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Accumulation of mercury in marine biota of Buyat Bay, north Sulawesi, Indonesia

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Abstract — Anthropogenic input of mercury (Hg) to marine environment is a great concern due to its potential impact may threat the marine ecosystem. In this paper, we evaluate Hg releases caused by mining in marine environment of Buyat Bay (BB), north Sulawesi, Indonesia, by quantifying the concentration of total mercury (THg) and methyl mercury (MeHg) in marine biota. The results showed that Hg was found in all samples and the concentration varied according to group of species. Bioaccumulation and biomagnifications occurred through the food webs in which the lowest concentration was found in the soft coral *Sinularia* sp. (1.3 μg/kg, range 0.45–2.28) and other producers (sea grass and seaweed) and the highest was in the carnivorous fish *Epinephelus merra* (359 μg/kg, range 211–572). As MeHg is found to accumulate in the carnivore fish sample in higher level than that in control, the methylation of inorganic Hg occurs in the marine environment of BB. That is plausible since all the Hg released from the anthropogenic sources in the region was inorganic form and there is absolutely no source of MeHg other then the spontaneous distribution.

Key words: methyl mercury, bioaccumulation, submarine tailings disposal (STD), Buyat Bay, Indonesia

Introduction

BB locates at the southeastern part of the Minahasa Peninsula, north Sulawesi, Indonesia. That bay is in between two short peninsulas, Ratatotok to the northeast and Bobokan to the southwest, and opens to the Maluku Sea to the south. The bay receives terrigenous runoff from upper land area of Ratatotok district through the Buyat River (BR) (Fig. 1). A fishing village, Buyat Pante (BPV) locates by the beach of BB. The village was inhabited by up to 230 people (54% male and 46% female) of 54 households. According to Berhimpon et al. (2005), the residents depend mainly on fish for their food consumption including various species of pelagic fish (eastern little tuna, yellowstripe trevally, mackerel) and demersal fish (grouper, trevally, and snappers).

From 1996 to 2004, BB received tailings (2000 t/day) of an industrial gold mine locates at the upper area of Buyat-Ratatotok district (Fig. 1). The mine exploited a gold deposit with As–Sb–Hg–Tl anomalies (Turner et al. 1994) that contain up to 6,000 ppb of Hg (PT NMR 1994, Blackwood and Edinger 2006, Edinger et al. 2006). The discharged tailings are treated one (45–55% solids, $<$75 μm diameter particles) containing Hg as fine-grained mercuric sulfide, which were disposed to BB using a submarine tailings disposal (STD) system through submarine pipelines (900 m from the beach) at 82 m of water depth. Although the STD system was designed to trap tailings below a seasonally stable thermocline, the tailings were found dispersed into water as shallow as 20 m, and as far as 4 km from the STD outfall (PT NMR 1998, Edinger et al. 2006). In addition, Hg-containing sediment transported from Kotabunan area and Totok Bay, where artisanal gold mines using Hg amalgamation to recover gold distribute (Fig. 1), that gives contribution to the bay (Blackwood and Edinger 2006, Edinger et al. 2006). However, the extent of contribution is un-quantified.

Scientific information on Hg distribution and speciation in marine biota is important as a major food source for human. From this point of view, the present study evaluates Hg accumulation in biota of BB, referring THg and MeHg concentrations. Finally, accumulation of Hg through food chain and potential impact to human are discussed. Related research on distribution and accumulation of Hg derived from gold mine at BB (Lasut et al. in preparation) will be published separately.

Materials and Methods

Samples and sampling procedure

Selection of the biota samples considered the trophic level of marine environment, which consists of trophic producers and consumers (herbivorous, carnivorous, omnivorous) groups. Table 1 shows the information of the samples (samples' name, their habitat, diet, sampling sites, tissue sample, and number of samples). Sampling was undertaken

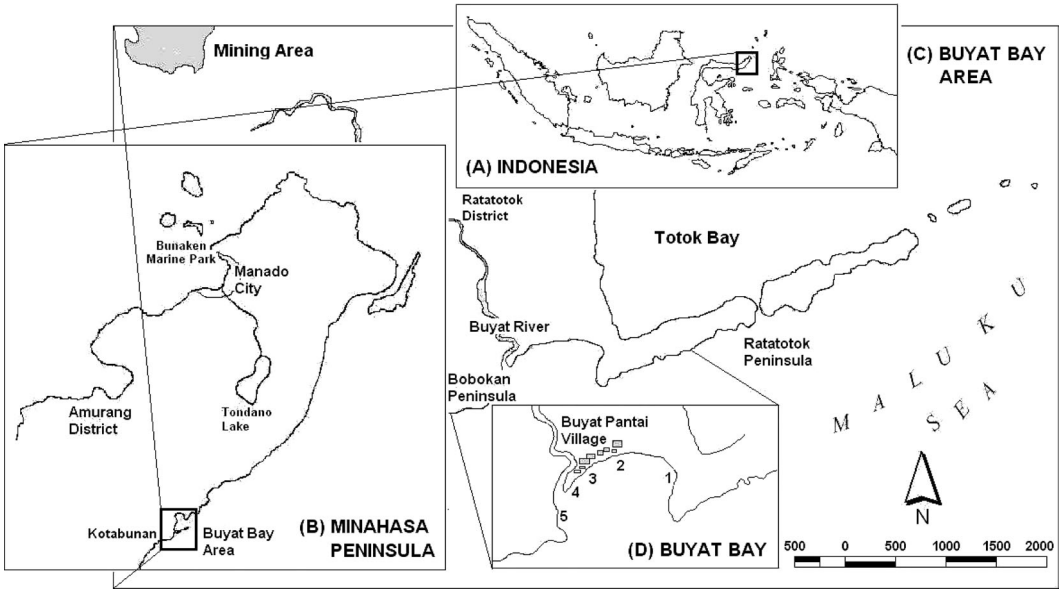

Figure 1. Map of the study areas and the sampling sites (#1–5) in Buyat Bay. A: Indonesia; B: Minahasa Peninsula; C: Buyat Bay Area; D: Buyat Bay, with sampling sites (#1–5).

in February, July, and August 2004 at BB during the lowest tide. The producer groups of seaweed and sea grass were collected using a stainless steel knife to cut some parts of them, as well as the consumer, soft coral. The intertidal bivalve (*Septifer* sp.), the gastropods, and the crabs were collected randomly in each point. The subtidal bivalves (*Tridacna* sp.) were collected using a hammer and chisel in 1.5 to 2 m depth under water. The crabs were collected along the beach at sampling sites of #1–5 (Fig. 1; D) and the other samples were done at selected sites where they were available at #1 (Fig. 1; D). The fishes were obtained from fishermen who caught them by angling inside and outside BB. Part of each of the samples was prepared for measurements; trunk for sea grass, thalli for seaweed, soft body part for bivalves and gastropod, muscle for fish, and the main body part for crab. However, whole body part of soft coral was used for measurement.

In order to maintain the samples in fresh condition during sampling work and transportation to the laboratory in Sam Ratulangi University, Manado City, Indonesia, all samples were put into sealed polyethylene plastic bags and stored in cool boxes with ice. All biological samples were freeze-dried prior to Hg analysis and moisture content of each sample was recorded at this step. Just prior to Hg measurement, the samples were digested in 5 to 10 times volume to the sample weight of 1 N NaOH at 60°C overnight.

Hg analysis

All Hg measurement was performed in the Laboratory of Natural Science, National Institute for Minamata Disease, Minamata City, Japan. The samples of seaweed and sea grass were stored at 4°C, while others were stored at −10°C prior to transportation from Laboratory in Sam Ratulangi University, to Japan. All samples were packed in a cool-box with freeze coolant gels during international transportation.

THg was quantified using cold vapor atomic absorption spectrometry (CV-AAS) (Akagi and Nishimura 1991). Sample (0.5 ml or less of 1N NaOH digested biological samples) was put into a 50 ml volumetric flask, to which 1 ml of water, 2 ml of a mixture of nitric acid and perchloric acid (1 : 1) and 5 ml of sulfuric acid were added sequentially. The flask was heated at 200°C for 30 minutes. After cooling, the digested mixture was filled up to 50 ml with water, which was used as a sample for total Hg analysis. Hg in the aliquot of the sample solution was vaporized by reduction in the presence of 0.15% (w/v) stannous chloride under vigorous bubbling for 30 seconds. The Hg vapor was then sent to the atomic absorption analyzer. This preparation was performed in an automated circulating airflow system (Akagi and Nishimura 1991, assembled by Sanso Co. Ltd., Tokyo, Japan) that enables Hg vapor to pass through the analyzer in the shortest time to provide a sharp peak.

MeHg concentration in each sample was determined by electron capture detector type gas chromatograph after extraction in KOH–ethanol (1 : 1) at 100°C for 60 min and concentration by a sequential extraction with dithizone, H_2S and dithizone (Ikingura and Akagi 1999, Matsuyama et al. 2004). Toluene layer after washing out of dithizone with 1 N NaOH was used MeHg determination with GC-ECD after acidifying with and removing 2 N HCl by suction.

Quality control

Each measurement was conducted twice with duplicate determination. For the reference material, DORM-2 (Dogfish meat by NRC) was analyzed for THg and MeHg concentra-

Table 1. Biota samples, habitat, sampling sites, and number of samples.

Biota Group	Scientific Name	Common English Name	Habitat	Diet	Sampling Sites	Tissue Sample	No. of Samples	Range of Body Size (cm)
Soft coral	*Sinularia* sp.	Finger coral	Rock/hard bottom	Plankton feeder	#1	Whole part	10	
Seaweed	*Turbinaria* sp.	Cup coral	Coral, rocks, shell, in shallow tropical reef flats	Producer	#1	Thalli	10	
Sea grass	*Enhalus acoroides*	Eel grass	Perennial	Producer	#1	Trunk	10	
Bivalve	*Septifer* sp.	Box mussel	Intertidal; attached to rocks, dead corals or the underside of stones	Suspension feeder/ omnivorous	#1	Soft part	9	
	Tridacna sp.	Giant clam	Subtidal; infaunal in rock/hard bottom	Suspension feeder/ omnivorous	#1	Adductor muscle	3	
Gastropod	*Nerita* sp.	Snail	Rock/hard bottom	Herbivore	#1	Soft part	14	
Crab	*Uca* sp.	Fiddler crabs	Intertidal, sandy beach	Carnivore	#1–5	Carapace	10	
Fish	*Priacanthus hamrur*	Crescent-tail big eye	Pelagic	Plankton feeder	Outside	Muscle	10	23.0–29.0
	Decapterus sp.	Mackerel Scad	Pelagic; deep water pelagic	Plankton feeder	Outside	Muscle	10	21.0–29.0
	Epinephelus merra	Honeycomb grouper	Demersal; semi-protected seaward reefs	Carnivore	Inside	Muscle	5	14.0–20.5
	Parupeneus multifasciatus	Manybar goatfish	Demersal	Carnivore	Inside	Muscle	2	18.5–24.0
	Lutjanus basmira	Snapper	Demersal	Carnivore	Inside	Muscle	3	14.0–16.8

tions. Measurement was done 6 times. The average value ±95% confidence interval obtained and those recommended value in parenthesis for THg was 4,670.0±110.0 ppb (4,640.0±260.0 ppb) and for MeHg was 4,260.0±100.0 ppb (4,470.0±0.32 ppb).

Results

Hg was found in all samples. Its concentration varied according to group of species (Fig. 2). Low concentrations were found in the trophic producer groups of sea grass and seaweed; their concentrations (average±standard deviation) were 4.8±1.3 ppb and 14.1±3.2 ppb, respectively. However, they were higher than in the consumer (plankton feeder) of soft coral (1.3±0.5 ppb). The intertidal and subtidal bivalves had relatively higher concentrations (56.1±9.9 ppb and 107.4±31.6 ppb, respectively) than those of the carnivorous intertidal crab (37.3±9.7 ppb), as well as the gastropod (93.7±45.2 ppb). The concentrations in fish group were relatively higher than those of all biota samples.

Concentration of THg in fish varied according to sampling location, diet, and body size. Figure 3 shows the concentrations in fish group from BB in relation to body size. Among the carnivorous demersal fish caught at inside the bay, *E. merra* had the highest concentration (354.8±135.4 ppb) than those of *P. multifasciatus* (126.2±12.9 ppb) and *L. basmira* (54.8±8.0 ppb). Among the plankton feeders pelagic fish caught at outside the bay, *P. hamrur* had higher concentration (198.9±72.3 ppb) than *Decapterus* sp. (170.5±53.7 ppb). The highest concentration was found in the carnivorous fish *E. merra*. In addition, an individual sample of the species reaches concentration of 573.6 ppb.

THg and MeHg concentration in fish meat are presented in Fig. 4. Correlation rate (*r*) between the MeHg with THg is 0.92. The average MeHg concentrations ranged from 53 ppb wet weight in *L*, *basmira* to 482 ppb wet weight in *E. merra*.

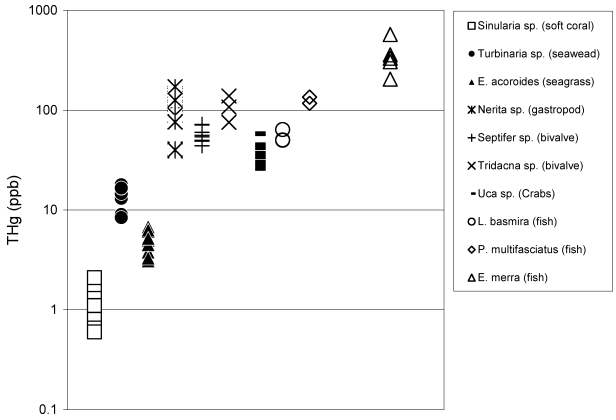

Figure 2. Accumulation of THg in biota of Buyat Bay (BB).

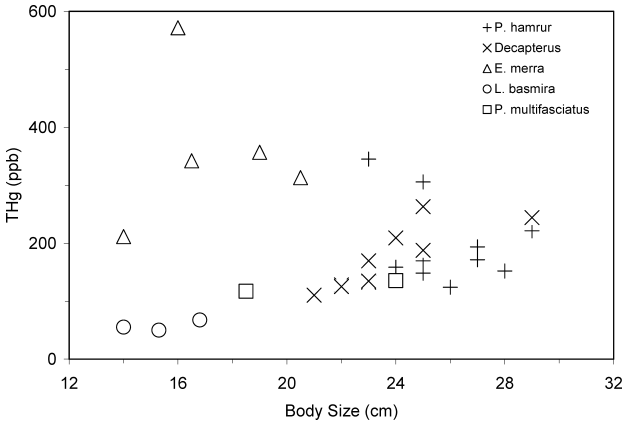

Figure 3. Concentration of THg in fish according to body size.

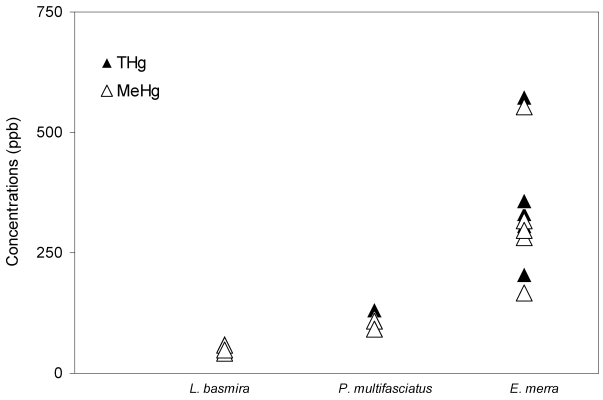

Figure 4. Concentration of Hg in fish collected from Buyat Bay. Correlation rate between THg and MeHg is 0.92.

Discussion

Accumulation of Hg through food chain

Hg was found in sediment of BB and exceeded the natural level. It may from various sources, such as tailings and transport from Kotabunan area and Totok Bay (Edinger et al. 2006). As sediments play a key role in controlling the metal concentrations in biota (Blanchette et al. 2001), this caused Hg accumulation in the marine biota of the bay, which was shown in the present study. Following the Hg introduction, it (in form of inorganic) is readily methylated by microorganisms, bioaccumulates in marine biota and consistently biomagnifies through food webs (Ikingura and Akagi 1999, Bustamante et al. 2006, Kinghorn et al. 2007, Yamaguchi et al. 2007). Microorganisms are believed to play an important role in the fate of mercury in the environment (Yamaguchi et al. 2007). The result of the methylation process is MeHg, the most stable and toxic to organisms including human (JPHA 2001). Conversely, certain microorganisms can demethylate MeHg (WHO 2000).

Accumulation of Hg in marine biota is correlated to trophic position (Desta et al. 2007) and lifestyle (Bustamante et al. 2006) where predators (consumers) showing higher tis-

sue concentrations than in their prey (Bustamante et al. 2006), except in the intertidal crabs. This was shown in the present study (Fig. 2). The difference in concentration between Lutjanids and *E. merra* may reflect the trophic level of each species.

Regarding the THg concentration in the intertidal crabs; that looks low due to a kind of fake that masked the true value by the character of sample as follows. Crabs were used for Hg determination as whole body since it is hard to separate soft part and shell. The Hg concentration in crab shell is 1/20 of that of muscle (Yasuda, unpublished data). The weight proportion of shell and soft part is hard to know, but if that is around half of whole weight, the true Hg concentration value could be 2/1.05 of that of whole body. Then, the Hg value for whole crab body would be lower than that in soft part by almost half, then the soft part Hg value could be comparable to or larger than the level of carnivorous fish *L. basmira*.

In the present study, process of methylation supposes to work in the BB environment as the input Hg is inorganic form. It was shown by the fact that THg and MeHg was found in the marine biota, including the fish. In particular, MeHg concentration in carnivore fish meat correlates with that of THg with a factor of 0.92 intimates such Hg derives from food of the fish, in other words, MeHg generated from the input Hg thorough anthropogenic activity accumulated through food web.

Potential impact to human

Hg methylation generally increases its toxicity as a result of its enhanced penetration through lipid membranes (Bustamante et al. 2006) of marine organisms and human. Through food webs where bioaccumulation occurred, concentration of the methylated Hg increases and magnified. At the end where human at the top of the webs, will accumulated the Hg and intoxication of the Hg occurred depend on the concentration. The typical and serious case was the incident of Minamata Disease in Japan (JPHA, 2001).

Consumption of fish is the main source of MeHg in humans (Malm 1998, Frery et al. 2001, Yokoo et al. 2003, Baker et al. 2004). Also, it is known that the more consumes fish the higher Hg concentration in their hair (for examples, Dickman et al. (1999) and Yokoo et al. (2003).

In the present study, THg concentration in fish of *E. merra* exceed the WHO's international human consumption advisory limit of THg in fish (500 ppb wet weight) and MeHg which almost in the same values of THg is relatively high. Berhimpon et al. (2005) reported that *Epinephelus* sp. was favorably consumed 71% by the BPV residents. It may be desirable to make any advice to avoid that kind of fish meat for consumption in the BPV.

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