ASSESSMENT OF SOIL CONTAMINATION IN CALETA VITOR AND SURROUNDING AREAS, NORTHERN CHILE, DUE TO HEAVY METAL ENRICHMENT CAUSED BY AN ABANDONED COPPER MINE

Carmen Gloria Seguel, Hernán Muñoz, Johan Segovia, Boris Ávalos and José Rojas Martín

SUMMARY

This work offers a vision of physicochemical properties of the soils of Caleta Vítor, Northern Chile, such as: organic matter content, pH, porosity, apparent density, particle density and contamination by the presence of Cu, Pb and Zn in the soils where the abandoned mine Compañía Minera San Carlos is located, areas surrounding the river and the beach. The environmental impact of this abandoned mine is analyzed by evaluating the enrichment factor of the metals and the corresponding geo-accumulation index. The information obtained in this study is compared with those reported by SERNAGEOMIN five years earlier. The results of the enrichment factors based on PEC reach values of up to 664 times above the probable effects of their concentration can be observed and, based on TEC, 3037 times above harmful effects due to the presence of Cu can be observed. The Igeo index calculation shows that the abandoned mine area and samples located in the river area and the beach closest to the mining area can be classified as extremely to highly contaminated with Cu and Pb, while they are not contaminated with Zn. It is also shown that almost all sites in the abandoned mining area have increased after five years their Cu concentration between 2 and 54 times; a similar situation is observed with Pb and to a lesser extent with Zn.

Introduction

Mining operations and, in particular, the legacy of abandoned mines are being studied worldwide because of their enormous environmental impact on soil, air, biota, groundwater, rivers, seas and human health (Pan *et al*., 2010). Chile has been for centuries a territory of vast mining activity, with massive deposits of porphyritic type concentrated in the northern sector of the territory. Until a few decades ago, as in other countries in Latin America and the world and due to the lack of legal regulation, national and foreign mining companies were not obliged to remedy the environmental impacts. A cadastral update of abandoned or paralyzed mining deposits in Chile published by Chile's National Geology and Mining Service (SERNAGEOMIN, 2010) reported 409 tailings deposits across the country, of which 324 were not active, and 14 of them may show a significant risk to human life and health. The most dangerous one in the country is in Caleta Vítor, located 30km south of the city of Arica, the northernmost city in Chile. Mining activity in Caleta Vítor began around 1955 with the installation of the San Carlos Mining Company as a copper ore processing plant. This mining company, located on the shores of the Pacific Ocean and adjacent to a river in Quebrada Vítor, expanded around 1978 its mining activities by extracting high-purity minerals imported from Bolivia, India, Spain, the USA, China and Perú (Clemente, 2008). The mining company was a mineral treatment plant, mainly for leaching, percolation, and agitation. The exact date of closure of its activities is unknown, but it is believed to have occurred during the 1980s or 1990s. The main objectives of this work are: 1) to evaluate the legacy of the San Carlos Mining Company in the soils of Caleta Vítor, through the determination of: pH, percentage of MO, bulk density, particle density, percentage of porous space of the soils, identification of soil types and quantification of the total concentration of the metals Cu, Pb and Zn; and 2) to evaluate the pollution of the area by means of the elements enrichment factor and geo-accumulation index.

Materials and Methods

Study area

The San Carlos Mining Company located in Caleta Vítor, is an area where the Vítor River of the Quebrada Vítor, flows into the Pacific Ocean. The local beach is a tourist attraction, and the local inhabitants have developed small agricultural and livestock crops a few meters from the abandoned plant and on the banks of the river. To this day, in the abandoned mine area it is possible to observe highly eroded remnant plant concrete structures and leaching terraces for spreading of tailings over a distance of at least 500m. In addition, rubble, white, yellow and green materials are scattered in

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Carmen Gloria Seguel (Corresponding autor). Doctor in Chemistry, Universidad de Concepción, Chile. Professor, Universidad de Tarapacá, Chile. Address: Departamento de Química, Facultad de Ciencias, Universidad de Tarapacá. Avda. General Velásquez 1775, Arica, Chile e-mail: cseguel@uta.cl
Hernán Muñoz.Hernán Muñoz. Environmental Chemical Engineer, Universidad de Tarapacá, Chile. Environmental Consultant, Arica, Chile.
Johan Segovia. Environmental Chemical Engineer, Universidad de Tarapacá, Chile. Environmental Consultant, Arica, Chile.
Boris Ávalos. Chemist, Universidad de Tarapacá, Chile. Professor Researcher. Universidad de Tarapacá, Chile.
José Rojas Martín. Engineer, Universidad de Tarapacá, Chile. Professor Researcher, Universidad Tecnológica de Chile.

EVALUACIÓN DE LA CONTAMINACIÓN DE SUELOS EN CALETA VÍTOR Y ÁREAS CIRCUNDANTES, NORTE DE CHILE, DEBIDO AL ENRIQUECIMIENTO EN METALES PESADOS CAUSADO POR UNA MINA DE COBRE ABANDONADA

Carmen Gloria Seguel, Hernán Muñoz, Johan Segovia, Boris Ávalos y José Rojas Martín

RESUMEN

Este trabajo ofrece una visión de propiedades fisicoquímicas de los suelos de Caleta Vítor, norte de Chile, tales como: contenido de materia orgánica, pH, porosidad, densidad aparente, densidad de partículas y de la contaminación por presencia de metales Cu, Pb y Zn en los suelos donde se emplaza la mina abandonada Compañía Minera San Carlos, áreas que rodean el río y la playa. El impacto ambiental de esta mima abandonada se analiza evaluando el factor de enriquecimiento de los metales y los correspondientes índices de geo acumulación. La información obtenida en este estudio se compara con los reportados por el SERNAGEOMIN cinco años antes. Los resultados de los factores de enriquecimiento basados en la PEC alcanzan valores de hasta 664 veces por encima de los cuales se pueden observar los efectos probables de su concentración y, basados en TEC, 3037 veces por encima de los cuales se pueden observar efectos nocivos debido a la presencia de Cu. Los cálculos del índice Igeo muestran que el área de mina abandonada y las muestras ubicadas en el área del río y la playa más cercana al área minera pueden clasificarse como extremadamente a altamente contaminada con Cu y Pb, y no contaminada con Zn. También se muestra que casi todos los sitios en el área minera abandonada después de cinco años, han incrementado su concentración de Cu entre 2 y 54 veces. Similar situación se observa con Pb y en menor medida con Zn.

AVALIAÇÃO DA CONTAMINAÇÃO DE SOLOS EM CALETA VÍTOR E ÁREAS CIRCUNDANTES, NORTE DO CHILE, DEVIDO AO ENRIQUECIMENTO EM METAIS PESADOS CAUSADO POR UMA MINA DE COBRE ABANDONADA

Carmen Gloria Seguel, Hernán Muñoz, Johan Segovia, Boris Ávalos e José Rojas Martín

RESUMO

Este trabalho oferece una visão de propriedades físico-químicas dos solos de Caleta Vítor, norte do Chile, tais como: conteúdo de matéria orgânica, pH, porosidade, densidade aparente, densidade de partículas e da contaminação por presença de metais Cu, Pb e Zn, em solos onde está localizada a mina abandonada, Companhia Mineira San Carlos, áreas em torno do rio e a praia. O impacto ambiental de esta mima abandonada é analisado avaliando o fator de enriquecimento dos metais e os correspondentes índices de geoacumulação. A informação obtida em este estudo é comparada com os relatados por SERNAGEOMIN cinco anos antes. Os resultados dos fatores de enriquecimento baseados na PEC alcançam valores de até 664 vezes, acima destes podem ser observados os efeitos prováveis de sua concentração e, baseados em TEC, alcançam 3037 vezes, acima destes podem ser observados os efeitos nocivos devido à presença de Cu. Os cálculos do índice Igeo mostram que a área de mina abandonada e as amostras localizadas na área do rio e praia, mais próxima da área mineira, podem ser classificadas como extremamente ou altamente contaminada com Cu e Pb, e não contaminada com Zn. Também se mostra que, após cinco anos, quase todos os locais na área mineira abandonada têm incrementado sua concentração de Cu entre 2 e 54 vezes. Similar situação se observa com Pb e, em menor medida, com Zn.

areas of the river close to the plant, as well as on the beach. With the rising tide and flooding of the river, particularly due to events in the Altiplano winter (January-March) the latter end up being incorporated into the water column and sediments of the Pacific Ocean.

Soil sampling

Soil samples from Caleta Vítor were collected during two samplings, carried out on March and October 2015. The study area was distributed in four main areas and the geographic coordinates of all sites were established using GPS (Garmin International Inc. Olathe, USA). Seven sites were located at the abandoned mine area (sites 1 to 7) and included areas of eroded leaching thanks, tailing dumped in a pile and waste rocks (these seven sites have the same geographic coordinates than the study carried out by SERNAGEOMIN five year before); five sites were located along the course of the Vítor river watershed (sites 8 to 11); a control or reference site (12) was located 4.7km northeast away from the abandoned mine area and, finally, four sites (sites 13 to 16) were along the beach. The sampled area is shown in Figures 1a and 1b.

Using a stainless steel hand shovel and quartering method, 32 soil samples (two per site) were taken from horizon A at a depth of 1-20cm, packed in polyethylene bags and transported to the laboratory for sample preparation. Representative subsamples of 100g from each quartering were oven-dried at 40°C for 24h and used for the determination of pH, organic matter, particle density, bulk density, porosity and quantification of the metals Cu, Pb and Zn.

Sample preparation and physicochemical characterization

All samples were finely grounded with a jaw crusher Hebro and LM2 sprayer (Labtech ESSA) before physicochemical characterization. The pH of the soil samples was measured potentiometrically using an HI9828 multiparametric portable (Hannna Instruments) after of appropriate saturation of the soil. The percentage of organic matter was determined by weight differences between samples dehydrated at 105°C for 24h (before dehydration, samples were treated with HCl 0.1M to eliminate inorganic carbon) and samples heated in a muffle to 550°C (loss of total organic carbon) for 2h. The total concentration of Cu, Pb and Zn at each site sampled was performed in triplicate and measured by atomic absorption

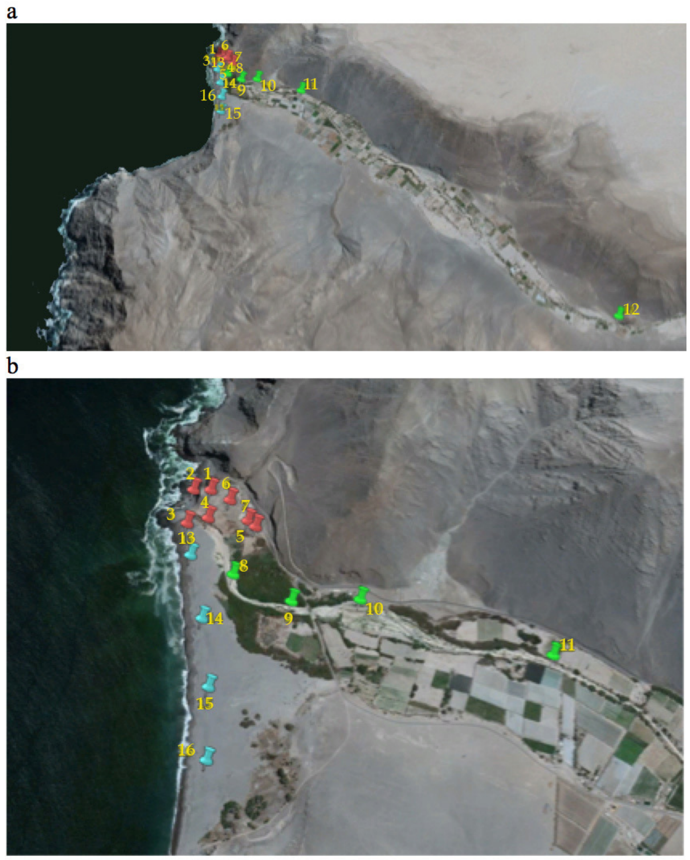

Figure 1. a: overview of all sites sampled in Caleta Vitor, b: partial view of the sampled areas. Red pins: mine area, green pins: river area, light blue pins: beach area.

spectrometry (Varian Spectra AA-240), according to protocol 3050B (USEPA, 1996). Recovery was 90 to 110% for all metals in the soil reference material (NIST SMR 2710).

Bulk density, particle density, organic matter and pore space

The environmental characteristic of soils depends on many physicochemical factors, such as texture, organic and inorganic matter content, pH, particle density, bulk density and pore spaces, among others. Bulk density (ρ_b) is defined as the mass of dry soil per unit bulk volume, including pore spaces and solids; it is related to soil textural class and soil porosity: soils with more organic matter content and high pores spaces percentage have lower ρ_b than those have higher pore space percentages (Schoonover and Crim, 2015). In this study ρ_b was quantified in soil samples excavated to 20cm deep, then oven dried to 105°C and weighed. The samples were transferred to 25ml volumetric flasks, weighed and subsequently eliminated to fill the flask with distilled water. Bulk density was calculated with the equation

$$\rho_b = (Ps/Pw) \times \rho w$$

where Ps: weight of volumetric flask with soil sample minus weight of volumetric flask, Pw: weight of volumetric flask with distilled water minus weight of volumetric flask, and ρw: water density at room temperature.

The particle density (ρ_s) of the soil is defined as the mass per unit of volume of soil solid without any pore space. This parameter depends on the mineral and organic soil composition. It was quantified by transferring 10g of sample soil to a 25ml volumetric flask. After weighing, boiling water was added until 2/3 full and the flask heated (without stopper) in a hot water bath to remove any air entrapped in the soil. After cooling to room temperature, the flasks were filled with water to complete their capacity. Finally, all the soil was removed from the volumetric flask and it was filled with distilled water and weighed. The particle density was calculated with the equation

$$\rho_s = (m_s/m_w - m_{s\text{-}a}) \times \rho w$$

where m_s: weight of soil sample, m_w: weight of water, $m_{s\text{-}a}$: weight of soil without air, and ρw: water density at room temperature.

Pore space (Po) in soil is related to particle density and bulk density (Danielson and Sutherland, 1986) through the equation

$$Po(\%) = (1 - \rho_b/\rho_s) \times 100$$

All factors influencing bulk density also affect pore space.

Indicator indices of heavy metal contamination

There are different indices usedcas indicators of soil contamination by anthropogenic activity. The geo-accumulation index (Igeo) defined by Müller (1981) and the enrichment factor (EF) are among the most commonly used indexes to assess the contamination/pollution level of heavy metal in soils and sediments. Igeo is calculated by the equation

$$Igeo = Log_2\ (C_n / (B_n \times 1.5))$$

where C_n: concentration of the n metal in the study area, and B_n: background value of the same metal at the control site or soil. The constant 1.5 is introduced to minimize the effect of possible variations in the background values attributable to lithological variation. The Igeo index has seven categories (Müller 1981).

The EF is defined as the ratio between a specific metal concentration and its background metal content. A different formulation for EF calculation defined as a ratio between metal concentration and their threshold effect concentration (TEC) or probable effect concentration (PEC), as defined by MacDonal *et al.* (2000) has been applied by Bird (2016) and is represented by the equation

$$EF = C/G$$

where C: concentration of the metal and G: the corresponding guideline values based on TEC (threshold effects concentration) or PEC (probable effects concentration) of the given metal.

In this study, the Igeo and EF have been applied to evaluate the legacy of Cu, Pb and Zn contamination in the soils of the abandoned San Carlos Mining Company area and its surroundings.

Results and Discussion

Copper

The abandoned mining area presented a wide range of total concentration of this heavy metal (Table I). The highest values (95,975mg·kg^{-1}) were found in flotation tailings, and in waste rock piles sites with concentrations ranging from 5,091 to 33,561mg·kg^{-1}. These sites were characterized by both acidic conditions with pH 3.4-4.41 and high (11.12-14.77%) organic matter (OM). The concentrations found in waste rock are in the range reported by Higueras *et al.* (2004) and Perlatti *et al.* (2015); however, no similar values of copper concentration have been reported for flotation tailings in abandoned copper mines or mines related to this metal. The OM of flotation tailings and waste rock piles is very high compared to those found by Carkovic *et al.* (2016). A high OM should favor the decrease of copper levels available in the environment through the formation of complexes; however, metal mobilization in the surface environment is favored by the acidic conditions found at these

TABLE I
PHYSICOCHEMICAL PARAMETERS OF THE STUDY AREA

Area	Sites	pH	%OM	Po(%)	g·cm^{-3}		mg·kg^{-1} dry weight		
					ρs	ρb	Cu	Pb	Zn
Mine	1	6.09	4.09	40.78	2.55	1.51	24,480	604	289
	2	6.85	1.39	44.03	2.68	1.50	1,230	16	41
	3	7.06	0.79	41.36	2.66	1.56	251	6	34
	4	6.66	1	41.35	2.66	1.56	419	4	28
	5	3.4	13.22	64.37	2.47	0.88	5,091	10	251
	6	4.41	11.12	57.05	2.98	1.28	95,975	323	810
	7	4.35	14.77	72.01	3.77	1.05	33,561	280	355
River	8	6.18	0.89	36.75	2.34	1.48	239	8	39
	9	6.5	1.49	40.48	2.52	1.5	350	5	39
	10	6.09	1.09	44.40	2.68	1.49	2,414	3	42
	11	6	0.98	60.73	3.92	1.52	38	3	43
	12*	7.03	1.21	66.69	4.42	1.48	37	4	44
Beach	13	6.33	1.09	42.44	2.71	1.56	349	5	32
	14	6.46	0.90	39.69	2.62	1.58	320	3	29
	15	6.53	0.99	39.55	2.68	1.62	60	2	92
	16	6.26	1.09	41.67	2.88	1.68	58	2	95

12*: Control or reference site located 4.7km northeast of the abandoned mine area.

sites, similar to those found in tailings reported by De la Iglesia *et al*. (2006). The other sites in the abandoned mining area have a pH that tends to be neutral (7.06-6.66), OM varies widely (4.09-0.79%), and the range of Cu concentrations varies from 24,480 to 251mg·kg^{-1}. Except for site 1, the concentrations are in the range found in other copper mine soils in Chile (Higueras *et al*., 2004) and in India (Punia *et al*., 2017). Sites along the course of the Vítor river watershed had a lower OM (0.89-1.49%) with less acidic pH (6-7.03). The Cu concentration range decreases as the distance to the mine area increases from 2,414mg·kg^{-1} (closest to the mine waste site) to 38mg·kg^{-1}. The control or reference point located 4.7km northeast of the mining area shows a concentration of 37mg·kg^{-1} and a slight increase of OM. The sites sampled in the beach area had a concentration range from 349 to 58mg·kg^{-1} showing the same decreasing concentration trends as the river area.

Comparing the results obtained in this study with the same sites sampled by SERNAGEOMIN in 2010, with the same geographical coordinates (Table II), it can be observed that after five years almost all the sites in the area have increased their concentration between 2 and 54 (site 8) times. According to this, it can be said that the rising tide and river, together with the climatic conditions of wind and humidity have contributed both to a larger dispersion of this metal, as well as to soil erosion and leaving the area more exposed to higher concentrations of Cu.

Lead

The total concentration range of Pb throughout the sampling area (Table I) varies from 2 to 604mg·kg^{-1}, values that are similar to those found in central-southern Poland (Lee *et al*., 2016). The highest concentrations were observed in only two sites in the mining area and comparing these results with those reported by SERNAGEOMIN (2010), four sites have decreased their concentration, and two others increased their concentration between 1.1 and 2.8 times. Both the river area and the beach area had very low concentrations (2-8mg·kg^{-1}).

Zinc

Like the two other metals, the total concentration of Zn (Table I) also shows a wide range, particularly in the mine area, from 810 to 28mg·kg^{-1} and the highest concentrations are found at the same sites as Cu. Compared to the SERNAGEOMIN (2010) study, after five years, site 1 increases up to 53 times its concentration, and sites 5 and 6 increase 1.3 and 23 times, respectively. Zn concentrations in the river area are very similar (39-44mg·kg^{-1}). The beach area shows enrichment of this metal as the distance from the mine area increases.

Relationship between bulk density, particle density, organic matter and pore space

When the organic matter content is high, the bulk density (ρ_b) and the particle density (ρ_s) are low. Similarly, soils with a high ratio of porous space (Po%) have less organic matter (MO%) than those that are more compact and have a less porous space. On the other hand, ρ_s is independent of porous spaces. Soils with high OM reached values between 1 to 1.5g·cm^{-3} and mineral soil may range from 2.4-2.9g·cm^{-3} (Schjønning *et al*., 2017). The experimental values obtained for these parameters regarding the sampled sites show a trend towards a decrease in ρb as ρs increases (Figure 2). Although the ρs values are in the range reported by Di Giuseppe *et al*. (2015), they were lower than expected, particularly in the soils of the mining area. In the mining area, deposits 6 and 7 have the highest ρ_s of 2.98 and 3.77g·cm^{-3}, respectively, indicative of a high ore content. Sediment samples from the riverbed and beach area show an average of ρ_b between 1.48-1.50g·cm^{-3} and 1.56-1.62g·cm^{-3}, respectively. When the OM content and percentage of pore space are high ρ_b is low, and ρ_s is independent of pore space. OM varies between 0.89 and 13.22 and Po% between 39.69 and 64.37. Sites 5, 6 and 7 have the highest MO and Po values and the lowest ρ_b. Arantes de Barros *et al*. (2013) has reported the same trends and the correlation between ρ_b and Po.

The kind of soil texture is also related to bulk density and pore space. Generally, fine textured surface soils such as silt loams, clays, and clay loams have lower bulk densities

TABLE II
TOTAL METAL CONCENTRATIONS FROM THE SERNAGEOMIN STUDY (2010) AND EXTRAPOLATION OF ENRICHMENT FACTORS

Area	Sites	Cu			Pb			Zn		
		mg·kg^{-1} dw	EF PEC	EF TEC	mg·kg^{-1} dw	EF PEC	EF TEC	mg·kg^{-1} dw	EF PEC	EF TEC
Mine	1	29.7	199.3	939.6	532	4.2	14.9	≤5	0.0	0.0
	2	329	2	10	73	1	2	41	0.1	0.3
	3	187	1	6	72	1	2	25	0.1	0.2
	4	1562	10	49	149	1	4	21	0.0	0.2
	5	2204	15	70	70	1	2	198	0.4	1.6
	6	1795	12	56.9	116	1	3	34	0.1	0.3

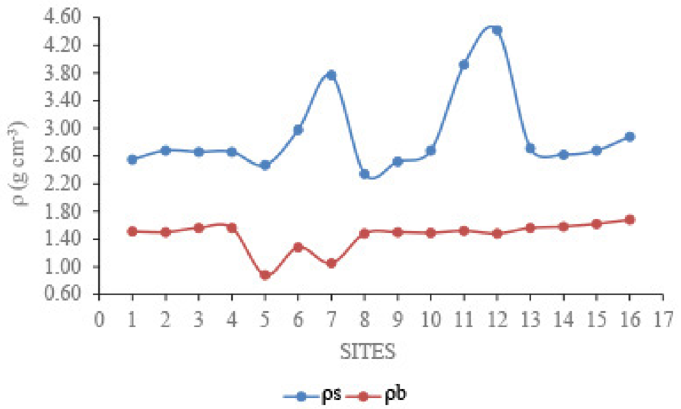

Figure 2. Bulk density and particle density distribution in the sampled area.

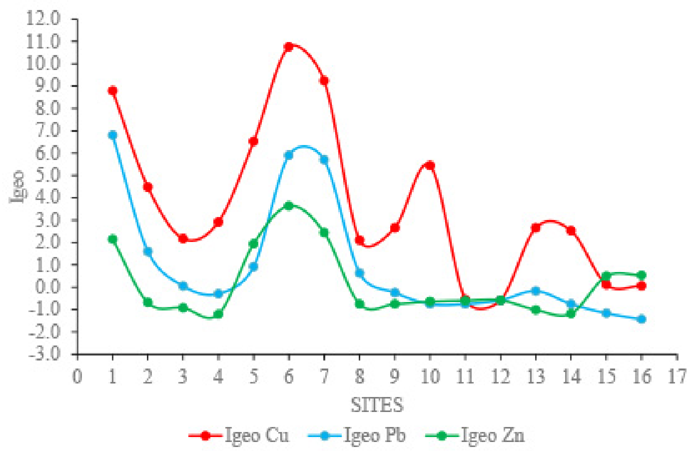

Figure 3. Enrichment factors based on PEC and TEC and index of geo accumulation of each metal in the sampled area.

(1.0-1.6-g·cm^{-3}) than sandy soils (1.2-1.8g·cm^{-3}) (Brady and Weil, 1999). Based on the results obtained from ρ_b and Po, and according to Kutilek *et al.* (1994), soil samples in the studied area can be classified as mainly sandy, sandy loam and, particularly, clayey soils. The highest porosity values were found in clay and silt loam soils, and the texture soils of sites 5 to 7 also show good correlation with OM.

Indicators of soil contamination

The geo-accumulation index (Igeo) of Cu, Pb, and Zn at the sampled area was calculated using the equation proposed by Müller (1981). The background value of the corresponding metal was the concentration obtained in the control sample, taken 4.7km northeast of the abandoned mining area. Figure 3 shows the Igeo values of the three metals. The Igeo for Cu shows a variation from -0.5 to 10.8 (Table III). Using the categorization defined by (Müller 1981), all the soil samples closest to the mine area (sites 1 to 7) may be classified as having an extremely high contamination to being strongly contaminated. Soil samples located in the riverbed and surrounding area may be categorized as extremely highly contaminated areas (site 10, a stockpile of precipitate of the plant) to uncontaminated (sites 11 and 12) and the samples corresponding to the beach area as uncontaminated. The Igeo values obtained for Pb ranged from -0.2 to 6.8 and the sites sampled can be classified as extremely contaminated, moderately contaminated to uncontaminated. Riverbed and beach area sites may be considered as non-Pb contaminated areas. Concerning Zn, most of the area sampled can be classified as uncontaminated. Oyebamiji *et al.* (2017) have found similar Igeo values for Cu, Pb and Zn in mining soils and surrounding areas.

To compare the degree of anthropogenic accumulation of metals in five years, an extrapolation of the Igeo accumulation index was made with six samples taken five years earlier by SERNAGEOMIN (2010) using the same metal background concentration of the control sample obtained in this study. The Igeo indices extrapolated from sites 1 to 6 show that the order of contamination is maintained: Cu>Pb>Zn. The categorization of contamination by means of this index remains the same after five years, although sites 2 and 5 have increased their Igeo values by 1.2 and 6 units respectively, it was also observed that there had been no significant variations in sites 1, 3 and 4.

Like for Cu, the Igeo value of Pb at site 1 maintains the same value five years later; however, with the exception of site 6, the Igeo values of the other sites decrease. In this way, four sites change their classification from heavily contaminated, extremely contaminated to uncontaminated. On the other hand, Zn shows that four sites show slight increases in Igeo values, increasing their degree of contamination after five years from not contaminated to heavily and moderately contaminate.

In this study, EF was quantified using the adapted equation proposed by Bird (2016) and the consensus values for threshold effect concentration (TEC) and probable effect concentration (PEC) in mg·kg^{-1} proposed by MacDonald (2000), TEC/PEC values being for Cu: 31.6/149; Pb: 35.8/128 and Zn: 121/459.

As it can be seen in Table III, the highest EF values were found in the area closest to the abandoned mine. Cu presented extremely high values, particularly in sites 1, 6 and 7 reaching an EF PEC up to 664 fold above that at which effects are likely to be observed. Similarly, these sites had extremely high EF TEC values; site 6 reaches a value of 3037 times above which it is unlikely that harmful effects will be observed in the presence of this metal. In general, the riverbed area had lower EF PEC. Site 10 had the highest EF PEC, being 16 times higher the probable effect concentration and the lowest value was obtained at the control or reference point (site 12). However, Cu continues to cause concern, especially for EF related to TEC at sites 9-10. All EF TEC or PEC for Cu exceed the values reported by Bird (2016). The EFs of Pb and Zn in all the sampled area were lower compared to Cu. Nevertheless, Pb presented high values of EF TEC particularly at site 1, 6 and 7 ranging from 7.8 to 16.9 above harmful threshold effects and EF PEC values also show likely concentration effects to be observed. The enrichment factor for river and beach area may be considered non-significant. Similar behavior it is observed with Zn in most of the sampled sites.

Conclusions

According to the results obtained almost all physicochemical properties of the different zones and surrounding areas of the San Carlos Mining Company abandoned mine are in the expected range. The mine area is significantly contaminated with Cu (95,975-33,561mg·kg^{-1}) and to a lesser extent with Pb (323-10mg·kg^{-1}) and Zn (810-231mg·kg^{-1}), as are the river and beach areas near the abandoned mine. This high pollution is also demonstrated by the extremely high values of Igeo indices and EF PEC for Cu, which reaches values up to 664 times above which the probable effects of its concentration can be observed,

TABLE III
TENRICHMENT FACTORS BASED ON PEC AND TEC, AND GEO-ACCUMULATION INDEX OF EACH METAL IN THE SAMPLING AREA

Area	Sites	Cu		Pb		Zn		Igeo		
		EF PEC	EF TEC	EF PEC	EF TEC	EF PEC	EF TEC	Cu	Pb	Zn
Mine	1	164.3	774.7	4.7	16.9	0.6	2.4	8.8	6.8	2.1
	2	8.3	38.9	0.1	0.5	0.1	0.3	4.5	1.6	-0.7
	3	1.7	7.9	0.0	0.2	0.1	0.3	2.2	0.1	-0.9
	4	2.8	13.3	0.0	0.1	0.1	0.2	2.9	-0.3	-1.2
	5	34.2	161.1	0.1	0.3	0.5	2.1	6.5	0.9	1.9
	6	644.1	3037.2	2.5	9.0	1.8	6.7	10.8	5.9	3.6
	7	225.2	1062.1	2.2	7.8	0.8	2.9	9.2	5.7	2.4
River	8	1.6	7.6	0.1	0.2	0.1	0.3	2.1	0.6	-0.8
	9	2.3	11.1	0.0	0.1	0.1	0.3	2.7	-0.2	-0.8
	10	16.2	76.4	0.0	0.1	0.1	0.3	5.4	-0.8	-0.6
	11	0.26	1.2	0.0	0.1	0.1	0.4	-0.5	-0.8	-0.6
	12*	0.25	1.2	0.0	0.1	0.1	0.4	-0.6	-0.6	-0.6
Beach	13	2.3	11.0	0.0	0.1	0.1	0.3	2.7	-0.2	-1,0
	14	2.1	10.1	0.0	0.1	0.1	0.2	2.5	-0.8	-1.2
	15	0.40	1.9	0.0	0.1	0.2	0.8	0.1	-1.2	0.5
	16	0.40	1.8	0.0	0.1	0.2	0.8	0.1	-1.4	0.5

12*: Control or reference site located 4.7km northeast of the abandoned mine area.

and EF TEC 3037 times above which harmful effects can be observed due to the presence of this metal. EFs of Pb and Zn in this area are lower compared to Cu, but Pb is still a cause for concern. Considering that the abandoned mine is located on the ocean shore and adjacent to a river in the Vítor watershed, not only the soils and surrounding areas would be contaminated, but also the sea and river-bed water, which would be favored by the erosion of acid soils.

Comparison of the results of this study, with those reported five years earlier SERNAGEOMIN (2010) shows that the order of contamination (Cu>Pb>Zn) remains the same over time and has increased considerably, rather than decreased. Almost all sites in the mining area have increased in Cu concentration, between 2 and 54 times (site 8), some sites show a decrease in Pb concentration and two other sites increases of 1.1 to 2.8 times, due to the conditions of high tides, wind, humidity, and erosion. Due to all the above-mentioned factors and considering that Caleta Vítor is popular with tourists and that local inhabitants cultivate small agricultural crops and livestock a few meters from the abandoned plant, it is necessary to implement strategic protection actions to avoid contamination transfer to the population, as well as the isolation of the area to minimize environmental impacts.

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