Atmospheric mercury data for the Coquimbo region, Chile: influence of mineral deposits and metal recovery practices

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Abstract

This work reports data of atmospheric mercury for northern Chile. The study was centered in the Coquimbo region, a realm rich in mineral deposits. Some of the mining districts have historic importance and have been exploited almost continuously since the Spanish colonial time (16–18th century). Two of these districts are particularly relevant: (1) Andacollo, initially exploited for gold, and then for copper and gold; and (2) Punitaqui, initially exploited for mercury, and then for copper and gold. The continuous mercury measurement procedures carried out during this survey, have proved to be an excellent tool to detect Hg signatures associated with the mining industrial activities. The combination of cumulative log-probability graphs and atmospheric mercury concentration profiles, allows clear differentiation between areas subjected to agriculture (2–3 ng Hg m\textsuperscript{-3}), from those in which mining and metal concentration activities take place (> 10 ng Hg m\textsuperscript{-3}, most data well beyond this figure). Gold recovery involving milling and amalgamation appear as the most contaminant source of mercury, and yield concentrations in the order of 10\textsuperscript{4}–10\textsuperscript{5} ng Hg m\textsuperscript{-3} (Andacollo). Second in importance are the vein mercury deposits of Punitaqui, with concentrations above 100 ng Hg m\textsuperscript{-3}, whereas the flotation tailings of the district yield concentrations near to 100 ng Hg m\textsuperscript{-3}. The large and modern open pit operations of Andacollo (Carmen: Cu; Dayton: Au) do not show high concentrations of atmospheric mercury.

Keywords: Mercury; Atmosphere; Air geochemistry; Coquimbo; Chile

1. Introduction

The Coquimbo region in northern central Chile (Fig. 1) is one of the richest in terms of mineral deposits and mining activity. The mineral deposits are not only important in number and/or size, but also in terms of historical significance, because some of them have been almost continuously exploited since the Spanish colonial time (16–18th century) (e.g., Andacollo: copper and gold). Thus, in many ways one may infer that the Coquimbo region has a long-lasting record of environmental disturbances derived from its mining industry, particularly in old mining sites such as
Andacollo (Fig. 1). Similar to other South American countries (e.g., Brazil, Colombia, and Venezuela) the artisanal gold mining operations have intensively used mercury, and since small-scale miners usually refine gold carelessly, part of this mercury escapes to the air (e.g., Lacerda and de Salomons, 1999; Hilson, 2000). In this respect, not more than 70% of mercury used in gold amalgamation is ever recovered, and therefore gets incorporated to the soils, waters, and the atmosphere. Apart from this, the precious (Au–Ag) and base metal deposits (Cu–Pb–Zn) are among the most significant geologic sources of atmospheric mercury (Gustin, 2003). Thus, given that the Coquimbo region has an important gold recovery industry, and a large number of ore deposits, we decided to study the influence of these factors into the pool of atmospheric mercury within this realm.

2. Physiography and climate

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 transversal valleys that communicate the Andean Mountains with the coast. The main valleys are flanked by mountain belts of about 50 km wide and altitudes ranging from 600 to 1000 m above sea level. The climate is strongly conditioned by the so-called Pacific anticyclone, which normally blocks the rain fronts that sweep central and southern Chile during the austral winter (Westerly winds). The Coquimbo region has a transitional climate between the extremely dry Atacama Desert and the more humid central part of Chile (Mediterranean climate). The coastal sector is characterized by a high percentage of cloudy days, whereas the interior is relatively free from the sea influence. The mean temperature in the coast is 14 °C, which increases towards the interior to 16 °C. The average precipitations along the coast are of 126 mm year⁻¹, whereas those of the interior are slightly higher (131 mm year⁻¹). However, these data are to be taken with much caution, because the snow fall in the Andes mountains is poorly recorded, and this region of Chile is characterized by strong annual variations induced

Fig. 1. General map of the study region showing location of profiles (P), towns, mining districts, and industrial activities.
by the influence of the Westerly winds (Veit, 1996). Increased activity of the Westerlies with more frontal activity during winter is in turn well correlated to El Niño years when both, rain and snow fall increase 3–5 times.

3. Geology, mineral deposits, and mining industry

The geology of the studied area comprises units ranging in age from Paleozoic to Tertiary. The Paleozoic rocks crop out along a narrow belt in the coast and mostly consist of monotonous mica schists series. These rocks are partially covered by Pliocene to Quaternary marine sedimentary rocks. Eastward from the coast the geology is dominated by volcanlastic, volcanic and sedimentary units of lower Cretaceous age: the Estratos del Reloj, Arqueros, and Quebrada Marquesa formations (e.g., Oyarzun et al., 1996, 1998; Oyarzúñ et al., 2001). These units were intruded by granitoids of middle Cretaceous age, which gave rise to a series of mineralized clusters (Fig. 1): (1) Talcuna; (2) Andacollo; and (3) Punitaqui; all of them of both historic and economic importance. The Talcuna district comprises stratabound Cu and Mn mineralizations. Andacollo is characterized by a central porphyry copper deposit and peripheral gold-(copper) vein and manto (stratabound) type deposits, and small mercury veins, whereas the Punitaqui district comprises shear-related copper–gold, and mercury-vein type deposits (Oyarzun et al., 1996, 1998; Oyarzúñ et al., 2001). Other districts in the region include those of Corral Quemado (Mn) and Tamaya (Cu). The latter was of major importance during the second half of the 19th century, when it became the world’s largest copper producer. The main characteristics of these districts are summarized in Table 1.

Andacollo has been a site of continuous use of mercury for gold recovery for at least the last three centuries, thus a brief insight into its mining history might be useful to understand the present environmental problems in this realm (Higueras et al., 2004). The district was already mined for gold during the Inca Empire, and the activity continued during colonial time (16–18th centuries). Prior to 1575 the Andacollo placer gold fields were already operating, and were regarded as the greatest gold resource of the colony (Cuadra and Dunkerley, 1991; Cuadra and Arenas, 2003). Hard rock mining was introduced before the end of the 16th century, and the main technological innovation consisted in the introduction of the water powered “trapiches” (an old Spanish word for mill), rock crushers consisting in two massive grinding stones mounted vertically on a horizontal axle and turning on top of a circular stone (Cuadra and Dunkerley, 1991). An improved version of the old trapiches is used at present by the small-scale mining operations that still exist in the district. These modern trapiches (electricity powered) crush ore up to 10 cm in diameter, and leaves a residue of 65% < mesh 200. The crushers are used for two purposes: (1) to crush ore for flotation of copper sulfides; and (2) to recover gold (within the trapiche) on

<table>
<thead>
<tr>
<th>District</th>
<th>Deposit type</th>
<th>Production (total)</th>
<th>Main ore</th>
<th>Mining duration</th>
<th>Ore processing</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Andacollo</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Small mining</td>
<td>Veins</td>
<td>~100 t (Au)</td>
<td>Au, Cu*</td>
<td>1575–present</td>
<td>Trapiche milling</td>
</tr>
<tr>
<td>Carmen</td>
<td>Porphyry Cu</td>
<td>100,000 t (Cu)</td>
<td>Cu</td>
<td>1997–present</td>
<td>Heap leaching</td>
</tr>
<tr>
<td>Dayton</td>
<td>Epithermal Au</td>
<td>20 t (Au)</td>
<td>Au</td>
<td>1996–2000&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Heap leaching</td>
</tr>
<tr>
<td><strong>Corral Quemado</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>District</td>
<td>Stratiform</td>
<td>~1,700,000 (~30% Mn)</td>
<td>Mn</td>
<td>1884–present</td>
<td>Gravitational concentration</td>
</tr>
<tr>
<td><strong>Punitaqui</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Azogues</td>
<td>Tension veins</td>
<td>Unknown</td>
<td>Hg</td>
<td>1785–1958</td>
<td>Unknown</td>
</tr>
<tr>
<td>Milagro/Los Mantos</td>
<td>Shear zone related</td>
<td>50,000 t&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Cu-Au</td>
<td>1994–1998</td>
<td>Flotation, heap leaching</td>
</tr>
<tr>
<td><strong>Talcuna</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Small mining&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Stratabound</td>
<td>~115,000 t&lt;sup&gt;e&lt;/sup&gt; (Cu)</td>
<td>Cu</td>
<td>1790s–present</td>
<td>Flotation</td>
</tr>
<tr>
<td>Small mining</td>
<td>Stratiform</td>
<td>Unknown</td>
<td>Mn</td>
<td>1790s–present</td>
<td>Gravitational concentration, AFD</td>
</tr>
<tr>
<td><strong>Tamaya</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>District</td>
<td>Veins</td>
<td>~10,000 t (Cu)</td>
<td>Cu</td>
<td>1871–1881&lt;sup&gt;f&lt;/sup&gt;</td>
<td>Direct smelting, AFD</td>
</tr>
</tbody>
</table>

<sup>a</sup>Cu extraction began in the 19th century.<br><sup>b</sup>Although the mine closed in 2000, the heap-leaching operation continues.<br><sup>c</sup>Cu, total Au production in 1996 reached 780 kg.<br><sup>d</sup>Two copper mines in operation at present (Coca-Cola and 21 de Mayo).<br><sup>e</sup>From ~1900 to present.<br><sup>f</sup>Main period.<br>AFD: Away from the district.
copper plates which are covered by a thin film of mercury. The operation requires 0.8 kg Hg day\(^{-1}\) and only 50–70\% of this mercury is later recovered. At present there are eight milling plants in Andacollo, with a total of 30 operating trapiches.

4. The survey

The survey was carried out along different roads and tracks of the Coquimbo region (Fig. 1), using a LUMEX RA-915+ analyzer for continuous Hg measurements. The analytical procedure is based on Zeeman atomic absorption spectrometry with high-frequency modulation of light polarization (ZAAS-HFM). Application of Zeeman background correction and a multipath analytical cell provide high selectivity and sensitivity of measurements. The instrument allows determination of Hg in air directly with an ultra low detection limit in real time. This detection limit is governed by shot noise and equals CaDL = 2 ng m\(^{-3}\) (average measuring time = 5 s) and CaDL = 0.3 ng m\(^{-3}\) (average measuring time = 30 s) for mercury determination in air. The dynamic range covers four orders of magnitude (2–30,000 ng m\(^{-3}\)). The real-time measurements are made with visualization of the process on a digital display (Sholupov and Ganeyev, 1995). On-line data recording is made by connecting the instrument to a lap-top computer, using specific software. The whole process is completed in the field with geographic location of single data using a GPS. The procedure involved geographic data acquisition (GPS SILVA Multinavigator) at every 500 s, and at singular points such as small villages, abandoned mineral dumps, or crossroads (among others). The statistical treatment of data was made using MINITAB 13.0, whereas the spatial distribution was plotted via SURFER 8.0. The collected data sets were investigated using the Lepeltier (1969) method, as it is ideal to deal with complex populations. This graphical approach, based on log \(X\) versus cumulative probability (cumulative log-probability graphics), nicely separates normal from transitional and anomalous populations. Since the \(Y\)-axis represents cumulative Gaussian distributions, each straight curve is representative of an individual data subset, having a log-normal distribution. The changes in slope (breaks) mark the boundaries between populations (Lepeltier, 1969; Sinclair, 1976).

In order to have a clean air reference value for Chile, we measured atmospheric mercury in the central part of the country (Valparaíso region). This 60 km long E–W profile was initiated in the town of Los Andes (at about 800 m above sea level; 32°48′S, 70°38′W) and ended at the ski resort of Portillo, well within the Andean mountains, at about 2800 m above sea level, an ideal unpolluted site to measure mercury for reference purposes. The first kilometers displayed comparatively high levels in the order of 20 ng Hg m\(^{-3}\), whereas mercury in the ski resort showed concentrations close to 2 ng Hg m\(^{-3}\), i.e., well within the order of what can be expected in the clean air of rural areas (1–4 ng Hg m\(^{-3}\); USEPA, 1997). The higher concentrations of the 2–20 ng Hg m\(^{-3}\) range can be explained in terms of the presence of the huge copper mining complex of La Andina (copper production 2002: 219,000 t Cu), which is located between Los Andes and Portillo.

The main survey was carried out in May 2003, and included a series of profiles in the Coquimbo region (Fig. 1): (1) From La Serena to Tongoy, Guanaqueros, Ovalle, and Tampillo (May 18; Tongoy–Ovalle profile: P1); (2) From La Serena to Andacollo, town, trapiches, and the Dayton gold mine (May 19; Andacollo profile: P2); (3) From Andacollo (Carmen copper mine) to the Punitaqui district (May 20; Andacollo–Punitaqui, profiles: P3 and P4); (4) From La Serena to the Talcuna copper district and Vicuña (May 22; Talcuna profile: P5); and (5) From Andacollo to the manganate district of Corral Quemado, and finally to the Andacollo El Toro gold mine (May 23; Andacollo–Corral Quemado profile: P6). Given that the factors affecting the variability of mercury emissions include sunlight, temperature, and atmospheric turbulence among others (e.g., Gustin, 2003), we provide meteorological information for each profile (Table 2). Conditions for data recording were excellent, with very low-to-low wind speeds and moderate temperatures. On the other hand, considering the nature of the measurement procedures, i.e., long-range regional profiles, there is a limitation

<table>
<thead>
<tr>
<th>Profile</th>
<th>Date</th>
<th>(T) min (°C)</th>
<th>(T) max (°C)</th>
<th>Wind direction (main)</th>
<th>Wind speed (min–max) in m s(^{-1})</th>
<th>Skies</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>05.18.2003</td>
<td>9.1</td>
<td>21.3</td>
<td>E</td>
<td>0.0–5.8</td>
<td>Sunny</td>
</tr>
<tr>
<td>P2</td>
<td>05.19.2003</td>
<td>3.8</td>
<td>13.5</td>
<td>NNW</td>
<td>0.4–6.7</td>
<td>Clouded</td>
</tr>
<tr>
<td>P3–P4</td>
<td>05.20.2003</td>
<td>6.9</td>
<td>10.5</td>
<td>SE</td>
<td>0.4–8.0</td>
<td>Clouded</td>
</tr>
<tr>
<td>P5</td>
<td>05.22.2003</td>
<td>13.4</td>
<td>17.2</td>
<td>ESE, SSW</td>
<td>0.9–5.4</td>
<td>Clouded</td>
</tr>
<tr>
<td>P6</td>
<td>05.23.2003</td>
<td>13.8</td>
<td>24.0</td>
<td>S</td>
<td>0.4–6.3</td>
<td>Sunny</td>
</tr>
</tbody>
</table>

See Fig. 1 for location.
regarding data interpretation. The atmospheric mercury measurements were carried out in different hours during a day (and in different days: 18th to the 23rd of May 2003), therefore the results may have been affected somehow by the different ambient temperatures and sunlight conditions (e.g., Gustin et al., 2002). However, the data sets are consistent, and in good agreement with the geological and industrial setting of the studied areas.

5. Results and discussion

Compared to unpolluted areas (Portillo: ~2 ngHg m$^{-3}$) many data populations from the studied areas in the Coquimbo region can be regarded as anomalous or highly anomalous (Figs. 2 and 3). We suggest that this increase in mercury levels is the consequence of: (1) the geological setting, which include numerous base metal deposits and (2) the mining and processing of ores. The presence of anomalous concentrations of mercury in many types of ore deposits has long been recognized, and the reason why is simple: the geologic and geochemical processes that lead to ore formation, also concentrate mercury in mineral phases that are specific to an ore deposit type; for example, in volcanic stratiform copper deposits (e.g., the Talcuna district), mercury may be present as an amalgam in copper (Rytuba, 2003). Because of this reason ore deposits constitute significant emission sources of mercury (Gustin, 2003). The rationale behind this fact is based on the following (Carr et al., 1986): as a host sulfide ore body weathers, mercury is partly converted to the gaseous state. This phase disperses through the permeable rocks or cover, allowing gaseous mercury to be detected on the surface. However, sorption phenomena to oxide phases such as goethite (FeO(OH)), or other minerals or organic components of the soil, may prevent the escape of mercury into the atmosphere (Carr et al., 1986). Although mercury is rare in porphyry copper deposits, it can be found in this environment, and in fact, the Andacollo porphyry is one of the three world cases in which the element has been reported (Rytuba, 2003). On the other hand, mining and metallurgical processing of ores constitute either a secondary or a pseudoprimary source of mercury. In the latter case the mercury that is already present in the ore is liberated to the environment during processing (e.g., milling, leaching, etc.). In this respect, although compared to gold amalgamation, cyanide leaching can be regarded as environmentally benign (Hilson, 2000), the process may still present some problems. For example, if the gold ore contains some mercury, this forms a mercury–cyanide complex, which will not be totally adsorbed on the activated carbon column, and will remain in the circulating load and accumulate over time. However, far more important than the probable accumulation of mercury via cyanide leaching-CIP recovery (e.g., Dayton operation) is the process of gold recovery via amalgamation (introduction of mercury to the system). We regard amalgamation as a secondary (fully anthropogenic) source of mercury, as opposed to the mercury present in the ore that is unintentionally liberated during processing (pseudoprimary mercury).

The Tongoy-Ovalle profile (P1) (Figs. 1 and 2) was the longest and covered a wide variety of environments, including rural areas, abandoned mines and smelters, and port facilities. The cumulative probability analysis shows the presence of three populations (Fig. 3). The poorly defined first break may represent the passage from rural-type data ( uncontaminated areas) to a transitional population. Given that the highs of the profile (Fig. 2) are found at La Herradura (huge stockpiles of iron ore from El Romeral mine), Tongoy (old decommissioned small copper smelters), Tamaya (abandoned Cu mine), and Panulcillo (copper flotation and heap-leaching plant), the 21.3 ngHg m$^{-3}$ break may truly indicate the passage from a transitional population to a well defined industrial-related one.

The Andacollo (Dayton Au operation and town) profile (P2) (Fig. 1) is particularly important as it concentrate the highest levels of atmospheric mercury (Fig. 2). The data can be clearly separated into two populations, with an anomalous one starting at 56.2 ngHg m$^{-3}$ (Fig. 3), basically developed within the town. Andacollo is a peculiar mining town, highly resembling the old pictures of the 19th century mining settlements; inside the town one may find abandoned flotation tailings, mineral heaps, and even trapiche installations along the urban perimeter. Apart from this, the modern mining installations (Au, Cu; open pits, and heap-leaching operations) are very near to the outer neighborhoods. Contrary to what might have been expected, the Dayton (Au) open pit did not show high levels of mercury, except for a few data from the Natalia pit in the order of 20–30 ngHg m$^{-3}$ (Fig. 2). The higher concentrations are detected in the town itself, at the entrance of the giant cyanide heap-leaching operation of Dayton, and particularly near to the trapiches. The latter are responsible for concentrations near to 10,000 and 100,000 ngHg m$^{-3}$ (due to instrumental restrictions the latter value is to be regarded as minimum). Given that: (1) the trapiches consume about 0.8 kg Hg per day; (2) there are around 30 of these mills on operation; and (3) only 50–70% of the mercury is finally recovered; one may wonder where all these 2628–4380 kg of “unrecovered mercury” go every year. Higuera et al. (2004) suggested for Almadén (Spain) a mechanism that may also apply to Andacollo. The gaseous mercury emitted by the sources, in this case trapiches, and heap-leaching operations, can be deposited in the surrounding soils as Hg$^{2+}$, either from direct deposition of emitted Hg$^{2+}$, or...
from conversion of emitted Hg$^0$ to Hg$^{2+}$ through ozone mediated processes (USEPA, 1997) (g: gas phase; aq: aqueous phase; p: particulate phase):

\[ \text{Hg}^0_{(g)} \rightarrow \text{Hg}^0_{(aq)} \]
\[ \text{Hg}^0_{(g)} + \text{O}_3_{(aq)} \rightarrow \text{Hg}^{2+}_{(aq)} \]
\[ \text{Hg}^{2+}_{(aq)} + \text{soot}/\text{possible evaporation} \rightarrow \text{Hg}^{2+}_{(p)} \]

Photolysis of inorganic Hg$^{2+}$ to Hg$^0$ at the soil surface may in turn contribute significantly to the emission of gaseous mercury to the atmosphere (Scholtz et al., 2003). In fact, even if part of the mercury in the
Fig. 3. Cumulative log-probability graphs for the different profiles. A, Tongoy, Guanaqueros, Ovalle, Tampillo (P1); B, Andacollo town, trapiches, marays, and Dayton gold mine (P2); C, Andacollo (Carmen copper mine) (P3); D, Punitaqui district (P4); E, Talcuna copper district and Vicuña (P5); F, manganese district of Corral Quemado and Andacollo (P6). PBL, Portillo baseline: 2 ngHg m$^{-3}$. WML, WHO maximum level: 1000 ngHg m$^{-3}$. 
soil becomes bound to an organic or inorganic matrix, the element would be eventually released by photo-reduction (Gustin et al., 2002), thus further contributing to the atmospheric pool. A quick check of the validity of these assumptions may be provided by the analyses of soil samples from the district, which yield results in the range of 3.4–47 μg g⁻¹Hg (Higueras et al., 2004). This result might indicate that although part of the soil’s mercury escapes to the atmosphere, a substantial portion remains attached. Alternatively, it is also probable that most of the mercury indeed escapes, but since new mercury becomes continuously adsorbed the soil fractions, a permanent stock forms. In any case, we must also bear in mind that the gold–mercury amalgams in the trapiche installations are treated by heating, a process that directly liberates mercury vapor to the atmosphere. Thus, one way or another, one may assume that the trapiches constitute the most important potential source of atmospheric mercury in the Andacollo district.

An illustrative profile of the interactions between the presence of ore deposits and atmospheric mercury are the Andacollo (Carmen) (P3) and Punitaqui (P4) profiles (Fig. 1). Measurements started at the main facilities of Carmen mine, the Andacollo porphyry copper deposit. Contrary to early assumptions indicating that the porphyry had some enrichment in mercury (e.g., Rytuba, 2003), the concentrations obtained in the pits were generally low (Fig. 2), and the only relatively high-level data were measured outside of the mine, i.e., at the entrance of the mine installations or within the town of Andacollo. The latter is well reflected in the anomalous population that forms at approximately 80 ngHg m⁻³ (Fig. 3). Given that conditions for data collection within the pits were perfect, and that the mercury enrichment of the porphyry is well supported by early works, we may infer that the element must have been concentrated in the uppermost levels of the deposit, retained in the oxide phase (e.g., Carr et al., 1986). Since stripping of the upper levels of the deposit was done early in Carmen, no important mercury should be currently present in the deposit, which might explain the lack of high concentrations and particularly, the anomalously low-level population between approximately 1 and 3 ngHg m⁻³ (Fig. 3). In fact, we may infer that these levels are indicative of strong mercury depletion. The same may apply to the Dayton case (Fig. 2).

The second leg (profile P4) comprised the historic district of Punitaqui (Fig. 1). Given that the district was the only mercury resource of Chile during the Spanish colonial time, so we expected to find truly anomalous concentrations in the vicinity of the mines. Punitaqui is a complex deposit comprising a shear-related Cu–Au deposit, and minor mercury veins associated with Riedel 1 type fractures (Oyarzún et al., 2001). Apart from this geologic setting, the mining site includes abandoned open pit and underground works, flotation tailings, and heaps (cyanide leaching). We detected variable levels of mercury (Fig. 2) and three data populations (Fig. 3): (1) low concentrations (up to 2 ngHg m⁻³) that represent clean agricultural areas (Punitaqui–Ovalle); (2) a transitional population between ~2 and 12 ngHg m⁻³ detected in the immediate vicinity of the mining complex; and (3) a truly anomalous population that reach concentrations well above 100 ngHg m⁻³. The latter is clearly related to the area in which both the copper–gold and mercury deposits occur (Fig. 2). Second in importance to these concentrations are the data related to the old tailings dumps, with mercury peaks approaching the 100 ngHg m⁻³ (Fig. 2). Soil samples obtained in the area yield results within the range of 2.5–35 μg g⁻¹Hg (n = 8), and an earlier soil geochemical survey of the district (Oyarzún et al., 2001) yielded a mean value of 2.2 μg g⁻¹Hg (n = 160), which indicates the existence of a district-wide heavily enriched substratum. The absence of trapiche installations in the Punitaqui district may explain the relatively lower concentrations of atmospheric mercury detected within this realm.

The Talcuna–Vicuña profile (P5) (Fig. 1) showed concentrations lower than expected (Fig. 2). The leg included the Quebrada Marquesa gully, in which the Talcuna district is located. The district comprises several copper and manganese mines (Oyarzún et al., 1998), and two of them are currently active (Coca-Cola and 21 de Mayo). Ore dressing includes crushing and flotation of copper sulfides. We observe two well-defined populations in the profile (Fig. 3): (1) low concentrations representing agricultural areas of the Elqui Valley (e.g., Vicuña), with levels below 3 ngHg m⁻³; and (2) relatively higher concentrations of up to 50 ngHg m⁻³, which are detected in relation to abandoned and active flotation tailings, and old mining sites (Las Rojas: abandoned small scale gold operations).

A final profile from Andacollo to Corral Quemado (P6) (Fig. 1) gave mostly background concentrations below 10 ngHg m⁻³ (Fig. 2). The area was an interesting target because of the presence of Corral Quemado, an important Mn district of the hot-spring type. The district is rich in iron oxides (Oyarzún et al., 1998) that could have acted as potential retention phases for mercury by adsorption (e.g., Carr et al., 1986). The only anomalous concentrations (Fig. 3) measured in this profile correspond to those that were collected either while exiting or entering the town of Andacollo (approximately above 100 ngHg m⁻³), and related to the town itself or to milling operations (above 158.5 ngHg m⁻³) (Fig. 2). The latter are responsible for the relatively complex log-probability graph (Fig. 3), in which concentrations >10 ngHg m⁻³ represent the anomalous populations of Andacollo, already studied in the P2 profile.
6. Conclusions

Compared to the reference value of Portillo, the studied sectors of the Coquimbo region generally display higher levels of atmospheric mercury. These concentrations are the result of the presence of mercury ore deposits, flotation tailings, and gold recovery installations (trapiche milling). The contacts between the different lower Cretaceous units are not reflected in our data. The levels of atmospheric mercury in the vicinity of ore deposits much depend on whether the ore has significant contents of primary mercury. Although most of the studied deposits give concentrations above those from the agricultural lands (2–3 ngHg m$^{-3}$), the levels vary significantly. For example, despite the hidden character of the mercury ores of Punitaqui (underground mining works) the sector displays a clear signature, with concentrations exceeding the 100 ngHg m$^{-3}$. On the contrary, the open pits of Andacollo (Carmen: Cu and Dayton: Au operations), give a minor signal oscillating around 10 ngHg m$^{-3}$. The same applies to Talcuna (Cu–Mn), whereas Corral Quemado (Mn) gives lower concentrations. An entirely different picture emerges from the industrial facilities. For example, the flotation tailings from Punitaqui give clear signals, with concentrations of up to 100 ngHg m$^{-3}$. A special mention deserves the old-fashioned gold recovery operations (trapiche) carried out at Andacollo, with extremely high levels of mercury in the order of 10$^3$–10$^5$ ngHg m$^{-3}$. The latter results are worrying because of two main reasons: (1) some of these gold operations are carried out within the limits of the town; and (2) these concentrations are well above the revised international air quality guidelines (maximum at 1,000 ngHg m$^{-3}$) (WHO Regional Office for Europe, 2000).

The combination of cumulative log-probability graphics and mercury distribution profiles allows clear differentiation of background and anomalous data sets, whereas the continuous Hg measurement procedures carried during this survey have proved to be an excellent tool to detect Hg signatures associated with the industrial activities. The procedure clearly allows differentiation of the areas subjected to agriculture (2–3 ngHg m$^{-3}$), from those in which mining-metal recovery takes place (at least above 10 ngHg m$^{-3}$). The latter suggests that under the proper atmospheric conditions (absence of strong winds) mercury tends to remain near to the potential source areas.

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References


Geochemists, Special Volume. 4, Richmond Printers Ltd., Richmond, BC, 95pp.

