Geochemical base line and pollution analysis of heavy metals in Taltal commune, northen Chile

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Abstract

Taltal is a coastal commune of 14,000 inhabitants located in northern Chile, where several abandoned mine wastes have been identified. The objectives of this study were to determine the geochemical baseline for Sb, V, Pb, As, and Cu and evaluate the heavy metal contamination for the soils in Taltal commune. Soil samples were collected at 175 sites. The samples were analyzed for total heavy metal concentrations, pH, and conductivity. Geochemical baseline concentrations of heavy metals were estimated following the upper-whisker limit method. The pollution levels of heavy metals were obtained using geo-accumulation index (Igeo), pollution index (PI), and enrichment factor (EF). The pH and the conductivity of the soils was found in the range of 7.23-9.74 and 8 and 35 $mScm^{-1}$, respectively. The geochemical baseline concentrations of Sb, V, Pb, As, and Cu were 0.180-22.907, 46.325-88.326, 2.770-187.874, 4.130-2,746.114, 8.08-1,591.353 mg kg−1, respectively. The Igeo values indicated that the soils were "moderately to strongly polluted" by Sb, V, Pb, As, and Cu. PI for Sb, V, Pb, As, and Cu was found in the range of 0.008-8.032, 0.094-3.815, 0.015-8.037, 0.002-8.010, 0.005-7.991, respectively. The EF for Sb, Pb, As, and Cu showed values above 5. The baseline values for Sb, V, Pb, As, and Cu in soils of Taltal were determined. It was concluded that the abandoned sites are contaminated with heavy metals.

Keywords: geochemical baseline, heavy metals, soils, mine wastes, pollution

1. Introduction

In Chile, guidelines values of heavy metals in soils has not been established yet, and the use of baseline values would contribute to increase the database necessary to establish threshold levels for the protection of environmental and human health. At the same time the use of baseline values will support the identification of zones contaminated with heavy metals. Due to anthropogenic contribution, it is very difficult to determine a background value (Gough *et al.*, 1994; Chen *et al.*, 1999; Facchinelli *et al.*, 2001). The baseline includes both the geogenic (background value), and the anthropogenic concentration (Darnley, 1997; Wei and Wen, 2012). The baseline is defined as 95% of the expected range of background concentration (Gough *et al.*, 1994). The baseline value has been used to define the concentration of an element on its surface environment (Salminen, 1997; Salminen and Gregorauskiene, 2000), and can be used as a reference to determine if a soil has been impacted by anthropogenic activities (Chen *et al.*, 1999; Gil *et al.*, 2004, 2010; Tarvainen and Kallio, 2002). Geoaccumulation index, enrichment factor, and pollution index are used to quantify the heavy metal contamination of soils and sediments (Müller, 1969; Hakanson, 1980; Szefer *et al.*, 1998; Gosar and Miler, 2011). The mining activities carry out by artisanal, small, and medium mining operations has lead to the occurrence of several abandoned mines sites across the world. A survey conducted by the Chilean Government (Cenma, 2014) identified 20 abandoned sites located in Taltal. These abandoned sites contain mainly tailings from metallurgy of copper, gold and silver ores and, are located in urban areas and close to natural reserves. However, the quantification of heavy metal pollution in Taltal still is a challenge due to the lacking of baseline concentrations. The objectives of this study were to determine the geochemical baseline and evaluate the heavy metal contamination for the soils in Taltal commune.

2. Methods

2.1. Study sites

This study was carried out in several sites located in Taltal commune, southern part of Antofagasta Region (North Chile). In this location there are a lot of abandoned sites which contain mine wastes such as copper and gold tailings.

2.2. Mine wastes and soil sampling

A stratified random sampling of soils and wastes was conducted on 151 sites. The samples were collected in plastic bags and kept to 4 °C prior to the analytical determination of their physical and chemical characteristics. The samples were analyzed for total heavy metal concentrations, pH, conductivity, and total Sulphur.

2.3. Wastes characterization

All the samples were dried at 105°C for 24 h, then passed through a 2 mm sieve before analysis. All analytical results were performed as the average of three replicates. The pH and electrical conductivity were determined in a 1:5 (w/v) suspension of soil in desionizated water (Milli-Q; resistivity ≥ 18 MOhm), using portable instruments from WTW. The heavy metal concentrations were analyzed by inductively coupled plasma–mass spectrometry (ICP-MS), after hydrochloric acid and nitric acid of 3:1 ratio (aqua regia).

2.4. Geochemical baseline calculation

The baseline levels in soils were calculate following the upper-whisker limit method (Tarvainen and Jarva, 2011). The upper-whisker value was calculated from the basic statistics of the soil data and was used as a limit to define the contamination. Concentrations observed above this limit can indeed be considered as abnormally high compared with the whole dataset. The upper limit of geochemical baseline variation for element X is estimated as follows:

$$BL = P_{75} + 1.5x[P_{75} - P_{25}]$$

where P_{75} is the 75_{th} percentile of element X concentrations and P_{25} is the 25_{th} percentile of element X concentrations.

2.5. Calculation of pollution levels

The pollution levels of heavy metals were obtained using different indices, such as geo-accumulation index (Igeo), pollution index (PI), and enrichment factor (EF).

2.5.1. Index of geo-accumulation

To quantify the heavy metal pollution in geo-matrices (Cevik *et al*., 2009), the index of geo-accumulation (Igeo), proposed by Müller and Erwin (1979), was used. The Igeo was calculated as follows:

$$I_{geo} = log_2\left[\frac{C_n}{1.5 \times C_{BL}}\right]$$

where C_n is the concentration of heavy metal in sample and C_{BL} is the geochemical baseline value of the same metal in the sample.

2.5.2. Pollution index

The pollution index (PI), which can be defined as the ratio between the sample and the baseline concentrations, was calculated to determine the degree of contamination of a given metal.

$$PI = \frac{C_n}{C_{BL}}$$

where C_n is a metal's concentration and C_{BL} is the baseline concentration of the metal in the sample.

2.5.3. Enrichment factor

The enrichment factor (EF) was used to estimate the anthropogenic contribution to the heavy metal content in the samples compared with an uncontaminated reference material (Chester and Stoner, 1973; Reimann and de Caritat, 2005; N'guessan *et al*., 2009). The EF was calculate by normalizing metal concentrations to Fe (Balachandran *et al*., 2005; Covelli and Fontolan, 1997). The chosen reference element was Fe because it is a semi-conservative element (Reimann and de Caritat, 2005; Yay *et al*., 2008). The EF was defined as the concentration ratio of an element (X) to a reference element (Fe) in a given sample, divided by the same ratio in a reference material (Baseline). The EF values for the metals in different soil samples were calculated as follows:

$$\mathrm{EF} = \frac{\left[\mathrm{C_n}/\mathrm{C_{Fe}}\right]_{\mathrm{sample}}}{\left[\mathrm{C_n}/\mathrm{C_{Fe}}\right]_{\mathrm{BL}}}$$

where C_n/C_{Fe} is the ratio of the total concentration of the metal to the reference element.

2.6 Chemical and Solutions

Standard stock solutions were prepared from salts in acidified ultra pure water (HCl, pH 1.7) daily. All containers, except those especially mentioned, were made of high density polyethylene (Nalgene) and subjected to a rigorous acid cleaning and were washed with ultra pure water before use. High purity chemical, and desionizated water was used for the preparation of all solutions.

3. Results and Discussion.

3.1. Chemical and physical characterization of soils and wastes

The soil contains 67.4 % sand, 26.3 % silt and 6.3 % clay, with pH and conductivity in a range of 7.23-9.74 and 8 and 35 $mScm^{-1}$, respectively, and low organic matter content (< 0.10 % as total organic carbon. Total concentrations of Sb, V, Pb, As, and Cu exceeding the EPA standard for metal on soils or regional baseline values were found on the 151 sampled sites (Table 1). The descriptive statistics to Sb, V, Pb, As, and Cu concentrations determined in samples of soils and wastes taken in the sites are shown in Table 1.

3.2. Baseline and Quantification of pollution

Igeo results for Sb, V, Pb, As, and Cu are presented in Fig. 1. The Igeo values indicated that the soils were "moderately to strongly polluted" by Sb, V, Pb, As, and Cu PI for Sb, V, Pb, As, and Cu was found in the range of 0.094-3.815, 0.015-8.037, 0.002-8.010, and 0.005-7.991, respectively. The variations in PI values of heavy metals in soil showed that in those areas of the city which are influenced by anthropogenic mining activities had exceptionally high concentrations of these elements

Table 1. Descriptive statistics to heavy metals concentrations determined in samples of soils

Element	Sb	V	Pb	As	Cu
Min	0,18	8,32	2,77	4,13	8,08
Max	184,00	337,00	1510,00	21996,00	12716,000
Mean	11,46	92,18	102,17	312,42	873,68
Median	2,61	82,90	30,00	18,70	132,00
15 th percentil	1,50	36,25	10,35	5,41	32,10
25 th Percentil	1,50	52,05	14,85	7,10	49,55
75 th Percentil	10,00	120,00	58,70	97,10	543,50
SD	25,37	59,39	219,49	1837,20	1784,45
BL	22,75	221,92	124,47	232,09	1284,42

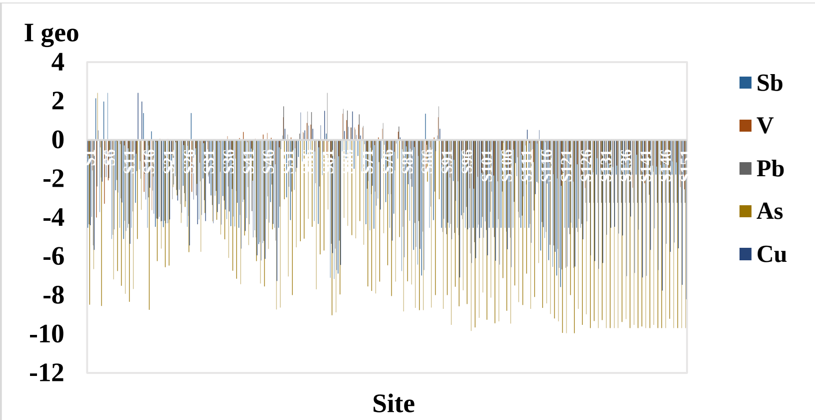

Figure 1. Index of geo-accumulation calculated to heavy metals measured in each sample taken in Taltal commune (Igeo <0: unpolluted; Igeo 0-1: unpolluted to moderately polluted; Igeo 1-2: moderately polluted; Igeo 2-3: moderately to strongly polluted; Igeo 3-4: strongly polluted; Igeo 4-5: strongly to very strongly polluted; Igeo > 5: very strongly polluted).

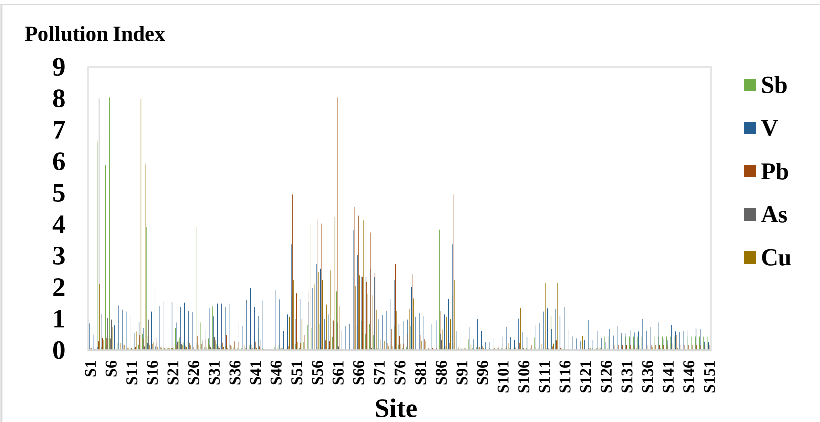

Figure 2. Pollution index calculated to heavy metals measured in each sample taken in Taltal commune (PI 0: none; PI 1: none to medium; PI2: moderate; PI3: moderate to strong; PI4 strongly polluted; PI5 strong to very strong; PI6 very strong).

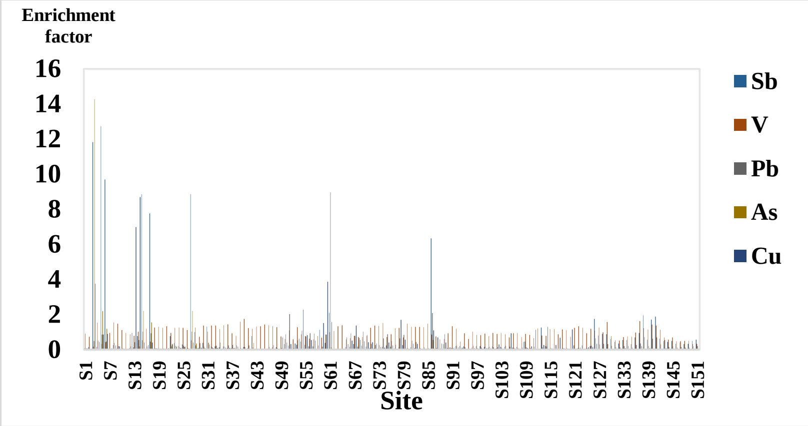

Figure 3. Enrichment factor calculated to heavy metals measured in each sample taken in Taltal commune. Enrichment factor by sampling site (EF < 1.5: non enrichment; EF 1.5-5: moderate anthropogenic enrichment; EF 5-20: significant anthropogenic enrichment; EF 20-40: very high enrichment; EF > 40: extremely enrichment).

The Figure 3 shows the EF for heavy metal for all the studied samples. The EF for Sb, Pb, As, and Cu showed values above 5. Then the soils were categorized as moderate anthropogenic enrichment to significant anthropogenic enrichment.

4. Conclusions.

The baseline values for Sb, V, Pb, As, and Cu in soils of Taltal were determined. It was found that the samples of soils taken on the several sites in Taltal contained elements such as Sb, V, Pb, As, and Cu, which exceeded the regional baseline values. According the results the abandoned site are contaminated with heavy metals and eventually could cause exposure to the population at such contaminants. It is thought that the mine wastes would have contaminated the soils at that sites. Therefore, it is necessary to implement remediation technologies in order to minimize the heavy metal contamination.

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