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RISK ASSESSMENT OF MAHIGA AND GUADALUPE RIVERS OF METRO CEBU, PHILIPPINES

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ABSTRACT

Two prominent urban rivers in Metro Cebu namely, Mahiga and Guadalupe were sampled and analysed *in situ* using a Multi-probe digital meter for their physico-chemical properties like pH, dissolved oxygen and temperature while linear alkyl benzene sulfonates (LAS) and ammonia were determined colorimetrically using UV-VIS spectrophotometer. Metal concentrations of the water samples were also analyzed using Ion-Coupled Plasma (ICP) Spectroscopy. The results of the study revealed that only Guadalupe River met the Department of Environment and Natural Resources Administrative Order 34 (DENR-DA 34, 1990) standard limit of 5 ppm for dissolved oxygen. Mahiga river failed both the DENR-DAO 34 and Environmental Protection Agency (EPA, 2012) standard for NH3 which is 0.50 ppm and 0.20 ppm, respectively. Further, the elevated LAS values were consistent with the high phosphorus concentrations in Mahiga and Guadalupe. The PEC/PNEC or Risk Quotients revealed that the urban rivers under study were at possible risk implying the need for immediate intervention to rehabilitate and save the river systems. Large scale environmental risk assessment is highly recommended.

Keywords: LAS, Urban Rivers, Risk Quotient, Physico-chemical Properties, Environmental Risk Assessment

INTRODUCTION

Urbanization due to rapid development of technology and economy poses significant risk to aquatic ecosystem health. These risks result from a variety of stressors, including physical (removal of vegetative cover, creation of impervious areas, in-stream modifications), chemical (discharges from industrial operations, atmospheric deposition, diffuse non-point sources from various land uses, accidents and spills) and biological (pathogens from human and animal waste, introduced species) (Zandbergen, 2008). Environmental risk assessment therefore is on the frontier to help environmentalists and government officials save and rehabilitate these river resources (Rohde *et al*., 2006) and seen as a way to integrate science, policy, and management to address this wide array of ecological problems (CENR, 2009).

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Metro Cebu is an urban area of four cities; Cebu, Lapu-Lapu, Mandaue and Talisay, including 5 municipalities with a population of more than 2 million (Mendoza, 1993 and Suico, 1997). The focused areas are the urban rivers, namely Guadalupe River in the South and Mahiga River in the North of Cebu City. The urban waters in Metro Cebu which come from waste water canals and creeks represent a combination of industrial, commercial, agricultural and domestic wastes. They were highly contaminated and threatened the health of the community and the environment (Dura, 1986). There had been no attempt for environmental river risk assessment for toxicity levels of these different pollutants in Cebu City urban rivers. Examples of the many toxic substances that can have adverse effects on fresh water habitats include detergents, phosphates and nitrogen containing compounds from fertilizers and synthetic hormones (NTP, 2011).

To date, however, there are no established standard toxicity test procedures specified by the Department of Environment and Natural Resources (DENR) in the Philippines for determining the potential hazards caused by chemicals and various substances on fresh water habitats. Instead, there is still heavy reliance on the use of chemical methods in determining the impacts of these substances (Espiritu *et al*., 2011). Hence, this study was conducted to assess the risk levels of Mahiga and Guadalupe Rivers of Metro Cebu in terms of physico-chemical properties of the two rivers in terms of dissolved oxygen (DO), pH and temperature of water samples, levels of ammonia, linear alkylbenzene sulfonates (LAS), and metal content and to evaluate the toxicity risk levels of water samples for LAS and ammonia based on the Risk Quotient .

MATERIALS AND METHODS

Sampling Site Selection

Sampling points were identified on the basis of accessibility. There were two sampling sites per river system. For the Guadalupe River, the first sampling site was the Guadalupe Bridge at Lower Kalunasan while the second was at Pahina Central near the Taboan Market. For Mahiga River, the first sampling site was the Mahiga Bridge near Country Mall, Banilad and the second sampling site was at Sitio Mahusay, Subangdaku, Mandaue near SM Hypermarket. Conditions of each sampling site were noted.

Sample Collection

Water samples were taken from a flowing part at the sides and at the middle of each sampling point. The water samples were contained in acid washed amber colored borosilicate glass bottles and filled up to the brim and tightly covered with stopper. Samples for each analysis were collected in separate bottles. The water samples were immediately brought to the laboratory ready for analysis. The unanalysed samples were stored in refrigerator.

Determination of Physical Parameters

Physico-chemical parameters such as Temperature, pH and Dissolved Oxygen (DO) were determined *in situ* using a digital multiparameter meter (Thermo Scientific). The digital multi-probe meter was calibrated using standards prior to sampling.

Figure 1.The sampling sites.

Ammonia Analysis by Phenate Method

Chemical analyses were done in triplicates to determine the precision of the data and the reproducibility of the result for the method and instrument used. Calibration curves were generated and quality control standards were used to determine the accuracy of the data. Ammonia was analyzed employing the Phenate Method as prescribed in the protocol of APPHA, AWWA (1989) using UV-VIS spectrophotometer (Shimadzu).

Linear Alkylbenzene Sulfonate (LAS) by Triphenylmethane Dye Method

Anionic surfactants (AS) are the major class of the surfactants used in detergents formulations. The pre dominant class of anionic surfactant is branched alkyl benzene sulphonate (ABS), linear Alkyl benzene sulphonate (LAS) and linear alkyl sulphate. An example of linear alkyl sulphate is Sodium dodecyl sulphate (SDS), which is a representative of anionic surfactant.

In the analysis of LAS, anionic surfactants formed 1:1 complex with cationic dyes like crystal violet. Such complexes are called ion association complex. The use of crystal violet as a dye is due its property of easy solubility in water to form ion association complex with the LAS and maximum extractability in organic solvent. SDS-CV ion associated complexes was extracted using benzene owing to its maximum extraction efficiency (Sar *et al.*, 2009). The reaction of CV with the anionic surfactant can be illustrated in the given reaction scheme in Figure 2.

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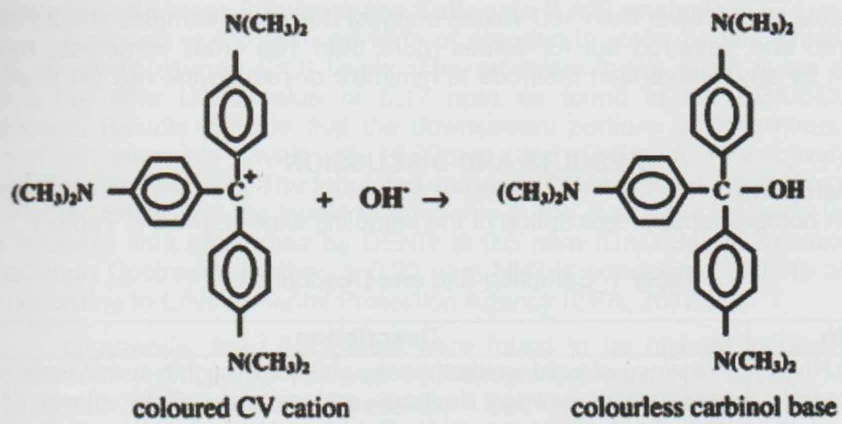

Figure 2. CV and AS in an ion association complex (Talman, *et al.*, 2005).

Exactly 75 mL water sample was placed in a separating funnel. Ten milliliters of crystal violet were added and the mixture was shaken. This is followed by the addition of 10-mL benzene. The contents were shaken for 1 minute and then allowed to settle for 30 minutes. The organic layer was collected and its absorbance was measured at a wavelength of 605 nm. In a similar manner, standard and blank solutions were also run in a separate separating funnel.

Metal Analysis Using ICP

About 100-mL of water samples were filtered using 0.5μm filter membrane and stored in polyethylene containers. These were reserved for metal determination using Ion Coupled Plasma – Atomic Emission Spectrophotometer (ICP-AES) analysis in Kagoshima University, Japan.

Toxicity Risk Assessment of River Water Samples

A simplified risk assessment was done as described in the Technical Report 21, GEF/UNDP/IMO Regional Program for the Prevention and Management of Marine Pollution Prevention in the East Asean Seas. Environmental Risk Assessment (ERA) for each River System was carried out using the values calculated from the Predicted Environment Concentration (PEC)/Predicted No Effect Concentration (PNEC) ratio criterion termed as the Risk Quotient (RQ). Predicted Environment Concentrations for each analyte under study was determined from their measured concentrations in the water samples. The PNEC values were obtained from EPA/ECOTOX database, and in the absence of values, the Water quality criteria of the Department of Environment and Natural Resources Department Administrative Order 34, s. 1990 (DENR DAO 34) Class C Waters, Water Quality Criteria for Aquatic Life Protection (US EPA), Canadian Water Quality Criteria were used.

The application factor for LAS toxicity was 1000 as the test was short termed and considered only one test organism species. Based on the values derived from PEC/PNEC ratios, the river systems were judged with the following criteria: PEC/PNEC > 1, Possible Risk; PEC/PNEC ratio < 1,

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No Possible Risk. Lower than 100 values suggest that more samples should be considered and gathered but for values more than 100 entail immediate risk reduction by any intervention methods to minimize or reduce the risk (Yi *et al,.* 2011).

RESULTS AND DISCUSSION

Water Sampling

A comprehensive description of the sampling sites is given in Table 1.

Table 1. Sampling Site and Description.

Site	Description
Mahiga River Upstream	Presence of solid wastes(mostly plastics); slightly turbid water; presence of sewage drainage and canals; stinky; plenty of household at the riverside; flowing water; presence of fecal matter
Mahiga River Downstream	Presence of solid wastes(mostly plastics); slightly turbid water; presence of sewage drainage and canals; stinky; plenty of household at the riverside; flowing water, presence of fecal matter
Guadalupe River Upstream	Slightly turbid water, non stinky environment, fish, shells, mayfly, green moss, and small crustaceans were seen.
Guadalupe River Downstream	Floating solid wastes; riverbank as dumpsite ; very turbid water; stinky; plenty of households at the riverside; presence of fecal matter; flowing water with stagnant ponds

The Physico-Chemical Parameters

The pH, DO and temperature are shown in Table 2. The pH's of all sites are within the acceptable range of 6.0-9.0 of DAO 34 in 1990. The measured DOs for Mahiga and Guadalupe Downstream using the DO meter are below the accepted level of 5 ppm required to sustain aquatic life (DAO 34, 1990). This can cause stress to aquatic life. In fact, the DO level in Guadalupe downstream is way below 2 ppm which is the critical level that can kill fish within 2 hours (Lenntech, 2011).

Table 2. pH, DO and temperature of the river samples.

Parameters	Rivers			
	Mahiga Upstream	Mahiga Downstream	Guadalupe Upstream	Guadalupe Downstream
pH	7.32	7.62	6.93	7.64
DO, mg/L	3.29	1.4	6.68	0.00
Temperature, °C	25.0	28.1	25.0	30.2

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Ammonia and Linear Alkylbenzene Sulfonate (LAS) analysis

Ammonia is the reduced form of nitrogen in water bodies which have poor dissolved oxygen (DO) levels. The ammonia levels in all rivers are all above the 48hr LC50 value of 0.17 ppm as found in the EPA/ECOTOX Database. Results indicate that the downstream portions of both rivers have very high ammonia levels of 10.29ppm and 9.48ppm respectively, for Guadalupe and Mahiga. The tabulated values in Table 3 show a possible risk to freshwater fishes and the levels of ammonia in the river samples were beyond the tolerable limit prescribed by DENR at 0.5 ppm (DAO 34, 1990) except in Guadalupe Upstream. Further, a 0.20 ppm NH_3 is considered toxic to aquatic life according to Environmental Protection Agency (EPA, 2012).

Meanwhile, the LAS Levels were found to be highest in Guadalupe Downstream (4.51 ppm), followed by Mahiga Upstream (4.45ppm), Mahiga Downstream (1.95ppm) and Guadalupe Upstream (0.711 ppm). Both urban rivers did not meet the DENR standard of 0.500 ppm surfactant for surface waters (DAO 34, 1990). Based on EPA/ECOTOX Database, the LC50 for LAS was found to be 500 ppb against Bluegill fish in 1998. The PNEC therefore for LAS is 50 ppb after the LC50 value is divided by an application factor of 1000.

Table 3. Mean levels of Ammonia and LAS.

Parameters	Rivers			
	Mahiga Upstream	**Mahiga Downstream**	**Guadalupe Upstream**	**Guadalupe Downstream**
Ammonia, ppm	5.23	9.408	0.331	10.29
LAS, ppm	4.45	1.94	0.711	4.51

Concentration of Metals in the River Water Samples

The concentration values of some major and trace elements including Na, Mg, K, Mn, Fe, Co, Cu, Zn, As and Pb in water samples are reported in Table 4.

Elevated levels of phosphorus in the rivers were of special concern. In fact, both phosphorus and nitrogen are important variables for classification of trophic state because they are the nutrients most likely to limit aquatic primary producers in streams and rivers. To control eutrophication, the USEPA (1986) recommended a limit of 0.05 mg/L for P in streams that enter lakes and 0.1 mg/L for P in flowing waters. The P concentrations were above the recommended upper concentration limit of 0.05 mg/L for Mahiga and Guadalupe Rivers. The phosphorus levels in the water can contribute to eutrophication in coastal waters. This is in agreement with the result for LAS which were also high for the said rivers. Phosphorus as phosphates in detergents are excellent builders (Hammond, 1991), and are often used as either sodium tripolyphosphate (dry detergents) or sodium/potassium phosphates (liquid detergents) (ReVelle and ReVelle,1988). These phosphates

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are capable of tying up calcium, magnesium, iron and manganese ions, thereby improving overall washing performance (Duthie , 2012).

Table 4. Concentration of metals in the river samples.

Metals	Guadalupe	Mahiga	Acceptable	Sources
Conc, ug/L	River	River	Limits, ug/L	
B	66.5	67.5	750	DAO, 1990
Na	3.19E+04	7.36E+04	-	BC EPD, 2006
Mg	2.67E+04	2.54E+04	150,000	WHO,2000
Al	8.95	9.12	100	BC EPD, 2006
Si	1.44E+04	1.21E+04	-	EPA, 2001
P	1.92E+02	1.49E+03	50-100	DAO, 1990
K	4.36E+03	1.04E+04	50,000	WHO, 2000
Ca	7.91E+04	1.14E+05	1,000,000	BC EPD, 2006
Ti	1.64	1.84	2,000	BC EPD, 2006
V	8.17	3.00	20	WHO, 2000
Cr	0.11	0.19	100	NPCC, 1982
Mn	0.64	2.03	1,000	NPCC, 1982
Fe	<0.0077	9.81	10,000	NPCC, 1982
Co	0.068	0.121	0.9	BC MWLAP, 2004
Ni	0.347	1.466	500	NPCC, 1982
Cu	<0.0475	<0.0475	1,000	NPCC, 1982
Zn	2.76	17.71	5,000	NPCC, 1982
As	2.61	2.95	10	DAO, 1990
Ag	<0.0435	<0.0435	500	NPCC, 1982
Cd	0.008	0.002	50	DAO, 1990
Sn	0.015	0.034	0.4	BC EPD, 2006
Pb	<0.0007	0.012	500	NPCC, 1982

Legend*:*

DAO–DENR Administrative Order, Philippines, BC EPD – British Columbia Environment Protection Division, Canada, WHO – World Health Organization, EPA –United States Environmental Protection Agency, NPCC – National Pollution Control Commission, Philippines, BC MWLAP – British Columbia Ministry of Water, Land and Air Protection, Canada

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River Water Risk Assessment for LAS

The LAS concentrations in the different rivers are all at a level with possible high risk (Table 5). The experimental PEC/PNEC ratios of Mahiga and Guadalupe , and are greater than 1, hence the risk must be reduced immediately.

Table 5. PEC/PNEC ratios (Risk Quotient) of LAS and their implications.

Rivers	PNEC, ppb (Database, OECE)	PEC, ppb	PEC/PNEC (EPA)	Remarks
Mahiga Upstream	50	4454	89.08	High risk
Mahiga Downstream	50	1940	38.80	High Risk
Guadalupe Upstream	50	7110	14.22	High risk
Guadalupe Downstream	50	4510	90.2	High Risk

River Water Risk Assessment for Ammonia

Ammonia concentrations in the different rivers are all at a level with high risk (Table 6). The PEC/PNEC ratios of Mahiga and Guadalupe Downstream are all above 100, hence, the risk must be reduced immediately. While that of Guadalupe Upstream is less than 100. All these Risk Quotient values indicate that the two rivers are at high risk for Ammonia levels.

Table 6. PEC/PNEC ratios of ammonia and their risk levels in the rivers.

Rivers	PNEC, ppb (Database, OECE)	PEC, ppb	PEC/PNEC Ratio	Remarks
Mahiga Upstream	17.0	5230	307.6	High risk
Mahiga Downstream	17.0	9408	553.41	High Risk
Guadalupe Upstream	17.0	331	19.6	High risk
Guadalupe Downstream	17.0	10290	605.29	High risk

CONCLUSIONS

The results of the risk assessment study revealed that Mahiga and Guadalupe Downstream have low DO levels which are below the 5 ppm limit to support aquatic life. The river systems are contaminated with ammonia and LAS which are beyond the standard limits set by the DENR-DAO 34 for both Class C and D surface waters. Risk Quotients revealed that the urban rivers under study were at possible risk implying the need for immediate intervention to rehabilitate and save the river systems.

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RECOMMENDATIONS

Activities involving the communities living along the two urban rivers focusing on environmental interventions to save these rivers must be done. Participation from the grassroots is very crucial as river clean up and sustainability will not be possible without the cooperation of the people who themselves are the main contributors of the pollutants being dumped into the river system. Information, education campaign must be done to make the community aware of the situation of the river.

Furthermore, involvement of the Local Government Unit is also recommended as enforcement and funds are also needed to mobilize activities related to the clean up and rehabilitation of the river. Included also would be ordinances to industries and agricultural establishments dumping their wastes into the river.

Additional recommendation would be further studies to monitor the physico-chemical parameters of the river for a longer period. Oxidative stress and other toxicity tests must also be done to determine the extent of pollution and its effect to aquatic life present in these two rivers.

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