Chapter 2

LITERATURE REVIEW

2.1. Heavy Metals : Definition, Nature and Sources

Heavy metal is defined as a metallic group of elements with an atomic density greater than 6 g cm^{-3} (Davies, 1980). They are also called *trace metals*, *trace inorganics*, *microelements*, and *micronutrients* (Forstner and Whittman, 1991). There are 69 elements in this category, of which 16 are synthetic elements not found in nature. This definition is still debatable and based on a rather arbitrary chosen physical parameter only. Consequently, it includes elements with widely different chemical properties. For example, lanthanides and the actinides are included, although these groups of elements are not generally accepted to be *heavy metals* when their chemistry is considered (Martin and Coughtrey, 1982). According to Alloway (1995) the term *heavy metal* is used with emphasis on the pollution and toxicity aspects rather than on their economic and environmental importance.

Some heavy metals (*e.g.* Cr, Co, Cu, Ni, Sn, Zn) are *essential* for life functions of plants and animals. Others, including the most common pollutants (*e.g.* Cd, Pb, Hg), have not yet been identified as serving beneficial function, are termed *non essential* metals (Davies, 1980). In relation to environmental pollution, both categories of heavy metals are considered to be toxic and can pose threats to biological systems (Wittmann, 1981).

There are two sources of heavy metals in the environment, *viz.* natural and anthropogenic. The primary natural source is from geochemical materials (Martin and Coughtrey, 1982). Heavy metals are released to the environment once their host rock or mineral is altered by weathering process (Carrol, 1970). Other natural sources are wind blown dust, volcanic eruptions, forest wildfires, sea-salt emissions, and vegetation (Nriagu, 1989; Vernet, 1991). In terms of environmental concern, anthropogenic sources are considered as more troublesome. A large amounts of heavy metals have been released by human activities and have caused adverse effects upon the environment. These activities are (i) metalliferrous mining and smelting, (ii) agriculture and horticulture materials, (iii) sewage and sludge, (iv) fossil fuel combustion, (v) metallurgical industries, (vi) industrial activities *e.g.* electronics and chemicals, (vii) waste disposal and (viii) other activities (Alloway, 1995). Among them, combustion of fossil fuels to produce electricity is considered as the main source. Combustion processes are important sources of atmospheric As, Cr, Cu, Mn, Zn, Be, Co, Hg, Mo, Ni, Sb, Se, Sn, and V. Half of the total amount of heavy metals produced by the combustion of fossil fuels is emitted by electric power station (Vernet, 1991). In the future, heavy metal emissions from electric power plants will increase due to the increasing demands for electricity. Presently, electricity consumption per capita is about 3×10^{10} Joules per year (Winteringham, 1992).

2.2. Heavy Metal Emissions from Coal-Fired Power Plants

Heavy metals occur naturally in coal. Their concentrations are varied, but relatively high when compared to their mean concentration in the earth's crust (Egorov *et al.*, 1978). In American coals from Illinois, for example, Cd concentration ranges from 4.0 to 128 mg kg^{-1} (Ruch *et al.*, 1974). It is also suggested that Bo, Se, and As are enriched in coal (Gluskoter et al., 1977). Straughan *et al.*, (1978) analyzed concentrations of 16 trace elements in various coal, rocks, and soils and indicated that Se, As, B, Cd, Hg, and Mo are enriched in coal relative to soil.

The amount of each heavy metal released from the power plant depends upon the characteristics of the element and its compounds, coal composition, power plant configuration, and the emission control devices available (Vernet, 1991). Table 2.1 shows estimates of the rate of atmospheric discharge per ton of coal combusted for some elements which vary greatly between elements in regard to the amount released and the fraction emitted relative to input from coal.

Table 2.1. Estimates of atmospheric emission of elements at coal-fired power plants

Element	Range of atmospheric emission	
	(g/ton coal)	(% of element in coal emitted)
Al	18 - 1000	0.2 - 14
Cr	0.2 -14	1 - 47
Zn	0.2 - 5	2 - 66
Ni	0.05 - 4.5	0.4 - 82
Co	0.01 - 0.4	0.5 - 56
As	0.002 -1.6	0.1 - 21
Pb	0.1 - 0.6	4 - 67

(Source : Elseewi *et al.*, 1986)

During combustion heavy metals are volatilized and expelled through smoke stacks, in conjunction with fly ash (Klein and Russel, 1973; Smith *et al.*, 1980; Chadwick *et al.*, 1987). Total contents of some heavy metals in fly ash are given in Table 2.2. It appears that this material contains appreciably more As, Cd and Bo, that

Table 2.2. Concentration of various heavy metals in fly ash (mg/kg)

As	Cd	Cr	Cu	Pb	Zn	B
70-110	5-10	10-140	80-230	90-380	90-130	130-430

(Source : Gillham and Simpson, 1973)

is normally found in soils (see also Table 2.4) but the differences are not so great. The other elements are even of the same order of magnitude, so that fly ash can not be regarded as a serious source of heavy metal contamination in soils (Purves, 1985). Considering higher concentrations of As, Bo, Cd, Cr, Co, Pb, Mo, Ni, and Se in fly ash than those normally found in soils, Phung *et al.*, (1985) have drawn similar conclusion other than B. Fly ash has been reported to contain relatively high concentrations of Mo with a range of 5.6 to 39 mg/kg dry soil (Doran and Martens, 1972).

2.3. Soil Contamination by Heavy Metals

All heavy metals occur naturally in soil. Since no one soil is identical with another considerable variation occurs not only between localities but also between areas, sites, and even over the same parent material. Soil contamination by heavy metals should be understood as an increase to the natural occurrence of that material in the environment (Martin and Coughtrey, 1982). Consequently, assessment of soil contamination by heavy metals must also be implemented under this restriction. According to Macklin (1992) soil contamination by heavy metals can be assessed in a number of ways such as comparing with levels in sediments before the industrial era, in recent deposits from unpolluted areas, or with a rock standard. Table 2.3 shows background concentrations of some of the more common heavy metal contaminants. The best way to assess the risk of heavy metals in soil is, however, by ascertaining the critical concentration which can trigger either phytotoxic or zootoxic concentrations, cause detrimental effects on the growth and activities of microorganisms, and cause adverse effect on human health (Gupta, 1991).

Table 2.3 Background concentrations of heavy metals in sediments and soils (mg/kg)

Metal	Shale and Clays	Sub-recent Rhine sediments	Lacustrine sediments	Soils
Zn	95	115	118	59.8
Cr	83	47	62	84
Ni	68	46	66	33.7
Cu	45	51	45	25.8
Pb	20	30	34	29.2
Co	19	16	16	12
Hg	0.2	0.2	0.35	0.098
Cd	0.2	0.3	0.40	0.62

(Source : Salomons and Forstner, 1984)

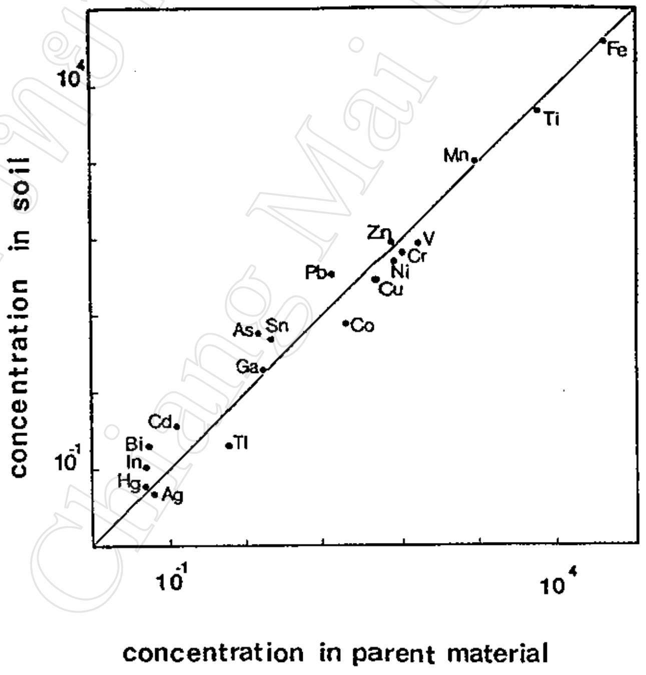

Figure 2.1. Relationship of concentrations of various heavy metals in soil and parent material (Source : Bowen, 1979).

Bowen (1979) has reviewed the 'normal' concentrations of heavy metals in soils and compared them with their concentrations in parent material (Figure 2.1). The data suggests that Fe, Ti, Mn, Zn, Ga, Ag, and Hg show close relationships between the parent material and soil concentrations; Tl, Co, Cu, Ni, Cr, and V appear to be somewhat depleted in soils relative to parent material; and In, Bi, Cd, Sn, and As are somewhat enriched in soils relative to parent materials. The normal ranges and typical levels of some potentially toxic heavy metals in uncontaminated soil are also reported by Mitchell (1964), Purves (1985), Kraemer (1976), and Straughan 1978) (Table 2.4).

Table 2.4. Normal ranges and typical levels of heavy metal concentrations in uncontaminated soils (mg/kg)

Heavy Metal	(a)	(b)	(c)	(d) common	(d) range
Arsenic (As)	1 - 14			6	0.1 - 40
Cadmium (Cd)	0.3 - 1.5	0.1	5	0.06	0.01- 7
Chromium (Cr)	15 -1000			100	5 - 3000
Copper (Cu)	2 - 100	3	100	20	2 - 100
Lead (Pb)	2 - 200	0.5	100	15	2 - 200
Zinc (Zn)	10 - 250	3	300	50	10 - 300
Boron (B)	2 - 100	1			
Nickel (Ni)		1		40	10 - 1000
Cobalt (Co)				8	1 - 40

(a) *Source* : Mitchell (1964)
(b) *Source* : Purves (1985)
(c) *Source* : Kraemer (1976)
(d) *Source* : Straughan *et al.*, (1978)

2.4. Risk of Soil Contamination by Heavy Metals

Ever since the discovery of the use of fire, humans have polluted the environment with heavy metal emissions. In ancient times these emissions increased by the use of metal working techniques (Renberg *et al.*, 1994), and during the 20th century they have increased dramatically (Bergback, 1992). In some areas they have even reached levels critical to the health of humans and other organisms (Nriagu, 1990). Therefore, it has become of interest to study the risk of these metals in the environment, especially in soils.

Heavy metal contamination of soils have received special attention because it can lead to adverse effect to plants, animals and people when it is above specific limits. Microfauna and microflora can be affected so that the organic will not be decomposed and mineralized (Greszta *et al.*, 1979). The availability and uptake of nutrients by plants can be reduced. Ultimately, the growth and quality of crops are also decreased and result in necrotic appearances (Legge and Krupa, 1986). Carroll and Loneragan (1969) found that heavy metals taken up by roots from soil are more harmful than those collected on exposed parts of the plants. For example, concentration of 500 mg/kg of Zn a plant taken from nutrient solution and sand culture can cause damage. In contrast, concentrations of up to a few thousand ppm of Zn in the plant taken up through the leaves, still do not cause plant damage (Guderian *et al.*, 1977). The same is true for Cd. According to Krause (1974), several hundred ppm of Cd applied to the leaves did not cause any visible symptoms, while much less than 5 ppm of Cd taken up through the roots gave rise to plant damage (Turner, 1973). According to Larcher (1980) heavy metal are harmful to most plant in terms of impairing stomata opening, depressing photosynthesis, disturbing respiration, and reducing growth. Higher plants are injured by relatively low concentration of heavy metals (Levitt, 1980). Plants grown on heavy metal contaminated soils have been found to accumulate As, B, Mo, Se, Zn, Cu, Hg, Ni, and Sb (Plank and Martens, 1974; Furr *et al.*, 1978; Page *et al.*, 1979). Bioaccumulation of trace elements was also found in aquatic organisms grown in polluted ponds (Guthrie and Cherry, 1979). Grazing animals are also in risk due to heavy metal contamination of soil. Large quantities of contaminated soil may be consumed during grazing (Field and Purves, 1964) and intakes of the order of 0.5 tons/cow/year have been reported (Healy, 1968).

Although trace elements are necessary for a number of biochemical function in humans, their intake at an excessive amounts will results in toxicity that is indicated by impaired growth, anemia, and susceptibility to many forms of diseases (Carrol, 1970). For example, chronic exposure to As in drinking water is related to skin cancer, (Bergolio, 1964) and lung cancer (Axelson *et al.*, 1978; Mabuchi *et al.*, 1979). Higher Pb levels in blood or other tissues is associated with poor intellectual performance and/or neurological abnormalities especially in children (Needlemen *et al.*, 1979; Burchfield *et al.*, 1980). It is also recognized that early pregnancy and prenatal exposure coupled with unusual susceptibility of young children to lesser amounts of Pb may produce subtle, fully irreversible neurological defects (Singhal and Thomas, 1980). Moreover, accumulation of Cd in kidneys can cause cancer and cardiovascular diseases. Its implication to human health is related to bone and renal diseases (Webb, 1979).

2.5. The Role of Soil Arthropods in Terrestrial Ecosystems

Most of arthropods are present in soil. They are largely diverse and range from minute pauropods feeding on fungi and plant debris, myriapods in damp soil to the principal predators, *e.g.* carabid ground beetles, staphylinid rove beetles, and spiders

(Brown, 1978). Arthropods play an important role in maintaining the integrity of soil ecosystems. They decompose litter, nutrients (Moore *et al.*, 1988) and skeletonize leaf material (Wallwork, 1970). Decomposition can be done directly by feeding on detritus and indirectly by ingesting microbes and adhering detrital material. According to Whitford (1996) the unique life histories and behavioral characteristic of these organisms, for instance termites and ants, determine the properties and formation of soil by affecting the spatial and temporal distribution of essential water and nutrient resources. Their abundance and diversity are, therefore, directly related to quantity of litter accumulation and soil organic matter.

2.6. Soil Arthropods as Bioindicators

Distribution and response of soil-inhabiting arthropods to various environmental stressor have been studied. Lauritz *et al.*, (1996) collected carabid beetles (Coleoptera: Carabidae) from an altitudinal gradient at Chimborazo, Ecuador. They found that *Bembidion andinum* Bates was the dominant species at 4,800 m, *Pelmetellus andinum* Bates at 4,500 m and *Agraphoderus integer* Bates at 4,250 m.

Vossel and Assman (1995) have studied communities of Chilopoda, Diplopoda, and Carabidae of two formerly grazed woodland areas (wood pasture) and an adjacent planted even-aged stands of oak-hornbeam forest in the 'Bentheimer Wald" near Bad Bentheim (southern part of Lower Saxony, Germany) using pitfall traps and bowl extractors. The formerly woodland grazed areas are best characterized as a *Stellario-Carpinetum peryclymenetosum*. The planted forest constitutes as a transition between the *Stellario-Carpinetum* and *Lonicero-Fragetum*. For all three animal groups, the number of detected species is greater in the wood pasture area than in the planted forest stand.

Coulson *et al.*, (1996) investigated the effects of summer warming on the total population densities of soil-dwelling microarthropods in the Arctic and compared these results with those from natural between year and between site variations. No significant effect of temperature elevation on oribated mite population emerged. In contrast, springtail numbers were significantly lower on tented versus control plots. Year to year variation in climate, interacting with physical differences between sites, produced an equal or greater effect on microarthropod numbers at any one site than the 8-10% increase in "heat availability" resulting from the summer tent treatment.

Baldi and Kisbenedek (1994) have studied the effect of edge effect on beetles communities. They report that the beetle communities sampled in the forest edge, interior edge and interior habitats differed significantly from each other. There were differences in calculated species number, diversity, and equitability. They also revealed that the effect of edge may have similar consequences on taxonomically distant group of beetles.

Wikars (1995) have investigated the effect of habitat destruction on carabid beetles population. It is concluded that breeding populations of the fire-adapted *Agonum quadripunctatum* were found in most of the fifteen investigated burned uncut forest, but not in any of the fifteen burned clear cut.

Zinkler and Platthaus (1996) have assessed the tolerance of soil-inhabiting Collembola to high carbon dioxide concentration. Behavioural changes of the dwelling species *Allacma fusca*, and *Orchesella cincta* could be observed during short term exposure (1 to 5 hours) and 10% CO_2 in soil gas, respectively. In contrary, the limit of the tolerable CO_2- concentration of *Falsomia candida* and *Tomocerus flavescens* from deeper soil layers was only reached at 25% CO_2 in soil gas.

Bouletrau and Sillans (1996) studied the interaction effects of low CO_2 concentration (0 and 5%) and temperatures (14 and 25 °C) on several life history traits in the two sibling species of *Drosophila melanogaster* and *Drosophila simulans*. They found that development duration was increased by CO_2, particularly at low temperature (14 °C), and viability reduced. At low temperature, body size was increased, although wing length variation was reduced by CO_2 in this condition. CO_2, unlike temperature, did not appear to be a powerful selective factor, but modified the expression of certain traits, being in some cases, beneficial to the flies.

Stone and Bocon (1995) examined the influence of soil moisture content on leaf dynamics and insect herbivory. They found that consumption of foliage by insects on the trees subjected to flooding compared to the non-flooded trees was not significantly different. However, the relative impact of insect herbivory was significantly greater on the non-flooded trees.

Verhoef (1996) investigated the effect of multiple stressor including the simultaneous effects of food, water shortage and low temperature on Collembola. It is advocated to perform multiple stressor studies including toxic substances such as heavy metals and organic toxicants.

Kizimirova and Slovak (1996) studied the effects of heavy metals and fluorine on phagocytosis and phenoloxidase activity in *Mamestra brassica* (Lepidoptera: Noctuidae). In copper-stressed larvae, increased and reduced percentage of plasmatocytes and granular cells, respectively, and a reduced phagocytosis of iron sacchrate were found. Cadmium- and fluorine treatment reduced phagocytosis of *Saccharomyces cerevisiae*. Cadmium showed a stimulatory effect and copper indicated an inhibitory effect of phagocytosis of *Candida tropicalis*.