Assessment of lead concentration in surficial sediments of an island harbor estuary in Western Visayas, Philippines by flame atomic absorption spectrophotometry (FAAS)

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Article Info

Submitted: July 24, 2023
Approved: Dec 15, 2023
Published: Dec 31, 2023

Keywords:
heavy metals
anthropogenic activities
lead contamination
Sediment analysis
Flame Atomic Absorption Spectrophotometry

Abstract

Lead contamination is an emerging problem in the Philippines due to marine activities such as boating and commercial fishing in most coastal areas like MacArthur's Wharf in Guimaras. The aquatic environment's health is assessed by considering sediment quality through Flame Atomic Absorption Spectrophotometry (FAAS). Four surficial sediment samples were collected at 0 m, 25 m, 50 m, and 75 m away from the innermost sections of the docking area of the wharf, and the Pb concentrations were 23.66 ppm, 15.34 ± 1.07 ppm, 12.31 ± 1.07 ppm, and 11.80 ± 1.07 ppm, respectively. All samples fulfilled the permissible lead concentration in sediments by the National Oceanic and Atmospheric Administration (NOAA) at <30.24 ppm, and the U.S. Environmental Protection Agency (U.S. EPA) at <40 ppm, implying that MacArthur's Wharf, Guimaras, is within the acceptable environmental standards.

Introduction. - Heavy metal (HM) contamination of aquatic ecosystems is developing into a possible global issue due to its hazardous impacts on the environment and public health [1]. Heavy metals are elements with high atomic weights and densities that pose a danger even at low concentrations [2]. In certain amounts, some play a vital role in the biochemistry and physiological functions of plants and animals but can be harmful to these organisms when exceeding the threshold value [2]. The study by Astatkie et al. (2021) stated that surficial sediments may act as an adsorptive basin, especially for metals that exceed the threshold value and do not naturally degrade [9, 4]. Thus, sediments are used as environmental indicators for the assessment of metal pollution in bodies of water [5].

All potential causes of sediment contamination with heavy metals include anthropogenic activities, such as dumping of domestic waste, drainage system inefficiencies, and natural occurrences like rock corrosion and weathering [3]. Lead (Pb) is a non-essential metal and one of the most hazardous and toxic contaminants in the environment [19]. It is largely found in the oil and gasoline industries [11, 2]. One study on the analysis of the water column of Iloilo-Guimaras Port concluded that the exceeding amounts of Cd, Cr, and Pb could be mainly attributed to oil spillage from motor boats [16]. Shipping activities and marine traffic in ports reportedly have increased the flux of Pb into the marine environment [10].

In maintaining proper and balanced physiological functions in aquatic species, heavy metals play vital roles at trace levels or in small amounts [12, 2]. Water bodies with excessive levels of heavy metals, however, harm aquatic life [2]. Later on, HMs like Pb could contribute to the long-term poisoning of the food chain [6]. Pb is found to be potentially carcinogenic to humans and animals, inducing damage to the brain, kidneys, liver, digestive system, endocrine system, and reproductive system [22].

One of the main wharves in Guimaras, MacArthur's Wharf, formerly known as "Buenavista Wharf," with coordinates of 10.6870° N, 122.6173° E, is located in the Iloilo Strait and is used to transport people, goods, and products to and from the island for industrial and commercial purposes, as well as to dock boats when they are not in use or require repair. Given their significance for international trade and economic activity, seaports have evolved into a coordinated land-sea region that is heavily influenced by human activity. Consequently, anthropogenic causes such as marine traffic, fishing, ship maintenance, and commercial activities may release pollutants into nearby seas and sediments. High Pb concentration in a port in Misamis Occidental was attributed to shipping and other anthropogenic activities in the area [10].

In addition, both residential and commercial buildings line the waterfront. According to the classification of water bodies and usage of marine waters of the Department of Environment and Natural Resources (DENR) Environmental Management Bureau, the surrounding waters of the wharf are categorized as Class SC which includes fishery water, recreational water, and marshy and mangrove areas. It has beneficial uses including boating and the propagation of fish and other aquatic resources intended for commercial and sustenance fishing.

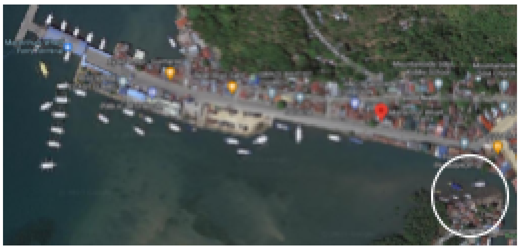

Figure 1. The docking area (encircled) of boats in MacArthur's Wharf, Guimaras

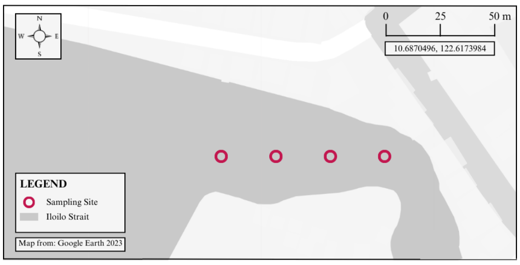

Figure 2. A close-up map of the docking area and the sampling sites (from GoogleEarth)

There are no sediment quality guidelines in the Philippines, but there are available standards developed by the National Oceanic and Atmospheric Administration (NOAA) [10], and the U.S. Environmental Protection Agency (U.S. EPA). Sediment Quality Guidelines (SQGs) are numerical chemical concentrations intended to be either protective of biological resources, predictive of adverse effects on those resources, or both. Heavy metal concentrations in the samples collected from the study area are assessed by comparing them with sets of SQGs. The study referred to two SQGs, the U.S. EPA and the NOAA Screening Quick Reference Table for Inorganics in Marine Sediment [13, 14].

The investigation of heavy metals in surficial sediments is beneficial in assessing the anthropogenic and industrial impacts posed by pollution on water ecosystems. Heavy metals, like lead, are known to atomize with good efficiency with either N_2O or acetylene flame type with FAAS detection limits. A detector receives a light beam from a cathode lamp directed through the flame. The absorbed light is measured to compare with the light wavelengths that originally passed through the sample. The principle is that since the light beam has the same wavelength as the metal being observed, the absorbed light energy represents the concentration of the metal in the sample [25]. FAAS is also known for its low operational costs and good analytical performance. Therefore, in this study, surficial sediments were gathered in the docking area of MacArthur's Wharf. Then, they underwent pretreatment and acid digestion before conducting the FAAS to determine the concentration levels of the heavy metal Pb.

The study aimed to determine Pb concentrations and its pollution and toxicity state in the surficial sediments of the docking area of MacArthur's Wharf, Buenavista, Guimaras with the following objectives:

(i) To determine the concentration of Pb in the surficial sediments of MacArthur's Wharf, Buenavista, Guimaras by FAAS; and

(ii) To assess the detected concentrations of Pb if it is within the permissible levels as set by the EPA Toxicity Classifications and the NOAA Screening Quick Reference Table for Inorganics in Marine Sediment.

Methods. - The study adopted a descriptive approach designed to assess whether the concentration of heavy metal Pb in the surficial sediments of the docking area of MacArthur's Wharf, Buenavista, Guimaras is within the permissible levels set by U.S. EPA and NOAA. The methodology is comprised of five parts: collection, pretreatment, digestion [15], preparation of the calibration curve, and FAAS analysis [16]. Surficial sediment samples were collected during the dry season from four separate sampling areas: 0 m, 25 m, 50 m, and 75 m from the innermost section of the docking area, the farthest that pump boats are stationed. The samples were then pretreated and digested before being analyzed through FAAS [15, 17].

Collection of Sediment Samples. The collection of sediment samples was done in January during the dry season. Four sampling sites with 25-m intervals from end to end of the docking area of the wharf surrounded by residential areas were marked: 0 m, 25 m, 50 m, and 75 m. Around 500 g of the upper 5 cm surficial sediment layer of each marked collection area was collected with a separate plastic spoon for each area and transferred to a decontaminated zip lock bag. The sediment samples were then kept in a styrofoam box filled with ice while being transported to the Philippine Science High School - Western Visayas Campus (PSHS-WVC) laboratory.

Pretreatment of Sediment Samples. Upon arrival at the laboratory, the sediment samples were then oven-dried at 50°C for 24 hours, ground to ensure homogeneity, and sifted through a 3-mm sieve (or ASTM sieve size No. 16-8) to separate coarse-grained sediments and concentrate dust particles in this fraction that may contain high levels of heavy metal [15].

Acid Digestion. Acid digestion was then done to the sediment samples following the U.S. EPA Method 3050B: Acid Digestion of Sediments, Sludges, and Soil [17].

Preparation of Calibration Curve. Pb solutions with concentrations of standard true values 0.05, 0.10, 0.30, 0.50, and 1.0 ppm were prepared following the standard addition method. The standard curve was created using the absorbance values measured for the working standards. It showed the relationship between the absorption of monochromatic light in the spectrophotometer and the known Pb concentration.

FAAS Analysis. The Pb concentrations in the sediment samples were then analyzed using the

Shimadzu AAS AA-7000F model with Lamp ID: Pb-1, wavelength of 283.3nm, slit width of 0.7nm, lamp Mode: BGC- D2, and low peak at 10mA. It uses an acetylene gas flow rate of 2.0 L/min and a support gas flow rate (compressed gas) of 15l/min. For each sample, the instrument performed two replicate analyses. The average of these replicates was subsequently calculated and utilized in assessing the sediment quality by established SQGs.

Data Analysis. The concentrations in ppm of analyte Pb in the sample were compared with the permissible concentrations set by the U.S. EPA Toxicity Classifications and the NOAA Screening Quick Reference Table for Inorganics in Marine Sediment [13, 14].

Safety Procedure. Possible harm from inhalation of fine sediment samples was mitigated by wearing safety gear such as safety goggles, face masks, and gloves. Handling of strong acids with fumes was done in a fume hood. The experiment was conducted with the guidance of a laboratory supervisor.

Results and Discussion. - The yielded actual concentrations slightly deviated from the standard target values of the calibration curve due to an inaccuracy during the preparation of the standard solutions.

Table 1. Target standard concentration, generated actual concentration, and absorbance values of lead as yielded from the FAAS

Target Standard Concentration (ppm)	Actual Concentration (ppm)	Absorbance
0.05	0.0247	0.0265
0.10	0.1105	0.0282
0.30	0.3325	0.0326
0.50	0.4839	0.0356
1.00	0.9986	0.0458

Nonetheless, a straight line was approximated through the data points using linear regression, and its equation was best described as $y = 0.0198x + 0.0260$. The line has a slope of 0.0198 and an r^2 value of 0.9983 from a linear fit.

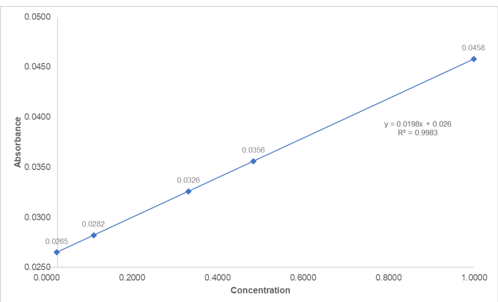

Figure 3. Standard Curve for Lead Concentration Analysis

The Pb concentrations were calculated by substituting their measured absorbance values into the equation of the standard curve. The instrument-run replicates of unknown concentrations of Pb are shown in Table 2.

Table 2. FAAS yielded concentration and absorbance of lead from samples

Sediment Sample	Concentration (ppm)	Absorbance
1	0.2366	0.0307
	0.2366	0.0307
2	0.1458	0.0289
	0.1609	0.0292
3	0.1155	0.0283
	0.1306	0.0286
4	0.1054	0.0281
	0.1306	0.0286

The statistical analysis of the Pb concentrations, including the mean and standard deviation is presented in Table 3. These values were calculated using the results from the two instrument-run readings of each of the four samples.

Table 3. Mean, standard deviation, standard error of the mean, and coefficient of variation of the two instrument-run readings of each sample.

Sediment Sample	Mean	SD
1	23.66	0.00
2	15.34	1.07
3	12.31	1.07
4	11.80	1.78

The average lead concentrations in the samples were assessed with the SQGs: U.S. EPA and NOAA Screening Quick Reference Table for Inorganics in Marine Sediment. For samples 1, 2, 3, and 4, the values are 23.66, 15.34, 12.31, and 11.80 ppm, respectively. The U.S. EPA provides three classifications for Pb concentration ranges: non-polluted, moderately polluted, and heavily polluted with values of less than 40, 40 to 60, and greater than 60 ppm. NOAA's SQGs for lead in marine sediment provided values of 30.24, 46.70, 112.0, and 218.0 ppm for Threshold Effect Limit (TEL), Effects Range Low (ERL), Probable Effect Limit (PEL), and Effects Range Median (ERM).

Table 4. NOAA and US.EPA Classification of Heavy Metal Concentrations in MacArthur's Wharf

Heavy Metal	NOAA (ppm)				EPA (ppm)		
	TEL	ERL	PEL	ERM	Non-Polluted	Moderately Polluted	Heavily Polluted
Pb	30.24	46.70	112.0	218.0	<40	40-60	>60

The lead concentrations in the docking area of MacArthur's Wharf were found to decrease with increasing distance from the innermost section. Sediment sample 1, located at 0 m from the innermost portion of the docking area, exhibited the highest concentration of lead with a value of 23.66 ppm. Such results concurred with the study of Qian et al. (2015) as it was observed that high concentrations of toxic metals are commonly found in sediments near industrialized coastal areas [18]. Pb in the sampling areas may be particularly attributed to domestic waste and run-off from surrounding residential areas, fishing boats and vessels, and passenger boats plying and stationed in the area [19]. Furthermore, studies have found that HM levels were significantly higher during the dry season in both water and sediment samples due to decreased water activity resulting in sediment accumulation [5]. In contrast, sample 4 showed the lowest amount since it was located further away from commercial and residential areas. However, the researchers were unable to collect sediment samples from other sampling sites, such as in commercial areas where frequent shipping activities occur.

The observed lead concentrations from all four samples were well within the permissible levels and complied with the standards set by the U.S. EPA and NOAA. According to the U.S. EPA toxicity classification, all sediment samples were found to be non-polluted as their concentrations were determined to be less than the set value of 40 ppm. For the NOAA Screening Quick Reference Table for Inorganics in Marine Sediment, the TEL, with a permissible level of lead at 30.24 ppm, is the level of sediment contamination at which benthic organisms begin to exhibit toxic responses. The PEL is the concentration at which the majority of benthic organisms exhibit toxic responses and has a permissible concentration of 46.70 ppm. Harmful effects on the surrounding environment are rarely observed at concentrations below the ERL value of 112.0 ppm, while concentrations above the ERM value of 218.0 ppm frequently result in harmful effects. Concentrations between ERL and ERM are those in which harmful effects would occasionally occur. The determined concentrations of all four samples were below both the TEL and ERL, indicating that benthic organisms in the area have not exhibited toxic responses, and harmful effects are rarely observed.

Pb in the sampling areas may be attributed to several sources, including domestic waste and run-off from surrounding residential areas, fishing boats and vessels, and passenger boats plying and stationed in the area. Sediments serve as an adsorptive sink wherein heavy metals and other particles accumulate as they get quickly removed from the water body [6, 20]. The Second State of the Coasts of Guimaras 2018 has reported total and fecal coliforms that exceeded the standard provided by the DENR for Class SC bodies of water [21]. Though their presence and contamination may suggest exceeding levels of Pb, detected Pb concentrations were well within the permissible levels. The State of the Coasts report also monitored the physicochemical properties of water, such as pH, temperature, and dissolved oxygen. It supported the current study's findings that the water quality standards were satisfied, and it suggested that heavy metals not be contaminated.

Few studies have addressed heavy metal pollution assessments in sediments in the Philippines. Although heavy metals are naturally occurring elements, anthropogenic activities such as mining and smelting operations, industrial production and usage, home and agricultural use of metals, and transportation are the main causes of environmental contamination and human exposure [22]. Bacteria can be used as heavy metal concentration bioindicators and thus as indicators of water and sediment quality [23]. The observed lead concentrations that are within permissible levels may oppose the monitored exceeding coliform levels that would otherwise suggest also exceeding levels of heavy metal concentrations. However, these low concentrations of heavy metal may be attributed to the nearby mangrove forestation.

One factor that may have affected the low presence of lead in the area is the nearby mangrove forestation which is approximately 30 m to 70 m away from the docking area. Studies have found that the roots of certain mangrove species have a high potential for absorbing heavy metals and could serve as a natural phytoremediation treatment [24]. However, current monitoring of the mangrove forestation of the area and its physicochemical properties was not taken into account, thus their relationship with the observed lead concentrations cannot be determined for certain.

Domestic waste and run-off due to industrial activities contributed to the high lead concentration in the innermost section of the docking area of the sample site. The low lead concentration of some parts may be attributed to the nearby mangrove forestation where the study of Nazli and Hashim (2010) found that the roots of some mangrove species have a high potential for absorbing heavy metals and could have served as a natural phytoremediation treatment [24]. In addition, the found lead concentrations that are within permissible levels may oppose the monitored exceeding coliform levels that would otherwise suggest also exceeding levels of heavy metal concentrations. All four samples were able to fulfill the permissible lead concentration set by the U.S. EPA and NOAA, implying that the sampling location, MacArthur's Wharf docking area, is not polluted with lead, benthic organisms in the area have not exhibited toxic responses, and harmful effects are rarely observed.

Limitations. Due to the rapid return of high tide upon arrival at the docking area, the researchers were unable to collect the intended three replicates per sample area distance (right side, left side, center), and only managed to collect samples from the center section of the docking area. Second, statistical analysis tools were not utilized for the assessment of the detected concentrations of Pb for any significant differences if it is within the permissible levels.

Conclusion. - The results obtained from the FAAS analysis showed that all four samples were able to fulfill the permissible lead concentration set by NOAA (at <30.24 ppm) and the U.S. EPA (at <40 ppm). Sediment sample 1 contained the highest lead concentration of 23.66 ppm. Samples 2 through 4 had concentrations of 15.34 ± 1.07 ppm, 12.31 ± 1.07 ppm, and 11.80 ± 1.07 ppm, respectively. The findings imply that MacArthur's Wharf, Guimaras, is not polluted with lead.

Recommendations. - The researchers recommend identifying a schedule for lower tides to have more time to collect samples from the docking area (right side, left side, center). It is also recommended that the researchers utilize statistical tools such as independent samples t-test for their assessment of the detected concentrations of Pb for any significant differences if it is within the permissible levels.

Acknowledgment. - The researchers would like to express their gratitude to the Sto. Rosario barangay officials for granting permission and providing assistance with the conduct of the sediment sampling in MacArthur's Wharf, Buenavista, Guimaras.

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