a screen with 2 mm openings and stored at the field moisture content in a 4 °C cold room until used.

### 2.2. Experiments

Soils were packed to the depth of 25 cm into acrylic columns of 30 cm length and 10 cm of diameter, according to their respective field bulk densities. A filter paper disk was placed on the perforated plate at the bottom of each column to prevent the loss of solid materials. The sewage sludge was obtained from a domestic water treatment plant located in Santiago (Chile), the sewage sludge ash was obtained by heating the sewage sludge at 500 °C for 2 h. Dependent on the treatment, 30 g of air dried sewage sludge or the ash equivalent of 30 g of air dried sewage sludge were incorporated into the surface 5 cm of the packed columns. The experimental controls received neither the sludge nor the ash treatment. The columns, were placed in vertical position, flooded once a week with one pore volume of distilled water, and drained by gravity from top to bottom, for a period of 12 weeks. In addition, 30 g of sludge and the ash equivalent of 30 g of sludge were leached in the same manner. The drainages from each weekly leaching cycle were analyzed for pH, electrical conductivity,  $SO_4$ ,  $PO_4$ , Na, K, Mg, Ca, Zn, Cu, Fe, Al, Ni, Cd, Pb, Mo, and Mn.

At the end of the leaching experiment, each soil column was cut open lengthwise and the profile was sectioned into five equal length segments for analysis of the soils' pH, electrical conductivity, and organic carbon, exchangeable cations, and P contents. A chemical fractionation of heavy metals was carried out in sludge and sludge ash, by using the methodology proposed by Chang et al. [13]. The sequential extraction with 0.5 M  $KNO_3$ , distilled water, 0.5 M NaOH, 0.05 M EDTA, and 0.5 M  $HNO_3$  allows to estimate the exchangeable, sorbed, organic, carbonate and residual fractions of heavy metals.

### 2.3. Chemical determinations

The bulk density, exchangeable cations, total porosity, and organic carbon content of the soils were determined by methods outlined in methods of soil analysis (American Society of Agronomy, Madison, WI). Briefly, the bulk density [14] was determined by the average air dried weight of soils in undisturbed soil cores of the 0–25 cm soil profile in 5 cm (diameter) × 5 cm (height) brass rings; the exchangeable cations were determined as the concentrations of Na, K, Mg, and Ca in ammonium acetate extracts [15]; and organic carbon was determined by the Walkley-Black method [16]. The pH and electrical conductivity of soils were measured in soil suspensions with soil to water ratio of 1:2.5 w/v. The total elemental contents of Na, K, Mg, Ca, Zn, Cu, Fe, Al, Ni, Cd, Pb, Mo, Mn, P and S were determined by digesting the soils with a concentrated  $HNO_3$ –HCl–HF mixture in a microwave oven and measuring the concentrations by ICP–OES spectroscopy (Perkin Elmer Optima 2000 equipment, MECESUP USA9903).

Table 1  
Properties of soils, sewage sludge and sludge ash

Soil	pH	Bulk density (g cm <sup>-3</sup> )	Pore volume (mL)	Organic carbon (%)	Electrical conductivity (μS m <sup>-1</sup> )	Exchangeable bases (cmol kg <sup>-1</sup> )			
						Na	K	Mg	Ca
Collipulli	5.4	1.36	1027	2.3	81	0.1	0.2	1.8	5.9
Metrenco	5.5	1.33	1056	1.8	29	0.2	0.3	1.5	4.0
Ralún	4.5	0.90	988	6.2	436	0.1	0.1	0.4	2.5
Diguillin	5.9	1.12	830	6.5	94	0.2	0.7	1.1	8.4
N. Braunau	5.5	0.82	834	11.0	20	0.1	0.1	0.2	1.1
Sludge	7.7	0.46	–	17.8	8520	1.5	2.5	10.7	65.9
Sludge ash	7.4	–	–	<0.1	3890	1.2	1.1	7.4	25.8

Comparable components of the sewage sludge and sludge ash were determined in the same manner. The concentration of the same elements in leachates was also determined by ICP–OES; the SO<sub>4</sub> and PO<sub>4</sub> concentrations in the drainage water were measured by ion chromatography (Waters 625LC), provided with a Waters IC Pak anion HR 4.5 mm × 75 mm column.

The absorbance of leachates was measured at 465 and 665 nm in an UV–vis Perkin Elmer Lambda 20 spectrophotometer.

### 3. Results and discussions

#### 3.1. Soils, sludge, and sludge ash

Prior to the sludge and ash treatments, the soils were acidic with pH varying from 4.5 to 5.9 and low in exchangeable bases contents varying from 1.5 to 10.4 cmol kg<sup>-1</sup> (Table 1). In contrast, the sewage sludge and sludge ash had pH of 7.7 and 7.4, respectively that were 2–3 orders magnitude higher in alkalinity than those of the soils. The exchangeable base content of the sewage sludge was 80.6 cmol kg<sup>-1</sup>, 10–54 times those of the soils. The Na, K, Mg and Ca in the sludge ash were soluble but not necessary in the exchangeable forms. Judging by their electrical conductivities, the soluble mineral contents of sewage sludge and sludge ash were orders of magnitude larger than the soils, even though the incineration of sewage sludge results in less soluble chemical forms, and consequently presents a lower electrical conductivity than sewage sludge. The total elemental contents of the Ca, Mg, K, and Na in soils follow the same trends as those in the exchangeable forms and the concentrations are in the same order of magnitude. The column pore volume was calculated considering the amount of soil into the column and the total porosity of each soil (Table 1).

#### 3.2. Releases from sludge and sludge ash

When the sludge and sludge ash were leached, the soluble Na and SO<sub>4</sub> were released quickly (Fig. 1). Judging from the shapes of the break through curves, the soluble Na and SO<sub>4</sub> in sewage sludge were depleted with one pore volume of water used to leach the soils. On the other hand, the soluble Na and SO<sub>4</sub> in sewage sludge ash are gradually released with 5–8 pore volumes of water. Slight differences in the total amounts released from the sludge and sludge ash for Na (19 mg versus 16 mg), and SO<sub>4</sub> (342 mg versus 319 mg), were observed.

One main domain is observed in sludge release, which is associated to highly soluble forms. On the other hand, two main domains are observed in sewage ash, the first associated to soluble forms which is less important than in sludge, and a second from 2 to 5 pore volumes which can be associated to slow equilibria between solid and water. In both samples the quantities released were a small fraction of the total amounts.

Organic and inorganic P forms are present in sludge, while in sludge ash, after calcination, only inorganic P forms are present. The P forms in both samples are released slowly and released at constant rates over time (Fig. 2). In sludge, release is probably controlled by slow equilibria between solid organic P forms and soil solution, and by solubility of inorganic P forms. The release of P forms from ash is mainly solubility controlled, which is reflected in the lower slope shown in Fig. 2. Consequently, at the end of 12 leaching cycles, small amounts of PO<sub>4</sub> were recovered from drainages of sewage sludge and sludge ash (18 and

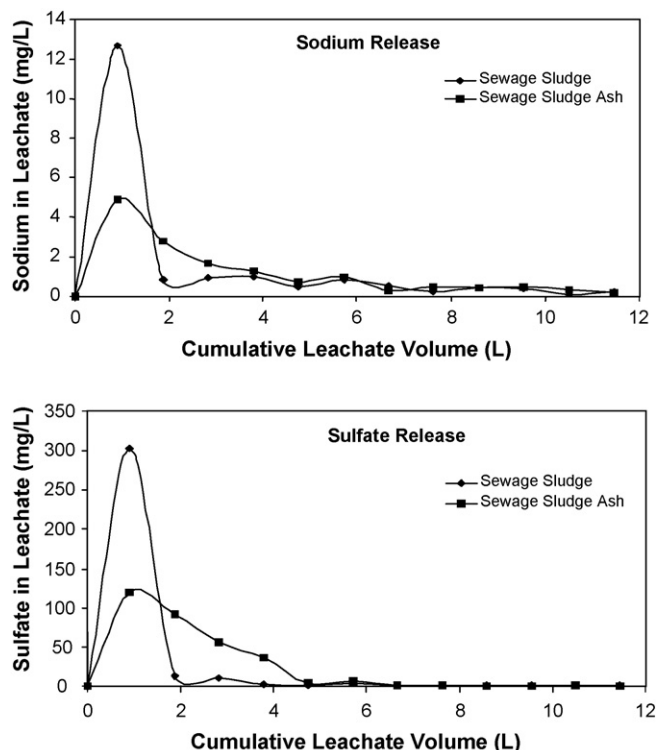


Fig. 1. Releases of Na and SO<sub>4</sub> from sewage sludge and sludge ash.

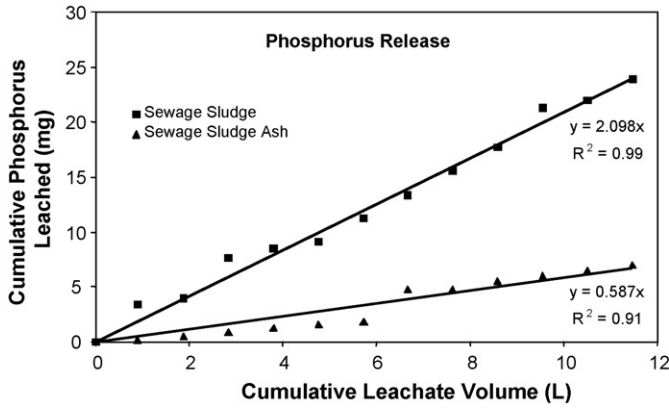


Fig. 2. Phosphorus release from sewage sludge and sludge ash.

6 mg, respectively) compared with their total contents (181 and 170 mg, respectively).

The patterns of Zn releases for the sludge and sludge ash were similar (Fig. 3). However, the amounts released by the sludge, 0.8 mg, were considerably higher than that of the sludge ash, <0.1 mg. Nevertheless, they were far below the total amounts of 53 and 49 mg in the sludge and sludge ash, respectively.

In all, only small amounts of the Na, SO<sub>4</sub>, P, and Zn were released when the sludge and sludge ash were subject to intense leaching for 12 weeks. Even though Cu and Zn are the main heavy metals in Chilean sewage sludge, also other heavy metals of environmental interest, such as Ni, Cd, Cr, Mo and Mn, were considered.

### 3.3. Soil attenuation

The pH of leachates in control and treated soils increases after 12 pore volumes; the final pH is about 1.5–2.0 units higher than the initial pH. The process is controlled by the soil; thus, after 12 pore volume the pH of treated soil leachates is only about 0.3 pH unit higher than those observed in the control columns. In all the experiments, after 12 pore volume, the leachate pH is basic, ranging between 7 and 8.

The leaching of organic matter was followed by measuring the absorbance of leachates after each pore volume at 465 and 665 nm. Only leachates from Ralun soil columns showed

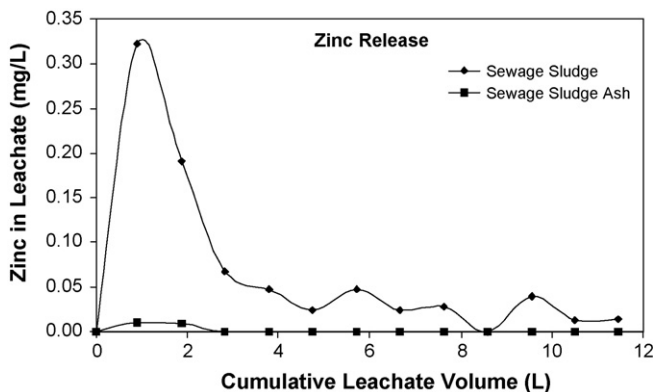


Fig. 3. Zinc release from sewage sludge and sludge ash.

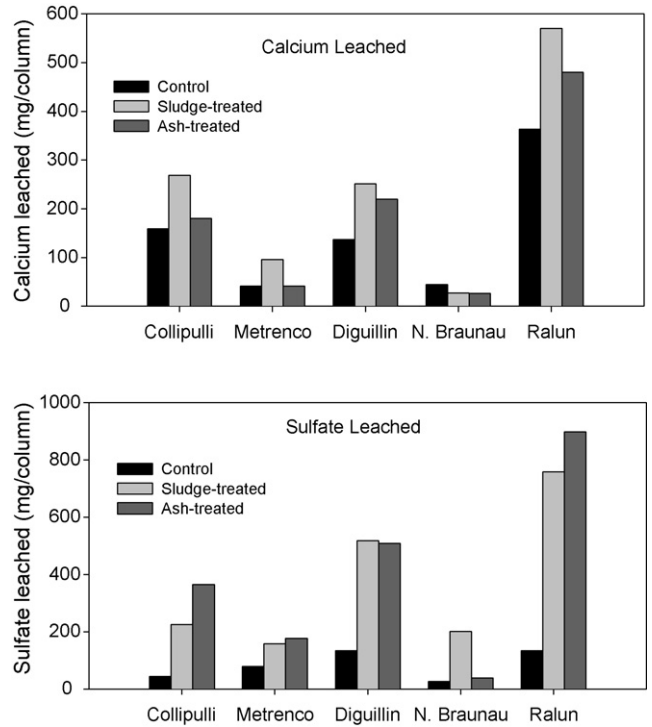


Fig. 4. Total amount of Ca and SO<sub>4</sub> leached from sewage sludge and sludge ash treated soils.

absorbance higher than zero, but the amount of organic matter leached was too low to be quantified. No significant loss of organic colloids was observed, because the mass balance demonstrates that the organic carbon remains constant in all columns considering the experimental errors of the Walkley-Black method.

Even without the applications of sludge or sludge ash, significant amounts of cations and anions such as Ca and SO<sub>4</sub> maybe leached from the soils (Fig. 4) and the amounts collected in the drainage water were dependent on conditions of soils. Sludge and sludge ash amendments consistently enhanced the leaching of minerals. However, collected amounts were significantly smaller than the total introduced through the addition of sludge or sludge ash, and are practically leached in the first 3 or 4 pore volumes of drainage water. Soil incorporation further reduced the mobility of the chemical constituents in the sludge and sludge ash (Fig. 5). For P and Zn, the amounts found in the drainage water (Fig. 5) were 2–3 orders of magnitude lower than the amounts present in the added sludge and sludge ash. As a result, nutrients such as the available P significantly increased with the application of sewage sludge and sludge ash for both the Ultisol and Andisol (Fig. 6).

The general trend in all the experiments was that only a small fractions of the total amounts incorporated by the addition of sludge or sludge ash were leached. As an example, the total input from sludge and ash, the total amount leached from them, and the total amount collected after 12 pore volumes for Collipulli and Nueva Braunau soils, are presented in Fig. 7. The total amount of heavy metals (Cu, Zn, Ni, Cd, Pb, Mo, Mn) leached after 12 pore volumes was <0.1% of the total input through sewage sludge or



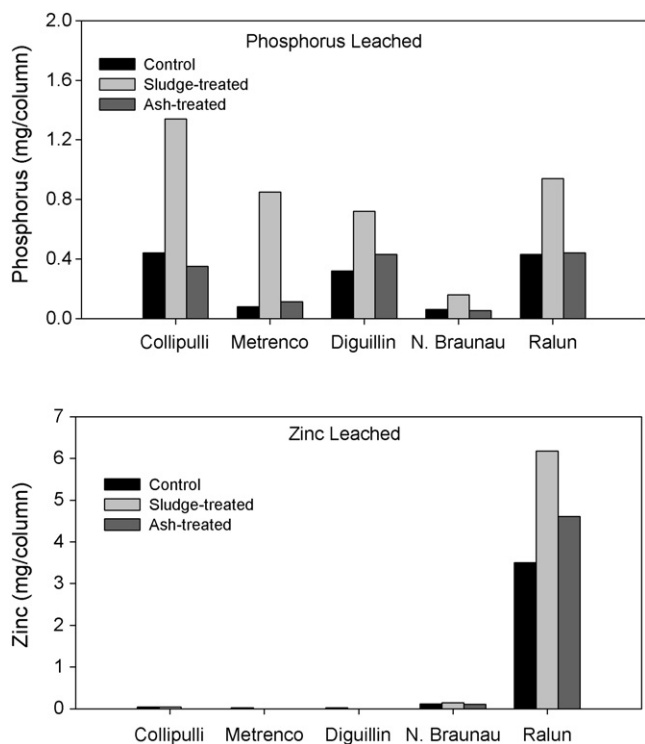


Fig. 5. Total amount of Zn and PO<sub>4</sub> leached from sewage sludge and sludge ash treated soils.

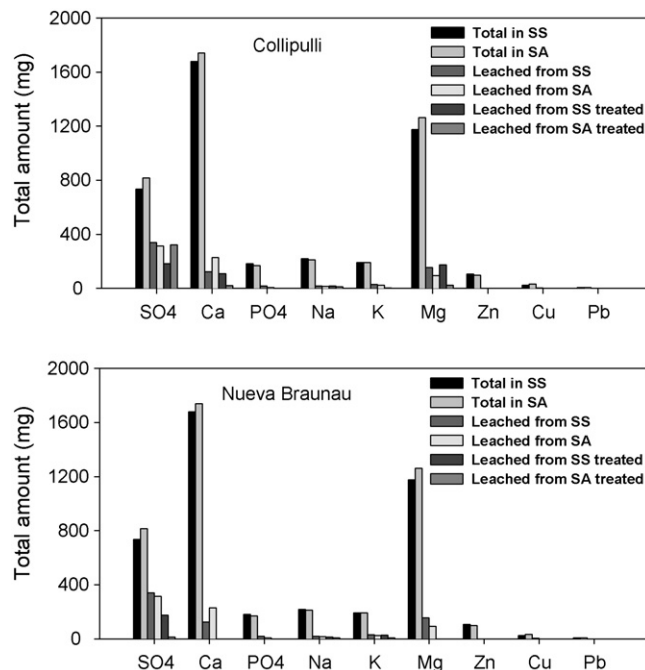


Fig. 7. Total amount of selected cations and anions in sewage sludge and the equivalent ash (Total in SS, SA), total amount leached from sewage sludge and sewage ash (leached from SS, SA), and leached from sewage sludge-treated columns and ash-treated columns (leached from ss treated, ash treated), for Collipulli and Nueva Braunau soils.

sewage ash (represented by Zn, Cu and Pb in Fig. 7). On the other hand, fractions leached of SO<sub>4</sub> (22–55%), Na (7–15%), K (2–30%), Ca (3–7%), and Mg (2–30%) are more significant.

The leaching of exchangeable bases behaves as predicted by cation exchange selectivity previously reported [17]. Phosphate is leached in very low amounts (<0.1%), even though sewage sludge and sludge ash present large P contents; this is due to the specific PO<sub>4</sub> adsorption, which is a characteristic of Chilean volcanic soils [12].

Fractionation experiments demonstrate that 86–99% of heavy metal chemical forms in sewage sludge are associated to organic matter complexes, carbonate and residual low soluble compounds, and that 95–99% is associated to carbonate and low solubility forms in sludge ash. All of them have low mobility, and consequently their leaching is mainly associated to the more soluble chemical forms, which are present only in very low concentration in both substrates.

#### 4. Conclusions

Results of column leaching experiments showed that volcanic soils in Chile were capable of retaining the inorganic mineral constituents, P, and Zn in sewage sludge and sludge ash when land applied. These constituents are essential inputs to enhance the productivity of volcanic soils that are frequently low in fertility. Cation exchange selectivity, specific anion adsorption and solubility are the processes that cause the reduction of leaching. In this regard, the volcanic soils will attenuate the sewage sludge borne pollutants and provide soils with nutrients that may be slowly released for crop production.

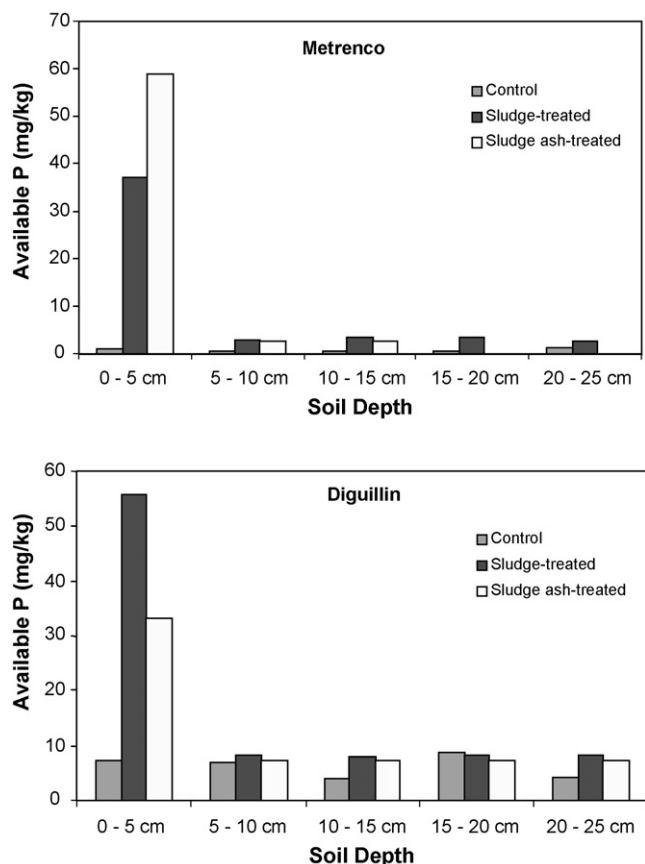


Fig. 6. Available P in the sewage sludge and sludge ash treated Ultisol (Metrenco) and Andisol (Diguillin).

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