Ecological Risk Assessment of Heavy Metals in the Bottom Sediments of Laguna de Bay, Philippines

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Abstract

The combination of pollution and ecological risk indices gives both qualitative and quantitative information on an ecosystem's status. This study utilized such a combination to assess the health of Laguna de Bay, Philippines by determining the physicochemical characteristics of its bottom sediments. Two very distinct regions of the lake were sampled: the east bay whose watersheds are mostly of agricultural land uses, and the west bay whose watersheds are dominated by urban areas. Samples of grabbed sediments were analyzed for their grain and particle size distributions, mineralogical compositions, and heavy metal concentrations. The finer sediment fractions were further analyzed for their chromium, nickel, copper, zinc, arsenic, lead, and cadmium concentrations and a representative sample was also analyzed for its mineralogical composition. Based on size analyses, all samples were dominated by sediments finer than 250 µm or medium sand. Mineralogical analysis of a representative sample indicated that the finer fractions of sediments have high concentrations of plagioclase and various clay minerals (montmorillonite and halloysite). Concerning heavy metals, the clay fractions registered higher concentrations. The sediments vary from being slightly to moderately contaminated based on a modified contamination index. Their potential ecological risks to biological resources can be considered as very high due to the high concentrations of heavy metals in the finest sediment fractions that are also the most bioavailable. These results highlight the importance of considering sediment compositions to provide a more complete assessment of lake ecosystems.

Keywords*:* Laguna de Bay, heavy metals, modified contamination index, ecological risk index

1. Introduction

The degradation of Laguna de Bay has been attributed to a host of factors; foremost of which is the intensification of economic activities within and around the lake. Water quality and ecology are threatened due to population expansion, deforestation, urbanization, and industrialization, which have resulted into intense land conversions within the lake's catchment and into wider land reclamations within the lake itself (Laguna Lake Development Authority [LLDA], 2016).

There are more than 5,009 industrial and agricultural establishments in the Laguna de Bay watershed areas that are directly and indirectly discharging waste products into the lake (LLDA, 2005). The rapid decline of water quality in the lake is due to the increasing waste inputs from agricultural run-off and soil erosion, domestic sources, and industrial effluents (Centeno, 1987; Bacallan, 1997).

Several studies have been conducted along the west and east bays of Laguna de Bay. According to the study by Vicente-Beckett *et al*. (1991), cadmium (Cd), lead (Pb), and zinc (Zn) were higher in the west bay at 0.20, 5.5, and 97 ppm, respectively, compared with the east bay at 0.12, 5.2, and 87 ppm, respectively. Results were also supported by Hallare *et al*. (2005) study that Cd, Pb, and Zn were higher in west bay at 0.08, 22.4, and 16.8 ppm compared with east bay at 0.02, 17.5, and 16.6 ppm. Also, chromium (Cr) and nickel (Ni) were higher in the west bay at 21.4 and 15.5 ppm compared with east bay at 14 and 9.7 ppm (Hallare *et al*., 2005). These findings reflect the significant variation across regions as the watershed of the west bay are categorized as a highly urbanized region where large-scale industrial activities are located. In contrast, the east bay watersheds are classified as suburban and agricultural regions.

The degradation of water in the lake is believed to have led to low productivity that resulted in biodiversity loss, destruction of water habitats, increased sedimentation, and elevated levels of hazardous and toxic substances that pose biological health effects (Tamayo-Zafaralla *et al*., 2002). This condition has caused various impacts on the provisions that the lake can provide. This study aimed to determine the concentration of heavy metals in bottom sediments and assess the quality of the lake through sediment quality indicators such as the contamination and enrichment factors. The initial results were used to further assess the ecological risks of heavy metals and the overall potential ecological

risk within Laguna de Bay. The results could be a basis in strengthening the local and national policy guidelines to come up with a programmatic intervention towards the improvement of the overall health of the Laguna de Bay.

2. Methodology

2.1 Study Area

The study was conducted in the east and west regions of Laguna de Bay. Land use in the watersheds of the east bay are classified mostly as sub-urban areas with land covers of mainly annual crops, a few portions of brush, shrub lands some built-up areas, and forests. In the west bay, the watersheds are almost entirely built-up zones for industrial, commercial, and residential purposes.

Nine sampling stations were each established in both the west and east bays (Figure 1). These were clustered based on the nearest towns/cities or on the ease of access from those places. The clustering is as follows: west bay clusters are Taguig, Muntinlupa, and San Pedro; east bay clusters are Victoria, Pila, and Santa Cruz.

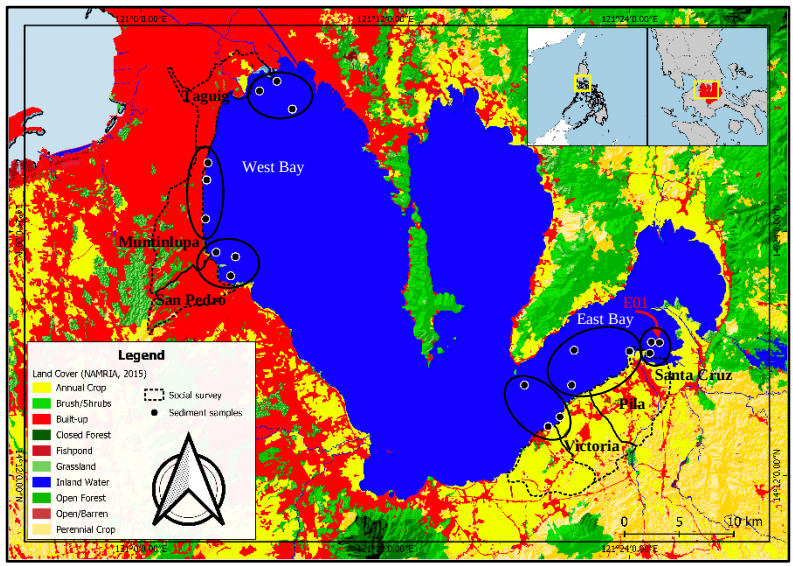

Figure 1. A modified map (National Mapping and Resource Information Authority, 2015) of Laguna de Bay showing the sampling site

2.2 Sampling Methods of Sediments

Sediment collection was done using a targeted or judgmental sampling design adopted from the United States Environmental Protection Agency (USEPA) (2002). A reconnaissance survey was conducted to assess the general features of the study area and identify the potential sampling stations. The sampling stations were established based on the possible sources of pollution, i.e., agricultural, industrial, or domestic. Three sediment samples were collected in every sampling station using the Ponar grab sampler. Approximately 1 kg of sediment samples per replicate was collected. The collected sediment samples were decanted from lake water and other unnecessary materials (i.e., twigs, plastic wastes, shells, etc.), and were secured in resealable clear polybags labeled with the necessary information. All samples were placed in a crate with cover to prevent contamination during transport to the laboratory.

2.3 Preparation of Sediment Samples

Sampling devices and sample containers were ensured to be free from contamination and external exposure. The moisture of sediment samples was removed through air drying for 48 h and was followed by oven drying at 60 °C for 8 h. Samples were then sieved using the following mesh sizes: 2 and 1.18 mm and 450, 250, 150, and 75 µm. The collected fractions for each compartment were weighed, and the percentage of the different sediment particles was calculated. Furthermore, the sieved sediment samples were utilized for particle size analysis to express the comparative dimension of solids that are not polycrystalline. Fractions from 150-250 µm, 75-150 µm and < 75 µm were manually pulverized up to 5 µm using an agate mortar and pestle. Approximately 1 g of sample per fraction was placed in a vial, added with water, and placed in an Ultrasonic Automatic Washer for 10 min to disaggregate the sediment samples. After disaggregation, the particle size of each sediment fraction was analyzed using a Laser Diffraction Particle Size Analyzer SALD-2100 (Shimadu, Japan).

2.4 Chemical Analytical Methods

2.4.1 X-ray Powder Diffraction Analysis

XRD analysis was conducted using a Desktop X-Ray Diffractometer Miniflex II (Rigaku, Japan) at the Graduate School of Engineering Science, Akita University, Japan. The analysis was carried out to determine the clay mineral

composition of samples. Hydraulic elutriation was used to separate clay fractions from other minerals. Ethylene glycol treatment was conducted to improve confirmatory tests for montmorillonite.

2.4.2 Q-ICP-MS Analysis

From each of the sediment fractions (<75, 75-150, and 150-250 µm), 0.1 g of sediments were taken and placed in a 15 mL Savillex Teflon vial, and added with 1 mL of concentrated HNO_3. These were then covered with caps, heated for 2 h at 120 °C, and allowed to cool down. The samples were added with 1 mL of concentrated HNO_3 and 1 mL of HClO, covered with caps, and heated at 120 °C for 6 h. The caps were then removed, and the samples were heated continuously until they dried up. After 6 h, the samples were allowed to cool down, added with 1 mL of concentrated HNO_3, 1 mL of HClO, and 1.0 mL of HF, covered with a cap, and heated again at 120 °C for 1 h. Thereafter, the caps of the vials were removed, and the samples were heated again at 120 °C until they dried up. The final solutions were obtained by adding 7.14 mL of $7NHNO_3$ and heating at 100 °C for 1 h. These were filtered using Advantec 5B 110 mm filter paper and were diluted 1,000 times.

Digested sediment samples were then analyzed using quadrupole inductively coupled plasma mass spectrometer (Q-ICP-MS), Agilent 7700x (Agilent Technologies, U.S.) at the Graduate School of Engineering Science, Akita University, Japan. The heavy metals such as total Cr, Ni, Cu, Zn, As, Pb, and Cd, among others, were identified. The accuracy of the data was validated using the certified reference materials JLk-1 (Imai *et al*., 1995) and JB-1a (Imai *et al*., 1995) as provided by the Geological Survey of Japan (GSJ). The recovery values of targeted metals indicated strong reliability based on comparisons of their certified and measured values (Table 1).

2.5 Statistical Analysis

Grain sizes were analyzed statistically in GRADISTAT version 8.0 using the calculation method of Folk and Ward (1957). The technique is used to determine the mean grain size distribution and classification to identify the differences among the sediments collected from the different sampling stations (Blott and Pye, 2001). Descriptive statistical analysis was used to determine the mean and standard deviation of heavy metal concentrations. The analysis was done using PAST software version 3.14 (Hammer *et al*., 2001).

Table 1. Comparison of the analytical results of lake water-sediment JB-1a and JLk-1 by the GSJ to the certified values (Imai *et al*., 1995)

	JB-1a (Imai *et al.*, 1995)			JLK-1 (Imai *et al.*, 1996)		
Elements	Measured value (ppm)	Certified value (ppm)	Recovery (%)	Measured values (ppm)	Certified values (ppm)	Recovery (%)
Li	10.1	10.9	93.1	52.1	51.5	101.2
Be	1.5	1.4	106.2	2.9	3.3	87.6
Sc	32.0	27.9	114.8	-	-	-
V	245.4	205.0	119.7	-	-	-
Cr	474.4	392.0	121.0	67.1	69.0	97.2
Co	42.2	38.6	109.4	18.0	18.0	100.0
Ni	153.2	139.0	110.2	35.4	35.0	101.1
Cu	62.7	56.7	110.5	63.4	62.9	100.8
Zn	101.1	82.1	123.1	-	-	-
Ga	20.6	17.9	115.2	24.0	21.4	112.1
As	4.1	2.3	178.8	29.0	26.8	108.2
Rb	43.3	39.2	110.6	-	-	-
Sr	513.9	442.0	116.3	-	-	-
Y	24.2	24.0	100.8	-	-	-
Zr	154.2	144.0	107.1	-	-	-
Nb	30.8	26.9	114.7	15.4	15.8	97.5
Mo	1.6	1.6	101.3	1.6	2.2	73.1
Cd	0.1	0.1	104.3	0.5	0.6	87.4
Sn	2.0	2.2	87.6	-	-	-
Sb	0.3	0.3	122.7	-	-	-
Cs	1.4	1.3	109.5	13.0	10.9	119.3
Ba	556.7	504.0	110.5	573.2	574.0	99.9
La	42.9	37.6	114.1	40.4	40.6	99.5
Ce	74.7	65.9	113.3	85.7	87.9	97.5
Pr	8.2	7.3	112.7	-	-	-
Nd	30.0	26.9	111.7	36.9	35.7	103.4
Sm	5.8	5.1	114.2	-	-	-
Eu	1.9	1.5	127.0	1.4	1.3	110.2
Gd	6.2	4.7	132.0	7.9	6.0	131.2
Tb	0.9	0.7	128.6	-	-	-
Dy	4.8	4.0	120.6	6.4	6.6	97.4
Ho	1.0	0.7	134.0	1.3	1.1	122.6
Er	2.7	2.2	126.1	3.8	3.6	105.8
Tm	0.4	0.3	112.9	-	-	-
Yb	2.4	2.1	115.6	-	-	-
Lu	0.4	0.3	109.3	0.5	0.6	87.6
Hf	4.0	3.4	116.9	2.5	3.8	66.1
Ta	1.7	1.9	86.9	-	-	-
W	2.1	1.8	112.3	-	-	-
Pb	7.2	6.8	106.7	43.6	43.7	99.8
Th	10.6	9.0	117.9	52.1	51.5	101.2
U	1.9	1.6	121.3	2.9	3.3	87.6

2.6 Assessment of Sediment Pollution

Contamination and enrichment factors were used to assess the status of heavy metal pollution in the sediments of Laguna de Bay and determine the possible sources of these heavy metal pollutants. The contamination factor (*Cf*) is widely utilized to assess metal contamination in an ecosystem (Equation 1). It is a single index indicator that provides a ratio between an element in a study site and the same element at a background site, reference value, or national criteria for a metal (Qingjie *et al*., 2008). However, *Cf* does not take into account the lithogenic and sedimentary inputs of the element of interest (Brady *et al*., 2015).

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

where:

Cf = contamination factor
C_i = concentration of metal of interest at a site
C_b = concentration of the same metal at a background or reference site

Enrichment factor (*Ef*) is a single element index that compares the ratio of the element of interest (Sucharovà *et al*., 2012). It is used to estimate the impact of anthropogenic inputs on sediments (Ho *et al*., 2010). The normalization of the studied element for the lithogenic and sedimentary inputs enhances the prediction of anthropogenic pollution with *Ef* (Duodu *et al*., 2016). According to Cevik *et al*. (2008), an enrichment factor that is greater than one is an indication that the studied element is an anthropogenic pollutant. In Sutherland (2000), *Ef* is mathematically expressed in Equation 2.

$$Ef = \frac{\left(\frac{M_c}{M_r}\right) sample}{\left(\frac{M_c}{M_r}\right) background} \tag{2}$$

where:

M_c = concentration of elements of interest
M_{ref} = concentration of the reference element

Following the review of Boes *et al*. (2011), Rubidium (Rb) was used as lake water-sediment reference material in this study. The value of Rb (84 ppm) as

background and reference material for the target elements, i.e. Cr (99 ppm), Ni (47 ppm), Cu (28 ppm), Zn (67 ppm), As (4.8 ppm), Pb (17 ppm) and Cd (0.09 ppm), was obtained from the recommended composition of the upper continental crust as adopted from the study of Ho *et al*. (2010).

Table 2. Indices and grades of contamination factor and enrichment factor depending on the quality of sediments

Contamination Factor		Enrichment Factor	
Sediment Quality	*Cf* Factor	Sediment Quality	*Ef* Classes
Low contamination	< 1	No enrichment	< 1
Moderate contamination	1 – 3	Minor enrichment	1 – 3
Considerable contamination	3 – 5	Moderate enrichment	3 – 5
Very high contamination	< 6	Moderately severe enrichment	5 – 10
		Severe enrichment	10 – 25
		Very severe enrichment	25-50
		Extremely severe enrichment	>50

2.7 Modified Degree of Contamination

The modified degree of contamination (mC_d) is a multi-element pollution index used in sediment quality assessment (Brady *et al*., 2015) (Table 3). This index was developed by Hakanson (1980) and Nemerow (1985) and first used by Abrahim and Parker (2008) However, Brady *et al*. (2015) recently proposed a pollution index using the enrichment factor instead of replacing the contamination factor. This modified index considers the non-conservative behavior and the background concentration of metals in the sediments. It also adjusted the thresholds to assess the contamination status of sediments accurately. Brady *et al*. (2015) expressed the modified degree of contamination mathematically in Equation 3.

$$mC_d = \frac{\sum_{i=1}^{n} Cf^i}{n} \quad (3)$$

where:

Cf^i = contamination factor for the individual element
n = number of metals tested

Table 3. Thresholds for sediment quality classification for multi-element indices (Adapted from Brady *et al*., 2015)

Class	Sediment qualification	Modified degree of contamination
0	Unpolluted	$mC_d < 1.5$
1	Slightly polluted	$1.5 < mC_d < 2$
2	Moderately polluted	$2 \leq mC_d < 4$
3	Moderately-heavily polluted	$4 \leq mC_d < 8$
4	Severely polluted	$8 \leq mC_d < 16$
5	Heavily polluted	$16 \leq mC_d < 32$
6	Extremely polluted	$mC_d > 32$

2.8 Potential Ecological Risk Index (RI)

The Table 4 shows the grading standards on different levels of potential and modified ecological risk (Guo *et al*., 2010; Suresh *et al*., 2012). The potential ecological RI measures the sensitivity of the biological community to the overall contamination in a site (Hakanson, 1980). It takes into account the contamination factor of elements, their potential ecological risk factors (*Er*), and the sedimentological toxic response factors (*Tr*: Ni = 42.8 ppm; Cd = 4.21; Cr = 160.4 ppm; Pb = 112.18; Cu = 108.2; Zn = 271; As = 4.6 based from PLE) (Manoj and Padhy, 2014). As proposed by Hakanson (1980), the equation for calculating RI is presented in Equation 4.

$$RI = \sum_{i=1}^{n} Er^{i} = \sum_{i=1}^{n} Tr^{i} \times Cf^{i} \quad (4)$$

where:

Er^i = potential ecological risk index of an individual element
Tr^i = biological toxic response factor of a particular element
Cf^i = contamination factor for every single element.

Table 4. Grading standards of potential and modified ecological risk index – adapted from Guo *et al*. (2010) as cited by Suresh *et al*. (2012)

Er^i	Ecological grade	*RI* or *MRI*	Ecological grade
<40	Low risk	<150	Low risk
40 – 80	Moderate risk	150 – 300	Moderate risk
80 – 160	Considerable risk	300 – 600	Considerable risk
160 – 320	High risk	-	
>320	Very high risk	>600	Very high risk

3. Results and Discussion

3.1 Grain Size of Sediment Samples

The samples collected from Laguna de Bay were composed of sediments that were mostly < 2 mm in grain size (Table 5) and characterized by particle sizes that are very coarse sand to finer fractions (Table 6). The sediments from east bay consisted predominantly of finer grains (67 to 75% of < 250 µm sediment sizes, fine sand). Sediments from west bay had similar grain size distributions (Table 5). However, the southernmost cluster of stations had significantly higher fractions of sediments that are < 75 µm (~38% of very find sand + silt + clay).

Table 5. Grain size distribution of sediment samples (in % distribution)

Grain Size	Laguna de Bay					
	East Bay			West Bay		
	Santa Cruz	Pila	Victoria	Taguig	Muntinlupa	San Pedro
> 2 mm	5.6	2.0	2.9	4.7	2.8	2.6
1.18 to 2 mm	3.6	1.5	3.2	3.6	1.0	1.9
450 to 1.17 mm	18.4	11.9	13.1	9.9	7.7	15.2
250 to 450 µm	21.5	36.7	38.0	37.4	28.3	18.7
150 to 250 µm	22.6	32.6	24.2	26.2	31.3	8.9
75 to 150 µm	21.1	13.4	12.9	14.9	18.7	14.1
< 75 µm	7.2	1.9	5.8	3.3	10.1	38.5

Table 6. Particle size distribution of sediment samples (in % distribution)

Particle size	Laguna de Bay					
	East Bay			West Bay		
	Santa Cruz	Pila	Victoria	Taguig	Muntinlupa	San Pedro
Very coarse sand	12.3	5.6	8.3	10.0	5.1	7.1
Coarse sand	13.3	8.5	9.4	7.1	5.5	11.0
Medium sand	23.5	38.0	39.4	38.4	29.2	20.4
Fine sand	28.3	36.2	27.7	30.2	36.3	12.7
Very fine sand + silt + clay	22.7	11.7	15.3	14.2	23.8	48.8

3.2 Mineral Compositions of Sediment Samples

Results of XRD analysis from the east bay revealed that clay fractions of sediment samples from Laguna de Bay were composed mostly of the clay minerals montmorillonite and halloysite, and the primary mineral plagioclase.

Figure 2 shows the XRD result of sediment analysis after the hydraulic elutriation and ethylene glycol treatment. Based on the relative intensity of the peaks in Figure 2, plagioclase was the most abundant primary mineral. All other detected peaks indicated montmorillonite and halloysite. These patterns were true for all sediment fractions of this representative sample. Having mostly clay in the samples was of special interest because clay minerals are effective in metal adsorption, mainly due to their negatively charged surface and high cation exchange capacity (Uddin, 2017).

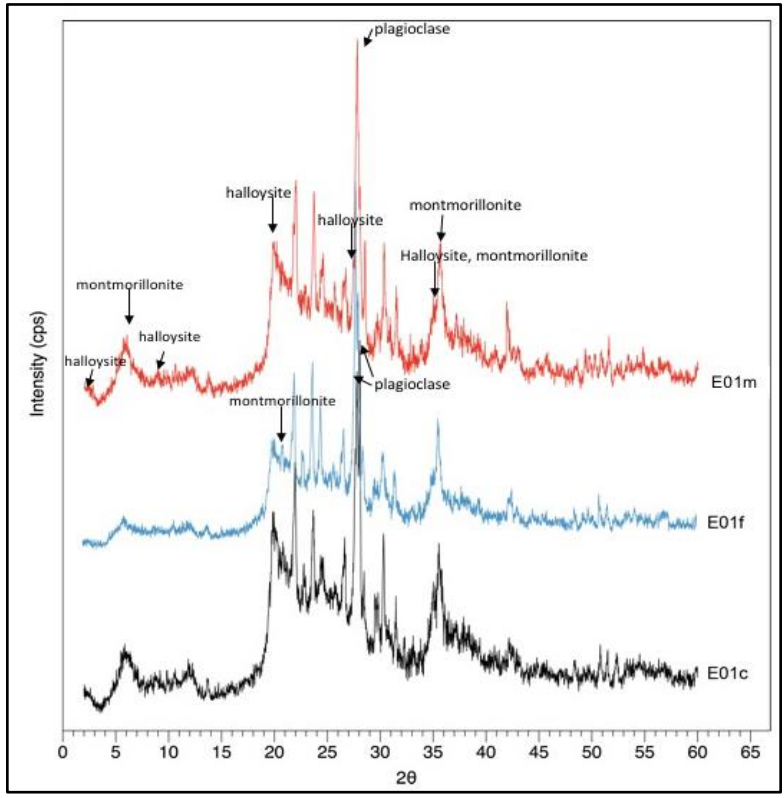

Figure 2. XRD diffractogram of the representative sediment sample with sediment particle sizes of 150-250 µm, E01c (black); 75-150 µm, E01 m (red); and < 75 µm, E01f (blue)

3.3 Concentration of Heavy Metals in Sediments

Results showed that heavy metal concentrations in < 75 µm sediment samples across sampling stations ranged from 21.4 to 252.9 ppm for Cr, 18.3 to 78.3 ppm for Ni, 66.8 to 147.1 ppm for Cu, 111.9 to 250.9 ppm for Zn, 4.8 to 5.9 ppm for As, 20.4 to 64.9 ppm for Pb, and 0.1 to 0.4 ppm for Cd (Table 7).

Table 7. Concentrations of Cr, Ni, Cu, Zn, As, Pb, and Cd in < 75 µm sediment samples

	Standards		East Bay			West Bay		
	A	B						
Metal (ppm)			Santa Cruz (n=18)	Pila (n= 18)	Victoria (n=18)	Taguig (n=18)	Muntinlupa (n=18)	San Pedro (n=18)
	33.3	76						
Cr			97.7 ± 55.6	252.9 ± 148.2	107.3 ± 17.1	172.8 ± 62.4	63.3 ± 34.2	21.4 ± 1.5
	-	24						
Ni			32.3 ± 12.3	67.7 ± 39.7	30.2 ± 4.9	31.2 ± 1.4	78.3 ± 97.1	18.3 ± 0.6
	35.7	50						
Cu			77.6± 27.2	66.8 ± 16.9	77.0 ± 2.9	79.8 ± 9.7	121.9 ± 40.7	147.1 ± 2.2
	123	14						
Zn			139.3 ± 17.2	138.6 ± 31.0	111.9 ± 2.9	197.0 ± 51.5	237.3 ± 29.8	250.9 ± 6.2
	5.9	11						
As			5.4 ± 1.7	5.3 ± 1.2	5.9 ± 1.9	5.3 ± 0.5	4.8 ± 0.7	5.1 ± 0.3
	35	48						
Pb			21.9 ± 3.1	20.4 ± 7.2	23.5 ± 4.9	27.6 ± 13.4	64.9 ± 26.8	38.8 ± 5.9
	0.6	0.65						
Cd			0.1 ± 0.2	0.1 ± 0.1	0.1 ± 0.0	0.2 ± 0.0	0.2 ± 0.1	0.4 ± 0.0

A = Canadian Council of Ministers of the Environment (CCME)'s interim sediment quality guideline (ISQG) and probable effect level (PEL) (CCME, 1999),
B = Taiwan Environmental Protection Agency (TEPA)'s sediment quality guideline upper and lower limits (TEPA, 2010), standard deviation (±)

Table 8. Concentrations of Cr, Ni, Cu, Zn, As, Pb, and Cd in 75 to 150 µm sediment samples

Metal (ppm)	Standards		East Bay			West Bay		
	A	B	Santa Cruz (n = 18)	Pila (n = 18)	Victoria (n = 18)	Taguig (n = 18)	Muntinlupa (n = 18)	San Pedro (n = 18)
Cr	33.3	76	63.1 ± 26.6	225.2 ± 113.1	90.9 ± 9.1	119.2 ± 39.5	40.9 ± 11.4	22.2 ± 0.9
Ni	-	24	24.4 ± 9.7	66.2 ± 33.5	24.8 ± 2.9	27.4 ± 2.1	24.8 ± 2.9	20.0 ± 0.4
Cu	35.7	50	65.3 ± 41.9	48.1 ± 16.6	51.4 ± 6.8	46.6 ± 7.4	81.0 ± 58.3	159.7 ± 3.1
Zn	123	14	115.6 ± 24.1	133.2 ± 13.4	142.6 ± 1.1	151.3 ± 17.9	224.9 ± 54.0	269.3 ± 4.2
As	5.9	11	6.3 ± 1.7	6.1 ± 0.7	7.9 ± 0.8	7.1 ± 0.7	8.7 ± 1.0	8.2 ± 0.3
Pb	35	48	24.1 ± 3.3	16.4 ± 1.9	15.5 ± 1.5	11.7 ± 0.4	31.5 ± 16.1	39.2 ± 2.0
Cd	0.6	0.65	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.0	0.2 ± 0.1	0.5 ± 0.0

A = Canadian Council of Ministers of the Environment (CCME)'s interim sediment quality guideline (ISQG) and probable effect level (PEL) (CCME, 1999),
B = Taiwan Environmental Protection Agency (TEPA)'s sediment quality guideline upper and lower limits (TEPA, 2010), standard deviation (±)

Table 9. Concentrations of Cr, Ni, Cu, Zn, As, Pb, and Cd in > 150 µm sediment samples

Metal (ppm)	Standards		East Bay			West Bay		
	A	B	Santa Cruz (n = 18)	Pila (n = 18)	Victoria (n = 18)	Taguig (n = 18)	Muntinlupa (n = 18)	San Pedro (n = 18)
Cr	33.3	76	50.2 ± 27.2	132.4 ± 81.6	34.4 ± 16.3	59.3 ± 33.1	28.7 ± 7.0	22.2 ± 0.3
Ni	-	24	22.9 ± 12.3	38.5 ± 19.8	12.9 ± 5.1	25.1 ± 4.1	23.7 ± 6.3	19.9 ± 0.2
Cu	35.7	50	70.1 ± 50.9	44.8 ± 17.9	45.2 ± 9.4	88.4 ± 62.7	56.2 ± 22.3	158.2 ± 2.7
Zn	123	14	112.9 ± 26.9	125.7 ± 29.8	165.7 ± 4.7	204.9 ± 71.4	241.0 ± 36.2	275.5 ± 3.6
As	5.9	11	5.9 ± 1.9	6.5 ± 0.6	9.3 ± 2.1	8.3 ± 0.6	11.8 ± 2.1	8.0 ± 0.2
Pb	35	48	22.4 ± 3.2	18.7 ± 2.1	12.7 ± 2.4	20.5 ± 14.0	24.9 ± 7.9	40.5 ± 8.5
Cd	0.6	0.65	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.3 ± 0.2	0.2 ± 0.0	0.5 ± 0.0

A = Canadian Council of Ministers of the Environment (CCME)'s interim sediment quality guideline (ISQG) and probable effect level (PEL) (CCME, 1999),
B = Taiwan Environmental Protection Agency (TEPA)'s sediment quality guideline upper and lower limits (TEPA, 2010), standard deviation (±)

In the 75 to 150 µm sediment samples, heavy metal concentrations ranged from 40.9 to 225.2 ppm for Cr, 20.0 to 66.2 ppm for Ni, 48.1 to 159.7 ppm for Cu, 133.2 to 269.3 ppm for Zn, 6.1 to 8.7 ppm for As, 11.7 to 39.2 for Pb, and 0.1 to 0.5 ppm for Cd (Table 8).

In the > 150 µm sediment samples, heavy metal concentrations ranged from 22.2 to 132.4 ppm for Cr, 12.9 to 38.5 ppm for Ni, 44.8 to 158.2 ppm for Cu, 112.9 to 275.5 ppm for Zn, 5.9 to 11.8 ppm for As, 12.7 to 40.5 ppm for Pb, and 0.1 to 0.5 ppm for Cd (Table 9).

3.4 Sediment Pollution Assessment

The contamination factor was used to provide a ratio between Cr, Ni, Cu, Zn, As, Pb, and Cd concentrations against the reference value in the area and to show how these target elements concentrated in the sampling stations. The result showed that Cu and As were considerably contaminated, while Ni, Zn, As Pb, and Cd weremoderately contaminated across sampling stations (Figure 3).

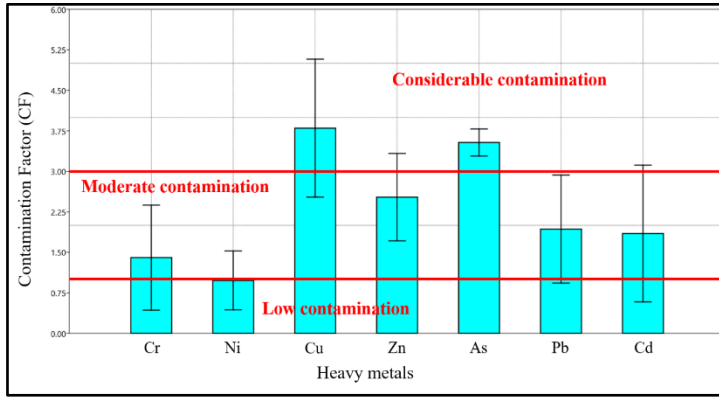

Figure 3. Contamination factor of seven heavy metals in Laguna de Bay

The enrichment factor was utilized to assess the anthropogenic contribution of metals to the sediments. The average enrichment factors computed for the metals in all the sampling stations are presented in Figure 7. Across sampling stations, Cu and As had moderate enrichment while Cr, Ni, Zn, Pb, and Cd had minor enrichment.

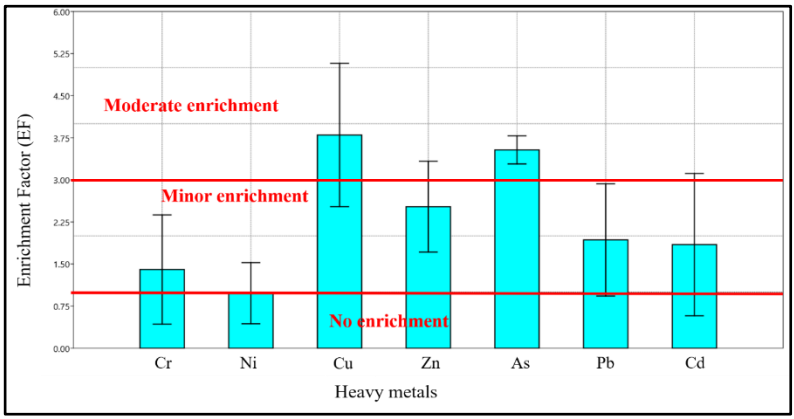

Figure 4. Enrichment factor of seven heavy metals in Laguna de Bay

Instead of using the contamination factor to compute the pollution index, the modified pollution index used the numerical value of the enrichment factor to consider the non-conservative behavior and the background concentration of metals in the sediments. The results of the modified degree of contamination revealed that Santa Cruz and Victoria are slightly contaminated while Pila, Taguig, Muntinlupa, and San Pedro are moderately contaminated (Table 10).

Table 10. The modified degree of contamination of all heavy metals across sampling stations in Laguna de Bay

Station	Modified degree of contamination	
	mC_d	Quality
Santa Cruz	1.8	Slightly contaminated
Pila	2.1	Moderately contaminated
Victoria	1.9	Slightly contaminated
Taguig	2.2	Moderately contaminated
Muntinlupa	2.8	Moderately contaminated
San Pedro	2.9	Moderately contaminated

3.5 Ecological Risk Assessment

Single and multi-element sediment quality indices only deal with anthropogenic inputs and estimated levels of contamination but not pollution. To overcome this limitation, the potential ecological risk index was used to determine the potential risk of pollution from individual elements in the site and to assess the overall potential impact on aquatic organisms.

Results showed that concentrations of Cu and Zn across stations posed a very high potential ecological risk. Concentrations of Pb in all stations presented moderate to very high risk. Concentrations of Cr in Santa Cruz, Pila, Victoria, and Taguig suggested high to very high risk. On the other hand, As and Cd in all stations had very low risk. Concentrations of Ni pose low to moderate risk (Table 11).

Table 11. Potential ecological risk of individual elements across sampling stations in Laguna de Bay

Station	ER^i of heavy metals						
	Cr	Ni	Cu	Zn	As	Pb	Cd
Santa Cruz	184.3	31.4	335.6	531.6	16.5	144.2	4.2
Pila	477.2	65.8	289.0	529.1	16.3	134.4	3.4
Victoria	202.5	29.4	333.3	427.1	18.2	154.7	5.4
Taguig	326.0	30.3	345.3	752.0	16.2	182.0	6.7
Muntinlupa	119.5	76.2	528.0	905.9	14.6	427.9	9.0
San Pedro	40.4	17.8	636.7	957.6	15.7	256.0	17.9

Results also revealed that the overall potential ecological risk to the biological community of the heavy metals studied is very high in all stations (Table 12).

Table 12. Overall potential ecological risk of heavy metals to the biological community across sampling stations in Laguna de Bay

Station	*RI* or *MRI*	Ecological Grade
Santa Cruz	1247	Very high risk
Pila	1515	Very high risk
Victoria	1170	Very high risk
Taguig	1658	Very high risk
Muntinlupa	2081	Very high risk
San Pedro	1942	Very high risk

3.6 Sediment Sizes and Environmental Implications

Sediment grain sizes, as recorders of environmental conditions, are good indicators for various parameters including distance from the shoreline, water depth, sediment fluxes, and even climatic changes. In general, larger sediment grain size is often taken to indicate near-coastal environments, shallow water conditions, and dry climates, while smaller sediment grain size implies longer distance from the coast, wet climate, and higher lake level stand (e.g., Menking *et al*., 1997; Wang *et al*., 2001; Chen *et al*., 2004).

Based on particle size analysis, all the sampled surface sediments at the study sites were dominated by fine sediment fractions. In both the west and the east bays, grain sizes that are finer than 250 μm, or particles of fine sand + silt +

clay were the most abundant materials. Considering that the sampling sites are not very distant from the shorelines, and that Laguna de Bay is a shallow lake, the higher abundance of very fine sediments indicate that the flux of materials being eroded from the watersheds are more skewed towards the finer fractions. This is a direct reflection of high soil losses that the watersheds are experiencing. The abundance of very fine sediments close to the shore also supports the general observation that shoaling in Laguna de bay has accelerated (Tamayo-Zafaralla *et al*., 2002). Local communities describe this condition as the lake having turned shallower and muddier or "maburak". Because sediments are sourced from the surrounding watersheds, faster shallowing of the lake indicates higher rates of soil loss from the surrounding terrestrial environments as well.

In a report by Santos-Borja and Nepomuceno (2006), forests used to be the primary land cover of the watershed around Laguna de Bay. However, by the time of their assessment, such cover had been drastically reduced to just 5%, with built-up/industrial, agricultural and other areas covering 29, 52 and 14%, respectively (Santos-Borja and Nepomuceno, 2006). Among those dominant land covers, agricultural use is known to enhance vulnerability to soil erosion, the identified major contributor to sedimentation in the Laguna de Bay. Longstanding studies on materials transfer in the lake and its watersheds is wanting. There are, however, a few estimates on the sedimentation rates and shoaling of the lake. In 1999, Siringan *et al*. (1999) estimated that the lake is shoaling at a rate of 3.6 mm/year with variable sedimentation rates of 1.38 to 2.07 mm/year. Hopefully, sediment size distribution studies are further expanded in the region to help contribute to the better understanding of sedimentation within the lake.

3.7 Abundance of Clays and Elevated Heavy Metal Concentrations

Sediments are important carriers as well as sinks of heavy metals in the hydrological cycle (Celo *et al*., 1999). Most heavy metal pollutants from anthropogenic activities accumulate in lake, river, and ocean sediments, where they are being adsorbed by clays and other fine-grained materials (Adamo *et al*., 2005; Chen *et al*., 2007). Clay minerals commonly occur as sheeted crystalline structures called phyllosilicates (Sherman, 2007). Montmorillonite, one of the clay minerals identified, is a group of very soft phyllosilicates that usually form as precipitate from the water solution as microscopic crystals. Another type of clay mineral identified is halloysite. Halloysite is a dioctahedral, 1:1 clay mineral which belong to the kaolin group (Joussein *et al*., 2005). Unlike montmorillonite, halloysite is characterized by low specific

surface area and cation exchange capacity (CEC) (Joussein *et al*., 2005). By nature, clay is negatively charged and has a high surface to volume ratio, which enables heavy metals to bind/sorb on its surface. Such characteristics have important implications to potential ecological risks especially considering that the finest sediment fractions are also the most bioavailable and have the highest resuspension rates. These finding should also be considered in managing spoils from dredging activities, particularly as provided for by Republic Act 6969 (LLDA, 2015).

The concentration of heavy metals in this study was relatively higher in the < 75 µm sediment fractions, mostly composed of clay minerals than in the coarser materials. The various sediment pollution indices presented earlier showed that Cu and As were considerably elevated in the study sites, and Ni, Zn, Pb, and Cd are moderately contaminated as well. In terms of enrichment, Cu and As were moderately enriched, while Cr, Ni, Zn, Pb, and Cd had experienced only minor enrichment across the sampling regions.

Laguna de Bay is a caldera within the Macolod Corridor, a volcanic field that formed during the Pliocene period (5 million years ago) and has remained active since (Vogel *et al*., 2006). Being a volcanic terrane, elevation in As is to be expected as with other geothermally associated elements that include sulfur and mercury. Thus, the abundance of As can be associated to geogenic sources. However, source attribution for the rest of the heavy metals can be the subject of future investigations, especially in how they relate to land use and its changes.

3.8 Limitations in Indices

Although the information on contamination and enrichment factors are essential, there are limitations on these indices, which may affect the overall conclusion of the study if not further analyzed. These indices are single element indices, and they ignore the impact that multiple contaminant elements can have on sediment health (Hakanson, 1980). The Hakanson modified contamination index can overcome this limitation. This modified index considers the non-conservative behavior and the background concentration of metals in the sediments. It also adjusts the qualification threshold of the sediment to qualify the contamination status of sediment accurately.

Results from the modified degree of contamination index revealed that Santa Cruz and Victoria are slightly contaminated while Pila, Taguig, Muntinlupa,

and San Pedro were moderately contaminated. The results validate the findings from the contamination factor that heavy metal tested were at low to considerable contamination level. However, multi-element indices have limitations as they only assess the level of contamination, not pollution (Brady *et al*., 2015). Hence, the potential ecological risk index was used to assess the risk of heavy metal pollution in the area, and the risk of heavy metal pollution poses to aquatic organisms. Based on the results of the ecological risk assessment, aquatic life in all sampling stations were already at very high risk to heavy metal pollution in the lake.

4. Conclusion

In any aquatic system, sediments that are both suspended in the water column and those that have settled at the bottom are important components of the environment. They play a major role in the source-sink dynamics and are indispensable in the assessment of organisms that depend on sediments during their embryonic and larval development. Hence, assessment of the Laguna de Bay's health in terms of its ecotoxicological potential would be incomplete if sediments are neglected as a factor in the evaluation.

This work assessed lake bottom sediments from two very distinct regions of the Laguna de Bay: The east bay whose watersheds are mostly of agricultural land uses, and the west bay whose watersheds are dominated by urban areas. Samples of grabbed sediments were analyzed for their grain and particle size distributions, mineralogical compositions, and heavy metal concentrations. In terms of grain and particle sizes, Laguna de Bay sediments are dominated by fractions that are 250µm or medium sand and finer (very fine sand + silt + clay), whether they were collected from the west of east bays. This lends support to the general observation that the lake has become shallower and muddier. Considering that the samples were collected very close to the shoreline and from relatively shallow depths, the higher abundance of very fine sediments indicate that the flux of materials being eroded from the watersheds are more skewed towards the finer fractions. This is a direct reflection of high soil loss that the watersheds of the lake are experiencing.

Geochemically, it was found that sediments finer than 75µm registered the highest heavy metal (Cr, Ni, Cu, Zn, As, Pb, and Cd) concentrations among the several fractions that were separated. These fine materials were found to be mineralogically composed of plagioclase and various clay minerals,

particularly montmorillonite and halloysite. The sediment pollution analysis revealed Cu and As at considerable level of contamination with moderate enrichment. The heavy metals such as Ni, Zn, Pb, and Cd are moderate with minor enrichment of Cr, Ni, Zn, Pb, and Cd, respectively. The abundance of As and other geothermally associated elements may be a reflection of the volcanic nature of the Laguna de Bay. However, source attribution for the rest of the heavy metals can be the subject of future investigations. Results from the modified degree of contamination index showed the east bay as being slightly contaminated, while the west bay is considered as moderately contaminated. These findings validate the initial claim that Laguna de Bay has a low to moderate level of contamination. However, potential ecological risk analysis revealed that aquatic life thriving in the lake are already at very high risk. This is especially true for certain stages of their development or for particular organisms that are sedentary. The very fine nature of the heavy metal polluted-sediments also make them very highly bioavailable. Hence, these results highlight the importance of considering sediment compositions to provide a more complete assessment of lake ecosystems.

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