Risk Assessment of Mercury in Soil and Surface Water in Brgy. Santa Lourdes, Puerto Princesa City, Palawan

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Abstract. Mercury sources influence human health, especially in urban areas with high population density and intensive anthropogenic activities. Barangay Sta. Lourdes, Puerto Princesa, Palawan in South-Eastern Philippines, was one of the mercury hotspots with cinnabar as a primary mineral. The mines had to close because of economic downturns during the 1970s. Several samples were taken from the area, and concentration distribution was determined to identify potential hazard exposure. Doses contacted through ingestion, inhalation, and dermal absorption were calculated using US EPA exposure parameters. The soil was found to be enriched in Hg with the highest Total Hg (THg) recorded at 977.70 ppm. The correlation of soil pH and Hg shows a 0.64 decrease in THg for every unit increase in pH. High THg was noted during the rainy season and tended to erode mercury-laden soil into the river. The highest risk is associated with ingestion and dermal absorption, with negligible risk through air inhalation. The samples near the abandoned quicksilver mines recorded the highest THg concentrations with a hazard index (HI) greater than 1, signifying possible adverse health risks for the nearby residents. Mercury soil contamination maps indicated sources of the contamination, which can help future studies for remediation.

1. Introduction

Mercury (Hg, from the Latin word hydrargyrum or ‘watery silver’) is a sulfur-loving and extremely biologically active element [1]. It is primarily produced from mercury-bearing ores (cinnabar, HgS), with the metal as the primary Cinnabar precipitate from ascending hot water and vapors that move into fracture rocks and forms at shallow depths where temperatures are relatively lower. These may be in rocks surrounding geologically recent volcanic activity and near hot springs and fumaroles.

The cinnabar mines in the Central Palawan, Philippines, is one of the twenty-six (26) mercury mineral belts globally [2,3]. Mercury is considered one of the least abundant minerals in the earth’s crust, with concentrations ranging from 0.01 to about 2 mg/kg [4,5]. Despite its scarcity, it is considered one of the most hazardous elements due to its serious health effects and potential to enter the food chain and bio-accumulate even at a low amount of exposure. It also has been placed on the priority list of 129 hazardous chemical substances by the United States Environmental Protection Agency (US EPA) [6].

In humans, mercury exposure through direct pathways such as ingestion, inhalation, or dermal contact can cause central and peripheral nervous system damage. Among the symptoms are insomnia,
tremors, memory loss, neuromuscular effects, headaches, and cognitive and motor dysfunction [7]. Indirect pathways include consumption of fish and edible plants that have been contaminated with methylmercury formed from biochemical transformation of mercury released from a mineral deposit into the soil and waters.

Five major mines have been identified in Central Palawan, with the largest, Palawan Quicksilver Mines, Inc. (PQMI), producing 140,000 kg of mercury annually from 1955 to 1976. The mercury deposit is mainly associated with the Tagburos opalite and appears as a product of siliceous replacement of serpentinitized ultramafic rocks [8]. The mine was closed in 1976 and has been abandoned since. Approximately 2 Million MT of mine-waste calcines (retorted ore) were produced during mining, and roughly 50% were dumped into nearby Honda Bay during the construction of a jetty 600 m long and 50 m wide meant to facilitate mine operations. About 2,000 people residing in the three barangays live nearby [7-10]. The mine pit’s imprint is a 20-hectare area with a lagoon or pit lake occupying 30% of the area, informal settler families surrounding the lake occupying about 6.35 ha, while the remaining 8.18 ha is being utilized as a sanitary landfill being managed by the Puerto Princesa City Local Government Unit (LGU). The pit lake environs pose potential geologic hazards such as landslides, slope undercutting, and erosion. Aside from this, there is an indicative presence of pollutants in the pit water due to sanitary landfill leachate. Based on a risk-assessment scale used by Tetra Tech EM, Inc, the area was ranked second in priority for rehabilitation efforts out of six (6) priority abandoned mines, out of 44 abandoned sites for rehabilitation in the Philippines [11]. The area near the landfill inside the perimeter of PQMI has recently been observed to show signs of cinnabar resurfacing in the topsoil, which became a cause for alarm due to possible mineralization effects from meteorological and other natural forces. Weathering and erosion of cinnabar result in sediments rich in mercury (i.e., mercuric ion or inorganic mercury form) that eventually find their way into streams and rivers. This situation poses a potential hazard to residents and wildlife.

However, even with studies confirming that weathering and erosion of cinnabar result in sediments rich in mercury and other mercury forms, there have been limited studies conducted in Palawan to assess the contamination of mercury ore deposits. Most of the previous studies were mainly focused on studying the environmental degradation caused by PQMI, especially in Honda Bay. This study involves looking into the extent of mercury soil contamination and conducting a risk assessment and hazard analysis, particularly for the residents near the area. The soil was characterized in different areas to determine the concentration of mercury and its pathway as a tool for determining the best approach for remediation, rehabilitation or even recovery of Hg. The soil sampling was conducted for five (5) months to identify the possible effects of meteorological conditions on mercury concentrations.

2. Experimental Methods

2.1. Study Area
Brgy. Sta. Lourdes (N: 9.8591, E: 118.7217) is one of the 66 barangays and located at the eastern side of Puerto Princesa City, Palawan. The topography is characterized by rolling hills and ridges on the eastern portion and becoming moderate toward the northeast and west portion, wherein the highest peak is 452 meters above sea level. The area is drained principally by Tagburos River, which flows southeast into Honda Bay, while Inawayan and Iratag Rivers flow toward the Puerto Princesa Bay at the south. With an annual rainfall of 35.6 mm and rivers near the mineralized areas, mercury’s possible spread through natural pathways was deemed an essential factor for the risk assessment [10].

2.2. Soil Sampling and Preparation
Nineteen (19) initial soil samples were obtained in June 2019 to establish baseline values in areas near the pit lake, landfill and along the course of the Tagburos River. After expanding the study area, sixteen (16) additional sampling locations were established in July. The sites were selected to capture likely high and low impact areas within the Hg anomaly area. Samples were collected from 10 to 30 cm of the soil layer removing organic materials (e.g. leaves, roots etc). A 1-kg sample was collected on a 2 m x 2
m grid using the five-spot mixing method (samples from a total of five spots: the center and four sub-points). To ensure a representative sample, composites were prepared and stored in double-sealed polyethylene bags for transport to Quezon City and preserved till analysis [12]. The samples were air-dried in a closed, dark room for a week. After removal of organic materials, the sample was coned and quartered for further analysis. A portion was taken for sieve analysis and soil type classification. At the laboratory, 20 grams of fresh soil from each sample were used for pH determination in 1:2.5 water slurry and measured using pen-type pH meter in triplicates. [13]

2.3. Soil Characterization

2.3.1. Total Mercury using, DMA-80. THg analyses were performed using a direct Hg analyzer (DMA-80). Quality assurance and quality control were performed using duplicates, method blanks, and certified reference material (GSD-1). Analytical accuracy for THg in soil was estimated from analyses of the geological standard of GSD-1.

2.3.2. X-Ray Fluorescence (XRF). XRF was used to determine the sample’s elemental composition without differentiating between the different chemical compounds present. A handheld X-ray fluorescence analyzer (Olympus Innov-x) was used to scan samples for 45 sec to collect data for 32 elements. The manufacturer’s reported detection limit for this instrument is 50 mg/kg for Hg. Alternative methods were used for lower sensitivities.

2.3.3. X-Ray Diffraction (XRD). For the detection of the samples’ mineral composition, XRD investigations were conducted at the Department of Mining, Metallurgical and Materials Engineering (DMMME) XRD laboratory, in which the rotating anode and cross-beam optics were used to enhance the X-ray intensity. XRD patterns were recorded using Rigaku Smartlab Diffractometer of 5–90° using Cu K α radiation with a step size of 0.010 [14,15].

2.3.4. Statistical Analysis. Descriptive data analysis, including minimum value, median, maximum value, geometric mean, standard deviation, and skewness, was carried out with Excel 2010 (Microsoft Inc., Redmond, USA) and SPSS 25 (SPSS Inc., Chicago, USA).

2.4. Risk Assessment

To better understand the influence of human activities in the study area, the 35 sampling locations were divided into four (4) land-use types: agricultural, agricultural with nearby structures, residential, and sanitary landfill. Majority of the area of Brgy. Santa Lourdes is covered by agricultural land. For the study, sampling points in agricultural areas where structures (i.e., makeshift house, school, church) are present within 250 m were considered under Case 2. On the other hand, agricultural lands without structures within 250 m were considered under Case 1. Sample points under residential areas are in Case 3, while Case 4 covers sampling areas near the Sanitary Landfill.

Risk assessment aims to measure the intensity, frequency, and duration of human exposures to mercury-contaminated soil. Adults and children are separated because of their behavioral and physiological differences. The assessment was carried out by measuring the average daily dose (ADD) of mercury through the following pathways:

1) direct ingestion of soil particles;
2) inhalation of soil particles through the mouth and nose;
3) dermal absorption.

The ADD, mg/kg day⁻¹, received through each pathway was adapted from the US Environmental Protection Agency (US EPA) guidelines. The parameters used are enumerated in Table 1. This model was chosen to cover hazard identification, dose-response analysis, exposure assessment, and risk characterization [16-18].
Table 1. Exposure parameters used for Risk Assessment through different exposure pathways for soil.

| Parameter                      | Unit | Child | Adult       |
|-------------------------------|------|-------|-------------|
| Bodyweight                    | Kg   | 15    | 70          |
| Exposure frequency            | days/year | 350  | 350; farmer: 270 |
| Exposure duration             | Years | 6     | 30          |
| Ingestion rate                | mg/day | 200  | 100         |
| Inhalation rate               | m³/day | 7.6  | 20          |
| Skin surface area             | cm²  | 2100  | 5700; farmer: 3,300 |
| Soil adherence factor         | mg/cm² | 0.2   | 0.07        |
| Dermal adsorption factor      | None | 0.001 | 0.001       |
| Particulate emission factor   | m³/kg | 1.36 x 10⁹ | 1.36 x 10⁹ |
| Conversion factor             | kg/mg | 10⁶  | 10⁶         |
| Averaging time                | Days | 365 x ED | 365 x ED |

2.4.1. Ingestion of Hg through Soil Particles

\[
ADD_{\text{ing}} = \frac{C \times IR_{\text{ing}} \times EF \times ED \times CF}{BW \times AT}
\]

where ADDing is the average daily intake of heavy metals ingested from the soil in mg/kg-day, C = concentration of heavy metal in mg/kg for soil. IR in mg/day is the ingestion rate, EF in days/year is the exposure frequency, ED is the exposure duration in years, BW is the bodyweight of the exposed individual in kg, AT is the time period over which the dose is averaged in days. CF is the conversion factor in kg/mg.

2.4.2. Inhalation of Hg through Soil Particulates

\[
ADD_{\text{inh}} = \frac{C \times IR_{\text{inh}} \times EF \times ED \times CF}{BW \times AT \times PEF}
\]

where ADDinh is the average daily intake of heavy metals inhaled from soil in mg/kg-day, C is the concentration of heavy metal in soil in mg/kg, IRinh is the inhalation rate in m³/day, PEF is the particulate emission factor in m³/kg. EF, ED, BW and AT are as defined in the earlier equation.

2.4.3. Dermal Contact with Soil

\[
ADD_{\text{derm}} = \frac{C \times SA \times AF \times ABS \times EF \times ED \times CF}{BW \times AT}
\]

where ADDderm is the exposure dose via dermal contact in mg/kg-day. C is the concentration of heavy metal in soil in mg/kg, SA is exposed skin area in cm², AF is the soil adherence factor in mg/cm², ABS is the fraction of the applied dose absorbed across the skin. EF, ED, BW, CF and AT are as defined in the previous equations.

2.4.4 Hazard Quotient and Hazard Index. Non-carcinogenic hazards are characterized by the hazard quotient (HQ), which is a unit-less number expressed as the probability of an individual suffering an adverse effect. It is defined as the quotient of ADD divided by the toxicity threshold value, which is referred to as the chronic reference dose (RfD) in mg/kg-day. For n pathways, the non-carcinogenic
Effect to the population results from the summation of all the $HQ_S$ called the Hazard Index ($HI$) as described by US EPA guidelines. An HI less than 1.0 indicates that there is no adverse health risk.

3. Results and Discussion

3.1. THg Concentrations at Brgy. Santa Lourdes

THg content of soils varied across the study area. THg concentrations were elevated, ranging from 0.06 to 977.70 ppm with samples from areas near to PQMI and Sulu Sea generally containing 10.0 ppm. On the other hand, samples near the other mines recorded lower THg concentrations which may be attributed to low grade cinnabar deposits in these areas.

![Figure 1. Project Location Map and High-Risk Sampled Locations.](image1)

Based from correlation tests using SPSS, it was found out that Hg has a significant correlation to Fe ($\rho = 0.025$), Mn ($\rho = 0.000$), Cu ($\rho = 0.002$), V ($\rho = 0.000$), Sr ($\rho = 0.004$), Rb ($\rho = 0.016$), Nb ($\rho = 0.002$), Y ($\rho = 0.009$), and Ca ($\rho = 0.006$).

In samples J_13 and M_23, relatively low concentrations of Mn were measured compared to the other samples, while no K and Ca were measured. On the other hand, S was only obtained in these two samples. Locations of these samples were believed to be areas where calcines were dumped from the old mine.

Samples from areas near the landfill have high Ni but relatively lower Hg concentrations. It was initially suspected that these areas would be major sources of Hg due to their reddish violet color. However, XRF data from samples M_02 and M_03 show that the soil’s color is due to the high presence of Ni.

XRD results indicate that Hg sulphides are the main Hg-bearing mineral in most samples, consistent with the fact that cinnabar ($\alpha$-HgS) was the primary ore mineral in the area. The incomplete roasting of cinnabar during retorting results in the presence of unconverted cinnabar in calcine, together with meta-cinnabar ($\beta$-HgS). This suggests that ore roasting converts cinnabar to meta-cinnabar by heating it above the cinnabar-meta-cinnabar inversion temperature of 345 °C [18-22]. Once formed, impurities (Zn, Se, and Fe) introduced during roasting impedes the conversion back to cinnabar thus stabilizes the meta-cinnabar [23,24]. This meta-cinnabar’s origin is consistent with the noted high levels of meta-cinnabar in the calcines analyzed and supports the proposed formation of meta-cinnabar through ore roasting [20].

Both polymorphs of HgS are extremely insoluble in water (Kps are ~10−36) [25] and kinetically resistant to oxidation [3, 26]. Physical weathering and erosion of cinnabar-bearing rocks and mine waste
calcines lead to transport of cinnabar/meta-cinnabar particulates by mine runoff water and their eventual deposition (Hg sulphides density is $\approx 8.0 \text{ g cm}^{-3}$ against the 2.5 to 3.5 g cm$^{-3}$ mean density of silicates) in streams and rivers. Notably, samples J_13 and M_23 contain meta-cinnabar, thus, indicating that erosion of calcines and downstream transport of HgS is ongoing in the area. On the contrary, pre-mining sediments contained only cinnabar. [27]

3.2. Non-Carcinogenic Risk of THg for Adults and Children

High risk samples are as summarized in Table 2. Sampling sites M_12, J_13 and M_23 recorded the highest HI values and are considered very high risk (VHR) areas. Samples M_15 and M_03 are medium high risk (MR). While samples M_08, M_17, J_12, M_02 and M_18 have relatively low HIs, they are still greater than 1 which means that there are still possible adverse health effects in these sampling sites.

| Case | Sample No. | THg$^{\text{ave}}$ | HI$^{\text{adult}}$ | HI$^{\text{child}}$ |
|------|------------|-------------------|-------------------|-------------------|
| 2    | M_12       | 307.42            | 40.16             | 40.52             | VHR               |
| 3    | J_13       | 352.53            | 40.03             | 46.67             | VHR               |
| 3    | M_23       | 117.46            | 13.34             | 15.48             | VHR               |
| 2    | M_15       | 67.409            | 8.81              | 8.89              | MHR               |
| 3    | M_03       | 62.47             | 7.09              | 8.23              | MHR               |
| 2    | M_08       | 29.37             | 3.84              | 3.87              | HR                |
| 1    | M_17       | 20.61             | 2.3               | -                 | HR                |
| 3    | J_12       | 16.997            | 1.93              | 2.24              | HR                |
| 4    | M_02       | 14.4              | 1.63              | 1.9               | HR                |
| 2    | M_18       | 8.998             | 1.18              | 1.19              | HR                |

Of the combined 26 sampling sites under agricultural areas in Case 1 and 2, only five (5) recorded HI ≥ 1 values, indicating that the majority of the land used for agriculture in Sta. Lourdes is low risk. However, farming and the presence of houses near these locations should be taken into consideration, especially M_12 that recorded exceptionally high HI (40.16 and 40.52 for adults and children, respectively), and that these are also near a school (M_15) and church (Iglesia Ni Cristo). Samples M_15 and M_12 are also near an old mine/prospect (Sulu Sea) implying the area is likely a source of a considerable quantity of Hg.

Four of the ten samples from residential areas recorded HI ≥ 1. These 4 samples are near the imprint of PQMI, indicating that the area is also likely a source of considerable Hg quantity. J_13 recorded the highest HI of 40.03 and 46.47 for adults and children, respectively, under Case 3 samples. It is followed by M_23. The population near these areas is very susceptible to mercury contamination.

Only one of four samples from the sanitary landfill (M_02) has an HI ≥ 1. Although the HI is low (HI = 1.19) compared to that obtained from the other Cases, the sanitary landfill has also a possibility of health risks, especially to the employees working at the landfill and the residents living nearby.

The results of the risk assessment coincide with the results obtained from the mapping of soil contamination shown in Figure 1. High THg were recorded from samples near PQMI (M_03, M_23, J_12 and J_13) and Sulu Sea (M_12, M_15). These samples recorded HI ≥ 1 values. Similarly, Hg particles that have been transported downstream (M_08, M_17, M_18) would also lead to possible health risks.

Compared with adults, children had more health risks due to mercury. More specifically, the average HI values for children were approximately 1.1 times higher than those of the adults. Children have different behavior and physical characteristics from adults that can increase their possibility of exposure to mercury, including their higher respiration rate, increased absorption ability of gastrointestinal tract, and repetitive hand or finger sucking (which is another pathway for children to ingest more soil particles).
The exposure pathway that has the highest contribution to the overall figure of risk is through ingestion of soil particles followed by dermal absorption. Meanwhile, risk caused by air inhalation was nearly negligible. Both children and adults recorded these patterns.

4. Conclusion
The THg analysis from samples in Brgy. Sta. Lourdes confirmed that the study area is enriched with mercury. The concentrations of mercury near old mines (PQMI and Sulu Sea) were significantly higher than those in the other sampling sites, indicating that the soil in the contaminated area is greatly affected by mining and smelting activities. Priority locations according to hazard index (HI) values are M_12, J_13, M_23, M_15, M_03, M_08, M_17, J_12, M_02 and M_18. The risk assessment in this study was able to identify that the main exposure pathway is by direct ingestion of soil particles, followed by dermal contact. Children had more health risks of mercury than adults. The average HI for children were approximately 1.1 times higher than those of the adults.

5. Recommendations
According to the 2011-2020 Comprehensive Land Use Plan (CLUP) of Puerto Princesa, Brgy. Sta. Lourdes, possible projects to be undertaken include (1) socialized housing projects, (2) retirees village, (3) centralized waste treatment plant for small hogs and poultry farms, and (4) series of ordinances regulating certain extractive economic activities such as quarrying. However, the high values of HI the risk analysis strongly indicate that exposure to the soil at these locations may result in adverse health effects. Should these plans push through, the results of this study warrant intervention in terms of soil use and planning. Moreover, very careful consideration needs to be undertaken as to the fitness for purpose.

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References
[1] Schluter K 2000 Review: evaporation of mercury from soils. An integration and synthesis of current knowledge Envi. Geol.39 (3) 249-71
[2] Rytuba J J 2003 Mercury from mineral deposits and potential environmental impact Envi. Geol. 43(3) 326–38
[3] Holley E A, James McQuillan A, Craw D, Kim J P, and Sander SG 2007 Mercury mobilization by oxidative dissolution of cinnabar (α-HgS) and metacinnabar (β-HgS). Chem. Geol. 240(3–4) 313–25
[4] Barringer J L, Szabo Z, and Reilly P A 2012 Occurrence and mobility of mercury in groundwater, Current perspectives in contaminant hydrology and water resources sustainability, IntechOpen 2013
[5] Bose-O'Reilly S, Drasch G, Beinhoff C, Rodrigues-Filho S, Roider G, Lettmeier B, 2010 Health assessment of artisanal gold miners in Indonesia. Sci. Total Environ. 408(4) 713-25
[6] Qiu G, Feng X, Meng B, Zhang C, Gu C, Du B and Lin Y 2013 Environmental geochemistry of an abandoned mercury mine in Yanwuping, Guizhou Province, China Envi. Res. 125 124–30
[7] Hernandez H 1968 The Geology of Cinnabar Deposits of Central Palawan. The Phil. Geologist XXII 91-105
[9] Williams T M, Weeks J M, Apostol A, and Miranda, C 1996 Assessment of mercury toxicity hazard associated with former cinnabar mining and tailings disposal in Honda Bay, Palawan, Philippines. Overseas Geology Series Technical Report WC/96/31 (British Geological Survey)

[10] Cruz N, Mojares E, and Villanueva A 1996 Report on the Preliminary Geological and Geochemical Survey Conducted at Barangay Sta. Lourdes and vicinity in Puerto Princesa City, Palawan in connection with mercury contamination (DENR Region IV - Mines Sector, Palawan)

[11] MGB-IVB 2017 PQMI Rehabilitation Project Annual Progress Report (MGB-MIMAROPA, Region IVB)

[12] Qiu G, Feng X, Meng B, Sommar J, and Gu C 2012 Environmental geochemistry of an active Hg mine in Xunyang, Shaanxi. Applied Geochemistry 27, 2280–8

[13] Floresta A, Amazon S, Lacerda L D, Souza M De, and Ribeiro M G 2004 The effects of land use change on mercury distribution in soils of Alta Floresta, Southern Amazon Environmental Pollution 129 247–55

[14] Zhao S, Duan Y, Yao T, Liu M, Lu J, Tan H, Wu L 2017 Study on the mercury emission and transformation in an ultra-low emission coal-fired power plant. Fuel 199 653–61

[15] Rahman A 2007 Bahan Ajar Pelatihan Analisis Risiko Kesehatan Lingkungan. Depok: Pusat Kajian Kesehatan Lingkungan and Industri Fakultas Kesehatan Masyarakat Universitas Indonesia

[16] Haq A, Achmadi U F, and Mallongi A 2018 Environmental health risk assessment due to exposure to mercury in artisanal and small-scale gold mining area of Lebak district. Glob. J. of Health Sci. 10 3

[17] Yang J, Ma S, Zhou J, Song Y, and Li F 2018 Heavy metal contamination in soils and vegetables and health risk assessment of inhabitants in Daye, China. J. of Int’l Med. Res. 46(8) 3374–87

[18] Baptista-Salazar C, Richard J, Hof M, Rejc M, Gosar M, and Biester H 2017. Applied geochemistry Grain-size dependence of mercury speciation in river suspended matter , sediments and soils in a mercury mining area at varying hydrological conditions. Appl. Geochem. 81 132–42

[19] Kullerud, G., 1965. The mercury-sulfur system. Carnegie I 64 194-5

[20] Kim C S, Brown GE Jr, Rytuba J J 2000 Characterization and speciation of mercury-bearing mine wastes using x-ray ab- sorption spectroscopy (XAS). Sci Total Environ 261 157–68

[21] Kim C S, Rytuba J J, and Brown G E 2004 Geological and anthropogenic factors influencing mercury speciation in mine wastes: An EXAFS spectroscopy study Applied Geochemistry 19 379–93

[22] Berna A, Gaona X, Valiente M. 2005 Characterisation of Almadén mercury mine environment by XAS technique J. Environ. Monit. 7 771–7

[23] Dickson F W, Tunell G, 1959 Stability relations of cinnabar and meta-cinnabar. Am. Mineralogist 44(5–6) 471–88

[24] Tauson V L, Akimov V V, 1997 Introduction to the theory of forced equilibria: General principles, basic concepts, and definitions. Geochem. Cosmochim. Acta 61 4935–43

[25] Schwarzenbach G, Widmer M, 1963 The solubility of metal sulfides I. Black mercuric sulfide. Helv. Chim. Acta 46 2613–28 (in German)

[26] Barnett M O, Turner R R, Singer P C, 2001 Oxidative dissolution of meta-cinnabar (β- HgS) by dissolved oxygen Appl. Geochem. 16 1499–512

[27] Rimondi V, Bardelli F, Benvenuti M, Costagliola P, Gray J E, and Lattanzi P 2014 Mercury speciation in the Mt. Amiata mining district (Italy): Interplay between urban activities and mercury contamination. Chem. Geol. 380 110–8