Abandoned tailings deposits, acid drainage and alluvial sediments geochemistry, in the arid Elqui River Basin, North-Central Chile

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Abstract

Two major pollutant sources related to hydrothermal ore deposits and mining operations exist in the Elqui river basin, Chile: (a) acid drainage from Andean epithermal El Indio Au–Ag–Cu–As district and nearby hydrothermal alteration zones, and (b) diffuse sediment dispersion from abandoned tailings deposits in usually dry creeks in the western belt of the basin. This work analyses the contribution of both sources to the current metal contents of the fine grained sediments of the rivers and creeks of the Elqui basin, including a group of chemical elements and data analysis techniques not considered in previous works carried out in the area. Analysis of “active sediments” (i.e., sediments in permanent contact with surface water) in the main channel and tributaries of the Elqui river reveals that both pollutant sources contribute to their exceptionally high Cu contents (between 0.1 and 0.2% in the minus 60 mesh fraction). However, As pollution (0.03%) is mainly derived from the El Indio district. Potentially toxic heavy metals (notably Cd, Pb, Hg and Mo) are present in low concentrations and do not represent major threats to ecology or human health. Nevertheless, ongoing erosion of abandoned tailings deposits may result in soil contamination and thus be detrimental to the export-oriented agriculture of the Elqui basin. Consequently, remediation of that source should be prioritized.

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1. Introduction

Metallic mining in Chile, mainly for Ag, Cu and Au, thrived in the 1830s, after the establishment of independence from the Spanish Crown in 1818. In the Elqui river basin, located in the Coquimbo region, north-central Chile, the remains of 19th century mining include scattered slags (from the process of smelting sulfide minerals) and piles of low-grade or barren rocks near old Cu and Ag mines, with normally low contents of toxic metals like As and Cd and barely affected by leaching processes due to the dominant arid climate (Oyarzún, 2001). The introduction of the flotation process around 1908 (Valenzuela, 2005) to-gether with the uptake of the “trapiche” or Chilean mill (originally used for wheat grinding in Europe), allowed a significant expansion of Cu and Cu–Au mining to exploit lower grade sulfide minerals. The trapiche was a relatively cheap and easy to install and operate device, which permitted amalgamation of gold while the sulfide minerals were dressed for the flotation stage. As mining expanded and the number of mines multiplied, a large number of tailing deposits were left behind in many places on the alluvial plains of the rivers and creeks throughout the whole basin. This occurred in practice with almost no regulation at all, and started to change only after the Environmental law was enacted in Chile in 1994 (De la Maza, 2001; Newbold, 2006).

Much of this material has been already eroded during the episodic winter floods affecting rivers and normally dry creeks. However, over a hundred deposits still remain and are a potential source of pollution in the Elqui basin. Moreover, this diffuse contamination coexists with Cu, Zn and As rich acid drainage from the El Indio Au–Cu–As district located at the NE heads of the basin and other minor Andean sources.

In the early 1970s El Indio, an extremely high grade Au–Cu–As district (Jannas et al., 1999) was discovered. The main deposit was mined for some 25 years and began its closure activities in 2000. A preliminary geochemical sampling performed by Oyarzún et al. (2003) revealed extremely high contents of Cu (over 0.1%), Zn (around 0.05%) and As (0.02%), in fine grained sediments contaminated by acid drainage. This was followed by a second study that confirmed the previous figures. Also a gypsum-rich bed, dated to ca. 9640 ± 40 years and containing abundant Cu, Zn and As (up to 1.6, 14.7 and 2.3%) was discovered in

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the Turbio river valley, the Andean tributary connecting the Toro and Elqui rivers. This probably represents the remnant of a temporary lake bed, and records old, natural acid drainage generation from El Indio (Oyarzun et al., 2004).

However, in addition to this natural polluting source, Oyarzun et al. (2006) also documented a significant increase in the Cu and As total contents of the Toro river water (i.e., 5.6 and 0.8 mg/L), the direct receptor of the district drainage, since the very beginning of full scale mining operations at the district. The well designed and carefully executed closure plan of El Indio was effective in reducing (at least temporarily) the As content of the Toro river drainage. However, neither water acidity nor its Cu content was reduced. Moreover, they have even shown some slight increasing trends lately, to judge from monitoring data of the Chilean water authority (Espejo et al., in press; Galleguillos et al., 2008). This fact is explained by the unfavorable environmental context of the district, i.e., highly altered and fractured rocks, hosting high sulfur minerals in an underground mine with some 100 km of tunnels and a high hydraulic gradient (Oyarzun et al., 2007). Nevertheless, the Puclaro irrigation dam, built in year 2000 on the Elqui river course, has performed as an effective sink for As, Cu, and Fe total contents of the river water (Galleguillos et al., 2008). Thus, although no major mining-agricultural conflicts for water resources availability exist in the Elqui river basin, water pollution is a source of concern for the farmers, in particular the contamination of agricultural lands by tailings materials transported via the irrigation channels (Oyarzún and Oyarzún, 2011).

Within this framework, this work analyses the contribution of both sources (i.e., diffuse contamination from Cu, Zn and As rich acid drainage from El Indio and scattered tailings deposits) to the metal contents of the fine grained sediments of the rivers and creeks of the Elqui basin. These two sources contribute under very distinct conditions of relief and climate, but are spatially closed and act within the same basin, where mining and modern agriculture coexist and that is representative of the arid belt of the Central Andes. Furthermore, the current research included a group of chemical elements and data analysis techniques not considered in previous works.

2. Material and methods

2.1. Study area

2.1.1. Geography, climate, hydrology and main water users of the basin

The Elqui basin is located between latitudes 29° 20′ and 30° 27′ S, at the narrowest segment of the Chilean territory, limited by the highest Andean peaks (east) and the Pacific ocean (west), and subjected to arid conditions produced by the Pacific anticyclone. Just 130 km separate the head of the basin at the Andean peaks (attaining over 6000 m) from the river mouth on the Pacific coast (Fig. 1). Therefore, flow regimes in the basin’s rivers are turbulent, due to their steep bed slopes. In addition, they have a torrential regime, controlled by snowfall on the Andes occurring mainly during the winter months, from May to August (about 200–300 mm) followed by snow melting in spring-summer (mainly December–January). In consequence, the Elqui river flow is at a minimum during winter (some 5.5 m$^3$ s$^{-1}$) and peaks by the end of December (about 9.6 m$^3$ s$^{-1}$) (DGA, Cade-Idepe, 2004).

Fig. 1. Elqui river basin and active sediments sampling locations (*only sampled in 2007; **only sampled in 2008). T: Toro and Turbio rivers; C: Claro river; E: Elqui river; N: Los Negritos creek; A: El Arrayan creek.
Structurally, the Elqui basin is underlain by two main tectonic and morphological blocks of similar width, separated by a major N–S, east dipping thrust fault near longitude 70°40′W. The western block attains some 2000 m altitude at its Eastern limit and progressively decreases to some 500 m at 20 km from the coast. In this part of the basin, precipitation falls as rain during the winter season. However, the mean annual precipitation value is meager (about 80 mm) except during El Niño (ENSO Cycle) episodes, separated by 5 to 10 years (DGA, Cade-Iinde, 2004). The eastern block corresponds to the mountain heights of the Andes that attain over 6000 m. The distribution of atmospheric precipitations (mainly as snow) is highly variable in this block, and few meteorological stations exist. However, it is estimated between 200 and 300 mm year⁻¹ in average.

The major part of the Elqui basin surface is made up of hard rock mountain massifs, and only 0.24% of its 9645 km² is used for agricultural purposes (that require both suitable land and water resources). Two dams exist, both for irrigation purposes: La Laguna, on the mountain river of the same name, with a capacity of 40 million cubic meters (M m³) and the larger Puclaro dam (200 M m³) in the middle reach of the Elqui river, located on the western tectonic block of the basin, some 50 km from the coast. In addition to the agricultural, agro-industrial and mining sectors, the Elqui river system provides drinking water to some 300,000 residents, 250,000 of them in the coastal cities of La Serena and Coquimbo, 24,000 inhabitants in the inland city of Vicuña (next to the river, at the eastern limit of the western block), and about 4200 persons living in 13 small villages (INE, 2002). The latter are supplied with tap water by local committees, which mainly withdraw water from shallow wells placed close to the streams.

2.1.2. Geology, ore deposits, and mining

The Elqui river basin exhibits geological traits and metallic belts that are characteristic of the 27° S–33° S tectonic segment of the Andean belt (Sillitoe, 1974). They include: a) dominant presence of intrusive, extrusive and volcaniclastic rocks of calc-alkalic affinities, a consequence of the oceanic tectonic plate subduction under the South American plate since Upper Paleozoic times (Charrier et al., 2007; Oyarzún, 2000); b) a series of Mesozoic–Cenozoic intrusive...
and volcanic rocks in N–S belts that become progressively younger eastward; c) strong faulting, with normal faults dominant in the western block and thrust faults in the eastern one (e.g., the Vicuña E-dipping thrust fault, that lifts up the eastern, Andean block of the Elqui basin); d) the absence of a N–S tectonic valley and of Quaternary volcanic activity, both traits being present north and south of this tectonic segment; and e) the presence of several N–S metallic belts, approximately coincident with the magmatic belts. Between 29°20′S and 30°27′S they include: Kiruna-type Fe, Cu–Fe–Au and Cu–Au deposits in the coastal belt; vein, “manto” type and

![Fig. 3. Frequency distributions for active sediments in 2007 (Panel A) and 2008 (Panel B).]
porphyry type Cu deposits, vein Ag and Au deposits and stratiform Mn ores in the central part of the basin, and Au–Ag–Cu–As deposits in the Andean tectonic block, close to the border with Argentina.

Current extractive activities include iron mining in the El Romeral Kiruna type deposit (magnetite, minor apatite and pyrite), some 21 km northeast of the city of La Serena and the Elqui river mouth, but outside the Elqui watershed boundaries (Oyarzun et al., 2003; Squeo et al., 2006). Copper is mined at the Santa Gracia (chalcopyrite and bornite) and Marquesa (chalcopyrite and bornite plus Mn minerals and minor Pb and As) creeks, but only the latter attains economic importance, due to the presence of the Talcuna Cu–Mn district, that has been mined since the 1880s (Boric, 1985). Ore deposits in the district crop out both at the Marquesa creek, as well as at its affluent the Las Cañas creek, and include vein type Cu and stratiform Cu and Mn deposits. The Cu ores contain unusual Pb as well as As, and are transitional to the Ag ores of the nearby Arqueros district (Oyarzun et al., 1998; Reyes, 1991). Current mining in the district is performed by three small to medium size companies that have a total production

![Fig. 4. Frequency distributions for non-active sediments (Panel C) and tailings deposits (Panel D).](image-url)
of some 40 t day\(^{-1}\) of copper concentrates, grading about 30% Cu and 800 g t\(^{-1}\) Ag. These operations generate some 1200 t day\(^{-1}\) of tailings materials. Although much of the tailings deposits accumulated by the mining operations of the district have been already eroded and partly incorporated to the Elqui river fluvial sediments (e.g., 2 M t of tailings materials were eroded by a flood in 1997), several M t still remain. Also, operational accidents have resulted in several spills, including the pollution of irrigation channels with 12,000 m\(^3\) of tailings materials in 2002 (Galleguillos, 2004).

In the Andacollo area (Oyarzún et al., 1996), Cu mining started in the 1950s. It was followed by a medium scale heap leaching operation, Carmen, that mined about 60 M t of supergene ore (0.8% grade) of a porphyry copper deposit, during the 1996–2011 period, and was recently expanded to mine about 400 M t of hypogene ore reserves (0.4% Cu) of the same deposit, at a rate of 60,000 t day\(^{-1}\). Its mineralogy includes chalcocite-pyrite plus supergene chalcocite with molibdenite and minor gold contents. Currently, Carmen is producing some 900 t day\(^{-1}\) of Cu concentrates (30% Cu) from its new operation plus 50 t of copper cathodes from the remaining of the supergene ores. The whole operation involves the accumulation of some 200 t day\(^{-1}\) of Cu concentrates (30% Cu) from its new operation plus 50 t of copper cathodes from the remaining of the supergene ores. The whole operation involves the accumulation of some 60,000 t day\(^{-1}\) of tailings materials. Besides, about 90 t of gold had already been mined from surrounding Au-deposits in the Andacollo district by 1996, when a medium scale operation began, which was active until 2006 at a rate of 16,000 t day\(^{-1}\), grading 0.7 g t\(^{-1}\) Au, and producing around 4 t year\(^{-1}\) of gold. Although mining has almost ceased, gold recovery from the heap leaching piles continues. These piles contain some 60 M t of processed materials. In addition, the Andacollo district is full of scattered tailings deposits generated by the small and artisanal mining activities.

Finally, the El Indio Au–Cu–As district (Au-minerals, Cu-sulfosalts), discovered in the early 1970s and mined for some 25 years until its closure in 2000, was famous for its exceptional Au grades (attaining over 200 g t\(^{-1}\) in the “direct shipping ores”). It contains complex high sulfidation enargite-pyrite and gold-quartz mineralization with alunite and a number of minor sulfophile metals like Zn, Sb, and Bi (Jannas et al., 1999). Also, Cu grades (about 5%) and As (contained in enargite) were high. The latter became the problematic side of the district, for the serious risk involved in term of occupational health and environment, as the rich ores needed to be roasted in order to eliminate the arsenic content, a process which gave rise to high air pollution. In addition to As pollution, drainage water in the district is contaminated by acid drainage rich in Cu, Zn, Fe and SO\(_4\), a consequence of oxidation of the highly sulfidic mineral paragenesis, but also enhanced by the extreme grade of advanced argillic alteration and fracturing that affect the igneous rocks of the district (Jannas et al., 1999). As previously stated, this contamination predated human activity, but was increased by the underground mining activities, and the closure operations performed in the district have not been entirely effective in stopping the acid drainage generation process (Galleguillos et al., 2008). Currently, the Vacas Heladas prospect at El Indio belt is assessed in order to start a heap-leaching operation by a joint venture international group.

### Table 1

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<tr>
<th>Metals</th>
<th>Cu</th>
<th>Mo</th>
<th>As</th>
<th>Pb</th>
<th>Zn</th>
<th>Cd</th>
<th>Hg</th>
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<td>39</td>
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<td>2</td>
<td>26</td>
<td>382</td>
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<td>0.12</td>
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<tr>
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<td>492</td>
<td>1.6</td>
<td>0.13</td>
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<td>95.9</td>
<td>1.3</td>
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<td>543</td>
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<td>125</td>
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<tr>
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<td>101</td>
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<td>141</td>
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<td>522</td>
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<td>112</td>
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<td>64</td>
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<td>13</td>
<td>84</td>
<td>10</td>
<td>516</td>
<td>2460</td>
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<td>320</td>
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<td>116</td>
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<td>Maximum</td>
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<td>13</td>
<td>578</td>
<td>63</td>
<td>426</td>
<td>4420</td>
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<td>4</td>
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<td>160</td>
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<td>0.39</td>
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<td>Average</td>
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<td>3.6</td>
<td>94</td>
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<td>SD</td>
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<td><strong>Worldwide average content of river sediments</strong></td>
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<td>Minimum</td>
<td>33</td>
<td>2</td>
<td>7.7</td>
<td>1.2</td>
<td>19</td>
<td>95</td>
<td>0.17</td>
<td>0.19</td>
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</table>

AS: active sediments; NAS: non-active sediments; TM: tailings material.
**Fig. 5.** Box plots diagrams for the nine studied elements.

**Fig. 6.** Intra-tailings deposit compositional variability (A: M-5; B: N-6; C: N-7; D: N-8; E: Q-9).
possible to analyze Sb, Cd, Mo, and Hg in the whole set of original samples due to the lack of enough material conserved after the first analytical procedure). The ICP-AES determinations of these four elements and sulfur were performed at the ALS Chemex Mineral Division Laboratory in Coquimbo, also using aqua regia sample digestion. Detection limits were 0.5 ppm for Cd; 0.01 ppm for Hg; 1 ppm for Mo; 2 ppm for Sb; 100 ppm for S. Standard QA/QC procedures (i.e., blanks and duplicates) were performed by the laboratory.

Data processing started with rather simple, standard statistical analysis methods (central tendency and dispersion parameters). In addition to the determination of ordinary statistical parameters, multivariate statistical methods were used. Given that some of the statistical techniques require normally distributed data (e.g., Thyne et al., 2004; Yidana et al., 2008) our analysis started with the Anderson-Darling and Ryan-Jones normality tests (MINITAB, 2008). Although parametric test suitable for not normal distributed data, was calculat- 
ed by the laboratory.

Data processing started with rather simple, standard statistical analysis methods (central tendency and dispersion parameters). In addition to the determination of ordinary statistical parameters, multivariate statistical methods were used. Given that some of the statistical techniques require normally distributed data (e.g., Thyne et al., 2004; Yidana et al., 2008) our analysis started with the Anderson-Darling and Ryan-Jones normality tests (MINITAB, 2008). Although the number of samples is rather low to establish definite conclusions, the majority of the distributions obtained may be assimilated to the lognormal type. Spearman's rho correlation coefficient, a non-parametric test suitable for not normal distributed data, was calculated (Kotegoda and Rosso, 2008) and a Q-mode hierarchical cluster analysis (HCA) was performed, on log-transformed and standardized, i.e., z-scale transformed variables, in order to avoid misclassification due to differences in data dimensionality (Chandra et al., 2006; Shrestha and Kazama, 2007), using MINITAB software. Ward linking method and Euclidean distance were used as measures of similarity, for they produce an efficient samples group classification (Güler et al., 2002; Thyne et al., 2004; Yidana et al., 2008). The clustering (i.e., linkage distance) was conducted following the Sneath's index of D_1/2/D_max < 2/3 (Astel et al., 2007; Shrestha and Kazama, 2007). This analysis was performed for the major four elements related to ore deposits in the basin which are also those presenting the higher contents in the samples analyzed: Cu, Zn, Pb, and As.

Table 3

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu</th>
<th>Mo</th>
<th>As</th>
<th>Sb</th>
<th>Pb</th>
<th>Zn</th>
<th>Cd</th>
<th>Hg</th>
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<td>S</td>
<td>0.07</td>
<td>0.30</td>
<td>0.18</td>
<td>0.35</td>
<td>0.37</td>
<td>0.06</td>
<td>0.20</td>
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Table 4

| Correlation coefficients for active sediments in 2008 (bold font indicates 0.05 significance). |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Cu   | Mo   | As   | Sb   | Pb   | Zn   | Cd   | Hg   |
| Mo   | 0.49 |     |     |     |     |     |     |
| As   | 0.61 | 0.64 |     |     |     |     |     |
| Sb   | 0.51 | 0.44 | 0.77 |     |     |     |     |
| Pb   | 0.27 | 0.41 | 0.12 | 0.04 |     |     |     |
| Zn   | 0.78 | 0.56 | 0.48 | 0.07 | 0.19 |     |     |
| Cd   | 0.69 | 0.52 | 0.39 | 0.05 | 0.02 | 0.87 |     |
| Hg   | 0.04 | 0.11 | 0.20 | 0.04 | 0.03 | 0.26 | 0.03 |
| S    | 0.23 | 0.41 | 0.33 | 0.44 | 0.65 | 0.56 | 0.10 | 0.01 | 0.16 |

Table 5

| Correlation coefficients for non-active sediments (bold font indicates 0.05 significance). |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Cu   | Mo   | As   | Sb   | Pb   | Zn   | Cd   | Hg   |
| Mo   | 0.67 |     |     |     |     |     |     |
| As   | 0.31 | 0.13 |     |     |     |     |     |
| Sb   | 0.68 | 0.34 | 0.42 |     |     |     |     |
| Pb   | 0.14 | 0.33 | 0.77 |     |     |     |     |
| Zn   | 0.63 | 0.28 | 0.79 | 0.61 | 0.56 |     |     |
| Cd   | 0.39 | 0.01 | 0.64 | 0.58 | 0.64 | 0.64 |     |
| Hg   | 0.78 | 0.71 | 0.18 | 0.53 | 0.16 | 0.55 | 0.14 |
| S    | 0.81 | 0.63 | 0.35 | 0.69 | 0.01 | 0.62 | 0.19 | 0.85 |

3. Results and discussion

3.1. General analysis of the data

Figs. 3 and 4 present the frequency distribution histograms for the concentrations of the nine elements in both types of sediments and tailings samples. For active sediments all the elements, except Pb in the spring samples and Sb in the autumn ones, present a log-normal aspect. This is also the case for all the elements in the non-active sediments and tailings samples.

Table 1 presents a general summary of the basic statistical parameters for the group of nine elements analyzed in sediments and tailings materials. Worldwide average figures for river sediments have been included for comparison purposes. This information is complemented with a graphic box-plot representation (Fig. 5). Of particular note are the unusually high Cu, Zn, and As contents, when compared to the worldwide averages, as well as to other rivers in the country (Segura et al., 2006). These results are also consistent with those of previous studies (Oyarzun et al., 2004, 2003).

For AS, they are mainly explained by the contributions of acid drainage from El Indio district and from neighbouring hydrothermal alteration zones, through the Toro–Turbio rivers, although the Inca- guazu river also contributes important Cu and Zn loads. A comparison of the average contents of the spring and autumn samples of active sediments shows that Cu, Zn and As, the main elements contained in acid drainage from El Indio district (Oyarzun et al., 2004, 2003), are higher in autumn, whereas the rest of the elements exhibit little difference. This fact may be explained considering that the autumn peak concentrations are a consequence of the oxidation and dissolution of sulfide minerals like enargite (Cu₃AsS₄) during the summer, when temperature is higher and liquid water is available.

The “Andean” metallic source is complemented by the contribution of the metallic districts of the western tectonic block through the dry creeks thattribute to the El Quin river and is intermediated by the tailings materials deposited on these creeks. In fact, due to the narrow alluvial plains of the dry creeks and to the abundant tailings material deposited on their surfaces, in particular on the Marquesa creek, their sediments are polluted to variable degrees and their metal contents reflect that of the tailings deposits. Except for the case of Andacollo, where different types of deposits coexist, the tailings materials are mineralogically and chemically homogeneous; likewise the ore bodies from which they come. This homogeneity is shown in Fig. 6, which represents the internal chemical variability in five tailings deposits (two or three composite samples were taken in each deposit).

A comparison of the relative enrichment of metals in both sources according to the data is presented in Table 2. Considering the average figures, AS compared to NAS are very enriched in As and Cd (by a 4 to 9 fold factor), and richer in Cu and Zn (a factor of 1 to 3), but have less
Pb, Hg, Mo, and S. If the medians are considered, the observed enrichment in As, Cd, Cu, and Zn is enhanced. The enrichment in Pb and Mo is only moderate, while S is higher in the AS. Comparing the average metal contents of TM and NAS samples, the former are highly enriched in As and Cd (3 to 5 fold), fairly enriched in Cu, Zn, Pb, Sb, and Hg (1 to 2 fold), but contain less Mo. However, taking into account the fact that the data approach the log normal distributions, the comparison of the medians is more illustrative. Thus, when they are considered, the relations for Cu, Pb, As, Sb, and Hg stand. In exchange, Zn and Pb exhibit similar contents in both types of samples, and Mo and S are higher in TM samples. Finally, the comparison of AS and TM samples is particularly important, as they represent the two principal sources of metalic pollution: the “Andean” El Indio district and the tailings materials of the western tectonic block, respectively. Comparison of averages indicates that active sediments are more enriched in Cu, As, and Cd, but less enriched in Pb, Sb, Hg, Mo, and S, but have a similar Zn content. Comparison of medians maintains the ratio for Cu, increases the enrichment in As, Sb, and Cd, and incorporates Zn into the group. On the other hand, the lower contents of Sb, Hg, Mo, and S in active sediments are maintained, indicating that these elements are mainly contributed by the tailings materials.

Among the Spearman’s rho coefficients presented on Tables 3 to 6, highlight the following results (over 0.7): 1. – active sediments, (a) spring campaign: Cu–Zn; autumn campaign: Cu–Zn, As–Sb, Zn–Cd; 2. – non active sediments: Cu–Hg, Cu–S, Zn–As, Pb–As, Pb–S, Mo–Hg; and 3. – tailing materials: Pb–As, Zn–Cd, and Pb–Cd. These results are also consistent with the participation of two principal metallic sources. The principal one is the El Indio enargitic Cu–Au–As mineralization district (Jannas et al., 1999), which contributes Cu, Zn, As, Sb, and Cd. This source is dominant in the active sediments, in particular in those of the autumn campaign, for the reasons stated before (i.e. active ore mineral weathering during summer). The second source is the Talcuna Cu (Mn) district in Marquesa creek (Oyarzun et al., 1998), where the Cu ore minerals present a polymetallic affinity, expressed in higher Pb contents, a metal also related to As in this district. The possibility of metal dispersion in the Talcuna district due to acid drainage is hampered both by the dry conditions prevailing in the western block and the low sulfur/metal ratios of this district. Therefore, the metallic contents exhibited by the non active sediments of the dry creeks is mainly due to the polluting effect of mobilization of the tailings deposits located on its normally dry alluvial plains, either by wind erosion or by episodic rains (related to the ENSO cycles). The contribution of these creeks is high in Cu, and in the case of Marquesa, also high in Pb and Zn, but moderate to low in As. Regarding Sb, Cd, Hg and Mo contents, they are moderate in the basin, although some high values for Hg and Mo appear in dry creeks sediments and tailings samples. A third minor source, expressed by the correlation coefficient, corresponds to the tailing deposits generated by low tonnage gold mining operations in the Arrayán and Negritos creeks, that produce higher Mo and Hg contents (the latter due to Hg used in gold amalgamation). The negative Cu–Hg and Cu–S correlations are particularly interesting, and could be explained by the Cu-poor characteristic of these gold deposits, that are, in contrast, rich in pyrite (FeS2). As a consequence, its tailings deposits exhibit a positive correlation of Hg with S (the latter, contained in pyrite) but a negative one of both elements with Cu.

The cluster analysis performed for the active sediments of both campaigns revealed the presence of two principal groups (Fig. 7). One of them gathers samples with low to moderate metals contents, mainly from the Claro river and from the lower part of the Elqui river, downstream the Puclaro dam. The other group mainly includes samples of the Turbio river and Elqui river (for the latter, upstream of the Puclaro dam). For non-active sediments and tailings samples, the cluster analysis also defines two major groups (Fig. 8). A first one mainly comprises sediments from the Marquesa creek, with a component of tailings from the Marquesa, Talca and Arrayán creeks. The second group includes non active sediments and tailings samples of the Santa Gracia and Arrayán creeks and by samples presenting lower metallic contents of Marquesa creek.

3.2. Geochemical traits of the rivers and creeks

The average and median metallic and sulfur contents for AS, NAS and TM samples in each of the rivers and creeks sampled in the current study are presented in Table 7. Also, the average pH of water in contact with AS is indicated. Special mention is merited by the following issues:

The Toro river AS samples, which are the most directly affected by acid drainage from El Indio district, exhibit relatively low Cu, Zn and Cd contents, a fact that contrasts with the high Cu and Zn water content of this river water (Oyarzun et al., 2006, 2003). This apparent contradiction is explained by the fact that the low pH of water favors
the presence of these elements under its ionic, soluble forms, preventing their transference to the fine grained sediments. In contrast, as most As is mobilized under a non ionic form (like As$_2$O$_3$), which is incorporated to the alluvial sediments at low pH, it therefore, attains its highest contents in the Toro river sediments.

The La Laguna river sediments present low Cu contents and moderate concentrations of the rest of the elements. In this case, low Cu is not a consequence of pH (7.6), but of the ore mineralogy of this sub basin.

There are extremely high Cu and Zn contents of the Turbio river sediments, as a consequence of the mixing of the Toro and La Laguna flows, resulting in neutral to slightly basic water pH, producing hydrolysis, precipitation and transference of both metals to the fine sediments. In contrast, As and Pb attain an average content between those of both conglomerates.

The extremely high Zn and high Cd contents of the Incaguaz river sediments, together with high Cu and moderate As and Mo, are not explained by the present geological literature and could be of interest in terms of mining exploration opportunities. In contrast, the Claro river sediments present low contents of all the elements tested.

The Puclaro dam plays an important role as a sink for Cu, Zn and As, which decrease to about 1/4, 1/2 and 1/5 of those in the upper course of the Elqui river. This role had already been established by Galleguillos et al. (2008) for water quality, but not until now in relation to sediments. Other elements are less affected or even increase in the lower course. This is the case for Pb and Hg, as a consequence of the inputs of the dry creeks (Marquesa and Los Negritos-El Arrayan, respectively) to the Elqui river sediments.

There is a striking similarity of the average Cu, Zn, Pb, As and Sb contents of NAS and TM of the Marquesa creek. It is not possible to explain this similarity in terms of lithogeochemical reasons: this sub basin is dominated by andesitic rock outcrops which have only moderate (Cu, Zn) to low (Pb, As, Sb) concentrations of these elements. In addition, as stated before, acid drainage is not generated at the Talavera district, due to mineralogical and hydrological conditions. Therefore, the only reasonable explanation is the incorporation of

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tailings materials to the alluvial sediments of the creek, a well documented process, as stated previously.

For the Santa Gracia creek, no significant incorporation of tailings materials to the alluvial sediments could be established on the basis of geochemical data. This fact may be explained both by the wider alluvial plain of this creek and by the comparatively minor mining activity developed in the area, in comparison with that of the Marquesa creek. The different geochemical patterns of the Marquesa and Santa Gracia creeks also include the high positive correlation coefficient between Cu–Zn (0.94), Cu–Pb (0.94) and Pb–Zn (0.83) of the Marquesa creeks sediments (that points to a single source, i.e., the tailings materials). In contrast, those of Santa Gracia exhibit a good Pb-Zn correlation (0.5), but a negative one of both elements with Cu (−1.0 and −0.5, respectively), suggesting the possible influence of two types of ore minerals.

The Arrayán creek connects the Elqui basin with the Andacollo sub basin, some 20 km southward, through the Los Negritos creek, offering the opportunity to sediments and tailings materials from Andacollo to be transported under the exceptional floods, occurring a few times each century. Abandoned tailings deposits are abundant in the Los Negritos creek, and sediments of El Arrayán creek are high in Cu and have moderate enrichment in Mo, Hg and S.

Finally, alluvial sediments of Los Negritos creek have in average three times the Cu content of the tailings materials sampled in the area (Andacollo). However, the latter have two times the Cd and four times the Zn and As contents of the sediments (an illustration of the mineralogical diversity of the Andacollo district).

4. Conclusions

Considering the tailings materials from the Andacollo sub basin, the Marquesa creek and the La Cantera basin in terms of the future wind erosion of these deposits.

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References


