

# Environmental assessment of copper–gold–mercury mining in the Andacollo and Punitaqui districts, northern Chile

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## Abstract

The Coquimbo region has been one of the richest producers of Cu, Au and Hg in Chile, and some of the deposits have been mined almost continuously since the 16th century. To assess the potential environmental contamination in this region, the authors measured the concentration of Cu, As, Cd, Zn and Hg in samples of stream and mine waters, stream sediments, soils, flotation tailings, and mine wastes in the Andacollo (Cu, Au, Hg) and Punitaqui (Cu–Au, Hg) districts. The concentration of Hg in the atmosphere in these districts were also measured. Although contamination is strongly controlled by the ore in each district, metal dispersion is modified by the degree of metallurgical processing efficiency as shown by the outdated Cu flotation system at Andacollo (stream sediments Cu 75–2200 µg/g). Conversely, more efficient procedures at Punitaqui resulted in less stream contamination, where stream sediments contained Cu ranging from 110–260 µg/g. However, efficient concentration by flotation of a given metal (e.g. Cu) may lead to the loss of another (e.g. Hg up to 190 µg/g in the tailings at Punitaqui), and therefore, to contamination via erosion of the tailings (downstream sediments Hg concentrations up to 5.3 µg/g). Continued use of Hg for Au amalgamation at Andacollo has led to significant contamination in stream sediments (0.2–3.8 µg/g Hg) and soils (2.4–47 µg/g Hg). Communities in this region are underdeveloped, and decades of inefficient treatment of flotation tailings and waste-rock stock piles has resulted in significant contamination of the surrounding landscape.

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## 1. Introduction

The Coquimbo region is located in the northern part of Chile and is one of the richest in terms of mineral

deposits and mining activity (Fig. 1). The mineral deposits are not only important in number or size, but also in terms of historical significance. Some of them have been almost continuously exploited for Cu, Au and Hg since the Spanish Colonial time (16th to 18th century), for example, Andacollo and Punitaqui (Fig. 1; Table 1). The Coquimbo region has a long record of mining-related environmental disturbances primarily as a result of runoff and downstream dispersion. Since the second

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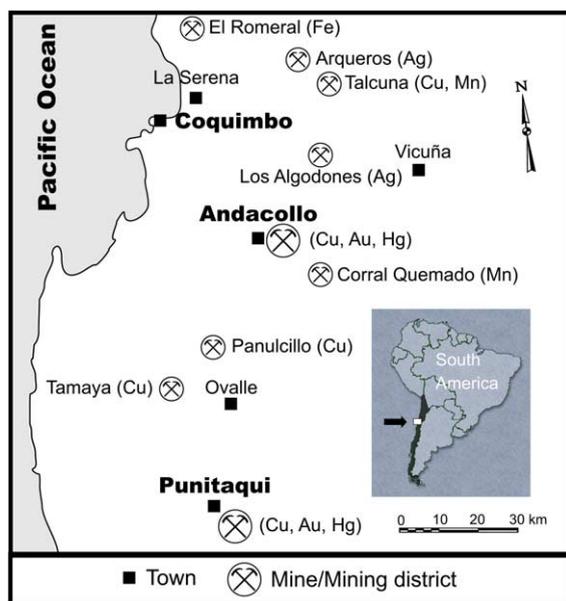


Fig. 1. The Andacollo and Punitaqui mining districts, and other important mining sites (past or present) in the Coquimbo region. See inset for location.

most important economic sector in this region is agriculture, mining-related contamination is important, particularly considering that mining and agriculture coexist in narrow strips of land flanked by mountain belts.

Similar to other South American countries (e.g. Brazil, Colombia, Venezuela), the mining operations have traditionally used metallic Hg for Au recovery. Since artisanal miners use crude, inefficient techniques, significant Hg escapes to the air and the surrounding environment (Hilson, 2000). For example, no more than 70% of the metallic Hg used in Au amalgamation at Andacollo is ever recovered, and therefore, part of it is lost to soil, water, and the atmosphere. Hard rock mining was introduced at Andacollo before the end of

the 16th century. The main technological innovation was the introduction of the water powered “trapiches” (Spanish for mill), or rock crushers similar to those used for wheat grinding, consisting of two massive milling stones mounted vertically on a horizontal axle, which turned on top of a circular stone (Cuadra and Dunkerley, 1991) (Table 1). An improved version of the old trapiches is presently used by the small-scale mining operations existing in the district. These modern, electricity-powered trapiches crush ore up to 10 cm in diameter, and leave a residue of 65% <200 mesh. The crushers are used for two purposes: (1) to crush ore for flotation of Cu sulfides; and (2) to recover Au (within the trapiche) on Cu plates which are covered by a thin film of Hg. In 1996–1997, two mining companies started operations at Andacollo (Table 1) (1) Carmen de Andacollo (a joint venture of Aur Resources Inc., Compañía Minera del Pacífico and Empresa Nacional de Minería), centered on the porphyry Cu deposit, and (2) Compañía Minera Dayton, a wholly owned subsidiary of Dayton Mining Corporation, that centered its operation on the exploitation of epithermal Au manto-type deposits. Both mines are of the open-pit type and leach piled ores. Given that these mines operate under environmental regulations, the study was centred on the old, heavily contaminated and traditional procedures used at Andacollo. Thus, this study is a ‘baseline’ geochemical survey of Andacollo, as it shows the type and extent of metal contamination induced by the older, traditional metallurgical process. Punitaqui is a different case, characterized by a long record of Hg production (late 1700s – late 1950s) from the Azogues deposit of the district (Table 1). Punitaqui was later mined for Cu and Au in the 1990s. At Punitaqui, the extent and origin of the potential contamination by Hg and Cu was evaluated. Although Andacollo and Punitaqui are some 80 km apart (Fig. 1), Hg produced at Punitaqui was probably used at Andacollo for Au recovery during the Spanish colonial time, and even later until Punitaqui ceased production of Hg.

Table 1  
Characteristics of the studied mining districts

| District           | Deposit type       | Production (total)       | Main ore            | Mining duration        | Ore processing           |
|--------------------|--------------------|--------------------------|---------------------|------------------------|--------------------------|
| <i>Andacollo</i>   |                    |                          |                     |                        |                          |
| Small mining       | Veins              | 100 t Au                 | Au, Cu <sup>a</sup> | 1575–present           | Trapiche milling         |
| Carmen             | Porphyry Cu        | 100,000 t Cu             | Cu                  | 1997–present           | Heap leaching            |
| Dayton             | Au epithermal      | 20 t Au                  | Au                  | 1996–2000 <sup>b</sup> | Heap leaching            |
| <i>Punitaqui</i>   |                    |                          |                     |                        |                          |
| Azogues            | Tension veins      | Unknown                  | Hg                  | 1785–1958              | Unknown                  |
| Milagro/Los Mantos | Shear-zone related | 50,000 t Cu <sup>c</sup> | Cu–Au               | 1994–1998              | Flotation, heap leaching |

<sup>a</sup> Cu extraction began in the 19th century.

<sup>b</sup> Although the mine closed in 2000, the heap leaching operation continues.

<sup>c</sup> Total Au production in 1996 reached 780 kg.

## 2. General environmental setting

The Coquimbo region is characterized by a mountainous landscape and a semi-arid climate. Except for a discontinuous coastal narrow belt, the region is dominated by E–W oriented valleys (the “*Valles Transversales*” system), which flow from the Andean mountains to the coast. The main valleys are flanked by mountain belts of about 50 km wide and altitudes of 600 to 1000 m above sea level. The climate is strongly conditioned by the Pacific anticyclone and the region has a transitional climate between that of the northern Atacama Desert and the more humid central part of Chile (Mediterranean climate). The average temperature on the coast is 14 °C, which increases towards the interior to 16 °C. The average precipitation along the coast is about of 126 and about 131 mm/a in the interior. However, this region is characterized by strong annual variations induced by the influence of the Westerly winds (Veit, 1996) that correlate with El Niño years, which bring intense rains and subsequent floods. Numerous tailings deposits studied here are subjected to weathering, erosion, and flash flooding. For example, the local streams of Andacollo and Punitaqui have an intermittent character, behaving as the Spanish

“ramblas”, which are dry most of the year, but behave as high-flow torrents during periods of strong rain.

## 3. Geologic background, mineral deposits, and ore mineralogy

The geology of the studied area is dominated by Lower Cretaceous volcanic and sedimentary rocks of the Estratos del Reloj, Arqueros and Quebrada Marquesa Formations. These rocks were intruded by granitoids (Coastal Batholith) during the Middle Cretaceous, which gave rise to a series of mineral deposits, among them those belonging to the Andacollo and Punitaqui districts. Andacollo is a complex district, including porphyry Cu, epithermal Au, Cu vein and Hg vein deposits (Oyarzun et al., 1996; Fig. 2). The porphyry Cu occurs in the central part with Au occurring in the west, and Hg in the east. The porphyry Cu deposit largely consists of chalcocite ( $\text{Cu}_2\text{S}$ ), pyrite ( $\text{FeS}_2$ ), chalcopyrite ( $\text{CuFeS}_2$ ), subordinate molybdenite ( $\text{MoS}_2$ ) and minor Au. Although Hg is rare in porphyry Cu deposits, Andacollo is one of the 3 porphyry deposits worldwide, where Hg has been reported (Rytuba, 2003). The Au

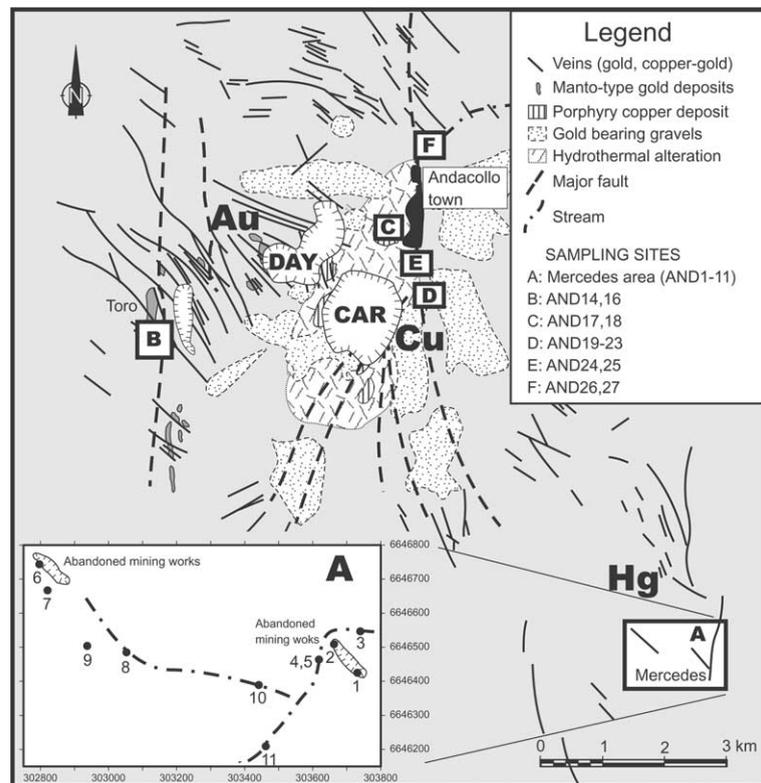


Fig. 2. The Andacollo district, showing location of the main geologic and metallogenic features, mining operations, and sampling sites. CAR, Carmen open pit; DAY, Dayton open pit. Exact location of samples in B–F (UTM data) can be requested from the authors.

epithermal deposit consists of Au-bearing pyrite and native Au, with minor chalcopyrite, sphalerite (ZnS), galena (PbS), and cinnabar (HgS). The Hg-bearing veins contain schwazite, Hg tetrahedrite ((Cu,Hg)<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub>), pyrite, chalcopyrite, bornite (Cu<sub>5</sub>FeS<sub>4</sub>), and galena. The Cu veins that occupy a marginal position within the district consist of pyrite, chalcopyrite and bornite. The Punitaqui district (Oyarzún et al., 2001; Fig. 3) corresponds to a complex case of shear-related, Cu–Au and Hg deposits. The Cu–Au ore consists of pyrite, tetrahedrite (Cu<sub>12</sub>As<sub>4</sub>S<sub>13</sub>), native Au, chalcopyrite, and native Cu, whereas the Hg ore consists of cinnabar.

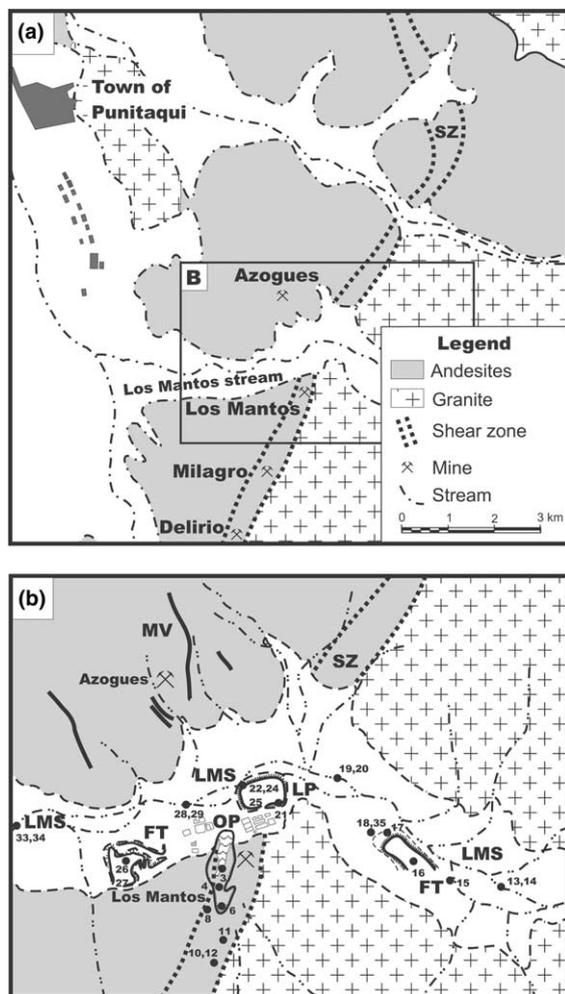


Fig. 3. The Punitaqui district. (a): general geologic map of the district showing location of the main mineral deposits cited in the text, and the town of Punitaqui. (b): The Los Mantos and Azogues mines showing location of mining works and sampling sites. FT: flotation tailings; LMS: Los Mantos stream (rambla); LP: leaching pile; MV: Hg-bearing veins; OP: open pit; SZ: shear zone.

#### 4. Methods

To assess metal contamination, the authors collected samples of stream and mine waters, stream sediments, soils, flotation tailings, leaching piles, gases, and mine waste from the Andacollo and Punitaqui districts in November, 2000. Unfiltered water samples were collected in 120 ml plastic flasks, and preserved with ultrapure HCl. No specific samples were collected for the Hg analyses. The stream sediment samples (~5 kg) were collected from the shores of the rivers, focusing on the silty fraction, and stored in plastic bags. The soil samples (~5 kg) were collected from the locally shallow C horizon, at a depth of 15–25 cm, and stored in plastic bags. Depending on the type of solid material (rock, wet sediment, dry soil), the samples were crushed, dried, and sieved to <64 μm (F samples) and 64–500 μm (I samples). The samples were analyzed by atomic absorption spectrometry at Geoanalítica Ltd., Chile with the following detection limits: As (0.5 mg/L waters, 10 μg/g solids), Cd (0.1 mg/L waters, 10 μg/g solids), Cu (0.2 mg/L waters, 1 μg/g solids), Hg (1 μg/L waters and 1 μg/g solids), and Zn (0.1 mg/L waters, 1 μg/g solids). Quality control at the laboratory was addressed by analyzing duplicate samples to check precision, whereas accuracy was determined by analysis of certified reference standards. Blank samples were also analyzed to check procedures. Given that the detection limit for Hg is relatively high, the data for waters may be of limited value. Gaseous Hg was analyzed using a LUMEX RA-915+ analyzer for continuous measurements. The analytical procedure is based on Zeeman atomic absorption spectrometry with high frequency modulation of light polarization. The instrument allows determination of Hg in air directly with a low detection limit in real time of 2 ng m<sup>-3</sup> (average measuring time = 5 s).

#### 5. Results and discussion

As shown by Seal and Hammarstrom (2003), the potential impact of mineral deposits depends on a series of variables, including ore mineralogy, mining methods, mineral processing (past and present), climate, and the level of development of a country. The mineralogy is key for understanding which metals may become naturally (geological processes) or industrially (mining and metallurgy) incorporated in to the environment. Metallic Hg has been intensively used for the recovery of Au in Andacollo and continues to be employed in the remaining semi-industrial trapiche installations. In addition, Hg is also present as an ore mineral (either cinnabar or schwazite) in the Andacollo and Punitaqui. Hydrothermal and supergene alteration processes are also environmentally relevant in the Andacollo and Punitaqui deposits. These processes were more extensive

at Andacollo (Fig. 2), and implied (1) a lower pH of supergene solutions, (2) subsequent metal leaching and transport, and (3) important formation of clays by hydrolysis of the feldspars (Oyarzun et al., 1996; Oyarzún et al., 2001).

5.1. The Andacollo district

One of the main environmental problems regarding the district is centered in the mining town of Andacollo (Fig. 2), which is home to 10,200 inhabitants. Andacollo

resembles many of the 19th century mining settlements, with abandoned mining wastes, mineral heaps, and even trapiche installations that are found in the town. The geochemical results for Andacollo show two main facts: (1) the Cu, and to a lesser extent, the metallic Hg signatures of the district, and (2) the intensive use of metallic Hg in the district to recover Au (Figs. 2 and 4; Tables 2 and 3). Additionally, both Cu and Hg concentrations are much higher than reference baselines from stream sediments and soils (Table 3). The concentration of Cu is significant in the waters, stream

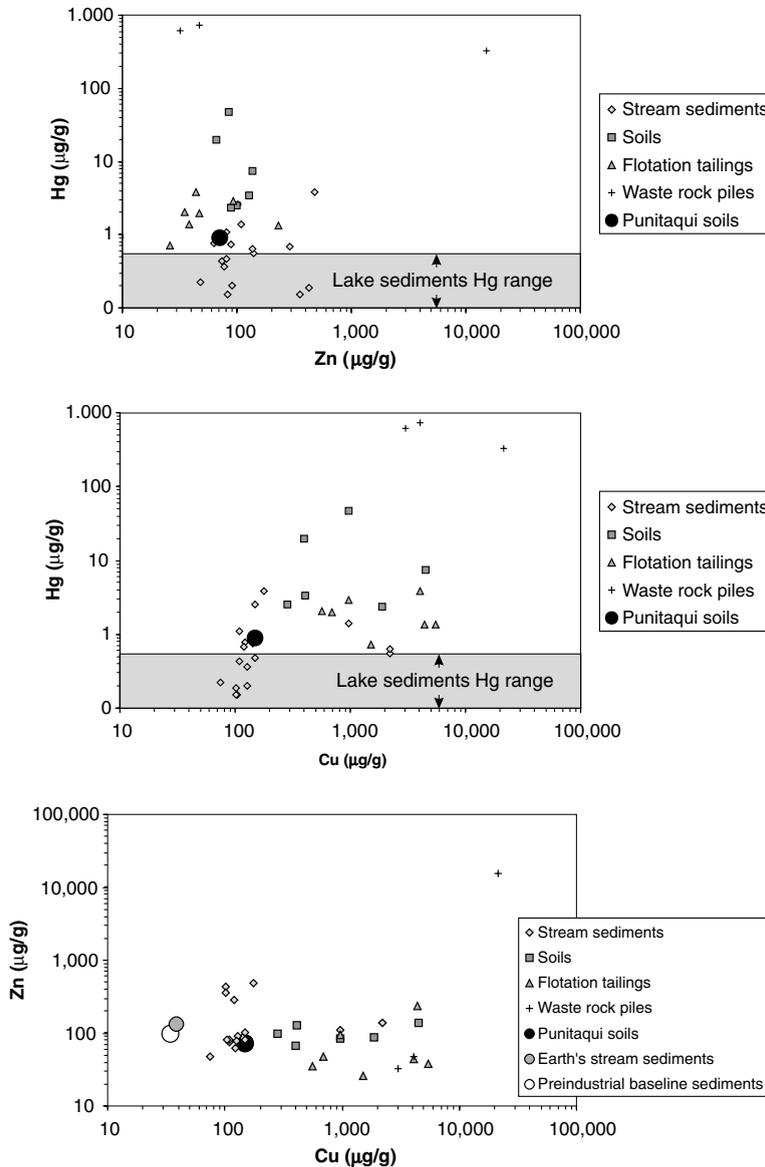


Fig. 4. Trace element concentration plots for Andacollo (floatations tailings and waste rock piles, this work), Punitaqui soils (Oyarzún et al., 2001), stream sediments (Callender, 2004) and lake sediments Hg range (Fitzgerald and Lamborg, 2004).

Table 2

Geochemical data for various samples from Andacollo. MCL, maximum contaminant level for drinking water (USEPA, 2004)

| Sample                        | Zn (mg/L)           | Cu (mg/L)           | As (mg/L)           | Cd (mg/L)           | Hg (mg/L)           | pH  |
|-------------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|-----|
| <i>Stream and mine waters</i> |                     |                     |                     |                     |                     |     |
| AND4B                         | <0.10               | <0.2                | <0.5                | <0.10               | <1                  | 7.0 |
| AND17                         | 31                  | 170                 | <0.5                | <0.10               | <1                  | 2.5 |
| AND19                         | <0.10               | <0.2                | <0.5                | <0.10               | <1                  | 6.0 |
| AND27                         | 3                   | 24                  | <0.5                | <0.10               | <1                  | 4.5 |
| MCL                           | 5                   | 1.3                 | 0.010               | 0.005               | 0.002               |     |
|                               | ( $\mu\text{g/g}$ ) |     |
| <i>Stream sediments</i>       |                     |                     |                     |                     |                     |     |
| AND3F                         | 88                  | 140                 | <10                 | <10                 | 0.7                 |     |
| AND3I                         | 74                  | 110                 | <10                 | <10                 | 0.4                 |     |
| AND5F                         | 100                 | 150                 | 10                  | <10                 | 2.6                 |     |
| AND5I                         | 81                  | 110                 | 10                  | <10                 | 1.1                 |     |
| AND8F                         | 63                  | 120                 | <10                 | <10                 | 0.8                 |     |
| AND8I                         | 48                  | 75                  | <10                 | <10                 | 0.2                 |     |
| AND10F                        | 90                  | 130                 | <10                 | <10                 | 0.2                 |     |
| AND10I                        | 82                  | 100                 | <10                 | <10                 | 0.2                 |     |
| AND11F                        | 81                  | 150                 | 15                  | <10                 | 0.5                 |     |
| AND11I                        | 77                  | 130                 | <10                 | <10                 | 0.4                 |     |
| AND14F                        | 430                 | 100                 | <10                 | <10                 | 0.2                 |     |
| AND14I                        | 480                 | 180                 | <10                 | <10                 | 3.8                 |     |
| AND16F                        | 360                 | 100                 | <10                 | <10                 | 0.2                 |     |
| AND16I                        | 290                 | 120                 | <10                 | <10                 | 0.7                 |     |
| AND24F                        | 140                 | 2200                | 16                  | <10                 | 0.6                 |     |
| AND24I                        | 140                 | 2200                | <10                 | <10                 | 0.6                 |     |
| AND26I                        | 110                 | 970                 | <10                 | <10                 | 1.4                 |     |
| <i>Soils</i>                  |                     |                     |                     |                     |                     |     |
| AND7F                         | 130                 | 410                 | 25                  | <10                 | 3.4                 |     |
| AND7I                         | 99                  | 290                 | 29                  | <10                 | 2.5                 |     |
| AND9F                         | 85                  | 960                 | 45                  | <10                 | 47                  |     |
| AND9I                         | 66                  | 400                 | 24                  | <10                 | 20                  |     |
| AND23F                        | 140                 | 4500                | <10                 | <10                 | 7.4                 |     |
| AND23I                        | 89                  | 1900                | <10                 | <10                 | 2.4                 |     |
| <i>Flotation tailings</i>     |                     |                     |                     |                     |                     |     |
| AND20A                        | 35                  | 570                 | <10                 | <10                 | 2                   |     |
| AND20B                        | 93                  | 970                 | <10                 | <10                 | 2.9                 |     |
| AND20C                        | 44                  | 4000                | <10                 | <10                 | 3.9                 |     |
| AND20D                        | 47                  | 690                 | <10                 | <10                 | 2                   |     |
| AND21                         | 38                  | 5500                | <10                 | <10                 | 1.4                 |     |
| AND22                         | 26                  | 1500                | <10                 | <10                 | 0.7                 |     |
| AND25                         | 230                 | 4400                | <10                 | <10                 | 1.4                 |     |
| <i>Waste rock piles</i>       |                     |                     |                     |                     |                     |     |
| AND1                          | 32                  | 3000                | 170                 | <10                 | 620                 |     |
| AND2                          | 47                  | 4000                | 290                 | <10                 | 720                 |     |
| AND6                          | 15,000              | 21,000              | 1400                | 18                  | 330                 |     |

sediments, and soils. Mine waters from an old cementation plant (AND17) display the highest concentrations of Cu, whereas those from a trapiche operation (AND19) are much lower (Table 2), which reflects the type of metallurgical procedures: acid treatment in the former and flotation in the latter. In any case, part of

the metals reach the Andacollo stream as shown by one concentration of 24 mg/L Cu (AND27). Sediments from the Andacollo stream are contaminated with Cu and Hg, with concentrations ranging from 970–2200  $\mu\text{g/g}$  Cu and 0.6–1.4  $\mu\text{g/g}$  Hg (AND24–26). Mercury is also elevated (AND3–11) in the vicinity of the Hg-bearing veins

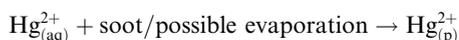
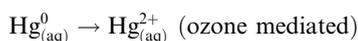
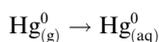
Table 3  
Concentrations of Zn, Cu, and Hg for Andacollo, Punitaqui, other mining districts, and earth materials

| Site  | Zn ( $\mu\text{g/g}$ ) | Cu ( $\mu\text{g/g}$ ) | Hg ( $\mu\text{g/g}$ ) | References                    |
|---|------------------------|------------------------|------------------------|-------------------------------|
| Andacollo (all) stream sediments                    | 48–480                 | 75–2200                | 0.2–3.8                | This study                    |
| Andacollo (Mercedes) stream sediments               | 48–100                 | 75–150                 | 0.2–2.6                | This study                    |
| Punitaqui stream sediments                          | 27–70                  | 110–260                | 0.3–5.3                | This study                    |
| Punitaqui soils                                     | 71                     | 149                    | 0.9                    | Oyarzún et al. (2001)         |
| West-Central Nevada Hg mines (USA)                  | –                      | –                      | 0.008–170              | Gray et al. (2002)            |
| Carson River (Nevada, USA), overbank flood deposits | –                      | –                      | 5.3–7                  | Miller et al. (1999)          |
| Pre-industrial baseline lacustrine sediment         | 97                     | 34                     | –                      | Callender (2004)              |
| Earth stream sediments                              | 132                    | 39                     | –                      | Callender (2004)              |
| Lake sediments                                      | –                      | –                      | 0.01–0.45              | Fitzgerald and Lamborg (2004) |

and mine workings of Mercedes (Fig. 2), with concentrations ranging from 0.2–2.6  $\mu\text{g/g}$ . Conversely, the area of the Mercedes Hg-vein deposits display lower Cu concentrations (75–150  $\mu\text{g/g}$ ), which reflects the Cu-poor character of the ore. Stream sediment samples collected near to Toro (one of the manto- and vein-type Au deposit) (AND14-16) (Fig. 2), contain the highest Zn concentrations for the district (290–480  $\mu\text{g/g}$ ), reflecting the presence of sphalerite (Table 2). Toro also has one of the highest concentrations of Hg in stream sediments (up to 3.8  $\mu\text{g/g}$ ; AND14I), which must be related to the introduction of Hg via the trapiche operations. One mine waste-rock sample (AND6; possibly from one of the manto-Au deposits) contained high Zn (15,000  $\mu\text{g/g}$ ), Cu (21,000  $\mu\text{g/g}$ ), As (1400  $\mu\text{g/g}$ ), and Cd (18  $\mu\text{g/g}$ ). Copper concentrations in soils (AND7-23) and in flotation tailings are high and suggest poor rates of Cu recovery during trapiche processing. The flotation tailings have Cu concentrations ranging from 570–5500  $\mu\text{g/g}$  (AND20-25). Similarly, the tailings samples contain Hg concentrations ranging from 0.7–3.9  $\mu\text{g/g}$ . The soils have high Hg concentrations, and the highest values are found at Mercedes (AND7, AND9; 2.5–47  $\mu\text{g/g}$ ) (Fig. 2). The mineralogy of Hg ore explains why some of the sampled soils are not as elevated in Hg (AND23F-I; 2.4–7.4  $\mu\text{g/g}$ ) as those from Mercedes (Fig. 2). At Mercedes Hg is mostly in the form of schwazite, which is resistant to physical and chemical weathering.

In situ measurements of Hg gas in trapiche installations ranged from 10,000 to 100,000  $\text{ng Hg m}^{-3}$  (due to instrumental restrictions, the latter value is regarded as a minimum). The trapiches consume about 0.8 kg Hg per day, and there are around 30 of these mills in operation. Considering that only 50–70% of this Hg is recovered, about 2628–4380 kg of unrecovered metallic Hg is lost to surrounding environments each year. Higuera et al. (2003) suggested for Almadén (Spain) a mechanism that may be applied also to Andacollo in the following way: the Hg gas emitted by the sources (e.g. trapiches, marays) can be deposited in the surrounding soils as  $\text{Hg}^{2+}$ ,

either from direct deposition of emitted  $\text{Hg}^{2+}$ , or from conversion of emitted  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  through ozone mediated processes (USEPA, 1997)



(g, gas phase; aq, aqueous phase; p, particulate phase).

Photolysis of inorganic  $\text{Hg}^{2+}$  to  $\text{Hg}^0$  at the soil surface may in turn contribute significantly to the re-emission of Hg gas to the atmosphere (Scholtz et al., 2003).

## 5.2. Punitaqui

The district is named after the small village of Punitaqui (9539 inhabitants), which is about 5 km to the NW. Similar to Andacollo, the village is poor and largely depended on the mining industry before the present upsurge of agricultural activities. Pressured by low Au prices, the mines at Punitaqui ceased operation in 2000, and presently agriculture (vineyards) is the only driving economic force in this area. Because mine wastes piles ( $\sim 500,000 \text{ m}^3$ ) are within 2 km of the town of Punitaqui, the town is potentially affected by mine-related contamination and runoff. The geochemical data for Punitaqui shows high concentrations of Cu and Hg in soils and sediments (Fig. 5; Tables 3 and 4).

The sampled stream waters (PNT13,19,28,33) generally show metal concentrations below detection limits (Fig. 3; Table 4). The neutral to weakly alkaline character of the waters may in part explain this behavior. The only water sample with high Hg concentration (PNT18; 18  $\text{mg/L}$ ) was obtained from a solution pond at a heap leaching operation, which explains this extremely high concentration. Concentrations of Cu and Zn in the stream sediments show no significant variation along the

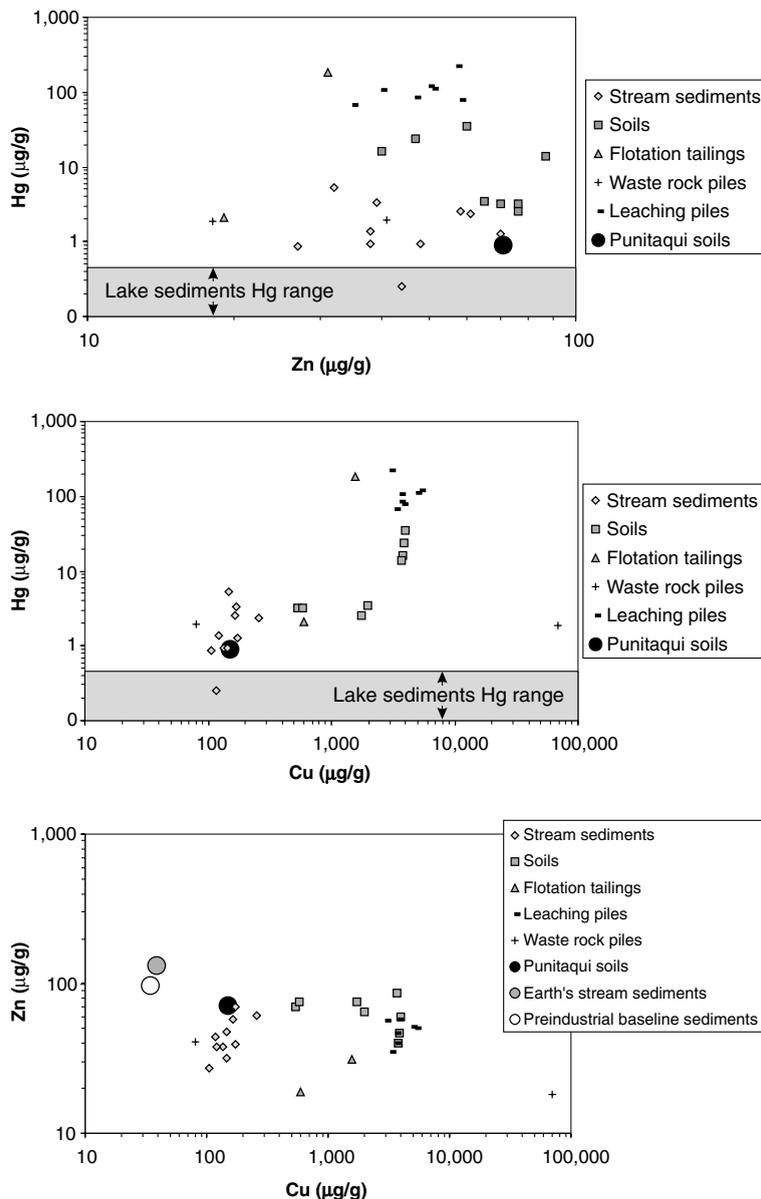


Fig. 5. Trace element plots for Punitaqui. Punitaqui soils (Oyarzún et al., 2001), stream sediments (Callender, 2004), lake sediments Hg range (Fitzgerald and Lamborg, 2004).

stream, whereas Hg increases downstream up to 5.3 µg/g (Fig. 6, Table 4). Hg was probably introduced to the stream via metallurgical activities. For example, the samples from flotation tailings and leaching piles, yield high concentrations of Hg of up to 220 µg/g (Table 4). Thus, Hg could have been transferred from the piles to the stream via erosion. In situ measurements of gaseous Hg indicate values approaching 100 ng Hg m<sup>-3</sup> near to the flotation tailings and heap-leaching operations.

The soil samples (Table 4) were taken in and near the open-pit operation at Los Mantos (Fig. 3). The samples

collected within the pit (PNT4, PNT6), and outside (PNT8) yield high concentrations of Cu (1700–4000 µg/g) and Hg (2.6–35 µg/g). These Hg concentrations are similar to those of a previous geochemical survey of the area (Oyarzún et al., 2001), showing a district-wide mean of 0.9 µg/g (*n* = 160). Considering that Cu in the same survey showed a much lower mean value of 150 µg/g, it may be concluded that: (1) the Los Mantos pit and tailings are the primary sources of Cu, and (2) the stream sediment results (Table 4) suggest limited geochemical dispersion of Cu downstream from Los Mantos. The other Cu source in

Table 4

Geochemical data for various samples from Punitaqui. MCL, maximum contaminant level for drinking water (USEPA, 2004)

| Sample                        | Zn (mg/L) | Cu (mg/L) | As (mg/L) | Cd (mg/L) | Hg (mg/L) | pH      |
|-------------------------------|-----------|-----------|-----------|-----------|-----------|---------|
| <i>Stream and mine waters</i> |           |           |           |           |           |         |
| PNT3                          | <0.10     | <0.2      | <5        | <0.10     | <1        | 8.0     |
| PNT13                         | <0.10     | <0.2      | <5        | <0.10     | <1        | 7.5–8.0 |
| PNT17                         | <0.10     | <0.2      | <5        | <0.10     | <1        | 7.0     |
| PNT18                         | <0.10     | 64        | <5        | 0.4       | 18        | 7.0–7.5 |
| PNT19                         | <0.10     | <0.2      | <5        | <0.10     | <1        | 7.0     |
| PNT22                         | <0.10     | <0.2      | <5        | <0.10     | <1        | 7.0     |
| PNT28                         | <0.10     | <0.2      | <5        | <0.10     | <1        | 7.0     |
| PNT33                         | <0.10     | <0.2      | <5        | <0.10     | <1        | 7.0     |
| MCL                           | 5         | 1.3       | 0.006     | 0.005     | 0.002     |         |
|                               | (µg/g)    | (µg/g)    | (µg/g)    | (µg/g)    | (µg/g)    |         |
| <i>Stream sediments</i>       |           |           |           |           |           |         |
| PNT14F                        | 38        | 140       | <10       | <10       | 0.9       |         |
| PNT14I                        | 48        | 150       | <10       | <10       | 0.9       |         |
| PNT15F                        | 61        | 260       | <10       | <10       | 2.3       |         |
| PNT15I                        | 44        | 120       | <10       | <10       | 0.3       |         |
| PNT20F                        | 70        | 170       | 12        | <10       | 1.3       |         |
| PNT20I                        | 38        | 120       | <10       | <10       | 1.4       |         |
| PNT29F                        | 58        | 160       | <10       | <10       | 2.6       |         |
| PNT29I                        | 27        | 110       | <10       | <10       | 0.9       |         |
| PNT34F                        | 39        | 170       | <10       | <10       | 3.3       |         |
| PNT34I                        | 32        | 150       | <10       | <10       | 5.3       |         |
| <i>Soils</i>                  |           |           |           |           |           |         |
| PNT4F                         | 40        | 3800      | <10       | <10       | 16        |         |
| PNT4I                         | 87        | 3700      | <10       | <10       | 14        |         |
| PNT6F                         | 47        | 3900      | 21        | <10       | 24        |         |
| PNT6I                         | 60        | 4000      | 25        | <10       | 35        |         |
| PNT8F                         | 65        | 2000      | 28        | <10       | 3.4       |         |
| PNT8I                         | 76        | 1700      | 24        | <10       | 2.6       |         |
| PNT11F                        | 70        | 540       | <10       | <10       | 3.2       |         |
| PNT11I                        | 76        | 580       | <10       | <10       | 3.2       |         |
| <i>Flotation tailings</i>     |           |           |           |           |           |         |
| PNT26                         | 19        | 600       | <10       | <10       | 2.1       |         |
| PNT27                         | 31        | 1600      | 37        | <10       | 190       |         |
| <i>Leaching piles</i>         |           |           |           |           |           |         |
| PNT16                         | 47        | 3600      | 40        | <10       | 86        |         |
| PNT21A                        | 50        | 5300      | 44        | <10       | 120       |         |
| PNT21BCD                      | 51        | 4900      | 39        | <10       | 110       |         |
| PNT21EF                       | 58        | 3800      | 29        | <10       | 79        |         |
| PNT24                         | 40        | 3600      | 40        | <10       | 110       |         |
| PNT25                         | 35        | 3300      | 28        | <10       | 67        |         |
| PNT35                         | 57        | 3000      | 23        | <10       | 220       |         |
| <i>Waste rock piles</i>       |           |           |           |           |           |         |
| PNT10                         | 18        | 69,000    | 37        | <10       | 1.9       |         |
| PUN12                         | 41        | 80        | 27        | <10       | 1.9       |         |

the district is the leaching pile of Los Mantos (3300–5300 µg/g Cu). However, despite these high contents, a pile subjected to cyanide leaching may be relatively harmless in terms of Cu mobilization because pH has to be kept above 10, and leaching and transport of Cu becomes severely reduced (e.g. Price, 2003).

## 6. Conclusions

Although the Andacollo and Punitaqui districts have distinctly different geochemical characteristics, they have one common problem: Hg. The stream sediment surveys showed high concentrations of Hg at Andacollo and

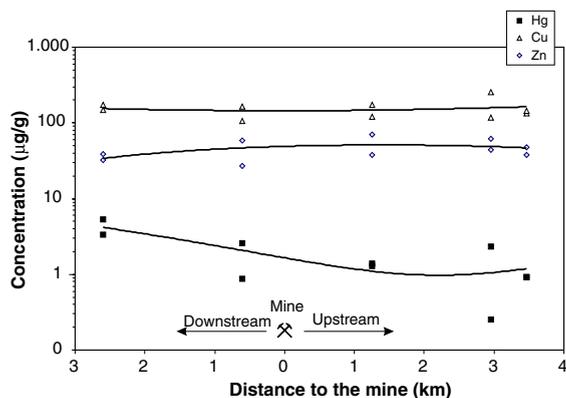


Fig. 6. Concentrations of Cu, Zn and Hg in sediments along the Punitaqui stream.

Punitaqui. However, the origin of Hg may be different in the two districts. As observed in Andacollo, high Hg concentrations are generally related to the amalgamation of Au. Punitaqui is different where Hg has a primary origin (ore) and must have been released first during Hg production from the Azogues deposit, and later during flotation and leaching of the Cu–Au ores. The authors did not find high concentrations of Cu in the stream sediments at Punitaqui, where the samples of flotation tailings apparently have lower Cu than those of Andacollo. This may indicate that flotation for Cu was more effective at Punitaqui. Based on this study, the following is suggested: (1) the nature of ore minerals in the two districts determine the general type of metal contamination, (2) metal contamination may be modified by the degree of metallurgical efficiency: poor metal recovery will eventually lead to metal dispersion (e.g. Cu in Andacollo), whereas more efficient procedures result in less metal contamination (e.g. Cu in Punitaqui), (3) efficient flotation for a given metal may lead to loss of another, and therefore, to unintentional contamination (e.g., Hg at Punitaqui), and (4) Au recovery by amalgamation during decades or even hundreds of years aggravate the environmental problems: although Hg escapes from the soils to the atmosphere, the continuous introduction of new Hg to the system keeps the supply of Hg high.

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#### References

- Callender, E., 2004. Heavy metals in the environment – historical trends. In: Lollar, B.S. (Ed.), *Treatise on Geochemistry 9, Environmental Geochemistry*. Elsevier, Amsterdam, pp. 67–105.
- Cuadra, W., Dunkerley, P.M., 1991. A history of gold in Chile. *Econ. Geol.* 86, 1155–1173.
- Fitzgerald, V.F., Lamborg, C.H., 2004. Geochemistry of mercury in the environment. In: Lollar, B.S. (Ed.), *Treatise on Geochemistry 9, Environmental Geochemistry*. Elsevier, Amsterdam, pp. 107–148.
- Gray, J.E., Crock, J.G., Fey, D.L., 2002. Environmental geochemistry of abandoned mercury mines in West-Central Nevada, USA. *Appl. Geochem.* 17, 1069–1079.
- Higuera, P., Oyarzun, R., Biester, H., Lillo, J., Lorenzo, S., 2003. A first insight into mercury distribution and speciation in soils from the Almadén mining district. *J. Geochem. Explor.* 80, 95–104.
- Hilson, G., 2000. Barriers to implementing cleaner technologies and cleaner production (CP) practices in the mining industry: a case study of the Americas. *Min. Eng.* 13, 699–717.
- Miller, J., Barr, R., Grow, D., Lechler, P., Richardson, D., Waltman, K., Warwick, J., 1999. Effects of the 1997 flood on the transport and storage of sediment and mercury within the Carson River Valley, West-Central Nevada. *J. Geol.* 107, 313–327.
- Oyarzún, J., Oyarzun, R., Pavicic, S., 2001. Estudio prospectivo en un distrito de Cu–Au–Hg asociado a zona de cizalla: Punitaqui. Chile. *Bol. Inst. Technol. Geomin. España* 112, 75–84.
- Oyarzun, R., Ortega, L., Sierra, J., Lunar, R., Oyarzún, J., 1996. The manto-type gold deposits of Andacollo (Chile) revisited: a model based on fluid inclusion and geological evidence. *Econ. Geol.* 91, 1298–1309.
- Price, W.A., 2003. Challenges posed by metal leaching and acid rock drainage, and approaches used to address them. In: Jambor, J.L., Blowes, D.W., Ritchie, A.I.M. (Eds.), *Environmental Aspects of Mine wastes*. In: *Short Course Series, 31*. Mineralogical Association of Canada, Vancouver, pp. 1–10.
- Rytuba, J.J., 2003. Mercury from mineral deposits and potential environmental impacts. *Environ. Geol.* 43, 326–338.
- Scholtz, M.T., Van Heyst, B.J., Schroeder, W.H., 2003. Modelling of mercury emissions from background soils. *Sci. Total Environ.* 304, 185–207.
- Seal, R.R., Hammarstrom, J.M., 2003. Geoenvironmental models of mineral deposits: examples from massive sulfide and gold deposits. In: Jambor, J.L., Blowes, D.W., Ritchie, A.I.M. (Eds.), *Environmental Aspects of Mine Wastes*. In: *Short Course Series, vol. 31*. Mineralogical Association of Canada, Vancouver, pp. 11–50.
- USEPA, 1997. Mercury Study Report to Congress: Volume III. Fate and Transport of Mercury in the Environment. Office of Air Quality Planning and Standards, and Office of Research and Development, Washington.
- USEPA, 2004. List of drinking water contaminants and MCLs. Available from: <<http://www.epa.gov/safewater/mcl.html>>.
- Veit, H., 1996. Southern Westerlies during Holocene deduced from geomorphological and pedological studies in Norte Chico, northern Chile. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 123, 107–119.