

Chapter I



INTRODUCTION

This study is to establish the base-line values for the two heavy metals, lead and mercury, in the aquatic ecosystem of the lower section of the Chao-Praya River which is the main river of Thailand. The Chao-Praya River originates from four major tributaries in the northern part of the country, merging to form one single river, the Chao-Praya River. It then flows down towards the Gulf of Thailand. The study includes the Bangkok area and the estuarine environment of the river.

Both lead and mercury are among the most threatening heavy metals, and have potential hazardous effects on the aquatic environment for many reasons. The physicochemical properties of the elements and the quality of the water both play a role in governing the outcome of the ecological deterioration of the receiving waters. In their various forms in the water, they react differently with other biochemical and geochemical species coexisting in the water. Some forms of lead and mercury are more toxic to organisms than others; some can also survive all of the self-purifying processes occurring therein. So a fundamental knowledge of the distribution of lead and mercury prevailing in the lower section of the Chao-Praya River is essential if the problems relevant to the protection of the water resources from contamination and consequent quality variation, are to be solved.

Objectives and Scopes of Thesis

The main objectives of the study on the distribution of lead and mercury in the lower section of the Chao-Praya River are as follows:-

1. To study the distribution and concentration of the total lead and mercury residues in various layers of different cores from different stations.
2. To study the distribution and concentration of the total lead and mercury in the water samples both in dissolved and particulate form from different seasons and stations.
3. To study the distribution and concentration of the total lead and mercury residues in organisms from various trophic levels in the food chain at different stations and in different seasons.

Merits of Thesis

The advantages gained from this study may be roughly outlined as follows:-

1. The establishing of the base-line values for the distribution of total lead and mercury concentration in the sediment cores, in the water and in the biological samples at various locations of the area studied and at different seasons.
2. The information on the trends of these two metals in the aquatic ecosystem of the area may be used in studying the ecological deterioration caused by these two metals and other related pollutants.
3. The information obtained may be used in setting the standard for the quality of the treated municipal and industrial water.

4. The information obtained may be used as a reference in further study regarding these two heavy metals or other related pollutants.

Method of the Study

The procedures of the study may be outlined as follows:-

1. Collection of sediment cores, water and biological samples in different seasons and at different stations.
2. Preservation and storage of the samples. Sediment core will be frozen, water samples stored in polyethylene bottles with HNO_3 (Con.) at a concentration of about 2 ml per 1.0 litre of water sample to keep the pH at about 2. The biological samples are classified, weighed wet, measured and then frozen.
3. Chemical analysis of the samples by various techniques.
4. Instrumental analysis for lead and mercury-lead by the use of the atomic absorption spectrophotometer, and mercury by the flameless atomic absorption spectrophotometer.
5. Interpretation of the results obtained.

Literatures Survey and Previous Study of Lead and Mercury in the Aquatic Environment

Sources of Lead and Mercury in the Aquatic Environment

The modes of entry of these two heavy metals into the aquatic environment are not well understood in many cases. They can be classified into two main categories, namely:-

- Natural sources
- Artificial sources



Natural Sources of Lead and Mercury

Many authors have reported that atmospheric fallouts, upland river flows, leaching from soil and destruction of mineral ores are among the most important natural sources of lead and mercury into the waters (Schell and Barnes, 1973, Wilkin, 1965, Kenneth et al., 1975). Smith (1975) and Williston (1968) reported the destruction of the geological formation bearing lead and mercury mineral ores, namely galena and cinnabar, by weathering and erosion processes. They also reported the values of 0.001-0.05 $\mu\text{gHg}/\text{m}^3$ of air in the San Francisco Bay area. Schell and Barnes (1973) also reported that the atmospheric washouts of mercury aerosol were 0.08×10^6 tons per year. Kenneth et al. (1974) reported that the lead aerosol concentration in some coastal metropolitans in California is about $100 \text{ ng}/\text{m}^3$ and there are higher concentration during the occurrence of smog. The mercury content in igneous rocks is generally 10-100 ppb and even higher in the sedimentary rocks from some areas. The tapping of geothermal energy might cause long-term hazards when associated with high atmospheric mercury content (Siegel et al. 1975). In Iceland, the mercury content associated with fumaroles, magnetic and non-thermal energy were 1.3-37, 4.8-7.6, and $0.02-1.0 \mu\text{gHg}/\text{m}^3$ respectively. In Hawaii, the measurement recorded were 1.0-40.7, 0.7-40.5 and $0.04-0.3 \mu\text{gHg}/\text{m}^3$.

Artificial Sources of Lead and Mercury

The most important source of lead and mercury into the aquatic environment is through man-made activities. The use of various forms of compounds of the two metals in industry and agriculture results in the increase of lead and mercury artificially introduced into the aquatic

environment. Lead and mercury may be brought into the air in vaporized forms from smoke and fumes from factories and houses, and as a result of the combustion of fossil fuels and garbage incineration (Joensuu, 1971). The resulting air-borne particles eventually fall to the ground and on to the water either by their own gravities or by association with rain-water, snow or other atmospheric particles (Saunders, 1975). The biggest source of mercury pollution in the United States stems from the manufacturing of chlorine (Schubert, 1973). The waste from some factories, thermal plants and dental practices can all find their ways into the environment. The use of lead compounds in industry also cause the rise in a lead-contaminated environment through direct and indirect disposal of wastes into the environment. The introduction of lead into the soil and the aquatic environment is mainly from industry, mines and leaded gasoline. More than 98% of the 400 million pounds of lead released into the environment in the United States yearly is from the combustion of leaded gasoline containing 1.9-2.6 gm. of lead per gallon (Schubert, 1973). The consumption of leaded gasoline was reported to be the main cause of the lead contamination of soils and vegetation along the highways--both of the surface and, to some extent the deep soils as well (Welch, 1975, Ward et al., 1975, Mierau, 1975). Dorn et al. (1975) studied the distribution of lead in soil, vegetation and animals in the vicinity of a lead-producing area and found that the lead was distributed differently in all the samples detected. The smelters contribute the major source of lead mercury in the receiving waters (Schell and Barnes, 1973). The introduction of methyl-mercury salts as seed-dressing and disinfectant in Germany in 1914, and as fungicide and slimeicide in Sweden in 1940, all gave rise

to mercury contamination in the environment, and also enhanced the concentration of lead contamination in the environment through the trace residues in the content and containers. These activities also increase the artificial input of both lead and mercury concentration in the water, even beyond the natural normal limit in certain areas.

Geochemistry of Lead and Mercury in the Aquatic Environment

Upon their arrival in the aquatic system, biogeochemistry of the two metals can only be determined by a spectrum of parameters: the introduced forms, the water quality, and the prevailing geochemical cycle of the receiving waters. The forms of lead in the water are not well understood but it is believed to be either in dissolved ionic form or in the chelated form with organic particles, or otherwise incorporated with sedimentary surfaces which finally settle down onto the bottom as chemical precipitates (Goldberg, 1963). In the report of Hall (1972) the lead-solubility of lead sulphide in molar at pH 2.5 is $10^{-7.5}$ and at pH 6.5 is $10^{-18.2}$. These values reveal that under low pH the solubility of lead is greater than under high pH. Besides being ionic lead, it can form compounds with carbonate and bicarbonate in the water under the influence of the biogeochemical processes of the water system. From investigations and researches which have been made, both in the field and in the laboratory, there is strong evidence that, whatever form of mercury is introduced, biogeochemical changes take place as a result of bacterial activities. The by-products resulting in the distribution of newly introduced forms of mercury in the water, especially in the upper layer of the sediment blanket. Most of the mercury compounds, except alkyl-mercury, is decom-

posed to an inorganic form as mercury metal, whereas the inorganic mercury gradually changes to the more toxic methyl-mercury. The process is known as methylation of mercury and take place in accordance with the concentration of the mercury ion and pH.

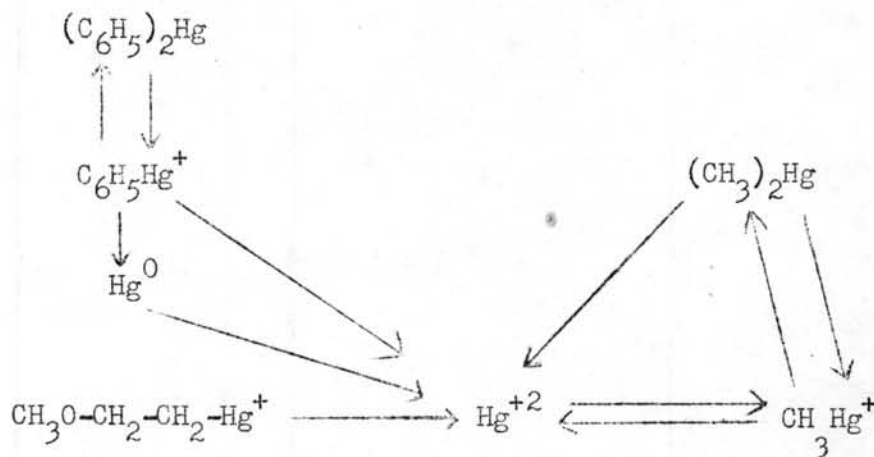


Figure 1. Methylation Diagram

(Jernel'ov, 1970)

These processes are known to take place only under aerobic conditions; but recently it was also suggested that in some cases the methylation of mercury may take place under anaerobic conditions. Nevertheless, the mechanisms of the process of the biogeochemical cycle of mercury within the aquatic system are not yet fully known, and research into this process is urgently required. The presence of sulphide ions and organic carbon can result in the formation of organic and polysulphide complexes with mercury in the water. This was noted by Lindberg and Harris (1974) in their study of the interstitial water in the sediments. In 1974, McLerran et al. reported that the enzymatic processes from bacterial activity were at a maximum during the summer months while Boylen et al. (1973)

reported the minimal activity during the winter months from their study of the lake cores.

Lead and mercury as well as other metals are known to be incorporated and adsorped quantitatively onto the surfaces of settleable particles such as clay, humic colloids, and mobile planktonic organisms. The surface phenomena of charged particles are of significance in introducing lead and mercury onto the sedimentary particles, whereas the incorporated species may linger on in the water for a period of time before they are taken up in the sediment blanket on the bottom of the water body. Lead as well as mercury shows a variable vertical concentration profile indicating a different post-depositional reaction in the sediment. The process depends on the physicochemical factors of the environment generated by a variable amount of organic material and different accumulation rates (Patricia et al. 1973, Ward et al. 1975). A lead profile model, based on the sedimentation is an excellent quantitative description of the past history of the lead input into the environment through the consumption of coal and leaded gasoline (Schell and Barnes, 1973, Edgington, 1976, Schubert, 1972).

Interaction of Lead and Mercury with Biota in the Aquatic System

Lead and mercury are two inorganic substances which aquatic organisms are particularly sensitive to because of the effects they have on their vital biochemical processes. The biota dwelling in the receiving water are capable of accumulating lead and mercury in their bodies in a higher concentration than the ambient water, the actual amount depending on the concentration of metals in the water, the time of exposure and many other

factors. The concentration of metal is low in the lower trophic level as compared to that in the upper trophic level of the food chain (Rex and Goldberg, 1962). These body concentrations are the result of their continuous exposure to the water and probably also to the food they ingest. The deposition of these two metals on the gills, mucus and skin also plays a significant role. Bacteria and viruses are generally capable of fixing trace amounts of lead and mercury on the outside of the fish and these traces are finally transformed biochemically to other mercury and lead compounds. Moreover surface absorption helps accumulate mercury on the surface of drifting phytoplanktons, which subsequently become contaminated food in the aquatic food cycle.

Dorn et al. (1975) pointed out that trees and grass can accumulate lead through foliar phenomena in their foliage that can cause a high level of lead and mercury in milk from cows feeding on such food. The death of fish living in natural water contaminated with these two metals is mainly attributed to asphyxiation and the precipitation of mucus on the gill surface (Mitrovic, 1971). Even 1.25 mgPb/l can cause serious damage to tissue and result in a retarded growth rate. Mitrovic (1971) also reported that in some fish that are highly sensitive to mercury poisoning. Mercury can accumulate in the kidneys and cause injury to membrane and skin. However, the more toxic organic mercury compounds are considerably much more hazardous due to the accumulation in the body and the attachment to the nervous system. The two tragedies in Minamata (1953) and Niigata (1964) resulted from the consumption of fish and shellfish contaminated by methylmercury (Nita, 1971). Similarly, in Iraq in 1972 and in the United States

in 1969, the same tragedies occurred (Schubert, 1973). Information about lead poisoning of water biota is still limited. Lead poisoning occurred in Europe years ago due to the use of lead pipes in municipal water systems. Lead has also been shown to produce chromosomal damage. In general, lead poisoning can be classified either as an acute manifest illness, a symptomatic chronic illness or an asymptomatic illness.

Being aware of the impairment occasioned by these two metals, environmentalists are increasingly directing their attention to and studying both the temporal and spatial distribution of lead and mercury pollutants introduced in the receiving waters together with their effects on water quality and aquatic organisms. The establishment of the base-line values for the distribution of the two metals in the aquatic ecosystem of the lower Chao-Praya River is of importance in assessing the type of treatment necessary to improve the quality of municipal and industrial water, and to determine the maximum pollution levels which can be tolerated by the water body system.

Definition of Term

$$\text{Concentration factor (C.F.)} = \frac{\text{Metal concentration in Biota}}{\text{Metal concentration in Water}}$$

$$\text{Part per billion (ppb)} = \mu\text{g/l}$$

$$\text{Part per million (ppm)} = \text{ng/mg or } \mu\text{g/g}$$