

EFFECT OF Pb POLLUTION ON SOILS AND CROPS

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EFFECT OF Pb POLLUTION ON SOILS AND CROPS



465273

**A Thesis Submitted to the
University of Dhaka
For the degree of
Master of Philosophy
In Department of Soil, Water and Environment**

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BY

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EFFECT OF Pb POLLUTION ON SOILS AND CROPS

I do hereby certify that the research work embodied in this thesis entitled “Effects of lead pollution on soils and crops” is the outcome of an original work and has been done by Mrs. Afroza Begum under my direct supervision. The laboratory research works have been done mostly in Department of Soil, water and Environment, University of Dhaka and Soil Science Discipline in Khulna University. I further declare that the dissertation meets the requirement and the standard for the degree of Master of Philosophy in Soil, Water and Environment.

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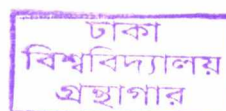


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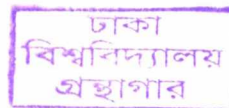
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Dedicated to
My Supervisor

Prof. Dr. S.M. Ullah
My Parents and Family
for
Inspiration and
Encouragement

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The Author

**WITH THE NAME OF
ALLAH THE MOST BENEFICIENT
AND THE MOST
MERCIFUL**

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ABSTRACT

An attempt was made to assess the levels of Pb and some other heavy metals in soils and plants influenced by motor vehicle exhausts along Dhaka- Manikganj- Khulna high ways. Thirty spots were selected from twelve different sites and at different distances along the highway. Soils and plants were collected from these sampling spots. Samples were analyzed for heavy metals particularly Pb, Cd, Zn, Cu and Mn. Other physical and chemical parameters were also determined to correlate the results.

Results obtained from the soil analyses showed a higher concentration of Pb (18.13ppm) and Zn (76.5ppm) at spots nearest to the highway but it decreased with increasing later distances from the highway. Other heavy metals were not found in toxic concentration except Mn.

In case of plants analysis it was observed that, accumulations of Pb and Cd were more in root than in shoot in grass and rice and more in shoot than root in arum and malancha. Among the plant parts, the highest Pb concentration was found in grass root (14.3ppm) and malancha shoot (10.57ppm). Highest cadmium concentration was found in grass root (0.65ppm) and in malancha shoot (0.82ppm).

Finally, it was observed that, Pb concentrations were more in plants than in soil. The soils and plants nearest to the highway were more contaminated than those away from the highway. Although roadside soils and plants in Bangladesh are not heavily polluted by heavy metals like developed countries, yet the possibility of Pb and Cd contamination of the food chain through motor vehicle exhausts can not be overlooked.

CHAPTER 1

INTRODUCTION

Plant and soil form an integrated system and technogenic contamination of soils is reflected in parts of plants. Soil contamination by heavy metals has several implications, not only for human health but also for many organisms. Economic activities introduce essential changes to the environmental system. These changes are noticed in large cities and urban landscapes by way of pollution. Heavy metals (HMs) represent one of the major environmental pollutants and contaminants of the soil. Evaluation of metal accumulation in soils and plants is of environmental importance due to their health effects on humans and other biota (Hadjiliadis, 1997).

Heavy metals are important environmental pollutants, particularly in areas with high anthropogenic pressure. Their presence in the atmosphere, soil and water, even in traces, can cause serious problems to all organisms. Heavy metal contamination of the environment is a serious concern for agricultural land, groundwater and ultimately for animal and human health.

A wide variety of contaminants enter into our environment due to extensive industrial production, energy and fuel production and intensive agriculture. Heavy metals are one of the most dangerous of these contaminants. Among heavy metals, lead is an element that is easily accumulated in soil and sediments. The level of Pb in the environment is currently of great concern. Although lead is not an essential element for plants, it is absorbed and accumulated (Kabata Pendias and Pendias, 1999; Kibria *et al.*, 2006, 2007).

Lead is one of the major heavy metals that has been known for ages and has gained considerable importance as a potent pollutant of the terrestrial and aquatic ecosystems. Besides natural weathering processes of geological materials and soils (Shea, 1996), the main sources of lead pollution are exhaust fumes of automobiles, chimneys of factories using lead, effluents from the

storage battery industry, mining, and smelting of iron ores, metal plating and finishing operations, fertilizers, pesticides and additives in pigments and gasoline (Erick *et al.*, 1999., Asamit, 1994., Dean *et al.*, 1972., Field and Lager, 1975). In urban areas automobile exhaust contributes substantially to the atmospheric pollution. Lead compounds are the major pollutants emitted by automobiles. Plants growing on highways are usually exposed to more lead than other localities. It has been predicted in Nigeria that at least 15,000 kg of lead is emitted into the environment through burning (Agbo, 1997). Hence automobile exhausts were believed to account for 80% of the air pollution. Lead is also available to plants from soil and aerosol sources. Plant roots have an ability to take up significant quantities of lead whilst simultaneously greatly restricting its translocation to above ground parts (Lane and Martin, 1977). The importance of this plant as a fodder not only for feeding of cattle but also other domesticated ruminants further prompts the interest in wanting to know the level of this metal in the plant tissue and in the soil where they grow. Moreover, leaded petrol is still in use in Bangladesh and a good number of commercial vehicles that ply the roads are not road worthy with high volume of exhaust released into the environment. Atmospheric deposition of lead has been reported as a major contributor to a lake sediment burden. The presence of lead and other heavy metals has been reported in soils and plants including leafy vegetables in Bangladesh (Gerzabek and Ullah, 1990).

Most edible crops are indiscriminate in their extraction of nutrients from the soil and thus will extract the non-desirable heavy metals along side the required essential nutrients. This may predispose the populace to heavy metals through the consumption of such agricultural products thereby serving as a point of entry of heavy metals into the food chain. Cadmium and lead are not known essential elements for crop plants. However, there are circumstantial evidences indicating that various plant species have the ability to absorb Cd and Pb by roots and translocate Cd and Pb from the roots to the shoots (Shute and Macfie 2006; Murakami *et al.*, 2007; Huang and Cunningham, 1996). Cadmium and

Pb are the most important pollutants with regard to their human-health effects via food chain contamination, as they are taken up and translocated to different plant parts where they can reach concentrations toxic to humans and animals (Florijin and Van Beusichem, 1993; Nordberg *et al.*, 1997). The Codex Alimentarius Commission, an international foods standards organization, has set a limit of $0.2 \text{ mg Cd kg}^{-1}$ in cereals and legumes for human consumption (Codex Alimentarius Commission, 2001). According to Joint FAO/WHO Food Standards Programme (2002), the maximum level of Pb in grain crops is 0.2 mg kg^{-1} . Therefore, minimizing the intake of Cd and Pb from food is an important health issue. For ecological safety and human health, Cd and Pb uptake by food crops needs to be understood in order to limit their accumulation in the food chain.

Soil physico-chemical properties such as texture, pH and organic matter play an important role in the solubility of Cd and Pb and thereby their availability to plants (Eriksson, 1990a; Eriksson *et al.*, 1996; Grant *et al.*, 1999; Adams *et al.*, 2004; Singh *et al.*, 1997; Kumar *et al.*, 1995; Basta and Tabatabai, 1992; Li and Shuman, 1996). Plant species and cultivars differ widely in their ability to absorb, accumulate and tolerate Pb (Kabata -Pendias, 2001; He *et al.*, 2006; Dunbar *et al.*, 2003; Huang and Cunningham, 1996; Romeiro *et al.*, 2006). Cadmium concentrations observed in plants are generally between $0.05\text{-}0.5 \text{ mg kg}^{-1}$ and the critical range for phytotoxicity is usually $5\text{-}10 \text{ mg kg}^{-1}$ dry matter (Sauberebeck, 1989).

The value set by several countries for consumption of leafy vegetables is 0.1 mg kg^{-1} fresh weight (Adriano, 2001). Normal Cd concentration values in plants of non polluted soils are between 0.1 and 1 mg Cd kg^{-1} of dry weight, while phytotoxic values are between 5 and $700 \text{ mg Cd kg}^{-1}$ of dry weight, depending on the plant and experimental conditions (Murillo *et al.*, 1999). The normal range and toxic levels of Cd in soil are from 0.1 to 2.4 and 5 to 30 mg kg^{-1} , respectively while the corresponding values for Pb are 5 to 10 and 30 to 300 mg kg^{-1} (Ashwathanarayana, 1999).

Vehicular traffic is the most widespread Pb sources, owing to the emissions from motor vehicle powered with leaded gasoline. Published results of several studies show Pb accumulation in crops, soils and spontaneous vegetation near the highways. Besides, Cd emitted as particulate matter by tyres appears to be a good tracer of proximal vehicular induced pollution (Daineset *et al.*, 1970; Lagerwerff and Specht, 1970; Kingston *et al.*, 1988; Page *et al.*, 1971; Quarles *et al.*, 1977).

Roadside is designated as disturbed environment, where the physiology and growth of plants often differ as compared to non road plants. Availability of water from road surface run-off has positive effects on roadside plants, particularly in arid and semiarid region (Frenkel, 1977).

There are about 3000 industrial units particularly in and around the cities of Bangladesh. Their wastes effluents contain organic toxins and heavy metals especially Cr, Zn, Pb, Cd Hg, Ni, As and Mn which pollute water system and agricultural lands. The Department of Environment of Bangladesh (DOE, 1991) has already identified 900 polluting industrial plants which do not have any treatment facilities for effluents and wastes and discharge highly toxic effluents directly to river waters. In addition, the 24,000 small and cottage industries in Bangladesh also causing pollution. Some of these metals are toxic to plants and some are toxic to both plants and animals (Page *et al.*, 1990; Roads *et al.*, 1989; Gerzabek and Ullah, 1990). Shamsad *et al.*, (1998) reported that Kawran Bazar is the most Pb polluted areas followed by Jatrabari and Motijheel Roads with higher automotive movement have higher concentration of total Pb level. Ali *et al.*, (1998) stated that Dhanmondi lake, which is located in densely populated central Dhaka, has been found to be heavily contaminated with Pb.

Heavy metal contamination in Bangladesh, particularly soil, has not yet reached a level for concern. Yet, heavy metal contamination of roadside soils

especially with lead through automobile exhausts is likely to become alarming in near future. The wastes and effluents from industries in the vicinity of big cities in Bangladesh contain organic toxins and heavy metals. These industrial contaminants increase heavy metal load in the surrounding agricultural soils (Joardar *et al.*, 2005). An oversupply of these contaminants produces toxic effect and might be lethal eventually to the organisms. These are very toxic because they are soluble in water and may be readily absorbed into living organisms (Kannan, 1997). Their uptake and accumulation in plants have been known to result in negative effects on plant growth (Breckle and Khale, 1992). It has been reported that Cd, Pb, Cu, Ni and Zn may interfere with the uptake and distribution of essential mineral nutrients in the plant (Trivedi and Erdei, 1992). These metals are taken up by plants and thereby enter into the food chain causing health hazards (Imamul Huq *et al.*, 2000). Metals are capable of causing significant damage to the environment and human health as a result of their potential to bioaccumulate and their ability to remobilize under changing land use regimes.

From the foregoing discussion, it is evident that considerable works have been done on the heavy metal contamination of soil and their uptake by plants by anthropogenic sources such as industrial operation and urbanization in most developed countries. However, there is paucity of information from developing countries like Bangladesh, and more so, relatively few studies have been reported on the heavy metal status of soils around Dhaka city (Ullah *et al.*, 1999; Kashem and Singh 1999; Kashem *et al.*, 2007). Most of the leaded gasoline driven vehicles were converted CNG (compressed natural gas) technology in Bangladesh. Hence, the assessment of lead contamination from automobile exhaust along roadsides in Bangladesh is of vital importance.

The interest in this study however lies in the soil as a source of lead and some other heavy metals for plants is heightened by the concern over airborne lead from automobile exhaust. The importance of this airborne source has been verified by the concentrations of lead in plants and soils along heavily traversed

highways. During the recent past, transportation by the highways has become the main means of communication. People living along the important highways of the country grow crops of various kinds in the depressions, basins and along the roadsides. Moreover, water-vegetables like malancha, aurum etc also grow naturally. There is a possibility of high level load of lead in plants growing along the expressway and potential danger to organisms that depend directly on the plant for food as well as to humans that eat the meat from these herbivores. Particularly, to the cattle that are either brought by herdsmen to feed on this plant growing along the expressway or those fed on the plant collected along the roadside highway in Dhaka-Manikganj- Khulna highways in Bangladesh. Keeping all these entire in mind, the present research work was undertaken with the following objectives:

- 1) To study the nutritional quality of soil and plant samples along Dhaka-Manikganj- Khulna highways as it varies specially as well as laterally away from the highway
- 2) To study the content of Pb and some other heavy metals (Cd, Zn, Cu and Mn) in soil at different distances laterally away from the highway to assess the level of contamination of soil by the above mentioned heavy metals
- 3) To evaluate the uptake or accumulation of the above mentioned heavy metals by plants (rice and some naturally growing roadside plants, ie, grass, aurum and malancha, etc.) to study the intensity of contamination at different distances laterally away from the highways
- 4) To evaluate the relationship among total heavy metals (Pb, Cd, Zn, Cu and Mn) and soil properties
- 5) To evaluate the relationship among total heavy metals in soil and different plant parts at different distances laterally away from the highway and
- 6) To study the effect of automobile exhausts on the nutritional status of soils and plants.

CHAPTER-2

RIVIEW OF LITERATURE

The present study included the dynamics of lead in soils contaminated by automobile exhausts along roadside in Dhaka-Manikgong-Khulna highways and their accumulation in some plants. Besides lead, some studies were also done on cadmium, zinc, copper and manganese. Pertinent literature is being reviewed below.

Many urban areas are being developed with growing industrialization and populations increase. This growth is due to different kinds of transport means. All transport vehicles emit different kinds of pollutants. Some of these are primary kinds having direct hazardous effects e.g., carbon monoxides, hydrocarbons, nitrogen oxide, particulate etc. Air pollution from motor vehicles in developing countries does not yet present a problem of the magnitude reached in highly developed countries. However, as urbanization and industrialization develop in these countries, the contribution to air pollution from motor vehicle emission could increase very rapidly (WHO, 1969).

Automobile pollution may be defined as pollution which includes air and noise pollution caused by a vehicular powered by either spark ignition or compression ignition of internal combustion engine or regenerating power to drive such vehicle by burning fuel (Galchhania, 1991). As urban area grows, so does the number of vehicles, which in turn means more pollution. Narrow roads, which were designed in pre-automobile age, poor geometric, congestion, formation of long queues at intersections and quite low speed, particularly near residential and shopping area aggravate the situation (Agarwal, 1991a).

Motor vehicles contaminate not only the air but also the soil environments by emitting the exhaust gases. The soil adjacent (within 100ft of the edge of the road) to major roads is thus polluted with heavy metals particularly Pb given

out along with gases from the automobile engines and Zn from tire wear burning (Williamson & Evans, 1973; Lussenhip, 1973 and Krzysztofiak, 1984).

2.1 POLLUTION: DEFINITION, TYPES, AND SOURCES

Definition

The term pollution is derived from a Latin word *polluere*, which means "to soil" or "to defile." Pollution may be defined as "an undesirable change in the physical, chemical, and biological characteristics of air, water and soil which effects human life, lives of his related other useful living plants and animals, industrial progress, living conditions and cultural assets"

Pollution is defined as the addition of (extraneous) materials to water, air or land, which adversely affect the natural quality of the environment. Pollutant is a substance, which may alter environmental constituents or cause pollution. A pollutant can also be defined as constituent in this wrong amount at the wrong place or at the wrong time (Shukla and Chandel, 1987).

Anything even beneficial substance in excessive amount can be a pollutant. A pollutant is something, which adversely interferes with health, comfort, amenities, property or environment of the people. Generally, most pollutants are introduced in the environment as sewage, waste, automobile exhausts, and accidental discharge or else they are by-products or residues from the production of something-useful (Misra and Dinesh, 1991).

Types of Pollution

There are many types of pollution such as air, soil, water, sound and nuclear pollution. Agricultural, industrial, environmental and residential land use, all produces residues and waste products. They pollute soil, air and water. These three are important component of the life support system. Soil pollution is associated mainly with the use of chemicals, such as fertilizers and growth

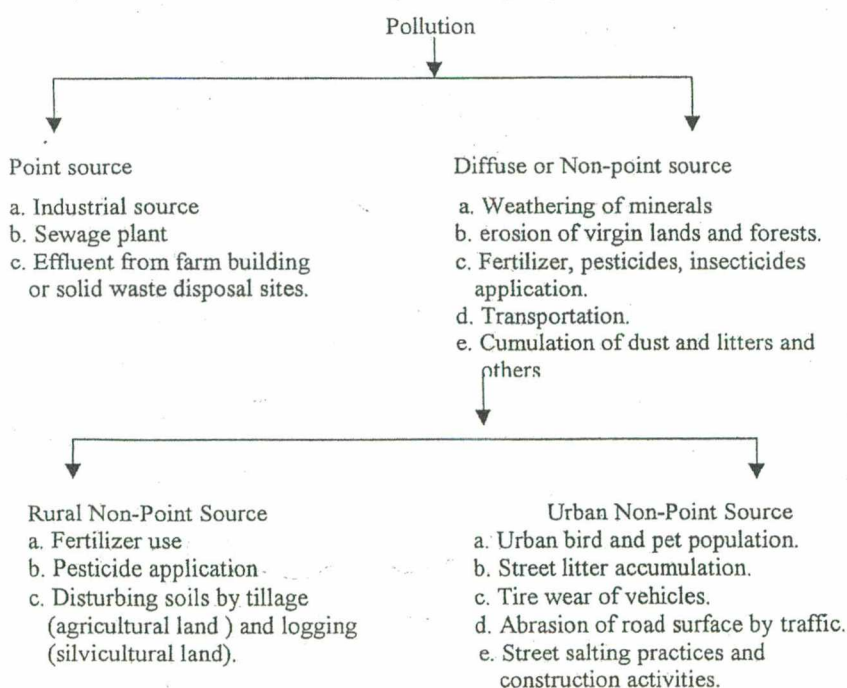
regulating agents in agriculture, by the dumping on land of large masses of waste materials from the mining of coal and minerals, by the dumping on land of domestic refuse and solids, particulate products from burning of automobiles, etc.

Air pollution is associated due to blasting, drilling, loading and conveying of coal in case of opencast mine. Industrial chimneys, power houses, burning of fuels, autoexhausts, etc. emit such pollutants into the atmosphere as suspended matters like smoke, dust and sprays, SO_2 , CO_2 , nitrogen oxides, fluorides and foul odor leading to air pollution in an around the quarry.

Many of the wastes of human society are disposed off in the bodies of water, rivers, lakes, oceans and some of the wastes are disposed off in air or land may eventually enter the water bodies. Water pollution by rainfall and by washing the soil surface, leaching the pollutants in water. By rainfall floating particles in air is precipitated into soil and water.

Sources of Pollution

Sources of pollution can be divided basically into two groups:



Sources: Misra and Dinesh, 1991.

2.2 HEAVY METAL POLLUTANTS: THEIR SOURCES AND DISTRIBUTION

Chemically, the metals have been classified variously, but biologically, the term heavy metal is used to denote certain category of metals, which are most deleterious ecologically. These heavy metals have a specific gravity of 4-5 times greater than that of water, and usually belong to atomic numbers 22-34; 40-52 and members of lanthanides and actinides of the periodic table (Murphy, 1981). "Heavy metals" are a group of metallic elements that exhibit certain chemical and electrical properties and are generally those having a density greater than 5 g/cm^3 (Forstner *et al.*, 1979). Most of the heavy metals are extremely toxic because, as ions or in certain compounds, they are soluble in water and may be readily absorbed into plants or animal tissue. After absorption, the metals tend to combine with biomolecules, such as proteins and nucleic acids, impairing their functions (Ming-Ho Yu, 2001). All heavy metals exist in surface water in colloidal, particulate and dissolved phases. The colloidal and particulate metal may be found in i) hydroxides, oxides, silicates and sulfides or ii) adsorbed to clay, silica or organic matter. The soluble forms are generally ions or unionized organometallic chelates or complexes. The solubility of trace metals in surface water is predominately controlled by the water pH, the type and concentration of ligands, on which the metal could be adsorbed, and the oxidation state of the mineral components and the redox environment of the system (Connell *et al.*, 1984).

SOURCES OF HEAVY METALS

The heavy metals are widely distributed in the environment, in soils, in plants and in animals. The concentrations of individual metal in living tissues are originally very low and must be maintained within narrow limits to permit the optimum biological performance of most organisms. Some heavy metals, namely Co, Cu, Fe, Mn, Mo and Zn are essential in trace amounts in plants and, in addition, Cr, Ni, and Sn for animals, whereas Cd, and Pb have been

shown not to be essential for either plants or animals (Greenland and Hayes, 1981). Practically, there are two major routes for input of trace elements into agro ecosystems: aerial (aerosols, particulate matter, re-suspended air borne dust etc.) and land application (fertilizers, pesticides, industrial wastes and effluents and other soil amendments). The output pathways can be represented primarily by losses through plant tissue removal for food, feed stuff and by leaching and erosion (Adriano, 1986).

The main sources of heavy metals are:

- Urban industrial aerosols created by combustion of fuels, metal ore Refining and other industrial process,
- Liquid and solid wastes from human and animals,
- Mining wastes, and
- Industrial and agricultural chemicals.

Although in some circumstances there are direct atmospheric inputs to plants, addition to the soil and subsequent transfer from soil to plants for most heavy metals is the major route of entry into the living tissues of plants, animals and human. Higher concentration of the metals in soils may raise the levels, which are toxic for plants and create animal and human health problems (Abadeen, 2002). Table-2.1 presents some major sources of heavy metals and other hazardous substances.

Table 2.1 : Some major sources of heavy metals and other hazardous substances (Schmidtke, 1981)

	Substances									
	As	Cd	Chlorinated Hydrocarbons	Cr	Cu	Pb	Hg	Misc ++ Organics	Se	Zn
Battery		*				*	*			*
Chemical			*	*	*		*	*		
Manufacturing			*			*	*		*	
Electrical and Electronics			*			*	*		*	
Electroplating and Metal Finishing		*		*	*					*
Explosive	*				*	*	*	*		
Leather				*				*		
Mining	*	*		*	*	*	*		*	*
Paint and Dye		*		*	*	*	*	*	*	
Pesticide	*		*			*	*	*		*
Petroleum and Coal	*		*	*		*				
Pharmaceutical	*					*				
Printing and Duplicating	*					*		*		
Pulp and Paper							*	*		
Rubber and Plastic					*	*	*	*		*
Textile				*	*			*		

++ => aerotein chloroplerin, diethysulfate, dinitrobenzene, dinitrophenol.

DISTRIBUTION OF HEAVY METALS IN SOIL AND PLANT

Heavy metals are present in all uncontaminated soils as the result of weathering from their parent materials. Heavy metals such as Cd, Cu, Ni, Pb, Zn etc. are found in soils at different concentrations. The distribution, availability and mobility of heavy metals in soil are influenced by various soil characteristics, soil composition and many other factors. Heavy metals are also found in plants. Trace metals or micronutrients, such as copper (Cu) and zinc (Zn) are regarded as being essential for plants. Recent evidence indicates that nickel (Ni) is also required for higher plants (Brady and Weil, 2002). Other heavy metals, notably cadmium (Cd) and lead (Pb). Are not essential elements (Stevenson, 1986)? However, interest in these trace elements has been sparked by problems of toxicity resulting from an oversupply of these elements, particularly in soils.

In agricultural soils, the concentration of one or more of these elements may be significantly increased in several ways, the most important of which are listed below:

- Pesticides
- Fertilizers
- Micrometrical additions
- Aerial Emissions
- Sewage Sludge
- Farm Slurries
- Other Inputs.

The heavy metal contents of soils in a few areas may be increased by the dumping of mine wastes and of dredging from rivers and estuaries, and the use of contaminated irrigation water.

2.3 BIOAVAILABILITY OF METALS IN SOILS

Heavy metal accumulation in soils is highly dependant on the availability of metals for plant uptake. Soils consist of a heterogeneous mixture of different minerals (primary minerals, clay minerals and hydrous oxides of Al, Fe, and

Mn); organic and organo-mineral substances, and other solid components. The binding mechanisms for heavy metals are therefore complex and vary with the composition of the soil, soil acidity, and redox conditions. Heavy metal behavior (e.g., mobility, bioavailability) depends upon several factors which can be classified as (Kabata-Pendias, 2001):

- Geochemical characteristics of a metal
- Plant ability to take up a metal
- Soil chemical equilibria
- Climatic and other environmental variables
- Agricultural or remedial soil management

Generally, the solubility of metal fractions is in the order (Li and Thornton, 2001) exchangeable > carbonate specifically adsorbed > Fe—Mn oxide > organic—sulfide > residual.

Furthermore, only a fraction of soil metal is readily available (bioavailable) for plant uptake. The bulk of soil metal is commonly found as insoluble compounds, unavailable for transport into roots. With the exception of Hg, metal uptake into roots occurs from the aqueous phase. In soil, easily mobile metals such as Zn and Cd occur primarily as soluble or exchangeable, readily bioavailable forms. Copper and Mo predominate inorganically bound and exchangeable fractions. Slightly mobile metals such as Ni and Cr are mainly bound in silicates (residual fraction). Soluble, exchangeable, and chelated species of trace elements are the most mobile in soils and govern their migration and phytoavailability (Kabata-Pendias, 2001). Others, such as Pb, occur as insoluble precipitates (phosphates, carbonates, and hydroxyoxides), which are largely unavailable for plant uptake (Pitchel, 1999). Binding and immobilization within the soil matrix can significantly restrict the potential for metal phytoextraction.

Despite the adverse effect on metal root uptake, soil inactivation with chemical amendments has been proposed as a temporary solution for the remediation of metal-contaminated soils, especially for Pb. Also, the effect of soil amendment on bioavailability is metal specific. Increased mobility of metals can be stimulated by plant roots; this includes changes in pH, reducing capacity, The amount and composition of exudates (Bernal, M.P. and McGrath, 1994) and use of chelating agents. Soil amendments can increase or decrease biological availability of the contaminant for plant uptake. Bioavailability and metal uptake can often be increased by lowering soil pH, adding chelating agents, using appropriate fertilizers (containing ammonium), altering soil ion composition, soil microorganisms and root exudates (Thangavel and Subbhuraam, 2004).

2.3.1 PROPERTIES AFFECTING TRACE ELEMENT MOBILITY

The soil properties determining the mobility of heavy metals in the environment are pH, organic matter contents, Eh, CEC and temperature

2.3.1.1 Soil pH: The lowering soil pH, increases concentration of heavy metals in solution increases via decreasing their adsorption. Soil pH is to be adjusted to provide a range of pH before planting. Sorption of heavy metals depends largely on pH; in general, sorption increases with increasing pH. That is, the lower the pH value is, the more metal can be found in solution and thus the more metal is mobilized. When pH falls to below 5, mobility is enhanced as a result of the increased proton concentration. At pH values above 7, some heavy metals tend to form hydroxyl complexes, which will increase the solubility of the metal in question (Legreton, 1993; McBride, 1995]. A soil that has high pH and high cation exchange capacity will be able to immobilize the trace elements added to it via the sewage sludge. An alkaline soil may not always remain alkaline; thus, if the pH drops at a later stage (i.e., becomes acidic), the trace elements may get released (Stennes, 1990).

2.3.1.2 Chelate amendments: Chelate additions (EDTA, HEDTA, DTPA, EGTA, EDDHA, NTA, citrate, and hydroxylamifile) are commonly used in soil washing technologies because they cause metal desorption from clay minerals and dissolution of certain precipitates such as Fe and Mn oxides. Chelates enhance metal phytoavailability and subsequent uptake and translocation in shoots. Two strategies have been proposed regarding the mode of chelate application. The chelates may be added at once a few days before harvest (Huan *et al.*, 1997) or gradually during the growth period (Kayser *et al.*, 2000).

Pierzynski and Schwab (1993) investigated the effects of chemical amendments on the potential of phytoextraction of several toxic metals e.g. Cd, Pb, and Zn. They showed that addition of limestone, cattle manure, and poultry litter to soil significantly reduced Zn bioavailability. Experiments indicate that biosurfactants have the potential to enhance metal bioavailability in contaminated soil and sediments (Mulligan *et al.*, 2003). EDTA amended soils increased Pb availability. Therefore, chelate application might pose a risk to the environment (McGrath and Zhao, 2003). If the metal availability could be locally improved by increasing reductase activity or the amount of chelating agents -e.g., phytosiderophores (Briat and Lebrun, 1992) without harmful effects on the environment, hyperaccumulators might be used safely for phytoremediation.

2.3.1.3 Fertilizers: Fertilization with N, P, and K more than doubled annual biomass production without reducing the shoot Ni concentration. This suggested that soil fertility management will be important for commercial phytoextraction (Li *et al.*, 2003).

2.3.1.4 Competition for sorption sites: Using the competition of metal ions in solution for sorption sites may also be a useful tool. For example, addition of phosphate to soil may help to extract Cr, Se, and As on exchange sites by binding to the sites, thereby increasing bioavailability.

2.3.1.5 Soil microorganisms: The soil microbes have been documented to catalyse redox reaction in metal mobility in soils and propensity for uptake into roots. For example, chemolithotrophic bacteria have been shown to enhance environmental mobility of metal contaminants via soil acidification or, in contrast, to decrease their solubility due to precipitation as sulfides (Kelley and Tuovinen, 1988). Several strains of *Bacillus* and *Pseudomonas* increased the total amount of Cd accumulated by *Brassica juncea* seedlings (Salt *et al.*, 1995). Furthermore, soil microorganisms have been shown to exude organic compounds, which stimulate bioavailability and facilitate root absorption of a variety of metal ions, including Fe (Bural *et al.*, 2000) Mn (Barber and Lee, 1974) and possibly Cd (Salt *et al.*, 1995). The microbial activity is stimulated by adding carbon substrates such as agricultural wastes (Frankenberger and Karlson, 1992) water, and nutrients. Growth of crops also provides these materials to the soil microbiota due to standard farming practices and the process of Cd loss from roots, called “rhizodeposition.” It is interesting that rhizodeposition increases after clipping plants (Terry and Zayed, 1994) this could partly explain the enhanced Se removal after cutting treatments, plus the enhanced biomass production.

2.3.1.6 Phytosiderophores: Plants possess highly specialized mechanisms to stimulate metal phytoavailability in the rhizosphere and to enhance uptake into roots (Romheld and Marschner, 1986). Thus, graminaceous species (sp. have been documented to exude a class of organic compounds termed siderophores (mugineic and avenic acids) capable of enhancing the availability of soil Fe for uptake into roots (Takagi *et al.*, 1984).

2.3.1.7 Root exudates: It is well established that roots of many plant species release specific metal-chelating or reducing compounds into the rhizosphere to mobilize Fe and, possibly, Zn (Marschner, 1995). For Zn/Cd/Cu/Pb hyper accumulators, there are very few studies on the role of root.

2.3.1.8 Organic matter: The organic matter binds heavy metals in soils most strongly onto soil constituents (Nemeth, 1993; Antoniadis and Alloway, 2002). The chemical composition of soil water determines which ligands are available for complexation, whether precipitation is likely to occur, and whether competitive sorption exists. For example, the presence of chloride ions in the soil solution has been shown to enhance the mobility of some heavy metals by the formation of soluble complexes. (Ashwortha and Allowaya, 2004).

2.3.1.9 Redox potential(Eh): The oxidation state of a given metal is determined by the redox potential. Different oxidation forms of a metal behave differently chemically. For example, chromium in the oxidation state (+6) is much more soluble and toxic than chromium in the oxidation state (+3) (Ashwortha and Allowaya, 2004; Saverbeck, 1991).

2.3.1.10 Cation exchange capacity (CEC): The CEC of a soil is a measure of the negative charge density of a soil as function of the soil's ability to adsorb positively charged ions, cations. Thus, a high CEC reflects a soil with a high sorption capacity. Quebec researchers (Milacic and Stupar, 1995) suggested that the maximum heavy metal concentration in soil is based on the CEC of the soil, which is a measure of soil's ability to retain heavy metal ions. CEC increases with increasing clay content of the soil. Thus, they recommend maximum heavy metal concentration for fine textured soils, such as clay and clay loam, rather than for coarse textured soils, such as sand. Texture reflects the particle size distribution of the soil and hence the ability of absorbing fine particles likes oxides.

2.3.1.11 Temperature: Several chemical reactions are temperature dependent and proceed at a higher rate, when temperature increases. It is now well established that determinations of the individual physicochemical forms and phase are required for understanding the role of trace metals in the environment or human health (Qureshi *et al.*, 2004; Adriano, 1986 and Fergusson, 1990).

2.4 EXCLUSION OF TRACE METALS TO FOSTER PHYTOSTABILIZATION

The bioavailability of metal ions depends on their solubility in the soil solution, i.e., their general solubility and the stage of equilibrium between the metal cation in bound form and the free soluble ion. Because the concentration of heavy metal ions in forest soils is usually so low that the solubility behavior of the metal salts will govern their concentration in the soil solution, the dominating factor for bioavailability of heavy metal ions in soils is their adsorption to soil structures.

The capacity of a given soil to bind given heavy metals depends on the amount and nature of binding sites in the soil structures and the pH of the soil solution. Generally, it can be stated that the lower is the pH value; the more soluble are the metal cations and the more binding sites are available in a given soil; the lower will be the solubility of the heavy metals. In the case of cadmium ions, the increase in solubility with decreasing pH values starts at a pH of 6.5. In the case of lead and mercury ions, it starts at a pH value of 4; ions of arsenic, chrome, nickel, and copper start to dissolve at pH values between these two extremes. Thus, the pH value of the soil solution in principle is one of the main factors governing the solubility of heavy metal cations in the soil solution; its influence on plants under heavy metal stress is well established (Gerth and Briimmer, 1997). Thus, increasing the pH could be a measure to reduce the bioavailability of heavy metals. This has been shown by Walendzik (1993) for spruce in the Western Sudety Mountains. Liming, however, may not always be a good solution because it may increase the rate of nitrogen mineralization and thus aggravate the NO load in the groundwater (Marschner *et al.*, 1989; Kreutzer and Hüttel, 1995 and Schuler, 1995). The approach of using waste materials such as fuel ash (Piha *et al.*, 1995) or sewage sludge (Borgegard and Rydin, 1989) to improve the growth of trees on mine spoils may not always be successful. Better results using municipal sewage sludge for establishing

sagebrush vegetation on copper mine spoils were reported (Sabey *et al.*, 1990). The simple addition of inorganic fertilizer may not work at all (Borgegard and Rydin, 1989).

Another way to decrease the bioavailability of heavy metals is to increase the binding sites for heavy metal ions in the soil, e.g., by amendment with humic substances or zeolites (Baydina, 1996) or expanded clay and porous ceramic material (Figge, 1995). When organic substances are added to the soil, it is very important to work with water-insoluble material, which is not available for rapid degradation by microorganisms (Herms and BrUmmer, 1984). The authors found that an addition of hay to a soil contaminated with heavy metals increased the solubility of Cu, Cd, and Zn, but this effect was not observed for Pb. Amendment of the soil with peat had the opposite effect.

Researchers have found that plant roots exude a variety of organic compounds. Root exudates that play important roles in nutrient solubilization (e.g., organic acids, phyto siderophores, and phenolics), restricting the passage of toxic metals across the root (e.g., citrate, malate and small peptides) and attracting beneficial microorganisms (e.g., phenolics, organic acids sugars). Often, the excretion of these organic molecules increases in response to soil stress.

In the soil environment, a heavy metal ion can undergo a number of processes and will distributed among its different chemical forms and physical phases (water-soluble mobile phase organic matter bound, oxide bound, etc.). It was found that trace elements that form stable complexes with ligands tend to be more toxic and remain in the soil for much smaller periods of time. This can result in phytotoxicity and increased movement of trace elements into the food chain.

The processes determining the speciation of trace elements in a soil environment are (Greenwood and Earnshaw, 1994; Essington and Mattigod, 1990; Essington and Mattigod, 1991).

- Precipitation and dissolution
- Sorption and desorption
- Complexation with organic compounds
- Complexation with inorganic compounds

2.5 ACCUMULATION OF METALS BY PLANTS:

The uptake of essential element is determined not only by the availability of the soil-held nutrients but by their being in proximity to the root surface. The amount of heavy metal taken up by plants or crops from the soil is, in the strictest sense, the criterion of its availability. However, plants vary greatly in the amount of a heavy metal they take up depending on species, stage of growth and environmental conditions. The availability of a heavy metal in a soil is as much a function of the plant as of the soil (Mitchell, 1964).

2.5.1 MOVEMENT FROM SOIL TO PLANT ROOT

Ions and molecules dissolved in water constitute the soil solution. The concentration and composition of the solution changes when (i) mineralization of soil organic matter releases nutrients, (ii) fertilizers and pesticides are applied, (iii) ions are taken up by plants, and (iv) rainfall and irrigation increase, and evaporation/transpiration decreases, the soil water content (Wild, 1996).

The main processes involved in the movement of nutrients from soil solution or from soil to plant root surfaces are: first, as root penetrates the soil they come in contact with soil colloids on which nutrients are held. This is termed as **root interception**. Second, some nutrients move to the roots with water as it is absorbed by plants. Such movement is called **mass flow**. Third, as nutrients are

absorbed by plant roots, a concentration gradient is set up between the zone immediately around the root surfaces and the soil zones farther away. In response to this gradient, **diffusion** of ions toward the root surfaces takes place. For cations such as K^+ and Ca^{2+} diffusion is by far the most important means of supplying nutrients to plant roots. Diffusion is also important for anions such as NO_3^- although mass flow also can be quite significant for these negatively charged ions, (Brady, 1990).

The relative importance of mass flow and diffusion has created some controversy among soil scientists interested in the uptake of ions by plants. No simple answer appears to be applicable to all types of ions, and the two processes can generally be regarded as additive, with one or the other being dominant in a particular case depending upon water regime and the sorption characteristics of both root and soil. With the heavy metal ions, which are firmly held on the absorbing complex, other processes may be involved in the immediate vicinity of the root. The root and associated microorganisms produce various organic chelating agents which are very effective in releasing heavy metals from the soil colloids; this would probably mean that greater diffusion gradients are established between the bulk solution and the concentration at the absorbing root (Misra and Dinesh, 1991).

2.5.2 ABSORPTION BY ROOTS

Root uptake of nutrients by plants requires intimate root soil association. The uptake of ions has been the subject of diverse investigations based both on solution and on the soil. Studies of the mechanism of absorption from solution have been mainly concerned with the macronutrients, but from the limited information on heavy metal ions it seems likely that the mechanisms are similar. There is, however, some controversy as to what extent the absorption of macro nutrient and heavy metal cations is under control of metabolic (physical) processes. With many ions including Mn^{2+} (Moore, 1972) and Pb^{2+} (Jarvis *et al*, 1977), an initial rapid phase is considered to be due to non-

metabolic processes. The plant does not simply absorb the essential nutrients in a passive way. In the soil solution nutrient solubility is markedly affected by root exudates and by microbial activity in the vicinity of the roots (rhizosphere). Furthermore, entrance of soluble nutrients into root cells is stimulated by plant root metabolism. A combination of active transport and ion diffusion makes possible the movement of ions from the soil solution to the vessels that can carry the nutrient upward in the plants. Respiration by the root cell supplies energy for this nutrient absorption (Brady, 1988).

The absorption of a heavy metal cation is promoted as pH increases and is inhibited by some alkali and alkaline earth cations and by other heavy metals. In soils, the effect of pH is in the opposite direction, and liming reduces uptake of the cations; this is due in part to the physiological effect of Ca^{2+} but largely to increased retention by soil colloids. The uptake of Cu from soils may sometimes be independent of pH (Loneragan, 1975), in which circumstances its behavior would be dominated by complexing with organic ligands in the soil solution. The uptake of Mo, as an anion, also has a different relationship to pH, depending of whether uptake is from solution or from soils. Thus with increasing pH, uptake from solution is reduced whereas from soils it is increased. The latter effect is due to decreased retention of Mo by hydrous Fe-Oxides and other inorganic colloids.

The adsorption of heavy metals from solution is largely derived from studies with inorganic forms. However, it has been shown that the absorption of several heavy metals, including Co, Cu, Ni, and Zn by mustard plant is reduced when EDTA or other chelation agents are present in the nutrient solution (De Kock and Mitchell, 1957). Similarly, the absorption of Cu by barley from solution has been reduced by adding each of three soluble organic fractions that were isolated from a peat soil. Those fractions were of molecular weight 200-400, 400-1500 and greater than 5000 and the effect increased in the same order (Mercer and Richmond, 1972). As heavy metals are frequently added to soils in

combination with organic matter as in sewage sludges, and sometimes as synthetic chelates there is increasing interest in the equilibria and metal ions in the soil solution and in effects upon plant uptake (Norvell, 1972).

2.5.3 TRANSPORT WITHIN THE PLANTS

Once in the root, metal ions can be stored or exported to the shoot. Metal transport likely occurs in the xylem, but metals may redistribute in the shoot via the phloem. For metals to enter the xylem, they must cross the casparian strip symplastically (intracellular) and this may be the rate-limiting step in metal translocation to the shoot.

2.5.4 INTERACTION WITHIN THE PLANTS

In addition to interaction during absorption, there are other processes within the plant between heavy metals and some major nutrients. These interactions, sometimes described as antagonisms, are discussed fully by Olsen (1972) and attention here is restricted to a few examples. In general very little is known about the mechanisms involved in interactions of this kind. Those between one heavy metal and other may be viewed as competition for sites in some compounds such as enzymes or those involved in translocation. In this way, Fe or Mn deficiency symptoms have been induced in plant given large amounts of Zn, Ni, or Cu (Leeper, 1978) in the growth media. Another better known interactions appear as Fe deficiency in plants growing on some acidic soils containing high level of available Mn.

The interactions between heavy metals and phosphate deserve some comment because of the high content of P in sewage sludge and the widespread use of phosphatic fertilizers have caused Zn deficiency in many crops. There is evidence that this is not a soil effect (Olsen, 1972) and that phosphate reduces

transport of Zn in the plant, most likely that from roots to shoots. Phosphate also interacts in a similar way with Cu and Fe in several plant species.

These interactions with phosphate raise the possibility that plants may be protected against injury from some heavy metals when the phosphate is high.

Orabi and Abuleenane (1980) concluded that P application increased Zn content in rice, particularly when applied as Zn-EDTA. The P content of the plants was affected by Zn application and increased by both sources (ZnSO₄ and Zn-EDTA). Qayyam *et al.* (1981) tested the effect of N, P and K on the uptake pattern of Zn and Cu in rice. Zn contents generally decreased with increasing rates of N P K, but increased significantly with increasing rates of K; Cu content generally increased with increasing rates of NPK, but were significantly reduced by higher rates of P. Homma and Hirata (1984) accomplishing an experiment with rice, concluded that at lower concentration, Cd is more rapidly absorbed than Zn (due to higher affinity of Cd) and at higher concentration; Zn ions are more rapidly absorbed than Cd (due to lower affinity of Zn).

Abdul-Rehman *et al.* (1988) observed Zn application enhanced N concentration and uptake in straw and unhusked grain and increased Zn concentration. Ammonium sulfate as N source has the highest unhusked grain yield. Smilde (1981) studied the heavy metal accumulation in crops grown on sewage sludge amended with heavy metals. The order of phytotoxic doses increased in the order of Cd < Ni < Cu < Zn.

The competitive interactions among heavy metals during absorption are complex and have been little studied. There is evidence from short-term experiments that the absorption of Zn²⁺ by wheat from solution is reduced strongly by Cu²⁺, but weakly Cu²⁺ (Chaudhury and Loneragan, 1972) and similarly that the adsorption of Cd²⁺ by ryegrass is reduced by Zn²⁺ and Mn²⁺ (Jarvis *et al.*, 1976). The competitive effects with Cd²⁺ were found in the presence of Ca⁺ in excess and at concentration commonly present in soil

solution. There is evidence that Zn sometimes depresses Cu uptake from soils and it is thought that this is due to a competitive interaction during uptake rather than a soil effect (Loneragan, 1975).

2.5.5 DIFFERENCE AMONG PLANTS

The characteristics and behavior of an individual plant species or variety are important in determining the amount of heavy metal that is taken up from soils. There are few reports of differing rates of absorption of Zn^{2+} and Mn^{2+} between species and varieties (Loneragan, 1975). Many comparisons have, however, been made between the content of individual heavy metals in the shoot of soil-grown plants and these often show wide differences both between species and varieties (Fleming, 1973; Loneragan, 1975). Although such differences may reflect differing rates of absorption, they will also be dependent on the extent of transport from roots to shoots. There is a wide divergence in lead uptake between species: uptake being greater in general in dicotyledonous than in monocotyledonous species (Suchodoller, 1967).

Grasses, leafy vegetation and trees containing higher lead concentrations, growing in the vicinity of highways compared to those away from the highways. Forage grasses may contain enough lead to pose a threat to the health of grazing animals. Highest proportions of heavy metals taken up by plants are rather retained in the roots as for instance, with Pb and Cd in ryegrass (Jones *et al.* 1973; Jarvis and Jones, 1978) and with Mn in some medics and clovers (Loneragan, 1975). The proportions retained vary with the metal and plant species. Furthermore, similar differences have been found within an individual species, notably in bentgrass (*Agrostis sp.*). Strains growing on soils contaminated by mine workings have evolved a tolerance to high level of Zn and retain higher proportions in their roots than other, non-tolerant strains. Other specific tolerances in bentgrass in high level of Cu, Ni, and Pb have also been described (Gregory and Bradshaw, 1965), and it seems possible that these may also be related to retention in the roots.

Flanagan *et al.* (1980) reported that lead deposition was more on pubescent bramble leaves in comparison to smooth rhododendron leaves. The differing responses of species and varieties to environmental changes will also contribute to differences in uptake of heavy metal from soils. These effects may be exerted either through the root or shoot, or through the whole plant.

2.5.6 DISTRIBUTION AMONG PLANT PARTS

Reference has already been made on the tendency of some heavy metals to be concentrated in the roots. The concentrations of heavy metals in the shoot will be affected not only by uptake and transport from the roots but also by the rate and stage of growth. Concentration will also differ in the various parts of the shoots, notably with the cereals in leaves and stems than in the seeds. In the later respect, Ni seems to differ from the other heavy metals in that it is often more concentrated in the seeds than in leaves and stems (Hunter and Vergnano, 1952).

Leaves of lettuce accumulate the highest concentration of lead (Motto *et al.*, 1970). Schuck and Locke (1970) reported higher concentration of lead in the outer leaves of cabbage. High concentrations of lead are found in the bark of trees. Heichel and Hankin (1976) reported that *Pinus strobus* L. trees retain 20 times more lead on bark than on foliage. Mankovaks (1977) considered variation in lead in foliage with height above the ground. The highest concentrations in spruce needles were recorded close to the ground surface; and two-year-old needles generally contaminated more metal than one-year-old needles.

The vegetative and generative organs have different affinities for lead. The fruits and flowers accumulate the least amount of lead. Lead content increases 4.5 times in leaves, 2.2 times in seeds, 1.2 times in pollen and 1.1 times in flowers (Ostroluca and Mankovska, 1985). In *Potamogeton pectinatus*, it has been found that plasmalemma acts as a barrier to lead (Sharpe and Denny,

1976). Large amount of lead can be taken up by plant roots but immobilized by dictyosome vesicles and deposited in the cell wall (Malone *et al*, 1974).

Siedlecka (1995) divided the metal accumulating into plants in three categories based on metal accumulative ability in different plant parts (Figure 2.1):

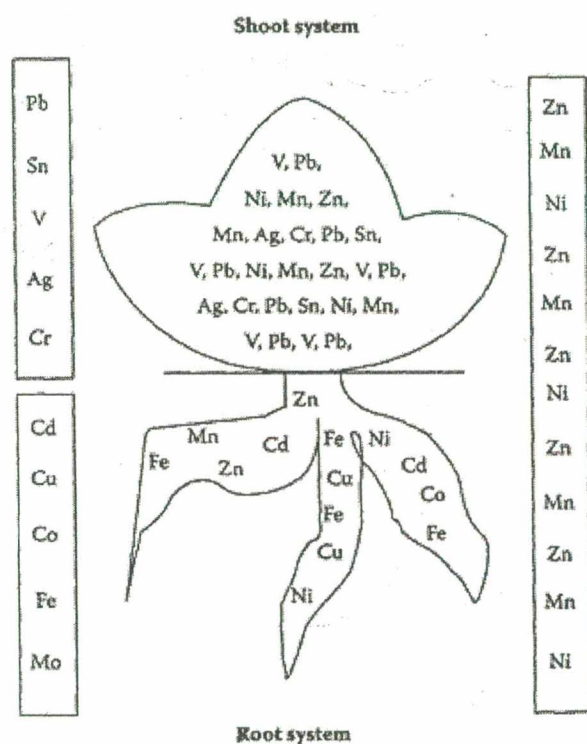


FIGURE 2.1: A generalized pattern of partitioning of metals in the root and shoot system. Silver, chromium, lead, tin, and vanadium accumulate more in shoot (stems and leaves) compared to roots and rhizomes. Cadmium, cobalt, copper, iron, and molybdenum accumulate more in roots and rhizomes than in shoot (stems and leaves). Nickel, manganese, and zinc are distributed more or less uniformly in root and shoot of the plant (Siedlecka, 1995).

- Accumulate more in roots/rhizomes: Cd, Co, Cu, Fe, and Mo in beetroot, carrot, radish, Jerusalem artichoke, and potato.
- Accumulate more in shoots (stems/leaves): Ag, Cr, Pb, Sn, and V in cabbage, cauliflower, tomato, rice, barley, oats, wheat, corn, pigeon pea, chick pea, soybean, peanut, broccoli, lettuce, spinach, and amaranthus.
- More or less uniform distribution in roots/shoots: Mn, Ni, and Zn in bush bean, broad bean, mung bean, and cucumber. Soils contaminated with multiple heavy metals can present a difficult challenge for phytoextraction. Although some hyperaccumulators appear to be capable of accumulating elevated concentrations of several heavy metals simultaneously, there is still considerable specificity in metal hyperaccumulation (Baker *et al.*, 2000).

The concept of using hyperaccumulator plants to take up and remove heavy metals from contaminated soils was first proposed by Chaney, 1983. However, it was not until the early 1990s that field experiments were carried out to test the potential of phytoextraction of metals with hyper accumulator plants (Brown *et al.*, 1995). Hyper accumulators take up a large quantity of toxic metals through their roots and transport them to the stems or leaves. The word “hyperaccumulator” was coined by Brooks (1995) and has been defined as metal accumulation exceeding a threshold value of shoot metal concentration of 1% (Zn, Mn), 0.1% (Ni, Co, Cu, Pb), or 0.1% (Cd) of the dry weight shoot biomass (McGrath, 1998).

2.6 TRANSFER COFFICINTS OF TRACE METALS

Transfer coefficients (concentration of metal in the aerial portion of a plant relative to total concentration in the soil) are a convenient way of quantifying the relative differences in bioavailability of trace elements to plants. Alloway and Ayres (1993) and Kloeke *et al.*, (1984) have given generalized transfer coefficients for soils and plants. However, soil pH, soil organic matter content, and plant genotype can have marked effects on metal uptake. The transfer

coefficients are based on root uptake of trace elements, but plants can accumulate relatively large amounts of trace elements by foliar absorption of atmosphere deposits on plant leaves.

Cd, Tl, and Zn have the highest transfer coefficients -a reflection of their poor sorption in the soil. In contrast, trace elements such as Cu, Co, Cr, and Pb have low coefficients because they are usually strongly bound to the soil colloids. The most toxic trace elements for high plants and several microorganisms are Hg, Cu, Ni, Pb, Co, Cd, and, possibly, Hg, Be, and Sn (Towers *et al.*, 2002). Although the occurrence and toxicity will depend on soil factors such as pH, plant genotype, and source of trace elements.

2.7 Lead contamination on soils and crops

2.7.1 Lead in nature

Lead is a bluish gray heavy metal with a low melting, a high resistance to corrosion and good electrical conducting capabilities. Lead is the member of Group xiv A in the periodic table. Its atomic number is 82 and atomic weight is 207.2. The oxidation states of Pb are 0, +2 and +4 (Cotton *et al.*, 1972 and Rai *et al.*, 1984). Pb (iv) exists only in extremely oxidizing conditions but not usually found within the range of environmental pH and redox condition. In the environment lead primarily exists as Pb (ii). Metallic lead Pb (o) exists in nature but its occurrence is rare. When exposed to air or water, thin films of lead compounds are formed that protect the metal from further attack.

2.7.2 LEAD ON ROADSIDE SOILS AND PLANTS

Due to the fact that until the end of the 1980s petrol contained tetraethyl lead Pb (C₂H₅)₄, road transport was the major source of atmospheric emission of such lead compounds as: lead (II) chloride, PbCl₂, lead (II) bromidechloride, PbBrCl, lead (II) chloride-hydroxide, Pb(OH)Cl and lead II bis(oxide)-bromide-chloride, (PbO)₂ PbBrCl. Most of them are unstable compounds. Several hours after emission, the following compounds are usually present:

lead II bis (oxide)-carbonate, $(\text{PbO})_2\text{PbCO}_3$, lead (II) carbonate PbCO_3 , lead (II) bromide-chloride, PbBrCl , and lead oxides PbOx ((Haar and Bayard, 1972). Lead (II) oxide PbO and lead (IV) oxide PbO_2 are sparingly water-soluble. In slightly acid media (e. g. in the presence of diluted sulfuric and hydrochloric acids) they do not pass into the solution, forming sparingly soluble salts (PbCl_2 and PbSO_4). However, the ionic form of lead existing in the soil is taken up by plants and is accumulated mainly in their roots (Jacson *et al.*, 1990). Addition of synthetic chelates increases lead uptake from the soil, which is used in its phytoextraction in industrial areas (Salt *et al.*, 1998). In the presence of phosphates, lead forms lead phosphates, which often causes phosphorus deficit in the soil and plant organs. Some lead ions form in the soil combinations with organic compounds, hardly available to plants. Due to problems with lead uptake by the root system, penetration through internal leaf cells, one of the major sources of this element are atmospheric dusts adsorbed on the outer plant surface (Jacson *et al.*, 1990; Kabata-Pendias and Pendias, 1999)

2.7.3 USES OF LEAD

Lead may be used in the form of metal, either pure or alloyed with other metals, or as chemical compounds. The commercial importance of lead is based on its ease of casting, high density, low melting point, low strength, ease of fabrication, acid resistance, electrochemical reaction with sulfuric acid, and chemical stability in air, water, and soil (King and Ramachandran, 1995; Shea, 1996; Sutherland and Milner, 1990). Lead is used in the manufacture of storage batteries; lead alloys used in bearings, brass and bronze and some solders; sheets and pipe for nuclear and x-ray shielding, cable covering, noise control materials; chemical resistant linings; ammunition; and pigments and lead compounds used in glass making, ceramic glazes, plastic stabilizers, and paints.

Consumption of lead in lead-acid batteries, including SLI (Start, Light, Ignition) batteries used in cars, trucks, and other vehicles and industrial type

lead acid batteries is the major use of lead today., such as tetraethyl lead in gasoline, water pipe, solder in food cans, lead shot and sinkers, and in house paints, have been or are being phased out due to environmental and health concerns (Larrabee, 1998).

The contents of Pb were 10-100 times higher than that of Cd and 11-17 times higher as compared to localities without air pollution. A survey was made for the accumulation of Pb from motor vehicle exhaust on soils and trees growing along a busy area of Baroda city, India. Plant and soils near the roadside had a higher concentration of Pb than at a distance of 4-6 meters. A good correlation existed between traffic volume, total and extractable soil Pb and Pb content of roots and shoots of the grass *Cynodon dactylon* in roadside of Delhi (Dutta and Mookerjee, 1981).

An enhancement of lead in the levels was found in roadside soil and vegetation due to combustion of leaded petrol by automobile exhaust in Baghdad city (Khalid *et al.*, 1981). Kovacs *et al.* (1981) monitored the heavy metal content, including Pb, Cu and Zn, in leaves of three tree species in urban and rural environments in Budapest. They reported that the leaves accumulate various heavy metals in quantities 1.2 to 9 times higher in an urban than in a rural environment. A survey for lead pollution was carried out in Baghdad city (Hanna and Al-Bassam, 1983). Palm leaves, which were collected from 25 different sites of the city, showed a relative increase in Pb deposition due to vehicles using leaded petrol.

A systematic study carried out on vegetables and other agricultural products used as food suggests a tentative classification of products exposed to roadside Pb pollution from automobile exhausts (Favretto, 1984). It was found that Pb contents decreased with distance from the source. Similarly, the distribution pattern of lead in the leaves of Banyan tree (*Ficus bengalensis*) L. from different traffic density regions of Calcutta was carried out (Datta and Ghosh,

1985). In high and medium traffic density regions, Pb content of leaves was high in winter than in summer months. Such changes due to seasonal variations were not marked in low and zero traffic density areas.

Nasralla and Ali (1985) found an accumulation of Pb in different parts of vegetables growing around six Egyptian traffic roads. Leafy vegetables such as lettuce and cabbage accumulated lead up to 78.4 ppm in their edible portions, with lowest Pb accumulation in carrot and radish. These findings suggested that Pb was accumulated in plants through both foliage and root systems, but lead absorption through foliage was more pronounced at locations close to the emissions source of Pb vapor and fine particle.

Al-Saleh and Taylor, (1994) determined the concentration of lead in the atmosphere and soil at 13 locations in the city of Riyadh during the working days (Saturday and Wednesday) and found that lead concentration in the atmosphere and soil was significantly higher in areas where the traffic density was consistently high than non residential areas. There was a significant relationship between the concentrations of airborne and soil lead.

The effect of high lead level on datepalm (*Phoenix dactylifera*) and tomato (*Lycopersicon esculentum*); in an area near a major highway showed that the contamination by lead decreases rapidly with increasing distance from the highway (Jaffer *et al.*, 1999). Atmospheric depositions appeared to be the main contributor to plant contamination by lead. Lead levels in the soil of study area varied from 0.0 to 0.14 ppm. This low level of lead could be due to low population and the relatively limited number of vehicles on the street.

2.7.4 SOURCES OF LEAD IN SOIL

Lead occurs naturally in the environment. The natural lead content of soil is inherited from parent rocks. Depending on the geophysical characteristic of the site, total Pb concentration in soils ranges from 10 to 200 mg kg⁻¹ (Chlopecka and Adriano, 1997).

However, human activities have caused elevated levels of the Pb in soils (Chen *et al.*, 2003). Environmental levels of lead have increased more than 1,000-fold over the past three centuries as a result of human activity (ATSDR, 2005). Lead released from natural sources, such as volcanoes, windblown dust, and erosion, are minor compared with anthropogenic sources. Soil as sink for anthropogenic Pb and the major anthropogenic sources of lead include combustion of coal and oil, mining and smelting activities, and manufacture of lead-containing products, waste incineration and manure usage in agriculture (ATSDR, 2005; Alloway, 1995).

Atmospheric deposition is the largest source of lead found in soils. Lead is released into the air during burning coal, oil or waste. The combustion of ethylated motor fuel containing tetraethyl lead (TEL), ethylene dibromide, ethyl bromide, and other additives, with a content of lead up to 0.78 g L^{-1} (Nriagu, 1990b), led to the emission of lead (II) bromide and oxide that contaminate soils and plants near busy roads. Lead is transferred continuously between air, water, and soil by natural chemical and physical processes such as weathering, runoff, precipitation, dry deposition of dust, and stream/river flow; however, soil and sediments appear to be important sinks for lead. Lead particles are removed from the atmosphere primarily by wet and dry deposition. The average residence time in the atmosphere is 10 days. Over this time, long-distance transport, up to thousands of kilometers, may take place. Lead is extremely persistent in both water and soil.

Industrial sources of lead can result from the mining and smelting of lead ores, as well as other ores in which lead is a by-product or contaminant. In these processes, lead may be released to land, water, and air. Electrical utilities emit lead in flue gas from the burning of fuels, such as coal, in which lead is a contaminant (ATSDR, 2005). The main Pb pollutants emitted from smelters occur in mineral forms (e.g., PbS, PbO, PbSO₄, and PbO. PbSO₄), while Pb in automobile exhausts is mainly in the form of halide salts (e.g., PbBr, PbBrCl, Pb(OH)Br, and (PbO)₂PbBr₂). Exhaust Pb particles are unstable and readily convert into oxides, carbonates, and sulfates (Kabata-Pendias, 2001).

Disposal of lead-containing products contribute to lead in municipal landfills. Lead-containing waste products include storage batteries, ammunition waste, ordnance, sheet lead, solder, pipes, traps, and other metal products; solid waste and tailings from lead mining; items covered with lead-based paint; and solid wastes created by mineral ore processing, iron and steel production, copper and zinc smelting, and the production and use of various lead-containing products (ATSDR, 2005). Most of the lead in inner city soils comes from old houses with paint containing lead and previous automotive exhaust emitted when gasoline contained lead.

Sewage sludges, especially those from metropolitan areas, usually have high levels of trace elements, including Pb (Alloway, 1995). Because of these high levels of Pb in sewage sludges, addition of large quantities of sludge to land can enrich the soil environment and possibly also increase the Pb contents of plants.

In some areas, soil contamination by lead is caused by horticulture applications of insecticides containing lead arsenate $PbHASO_4$ (Kalbasi *et al.*, 1995). A specific contamination problem arises at shooting ranges, hunting areas, and battlefields where metallic lead is spread in soil as more or less fragmented pieces (Rooney, 1997).

Other important sources of Pb in soils are Pb containing paints within the home and garden. Thornton (1990) reported that the geometric mean concentration of Pb in 4650 garden soils of Great Britain is 298 mg kg^{-1} (DW). The concentrations of Pb were higher in older home, which clearly indicates a gradual increase of this metal in garden soils. This phenomenon is closely related to hazardous Pb intake by children as a result of "hand-to-mouth" activity. The most serious soil Pb issue is associated with a direct transfer of Pb from contaminated soil to children, showing a significant relationship among Pb levels in soils and in children's blood (ATSDR, 2005).

2.7.5 LEAD CONCENTRATION IN SOIL

The terrestrial abundance of Pb indicates a tendency for Pb to concentrate in the acid series of magmatic rocks and argillaceous sediments in which the common Pb concentrations range from 10 to 40 mg kg⁻¹, while in ultramafic rocks and calcareous sediments its range is from 0.1 to 10 mg kg⁻¹ (Kabata-Pendias, 2001). The natural Pb content of soil derived from crustal rock, mostly as galena (PbS), typically ranges from < 10 to 30 mg kg⁻¹ soil (ATSDR, 2005). However, due to widespread Pb pollution, most soils are likely to be enriched in this metal, especially in top horizon. The concentration of lead in the top layers of soil varies widely due to deposition and accumulation of atmospheric particulates from anthropogenic sources. Kabata Pendias (2001) reviewed the world literature and reported that the natural Pb concentration in top horizons of different soils from various countries lie in the range from 3 to 189 mg kg⁻¹, while mean values for soil types range from 10 to 57 mg kg⁻¹ and average 32 mg kg⁻¹. In non contaminated soils, the mean values are taken to be from 15 to 17 mg kg⁻¹ for light soils, and from 17 to 22 mg kg⁻¹ for heavy textured soils (Kabata Pendias, 1998). Gough *et al.* (1998) found a relatively low Pb content of soils in Alaska. Although Pb in these soils ranges from 4 to 349 mg kg⁻¹ (DW), about 90 % of the samples contained only up to 20 mg kg⁻¹, with a geometric mean of 12. Low concentrations of Pb in soils from this remote region suggest that baseline values of this metal in most world soils should not be much higher than 20 mg kg⁻¹ (Kabata-Pendias, 2001). Agricultural soils can have a wide range of Pb content, depending on a number of factors, such as parent material and anthropogenic input. The geometric mean Pb content of surface soils from major agricultural production areas of the U.S. is 10.6 mg kg⁻¹, within the range from <1 to 135 mg kg⁻¹ (Holmgren *et al.*, 1993). The concentration of soil lead generally decreases as distance from contaminating sources increases. As a result of lead reactions with the soil, extractable lead in surface soil samples (0–5 cm depth) from an agricultural area near a car battery manufacturing plant (taken at 0.3 km from the source) decreased from 117 mg

kg⁻¹ to 1 mg kg⁻¹ within 1 year after the plant stopped operating (Schalscha *et al.*, 1987). Lead concentrations in soils collected from inner-city school in New Orleans were higher (median concentration of 96.5 mg kg⁻¹) than soils collected from mid-city (30 mg kg⁻¹) and outer city (16.4 mg kg⁻¹) elementary school (Higgs *et al.*, 1999).

2. 7. 6. CHEMICAL BEHAVIOUR OF LEAD IN SOILS

Forms and speciation of lead in soils

Lead availability and mobility depend on its physicochemical forms in soils. For this reason, understanding Pb availability and mobility in contaminated soils is important for evaluating the potential environmental and health effects of Pb. Lead in soils is usually present in different forms: (i) water soluble (ii) exchangeable (iii) adsorbed, chelated or complexed and precipitated; (iv) secondary clay minerals and metal oxides of low solubility, and (v) primary minerals (Ma *et al.*, 1997). In general, the water soluble metals represent the most mobile and potentially most dangerous fraction in the soil. The exchangeable fraction consists of those metals retained by electrostatic forces that are solubilized by an exchange reaction with excess positive ions present.

According to Ponizovsky and Mironenko (2001), the 'exchangeable' fraction cannot be taken as the amount of Pb(II) that can be exchanged, 'carbonate' fraction - as PbCO₃, and so on. Basing on the data obtained with the existing methods of fractionation Ponizovsky and Mironenko (2001) concluded some generalizations: (1) in slightly acidic and acid soils, up to 10-70% of the total amount of Pb can exist in exchangeable form, bound either with inorganic or organic compounds. (2) in neutral soils, the greatest part of lead may be 'bound to Fe-Mn oxides' and 'organic' fraction. (3) In slightly alkaline soils, lead is retained as 'carbonate', 'organic' and 'residual' fractions.

Li and Thornton (2001) reported a significant association of Pb with soil carbonate phase. Chlopecka *et al.* (1996) and Ram *et al.* (1994), however, found

most of the Pb to be bound to Fe and Mn oxide and the organic fraction. In contrast to these reports, Finžgar *et al.* (2007) found the quite low fraction of Pb bound to oxides. A strong association of Pb with organic matter was also described by Kabata-Pendias and Pendias, (1993). Lead distribution in different soil fraction in Mežica valley and Celje region of Slovenia (Finžgar *et al.*, 2007) was that 31.5-74.7 and 5.0-67.1 % of the total soil Pb was bound to soil organic matter and carbonates while 5.9-23.8 % remained in the residual fraction. This distribution pattern of Pb in different soil fractions was similar to that reported by Leštan and Grěman (2001) and Leštan *et al.*, (2003).

Reactions of lead with soil components

Metals ion can be held to the soil by adsorption onto the surface of mineral particles, by complexation with humic substances, and by precipitation reactions (Baird and Cann, 2005). Sorption of metals from aqueous solution onto solid surfaces is an important process that influences both accumulation and transport in the environment. Adsorption of Pb to soil materials was described by Langmuir and Freundlich adsorption isotherms by Trancoso *et al.*, (2007). These complex processes are dependent on many factors including (i) soil composition, (ii) pH, (iii) organic matter (iv) redox potential, (v) presence of cations and anions, (vi) presence of chelates and (vii) other miscellaneous factors like microbial activity and earthworm activity.

Finer soil particles have larger relative surface areas available for metal adsorption than the coarser particles, thus, metals usually tend to accumulate in the smaller grain size fractions in uncontaminated soils (Berrow and Mitchell, 1991; Kabata-Pendias, 1993). It is well known that metals, especially, Pb are concentrated in silt and clay fractions due to their relatively large surface areas (Queralt and Plana, 1992).

Soil pH is generally acknowledged to be an important regulating factor for metal partitioning and fractionation. Janssen *et al.* (1997) reported that soil pH was in fact the only soil parameter of significance for partitioning Pb and other

metals between the soil solution and soil solid phases. Finžgar *et al.* (2007) found that soil pH affected highly significantly the exchangeable Pb and Zn. In their study, more than 90% of the variability of Pb and Zn in the exchangeable fraction was explained by the variability of soil pH. Metal solubility tends to increase at lower pH and adsorption reactions become more important than precipitation and complexation reactions (Finžgar *et al.*, 2007). However, adsorption also tends to decrease with lowering soil pH, due to competition of protons (H^+) with metal cations for adsorption sites on soil colloids. The association between metal adsorption on exchangeable surfaces of soil colloids and pH is partly due to the competition of H^+ for adsorption sites at low pH resulting in decreased metal adsorption (Rieuwerts *et al.*, 1998). As a result, adsorption reactions of Pb are significant at soil pH 3-5 (Finžgar *et al.*, 2007). Precipitation and complexation reactions of Pb predominate at soil pH 6-7 (Rieuwerts *et al.*, 1998). Carlon *et al.* (2004) applied multiple regression analysis to literature data and obtained a soil pH-dependent regression equation of the soil-water distribution coefficient for Pb (ratio of sorbed Pb to dissolved Pb).

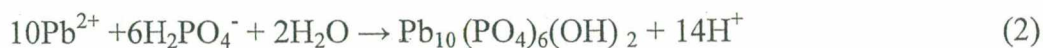
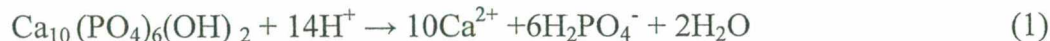
Soil organic matter retains metals by complexation, adsorption and ion exchange. The carboxylic groups of humic substances ionize as the pH rises and form more stable metal complexes. Lead generally tend to persist in the soil surface layers, although a significant quantity of Pb bound the soluble part of the soil organic matter can be transported with percolates through the soil profile (Rieuwerts *et al.*, 1998).

A number of studies was shown that phosphate minerals such as hydroxyapatite and phosphate rock effectively immobilized Pb from aqueous solutions and soils (Ma *et al.*, 1993; 1994 a,b, 1995). Ma *et al.* (1997b) reported the effects of phosphate rock on Pb extractability and speciation in 11 Pb contaminated soils. They found that addition of phosphate rock significantly reduced the $Ca(NO_3)_2$ and HOAc -extractable Pb from all soils indicating its

effectiveness in immobilizing Pb from various Pb contaminated soils. Ma *et al.* (1994b) reported the removal of Pb through dissolution of hydroxyapatite followed by precipitation as hydroxypyromorphite.

When phosphate is added to a Pb contaminated soil, soluble Pb-phases are precipitated to more stable Pb-phosphates such as pyromorphite. This reduces both the availability and mobility of Pb. These compounds are almost insoluble and geochemically stable over a wide pH range (Hettiarachchi and Pierzynski, 2004). Extended research has been performed on the formation as well as mobility and bioavailability of Pb-phosphates (Arnich *et al.*, 2002; Bautier *et al.*, 2001; Brown *et al.*, 2004; Cao *et al.*, 2003; Melamed *et al.*, 2003; Yang *et al.*, 2001; Zhu *et al.*, 2003).

The main mechanism of pyromorphite formation from hydroxyapatite (HA) is dissolution followed by precipitation (Melamed *et al.*, 2003).



Another possible formation route is by surface exchange, where Pb would absorb to the surface of the apatite particle and a cation exchange occur (Arnich *et al.*, 2002).



According to Shashkova *et al.* (1999) also, lead would be adsorbed first on the surface of the apatite particle, and then by diffusion, cation exchange would take place between apatite Ca^{2+} ions and Pb^{2+} ions in solution.

Thermodynamically, it is expected that Pb contaminated soil will eventually form pyromorphite if sufficient P is available. The formation of pyromorphite has been reported to be pH dependent (Laperche, 1996) where pH 5 is to prefer

rather than pH 6 or 7. Natural formation of pyromorphite is enhanced by an acidic pH and high organic carbon content in soil (Bautier *et al.*, 2001) which both increase the dissolution rate of P- and Pb-sources in soil.

Metals are more readily dissolved in waterlogged soils with low redox potential (Rieuwerts *et al.*, 1998). As total soil metal concentrations in soil solution increase, the fixation capacity of the soil solid phase becomes saturated and metals remain in soil solution.

Plants have evolved several strategies for increasing the bioavailability of metallic micronutrients by production of metal chelating compounds (i. e. siderophores). The bioavailability of metals may be facilitated by soil microorganisms producing polycarboxylic organic acids and other chelating metabolites (White *et al.*, 1997). Microbial and earthworm activities increase plant available Pb, root activity, aggregation of Pb forms within silica, oxide or other mineral matrixes (Rieuwerts *et al.*, 1998).

2. 7.7 FACTORS AFFECTING LEAD UPTAKE BY PLANTS

Lead is taken up from soils, at both low and high Pb concentration and this process is strongly governed by soil and plant factors (Kabata Pendias, 2001). Soil pH value, organic matters, clay minerals, oxides of iron or aluminium, redox conditions, etc have been shown to control the behaviour of Pb in soils and also the uptake of Pb by plants (Lasat, 2002).

The uptake of Pb by plant is frequently related to its concentration in soil. In general, increases in soil Pb content resulted in an increase in the uptake of Pb by plants. For example, Salim *et al.* (1993) showed that the concentration of Pb was increased in radish plants when treated with an increasing concentration of Pb in soil. Davies (1992) found that Pb uptake by radish was best predicted by total Pb in soil, and the regression of plant Pb on soil Pb concentration was not improved by adding other soil characteristics.

Soil pH probably is the single most important factor affecting the solubility, mobility, and phytoavailability of Pb. Increasing soil pH decreased Pb in plant roots, although no consistent trends occurred in the foliage. Chen *et al.* (2000) suggested that lime reduced the uptake of Pb by wheat via depression of solubility of Pb.

Organic matter tightly bounds Pb (Singh *et al.*, 1997; Kumar *et al.*, 1995) which may decrease the mobility of Pb in most soils and may reduce the uptake by plants. It has been suggested that the mobility of Pb is greater in sandy soils which tend to lack organic matter, than in organic soils. At low pH, organic matter is the only factor that may reduce the heavy metal mobility in soils because of metal-organic complexation (McBride, 1995). According to Van Erp and Van Lune (1991), Pb and Cu are bound strongly to organic matter and would be released slowly over time as the organic matter is decomposed.

Soil texture, in particular the clay content, has been shown to influence plant uptake of Pb as well as sorption of Pb by soil materials. Soils with higher clay contents, assuming other soil constituents are constant, generally have higher CEC and therefore, higher binding capacity for cations. Sorption studies of Pb by soils indicate that Pb is accumulated in silt and clay fractions due to their relatively large surface areas (Queralt and Plana, 1992).

Geochemical forms of Pb in contaminated soils affect its solubility, which directly influence its availability to plants (Zhang *et al.*, 1997). The geochemical behaviour of Pb indicates that phosphate, when present in sufficient amount, reduces Pb solubility and availability (Ruby *et al.*, 1994). Thus, phosphate minerals have potential to immobilize Pb in contaminated soils and their application to soils may alter the distribution of Pb between various physicochemical forms and hence reduce its availability (Ma *et al.*, 1997b).

The application of hydrous iron or manganese oxides can significantly reduce the solubility of Pb in soil and its uptake by plants (Khattack and Page, 1992; Mench *et al.*, 1994; Lee, 1996). Plant uptake of Cd and Pb by wheat (*Triticum aestivum*) grown in two polluted soils amended with calcium carbonate, calcium phosphate, hog compost, iron oxide, manganese oxide and synthetic zeolite was reported by Chen *et al.* (2000). They concluded that manganese oxide, calcium carbonate and synthetic zeolite can significantly reduce uptake of Pb and Cd in wheat while iron oxide does not affect plant uptake of Pb and Cd.

Pb uptake by wheat was enhanced by organic acids (acetic acids and malic acid). The enhanced influx of Pb into wheat roots was mediated by Ca^{2+} and K^{+} channels depended upon the plasma membrane P-type ATPase as well as enhanced diffusion of Pb towards roots by organic acids (Wang *et al.*, 2007).

Metal solubility and bioavailability can be increased by the application of synthetic chelates such as EDTA, HEDTA, NTA and citric acid to soil (Wu *et al.*, 1999b). The application of EDTA solubilizes large quantities of Pb from soil, which then diffuses down its concentration gradient into plant root, and can be taken by mass flow (Shen *et al.*, 2002). Application of EDTA (3.0 mmol of EDTA/kg soil) to Pb-contaminated soils significantly increased the concentrations of Pb in the shoots and roots of cabbage (*Brassica rapa* L.), mung bean (*Vigna radiata* L.) and wheat (*Triticum aestivum* L.) (Shen *et al.*, 2002).

Plant species differ significantly in Pb uptake and translocation. Huang and Cunningham (1996) reported that Pb uptake by ragweed roots was threefold higher than that by corn roots in a short term (60 minutes) hydroponic experiment. After 2 weeks of Pb (100 μM) exposure in hydroponics, root Pb concentration was 24000 mg kg^{-1} for ragweed and 4900 mg kg^{-1} for corn. In contrast to root Pb concentration, shoot Pb concentration was significantly

higher in corn (560 mg kg^{-1}) than in ragweed (30 mg kg^{-1}) (Huang and Cunningham, 1996).

Microbial activity and earthworm activity increase plant available Pb, root activity, aggregation of Pb forms within silica, oxide or other mineral matrixes (Rieuwerts *et al.*, 1998).

2.7.8 EFFECTS OF Pb ON CROPS AND VEGETABLES

Chen *et al.* (1991) reported that seed germination and respiration, shoot and root growth of seedlings and seedling chlorophyll content of brown rice were decreased by added Pb. All lead compounds greatly enhanced Pb uptake and plant tissue concentrations. $\text{Pb}(\text{OAc})_2$ produced the highest Pb concentrations in the roots, whereas concentrations in all above ground parts were highest in $\text{Pb}(\text{NO}_3)_2$ treated plants. The uptake and plant concentrations of Cu, Zn, Fe and Mn in wetland rice were markedly affected by Pb, with the effects varying with Pb compounds and plant organ.

Dry weight of shoot and root of *A. gangeticus* and *A. oleracea* were significantly affected by Pb application. In general, Pb application caused a decrease in the shoot and root weight of *A. gangeticus* and *A. oleracea* (Kibria *et al.*, 2009).

Kosobrukhov *et al.* (2004) also reported a considerable decrease in dry weights of different plant parts under Pb treatments.

Trivedi *et al.* (1992) reported that increasing Pb concentration had an adverse impacts on K uptake by rice plant. Lead reduced the contents of K significantly in straw and grains of rice.

Judel and Stelte (1977) reported that low doses (500ppm in soil) of highly soluble lead acetate increased the Pb content in the plants. At a moderate Pb concentration in soil ($<100 \text{ ppm Pb}$) positive correlation was observed between the increase of Pb accumulation and length of the growing period of plant species.

Strand *et al.* (1990) observed that at 100 mg Pb, 100 mg Cu and 2 mg Cd/kg soil increased plant uptake combined with yield reduction of 30% in barley grain, 40.3% in potato tubers and 71% in maize.

Juwarker and Shiende (1986) showed that height of plants, length of roots, length of grain, yield of *Hordenuin vulger* were reduced due to combined treatment of Pb and Cd.

Hibben *et al.* (1984) reported that radish leaves and lettuce accumulated more Pb than other vegetables.

Ludger and Jager (1985) investigated the effect of Pb, singly and in combination on yield of *Allium porrum* L. and *Pisam sativum* L. The dry matter production was reduced as a function of heavy metal concentration and combination. The mechanisms of combinations were mostly synergistic. The correlation between pollutant contents (m mol/shoot) and yield was higher than the correlation between heavy metal concentrations of soil or shoot (ppm) and yield. Results of regression analysis showed that the inhibition of copper translocation caused by Pb was responsible for the yield depression.

Tyksinski *et al.* (1993) analyzed Pb from vegetables grown in the city of poznan. It was found that 53.7% of leafy vegetables, 26.9% of rooty vegetables and 40% of vegetable crops grown for their fruit contained excessive concentrations of lead.

Mesmer *et al.* (1991) reported that excess Pb in *Triticum sativum* and *lens esculenta* alters several physiological and biochemical processes in both species. They further reported that Pb inhibits the growth of both shoots and root, but root growth inhibition was more pronounced than the shoot, inhibition percentage increased with higher Pb content and total chlorophyll content decreased.

2.7.9 EFFECT OF LEAD ON NUTRIENT UPTAKE

Plants cultivated in soil contaminated with heavy metals are subject to modification of the chemical composition of not only the content of heavy metals but also macronutrients (Ciecko *et al.*, 2004).

Huang and Cuningham (1996) reported that Mg concentrations in shoots for both corn and ragweed significantly decreased after 2 week of 20 μ M Pb treatment. Lead decreased the uptake of magnesium by *Cucumis sativus* seedlings and *Zea mays* (Walker *et al.*, 1997). Similar results were found by Kopittke *et al.* (2007a) with cowpea. In Pb treated rice plants there was no definite trend in the concentration of magnesium in various parts (Chatterjee *et al.*, 2004).

Kibria (2008) reported that Pb application significantly decreased Mg concentration in grain, straw and roots of rice and leaf, stem and root of Indian spinach. Kibria *et al.*, (2009) also stated Pb did not affect Mg concentration in both shoots and roots of radish.

Lead application in soil neither affected nor showed any definite trend of variation in nitrogen concentration in roots of *A. gangeticus*. Contrary to the results found for *A. gangeticus*, Pb application in soil significantly increased **nitrogen** concentration in shoots of *A. oleracea*. However, the values of nitrogen concentration in shoots of *A. oleracea* with 40-100 mg kg⁻¹ Pb application were not significantly different from each other. At the highest rate of Pb application (100 mg kg⁻¹), nitrogen concentration in shoots of *A. oleracea* increased by 26% compared with control. Nitrogen concentrations in roots of *A. oleracea* were significantly different among the treatments. The values of nitrogen concentration decreased with increasing Pb application up to 40 mg kg⁻¹ (Kibria *et al.*, 2009).

Zinc content of shoots and roots of *A. gangeticus* and roots of *A. oleracea* decreased significantly with increasing rate of Pb application showing a negative relation between Pb and Zn (Kibria *et al.*, 2009). On the contrary, shoots of *A. oleracea* increased with increasing Pb application. Kopittke *et al.* (2007a and b) showed negative effects between Pb and Zn in shoots and roots of cowpea and shoots of signal grass and Rhodes grass.

Shoots and roots of *A. oleracea* and roots of *A. gangeticus* showed to decrease significantly in **Mn** concentration with the increase of Pb application with the lowest values being obtained with the highest rate (Kibria *et al.*, 2009). Similar results were found by Kopittke *et al.*, (2007b) in shoots of signal grass and Rhodes grass. Mn concentration in shoots of *A. gangeticus* was not affected by Pb treatments (Kibria *et al.*, 2009).

Kibria (2008) reported that Pb application significantly decreased potassium concentration in straw and roots of rice, shoot and root of radish and leaf, stem and root of Indian spinach.

Kibria (2008) found Ca concentrations to be decreased in grain, straw and roots of rice, shoot and root of radish and leaf, stem and root of Indian spinach due to Pb application. Similar results were found by Huang and Cuningham (1996) with corn.

2.8 IMPACT OF CADMIUM ON SOIL AND CROPS

Atmospheric deposition of cadmium

Cadmium is released to the atmosphere from both natural and anthropogenic sources. Cadmium is widely distributed in the earth's crust and, consequently, may be released to the air from entrainment of dust particles, volcanic eruptions, or other natural phenomena (ATSDR, 1999). It has been estimated that worldwide anthropogenic emissions of cadmium exceed natural ones by a factor close to ten (Elinder, 1992; IARC, 1993). Industrial activities are the main sources of cadmium release to air (ATSDR, 1999), and major industrial

sources of cadmium emissions include mining and smelting operations (zinc, lead, copper, and cadmium), manufacture of phosphate fertilizers, production of iron and steel (which involves recycling scrap metals), fossil fuel combustion, municipal and sewage sludge incineration pigment manufacturing plants, etc (Alloway and Steinnes, 1999; Wilber *et al.*, 1992). It has been suggested that coal and oil used in classical thermal power plants are responsible for 50% of the total cadmium emitted to the atmosphere (Thornton, 1992).

Atmospheric cadmium is in the form of particulate matter, which may consist of very small particles if it is produced by combustion processes. The main forms of Cd in aerosol-size suspended particles are the oxide, sulphide, sulphate and chloride. These are stable compounds that do not undergo significant chemical transformation. The chief fate of airborne cadmium is to be dispersed by the wind and, subsequently, deposited onto soil and vegetation by both wet and dry deposition (ATSDR, 1999 Alloway and Steinnes, 1999). The transport of Cd and other metals emitted to the atmosphere depends upon the nature of the particulate forms emitted and the climatic conditions.

Concentrations of Cd in ambient air normally fall within the range 0.1-4.0 ng m⁻³ in rural areas and 2-150 ng m⁻³ in urban/ industrial areas (OECD, 1994). The OECD (1994) quote estimates of inputs to soils from the atmosphere ranging from 2-7 g Cd ha⁻¹ yr⁻¹. Jung and Thornton (1997) reported mean Cd concentrations of 0.9-1.7 mg kg⁻¹ (range <0.2- 7.8 mg kg⁻¹) in mining contaminated paddy soils near the Sambo lead-zinc mine in north-west Korea. Rice grain samples contained 0.1-0.5 mg Cd kg⁻¹, substantially higher than average values for rice in Korea. Some typical values for annual deposition of Cd reported in the literature for countries in Europe were (g ha⁻¹ yr⁻¹): Poland, 5.0 (Kabata-Pendias and Pendias, 1993); Sweden, 3.2 (Bergkvist *et al.*, 1989); England and Wales, 2.5 (Alloway *et al.*, 1997) and Europe, 3.0 (Pacyna, 1987).

Nriagu and Pacyna (1988) estimated the worldwide atmospheric deposition of Cd onto soil in 1988 to be within the range 2200- 8400 t Cd yr⁻¹.

Cadmium Concentration in Soil

In neutral soils, Cd concentration is largely influenced by the amount of Cd in the parent rock (Adriano, 2001). Based on the concentrations reported for common rocks, one can expect on the average, soils derived from igneous rocks would contain the lowest Cd (< 0.10 - 0.30 mg kg⁻¹), soils derived from metamorphic rocks would be intermediate (0.10-1.00 mg kg⁻¹), and soils derived from sedimentary rocks would contain the largest amount of Cd (0.30-11.00 mg kg⁻¹)(Adriano, 2001). In general, background Cd level in agricultural soils is about 1 mg kg⁻¹ or less (Adriano, 2001). The mean Cd contents reported from most analytical surveys of background levels of metals in soils lie in the range 0.06-1.1 mg kg⁻¹ with a calculated worldwide mean of 0.53 mg kg⁻¹ in surface soils (Alloway, 1995). Surface soils from major agricultural production areas of U.S. contain Cd within the range of <0.01 to 2.0 mg kg⁻¹ with geometric mean of 0.175 mg kg⁻¹ (Holmgren *et al.*, 1993). In the United Kingdom a 5-km grid survey of soils (5692 samples) showed an average Cd concentration of 0.7 mg kg⁻¹ (McGrath and Loveland, 1992). In Germany, background concentrations of Cd in 2947 soils from rural areas on a range of different geological parent materials showed median values of <0.3-1.0 mg kg⁻¹ with the highest concentrations occurring in the organic surface horizons of woodland soils (LABO, 1995). Govindaraju (1994) reported Cd contents in reference soils from different countries to range from 0.06 to 4.3 mg kg⁻¹. Soils from Sichote-Alin, Russia, contain Cd from 0.2 to 1.14 mg kg⁻¹, and the greatest concern was noticed in flooded soils (Motuzova and Pershikova, 1999). Approximately 9.5% of rice paddy soils in Japan are contaminated with Cd, coming primarily as effluents from nonferrous metal mines. The mean Cd concentration of surface paddy soils and unpolished rice in the most severely affected areas in Japan ranged from 1.12 to 6.38 and 0.78 to 1.06 mg kg⁻¹ dry weight basis respectively (Adriano, 2001).

In a study conducted by Kashem and Singh (1999), soils from several industrial sites around Dhaka city of Bangladesh contained Cd in the ranges 0.11 -1.80 mg kg⁻¹. It has become apparent that although Cd concentrations in non contaminated soils are typically <1 mg kg⁻¹, its level in soils may be substantially elevated due to human activities, or due to weathering of parent rocks having high Cd contents (Adriano, 2001).

CHEMICAL BEHAVIOR OF CADMIUM IN SOIL

Forms and speciation of cadmium in soil

Heavy metal bioavailability is determined by their chemical forms related to solubility in soil. It is important to be able to identify the forms of metals in the soil, especially in the soil solution, in order to have a complete understanding of the dynamics of the metal in agricultural and natural ecosystems. Cadmium in soil solution can be present in different physico-chemical forms, varying in size and charge. Dissolved Cd can be present as free, hydrated cations or as species complexed with organic or inorganic ligands. The term species refers to the chemical form in which an element is present in solution. The anions or molecules with which a cation forms a coordination compound are referred to as ligands. Ion pairs, complex ions, polymers, or micro particulates can reduce free ion species of heavy metals in solution (Green *et al.*, 1993). The process of identifying and quantifying these different species of metals in a sample is referred to as speciation. The speciation of individual elements in the solution phase using data for the total concentrations of all elements and ligands can be estimated by computer implemented models such as SOIL CHEM (Sposito and Coves, 1995), GEOCHEM-PC (Parker *et al.*, 1995), MINTEQA2 (Serkiz *et al.*, 1996) and others.

The risk from heavy metal contamination in a given soil relative to metal transfer to the food chain or migration to the ground water is evaluated by the partition of metals into different fractions (Han and Benin, 1997). The reversible fractions where metals are extracted by H₂O or by exchange reaction

are defined as mobile. The immobile fractions refer to inner sphere complexed where strong acids or digestions are required to release the fractions of metals (Almås *et al.*, 1999; Salbu *et al.*, 1998).

The free ion Cd^{2+} is more likely to be adsorbed on the surfaces of soil solids than other species, such as neutral or anionic species. The principal species of Cd in the soil solution is Cd^{2+} but the metal can also form the following complex ions: CdCl^+ , CdOH^+ , CdHCO_3^+ , CdCl_3^- , CdCl_4^{2-} , $\text{Cd}(\text{OH})_3^-$ and $\text{Cd}(\text{OH})_4^{2-}$ together with organic complexes (Kabata-Pendias, 2001).

Heavy metals are associated with various components of the soil in different ways, and these associations indicate their mobility in the soils as well as their bioavailability (Ahumada *et al.*, 1999). The nature of this association in solid phase of soil is referred to as solid speciation. In most soils, more than 99% of the Cd content is associated with the solid phase and less than 1% is found in the soil solution (Christensen and Haug, 1999). In general, under natural conditions, only a small portion of the metals in soils is in a plant available form (Kabata-Pendias and Pendias, 2001). Mobility of heavy metals relates to their capacity to pass from one soil compartment to another where the element is bound more or less energetically, the ultimate mobile compartment being the soil solution which determines the bioavailability of heavy metals (Moral *et al.*, 2002).

The distribution of Cd among various chemical forms is of importance with respect to its solubility, mobility and bioavailability. Heavy metals in exchangeable form have the most solubility. Metals associated with carbonates would be susceptible to change in pH, also are easily made soluble. An investigation into the effects of chemical forms of cadmium, lead and zinc on their uptake, revealed that exchangeable and carbonate forms exhibited stronger influence on the uptake than the total concentration in soil (Xian, 1989). Heavy metals in the other chemical forms, such as Fe-Mn oxides and

organics with very low solubility and high stability for biological activity, would not have direct bearings on their uptake by plants (Xian, 1989).

The degree of at which metals are associated with different chemical forms depends on such soil properties as pH, amount of organic matter, redox conditions and soil texture (Kashem and Singh, 2004; Rieuwerts *et al.*, 2006). In addition, the distribution patterns of heavy metals in soils depends on the nature of metals and their origin of source (Ma and Uren, 1998). The endogenous heavy metals frequently exist in solid phases (Ramos *et al.*, 1994), and the anthropogenically added heavy metals mainly exist on the surfaces of soils as reactive forms (Levi *et al.*, 1992; Ramos *et al.*, 1994). Narwal *et al.* (1999) found that in two naturally metal rich soils, the percentage of Cd extracted with NH_4OAc was higher at low pH (6.2) than at high pH (7.2) but the opposite was true for less available forms (organic or oxide bound fractions). He and Singh (1993b) reported that the addition of organic matter increased soil CEC and decreased soil pH, resulting in changes in the solid phases of Cd in soils. The solid phase transformation of Cd from the Fe-Mn oxide bound fractions to the exchangeable fraction occurred when organic matter at increasing rates was added to the soils. Mahler (1988) found that Cd, either native or sludge- derived, appeared mainly in the carbonate fraction. Kashem and Singh (2001a) and Chlopecka *et al.* (1996) reported that Cd from anthropogenic sources was more mobile than that derived from parent materials. The mobility of Cd was higher in the city sewage soil than tannery, pharmaceutical and paper mill waste contaminated soil (Kashem *et al.*, 2007a). Almas *et al.* (1999) found that in pig manure treated alum shale soil, ^{109}Cd and ^{65}Zn increased significantly in mobile fractions, with a corresponding reduction in the immobile fractions.

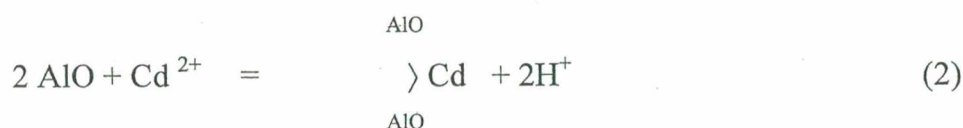
Reactions of cadmium with soil components

Cadmium in the solution phase existed as free ions and potentially the complexed species interact with the soil solid phases by adsorption-desorption phenomena or by precipitation-dissolution (solubility) and ion exchange phenomena (Helmke, 1999). As Cd leachability and availability to plants are related to Cd in the soil solution and to pools of solid Cd that can be made available through the soil solution, it is mandatory to understand and quantify the solid phase Cd and the reactions and processes that govern the distribution of Cd between the solid phase of the soil and the soil solution. Sorption is used as a collective term for various soil surfaces-related processes including surface complexation, ion exchange, and other processes related to binding by chemical or physical properties (Holm *et al.*, 2003). Desorption describes the reverse process that releases Cd from the solid phases into the soil solution. The relationship between these two processes determines the distribution of Cd between the solid phases of the soil and the soil solution. Cadmium distribution between the soil solid phase and the soil solution is a key issue in assessing the environmental risk of Cd in the terrestrial environment.

Adsorption is considered to be the dominating process governing Cd distribution between solid phases and soil solution. Cadmium adsorption processes can be broadly separated into two groups, depending on the affinity of the adsorbent for Cd (McBride, 1994). When Cd is bound by electrostatic forces simply to balance the negative charge on surfaces, this process is referred to as non-specific adsorption and the Cd ions adsorbed in this way are equivalent to the exchangeable Cd. For the second type of adsorption, Cd ions are bound much more tightly to the adsorbent surface. This process is termed as specific adsorption and the adsorbed Cd ions are much less easily removed from the surface of the adsorbent (Christensen and Haug, 1999).

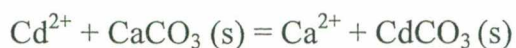
Many soil components such as metal oxides (Fe and Mn), layer silicates, calcite and hydroxyapatite, organic matter and biological colloids (microorganisms) are involved in sorption and desorption processes (McBride, 1989; Zachara *et al.*, 1992; Stevenson, 1994; Huang and Bollag, 1997).

Metal oxides possessing surface metal OH groups may interact with Cd ions by processes more specific than the electrostatic mechanism of ion exchange (McBride, 1989). These metal oxides have, therefore, specific adsorption sites for Cd ions. Poorly crystalline or microcrystalline materials such as allophanes, imogolite and Al-hydroxide gels also have remarkable ability for adsorbing Cd ions (Wada, 1989; Goldberg *et al.*, 1996). The affinity of Cd for O, or the tendency for these ions to form covalent bond is strong enough to liberate H⁺ from surface OH groups, resulting in the specific adsorption of Cd at the reaction sites of metal oxides and amorphous aluminosilicates, e.g.,



Layer silicates may play an important role in Cd adsorption due to permanent charge on the mineral surface (Zachara *et al.*, 1992). Cadmium adsorption on kaolinite appears to proceed largely through specific adsorption and in contrast, adsorption of Cd by smectites and vermiculites appears to be predominantly non-specific in nature (Christensen and Haung, 1999). Sakurai and Huang (1996) reported that a substantial percentage of Cd was adsorbed by the interlayer material through specific adsorption.

Cadmium can be bound by calcite through chemisorption (McBride, 1994) that involves exchange of Ca²⁺ by Cd²⁺ at the surface as shown below:



The reaction has been viewed as a chemisorption process rather than precipitation for the two reasons: (1) the reaction proceeds to a degree determined by the surface area of calcite and (2) the reaction occurs even when the suspension is under saturated with respect to solid CdCO_3 (Christensen and Haung, 1999). Cadmium fits well into the Ca site of hydroxyapatite and Cd is, thus, associated with this mineral in nature (Mc Bride, 1994).

Organic constituents form both soluble and insoluble complexes with Cd and thereby play a dual role in Cd transformation (Stevenson, 1994). Low molecular weight organic components (biochemicals, fulvic acids) serve as carriers of Cd in the solution. In contrast, high molecular weight organic components (e.g., humic acid, humin) function as a sink for Cd.

The sorption-desorption behaviour of Cd in soils (i.e. the dynamic equilibrium between Cd in the soil solution and that adsorbed on the solid phase of the soil) varies from soil to soil and is influenced by many factor including soil composition, pH, texture (and clay content), cation exchange capacity, cationic composition, competing trace metals and organic and inorganic ligands, and redox status.

The composition of the soil affects adsorption of Cd significantly, since various components in soil are able to sorb Cd as discussed before and will be present in different amounts in different soils. Boekhold and van der Zee (1992) and Gray *et al.* (1998) have identified organic matter as the soil parameter providing the strongest correlation with K_d values for Cd.. Cadmium Sorption can be expected to be greater by soils dominated by Mn oxides than by Fe oxide (Backes *et al.*, 1995). The effect of soil solution composition on sorption of heavy metals was reviewed (Naidu *et al.*, 1998).

Soil microbial activity is also believed to play a significant role in the Cd behavior in soils. Besides non-living inorganic and organic colloids, microorganisms such as bacteria have enormous surface areas on which to

immobilize metal ions in the environment (Huang and Bollag, 1997). Chammugathas and Bollag (1987) observed both binding of Cd and its subsequent release from soils under the influence of soil microorganisms. The rate and degree of these processes depend upon soil parameters of which the Eh-pH system is of greater importance

The effects of pH on soil adsorption of Cd are well known and extensively documented (McBride, 1994). Several studies have shown that many individual minerals and other components found in soils can bind Cd, but most studies on whole soil samples have shown that pH is the main parameter controlling the distribution. Anderson and Christensen (1988) found that pH was the most influential factor in controlling the distribution of Cd in soils. Increasing pH favours the adsorption of Cd to metal binding sites and decreases the partition of Cd to soil solution (Mc Bride *et al.*, 1997; Sauvé *et al.*, 2000a). Andersen *et al.* (2002) found the pH not to have any influence on the total Cd content in the soil, but a significant influence on the Cd in solution, and thus on the solubility of Cd in soil. Cadmium solubility decreases at high pH that favors a high sorption capacity (Sanchez-Martin and Sanchez-Camazano, 1993; Bockhold *et al.*, 1993; Egli *et al.*, 1999; Sterckeman *et al.*, 2000). Christensen (1989) and Chlopecka *et al.*, (1996) found that cadmium solubility increases as pH decreases. Cadmium released from soil increases substantially when pH drops below 4.5 (Bergkvist *et al.*, 1989; McBride *et al.*, 1997). This is especially true for sandy soils with low CEC, low acid neutralization capacity, and low ability of the subsoil to sorb Cd ions. Such soils may be vulnerable to Cd leaching. Temminghof *et al.* (1995) found for one soil that a pH decrease of one unit in the pH range 3.5 to 5.0 decreased Cd adsorption by 75% (equal to a four times increase for a one unit increase in pH). The actual effect of pH may depend on the specific soil and pH range, but undoubtedly pH is the most dominating of all factors, increasing adsorption dramatically with increasing pH. Christensen (1989) showed that 72% of the variation in K_d values among 63 soils sampled in the upper 1 m of agricultural soils in Denmark could be explained by

variation in soil pH alone. Sauvé *et al.*, (2000b) recently reviewed and compiled data from more than 70 studies and found by multiple linear regression analysis that approximately 50% of the overall variation in the K_d values for Cd could be explained by variations in solute pH. Thus, soil pH is the main factor controlling the distribution of Cd between solid and solution phases.

Adsorption of Cd could vary for different types of clay minerals (Finžgar *et al.*, 2007). The clay fraction of the soil mineral phase adsorbs metals through ion exchange and specific adsorption. It was reported that for soils with the same total Cd content, Cd was more soluble and more plant available in sandy soil than in clay soil (He and Singh, 1993b; Eriksson, 1989). Soils with high clays and CEC provide sorption sites for metals and strongly retain in the lattice. Cadmium solubility decreases with high clay content that favours a high sorption capacity (Sanchez-Martin and Sanchez-Camazano, 1993; Boekhold *et al.*, 1993; Egli *et al.*, 1999; Sterckeman *et al.*, 2000). But in contrast, an increasing Cd concentration in the soil solution was found by Andersen *et al.* (2002) as the clay percentage increased; that was explained by association of higher Cd content in a loamy sand and sandy loam soils.

A number of investigations have shown Cd solubility to be dependent on the cation- exchange capacity (Christensen, 1989; McBride *et al.*, 1997; Ma *et al.*, 1997a). The significance of CEC among other soil variables than pH on the Cd solubility has been reported as being the most important ones (Buchter *et al.*, 1989). Decreasing soil solution pH increase Cd in solution, but the CEC and content of clay and organic matter in the soil counteract this by binding Cd in the soil. Sánchez-Camazano *et al.* (1998) found a strong correlation of CEC with K_d values for Cd.

Cations present in the soil solution at the mM level can affect Cd adsorption in excess of what can be ascribed to ionic strength effects (Temminghof *et al.*, 1995). Calcium, which dominates among the cations of soils, seems to affect

adsorption of Cd at a level comparable to the effects caused by pH. Magnesium, potassium and sodium may also affect Cd distribution, but they are present in lower concentrations and hence of less competitive strength (Temminghof *et al.*, 1995).

Other trace metals present in the soil solution may compete with Cd for adsorption sites. This has been demonstrated for trace metals such as zinc, lead, nickel, cobalt and copper (Christensen 1987a; Homann and Zasoski, 1987). The presence of inorganic and organic ligands in the soil solution may decrease soil adsorption by formation of dissolved Cd complexes. Of the inorganic ligands, chloride (Cl^-) in particular has received more attention (Boekhold *et al.*, 1993; Temminghof *et al.*, 1995), because Cd readily forms complexes with chloride and some soils may have sufficient concentrations of chloride to result in significant complexation. Formation of complexes with Cl^- tends to shift Cd from the solid to the solution phase, thereby enhancing solubility and mobility (McLaughlin *et al.*, 1997a; Smolders *et al.*, 1998). The ability of chloride in enhancing Cd bioavailability has been demonstrated in field experiments (McLaughlin *et al.*, 1994a, 1996). Application of potash fertilizer (KCl) to soils may lead to concentration of chloride higher than 1M in the immediate vicinity of the fertilizer granules, which may locally decrease Cd adsorption dramatically due to complex formation (Sakurai and Huang, 1996; Onyatta, 1997).

Submergence of soils is reported to decrease the availability of heavy metals in soils attributed to the increase of adsorption of metals on hydrous Mn and Fe oxides (Brown *et al.*, 1989) and formation of insoluble compounds with sulfide (Van Den Berg *et al.*, 1998). The reduction of SO_4^{2-} to S^{2-} takes place at a low redox potential, which then forms a complex with metals and immobilizes them. Hydrous Mn and Fe oxides are thought to immobilize the heavy metals by providing sites for their sorption in most soils (Brown *et al.*, 1989). The adsorption of Cd and Zn on Fe and Mn hydroxide fractions was reported to be

the major mechanism of their solubility reduction in submerged conditions (Kashem and Singh, 2001b).

FACTORS AFFECTING CADMIUM UPTAKE BY PLANTS

The uptake of nutrients and metals by plant roots is affected by a complex interaction of soil and plant processes. As with all mineral ions, Cd is present in both the solid phase and liquid phase of the soil. Cadmium in solid phase is not available for plant uptake and must first be dissolved in the soil solution. The availability of soil Cd to food crops is dependent on the physical, chemical and biological processes that control the solubility and form of Cd in soil solution, especially in the rhizosphere. Important non biotic factors include soil pH, clay content, carbonates, Fe and Mn oxides, redox potential, type and content of organic matter, complexing ligands, and water content, as well as soil management practices, including crop rotations and soil amendments such as phosphate fertilizers, manures, sewage sludges and agricultural lime. Known important biotic factors include plant species, crop cultivar, root activity, rooting patterns and rhizosphere root-associated microorganisms (such as mycorrhizal fungi) (Oliver *et al.*, 1993; Grant *et al.*, 1995; Guo *et al.*, 1996). All of these factors interact to influence Cd availability to plants.

Total Cd content of soil is one of the important factors affecting the uptake of Cd by crops. It is a significant factor influencing grain Cd concentration of wheat and barley in long term sewage sludge experiments conducted by Adams *et al.*, (2004). Significant positive correlations between total Cd of soil and Cd concentrations in plant tissue have also been found for several crops such as Lettuce (*Lactuca sativa* L.), Swiss chard (*Beta vulgaris* L.), and corn (*Zea mays* L.) leaves (McBride (2002), rice (Kibria *et al.*, 2006) and radish (Kibria *et al.*, 2007).

Although various soil parameters are known to affect the availability of Cd, soil pH is considered as one of the major factors influencing the plant uptake of

cadmium from soils (Smith, 1994; Alloway, 1995). The effects of soil pH in regulating the availability of heavy metals, particularly Cd are well documented (Baerug and Singh, 1990; He and Singh 1993c, Eriksson and Söderström, 1996; Oliver *et al.*, 1996; Grant *et al.*, 1999). Soil pH is the single most important factor controlling the solubility, mobility and bioavailability of Cd in soils (Witter, 1989). The plant tissue concentration of Cd generally decreased with increased soil pH provided that other soil properties remained unchanged. This inverse relationship between soil pH and plant uptake of Cd is well established by several investigators (Eriksson, 1989; Jackson and Alloway, 1991; Oliver *et al.*, 1994; He and Singh, 1993c; Singh *et al.*, 1995; Guttormsen *et al.*, 1995). At higher pH values, the solubility of Cd salts in the soil solution declines due to the formation of low soluble compounds; as a result, the biological availability of soil Cd decreases (Salt *et al.*, 1995). The fact that the Cd content was higher in the plants grown on acid rather than on calcareous soils supported this notion (Preer *et al.*, 1995). In a large number of soil and plant samples collected from newly and long term cultivated field located in different locations of Norway, a significant but inverse relationship between soil pH and NH_4 -extractable Cd and between soil pH and Cd concentration in grasses was reported by He and Singh (1993a). Guttormsen *et al.*, (1995) found that the Cd concentration in carrots and Chinese cabbage consistently and significantly increased with decreased pH. However, the relationship may not always be so straightforward. The concentration may decrease or increase depending on the type of crops and soils used (He and Singh, 1994a). In a study, Smith (1994) found that in peeled potato tubers, potato peelings, oat straw, and ryegrass, cadmium concentrations generally decreased as simple linear functions of increasing soil pH over the range of pH values between 3.9 and 7.6. Plants grown in nutrient solution, however, showed an opposite response. Competition between H^+ and Cd^{2+} for uptake resulted in plant Cd concentrations increasing with increasing pH (Floriijn and Beusichem, 1993). Singh *et al.*, (1995) suggested that Cd concentration in wheat, carrot and lettuce can be reduced substantially by raising the soil pH to 6.5. But raising

the soil pH beyond this level had only a minor reduction in the metal concentration. The average magnitude of reduction in the Cd concentration in wheat grain and carrot root was about 55 and 62%, respectively when the pH was raised from 5.5 to 6.5 (Singh *et al.*, 1995).

Increasing pH generally enhances the sorption of Cd by soils (Shende *et al.*, 1993) and reduces plant uptake of Cd (Xian and Shokohifard, 1989). Increased sorption of Cd at higher levels of soil pH was also evident from the results of DTPA and NH_4NO_3 -extractable Cd which decreased in soils with increasing soil pH in a study by Singh *et al.* (1995). Liming of soil raises the pH, increasing cadmium adsorption to the soil and reducing bioavailability (He and Singh 1994; Thornton, 1992).

Adding synthetic chelating agents, such as EGTA and EDTA, to the soil polluted with the heavy metals enhanced plant uptake of Cd and Pb. This phenomenon can be employed for cleansing the soils of heavy metals (Salt *et al.*, 1995).

Soil type also affects uptake of cadmium by plants. For soils with the same total cadmium content, cadmium has been found to be more soluble and more plant-available in sandy soil than in clay soil (He and Singh, 1994a). Similarly, cadmium mobility and bioavailability are higher in noncalcareous than in calcareous soils (Thornton, 1992).

Fertilizer applications can influence Cd phytoavailability directly, through addition of Cd as a contaminant, or indirectly through immediate and long term effects on soil characteristics and crop growth parameters. Fertilizer application can affect soil pH and ionic strength of soil solution, which may increase phytoavailability of Cd. Addition of competing ions may displace Cd from sorption sites in the soil and increase solution Cd concentration. Fertilizer can influence movement of Cd to the root and possibly absorption into the

symplast. The addition of fertilizers having high Cd concentrations to agricultural land in general may cause significant increase in the uptake of Cd by crops through improvement in plant growth, rooting intensity and mass flow.

A number of investigators have shown that the application of Cd-containing fertilizers increased Cd uptake by crops (Grant *et al.*, 1999; Jones *et al.*, 1987; Jones and Johnston, 1989; Andersson and Siman, 1991). In other studies, in spite of an increase in Cd content of the soil with P application, the Cd concentration of crops was not increased by long term P fertilization (Baerug and Singh, 1990; He and Singh 1993c, d). The Cd concentration of the P fertilizer, the application rate, the soil type and the crops grown are important factors, when considering the relationship between added Cd and plant uptake. An intensive increase in the rate of the application of phosphate fertilizer leads to the accumulation of available Cd in the soil, which in turn affects the plant's Cd content (Al-Faiyz *et al.*, 2007). Pezzarossa *et al.* (1993) also reported that the uptake of Cd by plants increased with an increased application rate of phosphate fertilizers. Guttormsen *et al.*, (1995) reported that yearly application of Cd through fertilizer had resulted in an accumulation in sandy soil which was then reflected back in the increased concentration in the vegetable crops. The concentration of Cd in carrots tended to increase with increasing rate of Cd levels in fertilizers and the increase was more pronounced in carrot leaves. Singh (1990) found that the application of a Cd containing NPK fertilizer (40 mg Cd kg⁻¹) at the rate of 30 mg P kg⁻¹ soil did not increase the Cd concentrations in oat and rape. However, the same fertilizer at a higher rate of application (90mg P kg⁻¹ soil) increased the Cd concentrations in both crops. Thus, increased Cd in the soil leads to increased Cd in crop plants (Zarcinas *et al.*, 1999). As well as adding Cd to the soil system as a contaminant, P Fertilizer may influence Cd availability through its effects on soil pH, ionic strength of the soil solution and crop growth.

Nitrogen fertilizers can increase Cd concentration in plants, although the fertilizer does not normally contain significant levels of Cd (Eriksson, 1990b; Oliver *et al.*, 1993; Grant *et al.*, 1996; Grant and Bailey, 1997b). The increased crop uptake of Cd with N application may be due to increase in ionic strength of the soil solution, ion exchange reactions, or soil acidification. Basta and Tabatabai (1992b) reported that long term application of N fertilizer in continuous corn production reduced soil pH, base saturation and adsorption of Cd. Fertilizers with high NH_4^+ content depressed soil pH and increased the crop uptake of Cd (Eriksson, 1990; Willaert and Verloo, 1992).

The effect of fertilizers on Cd accumulation in crops tends to be greater in sand than in clay soils (Eriksson, 1990; He and Singh, 1995; Grant *et al.*, 1996). Sands have a lower sorption capacity and lower average soil-water content than clay soil, which may result in a higher Cd concentration in the soil solution and a higher Cd uptake by the plant.

Organic matter plays an important role in Cd phytotoxicity by reducing the bioavailability of Cd in soils due to high cation exchange capacity (CEC) and complexing properties (He and Singh, 1993b). A negative correlation was observed between Cd concentration in plants and organic matter content in soils (Chen and Aviad, 1990; He and Singh, 1993b). Although polymeric organic matter decreases the bioavailability of Cd to plants, organic complexing molecules of low molecular weight may increase it (Chen and Aviad, 1990).

The nutrient status of soils also affects the amount of Cd available to plants. In nutrient-enriched environments, the bioavailable fraction of metals may be reduced as a result of binding to nutrient anions. The uptake of heavy metals in plants may also be affected by competition, since nutrient cations compete with the metal for uptake sites (Greger, 1999). Thus, the uptake of Cd may decrease with increasing external nutrient to toxic heavy metal ratio. Greger *et al.*,

(1991) showed that the Cd net uptake in the roots of sugar beet (*Beta vulgaris* L.) was greater when the nutrient concentration was minimal, rather than optimal. Some studies show that metal accumulation may be depressed by competition with a certain nutrient cation. Trivedi and Erdei (1992) found that wheat (*Triticum aestivum* L.) plants with a high K supply accumulated less Cd and Pb than plants with a low K status. Calcium (Ca^{2+}) considerably inhibited Cd^{2+} uptake by roots of diverse plant species (Jensen, 1995). Cadmium and calcium (Ca) antagonistically reduced the uptake of each other in the submerged macrophyte coontail (*Ceratophyllum demersum* L.) (Tripathi *et al.*, 1995).

However, in the case of birch roots, a higher Ca^{2+} concentration in the medium promoted Cd^{2+} uptake, although Ca concentration in the root tissues did not affect the rate of Cd^{2+} absorption (Jensen 1995). The concentrations of other metals such as Zn, Pb, Cu and Ni in the soil have been shown to affect Cd uptake by plants (Abdel-Sabour *et al.*, 1988; Cataldo *et al.*, 1988). Zn^{2+} ions counteracted Cd^{2+} absorption (Oliver *et al.*, 1994). Cadmium uptake by wheat and other crops has been reported to decrease as a result of Zn fertilization (Oliver *et al.*, 1994; Grant *et al.*, 1999). When applied to soil, Zn decreased the Cd concentration in all wheat tissues, whereas phosphorus and nitrogen plus phosphorus fertilizers promoted Cd accumulation in wheat tissues (Choudhary *et al.*, 1995). Oliver *et al.*, (1994) showed that the Cd concentration in grains of wheat grown on Zn deficient soils could be reduced by the addition of Zn at planting. The authors suggest that low Zn concentrations in the soil may affect plant membrane integrity allowing increased uptake of Cd. It is also possible that Zn competes with Cd for uptake at the root surface. In addition to competition at the root surface, preferential binding of other metals, such as Pb, to soil surfaces can increase the concentration of Cd in the soil solution and, hence, uptake by the plant, although this has little practical significance in agricultural soils (Adriano, 2001). Florijin *et al.*, (1992) reported on the effects of the form of nitrogen nutrition on the uptake of Cd in lettuce varieties grown.

in nutrient solution culture. Cadmium uptake was found to increase when nitrogen was supplied in the form of NH_4 in contrast to a decreased uptake when supplied as NO_3 . Further work conducted by Willaert and Verloo (1992) supported these findings for soil grown plants, although the N effect in a study by Dunbar (2004) was attributed to the effects of N fertilizer on soil pH.

Recent studies have shown that the chloride (Cl) concentration in soils is another major factor that can determine Cd availability (Li *et al.*, 1994; McLaughlin *et al.*, 1994a, 1997b; Norvell *et al.*, 2000). An increase in Cl concentration in the soil or soil solution was shown to increase Cd concentration in soil solution and Cd uptake by plants, whether in laboratory or field experiments (Wegglar *et al.*, 2004; Boukhars and Rada, 2000). Chloride anions are known to reduce soil sorption of Cd, probably due to the fact that chloride forms relatively strong complexes with Cd (Boekhold *et al.*, 1993). It is generally accepted that the Cd uptake of plants is dependent on the chemical speciation of Cd in solution (Checkai *et al.*, 1987). Although initially it was argued that only “uncomplexed” free ion metal species are taken up by the plant, there is increasing evidence that also some metal complexes, such as chloro complexes, can be absorbed by the plant root, although at a lower efficiency (Boukhars *et al.*, 2000). In a study by Wegglar *et al.* (2004) on the effect of Cl in soil solution on the plant availability of biosolid -borne Cd, the principal Cd species in soil solution were free (ionic) Cd^{2+} , chloro, sulfate, and carbonate complexes, and a small fraction of organically complexed Cd, which is in agreement with other studies of biosolid-amended soils (Hirsch and Banin, 1990).

Plant species differ widely in their ability to absorb, accumulate and tolerate Cd (Kabata Pendias, 2001).

Among plant species the Cd concentration is generally higher in leafy plant species such as spinach and in root crops like carrots as compared to grain crops (Alloway *et al.*, 1990). In general, cadmium accumulates in the leaves of plants and, therefore, is more of a risk in leafy vegetables grown in contaminated soil than in seed or root crops. He and Singh (1994a) reported that, for plants grown in the same soil, accumulation of cadmium decreased in the order: leafy vegetables > root vegetables > grain crops. He and Singh (1994a, b) found Cd concentrations in spinach > carrot > rye grass > oat. Alloway *et al.* (1990) demonstrated that uptake of cadmium decreased in the order: lettuces, cabbages, radishes, and carrots. Mench *et al.* (1989) reported that tobacco (*Nicotiana tabacum* L.) took up Cd in its shoot from soil more than 3 to 10 times higher than maize did. Soybean and rice took up Cd in their shoots from soil more than 7 to 15 and 7 to 12 times higher than maize did (Murakami *et al.*, 2007).

The amount of Cd that enters the diet from a crop depends on the amount of Cd that the crop accumulates and whether Cd accumulates in the portion of the crop that is consumed. Distribution of Cd in the plant differs depending on the plant species and growing conditions (Jackson and Alloway, 1992). As well as differing in total accumulation, species differ in the distribution of Cd among plant parts. It has been noted that the uptake and translocation of heavy metal to consumable parts of crops varied greatly with plant species and with genotypes within a species (Li *et al.*, 1995; Dunbar *et al.*, 2003 and Liu *et al.*, 2005). Cadmium concentration of straw was greater than that of grain in oat (He and Singh 1994a) and rice (Kibria *et al.*, 2006). According to Nwosu *et al.* (1995), the metal burden of a crop depends on uptake by the root system, direct foliar uptake and translocation within the plant, and surface deposition of particulate matter.

Distribution of Cd in the plant may be related, in part, to Cd tolerance. High tolerance of rye grass to Cd toxicity may relate primarily to a low transport rate

of Cd into the shoot (Yang *et al.*, 1995). Cadmium may be complexed in Cd-binding peptides in roots and old leaves of lettuce and spinach, with the roots and old leaves acting as a barrier to the transport of Cd to young leaves (McKenna *et al.*, 1993). The shoot: root ratios of Cd are less than 1 when non-tolerant species are grown on contaminated soil and high shoot: root ratios are generally associated with hyper accumulator species (Brown *et al.*, 1994).

Accumulation of high levels of Cd in the root may limit the accumulation of Cd in edible above ground portions of the plant (Grant *et al.*, 1999). Cadmium has been found to be bound by cytoplasmic proteins that usually contain cysteine and are collectively called phytochelations. Excess concentration of Cd in plant tissue may trigger the formation of phytochelatin, which could lead to retention of Cd in the root (Grant *et al.*, 1999).

The uptake and translocation of Cd in plants vary greatly not only among plant species but also among cultivars within the same species (Liu *et al.*, 2005). He *et al.* (2006) showed large differences in Cd concentrations of brown rice among the 38 rice genotypes grown in Cd-contaminated soil. According to Wu *et al.* (1999a), more than a two fold difference (ranging from 0.48 to 1.17 mg kg⁻¹) was observed for Cd concentration in brown rice among 20 rice genotypes grown in South China. Morishita *et al.* (1987) showed a wide variation among 56 rice cultivars of different types in Cd concentrations of brown rice, ranging from 2.10 to 73.6 µg kg⁻¹, growing in a non contaminated area. The differences among the rice genotypes in the uptake of Cd may result from the differences in their root absorption abilities and exudation properties (He *et al.*, 2006). Significant cultivar differences in Cd uptake were also observed for both wheat and barley (Adams *et al.*, 2004). Important differences in Cd uptake and transfer among maize genotypes have also been shown (Florin and van Beusichem, 1993; Guo and Marschner, 1996). Sparrow

et al. (1992) reported differences in Cd uptake among commercially grown potato cultivars in Tasmania, with Kennebec averaging 0.24 mg kg^{-1} and Russet Burbank 0.15 mg kg^{-1} . McLaughlin *et al.* (1994b) reported that mean tuber Cd concentrations differed significantly in 14 commercial potato cultivars, and suggested that tuber Cd concentrations at some sites can be reduced by up to 50% by appropriate choice of cultivar.

Li *et al.* (1997) reported genetic variation of sunflower and durum wheat cultivars in their ability to absorb and translocate Cd to edible crop parts. Li *et al.* (1993) reported large genetic differences among 200 sunflower genotypes grown at four locations and tested for kernel Cd concentration. The average Cd levels in the five lowest genotypes were four fold lower than the Cd levels in the five highest genotypes. Significant differences in heavy metal uptake and distribution between flax cultivars have been shown by several authors (Li *et al.*, 1997). A great difference in Cd accumulation and tolerance has also been identified in *Thlaspi caerulescens* ecotypes of different origin (Lombi *et al.*, 2000).

Other plant factors, such as root surface area, root exudates, mycorrhization, phloem and xylem transport, and transpiration rate also affect the availability of Cd in soil and the uptake and translocation of Cd by plants (Shallari *et al.*, 1998).

2.9 IMPACT OF ZINC ON SOILS AND CROPS

Zinc is the first member of Group IIB (Zn, Cd, Hg) in the periodic table. Its atomic number 30 and atomic weights 65.38. It occurs in nature primarily as the sulfide, carbonate, silicate and oxide. The most important uses of the metal and its alloys are in galvanizing, die-casting and the manufacture of brass. Zinc oxide, zinc sulfide and other compounds are used in plastic, paints, cosmetics and agricultural application (USEPA, 1980a). The role of zinc as an essential nutrient is well established now. A number of enzymes are dependent on zinc.

It takes part in the synthesis of DNA, proteins and insulin. Hence zinc is essential for the normal functioning of the cells including protein synthesis, carbohydrate metabolism, cell growth and cell division (Dara, 1995).

At $\text{pH} > 7.5$, $\text{Zn}(\text{OH})_2$ is the principal species in both environments (Bodek *et al.*, 1988). The sorption of zinc on soil and sediment increases greatly as pH increases

Zinc is fairly uniformly distributed and easily adsorbed by mineral and organic substances, accumulating primarily in the soil surface layer. Zinc soil chemistry is quite complex in terms of its various combined ionic forms, with zinc being the most readily soluble of all the heavy metals in soils (Pais *et al.*, 1994). Cammarota (1980) and NRC (1979) reported that most of the Zn produced in the world comes from ores containing Zn sulfide a mineral. The higher concentration lies in ZnO (80.3%) and ZnS (67%) and it ranks fourth among metals of the world in annual consumption. Domingo and Kyuma (1983) reported 66 ppm for tropical Asia and 68 ppm for Bangladesh.

Zinc is used in the manufacture of dry cell batteries, parchment papers, glass, automobile tyres, television screens, printing and dyeing of textiles, as a flux in metallurgical operations, wood preservatives, agricultural micronutrient, fertilizers, insecticides, etc. Its uptake is promoted with decreasing soil pH. It is easily distributed to various plant parts (Bodek *et al.*, 1988; Markert, 1993). A 10% reduction in rice yield occurred, when extractable (0.1N HCl) Zn was 460 ppm in paddy soils in Hokaido, Japan (Chino, 1981). He also summarized the Zn toxic levels for rice tops as 100 to 300 ppm and rice roots as 500 to 1000 ppm.

Shuman *et al.* (1997) found rhizosphere soil Zn increased in the Mn oxide fraction indicating that it may have been adsorbed or occluded by the oxides freshly precipitated by the roots. This increase in Zn in the Mn oxide fraction

coupled with a decrease in more plant available fraction indicated that rice cultivars with high oxidizing power can alter the rhizosphere forms of metals so as to decrease their plant availability.

Lubben and Sauerbeck (1991), with their experiment of spring wheat, manured with sewage sludge for 18 years, found that Zn content of the grain was appreciably lower than those of straw, but in the unpolluted control grain was enriched in Zn. Zinc is an essential micronutrient with a sufficiency range of 20 to 100 mg/kg dry weight of tissue.

2.10 IMPACT OF COPPER ON SOILS AND CROPS

Copper is the first member of Group IB (Cu, Ag, Au) in the periodic table. Its atomic number 29 and atomic weights 63.57. Copper is a widely distributed metal in nature, and is extensively used by men. It is an essential metal required by almost all living organisms in some of their enzyme systems. Deficiency of copper may lead to certain physiological disorders in both plants and animals, but at higher concentrations it works essentially as a pollutant. Copper occurs in nature mostly in the form of oxides and sulfides (De, 2000).

Organic complexation, specific adsorption, precipitation, and ion exchange are important mechanism for sorption of copper into soils and sediment. The sorption process is strongly dependent on pH (Bodek *et al.*, 1988).

Copper is immobile in soils. Hiroki (1991) stated that Cu can prevent biological processes in ecosystems. Since soil pollution problems due to Cu is becoming increasingly serious, it is important to assess its deleterious effects on the soil ecosystems. Applied or deposited Cu is strongly fixed by organic matter, clay minerals, oxides of Fe, Al and Mn (Baker, 1979). For normal agricultural soils, total Cu is expected to range from 1 to 50 ppm and available Cu from 0.1 to 10 ppm, depending on the kind of extractant used (Baker, 1979). Domingo and Kyuma (1983) found 27 ppm Cu in Bangladesh soils.

Its major sources are from Cu Compounds and Cu chelates in agriculture, smelting for Cu, Fe and steel production and coal combustion from the industries (Duce and Windom, 1976).

Aoyama (1998) indicated that in apple orchard soils with heavy metal accumulation, the Cu mineralization of humified plant residues was inhibited by the pH-dependent water-soluble and exchangeable heavy metals, especially Cu. Copper in soil can occur in several forms (1) in the soil solution, ionic and complexed, (2) in normal exchange sites, (3) on specific sorption sites, (4) occluded in oxide material, (5) in organic residues and living organisms and (6) in the lattice structure of primary and secondary minerals.

Copper is an essential micronutrient with a sufficiency range of 5 to 30 mg/kg dry weight of tissue. Plant species vary in their tolerance to copper. Toxicity occurs, when tissue levels exceed 20 to 30 mg/kg. It is particularly toxic to roots, with relatively little being translocated to plant tops. The symptom of copper toxicity is chlorosis as high copper interferes with iron metabolism. Its deficiencies are most likely to occur on organic soils and on mineral soils with a high pH (>7.5) and or high (>2%) organic matter content (Pais *et al.*, 1994).

Chino (1981) reported that for rice, toxicity levels in tops were in the range of 20 to 30 ppm Cu, in roots toxic range was from 100 to 300 ppm. Chino *et al.*, (1966) found that the toxicity of metals in rice follow the order: Cu > Ni > Co > Zn > Mn, which correspondingly follows the order of the metal electro negativity.

Lubben and Sauerbeck (1991) observed higher concentrations of Cu in grain than in straw and chaff in spring wheat, roots were enriched in Cu, as compared with the soil, however, sewage sludge treatment induce a significant drop of Cu content rather than an increase.

Sarkunan *et al.* (1989) reported that rice plants receiving the highest levels of Cu were stunted in growth and the leaves were dark green similar to

phosphorus deficiency. Zinc application decreased Cu content in straw; while Cu addition enhances Zn content indicating that both antagonistic and synergistic interactions occur on the metal accumulation in rice (Chaudhury *et al.*, 1972).

Copper has a high bioaccumulation index and can accumulate in plants to high levels, which may pose environmental health problems (Pais *et al.*, 1994). It is essential for health (2-3 mg) but at higher levels, copper is an irritant of the stomach and intestine and can prove fatal at very high doses. It is usually more toxic to fresh water fish than any other heavy metal except mercury.

2.11 IMPACT OF MANGANESE ON SOILS AND CROPS

Manganese is one of the most abundant trace elements in the lithosphere. It exists in the soil in a wide range of oxidation states, depending on physiochemical conditions. Its solubility depends on soil pH and redox potential and availability increases significantly with a decrease in soil pH. Availability is also affected by the presence of organic ligands for neutral to alkaline soils. (Pais *et al.*, 1994).

Like other trace elements, Mn is not only important for plant, animal and human nutrition, but it has also several functions in plants. It activates many enzyme reactions involved in the metabolism of organic acids, phosphorus and nitrogen. In higher plant manganese activates the reduction of nitrite and hydroxylamine to ammonia. It is also involved in photosynthesis and functions along with Fe in the formation of chlorophyll. Its minerals are widely distributed the most common being the oxides, carbonate and silicates. Manganese uptake is in ionic form from soil solution. It is easily transported to different plant parts. Only the reduced form Mn^{+2} is taken up by plants which is promoted by anaerobic conditions and low pH (Islam and Ullah, 1973; Bodek *et al.*, 1988; Markert, 1993).

Jones (1972) reported the following ranges of Mn (in ppm, dry wt. of mature leaf tissue) for most agricultural crops, deficient, <20, sufficient 20-500, and toxic > 500. Melsted *et al.*, (1969) found the following critical levels of Mn (ppm), corn 15, soybeans 20, wheat 30 and alfalfa 25.

Manganese toxicity can be associated with Mn concentrations in plant tissues exceeding 500 ppm (dry wt. basis). However, most crop species appear to tolerate as much as 200 ppm Mn in their tissues without showing toxicity effects. Levels of Mn in potato foliage from 300 ppm to 1000 ppm in tops and 200 to 600 ppm in roots were reported (Chino, 1981).

Shuman *et al.* (1997) found that rice with higher oxidizing power decreased Mn in the Mn oxide fraction, since Mn reduced by submergence was oxidized by the oxygen supplied by the roots.

Manganese is widely distributed throughout the body but in low concentrations. Effects on reproduction are the first signs of manganese deficiency, which also affects skeletal development. It is normally considered the least toxic of the trace elements for poultry and mammals, with maximum tolerable levels varying from 400 to 2000 ppm depending on the species. Absorbed manganese is primarily excreted through feces, little is excreted in urine (Pais *et al.*, 1994).

CHAPTER 3

MATERIALS AND METHODS

The present study included two parts-

- i) To study the accumulation of lead and some other heavy metals (Cd, Zn, Cu and Mn) in some contaminated soils along Dhaka - Manikgonj- Khulna highway and
- ii) To study the accumulation of lead in grass and some crops of the same soils.

The laboratory analyses were conducted in the Department of Soil, Water and Environment, University of Dhaka and in Soil Science Discipline, Khulna University. The soil samples were collected along Dhaka-Manikganj-Khulna highway, mainly from Savar to Manikgonj and Fultala to Shonadanga. Soil and plant samples were collected from different locations along the highway. The selections of sampling sites were based on the parking of vehicles, roadside garage, and motor stand, industrial units, brick field as well as whereby vehicles pass. The samples were processed for physical and chemical analyses in the laboratory. In the laboratory the following parameters were analyzed:

1. The amount of different nutrients and some heavy metals content in soil.
2. The nutrients and heavy metals uptake by plants of that area.

Dynamics of lead in some roadside soils of Dhaka-Manikganj-Khulna highway.

Soil and plant samples in triplicate for this study from twelve different sampling sites were collected along Dhaka-Manikgonj and Khulna highway.

3.1 SELECTION OF SAMPLING SITES

Twelve sampling sites were selected in three districts in order to give a sufficient representation to each area whose average daily traffic (A.D.T) are quite different. Besides the type of highway, layout has been taken into account for site selection. The assessment of enrichment factors of heavy metals especially lead has been considered as “a background level” and the average level has been measured in soils and roots and shoots of plants at different distances from vehicular traffic. Samples were collected in August-September 2009. The sampling sites are presented in Figure 3.1 and Figure 3.2.

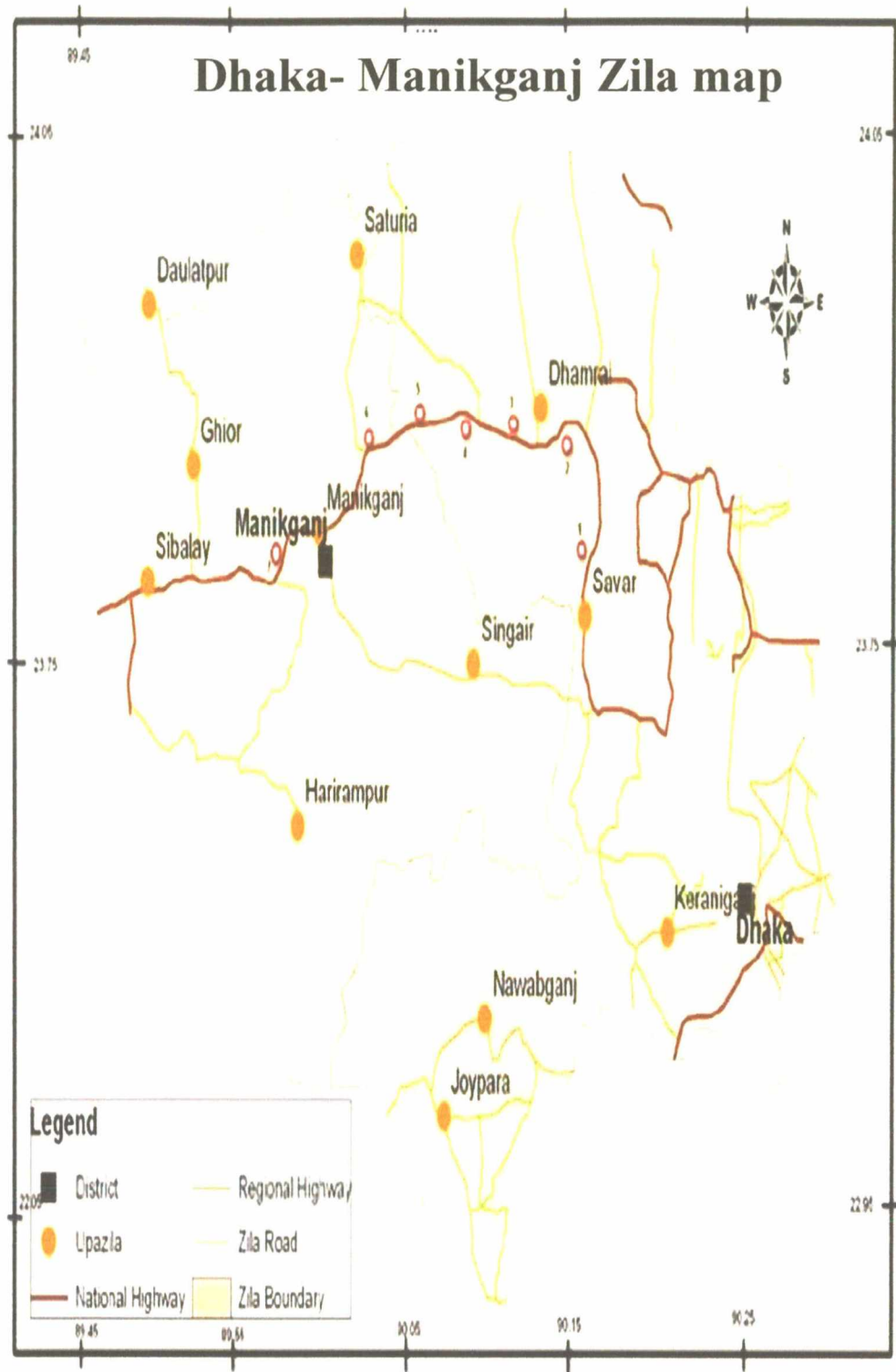


Figure 3.1 Dhaka- Manikganj Zila map Showing Sampling Sites

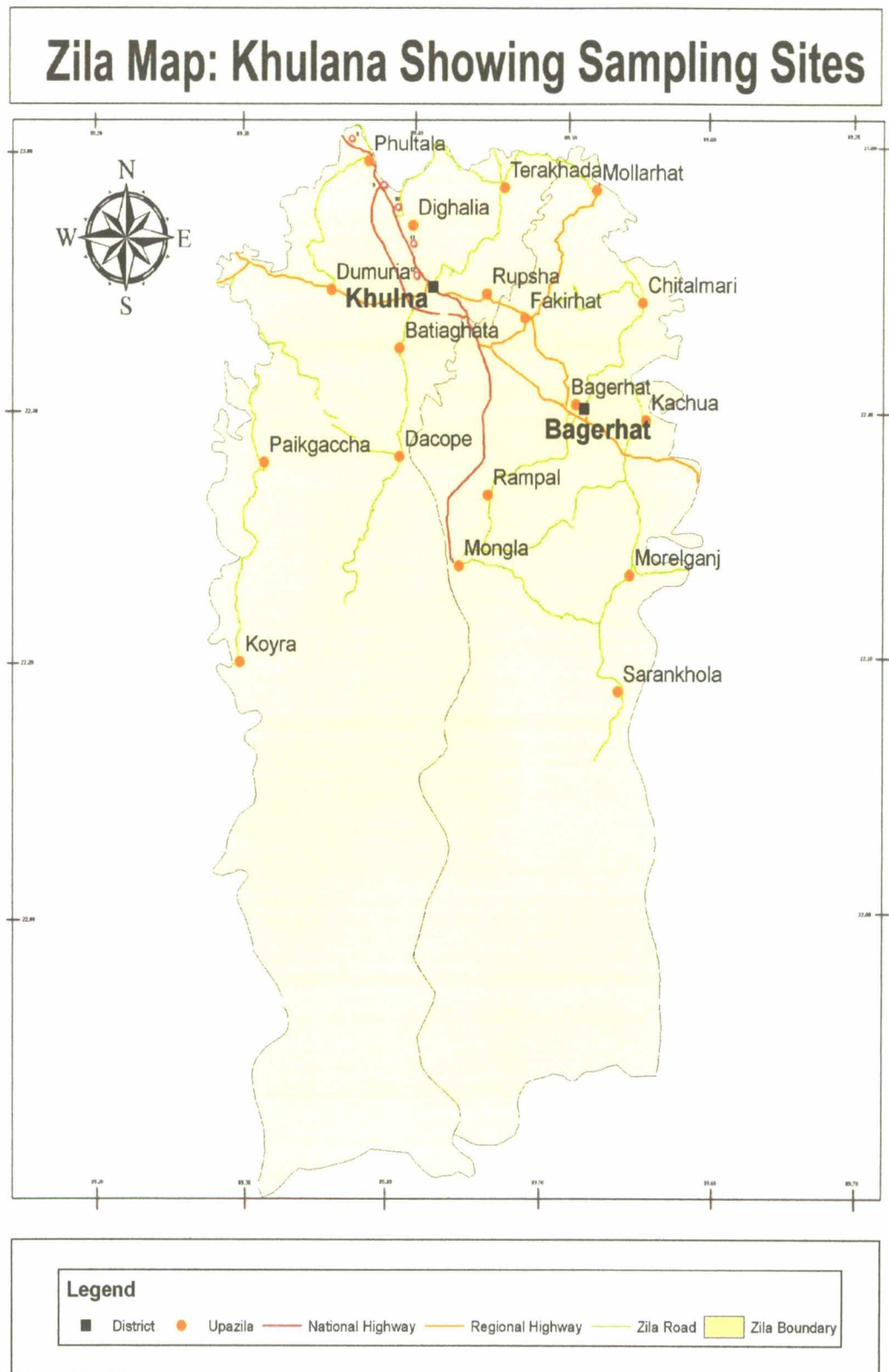


Figure 3.2 Khulna Zila map showing sampling sites

3.2 BRIEF DESCRIPTION OF THE SAMPLING SITES

In each sites A, B and C points were selected for sampling spot. The first one spot A was edge of the road, the second one spot B was 30 meter and the third one spot C was 50 meter away from the first spot.

Dhaka city is the largest city and the main industrial zone of Bangladesh. It is situated within $22^{\circ}14'$ and $22^{\circ}27'$ N latitude and between $91^{\circ}46'$ and $90^{\circ}53'$ E longitude. A large number of industrial operation including plastic, textiles, chemical, paint and dye manufacturing, pharmaceutical industry and petrol pumps are located along the roadsides of the Dhaka city i.e. Savar, Satoria, Dhamrai and Manikgonj area. Roadsides are thought to be polluted with emissions from heavy traffic in this area.

Khulna is the third largest metropolitan and industrial city in Bangladesh. Historically, Khulna has been established as a regional center for trade and commerce. Khulna has achieved tremendous industrial growth during the early and mid sixties having 950 major industrial units (URDP, 1999). Most of the industries discharge their wastes and effluents into the surrounding environment.

Since 1960s to date most of the large industries in Khulna such as Khulna newsprint mills, hard board mills; platinum, jubilee, crescent, peoples, star and Daulutpur jute mills; power plants, meghna, jamuna and padma oil depots were established in around Khalishpur -Fultula industrial belt. Moreover the main route of transport from Khulna to Dhaka and other districts is present in this zone.

Sampling sites

Before collecting the samples, the sampling sites were chosen along the highway where automobile pollution may occur. So, the sampling sites were chosen along the Dhaka-Manikganj-Khulna highway. Here all sampling sites are briefly described.

Twelve sampling sites were selected from three districts are:

Site-1:- This site was situated at the **Nabinagar, at Savar Sriti Sougndha**. The site lies at $23^{\circ} 54' 803''$ N latitude and $90^{\circ} 15' 52''$ E longitude. Grass was collected from the roadside of Nabinagar bus stand where Dhaka-Manikgonj and Dhaka-Ashulia link road is present. At this location only one spot -A was selected for sampling because of lacking of other two spots, spot B and C.

Site- 2:- The study area was in **Srirampur village** of Sutipara union at Dhamrai. This area lies at $23^{\circ} 55'$ N latitude to $90^{\circ} 07'$ E longitudes. There was a big rice field and the samples were collected from this field. An industrial unit was located in this area which was around 500m away from roadside. The main agricultural crop in this site was paddy rice. The wastes and effluents flowing through the drain were diverted to small plots by farmers for irrigation of paddy rice. Rice, grass and malancha were collected from this field.

Site-3:-This site was in Gangutia union, **Krishnopura village** at Dhamrai thana. . This area lies at $23^{\circ} 54' 00''$ N latitude to $90^{\circ} 04' 33''$ E longitude. A small piece of land was cultivated with some vegetables crops. Red amaranthus and Balsam apple along with soils were collected from 50m away from the roadside.

Site- 4:- The site was in Charkanda, Ghora under Gaigir union at Manikgonj district. This area lies at $23^{\circ} 53' 90''$ N latitude to $90^{\circ} 03' 39''$ E longitude. A small land was cultivated with chilies along roadside. There is a bus stand at this location and slum people are living here. Chilies with soils were collected from the above mentioned three spots.

Site- 5:- This study area is situated at 1.5 km west side of Manikgonj bus stand under Dighi Union, **Vatpur village** in Manikgonj. . This area lies at $23^{\circ} 52' 93''$ N latitude to $90^{\circ} 02' 27''$ E longitude. Most of the land in this study area on both side of the highway were used for Agricultural purposes. Most of the people used this land for rice and vegetables production. Basil was collected from the edge of the roadside.

Site- 6:- The sampling site was the Dighi Union of Manikgonj District. It is about 2km. away from the east of Tara Bridge ($23^{\circ}5'95''$ N latitude and $98^{\circ}57'80''$ E longitude). Two rice fields were present on both sides of the high way. But, most of the lands of this area were under water. Grass, malancha and rice were collected from the edge, 30 m and 50 m away from the edge of the roadside, respectively.

Site- 7:- The site was selected ($23^{\circ}50'93''$ N latitude and $89^{\circ}56'72''$ E longitude) at Baniajuri Union in Manikgonj. It was 6 to 7 km away from Tara Bridge. An agricultural field belonging to Gangacharan malaker along roadside area selected for sampling points. This field was used for 12 years for vegetables production. The samples were collected after harvesting of maximum vegetables. This field was used for the production of cabbage, reddish, cauliflower, chilies etc. Chilies and malancha from 30m and grass were collected from 50m distance from the edge of the roadside, respectably and grass and aurum were collected from the edge of the roadside. A large number of buses, tempos, cars, trucks, and other types of motor vehicles passes through for almost twenty four hours.

Site-8:-This site is present at Atra Gilatala, Fultala under Khanjahan Ali thana ($22^{\circ}55'30''$ N latitude to $89^{\circ}30'01''$ E longitude). The samples were collected from the roadside and from an agricultural field along the roadside. The field was cultivated with various types of vegetables, mainly ladies finger. Malancha was collected from the roadside and ladies finger was collected from 30m and 50m distances from the edge of the roadside. Many people live here and the people are mainly dependent on agriculture. Many buses, tracks, move from here.

Site-9 :- The name of the sampling site is, Payer Bazar, Fultala. It was about two km away from the site-8. This site lies at ($22^{\circ}56'42''$ N latitude to $89^{\circ}28'59''$ E longitude). There was a low land filled with water. A rail line passed away beside this field. First site (A) was selected along the highway at 0m distance. Natural grass , aurum and malancha, along with soil were

collected from this site. The second sampling site was 30m away from the road. From this site, grass, potato and arum were collected. The third sampling site was 50m away from the edge of the road. Malancha, potato, grass and arum were collected from this spot.

Site-10:- This site was selected at the Bederdanga, Fultala which lies at $22^{\circ} 57' 16''$ N latitude and $89^{\circ} 28' 58''$ E longitude. It is a residential area but many motor vehicles and trucks, tempos use this road always for their communication. Rice, grass and arum along with the soils were collected from the edge of the road and again grass, arum and rice were collected from the 30m away and rice, grass and arum were collected from 50ms away of the road.

Site-11:- The samples were collected from the Damodar high school at Fultala upazila . A large field covered with grasses and seldomly used play ground lies at $22^{\circ} 56' 57''$ N latitude and $89^{\circ} 28' 54''$ E longitude. Only grass along with soils were collected from the three spots A , B and C at a distance of 0m, 30m and 50m to investigate the contamination effect.

Site-12:- The spot is situated in Boyra-Sonadanga link road. The area lies at $22^{\circ} 50' 42''$ N latitude to $89^{\circ} 32' 00''$ E longitude. Grass, malancha ,rice and soils were collected from the edge of the road and rice plants with soils were collected from the 30m and rice and arum were collected 50m away from the first sampling site. It is a residential area. Hospital, bus stand and petrol pumps are situated around this spot.

3.3 COLLECTION OF SOIL SAMPLES FOR ANALYTICAL PURPOSES

From each sampling spot, soil samples were collected from 0-15cm depth with spade and trowel. The soil samples collected were making composite as suggested by the soil survey staff of the USDA (1951). After sampling soils, the collected soils were packed into polythene bags, tagged with rubber band and labeled properly by a marker pen. At the same time GPS reading of the sample area was also recorded (Table 3.1).

Table 3.1 Coordinates of the sampling sites

Sampling Site	Coordinates
1	23° 54' 803" N latitude to 90° 15' 525" E longitude
2	23° 55' 249" N latitude to 90° 07' 799" E longitude
3	23° 54' 00" N latitude to 90° 04' 33" E longitude
4	23° 53' 90"N latitude to 90°03'39"E longitude
5	23°52'93"N latitud to 90°02'27"E longitude
6	23° 51' 957" N latitude to 89° 57' 804" E longitude
7	23° 50' 93.5" N latitude to 89° 56' 726" E longitude
8	22° 55'39.2" N latitude to 89° 29' 52" E longitude
9	22° 56'42.7" N latitude to 89° 28' 59.0" E longitude
10	22° 57'16.2" N latitude to 89° 28' 58.4" E longitude
11	22° 56'57" N latitude to 89° 28' 54" E longitude
12	22° 50' 42" N latitude to 89° 32' 00" E longitude

3.4 COLLECTION OF PLANT SAMPLES FOR ANALYTICAL PURPOSES

For studying the influx of lead in plants, standing crops on natural vegetation from every sampling site were carefully uprooted with cutlass and a digger to ensure that the roots and other plant parts were not damaged. Sample was taken in triplicate and mostly for each species from 3 spots i.e., A, at the edge of the road, B at 30m and C at 50m away from A. The samples were collected in clean polythene bags separately after labeling it with marker pen containing spot No, distance (m) and name of the plant on polythene bags and were brought to the laboratory instantly on the same day.

**TABLE 3.2 NAME OF PLANT SAMPLES COLLECTED FROM
DIFFERENT SITES WITH DISTANCE**

Spot	Distance from road (m)	Plant	
		English Name	Scientific Name
1	0	Grass	<i>Cynodon dactylon</i>
2	0	Rice	<i>Oryza sativa</i>
		Grass	<i>Cynodon dactylon</i>
		Malancha	- <i>Alternanthera philoxioides</i>
	30	Rice	<i>Oryza sativa</i>
	50	Rice	<i>Oryza sativa</i>
		Malancha	<i>Alternanthera philoxioides</i>
3	50	Red amaranthus	<i>Amaranthus tricolor</i>
		Balsam apple	<i>Momordica charantea</i>
4	0	Maricha	- <i>Capsicum frutescens</i>
	30	Maricha	- <i>Capsicum frutescens</i>
	50	Maricha	- <i>Capsicum frutescens</i>
5	0	Basil	<i>Basella alba</i>
6	0	Grass	<i>Cynodon dactylon</i>
	30	Malancha	<i>Alternanthera philoxioides</i>
		Rice	<i>Oryza sativa</i>
	50	Rice	<i>Oryza sativa</i>
7	0	Grass	<i>Cynodon dactylon</i>
		Aurum	<i>Colocasia esculenta</i>
	30	Maricha	- <i>Capsicum frutescens</i>
		Malancha	<i>Alternanthera philoxioides</i>
		Aurum	<i>Colocasia esculenta</i>
	50	Grass	<i>Cynodon dactylon</i>
8	0	Malancha	<i>Alternanthera philoxioides</i>
	30	Ladies	<i>Abelmoschus esculentus</i>

Spot	Distance from road (m)	Plant	
		English Name	Scientific Name
		finger	
	50	Ladies finger	<i>Abelmoschus esculentus</i>
9	0	Grass	<i>Cynodon dactylon</i>
		Aurum	<i>Colocasia esculenta</i>
		Malancha	<i>Alternanthera philoxioides</i>
	30	Grass	<i>Cynodon dactylon</i>
		Potato	<i>Solanum tuberosum</i>
		Aurum	<i>Colocasia esculenta</i>
	50	Malancha	<i>Alternanthera philoxioides</i>
		Potato	<i>Solanum tuberosum</i>
		Grass	<i>Cynodon dactylon</i>
		Aurum	<i>Colocasia esculenta</i>
10	0	Aurum	<i>Colocasia esculenta</i>
		Rice	<i>Oryza sativa</i>
	30	Grass	<i>Cynodon dactylon</i>
		Aurum	<i>Colocasia esculenta</i>
		Rice	<i>Oryza sativa</i>
	50	Grass	<i>Cynodon dactylon</i>
		Rice	<i>Oryza sativa</i>
		Aurum	<i>Colocasia esculenta</i>

Spot	Distance from road (m)	Plant	
		English Name	Scientific Name
11	0	Grass	<i>Cynodon dactylon</i>
	30	Grass	<i>Cynodon dactylon</i>
	50	Grass	<i>Cynodon dactylon</i>
12	0	Rice	<i>Oryza sativa</i>
		Grass	<i>Cynodon dactylon</i>
		Malancha	<i>Alternanthera philoxioides</i>
	30	Rice	<i>Oryza sativa</i>
	50	Rice	<i>Oryza sativa</i>
		Aurum	<i>Colocasia esculenta</i>

3.5 PROCESSING OF SOIL SAMPLES

The soil samples collected for analytical purpose were dried in air for 3 days by homogeneously spreading on a clean piece of paper. Visible roots were discarded from the soil samples. After air drying, the larger aggregates were gently broken. Dried roots, stubble, concrete, grasses and other substances were discarded from the samples. Then the samples were ground with the help of wooden hammer and mortar and ground soils were screened to pass through a 2mm sieve. The sieved sample was then mixed thoroughly for making a composite sample. Then a portion of each of the soil samples were preserved in a plastic container and labeled properly showing the distance (m), sample number, date of collection. These soil samples were used for various physical analyses and the mouth of the container was well-capped.

Rest of the portions of soil samples (2mm sieved) was further ground and screened to pass through 0.5 mm sieve. All the soil samples were properly

passed through 0.5mm sieve. The sieved samples (0.5mm) were mixed thoroughly for making composite samples and preserved in the same way that was discussed as above. These soils were used for chemical analysis.

3.6 PROCESSING OF PLANT SAMPLES

Plant samples were collected from the roadsides (natural vegetation) and from farmers field. After removing any traces of soil and other plant material in the laboratory the samples were carefully washed at least three times with distilled water to remove soil particles and dust. After washing the roots of the plant samples were separated by cutting it with scissor. The roots and shoots were air dried and then cut into small pieces. The plant parts were then put into an envelope with proper labeling and kept in an oven at 70⁰c for 48 hours before dry weights were measured. After oven drying plant samples were ground in an electric grinder and the ground root and shoot samples were kept separately and root and shoot were mixed thoroughly for each species. The samples were kept in a plastic bag with proper labeling and stored in desiccators for further analysis.

3.7 LABORATORY ANALYSES

Generally, there were two main parts of laboratory analysis with the soil. One was physical analysis and the other was chemical analysis. The most convenient methods were used in these analyses. The methods that were used in the experimental analyses were as follows.

Digestion of soil samples with aqua-regia (HCl:HNO₃) (3.5:1)

Soil samples were digested with 10ml HCl+HNO₃ acid under a closed system (Jackson,1973).Aqua-regia decomposes nearly almost all complex forming soil

particles (clay minerals, organic substance, oxide, etc.) through which most of the ions go into solution and can be measured quantitatively.

Digestion of plant samples with HNO_3 : HClO_4 mixture (5:1)

0.5g and 0.2g of finely ground plant shoot and root samples were weighed, respectively, and digested with 10ml conc. HClO_4 - HNO_3 mixture (1:5) (both the chemicals were superpose).

3.7.1 LABORATORY ANALYSES OF THE SOIL SAMPLES:

The soils were analyzed in the laboratory to determine their physical and chemical properties. The methods used are as follows:

3.7.1.1 DETERMINATION OF SOIL PHYSICAL PROPERTIES

a) Moisture percentage- The percentage of moisture present in the air dried soil was determined by drying known amount of soil in an electrical oven at 105°C for 24 hours until constant weight was obtained and the moisture percentage was calculated from the loss of moisture from the sample as described by Black (1965).

b) Particle size analyses

The particle size distribution was determined by hydrometer method of Day (1965).

c) Textural class: Textural class of soils was determined from the Marshall's triangular coordinates as devised by the United States Department of Agriculture (USDA, 1951).

3.7.1.2 DETERMINATION OF SOIL CHEMICAL PROPERTIES

a) pH

The pH the soil was measured by using a Glass electrode pH meter. The ratio of the soil to water was 1:2.5 as suggested by Jackson (1973).

b) Organic matter

Organic carbon was estimated volumetrically in the soil samples by wet oxidation with $K_2Cr_2O_7$ and H_2SO_4 mixture and rapid titration with normal $FeSO_4$ solution (Black, 1965) using the correction factor based on 76 percent recovery and the organic matter was calculated by multiplying the percentage of organic carbon with conventional VanBemmelen's factor of 1.724 (Piper, 1966).

c) Total nitrogen

Total nitrogen in the soil and plant samples were determined by Micro-Kjeldahl digestion method and steam distillation with 40% NaOH. Evolved ammonia was collected in 4% boric acid with mixed indicator and the adsorbed NH_3 was estimated by back titration with N/100 H_2SO_4 as described by Jackson (1973).

d) Total phosphorus

The total phosphorus content of the soil and plant samples were determined spectrophotometrically from Perchloric-Nitric Acids digested extract, described in Haq and Alam, (2005) by spectrophotometer at 420 nm wave length, after developing the yellow color with vanadomolybdate as described by Jackson (1973).

e) Total potassium

The total potassium content of the soil samples in Perchloric-Nitric Acid digested extract were determined flame photometrically by Flame Analyzer (at 767 nm filter).

f) Total Cu, Mn, Zn, Pb, and Cd

Total Cu, Mn, Zn, Pb, and Cd contents of the soil and samples in the digested extract were determined with the help of a Atomic Absorption Spectrometer (Varian spectra AA-220).

3.7.1.2 LABORATORY ANALYSES OF THE PLANT SAMPLES:

A. Plant shoot and root analyses:

a) Total nitrogen:

Plant nitrogen (shoot and root) was determined by Micro-Kjeldhal's method of following H_2SO_4 acid digestion and steam distillation with 40% NaOH. Ammonia evolved was collected in boric acid containing mixed indicator and determined titrimetrically with a standard N/100 H_2SO_4 acid (Jackson, 1973).

b) Determination of Total Phosphorus, Lead, Cadmium, Manganese, Copper and Zinc :

After wet oxidation with $\text{HNO}_3\text{-HClO}_4$ acid mixture(5:1) (Jackson,1973). the total contents of P, Pb, Cd, Mn, Cu and Zn were determined by using the procedure as described previously for total soil analysis.

3. 8. DATA ANALYSIS

The significance of differences between the means of the treatments was evaluated by one way analysis of variance followed by Duncan's Multiple Range Test at the significance level of 5%. Pearson's correlation coefficient was estimated to test the relations among metal contents in soil and soil properties and between metal concentrations in plant tissues and metal content in soils. The statistical software Excel (Excel Inc., 2003) and SPSS version 12 (SPSS Inc., 2003) were used in the analysis.

CHAPTER 4

RESULTS AND DISCUSSIONS

The present work was carried out with two approaches

- i) Accumulation of lead and some other heavy metals (Cd, Zn, Cu and Mn) in some contaminated soils along Dhaka - Manikganj- Khulna highway and
- ii) Influx of the above metals in grass and some edible crops (rice, malancha and aurum).

4.1 RESULTS OF SOIL ANALYSIS

The general physical, chemical properties and heavy metals content of the soil samples are presented in Tables 4.1, 4.2 and 4.3, respectively.

4.1.1 PHYSICAL PROPERTIES OF THE STUDIED SOILS

4.1.1.1 Particle size of the soil samples

a) Sand: The percentage of sand content was 23.46%, 9.81% and 25.60% at spot 1A, 3C and 5A, respectively. The sand content varied from 19.04% to 22.22%, 20 to 30%, 13% to 37%, 19% to 41%, 29 to 60%, 27% to 62%, 31 to 35%, 13% to 26% and 17% to 27% at site 2, 4 and 6 to 12, respectively. The highest value of sand was obtained at spot 9A (62%) and the lowest value was obtained at spot 3C (10%).

b) Silt: The percentage of silt content was 57.75%, 65.25% and 51% at spot 1A, 3C and 5A, respectively. The silt content varied from 52 to 71%, 56 to 63%, 47 to 78%, 50 to 66%, 32 to 55%, 28 to 62%, 51 to 60%, 43 to 69% and 38 to 54% at spot 2, 4 and 6 to 12, respectively. The highest value of silt was obtained at spot 6C (77.62%) and the lowest value was obtained at spot 9A (27.5%). In most soils the percentage of silt contents increased with distances i.e., the highest value was obtained at spot C in most soils.

Table 4.1 Results of physical properties of soil samples

Sampling Site	Spot	Distance from road (m)	Particle Size Analysis (%)			Textural Class	%Moisture Content (air dry soil)
			Sand	Silt	Clay		
1	A	0	23.46	57.75	18.78	Silt loam	1.46
2	A	0	19.04	59.2	21.75	Silt loam	1.83
	B	30	22.22	52.15	25.62	Silt loam	2.30
	C	50	10.45	71.25	18.3	Silt loam	1.16
3	C	50	9.81	65.25	24.94	Silt loam	1.30
4	A	0	20.49	62.55	16.95	Silt loam	1.51
	B	30	26.92	56	17.08	Silt loam	0.99
	C	50	29.92	56.4	13.67	Silt loam	0.57
5	A	0	25.60	51	23.39	Silt loam	3.14
6	A	0	37.22	46.55	16.22	loam	2.58
	B	30	20.00	70.35	9.64	Silt loam	1.01
	C	50	12.65	77.62	9.72	Silt loam	1.48
7	A	0	35.39	45.5	19.11	loam	8.16
	B	30	18.51	65.5	15.98	Silt loam	4.04
	C	50	40.99	49.5	9.50	loam	9.44
8	A	0	33.44	42.8	23.75	loam	2.70
	B	30	59.82	32.4	7.77	Sandy loam	3.43
	C	50	29.47	54.5	16.02	Silt loam	2.20
9	A	0	61.8	27.5	10.67	Sandy loam	1.59
	B	30	35.93	47.6	16.46	loam	3.73
	C	50	26.88	62.15	10.96	Silt loam	4.21
10	A	0	34.79	51.3	13.90	Silt loam	2.38
	B	30	31.34	60.375	8.28	Silt loam	2.62
	C	50	30.74	52.2	17.05	Silt loam	2.09
11	A	0	25.97	43.4	30.62	Clay loam	2.51
	B	30	12.87	50	37.12	Silty clay loam	9.00
	C	50	18.47	69.3	12.22	Silt loam	9.26
12	A	0	27.35	38.1	34.54	Clay loam	8.16
	B	30	17.18	54.4	28.41	Silty clay loam	4.04
	C	50	19.76	45.15	35.08	Clay loam	9.44

c) **Clay:** The soils of spot 1A, 3C and 5A contained 19%, 30% and 23% clay, respectively. The percentage of clay content varied from 18 to 26%, 14 to 17%, 10 to 16%, 10 to 16%, 8 to 16%, 11 to 16%, 8 to 17%, 12 to 37%, 28 to 35% at site 2, 4 and 6 to 12, respectively. The highest value (37.12%) of clay was present at 11B and lowest value (8.28%) was obtained at 10B spot. There was no definite pattern of increasing or decreasing of soil particles with distances.

4.1.1.2 Textural Class: The textural classes of the collected soils are shown in Table - 4.1.

Site-1 (Nabinagar bus stand): The textural classes of the soil was silt loam at spot-1A.

Site-2 (Srirampur village): The textural classes of the soils of A, B and C spot at 2 sites were silt loam, silt loam and silt loam, respectively.

Site-3 (Krisnopura Village): The textural class of soils at site-3 was silt loam.

Site-4 (Charkanda Glona): The textural class of soils of site-4 was silt loam.

Site-5 (Vatpur village): The textural class of soil of site-5 was silt loam.

Site-6 (Dighi Union): The textural classes of soils were loam at spot 6A and silt loam at spot 6B and 6C.

Site-7 (Baniajuri): The textural classes of the soils were loam at 7A and 7C and silt loam at 7B.

Site-8 (Atra-Gilatala): The textural classes of the soils were loam, sandy loam and silt loam at spot 8A, 8B and 8C, respectively.

Site-9 (Payer Bazar, Fultala): The textural classes of the soils were sandy loam, loam and silt loam at spot 9A, 9B and 9C, respectively.

Site-10 (Bederdanga, Fultala): The textural classes of the soils were silt loam at all spots, of this site.

Site-11 (Damoder High School, Fultala): The textural classes of the soils were clay

4.1.2 CHEMICAL PROPERTIES OF THE STUDIED SOILS

The chemical properties of the studied soils are presented in Table 4.2.

4.1.2.1 pH: Soil pH ranged from 6.1 to 7.5, 6.5 to 6.9, 7.9 to 8.0, 7.7 to 8, 7.9 to 8.0 at sites 2, 4 and 6 to 12, respectively. The pH of the spot 1A, 3C and 5A was 7.6, 8.0 and 7.6, respectively.

The average pH of the studied soils were 7.6, 6.6, 8.0, 6.6, 7.6, 7.9, 7.8, 8.0, 7.9, 8.0, 7.8 and 7.9 at site 1 to 12, respectively.

The normal pH range for productive soil is from 6.5 to 8.4 (WHO 1996). In all spots the pH was within the normal range. The distribution of pH at different sites with distances are presented in Figure 4.1.

4.1.2.2 EC: The EC values of the studied soils ranged from 0.62 to 3.07 dS/m. The lowest value (0.62dS/m) was obtained at spot 2A and the highest value (3.07dS/m) was obtained at spot 3C. The soils were non saline to slightly saline.

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4.1.2.3 OM: The organic matter contents were 2.09 to 3.27%, 1.27 to 1.63%, 1.72 to 3.36%, 1.82 to 2.54%, 2.36 to 3.36%, 3.09 to 3.18%, 3.45 to 5.45%, 2.81 to 4.54% and 3.00 to 5.99% in site 2, 4 and 6 to 12 respectively. Spots 1A, 3C and 5A contained organic matter 2.72%, 2.72% and 2.18%, respectively.

The average organic matter content of the studied soils ranged from 1.39% to 4.11%. The average concentration of organic matter were 2.72%, 2.54%, 2.72%, 1.39%, 2.18%, 2.39%, 2.27%, 2.69%, 3.12%, 4.11%, 3.84% and 4.11% in soils at site 1 to 12, respectively.

Soils of Khulna contained the highest organic matter. The distribution of organic matter at different sites with distances was presented in Figure 4.2.

According to BARC (1999), the normal range of organic matter is <1.0 to 1.7% in soils of Bangladesh.

4.1.2.4 Total Nitrogen: The results of total nitrogen of soil were shown in Table 4.2. The total N content ranged from 0.20 to 0.28%, 0.14 to 0.17%, 0.17 to 0.31%, 0.20 to 0.22%, 0.22 to 0.34%, 0.31 to 0.42%, 0.20 to 0.39%, 0.25 to 0.39% and 0.28 to 0.50% in site 2, 4 and 6 to 12 respectively. Soils of Khulna

contained the highest nitrogen content that was related with higher organic matter content. The soils of Manikganj contained lower nitrogen percentage than the soils of Khulna. The highest (0.50%) nitrogen was obtained at spot 12A that was a rice field. The value may be due to the application of nitrogen fertilizer and also higher organic matter content. The distribution of total nitrogen at different sites with distances were presented in Figure 4.3.

Table 4.2 Some chemical properties and nutrient contents of the studied soils.

District	Sampling Site	Distance from road (m)	Sampling spot	pH	EC dS/m	%OC	%OM	Total N (%)	C/N	Total P (%)	Total K (%)
DHAKA-MANIKGANJ	1	0	A	7.6	0.90	1.58	2.72	0.20	8.06	0.07	0.19
	2	0	A	6.2	0.62	1.90	3.27	0.28	6.77	0.08	0.44
		30	B	7.5	1.64	1.32	2.27	0.20	6.72	0.08	0.23
	3	50	C	6.1	0.79	1.21	2.09	0.20	6.18	0.07	0.22
		50	C	8	3.07	1.58	2.72	0.15	10.26	0.06	0.42
	4	0	A	6.9	1.25	0.74	1.27	0.17	4.39	0.08	0.26
		30	B	6.5	0.96	0.95	1.63	0.14	6.77	0.09	0.23
	5	50	C	6.5	1.28	0.74	1.27	0.14	5.27	0.08	0.26
		0	A	7.6	1.33	1.26	2.18	0.31	4.10	0.07	0.20
	6	0	A	7.9	2.07	1.95	3.36	0.31	6.32	0.08	0.20
		30	B	7.9	2.30	1.00	1.72	0.20	5.10	0.07	0.29
	7	50	C	8	1.87	1.21	2.09	0.17	7.21	0.07	0.32
KHULNA	8	0	A	8	1.31	1.47	2.54	0.20	7.52	0.06	0.23
		30	B	7.7	1.56	1.42	2.45	0.20	7.25	0.08	0.32
	9	50	C	7.9	2.34	1.05	1.82	0.22	4.70	0.06	0.23
		0	A	8	1.49	1.37	2.36	0.22	6.11	0.06	0.19
	10	30	B	8	1.56	1.37	2.36	0.25	5.43	0.05	0.20
		50	C	8	1.04	1.95	3.36	0.34	5.80	0.10	0.19
	11	0	A	7.8	1.64	1.79	3.09	0.31	5.81	0.06	0.16
		30	B	7.9	1.62	1.79	3.09	0.42	4.26	0.06	0.27
	12	50	C	8	1.69	1.84	3.18	0.34	5.48	0.07	0.33
		0	A	8	2.08	2.00	3.45	0.20	10.21	0.08	0.21
	13	30	B	8	2.06	2.00	3.45	0.31	6.50	0.10	0.25
		50	C	8	1.89	3.16	5.45	0.39	8.06	0.07	0.18

4.1.2.5 C/N: The C/N ratio of the soils was shown in Table 4.2. The C/N ratio of the soils ranged from 4.10 to 10.26. The highest value was obtained at spot 3C and lowest value was obtained at 5A. There was no definite pattern of increasing or decreasing C/N ratio with distance.

4.1.2.6 Total Phosphorus: The total phosphorous content of soils of all sites and spots are presented in Table 4.2. The P content of soils at site 2 were 0.08, 0.08 and 0.07%, at site 4 soils were, 0.08, 0.09 and 0.08%, at site 6 soils were 0.08, 0.07 and 0.07%, at site 7 soils were 0.06, 0.08 and 0.06%, at site 8 soils were 0.06, 0.05 and 0.10%, at site 9 soils were 0.06, 0.06 and 0.07%, at soils of site 10 were 0.08, 0.10 and 0.07% and at site 12 soils were 0.06, 0.07 and 0.07, respectively. The soils of site 1A, 3C and 5A contained 0.07, 0.06 and 0.07% phosphorous, respectively. The distribution of total phosphorous at different sites with distances were presented in Figure 4.4.

4.1.2.7 Total potassium content: The total potassium content ranged from 0.22 to 0.44%, 0.23 to 0.26%, 0.20 to 0.32%, 0.23 to 0.32%, 0.19 to 0.20%, 0.16 to 0.33%, 0.18 to 0.25%, 0.24 to 0.24% and 0.21 to 0.29% for site 2, 4 and 6 to 12, respectively. The soils of 1A, 3C and 5A contained 0.19%, 0.42% and 0.20% potassium, respectively. The highest potassium (0.44%) was obtained at site 2A and the lowest potassium (0.16%) was obtained at site 9A. The distribution of total potassium at different sites with distances were presented in Figure 4.5.

The distribution of average content of organic matter, nitrogen, phosphorous and potassium were presented in Figure 4.6.

4.1.3 THE RESULTS OF THE HEAVY METALS OF SOIL SAMPLES

The results of the heavy metals of soil samples were presented in Table 4.3.

4.1.3.1 Lead :

Levels of heavy metals in soil samples collected from different sites along roadsides of Dhaka- Manikgonj and Khulna districts are given in Table 4.3.

The soils of 1A, 3C and 5A contained 19ppm, 9ppm and 46ppm Pb, respectively. The soils of sampling site 2, 4 and 6 to 12 contained lead 9, 14 and 8 ppm, 8, 6 and 5 ppm, 9, 12 and 21 ppm, 14.5, 6 and 9 ppm, 14, 19 and 8 ppm, 11, 10 and 19 ppm, 28, 17 and 12 ppm, 21, 11 and 9 ppm and 20, 14 and 13 ppm, respectively for each respective spots of each sampling site. It was shown that the value of lead in soils along roadsides ranged from 5 ppm to 46 ppm. The highest value was obtained at spot 5A that is along the edge of the sampling site 5(46ppm) and the lowest value was obtained at spot 4C(5ppm) at sampling site 4.

The average total Pb concentration of the studied soils ranged from 9ppm to 46ppm. The average concentrations of total Pb were 19ppm, 10.3ppm, 9ppm, 6.3ppm, 46ppm, 14ppm, 9.8ppm, 13.7ppm, 13.3ppm, 19ppm, 13.6ppm and 14.3ppm in soils at site 1 to 12, respectively.

Total Pb contents varied widely among the distances of the soils. The total Pb content ranged from 8 to 46 ppm, 6 to 19ppm and 5 to 21 ppm at 0m, 30 m and 50m distances i.e., spot A, B and C, respectively. The average accumulations of total Pb concentrations were 18.13ppm, 12.11ppm and 11.3ppm at 0m, 30m and 50m distances from the roadside. It showed a decreasing tendency with increasing lateral distances.

The distribution of total lead at different sites with distances was presented in Figure 4.7.

4.1.3.2 Cadmium :

Total Cd content in soils of site 1 was 0.3 ppm, soils of site 2 were 0.01, 0.8 and 0.02 ppm, soils of site 3 was 0.01, soils of site 4 were 0.3, 0.1 and 0.01 ppm, soils of site 5 was 0.81 ppm, soils of site 6 were 0.2, 0.1 and 0.01 ppm, soils of site 7 were 0.01, 0.2 and 0.3 ppm, soils of site 8 were 0.1, 0.01 and 0.01 ppm, soils of site 9 were 0.01, 0.01 and 0.02 ppm, soils of site 10 were 0.2, 0.03 and 0.02 ppm, soils of site 11 were 0.1, 0.01 and 0.1ppm and soils of

site 12 were 0.1, 0.01 and 0.01 ppm, respectively. The highest cadmium (0.8ppm) obtained at site 2B and 5A and the lowest value(0.01ppm) was found in most sites.

The average total Cd content of the studied soils ranged from 0.01ppm to 0.81ppm. The average concentrations of total Cd were 0.3ppm, 0.28ppm, 0.01ppm, 0.14ppm, 0.81ppm, 0.1ppm, 0.17ppm, 0.04ppm, 0.01ppm, 0.08ppm, 0.07ppm and 0.04ppm in soils at site 1 to 12, respectively.

Total Cd contents varied widely among the distances of the soils. The average accumulations of total Cd concentrations were 0.21ppm, 0.41ppm and 0.02ppm at 0m, 30m and 50m distances from the roadside.

The distribution of total cadmium at different sites with distances were presented in Figure 4.8.

Table 4.3 Results of some heavy metals of the studied soils

District	Sampling Site	Distance from road (m)	Sampling spot	Pb (ppm)	Cd (ppm)	Zn (ppm)	Cu (ppm)	Mn (ppm)	
DHAKA-MANIKGANG	1	0	A	19	0.3	96.5	36.5	295.5	
	2	0	A	9	0.01	74.5	26.5	206.5	
		30	B	14	0.8	109.5	32	481	
	3	50	C	8	0.02	64.5	32.5	236.5	
		50	C	9	0.01	63	31	302	
	4	0	A	8	0.3	92.5	33	360.5	
		30	B	6	0.1	110	27	287.5	
	5	50	C	5	0.01	102.5	22.5	266.5	
		0	A	46	0.81	77.5	24	389.5	
	6	0	A	9	0.2	73	28	310	
		30	B	12	0.1	50	20.5	342.5	
	7	50	C	21	0.01	64.5	31	428	
0		A	14.5	0.01	79	39	452		
KHULNA	8	30	B	6	0.2	68.5	32.5	250	
		50	C	9	0.3	66.5	27	334.5	
	9	0	A	14	0.1	54.5	22.5	273.5	
		30	B	19	0.01	54.5	14.5	246	
	10	50	C	8	0.01	61.5	33	425	
		0	A	11	0.01	68.5	14.5	195.5	
	11	30	B	10	0.01	63	27	402.5	
		50	C	19	0.02	96.5	31.5	347.5	
	12	0	A	28	0.2	75.5	19	409.5	
		30	B	17	0.03	61.5	24.5	448	
	Background level	Maximum tolerable level	50	C	12	0.02	57	26.5	320
			0	A	21	0.1	63	22.5	284.5
In excess of tolerable level	In excess of tolerable level	30	B	11	0.01	63	28	325	
		50	C	9	0.1	44.5	19	253.5	
Maximum tolerable level	Maximum tolerable level	0	A	20	0.1	89.5	24	294	
		30	B	14	0.01	78.5	29	301.5	
In excess of tolerable level	In excess of tolerable level	50	C	13	0.01	78.5	30.5	400	
				≤20	≤0.02	≤68	≤40	<20	
				≥20-<100	<0.02-≤3	>68-<300	≥40-≤100	>20-300	
				≥100	≥3	>300	≥100	≥300	

4.1.3.3 Zinc :

Total zinc contents of soils of site 1 was 96.5 ppm, soils of site 2 were 74.5, 109.5 and 64.5 ppm, soils of site 3 was 63 ppm, soils of site 4 were 92.5, 110 and 102.5 ppm and soils of site 5 was 77.5 ppm, soils of site 6 were 73, 50 and 64.5 ppm, soils of 7 were 79, 68.5 and 66.5 ppm, soils of site 8 were 54.5, 54.5 and 61.5 ppm, soils of site 9 were 68.5, 63 and 96.5 ppm, soils of site 10 were 75.5, 61.5 and 57 ppm, soils of site 11 were 63, 63 and 44.5 ppm and the soils of site 12 were 89.5, 78.5 and 78.5 ppm for respective spots of each sampling site. The highest Zn(109.5ppm) was obtained at spot 2B and the lowest Zn (57ppm) was obtained at spot 10C.

Total Zn contents varied widely among the distances of the soils. The average accumulations of total Zn concentrations were 76.5ppm, 73.1ppm and 69.9ppm at 0m, 30m and 50m distances from the roadside. It showed a decreasing tendency with increasing lateral distances.

The distribution of total zinc at different sites with distances were presented in Figure 4.9.

4.1.3.4 Copper :

Total Cu contents of soils of site 1 was 36.5 ppm. For site 2 soils were 26.5, 32 and 32.5, soils of site 3 was 31 ppm, soils of site 4 were 31, 33 and 27ppm, soils of site 5 was 24 ppm, soils of site 6 were 28, 20.5 and 31 ppm, soils of site 7 were 39, 33 and 27 ppm, soils of 8 soils were 22.5, 14.5 and 33 ppm, soils of site 9 were 145, 27, and 31.5 ppm, soils of site 10 were 19, 24.5 and 26.5ppm, soils of site 11 were 22.5, 28 and 196 ppm, soils of site 12 were 24, 29 and 30.5 ppm soils of respective spots of each sampling site. The highest value of copper (36.5ppm) was obtained at spot 1A and the lowest value of copper (14.5ppm) was obtained at spot 8B and 9A.

Total Cu contents varied widely among the distances of the soils. The average accumulations of total Cu concentrations in soils were 27.59ppm, 26.1ppm and 28.4ppm at 0m, 30m and 50m distances from the roadside.

The distribution of total copper at different sites with distances were presented in Figure 4.10.

4.1.3.5 Manganese:

Total manganese content of soils of site 1 was 295.5ppm, soils of site 2 were 206.5, 250 and 236.5 ppm, soils of site 3 was 302 ppm, soils of site 4 were 360.5, 288, and 267 ppm, soils of site 5 was 389.5 ppm, soils of site 6 were 310, 342.5 and 328 ppm, soils of site 7 were 452.5, 250 and 335 ppm, soils of site 8 were 273.5, 246 and 425 ppm, soils of site 9 were 195.5, 402 and 347 ppm, soils of site 10 were 409.5, 448 and 320 ppm, soils of site 11 were 285, 325 and 254 ppm, and soils of site 12 were 294, 301.5 and 400 ppm for respective spots of each sampling sites. The highest Mn(448ppm) was obtained at spots at 10B and the lowest Mn (195.5ppm) was obtained at spot 9A.

Total Mn contents varied widely among the distances of the soils. The average accumulations of total Mn concentrations in soils were 313ppm, 352ppm and 334ppm at 0m, 30m and 50m distances from the roadside.

The distribution of total manganese at different sites with distances were presented in Figure 4.11.

4.1.3.6. DISCUSSION ON SOIL PROPERTIES

From the study, it was clear that the concentration of soil nitrogen along the Dhaka- Manikganj-Khulna highway varied from 0.14% to 0.50% and the concentration did not follow any definite pattern so far along the highway as well as at different spots laterally away from the highway is concerned.

The highest concentration of soil nitrogen (0.50%) was found in Boyra-Sonadanga link road (spot-12A), where organic matter content was high (>3%). It was an agricultural field and the source of nitrogen also can be added in the soil through chemical fertilizer such as ammonium sulphate and urea.

In soil, nitrogen occurs in organic form (Corn forth, 1974; Sing *et al.*, 1891). Through the chemical nature of about total soil nitrogen is obscure; 20-40% of it is known of occur as found amino acids, 5-10% as combined amino sugars

(Richards, 1974). Only 1-3% of the total soil nitrogen exists in inorganic forms. mainly NH_4^+ and NO_3^- (Sing *et al.*, 1981).

From Table 4.4 the variance analyses of the values of general soil properties (pH and organic matter) and total N, total P and total K of soil showed that there were no significant differences with distances except phosphorous.

Correlation coefficient between total soil phosphorous and silt and total soil potassium and silt showed significant positive relationship ($r = 0.403$ and $r = 0.403$ respectively.) Total soil Cu showed significant positive correlation with silt ($r = 0.362$). Total soil Cu and total soil K showed significant negative correlation with sand ($r = -0.470$ and $r = -0.522$). (Table 4.5). Total soil nitrogen was highly significantly and positively correlated with soil organic matter ($r = 0.824$) (Table 4.6).

Table 4.4 Contents of some soil chemical properties and nutrients in soil at different distances laterally away from the highway.

Distance(m)	pH	OM(%)	Total N(%)	Total P(%)	Total K(%)
O	7.4a	2.9a	0.26a	0.69a	0.23a
30	7.4a	2.7a	0.28a	0.73a	0.24a
50	7.4a	2.9a	0.25a	0.07b	0.25a

Means followed by a common letter in a column are not significantly different at the 5% level by DMRT

Table 4.5 Correlation coefficient among the particle size with chemical properties and nutrient elements of the studied soils.

Element	Sand	Silt	Clay
Pb	0.087	-0.170	0.108
N	0.127	-0.360	0.313
P	-0.221	0.403*	-0.232
K	-0.470*	0.403*	0.138
OM	-0.010	-0.223	0.326
Cu	-0.522*	0.362*	0.272
Mn	-0.235	0.269	-0.025
Zn	-0.084	-0.045	0.188
pH	0.229	-0.221	-0.033
EC	0.004	-0.115	0.154

* denotes significant at 5% level

** denotes significant at 1% level

Table 4.6 Correlation coefficient (r) among the total nutrients, organic matter and heavy metal contents of top soils (0-15cm) along roadside, Dhaka- Manikgonj-Khulna.

	Nitrogen (N)	Phosphorus (P)	Potassium (K)	Organic Matter (OM)	Copper (Cu)	Manganese (Mn)	Zinc (Zn)	pH	EC	Cd
Lead (Pb)	0.149	-0.169	-0.219	0.075	0.131	0.227	0.027	-0.349*	0.090	0.504*
Cadmium (Cd)	-0.131	0.133	0.229	-0.229	0.298	0.257	0.389*	-0.040	-0.142	
EC	0.072	-0.214	0.139	0.114	-0.105	0.316	-0.143	0.536*		
pH	0.318	-0.252	-0.224	0.326	-0.082	-0.015	-0.122			
Zinc (Zn)	-0.231	0.288	0.059	-0.277	0.376*	0.121				
Manganese (Mn)	-0.115	0.307	0.091	-0.106	0.521**					
Copper (Cu)	-0.128	0.213	0.123	-0.184						
Organic matter (OM)	0.824**	-0.090	-0.045							
Potassium (K)	-0.105	0.017								
Phosphorus (P)	-0.156									

* denotes significant at 5% level

** denotes significant at 1% level

Contamination of soil by Pb and some other heavy metals such as Cd, Zn, Cu and Mn

According to Kolke(1980), the permissible limit of heavy metals in soils are 100ppm for Pb, 3ppm for Cd, 300ppm for Zn, 100ppm for Cu and 300ppm for Mn.

Lead and cadmium

The average concentration of Pb and Cd in the soil varied from 0.1 to 20ppm and 0.01 to 0.7ppm, respectively (Saurbeck, 1985). In the study total Pb and Cd content varied widely at different distances from roadside (Figure 4.7 to 4.8). Total Pb ranged from 5 to 46ppm and total Cd ranged from 0.01 to 0.8 ppm at the roadside.

Total Pb and Cd contents were 6 to 19ppm and 5 to 21ppm for Pb at 30 and 50m distances laterally away from the highway and 0.01 to 0.8ppm and 0.01 to 0.1ppm for Cd, respectively.

The average total Pb content of the studied soils ranged from 9ppm to 46ppm. The average concentrations of total Pb were 19ppm, 10.3ppm, 9ppm, 6.3ppm, 46ppm, 14ppm, 9.8ppm, 13.7ppm, 13.3ppm, 19ppm, 13.6ppm and 14.3ppm in soils at site 1 to 12, respectively.

The mean concentrations of total lead at 0m, 30m and 50m distances from the highways were 18.13, 12.11 and 11.30ppm, respectively.

The average total Cd content of the studied soils ranged from 0.01ppm to 0.81ppm. The average concentrations of total Cd were 0.3ppm, 0.28ppm, 0.01ppm, 0.14ppm, 0.81ppm, 0.1ppm, 0.17ppm, 0.04ppm, 0.01ppm, 0.08ppm, 0.07ppm and 0.04ppm in soils at site 1 to 12, respectively.

Total Cd contents varied widely among the distances of the soils. The average accumulations of total Cd concentrations were 0.21ppm, 0.41ppm and 0.02ppm at 0m, 30m and 50m distances from the roadside. It was observed that the highest mean concentration of lead (18.13ppm) was found near the edge of the highway and decreased with increasing distances.

The variance of analysis showed that there were significant differences of soil lead with distances (Table 4.7).

Table 4.7 Accumulation of lead and some other heavy metals at different distances laterally away from the highway

Distance(m)	Lead(Pb)	Cadmium(Cd)	Zinc(Zn)	Copper(Cu)	Manganese(Mn)
O	18.13a	0.21a	76.5a	27.59a	313a
30	12.11b	0.41a	73.16a	26.1a	352a
50	11.3b	0.02b	69.9a	28.4a	334a

Means followed by a common letter in a column are not significantly different at the 5% level by DMRT

It is interesting to note that, the concentration of Cd, Cu and Mn in the studied soils did not follow any definite pattern so far the distance from near the road to farther away from the road is concerned. The concentration of Pb and Zn decreases with increasing lateral distances.

Davidson and Osborn (1986) mentioned that, the transport of Pb, As and Cd depends on their physical- chemical properties, the particle size distribution and meteorological conditions such as rate of turbulent vertical air exchange and wind speed and the former two parameters are dominant in the long range transport of Pb, As and Cd. Rahn (1976) mentioned that, the residence time of Pb, As and Cd in the atmosphere were found to be about 7 days which is sufficient for transport over thousand kilometers. On the other hand, relatively higher concentrations of Pb in agricultural land could be due to other sources like pesticides, fertilizers, etc. Lau and Wong (1982) stated that, soils next to a minor agricultural area contained higher concentration of Pb than a commercial- residential area. The lowest concentrations were found at the grassland site followed by the commercial residential area while the highest Pb levels occurred in the agricultural area. They also mentioned that, besides the increased traffic volume, fertilizers, pesticides and animal manure might be the causes of Pb contamination of agricultural soils.

The lowest value of Pb in soil might be due to the higher content of organic matter in the soil as organic carbon exerts the maximum influence on the availability of Pb and due to its strong tendency to form metallo-organic complexes of low solubility. Olade (1987) mentioned that in stream sediments Pb is closely associated with organic matter. Lead shows little or no association with Fe-Mn precipitation but tends to readily form secondary lead sulfates and carbonates in soil overlying mineralization. Krishna Murti (1987) found that, the increase of lead occurring in the topsoil was from 14.0 to 24.0 mg/kg.

The metals originating from industrial activities are distributed in soil by the atmosphere within a distance that depends on the size of particles. The concentrations of these metals can vary greatly according to the strength and direction of wind, type of soil, composition, cation exchange capacity and pH (Al-Khashman and Shawabkeh, 2006). Usually, pH influences the CEC of soil which in turn, affects the heavy metal mobility and distribution in the soil samples. Kung and Ying (1990) found the presence of Cd, Pb, Hg, Zn and Cr contaminants in the surface soils around an industrial complex in Baoshang Wusong area, China.

The distribution of heavy metals in soil profiles, as well as their availability, are influenced by the nature of parent material, climate and their relative mobility depending on the nature of the metal species, their interaction with soil colloids, and soil characteristics such as soil pH, clay, organic matter content, etc (Colombo *et al.*, 1998; Naidu *et al.*, 2003; Krishna and Govil, 2007).

It is important to note that, Cd is a mobile element and the samples were collected in August–September, that was after the rainy season. So, for this reason Cd content may be low due to runoff and leaching loss high sand contents and low soil pH the content of Cd due to downward movement. Udom *et al.*, (2004) reported the loss of cadmium due to downward movement of water. Cadmium release from soil increases substantially when pH drops below 4.5 (Bergkvist *et al.*, 1989; McBride *et al.*, 1997). This is especially true for

sandy soils with low CEC, low acid neutralization capacity, and low ability of the subsoil to sorb Cd ions. Such soils may be vulnerable to Cd leaching. Smith (1991) showed evidence of such movement in a sandy soil treated with sewage sludge at intervals over a period of 25 years. Kabata-Pendias (2001) reported that cadmium is most mobile in acidic soil within the range of pH 4.5 to 5.5, whereas in alkaline soil Cd is rather immobile. The distribution of heavy metals in soil profiles is continuously being changed due to both anthropogenic activities and natural turn over in rock-soil-plant systems (Kashem *et al.*, 2007a). McBride (1995) noted that heavy metal mobility was most closely associated with metal-organic complexation and soil pH. Indeed, at low pH, organic matter is the only factor that may reduce the heavy metal mobility in soils because of metal-organic complexation (McBride, 1995). This agrees with the observation of Van Erp and Van Lune (1991) that Pb and Cu are bound strongly to organic matter and would be released slowly over time as the organic matter of the sludge is decomposed, whereas Cd and Zn are not bound as strongly to organic matter. McBride (1995) described this slow release of heavy metals as a “time bomb” because of high organic matter content of sewage sludge.

McGrath (2000) has investigated various metals and their pathways contributing to soil contamination in England and Wales from 1995 to 1997. The results showed that the greatest inputs of Cd, Pb, As and Hg were from atmospheric deposition, while animal manure supplied the most Zn and Cu. For ecological safety and human health, the Government of China has put forward a series of strategies to limit waste water, solid wastes, Cd containing phosphate fertilizers etc. used in agricultural systems to control air pollution and forbid the use of contaminated land for growing edible crops (Wang and Li, 1999).

Zinc and Copper

The concentration of Zn in soils collected along the Dhaka- Manikgonj-Khulna highway varied from 57 to 109.5 ppm.

Total Zn contents varied widely among the distances of the soils. The average accumulations of total Zn concentrations were 76.5ppm, 73.16ppm and 69.9ppm at 0m, 30m and 50m-distances from the roadside.

It was observed that the highest mean concentration of zinc(76.5ppm) was found near the edge of the highway and decreased with increasing distances. The variance of analysis showed that there were significant differences of zinc with distances (Table 4.7).

Some sites did not follow any definite pattern in Zn concentration from near the road to farther away from the road. The highest value of Zn (109.5pm) was found in a spot at 2B that is 30m away from the highway which might be due to the cause that, industrial wastes and sewage sludge and garbage were added there which contained high level of Zn.

The highest value of copper (36.5ppm) was obtained at spot 1A and the lowest value of copper (14.5ppm) was obtained at spot 8B and 9A.

Total Cu contents varied widely among the distances of the soils. The average accumulations of total Cu concentrations in soils were 27.59ppm, 26.1ppm and 28.4ppm at 0m, 30m and 50m distances from the roadside.

Le Riche (1968) mentioned that, zinc is almost present in the highest amount in sludge and the application of domestic sludge over several years have led to the accumulation of heavy metal especially Zn in the soil. The soils collected from agricultural land at 50 or 500 m away from the highway contained high Zn content, which might be due to the application of fertilizes, pesticides and other agrochemicals. Swaine (1962) found that, super phosphate fertilizers contained 70-3000 ppm Zn whereas farmyard manure contained 4-360 ppm Zn. As mentioned earlier, trace elements like Zn, Pb, Cu and Fe concentration in an agricultural soil could be higher than soils of commercial-residential area (Lau

manure. According to Swaine (1962) superphosphate contains trace to 2842 ppm Mn and farmyard manure contains 1 ppm Mn.

From Table 4.7 it was found that there were no significant differences of Mn content with distance calculated by DMRT.

From the above discussions, it was observed that the roadside soils were contaminated with Pb, Cd, Zn and Cu but not yet polluted except Mn and soil contamination with Pb and Zn was high near roadside and decreased with increasing lateral distances.

Correlations among total heavy metals and soil properties:

A correlation matrix for heavy metals and soil properties of the studied soils was calculated to see whether they were interrelated with each other and the results were presented in Table 4.6.

In the study, the concentrations of total Pb were significantly and inversely correlated with soil pH ($r = -0.349$) but were positively but not significantly correlated with clay and organic matter. From Table 4.6, it was found that Zn and Mn were significantly correlated with Cu. The correlation between Zn and Cu was $r = 0.376$ and between manganese was $r = 0.521$. The concentrations of total Pb were significantly and positively correlated with Cd ($r = 0.504$). The concentrations of total Cd were inversely correlated with soil pH ($r = -0.040$). The strong negative relationship between metal concentration and soil pH was also observed by many other investigators (Evans *et al.*, 1995; Singh *et al.*, 1995; Wang *et al.* 2003).

Wang *et al.* (2003) found that NH_4OAc extractable Cd, Zn and Ni decreased with increasing pH. More than 90 % of the variability of Pb and Zn in the exchangeable fraction was caused by the variability of soil pH (Finžgar *et al.*, 2007). A considerable number of other studies also tried to inter relationships between the mobility of metals and soil properties (Sauvé *et al.*, 1997; Janssen *et al.*, 1997). In general, soil pH and CEC were found to be important

predictors of metal extractability (Rieuwerts *et al.*, 2006), retention and movement in soils (Matos *et al.*, 2001; Udom *et al.*, 2004). Strong positive correlations of total contents of Cd and Pb with their mobile fractions and each other suggest overloading of geochemical system in the contaminated soils, where anthropogenically added metals remained weakly bound to soil constituents (Ramos *et al.*, 1994).

The relationships between Cd and soil properties are complex in that they are a result of parent material composition, natural and anthropogenic inputs of Cd as well as intrinsic soil properties which control the speciation and fate of Cd (Traina, 1999). According to Holmgren *et al.* (1993), at below approximately pH 7, Cd concentrations in mineral soils appear to be positively correlated to both soil pH and organic carbon content. Above pH 7, the correlation between Cd and organic carbon is less significant. In the present study, total Cd concentration was correlated negatively with organic matter and pH. In the present study, clay content did not exhibit any significant relationship with total and extractable metals. However, Chlopecka *et al.* (1996) did not observe any consistent relation between heavy metal concentrations and clay content, organic matter, carbonate content, pH and EC.

4.2 RESULTS OF PLANT SAMPLES

Fifty four different naturally growing plant samples were collected from thirty different spots. These different plant samples belong to 10 different species. Accumulation of nutrient elements (N and P) and heavy metals (Pb, Cd, Zn, Cu and Mn) from different plant species collected from different spots are shown in Table 4.8. The roots and shoots of plants were analyzed separately for the following parameters.

4.2.1 TOTAL NITROGEN :

and Wong 1982). A truck stand soil along the highway showed the second highest Zn content (128ppm) which obviously indicates that, motor wastes and fumes play a vital role in adding into the soils. Lagerweff and Specht (1970) mentioned that, Zn and Cd might also be added to soils adjacent to highways and the sources being tires and lubricants. Ardakani (1984) stated that, zinc and cadmium are added to lubricating oils and present in tires and galvanized parts of the vehicles. Zn content may decrease with increasing organic matter as Wild (1996) stated that, Zn form complexes with soil organic matter, but these are less stable than those formed by cadmium and much less than those formed by lead.

Manganese

The Mn concentration determined in the soils was higher than that of Zn concentration and it varied from 195 to 448 ppm.

The highest Mn(448ppm) was obtained at spots at 10B and the lowest Mn (195.5ppm) was obtained at spot 9A.

Total Mn contents varied widely among the distances of the soils. The average accumulations of total Mn concentrations in soils were 313ppm, 352ppm and 334ppm at 0m, 30m and 50m distances from the roadside.

From the result it was observed that Mn concentration in the collected soil samples was not in the normal range in most of the soils and so the collected soils were contaminated with Mn. It was clear from the study that, the Mn concentration did not follow any definite pattern so far the distance from near or farther away from the highway is considered. The high Mn content was found in the soils collected from 30m away from the highways which was a rice field area. However, soils along the highway did not show higher Mn contents compared to the soils at 50m away, which indicates that, automobile exhaust does not contribute to soil contamination by Mn. The exceptions where Mn content was higher along the roadside soil than that at 30 m away might be the addition of manure. In some cases, agricultural soils at 50 m away from the road showed high Mn content and obviously it had come from pesticides and

It was found from Table 4.8 that among the roots and shoots of the plants, the grass root accumulate more nitrogen (8.6%N) at sampling spot 9B and the shoot of malancha accumulates high level of nitrogen (7.1%) at sampling spot 7B.

On an average, the accumulation of nitrogen concentration in the roots of grass, rice, aurum and malancha were 3.0%, 2.2%, 3.2% and 4.0%, respectively and in the shoots of above plants were 2.9%, 3.2%, 3.2%, and 4.1%, respectively. The highest N concentration was found in **malancha root** and in **malancha shoot** among the above plants. The average concentrations of nitrogen in the roots of chilies, ladies finger, red amaranths balsam apple, basil, and potato contained 2.8%, 2.9%, 5.9%, 6.2%, 6.1% and 3.1% N and shoots of the above plants contained 3.7%, 2.7%, 5.2%, 2.9%, 4.2%, and 2.2% N (Table 4.9 to 4.13).

4.2.2 TOTAL PHOSPHOROUS :

It was found from the Table 4.8 that among the roots and shoots of plants, ladies finger contained the highest amount of phosphorous in both root and shoot i.e. 0.51% and 0.56%, respectively at spot 8B and 8C. The accumulation of P by the roots of the grass, rice, aurum and malancha were, 0.23%, 0.38%, 0.26%, and 0.35% and in the shoots of above plants were 0.27%, 0.27%, 0.28% and 0.40%, respectively. The shoot of chilies, Ladies finger, red amaranthus, balsam apple and potato contained 0.27%, 1.2%, 0.4%, 0.45%, 0.26%, and 0.15% phosphorous, respectively and the roots of the above plants contained 0.15%, 1.53%, 0.39%, 0.47%, 0.19%, and 0.21% Phosphorous, respectively (Table 4.9 to 4.13).

4.2.3 TOTAL LEAD :

From Table 4.8, it was observed that among the roots and shoots of different plant species the highest value of lead (25 ppm) was obtained in grass root at sampling spot 9B and 10B and the highest value of Pb (30ppm) was obtained in maricha shoot at sampling spot 4B. On an average, the accumulation of Pb

by the roots of the grass, rice, aurum and malancha were 14.3, 11.7, 7.1 and 8.6 ppm and in the shoot of the above plants were 8.7, 6.3, 8.1, and 10.57 ppm, respectively (Table 4.9 to 4.13).

4.2.4 TOTAL CADMIUM :

It was observed that among the roots and shoots of different plant species the highest value of cadmium (1.75 ppm) was obtained in grass root at sampling spot 10B and the highest value of Cd (3ppm) was obtained in maricha shoot at sampling spot 4B. The accumulation of Cd by the roots of the grass, rice, aurum and malancha were 0.65, 0.36, 0.53 and 0.41 ppm and in the shoot of the above plants were 0.75, 0.29, 0.73 and 0.82, ppm, respectively (Table 4.9 to 4.13).

4.2.5 TOTAL ZINC:

The highest zinc content was found in rice root (312.5 ppm) at spot 2C and among the shoots, the highest zinc was obtained in maricha shoot (2.42 ppm). The average concentration of Zn by the roots of grass, rice, aurum and malancha were 40.28, 107.93, 46.3 and 61.4 ppm and in the shoots of the above plants were 41.0, 43.67, 51.33 and 38.5 ppm, respectively (Table 4.9 to 4.13).

4.2.6 TOTAL COPPER :

Highest copper in roots of grass was 63 ppm at spot 10 C, and the highest copper in shoots of grass was 63 ppm at sampling spot 10 B.

On an average, the accumulation of Cu in the roots of grass, rice, aurum and malancha were 20.17, 41.61, 30.3 and 24.8 ppm and in the shoots of the above plants were 27.53, 28.52, 33.2 and 31.1 ppm, respectively (Table 4.9 to 4.13).

4.2.7 TOTAL MANGANESE :

Among the roots of the collected plant samples, the highest manganese content was observed in the roots of arum (625 ppm) and among the shoots, the highest

manganese content (840 ppm) was observed in rice shoot at sampling site 6C. On an average the accumulation of Mn in the roots of grass, rice, aurum and malancha were 138.17, 41.61, 253.3 and 167.3 ppm and in the shoots of the above plants were 145.33, 28.52, 177.2 and 161.60 ppm. respectively (Table 4.9 to 4.13).

The distribution of heavy metals in different plant parts with different distances were shown in Figures from 4.13 to 4.17 and correlation coefficient between soil heavy metals with distances and plant parts (root and shoot) were shown in Tables 4.19-4.23.

CONTAMINATION OF PLANTS BY Pb AND SOME OTHER HEAVY METALS

According to Sauerbeck (1985), critical level of Pb in plants is 10 to 20ppm, Cd is 5 to 10ppm, Zn is 150 to 200ppm and Cu is 15 to 20ppm and their common concentration in plants are 0.1 to 2.0ppm for Pb, 0.05 to 0.5ppm for Cd, 20 to 200ppm for Zn and 3 to 100ppm for Cu.

Lead

On an average Pb in the roots and shoots of plant parts at different distances from the highway were presented in Figure 4.13. From Figure 4.13 it was found that among the roots and shoots of the collected plant samples the average concentration of lead was high in grass root (20ppm) at 30m distance and malancha shoot (12ppm) at 30m distance.

On an average, the accumulation of Pb by the roots of the grass, rice, aurum and malancha were 14.3, 11.7, 7.1 and 8.6 ppm and in the shoot of the above plants were 8.7, 6.3, 8.1, and 10.57 ppm, respectively (Table 4.9 to 4.13). From the result, it was observed that among the plant parts, Pb concentration was more in root than shoot in grass and rice and it was more in shoot than root in aurum and malancha. Among the plant roots, the highest Pb concentration was found in grass (14.3ppm) and among the plant shoots the highest Pb concentration was found in the malancha shoot (10.57ppm) (Table 4.9 to 4.13). The amount was not at toxic level as the common concentration of Pb in plant is 0.1-2.0ppm and critical level is 10 to 20ppm (Sauerbeck, 1985). From Table 4.14 variance analysis showed that there were significant difference of Pb in rice root, grass root and grass shoot, aurum shoot and malancha shoot with distance.

It was observed that there were significant positive correlation between soil lead and Pb in rice root ($r = 0.846$) and in rice shoot ($r = 0.995$) at 0m distance. The Pb in the shoots of rice, grass, aurum and malancha showed significant positive correlation with soil Pb at 30m distance from roadside. The Pb in the

grass root and aurum shoot showed significant positive correlation with soil Pb at 50m distance. Most of the plant parts showed significant correlation for heavy metals with soils (Table 4.19). Correlation coefficient calculated between plant Pb content and that of soils showed very high value, thus substantiating the idea that, soil pollution by Pb could contribute to the pollution of the food chain.

In the study grass accumulated high amount of Pb and Cd than other plants _a finding similar to that of Ullah *et al.*, (1995). The reasons may be the due to the exposure of grass for a longer period of time and the main reason might be the motor vehicle exhaust or there might be the different mechanisms of absorption.

When plant samples were analyzed for this heavy metal, the results were rather astonishing. In most cases, it was observed that the plants collected along the highway mostly contained the high concentration of heavy metals and it showed a decreasing tendency with increasing lateral distance from the highway. Lubis *et al.*, (1988) found that rice plant grown along the highway contained 26.75-36.50 mg/kg Pb. Wild (1996) observed that, addition of lead salts to soils produce only small increase in uptake and most of this was retained in the roots. Among the accumulated lead, the insoluble part remains on the outside of the epidermis but the soluble part enters into the plant through stomata and other openings (Smith, 1971).

Above results indicated that Pb and other metal contamination of soil can lead to its accumulation in the vegetation which ultimately enter into food chain. Ward *et al.*, (1975) showed that, the vegetation growing in the areas of greater traffic density had higher Pb levels and the Pb levels in the vegetation decreased with increasing distance from the highway. Zimdahl (1976) outlined that, Pb remains largely as a superficial deposition or topical aerosol coating on plant surfaces. Moreover, Suchodoller (1967) mentioned that, there is a wide divergence in Pb uptake between species; uptake is greater in dicotyledonous

than in monocotyledonous species. Motto *et al.*, (1970) found the highest concentration of Pb in the leaves of lettuce. Bhatia and Choudhri (1991) showed that, plant growing on either side of the road with heavy traffic showed highest Pb content, which was above the acceptable level of toxicity. This corroborates to our observations.

It was found that grass accumulated more Pb than any other plant species. Other plants also accumulated higher concentration of Pb than the normal plant concentration which implies that all the collected plant species were contaminated with Pb. This signifies the differential accumulation of this heavy metal by species i.e. the accumulation of non essential heavy metal is regulated by plant through some mechanisms which are dependent on the species or variety. The difference in accumulation of Pb by the same species from one spot to another could be related to soil conditions, plant growth stages and plant parts.

The results of straw/root ratio of Pb concentration showed a limited translocation of Pb from the roots to the straw. Such limited translocation of Pb was also found in other plant species growing on contaminated soil (Nehnevajova, 2005). One reason of low Pb translocation capacity is the low mobility of Pb compared to Cd or Zn. Translocation of metals from root to shoots is performed in the xylem and it is driven by transpiration of water in the leaves. Xylem cells have a high cation exchange capacity, which would be expected to severely retard the movement of metal cations. Several pathways have been proposed to explain the movement of metals in the transpiration stream. Analysis of the xylem sap of certain metal accumulators showed that organic acids, like citric malic and malonic acids are involved in metal transport (Senden *et al.*, 1993).

Cadmium

It was observed that among the roots and shoots of different plant species the highest value of cadmium (1.75 ppm) was obtained in grass root at sampling

spot 10B and the highest value of Cd (3ppm) was obtained in maricha shoot at sampling spot 4B. The accumulation of Cd by the roots of the grass, rice, aurum and malancha were 0.65, 0.36, 0.53 and 0.41 ppm and in the shoot of the above plants were 0.75, 0.29, 0.73 and 0.82, ppm, respectively (Table 4.9 to 4.13).

In the study, cadmium concentration in grass varied from 0.01-1.5 ppm (Table-4.9). In grass root, mean concentration of cadmium was 1.46 ppm and in grass shoot, it was 1.15 ppm. So, from the background level, the grass samples did not show cadmium concentration more than critical levels for plants (5-10ppm) So, the results showed that there was no cadmium pollution in grass.

In case of rice, the cadmium concentration ranged from 0.01 to 0.75 ppm. The average cadmium in case of rice root was 0.36 ppm and in case of rice shoot was 0.29 ppm, respectively (Table 4.10). In case of aurum, the cadmium concentration ranged from 0.1 to 1.2 ppm. The average cadmium concentration in aurum root was 0.53 and in aurum shoot was 0.73 ppm (Table 4.11). In case of malancha, the cadmium concentration ranged from 0.1 to 1.9 ppm. The average concentration of cadmium in malancha root was 0.41 ppm and in malancha shoot was 0.82 ppm (Table 4.12). Besides other plants such as chilies, ladies finger, basil balsam apple potato contained high contents of cadmium (Table 4.8). The results showed that plant parts did not contain Cd more than critical level.

So, there was no cadmium pollution in plants. Correlation co-efficient between soil and plant parts at different sampling spots (A, B and C) i, e for 0m distance, 30 m distance and 50m distance laterally from the highway were presented in Table 4.20.

A positive and highly significant correlation was observed between soil Cd and Cd in the root and the shoot of rice; and between soil Cd and Cd in aurum root ($r=1^{**}$) at 0m distance. Positive relationships for metal content between soil and plants are expected results, because plants take nutritional elements from the soil via their roots.

From Anova Table 4.15, it was observed that there were significant differences of cadmium in roots and shoot of rice, grass and malancha with distances.

The variation of Cd and Pb uptake depend on the physical and chemical nature of the soil and absorption capacity of heavy metals by the plant (Bahemuka and Mubofu, 1999; Liu *et al.*, 2003, 2005). Soil properties influencing Cd and Pb uptake and accumulation in grain crops and other plant species were reported previously (Eriksson, 1990c; Li *et al.*, 1994). The uptake of metals is frequently related to their concentrations in soil. This is especially true for elements that are mobile (Bañuelos and Ajwa 1999). In general, increases in Cd and Pb content in soil resulted in increases in the uptake of Cd and Pb by plants. For instance, (Liu *et al.*, 2005) observed the Cd concentrations in brown rice range from 0.22 to 2.86 mg kg⁻¹ when grown in highly Cd contaminated soil (100 mg kg⁻¹).

The bioavailability of Cd in soil is highly dependent on soil pH, organic matter and total Cd concentration (Janssen *et al.*, 1997; Sauve *et al.*, 2000b). However, many factors and variables may have an effect on the absorption and storage of cadmium and lead in the grains of rice. Soil pH is an important factor that affects the concentration of the cadmium and lead of the soil solution because an increase of pH causes a decrease in the solubility of the lead and cadmium compounds. It is possible that the organic contaminant in city sewage enhanced Cd uptake. Zarcinas *et al.* (2004) also reported that Cd uptake was strongly correlated with organic matter. Rice root accumulated high quantities of Cd²⁺ when grown in non-pollution areas as in a medium containing this metal (Ruby *et al.*, 1994). This metal, as divalent cation, may compete with other cation

(including Ca^{2+} , Mg^{2+} , Fe^{2+}) in their transport across membranes. Other factors including the ionic exchange capacity and the competitive effect of the other metallic cations have an effect on the rate of absorption of lead and cadmium in rice (Alloway *et al.*, 1988). Li *et al.* (2005) indicated that the total uptake of cadmium and accumulation in grain was dependent on both soil type and genotype effects.

The percentage of total Cd and Pb uptake in the root was higher than that in shoot. Such a high Cd content in shoot could be the presence of Cd binding peptides in them (Wójcik and Tukendorf, 1999). Cadmium and Pb retention in the roots is an important mechanism in regulating or mobilizing their translocation to the straw and particularly to the grains. The mobility of Cd and Pb in roots may depend on adsorption to the cell wall (Nishizono *et al.*, 1989) and/or chelation to organic compounds (Wagner, 1993).

Retention of the highest amount of the metal taken up by roots, characteristic for numerous plant species (Meuwly and Rauser, 1992; Punz and Sieghardt, 1993), is considered as one of the detoxification mechanisms particularly in monocotyledones (Baker and Walker 1990; Verkleij and Schat, 1990). Cadmium concentration in roots can reach 80% of the total pool of the metal taken up (Baszynski and Krupa, 1992), but in the present study it was 9 to 20%.

Once in the shoot, it is possible that some Cd may be redistributed in the plant via the phloem, as suggested by a study of Zn transport in wheat (Herren and Feller, 1994) and data obtained with leaf-applied 109 ppm Cd (Cakmak *et al.*, 2000).

Potential transfer of metals from soil to plants may be an especially important issue in areas where agricultural production has been pushed onto marginal lands. The distribution of heavy metals in various parts of crops implies that it would be a high risk to human health if paddy rice were grown in soils heavily polluted with Cd since a large proportion of this metal accumulated in the edible parts. However, growing paddy rice in soil contaminated with Pb would be less risky because this metal is accumulated mostly in the roots with a only

very little translocation to the grain. Less contaminated soils can be utilized for production of crops, provided that they accumulate only small amounts of toxic metals in edible parts. Accumulation of heavy metals in edible parts of plants such as grain of rice may depend on genotypes. Therefore, further works may be conducted with different rice varieties and with widely different types of contaminated soils.

Kashem *et al.* (2008) reported that the concentration and accumulation of Cd in different parts of aurum increased with increasing Cd levels in the nutrient solution. Increases in Cd concentration in soil significantly increased Cd concentration and total Cd content in shoots and roots of durum wheat in another study by Jalil *et al.* (1994).

Zinc

The Zn concentration in the plant samples collected along the highway as well as laterally farther away from the highway varied from 22 to 290 ppm. The highest concentration was found in the plants collected near the highway.

The mean Zn concentration in grass, rice, aurum and malancha were 40.28, 107, 93, 46.3 and 61.4 ppm in case of root and 41, 43.67, 51.3 and 38.5 ppm in case of shoots of the above plants, respectively. The common concentration of Zn in plant is 20-100 ppm critical level of Zn is 150to200(Sauerbeck, 1985). Plant parts did not accumulate more Zn than the 'background level'.

Table 4.8 showed that plants collected near the edge of the high way contained more Zn and it decreased with increasing distances in most of the cases. In some cases plants of agricultural soils showed higher Zn concentration than those collected along the highway. The higher Zn concentration in plants collected near the highway might be due to the automobile exhausts and spillage was continuously being added to the soils and on plant foliages.

The variance analysis showed that Zn contents in grass root and shoot, aurum root and shoot and rice root showed significant differences with distances (Table 4.16).

There was highly significant positive correlation between Zn in malancha root and soil Zn at 50m distance ($r=1^{**}$) and highly significant negative correlation between soil Zn and Zn in malancha shoot ($r = -0.977$) and grass shoot ($r = -0.940$) collected from 0m and 30m distances, respectively (Table 4.21). In most plants, correlation co-efficient between Zn in plant parts and soil showed positive but not significant relationship which indicated Zn has the limited mobility in the plant and it can be accumulated in the root system when Zn has been applied to the soil. The clearest effect of excess Zn is reduction of root growth for the low tolerant plant. In Zn polluted soils, plants accumulate Zn, which can ultimately enter into food chain and pollute the environment.

Fytianos *et al.* (1985) observed contamination of roadside vegetation with Zn and Cd in Thessaloniki area in Greece. Das *et al.* (1989) found significantly higher contents of Zn along with Pb, Cu, Ni, Cd and Fe in the plants exposed 10 vehicle pollution than in control nursery plants. Lubis *et al.* (1988) found that rice plant grown along the highway contained 27.75 mg/kg Zn. Moreover, Maskina and Raudhawa (1983) stated that poultry manure, farmyard manure and other organic manure increase the Zn concentration in plant. In some cases, plants of agricultural soils 500m away from the highway showed higher Zn content than those collected at 50m away or along the highway. Atmospheric transport of airborne Zn particles exhausted from motor vehicles and their deposition on plant surface might be the cause of this high Zn concentration. Moreover, agricultural inputs such as fertilizers, pesticides and farm yard manure etc. may contribute to high Zn content in soils which is taken up by the plants entering into our food chain and polluting the environment. It was found that, on an average plant accumulated more Zn than the normal concentration in plant which is 20-100 ppm (Sauerbeck, 1985). In some spots, it also

accumulated the Zn that was in the normal range. This signifies the differential accumulation of Zn by plant species. The difference in Zn accumulation by the same plant species from one spot to another could be related to the soil conditions, plant growth stage and the plant parts.

Copper :

The mean copper concentration in roots of grass, rice, aurum and Malancha were 20.17, 50.8, 30.3 and 24.8 ppm, respectively and in shoots of the above plants were 27.53, 25.6, 33.2 and 31.1ppm, respectively. The normal concentration of copper in plant is 3-100ppm (Sauerbeck, 1985). So, plant parts did not accumulate more Cu than the background level (3-100 ppm). Rice root accumulate more Cu (50.8ppm) than any other parts of the plants(Figure-4.16). It has also been observed that the same plant species accumulate different amount of Cu in different spots that might be due to effect of soil conditions, plant growth stages and plant parts. The variance nalysis(Table 4.17) showed that Cu content in plant parts with distances had no significant differences except aurum root and grass root. Aurum root and grass root at 50 m distance significantly accumulate more Cu than the other two distances. There was no significant positive correlation between Cu in soil and plant(Table 4.22).

When plant samples were analyzed for this heavy metal, it was observed that, except the agricultural land, plants collected along the highway contained higher Cu than that of plants collected from 50m away from highway. Cu pollution of soils can lead to its accumulation in the vegetation which ultimately enter into the food chain. Das *et al.*, (1989) showed that, significantly higher content of Cu, Pb, Zn, Cd and Fe were found in the plants exposed to vehicle pollution than in control nursery plants. They also mentioned that, leaves accumulated higher concentration of Cu, Zn and Fe than

stems and flowers. The highest Cu content was found in plants of agricultural soils of 50m away where pesticides and fertilizers were applied.

It was found that rice plants accumulated more Cu (50.8ppm) than any other plant species (Table 4.13). This amount was in the range of the normal concentration of Cu in plant which is 3-100 ppm (Sauerbeck, 1985). It has also been observed that the same plant species accumulated different amount of Cu in different spots that might be due to the effects of soil conditions, plant growth stages and plant parts.

Manganese

When plant samples were analyzed for Mn content, the results showed that rice contained 409ppm Mn. The Mn content in the collected plant samples did not follow any definite pattern with increasing distance from the road and it is shown in Figure 4.17. Correlation coefficients (Table 4.23) between soil Mn and plant Mn showed that Mn in rice root and soil had strong positive correlation at 0m and 30m distances and between soil and malancha root had strong positive correlation at all distances. The variance analysis (Table 4.18) showed that there were significant differences of Mn concentration in plant parts with distances and increased with increasing distances in most cases. This is an indication that, the Mn contamination did not occur by automobile exhausts although Abasel and Cottenie (1985) observed that, soil contamination by zinc and Pb was quite pronounced along highways and in some cases contamination by Mn was observed but they did not find plant contamination by Mn as they investigated with soils and plants. The plants contained higher Mn than the normal content, which may enter into food chain and this Mn might have come from other sources.

It was observed from the results that most plants accumulated more Mn. The amount was higher than the normal concentration of Mn in plant which is 15-100 ppm (Allaway, 1968). It implies that, accumulation of this heavy metal in plant is regulated by plant through some mechanisms that are dependent on the plant species or variety. The difference in accumulation of Mn by the same

species from one spot to another could be related to soil conditions, plant growth stages and plant parts.

Table 4.8 : Nutrients and Heavy Metals Contents in Plants

Spot	Distance from road (m)	Plants	Plant Parts	%N	%P	Pb (ppm)	Cd (ppm)	Zn (ppm)	Cu (ppm)	Mn (ppm)
1	0	Grass	Root	1.9	0.26	12.5	0.01	32.5	2.5	10
			Shoot	2.7	0.19	7	0.1	60	28	31
2	0	Rice	Root	2.0	0.20	12.5	0.5	100	50	272.5
			Shoot	1.8	0.16	2	0.1	28	16	139
		Grass	Root	3.9	0.35	10.5	0.5	50	45	222
			Shoot	2.1	0.40	7	0.1	49	47	202
		Malancha	Root	3.9	0.18	12	0.29	70	25	110
			Shoot	3.0	0.35	18	1.9	40	37	60
	30	Rice	Root	1.8	0.20	17.5	0.01	75	44	512.5
			Shoot	1.9	0.26	9	0.01	39	16	205
	50	Rice	Root	2.2	0.29	10	0.15	312.5	50	400
			Shoot	1.8	0.28	7	0.01	52	30	229
		Malancha	Root	6.0	0.30	12	0.2	52	18	107
			Shoot	2.5	0.25	18	0.3	39	40	189
3	50	Red amaranthus	Root	5.9	0.39	9	0.5	60	35	60
			Shoot	5.2	0.40	17	0.4	47	20	58
		Balsam apple	Root	6.2	0.47	6	0.32	48	13	80
			Shoot	2.9	0.45	8	0.5	54	17	69
4	0	Chili	Root	1.8	0.16	5	0.23	90	52	131
			Shoot	4.2	0.39	3	1.0	242	25	143
	30	Chili	Root	2.7	0.10	7	0.26	69	42	140
			Shoot	3.9	0.28	30	2.4	71	48	151
	50	Chili	Root	3.9	0.12	5	0.01	90	32	170
			Shoot	3.5	0.17	6	0.4	70	42	110
5	0	Basil	Root	6.1	0.19	2.3	0.23	99	62	60
			Shoot	4.2	0.26	3	0.4	38	11	23
6	0	Grass	Root	2.2	0.29	5	0.01	47.5	10	42.5
			Shoot	4.1	0.30	5	0.01	49	12	51
	30	Malancha	Root	2.2	0.23	7.5	1.0	55	30	53
			Shoot	6.2	0.53	10	0.01	27	16	39
		Rice	Root	2.9	0.33	9	0.15	88	40	320
			Shoot	3.9	0.42	6.5	0.3	58	23	210
	50	Rice	Root	1.6	0.34	5	0.01	97.5	45	520
			Shoot	2.0	ND	7	0.4	48	10	846
7	0	Grass	Root	2.1	0.23	12.5	0.01	117.5	10	117.5
			Shoot	2.3	0.19	3	0.01	73	31	65
		Aurum	Root	3.1	0.39	9	0.3	33	30	90
			Shoot	1.3	0.17	8	0.1	30	44	80
	30	Chili	Root	2.8	0.20	5	0.5	86	4	132
			Shoot	3.3	0.23	3	0.5	127	21	46

Spot	Distance from road (m)	Plants	Plant Parts	%N	%P	Pb (ppm)	Cd (ppm)	Zn (ppm)	Cu (ppm)	Mn (ppm)
		Malancha	Root	7.0	0.40	9	0.5	80	29	310
			Shoot	2.1	0.21	6	0.2	25	38	215
		Aurum	Root	2.4	0.16	8	0.3	47	15	210
			Shoot	3.3	0.25	6	0.5	30	25	150
	50	Grass	Root	2.6	0.34	2.5	1.25	60	20	207.5
			Shoot	3.5	0.24	0	0.7	27	26	58
8	0	Malancha	Root	2.9	0.42	5	0.25	67.5	10	210
			Shoot	3.8	0.23	26	3	56	34	64
	30	Ladies finger	Root	2.8	0.51	12	0.25	28	10	59
			Shoot	2.6	1.12	4	0.3	22	2	52
	50	Ladies finger	Root	2.9	0.56	15	1.25	85	47.5	72.5
			Shoot	2.7	1.2	9	0.9	70	51.5	80.5
9	0	Grass	Root	2.2	0.22	7.5	0.25	42.5	7.5	37.5
			Shoot	2.6	0.20	20	1.2	21	13	69
		Aurum	Root	6.5	0.21	8	0.3	79	6.3	90
			Shoot	4.0	0.29	10	1.2	67	14	110
		Malancha	root	2.8	0.49	9	0.6	51	24	97
			shoot	3.0	0.29	13	1.2	42	36	69
	30	Grass	Root	8.6	0.12	25	0.9	35	17.5	142.5
			Shoot	2.7	0.14	2	0.4	44	20	95
		Potato	Root	2.6	0.23	12.5	0.25	107.5	20	162.5
			Shoot	1.8	0.15	10	0.9	51	25	88
		Aurum	Root	2.6	0.21	3	0.9	50	9	130
			Shoot	1.8	0.08	5	0.7	40	30	80
	50	Malancha	Root	5.4	0.26	6	0.3	51	26	315
			Shoot	3.1	0.36	10	0.8	29	25	204
		Potato	Root	3.5	0.19	10	0.3	42.5	42.5	205
			Shoot	2.6	0.15	4	0.2	65	40	312
		Grass	Root	5.4	0.20	15	0.5	27.5	27.5	87.5
			Shoot	2.8	0.5	4	0.1	26	18	192
		Aurum	Root	3.2	0.30	6	0.75	25	57.5	300
			Shoot	4.0	0.40	10	0.90	80	19	160
10	0	Aurum	Root	2.2	0.41	7.5	0.5	80	40	140
			Shoot	3.1	0.35	8	0.8	34	54	280
		Rice	Root	1.8	0.27	2.5	0.75	50	57.5	395
			Shoot	3.2	0.26	11	0.5	32	31	292
		Grass	Root	1.2	0.27	12.5	0.75	52.5	42.5	242.5
			Shoot	1.9	0.26	13	1.4	55	37	202
	30	Aurum	Root	1.7	0.19	10	0.25	37.5	22.5	625
			Shoot	2.2	0.18	6	0.8	20	21	262
		Rice	Root	2.0	0.51	2.5	0.5	55	45	622.5
			Shoot	2.2	0.24	3	0.1	24	23	387
		Grass	Root	1.8	0.40	25	1.75	67.5	17.5	85

Spot	Distance from road (m)	Plants	Plant Parts	%N	%P	Pb (ppm)	Cd (ppm)	Zn (ppm)	Cu (ppm)	Mn (ppm)
11	50	Grass	Shoot	4.5	0.53	27	1.8	78	63	210
			Root	1.8	0.35	15	0.5	60	65	310
			Shoot	3.1	0.38	10	0.2	24	26	124
		Rice	Root	3.5	0.29	19	0.17	40	60	350
			Shoot	7.4	0.30	7	0.01	42	50	210
		Aurum	Root	2.1	0.24	6.5	0.69	40	52	400
			Shoot	5.0	0.37	9	0.89	75	40	300
	0	Grass	Root	1.4	0.26	2.5	1.5	45	15	177.5
			Shoot	2.5	0.17	4	0.3	40	12	146
		Grass	Root	1.6	0.19	10	0.1	20	8	86
			Shoot	2.7	0.27	6	1.5	26	20	190
		Grass	Root	1.9	0.26	8	0.3	35	10	90
			Shoot	2.8	0.35	6	1.5	28	22	160
12	0	Rice	Root	3.0	0.50	19	0.62	90	45	350
			Shoot	3.9	0.25	8	0.20	40	30	410
		Grass	Root	2.9	0.27	20	0.1	39	54	300
			Shoot	2.6	0.22	4	0.22	37	33	141
		Malancha	Root	2.9	0.41	10	0.4	53	35	316
			Shoot	3.8	0.30	18	0.50	32	25	209
	30	Rice	Root	2.4	0.41	21.5	0.41	115	30	182.5
			Shoot	2.5	0.25	4	0.25	26	29	285
	50	Rice	Root	2.2	0.47	10	0.47	50	17.5	315
			Shoot	5.2	0.34	5	0.34	30	9	387
		Aurum	Root	.5	0.31	6	0.7	30	40	300
			Shoot	4.0	0.48	10	0.9	90	45	250

GRASS

Table 4.9 : Nutrients and heavy metals content in the roots and shoots of grass at different sites with distances

SITE	DISTANCE	at different sites with distances								
		Plant Parts	Pb (ppm)	Cd (ppm)	%P	%N	Zn (ppm)	Cu (ppm)	Mn (ppm)	
7	0m	Root	12.5	0.01	0.23	2.1	117.5	10	117.5	
6		Root	5	0.01	0.29	2.2	47.5	10	42.5	
2		Root	10.5	0.5	0.35	3.9	50	45	222	
1		Root	12.5	0.01	0.26	1.9	32.5	2.5	10	
9		Root	7.5	0.25	0.22	2.2	42.5	7.5	37.5	
10		Root	12.5	0.75	0.27	1.2	52.5	42.5	242.5	
11		Root	2.5	1.5	0.26	1.4	45	15	177.5	
12		Root	20	0.1	0.27	2.9	39	54	300	
			mean	10.3	0.39	0.26	2.1	46.25	12.5	147.5
		0m								
7	0m	Shoot	3	0.01	0.19	2.3	73	31	65	
6		Shoot	5	0.01	0.3	4.1	49	12	51	
2		shoot	7	0.1	0.4	2.1	49	47	202	
1		Shoot	7	0.1	0.19	2.7	60	28	31	
9		Shoot	20	1.2	0.2	2.6	21	13	69	
10		Shoot	13	1.4	0.26	1.9	55	37	202	
11		Shoot	4	0.3	0.17	2.5	40	12	146	
12		Shoot	4	0.22	0.22	2.6	37	33	141	
			mean	7	0.41	0.24	2.6	48	26.6	113
		30m								
9	30m	Root	25	0.9	0.12	8.6	35	17.5	142.5	
10		Root	25	1.75	0.4	1.8	67.5	17.5	85	
11		Root	10	0.1	0.19	1.6	20	8	86	
		mean	20	0.92	0.23	4	29	14	104.5	
	30m									
9	30m	Shoot	2	0.4	0.14	2.7	44	20	95	
10		Shoot	27	1.8	0.53	4.5	78	63	210	
11		Shoot	6	1.5	0.92	2.7	26	20	190	
		mean	11.6	1.23	0.31	3.3	49	34	165	
	50m									
7	50m	Root	2.5	1.25	0.34	2.6	60	20	207.5	
9		Root	15	0.5	0.2	5.4	27.5	27.5	87.5	
10		Root	15	0.5	0.35	1.8	60	65	310	
11		Root	8	0.3	0.26	1.9	35	10	90	
		mean	12.6	0.63	0.29	3	45.63	30.63	162.5	
	50m									
7	50m	Shoot	0.01	0.7	0.24	3.5	27	26	58	
9		Shoot	4	0.1	0.5	2.8	26	18	192	
10		Soot	10	0.2	0.38	3.1	24	26	124	
11		Shoot	6	1.5	0.35	2.8	28	22	160	
		mean	6.8	0.62	0.37	2.9	26	22	158	
GRAND MEAN		Root	14.3	0.65	0.23	3	40.28	20.17	138.17	
		Shoot	8.7	0.75	0.27	2.9	41	27.53	145.33	

Table 4.10 : Nutrients and heavy metals content in root and shoot of rice at different distances

SITE	DISTANCE	Plant Parts	Pb	Cd	%P	%N	Zn	Cu	Mn	
			(ppm)	(ppm)			(ppm)	(ppm)	(ppm)	
2	0m	Root	12.5	0.5	0.2	2	90	50	272.5	
		10	Root	2.5	0.75	0.27	1.8	50	57.5	395
		12	Root	19	0.62	0.5	3	90	45	350
			mean	11.3	0.62	0.32	2.2	76	50.8	304
2	0m	Shoot	2	0.1	0.16	1.8	28	16	139	
		10	Shoot	11	0.5	0.26	3.2	32	31	292
		12	Shoot	8	0.2	0.25	3.9	40	30	410
			mean	7	0.26	0.22	2.9	33	25.6	314
6	30m	Root	9	0.15	0.33	2.9	88	40	320	
		2	Root	17.5	0.01	0.2	1.8	75	44	512.5
		10	Root	2.5	0.5	0.51	2	55	45	622.5
		12	Root	21.5	0.41	0.41	2.4	115	30	182.5
			mean	12.6	0.26	0.36	2.2	83.2	39.7	409.3
6	30m	Shoot	6.5	0.3	0.42	3.9	58	23	210	
		2	Shoot	9	0.01	0.26	1.9	39	16	205
		10	Shoot	3	0.1	0.24	2.2	24	23	387
		12	Shoot	4	0.25	0.25	2.5	26	29	285
			mean	5.6	0.16	0.31	2.6	49	22.7	271.7
6	50m	Root	5	0.01	0.34	1.6	97.5	45	520	
		2	Root	10	0.15	0.29	2.2	312.5	50	400
		10	Root	19	0.17	0.29	3.5	40	60	350
		12	Root	10	0.47	0.47	2.2	50	17.5	315
			mean	11	0.2	0.35	2.3	166.6	43.12	396
6	50m	Shoot	7	0.4	0.01	2	48	10	846	
		2	Shoot	7	0.01	0.28	1.8	52	30	229
		10	shoot	7	0.01	0.3	7.4	42	50	210
		12	Shoot	5	0.34	0.34	5.2	30	9	387
			mean	6.5	0.19	0.29	4.1	43	24.37	418
GRAND MEAN		Root	11.77	0.36	0.38	2.2	107.97	44.54	369	
		Shoot	6.37	0.2	0.27	3.2	43.67	24.22	334.3	

Table 4.11 : Nutrients and heavy metals content in root and shoot of aurum at different distances

SITE	DISTANCE	Plant Parts	Pb (ppm)	Cd (ppm)	%P	%N	Zn (ppm)	Cu (ppm)	Mn (ppm)
7	0m	Root	9	0.3	0.39	3.1	33	30	90
9		Root	8	0.3	0.21	6.5	79	6.3	90
10		Root	7.5	0.5	0.41	2.2	80	40	140
		mean	8.1	0.4	0.33	3.9	64	25.4	106
7	0m	Shoot	8	0.1	0.17	1.3	30	44	80
9		Shoot	10	1.2	0.29	4	67	14	110
10		Shoot	8	0.8	0.35	3.1	34	54	280
		mean	8.6	0.7	0.27	2.8	43	37.3	130
7	30m	Root	8	0.3	0.16	2.4	47	15	210
9		Root	3	0.9	0.21	2.6	50	9	130
10		Root	10	0.25	0.19	1.7	37.5	22.5	625
		mean	7	0.48	0.18	2.2	44	15.5	321
7	30m	Shoot	6	0.5	0.25	3.3	30	25	150
9		Shoot	5	0.7	0.08	1.8	40	30	80
10		Shoot	6.0	0.8	0.18	2.2	20	21	262
		mean	5.7	0.67	0.17	2.4	30	25.3	165
9	50m	Root	6	0.75	0.3	3.2	25	57.5	300
10		Root	6.5	0.69	0.24	2.1	40	52	400
12		Root	6	0.7	0.31	5	30	40	300
		mean	6.3	0.71	0.28	3.4	31	50	333
9	50m	Shoot	10	0.9	0.4	4	80	19	160
10		Shoot	9	0.89	0.37	5	75	40	300
12		Shoot	10	0.9	0.48	4	90	45	250
		mean	10	0.9	0.41	4.3	81	37	236.6
GRAND MEAN		Root	7.1	0.53	0.26	3.2	46.3	30.3	253.3
		Shoot	8.1	0.73	0.28	3.2	51.33	33.2	177.2

Table 4.12 : Nutrients and heavy metals contents in roots and shoots of malancha at different distances

MALANCHASITE		DISTANCE	Plant Parts	Pb	Cd	%P	%N	Zn	Cu	Mn
SITE	(ppm)			(ppm)	(ppm)			(ppm)	(ppm)	
2	0m	root	12	0.29	0.18	3.9	70	25	110	
8		Root	5	0.25	0.42	2.9	67.5	10	210	
9		Root	9	0.6	0.49	2.8	51	24	97	
12		Root	10	0.4	0.41	2.9	53	35	316	
		mean	9	0.38	0.53	3.1	60.3	23.5	183.3	
2	0m	Shoot	18	1.9	0.35	3	40	37	60	
8		Shoot	26	3	0.23	3.8	56	34	64	
9		Shoot	13	1.2	0.29	3	42	36	69	
12		Shoot	18	0.5	0.3	3.8	32	25	209	
		mean	8.7	1.65	0.39	3.4	42.5	33	100.5	
	30m									
2		Root	10	0.2	0.26	4.1	85	35	120	
6		Root	7.5	1	0.23	2.2	55	30	53	
7		root	6	0.5	0.1	2.8	51	28	51	
		mean	7.8	0.56	0.19	3	63	27	74.7	
	30m									
2		Shoot	13	0.1	0.39	5.6	64	47	160	
6		Shoot	10	0.1	0.53	6.2	27	16	39	
7		shoot	13	1	0.56	7.1	35	17	36	
		mean	12	0.4	0.49	6.3	42	26	78.3	
	50m	Root	12	0.2	0.3	6	52	18	107	
7		Root	9	0.5	0.4	7	80	29	310	
9		root	6	0.3	0.26	5.4	51	26	315	
		mean	9	0.3	0.32	6.1	61	24	244	
	50m	Shoot	18	0.3	0.25	2.5	39	40	189	
7		Shoot	6	0.2	0.21	2.1	25	38	215	
9		shoot	10	0.8	0.36	3.1	29	25	204	
		mean	11	0.4	0.27	2.5	31	34.3	306	
GRAND MEAN			Root	8.6	0.41	0.35	4	61.4	24.8	167.3
			Shoot	10.57	0.82	0.4	4.1	38.5	31.11	161.6

Table 4.13 : Mean concentration of different elements of different plant parts with distances

GRASS

Plant Parts	Pb	Cd	%P	%N	Zn	Cu	Mn
	(ppm)	(ppm)			(ppm)	(ppm)	(ppm)
0m root	10.3	0.39	0.26	2.1	46.25	12.5	147.5
0m shoot	7.8	0.41	0.24	2.6	48	26.6	113
30m root	20	0.91	0.23	4	29	14	104.5
30m shoot	11.6	1.23	0.31	3.3	49	34	165
50m root	12.6	0.63	0.29	3	45.63	30.63	162.5
50m shoot	6.8	0.62	0.25	2.9	26	22	158

RICE

Plant Parts	Pb	Cd	%P	%N	Zn	Cu	Mn
	(ppm)	(ppm)			(ppm)	(ppm)	(ppm)
0m root	11.3	0.62	0.32	2.2	76	50.8	304
0m shoot	7	0.26	0.22	2.9	33	25.6	314
30m root	13	0.26	0.36	2.2	83.2	39.7	409.3
30m shoot	5.6	0.16	0.31	2.6	49	22.7	271.7
50m root	11	0.2	0.35	2.3	166.6	43.12	396
50m shoot	6.5	0.19	0.29	4.1	43	24.37	418

AURUM

Plant Parts	Pb	Cd	%P	%N	Zn	Cu	Mn
	(ppm)	(ppm)			(ppm)	(ppm)	(ppm)
0m root	8.1	0.4	0.33	3.9	64	25.4	106
0m shoot	8.6	0.7	0.27	2.8	43	37.3	130
30m root	7	0.48	0.18	2.2	44	15.5	321
30m shoot	5.7	0.67	0.17	2.4	30	25.3	165
50m root	6.3	0.71	0.28	3.4	31	50	333
50m shoot	10	0.9	0.41	4.3	81	37	236.6

MALANCHIA

Plant Parts	Pb	Cd	%P	%N	Zn	Cu	Mn
	(ppm)	(ppm)			(ppm)	(ppm)	(ppm)
0m root	9	0.38	0.53	3.1	60.3	23.5	183.3
0m shoot	8.7	1.65	0.39	3.4	42.5	33	100.5
30m root	7.8	0.56	0.19	3	63	27	74.7
30m shoot	12	0.4	0.49	6.3	42	26	78.3
50m root	9	0.3	0.32	6.1	61	24	244
50m shoot	11	0.4	0.27	2.5	31	34.3	306

Table 4.14: Accumulation of Pb(mg/kg) in roots and shoots of rice, grass, aurum and malancha at different distances laterally away from roadside

Distance(m)	Rice		Grass		Aurum		Malancha	
	Root	Shoot	Root	Shoot	Root	Shoot	Root	Shoot
0m	11.3a	7.0a	10.37b	7.0ab	8.1a	8.6a	9.0a	8.7a
30m	12.62a	5.6a	20.0a	11.6a	7.0a	5.7b	7.8a	12.0b
50m	6.72b	6.5a	12.62b	6.8b	6.3a	10a	9.0a	11.3b

Means followed by a common letter in a column are not significantly different at the 5% level by DMRT

Table 4.15: Accumulation of Cd(mg/kg) in roots and shoots of rice, grass, aurum and malancha at different distances laterally away from roadside

Distance(m)	Rice		Grass		Aurum		Malancha	
	Root	Shoot	Root	Shoot	Root	Shoot	Root	Shoot
0m	0.62a	0.26a	0.38b	0.41b	0.36a	0.70a	0.38a	1.65a
30m	0.26b	0.16b	0.91a	1.2a	0.48a	0.66a	0.56a	0.40b
50m	0.20b	0.19a	0.63a	0.62ab	0.71a	0.86a	0.33b	0.43b

Means followed by a common letter in a column are not significantly different at the 5% level by DMRT

Table 4.16: Accumulation of Zn(mg/kg) in roots and shoots of rice, grass, aurum and malancha at different distances laterally away from roadside

Distance(m)	Rice		Grass		Aurum		Malancha	
	Root	Shoot	Root	Shoot	Root	Shoot	Root	Shoot
0m	76.0b	39a	46.25a	48.0a	64.0a	43.6b	60.37a	42.5a
30m	83.25b	49a	29b	49.3a	44.8a	30.0b	63.66a	42.0a
50m	166.0a	43.0a	45.6a	26.0b	31.6a	81.6a	61.0a	31.0a

Means followed by a common letter in a column are not significantly different at the 5% level by DMRT

Table 4.17: Accumulation of Cu(mg/kg) in roots and shoots of rice, grass, aurum and malancha at different distances laterally away from roadside

Distance	Rice		Grass		Aurum		Malancha	
	Root	Shoot	Root	Shoot	Root	Shoot	Root	Shoot
0m	42.0a	38.5 a	12.5b	26.6a	25.4b	37.3a	23.5a	33.0a
30m	39.7a	22.7a	14.3b	34.3a	15.5b	25.3a	27.0a	26.6a
50m	43.1a	24.7a	30.6a	22.0a	49.8a	37.0a	24.3a	34.3a

Means followed by a common letter in a column are not significantly different at the 5% level by DMRT

Table 4.18: Accumulation of Mn(mg/kg) in roots and shoots of rice, grass, aurum and malancha at different distances laterally away from roadside

Distance	Rice		Grass		Aurum		Malancha	
	Root	Shoot	Root	Shoot	Root	Shoot	Root	Shoot
0m	304a	314a	147.5a	113a	106b	130b	183.3a	33.0b
30m	409.3a	271.7b	104.5b	165a	321a	165ab	74.7a	78.3a
50m	396a	418a	162.5a	158a	333a	236.6a	244a	306a

Means followed by a common letter in a column are not significantly different at the 5% level by DMRT

Table 4.19: Correlation co-efficient between Pb concentration(ppm) in soil and different plant parts at different distances laterally away from roadside

	Rice root	Rice shoot	Grass root	Grass shoot	Aurum root	Aurum shoot	Malancha root	Malancha shoot
Pb in soil at 0m distance	$r=0.846^{**}$	$r=0.995^{**}$	$r=0.309$	$r=-0.002$	$r=-0.869^{**}$	$r=-0.659^{*}$	$r=-0.212$	$r=0.213$
Pb in soil at 30m distance	$r=-0.438$	$r=0.579^{*}$	$r=0.381$	$r=1^{**}$	$r=0.842^{**}$	$r=0.659^{*}$	$r=0.911^{**}$	$r=-0.277$
Pb in soil at 50m distance	$r=-0.389$	$r=0.061$	$r=0.739^{*}$	$r=-0.532^{*}$	$r=-0.610^{*}$	$r=0.610^{*}$	$r=-0.904^{**}$	$r=-0.269$

* denotes significant at 5% level

** denotes significant at 1% level

Table 4.20: Correlation co-efficient between Cd concentration(ppm) in soil and different plant parts at different distances laterally away from roadside:

	Rice root	Rice shoot	Grass root	Grass shoot	Aurum root	Aurum shoot	Malancha root	Malancha shoot
Cd in soil at 0m distance	$r=0.999^*$	$r=0.975^{**}$	$r=-0.099$	$r=-0.26$	$r=1^{**}$	$r=-0.156$	$r=-0.442$	$r=0.108$
Cd in soil at 30m distance	$r=-0.812^{**}$	$r=-0.734^*$	$r=0.875^{**}$	$r=0.666^*$	$r=-0.523^*$	$r=-0.909^{**}$	$r=-0.861^{**}$	$r=-0.381$
Cd in soil at 50m distance	$r=-0.239$	$r=-0.990^{**}$	$r=0.430$	$r=0.955^{**}$	$r=0.359$	$r=-0.50$	$r=0.945^{**}$	$r=-0.629^*$

* denotes significant at 5% level

** denotes significant at 1% level

Table 4.21: Correlation co-efficient between Zn concentration(ppm) in soil and different plant parts at different distances laterally away from roadside:

	Rice root	Rice shoot	Grass root	Grass shoot	Aurum root	Aurum shoot	Malancha root	Malancha shoot
Zn in soil at 0m distance	r=0.270	r=0.963**	r=-0.106	r=0.392	r=-0.744	r=-0.973**	r=-0.464	r=-0.977**
Zn in soil at 30m distance	r=0.045	r=0.239	r=-0.951**	r=-0.940**	r=0.476	r=0.203	r=0.915**	r=0.995**
Zn in soil at 50m distance	r=-0.120	r=-0.676*	r=0.021	r=-0.615*	r=-0.989**	r=0.363	r=1**	r=-0.681*

* denotes significant at 5% level

** denotes significant at 1% level

Table 4. 22: Correlation co-efficient between Cu concentration(ppm) in soil and different plant parts at different distances laterally away from roadside:

	Rice root	Rice shoot	Grass root	Grass shoot	Aurum root	Aurum shoot	Malancha root	Malancha shoot
Cu in soil at 0m distance	$r=-0.733^*$	$r=-0.794^*$	$r=-0.319$	$r=0.235$	$r=0.397$	$r=0.442$	$r=-0.243$	$r=0.238$
Cu in soil at 30m distance	$r=-0.125$	$r=-0.292$	$r=-0.721^*$	$r=-0.961^{**}$	$r=-0.366$	$r=-0.366$	$r=0.204$	$r=0.493$
Cu in soil at 50m distance	$r=-0.378$	$r=-0.656^*$	$r=0.358$	$r=-0.269$	$r=-0.021$	$r=-0.507^*$	$r=-0.580^*$	$r=-0.541^*$

* denotes significant at 5% level

** denotes significant at 1% level

Table 4. 23: Correlation co-efficient between Mn concentration(ppm) in soil and different plant parts at different distances laterally away from roadside:

	Rice root	Rice shoot	Grass root	Grass shoot	Aurum root	Aurum shoot	Malancha root	Malancha shoot
Mn in soil at 0m distance	r=0.973**	r=0.49	r=0.129	r=-0.054	r=0.359	r=0.225	r=0.964**	r=0.699*
Mn in soil at 30m distance	r=0.920**	r=0.110	r=0.131	r=0.017	r=0.561*	r=0.348	r=0.927**	r=0.926**
Mn in soil at 50m distance	r=0.283	r=0.777	r=0.089	r=0.038	r=-0.950**	r=0.537*	r=0.966**	r=0.752*

* denotes significant at 5% level

** denotes significant at 1% level

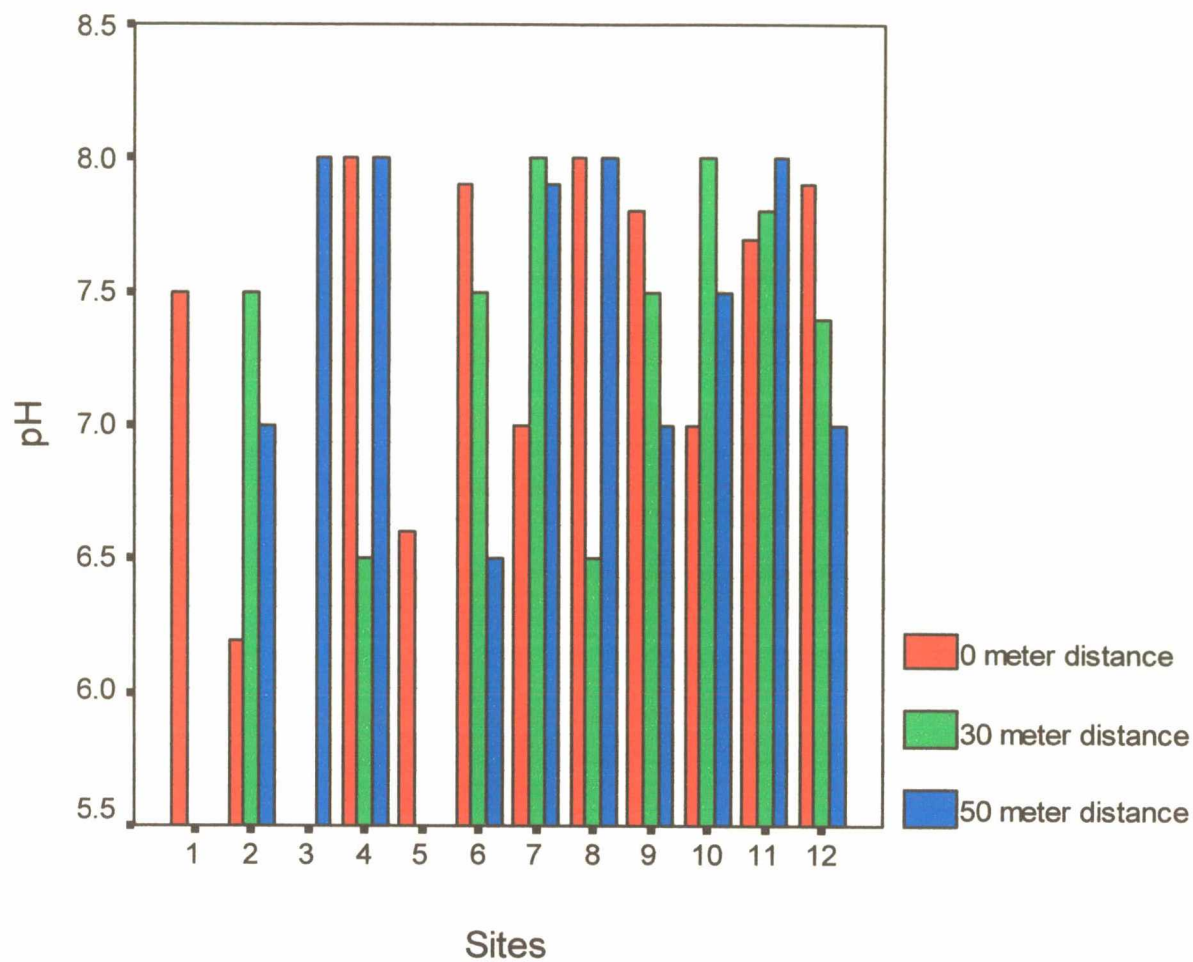


Figure 4.1 pH at different sites with distances

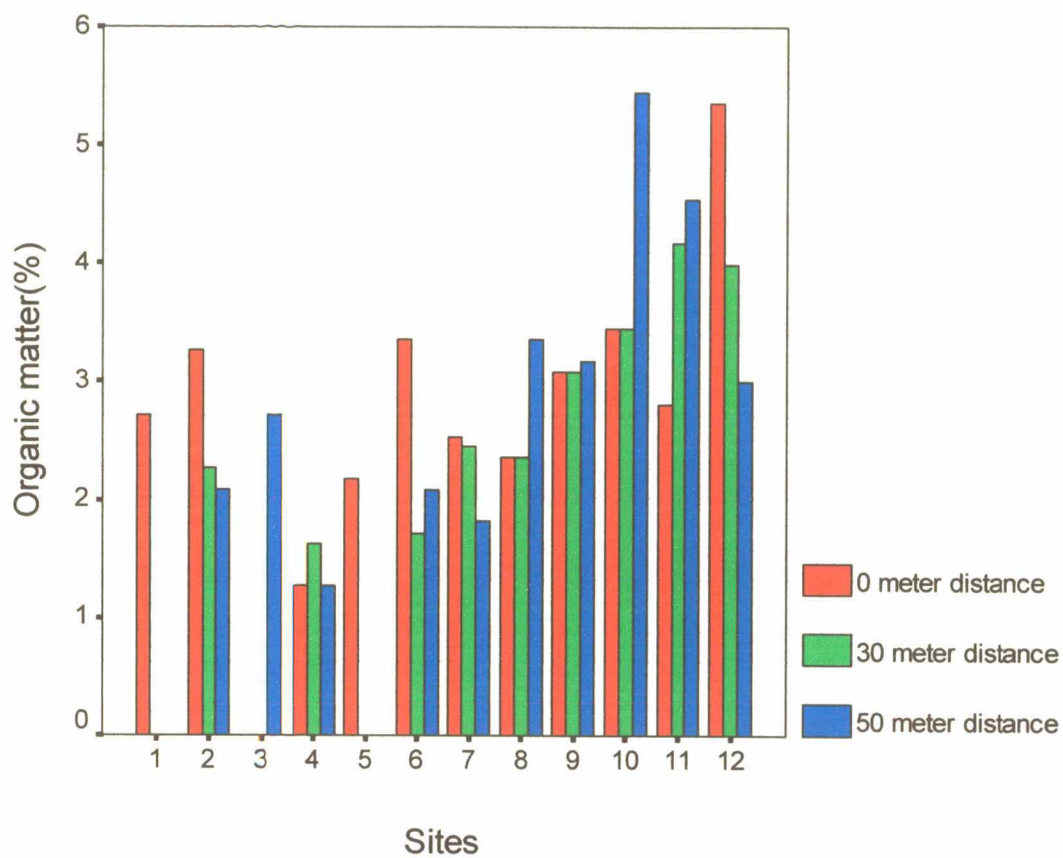


Figure 4.2 Distribution of organic matter in soil at different sites with distances

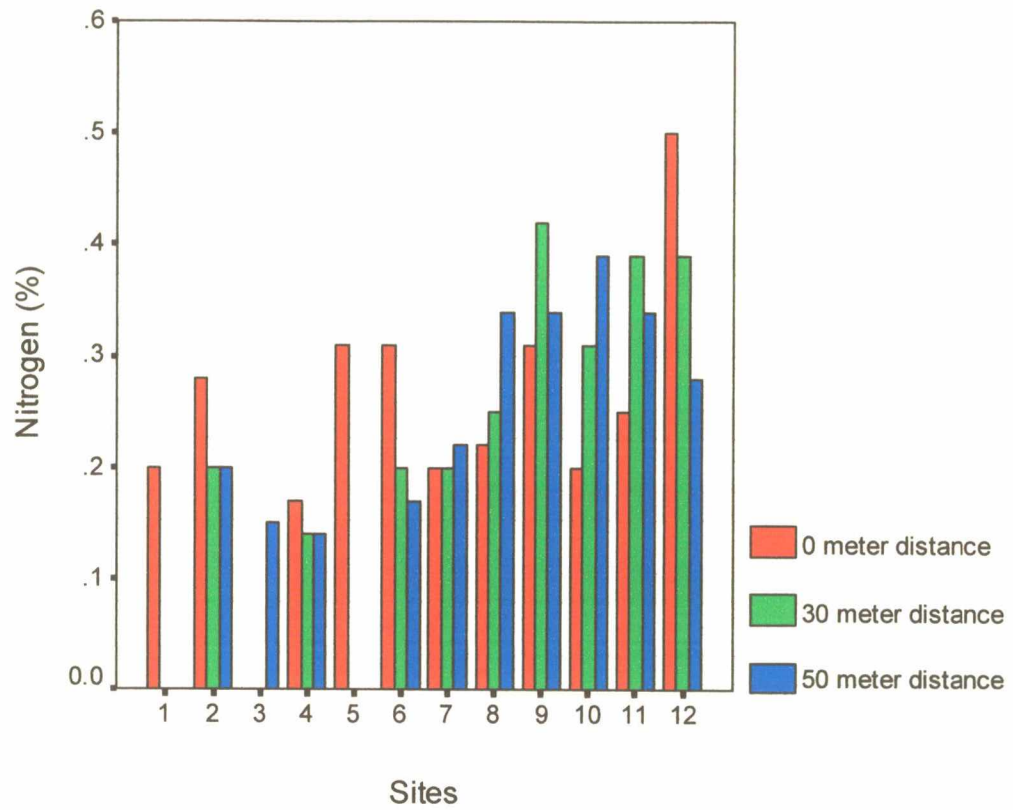


Figure 4.3 Distribution of nitrogen at different sites with distances

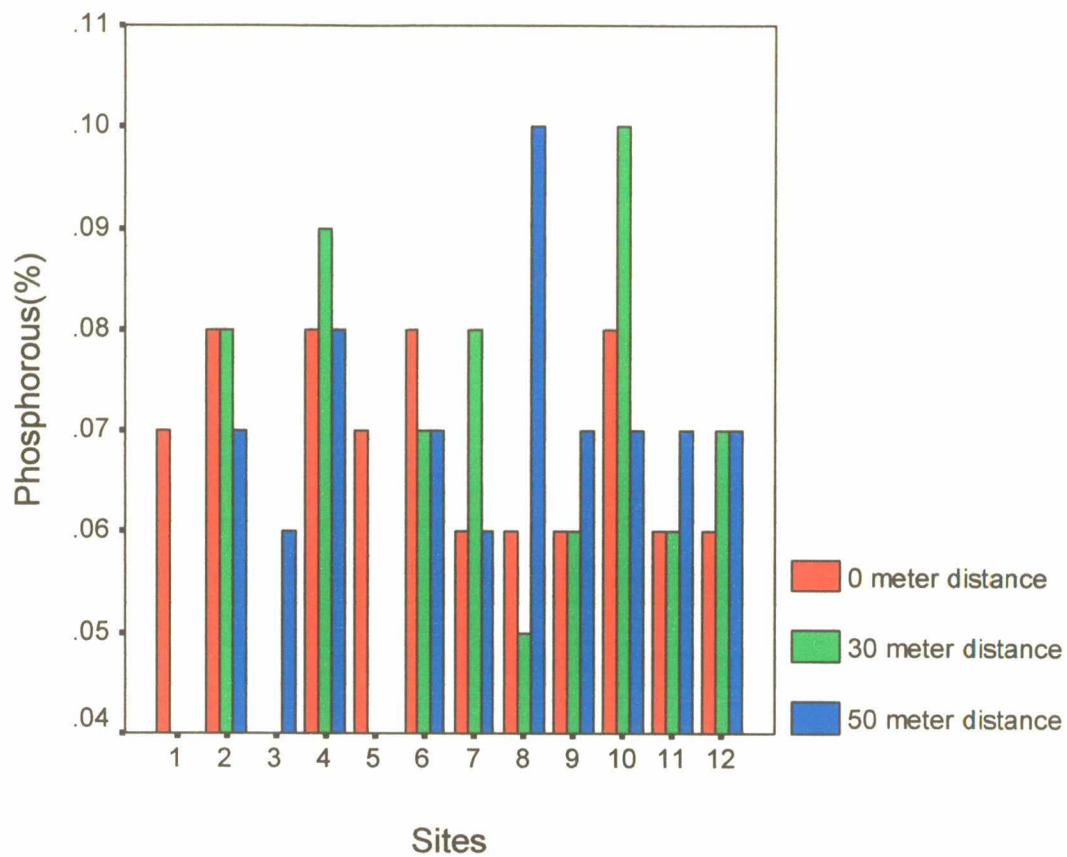


Figure 4.4 Distribution of phosphorous in soil at different sites with distances

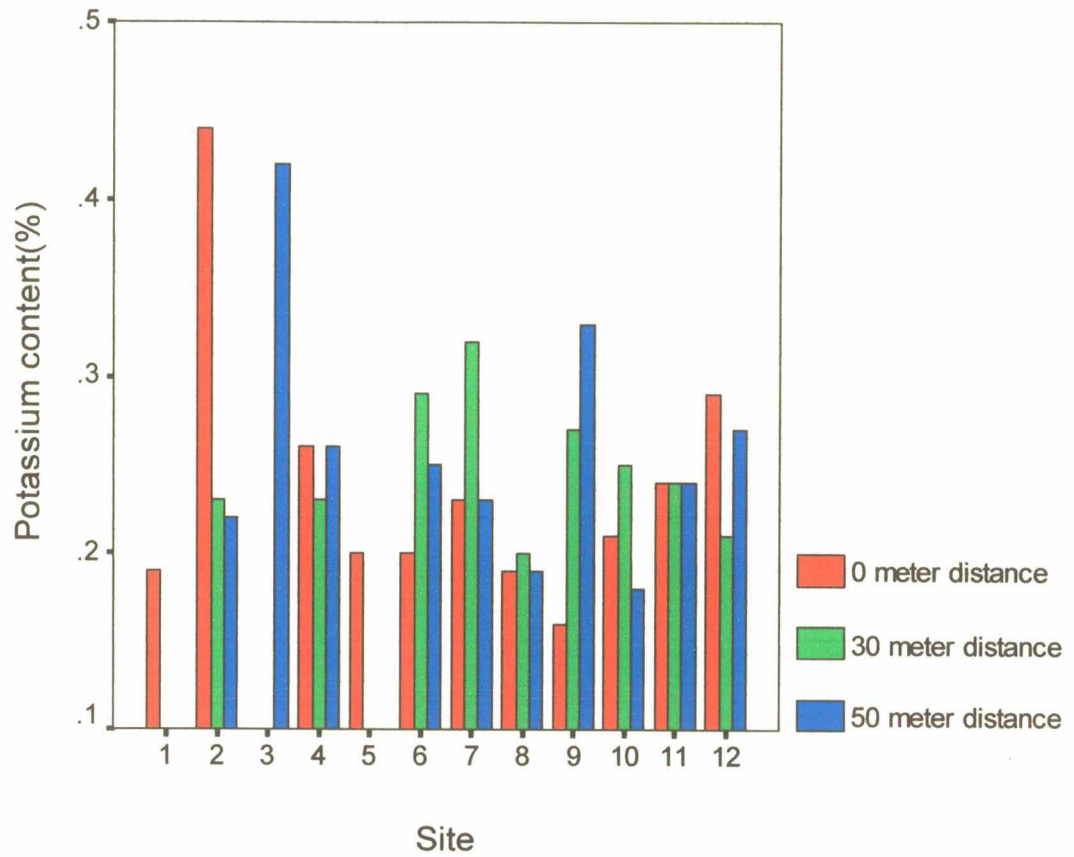


Figure 4.5 Distribution of potassium in soil at different sites with distances

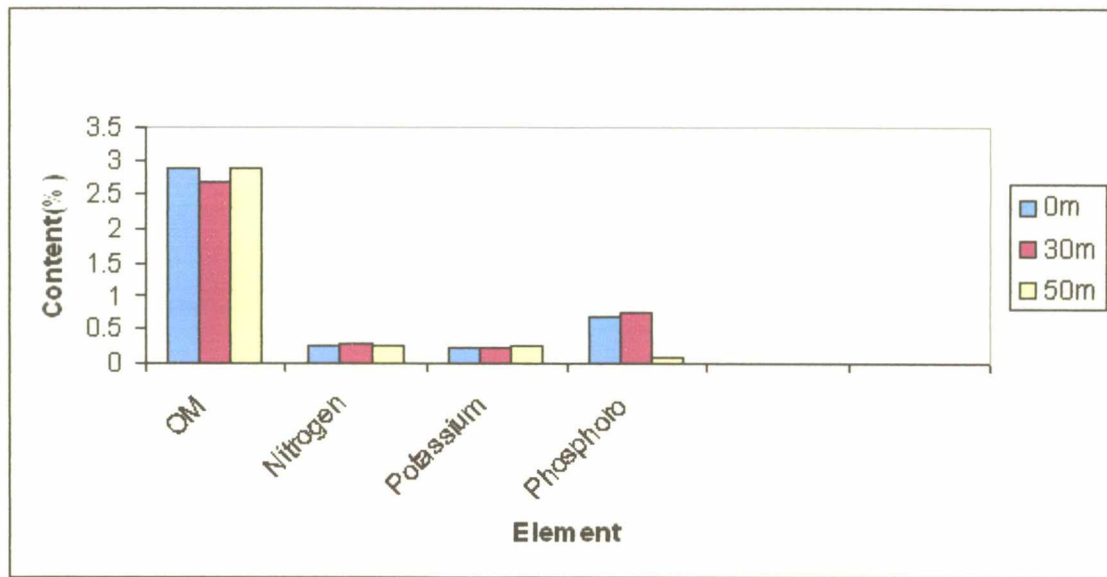


Figure 4.6 Distribution of soil chemical properties with distance

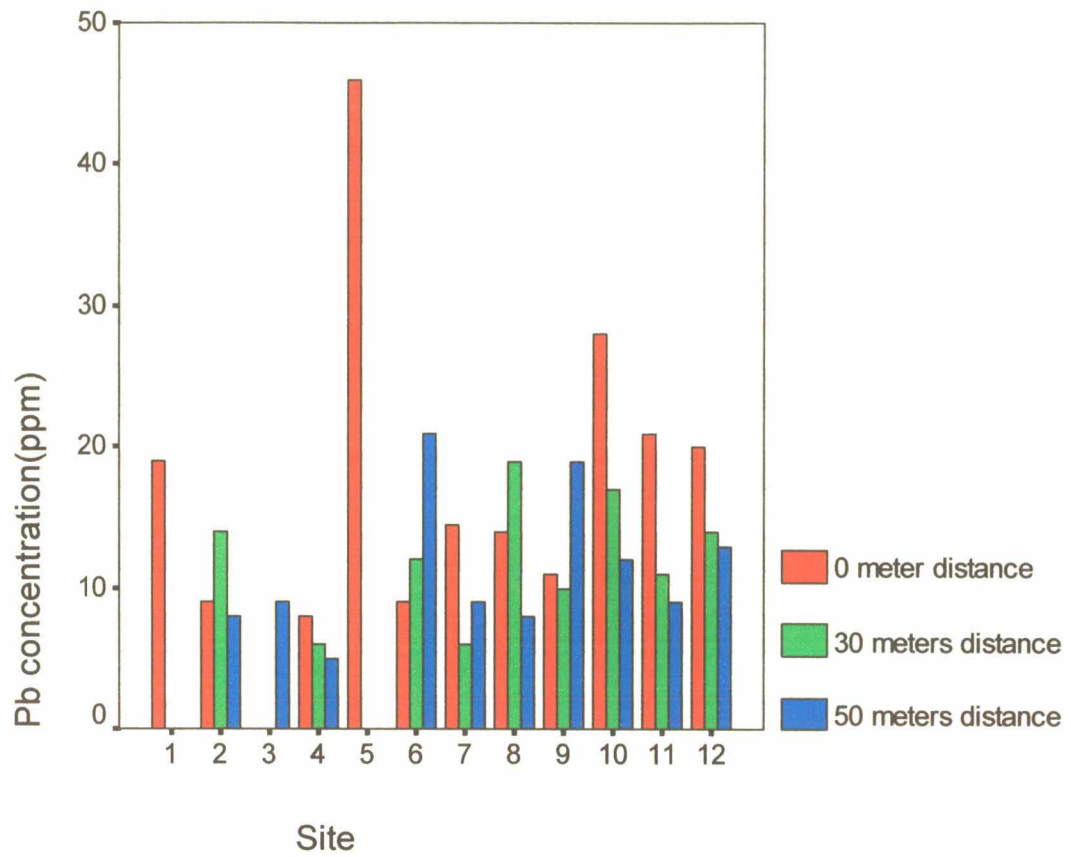


Figure 4.7 Distribution of lead in soil at different sites with distances

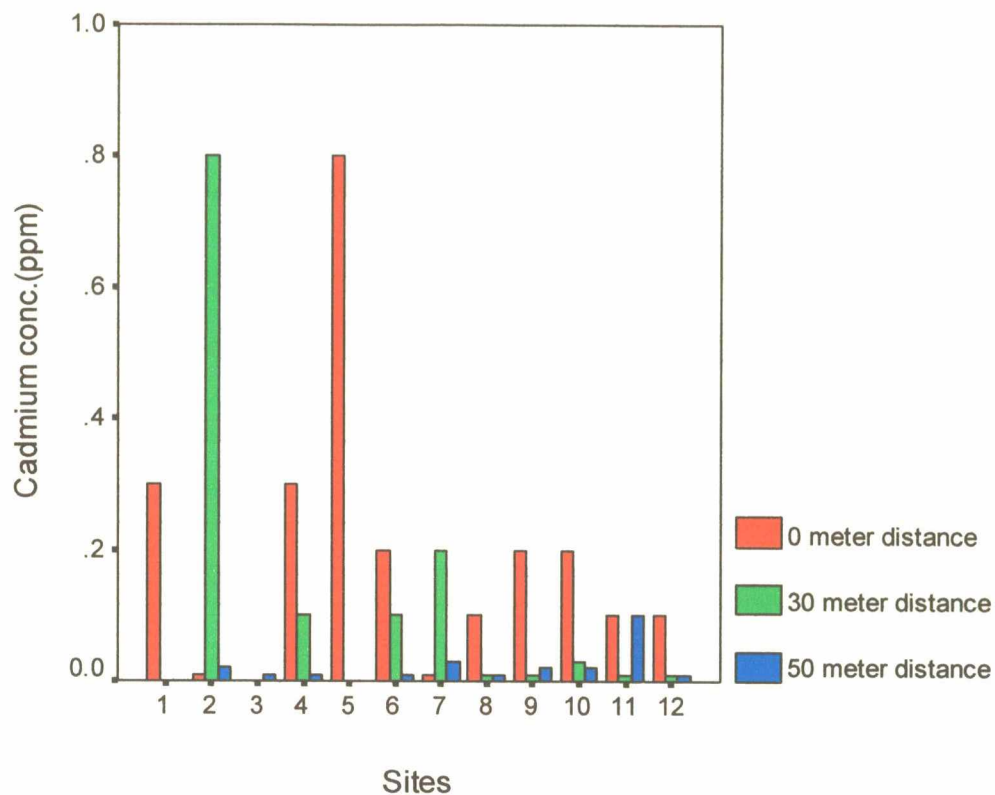


Figure 4.8 Distribution of cadmium in soil at different sites with distances

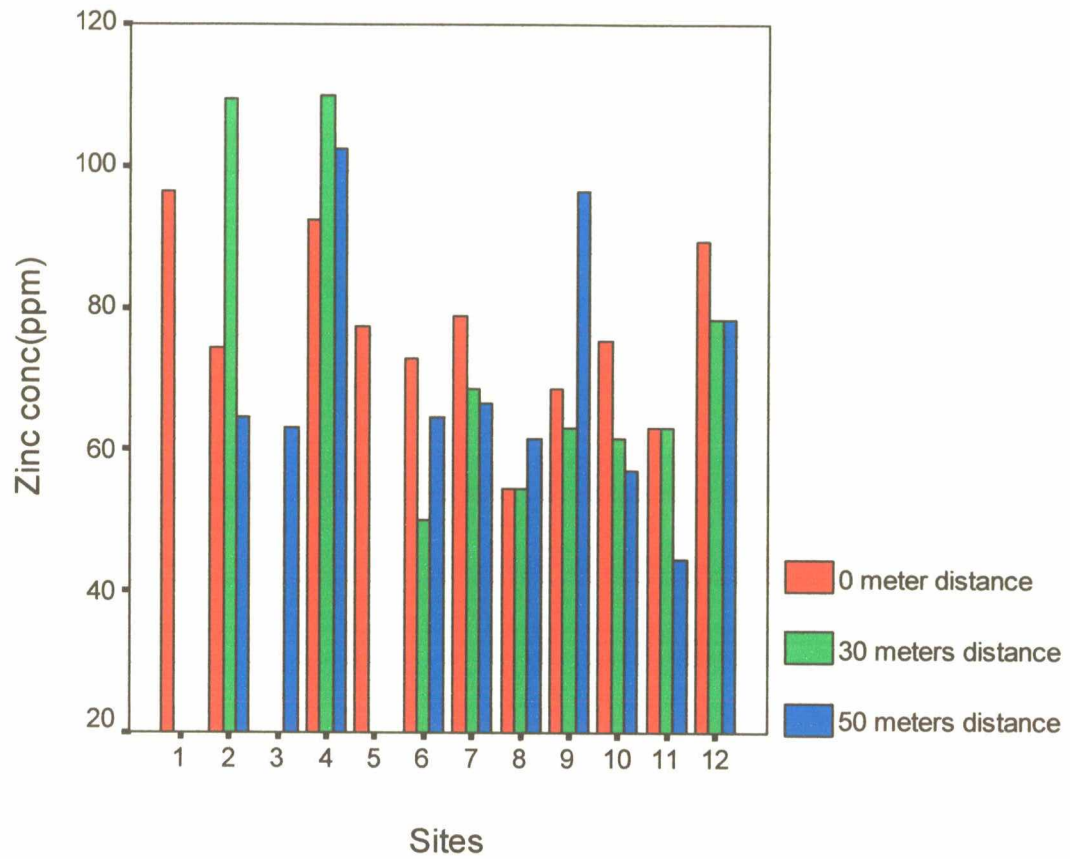


Figure 4.9 Distribution of zinc in soil at different sites with distances

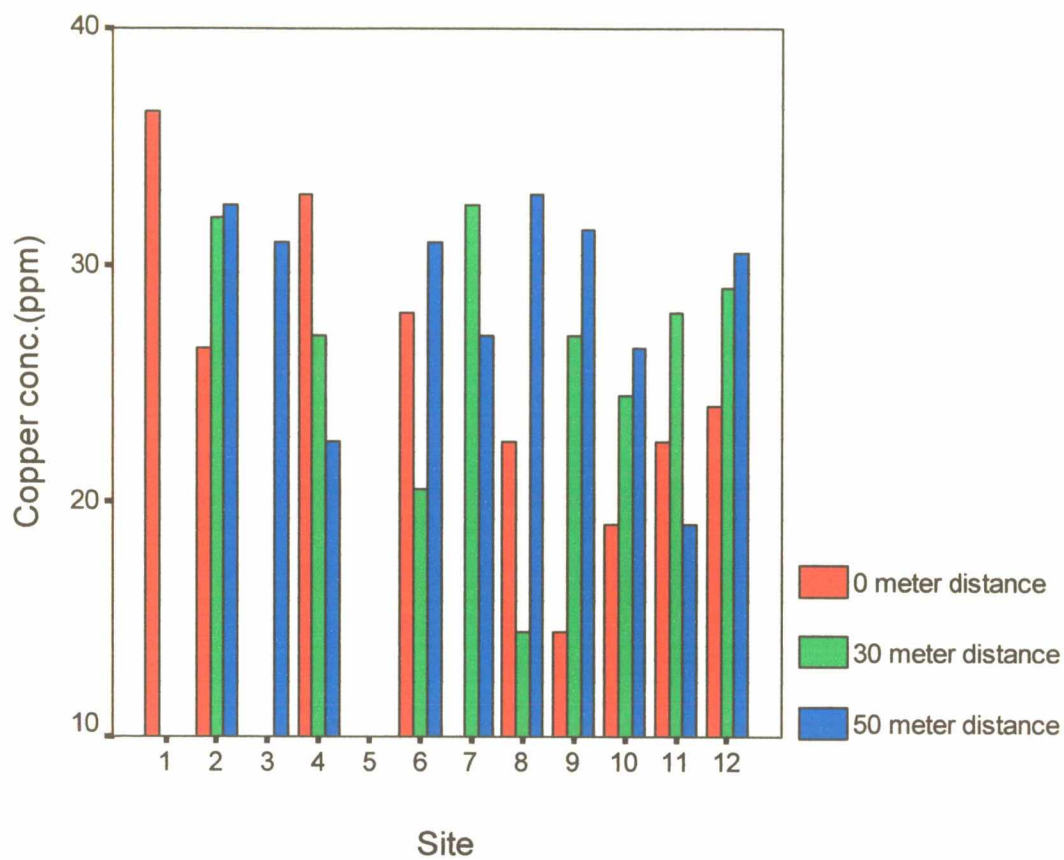


Figure 4.10 Distribution of copper in soil at different sites with distances

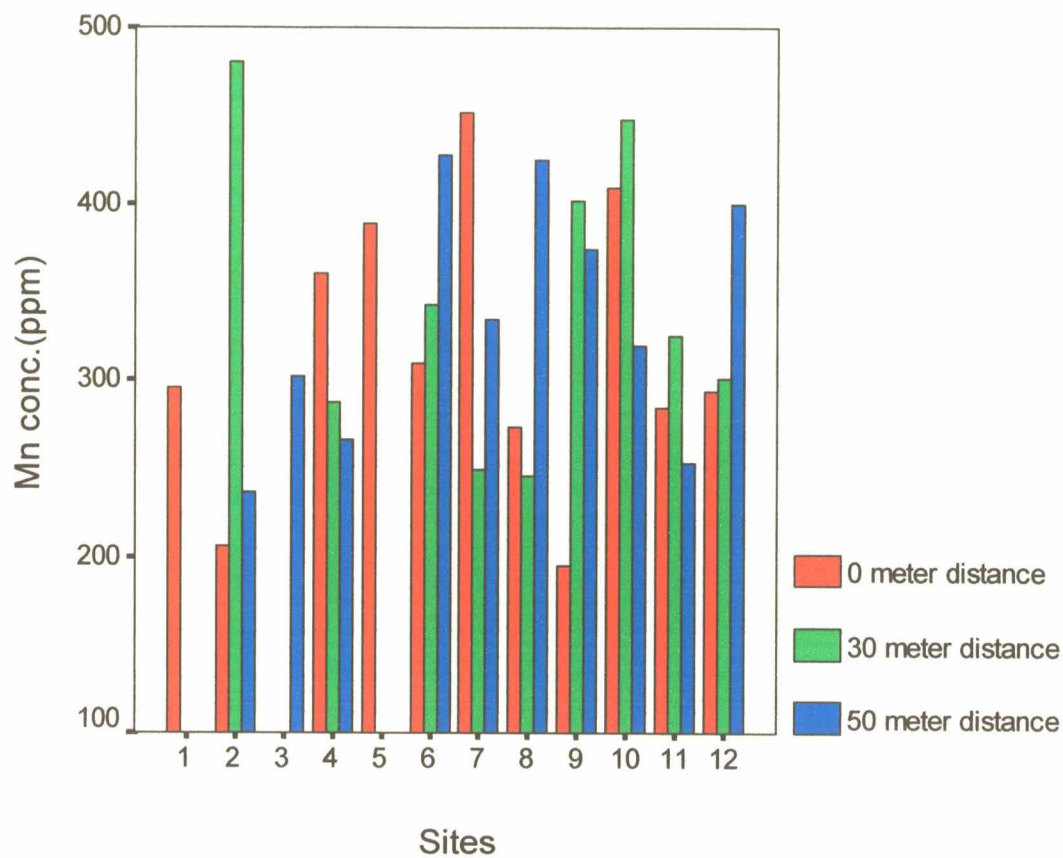


Figure 4.11 Distribution of manganese in soil at different sites with distances

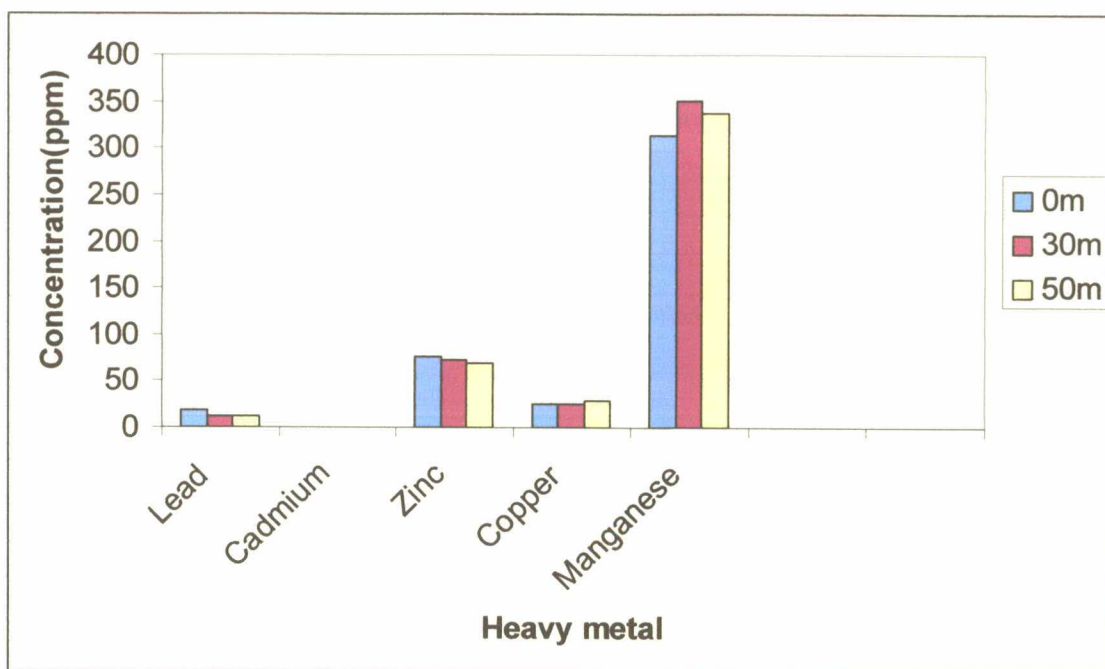


Figure 4.12 Distribution of some heavy metals in soil with distance

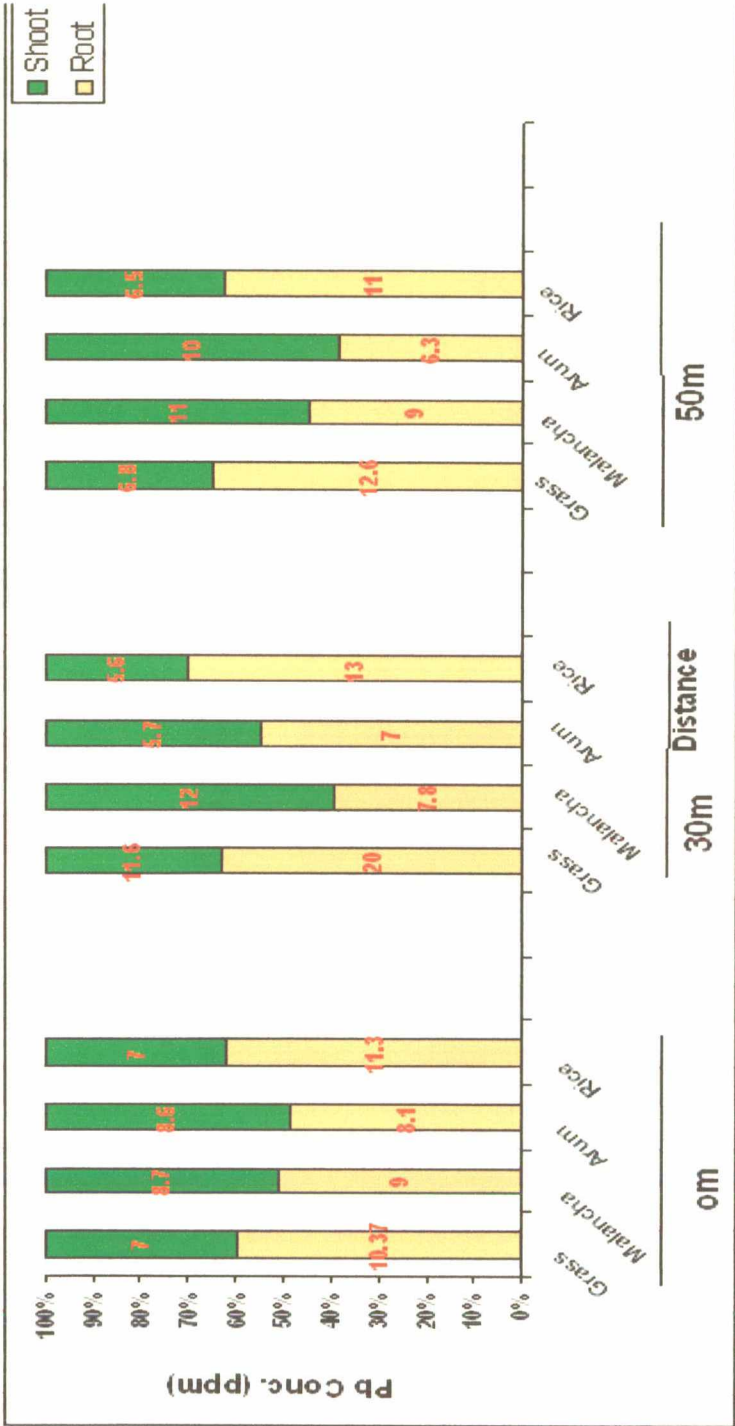


Figure 4.13 Lead concentration in different plant parts at different distances laterally away from the highway

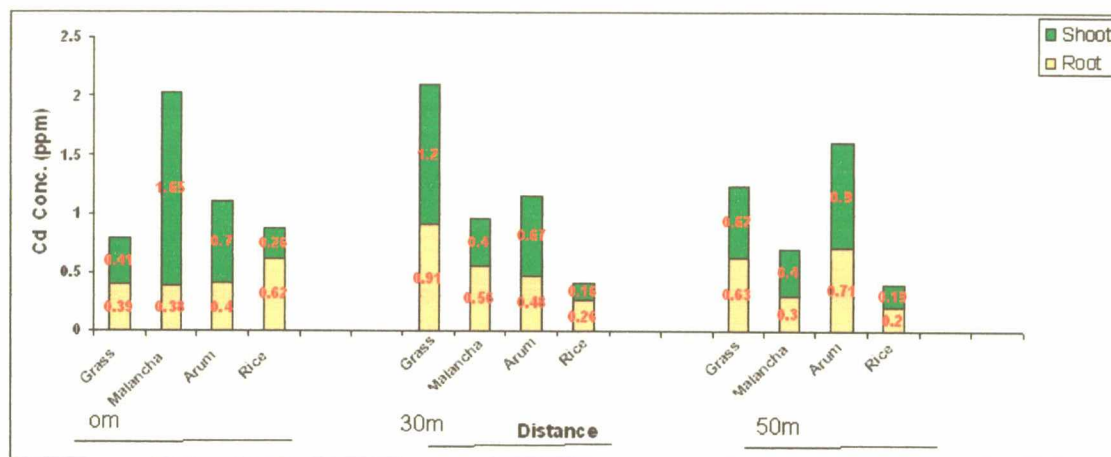


Figure 4.14 Cadmium concentration in different plant parts at different distances laterally away from the highway

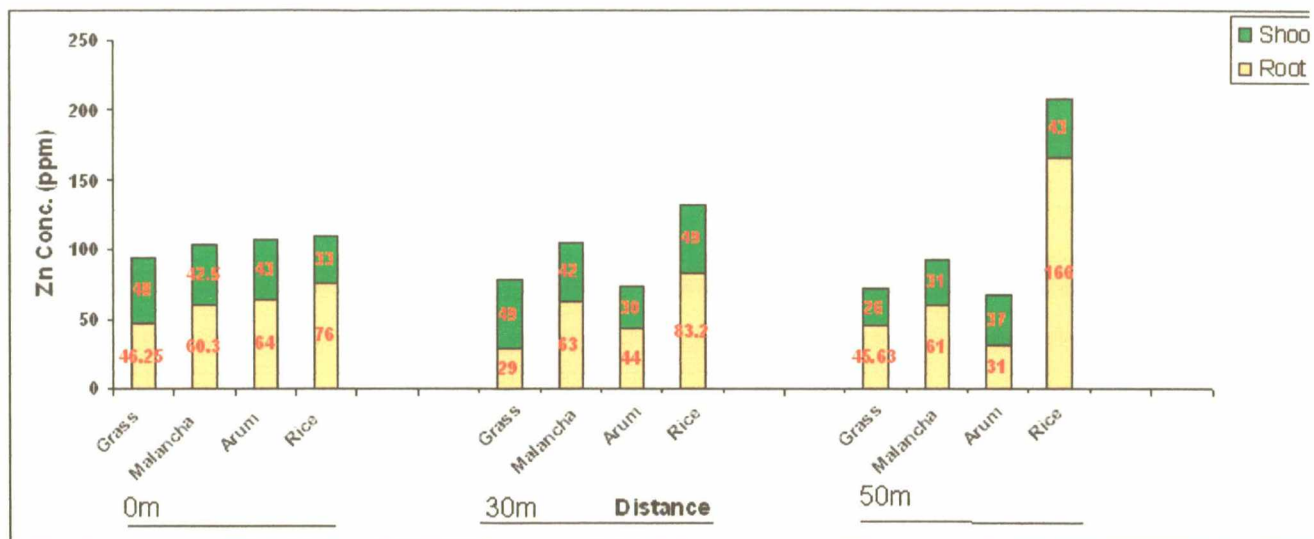


Figure 4.15 Zinc concentration in different plant parts at different distances laterally away from the highway

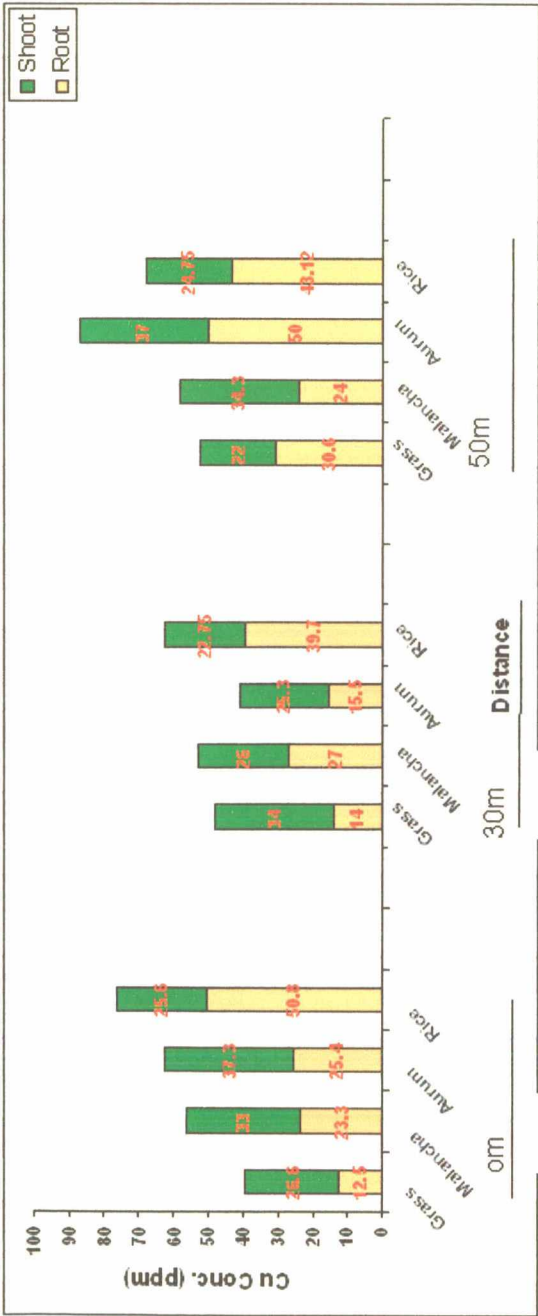


Figure 4.16 Copper concentration in different plant parts at different distances laterally away from the highway

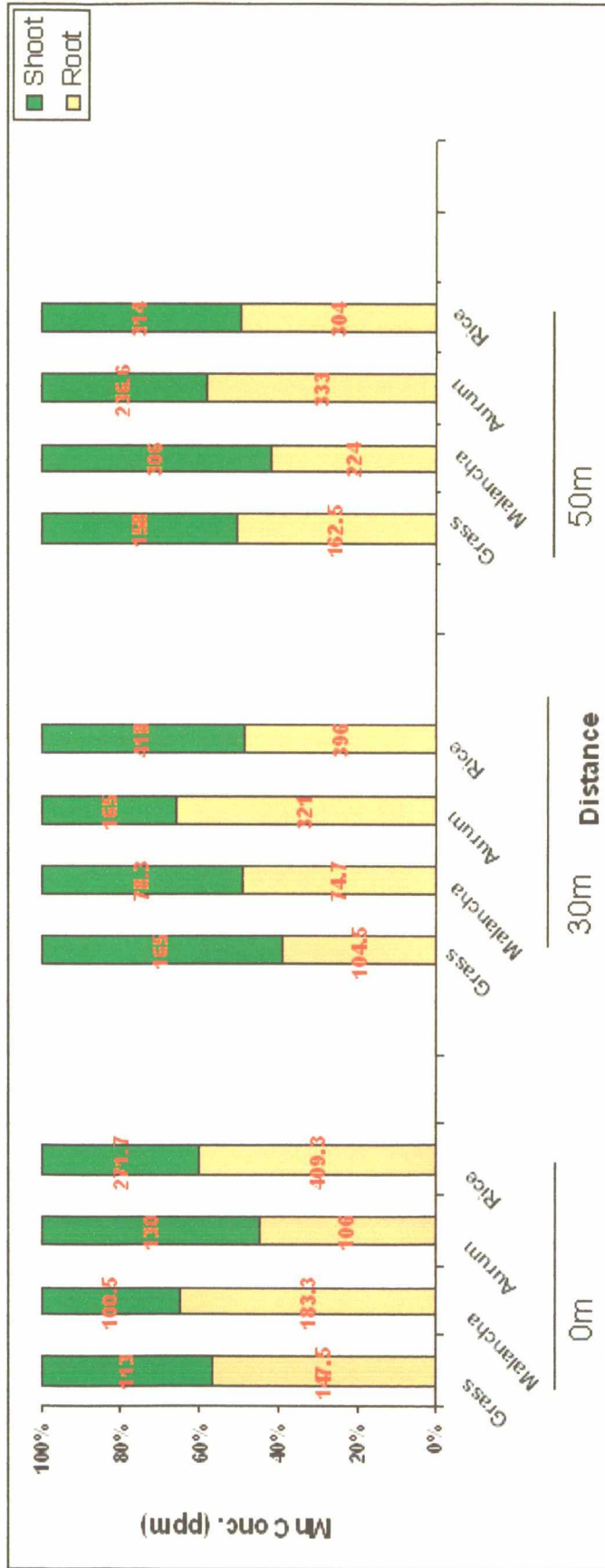


Figure4.17 : Manganese concentration in different plant parts at different distances laterally away from the highway

CHAPTER-5

SUMMARY AND CONCLUSION

5.1 Summary

Economic development has always accompanied with the problems of environmental pollution. With an improved living standard and increased demand on the transport sector, lead pollution is fast growing into a problem of serious dimensions in our cities and along the highway roadsides due to automobile exhausts. This is caused not only due to a rapid rise in the automobile pollution but also due to the narrow roads, slow moving traffic, unfavorable driving cycles, poor enforcement of laws relating to vehicle road-worthiness, poor emission control measures, etc.

An attempt was made to investigate the intensity of contamination of roadside soils and plants by the heavy metals particularly, Pb and some other heavy metals such as Cd, Zn, Cu and Mn along the Dhaka- Maikganj- Khulna highway. Texture, pH, EC and contents of organic matter, nitrogen, phosphorus and potassium in soils as well as nitrogen and phosphorous in plants were also determined.

The textural classes of the investigated soils ranged from sandy loam to clay loam. Most of the soils are silt loam and heavier textured found in site 11 and site 12. In most soils the percentage of silt contents increased with distances.

The pH of the soils ranged from 6.2 to 8. The average pH of the studied soils were 7.6, 6.6, 8.0, 6.6, 7.6, 7.9, 7.8, 8.0, 7.9, 8.0, 7.8 and 7.9 at site 1 to 12, respectively. Most of the soils are alkaline in nature and soil pH increased with increasing lateral distances in most of the soils.

The average concentrations of organic matter contents were 2.72, 2.54, 2.72, 1.39, 2.18, 2.39, 2.27, 2.69, 3.12, 4.11, 3.84 and 4.11% in soils at site 1 to 12, respectively.

General soil properties did not show any significant differences with distances.

The results obtained for heavy metals indicated that, roadside soils were contaminated with Pb and other heavy metals but not yet exceeded the permissible limits except Mn which was found above normal concentration in most cases.

The average concentrations of total heavy metals in soils were Pb-19, Cd-0.3, Zn-96.5, Mn-229.5 and Cu-36.5ppm at Nabinagar; Pb-10.3, Cd- 0.27, Zn-82.8, Cu-30.3 and Mn-308ppm at Srirampur village; Pb-9.0, Cd-0.01, Zn-63, Cu-31 and Mn- 302ppm at Krishnopura village; Pb-6.3, Cd-0.13, Zn-101.6, Cu-27.5 and Mn-304.8ppm at Charkanda; Pb-46, Cd-0.81, Zn-77.5, Cu-24 and Mn-389.5ppm at Vatpur village; Pb-14, Cd-0.1, Zn- 62.5, Cu-26.5 and Mn-360.1 ppm at Dighi union; Pb-9.8, Cd-0.17, Zn-71.3, Cu-32.8 and Mn-345.5ppm at Baniajuri union; Pb-13.6, Cd-0.04, Zn-57, Cu-23.3 and Mn-314.8ppm at Atra Gilatala; Pb-13.3, Cd-0.01, Zn-76, Cu-24.3 and Mn-315ppm at Payer Bazar; Pb-19, Cd-0.08, Zn-64.6, Cu-23.3 and Mn- 392.5 ppm at Bederdanga; Pb-13.6, Cd- 0.07, Zn- 56.8, Cu-23.16 and Mn-287.6ppm near Damodar High School; Pb-15.6, Cd-0.04, Zn-82.16, Cu-27.8 and Mn-331.8ppm at Boyra Sonadanga link road.

The average Pb concentrations were 18.13, 12.11 and 11.3mg/kg at 0, 30 and 50m distances from the roadside. It showed a decreasing tendency with increasing lateral distances. It was observed that the highest mean concentration of lead (18.13 mg/kg) was found near the edge of the highway and decreased with increasing distances.

Cadmium concentrations varied widely among the distances of the soils. The average concentrations of Cd were found 0.21, 0.41 and 0.02 mg/kg at 0, 30 and 50m distances away from the roadside.

Zinc contents varied widely among the distances of the soils. The average Zn concentrations in soils were 76.5, 73.1 and 69.9 mg/kg at 0, 30 and 50m distances from the roadside. It showed a decreasing tendency with increasing lateral distances.

Copper contents varied widely among the distances of the soils. The average Cu concentrations in soils were 27.59, 26.1 and 28.4 mg/kg at 0, 30 and 50m distances from the roadside.

Manganese concentrations varied widely among the distances of the soils. The average Mn concentrations in soils were 313, 352 and 334 mg/kg at 0, 30 and 50m distances from the roadside.

The analysis of variance (ANOVA) showed that there were significant differences of lead with distances. It is interesting to note that, the concentrations of Cd, Cu and Mn in the studied soils did not follow any definite pattern so far the distance from near the roadside to farther away from the road. The concentration of Pb and Zn decreases with increasing lateral distances.

From the above discussions, it was observed that the roadside soils were contaminated with Pb, Cd, Zn and Cu but not yet in harmful levels except Mn and soil contamination with Pb and Zn was found higher along the roadside and decreased with increasing lateral distances.

Correlation coefficient between total soil phosphorous and silt and total soil potassium and silt showed a positive relationship($r=0.403$ and $r=0.403$ respectively.) Total soil Cu also showed a positive correlation with silt ($r=0.362$). Total soil Cu and total soil K showed a significant negative correlation with sand($r=-0.470$ and $r=-0.522$)(Table 4.5). Total soil nitrogen was high significantly positive correlation with soil organic matter ($r = 0.824$).

The concentrations of Pb had inverse correlation with soil pH($r=-0.349$) but positively but not significantly correlated with clay and organic matter contents. From Table 4.6, it was found that Zn and Mn were significantly correlated with Cu. The correlation between Zn and Cu was $r = 0.376$ and between manganese was $r = 0.521$. The concentrations of Pb was significantly and positively correlated with Cd ($r= 0.504$).

The average concentrations of nitrogen in the roots of grass, rice, arum and malancha were 3.0, 2.2, 3.2 and 4.0%, respectively and in the shoots of above plants were 2.9, 3.2, 3.2, and 4.1%, respectively. The highest N concentration was observed in **malancha root** and in **malancha shoot** among the above plants.

The concentrations of P in roots of grass, rice, arum and malancha were 0.23, 0.38, 0.26, and 0.35% and that of shoots were 0.27, 0.27, 0.28 and 0.40%, respectively. Among the roots and shoots of the plants, the average concentrations of lead were high in grass roots (20 mg/kg) and in malancha shoots (12 mg/kg) at 30m distance away from the highway roadside.

On an average, the concentrations of Pb in roots of grass, rice, arum and malancha were 14.3, 11.7, 7.1 and 8.6mg/kg and those of shoots of the above plants were 8.7, 6.3, 8.1, and 10.57mg/kg, respectively. From the result, it was observed that among the plant parts, Pb concentration was more in roots than in shoots of grass and rice but it was found more in shoots than in roots of arum and malancha. Among the plant roots, the highest Pb concentration was found in grass (14.3 mg/kg) and among the plant shoots the highest concentration of Pb was found in shoot of malancha (10.57mg/kg). Among the roots and shoots of the collected plants, the average concentration of lead was found high in roots of grass (20 mg/kg) and in shoots of malancha (12 mg/kg) at 30m distance.

Analysis of variance (ANOVA test) showed that there were significant differences among the contents of Pb in rice roots, grass roots and grass shoots, arum and malancha shoots with distance.

It was observed that there were significant positive correlations between the contents of lead in soils and Pb in rice roots ($r=0.846$) and in rice shoot ($r=0.995$) at 0m distance. The concentrations of Pb in the shoots of rice, grass, arum and malancha showed significant positive correlations with soil Pb at 30m distance away from the roadside. The Pb in the grass root and arum shoot showed a significant positive correlation with soil Pb at 50m distance. Most of the plant parts showed significant correlation for heavy metals with soils.

The concentrations of Cd in the roots of grass, rice, arum and malancha were 0.65, 0.36, 0.53 and 0.41mg/kg and in the shoot of the above plants were 0.75, 0.29, 0.73 and 0.82mg/kg, respectively). The results also showed that plant parts did not contain Cd above permissible limit.

There were significant differences of cadmium in roots and shoots of rice, grasses and malancha with distances.

A positive and highly significant correlation was observed between soil Cd and Cd in roots and shoots of rice; and between soil Cd and Cd in arum root along roadside.

The mean concentrations of Zn in roots of grass, rice, arum and malancha were 40.28, 107.93, 46.3 and 61.4 mg/kg and in the shoots of the above plants were 41.0, 43.67, 51.33 and 38.5 mg/kg, respectively. Plants did not take up Zn more than the 'background level'.

The analysis of variance showed that Zn contents in roots and shoots of grass, arum and roots of rice were significantly different with distances.

A highly significant positive correlation was noticed between Zn in malancha root and Zn in soil at 50m distance ($r=1$) and highly significant negative correlation between soil Zn and Zn in malancha shoot ($r=-0.977$) and grass shoot ($r=-0.940$) collected from 0m and 30m distances,

respectively (Table 4.21). Positive but not significant correlation between Zn in plant parts and soil was obtained indicating a limited mobility of Zn in soil at this pH values.

On an average, the concentrations of Cu in the roots of grass, rice, arum and malancha were 20.17, 41.61, 30.3 and 24.8mg/kg but those of shoots of the above plants were 27.53, 28.52, 33.2 and 31.1mg/kg, respectively. Copper contents in different plant parts were not significantly different with distances except arum and grass roots. Arum and grass roots at 50 m distance significantly accumulated more Cu than those of other two distances. There were no significant positive correlations between Cu in soil and Cu in plants but some significant negative correlations were observed between them.

Concentrations of Mn in the roots of grass, rice, arum and malancha were 138.17, 41.61, 253.3 and 167.3mg/kg and in the shoots of the above plants were 145.33, 28.52, 177.2 and 161.60mg/kg, respectively.

Strong positive correlation (Table 4.23) between Mn in soil and Mn in rice root existed at 0 and 30m distances and between soil and malancha root at all distances.

The analysis of variances (Table 4.18) showed that there were significant differences of Mn concentration in plant parts with distances and increased with increasing distances in most cases.

The results indicated that the plants along the highway in all sites were contaminated by Pb, Cd, Zn and Cu having concentrations higher than the normal concentration in plants. It implies that, motor vehicle exhausts contributed to the Pb and Cd in the roadside plants. It was also found that grass root and malancha shoot accumulated more Pb than the other plants. Highest concentration of cadmium was found in malancha shoot. Accumulation of Pb

and Cd were much higher in roots than in shoots which decreased with increasing lateral distances.

DMRT tests computed from heavy metal contents in soils and plants at different distances along the highway showed that there were significant differences with some exceptions. It is also interesting to note that, plants are comparatively more contaminated by the motor vehicle exhausts than the soils.

5.2 Conclusion

The results of the present investigation showed the following specific indications=> Lead, Cadmium and Zn are emitted from the automobile exhausts.

=> Plants near the highway were more contaminated with heavy metals probably from automobiles exhausts.

=> Soil and plant spatially farthest from the highway except the agricultural land are less polluted.

=> Contamination of soil/plant with heavy metals increased with increasing traffic density but spatial variation from the highway did not show much difference.

Limited works were done of its kind in Bangladesh. Further works to see the temporal variation are needed as well. Moreover, situations in other highways are also needed to be studied. A thorough and more detailed study of the problem encompassing both temporal and spatial variations should be conducted to suggest what measures to be taken to address the problems arising from Pb and other heavy metals emitted from autoexhausts. Motor vehicle pollution in our country might be a serious problem in near future and the following alternatives should be taken to meet the challenge:

Use of electric, solar powered, ethanol or natural gas cars and vehicles

- * Shifting to gas turbine or ammonia filled spark ignition engine
- * *Alternative routes for congested areas, proper maintenance of self starting devices and batteries, better road condition and over all a civic sense/public awareness*
- * Intensive analysis of ecosystem components along highways and in urban environment.

CHAPTER- 6

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7. APPENDICES

Table 1: Permissible limit of heavy metals in soils (Kolke, 1980)

Elements	Concentrations(ppm)	Elements	Concentrations(ppm)
Lead(Pb)	100	Molybdenum(Mo)	5
Zinc(Zn)	300	Chromium(Cr)	100
Nickel(Ni)	50	Mercury(Hg)	2
Cadmium(Cd)	3	Arsenic(As)	20
Copper(Cu)	100	Cobalt(Co)	50
Boron(B)	25	Selenium(Se)	10

Table 2: Critical level of heavy metals in plants (Sauerbeck, 1985)

Elements	Concentrations(ppm)
Lead(Pb)	10-20
Zinc(Zn)	150-200
Nickel(Ni)	20-30
Cadmium(Cd)	5-10
Copper(Cu)	15-20
Cobalt(Co)	10-20
Mercury(Hg)	0.5-1

Table 3: Common heavy metal concentration in soils and plants (Sauerbeck, 1985)

Elements	Concentration in soils (ppm)	Concentration in plants (ppm)
Lead(Pb)	0.1-20	0.1-2.0
Zinc(Zn)	3-100	20-100
Nickel(Ni)	2-50	0.2-2.0
Cadmium(Cd)	0.01-0.7	0.05-0.5
Copper(Cu)	1-40	3-100