

## Chapter 2

### LITERATURE REVIEW

#### 2.1. BACKGROUND LEVEL OF HEAVY METAL IN SOIL

In soil, a certain number of elements are predominant or existing in appreciable quantities. Contents of oxygen, hydrogen, silicon, aluminum, iron, carbon, nitrogen, calcium, magnesium, sodium, potassium, phosphorus and sulfur vary widely from one soil to another. Content also varies from one horizon to another in the same soil profile (Martin and Coughtney, 1982). Other elements such as copper, lead, nickel, cobalt, molybdenum etc., are found only in traces in soils. Nevertheless, the majority of these elements play a primary role in plant nutrition and development. Because of the nature of parent rock, or climatic or topographic conditions, some of these elements can become very abundant in some soils.

The abundances of some heavy metal in various geological formations are summarized in Table 2.1.

Table 2.1 Average abundances of trace elements in soils, the earth's crust, sediments and igneous rocks (Bockris, 1977)

Elements	Soil (ppm)	Crust (ppm)	Sediments (ppm)	Igneous rock (ppm)
Zn	50	165	270	80
Pb	10	20	20	16
As	5	3.4	6.6	2

### *Lead*

The average lead content of igneous rock is about 15 ppm, which places this element in the category of a rare element. Fortunately, it is concentrated in sulphide deposits which occur commonly throughout the world and it is hence easily mined and smelted. In its natural state, lead is found mainly as galena (PbS).

The lead in the earth's crust is slowly released by the process of weathering of igneous rock and most of it ultimately finds its way into the ocean. The lead content in soil is of the order of its crustal abundance (15ppm) because of the stability of this element in the geochemical cycle. Natural levels can range from 1 to 100 ppm depending on the nature of the substrate from which the soil was formed.

In estimating the content of Pb in uncontaminated soil, Nriagu (1978) reported the mean as 17 ppm whilst Ure and Berrow (1982) reported 29 ppm. A statistical survey of soil data from Wales and England indicated that Pb content in the normal surface (0-15 cm) soil lies between 15 and 106 ppm. Severson et al. (1992) reported the mean Pb content of surface soil in the Frisian Islands Germany as 7.9 ppm and ranges of less than 4 ppm to 11 ppm. Data from several researches have supported the hypothesis that much of the observed Pb in soil in many areas originates from anthropogenic emissions such as mining activity.

According to Aubert and Pinta (1977), soils in the tropical humid zone have upper and lower limits of lead concentration from traces to 30 -50 ppm.

### *Zinc*

Tropical soils have about the same total zinc content as soils of other climatic regions. Contents range from traces to 400 ppm (Aubert and Pinta, 1977).

## 2.2. MINING ACTIVITIES AS A SOURCE OF HEAVY METAL CONTAMINATION IN SOIL

### United Kingdom

A comprehensive investigation of soils in Wales, where soils are polluted by appreciable quantities of Pb originating from Pb mining in the nineteenth century, was done by Alloway and Davies (Alloway and Davies, 1971). They found that alluvial soil in the Ystwyth river valley contained 90 ppm to 2,900 ppm (mean 1,419 ppm), whereas in neighboring control valley, the soil lead concentration varied from 24 ppm to 56 ppm (mean 42 ppm). Davies and Roberts (1975) published computer-drawn Pb isoline maps for an area in northeast Wales and calculated that there are 171 km<sup>2</sup> of land containing more than 100 ppm Pb in soil and 47 km<sup>2</sup> of soils with Pb contents ranging from 1,000 ppm to 10,000 ppm. A similar approach was used in a baseline survey in Missouri, USA (Davies and Wixson, 1985). The maximum soil Pb concentration was found to be 2,200 ppm, but 95 % of the samples contained less than 355 ppm. There is a strong association between concentrations larger than 355 ppm and old mine workings, dressing floors and railway ore loading places.

Coulbourn and Thornton (1978) found high concentrations of Pb in agricultural soil of the Peak District of Derbyshire. Within 100 m of an old smelter they reported mean soil Pb of 30,900 ppm, and within 100 m of an old ore washing floor a mean of 19,400 ppm.

### Korea

The extent of heavy metal pollution in agricultural soil near the abandoned mine land sites was investigated in mid-eastern Korea by Kim and Kim (1996). The

mean data for the metal concentrations (ppm) were as follows: 15.06±20.80 (Pb), 12.40±16.23 (Zn), 9.28±12.92 (Cu), 1.12±1.1 (As), 0.68±1.54 (Cd) 0.17±0.20 (Hg). The total number of analyzed samples is 65 for each metal. Their mean metal contents in soils, when compared to those measured previously from background agricultural soil in Korea, were found to be enriched by approximately 1.2 (As) to 8.0 (Hg) times. According to the analysis of inter-element relationships, a significant correlation was found between Pb and Cd. The pollution level generally decreased exponentially with increasing distance from the source.

#### **Case study in the southern Massif Central in France (Timsit and Lecomte, 1992)**

The case study of soil contamination from mining activity was carried out in an area situated in the southern Massif Central of France, in a rocky region with steep hills. The first mining activity in the area dates from the 12<sup>th</sup> century and the ore body was mined up to 1983. The soil survey data cover a long period from 1964 until 1990 through three investigation stages. Table 2.2 shows these systematic Pb and Zn survey data.

The authors of the research work reported that the region had a high potential in heavy metal mineralization and regional geochemical background values are high with average contents of 240 ppm Zn and 120 ppm of Pb. Numerous surface anomalies indicate mineral occurrence and the maxima are 6000 ppm for Zn and 2500 ppm for Pb. A large Pb-Zn anomaly existed before the start of mining in the soils of the studied site, which corresponded to the surface signature of the main ore body, with mean values of 690 ppm Zn and 110 ppm Pb. At this site the authors suggested

that the soil could be considered as "naturally contaminated" by Pb-Zn mineralization. At the present time the area downstream of the mining site shows very high Pb values (average 385 ppm, maximum 2,700 ppm) detected in the soils of the valleys, which can be considered as polluted. Comparing these values to those of the natural ore body, from which metals were leached and deposited downstream, it is also clear that a part of the budget is the consequence of mining either recently or earlier.

Table 2.2. Pb and Zn distribution in the area of southern Massif Central in France

Investigation stage	Characteristics	Mean content of Pb(ppm)	Mean content of Zn (ppm)
First prospect 1964	Regular grid 50 x 50 m	110	690
National inventory geochemical survey 1984	Systematic regional sampling 3 samples/km <sup>2</sup>	120	240
Environmental study 1988-1990	Mining area	400	385
	Local background	170	200

**Case study of soil lead distribution in an abandoned smelter in Socorro, New Mexico (Haneberg et al., 1993)**

Lead-bearing carbonates from the nearby Magdalena district were the major source of material when the Socorro smelter began operation in 1882. The complex grew to include three furnaces with a capacity of 227,000 kg/day, and operated until financial difficulties forced closure in 1894. Contamination assessment work at the smelter area estimated that smelter waste exceeded  $3 \times 10^8$  kg, and elevated concentrations of As, Cu, Pb, Hg and Zn were reported. The background level for soil Pb was estimated to be between 20 and 70 ppm. An emergency removal order was issued by the EPA in June 1990, and soil in excess of the EPA action level of 500-1,000 ppm total Pb has since been removed. Soil Pb concentrations from three 30.5 m x 30.5 m squares at an abandoned smelter site in Socorro, were determined by the Bureau of Mines and Mineral Resources (Bureau) in order to compare with the Pb values obtained by the US. Environmental Protection Agency. Results agreed within several hundred ppm. The soil Pb levels range from 400 ppm to 7,200 ppm. The analysis showed that differences between average analytical results for soil Pb obtained by EPA and the Bureau, were statistically insignificant. The obtained data were used for designing the appropriate remedial strategy for a given site. One common treatment was to simply excavate areas with mean value greater than 500 ppm, bury the soil somewhere else, and regrade the land surface. Based on data of the EPA and the Bureau the authors suggested the mean values could be reduced below the 500 ppm action level by removing somewhere between 50-100 % of the soil in squares with average values between 500 and 1,000 ppm.

### 2.3 DISTRIBUTION OF HEAVY METALS IN SOIL PROFILE- SURFACE ENRICHMENT

There are many factors separately or jointly influencing the distribution of heavy metals in soil. They may be straightforward weathering, leaching of soluble constituents, variable water table, plant extraction, surface enrichment, size sorting with clay movement down the profile and possibly also effects of microbiological activity.

The surface layers of most Scottish soils studied have a significantly higher Pb content than the underlying layers. The same situation also has been reported in England (Firman, 1995). Many researchers have deduced that among heavy metals, Pb tends to show a highest surface enrichment.

Lead appears to be accumulated naturally in surface horizons of soil. Alloway (1995) reported after Wright et al. that Pb showed the greatest proportional accumulation in the surface horizon of soil in eastern Canada. Colbourn and Thornton (1978) used the top soil enrichment ratio (concentration of heavy metal in top soil/concentration of heavy metal in subsoil) to assess the surface enrichment characteristic of heavy metal. In normal agricultural areas of the UK, this ratio of Pb ranged from 1.2 to 2.0, whereas in locations affected by mining, values between 2 and 20 were common.

According to Alloway (1995) there is a little evidence that Pb is readily lost from soil profile by leaching. Most heavy metals, including Pb, remain in an insoluble or stable form in surface layers after application of sewage sludge. The scientists demonstrated that soils have rather large capacities for the immobilization of Pb, that

the organic fraction was largely responsible for the observed fixation of the metal, and in the case of vehicle exhausts, Pb tends to remain near the soil surface. Research data lead to the objective of finding methods to reduce the Pb content of surface soils and thereby reduce the amount of Pb available for direct ingestion by children. For an effective treatment soil pH had to be reduced to 2.5-3 by leaching with HCl or by applying solid or dissolved FeCl<sub>3</sub> to the soil surface.

#### 2.4 GUIDELINE FOR HEAVY METAL LEVEL IN SOIL

No regulatory guidelines exist for contamination of soil, vegetation and many other essential components that allow an ecosystem to function. This presents a problem in making decisions as to what levels of pollutants found in this medium are acceptable. Most environmental guidelines are developed using acute toxicity testing, particularly for aquatic environments, and are used to assess intermediate conditions (Pilgrim and Hughes, 1994). However, to adequately interpret the present data, a more comprehensive understanding of the long term effects and ultimate fate of these metals in the ecosystem and biota is needed.

In Thailand as well as in almost of the other developing countries, there are detailed water quality standards and regulations, but the standards or regulations for assessment of soil contamination are still lacking.

The most well known guidelines for assessing soil contamination are that from the Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL) of the UK Department of Environment and that from the Netherlands



Housing Ministry. These guidelines, applied for Pb and Zn, are listed in Table 2.2 and Table 2.3.

Another set of so-called non-regulatory guidelines, which are used in some regions of other countries such as Canada or France, are also used for assessment of heavy metal contamination in soil, plants, water etc. The Ontario Ministry of Environment (1989) has developed non-regulatory guidelines, referred to as "Upper Limits of Normal" (ULN). These guidelines are expected maximum concentrations of metals found in vegetation, soil, snow and other environmental media in rural and urban areas of Ontario that are not directly influenced by a major point source.

Table 2.2. UK Department of the Environment ICRCCL "trigger" concentration for metals in contaminated land

Metal	Classification as	Threshold trigger concentration (ppm)
Pb	Contaminant which poses a hazard to human health	500
Zn	Phytotoxic contaminant not normally hazardous to human health	300

Table 2.3 Guide values and quality standards used in the Netherlands for assessing soil contamination.

Metal	Reference (A) value	Intervention (C) value
Pb	85	530
Zn	140	720

\* A = Reference value based on concentration found in natural reserves where the only contamination is from atmospheric deposition.

C = Intervention values where the soil must be cleaned-up

Ref. Netherlands Ministry of Housing, Physical Planning and Environment, *Environmental Quality Standards for Soil and Water*, Netherlands Ministry of Housing, Physical Planning and Environment, Leidschendam, Netherlands, 1991.

Concentrations of metals that exceed the ULN guidelines are not necessarily toxic to plants, animals or people. However, these guidelines are useful as background benchmark and are also an excellent start towards a national set of ecosystem or multi-media guidelines that can be used in risk assessment.

The non-regulatory guidelines as well as ULN can be a useful tool for risk assessment in the countries where the complete national standards are not yet available. It will play an important role in the setting up of national guidelines.

## 2.5 PLANTS AS MONITORS OF SOIL CONTAMINATION

One way by which heavy metals enter the plants from the soil is via roots. The metal content in plant tissues presents a picture of a plant's soil environment through time. For assessing of the potential of plants for monitoring heavy metal

contamination of the environment it is necessary to understand the processes that are involved in metal uptake by plants from soil.

In broad terms there is a positive relationship between the concentration of heavy metals in soil and that in plants. There is also general agreement that only a small proportion of the Pb in soil is available for uptake by plants (Alloway, 1995).

Walker (1975) pointed out that although lead concentrations exceeding 10 ppm in soil were normally toxic to plants, certain strains that could tolerate them exist in old mining areas. Specimens of the grass, *Agrostis tenuis*, taken from such sites showed resistance not only to lead, but also to copper, zinc, nickel. Tolerance to lead is often associated with tolerance to other heavy metals.

#### **2.5.1 Concentration differences at biological levels**

In biomonitoring studies, the use of tree leaves has been favored with the correct assumption that they can be obtained high above the ground, not subjected to soil contamination and splashing (Martin and Coughtrey, 1982)

A lot of plant species can hyperaccumulate an element in particular, i.e., accumulate more than 1,000  $\mu\text{g}$  element/ g dry weight (Ernst, 1994). As an example, the concentration of lead in leaves is low in most plants (1  $\mu\text{g}$  element/ g dry weight) but it can increase above 10,000  $\mu\text{g}$  element/ g, as in leaves of *Munuartia verna* growing on ore outcrops (Ernst, 1994). Taxon-specific accumulation is well known for several elements such as zinc in the families of *Betulaceas* and *Salicaceae* or nickel in the taxon *Alyssumn*.

In two aspects, the inhomogeneous distribution of elements in the different organs of a single plant is very important for vascular plants. Firstly, the analysis of

organs may give valuable information about the degree of exposure and the way of pollutants entering the plant. Secondly, on this basis the most suitable "critical" organ of a plant may be defined for use in monitoring studies.

Martin and Coughtrey (1982) discussed that the concentration of Cd was higher in the leaves of *Corylus avellana*, but that of Pb is significantly higher in the twigs while Zn and Cu were evenly distributed.

Investigating distribution between organs within different vascular plants from a birch forest area near a Cu smelter, Lobersli and Steinnes (1988) proved that *Betula pubescens* is a good indicator of environmental pollution. Cu and Zn in the leaves and Cu, Zn, Cd and Pb in the twigs were decreasing with the distance from a smelter.

Another study of *Betula* species conducted by Djingova and Kuleff (1994) demonstrated higher concentration of Co, Ga and Au in the leaves and of As, Bi, Sb and La in the twigs and even distribution of Cd and Fe.

Thus it seems that Pb, and probably As and Sb, are located in the twigs of deciduous trees and shrubs while there is strong evidence that U, Co and Cd are found in higher concentration in leaves, irrespective of the type of pollution.

With grasses and herbage, the investigations of different organs concern the distribution of elements in roots, stems, leaves and seeds. Thornton (1983) studied the influence of soils heavily contaminated with Cd and Zn found highest concentrations in the roots, stalk, leaves, calyx, petals, capsules and head and established highest values of P, Na, Ca, Mg, Mn and Zn in the leaves, of P and N in the seeds and only Fe in the roots.

The investigations of herbage are mainly directed towards studying the distribution between roots and aerial parts, aiming to discover the ways pollutants are entering the plant.

In this respect the pot experiments of Aspiazu and Romero (1986) with *Lolium multiflorum* grown on fertile soil with different additions of heavy metals are very interesting. They proved that using smaller additions, all elements (Zn, Co, Cd, As, Pb) were accumulated in the root, but with higher additions, the uptake at the top increased and except for Pb and Cu, the elements were translocated and stored in the above-ground parts.

Analyzing several weed species collected near the Metallochimia Factory (near Budapest) Kovacs et al. (1993) established highest concentration of Zn in the leaves and of As and Pb in the roots of *Ambrosia elatior*, *Atriplex tatarica* and *Convolvulus arvensis*. The concentrations of Cd and Ni generally were similar in leaves. In the case of *Lolium perenne* roots accumulated Cd, Cr, Cu, Fe, Pb and Zn. The presented accumulation capacities of the investigated weed species proved that the root systems of *Lolium perenne*, *Plantago lanceolata* and *Taraxacum officinale* were very effective accumulators of heavy metals.

The results of the different authors concerning distribution in herbage lead to the more general conclusion that at normal levels, or in slightly polluted areas, most of the heavy metals are accumulated in roots, through the above-ground parts also react to the pollution.

### 2.5.2 Seasonal variation in the heavy metal content of plants

When soil contamination is severe and toxic heavy metals reach above-ground parts of plants via root absorption, some degree of seasonal variation in metal content can be expected.

Seasonal changes in the elemental contents of deciduous trees and shrubs have been an object of investigation in a number of papers. Markert (1989) established differences of up to 159 % within two months for Mg, Ca, Sr, Ba and Zn in *Vaccinium myrtillus*. In many cases, however, such drastic changes have not been observed. Capannesi et al. (1993) concluded that the seasonal changes of Pb in *Quercus ilex* as well as of Eu, Sb, As and Hg were far less important than site by site variations. Most of the results from the studies of the seasonal behavior of heavy metals (Pb, Cd, Cu, Fe, etc.) in *Malus pumila*, *Pyrus communis*, *Prunus cerasifera*, *Aesculus hyppocastanum*, *Celtis orientalis*, *Tilia tomentosa* and *Populus nigra*, lead to the assumption that in the case of deciduous trees in the temperate northern hemisphere, heavy metals increase with the season from May to October reaching maximum concentrations before leaf fall (Djingova and Kuleff, 1994). There are some contradictory results for specific elements and/ or species but generally maximum is detected in September - October and a possible minimum during the preceding summer months.

The investigation of grasses proves a quite different behavior. Thornton (1983), Martin and Coughtrey (1982) established lowest concentration of heavy metals in pasture herbage and grass species in spring and highest in winter.

As is apparent from the foregoing discussion, seasonal variation in metal concentrations of plants may not be restricted to grossly contaminated sites. It has also been observed in sites affected by sewage sludge and other agricultural applications of heavy metals such as zinc and copper. In comparison with a reviews from previous studies the data from these conditions are sometimes still conflicting (Martin and Coughtrey, 1982).

Thus in the general case of monitoring heavy metal pollution using vascular plants in temperate climates, it seems that sampling of common pasture grass should be performed in winter, of deciduous trees in early autumn, while for non-grass herbage spring is also possible. With conifers cumulative effects over the years may be expected.

These final conclusions made on the basis of the reviewed literature, are correct but an additional question should be posed. Is it possible to standardize the exact period of sampling in the case of comparative studies, including regions with various altitudes and latitudes. Due to climatic variations, differences in the stage of development of the plants are to be expected. This question is directly connected with the proper organization of global monitoring studies using vascular plants.

## **2.6. ATOMIC ABSORPTION SPECTROMETRY (AAS) FOR THE ANALYSIS OF SOLUTIONS**

Atomic absorption spectrometry makes use of the fact that the atom of an element absorbs light at a wavelength which is characteristic of that element and determined by its outer electronic structure. The extent of that absorption is a measure

of the number of atoms in the light path. As illustrated in Figure 2.1 an atomic absorption spectrometer requires:

- A source of light, A;
- An energy source such as a flame to decompose the samples into its constituent atoms, i.e. a flame atomizer, B;
- A monochromator, C, to isolate the required wavelength;
- A photomultiplier detector, D;
- The readout device, E;

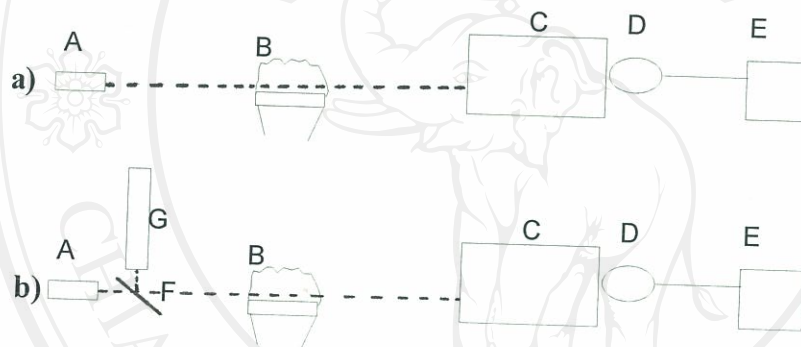


Figure 2.1. Schematic diagram of flame atomic absorption instrumentation.

- a) A: the hollow cathode lamp; B: the flame atomizer; C: the monochromator; D: Detector; E: the read out device.
- b) The deuterium background correction lamp G and the beam combiner F.

The light source, A, is usually a hollow cathode discharge lamp (HCL), whose cathode is composed of the element to be determined, but, exceptionally, can be an electrodeless discharge lamp excited in a microwave cavity for elements as As, Sb or Se or a metal vapor discharge lamp for mercury or alkali metals. All employ the element to be determined as the source of the spectrum emitted. The light emitted is thus the characteristic spectrum of that analyte, Pb, for example. The light is passed



through the flame, B, into which a fine mist or aerosol of the sample solution is sprayed by pneumatic nebuliser. The flame desolvates the sample mist and decomposes the resulting droplets into atoms of the analyte, Pb. The Pb atoms in the flame absorb the Pb spectral radiation at a characteristic wavelength isolated by the monochromator, C, and the decrease in the amount of light reaching the detector when sample atoms are present in the flame is a measure of the concentration Pb atoms.

Thus

$$\text{Absorbance} = \log(I_0 / I_T) = k c$$

where -  $I_0$  is the intensity of the incident beam;

-  $I_T$  is the intensity of the transmitted beam;

-  $c$  is the concentration of atoms in the atomizer;

-  $k$  is a constant.

The linear relationship between the measured absorbance and the concentration of analyte atoms in the flame, which is proportional to the concentration of atoms in the sample solution, holds in practice over some two orders of magnitude. The precise relationship between absorbance and solution concentration of the analyte is established by analyzing a series of standard solutions with known analyte concentrations covering the range required or, in some cases, by the method of standard addition.

#### Background correction systems

In AAS, part of the signal arises from molecular absorption and a further part is caused by scattering. Light from the hollow cathode lamp can be scattered out of the

path to the monochromator by particulate species such as aerosol droplets and clotlets in flame AAS.

The most common method of background correction makes use of a continuum light source such as a hydrogen or deuterium lamp to measure the background absorption. One instrument layout in Figure 2.1b illustrates the use of alternate measurements of total absorption using the hollow cathode lamp (A) and background absorption by using the deuterium lamp (G). Instrument subtraction of the two signals provides a background-corrected atomic absorption signal. The intensity of deuterium and hydrogen lamps falls off above about 300 nm. At wavelength above 350 nm they are ineffective, and barium filament lamps was used. The G lamp on the instrument at the Geology Department-Chiang Mai University, works at 553.6 nm (barium). Above this wavelength, however, scattering losses are usually small but molecular absorption effects still occur.