

Characterization of the Potential Mercury Contamination in the Apolobamba Gold Mining Area, Bolivia

Caracterización de la contaminación potencial por mercurio en el área minera de Apolobamba, Bolivia

Caracterização da potencial contaminação por mercúrio na área mineira de Apolobamba, Bolívia

AUTHORS

Acosta J.A.^{1*}
ja.acosta@upct.es

Martínez-
Martínez S.¹

Faz A.¹

Millán R.²

Muñoz M.A.¹

Terán T.¹

Vera R.²

* Corresponding Author

¹ Departamento de Ciencia y Tecnología Agraria. Universidad Politécnica de Cartagena. Paseo Alfonso XIII, 52. Cartagena. 30230. Murcia. Spain.

² Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas. Madrid. Spain.

Received: 25.03.2011 | Revised: 11.07.2011 | Accepted: 12.07.2011

ABSTRACT

A large amount of Hg is used for gold extraction through the amalgamation process in the Apolobamba gold mining area located in the northwest part of La Paz, Bolivia. This mining operation may produce a very serious impact on the ecosystems, as well as on the health of miners and inhabitants, mainly due to the primitive methods used in the gold recovery. The objective of this work was to characterize the potential contamination of total Hg in soils, sediments, water, and plants in a mining area of Bolivia. Results showed that there was atmospheric deposition of Hg in the study area. Accumulation of this metal in the studied soils and sediments was one of the highest in the world, but Hg in aquatic solution was below the detection limit of the analytical method of the studied lakes and rivers. The highest concentration of Hg was found in the river sediments of the Sunchullí-Viscachani (102 mg kg⁻¹), and in the sediments of Sunchullí and Viscachani lakes (12.3 and 11.7 mg kg⁻¹, respectively). These concentrations may pose a serious problem for aquatic life, related ecosystems and human health. Therefore, there is a need to study Hg availability and speciation in soils and sediments to better understand the cycling of Hg in the area.

RESUMEN

Una gran cantidad de Hg se utiliza para la extracción de oro mediante el proceso de amalgamación en la zona minera de Apolobamba, localizada al noroeste de La Paz, Bolivia. Este tipo de actividad puede estar generando un impacto muy grave tanto para los ecosistemas, como para la salud de los mineros y habitantes de la zona, principalmente debido a los métodos poco tecnificados utilizados en la recuperación del oro. El objetivo de este estudio fue caracterizar la contaminación potencial que supone la presencia de Hg total en suelos, sedimentos, agua y plantas. Los resultados mostraron que existía una deposición atmosférica activa de Hg. La acumulación de este metal en los suelos y sedimentos estudiados fue una de las más altas a nivel mundial; sin embargo, el Hg en la solución acuosa estuvo debajo del límite de detección del método analítico utilizado en los lagos y ríos estudiados. La mayor concentración de Hg se encontró en los sedimentos del Río Sunchullí-Viscachani (102 mg kg⁻¹) y en los sedimentos de los lagos Sunchullí y Viscachani (12,3 y 11,7 mg kg⁻¹, respectivamente). Estas concentraciones pueden suponer un grave problema para los animales acuáticos, los ecosistemas asociados y la salud humana. Por lo tanto, existe una urgente necesidad de estudiar la biodisponibilidad y la especiación del Hg en suelos y sedimentos para comprender mejor el ciclo del Hg en esta área.

RESUMO

Na zona mineira de Apolobamba, localizada a Noroeste de La Paz, utilizam-se grandes quantidades de Hg no processo amalgamação para extração de ouro. Este tipo de actividade pode ser responsável por graves impactos quer para os ecossistemas quer sobretudo para a saúde dos mineiros principalmente devido às tecnologias pouco avançadas que são utilizadas na recuperação do ouro. O objectivo deste estudo foi a potencial contaminação que pressupõe a presença de Hg total nos solos, sedimentos, água e plantas. Os resultados obtidos mostraram a existência de uma deposição atmosférica activa de Hg. A acumulação deste metal nos solos e sedimentos estudados foi uma das mais elevadas a nível mundial; contudo, os teores de Hg na solução aquosa encontravam-se abaixo do limite de detecção do método analítico utilizado, para os lagos e rios estudados. A maior concentração de Hg foi detectada nos sedimentos do rio Sunchullí-Viscachani (102 mg kg⁻¹) e nos sedimentos dos lagos Sunchullí e Viscachani (12,3 y 11,7 mg kg⁻¹, respectivamente). Estas concentrações sugerem graves problemas para as espécies aquáticas, ecossistemas associados e saúde humana. Existe assim, uma necessidade urgente de estudar a biodisponibilidade e especiação do Hg nos solos e sedimentos, para melhor compreender o ciclo do Hg nesta zona.

KEY WORDS
Pollution, soil, environmental impact, sediments, water, heavy metals

PALABRAS CLAVE
Polución, suelo, impacto ambiental, sedimentos, agua, metales pesados

PALAVRAS-CHAVE
Poluição, solo, impacto ambiental, sedimentos, água, metais pesados

1. Introduction

The “Apolobamba Integrated Management National Area (ANMINA)”, located in the northwest part of the Department of La Paz, Bolivia, is a very important gold mining region. Currently, gold is extracted using a Hg amalgamation technique that represents a highly economical and practical technique since 1556 (Enríquez 2001). Hg amalgamation is based on the formation of a gold-Hg alloy which is subsequently heated to volatile Hg to obtain pure gold. Unfortunately, this method leads to massive Hg contamination in the mining area (Ramírez and Terán, 2002).

More than 40 000 tons of Hg were disseminated in the environment during the colonial time in Bolivia (Enríquez 2001). At least 25-50 tones of Hg per year are discharged in the environment in Bolivia (Ministerio de Minería Metalurgia de Bolivia 1993). In addition, the use of firewood of diverse plant species as fuel for heating ovens caused a successive deforestation and degradation of the region (Ramírez and Terán, 2002).

The studied area has around 100 mining cooperatives and they are all located in alluvial plains in the Andean Bolivian Plateau. Mining operations use very primitive equipment and are carried out mostly by women and children. Miners work at night and even in abandoned mines in order to be able to survive (Enríquez 2001). The houses are located next to the mines and along the river. The inhabitants of these areas consume fish from the lakes and rivers, and they use the waters for the livestock, domestic purposes, and irrigation.

Studies were first initiated during the 1980s to determine the environmental impact of the mining activities. In 1993, the National Secretary of the Environment (SENMA) carried out an evaluation of the mining and industrial sectors in Bolivia and concluded that the main impacts on the environment derived from the mine activity were: consumption of exhaustible and scarce resources (land use, removal of minerals, and water use); transformation of the landscape; pollution of surface water, groundwater and soils; and accumulation of solid wastes and emissions of dust containing heavy metals that can contaminate water and soils (Enríquez 2001). Recent exploratory studies also found significant Hg contamination

in sediments, river waters and other water bodies (Maurice-Bourgoin et al. 2001), and fish (Alanoca and Maurice-Bourgoin 2000).

Although previous research efforts pointed out the importance of determining the most suitable preventive measures in the area (Alanoca and Maurice-Bourgoin 2000; Maurice-Bourgoin et al. 2001), local and national authorities have had great difficulties controlling the mining operations. This is due to the isolated occurrence of many small cooperative mines, the absence of serious efforts by qualified staff, and the lack of infrastructures. All of these factors collectively contributed to the development of the present critical environmental conditions.

Hg is among the most highly toxic trace metals in the food chain and many national and international agencies and organizations are interested in developing methods for its possible emission control (Horvat et al. 2003). Hylander et al. (1994), studying the Hg content of the Pantanal ecosystem in Brazil, indicated that Hg originated in the amalgamation process showed higher bioavailability than Hg naturally present in soil minerals. These authors found that catfish (*Pseudo-platyostoma coruscans*) had a Hg content above the limit for human consumption (0.5 ppm w.w.) and significantly above the natural background level.

Hg transfer and transport in watersheds are well understood (USEPA, 2000). The elemental Hg (Hg⁰) can travel from its source to the final receptor following a multi-step sequence, which includes emission to the atmosphere, transportation and deposition. Travníkov (2005) studied the dispersion of Hg in the atmosphere of the Northern hemisphere, and suggested that the contribution of external anthropogenic and natural sources to Hg deposition to different continents varies from 30 % to 70 % of the total value. This author concluded that the contribution of the intercontinental atmospheric transport of Hg is comparable with that of regional pollution even in industrially developed regions of the Northern hemisphere.

In general, Hg is believed to be relatively inert with a strong volatility under most atmospheric conditions (Zang-Ho et al. 2005). Thus, Hg⁰ is not

2. Material and Methods

easily oxidized to less volatile forms by the major oxidants (O_3 , OH, etc.); so its residence time is estimated in the range of 1–2 years (Lindquist and Rhode 1985).

Recent estimates of global anthropogenic emission of Hg are in the range of 2 000–2 600 Mg yr⁻¹ (Pirrone et al. 1996; Pacyna and Pacyna, 2002; Pacyna et al. 2006). The global oceanic emission is estimated to be 800–2 600 Mg yr⁻¹ (Bergan et al. 1999; Mason and Sheu, 2002; Lamborg et al. 2002) and the global natural terrestrial emission is estimated to be 1 000–3 200 Mg yr⁻¹ (Lindberg et al. 1994; Bergan et al. 1999; Shia et al. 1999; Mason and Sheu, 2002; Lamborg et al. 2002; Seigneur et al. 2004). These estimates give a global natural Hg emission of 1 800–5 800 Mg yr⁻¹.

The objective of this work was to determine the total Hg in soils, sediments, plants, and waters in three selected areas affected by gold mining in comparison to regulatory threshold levels.

Study area and sites descriptions

The study area is located in the protected area of “Apolobamba”, 68° 30′–69° 20′ west and 14° 40′–15° 10′ south, La Paz Province, Bolivia. Three different gold mining districts affected by Hg pollution (Campo, 2003) were selected for our study: Sunchullí-Viscachani, Katantica, and Sural (Figure 1).

In order to determine the extension of Hg pollution in the study area, soil, sediment, water and plant samples were collected. In addition, for comparing surface Hg with subsurface Hg concentration, and therefore evaluating atmospheric deposition, soil profiles were selected and sampled. Each soil, sediment, water, and plant sample was collected in triplicate and mixed in the field.

Soil samples were taken using a soil spade, with the caution of avoiding contamination between samples, cleaning the spade before use for each sample. Soil samples were taken between 0 to 15 cm depth. Sediment samples were

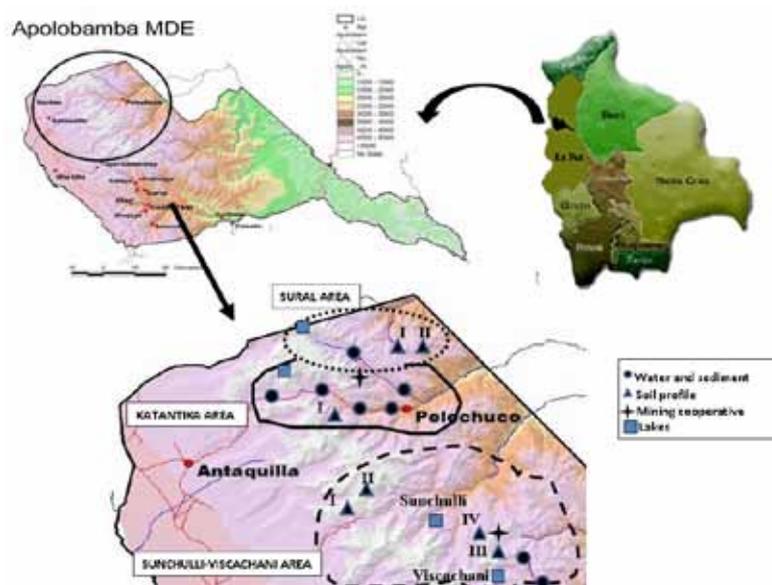


Figure 1. Sampling map and location of the three studied areas. Surface soil samples were collected around the lakes and mining cooperatives (not shown in the map).

taken using a long spade, in order to take the samples separated from the river or lake shore and as closer as possible to the center of the river bed, and as far as possible from the lake's shore. Plant samples from the same species were taken and stored in polyethylene bags with some holes to avoid water condensation and putrefaction. They were pressed and dried for its identification.

Soil and sediment samples were stored in polyethylene bags, while water samples were stored in hydrochloric acid washed high-density polyethylene bottles. All samples were stored at 4 °C and water samples were kept in light dark conditions using opaque bottles prior to sample preparation and analysis.

- The Sunchullí-Viscachani area

Four soil profiles were sampled in the Sunchullí-Viscachani area. Soil profiles were classified according to the World Reference Base (WRB 2006): a Fibric Histosol (Profile I), an Haplic Cambisol (Profile II), and two Haplic Regosols (Eutric) (Profile III and IV) (Table 1). Profile I (formed by three horizons: H1 (0-12 cm), H2 (12-23 cm), and R (>23 cm)) and Profile II (formed by four horizons: H (0-9 cm), Ah (9-24 cm), Bw (24-40 cm), and C/R (>40 cm)) were located 6 km northwest from Sunchullí Lake and 18 km from the main mining operation site, in the north face side of the mountain range (Figure 1). These profiles were sampled to find out whether there was a long distance atmospheric deposition of Hg in the area. Profile III (formed by four horizons: Ah (0-11 cm), AC (11-22 cm), and C (>22cm)) and Profile IV (formed by four horizons: Ah (0-12 cm), C1 (12-32 cm), 2C2 (32-54 cm), and 2C3 (>54 cm)) were located less than 500 m from the main mining operation site.

Three surface soil samples were taken around Sunchullí Lake (0-15 cm depth), located 5 km northwest from the main mining operation site. In order to evaluate the accumulation of Hg on the water bodies bed, seven sediment samples were taken: three in

Sunchullí Lake, two in Viscachani Lake, and four in the Sunchullí River (two upstream and two downstream a discharge point). Seven water samples were collected in the same location where the sediments were taken: three from the Sunchullí Lake, two from Viscachani Lake, and two from the Sunchullí River. The most abundant plant species (*Aciachne sp.*) growing in the main mining operation area was sampled, including roots and aerial part. This species is the most common plant growing in the *Pycnophyllum* grasslands from Bolivia (Seibert, 1993; Muñoz and Faz, 2009), which is dominant in the Apolobamba highlands. Two mine residual samples from a pyramidal pile of 5x6 m base and 2 m high close to the mining operation area were collected; also three soil samples were sampled from this site for analysis.

- The Katantika area

The Katantika area is located in the north part of the Apolobamba gold mine area, close to the Sural, and includes three different rivers: the Pelechuco River, the biggest one, the Turcos River, and the Rayo Rojo River. The mining activity in this area, like in the other areas, is principally associated with gold extraction but in this case the extraction is carried out from two different materials: auriferous grey quartz and alluvial deposits coming from upstream and located at the bottom of the rivers.

In the Katantika area, a soil profile (Profile I), formed by two horizons: Ah (0-42 cm) and C (> 42 cm) and located 1 km from the mining operation, was studied and classified as an Haplic Umbrisol (WRB, 2006). Two sediment samples in the Katantika Lake and four in the Pelechuco River (two samples upstream and two downstream a discharge point) were collected. Six water samples were taken at the same point than the previous sediments and finally, one mine solid residue from three pyramidal piles of 3x4 m base and 1 m high close to the mining operation area was collected. In addition, a sediment sample and a water sample were also collected in a small

stream draining from the main Katantika mining operation area.

- The Sural area

The smallest gold mining area included in this study, the Sural area, is located in the north-west part of Apolobamba. In this region the principal gold extraction is from alluvial deposits in the lower part of the river, and the gold distribution is controlled by the sediment structure affected by surface runoff. Profile I, formed by two horizons: Ah (0-9 cm) and R (> 9 cm), and Profile II, formed by the horizons H (0-27 cm) and R (> 27 cm), were taken 5 km southeast from the Sural Lake and 1 km east from the Sural River, and were classified as a Lithic Leptosol and a Fibric Histosol, respectively (WRB, 2006). Two superficial soils located 1 km from the mining operation area, two sediments, and two water samples were collected in the Sural Lake. One water sample in the Sural River was also taken. Finally, one plant sample (*Aciachne sp.*), including roots and aerial part, was collected in the shore of the Sural River.

Analytical treatment

Soil samples were dried at 30 °C for 24 h, passed through a 2 mm steel sieve, and grounded with a mechanical agate mortar (Retsch RM 100) for 10-15 min before analyses. Sediment samples were dried and grounded but not sieved because they were composed of particles less than 2 mm. Plants were washed with deionized water, oven-dried at 70 °C for 48 hours and grounded for Hg analysis.

Soils and sediments were characterized for: pH (Peech 1965), organic carbon (Anne 1945; Duchafour 1970), total nitrogen (Duchafour 1970), electrical conductivity (Bower and Wilcox 1965), particle size distribution using Robinson Pipette method (FAO-ISRIC, 2006), and cation exchange capacity (Chapman 1965).

The water samples were filtered and stored in the refrigerator at 4 °C. An Advanced Hg Analyser (AMA-254, LECO company) was used, with a detection limit of 0.5 ppb on weight basis. This

equipment uses solid samples, thus it is not necessary any digestion of the samples. Reagent blanks and reference materials were used as the quality control samples during the analysis. Certified reference materials (CRM) were used to determine the accuracy and precision of the measurements and to validate the applied method. They were obtained from the Community Bureau of Reference (BCR). These certified reference materials consist of SRM 2709 (soil, $1.40 \pm 0.08 \text{ mg kg}^{-1}$ of Hg), CRM 62 (*Olea europaea*, $0.28 \pm 0.02 \text{ mg kg}^{-1}$ of Hg), and BCR 281 (*Rye grass*, $0.020 \pm 0.002 \text{ mg g}^{-1}$).

Bolivia and Spain do not have any legislation allowing the classification of a polluted soil according to its Hg concentration. Therefore, reference values from Holland (0.3 mg kg^{-1}), Belgium (0.55 mg kg^{-1}), France (1 mg kg^{-1}), Germany (2 mg kg^{-1}), United Kingdom (1 mg kg^{-1}) and Switzerland (0.8 mg kg^{-1}) have been used to evaluate the degree of Hg enrichment of the sediment and soil samples (NMHPPE 1994; BWRHABTGG 1995; Barth and L'Hermite 1987; BAFUB 1987). It should be kept in mind that these guidelines pertain to soil samples and not sediments.

3. Results and Discussion

The Sunchullí-Viscachani area

The Hg contents of the topsoil from the four profiles in this area were 0.38, 2.58, 9.94, and 2.96 mg kg⁻¹. In comparison, the concentrations in the subsoil were 0.09, 0.34, 1.27 and 0.23 mg kg⁻¹ (Table 1). These results suggest that atmospheric deposition of Hg could have taken place

in this area for all the studied profiles. However, some studies have shown that in many tropical areas Hg is frequently high in soils, possibly as a result of the atmospheric deposition of Hg over thousands to perhaps millions of years (Lechler et al. 2000). Thus, it is possible that the observed values from Profile I represent the natural accumulation of Hg in the topsoil.

Table 1. Properties and Hg contents of soil profiles, surface soils, plant, mine wastes, water and sediments in the Sunchullí-Viscachani area

	pH	E. C. (dS m ⁻¹)	O.C. (g kg ⁻¹)	C.E.C. (cmol ₊ kg ⁻¹)	T. N. (g kg ⁻¹)	Clay (g kg ⁻¹)	Hg (mg kg ⁻¹)
Profiles							
Fibric Histosol							
Profile I - H1 (0-12 cm)	5.55	0.20	96.6	30.57	7.7	176.8	0.38
Profile I - H2 (12-23 cm)	5.77	0.21	45.4	11.90	3.4	112.0	0.09
R (>23 cm)	--	--	--	--	--	--	--
Haplic Cambisol							
Profile II - H (0-9 cm)	6.91	0.25	6.2	5.26	0.8	69.3	2.58
Profile II - Ah (9-24 cm)	5.41	0.06	27.6	9.80	2.6	146.5	0.05
Profile II - Bw (24-40 cm)	6.61	0.05	16.8	7.43	1.5	81.5	0.08
Profile II - C/R (> 40 cm)	5.44	0.19	19.2	5.76	1.4	89.7	0.34
Haplic Regosol (Eutric)							
Profile III - Ah (0-11 cm)	5.13	0.16	39.2	12.36	3.4	156.0	9.94
Profile III - AC (11-22 cm)	5.27	0.12	27.0	11.01	2.1	127.3	0.05
Profile III - C (> 22 cm)	5.88	0.06	5.8	3.63	0.5	79.6	1.27
Haplic Regosol (Eutric)							
Profile IV - Ah (0-12 cm)	5.09	0.73	71.0	14.41	5.9	208.5	2.96
Profile IV - C1 (12-32 cm)	4.55	0.51	40.1	15.78	3.6	259.5	1.97
Profile IV - 2C2 (32-54cm)	5.31	0.17	20.8	12.28	1.6	161.9	0.22
Profile IV - 2C3 (> 54 cm)	5.12	0.32	16.3	11.64	1.5	125.1	0.23
Soils							
Soil 1	5.54	0.18	102.0	29.95	8.7	169.2	203
Soil 2	5.85	1.29	8.0	1.15	0.7	30.7	12.8
Soil 3	4.52	0.27	50.8	23.66	6.3	127.4	5.13
Plant							
Plant	--	--	--	--	--	--	1.84
Mine waste							
M1	6.35	3.26	34.2	1.50	0.3	35.6	NM
M2	2.18	5.72	02.3	0.59	0.4	21.8	3.45

Sunchullí River							
Sediment (1) upstream discharge	6.34	0.230	11.6	4.18	1.2	40.8	4.14
Sediment (2) downstream discharge	4.85	1.180	16.6	2.99	0.9	52.8	102
Water (1) upstream discharge	6.96	0.150	--	--	--	--	BDL
Water (2) downstream discharge	6.91	0.148	--	--	--	--	BDL
Sunchullí Lake							
Soil (4)	7.88	1.22	7.6	2.96	1.2	61.5	0.78
Soil (5)	6.63	0.06	6.6	6.68	1.5	177.6	1.2
Soil (6)	7.51	0.82	7.9	3.59	1.8	101.0	0.06
Sediment (3)	7.19	0.41	10.6	1.18	0.5	12.9	12.3
Sediment (4)	6.31	0.11	18.3	7.17	2.7	339.4	0.1
Sediment (5)	7.02	0.21	11.9	3.29	1.2	76.8	4.14
Water (3)	6.96	0.203	--	--	--	--	BDL
Water (4)	6.90	0.187	--	--	--	--	BDL
Water (5)	7.06	0.192	--	--	--	--	BDL
Viscachani Lake							
Sediment (6)	5.74	0.56	218.3	34.74	16.7	205.1	11.7
Sediment (7)	5.77	0.04	89.5	42.56	9.0	277.2	23.7
Water (6)	6.57	0.048	--	--	--	--	BDL
Water (7)	6.65	0.045	--	--	--	--	BDL

BDL: below the detection limit ($0.5 \mu\text{g L}^{-1}$); NM: not measured due to saturation of equipment; E.C.: electrical conductivity; O.C.: organic carbon; T.N.: total nitrogen; C.E.C.: cation exchange capacity.

Oppositely, Profiles II, III, and IV showed a much higher concentration in the topsoil than in the subsoil, indicating active atmospheric deposition of Hg; therefore, for these profiles the Hg was originated from the atmospheric deposition and not from the bedrock. The Hg can be transported in small particles in the air and cause problems in the breathing system (Peñaloza and Reinhardt, 2000). These particles could reach the agricultural soils and pastures near the mine areas by atmospheric transport.

According with the used regulations, all the surface horizons have a Hg concentration higher than the reference values (NMHPPE, 1994; BWRHABTGG, 1995; Barth and L'Hermite 1987; BAFUB 1987), except for Profile I. Therefore, all

the profiles in the area studied can be considered as anthropogenic Hg-enriched with the exception of the Fibric Histosol (Profile I).

As shown in **Table 1**, the effect of atmospheric Hg deposition in the Sunchullí-Viscachani area was visible in the soil surface layers (Soils 1, 2 and 3) with a highest concentration up to 203 mg kg^{-1} . This and other analytical data confirm that this area likely make one of the most heavily polluted area with Hg in the world, which poses a very high risk for human population and terrestrial ecosystems. In fact, some authors have reported maximum levels of Hg of 3.4, 1.9, 54, 4.2, 40, and 2.4 mg kg^{-1} in surface soils of Hg mining or ore deposits from Great Britain, Canada, Czechoslovakia, U.S., and U.S.S.R. (Kabata-Pendias and Pendias 1995).

The Hg contents were varied in the Sunchullí Lake sediments. According to the already mentioned regulatory schemes, sediments could be classified as seriously enriched except for Sediment 4 (**Table 1**). The Hg found in the lake sediments come from both places, where the miners use primitive amalgamation processes, and from atmospheric deposition due to distance from the bigger mining operations, as showed the concentration of soil samples taken in the surroundings of the lake (Soils 4, 5, and 6), which ranged between 1.2 and 0.06 mg kg⁻¹.

Based on the analytical data, it is interesting to observe that the Hg concentrations in water do not seem to be high enough to be detected by the analytical method. Taking into account the detection limit of the method, the values were lower than the levels allowed (0,5 µg L⁻¹) by the European Community (DVGW 1985). Contents of Hg in the sediments (Sediments 3, 4, and 5) varied from 12.3 to 0.1 mg kg⁻¹. If these values are compared with those obtained by Alanoca and Maurice-Bourgoin (2000) for Tuichi River waters (0.0145 and 0.047 mg kg⁻¹) in Bolivia, we can suggest that the sediments of the Sunchullí Lake are enriched with great amounts of Hg.

The highest concentration of Hg (23.7 mg kg⁻¹) was obtained in the Sediment 7 of the Viscachani Lake area, which is similar to the Madeira River (Brazil) sediments concentration (19.83 mg kg⁻¹) (Pfeiffer et al. 1991). This sample was collected close to an area where the primitive amalgamation processes were carried out. Hg levels in the sediment samples of the lake were very high (23.7 and 11.7 mg kg⁻¹) and largely exceeded the thresholds levels established by the already mentioned regulations (NMHPPE 1994; BWRHABTGG 1995; Barth and L'Hermite 1987; BAFUB 1987) and the values reported in the literature (Filho and Maddock 1997; Barbo et al. 2004).

Hg contents of the lakes and river waters of the Sunchullí-Viscachani area were below the detection limit (**Table 1**). However, Sediments 3 and 5 from the Sunchullí Lake had high Hg contents, which we consider to be a potential high risk for the ecosystem. In the Sunchullí River, Sediment

2 was taken close to a point of discharge; the Hg concentration in this sediment was 102 mg kg⁻¹ which was the highest of all the sediments we analyzed.

Hg content of the plant (*Aciachne sp.*) was 1.84 mg kg⁻¹. According to Kabata-Pendias and Pendias (1992), the background levels of Hg in vegetables and fruits vary from 2.6 and 86 µg kg⁻¹. Therefore the reported value showed a potential accumulation of Hg in plant tissues for this species in the studied area. Recent works have shown that plant foliage can be a significant sink of atmospheric Hg (Hanson et al. 1995; Ericksen et al. 2003; Schwesig and Krebs 2003) and that litterfall can be an important source of Hg to the terrestrial ecosystem (Frescholtz et al. 2003). Plants differ in their ability to take up Hg and can also develop a tolerance to high Hg concentration in their tissues when grown in soils overlying Hg deposits (Kabata-Pendias and Pendias 1992).

The Katantika area

The Hg concentration in the Katantika area (**Table 2**) was lower than in the Sunchullí-Viscachani area. Profile I samples showed values of Hg lower than the reference concentration given by the used international regulation, therefore no Hg enrichment was observed in this profile. However, Sediment 1, located next to the mine (**Figure 1**), presented a Hg concentration of 2.24 mg kg⁻¹ and confirmed that the Katantika Lake exhibited a Hg enrichment. In the case of the Pelechuco River, Hg was no detected in the water of the river. Only in the water sample collected from the mining operation drainages towards the Pelechuco River (Water 7) the presence of Hg was detected (1.93 µg L⁻¹) (**Table 2**), since the sampling site was close to a mining operations area. Taking into account the levels allowed (0.5 µg L⁻¹) by the European Community (DVGW 1985) this water sample was polluted by Hg. Due to the cumulative contribution of the spills along the river, sediments of the lower basin had higher concentrations of Hg (**Table 2**).

Table 2. Properties and Hg contents of the soil profiles, lake sediments, lake and river waters, and the mine samples in the Katantica area

	pH	E. C. (dS m ⁻¹)	O.C. (g kg ⁻¹)	C.E.C. (cmol _c kg ⁻¹)	T. N. (g kg ⁻¹)	Clay (g kg ⁻¹)	Hg (mg kg ⁻¹)
Profile							
Haplic Umbrisol							
Profile I - Ah (0-42 cm)	4.75	0.15	75.2	24.68	4.3	109.2	0.08
Profile I - C (> 42 cm)	6.40	0.04	06.6	4.14	0.5	55.0	0.02
Katantica lake							
Sediment (1)	6.48	0.32	16.7	4.56	1.7	68.2	2.24
Sediment (2)	5.18	0.67	87.6	31.35	8.1	138.7	0.20
Water (1)	6.87	0.035	--	--	--	--	BDL
Water (2)	6.79	0.047	--	--	--	--	BDL
Pelechuco River							
Sediment (3) upstream discharge	6.35	0.07	08.4	1.99	1.0	19.0	0.08
Sediment (4) upstream discharge	7.27	0.29	6.2	1.11	0.3	12.5	0.04
Sediment (5) downstream discharge	7.03	0.55	6.3	0.96	0.3	10.0	8.55
Sediment (6) downstream discharge	7.41	0.27	33.1	4.84	3.6	418.7	6.85
Water (3) upstream discharge	6.51	0.068	--	--	--	--	BDL
Water (4) upstream discharge	6.97	0.051	--	--	--	--	BDL
Water (5) downstream discharge	7.13	0.037	--	--	--	--	BDL
Water (6) downstream discharge	7.18	0.072	--	--	--	--	BDL
Water from mining area towards river (7)	6.93	0.069	--	--	--	--	1.93*
Mine area							
Sediment (7)	6.40	0.30	4.7	0.31	0.3	7.0	31.80
Residual (1)	4.90	0.30	6.3	0.81	0.3	0.0	17.23
Water (8)	5.70	0.086	--	--	--	--	0.73*

BDL: below the detection limit (0.5 µg L⁻¹); NM: not measured due to saturation of equipment; E.C.: electrical conductivity; O.C.: organic carbon; T.N.: total nitrogen; C.E.C.: cation exchange capacity. * Concentration in µg L⁻¹.

The Hg concentration in the residual from the mining operation was 17.23 mg kg⁻¹. The Hg level in water associated with the mining site (Water 8) was 0.73 µg L⁻¹. If this value is compared to the one obtained in the Tapajos River, Brazil, which was less than 1.7 and 1.9 ng L⁻¹ for

the wet and dry seasons, respectively (Roulet et al. 1998), the aquatic ecosystems of Pelechuco River can be affected for a potential source of Hg pollution. In addition, according with the European regulation (DVGW 1985), this water sample is polluted by Hg.

The Sural area

When comparing the data of the soil profiles from the Sunchullí-Viscachani area with the Hg concentration in the soil profiles from the Sural area, atmospheric deposition of Hg does not occur in the areas close to Profiles I and II (Table 3). This is likely due to the fact that the extraction of gold in this area is less developed than in the other studied areas, and thus the deposition of Hg occurs near the emission source. Therefore, we can suggest that only the nearby terrestrial ecosystems and the workers could be at risk, since the amalgamation is a local process.

The Hg concentrations of the surface soils from the Sural Lake were similar to the surface soils of the Sunchullí Lake area. Hg concentrations in sediments and surface soils did not reach high

values ($< 0.6 \text{ mg kg}^{-1}$, Table 3). Hg contents in the water of the lake were also similar to the values found in the Sunchullí Lake, which was $< 0.5 \mu\text{g L}^{-1}$.

Content of Hg in the plant tissues was 0.16 mg kg^{-1} which was lower than the value reported for the plant sample in the Sunchullí-Viscachani area. This is likely due to the plant growth on soils with low concentrations of Hg and a low impact of atmospheric deposition. In general, Hg content of plants is high when Hg content of soil is also high, but this relation does not always stands (Siegel et al. 1987).

Hg water concentration in the Sural River was below the detection limit. Therefore, this water does not currently pose any risk for aquatic ecosystems and human health (Table 3).

Table 3. Properties and Hg content of the two surface soil, sediment, water, and plant samples in the Sural area

	pH	E. C. (dS m^{-1})	O.C. (g kg^{-1})	C.E.C. ($\text{cmol}_+ \text{ kg}^{-1}$)	T. N. (g kg^{-1})	Clay (g kg^{-1})	Hg (mg kg^{-1})
Profile							
Lithic Leptosol							
Profile I – Ah (0-9 cm)	5.09	0.37	43.7	15.21	4.6	95.7	0.06
Profile I – R (>9 cm)	--	--	--	--	--	--	--
Fibric Histosol							
Profile II – H (0-27 cm)	4.04	0.11	59.8	61.01	17.0	150.8	0.07
Profile II – R (>27 cm)	--	--	--	--	--	--	--
Sural lake							
Soil (1)	7.32	0.43	8.4	4.96	1.2	71.6	0.62
Soil (2)	7.38	0.13	7.9	3.97	1.5	204.9	0.02
Sediment (1)	6.94	0.17	11.8	5.56	1.0	127.1	0.07
Sediment (2)	6.18	0.14	62.9	11.42	4.4	504.9	0.23
Water (1)	6.81	0.034	--	--	--	--	BDL
Water (2)	6.83	0.055	--	--	--	--	BDL
Sural River							
Water (3)	6.85	0.061	--	--	--	--	BDL
Plant	--	--	--	--	--	--	0.16

BDL: below the detection limit ($0.5 \mu\text{g L}^{-1}$); NM: not measured due to saturation of equipment; E.C.: electrical conductivity; O.C.: organic carbon; T.N.: total nitrogen; C.E.C.: cation exchange capacity.

4. Conclusions

Analytical data have confirmed a high level of Hg pollution in two of the three areas studied. Among the three sites, the Sunchullí-Viscachani area must have received a very high amount of atmospheric deposition of Hg as well. This may be due to the open topographic position in comparison to the other two areas. Therefore, the risk for the ecosystems and inhabitants of the region is very high.

Hg contents of the majority of water samples from lakes and rivers of the three areas were below the detection limit. However, Hg concentrations found in some sediments were high, indicating that an enrichment of Hg in the sediments has occurred. The highest concentration of Hg was found in the river sediment of the Sunchullí-Viscachani area. This points out the degree of contamination in the mining area. In our view, this area is likely one of the heavily Hg-contaminated sites in the world. Accumulation of Hg was also found in plants tissues. Therefore, there is an urgent need to study Hg transformation of inorganic Hg to organic Hg species (MeHg), i.e bioaccessibility and speciation in soils and sediments in the Apolobamba area.

5. Acknowledgements

This study was carried out with the assistance of the Spanish Agency for International Cooperation within the framework of the Araucaria-Apolobamba Program.

REFERENCES

- Alanoca L, Maurice-Bourgoin L. 2000. Estudio de la contaminación por mercurio en la cuenca alta del Río Tuchi. La Paz, Bolivia.
- Anne P. 1945. Sur le dosage rapide du carbone organique des sols. *Annales de Agronomie* 2:162-172.
- BAFUB 1987. Available from: www.gama-peru.org/libromedmin/.
- Barbo ES, Angélica RS, Silva AP, Faial KRF, Mascarenhas AFS, Santos ECO, Jesus IM, Loureiro ECB. 2004. Assessment of Mercury Levels in Soils, Waters, Bottom Sediments and Fishes of Acre State in Brazilian Amazon. *Water, Air, Soil Poll.* 147:61-77.
- Barth H, L'Hermite P, editors. 1987. *Scientific Basis for Soil Protection in the European Community*. Commission of the European Communities. London: Elsevier Applied Science.
- Bergan T, Gallardo L, Rodhe H. 1999. Mercury in the global troposphere: a three-dimensional model study, *Atmospheric Environment* 33:1575-1585.
- Bower CA, Wilco Wilcox LV. 1965. Soluble salts. In: Black CA, editor. *Methods on Soil Analysis*. Madison, Wisconsin, U.S.A.: American Society of Agronomy. p. 933-940.
- BWRHABTGG, 1995. *Besluit van de Vlaamse Regering Houdende Achtergrondwaarden. Bodernsaneeringsnomen en Toepassingen van Gereinigde Grond*. Brussels, Belgium: Ministry of Environment and Employment.
- Campo L. 2003. Programa Araucaria. Componentes Programa Araucaria, Resultados Cartográficos. p. 29-47.
- Chapman HD. 1965. Cation exchange capacity. In: Black CA, editor. *Methods of Soil Analysis*. Madison, Wisconsin, U.S.A.: American Society of Agronomy. p. 891-900.
- Duchaufour P. 1970. *Precis de Pedologie*. Paris: Masson. 481 pp.
- DVGW. 1985. Available from: www.gama-peru.org/libromedmin/.
- Enríquez JC. 2001. *Minería, Minerales y Desarrollo Sustentable en Bolivia*. La Paz, Bolivia: Servicios Ambientales.
- Ericksen JA, Gustin MS, Schorran DE, Johnson DW, Lindberg SE, Coleman JS. 2003. Accumulation of atmospheric mercury in forest foliage. *Atmos. Environ.* 37:1613-1622.
- FAO-ISRIC. 2006. *Guidelines for Soil Description (revised)*, fourth ed. Rome: F.A.O. 97 pp.
- Filho SR, Maddock JEL. 1997. Mercury pollution in two gold mining areas of the Brazilian Amazon. *J. Geochem. Explor.* 58:231-240.
- Frescholtz TF, Gustin MS, Schorran DE, Fernandez GCJ. 2003. Assessing the source of mercury in the foliar tissue of Quaking Aspen. *Environ. Toxicol. Chem.* 22:2114-2119.
- Hanson PJ, Lindberg SE, Tabberer TA, Owens JG, Kim KH. 1995. Foliar exchange of mercury vapor: evidence for a compensation point. *Water Air Soil Pollut.* 80:373-382.
- Horvat M, Nolde N, Fajon V, Jereb V, Logar M, Lojen S, Jacimovic R, Falnoga I, Faganeli J, Drobne D. 2003. Total mercury, methylmercury and selenium in mercury polluted areas in the province Guizhou, China. *Sci. Total Environ.* 304:231-256.
- Hylander LD, Silva EC, Oliveira LJ, Silva SA, Kuntze EK, Silva DX. 1994. Mercury levels in Alto Pantanal: A screening study. *Ambio* 23:478-484.
- Kabata-Pendias A, Pendias H. 1995. *Trace Elements in Soils and Plant*. Boca Raton, USA: CEC Press. 365 pp.
- Lamborg CH, Fitzgerald WF, Damman AWH, Benoit JM, Balcom PH, Engstrom DR. 2002. Modern and historic atmospheric mercury fluxes in both hemispheres: Global and regional mercury cycling implications. *Global Biogeochem. Cycles* 16(4): 1104.
- Lechler PJ, Miller JR, Lacerda LD, Vinson D, Bonzongo JC, Lyons WB, Warwick JJ. 2000. Elevated mercury concentrations in soils, sediments, water, and fish of the Madeira River basin, Brazilian Amazon: a function of natural enrichments?. *Sci. Total Environ.* 260:87-96.
- Lindberg SE, Owens JG, Stratton WJ. 1994. Application of throughfall methods to estimate dry deposition of mercury. In: Watras CJ, Huckabee JW, editors. *Mercury Pollution: Integration and Synthesis*. Chelsea, MI: Lewis Publishers. p. 261-271.
- Lindquist O, Rhode H. 1985. Atmospheric Mercury—a review. *Tellus* 37B:136-159.
- Mason RP, Sheu G. 2002. Role of ocean in global mercury cycle. *Global Biogeochemical Cycles* 16:1-14.
- Maurice-Bourgoin L, Aalto R, Fraizy P, Barnaud V, Guyot JL. 2001. Modulation of Mercury Transport trough Fluvial System by Channel-Floodplain Interaction: A case study for the Beni River, Bolivian Amazonia. In: 6th Int. Conference on Mercury as a global pollutant; 2001 Oct 15-19; Akagi, Minamata, Japan.

- Ministerio de Minería Metalurgia de Bolivia. 1993. Desarrollo de la Minería y la Metalurgia en Bolivia: Fondo y Perfil Preliminar del Proyecto, "Regulaciones Ambientales para la Industria Minera. Swedish Geological, SGAB International AB.
- Muñoz MA, Faz A. 2009. Soil-plant conservation in the vicuna (*Vicugna vicugna*) habitat in Apolobamba, Bolivia: biodiversity in high altitude grasslands. In: Faz Cano A, Arocena JM, Mermut AR, Ortiz Silla R. editors. Land Degradation and Rehabilitation-Dryland Ecosystems. Reiskirchen: Catena Verlag. Advances in Geology 40:97-108.
- NMHPPE. 1994. Netherlands Ministry of Housing. Physical Planning and Environment. Leidschendam, Holland.
- Pacyna EG, Pacyna JM, Steenhuisen F, Wilson SJM. 2006. Global anthropogenic mercury emission inventory for 2000. *Atmospheric Environment* 40:4048-4063.
- Pacyna J, Pacyna E. 2002. Global emissions of mercury from anthropogenic sources in 1995. *Water, Air and Soil Pollution* 137:149-165.
- Peech M. 1965. Hydrogen-ion activity. In: Black CA, editor. *Methods of Soil Analysis*. Madison, Wisconsin, U.S.A.: American Society of Agronomy. p. 914-916.
- Peñaloza M, Reinhardt I. 2000. Problemas ambientales de la minería Boliviana. Estudio de caso de la minería en el área de la ciudad de Potosí, Proyecto IDRC - WRI - CIPMA: Identificando los Impactos Económicos y Ambientales de la Liberalización del Comercio: Una Aplicación al Sector Minero. Fundación MEDMIN.
- Pfeiffer WC, Maim O, Souza CMM, Drude de Lacerda L, Silveira EG, Bastos WR. 1991. Mercury in the Madeira River ecosystem, Rondonia, Brazil. *For. Ecol. Manage.* 38:239-245.
- Pirrone N, Keeler GJ, Nriagu JO. 1996. Regional differences in worldwide emissions of mercury to the atmosphere. *Atmos. Environ.* 30:2981-2987.
- Ramírez V, Terán N. 2002. Informe de trabajo de campo: Inventariación de actividades Mineras e impactos ecológicos y socioeconómicos en el Área Natural de Manejo Integrado Apolobamba. La Paz, Bolivia: Conservación Internacional/CEPF.
- Roulet M, Lucotte M, Canuel R, Rheault I, Tran S, De Freitas Gog YG, Farella N, Souza do Vale R, Sousa Passos CJ, De Jesus da Silva E, Mergler D, Amorim M. 1998. Distribution and partition of total mercury in waters of the Tapajós River Basin, Brazilian Amazon. *Sci. Total Environ.* 213:203-211.
- Schwesig D, Krebs O. 2003. The role of ground vegetation in the uptake of mercury and methylmercury in a forest ecosystem. *Plant. Soil.* 253:445-455.
- Seibert, P. 1993. *Ecología en Bolivia*. Instituto de Ecología-Universidad Mayor de San Andrés. *Revista de Ecología* N° 20. La Paz. 84 pp.
- Seigneur C, Vijayaraghavan K, Lohman K, Karamchandani P, Scott C. 2004. Global attribution for mercury deposition in the United States. *Environmental Science & Technology* 38:555-569.
- Shia RL, Seigneur C, Pai P, Ko M, Sze ND. 1999. Global simulation of atmospheric mercury concentrations and deposition fluxes. *Journal of Geophysical Research* 104:23747-23760.
- Siegel SM, Siegel BZ, Barcigiani C, Aratani K, Penny P, Penny D. 1987. A contribution to the environmental biology of mercury accumulation in plant. *Water Soil Pollution* 33:65-75.
- Travnikov O. 2005. Contribution of the intercontinental atmospheric transport to mercury pollution in the Northern Hemisphere. *Atmos. Environ.* 39:7541-7548.
- USEPA. 2000. Mercury transport and fate in watersheds. US EPA Office of Research and Development's Science to Achieve Results (STAR). A product of the National Center for Environmental Research Vol. 4(1):1-8.
- WRB. 2006. World Reference Base for Soil Resource. Rome: F.A.O. 90 pp.
- Zang-Ho S, Ki-Hyun K, Min-Young K, Meehye L. 2005. Modelling study of reactive gaseous mercury in the urban air. *Atmos. Environ.* 39:749-761.