ORIGINAL PAPER

ENVIRONMENTAL ASSESSMENT OF HEAVY METALS ACCUMULATION IN THE NEARSHORE AND TYPICAL ESTUARINE ENVIRONMENT IN DAVAO CITY PHILIPPINES

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Abstract. *The Department of Environment and Natural Resources, and the United Nations Educational, Scientific and Cultural Organization (UNESCO) classified the bodies of water in Davao as Class SB for seawater environment along the Davao Gulf and Class B or recreational water on the downstream area of the Davao River. Under these classifications, both bodies of water can be used by the public for recreational and other important activities. However, with the development in the City, the quality of these bodies of water is threatened by and affected with the accumulation of various pollutants particularly heavy metals.*

In order to assess the current heavy metal pollution in the aquatic environments, scientific investigation was conducted to determine the concentrations of the following heavy metals: Cadmium (Cd), Lead (Pb), Manganese (Mn), Iron (Fe), Zinc (Zn) and Copper (Cu) in two environmental sampling units, the typical estuarine (downstream) and near shore environments along Davao gulf. Surface water and sediments were sampled in these sites.

Results show that the surface water environment contained substantial amount of Cd, Pb, Mn, Fe and Zn. Of these heavy metals, the concentrations of Cd and Pb were found to be higher than the maximum allowable limits for both fresh and marine water. In addition, significant enrichments of Cd, Cu, Fe, Mn and Zn were detected on the surface sediments of the downstream environment. Results revealed that except for the Pb level, the mean concentrations of most heavy metal (Cd, Cu and Zn) in the surface sediments were substantially higher compared to the threshold effects limit. The findings demonstrate the accumulations of heavy metals in the aquatic resources which call for immediate review of the current classifications of the bodies of water in the region.

Keywords: *Environmental Assessment, Heavy Metals Accumulation, Nearshore, Typical Estuarine Environment.*

1. INTRODUCTION

The growing industrialization and urbanization in many cities across the globe in the absence of centralize waste water system has resulted to accumulation of various pollutants on surface water environment due to mishandling of waste by some industries such as: Disposal of untreated waste water to river beds, estuaries or in the sea. In effect, substantial damage to the environment and its resources occur and given the persistence and toxicity of these pollutants, they can seriously damage human health and quality of life [1]. Some of the pollutants that can accumulate on water systems are heavy metals [2-6]. In Davao City,

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bodies of water vulnerable to heavy metals contamination are Davao River, Talomo River and Davao Gulf.

Davao City is a place of over 1.2 million people which is strategically located in the Asia-Pacific rim serving as gateway to both the western and eastern hemispheres of the world. The City is one of the sprawling metropolis in the Philippines where economic system has been opened up to global competition resulting to diverse economy, that featured sound mix of agricultural (roughly 45%), industrial (15%) and services (at around 35%) industries. The City's economy is steadily growing in the last two decades shifting the counting investments from millions in the 80's to billions in the 90's up to the present [7].

In this study, the researchers have chosen two environmental units for assessment; the near shore (some parts of Davao gulf) and typical estuarine (downstream) environment located at Davao and Talomo river. It aimed to determine if the concentration of accumulated heavy metals of these areas exceeded the standard maximum limits posted by the Environmental Management Bureau (EMB) - Department of Environment and Natural Resources (DENR) and United States Environmental Protection Agency (US EPA). At present, pursuant to DENR Administrative Order (DAO) No. 34, the Davao Gulf along Coaco beach to Bago Aplaya was classified as Class SB [8]. Under this classified water bodies, the area can be regularly used for recreation or fishery allowing the public to use the bodies of water for bathing, swimming, diving and/or for fishing (DENR AD No. 34 S. 1990). Whereas, the Davao River and Talomo River Downstream were classified as Class B or recreational water class I which are used primarily for contact recreation such as bathing, swimming, skin diving and so on.

The heavy metals tested from the collected samples are Cadmium (Cd), Copper (Cu), Iron (Fe), Lead (Pb), Manganese (Mn), and Zinc (Zn). These pollutants when present in excess concentrations can contribute to variety of adverse health effects. Accumulation of these substances in the body can lead to the decline in mental, cognitive, and physical health of the humans [9].

The results of this research can serve as basis for the government agencies in making necessary guidelines to control the transport and disposal of toxic and hazardous substances. Results can also be used to strengthen and implement existing public policies in protecting the environment.

2. MATERIALS AND METHODS

This study utilized the descriptive type of research design. Quantification of the accumulated heavy metals on the near shore and typical estuarine environment in Davao City were done on the collected samples. Descriptive assessment was done by comparing the reported results with the existing guidelines and quality standards both for surface water and sediments test materials.

Surface water samples from the four pre-determined stations were collected in a previously cleaned and dried bottle using the "direct method". In this method, collection of water samples was done under water (about 1-2 cm in depth) until full to avoid surface debris and the containers were properly labeled for the sampling station, time and date. Collected test materials were then placed in water cooler at about 4^0C for preservation. Samples were immediately transported to the Science Resource Center – University of Immaculate Conception for laboratory testing.

Surface sediments samples from two sampling stations were taken using the "shovel technique". In the process, intact sediments samples were collected in a way to minimize

disturbance and retain the orientation and packing of the solid materials. Samples taken were then placed in handy plastic bag, sealed and were labeled appropriately for the sampling station, time and data[5]. Collected solid in plastic bags were then placed in water cooler at about 4 °C for initial preservation. Samples were immediately transported to the Science Resource Center – University of Immaculate Conception for air drying prior to laboratory testing.

Analysis of surface water for the level of pH, Salinity, Cd, Fe, Pb, Mn, and Zn followed standard procedures for testing water and waste water. Atomic Absorption Spectrophotometry (AAS) was use for the detection of heavy metals concentration while Glass Electrode Method was used for the pH analyses. Except for the tests of salinity, previously dried surface sediments samples were analyzed using Standard procedures from Perkin Elmer Manual and Standard Analytical procedures of the Mines and Geosciences Bureau Laboratories.

The researchers used standard methods of measurement in quantifying the heavy metals of the collected samples. Summary of each method is presented in Table 1.

Table 1. Methods of Analysis

Parameter	Method of Analysis
pH	Glass Electrode Method
Cadmium	AAS
Lead	AAS
Iron	AAS
Manganese	AAS
Zinc	AAS
Copper	AAS

Data obtained from this research were analyzed using descriptive statistical methods. The computed mean concentration of pollutant was then compared to the Water Quality Criteria for heavy Metals in both surface water and sediments.

3. RESULTS AND DISCUSSION

3.1. ACCUMULATION OF POLLUTANTS

Presented in Table 2 are results of the physical characteristics and heavy metal concentrations of typical estuarine and near shore environment in Davao City. Results obtained show that water samples taken from four different stations were basic having pH ranging from 7.6 – 8.1. At this pH, most of the heavy metals are insoluble in form. Whereas, salinity concentrations of typical estuarine environment ranges from 2984 - 4317 mg/L which indicates that the tests samples were mixture of fresh and sea water (brackish water). However, collected samples from near shore along Davao gulf reflect high concentration of salinity ranging from 31807 to 36508 mg/L. The salinity concentrations are common levels for seawater.

The overall results reflected in Table 2 indicated that heavy metals were substantially present both in surface water of typical estuarine and near shore environment in Davao City. Heavy metals accumulation from tested surface water has the following concentration range:

Cd, 0.01 - 0.09 mg/L; Pb, 0.14 to 0.55 mg/L; Fe, 0.05 – 0.30 mg/L; Mn,0.02 – 0.11 mg/L, and Zn, 0.01 – 0.09 mg/L.

On the other hand, it can be observed that significant variation of heavy metal concentrations was detected between two sampling units (typical estuarine and marine water). The varied concentrations of heavy metals from different sampling units can be explained based on the movement characteristics of salt water underlying the layer of fresher water in an estuary which tends to move sediments in an unusual way. This movement of bodies of water can carry pollutants in the surface sediments from estuary to near shore (vice-versa) environment.

As the denser salt water moves along the bottom toward the head of the estuary to replace water carried away by freshwater surface flow, it takes with it some of the nutrients the river has brought downstream, thus dispersing them over a wider area in the estuary. Similarly, if the river is polluted, contaminants can be carried downstream in the fresh or brackish surface layer, then back toward the head of the estuary after they settle out and into the near and offshore (deeper) salt water. Moreover, valuable nutrient-bearing sediments are also capable of carrying and dispersing a variety of dangerous pollutants, including pesticides and heavy metals [10 -].

Table 2. Physical characteristics and mean concentrations of heavy metals from typical estuarine and near shore environment.

Parameters Tested	Typical Estuarine		Near shore	
	Station 1	Station 2	Station 3	Station 4
pH	7.6	7.6	7.7	8.1
Salinity [mg/L]	2984	4317	31807	36508
Cadmium [mg/L]	0.01	0.02	0.06	0.09
Lead [mg/L]	0.14	0.17	0.40	0.55
Iron [mg/L]	0.13	0.05	0.30	0.29
Manganese [mg/L]	0.11	0.02	0.04	0.05
Zinc [mg/L]	0.02	0.01	0.09	0.07

Level of Cd was found to be higher in near shore environment compared to the typical estuarine samples. The presence of Cd on both sampling units may have been due to generated domestic and industrial waste. Common sources of Cd metal and its soluble compounds are waste incinerators and furnaces, phosphate-containing fertilizers, refuse dumps and sewage sludges [11].

Similar conditions were noted for the concentrations of Pb. Levels of Pb were relatively high on samples from near shore compared to estuary-like environment. This indicates that accumulated Pb was generated from untreated waste water wherein it was trapped and retained in seawater. Common sources of Pb from human activities includes: paints and ceramic products, caulking, gasoline, solder, lead-acid storage batteries used for motor vehicles and others. Though under normal conditions metallic Pb and compounds of lead bound to sulfide and phosphates are insoluble with water but Pb substances, such as Pb (II)carbonate ($PbCO_3$) and lead(II)acetate[$Pb(CH_3COO)_2$] are soluble in aquatic medium [12].

Iron in vulnerable aquatic environment in Davao City has concentrations ranging from 0.05 to 0.30. In the tests, the Fe has higher concentration in near shore station compared with the other sampling stations. Though Fe naturally occur in iron minerals such as: magnetite,

hematite, goethite and siderite, Fe alloy is also widely applied worldwide for commercial purposes for the processing of containers, cars, laundry machines, bridges, buildings, and even small springs [13, 14]. Manganese concentrations in station 1 (typical estuarine) was higher compared with the estuarine like environment (station 2). Accordingly, Mn is a natural substance found in surface water. In fact, seawater has 10 ppm Mn thus, the level of Mn may have reflected the natural Mn background for the samples tested.

The tested near shore environment depicted higher concentrations of Zn compared to typical estuarine. Common sources of Zn are: sulfidic zinc ore, dumps of the past mining operations, but anthropogenic and natural emissions occur at a ratio of 20 to 1. The solubility of zinc depends on temperature and pH of the water. When the pH is fairly neutral, zinc in water is insoluble but the solubility of Zn increases with increasing acidity. Some zinc water soluble compounds are: zinc chloride ($ZnCl_2$), and zinc oxide (ZnO), or zinc vitriol ($ZnSO_4 \cdot 7H_2O$). Since heavy metal accumulated in rivers and gulf catchments can be classified as soluble and insoluble, it is therefore best to assess the quality of surface water in Davao City by including the surface sediment in the determination of heavy metals. By considering both water and sediment analysis in determining the status of water quality, resources could better be targeted for those bodies of water where levels of pollution are greater. Results of the concentrations of heavy metals accumulated in surface sediments from typical estuarine environment in Davao City are shown in Table 3.

Table 3. Physical characteristics and mean concentrations of heavy metals from surface sediments in typical estuarine environment in Davao City.

Parameters	Station 1	Station 2
pH	8	6.6
Cadmium [µg/g]	1.56	1.38
Lead [µg/g]	12.3	7.8
Iron [%]	3.98	3.13
Manganese [µg/g]	776.67	660
Zinc [µg/g]	120	136.67
Copper [µg/g]	55.00	34.13

Data show that the tested environmental units had accumulated high amounts of heavy metals. It can be noted that between the two sampling stations, station 1 has higher concentrations of Cd, Pb, Fe, Mn and Cu compared with station 2 except for Zn. Moreover, of the six heavy metals tested, Fe has the highest concentration. The concentration range of Fe was found to be at 3.13 %– 3.98% which is apparently higher than the Fe present in the surface water with 0.05 ppm – 0.13 ppm on the same site. This was followed by Mn, Zn and Cu which have significant higher concentration in sediments than in surface water with concentration ranging from 660 – 776.67 ppm, 120 - 136.67 ppm and 34.13 – 55.00 ppm, respectively. The results have indicated enriched concentration of Fe, Mn, Zn and Cu causing deterioration to the quality of the surface sediments. These elevated concentrations of heavy metals may have been due to the generated domestic waste. According to the region XI EMB, though industries operating by the Davao river have waste water treatment systems but large volume of the pollutants are coming from households, particularly in the slum areas [7].

The same is true for the concentrations of Cd and Pb which has enriched concentrations in the surface sediments than in surface water. Cd has a concentration range of 1.38 – 1.56 ppm compared with the surface water showing a concentration range of 0.01 to

0.02 ppm. On the other hand, Pb has concentration range of 7.8 to 12.3 ppm as compared to the surface water which was 0.14 to 0.17 ppm.

3.2. ENVIRONMENTAL ASSESSMENT

In assessing the degree of accumulation of the pollutants from typical estuarine and near shore environment in Davao City, the researchers limit its evaluation on the specific heavy metals with available maximum allowable values posted by both the US EPA and EMB.

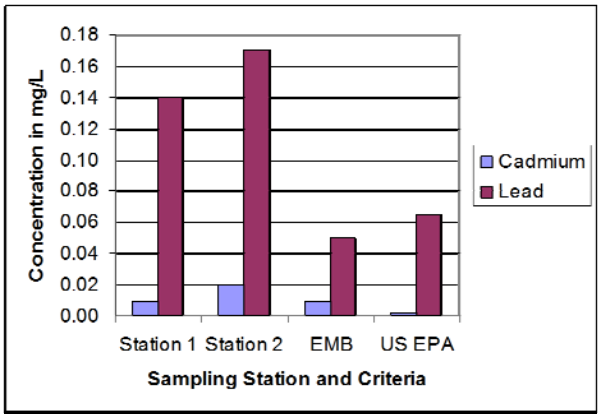

Figure 1. Assessment on the surface water quality standard of the typical estuarine environment.

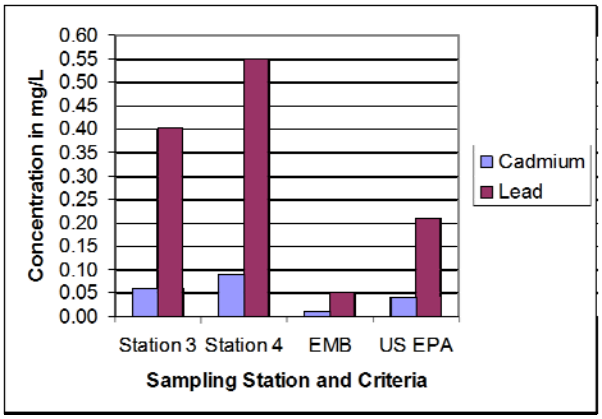

Figure 2. Assessment on the surface water quality standard of the near shore environment.

As it is shown in the graph, the levels of Cd (except in station 1) and Pb in the typical estuarine and near shore environments in Davao City did not conform to the standard limits of the EMB and US EPA. This means that the concentration of heavy metals exceeded the allowable maximum concentration of both agencies.

The current accumulation of deleterious substances in these bodies of water indicates that both catchments may have received gradual unauthorized disposal of untreated commercial, industrial and domestic wastes which affect the quality of the surface water in the area. Consequently, the current water classifications of Davao Gulf as Class SB and Class B for Davao River (Typical estuarine environment) are now uncertain and must be reviewed by proper government agencies.

It was found out that except for the concentration of Pb in the surface sediments, the concentrations of Cd, Cu and Zn in both stations were higher than the Threshold Effects Limit (TEL). These results have indicated that human and animals exposed to this type of environment will relatively be affected with some unfavorable health effects. Furthermore, these results proved that the concentrations of these heavy metals are not derived from its natural background but due to man made activities occurring in the area.

The biological accumulations of non essential heavy metals such as Cd and Pb have little or no beneficial role in the human body and often considered toxic or lethal.

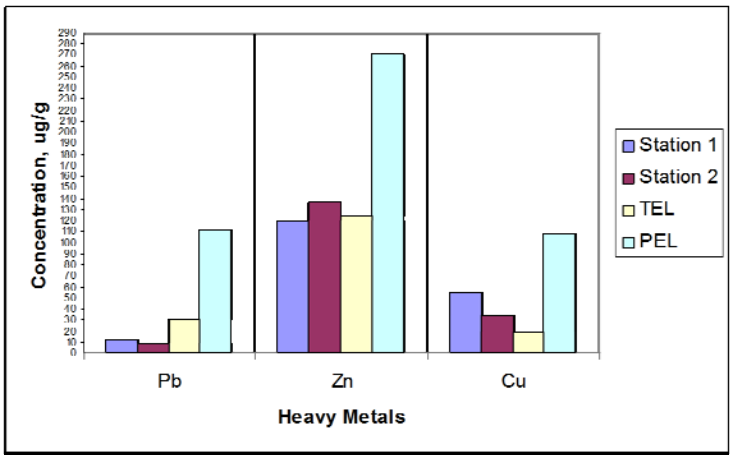

Figure 3. Assessment of Surface Sediments Quality Standard in Typical Estuarine Environment.

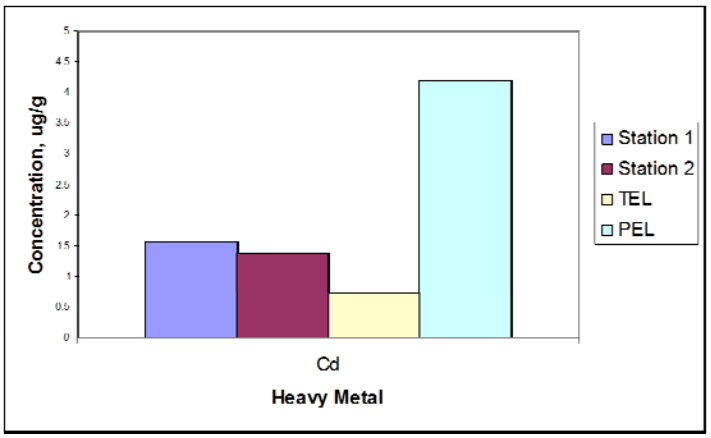

Figure 4. Assessment of Surface Sediments Quality Standard in Typical Estuarine Environment for Cd.

Many heavy metals cause nervous-system damage resulting to learning disorders in children. It could also lead to liver or kidney damage, allergic dermatitis, gastrointestinal distress, delays in physical or mental development.

4. CONCLUSIONS

Surface water samples had pH values ranging from 7.6 – 8.1. The salinity values of typical estuarine environment ranges from 2984 – 4317 mg/L indicating that the tests samples were mixture of fresh and sea water (brackish water) while the salinity values of test samples collected along the near shore environments was found to be at 31807 to 36508 mg/L.

Heavy metals were substantially present both in the surface water of the typical estuarine and near shore environments in Davao City. Heavy metals concentrations from tested surface water had the following concentration range: Cd, 0.01 - 0.09 mg/L; Pb, 0.14 to 0.55 mg/L; Fe, 0.05 – 0.30 mg/L; Mn, 0.02 – 0.11 mg/L and Zn, 0.01 – 0.09 mg/L.

The basic characteristics of the environments from the sampling units may have allowed the enriched deposition of heavy metals in the surface sediments. The concentration range of Fe in the surface sediment was found to be the highest at 3.13 % (3,130 ppm) – 3.98% (3,980 ppm) among the tested heavy metals. Manganese, Zn and Cu were found to be significantly higher in sediments than in surface water with concentration ranging from 660 – 776.67 ppm, 120 - 136.67 ppm and 34.13 – 55.00 ppm, respectively. Likewise, elevated

concentrations of Cd and Pb were detected in the surface sediments. Cadmium had concentration range of 1.38 – 1.56 ppm while Pb had concentration range of 7.8 – 12.3 ppm.

The computed mean concentrations of Cd and Pb from both sampling units did not conform to the quality standard for fresh and marine water. Though, no standard limits were posted for the heavy metals Mn, Fe and Zn substantial concentrations of these parameters were detected in the surface water samples.

Elevated (very high) concentrations of heavy metals are detected in the surface sediments from the typical estuarine environment in the City. Though, the level of Pb is lower than the TEL, it was noticeable that the levels of Cd, Cu and Zn exceed the TEL standards.

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