CHAPTER II

REVIEW OF LITERATURE

2. 1 Properties of Lead

Lead is a heavy metal in group IVA of the Periodic Table which has an atomic number of 82 and atomic mass of 207.2. Regarding physical properties, lead (Pb) is flexible, malleable, easily melted, cast rolled and extruded. Its color ranges from bluish-white, silvery to grayish. Lead can slightly dissolve in water but fairly rapidly dissolves in nitric acid and hot sulfuric acid. The density of lead is 11.34 g/cm^3 and its melting and its boiling points are 327.4°C and 1740 °C respectively (Windholz, 1976).

2.2 Sources of Lead

There are many ways by which lead can enter the environment. These sources might come from primary to secondary smelting operation; fabricating process- as a result of ways in which it is used; in the combustion of coal and other natural products and in the disposal of discarded and unwanted materials incorporating lead products (Hepple, 1971). Specifically, the most common sources of lead in soil are as follows:

a). *Parent Material* - The parent geological material from which soils are derived. The mean level of lead in an unpolluted soil approximates the concentration in the Earth's upper lithosphere.

b). *Dry and wet deposition of airborne lead.* This lead arises from vehicular emission and exists in the air in a particulate form. Lead emitted from vehicles is transported in aerosols to a certain distance depending on the particle size and the meteorological conditions of the area. Lead is added to gasoline because this is the most convenient and economic method of increasing the octane ratings of all grades of gasoline. In particular, Pb is usually responsible in obtaining the final six to eight octane numbers in the high grade petrol on which development of high compression engines has been based.

As stated by Lauther and Commins (1971) of the 9000 tons of lead at present being added to petrol in the UK, about a quarter was retained in the motor car itself in the exhaust system, the engine oil and filter. The rest of the lead is discharged in the exhaust with the gaseous products of combustion, the lead itself, being mainly in a form of fine particles of lead compounds, which contribute 1/3 by weight of the solids in the exhaust. Half the lead containing particulate matter falls to the ground within few hundred feet of roadways and is then washed away and dispersed in soil and drains. Fine particles are dispersed in the atmosphere and may be carried considerable distances by air movements before they are eventually dispersed.

c). *Disposal of Unwanted materials incorporating lead products*- Lead for batteries is one of the major uses which are normally used for motors, cars, electric vehicle trucks and other appliances . When worn out, these are usually improperly disposed leading to incorporation of lead into the soil..

d). *Disposal of Sewage sludge to land* - Spreading of sludge on land is a common agricultural practices are common practice. However, lead is typically incorporated in the sewage sludge which causes contamination of soil.

2.3 Lead Concentration in Soil

Lead is a constituent of the earth's crust. It has always been present in soils, rivers, lakes and seas; and in the air following the burning of wood and coal and plants, both edible and inedible. As indicated, the mean concentration of lead in unpolluted soil relates closely to concentrations in the parent geological material. Consequently, in non-mineralized areas (most areas in practice) concentration of lead ranges from 2 - 200 mg/kg with most samples being in the range 5 to 25 mg/kg (US Geological Survey, 1976).

However, due to widespread lead pollution, most soils are likely to be enriched in this metal, especially in the top horizon. There is much data available in the literature on soil Pb, but sometimes it is difficult to separate the data for the background Pb levels in soils from those that anthropologically influenced the amounts of Pb in surface soil (Kabata-Pendias and Pendias, 1984). However, they stated that for the natural Pb occurrence on top horizon of different soils from various countries show that the amounts ranges from 3 to 189 ppm, while mean values for soil types range from 10 to 67 ppm and an average of 32 ppm. High Pb levels (above 100 ppm) have been reported only in Denmark, Japan , Great Britain and Ireland and most probably reflects the impact of pollution. Davies (1980) stated that an upper limit of Pb content of a normal soil could be established as 70 ppm. Furthermore, it is stated that surface soil of US averages 20 ppm. Therefore, the anthropological mean Pb concentration in the world scale could be estimated as 25 ppm (Kabata-Pendias and Pendias, 1984)

2.4 Lead as Trace Element

Among all chemical contaminants, trace elements are believed to be of specific ecological, biological or health significance. These are elements which are not precisely defined since trace elements refers to those elements whose terrestrial abundance is low (most often below 0.1%) as well as those which occur in living matter only in trace amounts. They are also called microelements and when they are essential to vital processes, they are called as micronutrients Lead is considered as one of the listed most hazardous trace metals in the biosphere together with Ag, Au, Cd, Cr, Hg, Mn, Sb, W, and Zn. Likewise, have also great risk to the environmental health together with other chemicals such as Be, Cd, Cr, Cu, Hg, Se, V, and Zn (Kabata Pendias and Pendias, 1984)

2.5 Soil Contamination of Lead

The atmospheric deposition of trace elements, mainly heavy metals contributes to contamination of all other components of the biosphere e.g. water, soils and vegetation. Airborne lead is progressively removed from the atmosphere by wet and dry deposition processes causing contamination of other environmental media. This wet and dry deposition of lead had been widely reviewed ; especially by Ruhling & Tyler (1969), Folkeson (1979) and Thomas (1979) through a research conducted using mosses and lichens as bioindicators because these organisms are the most sensitive to atmospheric pollution of trace metals, although sensitivity varies decidedly among species.

Since soils are strong accumulators of lead, the analysis of lead in soil is an excellent indicator of accumulated deposition in the vicinity of a source of metal. Soil contamination with heavy metals is usually quite permanent, as has been reported by Davies (1980), Johnson et. al. (1975), Purves (1977) and Kitagishi & Yamane (1981). Therefore, it is necessary to emphasize that a soil heavily contaminated, especially by trace metals, is likely to be the sink of these contaminants resulting in degradation of biological and chemical properties of the soil. These metals are usually depleted slowly by leaching, plant uptake, erosion and deflation. The first half-life for heavy metals like lead is 740 to 5900 years as calculated by Iimura et. al. (1977) for soil in lysimetric conditions.

There are several indications that the composition of surface soil may be influenced by both local contamination and long- range transport of pollutants, Purves (1977) concluded that the extent of soil contamination in the urban environment is now so great that it is possible to identify most soils as urban or rural on the basis of their contents of few trace metals that are known to be general urban contaminants. The regional contamination of soils as reported most commonly, occurs mainly in industrial regions and within centers of large settlements with factories, motor vehicles and municipal waters which are the most important sources of these trace elements.

2.6 Lead as Pollutant

It had been well known for long time that lead is toxic in some of its forms. There have been many serious suggestions that with the increasing quantities of leaded gasoline/petrol being used, the concentration of lead in the general atmosphere of large towns might have risen to the point that it contributed a public health hazard as stated by

Lauther, et.al., (1971). Lead is not readily taken up and translocated by plants and hence elevated levels of lead in soil will have little effect upon the content of the plants(normally about 3 mg/kg) dry weight. and secondly lead does not produce toxic effects upon plant growth (Harrison and Parker, 1977)

One of the environmental problems that relates to the quantitative accumulation of metals is contamination of plant parts used as food. Soil contaminated with heavy metals like lead can produce apparently normal crops that may be unsafe for human and animal consumption as stated by Kabata-Pendias and Pendias (1984). Kloke (1979) calculated that if the content of lead and other heavy metals like Cd and Hg in the soil is higher than the threshold values, it can be expected that the content of these metals in human diet will exceed the weekly tolerable intake established by FAO/WHO.

The awareness of these problems and their effects on health and well-being or organisms, including man, coincided with the development of the technical means to investigate geochemical properties and relationships more thoroughly and economically in respect to industrial emission, agricultural practices and general environmental conditions.

2.7 Chemistry of Lead

Lead is added to the gasoline as the organic tetralkyllead additives tetramethyllead (TML), tetraethyllead (TEL)and mixed alkyls triethylmethyllead, diethyldimethyllead and ethyltrimethyl lead. The organic tetraalkyllead compounds are volatile and exist in the air in vapor phase, whilst the inorganic salts are emitted as particles. These TML and TEL compounds occur in atmosphere at levels ranging from 5 - 200 ng/m^3. Lead mainly occurs as PbBrCl in fresh exhaust particles (Ewers and Schlipkoter , 1991). As stated by Hepple (1971a), there is no Pb addition in diesel, kerosene (paraffin) or fuel oil.

Lead added to the soil , may react with available soil anions such as $SO_4^{2-}PO_4^{3-}$ or CO_3^{2-} to form sparingly soluble salts (Laxen and Harrison, 1977). Compounds such as basic lead carbonate, $Pb_3(OH_2(CO_3)_2$ (log Ks= -46.8 at 25°C) and pyromorphite-group minerals are formed at near neutral pH. In fact, powder diffraction (XRD) studies by Olsen and Skogerboe (1975), have shown the more soluble $PbSO_4$ to be the major crystalline lead compound in contaminated soil.

Pb had highly chalcophilic properties and thus its primary form in the natural state is galena (PbS). Pb mainly occurs a Pb^{2+} , although its oxidation state , +4, is also known and it forms several other minerals which are quite insoluble in natural waters. During weathering Pb sulfides slowly oxidize and have the ability to form carbonates and also to be incorporated in clay minerals, in Fe and Mn oxides, and in organic matter. The geochemical characteristics of Pb^{2+} somewhat resemble those of the divalent alkaline-earth group of metals. Thus, Pb has the ability to replace, Ba, Sr, and even Ca. , both in minerals and in sorption sites (Kabata-Pendias and Pendias, 1984)

2.8 Analytical Method by AAS

There are many methods by which lead in the environment could be determined. However, Atomic Absorption Spectroscopy (AAS) is one of the simplest and is used for the analysis of a large variety of materials containing from trace elements (ppm) to major (> 1%) inorganic constituents (Ure, 1991). These include agricultural and biological samples, geological samples, petroleum products, glass and its raw materials, cement, ferrous materials, alloys, water and air.

Basically, AAS refers to the absorption of energy from light source, with a consequent decrease in the radiant power transmitted through the flame. AAS makes use of the fact that the free atoms of an element absorb light at wavelengths characteristics of that element and that the extent of the absorption is a measure of the concentration of these atoms in the light path. A hollow-cathode discharge lamp, whose cathode made of the element (Pb for example) that is to be determined, is used .

It emits a spectrum characteristic of the cathode element (Pb). The production of the atoms from the chemical compounds requires a source of energy such as a flame that can vaporize and dissociate the sample compounds into a gaseous elemental state in which atomic absorption of radiation takes place.

The analytical application of AAS generally involves obtaining the sample in an appropriate solution for measurement and calibrating the instrument properly. Frequently, the releasing agents will have been added or a solvent extraction will be required to concentrate the element and increase the sensitivity. The standard should be treated in the same manner .

Instruments can be calibrated by preparing standard solutions over the concentration range of interest and measuring the absorption or emission of these under the same conditions as sample measurements. At least one standard should be run in each set of samples to determine any correction that should be applied to the calibration curve because the variables of flame stoichiometry, aspiration rate and the positioning of the burner are difficult to reproduce precisely (Harrison and Laxen, 1977).

The method of analysis selected will depend upon the degree of pollution of the soil or sediment. In unpolluted and scarcely polluted soils and sediment a substantial proportion of the lead is firmly bound in the silicate lattices of refractory minerals and can only be released by the use of hydrofluoric acid. Hence Harrison and Laxen (1977) found HF/HNO_3 to be the most efficient of the range of reagents for extraction of lead from soils. In a heavily polluted soil, the major part of the lead is far more readily extracted and HNO_3 or HNO_3/HCl is of quite adequate efficiency. Soil is digested in the acid which is evaporated to dryness, causing oxidative decomposition of the organic material present. The digest is then leached with dilute acid and filtered to provide a sample for analysis. Some of the sediments contain a very high proportion of organic material which may necessitate the use of $HClO_4$ for complete oxidation. Due to the risk of explosion the use of the reagent is recommended only after prior digestion with HNO_3 until all HNO_3-oxidizable material is destroyed, and evaporation of $HClO_4$ to dryness is not advised. (Harrison and Laxen, 1977)

2.9 Factors of Lead Mobility in Soil

There are several mechanisms by which lead may be immobilized in soils. When incorporated in the soil, lead is of very low mobility. Hence, once contaminated, a soil is liable to remain polluted with lead. This might have adverse consequences for soil fertility if the degree of contamination is great. Factors such as low cation exchange capacity, low organic matter content and low pH cause enhanced lead mobility and hence, increased availability for uptake. Their degree of mobility, activity and bioavailability is influenced by many factors particularly pH, temperature, redox potential, CEC of solid phase, competition with other metal ions, composition and quantity of soil solution (Trangmar, et. al, 1985, Woperies et. al, 1988). Usually metals are present in soil as part of the parent material and soil of secondary origin; precipitated with other compounds in soil ; and the sorbed and exchange sites, metal oxides or hydroxides, clay mineral content and organic matter content which can serve as exchangers (Schmith and Sticher, 1991). The influence of these factors are specifically discussed below:

Organic Matter Content

Lead may be complexed by soil organic matter such as humic and fulvic acids which are themselves adsorbed onto soil solids. Flemming et. al. (1968) as cited by Kabata-Pendias and Pendias (1984) reported that the characteristic localization of Pb near the soil surface in most soil profiles is primarily related to the surfacial accumulation of organic matter. The greatest Pb concentration is also found in the organic top horizon of cultivated soil. In this case therefore, organic matter could be considered as one of the important sinks of Pb in polluted soil.

Furtheremore,Tyler (1971), Anderson (1976a), Doelman and Haanstra (1979) and Hughes et. al (1985) showed that accumulation of Pb in surface soil is of great ecological significance because this metal is known greatly to affect the biological activity of soils. The increased levels of lead are likely to inhibit the enzymatic activity of the microbiota and as a consequence, markedly increase the accumulation of incompletely decomposed soil organic matter particularly those materials that do not decompose readily like cellulose. The steadily increasing amounts of Pb in surface soils, both arable and uncultivated, have been reported for various terrestrial ecosystems. The accumulation of Pb in surface soil exposed to various pollution sources at some sites has already reached a value about 2% of the dry material (Kabata-Pendias and Pendias, 1984). They also reported that the levels of Pb in soils that are toxic to plants are not easy to evaluate, however, several authors have given quite similar concentrations, ranging from 100 to 500 ppm.

Furthermore, different soil types, plant species and growing conditions contribute to the divergent influences of soil contamination on trace element status in plants as cited by Kabata Pendias and Pendias (1984). Some authors use a term " soil resistance to heavy metal contamination" which is related to the critical levels of metallic pollutants that exhibit toxic effects on plants and environments. However, the recent report (Zimdahl and Skogerboe, 1977) concludes that the majority of lead immobilized in soil is associated with the organic matter content. High organic matter content of soil has a complex influence on the behavior of trace elements. Increased organic matter content in Pb-amended plots is due to enhanced preservation of stable humus. Perhaps because a newly formed Pb-organic complexes with the humic and pulvic acids are protected from microbial attack. (Zimdahl and Hassett, 1977). However, it is also evident that Pb complexes with low molecular weight humic substances were mobilized in the soil solution.

pH

The change in pH may play a significant role in the rate of availability of certain trace elements. Usually the resistance of non-acid heavy soil with a higher organic matter content exceeds several times the resistance of a light sandy acid soil. Loamy neutral soil may accumulate higher amount of trace elements with much less environmental risks. However, a general chemical imbalance of such soil usually results in decreased biological activity, decreased or increased pH and as a further consequence, degradation of organic and mineral sorption complexes.

In general, with the increasing pH, the capacity of the soils for most metal ions is increased and the mobility of the cations is decreased. The relative mobility, dependent on the pH of some trace elements in soils, has been investigated by Fuller (1977). Low pH dissolves lead and mobilizes them, increasing possibility for uptake by the flora and fauna and then increasing mobility of lead. (Smith and Sticher , 1991)

Soil Type

The grain size of soil will also play an important role in the organic matter content of the soil. Thus, in the above premises, the understanding of soil properties like soil textural type, in relation to Pb availability in soil could be a significant tool to assess environmental risks. As stated by Smith and Sticher (1991), the amount of metal adsorbed is dependent on the type of soil component. It appears that clay minerals adsorb far smaller quantities than other sorbents such as oxides and organic matter. Although Pb species can vary considerably from one soil type to another, it may be concluded from the results given by Norrish (1975), Riffaldi. et. al. (1976), Tidball (1976) and Schnitzer and Kerndorff (1981) that Pb is associated mainly with clay minerals, Mn Oxides, Fe and Al hydroxides and organic matter.

2.10 Risk Assessment of Lead by Lead Immobility Model

Risk assessment means "the measure of the probability of the magnitude of impairment, including death" (Esmen, 1984) at a specified level of exposure. In the context of standard setting and enforcement one can distinguish two types of risk assessment: (1) assessment of exposure effect/response relationships in order to produce basic data for standard setting and (2) assessment of whether the actual exposure exceeds exposure standards. In particular, there are internationally accepted standards where all of the assessment of risk of several factors is based. Say for example additives in food, lead threshold level and other standards , the limit of which are internationally agreed upon Acceptable Daily Intake (ADI), usually established by the WHO and the FAO on the basis of a reasonably adequate toxicological database The FAO/WHO (1972) established some provisional units for weekly intake of Pb, Hg, As. Cd. However, the documentation is still rather poor.

The threshold limit/values recommended by Sewage Sludge Regulation for Water Resources (DVWK, 1988) for the accumulation of lead in soil, will be the basis in the setting up of a standard for risk analysis. As stated by Ewers and Schlipkoter (1991), atmospheric lead deposited on soil is retained in the upper (2-5 cm) soil layers, especially when there is at least 5% organic matter and a pH of 5 or above. A high organic fraction and a high soil pH are the most important factors in immobilizing lead. In the GIS processes, many applications of GIS are in environmental modeling where GIS is used to process data or to make maps of input data or model results. The environmental modeling , as one of the scientific tools for this prediction and assessment , is also a well-established field of environmental research. As with all GIS applications, the needs of environmental modeling are best handled not by integrating all forms of geographic analysis into one GIS package, but by providing appropriate linkages and hooks to allow software components to act in a federation.. In the risk and hazard assessment , the linkage with GIS is frequently found, but the majority of cases, GIS and environmental models are not really integrated, they are just used together (Hunsaker et. al, 1993)

2.11 Risk Assessment Using GIS

One of the strongest and most successful application areas for GIS has been in addressing problems for the environment. GIS is a rapidly developing technology for handling, analyzing and modeling geographic information. It offers an integrated approach to data handling problems, which are often severe. The use of GIS in environmental risk assessment provides a framework to enable (1) quantitative basis for balancing and comparing risk associated with environmental hazards and (2) a systematic means of improving the estimation and understanding those risks.(Hunsaker et. al. ,1993) . The GIS have the ability to integrate spatial variables into risk assessment models. Maps are powerful visual tools to communicate risk information (Fedra, 1993).

The mapping of risks, as rather abstract concepts, makes it much easier to communicate. The data structure can be conceptualized as a set of " floating maps" with common registration, allowing the user to "look" down and across the stack of maps. The spatial relationships of the data can be summarized (database inquires) or manipulated (analytical processing). Such system can be formally characterized as internal reference (Berry, 1993). Furthermore, the GIS forms a "toolbox" for processing maps that embodies fundamental concepts and stimulates creative applications. This toolbox is a flexible as conventional mathematics in expressing the relationships among variables. But with a GIS, the variables are entire maps. (Berry, 1993) The map analysis toolbox helps resource managers to define and evaluate spatial considerations in land management. For example, a map of unusually high concentration of lead in soil can be generated from a set of soil sample data. These hazardous areas can then be combined with population data to determine the high risk areas. The map can also be used to identify the source of air pollution.

GIS on the other hand frequently allows geographic entities to have multiple attributes. It frequently includes capabilities for stirring and handling relationships between entities and includes the capabilities of digital cartography in its input and output subsystems (Goodchild, 1993) . They are tools to capture, manipulate , process and display spatial or geo-referenced data. They contain both geometry data (coordinates and topographical information) and attribute data, that is the information describing the properties of geometrical spatial objects such as points, lines and areas (Fedra, 1993). It is also a data integrator by which other useful preprocessing functions include the ability to extract information in a user-defined window; scale and projection change, including knowledge of such coordinate systems as UTM (Universal Transverse Mercator) and SPC (State Plane Coordinate) and capabilities for esampling.

As a principal medium for the summary and representation of risks/hazards posed by natural processes, the hazards/risks in the map portrayed in ordinal zones such as high, medium, and low values are the probability of occurrence of such hazards/risks in individual cells. These values could be formed into risk indices which involve the ranking or weighing by assigning values that indicate the relative suitability of the researchers rating. The maps or overlays of spatial information like lead concentration (ppm), soil pH, organic matter content and soil grain size could be a principal medium for summary and representation of hazards posed by natural process and the results of which are the risk assessment of the concerned area under study.