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Solid-phase partitioning of mercury in artisanal gold mine tailings from selected key areas in Mindanao, Philippines and its implications for mercury detoxification

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Abstract

The solid-phase partitioning of mercury could provide necessary data in the identification of remediation techniques in contaminated artisanal gold mine tailings. This study was conducted to determine the total mercury content of mine wastes and identify its solid-phase partitioning through selective sequential extraction coupled with cold vapor atomic absorption spectroscopy. Samples from mine tailings and carbon-in-pulp (CIP) process were obtained from selected key areas in Mindanao, Philippines. The results showed that mercury use is still prevalent among small-scale gold miners in the Philippines. Tailings after ball mill-gravity concentration (W-BM and Li-BM samples) from Mt. Diwata and Libona contained high levels of mercury amounting to 25 and 6.5 mg/kg, respectively. The most prevalent form of mercury in the mine tailings was elemental/amalgamated mercury, followed by water soluble, exchangeable, organic, and strongly-bound phases, respectively. In contrast, mercury content of CIP residues were significantly lower at only 0.3 and 0.06 mg/kg for P-CIP (Del Pilar) and W-CIP (Mt. Diwata), respectively. The bulk of mercury in P-CIP samples was partitioned in residual fraction while in W-CIP sample, water soluble mercury predominated. Overall, this study has several important implications with regards to mercury detoxification of contaminated mine tailings from Mindanao, Philippines.

Keywords: gold extraction; mercury remediation; small-scale mining; heavy metal speciation; mine tailings

1. Introduction

With an estimated 15 million artisanal and small-scale gold mines (ASGM) in more than 70 countries, mercury contamination of the soil, sediments and water bodies in these mining areas is a very serious environmental problem (Velásquez-López et al., 2011). This is primarily because ASGM still employ amalgamation, a process whereby mercury is either added into the "heavy" products of gravity concentrators (e.g., sluice boxes and panning) or directly into the ball mill during grinding to agglomerate the liberated fine particles of gold forming relatively large mercury-gold amalgams that could be recovered by hand. Because mercury is always added in excess to recover as much of the gold as possible, amalgamation eventually produces mercury-contaminated mine tailings and waste waters. Although amalgamation had recently been replaced by cyanidation processes like carbon-in-pulp (CIP) or carbon-in-leach (CIL), the majority of ASGM worldwide, including the Philippines, still employ mercury for gold recovery (Appleton et al., 1999; Appleton et al., 2006). Swain et al. (2007) estimated that around 1000 tons of mercury is released into the environment annually by ASGM due to poor mining practices.

Mercury is an extremely toxic compound not only to the surrounding ecosystem but also to the health of the small-scale miners, their families and other individuals living close to the mining operation. It is released into the environment during amalgamation by careless handling, disposal to inadequate tailings pond, direct discharge to rivers, direct vaporization, and many others (Orbeta et al., 2002). Several individuals who have either developed adverse symptoms or died due to mercury-poisoning had been reported in the literature (Williams et al., 1995). In the Philippines, for example, Drasch et al. (2000) noted that exposed ball mill operators and amalgam smelters in Mt. Diwata, Mindanao, Philippines complained of metallic tastes, fatigue, tremors, memory problems, restlessness, weight loss, and insomnia, all of which are known symptoms of mercury-poisoning. It was also reported by Akagi et al. (2000) that children living near an artisanal gold processing and refining plant in Apokon, Tagum, Davao del Norte, Philippines, were generally underweight, and have gingival discoloration, adenopathy as well as dermatologic abnormalities.

Like other heavy metals and metalloids, mercury toxicity is closely related to its chemical form (i.e., methyl mercury is more toxic than metallic/ionic mercury) while its mobility is strongly dependent on its solid-phase partitioning with different mineral phases in sediments and soils (Bakir et al., 1973; Millán et al., 2006; Tabelin et al., 2012a, b). One of the most commonly used method to determine the solid-phase partitioning of mercury is sequential extraction, a technique that involves treatment of the sample with a series of solvents that specifically attack certain minerals in the sample matrix (e.g., carbonates, sulfides and oxides) (Gavilan-Garcia et al., 2008; Tabelin and Igarashi, 2009; Tabelin et al., 2014; Tessier et al., 1979). This technique has been successfully employed to estimate the mobility and potential bioavailability of mercury in contaminated soils of the Idrija mercury mine region (Kocman et al., 2004) and in some gold mining areas in Mexico (Gavilan-Garcia et al., 2008).

Aside from identifying the sources of mercury in contaminated soils and sediments, knowledge of the solid-phase partitioning of this element in contaminated ASGM tailings could aid in the development of more efficient detoxification or immobilization techniques. A high proportion of soluble mercury in contaminated soils, for example, could be effectively remediated by soil washing, phytoextraction and electro-remediation approaches. Mercury in soils with high non-available Hg content can be remediated via stabilization/solidification, which mainly involves the mixing of mercury contaminated soil or waste with chemical binders such as cement, sulfide-/phosphate-based materials, polyester resins, or polysiloxane compounds to create a slurry, paste, or other semi-liquid phase that is cured into a solid form (US EPA, 2007). Vitrification, thermal desorption technology and immobilization can also be applied when contaminated soils contain very high elemental mercury (Wang et al., 2012). For dissolved mercury in waste waters, it could be precipitated at around neutral to slightly alkaline pH conditions similar to most heavy metals associated with pyrite-rich wastes like mine tailings (Tabelin and Igarashi, 2009; Tatsuhara et al., 2012). Dean et al. (1972), for example, immobilized high concentrations of dissolved mercury as an oxide by precipitation at around pH 7 under oxidizing conditions. In case mercury concentrations are in trace amounts, it could be immobilized using adsorbents with strong negative surface charges like zeolite (Chojnacki et al., 2004) and perlite (Ghassabzadeh et al., 2010).

One complication in the remediation of mercury-contaminated ASGM tailings, sediments and soils is their site-specific nature. This is primarily because ore type, mineral processing and extraction techniques largely vary from area to area in small-scale mining operations. Because of this, elucidation of dissolved mercury concentration as well as the solid-phase partitioning of this element in each site is crucial for the development of suitable site-specific remediation options. Unfortunately, there are no studies available in literature about the solid-phase partitioning of mercury in contaminated ASGM tailings in the Philippines. Also, treating the source of mercury contamination associated with ASGM tailings is the most appropriate and economically way of dealing with the problem. In this context, this study aims to determine the total mercury concentration and its solid-phase partitioning in ASGM tailings in some selected key areas in Mindanao, Philippines. The solid-phase partitioning of mercury was investigated by sequential extraction coupled with Cold Vapor Atomic Absorption Spectroscopy (CVAAS). The particle size distribution of mercury contaminated mine tailings was also determined.

2. Materials and Methods

2.1 Study area and sample collection

The ASGM tailings samples were collected from Barangay Gango, Libona, Bukidnon; Barangay del Pilar, Cabadbaran City, Agusan del norte; and Barangay Mt. Diwata (Mt. Diwalwal), Monkayo, Compostela Valley as shown in Figure 1. In the Philippines, the usual process employed by small-scale gold miners to recover gold is amalgamation during ball milling followed by the recovery of mercury-gold amalgams by gravity concentration techniques like panning and sluice boxes. Because the processed ores after ball milling still contain considerable amounts of "unliberated" gold, these are sold to other players for reprocessing using cyanidation (i.e., CIP process). The samples from Cabadbaran City were collected in an open field of a closed compound near the processing plant, is already covered with vegetation. The CIP plant in this area stopped its operation for over a year because the city government of Cabadbaran banned all types of mining in the area. In the case of Mt. Diwalwal, ball mill tailings samples were collected inside a residential quarter while the CIP residues were obtained in a tailings pond beside the CIP processing plant. The samples from Libona, Bukidnon

were collected from a common tailings pond, which has already been in operation for more than 10 years. Table 1 presents the details of sample labelling, location and type of tailings collected from each site. The sampling method was carried out randomly for each key area in Mindanao. About 3-7 kg of mine tailings was collected and placed in a Ziploc bag and stored in a sampling cooler bag. All precautions for proper sampling were carefully followed throughout the sampling processes. The collected samples were refrigerated until treatment and analysis commenced. Also, the samples were sieved through a 2 mm-aperture screen prior to homogenization and analysis.
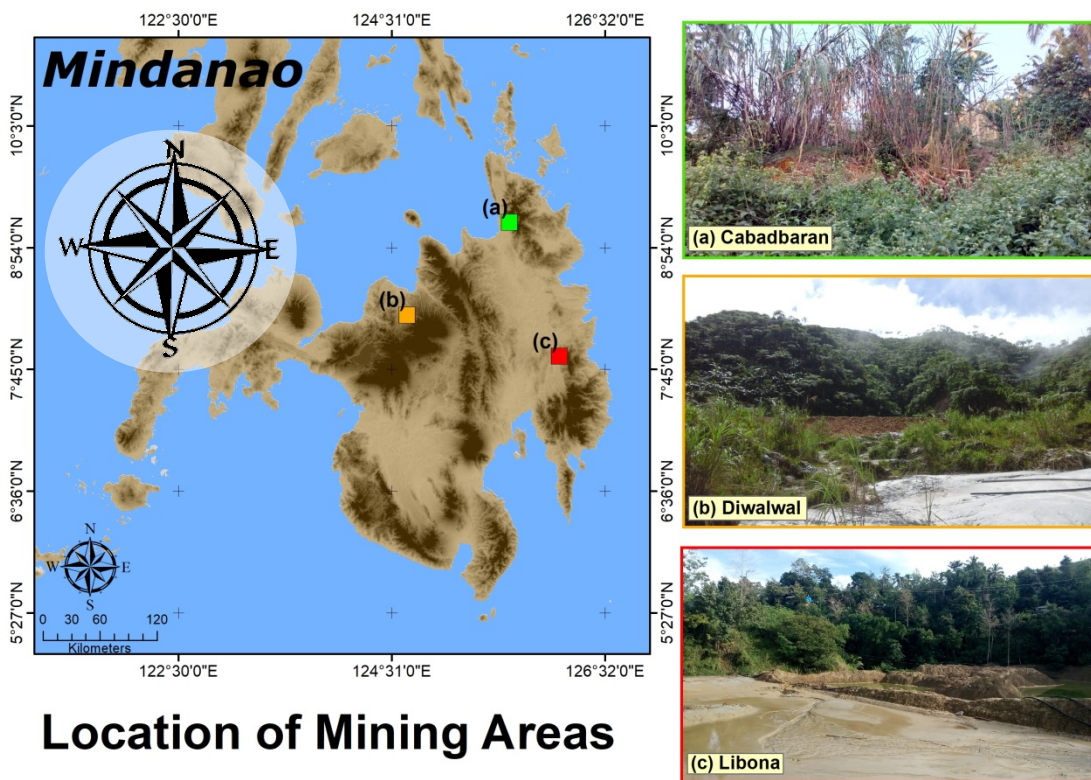

Figure 1. Map of Mindanao, Philippines and locations of key artisanal gold mining areas on the island.

Table 1. Sample name, locations and gold extraction methods

Sample Name	Sample Location	Source (Gold Extraction Method)
Li-BM	Barangay Gango, Libona, Bukidnon	Ball mill tailings
P-CIP	Barangay Del Pilar, Cabadbaran City, Agusan del Norte	Ball mill tailings and Carbon-in-Pulp residue
W-BM	Barangay Mt. Diwata, Monkayo, Compostela Valley	Ball mill tailings
W-CIP	Barangay Mt. Diwata, Monkayo, Compostela Valley	Ball mill tailings and Carbon-in-Pulp residue

2.2 Standards, reagents, and apparatus

Chemical reagents (hydrochloric acid (HCl) (37%), nitric acid HNO_3 (65%), magnesium chloride hexahydrate $MgCl_2 \cdot 6H_2O$, sodium hydroxide pellets NaOH, solid sodium sulfide HNa_2S^+, glacial acetic acid, and standard gold solution (1000 ppm)) used throughout the study were of analytical-grade. Double-distilled water was used throughout the experiment, and glasswares were thoroughly washed with detergent and tap water, soaked in 5% HNO_3, triple-rinsed with double-distilled water, and dried in a clean oven.

2.3 Determination of Particle size distribution of mine tailings and CIP residues

Particle size determination of samples was carried out using a particle size analyzer with dynamic light scattering capabilities. A suspension in water of the samples was prepared as actual specimens to be measured. The determination of the size fractions of mercury contaminated mine tailings could give possible insights into the distribution of mercury in the various size fractions.

2.4 Determination of Total Mercury Concentration

Representative samples of ASGM tailings and CIP residues were digested following the standard procedure based on ISO 11466:1995 for total mercury determination. The analysis of mercury was carried out using cold vapor atomic absorption spectroscopy (CVAAS).

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2.5 Sequential Extraction Procedure

The solid-phase partitioning of mercury was determined by the sequential extraction procedure employed by Gavilan-Garcia et al. (2008), which was based on the techniques developed and/or used by five research groups: Tessier et al. (1979), Di Giulio and Ryan (1987), Wallschläger et al. (1998), Ebinghaus et al. (1999) and Bloom et al. (2003). This sequential extraction procedure is divided into two routes (Figure 2). Route 1 only has two sequential steps: (1) water soluble species (F1), and (2) elemental species (F2*). The value of elemental/amalgam (F2*) was obtained by subtracting the concentration extracted in F1 and the concentration of mercury in the residue F2 from the total mercury concentration. In comparison, Route 2 divided mercury into six fractions: (1) water soluble species (F1), exchangeable species (F2), strongly bound species (F3), organic species (F4), sulfide fraction (F5) and residual (F6). For mercury in the sulfide fraction (F5), this was obtained by subtracting F1, F2, F3, F4 and F6 from the total mercury concentration since excess sulfide from F5 could generate interference during CVAAS analysis (Gavilan-Garcia et al., 2008). All experiments were done in triplicates to ascertain that differences and trends observed were statistically significant. Solutions for mercury determination by CVAAS were preserved by adding HNO_3 (2% (v/v)) and $AuCl_3$ (1 ppm of Au). Figure 2 presents the general flow of the sequential extraction procedure used in this study.

Table 2. The sequential extraction procedure used in this study based on Gavilan-Garcia et al. (2008).

Fraction	Extracting solution(s)	Extraction process	Target phase(s)	Potential mercury (Hg) species
F1	DI water	Shaken in a water bath for 120 minutes	Water Soluble	$HgCl_2$
F2*	Aqua regia	Heated first at 180°C for 3 h and then reacted with aqua regia for 15 h	Elemental/Amalgam	amalgamated Hg
F2	0.2 M Magnesium Chloride ($MgCl_2$)	Shaken in a water bath for 120 minutes	Exchangeable Hg	$HgSO_4$ & HgO
F3	HCl (conc.)	Shaken in a water bath for 120 minutes	Strongly bound Hg	Hg bounded to Fe/Mn oxides
F4	0.2 M NaOH + 4% (v/v) solution of glacial acetic acid	Shaken in water bath for 120 minutes with NaOH solution followed by another 120 minutes with glacial acetic acid	Organic Hg	Organic Hg
F5	Saturated solution of Na_2S	Shaken in water bath for 24 hrs	Sulfide fraction	HgS
F6	HNO_3 conc. and HCl (conc.)	Digestion with concentrated HNO_3 and HCl at 85°C for 45 minutes	Residual Hg	HgSe & residual

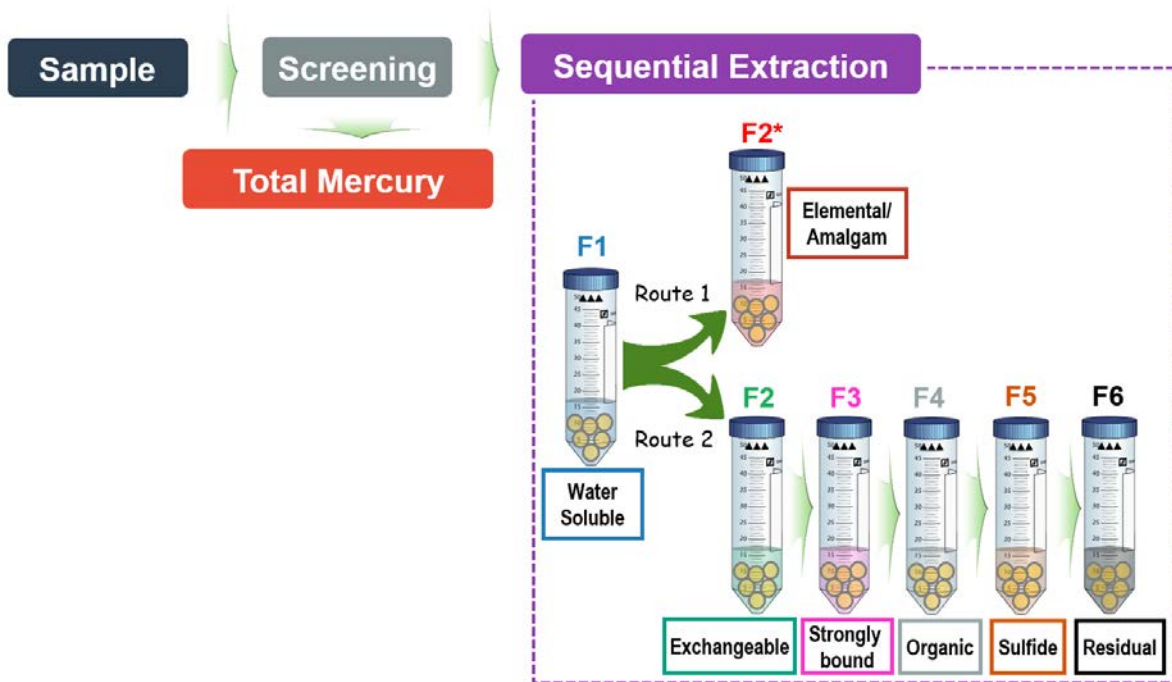**Figure 2.** Flowchart of the sequential extraction procedure to determine the solid-phase partitioning of mercury.

3. Results and Discussion

3.1 Particle Size Distribution of Mine Tailings and CIP Residues

Regardless of the site, almost all of the samples passed through a 75 μm-aperture screen after drying and homogenization. In general, tailings from the ball mill have bigger particles than the CIP residues. For example, Li-BM had a D_{80} of 25 μm while W-CIP had D_{80} of 0.2 μm (Figure 2). These results are to be expected because regrinding is required to liberate more gold prior to CIP process. Comparison of the two CIP residues also showed that the sample from Barangay Mt. Diwata, Monkayo, Compostela Valley have finer particles (D_{80} = 0.2 μm) than those from Barangay Del Pilar, Cabadbaran (P-CIP) (D_{80} = 0.4 μm). These results could be attributed to differences in mechanical strength of rocks hosting the ore of gold. In addition, Li-BM and P-CIP samples showed gap-graded distribution of particles while the samples from Mt. Diwalwal (W-BM and W-CIP) exhibited well-graded distribution of particles.
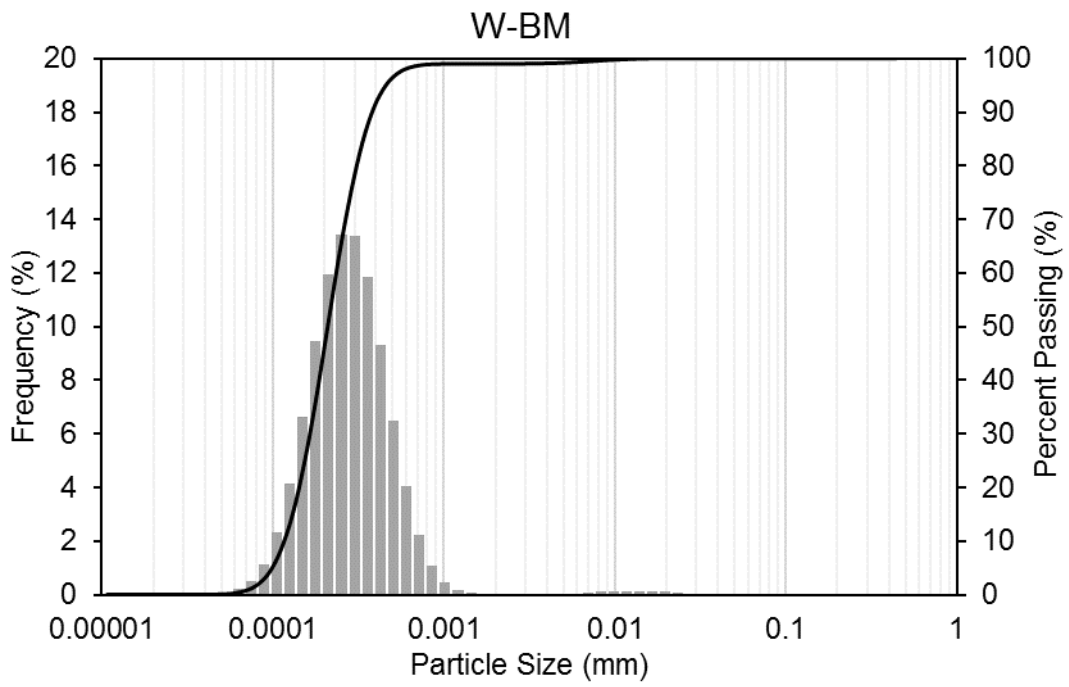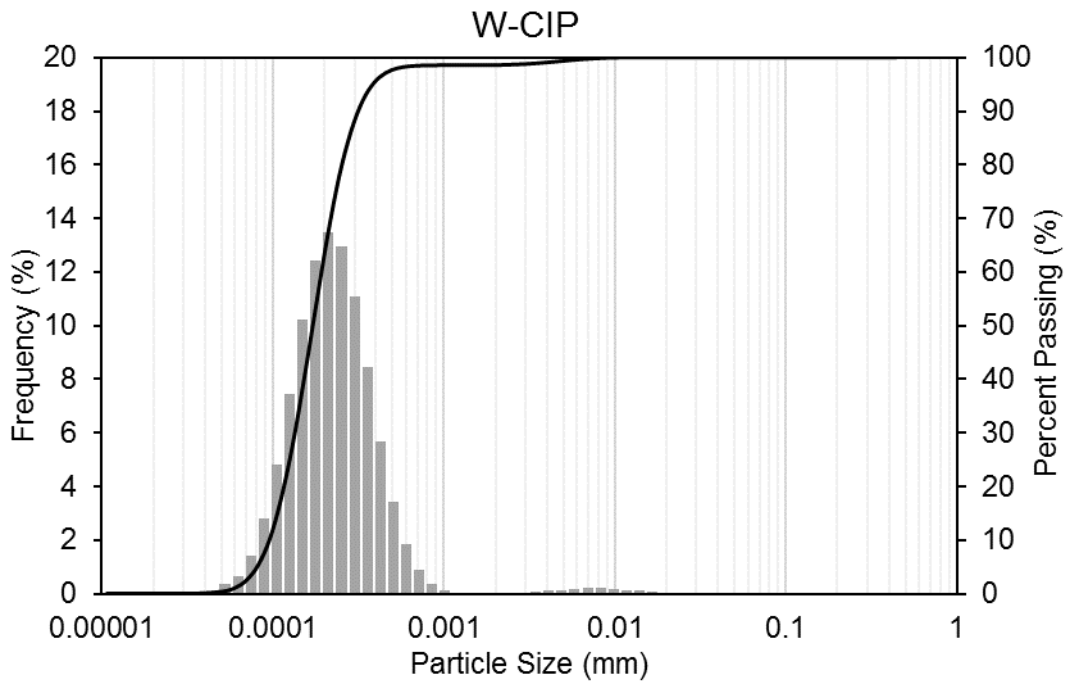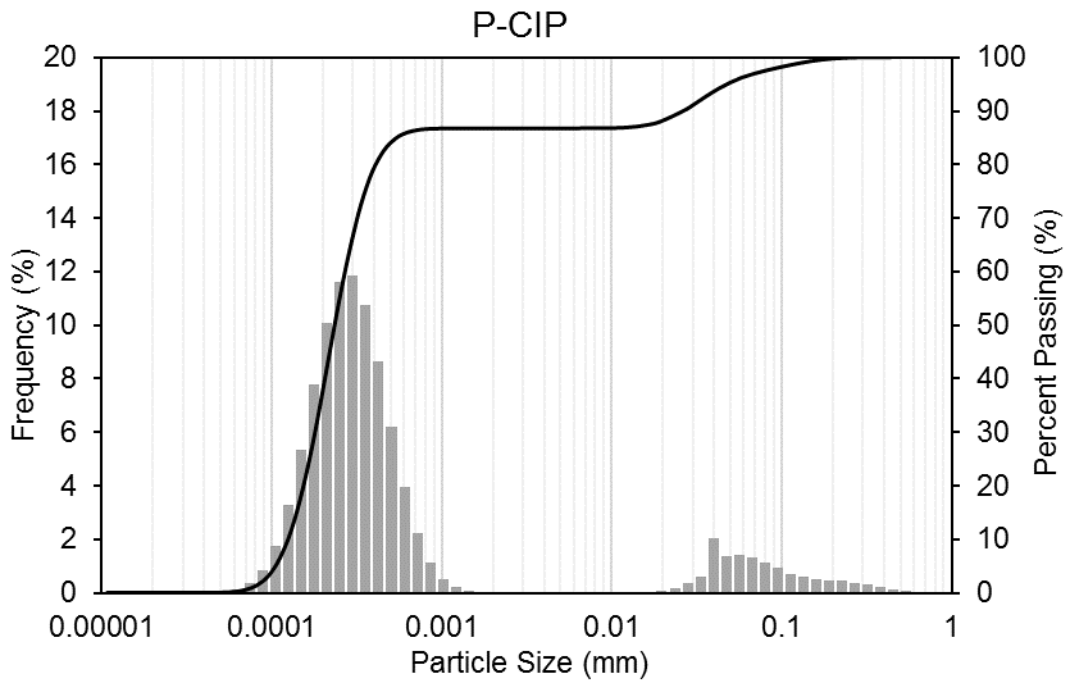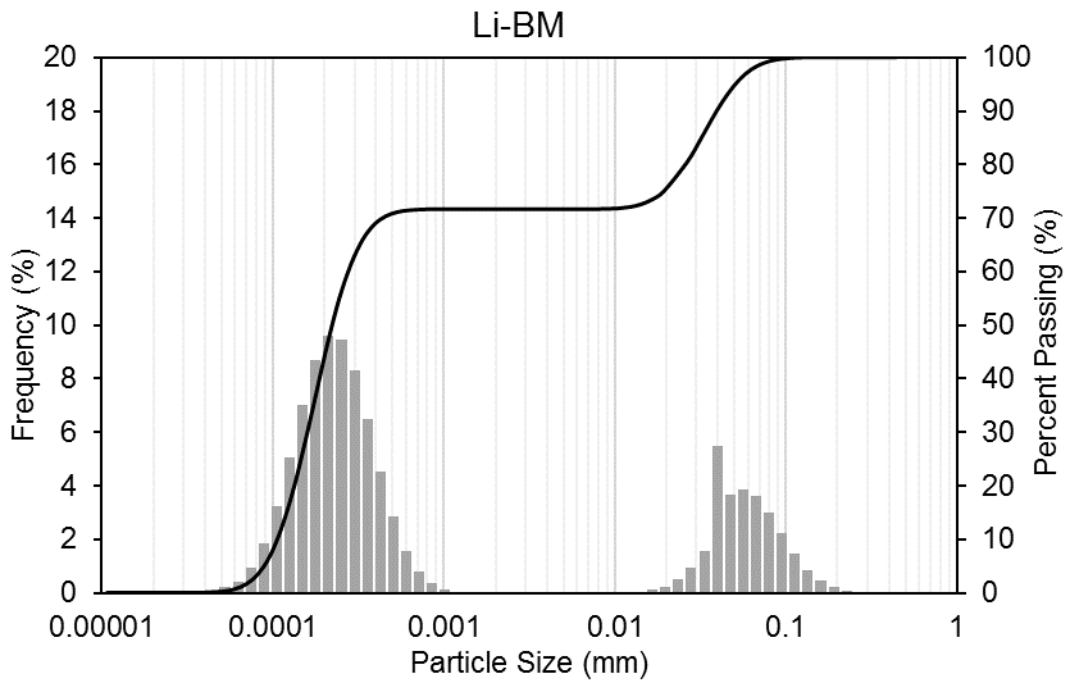
Figure 3. Particle size distributions of tailings and CIP residues.

3.2 Total Mercury Content of Tailings and CIP residues

The results of the total mercury determination confirmed the presence of mercury in ASGM tailings and CIP residues. The ball mill samples from Libona (LiBM) and Mt. Diwata (WBM) showed high levels of mercury with total mercury concentrations amounting to about 6.5 and 25.024 mg/kg, respectively. These values far exceeded the acceptable local and international standards for elemental and methylated mercury in residential soil and even for parkland and commercial land use. The higher mercury content of ball mill samples compared with the CIP residues could be attributed to two things: (1) mercury "trapping" of the larger particles of the ball mill samples (de Andrade Lima et al., 2008), and/or (2) dissolution of mercury by cyanide (CN^-) during CIP (Nsimba, 2009; Velásquez-López et al., 2010). Also, the high mercury contents of tailings mean that these wastes are hazardous not only to the gold miners but to residents living downstream of the mines. This is because when mercury-contaminated wastes is disposed of into aquatic bodies like rivers, mercury could be bio-assimilated by aquatic organisms like fish and shellfish and converted to the more toxic methylmercury, which has carcinogenic properties as well as immunological, reproductive, renal, cardiovascular and hematopoietic toxicity (Appleton et al., 1999). The reported median concentrations of mercury in the blood of ASGM workers are significantly higher than those living downstream in Monkayo, Philippines (Drasch et al., 2000).

On the other hand, CIP residues from Del Pilar (P-CIP) and Mt. Diwata (W-CIP) have less than 1 mg/kg concentration of mercury with total mercury concentrations of 0.3 and 0.06 mg/kg, respectively. The abrupt reduction of mercury concentration from ball mill tailings to CIP residues suggests that mercury is released during the continued processing of gold. This release of mercury from the ball milling tails during CIP is facilitated either by physical (e.g., reduction in size) and/or chemical (i.e., solubization by CN^-) processes as explained previously. A previous study by Shaw et al., (2006) showed that CN^- mobilized mercury from the tailings and transported it through the pore-water as mercury–cyanide complexes (predominantly $Hg(CN)_2$). Thus, the release of mercury into the surrounding aquatic environment is directly dependent on the rate of CN^- leaching (Shaw et al., 2006). However, these complexes are relatively weak and would dissociate under mildly acidic conditions

(pH 4 to 6) (Nsimba, 2009). Unstable metal-cyanide complexes could also adsorb to common mineral components of soils and sediments such as the oxides of iron, aluminum, silicon, and manganese as well as clays, which in most systems would inhibit their migrations (Kuyucak and Akcil, 2013).

3.2 Solid-phase Partitioning of Mercury

The speciation of mercury determines its toxicity, transport pathways and residence time in different compartments of the environment (O'Driscoll et al., 2005). Table 3 presents the level of mercury in the different functional phases of tailings and CIP residues. The prevalent form of mercury in all types of samples was elemental mercury (F2*) as shown in Figure 4 with W-BM exhibiting the highest amounts. The very high elemental mercury in the tailings is to be expected because of the excessive amounts mercury introduced during amalgamation. In comparison, relatively low elemental mercury after CIP suggest that most of mercury added during amalgamation was solubilized by CN^-, which could render mercury mobile in the environment. It should be noted that because of the very strong extracting solution used in F2* (i.e., aqua regia), mercury partitioned in this fraction included a substantial portion of those found in phases F2-F6. To further identify other possible phases important in the solid-phase partitioning of mercury, the second sequential extraction route (i.e., Route 2) was conducted. Strongly bound (F3) and sulfide (F5) fractions were also found in Li-BM and P-CIP samples in relatively significant amounts, but these fractions are not a problem because of their high stability, low solubility and limited bio-availability (Wang et al., 2012, Gavilán-García et al., 2008). Mercury in the sulfide fraction was observed only in Li-BM and P-CIP samples while residual mercury was only detected in P-CIP samples. In the former, mercury could be incorporated into iron sulfide (e.g., pyrite) (Morse & Luther, 1999) while in the latter, the presence of both strongly-bound and sulfide forms of mercury hints that there is a complex inter-conversion of this element from one form to another. In comparison, only water soluble and elemental/amalgamated phases of mercury were observed in W-CIP samples, in which the latter was the most dominant. Water soluble (F1), exchangeable species (F2) and organic forms (F3) of mercury were also detected in Li-BM and W-BM samples. The presence of mercury in water soluble, organic, and exchangeable forms presents a

potential health and environmental risk since these forms of mercury are easily transformed and redistributed in the environment (Gavilán-García et al., 2008).

Moreover, the solid-phase partitioning of mercury after deposition into the tailings through small scale gold mining operations could be influenced by various environmental factors such as pH and temperature as well as geochemical factors like humic acid content of the soil and the presence of microorganisms. For example, mercury in elemental/amalgamated form could be oxidized to dissolved mercury (Hg^{+2}) (Gavilan-Garcia et al., 2008), a cation with high solubility that reacts with chloride, oxygen and sulfur to form mercury salts like HgS, $HgCl_2$ or Hg_2Cl_2 (O'Driscoll et al., 2005). The solubility of mercury compounds ranges from negligible for HgS to very soluble particularly for $HgCl_2$ (Rodriguez et al., 2012). In the case of organic mercury compounds, methylmercury is the predominant species that could be formed by microorganisms in aquatic environments (Ullrich et al., 2001).

Table 3. Solid-phase partitioning of mercury in ASGM tailings and CIP residues

Sample	Mercury content (μg/g)						
	F1	F2*	F2	F3	F4	F5	F6
Li-BM	0.130	5.738	0.101	0.203	0.101	0.227	0
P-CIP	0	0.254	0	0.022	0	0.016	0.008
W-BM	0.030	24.968	0.013	0.004	0.009	0	0
W-CIP	0.001	0.059	0	0	0	0	0

Note: F1: Water soluble, F2: Elemental/amalgamated Mercury, F2*: Exchangeable species, F3*: Strongly bound species, F4*: Organic Mercury, F5*: Sulfide fractions, F6*: Residual Hg
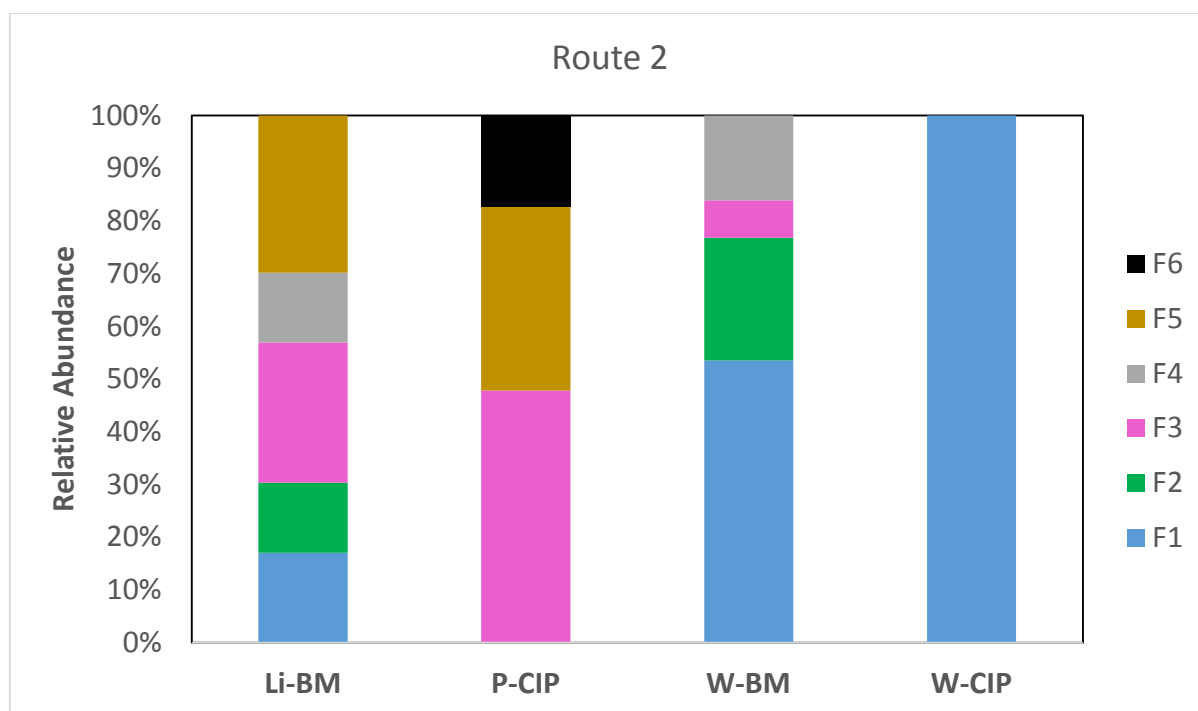
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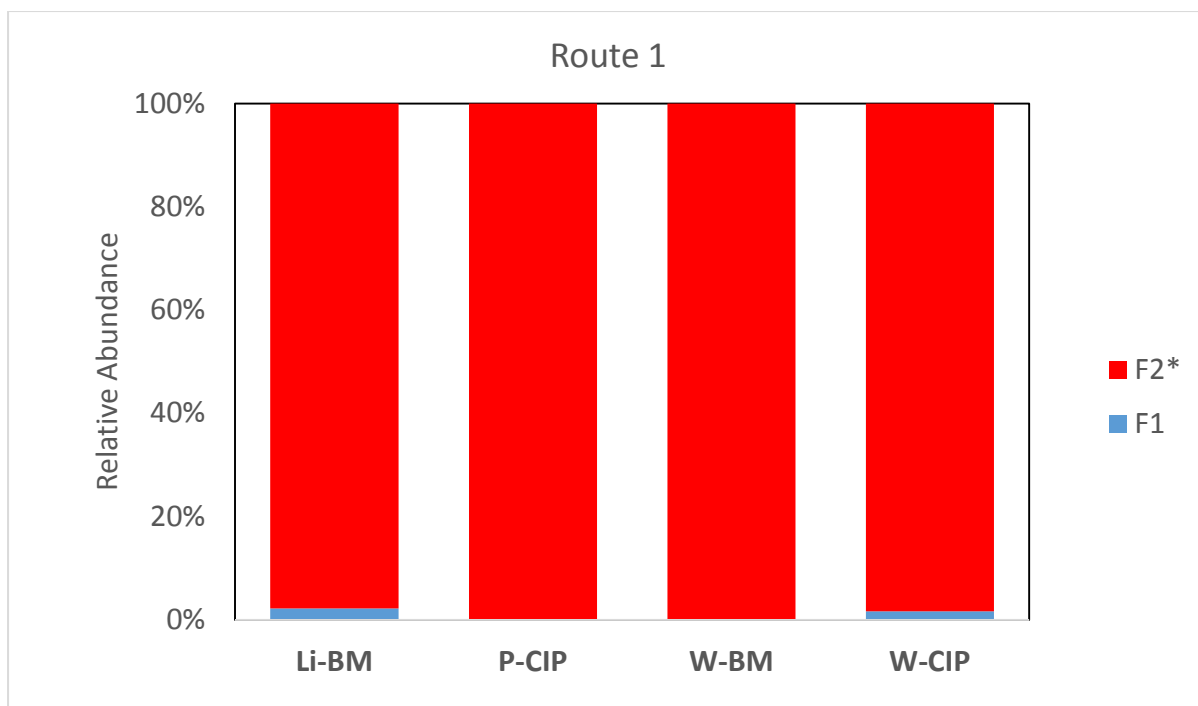
Figure 5. Solid-phase partitioning of mercury in mine tailings and CIP residues for route 1 (A) and route 2 (B)

Note: F1: Water soluble, F2*: Elemental/amalgamated mercury, F2: Exchangeable species, F3: Strongly bound species, F4: Organic mercury, F5: HgS, and F6: Residual mercury

4. Conclusions

The results of this study have several important implications with regards to mercury detoxification of contaminated ASGM tailings and CIP residues in Mindanao, Philippines. First, mercury use is still prevalent among ASGM operations to recover gold through amalgamation despite its ban in the 1980s. With regards to this, the government should strictly implement the ban on mercury use among ASGM operators and limit its proliferation in the black market. Specifically, the concerned local government units should make sure that common tailings ponds be contained so as to prevent outflows and limit direct human contact with the mercury-contaminated tailings. Second, thousands of tons of ASGM tailings containing mercury are accumulating over time without proper disposal and treatment. Environmental regulatory bodies should constantly monitor the levels of mercury in the effluents and/or drainage systems as well as in soils and sediments around ASGM areas. Strict ban on the disposal of tailings into the bodies of water and in open fields should be implemented. Third, elemental mercury is the predominant form of mercury in the studied areas. Solidification and stabilization (S/S) must be explored as among the most feasible techniques to remediate the contaminated tailings and residues, which could be done by adding additives such as cement, pozzolans, and clay-based materials. Soil washing, acid extraction, phytoextraction, and electro-remediation techniques may be considered prior to stabilization as the mine tailings also contained significant amounts of bio-available forms of mercury.

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References

Akagi, H., Castillo, E. S., Cortes-Maramba, N., Francisco-Rivera, A. T., & Timbang, T. D. (2000). Health assessment for mercury exposure among schoolchildren residing near a gold processing and refining plant in Apokon, Tagum, Davao del Norte, Philippines. *Science of the Total Environment*, *259*(1), 31-43.

Appleton, J. D., Williams, T. M., Breward, N., Apostol, A., Miguel, J., & Miranda, C. (1999). Mercury contamination associated with artisanal gold mining on the island of Mindanao, the Philippines. *Science of the Total Environment*, *228*(2), 95-109.

Appleton, J. D., Weeks, J. M., Calvez, J. P. S., & Beinhoff, C. (2006). Impacts of mercury contaminated mining waste on soil quality, crops, bivalves, and fish in the Naboc River area, Mindanao, Philippines. *Science of the total environment*, *354*(2), 198-211.

Bakir, F., Damluji, S. F., Amin-Zaki, L., Murtadha, M., Khalidi, A., Al-Rawi, N. Y., Tikriti, S., Dhahir, H. I., Clarkson, T. W., Smith, J. C., and. Doherty, R. A. (1973) Methylmercury Poisoning in Iraq. Science, New Series, 181, (4096), 230-241.

Bloom, N. S., Preus, E., Katon, J., & Hiltner, M. (2003). Selective extractions to assess the biogeochemically relevant fractionation of inorganic mercury in sediments and soils. *Analytica Chimica Acta*, 479(2), 233-248.

Chojnacki, A., Chojnacka, K., Hoffmann, J., & Gorecki, H. (2004). The application of natural zeolites for mercury removal: from laboratory tests to industrial scale. *Minerals Engineering*, *17*(7), 933-937.

Dean, J.G. Bosqui, F.L. Lanouette, K.H. (1972). Removing heavy metals from wastewater. *Environmental Science and Technology* 6(6), 518-522.

Di Giulio, R. T., & Ryan, E. A. (1987). Mercury in soils, sediments, and clams from a North Carolina peatland. *Water, Air, and Soil Pollution*, 33(1-2), 205-219.

de Andrade Lima, L., Bernandez, L., Barbosa, L. (2008). Characterization and treatment of artisanal gold mine tailings. *Journal of Hazardous Materials*, 150, 747-753.

Drasch, G., Böse-O'Reilly, S., Beinhoff, C., Roider, G., & Maydl, S. (2001). The Mt. Diwata study on the Philippines 1999—assessing mercury intoxication of the population by small scale gold mining. *Science of the Total Environment*, *267*(1), 151-168.

Ebinghaus, R., Turner, R., De Lacerda, L., Vasiliev, O., & Salomons, W. (1999). Mercury contaminated sites: Characterization, risk assessment and remediation. Springer–Verlag Publishers.

Gavilán-García, I., Santos-Santos, E., Tovar-Gálvez, L. R., Gavilán-García, A., Suárez, S., & Olmos, J. (2008). Mercury speciation in contaminated soils from old mining activities in Mexico using a chemical selective extraction. *Journal of the Mexican Chemical Society*, *52*(4), 263-271.

Ghassabzadeh, H., Mohadespour, A., Torab-Mostaedi, M., Zaheri, P., Maragheh, M. G., & Taheri, H. (2010). Adsorption of Ag, Cu and Hg from aqueous solutions using expanded perlite. *Journal of hazardous materials*, *177*(1), 950-955.

Kocman, D., Horvat, M., & Kotnik, J. (2004). Mercury fractionation in contaminated soils from the Idrija mercury mine region. *Journal of Environmental Monitoring*, *6*(8), 696-703.

Orbeta, A. C., Israel, D. C., & Asirot, J. (2000). *Mercury pollution due to small-scale gold mining in the Philippines: an economic analysis* (No. 2000-06). PIDS Discussion Paper Series.

Millán, R., Gamarra, R., Schmid, T., Sierra, M. J., Quejido, A. J., Sánchez, D. M., ... & Vera, R. (2006). Mercury content in vegetation and soils of the Almadén mining area (Spain). *Science of the Total Environment*, *368*(1), 79-87.

Morse, J. W., & Luther, G. W. (1999). Chemical influences on trace metal-sulfide interactions in anoxic sediments. *Geochimica et Cosmochimica Acta*, *63*(19), 3373-3378.

Nsimba, E. B. (2009). *Cyanide and cyanide complexes in the goldmine polluted land in the east and central rand goldfields, South Africa* (Doctoral dissertation)

O'Driscoll, N. J., Rencz, A., & Lean, D. R. (2005). The biogeochemistry and fate of mercury in the environment. *Metal ions in biological systems*, *43*, 221-238.

Quiwa, N.D., Palaganas, U.M., Pioquinto, W.P. (1987) Report on the geological survey and topographic mapping of Diwalwal Gold Rush Area, Monkayo, Davao del Norte, Philippines. Mines and Geosciences Bureau (MGB)

Rodríguez, O., Padilla, I., Tayibi, H., & López-Delgado, A. (2012). Concerns on liquid mercury and mercury-containing wastes: A review of the treatment technologies for the safe storage. *Journal of environmental management*, *101*, 197-205.

Shaw, S. A., Al, T. A., & MacQuarrie, K. T. (2006). Mercury mobility in unsaturated gold mine tailings, Murray Brook mine, New Brunswick, Canada. *Applied Geochemistry*, *21*(11), 1986-1998.

Swain, E.B., Jakus, P.M., Rice, G., Lupi, F., Maxson, P.A., Pacyna, J.M., Penn, A., Spiegel, S.J., & Veiga, M.M. (2007). Socioeconomic consequences of mercury use and pollution. *Ambio*, 36, 45-61.

Tabelin, C.B., & Igarashi, T. (2009). Mechanisms of arsenic and lead release from hydrothermally altered rock. *Journal of Hazardous Materials*, 169, 980-990.

Tabelin, C.B., Basri, A.H.M., Igarashi, T., & Yoneda, T., (2012a). Removal of arsenic, boron, and selenium from excavated rocks by consecutive washing. *Water Air Soil Poll.*, 223, 4153-4167.

Tabelin, C.B., Igarashi, T., & Takahashi, R., (2012b). Mobilization and speciation of arsenic from hydrothermally altered rock in laboratory column experiments under ambient conditions. *Appl. Geochem.*, 27, 326-342.

Tabelin, C.B. Hashimoto, A. Igarashi, T. Yoneda, T. (2014). Leaching of boron, arsenic and selenium from sedimentary rocks: II. pH dependence, speciation and mechanisms of release. *Science of the Total Environment*, 473-474, 244-253.

Tatsuhara, T., Arima T., Igarashi, T., & Tabelin, C.B., (2012). Combined neutralization-adsorption system for the disposal of hydrothermally altered excavated rock producing acidic leachate with hazardous elements. *Eng. Geol.*, 139-140, 76-84.

Tessier, A., Campbell, G.C., & Bisson, M., (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, 51, 844-850.

Ullrich, S. M., Tanton, T. W., & Abdrashitova, S. A. (2001). Mercury in the aquatic environment: a review of factors affecting methylation. *Critical reviews in environmental science and technology*, *31*(3), 241-293.

United States Environmental Protection Agency (US EPA). Treatment Technologies for Mercury in Soil, Waste, and Water, EPA- 542-R-07-003, 2007.

Velásquez-López, P.C., Veiga, M.M., Klein, B., Shandro, J.A., & Hall, K. (2011). Cyanidation of mercury-rich tailings in artisanal and small-scale mining: identifying strategies to manage environmental risks in Southern Ecuador. *Journal of Cleaner Production*, 19, 1125-1133.

Wallschläger, D., Desai, M. V., Spengler, M., & Wilken, R. D. (1998). Mercury speciation in floodplain soils and sediments along a contaminated river transect. *Journal of Environmental Quality*, 27(5), 1034-1044.

Wang, J., Feng, X., Anderson, C., Xing, Y., Shang, L. (2012). Remediation of mercury from contaminated sites – A review. *Journal of Hazardous Materials*, 221-222, 1-18.

Williams, M., Apostol, A., & Miguel, J. (2002). *Mercury contamination in artisanal gold mining areas of Eastern Mindanao, Philippines: A preliminary assessment.* Quezon City Philippines: British Geological Survey.