#### Chapter 2

#### LITERATURE REVIEW

#### 2.1. ROLES OF HEAVY METALS

Purve (1985) classified essential mineral elements for plants and animals into two groups: major and essential. The major elements include calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), phosphorus (P), sulfur (S), and chlorine (Cl). Essential trace elements, sometimes described as micronutrients, consist of copper (Cu), manganese (Mn), iron (Fe), zinc (Zn), molybdenum (Mo), cobalt (Co), selenium (Se), iodine (I), and boron (B). All of these are required for the normal growth and maintenance of health in plants and animals. Cobalt and selenium are specifically necessary for animals, and boron for plants.

When these mineral elements are excessive in the environment, they may cause toxicity to plants and animals, including humans by accumulating in their tissues and causing health damage later. Mason (1996) reviewed the well-known Minamata disaster in Japan in the 1950's, which is one of the earliest cases indicating the toxicity of heavy metals in the environment. Many others authors such as Cardwell, *et al.*, (1976) and Sorensen (1991) also summed up and pointed out substantial evidence for poisoning by heavy metals to fish, animals, and plants while some cases have resulted in changed ecosystems or reduced populations of plants and animals.

# 2.2. SOURCES OF HEAVY METALS RELEASED INTO THE ENVIRONMENT

There are two main sources, natural and man-made, of heavy metals released into the environment. Natural sources predominantly come from rock weathering, volcanic eruptions, and decomposing plants and animals. Man-made sources are more serious and include industrialization, urbanization, mobilization, and intensive agricultural development.

#### Arsenic (As)

Arsenic released into the environment has been summarized by Moore and Ramamoorthy (1984) and Nriagu (1994). It is mostly added to soil by modern industry, mining operations, agriculture (pesticides), forestry, and manufacturing. Coal burning has contributed about 2,900,000 metric tons of arsenic in the last 70 years. Total anthropogenic contributions have been estimated to be 11,000 tons a year. This is about 2.5 times the contribution from natural rock weathering. Both oxidation states of arsenic (3<sup>+</sup>) and arsenic (5<sup>+</sup>) are volatilized during coal combustion with an enrichment of the smaller particles. Any retention of arsenic by soil occurs by adsorption, especially if the soil contains iron or aluminum oxides.

Bignoli and Sabbioni (1984) stated that arsenic in soil is highly mobile, resulting in possible ground water contamination. The mobilization of arsenic in sediments, muds, and soils has been studied by Clement and Faust (1981), Mok and Wai (1990), and Masscheleyn *et al.* (1991). Mobilization is affected by the pH and redox potential of the media. In pH ranging from 2 to 11, arsenic (5<sup>+</sup>) and arsenic (3<sup>+</sup>)

released from sediment to the overlaying waters follows a pattern of substantial release with decreasing pH, the release of arsenic also increases sharply at high pH. Solubility reaches a maximum under highly oxidized (500mV) conditions and decreases significantly upon reduction.

The effects of temperature on the mobilization of arsenic had been reviewed by Nriagu (1994). In both anaerobic and aerobic systems, lower temperatures produced small As distribution coefficients e.g. 9.9 x 10<sup>-3</sup> at 25°C to 3.5 x 10<sup>-3</sup> at 4°C (anaerobic conditions) and 1.4 x 10<sup>-3</sup> at 20°C to 0.6 x 10<sup>-3</sup> at 10°C (aerobic conditions). The mobilization of arsenic during water-sediment interaction in a river will be affected by the water temperature. When temperature decreases, less arsenic will be released to the overlaying water.

The World Health Organization (WHO, 1993) recommends that the acceptable concentration of arsenic in drinking water be not more than 10 micrograms per liter (ppb). In Thailand, the Ministry of Industry (1978) and the Ministry of Public Health (1981) indicate that a maximum acceptable concentration of arsenic in drinking water and agricultural supply be not over 50 ppb. The Environment Canada (1987) had stated that the maximum allowable concentration of arsenic for fisheries and aquatic life should be not more than 50 ppb.

#### Lead (Pb)

Lead enters the environment from a variety of natural and human sources.

Natural processes such as soil weathering and erosion, volcanoes, and forest fires contribute to significant releases of lead. Natural processes rarely result in elevated

concentrations in the environment. Human activities, including mining, and burning fossil fuels, release the most lead which frequently results in incidents of local contamination (Ernst, 1996). Ernst reported that higher than normal lead concentrations in Atlantic Canada, were found frequently in urban areas, along side roads, near mining, smelting, and shipping facilities, and at industrial sites including battery manufacturing operations. Allen *et al.* (1996) pointed out that lead contamination in surface water in west-central Indiana impacted by acidic drainage, contained 811 mg/l of lead. Like other heavy metals, lead dissolves more readily in acidic waters (Masson,1996).

Train (1979) pointed out that lead is a toxic metal that tends to accumulate in the tissues of man and other animals. The toxicity of Pb in water is affected by pH, hardness, organic materials, and the presence of other metals. WHO (1993) notes that the acceptable concentration of lead is 10 ppb in drinking water. In Thailand, lead is also required by the Ministry of Industry (1978) to be not over 50 ppb for drinking purposes.

#### Mercury (Hg)

Mason (1996) summed up that weathering of rocks releases about 3,500 tons mercury per year, and gases from volcanic areas 25,000 to 150,000 tons. The world's production is around 10,000 tons a year. Sorensen (1991) estimated that fossil fuels may contain as much as 1 milligram of mercury per liter and releases about 5,000 tons of mercury annually when burned.

Environmental pollution with mercury from industries became widely

recognized in the early 1950's. Mason (1996) reviewed the Minamata disaster in Japan, in which many animals and people died or were damaged from that disaster. Goldwater (1971) said that the deaths of Napoleon, Ivan the Terrible, and Charles II of England could have been the result of mercury poisoning.

Bonzongo et al., (1995) proved that mining activities resulted in high mercury concentrations in water in the Carson River-Lahontan Reservoir, Nevada. Total mercury levels increased from a background concentration of 4 ng/l upstream from the mining activity, to peak values of 1,500 to 2,100 ng/l downstream from mercury contaminated mine tailing piles. Methyl mercury concentration in the surface water varied from 0.1 to 7 ng/l. In both cases, peak values were associated with the highest concentration of total suspended solids.

WHO (1990) stated that mercury is a toxic metal which is bioaccumulated in living tissues and has no known biological function. WHO (1993) notes that the acceptable concentration of mercury be not more than 1 ppb in drinking water. In Thailand, the Ministry of Industry (1978) has also stated it should not be over 1 ppb.

#### Chromium (Cr)

Train (1979) ranked chromium as the 17<sup>th</sup> most abundant nongaseous element in the earth's crust. It has oxidation states ranging from Cr<sup>2+</sup> to Cr<sup>6+</sup>, with Cr<sup>3+</sup> found most commonly in nature. Chromium is rarely found in natural waters.

Moore and Ramamoorthy (1984) found that dissolved concentration of Cr generally varies from 1-2  $\mu$ g/l in unpolluted lakes, rivers, and 0.05-0.5  $\mu$ g/l for marine water. WHO (1993) indicates that the acceptable concentration of Cr in drinking

water is 50 ppb. Thailand also has the same value while a concentration of 2-20 ppb of Cr is accepted for fisheries and aquatic life in Canada (Environment Canada, 1987), and 5-20 ppb in Russia (Committee for Fisheries, 1993).

### Molybdenum (Mo)

The environmental effects of molybdenum from mining activities have been documented. Jackson et al. (1975) found significant increases of Mo levels in Lucerne near Brighton, which had been irrigated with water containing 213 ppm of Mo. Purves (1985) stated that the level of Mo, which is normally regarded as toxic to livestock, was 10 ppm in dry matter, while a range of 5-8 ppm was found in cattle forages.

# Manganese (Mn) and iron (Fe)

Manganese and iron are major elements of the earth's crust. Iron is the second most abundant metallic element in the earth's crust. However, concentrations of iron present in surface water generally are small. In underground water, Fe<sup>2+</sup> is the most common metal. There is about one-fiftieth as much manganese in the earth crust as there is iron. In natural water, Mn<sup>2+</sup> predominates in most situations and is more stable in aerated water. It is often present at more than 1 mg/l in streams that have received acid drainage from coal mining. When acidity is gradually neutralized, ferric hydroxide precipitates first and manganese disappears from solutions after a longer time.

The WHO (1993) set an allowable manganese concentration in drinking water of 0.5 mg/l, and 0.3 mg/l for iron. In Thailand, a recommended concentration of

manganese is from 0.3-0.5 mg/l and 0.5-1.0 mg/l for iron.

# 2.3. HEAVY METAL POLLUTION FROM COAL MINING AND POWER PLANTS

Deposits of coal lie at various depths and have been exploited by man for a very long time. Mining operations increase the surface area of a deposit, facilitate and increase the passage of groundwater, and may thus cause vast environmental changes. Fyfe et al. (1993) reported that fossil fuels (oil, natural gas, coal) are the largest sources of energy, and are also the largest sources of carbon dioxide, which threatens to change world climate, temperature, and rainfall distribution by global warming. Moreover, fossil fuel combustion also creates large amounts of atmospheric trace elements (Mastradone et al., 1982; Fyfe et al., 1993; Fendar et al., 1995.) which cause substantial environmental impact; including reducing yields of agricultural crops (Jones et al., 1987).

Nriagu and Pacyna (1988), Purves (1985), Fendar and Kharat (1995) have shown that many trace elements are released into the atmosphere and are then deposited on soil, on vegetation cover, and in water basins in the area surrounding thermal power plants. Poisoning by coal smoke containing arsenic and fluoride was revealed by An *et al.* (1997).

Lead contamination from coal ash was reported by Walraven et al. (1997). A major source of lead contamination in Graft-De Rijp village (Netherlands) came from remnants of the "old" town which had building materials such as lead sheets, glazed roof tiles, and paint, coal ashes, and alkyl-leaded petrol. In addition, high zinc, copper,

and arsenic are strongly related to lead pollution, which is predominantly found in the topsoil (0-0.5 m) of the "old" town centre of Graft-De Rijp. De-Moraes-Flores and Martins (1997) have shown that lead concentrations in eggs of *Gallus domesticus* surrounding the two major coal power plants (Candiota and Charqueadas) in the state of Rio Grande Do Sul (RS), Brazil, ranged from 0.16 ppm (shells) to 3.16 ppm (yolk).

Mercury contamination from power plants was identified by Fthenakis et al. (1995). This study showed that the effects of emissions of a single large power plant may double the background exposures to methyl mercury resulting from consuming fish obtained from an area near the power plant.

The amount of arsenic in coal combustion is well documented. Querol et al. (1997) analyzed trace elements from raw coal from the Cayirhan mine, Beypazari Basin, Turkey and showed that arsenic, boron, chromium, nickel, and zinc were enriched when compared to world-wide averages of coal. Nriagu (1994) and Ratanasthien et al. (1991) reported that more arsenic was present in fly ash (213 mg/kg and 6300 mg/kg) than in bottom ash (18.3mg/kg and 168mg/kg).

Environmental contamination of arsenic from coal combustion has been studied. Hatcher et al. (1992) collected lake sediment and macrozoobenthos near a coal ash disposal basin on the western shoreline of Lake Erie (USA). They showed that arsenic and cobalt were significantly more concentration sediment nearest the coal ash basin. Arsenic and bromine were significantly higher in oligochaetes. Other cases of environmental contamination by arsenic were studied by Yager et al. (1997).

## 2.4. RESEARCH AT MAE MOH MINE AND POWER PLANT

At Mae Moh Mine and Power Plant, Ratanasthien et al. (1991) revealed that the elements with over 100 ppm were As, Ba, Mn, Rb, Sr, and vanadium (V). The highest concentrations of the elements As, Co, Cr, Ni, and U were found in the finest fly ash particles analyzed. Huyen (1995) pointed out that heavy metal concentrations in soil surrounding Mae Moh Power Plant were relatively high. Hastuti (1998) also reported that arsenic needs to be considered as a major source of pollution to the health of human beings and animals. Badulis (1998) analyzed the potential environmental risk for arsenic and lead in mine waste and found that arsenic and lead in power plant ash leachates was higher than in WHO and Thai water standards.