

Active and legacy mining in an arid urban environment: challenges and perspectives for Copiapó, Northern Chile

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Abstract Urban expansion in areas of active and legacy mining imposes a sustainability challenge, especially in arid environments where cities compete for resources with agriculture and industry. The city of Copiapó, with 150,000 inhabitants in the Atacama Desert, reflects this challenge. More than 30 abandoned tailings from legacy mining are scattered throughout its urban and peri-urban area, which include an active copper smelter. Despite the public concern generated by the mining-related pollution, no geochemical information is currently available for Copiapó, particularly for metal concentration in environmental solid phases. A geochemical screening of soils ($n = 42$), street dusts ($n = 71$) and tailings ($n = 68$) was conducted in

November 2014 and April 2015. Organic matter, pH and elemental composition measurements were taken. Notably, copper in soils (60–2120 mg/kg) and street dusts (110–10,200 mg/kg) consistently exceeded international guidelines for residential and industrial use, while a lower proportion of samples exceeded international guidelines for arsenic, zinc and lead. Metal enrichment occurred in residential, industrial and agricultural areas near tailings and the copper smelter. This first screening of metal contamination sets the basis for future risk assessments toward defining knowledge-based policies and urban planning. Challenges include developing: (1) adequate intervention guideline values; (2) appropriate geochemical background levels for key metals; (3) urban planning that considers contaminated areas; (4) cost-effective control strategies for abandoned tailings in water-scarce areas; and (5) scenarios and technologies for tailings reprocessing. Assessing urban geochemical risks is a critical endeavor for areas where extreme events triggered by climate change are likely, as the mud flooding that impacted Copiapó in late March 2015.

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Introduction

The world's urban population will increase from 3.9 (2014) to 5.8 billion people by 2050 according to the

United Nations World Urban Prospects (2014). The expansion of cities is posing sustainability challenges on a global scale, especially in developing countries where residential developments compete with industrial and agricultural use of the land. Environmental pollution from current and past industrial growth in urban and peri-urban areas exposes the urban population to health risks that prompt careful evaluation and response. Special attention is needed in arid areas with the presence of active and legacy mining (Gomez-Alvarez et al. 2011; Park et al. 2014). While active mining drives the local economy and urban expansion, traces of legacy mining—like abandoned tailings—may compromise human and environmental health.

Tailings that have not been closed under environmentally sound plans are likely to become the source of toxic metals in arid environments (Bes et al. 2014; Varrica et al. 2014; Nkosi et al. 2015; Sobrino-Figueroa et al. 2015). Indeed, metal-rich particles are easily mobilized and may reach residential and agricultural areas by wind-driven transport or by water erosion during infrequent but intense storms. Metal-rich particles increase the exposure to metals via inhalation, ingestion and absorption (Mielke and Reagan 1998; Boyd et al. 1999; Mielke et al. 1999). Thus, polluted urban soils and dusts have been considered a matter of public health in many parts of the world (Bloemen et al. 1995; Kelly et al. 1996; Sánchez-Martin et al. 2000; Norra et al. 2006; Wong et al. 2006; Glennon et al. 2014). Furthermore, exposure to toxic metals is likely to be enhanced when tailings, housing and agricultural activities are intermingled, as it is the case of the city of Copiapó, our study site, located in the Atacama Desert in Northern Chile.

Silver mining flourished around Copiapó in the early nineteenth century, when the population was of ~10,000 inhabitants. Copper mining thrives today in the area, while agriculture has expanded vigorously despite its aridity (18 mm/year of rainfall). Agricultural and industrial water use has increased, leaving a dry river bed for the past few years, as available surface water only flows through the channel networks. Urban expansion has been largely unplanned, leaving ~30 tailings from legacy mining operations scattered through the urban and peri-urban area of Copiapó, many near the reaches of the Copiapó River. At the same time, atmospheric pollution from an

active copper smelter has prompted public concern, for the present-day population of ~150,000 inhabitants.

In this study, we report a first geochemical screening of metals in solid phases such as soils, street dusts, and tailings in the arid urban and peri-urban area of Copiapó. We identify challenges for defining knowledge-based policies, control technologies and improved urban planning. Furthermore, evaluating environmental and health risks is a critical task for urban areas likely to suffer extreme events triggered by climate change, like the mud flooding that impacted Copiapó in late March 2015.

Materials and methods

Study area

The city of Copiapó (between 70°15′–70°25′W and 27°18′–27°26′S) is located in one of the driest places in the world, the Atacama Desert (NASA 2002). It has a mean annual rainfall of 18 mm, concentrated in winter (June and July), and a mean annual temperature of 16.1 °C. Mining represents the biggest contribution to the gross domestic product (GDP) of the region, while more than 30 tailings in the urban and peri-urban area of Copiapó have been considered as environmental liabilities by the Chilean mining agency (Cadastre by the National Geology and Mining Agency of Chile, SERNAGEOMIN 2015). Most of them do not have a protective surface layer and have not been closed under environmentally sound plans. Additionally, a copper smelting operation is located only 8 km east from Copiapó's downtown (see Fig. 1).

Sampling and sample pretreatment

Samples of soil in urban and peri-urban areas, street dust, and from one mine tailing were obtained throughout the city of Copiapó in November 2014. In addition, samples from 8 other mine tailings were collected in April 2015 (Fig. 1). A sampling strategy modified from Li et al. (2004) was used for soil samples. Composite soil samples of 0–15 cm deep were obtained at every site of interest by quartering 4 different samples taken within a distance of about 5 m from each other using a stainless still auger.

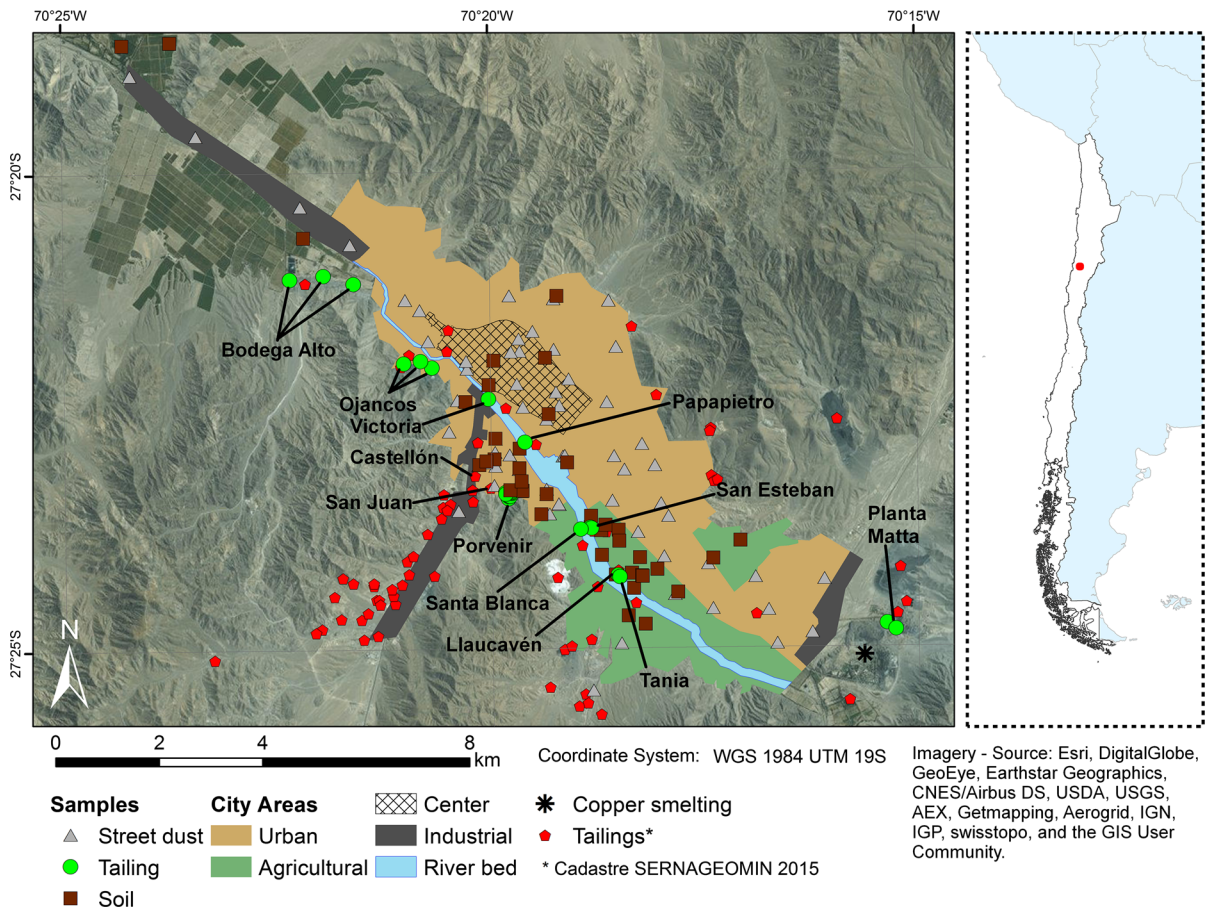


Fig. 1 Location of the city of Copiapó, sample sites, areas of the city and main tailings located in the urban and peri-urban areas

Sampling sites included city squares and parks (residential/park soils), agricultural areas in peri-urban parts of the city, and agricultural areas located near (<1 km) tailings. Street dust samples were collected from both sides of the streets by sweeping with a plastic brush ~1 m² as described in Banerjee (2003) and Al-Khashman (2007). Street dust sampling sites were located within a 1 × 1 km² grid throughout the city, and with a denser grid (500 × 500 m²) in El Palomar, a residential area close to several tailings in the southwest of the city. The surface of the tailings was sampled using a stainless steel auger (0–15 cm depth). Nine tailings were chosen for sampling, aiming at filling the main gaps in data availability, and for their proximity to the City center and the Copiapó riverbed. One of them, the Porvenir tailing, was extensively sampled because it had also been described as a potentially

contaminated and harmful tailing, but it had sparse chemical characterization (Soubllette et al. 2011), while the other 8 tailings were sampled each at 3 or less points to preliminary assess their metal composition. In the Porvenir tailing, samples were collected on top and around it from points spatially distributed in a systematic way.

In total, 42 composite soil samples, 71 street dust samples, 30 Porvenir tailing samples and 38 samples from other tailings were obtained. All samples were pretreated, which means they were oven-dried (40 °C) and sieved (<2 mm) in the laboratory.

Analytical methods

Metals' concentration was measured in the pretreated samples (dried and sieved through a 2-mm mesh) with X-ray fluorescence spectroscopy (XRF) with a

portable Innov-X Delta DS6000 equipment using two methods (two beam mining and soil 3 beam). In this aim, a fraction of pretreated sample was placed in a plastic cup of 23 mm high and 39 mm of diameter, and measured with both methods.

Physicochemical properties such as organic matter (OM) content and pH were also measured. The OM content was determined by oxidation with a mixture of dichromate and sulfuric acid (Nelson and Sommers 1996), and pH was determined by measurement on aqueous soil suspension in a 1:2.5 volume fraction with a pH meter (Pansu and Gautheyrou 2006). X-ray diffraction (XRD) analyses were performed with a diffractometer (D2 Phaser, Bruker AXS, Germany) at 30 kV and 10 mA using Cu-K α radiation for a selection of the samples (25 soil and street dust samples, and 27 tailing samples). For XRD analyses, pretreated samples were micronized with a mill using agate grinding elements (McCrone Micronising Mill, Westmont, IL, US).

For descriptive statistics, values under the estimated limit of quantification (LQ) were replaced with LQ divided by 2 (LQ/2). As street dust samples were spatially distributed in a 1-km² grid, maps of dot plots were made to visually represent the spatial distribution of the concentrations, using ArcGIS 10.3.1 (ESRI, Redlands CA).

Data validation

An analysis was performed to evaluate XRF analytical and quantification performance as recommended by the US Environmental Protection Agency Method 6200 (Sackett and Martin 1998). Systematic analysis of certified reference materials (CRM, NIST 2702, marine sediment and NIST 2781, domestic sludge) was performed; then, accuracy and uncertainty of measurements were calculated with the use of control charts, to validate the method for the studied elements. Moreover, the analytical uncertainty for the actual samples was verified for the 3 studied matrices (soil, street dust, tailings) with duplicate analysis of one sample for each matrix for 5 different days.

The uncertainty values along with the mean measured concentrations (of both certified reference materials and the 3 samples of the 3 matrices) were used to estimate an actual limit of quantification (LQ) for each element. The LQ was estimated as the threshold from which higher concentration values

showed lower uncertainties (<60 %). This LQ is different than the instrumental limits of detection, and is usually higher. In addition, the certified standard material IAEA-457 (marine sediment) was also analyzed as a quality control.

Results were deemed valid for As, Co, Cu, Fe, Mn, Pb and Zn for a specific method (two beam mining or soil 3 beam), and LQ along with the frequency of quantification for the different sample types measured is shown in Table 1.

A comparison between results from XRF and inductively coupled plasma mass spectrometry (ICP-MS) was performed for the elements with validated method measurement, except for Co. ICP-MS measurement after microwave acid digestion (9 HNO₃:3 HCl) was used to analyze total metals' concentrations of 34 of the samples used in this study. The comparison between XRF and ICP-MS data showed coefficients of determination of 0.92 (As), 0.93 (Cu), 0.85 (Fe), 0.97 (Mn and Pb) and 0.96 (Zn), as shown in the Online Resource 1 to 6. However, Fe and Mn showed systematically higher values when measured with XRF compared to ICP-MS. This could be due to the incorporation of Fe and Mn into the silicate matrix of the samples, as hydrofluoric acid (HF), which digests silicates, was not used.

Results and discussion

Physicochemical properties of the samples

Descriptive statistics of the samples physicochemical properties are shown in Table 2. The pH mean value was close to 7.0 for all 3 matrices. A wide range of pH values was found in tailing samples (3.5–8.8), while a narrower range (7.0–8.4) was found in soil samples. The minimum overall value was reported in a Porvenir tailing sample (pH 3.5), while the maximum was found in a street dust sample (pH 9.3).

Higher concentrations of OM with a mean of 4.5 %, and a broader range of values (0.9–18.9 %) were found on street dust samples compared to soils (with a mean of 2.8 %) and tailings (with a mean of 0.7 % for the Porvenir tailing and 1.0 % for the others). The high values and variability of OM content in dust samples could be attributed to the presence or absence of surrounding vegetation in the streets sampled, such as trees and shrubs, and could also be related to different

Table 1 Frequency of quantification (%) for selected elements in the different sample types, and estimated limit of quantification (LQ) in mg/kg (obtained with XRF analysis)

Sample type	No. of samples	Frequency of quantification (%)						
		As	Co	Cu	Fe	Mn	Pb	Zn
Agricultural soils in peri-urban areas	7	43	57	100	14	100	86	86
Agricultural soils near tailings	17	29	41	100	24	100	88	82
Residential/park soils	18	33	44	100	22	100	61	67
Street dust	71	13	75	100	39	100	83	99
Porvenir tailing	30	20	100	100	100	83	50	40
Other tailings	38	63	97	100	92	95	50	50
		Estimated LQ (mg/kg)						
		36	12	12	35,000	276	22	103

Table 2 Mean, median, relative standard deviation (% RSD), maximum and minimum values for pH and percentage organic matter content in soils, street dusts and tailings

Sample type	pH					% Organic matter (OM)				
	Mean	Median	% RSD	Max	Min	Mean	Median	% RSD	Max	Min
Soil (<i>n</i> = 42)	7.7	7.6	4.6	8.4	7.0	2.8	2.5	65.5	8.1	0.5
Street dust (<i>n</i> = 71)	6.8	6.7	8.4	9.3	5.8	4.5	3.4	80.1	18.9	0.9
Porvenir tailing (<i>n</i> = 30)	7.1	7.5	19.7	8.8	3.5	0.7	0.6	97.5	3.8	0.1
Other tailings (<i>n</i> = 38)	7.5	7.8	14.7	8.7	3.9	1.0	1.0	73.3	4.5	0.1

n is the number of samples collected for the different matrices

particle size distribution, as OM may be associated with smaller particles. Samples from the Porvenir tailing had the lowest OM concentrations, similar to values obtained for other tailings. The remaining tailing samples were grouped as “Other tailings” due to the small amount of samples available for each of the 8 other tailings sampled (with 38 samples in total). These results show that tailings have a smaller OM content compared to other matrices, which could make phytoremediation even more difficult considering the aridity of the area and that the potential for revegetation decreases for smaller OM contents (Cordova et al. 2011).

Metals in urban and agricultural soils

Table 3 shows the mean and the range of the metal concentrations obtained with XRF for the three types of soil samples: agricultural in peri-urban parts of the city, agricultural near tailings and residential/park soil. A comparison was performed between the

results and the Canadian and Brazilian guidelines (CCME 2003; Companhia de Tecnologia de Saneamento Ambiental 2005). International soil guideline values vary widely, as they are based on country-specific health and environmental goals and local geochemical contexts. For this study, the Canadian guideline was chosen as an example of a conservative limit at which no appreciable human health risk is expected. The Brazilian guideline was chosen because it represents a closer reality in Latin America and it has been used previously as an intervention value by Chilean authorities (SEREMI MINSAL 2011). Chile has not adopted a soil quality standard or guideline yet. Table 4 shows the two mentioned guidelines for the metals studied, except for Fe and Mn that do not have guidelines in those countries. The US EPA’s regional screening level (RSL) (US EPA 2015) is also displayed as additional information, but it was not included in the comparison analysis because it has no reference values for agricultural soil. The comparison between the results

Table 3 Mean and range (mg/kg, dry weight) of metal concentration obtained with XRF for the different types of samples

Sample type	Mean and range of concentrations (mg/kg)						
	As	Co	Cu	Fe	Mn	Pb	Zn
Agricultural soils (<i>n</i> = 7)	32.1 (<36–63)	13.3 (<12–21)	209 (78–349)	21,180 (<35,000–43,257)	1049 (736–1178)	50.4 (<22–102)	176 (<103–307)
Agricultural soils near tailings (<i>n</i> = 17)	25.8 (<36–52)	10.7 (<12–15)	379 (68–2116)	25,618 (<35,000–84,349)	1501 (711–4591)	39.6 (<22–74)	126 (<103–175)
Residential/park soils (<i>n</i> = 18)	36.8 (<36–125)	12.7 (<12–35)	201 (64–570)	24,657 (<35,000–67,775)	1236 (717–2321)	50.0 (<22–417)	147 (<103–655)
Street dust (<i>n</i> = 71)	28.5 (<36–489)	15.2 (<12–38)	690 (111–10,224)	29,732 (<35,000–110,847)	779 (518–1283)	54.7 (<22–275)	257 (<103–2743)

n is the number of samples collected for different matrices

Table 4 Canadian and Brazilian soil quality guidelines and US EPA screening levels for different land uses, metal concentration in mg/kg (dry weight)

Guideline	Land use	Element concentration (mg/kg)				
		As	Co	Cu	Pb	Zn
Canada ^a	Agricultural	12	40	63	70	200
	Residential/parks	12	50	63	140	200
	Commercial	12	300	91	260	360
	Industrial	12	300	91	600	360
Brazil ^b	Agricultural	35	35	200	180	450
	Residential	55	65	400	300	1000
	Industrial	150	90	600	900	2000
USA ^c	Residential	0.68	2.3	310	400*	2300**
	Industrial	3	35	4700	800*	35,000**

* Lead and compounds (US EPA 2015)

** Zinc and compounds (US EPA 2015)

^a Numerical limits recommended to support and maintain designated uses of the soil environment (CCME 2003)

^b Companhia de Tecnologia de Saneamento Ambiental (2005)

^c Screening level regions 3, 6, 9 (US EPA 2015)

of this study and the Canadian and Brazilian guidelines is shown in Table 5.

In the case of Cu, which was quantified in all soil samples (as shown in Table 1), 100 % exceeded the Canadian guideline for each sample type, and between 11 and 59 % of the samples, depending on the soil type, exceeded the Brazilian guideline. The mean Cu in soils was about 3 times the Canadian guideline for residential/park areas and agricultural soils in peri-urban areas, and 6 times higher for agricultural soils near tailings. The concentrations of Pb also outranged the limits of both soil quality guidelines in some cases. Mean Pb concentrations were below the guidelines limits, but 29 % of agricultural soils and 6 % of

agricultural soils near tailings exceeded the Pb Canadian guidelines and 6 % of residential/park soils exceeded both countries' limits. Although soils in residential/parks areas have higher mean values and a wider range of Pb concentrations compared to agricultural areas near tailings, both Canadian and Brazilian residential guidelines are about twice their corresponding agricultural guideline. For Zn, between 0 and 29 % of soil samples exceeded the Canadian guideline depending on the sample type, and all the samples had lower concentrations compared to the Brazilian guideline. Mean concentrations of Zn were below the Canadian guideline for all types of soils, but samples containing concentrations higher than the

Table 5 Percentage of samples that exceed Canadian and Brazilian soil guidelines

Sample type	Land use for guideline comparison	Percentage (%) of samples exceeding the guidelines (Canada/Brazil) per element				
		As	Co	Cu	Pb	Zn
Agricultural soils (<i>n</i> = 7)	Agricultural	43 ^a /43 ^a	0/0	100/57	29/0	29/0
Agricultural soils near tailings (<i>n</i> = 17)	Agricultural	29 ^a /29 ^a	0/0	100/59	6/0	0/0
Residential/park soils (<i>n</i> = 18)	Residential/parkland	33 ^a /17	0/0	100/11	6/6	17/0
Street dust (<i>n</i> = 71)	Residential/parkland	13 ^a /3	0/0	100/37	7/0	42/3

The “/” separates the percentage obtained for Canada and Brazil guidelines

^a Percentages calculated as frequency of quantification because the LQ estimated was higher than the guideline for the respective land use

limit were located in agricultural soils away from tailings and mainly in the residential/parks areas. For As, the Canadian guideline (12 mg/kg) is lower than the LQ (36 mg/kg), and As was quantified in only 15 of the 42 samples. Therefore, all soil samples in which As was quantified by XRF outranged the Canadian guideline. For the Brazilian guideline, the agricultural value was also lower than the LQ; thus, all agricultural samples quantified showed concentrations above the guideline. For residential/parks samples, the As Brazilian guideline was higher than the LQ, and less samples (17 %) were above the guideline.

As shown in Table 5, for every metal and soil type studied, the Canadian guideline had a higher (or equal) percentage of samples outranging the guideline, compared to the Brazilian guideline. This is because the Canadian guideline has lower guideline values, or is a more conservative limit. This makes evident the need to define an appropriate guideline for Chilean soils.

Due to traffic and industrial atmospheric emissions, urban soils may receive higher metal loads than rural or agricultural soils (Massas et al. 2010). Other studies have grouped Cu, Pb and Zn in one cluster linked to anthropogenic sources (Manta et al. 2002; Imperato et al. 2003; Moller et al. 2005), as it appears to be the case of Pb and Zn observed in this study. Nonetheless, the proximity of many tailings and the prevalence of wind-driven dispersion can be considered as key factors in the occurrence of metals in Copiapó, particularly for Cu in soils of urban and peri-urban sites.

Metals in street dust samples

There are no established guidelines of metal concentrations for street dusts. Thus, Table 5 compares street

dust concentrations to residential guideline values for soils (Table 4). Some street dust samples widely exceeded the Canadian limit for residential soil for Cu, Pb and Zn. For Pb, the mean value was below the Canadian guideline, while only 7 % of the samples exceeded the Pb guideline. On the other hand, Cu and Zn had higher mean values when compared to the Canadian guideline, and for Cu, all 71 samples exceeded the soil guideline. The large Cu concentrations in street dusts could be attributed to the presence of Cu tailings in the area and the current and past atmospheric emissions from the local Cu refinery. The effect of these sources may be enhanced by the low mean annual rainfall (18 mm/year). Other studies have linked high Cu, Pb and Zn in street dust samples to corrosion and abrasion of vehicles parts such as brake linings (e.g., Massas et al. 2010). Regarding As, the LQ (36 mg/kg) is higher than the Canadian guideline (12 mg/kg), causing the same scenario found for the comparison of soil samples; but in this case, only 13 % of street dust samples showed concentrations higher than the LQ and thus outranged the guideline. For the comparison with the Brazilian guidelines, samples hardly exceeded the guideline, except for Cu, for which 37 % of the street dust samples were above that limit, while the mean concentration (690 mg/kg) was also above the Brazilian guideline (400 mg/kg).

Street dust samples showed higher Co, Cu, Fe, Pb and Zn concentrations compared to soil samples (Table 3), particularly for Cu. The average concentration of Cu in street dust samples was about 690 mg/kg, compared to an average of 275 mg/kg for soil samples, while the maximum Cu concentration (10,224 mg/kg) was about 5 times higher than the

maximum obtained for soils samples (2116 mg/kg). It has been observed that fine particles in dust contain higher metal concentrations due to their high specific surface area (Wang et al. 2006). Several studies have also shown that as the particle size decreases, metal concentrations increase (e.g., Al-Rajahi et al. 1996; Ljung et al. 2006). In this study, Cu smelting emissions and wind-driven dust from tailings could enrich the fine fraction of dust. Another factor that could explain high Cu concentrations in street dusts is the higher levels of OM concentrations compared to the other sample types; indeed, Cu has a strong affinity with OM, which could result in the observed metal enrichment.

Metals in tailings

For tailings, the value of upper confidence limit 95 % (UCL 95 %) for metal concentrations was calculated, based on US EPA (2002) guidelines, and used for comparison with other tailings from Copiapó reported by Soublette et al. (2011), while the comparison with the Canadian and Brazilian guidelines was performed for the industrial land use. This comparison was made because mining operations and liabilities are normally considered as industrial sites, but according to the Copiapó city master plan, most of the tailings are scattered within the residential and agricultural zones, mainly near the riverbed and the hillsides surrounding the city (Fig. 1).

The values of UCL 95 % and the range of metal concentrations measured by XRF are displayed in Table 6 for the Porvenir tailing and the 8 other tailings sampled in this study, shown as a group. Results on metal concentrations measured by ICP-OES for 4 other tailings (Castellón, San Juan, Tania and Llaucavén) reported by Soublette et al. (2011) are also shown in Table 6.

The tailings showed large differences in their composition; in particular, the Llaucavén tailing had the highest UCL 95 % values for As (138 mg/kg), Cu (6903 mg/kg) and Pb (321 mg/kg). Arsenic could not be quantified in some tailings, but all tailing samples where As was quantified exceeded the Canadian guideline for industrial soils (12 mg/kg, Table 4). Co, Cu, Fe and Mn were quantified in a large majority of the tailing samples analyzed in this study, while Pb and Zn were only quantified in about half of the samples (Table 1). For Cu, every sample exceeded the Canadian guideline, with concentrations over 24 times

higher than the guideline value of 91 mg/kg. On the other hand, for Co and Pb, all tailings showed concentrations below the Canadian guideline for industrial soils (300 and 600 mg/kg, respectively). Metal concentrations in tailings measured with XRF in this study (Porvenir and Other tailings) showed the highest Fe and Mn concentrations, probably because of a systematic difference of XRF measurements with the ICP-OES method used for the 4 tailings reported by Soublette et al. (2011). For Zn, only one tailing (Porvenir) exceeded the Canadian guideline of 360 mg/kg, with a UCL 95 % concentration of 1023 mg/kg. When compared to the Brazilian guidelines for industrial soils, only two elements showed higher concentrations: Cu and Co. For Cu, every tailing exceeded the guideline, which is more than 6 times higher than the Canadian guideline. For Co, two tailings (Porvenir and San Juan) showed higher concentrations than the Brazilian guideline (90 mg/kg), unlike the comparison with the Canadian guideline, which has a higher value (300 mg/kg).

The large variation in elemental concentrations observed across tailings suggests diverse ore compositions, mineral extraction and/or leftover rock treatment before waste disposal. All tailings exhibited very high concentrations of Cu (UCL 95 % between 1200 and 6900 mg/kg), suggesting that inefficient methods were used at the time of ore processing. Large residual concentrations of Cu in the tailings hint a possibility of reprocessing depending on the market outlook. The high Fe concentrations (UCL 95 % of 52,000–444,000 mg/kg) represent the main component of the leftover rock.

In Chile, there are no soil quality guidelines, while comparison with international standards raises concerns due to dissimilar values and different contexts of application. Generating guideline values that consider background concentrations that naturally occur in different areas of the country is a challenge that should be addressed urgently. Furthermore, having tailings adjacent or immersed in residential areas is a source of additional difficulties regarding which guideline should be used for comparison of contamination level and risk assessment.

Geochemical mapping

The spatial analysis of the metal distribution in street dusts showed enrichment of metals in different areas

Table 6 Summary of metal concentration in Porvenir tailing and 8 other tailings (this study) and 4 other tailings studied by Soubllette et al. (2011), in mg/kg (dry weight)

	Porvenir ^a	Other tailings ^a	Castellón	San Juan	Tania	Llaucavén
As	76.5 (<36–543)	123 (<36–400)	^b (<1.2–31.6)	^b (<1.2–4.5)	87.2 (<1.2–102.1)	138 (<1.2–166.4)
Co	144 (17–345)	71.1 (<12–181)	55.8 (23.8–75.2)	168.8 (23.1–274.2)	44.9 (14–49.9)	49.7 (9.2–97.6)
Cu	2163 (90–10,002)	3500 (88–8026)	3095 (582.7–4901)	1190 (323.7–1592)	3126 (1754–3579)	6903 (441.7–15,219)
Fe	443,858 (38,317–872,296)	206,058 (<35,000–591,364)	52,173 (20,029–63,480)	95,951 (51,536–131,020)	87,089 (47,086–107,941)	86,449 (4351–156,402)
Mn	2286 (<276–6604)	3198 (<276–14,265)	579.8 (319.7–708.1)	538.7 (98.7–684.9)	1644 (625–2228)	261.6 (90.1–388.1)
Pb	85.2 (<22–577)	137 (<22–645)	14.1 (1.2–22.3)	133.1 (1.4–204.4)	97 (17.5–150.6)	321.1 (1.9–940)
Zn	1023 (<103–4190)	306 (<103–1040)	56.5 (0.3–68.5)	76.7 (7.6–124.7)	338.6 (84.6–450.8)	113.4 (16.1–241.9)

The values correspond to the upper confidence limit 95 % (UCL 95 %) and range (maximum and minimum values)

^a Metal concentrations in samples collected in Porvenir (*n* = 30) and other tailings (8 tailings, *n* = 38) were measured by XRF in this study, while metals in the other 4 tailings were measured by ICP-OES

^b More than 50 % of the samples were below the detection limit

of the city, which can be related to the proximity of tailings and the copper smelter. For Cu, Fe and Co, a similar distribution was found (as illustrated for Cu in Fig. 2a). Higher concentrations were predominant in the southeastern agricultural area and the southwestern industrial area. These areas are located near tailings and the copper refinery. For Fe and Co, there was also a slight enrichment in the northwestern area, which is categorized as industrial (Fig. 1). As opposed to this distribution, Pb and Zn (Figs. 2b, 3a) showed enrichment in the northwestern industrial area, with some differences between those two metals: An enrichment of Pb was also found in downtown Copiapó, while an enrichment of Zn was observed in the southwestern and industrial areas. This is consistent with the common association of these two metals with traffic and industrial emissions (Massas et al. 2010). For Mn (Fig. 3b), a different distribution was found, with enrichment in the southern end of the city area.

XRD analyses

Major XRD crystalline phases identified in 25 soils and street dust samples usually included quartz,

feldspars, phyllosilicates and calcite, while some samples also contained halite, magnetite, gypsum and siderite. XRD analyses of 27 samples from abandoned tailings also included the major phases found in soils and street dusts, plus a more diverse range of other crystalline phases, such as olivine, hematite, andradite, nantokite and pargasite. Sulfide phases were not detected in significant amounts. Furthermore, the prevalent detection of calcite in soils, dusts and tailings along with the arid conditions of Copiapó resulted in a lower potential for the generation of acid mine drainage conditions and transfer of contaminants to the aqueous phase.

Conclusions and perspectives

A first geochemical screening was conducted for Copiapó, a city that serves as a model of mining, aridity and unplanned urban growth. This overview of metal contamination was conducted for three different matrices: soils, street dusts and tailings. The comparison of soil concentrations with international guidelines showed that the guidelines were exceeded for some metals, especially for Cu, for which the

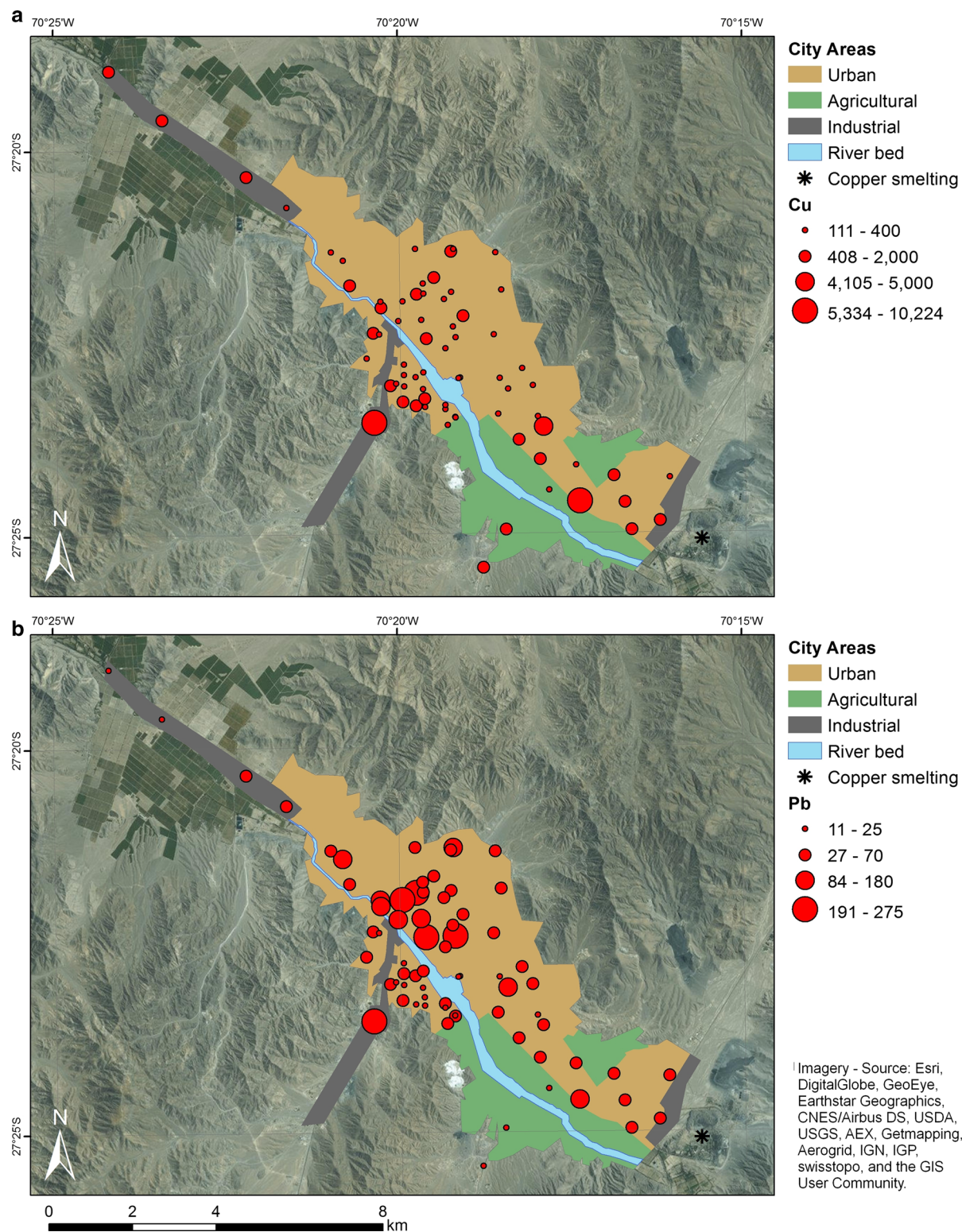


Fig. 2 Distribution of metal concentration obtained with XRF for street dust samples in the city of Copiapó, for **a** Cu and **b** Pb, in mg/kg (dry weight)

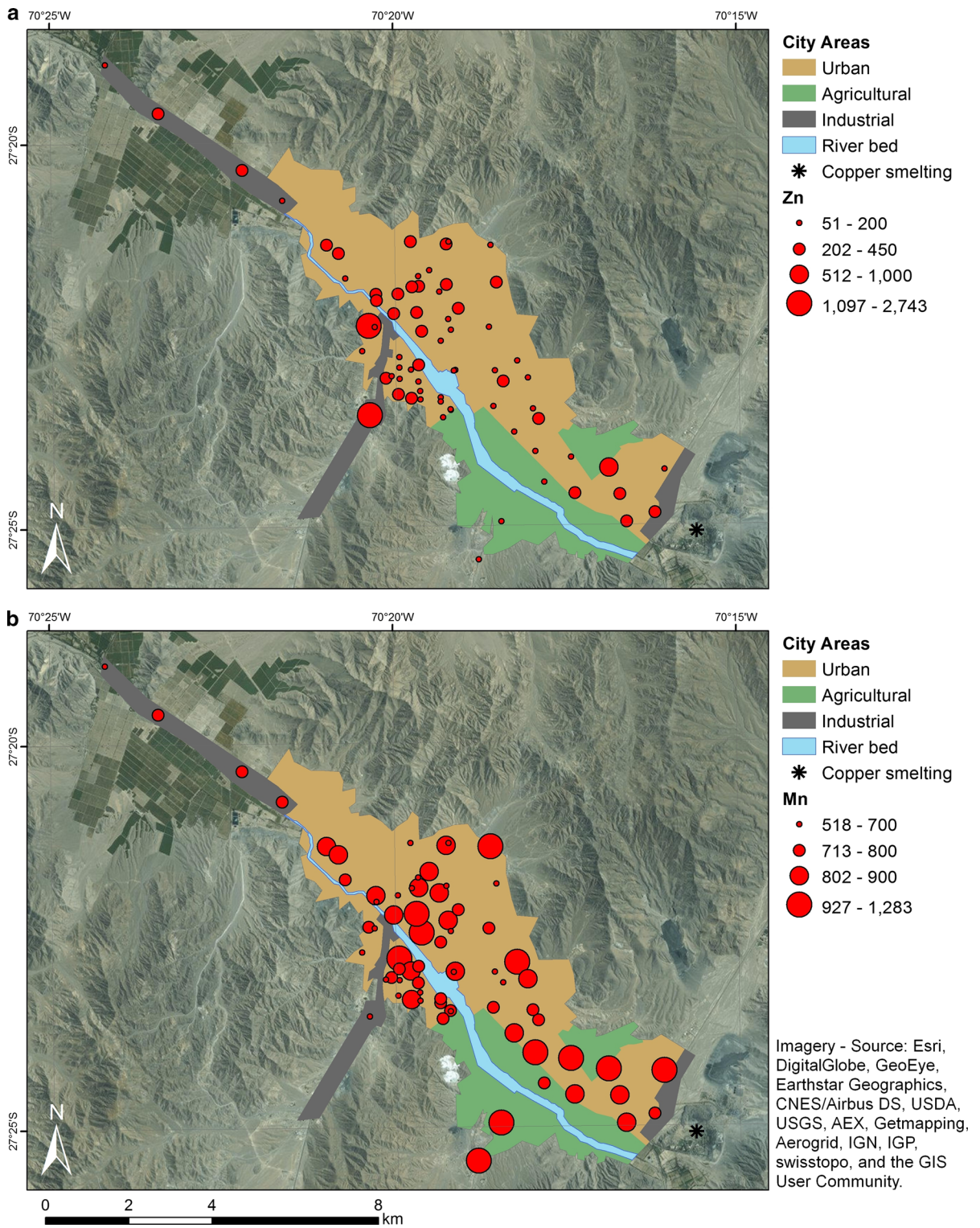


Fig. 3 Distribution of metal concentration obtained with XRF for street dust samples in the city of Copiapó, for **a** Zn and **b** Mn, in mg/kg (dry weight)

Canadian guideline was exceeded in all soil samples. Fewer samples exceeded the guidelines for As, Pb and Zn, while no sample exceeded the guidelines for Co. Although these guidelines are intended for comparing with soils, street dust samples were compared with the residential guidelines as a reference. This comparison also showed that Cu concentrations in street dust samples often exceeded the limits, as well as concentrations of As, Pb and Zn in some samples.

Metal concentrations of street dust samples were mapped to identify areas of metal enrichment or hot spots, as street dust samples were collected over a 1-km² grid throughout the city. Enrichment areas were found in the proximity of tailings and a copper smelter, especially for Cu, Fe and Co in street dusts. Areas of Zn and Pb enrichment were also identified, although these metals showed a different spatial distribution pattern compared to Cu. High concentrations of Zn and Pb were observed in the industrial area (probably due to industrial emissions) and downtown Copiapó. Some areas of lower metal enrichment were also identified, which might constitute possible candidates for future residential developments.

Tailings located within and near the city are an important potential source of metal contamination, as higher maximums of metal concentrations were found in the tailings compared to soil or street dust samples for every metal except Cu, for which street dust samples showed higher maximums. However, XRD analyses showed a prevalent detection of calcite resulting in a lower potential for the generation of acid mine drainage conditions. Wind-driven transport and aridity are likely key factors controlling the occurrence and distribution of these contaminants in the area.

As perspectives of this study, finding innovative engineering solutions and cost-effective alternatives to pollution and dispersion of metals from abandoned urban tailings is a critical challenge for Copiapó, for reducing potential health threats. Control technologies could include cover or encapsulation (dry in situ stabilization or geomembrane coverage), toxicity and mobility reduction (e.g., soil amendment or phytoremediation), and tailing reprocessing for Cu extraction. Phyto-based technologies should be critically scrutinized and tested before being adopted, considering the low OM content in tailings and water scarcity intensified by urban, mining and agriculture consumption. Reprocessing also needs a careful evaluation of

the conditions that would make it technically and economically feasible; the high concentration of Cu in some tailings could render reprocessing as an attractive remediation alternative.

Further studies are still needed as more than 30 tailings are located in the Copiapó urban and peri-urban area and can act as a source of contaminants, but they have not been studied completely. This study prompts confirmatory sampling and an analytical effort with a denser grid in areas of high metal enrichment. Additional studies are also needed for sites far from pollution sources to determine naturally occurring background levels. This screening sets the basis for future risk assessments toward defining knowledge-based policies and urban planning. City planners and regulators, together with scientists, need to consider the dynamics of pollutant occurrence, dispersion and exposure pathways to improve urban planning and minimize the risks to human health in Copiapó.

Besides confirmatory sampling and more analytical efforts, challenges include developing (1) adequate intervention guideline values, (2) appropriate background levels for key metals, (3) urban planning that considers contaminated areas, (4) cost-effective control strategies for abandoned tailings in water-scarce areas and (5) scenarios and technologies for tailing reprocessing. Assessing urban geochemical risks is a critical endeavor for areas where extreme events triggered by climate change are likely, as the mud flooding that impacted Copiapó in late March 2015.

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