

ASSESSMENT OF POSSIBLE INDIRECT RISK OF NATURALLY OCCURRING MERCURY AND CADMIUM THROUGH *Mugil* Sp. AND *Geloina* sp. CONSUMPTION IN SEGARA ANAKAN ESTUARINE ECOSYSTEM

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ABSTRACT

Estuarine ecosystem of Segara Anakan is located in south coast of Central Java, shielded from Indian Ocean by Nusakambangan island. The ecosystem of Segara Anakan estuary, Central Java, Indonesia, is influenced by fresh water inflow from Citanduy river basin and Indian sea water mostly by tidal actions through the western opening. The runoff materials continuously entering Segara Anakan from Citanduy catchment area, which geologically consist of weathering products of quarternary volcanic rocks from Galunggung mountain, West Java. Therefore various natural heavy metal contaminants are bound to the estuarine sediments, redistributed and accumulated within the ecosystem. In the present work, the effects of environmental stresses to mercury and cadmium abiotic distribution, and their availability to biotic ecosystems were studied, and consumers indirect risk assesment was carried out. In the laboratory scale studies on the distribution of mercury and cadmium in an estuarine simulation of water-field sediment, it was observed that the metal distribution coefficient decreases as the salinity and the acidity of the medium increases. Monitoring results confirmed that the highest levels of Hg and Cd in water and sediment samples were obtained in dry season. Consequently, the highest levels of Hg and Cd in biotic ecosystem, represented by *Mugil* sp. and *Geloina* sp., also obtained in dry season. The body burden of Hg in people of Segara Anakan villages, as indicated by the levels in hair and mother milk samples, taken at the end of the study (dry season 2004), were relatively low, but the levels of Cd in mother milk samples were significantly higher than that of control samples of Jogyakarta ($P = 0.05$). Consequently, the risk quotient for babies were exceeding the FAO/WHO PTWI. Based on the risk assesment carried out for babies and adults, at the present time it is advisable to consume *Mugil* sp. and *Geloina* sp., taken in wet season only and not in dry season.

Keywords: mercury, cadmium, estuarine, risk, distribution

INTRODUCTION

Segara Anakan Estuary is located in the south coast of Central Java, shielded from Indian Ocean by Nusakambangan island. It continuously collects the inflowing fresh waters from volcanic area of West Java, mostly of Citanduy river basin, and seawater from the Indian ocean, mostly by tidal actions through the western opening. Since geologically, soil materials of Citanduy river basin consist of weathering products of quarternary volcanic rocks, ash and debris from the eruption of Galunggung mountain [1]. Various natural heavy metal contaminants associated with the run off are continuously entering Segara Anakan estuarine ecosystem, sedimented, redistributed and accumulated in the ecosystem.

It is well documented that the presence of excessive concentration of heavy metals in waters poses a potential hazard to the related ecosystem.

After Minamata and Itai-itai disaster, much attention was given to mercury and cadmium, which is considered to be the most toxic heavy metals. A survey on market food basket done by Australian National Food Authority [2] showed that seafoods are the major source of mercury in the diet. Since local people lived in Segara Anakan has been exposed to Hg and Cd for quite a long time, there are concern of possible effect due to seafood ingestion.

Mercury induced toxic effects in several organ systems, however,. neurotoxicity is considered the most sensitive endpoint in humans. The ingested mercury may be stored and transfered into fetus and infants by placental exposure and intake of their mother milk. In order to prevent greater risks of *in utero* methylmercury exposure, long-term mercury biomarkers has to be used. For that reason, the FAO/WHO JEFCA committee confirmed the validity of mercury level in cord blood as short-

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term, and maternal hair as longer-term biomarkers [3].

Cadmium induced variety of progressive histopathological changes in the kidney, caused an increase in urinary cadmium. Therefore, the urinary Cd levels may serve as biomarkers, however, Honda *et al.* [10] consider that human breast milk may serve as Cd biomarker as good as urine samples.

The 61st FAO/WHO joint meeting of Expert Committee on Food Additives, JEFCA, held recently in Rome [3], recommended current provisional tolerable weekly intake, PTWI for cadmium at 7 µg/kg body weight, while PTWI for mercury was recommended at 1.6 µg/kg body weight.

The main objective of the present paper is to assess the possible risks of the indirect exposure of mercury and cadmium to human adults and babies through food chain in Segara Anakan estuary, especially through the most consumable seawater spawner fish *Mugil sp.*, and sessile mussel *Geloina sp.* Since the risk assessment is based on dose-effect relationship, the fate and distribution of mercury and cadmium in abiotic and biotic

ecosystems of Segara Anakan is monitored. Insight understanding on the bioavailability of mercury and cadmium under the influence of tropical climate, the effect of factors (salinity and pH) influencing their environmental distribution were also studied. The human body burden of Hg and Cd is reflected by the levels of Hg and Cd in biomarkers, i.e. hair and mother milk. The human risk quotient is calculated based on the amount of ingested mercury and cadmium per week to the FAO/WHO PTWI of Hg and Cd.

EXPERIMENTAL SECTION

Material

The study was carried out from July 2003 up to May 2004, covering dry season, changing period from dry season to wet season, wet season and changing period from wet season to dry season. To represent Segara Anakan Estuarine condition, 8 sampling sites were chosen: Citanduy, Majingklak, Palindukan, Karanganyar, Muaradua, Motean, Klaces and Gombol (Fig.1).

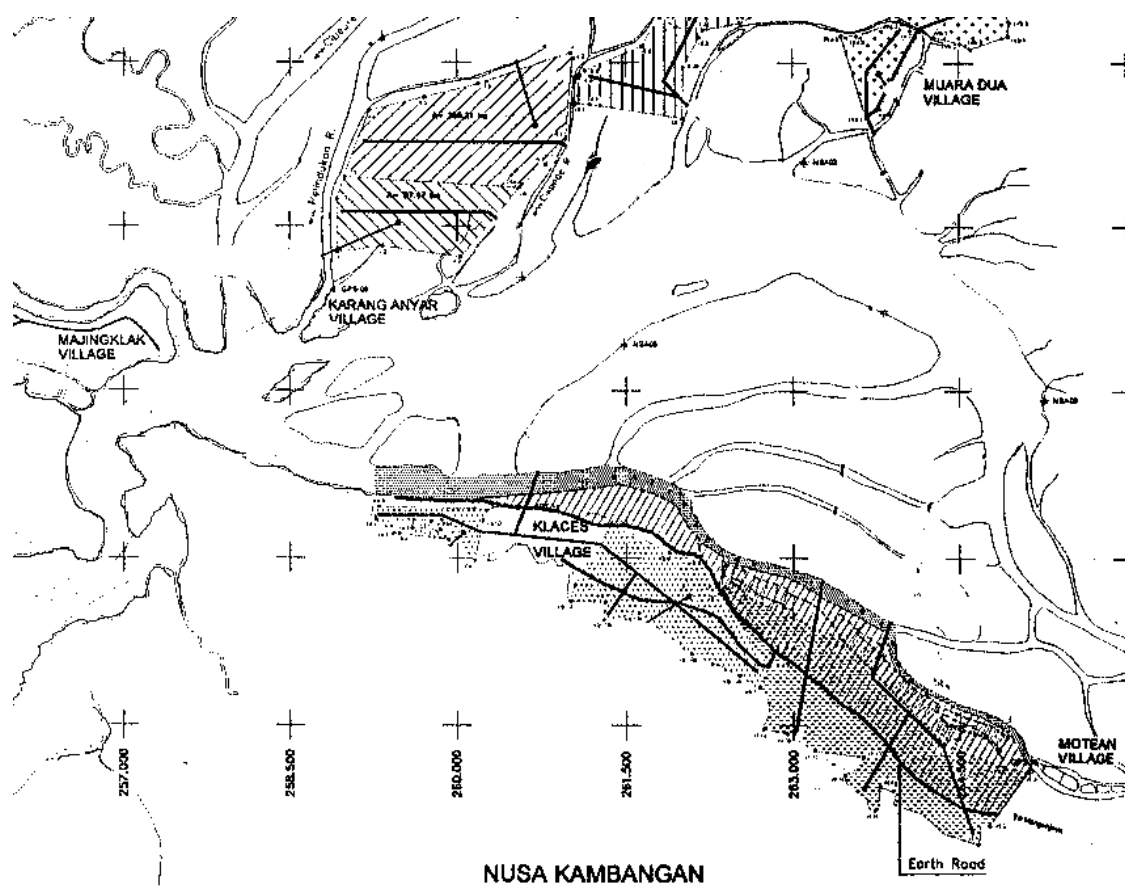


Figure 1 Map of Segara Anakan Estuarine

Samples

To know the level of mercury and cadmium in Segara Anakan ecosystem, field samples of surface water, top 5 cm sediment layers, *Mugil* sp. and *Geloina* spp were taken in 3 month intervals.

Surface water samples were collected in polyethylene containers, acidified with concentrated HNO₃ up to pH<2, transported to the laboratory at the same day and processed as soon as possible. Sediment samples were transported to the laboratory at the same day and kept refrigerated. *Mugil* sp. were transported in a refrigerated container as soon as possible to the laboratory, while *Geloina* sp. were collected alive and transported to the laboratory in a container with moist sediment and enough water. They were processed as soon as possible.

At the end of the study, May 2004, (dry season), hair and mother milk samples were collected from local residences in Motean, Klaces, Karanganyar and Muaradua, including information of their weekly diet and cosmetics usage.

Analytical Procedures

The quality of reagents used in this study were of pro analysis. Determination of mercury was done in cold vapor AAS Perkin Elmer model 3400 system with limit of detection 1.18 µg/L. The Flame/Zeeman Atomic Absorption Spectrophotometry Hitachi Model 180-60/80 was used for Cd determination. The limit of detection for Cd was 0.012 mg/L.

Salinity, pH, and temperature were measured on site using TPS Conductivity-Salinity-pH-Temperature meter Model WP-81 equipped with pH and reference electrode. Calibration for pH was done by primary pH standard solutions of Citrate (0.05 M) for pH 3.78, and of KH₂PO₄ + Na₂HPO₄ (1:1) for pH 6.86, and (1:3.5) for pH 7.41. Calibration for salinity was done against 0.01 to 0.5 M KCl solutions giving salinity from 0.8 to 40 [4]. Furthermore, the salinity was cross checked in Gadjah Mada University (GMU) laboratory using Horiba Conductivity meter DS-8F (digital). The temperature was cross checked by fine mercury thermometer

Mercury and cadmium in filtered surface water were complexed with APDC. The complex was extracted with CHCl₃, and then re-extracted with water at pH 4. This aqueous solution was subjected into Flame/Zeeman Atomic Absorption Spectrophotometry Hitachi Model 180-60/80 for Cd determination, and into cold vapor AAS Perkin Elmer model 3400. For Hg determination after reduction with borohydride in acidic condition. The Limit of quantitation (LOQ) for Hg and Cd were

0.02 µg/L and 0.24 µg/L respectively. The range of recoveries were 60-73%.

Sediment, edible part of *Mugil* sp. and *Geloina* sp., hair and mother milk samples were wet digested using a mixture of HNO₃:HCl 3:2, then determined their mercury and cadmium as mentioned above. The LOQ for Hg and Cd in sediment were 0.1 mg/kg and 1.2 mg/kg respectively, while the LOQ in biota were 0.03 mg/kg and 0.3 mg/kg respectively. The recoveries in sediment were between 90-109% and fish edible part were between 72-86%.

Experimental design

A. Factors influencing Mercury and Cadmium Distribution in Water-Sediment System

(i). The effect of salinity on Hg and Cd sorption isotherm

Four series of polyethylene bottles added with 1 gram field sediments of Gombol, Segara Anakan, were used in this study. Two series for high salinity. and the other two for lower salinity. The aqueous phase in high salinity series was solutions of HgSO₄ and CdSO₄ in seawater at concentrations of 0, 0.06, 0.30, 0.60, 0.80, 2 mg/L Hg, and 0, 0.7, 1.8, 3.6, 7.2, mg/L Cd, while in the lower salinity series, was similar solution in a mixture of seawater + Aqua™ drinking water (1+1). After the addition of 25 mL of the appropriate solutions, these bottles were shaken for 24 hours, centrifuged and decanted. The concentration of Hg and Cd in this solution was respectively determined in a cold vapor-AAS system and in flame AAS system

(ii). The effect of acidity on Hg and Cd desorption isotherm

In this study, the soil was enriched with solution of HgSO₄ and CdSO₄ up to concentration of 0, 1.5, 7.5, 15, 20, 50 µg Hg and 0, 17.5, 45, 90, 180 µg Cd per g soil and let stand overnight. The desorption was carried out at lower salinity with different pH. Two series of these soils were diluted with 25 mL low saline water at pH 5, while the other two were diluted with low saline water at pH 2, shaken for 24 hours, centrifuged and the supernatant were subjected to AAS.

B. Integrated Physicochemical Monitoring and Biomonitoring in Segara Anakan, Central Java, Indonesia

The climatic conditions of the surrounding area of Segara Anakan was obtained from Cilacap meteorological station. The effect of the changes in climatic condition to surface water were monitored by measuring its physicochemical characteristics, such as salinity, pH, temperature, total suspended solids (TSS) and total solids (TS). Salinity, pH and

temperature were measured on site at low tide in two weeks interval. While the total suspended solids (TSS) and total solids (TS) were measured at 3 months intervals. Mercury and cadmium levels of surface water, top 5 cm sediment layer, *Geloina sp.* and *Mugil sp.* were measured simultaneously in every 3 months interval. While mercury and cadmium levels of hair and mother milk samples of the local residents were measured only at the end of the study. Information on the texture and organic matter content of the collected top 5 cm sediment layer were obtained from soil laboratory, Faculty of Agriculture, Gadjah Mada University.

Data Evaluation

The influence of climate changes to mercury and cadmium behaviours in the abiotic ecosystem were compared to the laboratory studies on factors influencing mercury and cadmium distribution in water-sediment system. The bioavailable fraction obtained in these abiotic system was then used to evaluate the level of mercury and cadmium in *Geloina sp.* and *Mugil sp.* at the appropriate climate condition.

Consumer risk assessment of mercury and cadmium for local residents of Segara Anakan villages was carried out by comparing the indirect exposure by food intake to their PTWI [3]. Since seafood is the major source of mercury and cadmium, only the indirect exposure due to the intake of *Geloina sp.* and *Mugil sp.* will be considered, and risk quotient will be reported as % of PTWI.

The body burden of the ingested mercury and cadmium in local residents of Segara Anakan could be reflected as levels in biomarkers, such as hair and mother milk samples. The results obtained in this risk assessment can be used by the regulatory bodies to decide whether a more comprehensive evaluation, followed by risk reduction measure is required.

RESULT AND DISCUSSION

Factors influencing Mercury and Cadmium Distribution in Water-Sediment System

Laboratory scale experimental data presented in Table 1 showed that distribution coefficients, K_D

(heavy metal concentration ratio between sediment and water) depend largely on the salinity of the aqueous phase. For both Hg and Cd, the distribution coefficient, K_D , decreases as salinity increases. Similar results have been reported in several references [5, 6, 7]. Decrease in K_D indicating the formation of more stable water soluble species. Thermodynamically this possibility is expressed as highest complex. Since $HgCl^+$ and $CdCl^+$ has highest formation constants, 1.58×10^7 and 1.00×10^2 respectively, they seems responsible for the observed decreasing distribution coefficients.

As expected, acid addition to the system resulted in decreasing of Hg and Cd distribution coefficient, K_D , suggesting that solid particles of estuarine sediment are negatively charged. This phenomena are in agreement with the fact that the sediment particles of Segara Anakan consist mainly of aluminosilicate minerals and humic materials, which are negatively charged. Therefore acid addition will release the heavy metals adsorbed in the sediment through hydrogen bonding and electrostatic interaction. This trends were observed also other studies [5-7].

Table 1 further shows significantly lower K_D experimental values for Hg and Cd obtained from desorption experiments than that of adsorption experiments. These data demonstrate that sediment does not permanently sequester metals, it could also functioning as a source of heavy metals.

The influence of Climate Changes to Physicochemical Characteristics of Segara Anakan Estuary

Since estuarine water is principally a mixture consisting of fresh and saline water, it is reasonable to expect that fluctuation in climate conditions will influence the characteristics of the overlaying surface water of Segara Anakan. Any changes in its physicochemical characteristics will alter the species of heavy metals present of both the distribution and the bioavailability, which in other turn, will influence the toxicity. Based on the climate data and their effects to the physicochemical characteristics of the estuarine water in Segara Anakan presented in Table 2, several remarks are made.

Table 1 Sorption-desorption distribution coefficient, K_D , of Hg and Cd in field sediment-seawater system

	Hg			Cd		
	Seawater	Mix. of seawater: aqua (1:1)	Acidified mix. of seawater: aqua (1:1)	Seawater	Mix. of seawater: aqua (1:1)	Acidified mix. of seawater: aqua (1:1)
Sorption	3.4	231.7	n.a.	68.2	184.1	n.a.
Desorption	n.a.	89.1	12.6	n.a.	124.4	39.1

n.a. not assessed

Table 2 The influence of climatic changes to physico chemical characteristics of surface water in Segara Anakan Estuarine

Parameters	Dry season		Changing 2003		Wet season		Changing 2004	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Rainfall (mm)	0	0	277-606	488	238-388	298	187	187
Salinity (‰)	19 - 28	25	0.7 - 18	8	0.1 - 5	2	6 - 26	11
TS (g/L)	23 - 38	30.6	3 - 24	13.2	0.6 - 5	2.3	0.7 - 27	10.7
TSS (g/L)	0.05 - 0.2	0.2	0.5 - 5	2.2	0.04 - 1.3	0.4	0.3 - 5	1.6
pH	7.1 - 7.6	7.3	6.5 - 7.3	7	6.9 - 7.4	7.1	6.7 - 7.4	7.1
Temperature (°C)	26 - 31	28.5	28 - 32	30.1	27 - 32	29.9	30 - 31	30.6

Table 3 Mercury and cadmium levels in Segara Anakan Ecosystems

	Dry season		Changing 2003		Wet season		Changing 2004	
	range	mean	range	mean	range	mean	range	mean
Abiotic ecosystem								
<i>Water</i>								
Hg (mg/L)	0.01 - 0.02	0.01	n.d. ¹⁾		n.d.		0.003-0.01	0.007
Cd (mg/L)	0.03 - 0.04	0.03	n.d. ²⁾		n.d.		n.d.	
<i>Sediment</i>								
Hg (mg/kg,dry)	0.7 - 4.7	2.1	0.7 - 1.1	0.9	0 - 4.9	1.6	0.6 - 1.1	0.9
Cd (mg/kg,dry)	n.d.		n.d.		n.d.		n.d.	
Biotic ecosystem								
<i>Mugil spp</i>								
Hg (mg/kg,dry)	n.a. ³⁾		0.5	0.5	n.d.		1.2	1.2
Cd (mg/kg,dry)	7	7	7.5	7.5	n.d.		n.d.	
<i>Geloina spp</i>								
Hg (mg/kg,dry)	n.a.		0.04	0.04	n.d.		1.5 - 4.0	2.8
Cd (mg/kg,dry)	9.3	9.3	7.9 - 9.4	8.7	n.d.		n.d.	

¹⁾ not detected at LOD of Hg 1.18 µg/L ²⁾ not detected at LOD of Cd 0.012 mg/L ³⁾ not assessed

No rainfall was reported from July up to September 2003, therefore this period is considered as dry season. During this period, the riverine fresh water input into the Segara Anakan was relatively low, consequently the salinity of the surface water was high. The total suspended solids, TSS was low and total solids, TS, was high. The TS were identified as salt. Upon interfacing with high salinity surface water, the dispersed humic materials and aluminosilicates in fresh water from inland precipitated, causing low in TSS.

The rainfall was started at October 2003, followed by continuous heavy rain from November to December 2003, causing fluctuation of water salinity, lowering TS and increasing TSS. Although less rainfall was reported between January and March 2004, due to rain water saturation in the catchment area, the fresh water flooding into the Segara Anakan estuary, tend to decrease the water salinity, but increase the TS which were mostly consist of run off from inland. Due to its size, these solid particles were precipitated, leaving a relatively clear water with low TSS. In April 2004,

the rainfall was even less, causing increase in salinity, TS, and TSS.

As presented in Table 2, only small fluctuation was observed for temperature and pH of the surface water through out the study period. It seems reasonable to conclude that water salinity is strongly influenced by the climate changes, responsible for promoting the formation of the suspended solid as well as the solid particles in Segara Anakan estuary. These changes in physicochemical characteristics of surface water, may influence the distribution of Hg and Cd in Segara Anakan ecosystem as observed in the laboratory scale studies.

Field Distribution of Mercury and Cadmium in Segara Anakan Estuary

Field monitoring (July 2003 - May 2004) data of mercury and cadmium in Segara Anakan are presented in Table 3. It showed that in abiotic ecosystem, the mean value of the sediment-water concentration ratio for Hg observed in field experiment is within the range of K_D obtained in laboratory experiments presented in Table 1.

The data presented in Table 3 confirm earlier observation that the Hg and Cd adsorption decreases as the water salinity increases (see Table 1). It was observed that more dissolved species of Hg and Cd were determined in dry season (July – September 2003) and in the changing period (October – December 2003), where the salinity was relatively high,. On contrary, due to the lower salinity, especially in surface water of wet season, no Hg and Cd were detected.

Wasserman *et al.* [8] reported that under tropical climate, most mercury in sediments of Sepetiba Bay, Brazil, was inorganic mercury, and only less than 10 % was in the form of methyl mercury. Due to similar tropical climate, it can be assumed that mercury species in the sediment of Segara Anakan is similar to that of Wasserman *et al.* [8] work. Most of mercury in the estuarine sediment of Segara Anakan may present as inorganic species, which are easily converted to metal chloride complexes, therefore Hg and Cd in water phase was detected only when the salinity is relatively high.

Heavy metals were transported downstream as bounded metals to finely suspended materials [9]. Upon reaching saline water, most of these suspended materials will be deposited as sediment. Therefore, highest levels of mercury in the top 5 cm sediment layers of Segara Anakan estuary were observed during the dry season, and lower levels were observed during the wet season, even though the TSS were higher than dry season. However, during this study, no cadmium was detected in the sediment.

In the biotic ecosystem, a relatively high variability of mercury and cadmium levels were observed. As expected, due to the higher level of mercury and cadmium in abiotic ecosystem during dry season, higher levels of both mercury and cadmium in the edible part of *Mugil sp.* as well as *Geloina sp.*, were observed in dry season (not in wet season).

The fact that even though no cadmium was detected in sediment investigated (the limit of quantification, LOQ, for Hg and Cd in sediment were 0.1 mg/kg and 1.2 mg/kg, respectively), but detected in both biota, *Mugil sp.* and *Geloina sp.*, indicate that soluble species of Hg and Cd contribute more to the intake of the metals, and further, into the burden of *Mugil sp.* and *Geloina sp.* Despite the differences in their feeding habits, in high salinity, no significant difference was observed between the levels of Hg and Cd in *Mugil sp.* and *Geloina sp.*

Since local people lived in Segara Anakan has

been exposed to Hg and Cd for quite a long time, there are concern of possible effect due to seafood ingestion. Mercury can induce toxic effects in several organ systems (nervous system, kidney, liver, reproductive organs), however, neurotoxicity is considered the most sensitive endpoint. In humans, indices of neurotoxicity include neuronal loss, ataxia, visual disturbances, impaired hearing, paralysis and death. For the general population, greater risks are faced by fetus and infants due to placental exposure and ingestion of their mother milk. The FAO/WHO JEFCA committee confirmed the validity of mercury in cord blood as short-term, and maternal hair as longer-term biomarkers of *in utero* methylmercury exposure [3].

Chronic oral exposure to cadmium can result in a variety of progressive histopathological changes in the kidney, including proximal tubule epithelial cell damage, interstitial fibrosis, and glomerular basal cell damage with limited tubular cell regeneration. Tubular dysfunction results in increased urinary cadmium excretion. For cadmium, the urinary Cd levels may serve as biomarkers for the changes in renal function and bone/calcium metabolism, although appreciable uncertainty remains regarding the long-term health significance of these changes [3]. In Japan, for example, Honda *et al.* [10] observed a significant correlation ($r = 0.451$ at $P < 0.001$) between cadmium level found in samples of human breast milk and the level detected in the corresponding urine samples. For this reason, Honda *et al.* [10] consider that human breast milk may serve as Cd biomarker as good as urine samples.

Based on those studies, in this study, hair and mother milk samples are considered as biomarkers for mercury and cadmium body burden. The total mercury levels of hair samples of residences in Segara Anakan estuary, claim of not using any cosmetics, taken at the end of this study, were in the range of 0.8 to 4.1 mg/kg (Table 4). These levels are much lower than the levels obtained in epidemiological studies carried out by FAO/WHO JEFCA in Faroes Island and Seychelles Island [3]. In that study, the estimated maternal hair-mercury level was 14 mg/kg, is considered to be without appreciable adverse effects in the offspring. Compared to total mercury detected in hair samples of people in fishing villages in Tapajos River basin, Amazon, reported by Harada *et al.* [11], 14.1 - 20.8 mg/kg, the mercury levels in hair samples of Segara Anakan were again much lower. Moreover, the levels of Hg in mother milk samples of Segara Anakan were not significantly differ ($P = 0.05$) from that in control samples taken from Jogjakarta (Table 4).

Table 4 Hg and Cd levels of human hair and mother milk samples from Segara Anakan Residence

	Hg				Cd			
	Hair		Mo. Milk		Hair		Mo. Milk	
	Range mg/kg	Mean mg/kg	Range mg/L	Mean mg/L	Range mg/kg	Mean mg/kg	Range mg/L	Mean mg/L
Klaces	0.8-2.5	1.4	0.03-0.04	0.04	1.5-1.8	1.5	0.12-0.17	0.15
Karang Anyar	1.6-3.8	2.5	0.03-0.07	0.06	1.2-4.1	2.9	n.a	
Muaradua	2.5-3.9	3	0.04	0.04	1.6-3.6	2.4	0.13	0.13
Motean	1.8-4.1	3	0.02-0.04	0.03	0.8-2.1	1.5	0.08-0.18	0.12
Control	n.a		0.03	0.03	n.a		0.07	0.07

Table 5 Consumer risk assessment of Mercury and Cadmium intake from Mugil sp. and Geloina sp. by local residents of Segara Anakan estuary.

Consumer exposure from:	Hg intake ($\mu\text{g}/\text{week}$)				Cd intake ($\mu\text{g}/\text{week}$)			
	Dry 2003	Chg 2003	Wet 2004	Chg 2004	Dry 2003	Chg 2003	Wet 2004	Chg 2004
Mugil. sp.	n.a	40.5	(4.0)*	97.2	567	607.5	(40.5)*	(40.5)*
Geloina. sp.	n.a	1.0	(1.3)*	71.1	236.0	220.8	(12.7)*	(12.7)*
Total		41.5	5.3	168.3	803.0	828.3	53.2	53.2
PTWI for adult (60 kg body weight)	96				420			
Risk Characterization (% of PTWI)		43	6	175	191	197	13	13

Calculated based on LOQ.

The cadmium levels in mother milk samples taken from mothers in Segara Anakan villages are in the range of 80 – 180 $\mu\text{g}/\text{L}$ (Table 4). These levels were significantly higher compared to the geometric mean concentration of $0.28 \pm 1.82 \mu\text{g}/\text{L}$ reported by Honda *et al.* [10]. Compared to control samples taken from Jogjakarta, the levels of Cd in mother milk samples of Segara Anakan were significantly higher ($P = 0.05$), therefore, the indirect risk of cadmium for babies should be accounted.

Seafood Consumer Risk Assessment of Mercury and Cadmium

Risk assessment is a scientific attempt to estimate the probability of the effect following exposure to a substance, and the quantification of the risk probability is based on dose-effect relationship for that substance.

Due to their toxicity, the FAO/WHO Expert Committee on Food Additives, JEFCA [3], recommended provisional tolerable weekly intake, PTWI for cadmium at a level of 7 $\mu\text{g}/\text{kg}$ body weight, since there is no excess prevalence of tubular disfunction could be predicted to occur at that level. While a PTWI value for mercury of 1.6 $\mu\text{g}/\text{kg}$ body weight was considered to be sufficient in protecting fetus development of the most sensitive subgroup of the population. PTWI can be considered as an estimate of weekly intake over a lifetime without appreciable health risks. Therefore

the exposure level should be lower than the PTWI. If the risk characterization is expressed as percentage of PTWI, to be safe, the exposure should be less than 100% of PTWI.

It can be seen from the previous data presented in Table 3, that salinity influenced the bioavailability of Hg and Cd, and therefore the intake calculation and risk characterization are classified in salinity levels.

The indirect exposure through food can be calculated by

$$\text{Exposure} = \sum (\text{C of each intake media} \times \text{intake rate of each media})$$

Based on the information from local residents in Segara Anakan, it can be assumed that the adults eat around 3 *Mugil sp.* and 3 *Geloina sp.* per week. In the present study, the mean of fresh weight of *Mugil sp.* and *Geloina sp.* of Segara Anakan were found to be $60 \pm 25 \text{ g}$ and $30 \pm 10 \text{ g}$, respectively, therefore the intake rate of *Mugil sp.* and *Geloina sp.* were 180 g and 90 g per week respectively.

The mercury and cadmium exposure from the intake of *Mugil sp.* and *Geloina sp.*, and their risk characterization for adults of 60 kg are presented in table 5. As expected, In lower salinity (= 8, at changing period of 2003, Table 1), the Hg intake was 43 % of FAO/WHO PTWI, but in higher salinity (=11, at changing period of 2004, Table 1), it was 175 %. Also the Cd intake were higher in high salinity, 191% at dry season and 197% at changing period of 2003, which are higher than the PTWI.

In the lowest salinity (= 2, Table 1), Hg and Cd were not detected, suggesting that the concentration of Hg and Cd in these biota are less than their LOQ, ≤ 0.03 mg/kg and ≤ 0.3 mg/kg, respectively. Therefore the intake are calculated based on their LOQ. The obtained risk for Hg was 6 % (at wet season 2004) and Cd 13 % of the FAO/WHO PTWI, at wet season and at changing period of 2004. The calculated Hg and Cd intake for babies age up to 3 months, who consumes solely mother milk around 200 mL per day, having weight around 5 kg, were more than 700 and 500% of the FAO/WHO PTWI, respectively. Therefore a recommendation in consumption pattern of seafood in this area at present is required.

From those risk characterizations, it is advisable for the safety of babies and adults in Segara Anakan at the time being, to consume *Mugil sp.* and *Geloina sp.* only in wet season (not in dry season). It has to be noted that this is calculated based on those two species only.

CONCLUSION

- In the laboratory scale studies of mercury and cadmium distribution in an estuarine simulation of water-field sediment system, it was observed that the distribution coefficients, K_D , were influenced by salinity and pH. The distribution coefficient of both Hg and Cd were decreasing with increasing salinity and acidity, indicated the formation of more soluble species in more saline water.
- Monitoring results confirmed that due to higher salinity, highest level of Hg and Cd in water column and top 5 cm sediment layer samples were obtained in dry season. Consequently, the availability of Hg and Cd was highest in dry season, therefore highest level of Hg and Cd in biotic ecosystem, represented by *Mugil sp.* and *Geloina sp.*, were obtained in dry season.
- The mercury body burden of local residents in Segara Anakan villages, as indicated by the Hg levels in hair samples, were lower than those obtained from other studies carried out in Australia and Brazil. Also, the Hg levels in mother milk samples were not significantly differ (P0.05) from that of control samples taken from Jogjakarta. However, the levels of Cd in hair samples, were higher than those obtained from other studies carried out in Japan. Also, the Cd levels in mother milk samples were significantly higher from that of control samples from Jogjakarta (P0.05). Consequently, the risk quotient for babies were higher than FAO/WHO PTWI.
- Risk characterization of Hg and Cd for adults showed positive correlation between risk and

salinity, higher risk were obtained at higher salinity. Therefore, based on the risk assessment carried out for babies and adults, it is advisable to consume *Mugil sp.* and *Geloina sp.* only in wet season and not in dry season.

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REFERENCES

- White, A.T., Martosubroto, P., and Sadorra, M.S.M., 1989, *The Coastal Environmental Profile of Segara Anakan, Cilacap, South Java, Indonesia*, International Center for Living Aquatic Resources Management
- NFA, 1994, http://www.austlii.rdu.au/NationalFoodAuthority1994<14_4.htm
- FAO/WHO of the United Nations, 2003, JOINT EXPERT COMMITTEE ON FOOD ADDITIVES, Sixty-first meeting, Rome, 10-19 June 2003
- American Public Health Association, American Water Works Association, Water Environment Federation, 1992, *Standard Methods for the Examination of Water and Wastewater*, 18th Ed, Ed. Greenberg, A.E., Clesceri, L.S. and Eaton, A.D., APHA, Washington DC
- Cantwell MG, and Burgess RM., 2001, *Environ Toxicol Chem.* 20(11), 2420-7
- Riba, I., E. Garcia-Luquea, J. Blascob and T.A. DelVallsa, 2003, *Chemical Speciation and Bioavailability* 15 (4) 101
- Verslycke T, Vangheluwe M, Heijerick D, De Schamphelaere K, Van Sprang P, and Janssen CR., 2003, *Aquat Toxicol.* 64 (3), 307-15
- Wasserman JC, Amouroux D, Wasserman MA, and Donard OF., 2002, *Environ Technol.* 23(8), 899-910
- Gray JE, Theodorakos PM, Bailey EA, and Turner RR. 2000, *Sci Total Environ.* 260 (1-3), 21-33
- Honda R, Tawara K, Nishijo M, Nakagawa H, Tanabe K, and Saito S., 2003, *Toxicology.* 186(3), 255-9
- Harada M, Nakanishi J, Yasoda E, Pinheiro MC, Oikawa T, de Assis Guimaraes G, da Silva Cardoso B, Kizaki T, and Ohno, H., 2001, *Environ Int.* 27(4), 285-90