Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 15 March 2022 doi:10.20944/preprints202203.0205.v1

Article

Modelling the origin, fate, and ecological and health impacts of heavy metals from an abandoned mercury mine in a paradise island in the Philippines

Reymar R. Diwa [1,2], Custer C. Deocaris [2,,3, 5], Lhevy D. Geraldo [3,*] and Lawrence P. Belo [4,5,*]

[1] Research and Development Center, Rizal Technological University, Mandaluyong City 1550, Philippines; reymar.diwa@gmail.com (R.D.)
[2] Atomic Research Division, Philippine Nuclear Research Institute, Department of Science & Technology, Diliman, Quezon City 1101, Philippines; ccdeocaris@pnri.dost.gov.ph (C.D.)
[3] Earth and Space Sciences Department, College of Arts and Sciences, Rizal Technological University, Mandaluyong City 1550, Philippines;
[4] Department of Chemical Engineering, De La Salle University, Manila 1004, Philippines;
[5] BANToxics, Barangay Central, Quezon City, 1100 Philippines
* Correspondence: ldgeraldo@rtu.edu.ph (L.G.); lawrence.belo@dlsu.edu.ph (L.B.); Tel.: (+63917 8362356)

Abstract: A recent survey that determined heavy metal concentrations in an abandoned Hg mine in Palawan, Philippines, found the occurrence of Hg with As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Tl, V, and Zn. While the Hg originated from the mine waste calcines as supported by previous studies, the critical knowledge about the origin of the other heavy metals remains to be unknown. Our study investigated the sources of heavy metal pollution surrounding the abandoned Hg mine; and assessed the soil and sediment quality, ecological risks, and health risks associated with these toxic metals. Multivariate analyses, such as hierarchical cluster analysis (HCA), principal component analysis (PCA), and Pearson correlation analysis, were used to identify the heavy metal sources from the results of a previous paper. Our results showed that Fe, Ni, Cr, Co, and Mn are associated with the ultramafic geology of the study, whereas As, Ba, Cd, Cu, Pb, Sb, Tl, V, and Zn are likely due to historical mining and processing of cinnabar from 1953-1976. The mine waste calcines were used as construction material for the wharf and as land filler for the adjacent communities. The modified contamination factor (mC_{deg}) showed that the coast of Honda Bay is highly contaminated, while the inland areas, including the rivers, are very- to ultra-highly contaminated. There is a considerable ecological risk associated with the heavy metals, wherein Ni, Hg, Cr, and Mn contribute an average of 46.3 %, 26.3 %, 11.2 %, and 9.3 % to the potential ecological risk index (RI), respectively. The overall mean hazard index (HI) for both adults (1.4) and children (12.1) exceeded 1, implying the probability of non-carcinogenic adverse effects. The mean total cancer risk over a lifetime (LCR) for both adults (1.19×10^{-3}) and children (2.89×10^{-3}) exceeded the tolerable threshold of 10^{-4}, suggesting a potentially high risk for developing cancer mainly by Ni, Co, and Cr exposure.

Keywords: heavy metals; soil; sediments; soil pollution; multivariate analysis; health index; potential ecological risk; abandoned mine

1. Introduction

Palawan Province is the largest province in the Philippines with a total area of 14,649.73 km^2 and is composed of over 1700 islands: Calamian Island group in the north, Cuyo Island group in the northwest, and the Balabac-Bugsuk group in the southwest. The island is also considered as the last ecological frontier in the Philippines with the immense biodiversity of corals, seagrass meadows, mangroves, marine mammals, freshwater fishes, amphibians, reptiles, birds, and terrestrial mammals [1,2]. In 1990, UNESCO also designated Palawan as "Man and Biosphere Reserve" (1997) [3].

There is also an abundance of mineral reserves in this paradise island. In a mineralogical survey, nickel, chromium, gold, copper, cobalt, mercury, and rare earths abound in Palawan [4] indicating that the island is an ideal site for conducting mining operations.

© 2022 by the author(s). Distributed under a Creative Commons CC BY license.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 15 March 2022 doi:10.20944/preprints202203.0205.v1

In fact, in the past decades, multi-national companies, *i.e.*, Rio Tuba Nickel Mining Corporation (RTNMC), Berong Nickel Corporation, Celestial Nickel and Exploration Corporation (CNMEC), MacroAsia Corporation, LEBACH, Narra Nickel Mining and Development, Inc. (NNMDC), Tesoro Mining and Development, Inc. (TMDI), and McArthur Mining, Inc. (MMI) [5], contributed to the regional economic development through their mining operations. As of this writing, the open pit-mining activities for laterites in Palawan are still operation in the southern part of the main island. With the need to boost the local economy in response the COVID-19, it is expected that the national government will new mining operations in Palawan [6].

To strengthen protection of the environment from unregulated mining practices in the country, especially in Palawan, various legislative and policy instruments were passed to include Republic Act 7942 (Philippine Mining Act of 1995), Department of Environment and Natural Resources (DENR) Administrative Order No. 2010-21 (Mining Act IRR), and Executive Order No. 79, s. 2012 (Institutionalizing and Implementing Reforms in the Philippine Mining Sector, Providing Policies and Guidelines to Ensure Environmental Protection and Responsible Mining in the Utilization of Mineral Resources) [7]. While the local government and mining companies worked to address the long-term environmental effects like erosion, biodiversity loss, and contamination of groundwater by chemicals from the mining processes, there are still abandoned mines, like that of the Palawan Quicksilver Mines, Inc. (PQMI), that need rehabilitation. PQMI extracted a huge amount of mercury (Hg) deposits through open-pit mining from 1953 to 1976, and around 2,900 metric tons of mercury and 2,000,000 metric tons of mine waste calcines were produced. and the mining site was abandoned with no plans of rehabilitation The mining operations stopped in the 1970s due to declining price of mercury in the world market [8]. Remnants from the mining company operations, such as the mine waste calcines, were used to build the peninsula or jetty in Honda Bay, the artificial lagoon, and some landfills. Through time, with weathering and erosion, mercury seemed to aquatic environment of Honda Bay [9,10].

While existing research were conducted to assess the extent of mercury contamination in the surrounding area of the abandoned mine, detailed health and environmental impacts of *ad mixture* of the heavy metals and their possible origins remain unknown. Therefore, this study employed multivariate analyses, such as hierarchical cluster analysis (HCA) and principal component analysis (PCA), to determine the possible ecological and health risks associated to the heavy metals in soils and sediments [11–14]. To our knowledge, this is the most detailed study on the long-term health impact and source apportionment of heavy metals in the island paradise billed as "one of the most beautiful islands in the world" [15]. Specific policy recommendations from our results are provided in this paper.

2. Materials and Methods

2.1. Study Area

The study area, covering the villages of Santa Lourdes and Tagburos, is located 14 km north of Puerto Princesa City, the capital of Palawan. The villages are home to more than 12,200 people in 2015. The open pit-mining of cinnabar for Hg from 1953 to 1976 resulted to an artificial lake known as PQMI pit lake [10,16]. The lake is traversed to the south by the Tagburos River that drains to Honda Bay. The numerous islands adjacent the bay lodge many world-famous resorts for tourists. The bay is also a rich fishing ground for small-scale fisherfolks and commercial fishing companies.

2.2. Sediment Heavy Metal Data

We analyzed the most recent dataset of heavy metal concentrations in surface soils and sediments collected from the study area after the 2021 work of Samaniego et al. [16]. A total of 32 samples were collected from September 2018 to October 2019 at the following sites: soil samples from PQMI, the surrounding agricultural soils, and Honda Bay wharf; and sediment samples from Tagburos river and Honda Bay coast (Figure 1). The <63 μmsize fraction of the samples was analyzed for heavy metals using Inductively Coupled Plasma Mass Spectrometry (ICP MS). Table 1 summarizes the concentrations of the heavy metals in the study area.

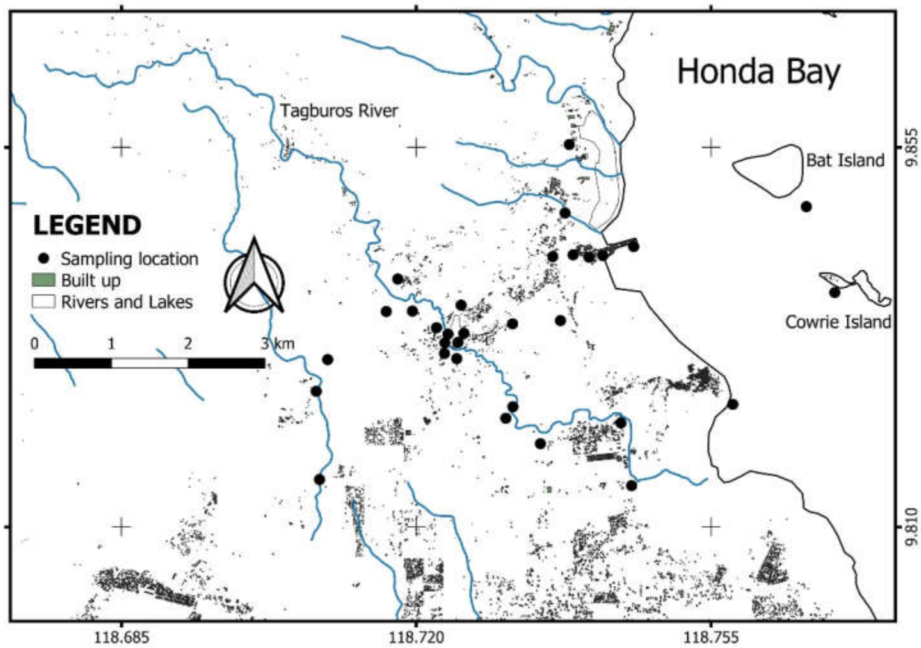

Figure 1. Samples were collected in the following areas: PQMI pit lake (n = 4), Honda Bay Wharf (n = 3), along Tagburos River (n = 9), agricultural soils (n = 6), along the coast of Honda Bay (n = 6), and other rivers (n = 4).

Table 1. Mean heavy metal concentrations found in the sampling areas (mg kg^{-1}) analyzed by Samaniego et al. [16].

Location	PQMI	Tagburos River	Wharf	Honda Bay	Agricultural soils	Other rivers
n	*4*	*9*	*3*	*6*	*6*	*4*
As	7.75	4.89	50.67	16.33	5.75	5.75
Ba	29.5	52.11	29.33	7.5	38.33	47.75
Cd	0.21	0.28	0.34	0.21	0.16	0.175
Co	124.7	98.52	27.7	33.67	111	119.25
Cr	1479.75	513.33	1164.33	205	731.67	514.75
Cu	58.72	83.75	116.87	60.28	50.72	67.45
Fe	138700	76700	161500	29600	108100	91725
Hg	124.5	36.7	357.3	3.5	7.4	10.5
Mn	860.5	2559.44	267.67	270.67	1751	1922.75
Ni	2530.75	904.22	414.67	361.67	1375.17	2019.75
Pb	18.5	33.67	36.4	10.52	11.95	10.88
Sb	3.38	2.46	30.18	4.32	0.77	1.15
Tl	1.88	0.15	20.88	0.08	0.14	0.17
V	103	159.89	112.67	27.5	135.5	140
Zn	99.25	109.22	114	37	63.33	88

2.3. Multivariate Analysis

To identify the sources and apportionment of the heavy metals, we performed multivariate analyses, such as hierarchical cluster analysis (HCA), principal component

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 15 March 2022 doi:10.20944/preprints202203.0205.v1

analysis (PCA), and Pearson correlation using R ver. 4.0.4. HCA groups similar variables of a dataset to homogenous clusters that differ from each other [17]. PCA reduces the dimensionality of several intercorrelated quantitative variables into a new set of variables, called principal components, without significant loss of data [14,18]. Pearson correlation measures the degree of linear correlation between two data sets.

The calculation of distance between the variables for clustering by HCA was performed using the Canberra method. The clusters were then linked together to form the dendrogram using the Single method. The *princomp* syntax in R was used to calculate the eigenvalues, proportion of variance, and factor loadings of the principal components.

2.4. Risk Assessments

The authors used various indices to assess the soil and sediment contamination and ecological and health risks associated with the heavy metals.

2.5. Soil and Sediment Contamination

The soil and sediment quality were assessed using contamination factor (*CF*) and modified contamination factor (mC_{deg}). *CF* is a single index indicator that reflects anthropogenic inputs in heavy metal pollution, although it doesn't consider lithogenic and sedimentary inputs of the metals [19,20]. It is calculated using Equation 1,

$$CF = \frac{C_i}{C_b} \tag{1}$$

where C_i is the concentration of the metal and C_b is the background or reference concentration of the same metal [21]. Due to the absence of pre-industrial concentration of the heavy metals in Palawan, we used the average concentrations in the Earth's upper continental crust as the reference concentrations [22]. The qualitative ratings of *CF* of the heavy metals are as follows: < 1 low contamination; 1 – 3 moderate contamination; 3 – 6 considerable contamination; and > 6 very high contamination.

To assess the overall degree of soil and sediment contamination, mC_{deg} was used to combine the contamination risks by the individual heavy metals. It is a multi-element index that takes into account the synergistic effects of the heavy metals by reducing their contribution into a single value [23]. It is basically the mean of *CF* of the heavy metals and is calculated using Equation 2,

$$mC_{deg} = \frac{1}{n}\sum_{i=1}^{n} CF_i \tag{2}$$

where *CF* is the contamination factor and n is the number of heavy metals. An mC_{deg} rating of < 1.5 signify very low contamination; 1.5 – 2 low contamination; 2 – 4 moderate contamination; 4 – 8 high contamination; 8 – 16 very high contamination; 16 – 32 extremely high contamination; > 32 ultra-high contamination [24].

2.6. Ecological Risk Assessment

The ecological risks associated with the heavy metals were assessed using the potential ecological risk index (RI). RI measures the vulnerability of organisms to heavy metal contamination [21]. It is calculated using Equation 3,

$$RI = \sum_{i=1}^{n} Er^i = \sum_{i=1}^{n} Tr^i \times Cf^i \tag{3}$$

where Er^i is the potential ecological risk factor of the heavy metal, Tr^i is the biological toxic response factor of the heavy metal (Tr^i: 40 -Hg, 30 – Cd; 10 – As; 5 - Cu, Ni, Pb; 2 – Cr, V;

1 - Zn), and Cf^i is the contamination factor of the individual heavy metal (Manoj and Padhy 2014). RI is rated as < 150 low risk; 150 – 300 moderate risk; 300 – 600 considerable risk; and > 600 very high risk. The ER^i of the individual heavy metals are classified as < 40 low risk; 40 – 80 moderate risk; 80 – 160 considerable risk; 160 – 320 high risk; and > 320 very high risk [12,21,25].

2.7. Human Health Risk Assessments

Health risk assessments are useful tools to estimate the risks posed by human exposure to toxic metals [26,27]. The heavy metals analyzed have toxicological and carcinogenic effects on humans, except for Fe and Tl [28–31]. We assessed the non-carcinogenic and carcinogenic risks of heavy metal exposure of resident adults and children in PQMI, agricultural soils, the wharf, Tagburos River, and other rivers based on guidelines by the United States Environmental Protection Agency using Hazard Index (*HI*) and Carcinogenic Risk (*CR*). These indices quantify the human health risks of heavy metal contamination in soil via ingestion, dermal, and inhalation exposures pathways.

CDI is the dose received through each of the heavy metal exposure pathways [31,32]. *HQ* is the measure of the potential non-carcinogenic toxicity to occur to an individual due to exposure to heavy metals. The risks associated with heavy metals are additive [33]. Thus, we computed for the Hazard Index (*HI*) which is the sum of the *HQ* of the heavy metals for the three exposure pathways. An HI > 1 indicates a probability of developing non-carcinogenic effects which tends to increase with the value [32,34]. Carcinogenic Risk (*CR*) estimates the probability of developing cancer for individuals as a result of exposure to carcinogenic metals. The total cancer risk over lifetime (*LCR*) is the sum of the *CR* by the individual heavy metals. The range of carcinogenic risk can be characterized as follows: very low (< 10^{-6}); low (10^{-6}–10^{-5}); medium (10^{-5}–10^{-4}); high (10^{-4}–10^{-3}); and very high (> 10^{-3}) [24]. *CDI*, *HI* and *LCR* are calculated using **Equations 4 to 10**. The definition of variables and their values are summarized in **Table 2**.

Chronic daily intake (*CDI*):

$$CDI_{Ing} = \frac{C_{soil} \times RI \times EF \times ED}{BW \times AT} \times 10^{-6}, \tag{4}$$

$$CDI_{Derm} = \frac{C_{soil} \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6}, \tag{5}$$

$$CDI_{Inh} = \frac{C_{soil} \times EF \times ET \times ED}{PEF \times BW \times AT}, \tag{6}$$

Non-carcinogenic risk:

$$HI = \sum HQ, \tag{7}$$

$$HQ = \frac{CDI}{RfD}, \tag{8}$$

Carcinogenic Risk:

$$CR = CDI \times SF, \tag{9}$$

$$LCR = \sum CR, \tag{10}$$

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 15 March 2022 doi:10.20944/preprints202203.0205.v1

Table 2. Values of variables for the assessment of health risks by heavy metal exposure.

Variable	Value
C_{soil} (mg kg^{-1}): heavy metal concentration in soil	Table 1
ABS (unitless): dermal absorption factor	0.03 for As and 0.001 for other metals
AF (mg cm^{-2}): soil to skin adherence factor	0.07 for Adults, 0.2 for Children
AT (d): averaging time	ED x 365 for non-carcinogenic and 70 x 365 for carcinogenic
BW (kg): body weight	70 for Adults, 15 for Children
ED (yr): exposure duration	23 for Adults, 6 for Children
EF (d yr^{-1}): exposure frequency	350 for residential
ET (h d^{-1}): exposure time	24 for residential
RfD (mg kg^{-1} d^{-1}): chronic reference dose	Table S1
RI (mg d^{-1}): ingestion rate	100 for Adults, 200 for Children
PEF (m^3 kg^{-1}): soil-to-air particle emission factor	1.36 x 10^9
SA (cm^2 event^{-1}): skin surface area available per event of heavy metal exposure	5700 for Adults, 2800 for Children
SF (mg kg^{-1} d^{-1}): carcinogenicity slope factor*	1.5 for As, 6.3 for Cd, 9.8 for Co, 0.5 for Cr, 0.84 for Ni, 0.005 for Pb

* Diami et al. 2016 [35]; Doležalová Weissmannová et al. 2019 [24]; Luo et al. 2012 [36]

3. Results and Discussion

3.1. Heavy metal concentration and source identification

The soil and sediment samples were collected and analyzed by Samaniego et al. [16] from the following areas in the study site: PQMI, Tagburos River, wharf, Honda Bay, agricultural soils, and other rivers as shown in Figure 1. The descriptive statistics of the heavy metals in the soils and sediments are summarized in Tables 1 and 3. PQMI and the wharf have the highest heavy metal concentrations, particularly Hg. The most notable result is that the mean As, Cd, Co, Cr, Cu, Hg, Ni, Sb, and Tl concentrations are equivalent to 3.1, 2.5, 5, 8.3, 2.6, 1799.7, 27, 17.6, and 4.3 times of the mean concentrations in the upper continental crust [22]. Comparing heavy metal concentrations in surface soils of another site affected by industrial activity in Ostrava, Czech Republic [24], we our study area in Palawan had higher concentrations of Cr, Cu, Hg, and V.

It is certain that the Hg in the study area is sourced from historical Hg mining by PQMI. As mine waste calcine has been seen the largest source of Hg contamination in the abandoned mine due to low efficiency of Hg recovery during calcination [10], what is intriguing is the existence of other toxic metals. To identify the sources of these heavy metals, we performed multivariate analyses such as HCA, PCA, and Pearson correlation analysis. These are useful tools for finding the causes of heavy metal pollution by grouping them according to similarity in their sources [12–14,25,37–39].

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 15 March 2022 doi:10.20944/preprints202203.0205.v1

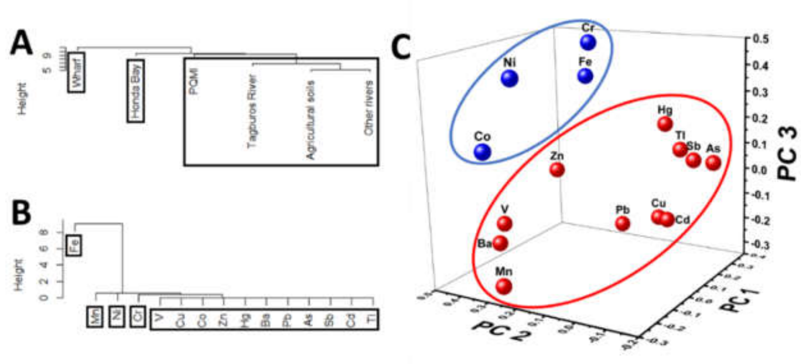

Figure 2. The sampling areas and heavy metals are clustered by the HCA and PCA according to similarity in heavy sources. (**A**) The wharf formed its own cluster; Honda Bay formed the second cluster; and PQMI pit lake, Tagburos River, agricultural soils, and other rivers formed the third cluster. (**B**) The heavy metals are also clustered into five groups wherein Fe, Mn, Ni, and Cr formed their own individual clusters and V, Cu, Co, Zn, Hg, Ba, Pb, As, Sb, Cd, and Tl formed the fifth cluster. (**C**) The PCA incorporated Fe, Ni, Cr, and Co into the first cluster and the rest of the heavy metals to the second cluster.

HCA grouped the sampling areas into 3 clusters. The first cluster consists of the wharf; second cluster, Honda Bay; and the third cluster, PQMI, Tagburos River, agricultural soils, and other rivers (**Figure 2A**). We found a striking relationship among the sampling areas of the clusters that corresponds to the degree of Hg contamination, exposure pathways, and external influence on Hg concentration. The wharf in first cluster has the highest heavy metal concentration from the calcine that had been immobilized by cement. It has been reported that the construction of the wharf used half of the total calcines produced by the entire operation of the Hg mine [10,40]. Honda Bay in the second cluster has the lowest Hg since it is farthest from the source. Lastly, the third cluster results from mobilization of mine waste calcines in PQMI thorough utilization as land fillers in nearby communities and erosion that eventually travel through Tagburos River and other rivers. mining activities had a significant effect to the chemistry of PQMI soils upstream of Tagburos River causing enrichment of Cr, Ni, and Mn [10].

Table 3. Comparison of the mean heavy metal concentrations in the upper continental crust, in other area affected by industrial activities, and in this study (mg kg^{-1}).

Location	Upper Continental Crust*	Ostrava, Czech Republic		This Study	
		Median	Range	Mean	Range
As	4.8	-	-	14.93	4.17-50.67
Ba	624	-	-	34.09	7.50-52.11
Cd	0.09	0.21	0.05-1.18	0.23	0.16-0.34
Co	17.3	-	-	85.81	27.70-124.70
Cr	92	17.46	3.03-64.02	768.14	205.00-1479.75
Cu	28	21.22	4.88-98.83	72.97	50.72-116.87
Fe	50400	-	-	101054	29600-161500
Hg	0.05	0.19	0.08-1.31	89.98	3.50-357.30
Mn	1000	-	-	1272.01	267.67-2559.44
Ni	47	-	-	1267.71	361.67-2530.75
Pb	17	37.71	11.09-174.03	20.32	10.52-36.40
Sb	0.4	-	-	7.04	0.77-30.18
Tl	0.9	-	-	3.88	0.08-20.88
V	97	96.72	43.45-181.79	113.09	27.50-159.89
Zn	67	204.57	63.16-373.58	85.13	37.00-114.00

*Rudnick & Gao [22]

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 15 March 2022 doi:10.20944/preprints202203.0205.v1

The clustering of sampling areas gives clues about the degree of heavy metal exposure, but it does not tell anything about the sources of the heavy metals. To investigate their sources, we used the HCA again to produce clusters according to similarity in sources (**Figure 2B**). The heavy metals are primarily grouped to five clusters: cluster 1 (Fe), cluster 2 (Mn), cluster 3 (Ni), cluster 4 (Cr), and cluster 5 (V, Cu, Co, Zn, Hg, Ba, Pb, As, Sb, Cd, and Tl). Despite forming clusters of their own, Fe, Mn, Ni, and Cr are all related to the geology of the study area. It belongs to the mantle component of the Palawan Ophiolite Complex that is dominated by harzburgites with few Cr-rich spinel [41,42]. Ultramafic rocks like the harzburgites have Cr and Ni concentrations reaching 2980 mg kg^{-1} and 10,900 mg kg^{-1}, respectively [43,44]. Meanwhile, Mn is related to the occurrence of red chert and dark manganiferous chert located northeast of the study areas [45]. The fifth cluster consisting of Hg and other heavy metals can be attributed to calcine from historical Hg mining and processing.

PCA reduced the dimensionality of the dataset into 5 principal components that control the heavy metal pollution in the study area. Three of the five principal components have eigenvalues greater than one that control 95.9 % of the total variance in the dataset. The eigenvalues, proportion of variance, cumulative variance, and factor loadings are summarized in **Table S2**. As PCA complements the our findings from HCA, the relationship of the factoring loadings of the first three principal components is shown in **Figure 2C**. The clustering of heavy metals by the PCA is like the clustering by HCA, although the PCA associated Co with Fe, Ni, and Cr and Mn to the cluster of Hg, directly implying that the heavy metals other than Fe, Ni, Cr, Co, and probably Mn were sourced from Hg mining and processing from 1953 to 1976.

The association of other heavy metals with Hg is supported by the Pearson correlation coefficients *r* (**Table S3**). Hg has strong positive correlation with As (r=0.91), Cd (r=0.80), Cu (r=0.84), Pb (r=0.71), Sb (r=0.95), and Tl (r=0.97).

3.2. Mechanism of heavy metal transport

The mine had not undergone rehabilitation even after its abandonment in 1976. Its exposure to weathering, especially during rains, has led to heavy metal run-off into the Tagburos River [40]. Unexpectedly, the occurrence of heavy metals upstream of the abandoned mine is against the natural flow of water although this unusual distribution pattern may not be due to natural causes but rather anthropogenic. The calcines were used as land fillers/topsoil in the adjoining communities in the area [8,46]. Half of the approximate two million tons of mine waste calcines produced by the mercury mine was also dumped in Honda Bay to construct the wharf [10,40]. Mangroves at the mouth of Tagburos River, which served as a major sink of the heavy metals from the eroded calcines carried by the river [46], may explain the considerably lower concentrations of heavy metals at Honda Bay than the inland areas.

3.3. Sediment pollution and risks associated with heavy metals

We used various indices to assess the heavy metal contamination in soil and sediments and the ecological and human health risks associated with these toxic metals. The contamination factor (CF) indicates that there is very high contamination by Hg, Ni, Sb, and Cr; considerable contamination by Co, Tl, and As; moderate contamination by Cd, Cd, Fe, Mn, Z, Pb, and V; and low contamination by Ba (**Figure 3A**). The modified contamination factor (mC_{deg}) that combines the contamination caused by all the heavy metals indicates that PQMI, the wharf, and Tagburos River have ultra-high contamination; the other rivers have extremely high contamination; the agricultural soils have very high contamination; while Honda Bay has high contamination (**Figure 3B**). Individually, Hg (95.9 %) presented the highest contribution to the contamination, followed by Ni (1.4 %) and Sb (0.9 %).

According to the potential ecological risk index (RI), all the sampling areas have highly strong ecological risks (**Figure 3C**). The mean potential ecological risk factors (ER)

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 15 March 2022 doi:10.20944/preprints202203.0205.v1

of the individual metals show that Ni (6339), Hg (3599), Cr (1536), Mn (1272), and Cu (365) presented very high risk; V (226) has high risk; As (149), Pb (102), and Zn (85) have considerable risk; and Cd (7) has low risk (**Figure 3D**).

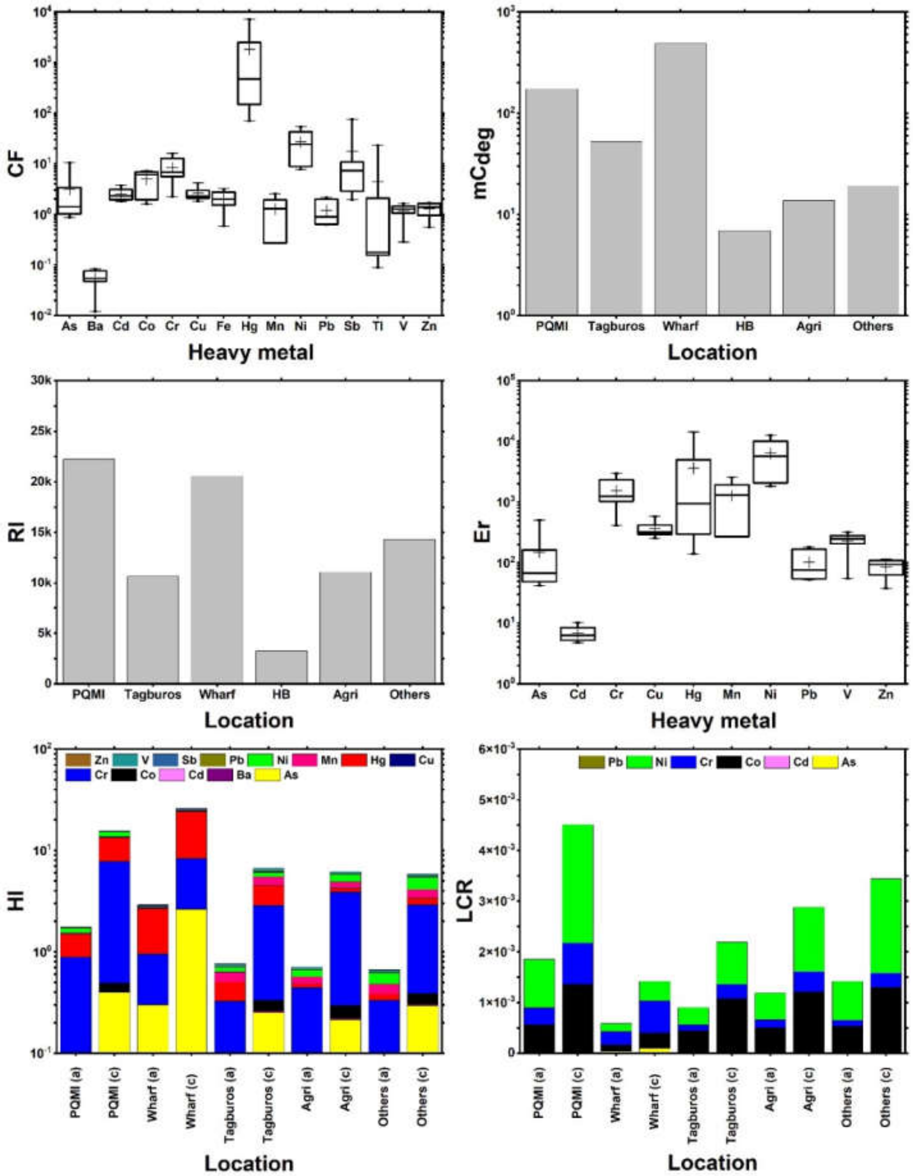

Figure 3. The ecological risks were assessed using contamination factor (CF), modified contamination factor (mC_{deg}), potential ecological risks index (RI). (**A**) mC_{deg} indicates that the study area has high (4-8) to ultrahigh (≥32) levels of heavy metal contamination. (**B**) The statistics of individual CF of the heavy metals showing the mean (square), 25th, 50th, and 75th percentile (rectangle), 1st and 99th percentile (x) and range (vertical line) indicate that the mean Hg, Ni, Sb, and Cr in the study area have very high contamination. (**C**) The potential ecological risks shows that all the areas have very high ecological risks. (**D**) The statistics of ER of the individual heavy metals indicate that Ni, Hg, Cr, Mn, and Cu posed the highest ecological risk. (**E**) HI suggests a strong potential for children to develop non-carcinogenic effects due to heavy metal exposure as well as for adults living near PQMI and the wharf. (**F**) The LCR for adults and children exceeded the 10^{-4} limit suggesting a very strong potential for developing cancer.

The hazard index (HI) measures the potential non-carcinogenic effects of heavy metal exposure. The HI for adults ranged from 0.67-2.89 while it ranged from 5.84-26.09 for

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 15 March 2022 doi:10.20944/preprints202203.0205.v1

children. As a rule, the higher values of HI and HQ above 1 suggests a higher level of concern. The result of the modelling suggests the probability of adverse effects to adult and children in residents living nearby PQMI and the wharf as well as to children in agricultural areas and around Tagburos river and the other aquatic systems (**Figure 3E**). We found that children are 9 times more vulnerable to non-carcinogenic effects of heavy metals than the adults. The mean HQs of Cr and Hg for children alone are >> 1. The mean HQ contribution of the heavy metals to the overall HI for both adults and children is in the order of Hg (38.8 %) > Cr (35.9 %) > Ni (7.6 %) > As (6.3 %) > Mn (5.0 %) > V (2.6 %) > Sb (2.3 %) > Pb (0.7 %) > Co (0.5 %) > Cu (0.2 %) > Ba (0.06 %) > Zn (0.03 %) > Cd (0.03 %).

The total cancer risk over lifetime (LCR) for both adults and children in all the sampling areas exceeded 10^{-4}, suggesting a potentially great risk for developing cancer (**Figure 3F**). The LCR for adults ranged from 5.83×10^{-4} - 1.85×10^{-3} and for children 1.41×10^{-3} - 4.51×10^{-3}. The mean cancer risk (CR) by the individual heavy metals show that Co and Ni have very high risk to children and high risk to adults, Cr has high risk to both adults and children; As has medium risk to both adults and children; Cd has very low risk to adults and low risk to children; Pb has very low risk to adults and children. The mean CR contribution of the heavy metals to LCR for both adults and children is Ni (46.3 %) > Co (35.9 %) > Cr (16.8 %) > As (0.9 %) > Cd (0.06 %) > Pb (0.01 %).

The results of our health risk analyses differ significantly from the work of [45] that didn't account the carcinogenicity of Co, Cr, and Ni which we found to cause high to very high risk CR to both adults and children. As the hazards caused by multiple heavy metals is also interactive, their failure to account the carcinogenic effects of all the possible metals through the LCR led them to conclude that there is no overall risk for the population to develop cancer that we've shown here otherwise. Their work also used the mean concentrations of the heavy metals in the entire study area instead of by sampling vicinity. This caused a massive underestimation of the health risks especially for areas with significantly higher concentration of heavy metals.

3.4. Policy recommendations for rehabilitation and mitigation of environmental impact

The abandonment of PQMI Hg mine in 1976 was a lost opportunity for proper mine rehabilitation causing the mine wastes to be exposed to the environment [40]. Despite the danger of Hg mining and processing, strong economic activity brought by the mining resulted to rapid urbanization in the area. The area surrounding the abandoned mine is home to more than 12,200 people in 2015. Our findings suggest a very strong potential to cause adverse health effects to residents due to heavy metal exposure which is supported by a recent work of [45]. Here, we present some key recommendations that the government through the Department of Environment and Natural Resources (DENR) and the local government of Palawan can adopt to mitigate the harmful effects of the heavy metals to the environment and the population:

- Land use plan in the affected areas should be reviewed to mitigate potential harm to the community without affecting key sources of employment. The local government should commit to achieving environmental justice through fair treatment and meaningful involvement of all people in decisions that affect public health and the environment. It is also reasonable for the residents who developed illnesses induced by the toxic metals to be compensated.
- Planting crops that accumulate heavy metals should be avoided. The toxic heavy metals can end up in the food chain and cause severe toxic effects to humans. Vegetable consumption account for 90 % of heavy metal exposure to humans [47–49]. The capacity of plants to accumulate heavy metals also differ by heavy metal [50]. In general, leafy vegetables have higher heavy metal uptake than non-leafy vegetables [40,51]. Future studies on bioaccumulation of heavy metals in food crops as well as fish products from Honda Bay can be pursued.
- As Palawan is a growing hub for shrimp aquaculture, deforestation of mangroves should be minimized since shrimps grow in these areas [52–55]. Since mangroves at

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 15 March 2022 doi:10.20944/preprints202203.0205.v1

the mouth of the Tagburos River act as the heavy metal filter at Honda Bay [46], the mangrove density must be enhanced.

- Intervention engineering of the wharf to prevent the heavy metals from seeping into the environment. Activities that can cause the mobilization of the heavy metals in the wharf such as major construction and dredging must also be prohibited.
- Market-based incentives necessary for reducing and rehabilitation of heavy metal-polluted areas can be devised. Markets incentives not limited to pollution fees and pollution taxes can be developed and enforced in industries in Palawan. As tourism draws immense income from the region, a larger portion of the revenue can be allocated for Honda Bay rehabilitation.

4. Conclusions

The present heavy metal pollution in the study area is a result of failure to rehabilitate the Hg mine after abandonment as well as the inconsiderate use of the calcines as construction material and land filler. The distribution of heavy metals may be traced from erosion of weathering-exposed mine waste calcine and anthropogenic activities like application of the calcines as construction material and land filler. There is ultra-high ecological risk associated with both biodiversity and human health. Hg and Cr contributed most to non-carcinogenic risks while Ni, Co, and Cr posed the highest risk of carcinogenic effects. The policy suggestions based on the Honda Bay could be transferable to similar sites.

Supplementary Materials: The following supporting information can be downloaded at: https://zenodo.org/record/6353923#.Yi93GXxBzSI , Table S1: Chronic reference dose (RfD, mg kg^{-1} d^{-1}) for different heavy metal exposure pathways for the assessment of non-carcinogenic risks.; Table S2: Eigenvalues, proportion of variance, cumulative variance, and factor loadings of the five principal components identified by the PCA.; Table S3: Pearson correlation matrix of the heavy metals. A correlation $r \geq 0.700$ was deemed as strong correlation for this study.

Author Contributions: Conceptualization, R.D., C.D. and L.B.; methodology, R.D., C.D. and L.B. software, R.D.; validation, R.D., C.D. and L.B.; formal analysis, R.D.; resources, R.D., C.D., L.G. and L.B.; writing—original draft preparation, R.D, C.D., L.G. and L.B.; writing—review and editing, R.D, C.D., L.G. and L.B.; visualization, R.D, C.D., L.G. and L.B.; supervision, C.D. and L.B. All authors have read and agreed to the published version of the manuscript.

Acknowledgments: The data analyzed was from a Department of Science and Technology - Philippine Council for Industry, Energy and Emerging Technology Research and Development (DOST-PCIEERD)-funded project to Dr. Jessie Samaniego of the Philippine Nuclear Research Institute. We are thankful to our colleagues in Rizal Technological University, Philippine Nuclear Research Institute, De La Salle University, and BAN Toxics for their invaluable contribution to this research paper.

Conflicts of Interest: “The authors declare no conflict of interest.”

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 15 March 2022 doi:10.20944/preprints202203.0205.v1

References

1. Förderer, M.; Langer, M.R. Exceptionally Species-Rich Assemblages of Modern Larger Benthic Foraminifera from Nearshore Reefs in Northern Palawan (Philippines). *Rev. Micropaléontologie* **2019**, *65*, 100387, doi:10.1016/j.revmic.2019.100387.
2. Zafra, M.A.G. *Developing the Philippine Blue Economy: Opportunities and Challenges in the Ocean Tourism Sector*; Asian Development Bank, 2021;
3. Sandalo, R.M.; Baltazar, T. *The Palawan Biosphere Reserve: Philippines*; South-South Cooperation Programme on Environmentally Sound Socio-Economic Development in the Humid Tropics, 1997;
4. Reyes, R.; Santos, G.; Magsambol, W.; Ramos, A.; Petrache, C.; Tabora, E. Heavy Mineral Survey for Rare Earths in the Northern Part of Palawan. *Phil. Nuclear Journal* **1992**, *9*, 25–44.
5. Novellino, D. Mining Expansion and the Responses of Indigenous Peoples. In *Palawan and its global connections*; Eder, J.F., Evangelista, O.L., Eds.; Ateneo de Manila University Press: Quezon City, 2014; pp. 254–286 ISBN 978-971-550-700-4.
6. Laririt, P. Puerto Princesa Is a Cautionary Tale as Duterte Opens New Mining Areas Available online: https://www.rappler.com/newsbreak/in-depth/puerto-princesa-palawan-cautionary-tale-rodrigo-duterte-opens-new-mining-areas/ (accessed on 16 February 2022).
7. Marcelo, C.; Bunye, T.-P.A.O. Mining in the Philippines Available online: https://www.lexology.com/library/detail.aspx?g=7537d507-42c3-4274-bd2a-d66507c629d6 (accessed on 5 February 2022).
8. Gray, J.E.; Greaves, I.A.; Bustos, D.M.; Krabbenhoft, D.P. Mercury and Methylmercury Contents in Mine-Waste Calcine, Water, and Sediment Collected from the Palawan Quicksilver Mine, Philippines. *Environ. Geol.* **2003**, *43*, 298–307, doi:10.1007/s00254-002-0626-8.
9. Langcay, M.L.; Clemente, E.D.; Arranz, C.G. Risk Assessment of Mercury in Soil and Surface Water in Brgy. Santa Lourdes, Puerto Princesa City, Palawan. *IOP Conf. Ser. Earth Environ. Sci.* **2021**, *690*, 012043, doi:10.1088/1755-1315/690/1/012043.
10. Samaniego, J.; Gibaga, C.R.; Tanciongco, A.; Rastrullo, R. Total Mercury in Soils and Sediments in the Vicinity of Abandoned Mercury Mine Area in Puerto Princesa City, Philippines. *Appl. Sci.* **2020**, *10*, doi:10.3390/app10134599.
11. Belo, L.P.; Orbecido, A.H.; Beltran, A.B.; Vallar, E.A.; Galvez, M.C.D.; Eusebio, R.C.; Ledesma, N.A.; Deocaris, C.C. Water Quality Assessment of Meycauayan River, Bulacan, Philippines. *Sylvatrop* **2018**, *28*.
12. Diwa, R.; Deocaris, C.; Belo, L. River Influx Drives Heavy Metal Pollution in Manila Bay, Philippines: An Insight from Multivariate Analyses. **2021**, doi:10.20944/preprints202106.0470.v1.
13. Diwa, R.; Deocaris, C.; Orbecido, A.; Beltran, A.; Vallar, E.; Galvez, M.C.; Belo, L. Meycauayan, an Industrial City in Bulacan, Philippines: Heavy Metal Pollution in Soil and Surface Sediments and Their Relationship to Environmental Indicators. **2021**, doi:10.20944/preprints202106.0439.v1.
14. Galvez, M.C.D.; Vallar, E.; Castilla, R.M.; Mandia, P.; Branzuela, R.; Rempillo, O.; Orbecido, A.H.; Beltran, A.; Ledesma, N.; Deocaris, C.; et al. Principal Component Analysis of Heavy Metals in Atmospheric Aerosols from Meycauayan, Bulacan, Philippines. **2022**, doi:10.20944/preprints202202.0120.v1.
15. Legaspi, J. Palawan Is One of the World's Best Islands, According to Travel+Leisure Magazine – Manila Bulletin Available online: https://mb.com.ph/2021/09/18/palawan-is-one-of-the-worlds-best-islands-according-to-travelleisure-magazine/ (accessed on 5 February 2022).
16. Samaniego, J.; Gibaga, C.R.; Tanciongco, A.; Rastrullo, R. Assessment of Trace Elements in Soils and Sediments in the Abandoned Mercury Mine Site in Puerto Princesa City, Philippines. *ASEAN J. Sci. Technol. Dev.* **2021**, *38*, 43–49, doi:10.29037/ajstd.682.
17. Yim, O.; Ramdeen, K.T. Hierarchical Cluster Analysis: Comparison of Three Linkage Measures and Application to Psychological Data. *Quant. Methods Psychol.* **2015**, *11*, 8–21, doi:10.20982/tqmp.11.1.p008.
18. Abdi, H.; Williams, L.J. Principal Component Analysis. *WIREs Comput. Stat.* **2010**, *2*, 433–459, doi:10.1002/wics.101.
19. Brady, J.P.; Ayoko, G.A.; Martens, W.N.; Goonetilleke, A. Development of a Hybrid Pollution Index for Heavy Metals in Marine and Estuarine Sediments. *Environ. Monit. Assess.* **2015**, *187*, 306, doi:10.1007/s10661-015-4563-x.
20. Pandey, B.; Agrawal, M.; Singh, S. Ecological Risk Assessment of Soil Contamination by Trace Elements around Coal Mining Area. *J. Soils Sediments* **2016**, *16*, 159–168, doi:10.1007/s11368-015-1173-8.
21. Hakanson, L. An Ecological Risk Index for Aquatic Pollution Control.a Sedimentological Approach. *Water Res.* **1980**, *14*, 975–1001, doi:10.1016/0043-1354(80)90143-8.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 15 March 2022 doi:10.20944/preprints202203.0205.v1

22. Rudnick, R.L.; Gao, S. 3.01 - Composition of the Continental Crust. In *Treatise on Geochemistry*; Holland, H.D., Turekian, K.K., Eds.; Pergamon: Oxford, 2003; pp. 1–64 ISBN 978-0-08-043751-4.
23. Gargouri, D.; Gzam, M.; Kharroubi, A.; Jedoui, Y. Use of Sediment Quality Indicators for Heavy Metals Contamination and Ecological Risk Assessment in Urbanized Coastal Zones. *Environ. Earth Sci.* **2018**, *77*, 381, doi:10.1007/s12665-018-7567-3.
24. Weissmannova, H.D.; Mihocova, S.; Chovanec, P.; Pavlovsky, J. Potential Ecological Risk and Human Health Risk Assessment of Heavy Metal Pollution in Industrial Affected Soils by Coal Mining and Metallurgy in Ostrava, Czech Republic. *Int J Env. Res Public Health* **2019**, *16*, 4495.
25. Elvira, M.V.; Diwa, R.R.; Deocaris, C.C.; Fukuyama, M.; Belo, L.P. *West-to-East Heavy Metal Transport in Bottom Sediments Affecting the Toxicity Indices of Asiatic Clam (Corbicula Fluminea) in Laguna De Bay, Philippines*; Social Science Research Network: Rochester, NY, 2022;
26. Khan, S.; Cao, Q.; Zheng, Y.M.; Huang, Y.Z.; Zhu, Y.G. Health Risks of Heavy Metals in Contaminated Soils and Food Crops Irrigated with Wastewater in Beijing, China. *Environ. Pollut.* **2008**, *152*, 686–692, doi:10.1016/j.envpol.2007.06.056.
27. Li, Z.; Ma, Z.; van der Kuijp, T.J.; Yuan, Z.; Huang, L. A Review of Soil Heavy Metal Pollution from Mines in China: Pollution and Health Risk Assessment. *Sci. Total Environ.* **2014**, *468–469*, 843–853, doi:10.1016/j.scitotenv.2013.08.090.
28. Beyersmann, D. Interactions in Metal Carcinogenicity. *Toxicol. Lett.* **1994**, *72*, 333–338, doi:10.1016/0378-4274(94)90045-0.
29. Kim, H.S.; Kim, Y.J.; Seo, and Y.R. An Overview of Carcinogenic Heavy Metal: Molecular Toxicity Mechanism and Prevention. *J. Cancer Prev.* **2015**, *20*, 232–240, doi:10.15430/JCP.2015.20.4.232.
30. Sultana, M.S.; Rana, S.; Yamazaki, S.; Aono, T.; Yoshida, S. Health Risk Assessment for Carcinogenic and Non-Carcinogenic Heavy Metal Exposures from Vegetables and Fruits of Bangladesh. *Cogent Environ. Sci.* **2017**, *3*, 1291107, doi:10.1080/23311843.2017.1291107.
31. USEPA Regional Screening Levels (RSLs) - Generic Tables Available online: https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables (accessed on 5 February 2022).
32. Hu, B.; Wang, J.; Jin, B.; Li, Y.; Shi, Z. Assessment of the Potential Health Risks of Heavy Metals in Soils in a Coastal Industrial Region of the Yangtze River Delta. *Environ. Sci. Pollut. Res.* **2017**, *24*, 19816–19826, doi:10.1007/s11356-017-9516-1.
33. Xu, X.; Li, Y.; Wang, Y.; Wang, Y. Assessment of Toxic Interactions of Heavy Metals in Multi-Component Mixtures Using Sea Urchin Embryo-Larval Bioassay. *Toxicol. In Vitro* **2011**, *25*, 294–300, doi:10.1016/j.tiv.2010.09.007.
34. USEPA *SUPPLEMENTAL GUIDANCE FOR DEVELOPING SOIL SCREENING LEVELS FOR SUPERFUND SITES - OSWER 9355.4-24*; USEPA, 2002; p. 106;.
35. Diami, S.M.; Kusin, F.M.; Madzin, Z. Potential Ecological and Human Health Risks of Heavy Metals in Surface Soils Associated with Iron Ore Mining in Pahang, Malaysia. *Environ. Sci. Pollut. Res.* **2016**, *23*, 21086–21097, doi:10.1007/s11356-016-7314-9.
36. Luo, X.-S.; Ding, J.; Xu, B.; Wang, Y.-J.; Li, H.-B.; Yu, S. Incorporating Bioaccessibility into Human Health Risk Assessments of Heavy Metals in Urban Park Soils. *Sci. Total Environ.* **2012**, *424*, 88–96, doi:10.1016/j.scitotenv.2012.02.053.
37. Casado-Martínez, M.C.; Forja, J.M.; DelValls, T.A. A Multivariate Assessment of Sediment Contamination in Dredged Materials from Spanish Ports. *J. Hazard. Mater.* **2009**, *163*, 1353–1359, doi:10.1016/j.jhazmat.2008.07.106.
38. Reid, M.K.; Spencer, K.L. Use of Principal Components Analysis (PCA) on Estuarine Sediment Datasets: The Effect of Data Pre-Treatment. *Environ. Pollut.* **2009**, *157*, 2275–2281, doi:10.1016/j.envpol.2009.03.033.
39. Varol, M. Assessment of Heavy Metal Contamination in Sediments of the Tigris River (Turkey) Using Pollution Indices and Multivariate Statistical Techniques. *J. Hazard. Mater.* **2011**, *195*, 355–364, doi:10.1016/j.jhazmat.2011.08.051.
40. Maramba, N.P.C.; Reyes, J.P.; Francisco-Rivera, A.T.; Panganiban, L.C.R.; Dioquino, C.; Dando, N.; Timbang, R.; Akagi, H.; Castillo, Ma.T.; Quitoriano, C.; et al. Environmental and Human Exposure Assessment Monitoring of Communities near an Abandoned Mercury Mine in the Philippines: A Toxic Legacy. *Mercury Cycl. Contam. Trop. Non-Mar. Ecosyst.* **2006**, *81*, 135–145, doi:10.1016/j.jenvman.2006.02.013.
41. Raschka, H.; Nacario, E.; Rammlmair, D.; Samonte, C.; Steiner, L. Geology of the Ophiolite of Central Palawan Island, Philippines. **1985**, 375–389.
42. Yumul, G.P.; Dimalanta, C.B.; Marquez, E.J.; Queaño, K.L. Onland Signatures of the Palawan Microcontinental Block and Philippine Mobile Belt Collision and Crustal Growth Process: A Review. *J. Asian Earth Sci.* **2009**, *34*, 610–623, doi:10.1016/j.jseaes.2008.10.002.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 15 March 2022 doi:10.20944/preprints202203.0205.v1

43. Alloway, B.J.; Ayres, D.C. Chemical Principles of Environmental Pollution, B.J. Alloway and D.C. Ayres. *Water. Air. Soil Pollut.* **1998**, *102*, 216–218, doi:10.1023/A:1004986209096.
44. Naldrett, A.J.; Cabri, L.J. Ultramafic and Related Mafic Rocks; Their Classification and Genesis with Special Reference to the Concentration of Nickel Sulfides and Platinum-Group Elements. *Econ. Geol.* **1976**, *71*, 1131–1158, doi:10.2113/gsecongeo.71.7.1131.
45. Samaniego, J.O.; Gibaga, C.R.L.; Tanciongco, A.M.; Devanadera, M.C.E.; Paro, F.R.C.; Adil, J.H.; Montano, M.O.; Quierrez, R.N.M.; Gutierrez, A.C.S. Health Risk Assessment of Trace Metals in the Vicinity of an Abandoned Mercury Mine in Puerto Princesa City , Philippines. *Philipp. J. Sci.* **2022**, *151*, 671–682.
46. Williams, T.M.; Weeks, J.M.; Jr., A.N.A.; Miranda, C.R. Assessment of Mercury Contamination and Human Exposure Associated with Coastal Disposal of Waste from a Cinnabar Mining Operation, Palawan, Philippines. *Environ. Geol.* **1999**, *39*, 51–60, doi:10.1007/s002540050436.
47. Ferré-Huguet, N.; Martí-Cid, R.; Schuhmacher, M.; Domingo, J.L. Risk Assessment of Metals from Consuming Vegetables, Fruits and Rice Grown on Soils Irrigated with Waters of the Ebro River in Catalonia, Spain. *Biol. Trace Elem. Res.* **2008**, *123*, 66–79, doi:10.1007/s12011-008-8113-z.
48. Kim, H.; Song, B.; Kim, H.; Park, J. Distribution of Trace Metals at Two Abandoned Mine Sites in Korea and Arsenic-Associated Health Risk for the Residents. *Toxicol. Environ. Health Sci.* **2009**, *1*, 83–90, doi:10.1007/BF03216468.
49. Martorell, I.; Perelló, G.; Martí-Cid, R.; Llobet, J.M.; Castell, V.; Domingo, J.L. Human Exposure to Arsenic, Cadmium, Mercury, and Lead from Foods in Catalonia, Spain: Temporal Trend. *Biol. Trace Elem. Res.* **2011**, *142*, 309–322, doi:10.1007/s12011-010-8787-x.
50. Singh, R.; Singh, D.P.; Kumar, N.; Bhargava, S.K.; Barman, S.C. Accumulation and Translocation of Heavy Metals in Soil and Plants from Fly Ash Contaminated Area. *J. Environ. Biol.* **2010**, *31*, 421–430.
51. Li, Y.; Wang, Y.; Gou, X.; Su, Y.; Wang, G. Risk Assessment of Heavy Metals in Soils and Vegetables around Non-Ferrous Metals Mining and Smelting Sites, Baiyin, China. *J. Environ. Sci.* **2006**, *18*, 1124–1134, doi:10.1016/S1001-0742(06)60050-8.
52. Alonso-Pérez, F.; Ruiz-Luna, A.; Turner, J.; Berlanga-Robles, C.A.; Mitchelson-Jacob, G. Land Cover Changes and Impact of Shrimp Aquaculture on the Landscape in the Ceuta Coastal Lagoon System, Sinaloa, Mexico. *Ocean Coast. Manag.* **2003**, *46*, 583–600, doi:10.1016/S0964-5691(03)00036-X.
53. Dewalt, B.R.; Vergne, P.; Hardin, M. Shrimp Aquaculture Development and the Environment: People, Mangroves and Fisheries on the Gulf of Fonseca, Honduras. *World Dev.* **1996**, *24*, 1193–1208, doi:10.1016/0305-750X(96)00033-2.
54. Ha, T.T.T.; van Dijk, H.; Bush, S.R. Mangrove Conservation or Shrimp Farmer's Livelihood? The Devolution of Forest Management and Benefit Sharing in the Mekong Delta, Vietnam. *Ocean Coast. Manag.* **2012**, *69*, 185–193, doi:10.1016/j.ocecoaman.2012.07.034.
55. Primavera, J.H. Socio-Economic Impacts of Shrimp Culture. *Aquac. Res.* **1997**, *28*, 815–827, doi:10.1046/j.1365-2109.1997.00946.x.