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The mercury and cadmium levels in the waters of the two major rivers in Cagayan De Oro City, Philippines

Romeo M Del Rosario, Dionel O Albina, Ronnie L Besagas*, Myrna S Ceniza, Antonio Y Asoy, Noel T Dael, Luna Villa R Migalang

University of Science and Technology of Southern Philippines, Cagayan de Oro City, Philippines

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Abstract

The Cagayan de Oro River and the Iponan River are two major rivers in the City of Cagayan de Oro—a highly urbanized city in the southern part of the Philippines. The waters of these two rivers were monitored at the downstream, midstream, and upstream portions for 8 months to establish the levels of mercury and cadmium. A total of 11 samples have been taken and analyzed for mercury using AAS equipped with a mercury/hydride system and for cadmium using flame AAS. The analysis methods used were validated in terms of detection limit, quantitation limit, signal-to-noise ratio, and percent recovery using USEPA-based procedure. On the average, the mercury for the Cagayan de Oro River came out at a concentration of 0.073 ppb and was highest at the downstream; for the Iponan River, it averaged at 0.067 and was highest at the upstream. The cadmium for the Cagayan de Oro River turned out at 0.048ppm and was uniform throughout; for the Iponan River, it was 0.033ppm and relatively somewhat higher at the upstream. Risk characterization based on the ANZECC guideline trigger values yielded risk quotients that indicated no risk to the two river ecosystems as far as mercury, but an enormous risk is suggested due to cadmium for both river ecosystems.

***Corresponding Author:** Ronnie L Besagas ✉ rlbesagas@ustp.edu.ph

Introduction

Two of the major rivers in Cagayan de Oro City, Philippines are the Cagayan de Oro River and the Iponan River. Figs. 1 and 2 show portions of these two Rivers. The Cagayan de Oro River itself, not just a tributary to it, has been considered as a possible source of water for processing into drinking water. This is likely when the supply of groundwater becomes scarce in relation to demand. On the other hand, the Iponan River has recently improved in appearance after the suspension of all the gold mining in the top upper portion of the river. The mining is mainly hydraulic mining and some panning that has resulted in excessive siltation up to the coastal area where the river empties.

Water is a resource vital to all life on earth. Pollutants that find their way into the water will, therefore, have negative impacts on living organisms, including man. The impact can be in the form of toxic effects that can be made severely more serious through bioaccumulation and biomagnification. Two such pollutants are mercury and cadmium which are naturally occurring and non-biodegradable (Chen & Chen, 2001; Järup, 2003; Martin & Griswold, 2009; USEPA, 2014). These are heavy metals that are dangerous not so much in their elemental forms but in the form of water-soluble compounds.

They can cause various ailments like kidney damage, neurological disorders, lung damage, fragile bones, among a host of other ill effects. Mercury is found in many rocks including coal. When coal is burned, mercury is released into the environment. Coal-burning power plants are the largest human-caused source of mercury emissions to the air in the United States, accounting for over 50 percent of all domestic human-caused mercury emissions. Cadmium occurs naturally in ores together with zinc, lead, and copper. Coal and mineral fertilizers also contain some cadmium. As early as the 1950s, anthropogenic activities have been a major player in bringing these pollutants into bodies of water. Consider the worst bioaccumulation incident that happened in Japan, the Minamata disease in 1953.

This was the result of consuming fish and shrimps contaminated with methyl mercury from wastewater discharged by nearby chemical producing factories. The Itai-itai disease in 1955 was the result of consuming rice and fish contaminated with cadmium from wastewater discharged by nearby mining activities.

This paper examines the extent with which these two metals have polluted the two selected major rivers in the city and evaluates which of the two rivers is more contaminated. Local studies conducted so far only have limited information about these two metals (Abasolo, Ontal, & Rusiana, 2006; Pasia, Miranda, & Navarro, 2006; Ebarat & Sabornido, 2009; Betancor, Gomez, & Salon, 2013; Ampit, Cuerquis, & Quirante, 2013). The Environmental Management Bureau-Region 10 does not have data either on these metals for the two rivers and the other rivers in Cagayan de Oro City.

Fig. 1. An upstream part of the Cagayan de Oro River.

Fig. 2. An upstream portion of the Iponan River.

Materials and methods

Sampling

The two rivers were monitored for a period of 8 months (February to September, 2015) with sampling conducted at a frequency of 1~2 times per month. For each river, there were three sampling stations established: downstream, midstream, and upstream. These stations are shown in Fig. 3 for the Cagayan de Oro River and in Fig. 4 for the Iponan River.

Dip sampling using a polyethylene bucket was employed for the river waters. All water samples were collected in acid washed polyethylene bottles. Upon reaching the laboratory, the water samples were filtered using a 0.45 µm glass fiber filter in order to determine only the dissolved metals, as much as possible, which are considered more bioavailable. The pH of the samples were then adjusted to less than 2 for preservation purposes. Actual analyses followed within the next few days.

Fig. 3. The sampling stations along the Cagayan de Oro River (left to right: downstream, midstream, and upstream; no coordinates for upstream because no network signal).

Fig. 4. The sampling stations along the Iponan River (left to right: downstream, midstream, and upstream).

Determination of metals

Mercury was analyzed using a PerkinElmer AAnalyst 200 atomic absorption spectrophotometer coupled to a PerkinElmer MHS 15 mercury/hydride system making use of sodium borohydride as the reducing agent. Cadmium was determined using the same atomic absorption spectrophotometer but in the flame mode with acetylene gas as the fuel.

Prior to the actual determination, the methods used were validated following a USEPA-based guideline (DNR, 1996) by determining the method detection limit (*MDL*), the limit of quantitation (*LoQ*), the signal-to-noise ratio (*S/N*), and the recovery (%). For mercury, the following were the results: *MDL*, 0.121 ppb; *LoQ*, 0.386 ppb; *S/N*, 13.50; and% recovery, 104.2. For cadmium, the data obtained were: *MDL*, 0.039ppm; *LoQ*, 0.125ppm; *S/N*, 7.19; and% recovery, 89.7. When an analysis result was below the *MDL*, it was reported as *ND* (i.e., not detected). When it was above the *MDL* but below the *LoQ*, it was indicated as *<LoQ* (i.e., detected but less than the limit of quantitation).

When results were a mix of data (i.e., at least any two of the following: *ND*, *<LoQ*, and something numerical), attempt was made to translate the *ND* and *<LoQ* results into some numerical figs so that the data could be averaged and processed for further interpretation. An *ND* would be given the value equivalent to the average of 0 (i.e., nothing at all) and the *MDL*; a *<LoQ* would be assigned a value equivalent to the average of the *MDL* and the *LoQ*.

To estimate the ecological impact of the results, risk characterization was employed. The concentrations obtained for the two metals were translated into risk quotients (RQs) which were calculated by dividing the determined concentration by the guideline value indicated for freshwater by the Australian and New Zealand Environment and Conservation Council (ANZECC, 2000) as follows

$$Risk\ Quotient\ (RQ) = \frac{Measured\ Environmental\ Concentration\ (MEC)}{Predicted\ No\ Effect\ Concentration\ (PNEC)}$$

An RQ value that is less than or equal to 1 indicates that the environmental condition is favorable but a value greater than 1 means that the condition poses potential harm to the system. While the ANZECC trigger values are not intended for the Philippine condition, they provide tentative references for ecological management purposes.

In contrast to regulatory standards, such as the ones indicated in the DENR DAO 34 (DENR-EMB, 1990), ecological management standards are generally stricter since they do not take into consideration prevailing socio-economic factors.

Results and discussions

There were, all in all, 11 samples taken during the period of 8 months in 2015. For both mercury and cadmium, the results were a mix of *ND* and <*LoQ*. Translating the data into quantitative results is a weakness in this research. But, at the same time, it is risking to err on the side of caution. The results of the averaging are shown in Table 1.

Table 1. Averaged Results of the Mercury and Cadmium Concentrations in Water.

		Mercury (Hg), ppb		Cadmium (Cd),ppm	
River	Sampling Station	Mean	Standard Deviation	Mean	Standard Deviation
Cagayan de Oro River	Downstream	0.096	0.078	0.048	0.032
	Midstream	0.061	0.000	0.048	0.032
	Upstream	0.061	0.000	0.048	0.032
	Overall Mean	0.073	0.026	0.048	0.032
Iponan River	Downstream	0.061	0.000	0.031	0.025
	Midstream	0.061	0.000	0.031	0.025
	Upstream	0.079	0.058	0.037	0.029
	Overall Mean	0.067	0.019	0.033	0.026

Average-wise, all the mercury concentrations for both rivers are below the detection limit of the method. Considering that the actual results ranged from *ND* to <*LoQ*, this likely means that mercury is present but at very low concentrations—lower than 0.121 ppb which is the *LoQ*. On the other hand, cadmium is definitely present in the waters of the Cagayan de Oro River on the basis of an average of 0.048ppm that is above the *MDL* of 0.039ppm. This is not, however, so definite in the case of the Iponan River whose cadmium averaged at 0.033ppm which is near but still below the *MDL* of 0.039ppm. It is, however, very likely.

To get estimates on the impacts of the two metals on the aquatic ecosystem, risk characterization was utilized by way of calculating the risk quotients (RQs) based on the ANZECC guideline values for freshwater. These values at 95% protection are 0.6 ppb for mercury and 0.2 ppb for cadmium. These values actually indicate the greater harm that the latter can pose on the water ecosystem. Table 2 summarizes the RQs obtained.

Table 2. Calculated Risk Quotients for the Metals at Different Segments of the Rivers.

		Risk	Quotient
River	Sampling Station	Mercury (Hg)	Cadmium (Cd)
Cagayan de Oro River	Downstream	0.16	240
	Midstream	0.10	240
	Upstream	0.10	240
	Overall Mean	0.12	240
Iponan River	Downstream	0.10	155
	Midstream	0.10	155
	Upstream	0.13	185
	Overall Mean	0.11	165

With RQs of only about 0.1, all the waters of the two rivers are not under any harm due to mercury. The big problem is with cadmium which is very high for the Cagayan de Oro River at an overall mean of 240 (calculated after converting the level of the metal into ppb from ppm). While somewhat lower, the same can be said about the cadmium in the Iponan River. Considering that the concentrations used are just estimates from the *ND* and the <*LoQ*, these are not clear signals about the harm that cadmium is posing on the 2 aquatic ecosystems. But they can be considered as clear warnings that something is likely doing havoc in the aquatic systems under consideration and should be given further attention.

The nature of heavy metals, like mercury and cadmium, is that they are not biodegradable. Therefore, they can be bioaccumulated by aquatic organisms and even by terrestrial organisms that make use of the river waters directly. Through the food chain, there is also a big likelihood of biomagnification. The perturbations of these 2 metals by society are occurring not just locally but also globally and the critical pathway by which they endanger human health is through the food being consumed (Olsen, 2000).

The danger is not confined to the river waters only. River waters finally discharge into the coastal waters and there continue to bring environmental havoc by adding to the heavy metal pollution load in the seawater.

Marine organisms bioaccumulate and biomagnify the metals posing increasing risks. With harvests from the sea making up a big component of the food supply, terrestrial animals, including man, are part of the receiving end of these pollutants.

Conclusions and recommendations

The findings disclose that the waters of the Cagayan de Oro River and the Iponan River are not endangered by mercury. The same findings, however, strongly suggests that the waters of the two rivers are in great danger due to cadmium. The Cagayan de Oro River is in even greater danger due to the relatively higher cadmium content in its waters.

The case of the alarming risk quotient for cadmium may be considered more as a serious warning since the analysis method for the metal is not very sensitive at the low ppb levels like that for mercury. Nevertheless, it is sufficient as a signal for the need to further validate the results and trace how the cadmium is getting into the waters of the two rivers. It is important to use an instrumentation technology with better capability for trace analysis like a graphite furnace atomic absorption spectrophotometer or, better still, an inductively coupled plasma emission spectrometer.

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