Assessment of Trace Elements in Soils and Sediments in the Abandoned Mercury Mine Site in Puerto Princesa City, Philippines

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ABSTRACT An abandoned mercury mine area in Puerto Princesa City, which was previously operated by Palawan Quicksilver Mines, Inc. (PQMI) from 1953 to 1976, is known for its unrehabilitated open-pit of mercury-rich rocks and exposed mine waste calcine stockpiles in the vicinity. In order to establish an understanding on the geology of the abandoned mercury mine deposit and to obtain clues in determining the possible metal pollutants in the area, measurement of trace element concentrations of soil and sediments collected from the PQMI vicinity were conducted. Soil and sediment samples were analyzed for heavy metals, rare-earth elements and naturally occurring radioactive elements and determined its contamination factor as part of risk assessment. Analytical results showed that aside from mercury, several heavy metals (nickel, chromium, manganese) were found to be anomalous due to the geology of the area. Statistical analyses show that chromium, nickel and antimony present the highest contamination factor among the sampling groups. Mercury is found to have negative bias with higher rare earth elements concentration but positively correlated with arsenic, antimony, and thallium. In general, there is low concentration of rare earth elements (except for scandium) in comparison with its respective average crustal concentration. Due to the nature of geology in the area, naturally occurring radioactive elements influence is also minimal. The results of this study, especially on the assessment of soil and sediment pollutants, are recommended as guidance to its mine rehabilitation.

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1. INTRODUCTION

The Philippines, with its geological nature, hosts several economic metallic deposits, some of which were extracted by private mining companies. Mining wastes are rampant in several areas that are not environmentally monitored, especially in abandoned mine sites (Samaniego et al. 2020b). One of these metallic deposits that was not rehabilitated after its mining period is found in Puerto Princesa City in the island of Palawan. Palawan Island is geologically divided into two main tectonic blocks; the North Palawan Block and South Palawan Block (Suggate et al. 2014). The lithologies in Puerto Princesa City are part of South Palawan Block, which include Palawan Ophiolite (ultramafics Block) and the South Palawan Block (Gibaga et al. 2020). The Northern Palawan Block contains old continental rocks rifted from mainland China after the opening of the South China Sea (Aurelio et al. 2014; Suggate et al. 2014; Padrones et al. 2017), while the South Palawan Block is dominated by ophiolite derived from an ocean basin believed to be of Cretaceous age that was thrust to the present day Palawan Island (Yumul et al. 2009; Suggate et al. 2014; Gibaga et al. 2020). Puerto Princesa City is underlain by Palawan Ophiolite (ultramafics, gabbros, and basalts), Iwahig Formation (Pliocene limestone and conglomerates), and Tagburos Opalite (Peña 2008). The Tagburos Opalite, which is the youngest lithology in South Palawan Block, refers to the yellowish to mocha brown siliceous rocks presumed to have been deposited during the Pleistocene (Williams et al. 1999). This opalite body is surrounded by serpentinized ultramafic rocks of Palawan Ophiolite to the north and is overlain by conglomerate-sandstone beds of Iwahig Formation to the south and quaternary alluvium to the east (Antonio et al. 1976). The origin of several hot springs in Puerto Princesa City is still a subject of discussion, but it is believed to be related to the hydrothermal fluids that brought forth the mercury (Hg) mineralization in central Palawan (Peña 2008).

The only naturally occurring deposit of Hg in the Philippines can be found in Puerto Princesa City. It mostly occurs in cinnabar (HgS) ores hosted by opalite bodies deposited along fractures and weak zones in the bedrock (Williams et al. 1999). The Hg deposit which is located in the village of Santa Lourdes in Puerto Princesa City was owned and operated by the Palawan Quicksilver Mines, Inc. (PQMI) from 1953 to 1976. It has Hg grades of as high as 10.65 lbs/ton (Zerda 1972). The Hg mining in the area was stopped due to the declining price of Hg in the world market in the 1970s. Due to the abandonment and lack of rehabilitation in the mine site, Hg contamination in soils, sediments and water is a prevailing issue in the surrounding community. While Hg assessment and characterization studies have been conducted in the past on this abandoned mine site, the extent of contamination by other trace elements in relation with its geology has not been evaluated. This study aims to char-

acterize the trace elements (heavy metals, rare earth elements, and naturally occurring radioactive elements) in the soils and sediments to have an understanding on their behavior in the abandoned PQMI mine site and to have clues in determining Hg contamination.

2. MATERIALS AND METHODS

2.1 Study area

The study area, Puerto Princesa City, is located in the central portion of Palawan Island in the Philippines (Figure 1). Specific study area is situated about 14 km north of Puerto Princesa City proper (118°43'N, 9°50'E), and encompasses two villages: Santa Lourdes and Tagburos. The former open pit area is traversed by Tagburos River, which drains to Honda Bay coast, a local fishing area and tourist spot. In this area, the Hg deposit in the form of cinnabar is hosted by Tagburos Opalite formation. The opalite rocks were observed as veins cutting the weathered ultramafic bedrock and cinnabar was found to have precipitated in cavities and linings of the siliceous vein. After abandonment of the PQMI mine site, the open pit was naturally filled with water and now forming a lake.

2.2 Soil and sediment sampling

A total of 33 soil and sediment samples were collected from September 2018 to July 2019 within the vicinity of the PQMI area from seven (7) sampling groups, namely: a pit lake, Tagburos River, Honda Bay wharf, Honda Bay, mine waste calcine, other rivers, and surrounding soils (Figure 1, Table 1). Six (6) soil samples were collected from the vicinity of the mining site, while nine (9) surface sediments were collected from Tagburos River, and four (4) from other nearby rivers not traversing the pit lake in the area. A representative mine waste calcine sample was collected from the stockpile near the pit lake and from the scattered calcines situated 500 m northeast of the pit lake. From the coastline of Honda Bay, six (6) samples were collected, along with another three (3) from the nearby wharf. Lastly, five (5) soils from roadcuts and/or exposures were also obtained from the surrounding vicinity.

Samples were collected using a plastic trowel, from the top 10 cm of the soil surface and surface sediment of rivers and were placed in polyethylene resealable plastic bags. All samples were prepared by air-drying and sieving up to U.S.

Standard 230 mesh (63 μm), to separate the silt-clay (<63 μm) size particles from the sand fraction. Only the <63 μm fractions were analyzed for Hg and trace element contents to minimize sediment size bias.

2.3 Elemental analyses

All soil and sediment samples were analyzed for trace elements, including heavy metals, rare earth elements (REEs) and naturally occurring radioactive elements using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS; Agilent Technologies, USA). A sample of around 1 g was prepared using a multi-acid (4-acid) digestion procedure that included dissolution in hot nitric acid (HNO₃) followed by mixture of hydrofluoric acid (HF), perchloric acid (HClO₄), and hydrochloric acid (HCl) to stabilize elements as an ionic solution. Multi-element certified reference material (OREAS 44P) was digested and analyzed along with samples to serve as quality control.

Total Hg concentration in soil and sediments was determined using a direct mercury analyzer DMA-80 evo (Milestone Srl, Italy) following the U.S. EPA Method 7473

TABLE 1. Soil and sediments sampling locations in PQMI and vicinities and its descriptions.

Sampling point	Coordinates	Sampling group
1	9°52'50.87"N, 118°44'49.92"E	Honda Bay sediment
2	9°52'22.43"N, 118°46'2.72"E	Honda Bay sediment
3	9°50'55.56"N, 118°45'57.61"E	Honda Bay sediment
4	9°50'19.38"N, 118°46'9.93"E	Honda Bay sediment
5	9°49'31.66"N, 118°45'26.65"E	Honda Bay sediment
6	9°47'54.11"N, 118°46'21.27"E	Honda Bay sediment
7	9°50'35.22"N, 118°44'19.51"E	Honda Bay wharf
8	9°50'34.27"N, 118°44'25.91"E	Honda Bay wharf
9	9°50'34.9"N, 118°44'31.86"E	Honda Bay wharf
10	9°50'14"N, 118°43'32.1"E	Mine waste calcine
11	9°49'37.65"N, 118°42'30.77"E	Other rivers
12	9°50'53.26"N, 118°44'15.89"E	Other rivers
13	9°50'34.72"N, 118°44'10.84"E	Other rivers
14	9°49'0.42"N, 118°42'32.14"E	Other rivers
15	9°50'1.64"N, 118°43'26.56"E	Pit lake
16	9°49'58.11"N, 118°43'25.19"E	Pit lake
17	9°49'58.15"N, 118°43'30.84"E	Pit lake
18	9°50'1.94"N, 118°43'33.2"E	Pit lake
19	9°50'7.5"N, 118°44'14.2"E	Surrounding soils
20	9°50'11.37"N, 118°43'0.48"E	Surrounding soils
21	9°49'51.04"N, 118°42'35.6"E	Surrounding soils
22	9°51'21.89"N, 118°44'17.5"E	Surrounding soils
23	9°50'6.12"N, 118°43'53.96"E	Surrounding soils
24	9°50'11.46"N, 118°43'11.45"E	Tagburos River
25	9°49'15.44"N, 118°44'5.81"E	Tagburos River
26	9°49'31.12"N, 118°43'54.31"E	Tagburos River
27	9°50'6.12"N, 118°43'53.96"E	Tagburos River
28	9°49'26.35"N, 118°43'51.08"E	Tagburos River
29	9°49'24.24"N, 118°44'39.45"E	Tagburos River
30	9°48'57.56"N, 118°44'44.05"E	Tagburos River
31	9°49'53.58"N, 118°43'25.06"E	Tagburos River
32	9°50'4.58"N, 118°43'21.81"E	Tagburos River
33	9°49'51.38"N, 118°43'30.34"E	Tagburos River

FIGURE 1. Location map of sampled points for trace elements and mercury near the abandoned PQMI mine area. Inset shows location of study area with respect to Philippine map.

(mercury in solids and solutions by thermal decomposition, amalgamation, and atomic absorption spectroscopy). Soil samples were weighed (0.10 g) and placed in a nickel boat without any pre-treatment. The boat is then introduced to the direct mercury analyzer where it is initially dried at up to 250°C, and then thermally decomposed at 900°C in a continuous flow of oxygen. The total Hg content is determined using atomic absorption spectrometry at 254 nm. Mercury analysis results from DMA-80 were validated using certified reference material for stream sediments (GSD-1) prepared by the Institute of Geophysical and Geochemical Exploration of China.

2.4 Risk assessment of soil and sediment pollution

Heavy metal contamination for each sampling group was identified by calculating the contamination factor (C_f^i) of each element following the procedure proposed by Hakanson (1980). The contamination factor is a heavy metal index derived by simply getting the ratio of the concentration of the metal in the sample (C_{0-1}^i) and its average upper crustal background level (C_n^i), as shown in Equation 1.

$$C_f^i = \frac{C_{0-1}^i}{C_n^i} \quad (1)$$

Values for upper crustal average for the heavy metals were based on the work of Taylor (1964), as presented in Table 2. There are four classes of contamination levels recognized by Hakanson (1980): (i) Low contamination factor for $C_f^i < 1$, (ii) Moderate contamination factor for $1 < C_f^i < 3$, (iii) considerable contamination factor for $3 < C_f^i < 6$, and (iv)

very high contamination factor for $C_f^i > 6$. Spearman's correlation coefficient was used in detecting the relationships among the trace metals analyzed.

3. RESULTS AND DISCUSSION

3.1 Anomalous concentrations of Hg, Ni, Cr, and Mn in PQMI rocks

The analytical results of heavy metal analysis for the soil and sediment sampling at the abandoned PQMI mine area are given in Table 2. It was observed that there are anomalous concentrations of Hg, nickel (Ni), chromium (Cr), and manganese (Mn) for most sampling groups. Ni and Cr are highest in both sediments obtained in the vicinity of pit lake and in the mine waste calcines, while Mn is elevated in Tagburos River and nearby rivers. Hg is particularly high in Honda Bay wharf and in the mine waste calcine.

The anomalous concentration of these heavy metals can be inferred by inspecting the general geology of Puerto Princesa City, particularly following the lithology traversed by the Tagburos River (Figure 1). The presence of ultramafic rocks of Palawan Ophiolite in the upstream portion of Tagburos River can explain the high Cr and Ni concentrations while the high Mn content of the sediment samples can be attributed to the occurrence of interbedded red chert and dark manganiferous chert in the former Sulu Sea mine located approximately 4 km northeast of the pit lake. High Hg content in Honda Bay wharf is caused by the mine waste calcine being used in the construction of the wharf (Gray et al. 2003; Samaniego et al. 2020a). The 600 m long wharf previously served as a port for Hg mining operations and now serves as a port for tourist and fishing boats.

TABLE 2. Heavy metal concentrations of sediment samples collected in different sapling groups in the vicinity of abandoned PQMI mine area.

Trace element	Pit lake	Tagburos River	Honda Bay wharf	Honda Bay	Mine waste calcine	Other rivers	Surrounding soils	Crustal average*
n	4	9	3	6	1	4	6	
Al (%)	2.19	3.00	0.75	0.61	2.55	2.92	2.97	8.23
As (mg/kg)	7.75	4.89	50.67	16.33	4.00	5.75	5.75	1.80
Ba (mg/kg)	29.50	52.11	29.33	7.50	20.00	47.75	38.33	425.00
Bi (mg/kg)	<0.05	<0.05	0.38	<0.05	0.07	0.098	0.08	0.17
Cd (mg/kg)	0.21	0.28	0.34	0.21	0.03	0.18	0.16	0.20
Co (mg/kg)	124.70	98.52	27.70	33.67	131.10	119.25	111.00	25.00
Cr (mg/kg)	1479.75	513.33	1164.33	205.00	2972.00	514.75	731.67	100.00
Cu (mg/kg)	58.72	83.57	116.87	60.28	46.00	67.45	50.72	55.00
Fe (%)	13.87	7.67	16.15	2.96	23.29	9.17	10.81	5.63
Ga (mg/kg)	5.32	8.44	3.95	1.45	7.00	8.20	7.98	15.00
Hg (mg/kg)	193.72	26.40	397.24	1.56	171.20	10.14	5.04	0.08
Mn (mg/kg)	860.50	2559.44	267.67	270.67	517.00	1922.75	1751.00	950.00
Mo (mg/kg)	0.85	0.67	2.20	1.77	0.70	0.45	0.47	1.50
Ni (mg/kg)	2530.75	904.22	414.67	361.67	2202.00	2019.75	1375.17	75.00
Pb (mg/kg)	18.50	33.67	36.40	10.52	2.90	10.90	11.95	12.50
Sb (mg/kg)	3.38	2.46	30.18	4.32	4.25	1.14	0.77	0.20
Sn (mg/kg)	23.22	1.61	3.93	<0.50	0.50	1.175	<0.50	2.00
Sr (mg/kg)	17.55	30.13	70.20	2747.58	2.70	21.90	18.97	375.00
Tl (mg/kg)	1.88	0.15	20.08	<0.08	1.41	0.17	0.14	0.45
V (mg/kg)	103.00	159.89	112.67	27.50	105.00	140.00	135.50	135.00
W (mg/kg)	<0.10	<0.10	1.20	0.17	0.50	0.70	<0.10	1.5
Zn (mg/kg)	99.25	109.22	114.00	37.00	45.00	88.00	63.33	70.00

*Taylor (1964)

The heavy metals generally showing very high contamination factors in the area were Cr, Ni, and antimony (Sb). Those with considerable degrees of contamination included arsenic (As), cobalt (Co), and thallium (Tl). Due to the naturally high background of Hg in the area, its contamination factor expectedly reached very high values, ranging 44–4,466 (not included in Figure 2). All other analyzed heavy metals had $C_f^i < 3$ for almost all sampling groups, indicating a low probability of them becoming pollutants.

3.2 Rare earth elements and radioactive element concentrations in Hg deposits

From the results of the REEs and radioactive elements analysis of sediment samples obtained in the vicinity of the pit lake, it was found that there is generally a low concentration of REEs and radioactive elements for all sampling groups in comparison with average crustal concentrations (Figure 3, Table 3). The average amount of light rare earth elements (LREE); lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), and samarium (Sm) were particularly very small in comparison with the crustal average, as well as uranium (U) and thorium (Th). There is an observed overall decrease in the concentration of elements, from La to lutetium (Lu), with increasing atomic weight. Only the average value of scandium (Sc) for all samples is higher than the crustal average, which can be attributed to laterite formation of the bedrock in the Puerto Princesa City area.

By contrasting the analyzed content in the sampling groups, the sediments obtained from Honda Bay wharf, Honda Bay, and mine waste have generally less REE than that from the pit lake and rivers (Figure 3). The sediments obtained in the periphery of the pit lake, and the sediments in Tagburos River and other tributaries can be representative of the concentration of original ultramafic bedrock of Puerto Princesa City. By normalization of the REE values of the pit lake and rivers with that of Carbonaceous Ivuna (CI) chondrite, there is a general trend of LREE enrichment and heavy rare earth elements (HREE) depletion with a slightly negative europium (Eu) anomaly (Figure 4). This behavior is similar to the REE trend observed in ultramafic rocks of ophiolite bodies in Naga Hills Ophiolite in India (Dey et al. 2018), Samail Ophiolite in Oman (Pallister and Knight 1981), and Zagros Ophiolite in Iran (Moghadam and Stern 2011).

Similarly, by normalizing the REE values with the crustal average, the enrichment and depletion pattern of

FIGURE 2. Contamination factor calculated for each heavy metal for each sampling group.

elements can be observed with respect to alteration processes. From Figure 5, the REE geochemistry of the sampling groups reveals three (3) distinct patterns indicative of their provenance, showing which groups are quite similar to each other. In general, all of the patterns follow a trend of relatively depleted LREE and higher values of HREE. The level of disparity between the light and heavy REE is what differentiates the patterns from each sampling group.

These behaviors of REE can be related to the weathering processes in the area (fluvial action and chemical weathering processes). However, since REEs are generally immobile elements (Middelburg et al. 1988) except for deep/strong weathering processes (Aide and Aide 2012; Chang et al. 2016), these REE trends can only be attributed to the original bedrock composition.

Samples from the pit lake, Tagburos River, nearby rivers, and soils showed very similar upper continental crust (UCC)-normalize REE patterns and they have the highest disparity between levels of HREE and LREE. The heavy REE (Eu to Lu) is in the range of 0.8–1.1, which coincides very closely to the values of the upper continental crust, while the light REEs go from 0.2 to 0.6, from La to Sm, respectively. These results for the four groups involved strongly suggest their same provenance and characteristics based on REE geochemistry. The REE fractionation for these four sampling groups can be correlated with two factors: (1) alteration processes that occurred due to hydrothermal activity that brought about the mercury mineralization, and/or (2) weathering processes. The same signature between the river sediments and the soil cover suggest that weathering processes related to fluvial action do not affect the REEs in the sediments. From the results, there is a higher degree of depletion of light rare earth elements than HREE. This is analogous to the trend of REE concentration in the phyllic alteration zone from hydrothermal processes in the Rangan area volcanic belt in Iran (Parsapoor et al. 2009). Heavy REE already has fixed a concentration in the crystal lattice of silicic minerals in these zones, such as quartz. Since there is no known secondary mineral formed from hydrothermal alteration that can incorporate LREE in their structure, LREE depletion can prevail.

The values for Honda Bay wharf and mine waste calcine display almost horizontal lines, indicating REE trends similar to the crustal average values, albeit diluted approximately 10 times. These two sampling groups are allegedly

FIGURE 3. Comparison of REE concentrations in sampling groups versus crustal average.

TABLE 3. REEs and radionuclide concentrations of sediment samples collected in different zones in the vicinity of PQMI lake as opposed to crustal average.

Trace element (mg/kg)	Pit lake	Tagburos River	Honda Bay wharf	Honda Bay	Mine waste calcine	Other rivers	Surrounding soils	Crustal average*	CI Chondrite**
La	2.94	5.03	1.54	1.60	1.01	6.34	5.39	31.00	0.237
Ce	7.33	13.53	3.11	3.17	3.21	12.91	14.15	63.00	0.613
Pr	2.15	1.85	0.23	1.00	0.91	2.21	1.89	7.10	0.093
Nd	8.88	8.43	0.99	4.97	3.69	9.41	9.24	27.00	0.457
Sm	2.72	2.53	0.25	1.30	0.72	2.62	2.63	4.70	0.148
Eu	0.94	0.85	0.08	0.43	0.21	0.88	0.92	1.00	0.056
Gd	3.42	3.19	0.29	1.56	0.69	3.17	3.33	4.00	0.199
Tb	0.61	0.57	0.05	0.25	0.11	0.57	0.57	0.70	0.036
Dy	3.69	3.42	0.30	1.56	0.62	3.42	3.45	3.90	0.246
Ho	0.75	0.74	0.07	0.33	0.13	0.73	0.77	0.83	0.055
Er	1.98	2.02	0.19	0.87	0.39	1.95	2.07	2.30	0.160
Tm	0.33	0.32	0.04	0.13	0.05	0.32	0.30	0.30	0.025
Yb	1.75	1.85	0.18	0.82	0.36	1.74	1.90	2.00	0.161
Lu	0.27	0.27	0.03	0.12	0.05	0.26	0.27	0.31	0.025
Sc	20.10	19.18	5.43	4.88	29	20.05	22.47	14.00	
Y	9.08	15.62	2.60	3.55	1.96	17.54	17.30	21.00	1.500
Th	0.47	0.84	0.26	0.22	0.81	1.23	0.86	6.00	
U	0.22	0.39	0.50	0.36	0.27	0.33	0.21	2.70	

*Weng et al. (2015), **McDonough and Sun (1995)

of similar nature, namely waste products of mining activity in the past because some of the mine tailings were used to construct the wharf. All REEs in the two sampling groups lie in the range of 0 to 0.2 and their similar trend supports their same origin and identical characteristics, given that they have the highest concentration of Hg in all of the sediments. It can be inferred that the calcination of the mined ores that produced these sediments have leached most REEs.

The UCC-normalize REE pattern of the Honda Bay sediments show all HREEs around 0.4 while the LREEs increase from 0 to 0.3 from La to Sm, respectively. This pattern is an intermediary of the two aforementioned major groups. This probably resulted from the dilution of terrestrial sediments similar to those from the rivers and soil with marine sediments that have relatively lower amounts of REEs.

The minimal concentration of radionuclides in all sampling areas in comparison with the crustal average are re-

lated to the nature of U and Th as incompatible elements. Incompatible elements are those that preferentially stay in the melt during magmatic differentiation and are subdivided into two categories: large ion lithophile elements (LILE) and high field strength elements (HFSE). U and Th belong to the HFSE category and are incompatible because of their high cationic charge. U and Th are enriched in silicic rocks. Since Puerto Princesa City is underlain with ultramafic rocks, U (0.21–0.50 mg/kg) and Th (0.22–1.23 mg/kg) occur in small amounts compared with the crustal average.

3.3 Correlation of Hg, other heavy metals, total REE (Σ REE) and radioactive elements

The possible relationships between the trace elements were assessed by linear correlation. The Pearson correlation coefficient (r) was calculated between the Hg, pollut-

FIGURE 4. Chondrite-normalized REE concentrations in pit lake and rivers.

FIGURE 5. Crustal average-normalized REE concentrations in all sampling groups.

TABLE 4. Pearson correlation coefficients of significant trace elements with each other.

	Co	Cr	Ni	Fe	Sb	Tl	Hg	ΣREE*	Th	U
As	-0.805	-0.074	-0.604	0.121	0.977	0.957	0.777	-0.657	-0.648	0.145
Co		0.438	0.902	0.372	-0.685	-0.610	-0.317	0.570	0.749	-0.654
Cr			0.555	0.944	0.097	0.116	0.488	-0.468	0.031	-0.431
Ni				0.490	-0.501	-0.426	-0.057	0.348	0.526	-0.580
Fe					0.306	0.350	0.647	-0.445	0.071	-0.609
Sb						0.992	0.867	-0.679	-0.572	-0.029
Tl							0.886	-0.611	-0.508	-0.137
Hg								-0.667	-0.510	-0.291
ΣREE									0.669	-0.352
Th										-0.564

*ΣREE refers to the total amount of rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, and Y).

ing heavy metals (As, Co, Cr, Ni, Sb, and Tl), iron (Fe), REEs, and the radioactive elements (Table 4). Fe was considered in order to assess the possible interaction with reactive Fe and iron hydroxide (Fe-OH) phases. Fe and Cr had a very strong positive correlation ($0.9 < r < 1$) because of their co-occurrence in mineral phases like chromite, which is abundant in the ultramafic bedrock. Nickel and cobalt also exhibit a very strong positive correlation as these two can be associated together in lateritic soils (Putzolu et al. 2018). As, Pb, and Tl have a three-way very strong positive relationship with each other while they all have a strong positive correlation ($0.7 < r < 0.9$) with Hg that probably occurred as accessory metals with Hg in the deposit given their association. Each of the REE (except Sc) along with total REE content for the sampling groups have close r values with respect to Hg, where they exhibit a strong negative correlation. The REEs tend to deplete with the increase in Hg pollution in the sediments that could indicate their non-affinity to Hg during its deposition. The radioactive elements, with their low concentration in all the samples tend to generally not associate with any of the investigated elements except for Th and Co.

3.4 Recommendation to control the impact of pollutants in the PQMI mine area

These findings confirmed the contamination of heavy metals in the soil, such as Ni, Cr, Mn, and Hg, which are inherent in the geology of the area. In order to curb the elevated values of these elements, particularly Hg, soil remediation techniques such as phytoremediation is recommended as a low investment, in situ type of solution. Revegetation of the mined-out area with hyperaccumulator species endemic to the pit lake vicinity is yet another area of study. The above mining rehabilitation techniques, if implemented, can reduce soil erosion and soil particle suspension.

4. CONCLUSIONS

This study presented the characteristics of heavy metals, rare earth elements, and radioactive elements in the soil and sediments of the abandoned mercury mine in Puerto Princesa City, Palawan. Aside from Hg, there are considerably higher concentrations of Ni, Cr, and Mn in the area due to its geology, particularly following the lithology traversed by the Tagburos River. The presence of ultramafic rocks of Palawan Ophiolite in the upstream portion of Tagburos River explains the high Cr and Ni concentrations while the

high Mn content of the sediment samples can be attributed to the occurrence of interbedded red chert and dark maniferous chert in the northeast of the pit lake. High concentrations of Ni, Cr, and Hg are manifested with the calculated highest contamination factor among the measured trace elements. The areas dumped with mine wastes were distinguished by their very depleted REE signature as opposed to the similar patterns exhibited by all other terrestrial sediments due to their parent rock origin. Past mining activities had an impact on the REE distribution in the area by leaching it in the process and REEs tend to deplete with the increase in Hg pollution in the sediments, which could indicate their non-affinity to Hg during its deposition. REEs were found to have a negative correlation with Hg. The concentration of U and Th found in the soil and sediments were within expected values in an ultramafic area and disturbance of the ground from mining did not enhance their concentrations. Mine rehabilitation activities, such as revegetation to reduce soil erosion and soil particle suspension and phytoremediation to remove heavy metals in soil, need to be implemented based on the results of this study.

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AUTHORS' CONTRIBUTIONS

JS, CRG: conception and design of study and supervision, sample acquisition, analysis, interpretation of data. AT, RR: sample acquisition, analysis, interpretation of data, drafting the manuscript. All authors have read and approved the final version of the manuscript.

COMPETING INTERESTS

The authors declare that there is no conflict or competing interests regarding the publication of this manuscript.

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