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DETERMINATION OF MERCURY IN ENVIRONMENTAL SAMPLES IN MUAR RIVER ESTUARY

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Abstract: This study was carried out at the Muar River Estuary, Johore, Malaysia. Water samples, sediment and biota that are *Crassostrea iredalei*, *Perna viridis* and *Anadara granosa* were collected during monsoon season in November 2005. All the samples were analyzed for the mercury concentration by using cold vapor atomic absorption spectrophotometer (CV-AAS). The temperature was between 28.70°C to 29.83°C, salinity at 12.78-29.96 ppt, dissolved oxygen at 5.0-6.83mg/L and pH at 6.71-7.93. The report of water samples show that the dissolved mercury in water samples was between 0.271µg L^{-1} and 0.8261tg L^{-1} while the total mercury in sediment was between 0.560-3.513µg g^{-1} dry weights. For biological sample, the average concentration of mercury in *Crassostrea irredelei* was 1.854 ± 1.012 µg g^{-1}. *Perna viridis* was 0.366 ± 1.125 µg g^{-1} and *Anadara granosa* was 1.178 ± 1.182 µg g^{-1}. The water at Muar River Estuary is still in safety level of mercury but biota especially *Crassostrea irredelei* and *Anadara granosa* are not safe to be taken due to the total mercury concentration was exceeding (WHO) level of 0.5 µg g^{-1}.

Keywords: *biota, CV-AAS, dissolved oxygen.*

1.0 Introduction

1.1 Estuary

An estuary is an inlet of the sea reaching into a river valley as far as the upper limit of tidal rise. Besides, an estuary also is a semi-enclosed arm of the sea merging with the river valley that is influenced by tides and by the mining of fresh and sea water. They fill up with sediment which acts as actual geomorphic-hydrologic features and they become extinct. Estuary can be defined more precisely in physiographic or geomorphologic terms as a river valley that is open to the ocean. By implication, it is commonly a former or “drowned” river valley into which the ocean saline water penetrates and which may or may not have some form of sediment bar at the entrance.

Usually, estuary being divisible into three sectors: a marine or lower estuary which is free connection with the open sea; a middle estuary which subject to strong salt and fresh water mixing and an upper or fluvial estuary which characterized by fresh water but subject to daily tidal action. The limits between these sectors are variable and subject to constant changes in the river discharge. The key feature of an estuary is that it is an interface between sea water and fresh water and there is an influence of the ocean tide creating a dynamic relationship between the two waters. Typically, estuaries are often characterized by sedimentation of silt from the river, which provides a unique habitat, for example, for wading birds. Estuaries are more likely to occur on submerged coastlines, where the sea level has raised in relation to the land, as this process floods valley to form raise. Estuaries provide important ecology benefit by filtering out pollutant, which means higher water quality, controlling erosion by trapping sand and silt that would otherwise wash into the ocean and soaking out storm and flood water that would destroy communities. However, estuaries can be easily destroyed through anthropogenic activities. This anthropogenic chemicals including mercury will direct emit into the river then to estuary and cause contamination. Mercury is considered as global pollutant element and many of its compounds are highly toxic and readily released into the environment because of their high volatility and mobility. Mercury is one of the hazardous, prevalent and toxic elements to the environment ecosystem. This element can exist as diverse dissolved chemical species in natural water as well as rivers, lake and ocean.

Biomass, particularly trees are accumulate and harbour a substantial fraction of biosphere mercury. When forest fires heat these fuels to temperatures well above the boiling point of mercury (57 °C), the mercury may be released to the atmosphere as either Hg^{2+} or the decomposed Hg^0. The Hg^0 released may be oxidised in the atmosphere over time to Hg^{2+}, which is also quite soluble in water and so dissolves in the moisture in the air when released in this fashion. Forest fires and rain are responsible for the transport and deposition of mercury over much of the world surface, regardless of its source (Lee et al. 2004). Inorganic and organic species of mercury are generated in different industrial activities, mainly pharmaceutical, paper, electrochemical (batteries) and plaguicide industries (Sanchez et al. 1998). According to Regional Water Quality Control (RWQC), the source of mercury come from residents (46%), water supply (22%), dentist (9%), storm water (3%), permitted industries (6%), unknown sources (11%) and employee-related human waste (3%). Currently, in the US, the main anthropogenic emissions of mercury to the atmosphere are attributed to burning of fossil fuels and municipal waste, whereas in the past the chlor-alkali and the wood pulping industries producing significant amounts of atmospheric mercury. Mercury has a special place in the list of environmental pollutants, since its adverse health effects have been convincingly demonstrated in several unfortunate poisoning incidents. The strongly toxic compounds of mercury have been exploited for bactericides, fungicides and insecticides and its brilliant hues have lead to mercury use in paints. It is also an excellent preservative and disinfectant, accounting for its presence in many chemical reagents and other applications in forms such as mercurochrome and thimerosal (Viorica et al. 2004).

Muar river estuary is a famous place for seafood and even seafood source such as oysters, fish and blood cockle. So, it is very important to carry out the studies to determine the mercury concentration in the water due to the development of the industrial areas at this river. Industrial areas have a high tendency to emit the pollutant to the Muar River Estuary. This will cause the water contamination and then to the aquatic organism bioaccumulation via food chain.

Hence, the objectives of this study are to determine the concentration of dissolved mercury (industries, township and primary forest) in water, total mercury in biota and sediment samples at Muar River estuary and to see the effects of physical and biogeochemical factors on the distribution of Hg within the estuarine zone of the river mouth.

1.2 Objective

The main objectives are to determine the concentration of total mercury in water, sediment and biota samples at Muar river estuary and then investigate the relationship between mercury concentrations with hydrological parameters.

2.0 Experimental details

2.1 Study area

The sampling location was located at Muar River Estuary and it is geographically located at $02^0$03'N, $102^0$34'E, Muar, Johor. Muar River Estuary is a very unique sampling location due to existence of industrial areas, primary forests and township of Muar (Figure 1). An industrial and town area is located oppositely while mangrove was located near to sea. The types of industries that located at the industrial area included semiconductor industries, steel mill industries, electrical industries, distillery industries, food industries, oil stations. Sampling was carried out on November 2005 at 11.00am to 2.30pm which the water was in high tide condition. Water and sediment sample was collected by using Van Dorm sampler and Ekman grab while the biological samples were

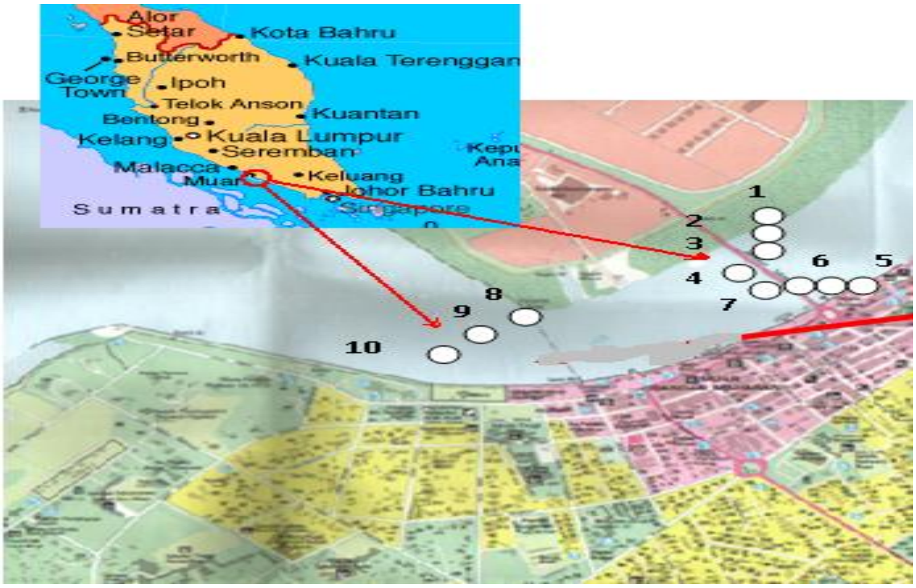

Figure 1: Sampling area and stations at estuary, Muar River.

Table 1: Coordinate of sampling stations

Stations	Coordinates
1	N 02^{o}03.379’ E 02^{o}34.220’
2	N 02^{o}03.238’ E 02^{o}34.341’
3	N 02^{o}03.305’ E 02^{o}34.221’
4	N 02^{o}03.250’ E 02^{o}34.226’
5	N 02^{o}03.233’ E 02^{o}34.244’
6	N 02^{o}03.204’ E 02^{o}34.292’
7	N 02^{o}03.331’ E 02^{o}34.368’
8	N 02^{o}03.230’ E 02^{o}34.413’
9	N 02^{o}03.234’ E 02^{o}34.277’
10	N 02^{o}03.222’ E 02^{o}34.176’

collected from the feeding and mangrove area. Coordinates of sampling stations are given on Table 1.

2.2 Chemicals

This study, used chemicals are Tin chloride, Sulfuric acid, Hydrochloric acid, Bromine chloride, Hydroammonium Chloride ($NH_2OH.HCI$), stock solution of mercury, Potassium chromate, Nitric acid, Boric acid, Calcium chloride and Hydrofluoric acid.

2.3 Instruments

Used instrument are YSI**,** GPS, 45 µm cellulose acetate millipore membrane, Van Dorn Sampler**,** aluminium foil**,** Polyethylene bottle**,** Borosilicate glass**,** ice box**,** pipette 10ml micro pipette, pH meter, dropper, 250ml cylinder, vacuum pump, Teflon beakers, 250ml cylinder flask, hot plate, microwave and cold vapor atomic absorbent spectrophotometer. All the containers and equipment used in this analytical work were washed with Trooper, tap water and distill water. Then, the equipment and containers were immersed in 10% nitric acids for at least 24 hours. Next, the container was taken out and soaked in 1.0% hydrochloric acids solution to remove all trace of oxidizing compound (e.g. Chlorine) that can destroy microbe and stored double-bagged until used (Coquery et al.1991; Mark et al. (2004)**.**

2.4 Mercury standard solution

1mL of stock solution mercury was pipetted into volumetric flask and diluted to 1000mL with 2% HNO_3 solution. This solution was used as an intermediate solution (1000 µg L^{-1}). A primary standard stock solution 1000 mg L^{-1} was used; secondary stock solution of 10 mg L^{-1} was prepared by dilution and working solutions of 5, 10, 20, 40 and 80 µg L^{-1} was used. Bromine monochloride was prepared by adding 10.8g of reagent grade KBr into 1L volumetric flask containing 1L of concentrated hydrochloric acid. Stir bar was placed into beaker and stirred for an hour. 15.2g reagent grade Potassium Bromate ($KBrO_3$) was added slowly while stirring. This process will produce large free halogens and the color will change from yellow to red then yellow. Finally, the solution was allowed to stir for another additional hour. Hydroammonium Chloride ($NH_2OH.HCI$) solution was prepared by adding 30g of $NH_2OH.HCI$ into deionize water in 100ml volumetric flask and the solution was purging with mercury free nitrogen. Then, tin chloride solution was prepared by dissolving $SnCl_2$ (25%) in hydrochloride acid (20% v/v) by heating. Finally, for potassium bromide, it was prepared by diluting 10g of potassium bromide into 100ml deionize water and mixed well.

At each sampling site, all the containers were rinsed several times with estuary water before the sample was taken. Then, the physical and chemical parameters were measured by using hydrolab or YSI. Next, water samples were collected 1 meter from surface water with Van Dorm sampler. Sample that had been collected was filtered through 0.45 µm cellulose acetate milipore filter, preserved with 2ml HNO_3 L^{-1}, warped with aluminium foil and storage in ice chest at 4 to 6^oC and stored in dark until analysis. Filters were stored frozen in milipore filter holder.

2.5 Determination of total mercury in water samples

100mL water sample was placed in a pre-cleaned 250 mL glass flask. Then, the water sample was acidified with 1mL 1.0% hydrochloric acid. 2mL of 5.0% BrCl solution was added to oxidize all mercury compounds to Hg^{2+} and the sample was exposure to UV radiation for 3 hours to remove organic color. Then, the sample was pre-reduced with 60 µm $NH_2OH.HCI$ to remove the excess of Chlorine and Bromide, which might create problem during analysis. Finally, 1mL $SnCl_2$ in 2% HNO_3 was added to the samples to convert "reducible" or "free" inorganic Hg^{2+} to Hg^0 and the water samples was detected by CV-AAS (Viorica et al. 2004; Parker et al. 2005).

2.6 Determination of total mercury in biological samples

All the biological samples (*Anadara granosa, Crassostrea iredalei* and *Perna viridis*) were dried at 60^oC until constant weight. Then, 0.5g of each sample weighted in Teflon beaker. Next, the samples were placed on the hot plate and 4mL of HNO_3 was added followed with 2mL of H_2SO_4. The sample was heated constantly for 3 hours at 90^oC. 1mL of 10% (w/v) $K_2Cr_2O_7$ was added at the end of heated. Then, the samples were diluted to 50mL with deionize water and 2mL $SnCl_2$ was added. Finally, all the samples were analysed by using CV-AAS.

2.7. Calculation of mercury concentration

Concentration of mercury in sediment and biological sample was calculated by using the formula below:

$$\text{Mercury concentrations } (\mu g\ g^{-1}) = \frac{Conc\ (\mu g\ ml^{-1}) \times the\ volume\ of\ \ diluted\ (50ml)}{weight\ of\ \ dry\ sample\ (g)}$$

3.0 Results and discussion

3.1 Hydrology of Muar River Estuary

A field sampling of estuarine water, sediment and the biological samples collected was carried out on 21st November 2005, monsoon season. Before the samples were collected, the in situ water parameter was measured by using Hydrolab. Hydrology parameters that was taken into account include temperature, conductivity, turbidity, salinity, dissolved oxygen, pH and depth. There was a raining before the day of sampling activity carried out. The weather was clear and the water level of Muar estuarine was high tide. The depth of water collection was in the range 1.589m to 2.096m. From the hydrology parameters measured, the water temperature variation was in the range 28.70^{0}C to 29.83^{0}C. The highest temperature was achieved by the mangrove and the lowest was found in industrial area.

3.2 Dissolved mercury in water

Based on obtained result in Table 2, mangrove area (sample no 8, 9 and 10) has the highest dissolved mercury concentration compared to town and industrial area which have quite similar dissolved mercury concentrations.

Table 2: Dissolve mercury in water

Stations	Hg Conc. (µg L^{-1})
1	0.379
2	0.309
3	0.427
4	0.271
5	0.373
6	0.390
7	0.661
8	0.786
9	0.632
10	0.826

The dissolved mercury concentration in Muar River estuary was between 0.271-0.826µg L^{-1}. Station 4 has the lowest dissolved mercury concentration while station 10 is the highest. Industrial and town areas have a quite constant dissolved mercury concentration. The dissolved mercury concentration of water increases from station 6 to station 10. Mangrove area has the highest dissolved mercury concentrations compared to others to sampling areas. The research in Klang River (DOE 1996a & 1996b) shown that the concentration of dissolved mercury was in the range 0.1- 2.3µg L^{-1}. This value was highest than the dissolved mercury concentration in Muar River Estuary.

Four sediment samples were collected during the time of sample collection. Obtained mercury results in the sediments are shown in the Table 3. Mercury concentration in the sediment samples are between 0.560- 3.513µg g^{-1} dry weights. Station 1 has the lowest while station 8 has the highest mercury concentrations.

Table 3: Total mercury in sediments samples

Stations	*Hg Conc. (µg L^{-1})*
1	0.560±0.60
2	1.47±0.780
8	3.513±0.03
9	2.635±0.05

Obtained mercury results in biota are shown in Table 4. Mercury concentration in biota (*Crassostrea iredalei*, *Perna viridis*, *Anadara granosa*) at Muar River estuary was between 0.158-3.481µg g^{-1} dry weights while the mean mercury concentration was 0.366-1.854µg g^{-1} dry weights. Both *Crassostrea iredalei* and *Perna viridis* was collected at station 2 while *Anadara granosa* was collected at station 8. When the comparison was done, its show that *Crassostrea iredalei* has the highest mercury concentration compare with *Perna viridis* which are from same station and *Anadara granosa* from the sea. *Anadara granosa* have higher mercury concentration when compared with *Perna viridis*.

Table 4: Concentration of mercury in biological samples at Muar River Estuary

Sample	Hg conc. (µg g^{-1})
Crassostrea iredalei (n=11)	1.854 ± 1.012
Perna Viridis (n=9)	0.366 ± 1.125
Anadara granosa (n=5)	1.178 ± 1.182

3.4 Hydrology of Muar River Estuary

Obtained hydrological parameters of Muar River Estuary are shown in Table 5. As the sampling point getting closer to the mouth of estuary, the dissolved oxygen increased constantly from industrial area to mangrove zone. The lowest dissolved oxygen reading was showed by station #1, 5.0 mgL^{-1} and the highest was found in station #8, 6.83mgL^{-1}. Higher dissolved oxygen level in mangrove indicates an adequate supply and available of oxygen to support marine species growth and activity. Dissolved oxygen level is controlled by water mixing, temperature, salinity and decomposition of organic matter. pH values at Muar River Estuary was constantly increased from station #1 to station #10. The pH values were in between 6.71 to 8.03, which mangrove area has the highest pH value while industrial area has the lowest. The pH values for estuaries typically increase as salinity rises. This can be explained by analysing the salinity measurement in this study area. Runoff from domestic and industrial area may attribute to these pH levels recorded. For turbidity of Muar River Estuary, its reading ranged from 13.92g L^{-1} in industrial to 27.49 g L^{-1} in mangrove zone. The turbidity showed linear increase from station #7 to station #10.

Table 5 showed that the mangrove area has a high dissolved oxygen, temperature, salinity, pH and turbidity. This is because dissolved mercury concentrations were influenced by dissolved oxygen, temperature, salinity pH and turbidity. In these studies, mangrove area contains high salt water because it was closer�against to the sea. From the obtained results, it has shown that concentration of dissolved mercury increase with the increase of salinity (Nguyen et al. 2005).

Table 5: Hydrological parameters of water samples

St. no.	Temp. ^{0}C	Cond. µs cm^{-1}	Turbi. g L^{-1}	Sal.. ppt	DO mg L^{-1}	pH	Depth. m
1	29.12	24.01	14.46	13.3	5.00	6.71	1.70
2	29.03	22.20	13.92	12.7	5.28	6.77	1.58
3	29.22	35.26	21.18	21.2	5.97	7.05	2.08
4	28.70	29.29	18.05	19.9	6.03	7.07	2.07
5	29.09	36.75	22.13	21.0	5.93	7.17	1.72
6	29.10	34.38	21.32	21.7	6.23	7.29	1.84
7	28.97	41.17	25.46	24.8	6.34	7.44	1.90
8	29.83	45.42	27.12	26.4	6.83	7.75	1.96
9	29.62	45.92	27.42	29.9	6.36	7.93	1.90
10	29.63	46.03	27.49	27.0	6.47	8.03	2.09

This is different compare with the previous studies and they shown that the concentration of dissolved mercury was increased with the decrease of salinity. This is because increase salinity has been associated in the rate of mercury methylation and in equilibrium methyl mercury concentration (Compeau, et al. 1985). Anionic components of the sea water also have an effect on the speciation of mercury in aquatic system. This is because anionic may influent the transfer of the methyl groups and thus directly affects the microbial communities that interact with mercury. The DO level is controlled by mixing at the air /water interface, temperature and salinity of water, the level of photosynthesis (which produce oxygen), and decomposition of organic material (depletes oxygen). High dissolved oxygen content resulting the high oxidation state of mercury (Hg^{2+}). These mean that when the concentration of dissolved oxygen was high, the mercury has an ability to go oxidation state from Hg^0 to Hg^{2+} easily and mercuric salts dissolved in aquatic environment and highest solubility of mercury occurs in oxygenated environments (Anderson et al. 1976; Gilmour et al. 1991). The oxidation rate might influence the dissolved mercury concentration in water since Hg^0 is a volatile mercury species and Hg^{2+} might change to organic mercury form which carried by tidal and wave to mangrove area before deposited or uptake by biota surrounded them. Another researcher explained that, organic mercury complex have a high stability and weakly affect by the pH (Scheuhammer et al. 1998).

Turbidity can be used to explain in term of the dynamic process that circulate and mix estuaries waters and this influenced the mercury form in aquatic environment. Turbidity is one of the most important factors in the deposition of sediment in estuaries (Walne, 1974). High turbidity zone of the mangrove which is show on these studies may result the formation of the organic mercury due to the high concentration of organic substance and this view is similar to other researcher and they proved that high turbidity zone probably show high concentrations of dissolved MeHg and particulate MeHg due to the intense methylation rate, flocculation and sedimentation. Besides, dissolved MeHg content is high when the high temperatures occur due to the higher methylation rate (Vale et al. 2005).

In the Table 5, pH in mangrove area was categorized as alkaline condition (7.75- 8.03) and it has matched with other researcher proven view, mangrove which near to the sea has pH of sea water approximately 8.0 (Vale et al. 2005). pH has a weak effect on the dissolved mercury concentration compare to others hydrological parameter.

Beside, mangrove is a place of suspended matter and organic matter deposition. Roots of mangrove plant able to capture the particulate passed through them. Thus, organic matter in natural water has an ability to modify the solubility, the redox potential and the precipitation behaviors of metals (Hg). This is because organic matter will undergo complex mechanism with sedimentary compound and result the transport of heavy metal. However, the stability of metal organic complexes in natural water is higher than that of corresponding inorganic-metal complex (Reuter et al. 1977). Besides, mangrove area has a high tendency to produce organic mercury from the association with the organic matter that captured. Organic mercury formed may transform water soluble and the organic molecule can be absorbed by mineral particles by physical adsorption, cation exchange and chemical reaction (Stoeppler et al. 1978)

4.0 Conclusion

Dissolved mercury in Muar River Estuary was in the range 0.271µg L^{-1} to 0.826µg L^{-1}. Total mercury concentration in the sediments is between 0.560µg g^{-1} to 3.513µg g^{-1} dry weights. On the other hand, the total mercury concentration in biota was between 0.366µg g^{-1} to 1.854µg g^{-1}. From the data analysis, the dissolved mercury concentration in water was influenced by dissolved oxygen, pH, salinity, turbidity and the water temperature. This hydrological parameters influnced the total mercury concentration in sediment except the sediment pH. The accumulation of mercury in tissues of *Crassostrea irredelei*, *Perna viridis* and *Anadara granosa* were found in the early stage. *Crassostrea irredelei* and *Anadara granosa* in Muar River Estuary is contaminated with the total mercury and the concentration is above the ADI (WHO) level, 0.5µg g^{-1}. Then, it is not safe for consumption.

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