ACCUMULATION AND TRANSFORMATION OF LEAD IN THE URBAN ECOSYSTEM DUE TO AUTOMOBILE EMISSIONS AND ITS REMEDIATION MEASURES

BY

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CERTIFICATE

This is to certify that the thesis entitled **"ACCUMULATION AND TRANSFORMATION OF LEAD IN THE URBAN ECOSYSTEM DUE TO AUTOMOBILE EMISSIONS AND ITS REMEDIATION MEASURES"** submitted to the Avinashilingam Institute for Home Science and Higher Education for Women - Deemed University, Coimbatore, for the award of the Degree of **DOCTOR OF PHILOSOPHY IN LIFE SCIENCES (BOTANY)**, is a record of original research work done by **SEEMA GEORGE** during the period of her study in the Department of Life Sciences (Botany), Avinashilingam Institute for Home Science and Higher Education for Women - Deemed University, Coimbatore, under my supervision and guidance and the thesis has not formed the basis for the award of any Degree / Diploma / Associateship / Fellowship or similar title of any candidate of any University.

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DECLARATION

I hereby declare that the matter embodied in the thesis entitled **"ACCUMULATION AND TRANSFORMATION OF LEAD IN THE URBAN ECOSYSTEM DUE TO AUTOMOBILE EMISSIONS AND ITS REMEDIATION MEASURES"** is the result of investigation carried out by me in the Department of Life Sciences (Botany), Avinashilingam Institute for Home Science and Higher Education for Women - Deemed University, Coimbatore, under the supervision of **Dr.RITA JOSEPH**, M.Sc., B.Ed. (Kerala), M.Phil., Ph.D. (Bharathiar), Professor and Head, Department of Botany, Avinashilingam Institute for Home Science and Higher Education for Women - Deemed University, Coimbatore, and it has not been submitted for the award of any Degree / Diploma / Associateship / Fellowship of any other University or Institute.

Signature of the Supervisor **Signature of the Candidate**

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ABBREVIATIONS

NH	-	National Highway
SH	-	State Highway
IC	-	Inner City
S	-	Soil
BS	-	Black Soil
RS	-	Red Soil
EC	-	Electrical Conductivity
bdl	-	below detectable limit
Pb	-	Lead
M_1	-	Moisture – I (field capacity moisture)
M_2	-	Moisture – II (alternate wetting and drying)
E	-	East
W	-	West
N	-	North
S	-	South
CCP	-	Composted Coir Pith

CHAPTER I

INTRODUCTION

Just go out for a breath of air
And you'll be ready for medicare

- Tom Lehrer

Global environmental change is interwoven with a complex web of social, economic, political and scientific implications. It is clear that with ceaseless repetitions, even seemingly innocuous actions – such as driving a car or cutting down a tree-can influence the physical and chemical systems that govern the earth. Driving a private car is probably a typical citizens' most "polluting" daily activity. Ecosystem damage and potential human health threats from a myriad of contaminants are creating increasing concern world wide. The omnipresence of automobiles makes it a very important source.

The rapid urbanization along with the rise in industrial and commercial activities has increased the demand for transport. At the present time, virtually all of the world's transportation needs are supplied by fuels derived from petroleum, also known as crude oil. Gasoline, diesel and jet fuel are the transportation fuels that are produced from petroleum.

Roads are commonly called the arteries through which the life blood of economy flows. They do not produce any wealth but act as a catalyst in transportation of economy from poverty to prosperity. Road transportation is

one of the basic infrastructures needed for the integrated development of rural areas. Road system activates the process of modernization and technological changes even in economic activities of a traditional society. On the other hand, automobiles are the major sources of environmental degradation. It is estimated that 60 per cent of air pollution in urban areas is contributed by automobiles, the main offenders being the two and the three wheelers, as they emit twice as much as highly toxic gas as other vehicles (Chamberlain et al, 1979).

The many types of vehicles, fuelled by a variety of products, emit varying amounts of both simple and complex pollutants mainly at the ground level and dispersion is very limited. Lead (Pb), a toxic heavy metal, is introduced into the environment mostly from petrol driven vehicles.

Automobile emissions are the major source of Pb pollution in the urban environment (Plate 1). Lead comes in the category of those heavy metals which are known to be toxic even when present in traces. Lead is virtually indestructible and non-biodegradable. It is one of the softest and heaviest metals available (Krishnayya and Bedi, 1984).

Numerous investigations of heavy metals in the vicinity of busy streets and highways have identified elevated concentration of heavy metals in soils, plants and air that are related to traffic density, mode of vehicle operation and distance from the highway.

Plate 1



Emission from a heavy vehicle - a threat to the environment

Soil is the major sink for metal pollutants which have lengthy residence times. A high metal content in soil frequently reflects an anthropogenic impact. These heavy metals may adversely affect the soil ecology, agricultural production or product quality and ground water quality. Introduction of heavy metal in agricultural soils is of concern from food chain point of view (Petruzzelli *et al.*, 1989).

Lead accumulation in soil results in plant uptake at high proportions. Positive relations exist between atmospheric heavy metal deposition and heavy metal concentration in several agricultural plant species (Hovmand *et al.*, 1983).

Auto-exhaust pollution inhibited the growth parameters such as length and number of branches and leaves and diameter of stem in *Malchra capitata, Alternanthera triandra* and *Xanthium strumarium* (Salgare and Swain, 1991). Lead accumulated more in leaves and shoots than in roots of sorghum, maize and wheat cultivated adjacent to a state highway (Saxena *et al.*, 1991).

The concentration of Pb in soil and plants positively correlated with traffic density. *Chloris barbata, Vernonia cinerea* and *Euphorbia hirta* accumulated more lead. At stations with maximum traffic density, chlorophyll content remained significantly less in a few plants exposed to automobile exhausts (Ramakrishnaiah and Somashekar, 1997).

Phytoremediation is a new technology that uses specially selected metal – accumulating plants for removing heavy metals from contaminated

soil, allowing preservation of top soil and eliminating costly excavation and disposal. Through screening and selection, several metal accumulating lines of crop plants have been identified which, in combination with soil and foliar amendments that enhance metal uptake, have been successful in remediating metal contaminated soils.

Lead may mobilize from the soil when lead-bearing soil particles run off to surface waters during heavy rain. The downward movement of Pb from soil by leaching is very low under most natural conditions. The conditions that induce leaching are the presence of Pb in the soil, at concentrations that either approach or exceed the sorption capacity of the soil, the presence of materials in the soil that are capable of forming soluble chelates with Pb and a decrease in the pH of the leaching solution. Seasonal concentration and speciation studies of heavy metals in the ground water of Agra city indicated that iron, lead and zinc was found maximum during winter (Chauhan *et al.*, 1999).

Lead contamination is of great concern because of its adverse effects on human health. The Pb from vehicular exhausts result in an increased level of Pb in the urban environment from where Pb enters human body through gastro-intestinal and respiratory routes. Lead is a cumulative neurotoxin. Lead poisoning, also called plumbism or saturnism, has proved to be more dangerous to children than adults. It remains one of the most common environmental hazards inspite of good scientific knowledge on its toxicity and control measures.

Pollution of any sort is no respecter of national boundaries. This is particularly true of air-borne pollutants. It is also true of contaminated soils which inevitably contribute to air and water pollution through dust and run-off transfers.

A lot of advertisement can be made about pollution and a great awareness can be created in the society in large cities on pollution, but pollution cannot be effectively controlled in the absence of authentic data on air, water or, soil pollution and its abatement.

To respond to the challenge of the evolving chemosphere in which we live, we need to develop more adequate databases from which we can derive more adequate and more credible environmental and health risk assessments and the knowledge of which will enable us to use and adopt effective reliable and economic measures for their remediation and control. Hence the present investigation was carried out with the following objectives.

Objectives

- To assess the status and distribution of lead in an urban ecosystem.
- To examine the chemistry and biotransformation of lead in urban soil.
- To study the adsorption, transport and mobility of lead in soil and its potential in ground water pollution.
- To develop and evaluate remediation technologies using agroindustrial waste and plants for managing lead contamination.

REVIEW OF LITERATURE

CHAPTER II

REVIEW OF LITERATURE

Economic losses through damage to environment has stimulated considerable research on the effects of individual air pollutants on soil, water and plants where much of the research has been developed because of the concern about the effects on human health. Environmental lead pollution is clearly attributable to anthropogenic sources, mainly from exhaust gases of vehicles. Lead, a toxic heavy metal, present in petrol and in air as fine particle has now become an ubiquitous pollutant which causes several dangerous effects on living organisms. It can affect the central nervous system, cause renal damage and hypertension. Children are 3 times more at risk than adults.

The literature pertaining to the accumulation of lead (Pb) in soil, water, plant and man due to substantial auto-exhaust activities as relevant to the present investigation is reviewed and presented in this chapter.

2.1 ORIGIN OF LEAD IN THE ENVIRONMENT

2.1.1 Early use of lead compounds

The relationship of man and metal is as old as man himself. Lead never dominated any age in history, it was nevertheless present in all metal ages and was put to various uses with or without the knowledge about its deleterious effects. Lead production in ancient times peaked during the Roman period (500 BC to 500 AD) at around 27,000 tons y^{-1}. During the iron

age (1200-500 BC), production was 12,500 tons y^{-1} and after the fall of Roman Empire consumption dropped to 8500 tons y^{-1} during 500-1000 AD. The floor of the hanging gardens of Babylon was made of Pb to help retain the moisture in the ground (Nriagu, 1983).

The analysis of Roman wines suggests that it had 20 mg lead / litre. The usage of Pb in Roman Empire exceeded 550 g / person / year, hence Pb earned the status of Roman metal. Hippocrates, Galen and many other ancient physicians included Pb in their pharmacopia. Paracelcus (1493-1541) boasted that he could cure 200 diseases with Pb claiming that it cures fistulas, cancer and similar ulcers (Shilpi, 1993). Lead is one such material whose reckless use by man has contributed to pollution the world over.

2.1.2 Present use of lead compounds

Though the toxicological properties have been well documented, the use of Pb compounds in our daily life continues unabated. Its ductility, high strength, high density, impermeability to radiation and other properties make it a very useful metal. Nowadays Pb is used in piping, building materials, paints, ammunition, castings, storage batteries, metal products and chemicals.

Postel (1986) in an estimate on the annual global emission of metals to atmosphere from human activity found it to be 20,00,000 tons as compared to 6000 tons by natural sources. Brown (1986) reported that elevated levels of heavy metals in soil, vegetation and ambient air in urban areas are due to the burning of fossil fuels, automobile exhausts and industrial emissions. The

environmental contaminations by Pb from various sources such as industries and heavy traffic results in elevated concentrations in biological and non-biological systems (Scoullos, 1986).

Nriagu (1990) stated that the use and subsequent emissions of metals into the environment have increased rapidly during the last centuries. According to Tong (1990), the concentrations of Pb was found to vary with housing age and higher levels of contamination in older neighbourhood and this result is probably ascribable to the accumulation of residues from leaded gasoline and lead based paint.

Recent metal emissions are added to earlier emissions and the resulting environmental state is a product of accumulated emissions over time (Bergback *et al.*, 1992). Emissions of heavy metals into the atmosphere as a result of human activities now exceed the natural processes and the presence of trace elements in soils reflects their sources both from parent material and anthropogenic addition. Depending on the location and traffic intensity, contaminated zones can extend upto several 100 meters from the road (Senesi and Loffredo, 1997).

The addition of organo-lead compounds such as lead tetraethyl [Pb $(C_2H_5)_4$] and lead tetramethyl [Pb $(CH_3)_4$], as antiknock agents to petrol which is currently on the increase, is one of the major sources of Pb pollution (Samir, 1999).

Although these sources account for the majority of Pb deposited on land, atmospheric fallout is usually the most important source of Pb in fresh water and marine environment. Other major anthropogenic inputs include non-ferrous metal production and iron/steel production whereas wind blown dust is the main source of natural emission.

2.2 AUTOMOBILE EMISSION AS A SOURCE OF LEAD IN THE ENVIRONMENT

Lead emissions into the atmosphere clearly indicate that on a world wide basis anthropogenic pollution sources widely dominate the natural sources, combustion of gasoline being responsible for more than 90 per cent of the emissions. Lead dominates the road side environment because of its common use in gasoline as lead tetraethyl.

According to Krishnayya and Bedi (1984), Pb is introduced into the environment from a variety of sources but mostly from petrol driven vehicles. Nriagu and Pacyna (1988) characterized human activities such as fossil fuel combustion and mining to have increased the mobilisation and discharge of trace elements into the environment.

Chang *et al.* (1989) reported significant reductions of Pb levels in road side soils and dusts following the lowering of Pb levels in petrol (0.84, 0.6, 0.4, 0.25 and 0.15 Pb mg l^{-1} of petrol in 1980, 1981, 1983, 1985 and 1987 respectively). Lead contamination of surface soil decreases with distance from the urban area, the principal sources of contaminant Pb being automotive emissions (Merry and Tiller, 1991).

Gajghate and Hasan (1997) indicated that quality of Pb emission from vehicles to environment depends on various factors namely, Pb content of petrol, wind speed, quality of roads and speed of vehicles. Brian *et al.* (1997) indicated that inspite of 75 per cent reduction of Pb in Sydney air more than 90 per cent derives from automobile emissions.

Lead in the tetraethyl [$(CH_3CH_2)_4Pb$] form is used as an antiknock additive to gasoline to increase its octane number. Higher the octane number, lesser the rattling. Thus pure linkage alkane gasoline has an octane number of 68 only. Addition of tetraethyl lead, TEL to gasoline increases its octane rating from 68 to 98. TEL is a mixture of about 60 per cent tetraethyl lead or tetramethyl lead, 35 per cent ethyl dibromide and ethyl dichloride, 2 per cent dye, rest solvent and stabilizer. A quantity of 0.66 g/l of TEL is added to gasoline (Sindhu, 1998).

Gajghate *et al.* (1998) evidenced that gasoline based auto-exhaust is the predominant source of Pb pollution in Kanpur city. Dayal and Nandini (2000) reported that vehicles are the primary sources of air pollution in Bangalore city and that the increase of vehicles on road increases the vehicular emissions, adding to the deteriorating ambient air quality.

2.2.1 Impact of traffic load on lead emissions

Aerosol samples along a street of Belgium on traffic free period and on days with intense traffic evidenced the strong influence of automobile exhaust gases (Janssens and Dams, 1975). According to David and Babur (1992) roads with high traffic load had much Pb levels than residential roads.

Piron *et al.* (1992) reported Pb values ranging from 180 µg/g near a road with heavy traffic density of 24,000 vehicles / day in Northern part of France, whereas, Singh *et al.* (1997a) reported a concentration of only 44 µg/g near an Indian Highway with a daily traffic density of approximately 20,000 vehicles. Wong *et al.* (1996) reported that metal concentrations were correlated with traffic volumes, indicating that car exhausts would be the major source of trace metal pollution in urban soils in Hongkong, resulting from the particulate deposits derived from vehicles.

2.3 ENVIRONMENTAL CHEMISTRY OF LEAD

Lead is a member of the group IV elements (C, Si, Ge, Sn and Pb) of the periodic classification and is truly metallic when compared to carbon and silicon. Lead, unlike C and Si does not bind to another identical atom, shows marked decrease in covalency and has stable (+2) and (+4) oxidation states. Lead forms alkyl and aryl compounds. Unlike other carcinogens and killers as pesticides, most chemicals, waste oils and even radioactive materials, Pb does not breakdown over time. It does not vaporize and it never disappears.

Lead compounds derived from vehicular emissions are mostly inorganic and consequently exist in a particulate form. Lead, in the tetraethyl form is added to petrol to increase its octane rating thereby to reduce the engine knocking. Ethylene dibromide and ethylene dichloride are further added to petrol to remove the lead from engine cylinders. The predominant lead product exhausted from automobiles is lead halide, which undergoes

chemical changes quite rapidly with other exhaust gases in the atmosphere (Tsuchiya, 1979).

Singer and Hanson (1969) found a general decrease in exchangeable Pb with increase in soil depth due to low solubility and mobility of Pb in soil. Lee and Chiou (1990) reported that amounts of exchangeable Pb and Cd were higher in acid soil than in alkaline soil and the two metals did not increase or decrease gradually in accordance with distance.

Gupta *et al.* (1995) observed that the effect of EC and pH on the total Pb and its fractions were negative, whereas the cation exchange capacity (CEC) and organic carbon were significantly positive. Exchange of Ca or Pb with adsorbed cations usually takes place and limits their mobility in soil profile (Balba, 1997).

2.3.1 Fractions of Lead

The behaviour of trace metals is strongly linked to their speciation. Carbonate bound lead may have lesser mobility due to lesser solubility as the PKsp (logarithm of solubility product) value of $PbCO_3$ is quite low as compared to other lead compounds (Santillian and Jurinak, 1975). Similarly, the strong affinity of lead with humic acid is reported by Takenaga and Aso (1975). Delineating the speciation of metals in soils is considered essential for understanding the mobility, bioavailability and toxicity of the metals and to develop useful environmental guidelines for potential toxic hazards (Davies, 1980 ; Davies, 1992). According to McLaren *et al.* (1981) the strong

adsorption of Pb by oxide minerals present in soil can increase the amount of Pb bound to Fe-Mn oxide in soil.

The effect of pH on the Pb status of soil was found to be negative (Garcia, 1984). Trace elements in soils are normally found in many different physico-chemical forms and may be associated with various soil components such as clays, hydrous oxides, carbonates and soil organic matter (Lake *et al.*, 1984 ; Tessier and Campbell, 1988). The effect of CEC and organic carbon on the Pb status of soil were found to be positive (Kuhad *et al.*, 1989). Gajghate and Saxena (1991) indicated that $PbNO_3^+$ ions are the major species involved in surface association. Lead has the tendency to form compounds of low solubility with the major anions found in natural water.

Solubility of lead and lead compounds as tabulated by Agency for Toxic Substances and Disease Registry (ATSDR), 1992

Element/Compound	Solubility	
	Water	Organic solvents
Lead	Insoluble	Insoluble
Lead acetate	221 g/100 ml at 50°C	Soluble in glycerol, very slight in alcohol
Lead chloride	0.99 g/100 ml at 20°C	Insoluble in alcohol
Lead chromate	0.2 mg / l	Insoluble in acetic acid
Lead nitrate	37.65-56.5 g/100 ml at 0°C	1 g in 2500 ml absolute alcohol 1 g in 75 ml absolute methanol
Lead oxide	0.001 g/100 cc at 20°C (Litharge)	Soluble in alkali chlorides
	0.0023 g/100 cc at 23°C (Massicol)	Soluble in alkali (Massicol)
Lead sulfate	42.5 mg/l at 25°C	Insoluble in alcohol

Speciation may also consider the type of bonding between an element and other solid components. For example, an element in ionic form may bind to colloidal-size fractions of soil such as clay minerals or organic matter by columbic forces, whereas covalent bonds may be formed with surface ligands on hydrous oxide surfaces (Fendorff *et al.*, 1994). Ligands can form either inner or outer-sphere complexes with cations on an absorbent (Ritchie and Sposito, 1995).

The amounts of exchangeable Fe-Mn bound, oxide bound, organic matter bound, carbonate bound and residual lead were 0.00 to 1.44, 0.00 to 7.92, 0.00 to 13.68, 0.00 to 0.39 and 0.00 to 1.52 respectively, with the total Pb content as high as 24.00 ppm (Gupta *et al.*, 1995). According to Herbert (1997), dissolved metal concentrations are more indicative of the bioavailable fractions of total metals present in water. Sauve *et al.* (1997) indicated that most of the Pb in soil is insoluble, precipitated or bound to soil solids. In most solutions only a small fraction of Pb will be present as free ionic species (Pb^{2+}), most of the soluble Pb being complexed with dissolved organic matter.

2.4 FACTORS INFLUENCING THE DYNAMICS OF LEAD IN THE ENVIRONMENT

Environment keeps on changing over a period of time. The availability of heavy metals are governed by different environmental factors.

2.4.1 Fallout from automobiles

The quantity of Pb consumed by a car engine is a fraction of the concentration of Pb in petrol, rate of petrol consumption, the size, the efficiency, the running speed of the engine and the engine load. The proportion of Pb exhausted depends upon the age, temperature and physical state of exhaust system and the manner in which the car is operated. The amounts exhausted can range from 20-300 per cent with an average around 75 per cent (Chamberlain *et al.*, 1978). Moreover, the fall in atmospheric Pb concentrations with distance from road is in part due to deposition and in part due to upward movement of plume. The large particles deposit close to the road (> 90 per cent within 1.5 m when the size > 5 μm). Some of the factors that have a bearing on the measured levels of Pb arising from petrol are traffic density, amount of Pb in petrol, driving mode, traffic turbulance, bouyancy of the exhaust gases, petrol consumption, age and condition of the car (Little and Wiffen, 1978 and Chamberlain *et al.*, 1979).

2.4.2 Distance from source

A significant drop in soil Pb concentration from 1130 μg g^{-1} in the top 0-2 cm to 350 μg g^{-1} in the 8-10 cm of soil profile was noted by Fergusson *et al.* (1980). It has been observed that the street dust levels fall off with distance from busy roads, with traffic density and distance from central city area (Fergusson and Simmonds, 1983 ; Hamilton *et al.*, 1984 and Davies *et al.*, 1987). The concentration of Pb is highest close to the roadways and decreases almost exponentially with the distance of the road, suggesting

that even though Pb is considered relatively immobile (Adriano, 1986), some migration into deeper layers occur in polluted areas.

2.4.3 Seasonal or climatic factors

Chaney *et al.* (1984) and Fergusson (1986) discussed that Pb levels in plants tend to increase in the autumn and winter. The reasons are, loss of vegetative material during winter, older leaves taking in aerosol Pb more readily than new leaves, reduced wind speed giving more opportunities for aerosol deposition and the amount and the intensity of rainfall which varies with season.

Mooniaruck *et al.* (1996) inferred that concentrations of suspended particulate Pb in traffic dense area were higher in summer than in winter. Von and Fuggle (1996) characterized a fall in the Pb concentration to a minimum during summer and a considerable increase during winter. Significant differences of air-lead levels were observed on week days and on week ends. Maximum concentrations of Pb commonly occurred during winter, whilst minimum concentrations were observed in summer (Ki and Dong, 1997).

2.4.4 Wind as a factor for lead dispersion

Wind promotes the dilution and dispersion of air pollutants. Wind speed is a significant factor in determining the atmospheric levels of lead. Low air Pb concentration because of wind does not mean that the element is not being

emitted from the source, but rather it is more rapidly dispersed and diluted (Simmonds *et al.*, 1993).

2.5 LEAD IN THE ATMOSPHERE

The input of a broad spectrum of atmospheric constituents to the earth's environment is large enough to alter earth's composition and to cause adverse effects on human health, where automobile emissions play a major role.

Hovmand *et al.* (1983) indicated a positive relationship between atmospheric heavy metal depositions and heavy metal concentrations in several agricultural plant species.

El-Shobokshy (1984) reported that in Riyadh, the average concentration of Pb during working day is twice the International standards. Lead is one of the most common heavy metals found in flue gases from hazardous waste incinerators and combustion processes and is listed as a regulated hazardous air pollutant under the U.S. Clean Air Act (Wallace *et al.*, 1985).

Lead particles are emitted from automobiles to the atmosphere as lead halides (eg. PbBrCl) and as double salts with ammonium halides (eg. 2Pb BrCl NH_4Cl) ; lead particles are emitted from mines and smelters primarily in the form of $PbSO_4$, $PbO.PbSO_4$ and PbS. In the atmosphere, lead exists primarily in the form of $PbSO_4$ and $PbSO_3$. However, the chemical composition of lead changes in dispersion is not clear (EPA, 1986).

The Pb involving industry and vehicular exhausts results in an increased level of Pb in the urban environment from where Pb enters human body through gastro-intestinal and respiratory routes (Gupta and Kaushik, 1992).

Richard and Marino (1994) stated that atmospheric pollution caused by use of leaded gasoline has lead to the contamination of Chaleauneuf-du-pape wine. Isabelle *et al.* (1995) found that 44 per cent of children in Mexico city had blood lead levels exceeding 10 µg / dl, the major predictors of blood lead levels were exposure to air borne Pb from vehicular exhausts.

2.5.1 Residence time of lead in the atmosphere

The lifetime of aerosols in the air which contain heavy elements, is a function of the particle size. The smallest particles, 0.001-0.08 µm, have a lifetime of < 1 hour, because of coagulation into bigger particles, whereas in the accumulation range, 0.08-1.00 µm, the lifetime is 4-40 days and the large particles of 1.00 µm, have a life time of minutes to days (Willeke and Whitby, 1975 and Graedel, 1980).

2.6 LEAD IN SOIL

Lead is probably the least mobile of the heavy elements. Lead is also said to limit the enzymatic activity of microbiota and as a result, organic material which has been incompletely decomposed, tends to accumulate Pb in soil. The decontamination time of heavy metals varies from 100 to several 100 years (Gupta *et al.*, 1997). Friedland and Johnson (1985) estimated that,

at current accumulation rates, forest floor Pb amounts will double in 30-40 years. At current leaching rates, mean residence time of Pb in forest floor is approximately 500 years. The ratio of Pb input to output of the forest is 60 : 1.

The major mechanism for the accumulation of heavy metals in soils lead to partitioning in different categories which have different behaviour with respect to remobilization under changing environmental conditions (Forstner, 1985).

Nriagu (1990) suggested that agricultural soils generally receive their trace metal pollution from the atmosphere. Hamon *et al.* (1995) indicated that the concentration of dissolved organic carbon in the soil solution influenced total metal concentrations in the solutions and metal speciation which inturn influenced the amount of metals absorbed by radish. Also, the rate of metal uptake by plants did not increase exponentially as the plants grew. Zhang *et al.* (1996) found that the average Pb content in the soils of Changchun was increased from 36.35 µg/g in 1987 to 64.24 µg/g in 1993. Petukhova and Kuznetsov (1997) reported a high content of Pb in the soil near the main highways of Belarus. Nogales *et al.* (1997) concluded that Pb availability was higher after the addition of inorganic Pb to the soil and also increased the Zn and Cu uptake by plants. One important factor responsible for the fate of trace metals in soil seems to be the organic matter of the soil and / or the organic matter of the soil solution (Bourgeois *et al.*, 1997).

2.6.1 Sorption kinetics of lead in soil

Soil sorption is of great importance for the physio-chemical extraction of toxic elements from underground water and soil. Adsorption-desorption reactions play an important role in controlling the concentrations of metal contaminants in ambient solutions. Movement of heavy metals within the soil profile is mainly in the solution phase. Soil-chemical reactions controlling mobility of heavy metals and their subsequent uptake by plants can be broadly classified as adsorption / desorption or solubility / precipitation, which are inturn controlled by the concentration and ionic species in the solution and the nature of surface phases present. Adsorption / desorption has provided useful means of describing heavy metal reactions in soils, but the boundary between adsorption and solubility is sensitive to small changes in soil components and soil conditions (Brummer *et al.*, 1983). The amount of adsorption normally increases with decreasing solid to liquid ratio (Tan and Teo, 1987). Reaction rates strongly influence element speciation and bioavailability in the environment (Taylor *et al.*, 1995).

The factors influencing sorption of Pb in soil as reviewed by various authors :

Factors influencing sorption of Pb in soil	Authors
pH of the soil	Gerriste and van Drivel, 1984 Naidu *et al.*, 1994 Hooda and Alloway, 1996 Ann, 1997 Balba, 1997
Organic matter	Gerriste and van Drivel, 1984 Elliott *et al.*, 1986 Swift and McLaren, 1991 Hooda and Alloway, 1996
Cation exchange capacity	Butcher *et al.*, 1989 Hooda and Alloway, 1996
Soil content of iron oxides, aluminium and carbonate	Elliott *et al.*, 1985 Swift and McLaren, 1991 Balba, 1997

Sorption or desorption of trace metals by soils occurs predominantly on (from) charged surfaces colloidal material, including organic matter, clay minerals and Fe and Al (hydr) oxides (Armour *et al.*, 1990). The major sorbing surfaces will differ between soils and vary with pH for a particular soil (Mann and Ritchie, 1993). Ionic strength and electrolyte cations have frequently shown to affect adsorption of heavy metals to soil components and soil. Due to the competitive binding of electrolyte cations, adsorption of heavy metals generally decreased with increases in electrolyte concentration and cation valence (Zachara *et al.*, 1993).

The kinetics of heavy metal sorption on soil and soil constituents are fast initially and then the reaction rates decreases, the fast reaction commonly associated with adsorption. For the slow reaction of heavy metals three mechanisms have been proposed : slow diffusion to sorption sites with

restricted access, precipitation on the surface (Fuller *et al.*, 1993) and sorption to sites of lower reactivity (Verburg and Baveye, 1994).

Abd and Wada (1981) showed that selectivity of trace metal adsorption by soils is connected to composition of clay minerals and humus content. According to Mench *et al.* (1997), the amount of trace elements sorbed on a solid phase depends mainly on the nature of the solid, pH and concentration between the toxic element and the sorbent. Sorption, ion exchange and precipitation can be used to convert soluble and pre-existing high soluble solid phase forms to more geochemically stable phases which are less available to root uptake. In the absence of soluble complexing species, Pb is almost totally sorbed as precipitated species at pH > 6.0. In acidic environment, humic acid sorbs Pb stronger than clays. The trend is reversed at pH < 6.5 where soluble Pb-humate complexes are formed. Clays seem to strongly compete with soluble Pb-humates for retention on solid phase.

2.6.2 Mobility of lead in the soil

The mobility of elements in soils is one of the key properties that determines their concentrations and their positions in their soil profile.

The bio-availability and mobility of metals in soil systems are fractions of metal species in soil solutions and the distribution of metals in the solid soil components (Roger *et al.*, 1983). Organic matter addition to the soil, increases the soils adsorbing capacity and the resulting increase in the concentration of potential ligands in aqueous phase enhances the metal

cations' solubility and hence their mobility (Elliott and Denneny, 1982 ; Baham and Sposito, 1986 and Campanella *et al.*, 1989). McCarthy and Zachara (1989) observed that the mobility of ions in the subsurface is generally very low, but the migration of trace elements may be enhanced by colloid facilitated transport.

2.7 LEAD IN WATER

Lead in drinking water is often considered to be a potential pollutant. The excessive limit for Pb in drinking water, as fixed by various sources is reviewed :

S.No.	Safer limit for Pb in drinking water	Source
1	0.05 mg/l	USPHS, 1962
2	0.1 mg/l	WHO, 1971
3	0.1 mg/l	Ministry of Health, Govt. of India, 1971
4	0.05 mg/l	EPA, 1977

The concentrations of heavy metals in rain water are related to their levels in atmospheric aerosols and their speciation. The intensity and duration of the rain also influences the level. Slow and even rainfalls have the best washout characteristics and produces the highest concentration of element in water. Autumn and winter rainfalls usually have higher levels of heavy metals than summer rainfall (Lazrus *et al.*, 1970).

The chemistry of Pb in water is a combination of precipitation equilibria complexing with organic and inorganic ligands. The degree of

mobility of Pb depends on the physico-chemical state of the complexes formed. Hydrolysis of precipitates [Pb_3 $(PO_4)_2$ and PbS] above pH 6 solubilizes Pb as Pb $(OH)^+$. At pH 8.5, Pb $(OH)^+$ is the major species occurring in water. Although the Pb^{2+} and Pb $(OH)^+$ ions are present in equal concentrations at pH 6, $Pb(OH)^+$ predominates at pH 8 (Ramamoorthy and Kushner, 1977).

Lead forms moderately strong chelates with organic ligands containing S, N and O donor atoms. Wilson (1976), reviewing the metal concentration in river waters around the world, reported that Pb shows variable levels of binding (15-83 per cent) in association with suspended solids. The physico-chemical speciation of Pb in drinking water indicates little or no free ionic lead. A significant portion of Pb is bound to colloids either as hydrous iron oxides or as organic macromolecules depending on the composition of water. A substantial fraction is in non-ion-exchangeable form.

Urban surface water usually contains Pb from atmospheric wash outs and road run-offs due to pollution from vehicular emission. The concentrations are usually higher in areas closer to the land and in confined areas such as in harbours and channels because of additional sources of Pb from urban run off and sewage (Bernhard, 1980 ; Burnett *et al.*, 1980 ; Mart *et al.*, 1980 ; Schaule and Patterson, 1981 and Smith, 1986).

Hart and Davies (1981) studied the speciation of Pb in fresh waters of Australia. In the fresh water, about 45 per cent of total Pb was present in particulate form. The calculated equilibrium distribution of ion-exchangeable

species showed that $PbCO_3$ accounted for about 80 per cent with smaller concentrations from Pb^{2+} and $Pb(OH)^{+}$. Organic matter, at concentration more than 5 mg/l did not significantly influence speciation. A change in the pH of sea water affects the relative proportions of the inorganic lead species (Stumm and Brauner, 1975 ; Whitfield and Turner, 1980 and Byrne, 1981).

The pH and EC of water sources reported by various sources / authors :

S.No.	Various water sources	pH range	EC range (m mhos/cm)	Sources / Authors
1.	Drinking water	7.0-8.5	600.00	ISI, 1983
2.	Drinking water	7.5	600.00	WHO, 1984
3.	Hand pump water, Aligarh	7.0-8.3	98-218.3	Ajmal and Raizuddin, 1986
4.	River koshi, Purnia	7.1-8.0	-	Pandey *et al.*, 1993
5.	Ground water, Singhari	7.3-8.4	507-1222	Jain, 1997

As water pH increases, metal concentration decreases. Levels of Pb are highest in surface water, presumably due to atmospheric input, and then falls with depth (Sigg, 1985).

In the natural environment, the divalent form (Pb^{2+}) is the stable ionic species of Pb. Hydroxide, carbonate, sulphide and more rarely sulphate may act as solubility controls in precipitating Pb from water. A significant fraction of Pb carried by river water is expected to be in an undissolved form. This can consist of colloidal particles or larger undissolved particles of lead carbonate, lead oxide, lead hydroxide and other lead compounds incorporated in other components of surface particulate matter run-off. The ratio of Pb in

suspended solids to lead in dissolved form has been found to vary from 4 : 1 in rural streams to 27 : 1 in urban streams (EPA, 1986).

Thomas and Greene (1993) detected that the presence of Pb in rain water from urban area roof catchments was mainly due to diffused pollution from atmospheric deposition. Organic matter and hydrous oxides, as ionic sorption sites strongly affect metal mobility in the soil profile (Abdel, 1997). Sadiq and Alam (1997) concluded that $PbCO_3$ minerals can limit Pb solubility in saline ground waters.

2.8 LEAD IN PLANTS

2.8.1 Accumulation of lead in plants

Several plants of terrestrial and aquatic ecosystems are known to bioconcentrate toxic trace elements.

The chemical form, level and particulate size of atmospheric Pb and the nature of soil Pb could play an important role in the uptake of Pb by plant tissue. Lead content of washed foliage ranged from 1.3 to 1120 ppm and lead content in twigs, which were generally low ranged from 1.8 to 320 ppm (Kenneth and Clair, 1980). Czuba and Hutchinson (1980) evidenced that leafy crops especially lettuce (*Lactuca sativa* L.) and celery (*Apium graveolens*) accumulated higher Pb levels in their foliage compared with levels in root crops.

The accumulation of Pb and Cd in edible vegetables was reported by Zurera *et al.* (1987). Eltner *et al.* (1988) stated that Pb and Cd are passively

absorbed by plants, accumulate in various amounts and adversely affect the metabolic activities. Higher accumulation of heavy metals in different parts of rice plants were observed by Ray *et al.* (1988). Lead accumulated more in leaves and shoots than in roots of sorghum, maize and wheat cultivated adjacent to a state highway. Leaf surface of sorghum had deposited more Pb but accumulated Pb was significantly high in maize (Saxena *et al.*, 1991).

Rice, wheat, barley, oats, corn, chickpea, pigeon pea, beet root, radish, carrot, tomato, spinach, peanut, soybean, tobacco, alpha alpha and oil seeds are reported to accumulate trace elements when grown in metal contaminated agro ecosystems (Rivai *et al.*, 1990a ; Rivai *et al.*, 1990b and Wagner, 1993). Trace metal accumulation in plant parts can be divided into three categories (Siedlecka, 1995).

i. Accumulate more in roots/rhizomes than in shoots (stems/leaves) : cadmium, cobalt, copper, iron and molybdenum, eg. beet root, radish, carrot and potato.

ii. Accumulate more in shoots when compared to roots/rhizomes : silver, chromium, lead, tin and vanadium, eg. cabbage, cauliflower, tomato, rice, barley, oats, wheat, corn, pigeon pea, chickpea, soybean, peanut, broccoli, lettuce, spinach and amaranthus.

iii. More or less uniform distribution in roots/shoots of the plant: manganese, nickel, and zinc, eg. bush bean, broad bean, mung bean and cucumbers.

Singh *et al.* (1997b) found that the accumulation of Pb in various tissues of plant is related to atmospheric levels of Pb ; *Polyalthia longifolia* being sensitive to atmospheric levels of Pb may serve as an excellent bioindicator of atmospheric Pb contamination.

The different concentrations of Pb accumulation in various plants as observed by Naik and Deshpande (2000) is as follows :

S.No.	Plant species	Concentration of Pb (ppm)
1a.	*Polyalthia longifolia* (from road side)	0.45
b.	*Polyalthia longifolia* (from residential area)	0.07
c.	*Polyalthia longifolia* (from unpolluted fields)	-0.03
2.	*Sterculia foetida*	0.04
3.	*Zizyphus rotundifolia*	0.09
4.	*Mangifera indica*	0.13
5.	*Leucaena latisiliqua*	0.09

2.8.2 Translocation of lead in plants

There are atleast three different pathways for the uptake of metal into wood and the most significant is from the soil via roots (Lepp, 1975). Lord *et al.* (1979) stated that entry of Pb in the plant system is mostly through stomatal pores. Ira and Anjali (1980) inferred that uptake of Pb through underground portions may be high but translocations to above ground portions are lower when compared to other metals like Zn and Cd. Lindberg and Harris (1981) concluded that Pb was absorbed internally by leaves or irreversibly adsorbed onto leaf surfaces.

According to William and Thomas (1981) Pb concentration in the biota was in the following order : lichens > mosses > tree twigs > roots > barks > leaves = bracket fungi > wood. This was further supported by Turner *et al.* (1985), that Pb in the biota was mainly contained in the fine roots > bark > foliage > wood. Chappelka *et al.* (1991) found that transport of Pb from plant root is low, which restricts the influence of root uptake on Pb levels in higher plants. Lead translocation from roots to shoots was limited in plants growing in Pb contaminated soils (Huang and Cunningham, 1996).

2.8.3 Effect of lead on growth and retardation of plants

Synergestic interaction of Pb and Cd in corn resulted in decrease in root length, plant height and new foliage growth (Hasset *et al.*, 1976). Wong *et al.* (1984) inferred that inhibition of root growth of crops (*Brassica parachinensis* and *B. chinensis*) was observed when treated with aqueous extracts of roadside dust and salts. Juwarkar and Shende (1986) inferred that in Barley (*Hordeum vulgare*) the root length, height of plants, length of earhead and grain yield were synergistically reduced due to combined effect of Pb and Cd. Saxena (1991) evidenced that motorway pollution reduced viability, germination, yield, seedling vigour and seed weight in crops along National Highways.

Inhibition of plant growth by heavy metals is attributed to reduction in physiological processes (Van and Clijsters, 1990 and Mishra *et al.*, 1994). Handique and Baruah (1995) reported significant loss of pollen viability in tomato, pea and pigeon pea, following treatments with Hg and Pb (at a

concentration of 10 and 20 ppm respectively). The magnitude of loss of viability is related to concentration and duration of treatment.

The influence of Pb treatment on gram, lentil, wheat and matra showed considerable retardation of shoot and root growth (Gupta and Sharma, 1997). Effect of automobile emissions on two common avenue trees, *Azadirachta indica* A. Juss and *Polyalthia longifolia* Benth and HK, collected from heavy traffic density area showed significant changes in cuticular and epidermal structures and a two fold increase in stomatal frequency (Pal *et al.*, 2000).

2.8.4 Mutagenic effects of lead in plants

Treatment of two lead salts on *Crepis capillaris* shows that Pb (NO_3) and PbI_2 are mutagenic at the same concentration of 4.10^{-4} M (Reutova and Shevchenko, 1991). Lerda and Marcos (1992) observed that Pb reduces root growth and the frequency of mitotic cells in meristematic zones and increases the frequency of aberrant cells in *Allium cepa*.

Effects on Pb (NO_3) on *Pisum sativum* L. exhibited a striking fall in mitostatic indices, various types of chromosomal anomalies indicating the role of spindle abnormality, strong chelating property, disturbances in cell plate formation, inactivation of spindle apparatus leading to polyploidy and aneuploidy and considerable decrease in growth index value (Sengupta and Ghosh, 1996).

2.8.5 Effect of lead on primitive plants

TriEthyl Lead (TriEL), a primary derivative of Tetra Ethyl Lead (TEL) causes severe inhibitory effects to the chrysophyte, *Poterioochromonas malhamensis* (Gerhard, 1981). Sphagnum moss exerts strong species specific effects on the uptake of metals by vascular plants (Vedagiri and Ehrenfeld, 1991).

2.9 LEAD IN HUMAN BEINGS

Lead poisoning remains one of the most common environmental hazard inspite of good scientific knowledge on its toxicity and control measures. Lead is a cumulative neurotoxin. Tetramethyl lead and tetraethyl lead are added to gasoline to reduce knocking and are emitted into the air with the exhausts as volatile lead halides. Absorption of Pb occurs primarily in the respiratory tract and major portion is absorbed by pulmonary circulation. Once lead enters the human body it tends to concentrate in the bones. When the body feels shortage of essential elements like calcium or phosphorus, the blood leaches out these minerals from the bones and supplies it to the relevant organs. In this process lead too becomes liable and enters the blood stream. It then concentrates in the tissues where it elicits toxic effects. Lead content of blood and water should not exceed 0.25 ppm and 0.05 ppm. Beyond these limits the symptoms of lead poisoning begin to manifest themselves (Sodhi, 2000). It is also widely accepted that children are a more susceptible target group for Pb than adults.

2.9.1 Haemotological risks

Hisao and Makato (1981) reported a significantly higher mean Free Erythrocyte Protoporphyrin (FEP) at various normal haemoglobin levels in female workers than the male workers, seemed to eliminate the possibility that a relative iron deficiency in women may play a role in the sex-related difference in the FEP response to Pb. Inner city people have higher blood levels than suburban and suburban higher than rural (Taskenin *et al.*, 1981 ; McBride *et al.*, 1982 ; Brunekreef *et al.*, 1983 ; Elwood *et al.*, 1984 ; Schutz *et al.*, 1984 ; Skerfving *et al.*, 1986 and Heany *et al.*, 1988). The umbilical cord blood of infants born in Boston during a three month period showed a positive correlation with Pb consumption in the city, maternal characters and soil Pb (Rabinowitz and Needleman, 1982, 1983 and 1984). In fresh serum about 4999 out of 5000 parts of added Pb were bound, which suggest that the free Pb^{2+} concentration is around 1/5000th of total Pb concentrations in the serum of normal subjects (Al-Modhefer *et al.*, 1991).

The studies on genetic pattern of glucose 6 phosphate dehydrogenase (G6PD) by Cocco *et al.* (1991) showed that Pb poisoning affected blood cholesterol of G6PD deficient subjects differently from normal ones. Environmental Pb levels were elevated near heavy traffic and automobile emissions were considered to be a major source of increased blood levels of children attending schools near heavy traffic at Cape Town (Debbie *et al.*, 1991). Day (1996) indicated that women who once lived in Pb

polluted environment may pass the poison to the unborn offspring long afterwards by flushing out Pb in the blood stream during pregnancy.

2.9.2 Dental Risks

A study by Fergusson *et al.* (1988) in the deciduous teeth of 996 children demonstrated a relationship between dentine Pb and social background, the length of time of residence along busy streets and pica.

Paterson and Fulton (1988) mentioned a tendency to higher Pb levels in carious teeth. Nandita *et al.* (1995) reported that the Pb content in Delhi was higher followed by Bhilai and Shillong. The Pb concentrations in teeth were lower in Bhilai and higher in Delhi and Shillong indicating environmental Pb and fluoride are interrelated among two forms of dental disorders - exfoliated teeth and dental caries. Pearce (1997) showed the link between Pb pollution from traffic fumes, tap water and tooth decay, the incidence of tooth caries increased in children and adults with high concentration of Pb.

2.9.3 Neurological Risks

In severe situations of Pb poisoning can cause neurological effects such as restlessness, hyperactivity, confusion and impairment of memory as well as coma and death (Grandjean and Nielson, 1979).

The psychological examination of employees from a factory producing antiknock additive for gasoline support the hypothesis of a special neurotoxicity of alkyl lead compounds (Kiesswetter *et al.*, 1990). According to

Stacey *et al.* (1994), Pb is known to affect both the immune and the nervous system. Motluk (1996) revealed neurological damage as immediate effects of Pb poisoning in children.

2.9.4 Nephrological Risks

In the renal system, the initial damage occurs to the peripheral tubular system. The effects are aminoaciduria, glucosuria, hyperphosphaturia and also hyperphosphatanemia. Chronic Pb nephropathy may develop where the kidney contracts with anteriosclerotic changes, glomerular atrophy and renal failure (Piotrowski and Coleman, 1980 ; Newland and Dawn, 1982 ; Royal Society of New Zealand, 1986 and Hutton, 1987). Reversible renal to tubular dysfunction is seen in children with acute Pb exposure. Continuous Pb exposure gradually alters the morphology of kidney. Nuclear inclusion bodies present in kidney are indicature of Pb exposure at doses as low as 1 per cent (Shilpi, 1993).

2.9.5 Reproductive Risks

Still births (Piotrowski and Coleman, 1980) and cot deaths–sudden infant death syndrome (Boeckx, 1986 and Erickson *et al.*, 1983) are other health effects where Pb has been implicated. For pregnant women, elevated Pb concentrations increase the risk of hypertension and birth defects (Rabinowitz, 1988). Plumbism in father also affects the survival, vigour and fertilization of the offspring, whereas in women exposed to Pb, pregnancy is

most likely to result in miscarriage or stillbirth. If the child is born living, there is a higher infant mortality (Sodhi, 2000).

2.9.6 Hair lead

Wilhelm *et al.* (1989) stated that elemental analysis of hair is an important factor for screening populations. Studies of Hongo *et al.* (1990) reveals that scalp hair is strongly influenced by external environment. Santos *et al.* (1994) showed that human scalp hair Pb concentration is an indicative of population exposure to Pb. Batzeviich (1995) pointed out that human scalp hair trace element concentration is highly influenced by geochemical and nutritional factors. Jaydip and Das (1996) analysed the mean baseline scalp hair elemental concentration to 2.49 µg/g for Pb. Vassilieva *et al.* (1997) established that accumulation of metals in hair and nails and secretions through urine and saliva are definitely correlated.

2.9.7 Behavioural Risks

Performance deficity, hyperactivity, insomnia and abnormal social behaviour are the consequence of Pb exposure. Lead is also associated with aggressive behaviour (Shilpi, 1993).

2.10 GENERAL EFFECTS

Daniel *et al.* (1981) reported that positive correlation exists between air and hair Pb, Hg and Se and there is a significant difference between learning

disabled and control group children's trace metal hair content and blood pressure.

The effect of Pb on the biosynthesis of haem shows that Pb influences the activity of enzymes (Fell, 1984). Hudson *et al.* (1984) reported that the harmful effects caused by Pb also include histopathological and haemotological changes. There is no evidence available that Pb has carcinogenic or teratogenic effects on human beings (Royal Society of New Zealand, 1986). Urinary delta–aminoluvelinic acid in urban and suburban children of Rhotak city area as an exposure to Pb showed that the level of significance decreased with increase in age and became non significant in 4-5 years age group (Kausic *et al.*, 1995).

2.10.1 Pathways of lead transfer

Potentially there are 3 major pathways of Pb transfer in the urban environment : inhalation of contaminated dust particles, direct ingestion of soils (especially with children) and through consumption of agricultural produce, poultry and animals. The amount of contaminant (Pb) transfer through food or meat consumption depends largely on the extent and mechanisms of soil contaminant uptake which is controlled by soil chemical and mineral characteristics - soil mineral type, soil texture, pH and sorption – desorption behaviour (Naidu, 1996).

Michael and Charles (1996) have demonstrated high Pb levels in the dust from play grounds in high traffic density areas and the relationship of

dust lead levels to child hand-wipe Pb levels. A major pathway for Pb exposure to children involves incidental ingestion of soil (Jones *et al.*, 1997 and Lena and Gade, 1997).

2.11 EFFECT OF LEAD ON ANIMALS

Low doses of Pb given to immature animals have been reported to increase the amount of non-adrenalin in various parts of central nervous system (Golter and Michaelson, 1975). Prolonged exposure of different species of fishes to lead salts in water resulted in significant reduction in erythrocyte count, heamotocrit value and blood haemoglobin level (Tewari *et al.*, 1987). Exposure of *Colisa faciatus*, a fresh water teleost to 15 mg/l lead nitrate for 96 hours showed a marked reduction in spermatogenic activity and haemorrhage in testis (Anil, 1987). Lead has become a serious threat to wildlife and ecosystem (Wiemeyer *et al.*, 1988).

In 1989, Setia *et al.* reported that blood Pb concentrations in buffalo calves after 20 days of induced Pb toxicity was 48.33 ± 1.45 µg / 100 ml and clinical symptoms were related to damage to central nervous system. Fox *et al.* (1991) showed that moderate level developmental Pb exposure produces long term selective rod defects and degeneration in the retinas of monkeys and rats. Lead also accumulates in the body of fishes from the surrounding water and detritus and thereby causes adverse and physiological effects (Alam and Maughan, 1995).

2.12 EFFECT OF LEAD ON BIRDS

The impact of lead on birds is reviewed.

Mallard ducks dosed with a single shotgun pellet for one month showed about 1 ppm Pb in blood, 2.5 in liver and 0.5 in brain (Dieter and Finley, 1979). Pigeons gave much more magnified Pb pollution than atmospheric concentration indicated (Gen *et al.*, 1981). In *Columba livia*, Pb concentrations increased according to the locality in the order : rural < suburban < urban. The trialkyl lead in the kidney and liver tissues of urban pigeons probably derives from exhaust of vehicles and that the body burdens is particularly high in those of urban area (Johnson *et al.*, 1982). Absorbed Pb accumulates primarily in bone of birds; of the soft tissues, kidney accumulates highest levels (Custer *et al.*, 1984).

2.13 EFFECT OF LEAD ON MICROBES

When metals are introduced into the environment, biological activity of micro organisms play an important natural role in metal sequestration and immobilization (Beveridge, 1989).

Biosorption of heavy metals by isolated pure cultures indicates that no single mechanism is responsible for metal uptake. In general, two mechanisms are known to occur viz., adsorption which refers to the binding of material onto the surface of the cell and absorption which implies penetration of metal into inner matrix of cell cytoplasm (McHale and McHale, 1994). Brady and Duncan (1994) opined that *Saccharomyces cerevisiae* has been utilised extensively as biosorbent due to its ability to accumulate heavy metals.

Stephen *et al.* (1996) indicated *Pseudomonas aeruginosa* as an effective organism that could remove Pb.

Mechanism of metal ion accumulation differs according to microorganisms and metal ions. Various types of biomass prepared from algae (Pascucci and Saneddon, 1993), fungi (Sag and Kutsal, 1997) and bacteria (Hu and Reeves, 1997) have been explored for their potential application as biosorbents of metal ions. An increase in Pb (II) biosorption rates with increasing pH has been observed in studies employing *Rhizopus arrhizus* (Sag and Kutsal, 1997). Studies by Suh *et al.* (1998) have shown that *Aureobasidium pullulans* accumulates Pb (II) only on the surface, while in *Saccharomyces cerevisiae,* Pb (II) accumulation site exists both on cell surface and in the inner cellular parts. Mode of Pb (II) accumulation is closely related to cell dry weight and initial Pb (II) concentration. Pseudomonas strain PTM is found to be an effective organism in the removal of Cu (II) and Pb (II) when compared to yeast (Ramraj *et al.*, 2000).

2.14 ENVIRONMENTAL IMPACT ASSESSMENT

Development and environment are inseparably linked to each other having its impact on the environment. In order to assess the changes caused by human activities, effective and reliable monitoring systems are required to recognize and predict hazardous effects. Risk assessment is fundamentally a probabilistic quantification of hazard evaluation.

2.14.1 Plants as biomonitors

Plants have shown phytotoxicity to the contaminants of Pb (Rolfe and Bazzaz, 1975). Laaksovirta *et al.* (1976) demonstrated that concentration of heavy metals accumulated in lichens correlate with traffic density. Anbazhagan *et al.* (1990) reported that leaf area can be used as an indicator of auto-exhaust pollution using *Calotropis procera*. Common dandelion (*Taraxacum officinale*) has been particularly useful as a phytomonitor of trace metals (Kabata and Dudka, 1991 and Rule, 1994).

Takala *et al.* (1994) points out that *Hypogymnia physodes* (lichen) has been widely used to monitor the deposition of air borne pollutants. Screening of two road side plants viz., *Azadirachta indica* and *Dalbergia sissoo* for their utility as bioindicators of auto-exhaust pollution showed that the plants were hypostomatic. *i.e.* stomata were present on the lower epidermis only (Sharma and Roy, 1995). Rule *et al.* (1997) suggested Moth mullein (*Verbascum blattaria*) and Goldenrod (*Solidago canandensis*) as potentially useful phytomonitors for metal uptake.

Agrawal and Agrawal (1999) discussed that increased mortality, declining vigour and changes in genetic and species diversity are often the harmed impacts of air pollutants on herbs, shrubs and trees. According to Sharma (1999), dominant species in an area are the most important indicators as they receive full impact of habitat for over longer periods.

Heavy metal pollution of water, monitored by algae, *Cladophora* and *Stigeoclonium*, showed that the former was completely absent and the latter had abundant growth in waters polluted with heavy metals. *Chlorella* is used to monitor toxic substances in water bodies (Sharma, 1999).

"Moss bags", epiphytic lichens and mosses accumulate heavy metals and are used for monitoring air pollution (Sharma, 1999).

2.14.2 Animals as bioindicators

Beyer *et al.* (1982) suggested that Cd, Cu and Pb were concentrated by earthworms. Urbini *et al.* (1997) characterized wasps (*Polistes* genus) as bioindicators for Pb pollution. Earthworm accumulates heavy metal when exposed to heavy metal contamination in soil and hence tissue heavy metal concentration may be an indicator of heavy metal contaminated soils. Fish, Daphnia and Silver carp indicate heavy metal pollution levels in water (Sharma, 1999).

2.15 REMEDIATION OF LEAD CONTAMINATED SOILS

Toxic metal contamination of soil posses a major environmental and human health concern which is still in need of an effective and affordable technological solution for remediation strategy. Alternative *in situ* technologies have been proposed that may limit the availability of ingested Pb by the precipitation of insoluble Pb minerals or high affinity adsorption of Pb in the soil matrix (Ruby *et al.*, 1994).

2.15.1 Physical in situ remediation

The major physical *in situ* technologies are soil mixing, soil washing and solidification.

2.15.1.1 Soil mixing

The simplest technique for reducing the hazard associated with heavy metals in soils is mixing the contaminated soil with uncontaminated soil, which can be achieved by importing clean soil and mixing it with contaminated soil or redistributing clean materials already on site (Musgrove, 1991). Another dilution technique relies on deep ploughing, during which the vertical mixing of surface contaminated soils with less contaminated subsoils reduces the surface contamination. However, the heavy metal concentration of the soil will remain the same (Burns *et al.*, 1996). The effectiveness of integrating pneumatic fracturing and *in situ* bioremediation for the treatment of gasoline – contaminated, low permeability soil was demonstrated by Venkatraman *et al.* (1998).

2.15.1.2 Soil washing

A basic requirement of any extraction procedure should be the ability of the extractant to dissolve specific component of a soil or sediment (Chao, 1984).

Soil washing or extraction is applied widely for the remediation of heavy metal contaminated soils in Europe (Tuin and Tels, 1991). Soil

washing, which is very useful for off-site treatment of soil, can also be used on-site using mobile equipment (Bromhead and Beckwith, 1994).

Sequential extraction procedures have been developed which also include successive leaching of metal from interstitial waters and from different forms of particulate-bound sediment fractions (Krishnamurthi *et al.*, 1995).

2.15.1.3 Solidification

Solidification involves the stabilization of the contaminated soil using cement, fly ash, gypsum, asphalt or vitrification and the technique has been applied in field scale remediation (Allan and Kukacka, 1995). However, there is a major question of long-term resistance to the breakdown of the solidified mass (Peters and Shem, 1992).

2.15.2 Chemical in situ remediation

2.15.2.1 Adsorption and desorption

Hydrous oxides of Fe, Al and Mn are known to specifically adsorb heavy metals, thus enhancing the metal immobility in soils (McKenzie, 1980 and Fu *et al.*, 1991). The IA and 13x type zeolites were shown to reduce the Pb content of plant tissues of several species (Gworek, 1992).

The influence of pH on minimizing metal uptake can be attributed to the roles that ionic speciation in soil solution and surface charge characteristics of soil particles play in metal adsorption (Naidu *et al.*, 1994). Arnfalk *et al.* (1996), after comparing several clay minerals and soils for their

effectiveness in metal uptake, concluded that the relative order of metal uptake was the same for Cr (III), Cd and Pb.

Organic and inorganic amendments and chemicals, are known to immobilize a range of heavy metals. Chelate ion-exchange resin, cation exchange resin, ferrous sulphate, silica gel, lime, gypsum and naturally occurring clay minerals such as bentonite, kaolin, zeolite and green sand have been found to immobilize heavy metals(Balba, 1991).

Chemical treatment of seedlings of *Brassica juncea* with putrescine and ammonium nitrate, decreased the Pb and Cd accumulation in leaf (10-20%) and shoot (40-60%) tissues depending upon the external metal levels. Putrescine significantly decreased the metal accumulation and translocation under saline conditions (Mishra and Singh, 2000).

2.15.2.2 Clay and minerals

Clays are naturally occurring non-toxic materials with large specific surface areas and significant electric charge. They may be modified to render them hydrophobic and organophilic. Churchman *et al.* (1996) reported that many Australian clays have an appreciable sorption capacity for heavy metals. Wang (1996) opined that among all the soil amendments, zeolite, an aluminosilicate mineral was very promising for the remediation of heavy metals in China.

2.15.3 Phytoremediation

Phytoremediation is an emerging technology for the remediation of contaminated soils. Some plants have inherent capacity to absorb and hyper accumulate heavy metals in their tissues (Baker, 1981). Such capacity can be harnessed to remove toxic metals from contaminated soils allowing preservation of top soil and eliminating costly excavation and disposal.

Different phytoremediation technologies such as phytostabilization, rhizofiltration and phytoextraction have been proposed by Cunningham *et al.* (1995).

a. Phytostabilization : Plants can be planted to revegetate the land, stabilize the soil and reduce bioavailability of metals. Plants need to be tolerant of metals in this case, but accumulation may be disadvantageous.

b. Rhizofiltration : The roots of plants can be used to adsorb or absorb metals from a contaminated solution and the metals removed by harvesting the whole plant. In this case tolerance and translocation are largely irrelevant.

c. Phytoextraction : Plants can be grown on contaminated soil and the aerial parts harvested. In this case, plants need to be tolerant only if the soil metal content is very high but they need to accumulate very high concentrations (more than 1000 mg/kg) in their aerial parts and in practice need to be hyper accumulators.

Chaney and Oliver (1996) have defined that Ni hyper accumulator is the occurrence of >1000 mg/kg of Ni in dry leaves collected at the nature

habitat of the plant, while normal plants start to suffer Ni phytotoxicity at 50-100 mg/kg. Most hyper accumulators have been found to be endemic metallophytes or plants which occur only on soils with very high metal concentrations. However, the use of metal concentration in dry plant tissues as a criterion for identifying plant species that can be good phytoremediators, does not take into account the metal concentration in the roots.

The most efficient plants in taking up heavy metals were spinach, potato and beet root which accumulated more heavy metals in shoots than in storage or fruit parts (Sara and Ramasamy, 1998). Through phytoremediation using *Brassica juncea* combined with soil amendments, the average surface soil lead concentration was reduced by 13 per cent (Blaylock *et al.*, 1999).

2.15.3.1 Coir pith as an amendment for soil remediation

India is one of the major coconut cultivating countries in the Asian continent covering over 1428.7 thousand hectares of land, producing 7.5 metric tons of coir pith annually. Coir fibre is obtained from the fruit of the coconut palm and consists of a mass of fibrous tissue. Coir pith is the binding material of coir fibre. Extraction of one kilogram of coir fibre generates two kilogram of coir pith which is considered a waste.

Incorporation of coir pith reduced the bulk density and increased the infiltration rate and hydraulic conductivity of the soil (Mayalagu *et al.*, 1983).

The addition of coir pith lowered the pH of saline sodic soil from 9.2 to a desirable level of 8.4.

Coir pith application improved the availability of nutrients by reducing the pH of sodic soil. Composted coir pith enhanced the water holding capacity and porosity of the soil (Selvi and Augustine, 1992). Coir is a biodegradable organic fibre material. Further the material is acidic in nature (pH 5.4) and hence its application with soil shall enable the release of fixed and mineral potassium for crop use (Savithri *et al.,* 1993).

Batch and column studies using coconut husk fibres and palm pressmud fibres showed that both the substrates could be used as barriers in landfill to maximize immobilization of toxic metal such as Cr (VI) in leachates. Batch test showed pH range for effective Cr (IV) removal was between 1.5 and 5.0 (Tan *et al.*, 1993).

Composted coir pith not only ensures continuous supply of nutrients to soil but also improves the physical characteristics of soil and increases the microbial population (Venkitasamy *et al.*, 1995). Application of composted coir pith increased the yield of ragi (Lavanya and Manickam, 1991), rice (Pakiaraj and Venkataraman, 1991), soyabean (Rita *et al.*, 1996), paddy (Thilagavathy and Manickam, 1996) and rice (Bagavathi and Durairaj, 1996) by maintaining the soil fertility status.

MATERIAL AND METHODS

CHAPTER III

MATERIALS AND METHODS

Lead (Pb), a toxic heavy metal, is introduced into the environment mainly through automobile emissions. It may persist in the soil for long time and / or undergoes various biological and chemical transformation resulting in ground water pollution. Urban environment is the most vulnerable because of the high intensity of vehicles used by a large population. Therefore, a study was undertaken to examine the accumulation and transformation of lead in urban environment due to automobile emission. An attempt was also made to develop remediation strategies for managing the Pb contaminated environment. The details of the materials used and methodology adopted are described in this chapter.

3.1 DESCRIPTION OF THE STUDY AREA

Coimbatore, is at 10°N 77°E and 426.72 m.a.s.l and is the second largest industrial centre in Tamil Nadu. It enjoys a salubrious climate as it is exposed to the Palghat gap of the Western Ghats. This has attracted a large number of textile mills to the region and Coimbatore is rightly called "**The Manchester of South India**". The region is also well known for the manufacture of varied goods which has earned it the title "**The Detroit of the South**". The minimum and maximum temperatures prevail between 21°C and 34°C, with an annual rainfall of 714 mm.

3.2 STATUS OF LEAD IN URBAN ENVIRONMENT

3.2.1 Collection and processing of the samples

3.2.1.1 Soil samples

A major survey was undertaken in Coimbatore urban environment to study the status and distribution of Pb in the soil.

Surface (0-15 cm) and subsurface (15-30 cm) soil samples were collected from different locations over a distance of 1 to 2 kilometers along the National Highway 47, which connects, Coimbatore to Palghat, Kerala and State Highway 10 which connects Coimbatore to Pollachi. The location of the sampling sites is depicted in Figure 1. Surface and subsurface soil samples were also collected from 4 major areas of Coimbatore inner city, covering the east (Avinashi road), west (Saibaba Colony road), north (Mettupalayam road) and south (Town Hall road) directions of the city. Replicate samples were collected from each location, following sampling protocol.

The soil samples were air dried for 2-3 days at 25°C and passed through a 2 mm nylon sieve. The homogenized soil samples were stored in polythene bags until further analysis.

3.2.1.2 Water samples

The water samples were collected from ponds, stagnated surface water bodies, wells and borewells along National Highway 47, State Highway 10 and from Coimbatore inner city. The samples were collected in new one litre polythene containers which were previously rinsed with sampling

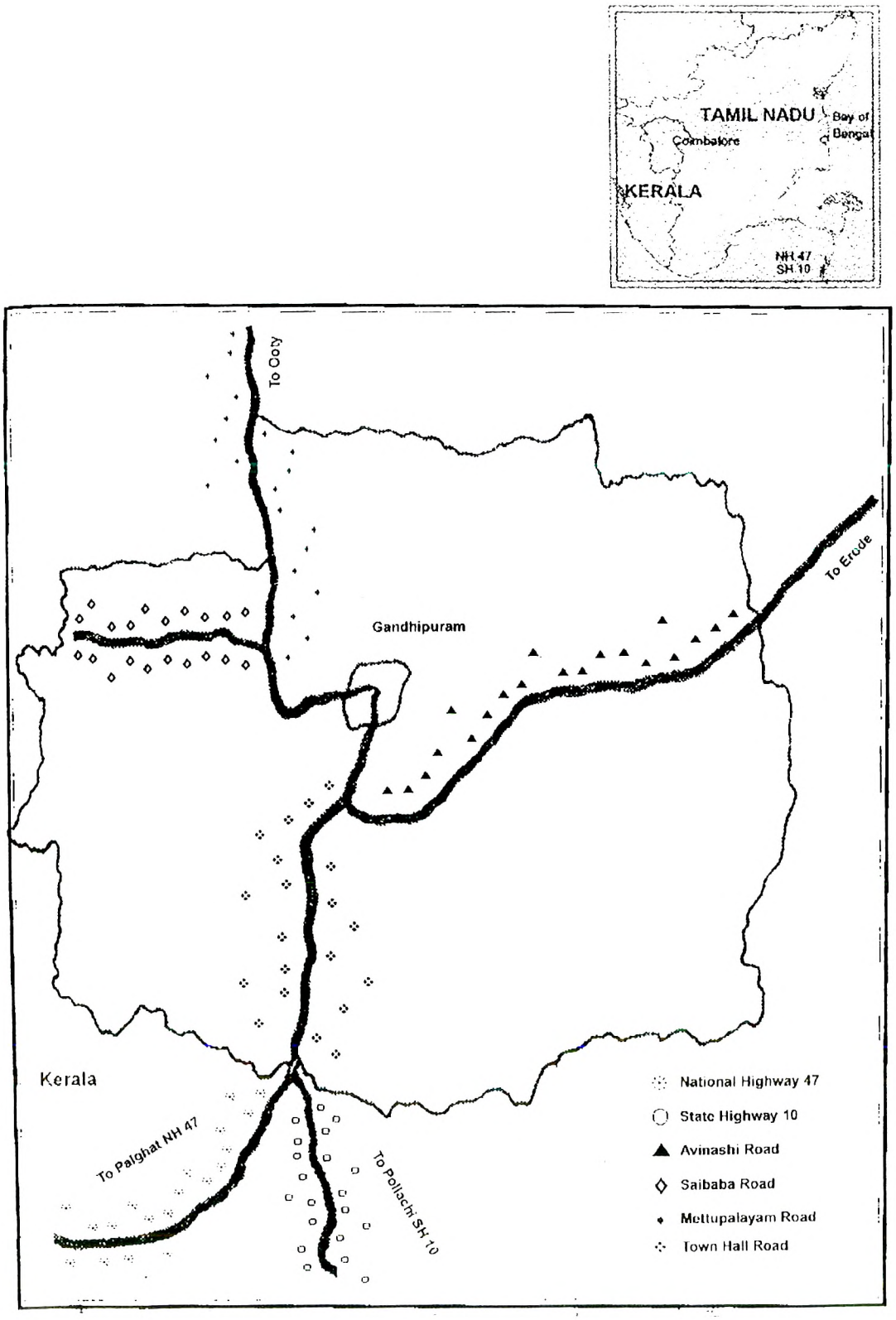


Figure 1. City map of Coimbatore showing the locations of the study area and sampling sites

water before taking the samples. After measuring the pH and EC, the water samples were acidified with concentrated HNO_3 (2 ml l^{-1}) to a pH around 3.0 to stabilize the original valence state of Pb. The samples were stored at 4°C and analysed within a week.

3.2.1.3 Plant samples

Predominant plant species, *Cyanodon dactylon* from highways and *Boerhaavia diffusa* from the inner city were collected from sites adjacent to soil sampling. *Cyanodon dactylon* also known as 'Doob grass' belongs to the family Poaceae and is commonly found along National Highway 47 and State Highway 10. Whereas, *Boerhaavia diffusa* known as 'Spreading hogweed' belonging to the family Nyctaginaceae, is grown as a common species along the road sides of Coimbatore inner city and hence was taken for the present study. The plants were washed with 1 per cent HCl and dried in a hot air oven at 70 °C for 8 hours and ground to pass a 0.425 mm screen using a stainless steel Wiley Mill. The samples were stored in plastic containers until further analysis.

3.2.1.4 Biological samples (Human tissues)

Blood (5 ml), hair (0.1-0.2 g) and nail (0.1-0.2 g) samples were collected from 50 automobile personnel having 5-25 years of experience in driving heavy vehicles along highways, apart from a reference group of 3 persons. The collected blood, hair and nail samples were immediately analysed for lead.

3.3 LABORATORY EXPERIMENTS

3.3.1 Transformation of lead in the urban soils

The chemistry and biotransformation of lead in urban soils under different moisture conditions were studied through laboratory closed incubation studies.

Bulk soil samples were collected from uncontaminated sites within Coimbatore urban limit. The soils represent two major groups that occur in Coimbatore district *viz.,* black soils (*Typic chromustert*) and red soils (*Typic haplustalf*). Some important characteristics are given in Table I. These soils were used in laboratory and pot experiments.

For this experiment 100 g of air dried black and red soils (< 2mm) was placed separately in 150 ml plastic cups. Lead at a rate equivalent to 0, 500 and 1000 mg Pb kg^{-1} soil was added as $Pb(NO_3)_2$ and thoroughly mixed. Two different moisture contents *viz.,* i. field capacity moisture and ii. alternate wetting and drying were imposed.

For field capacity moisture (M_1), water was added to the soil to achieve a final moisture content equivalent to field capacity (0.46 g g^{-1}). This moisture content was maintained throughout the incubation experiment for a period of 60 days. For alternate wetting and drying (M_2), initially the soil moisture content was maintained at field capacity. It was then allowed for drying until some hairline cracks occurred in the soil. The soil was then again wetted with required water. The alternate wetting and drying process was repeated for a period of 60 days. Soil samples were collected at a months interval.

Table I. Some important characteristics of experimental – urban soils

Characteristics	Black soil	Red soil
I. Physical		
1. Bulk density (Mg m^3)	1.38	1.41
2. Clay (%)	30.60	18.20
3. Silt (%)	12.20	21.80
4. Fine sand (%)	22.30	-
5. Coarse sand (%)	33.00	63.40
6. Texture	Sandy clay loam	Sandy loam
II. USDA Classification	*Typic chromustert*	*Typic haplustalf*
III. Chemical		
1. pH (1 : 2.5 H_2O)	7.67	6.30
2. EC (dSm^{-1})	1.62	0.53
3. Organic matter (%)	1.15	0.73
4. CEC (Cmol (p+) kg^{-1})	32.30	18.50
5. Total N (mg kg^{-1})	410.00	380.00
6. Total P (mg kg^{-1})	205.00	216.00
7. Total K (mg kg^{-1})	986.00	824.00
8. Total Pb (mg kg^{-1})	-	-
9. Total Fe_2O_3 (%)	2.87	4.22
10. Total Al_2O_3 (%)	4.24	6.70

The transformation of Pb was studied by determining changes in different fractions of Pb *viz.,* water-soluble-Pb, exchangeable-Pb, organic-Pb, iron-oxide bound-Pb and residual-Pb were examined following a sequential fractionation procedure according to Noble and Hughes (1991).

3.3.2 Adsorption of lead in urban soils

The adsorption of Pb in black and red soils at two different pHs *viz.,* 6 and 8 were determined by laboratory batch experiments.

Preliminary experiment was carried out to determine the equilibrium period required for achieving maximum adsorption. It has been shown that the adsorption of Pb was rapid and more than 90 per cent of adsorption of Pb occurred within 24 hrs. Therefore, a shaking period of 24 hrs was adopted in the batch experiment.

Both black and red soils were incubated after adding different levels of 0.1 M HCl or 0.1 M NaOH for three days. Then the resultant pHs were measured. The soil pHs of 6 and 8 were used in the adsorption study. Triplicate soil samples of 2 g (air dried, < 2 mm) of each soil (with pH 6 and 8) were shaken with 50 ml of different concentrations of Pb (0, 250, 500, 750 and 1000 mg kg^{-1} soil) for 24 hrs. After shaking the reaction mixtures thoroughly, they were centrifuged at 8000 rpm for 10 minutes, and filtered through Whatman No. 1 filter paper. The equilibrium Pb concentration was determined using Atomic Absorption Spectrophotometer. Lead adsorbed was calculated as the difference between the amount added and that remaining in the equilibrium solution.

3.3.3 Transport and mobility of lead in urban soils (Column experiment)

The transport and mobility (leaching) of lead in soil (black and red) and its possible impact on ground water quality were examined through an open column experiment.

The experimental device consisted of Poly Vinyl Chloride (PVC) tubes (5 cm internal diameter; 40 cm height). The bottom of the tubes were covered with nylon mesh and muslin cloth. The columns were gently packed with soils (air dried, < 2 mm) to a height of 30 cm having surface (0-15 cm) and subsurface (15-30 cm) layers with a bulk density of 1.2 Mg m^3 and 1.35 Mg m^3, respectively. These bulk densities were created to mimic the field environment.

Ten ml solutions containing varied levels of Pb (0, 250, 500, 750 and 1000 µg g^{-1}) were added on the surface soil and equilibrated for three days. Each treatment had three replicated columns which were randomly placed.

The soils were leached with 500 ml of distilled water and the leachates were collected in conical flask. The leachate collected was digested using aquaregia and the total Pb was measured using Atomic Absorption Spectrophotometer.

The soil samples were collected from both surface and subsurface layers carefully, and the pHs and Pb accumulation in the soils were determined.

3.3.4 Remediation Experiments

Technologies for remediating lead contaminated urban soils were evaluated through laboratory and pot culture experiments.

3.3.4.1 Availability of Lead in Plants

Biological wastes (farm yard manure, compost etc.) are known to reduce the phyto availability of heavy metals and thus its toxicity. Therefore, the effectiveness of coir pith, a waste from coconut industry, in reducing the Pb availability in soil was evaluated. The coir pith was composted as described below and used in the followed experiments.

Procedure for composting coir pith

An area of 8 m x 3 m was selected. One hundred kilogram of coir pith (approximately 2 cm height) was spread uniformly on the marked area. 300 g of spawn (*Pleurotus sajor caju*) was spread on the coir waste. This layer was covered with another hundred kilogram of coir waste, over which one kilogram of urea was applied. The process of sandwitching *Pleurotus* and urea, alternatively with one hundred kilogram of coir waste was repeated, until the heap reached a height of 1 m. To compost one tonne of coir waste, 1500 g of *Pleurotus* and five kilogram of urea were required. Water was sprinkled on the heap to maintain the moisture content to 200 per cent. The heap was maintained for 30 days for decomposition. At the end of 30 days, the coir waste turned into a black mass of compost with reduced C : N ratio and increased nutrient content.

Then 100 g of black soil was incubated with Pb at 1000 mg kg^{-1} as $Pb(NO_2)_3$ in the presence and absence of composted coir pith in small plastic cups for a period of 60 days. A control was maintained simultaneously. The samples were replicated and the treatments were given as follows :

T_1 – control soil
T_2 – 1000 mg Pb kg^{-1} soil
T_3 – 1000 mg Pb kg^{-1} composted coir pith @ 50 g kg^{-1} soil + soil

At fortnight intervals samples were withdrawn from the incubation cups and analysed for plant available Pb. The sample (1g) was extracted with 25 ml of Diethyl Triamine Penta Acetic Acid (DTPA) and analysed for Pb content (Lindsay and Norvell, 1978).

3.3.4.2 Pot experiment on Phytoremediation

Phytoremediation is an emerging technology in which plants, capable of extracting large amounts of metal and / or tolerating high concentration of metals in soil, are used. In this study castor (*Ricinus communis*), a naturally grown plant was evaluated for Pb uptake, accumulation and tolerance in pot experiment.

Syntex / mud pots with a capacity of 3 kg were used. Two kilograms of black soil (air dried, < 2mm) was weighed and transferred into each pot. The soil was then artificially contaminated with different rates of Pb (0, 250, 500, 750 and 1000 mg Pb kg^{-1} soil) using $Pb(NO_3)_2$ solution, in the presence and absence of composted coir pith at a rate of 12.5 t ha^{-1}.The following

treatments in triplicate were imposed with a total of 30 pots which were randomly placed in a factorial design.

After a week in each pot, three seeds of castor were sown and enough water was added to maintain the field capacity moisture content, throughout the experimental period.

After 45 days of sowing, the plants were uprooted and the growth parameters such as root length, shoot length, number of leaves and biomass were recorded.

The plant samples (root, shoot and leaves) were dried in an oven at 60°C and analysed for Pb content. After the harvest the soil samples were collected from pots and analysed for pH and DTPA extractable Pb.

Treatments

T_1 - Control (soil alone)
T_2 - 250 mg Pb kg^{-1} of soil
T_3 - 500 mg Pb kg^{-1} of soil
T_4 - 750 mg Pb kg^{-1} of soil
T_5 - 1000 mg Pb kg^{-1} of soil
T_6 - Composted coir pith (ccp) alone (50g)
T_7 - 250 mg Pb kg^{-1} of soil + 50 g ccp
T_8 - 500 mg Pb kg^{-1} of soil + 50 g ccp
T_9 - 750 mg Pb kg^{-1} of soil + 50 g ccp
T_{10} - 1000 mg Pb kg^{-1} of soil + 50 g ccp

The castor plants were uprooted at 45 days after sowing and the growth parameters such as root length (cm), shoot length (cm), number of leaves and biomass in terms of plant fresh weight (g) were recorded.

The accumulation of Pb in different parts (roots, shoots and leaves) of castor as influenced by application of different rates of $Pb(NO_3)_2$ with and without composted coir pith amendment were analysed. The uprooted plants were oven dried at 60°C to get a constant weight. The roots, shoots and leaves were separately digested with aquaregia (HCl : HNO_3 1:3), made up to 50 ml with double distilled water, filtered through Whatman No. 42 filter paper and were analysed for lead using AAS.

3.5 CHEMICAL ANALYSIS

3.5.1 pH and EC

The pH and Electrical Conductivity (EC) of soil were measured in H_2O (1 : 2.5) after one hour equilibration using ELTOP digital pH meter (3020) and Delux Conductivity meter -601 E, respectively. The pH and EC were directly measured in water samples immediately after collection (Jackson, 1973).

3.5.2 Analysis of lead

3.5.2.1 Lead in soil

One gram of soil was digested with 10-15 ml freshly prepared aquaregia (HCl: HNO_3 at 3:1) at 110°C for 2 hours in a hot plate and made up to 50 ml using double distilled water. After filtration (Whatman No.42) and

centrifugation (8000 rpm ; 10 min), total Pb concentration was measured using an Atomic Absorption Spectrophotometer (Varian SpectrAA-200) with air- acetylene flame (USEPA, 1977). The wavelength at 358 nm was used with a spectral slit width of 0.2 nm. Moisture factor was applied to express the results on oven dry weight basis.

3.5.2.2 Lead in water

The water soluble (or solution phase) Pb fraction was determined in the water samples after filtration through Whatman No. 42 filter paper. To determine the total Pb content, the water samples were digested using aquaregia at 1 : 2 ratio at 110°C for about 2 hours, since the results of Mahimairaja *et al.* (1997) showed that the determination of heavy metals in undigested and filtered water samples recorded reduction in the recovery of total metal content. Acid digestion recovers metals both in solution and in colloidal particles. Therefore water samples were subjected to acid digestion. After filtration and appropriate dilution, Pb was determined using an Atomic Absorption Spectrometer (USEPA, 1977).

3.5.2.3 DTPA extractable Pb

Ten g of soil was extracted with 50 ml of DTPA extract for 2 hrs. After centrifugation (8000 rpm : 10 min) and filtration (Whatman No. 42) the Pb content was determined using Atomic Absorption Spectrophotometer (Lindsay and Norvel, 1978).

3.5.2.4 Lead in plants

One gram of dried sample was digested with 15-20 ml aquaregia at 110° for 2 hours, and made up to 50 ml using double distilled water. After filtration (Whatman No. 42), the Pb content was determined in the extract using an Atomic Absorption Spectrophotometer.

3.5.2.5 Lead in human tissues

The samples of blood (5 ml), hair (0.1 - 0.2 g) and nail (0.1 - 0.2 g) collected from automobile personnel were immediately digested with 5 ml aquaregia at 110°C for one hour and made up to 25 ml (using double distilled water) and filtered through Whatman No. 42 filter paper. Then the Pb content was measured through an Atomic Absorption Spectrophotometer.

3.5.2.6 Fractionation of lead

A sequential fractionation procedure according to Noble and Hughes (1991) was adopted to determine the various fractions (species) of Pb. Duplicate one gram of air dried soil sample was shaken end-over-end with 25 ml of double distilled water (repeated two times and the data combined) at 20 ± 2°C for 2 hours in a 50 ml polypropylene centrifuge tube. The tube was then centrifuged at 8000 rpm for 10 minutes and filtered through Whatman No.40 filter paper.The soluble-Pb in the water extract was determined using AAS (air - acetylene).

To the residue in the tube 25 ml of 0.5M KNO_3 was added and shaken for 16 hours and then centrifuged and filtered. The exchangeable and sorbed Pb was determined in the extract. This was followed by extraction with 0.5 M NaOH for 16 hours and 0.05M Na_2EDTA for 6 hours and the fractions of organic -Pb and iron oxide bound Pb respectively were determined. Finally, the sample residue was digested with 4M HNO_3 at 80°C for 16 hours and the fractions of residual-Pb content was determined. The amounts of Pb extracted by each extractant were computed by the following equation.

$$\text{Pb extracted (mg kg}^{-1}) = C \times (25 + M) - (C^a \times M)$$

where

C = concentration of Pb in the extraction solution (µg/g)

C^a = concentration of Pb in the extractant of preceeding step of the sequence (µg/g)

M = Mass of the entrained solution carried over from the previous extraction solution (µg/g)

25 = Volume of extractant (ml)

3.6 STATISTICAL ANALYSIS

Analysis of variance was used to compare treatment means wherever necessary. The least significant difference (LSD) between means was calculated. The LSD was used in conjuction with Duncan's multiple range test (Panse and Sukhatme, 1985).

RESULTS

CHAPTER IV
RESULTS

Environmental pollution due to Pb is a cause of concern in most of the developed and developing countries. Automobile emissions are the major source of Pb pollution in the urban environment soil contamination which can have dire consequences, such as loss of ecosystem and agriculture productivity, tainted water sources, diminished food chain quality, economic loss and human and animal illness. The present study was undertaken to investigate the extent of Pb contamination in soil, water and plants along NH 47 (Plates 2 and 3), SH 10 (Plates 4 and 5) and inner city and its effect on human tissues.

Results pertaining to the analysis of pH, EC and Pb of soil and water and Pb content in plant and human tissues are explained in this chapter.

4.1 Status of Pb pollution in the urban environment

4.1.1 Estimation of pH, Electrical Conductivity and Lead content of soil samples

4.1.1.1 Analysis of pH, Electrical Conductivity and Lead content of soil collected along National Highway 47 (Table II)

pH of soil

The pH of the surface and subsurface soil samples collected along NH 47 ranged from 6.92 to 8.80 and 6.20 to 9.34. The minimum and maximum values were recorded at sites 19 and 1 for surface soils and at sites 8 and 1 for subsurface soils.

Table II. pH, EC and Pb content of soil collected along National Highway 47

Site	pH		EC (dSm^{-1})		Pb ($mg\ kg^{-1}$)	
	Surface soil	Subsurface soil	Surface soil	Subsurface soil	Surface soil	Subsurface soil
1.	8.80	9.34	0.30	0.22	26.43	49.93
2.	8.45	6.22	0.97	0.32	44.92	61.68
3.	7.25	8.00	1.39	0.41	32.18	49.93
4.	7.48	7.88	2.08	0.37	40.43	41.68
5.	7.70	8.04	0.23	0.33	32.18	27.43
6.	7.90	7.90	0.11	0.10	26.42	71.18
7.	7.60	7.87	0.27	0.14	48.68	66.88
8.	7.50	6.20	0.73	0.22	54.93	41.85
9.	8.35	7.75	0.21	0.40	61.68	54.93
10.	8.00	7.90	0.30	0.23	52.68	53.68
11.	8.23	7.04	0.55	0.20	29.93	44.93
12.	8.35	8.13	0.27	0.15	51.75	55.43
13.	7.75	7.36	1.60	2.38	45.93	36.68
14.	7.97	8.07	1.08	0.92	95.43	77.68
15.	8.31	8.17	1.43	0.67	25.93	121.43
16.	8.45	8.24	0.90	0.73	45.64	104.18
17.	8.53	7.29	0.29	1.75	65.68	26.25
18.	8.50	8.00	0.80	0.45	129.68	94.93
19.	6.92	6.27	0.29	0.25	158.93	19.93
20.	8.57	8.10	0.80	1.11	52.18	216.68
SEd	0.11		0.03		0.25	
LSD (5%)	0.21		0.07		0.49	

Electrical Conductivity of soil

The EC of the surface and subsurface soils ranged from 0.11 to 2.08 and 0.10 to 2.38 dSm^{-1}, recording minimum and maximum values at sites 6 and 4 for surface samples and at sites 6 and 13 for subsurface soils.

Lead content of soil

The concentration of Pb in soil samples collected along NH 47 ranged from 25.93 to 158.93 mg kg^{-1}, recording minimum value at site 15 and maximum at site 19. Whereas, the Pb concentration in subsurface soil ranged from 19.93 to 216.68 mg kg^{-1}, recording minimum and maximum values at sites 19 and 20 respectively (Figure 2).

4.1.1.2 Analysis of pH, Electrical Conductivity and Lead content of soil collected along State Highway 10 (Table III)

pH of soil

The surface and subsurface soils collected along State Highway 10 showed pH values ranging from 7.79 to 8.92 and 7.80 to 8.60, recording minimum and maximum values at sites 13 and 20 for both surface and subsurface soils.

Electrical Conductivity of soil

The EC of the soils ranged from 0.10 to 1.73 dSm^{-1}, recording minimum and maximum values at sites 3 and 8 for surface samples and for subsurface soils, the EC values varied from 0.12 to 1.00 dSm^{-1}, with minimum and maximum values being recorded at sites 7 and 8 respectively.

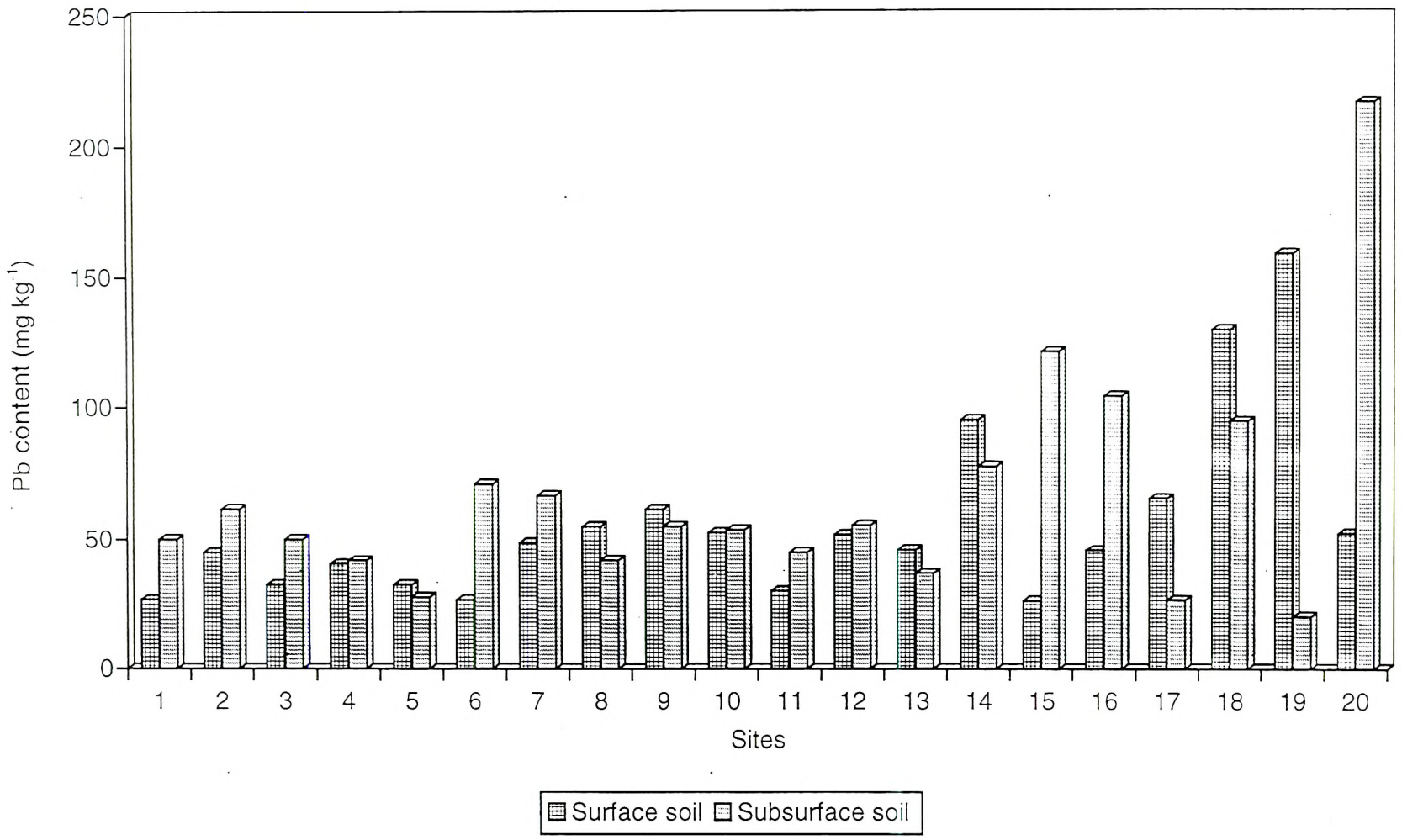


Figure 2. Pb content of soil samples collected along NH 47

Table III. pH, EC and Pb content of soil collected along State Highway 10

Site	pH		EC (dSm^{-1})		Pb ($mg\ kg^{-1}$)	
	Surface soil	Subsurface soil	Surface soil	Subsurface soil	Surface soil	Subsurface soil
1.	8.44	8.39	0.26	0.28	129.43	59.93
2.	8.05	7.86	0.12	0.25	36.68	53.68
3.	8.30	8.33	0.10	0.13	52.68	126.18
4.	8.08	8.33	0.25	0.23	32.18	111.93
5.	8.10	8.40	0.18	0.13	48.68	52.68
6.	7.90	8.19	0.19	0.13	97.43	94.18
7.	8.07	8.22	0.25	0.12	77.68	49.68
8.	8.35	8.40	1.73	1.00	123.68	157.68
9.	7.95	8.00	0.90	0.40	31.93	30.18
10.	8.16	8.16	0.25	0.22	39.68	38.68
11.	8.15	7.94	0.15	0.20	139.18	138.68
12.	7.90	8.04	0.38	0.17	127.68	178.93
13.	7.79	7.80	0.51	0.31	165.93	48.18
14.	8.10	7.84	0.28	0.26	221.42	324.68
15.	8.15	8.08	0.60	0.38	145.18	114.18
16.	8.23	8.16	0.20	0.24	52.18	63.18
17.	8.13	8.13	0.16	0.16	116.43	31.93
18.	8.02	8.02	0.27	0.14	86.18	77.68
19.	7.95	8.33	0.26	0.14	82.93	73.68
20.	8.92	8.60	0.70	0.42	64.93	48.18
SEd	0.12		0.02		0.23	
LSD (5%)	0.23		0.05		0.45	

Lead content of soil

Lead content in the soils collected along State Highway 10 varied from 31.93 to 221.42 mg kg^{-1} for surface soils and 30.18 to 324.68 mg kg^{-1} for subsurface soils. The minimum and maximum values were observed at sites 9 and 14 for both surface and subsurface soils (Figure 3).

4.1.1.3 Analysis of pH, Electrical Conductivity and Lead content of inner city soils

4.1.1.3.1 Avinashi Road (East) (Table IV)

pH of soil

The pH of the surface and subsurface soils collected from Coimbatore inner city along Avinashi road varied from 7.69 to 8.30 and 7.56 to 8.46. The lowest pH values of surface soils were noticed at two sites 8 and 17 and the highest at the site 4. The subsurface soil samples showed the minimum value at site 8 and maximum value at site 4.

Electrical Conductivity of soil

The EC of the surface soil varied from 0.13 to 1.64 dSm^{-1}. The minimum and maximum values were observed from the sites 2 and 20. The lowest and the highest values of subsurface soil were noticed as 0.13 and 2.40 dSm^{-1} at sites 2 and 7 respectively.

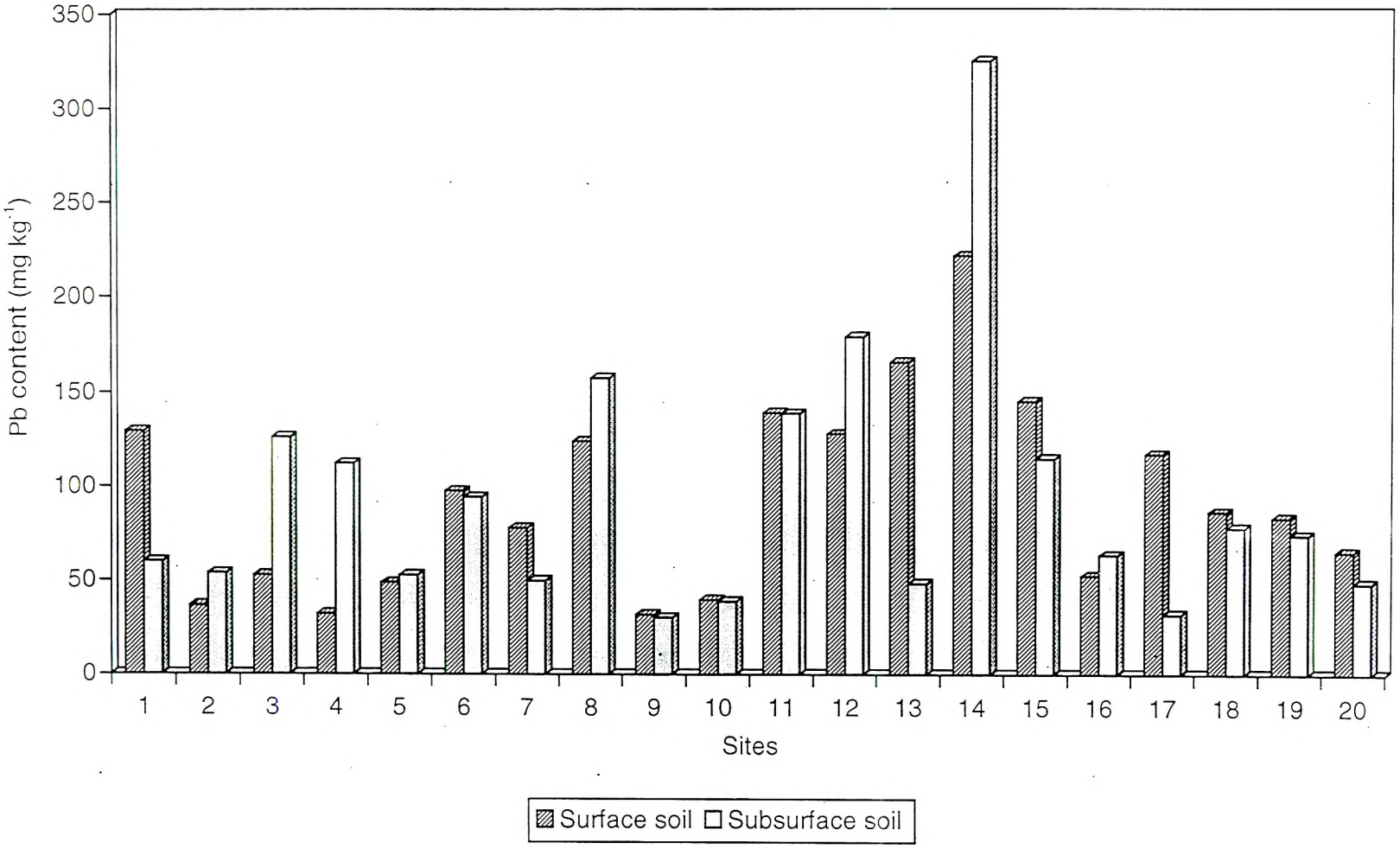


Figure 3. Pb content of soil samples collected along SH 10

Table IV. pH, EC and Pb content of soil collected along Avinashi Road (East)

Site	pH		EC (dSm^{-1})		Pb ($mg\ kg^{-1}$)	
	Surface soil	Subsurface soil	Surface soil	Subsurface soil	Surface soil	Subsurface soil
1.	7.80	7.85	0.42	0.56	61.93	55.68
2.	7.72	8.00	0.13	0.13	40.93	33.43
3.	8.26	8.30	0.30	0.35	83.93	33.93
4.	8.30	8.46	0.17	0.14	91.68	39.43
5.	8.21	8.01	0.40	0.65	52.18	44.18
6.	7.99	7.70	0.50	1.24	70.68	59.43
7.	7.85	7.74	1.19	2.40	112.58	82.68
8.	7.69	7.56	0.59	0.63	61.18	58.18
9.	7.90	7.80	0.48	0.62	27.68	43.43
10.	7.80	7.90	0.49	0.65	73.43	43.43
11.	7.74	7.73	0.73	0.93	58.18	59.68
12.	7.70	7.62	0.52	0.69	55.68	77.68
13.	7.72	7.72	1.05	0.91	62.18	52.43
14.	7.86	7.86	0.46	0.47	63.93	50.68
15.	8.00	7.78	0.54	1.07	62.68	30.43
16.	7.85	7.76	0.27	0.75	60.93	46.93
17.	7.69	7.67	0.64	0.80	66.93	78.93
18.	7.90	8.00	0.31	0.26	62.68	77.93
19.	8.05	8.05	0.36	0.22	83.93	96.18
20.	7.76	7.84	1.64	1.42	52.18	85.68
SEd	0.09		0.04		0.16	
LSD (5%)	0.17		0.07		0.31	

Lead content of soil

High concentration of Pb was observed in the soils along the busy traffic Avinashi road. The concentration of Pb in soil samples ranged from 27.68 to 112.58 mg kg^{-1}, recording minimum and maximum values at sites 9 and 7 for surface soils, whereas, the concentration of Pb in the subsurface soils ranged from 30.43 to 96.18 mg kg^{-1}, with minimum value at site 15 and maximum value at site 19 (Figure 4).

4.1.1.3.2 Saibaba Colony Road (West) (Table V)

pH of soil

The pH of the soil samples collected from Saibaba Colony road ranged from 7.42 to 8.17, recording minimum and maximum values at sites 20 and 15 for surface soil samples.The subsurface soil samples showed a range of pH from7.45 to 8.38 with minimum value at sites 8 and 9 and maximum at site 15.

Electrical Conductivity of soil

The EC values varied from 0.18 to 2.34 dSm^{-1} and from 0.20 to 1.39 dSm^{-1}, recording minimum and maximum values at sites 11 and 19 for surface soils and at sites 6 and 19 for subsurface soils.

Lead content of soil

The concentration of Pb in surface soils ranged from 25.43 to 128.93 mg kg^{-1}, recording the minimum and maximum values at sites 14 and 18, whereas, the Pb concentration in the subsurface soils varied from 23.18 to

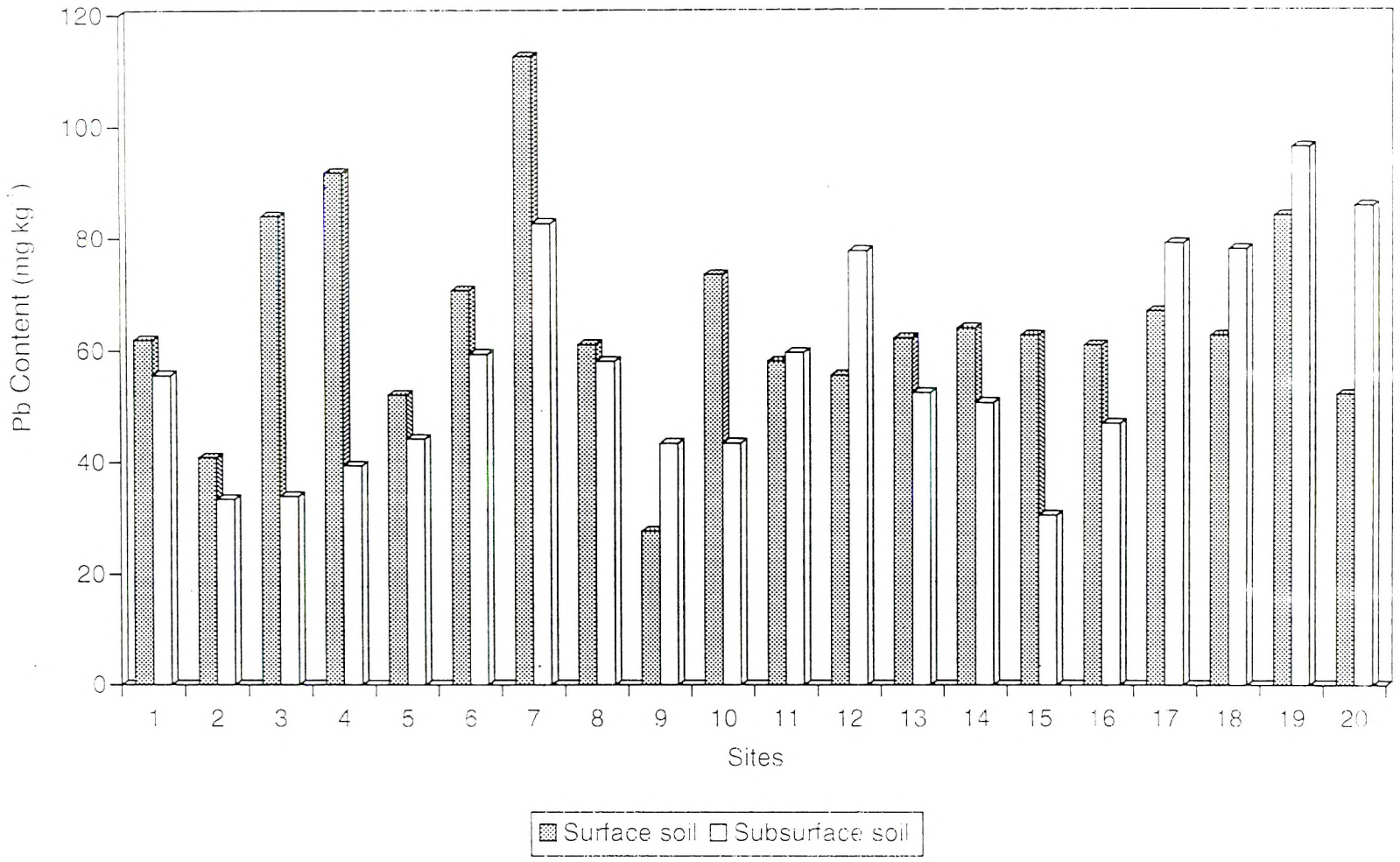


Figure 4. Pb Content of soil samples collected along Avinashi road

Table V. pH, EC and Pb content of soil collected along Saibaba Colony Road (West)

Site	pH		EC (dSm^{-1})		Pb ($mg\ kg^{-1}$)	
	Surface soil	Subsurface soil	Surface soil	Subsurface soil	Surface soil	Subsurface soil
1.	7.50	7.53	0.78	1.10	76.18	84.18
2.	8.00	7.76	0.42	0.58	52.68	40.68
3.	7.72	7.72	0.45	0.48	47.93	52.93
4.	7.75	7.86	0.65	0.71	27.18	23.93
5.	8.15	8.05	0.21	0.25	37.93	46.93
6.	8.07	7.82	0.26	0.20	48.68	42.96
7.	7.95	7.86	0.52	0.35	64.43	51.68
8.	7.50	7.45	1.29	0.71	41.18	41.68
9.	7.74	7.45	0.51	0.55	51.93	46.93
10.	7.50	7.80	0.38	0.53	42.43	40.68
11.	8.15	8.11	0.18	0.62	94.18	84.93
12.	7.82	7.65	0.95	1.39	37.68	24.43
13.	7.52	8.07	0.69	0.33	47.68	40.43
14.	7.52	7.85	0.95	0.78	25.43	23.18
15.	8.17	8.38	0.40	0.31	51.93	51.43
16.	7.98	7.84	0.20	0.92	45.68	55.68
17.	7.74	7.82	0.65	0.53	69.93	60.18
18.	7.78	7.90	1.15	1.29	128.93	118.68
19.	7.55	7.55	2.34	3.28	103.93	91.18
20.	7.42	7.90	0.88	0.82	72.68	105.68
SEd	0.14		0.06		0.32	
LSD (5%)	0.27		0.21		0.63	

118.68 mg kg^{-1} with the minimum and maximum values recorded from the same sites 14 and 18. The surface soils had higher concentration of Pb than the subsurface soils (Figure 5).

4.1.1.3.3 Mettupalayam Road (North) (Table VI and Plate 6)

pH of soil

The pH of the soils collected along the northern direction of the inner city covering the Mettupalayam road ranged from 7.22 to 9.93 and 7.38 to 8.54 with minimum and maximum values at sites 15 and 2 for surface soil samples and at sites 9 and 1 for subsurface soil samples.

Electrical Conductivity of soil

The EC of the soil samples ranged from 0.21 to 2.06 dSm^{-1}, recording the lowest and the highest values at sites 8 and 4 for surface soils. The EC of the subsurface soils showed a minimum value of 0.16 dSm^{-1} at 2 sites, 12 and 18. The highest EC value was 1.90 dSm^{-1} which was recorded from the site 4.

Lead content of soil

The Pb content in surface soils collected from Mettupalayam road ranged from 21.18 to 76.18 mg kg^{-1}, recording the minimum and maximum values at sites 14 and 11. Whereas, the concentration of Pb in the subsurface soils ranged from 23.93 to 67.43 mg kg^{-1}, recording the minimum and maximum values at sites 19 and 2. Similar concentrations of Pb were observed for both surface and subsurface soils (Figure 6).

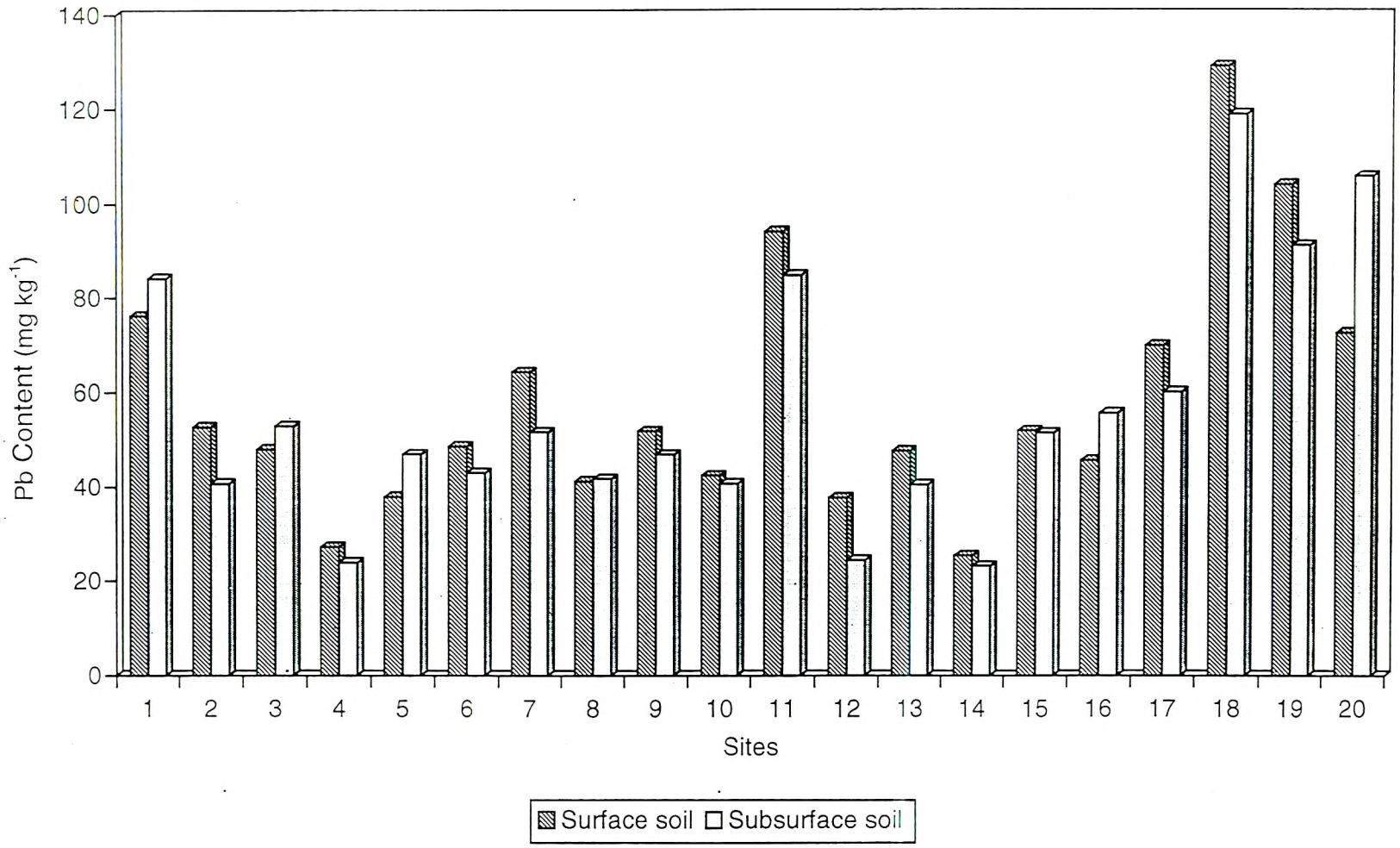


Figure 5. Pb Content of soil samples collected along Saibaba Colony road

Table VI. pH, EC and Pb content of soil collected along Mettupalayam Road (North)

Site	pH		EC (dSm^{-1})		Pb ($mg\ kg^{-1}$)	
	Surface soil	Subsurface soil	Surface soil	Subsurface soil	Surface soil	Subsurface soil
1.	7.70	8.54	1.56	1.06	40.18	25.93
2.	9.93	8.10	1.08	0.89	39.93	67.43
3.	8.12	7.56	0.74	1.22	29.18	40.18
4.	7.84	7.62	2.06	1.90	24.93	29.93
5.	7.45	7.78	0.75	0.40	28.68	37.68
6.	7.63	7.67	0.45	0.34	63.68	52.68
7.	7.91	7.64	0.30	0.59	28.43	43.93
8.	8.10	7.58	0.21	0.29	53.93	28.43
9.	8.00	7.38	0.75	0.58	31.43	41.18
10.	7.74	7.48	0.48	0.46	25.68	49.93
11.	8.00	7.85	0.67	0.34	76.18	47.93
12.	7.50	7.46	0.30	0.16	67.43	32.93
13.	7.86	8.06	0.28	0.21	35.93	31.68
14.	7.70	8.24	0.34	0.18	21.18	36.38
15.	7.22	7.80	1.43	0.55	36.93	37.18
16.	7.66	7.60	0.83	0.51	32.43	51.18
17.	7.80	7.91	0.23	0.22	36.93	46.68
18.	7.85	7.93	0.25	0.16	44.93	29.93
19.	8.19	7.99	0.27	0.24	39.93	23.93
20.	8.00	7.80	0.46	1.13	56.68	51.43
SEd	0.09		0.04		0.18	
LSD (5%)	0.18		0.08		0.36	

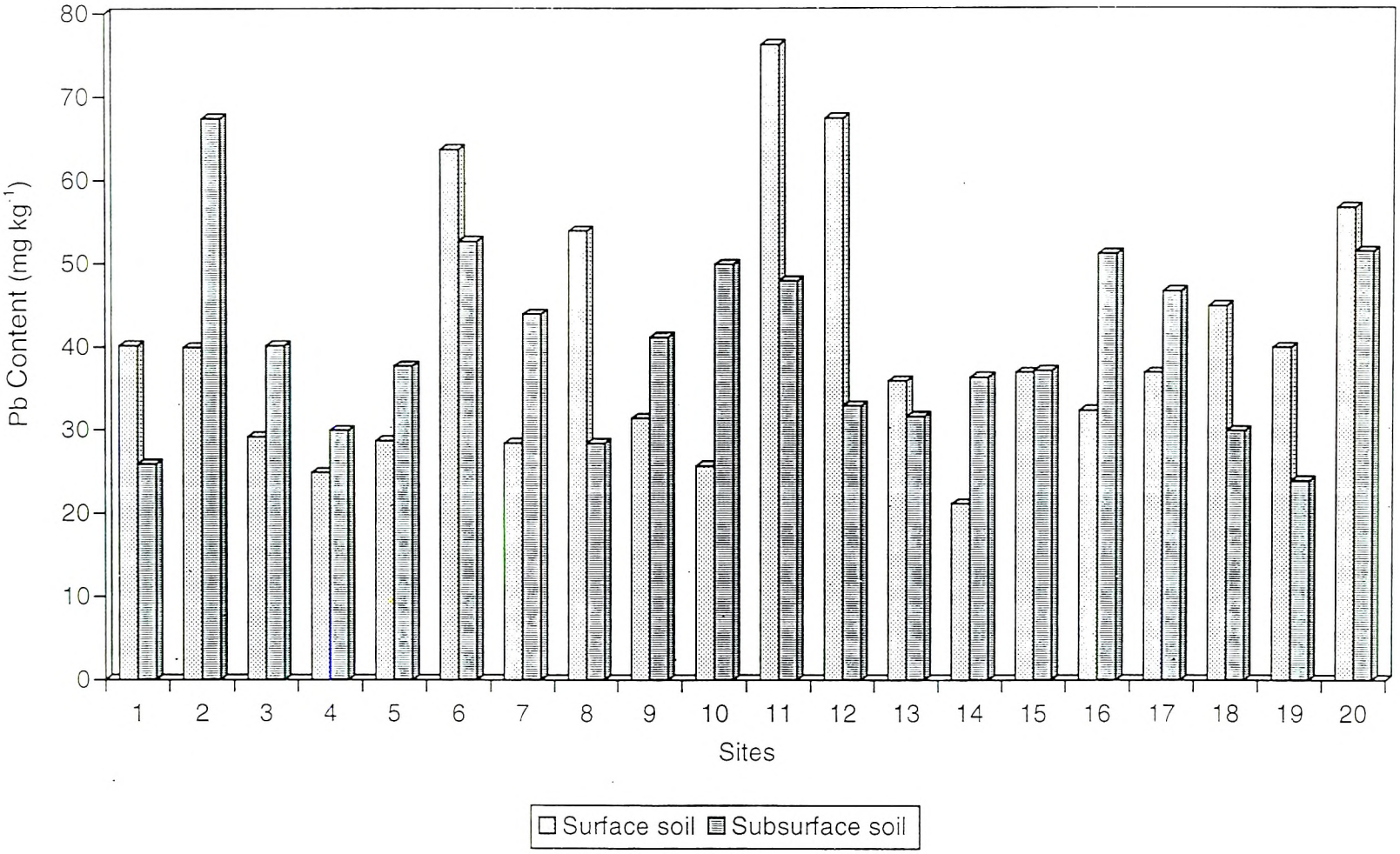


Figure 6. Pb Content of soil samples collected along Mettupalayam road

4.1.1.3.4 Town Hall Road (South) (Table VII)

pH of soil

The pH of the soil samples collected along Town Hall road ranged from 7.30 to 8.14, whereas, the pH of the subsurface soils ranged from 6.73 and 8.35. The minimum and maximum values were recorded at sites 5 and 1 for surface soils and at sites 19 and 20 for subsurface soils.

Electrical Conductivity of soil

The EC of the surface soils varied from 0.27 to 3.95 dSm^{-1} and the subsurface soils showed variations from 0.30 to 2.20 dSm^{-1}. The minimum and maximum values were recorded at sites 20 and 2 for surface soil and at sites 1 and 2 for subsurface soils.

Lead content of soil

The Pb concentrations were generally higher in soils collected along Town Hall road. Lead concentrations varied widely from 15.93 to 278.93 mg kg^{-1} in surface soils and from 6.43 to 266.18 mg kg^{-1} in subsurface soils. The minimum and maximum concentrations were observed at sites 14 and 3 for surface soil samples. The sites 3 and 17 showed the maximum and minimum concentrations of Pb in subsurface soils (Figure 7).

Table VII. pH, EC and Pb content of soil collected along Town Hall Road (South)

Site	pH		EC (dSm^{-1})		Pb ($mg\ kg^{-1}$)	
	Surface soil	Subsurface soil	Surface soil	Subsurface soil	Surface soil	Subsurface soil
1.	8.14	8.01	0.55	0.30	119.18	102.43
2.	7.72	7.78	3.95	2.20	87.86	179.43
3.	7.84	7.90	0.98	0.47	278.93	266.18
4.	7.93	7.85	0.60	0.54	65.68	52.43
5.	7.30	7.23	0.95	1.46	65.68	40.43
6.	7.41	7.47	0.80	1.83	72.43	53.18
7.	7.52	7.54	0.63	0.69	42.43	48.18
8.	7.76	7.53	0.44	0.98	60.68	191.43
9.	7.75	7.78	0.36	0.36	144.68	104.93
10.	7.73	7.64	0.47	0.77	63.68	63.68
11.	7.58	7.42	1.11	1.74	79.43	63.68
12.	7.78	7.78	0.56	0.59	67.43	40.93
13.	8.09	8.10	0.29	0.38	35.93	11.68
14.	7.54	7.62	1.92	0.94	15.93	10.18
15.	7.86	7.94	0.88	0.81	60.43	51.43
16.	7.86	7.86	0.49	0.51	42.18	68.68
17.	7.49	7.52	0.51	0.44	92.18	6.43
18.	7.61	7.63	0.47	0.51	54.18	78.68
19.	7.64	6.73	0.43	0.48	62.93	86.68
20.	8.06	8.35	0.27	1.70	65.18	103.93
SEd	0.07		0.04		0.17	
LSD (5%)	0.14		0.08		0.34	

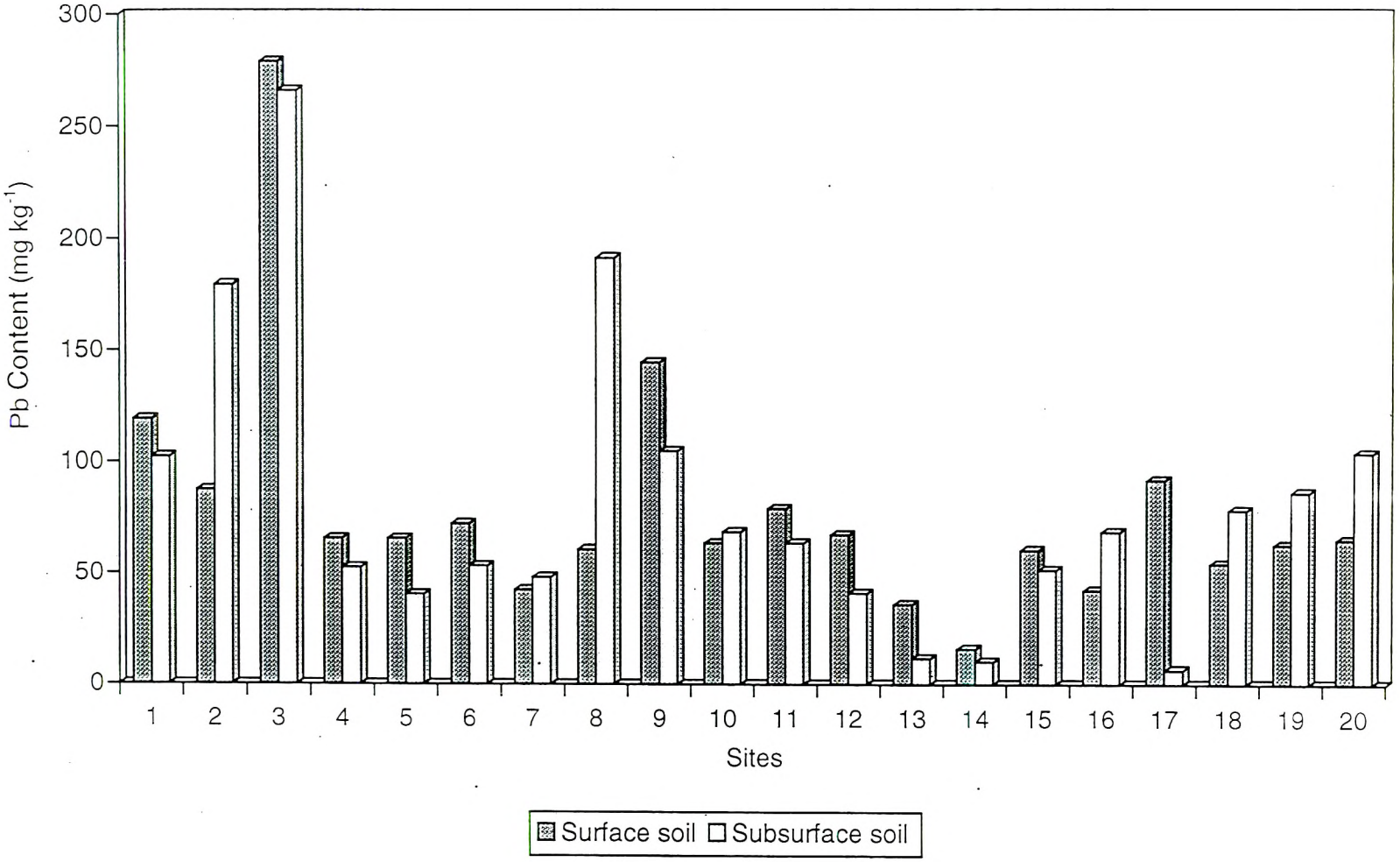


Figure 7. Pb Content of soil samples collected along Town Hall road

4.1.2 Estimation of pH, Electrical Conductivity and Lead content of water samples

4.1.2.1 Analysis of pH, Electrical Conductivity and Lead content of water samples collected along National Highway 47 (Table VIII)

pH of water

The pH of the water samples collected along National Highway 47 ranged from 7.50 to 8.95. The minimum and maximum values were observed at sites 17 and 19 respectively.

Electrical Conductivity of water

The EC of the water samples ranged from 0.13 to 1.99 dSm^{-1}, recording the minimum and maximum values at sites 11 and 8 respectively.

Lead content of water

The Pb concentrations in water samples along National Highway 47 ranged from 1.09 to 1.57 mg l^{-1}. The minimum concentration of Pb was observed at site 15 and the maximum concentration at site 10 (Figure 8).

4.1.2.2 Analysis of pH, Electrical Conductivity and Lead content of water samples collected along State Highway 10 (Table IX)

pH of water

The pH of the water samples collected from State Highway 10 ranged from 7.46 and 8.79. Among these samples the minimum value was recorded at site 19 and the maximum at site 14.

Table VIII. pH, EC and Pb content in water samples collected along National Highway 47

Site	pH	EC (dSm^{-1})	Pb ($mg\ l^{-1}$)
1.	8.52	0.55	1.37
2.	8.56	0.52	1.24
3.	8.51	0.51	1.19
4.	8.57	1.35	1.42
5.	7.81	1.63	1.49
6.	7.93	1.02	1.47
7.	7.80	1.18	1.49
8.	7.83	1.99	1.17
9.	8.77	0.89	1.54
10.	8.82	0.93	1.57
11.	7.66	0.13	1.42
12.	8.12	0.42	1.42
13.	7.95	1.01	1.19
14.	8.54	0.94	1.34
15.	7.83	1.30	1.09
16.	7.98	0.91	1.34
17.	8.95	0.16	1.19
18.	8.27	1.47	1.24
19.	7.50	1.24	1.34
20.	7.56	0.99	1.42
SEd	0.14	0.05	0.08
LSD (5%)	0.28	0.11	0.18

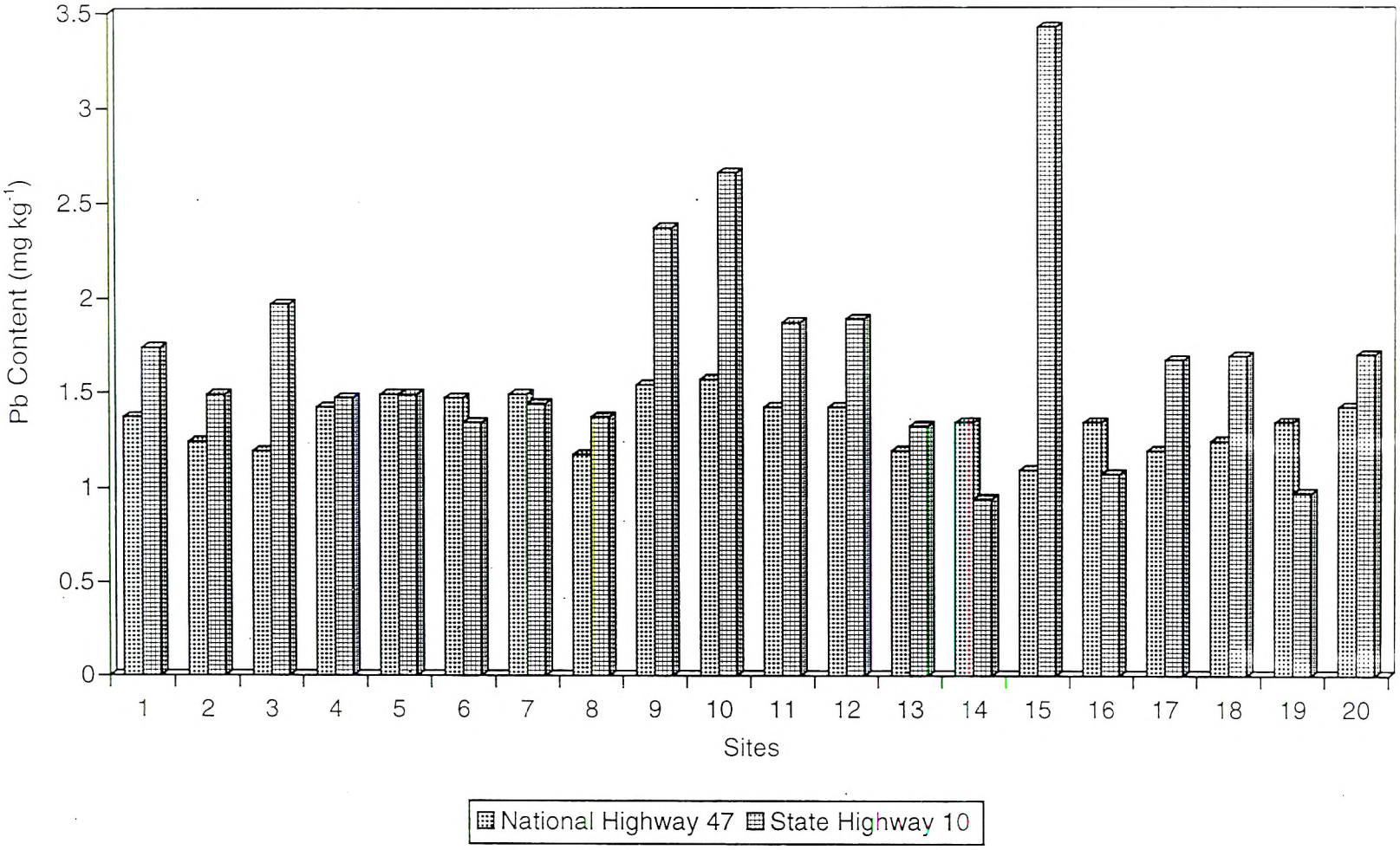


Figure 8. Pb content of water samples collected along Highways (NH 47 and SH 10)

Table IX. pH, EC and Pb content in water samples collected along State Highway 10

Site	pH	EC (dSm^{-1})	Pb ($mg\ l^{-1}$)
1.	8.38	1.09	1.71
2.	8.10	2.35	1.49
3.	8.24	0.21	1.97
4.	8.00	0.07	1.47
5.	8.18	0.21	1.49
6.	8.05	0.12	1.34
7.	8.10	0.11	1.44
8.	8.59	1.54	1.37
9.	8.15	1.05	2.37
10.	8.61	0.47	2.66
11.	8.46	0.91	1.87
12.	8.31	0.87	1.89
13.	8.35	1.85	1.32
14.	8.79	1.80	0.94
15.	7.81	0.16	3.42
16.	7.75	0.06	1.07
17.	7.69	4.19	1.67
18.	8.26	2.04	1.69
19.	7.46	0.44	0.97
20.	7.84	1.52	1.07
SEd	0.16	0.08	0.06
LSD (5%)	0.33	0.16	0.12

Electrical Conductivity of water

The EC of the water samples ranged from 0.06 to 4.19 dSm^{-1}, recording the minimum and maximum values at sites 16 and 17 respectively.

Lead content of water

The concentration of Pb in water samples ranged from 0.94 to 3.42 mg l^{-1}. The minimum concentration was recorded at site 14 and the maximum at site 15 (Figure 8).

4.1.2.3 Analysis of pH, Electrical Conductivity and Lead content of inner city water

4.1.2.3.1 Avinashi Road (East) (Table X)

pH of water

The pH of the water samples collected from Avinashi road ranged from 7.36 to 9.15. The minimum and maximum values were observed at sites 18 and 10 respectively.

Electrical Conductivity of water

The EC of the water samples ranged from 0.11 to 1.89 dSm^{-1}. The minimum and maximum values were observed at sites 3 and 4.

Table X. pH, EC and Pb content in water samples collected along Avinashi Road (East)

Site	pH	EC (dSm^{-1})	Pb ($mg\ l^{-1}$)
1.	7.80	0.61	1.12
2.	8.41	1.40	0.82
3.	8.16	0.11	1.54
4.	8.60	1.89	1.74
5.	7.81	0.15	1.74
6.	8.13	0.39	1.57
7.	8.02	1.14	1.14
8.	8.35	1.20	1.49
9.	8.05	0.21	0.97
10.	9.15	0.20	1.14
11.	8.32	0.24	0.90
12.	7.81	0.36	1.11
13.	7.83	0.29	1.60
14.	8.20	0.36	1.32
15.	7.75	1.32	1.15
16.	8.20	0.46	0.93
17.	8.16	0.23	1.45
18.	7.36	0.60	1.62
19.	8.70	1.00	1.53
20.	8.23	0.21	1.18
SEd	0.15	0.05	0.07
LSD (5%)	0.31	0.10	0.14

Lead content of water

The concentration of Pb in water samples ranged from 0.82 to 1.74 mg l^{-1}. The minimum concentration was observed at site 2 and the maximum concentration was noticed from the sites 4 and 5 (Figure 9).

4.1.2.3.2 Saibaba Colony Road (West) (Table XI)

pH of water

The pH of the water samples collected along Saibaba Colony road ranged from 7.20 to 8.10. The minimum and maximum values were observed at sites 1 and 15 respectively.

Electrical Conductivity of water

The EC of the water samples ranged from 0.06 to 2.56 dSm^{-1}. The minimum and maximum values were observed at sites 1 and 6 respectively.

Lead content of water

The concentration of Pb in water samples along Saibaba Colony road ranged from 1.07 to 1.45 mg l^{-1}. The minimum concentration of Pb was recorded at site 13 whereas, the maximum concentration was recorded at site 9 (Figure 9).

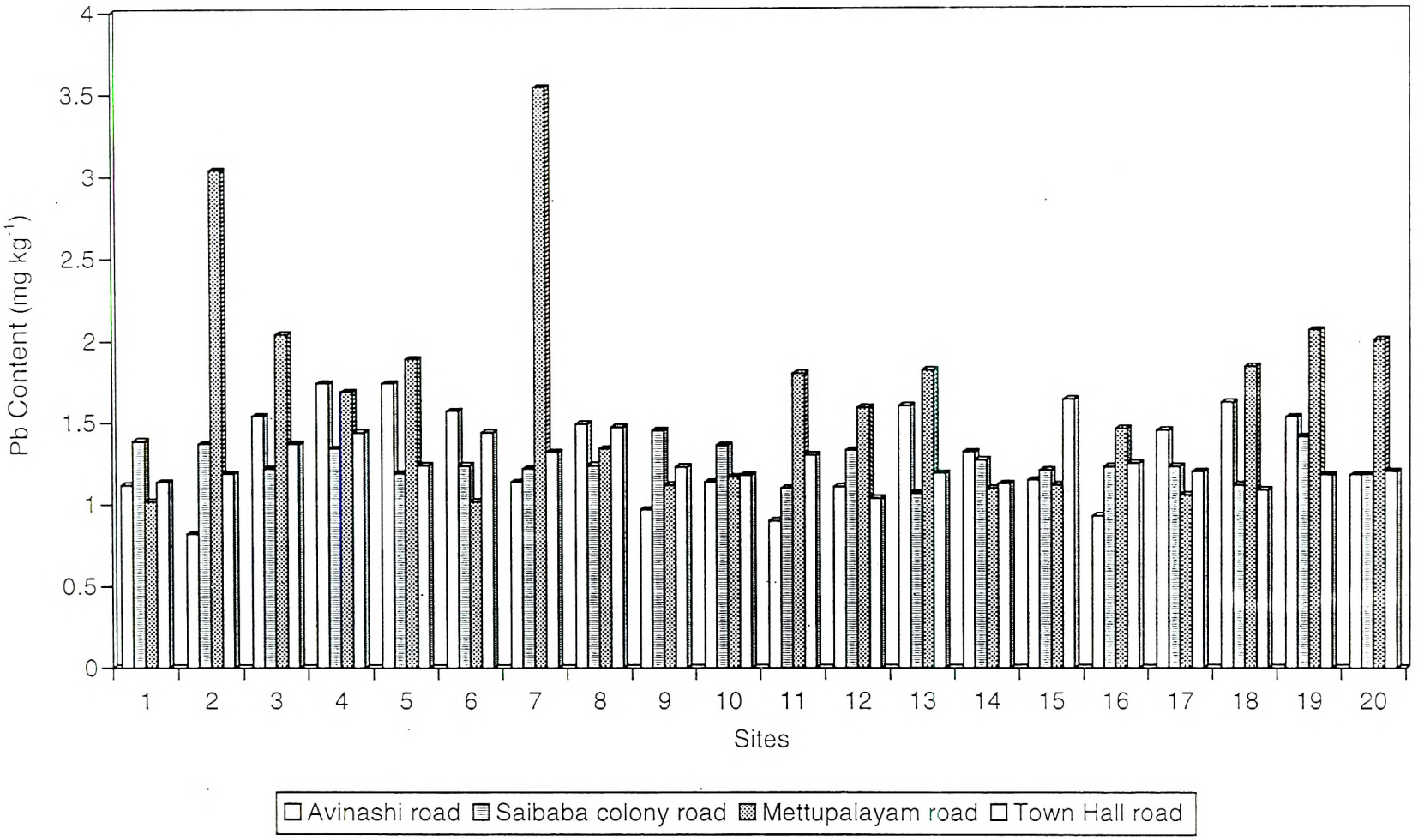


Figure 9. Pb Content of water samples collected along Inner city

Table XI. pH, EC and Pb content in water samples collected along Saibaba Colony Road (West)

Site	pH	EC (dSm^{-1})	Pb ($mg\ l^{-1}$)
1.	7.20	0.06	1.39
2.	7.50	0.09	1.37
3.	7.56	1.98	1.22
4.	8.05	1.88	1.34
5.	7.70	1.56	1.19
6.	7.83	2.56	1.24
7.	7.73	0.08	1.22
8.	7.87	1.95	1.24
9.	7.33	0.14	1.45
10.	7.56	0.16	1.36
11.	7.48	1.27	1.10
12.	7.62	1.62	1.33
13.	7.41	2.54	1.07
14.	7.98	1.55	1.27
15.	8.10	1.80	1.21
16.	7.26	1.86	1.23
17.	7.52	0.56	1.23
18.	7.43	1.24	1.12
19.	7.76	1.94	1.41
20.	7.68	1.30	1.18
SEd	0.13	0.03	0.08
LSD (5%)	0.27	0.07	0.16

4.1.2.3.3 Mettupalayam Road (North) (Table XII and Plate 7)

pH of water

The pH of the water samples collected along Mettupalayam road varied from 7.28 to 8.25. The minimum and maximum values were observed at sites 20 and 4 respectively.

Electrical Conductivity of water

The EC of the water samples varied from 0.10 to 3.78 dSm^{-1}. The minimum and maximum values were observed at sites 1 and 2 respectively.

Pb content of water

The concentration of Pb in the water samples ranged from 1.02 to 3.54 mg l^{-1}. The minimum concentration was recorded at two sites 1 and 6 and the maximum concentration of Pb was recorded at site 7 (Figure 9).

4.1.2.3.4 Town Hall Road (Table XIII)

pH of water

The pH of the water samples collected from Town Hall road varied from 7.78 to 8.88. The minimum value was observed at sites 12 and 18 and the maximum value at site 2.

Electrical Conductivity of water

The EC of the water samples ranged from 0.08 to 1.23 dSm^{-1}. The minimum and maximum values were observed at sites 7 and 3 respectively.

Table XII. pH, EC and Pb content in water samples collected along Mettupalayam Road (North)

Site	pH	EC (dSm^{-1})	Pb ($mg\ l^{-1}$)
1.	7.62	0.10	1.02
2.	7.33	3.78	3.04
3.	7.70	0.16	2.04
4.	8.25	1.87	1.69
5.	7.66	0.37	1.89
6.	8.12	1.89	1.02
7.	7.36	0.15	3.54
8.	7.92	1.41	1.34
9.	7.46	3.68	1.12
10.	7.40	0.57	1.17
11.	7.58	0.68	1.80
12.	7.79	0.42	1.59
13.	7.85	0.56	1.82
14.	7.39	1.37	1.10
15.	7.32	3.32	1.12
16.	7.30	0.42	1.46
17.	7.46	1.36	1.06
18.	7.38	0.55	1.84
19.	8.00	0.79	2.06
20.	7.28	0.98	2.00
SEd	0.10	0.04	0.06
LSD (5%)	0.21	0.08	0.12

Table XIII. pH, EC and Pb content in water samples collected along Town Hall Road (South)

Site	pH	EC (dSm^{-1})	Pb ($mg\ l^{-1}$)
1.	8.54	0.78	1.14
2.	8.88	0.26	1.19
3.	7.95	1.23	1.37
4.	8.08	0.73	1.44
5.	8.70	0.55	1.24
6.	7.95	0.10	1.44
7.	8.17	0.08	1.32
8.	8.04	0.41	1.47
9.	8.50	0.72	1.23
10.	8.06	0.22	1.18
11.	8.23	0.60	1.30
12.	7.78	0.12	1.04
13.	7.80	1.20	1.19
14.	8.00	1.01	1.13
15.	7.85	0.74	1.64
16.	8.50	0.23	1.25
17.	8.20	0.56	1.20
18.	7.78	0.21	1.09
19.	8.38	0.34	1.18
20.	7.99	0.40	1.20
SEd	0.08	0.03	0.07
LSD (5%)	0.17	0.05	0.15

Lead content of water

Lead concentration in the water samples ranged from 1.04 to 1.64 mg l^{-1}. The minimum and maximum values were recorded at sites 12 and 15 respectively (Figure 9).

4.1.3 Estimation of Lead content in Plants

To analyse the Pb concentrations, two plants were randomly selected from different locations. *Cyanodon dactylon* (Plate 8) was collected from National Highway 47 and State Highway 10 and *Boerhaavia diffusa* (Plate 9) from inner city (East, West, North and South).

4.1.3.1 Lead content of *Cyanodon dactylon* collected from Highway (Table XIV)

4.1.3.1.1 National Highway 47

The concentration of Pb in *Cyanodon dactylon* collected along National Highway 47 ranged from 13.43 to 79.93 mg kg^{-1}. Minimum concentration of Pb was recorded in plants collected from the site 6 and maximum concentration of Pb was recorded in plants collected from the site 5 (Figure 10).

4.1.3.1.2 State Highway 10

Lead content in plants collected from State Highway 10 ranged from 36.18 to 136.93 mg kg^{-1}. The minimum and maximum values were observed at sites 6 and 10 respectively (Figure 10).

Table XIV. Lead content in *Cyanodon dactylon* collected along Highways

Site	Pb (mg kg^{-1})	
	National Highway 47	State Highway 10
1.	35.68	112.18
2.	20.43	115.68
3.	16.93	45.18
4.	18.93	113.68
5.	79.93	111.68
6.	13.43	36.18
7.	52.68	82.43
8.	30.18	103.93
9.	16.93	131.93
10.	18.68	136.93
11.	25.18	67.43
12.	43.68	40.68
13.	30.43	77.43
14.	23.18	38.18
15.	42.18	77.68
16.	57.18	79.93
17.	35.43	70.93
18.	21.68	78.93
19.	34.43	44.93
20.	42.18	38.18
SEd	0.15	0.16
LSD (5%)	0.31	0.33

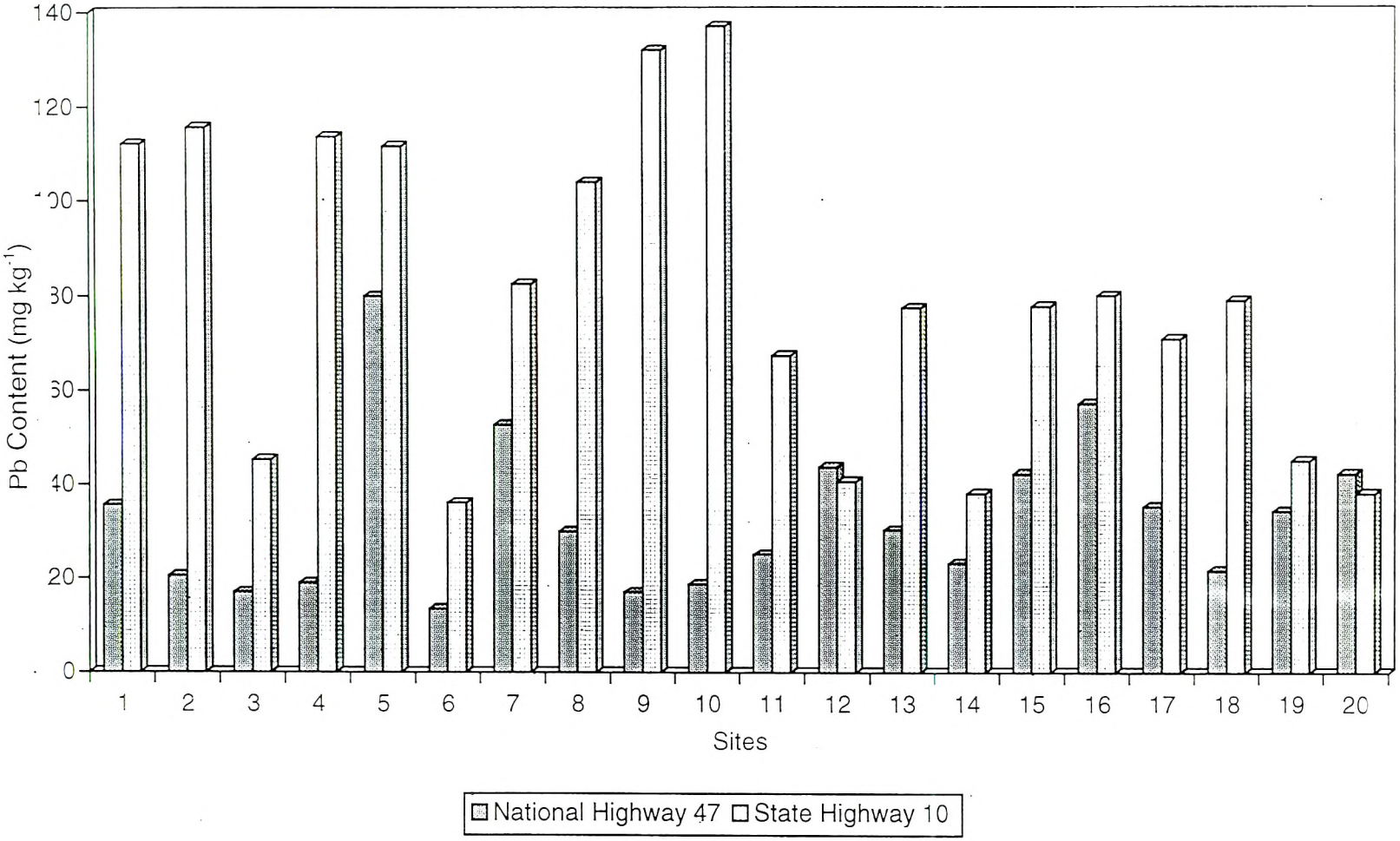


Figure 10. Pb content in *C. dactylon* collected from NH 47 and SH 10

4.1.3.2 Lead content of *Boerhaavia diffusa* collected from inner city (Table XV and Figure 11)

4.1.3.2.1 Avinashi Road (East)

The concentration of lead in *Boerhaavia diffusa* collected along Avinashi road varied from 25.18 to 78.43 mg kg^{-1}, recording the minimum concentration at site 19 and maximum at site 16.

4.1.3.2.2 Saibaba Colony Road (West)

Lead content in plants from Saibaba Colony road varied from 23.18 to 51.68 mg kg^{-1}. The minimum and maximum concentrations of Pb were recorded at sites 12 and 20 respectively.

4.1.3.2.3 Mettupalayam Road (North)

The concentration of Pb in plants along Mettupalayam road varied from 15.43 to 44.18 mg kg^{-1}. The minimum concentration was recorded at site 11 and the maximum concentration was recorded at site 5.

4.1.3.2.4 Town Hall Road (South)

Lead concentration of plants along Town Hall road varied from 25.43 to 68.18 mg kg^{-1}, recording the minimum and maximum concentrations at sites 9 and 5 respectively.

Table XV. Lead content in *Boerhaavia diffusa* collected along Coimbatore Inner city

Site	Pb (mg kg^{-1})			
	Avinashi Road (East)	Saibaba Colony Road (West)	Mettupalayam Road (North)	Town Hall Road (South)
1.	35.93	29.68	24.93	43.43
2.	34.68	49.93	33.68	27.93
3.	34.93	49.93	29.43	53.43
4.	35.18	28.68	23.18	27.93
5.	44.68	40.43	44.18	68.18
6.	34.43	32.68	26.68	28.68
7.	32.93	28.13	29.44	41.93
8.	35.93	33.43	29.44	31.68
9.	34.18	24.93	25.93	25.43
10.	64.43	33.43	39.93	32.68
11.	54.43	25.68	15.43	50.43
12.	57.68	23.18	25.10	29.43
13.	38.18	27.43	31.43	30.43
14.	36.68	27.43	23.18	30.43
15.	46.68	49.93	24.93	28.68
16.	78.43	49.93	26.46	31.68
17.	33.93	26.68	39.93	32.18
18.	35.93	25.68	29.93	29.18
19.	25.18	43.18	29.93	29.18
20.	33.68	51.68	26.93	30.18
SEd	0.30	0.22	0.38	0.24
LSD (5%)	0.60	0.45	0.77	0.47

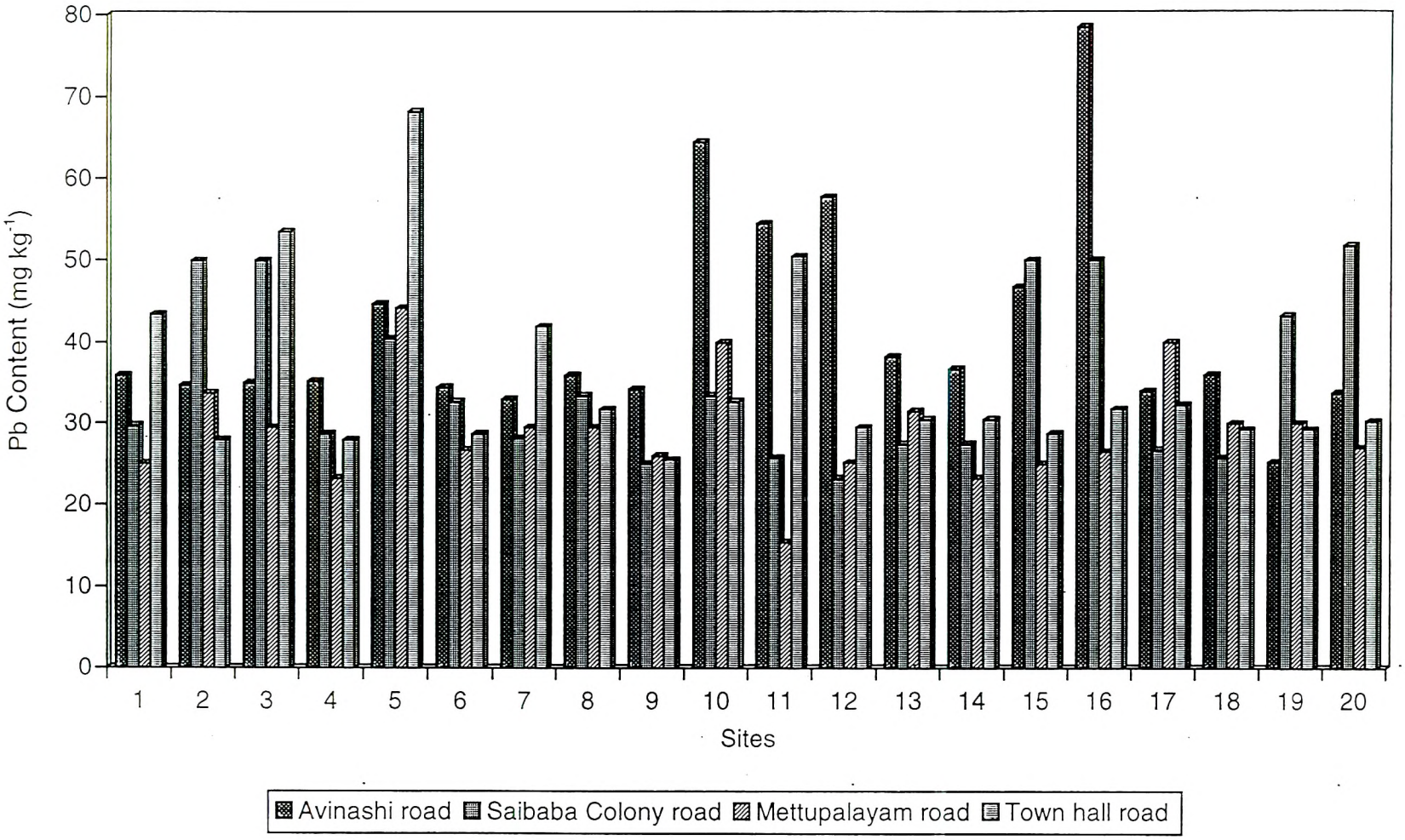


Figure 11. Pb content in *B. diffusa* collected from Inner city

4.1.4 Estimation of Pb concentration in biological samples (human tissues)

The impact of Pb contamination in soil, water and plant of urban environment on Pb accumulation in human tissues, particularly in blood, hair and nail samples of automobile personnel, was examined. The Pb content in blood, hair and nail of persons associated with automobiles is presented in Table XVI.

4.1.4.1 Lead content in blood samples

The levels of Pb in the blood of automobile personnel (Plate 10) ranged from 0.40 $\mu g\ ml^{-1}$ to 1.05 $\mu g\ ml^{-1}$. The different years of service did not influence the blood Pb of the personnel significantly. In fact the blood Pb of reference group did not differ significantly from personnel associated with automobiles (Figure 12).

4.1.4.2 Lead content in hair samples

Lead content in the hair of automobile personnel (Plate 11) ranged from 23.75 to 141.06 $\mu g\ g^{-1}$ against the reference group which ranged from 9.69 to 26.50 $\mu g\ g^{-1}$. Similar to blood-lead, the years of service had no significant effect on hair-Pb content, though the highest level of hair-Pb was found in persons with 5 years of service in driving heavy vehicles (Figure 13).

Table XVI. Lead content in blood, hair and nail samples of automobile personnels

S.No.	Year of service	Blood ($\mu g\ ml^{-1}$)	Hair ($\mu g\ g^{-1}$)	Nail ($\mu g\ g^{-1}$)
1.	5	0.80	50.08	128.57
2.	5	0.60	27.50	200.00
3.	5	0.72	61.50	136.00
4.	5	0.56	141.06	174.60
5.	5	0.64	48.73	155.33
6.	5	0.55	126.00	178.57
7.	5	0.78	50.30	92.37
8.	5	0.40	23.75	118.75
9.	5	0.47	44.35	162.43
10.	5	0.70	39.00	183.33
11.	10	0.55	71.42	185.71
12.	10	0.65	46.33	90.00
13.	10	0.45	50.00	106.50
14.	10	0.43	62.37	117.36
15.	10	0.70	48.38	287.50
16.	10	0.57	35.50	65.30
17.	10	0.52	48.83	180.45
18.	10	0.65	79.30	126.55
19.	10	0.60	49.20	130.55
20.	10	1.05	33.69	167.85
21.	15	0.60	30.30	120.00
22.	15	0.45	55.55	285.00
23.	15	0.55	68.30	104.95
24.	15	0.62	30.52	127.65
25.	15	0.72	53.06	178.50
26.	15	0.85	112.50	205.00
27.	15	0.55	60.33	196.30
28.	15	0.49	36.00	90.00
29.	15	0.72	33.10	157.00
30.	15	0.55	47.72	97.91
31.	20	0.62	47.36	136.20
32.	20	0.50	37.50	92.50
33.	20	0.82	50.36	126.30
34.	20	0.55	37.05	109.55
35.	20	0.55	110.00	197.33
36.	20	0.95	132.70	265.00
37.	20	0.61	36.20	165.71
38.	20	0.48	28.75	140.35
39.	20	0.41	37.33	120.00
40.	20	1.00	137.50	195.83
41.	25	0.51	28.33	112.36
42.	25	0.60	45.83	105.00
43.	25	0.60	27.50	61.11
44.	25	0.75	42.00	198.00
45.	25	0.55	71.25	142.85
46.	25	0.53	70.60	173.27
47.	25	0.65	44.73	130.35
48.	25	0.60	46.42	237.50
49.	25	0.78	55.50	200.00
50.	25	0.90	32.50	240.00
1.	Reference group	1.00	14.06	50.00
2.		0.60	26.56	42.85
3.		0.40	9.69	45.83
SEd		0.01	0.15	0.09
LSD (5%)		0.03	0.30	0.17

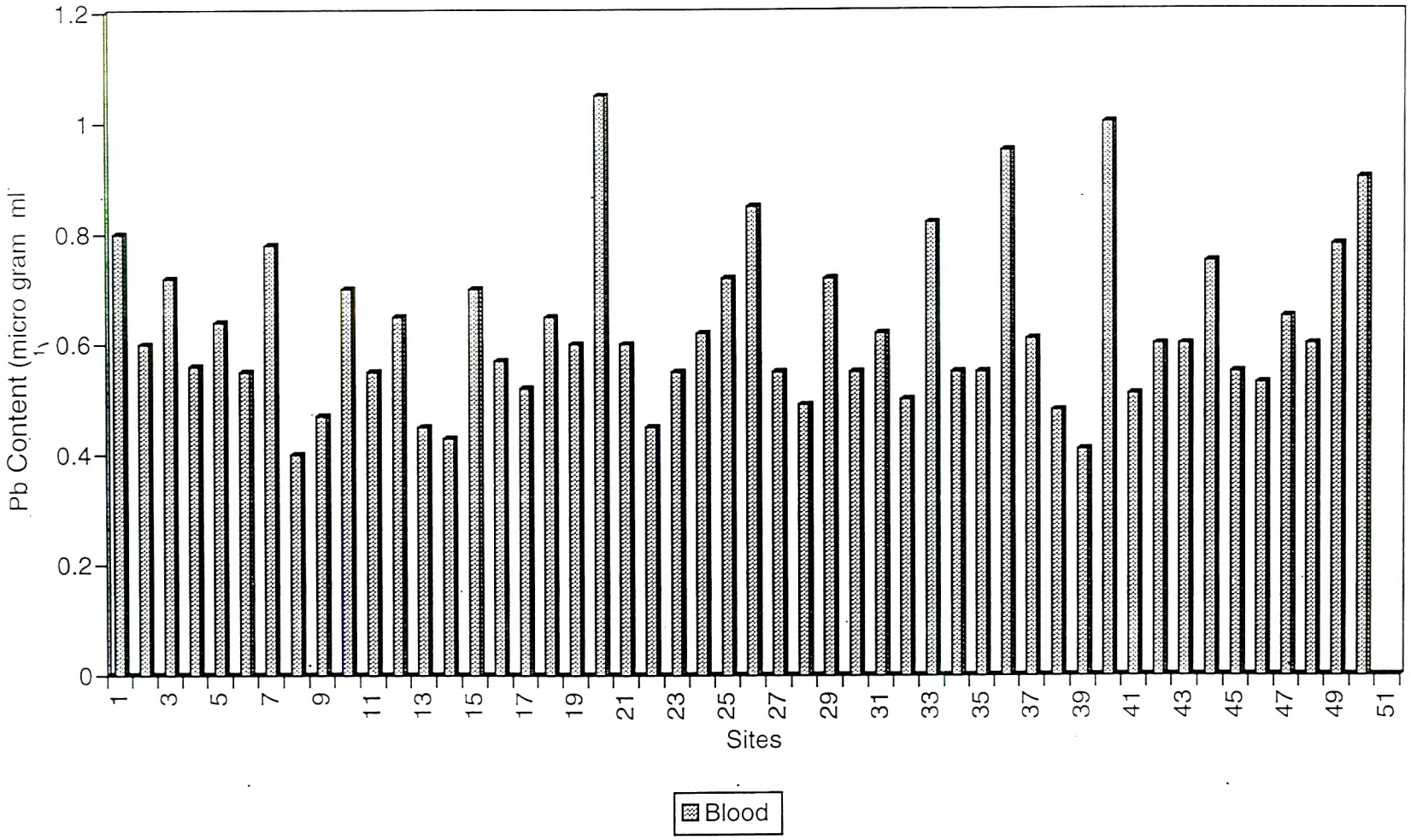


Figure 12. Pb Content in biological samples (Blood)

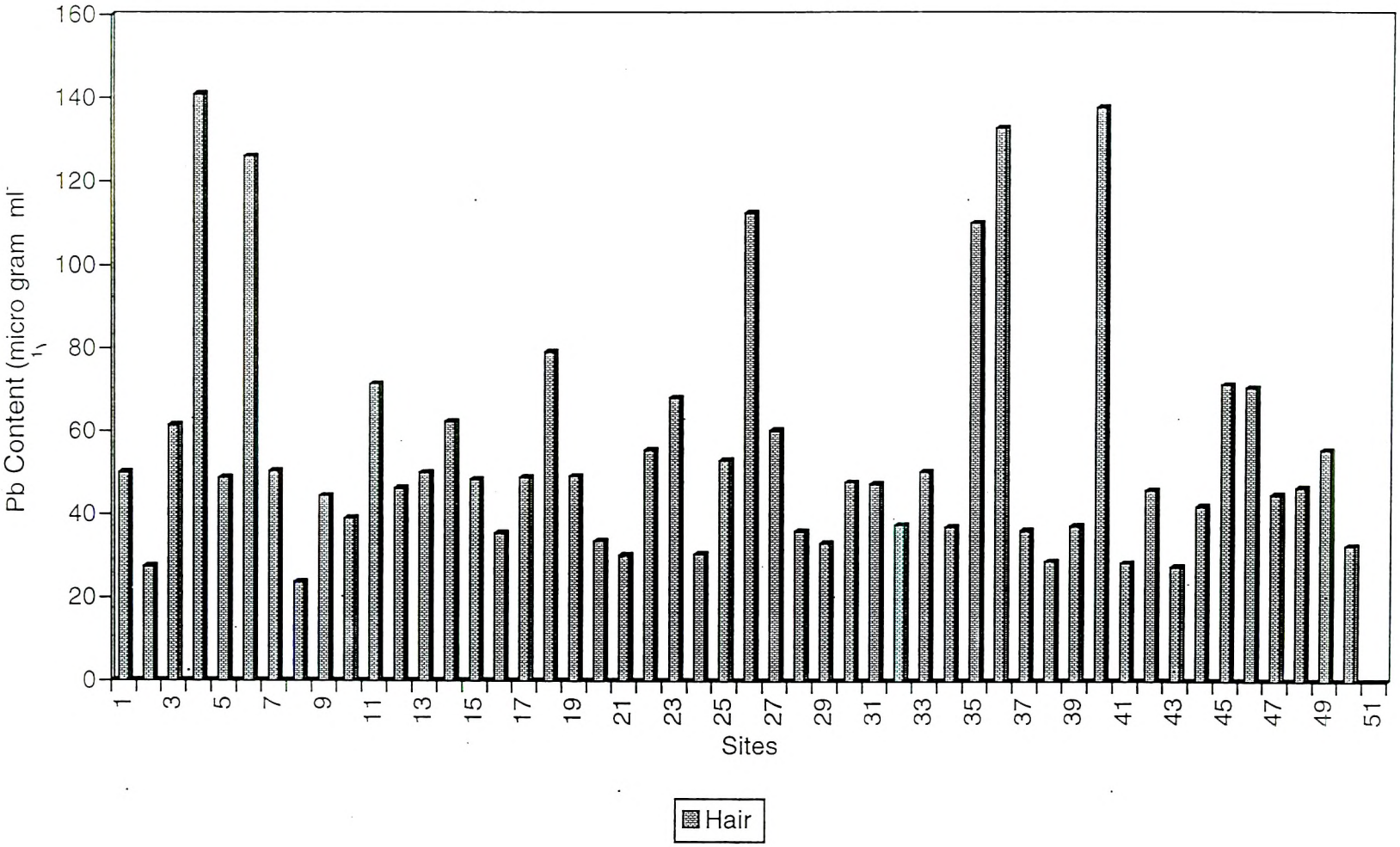


Figure 13. Pb Content in biological samples (Hair)

4.1.4.3 Lead content in nail samples

The Pb levels in the nail samples varied widely from 61.11 to 287.50 μg g^{-1}. The reference group had nail-Pb concentration ranging from 42.85 to 50.00 μg g^{-1}. All the nail samples of the automobile personnel (Plate 12) exceeded the nail-Pb levels of the reference group and a multifold increase was observed in the nail-Pb content of automobile personnel due to automobile exhaustion (Figure 14).

4.2 Transformation of lead in urban soils (black and red soils)

The transformation of lead added through Pb (NO_3) in black and red soils under two different moisture conditions was studied through a laboratory closed incubation experiment. The transformation was examined mainly by measuring the concentration of various fractions of Pb at an interval of 30 days.

4.2.1 Changes in soluble fractions (H_2O-Pb)

The soluble fractions of Pb as extracted in water (H_2O-Pb) showed that initially the concentration of H_2O-Pb was below detectable limit (bdl) in all the treatments. At 30^{th} and 60^{th} days notable changes in H_2O-Pb were observed. In general, the concentration ranged from 0.32 (BS-Control + M_2 + T_{30}) to 6.26 (BS + Pb @ 1000 mg kg^{-1} + M_1 + T_{60}) mg kg^{-1} in black soil and from 0.65 (RS – Control + M_1 + T_{30}) to 6.44 (RS + Pb @ 1000 mg kg^{-1} + M_1 + T_{60}) mg kg^{-1} in red soil. The higher values were associated with higher rate of application of Pb (1000 mg kg^{-1}). The control soil (without Pb) recorded significantly lower values at all times (Table XVIIa).

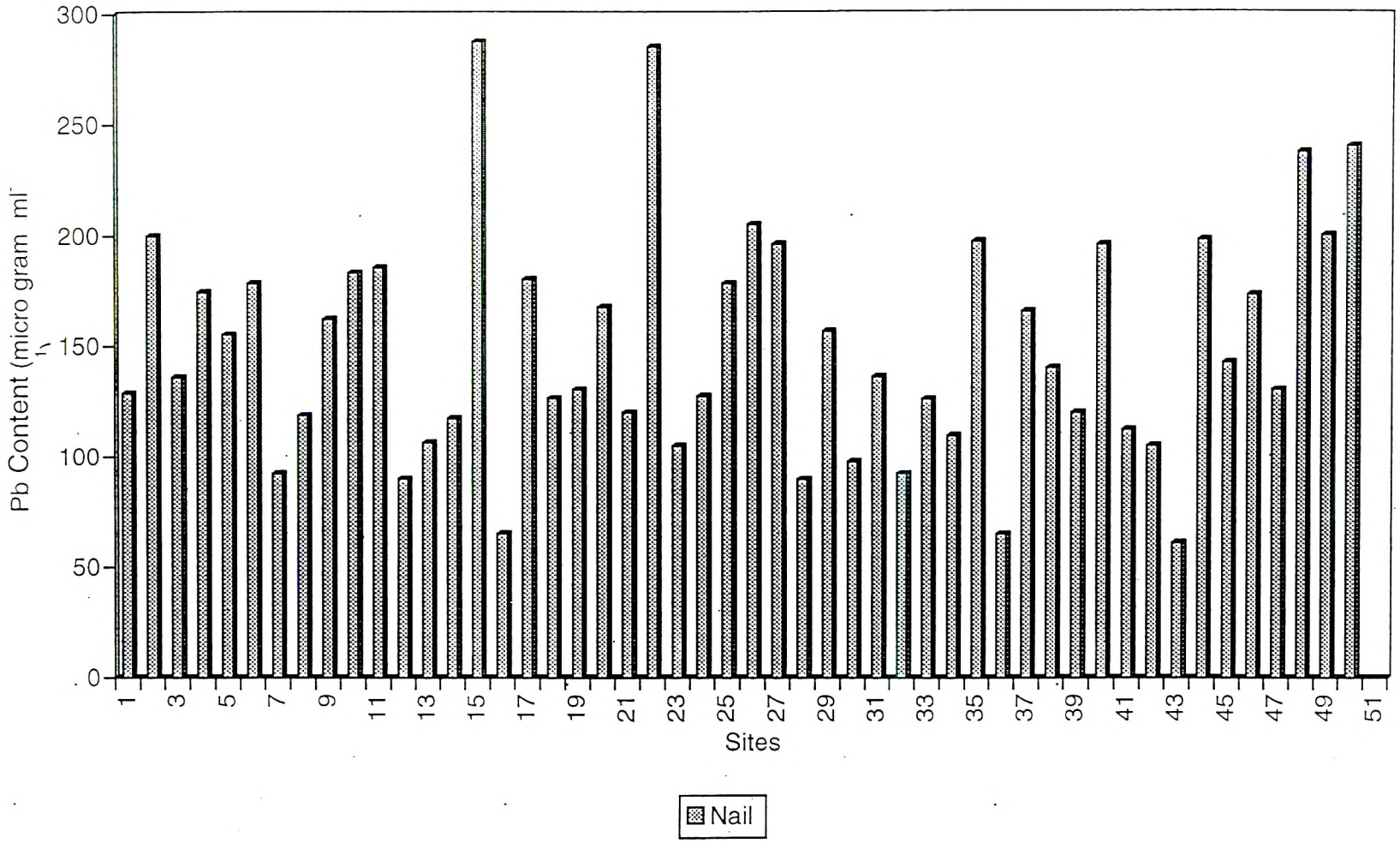


Figure 14. Pb Content in biological samples (nail)

Table XVII. Studies on the transformation of lead in black and red soils using closed incubation experiments

a. Changes observed in soluble fractions (H_2O-Pb) (mg kg^{-1})

Treatment	M_1			M_2		
	T_0	T_{30}	T_{60}	T_0	T_{30}	T_{60}
1. BS-Control	bdl	0.58	0.65	bdl	0.32	bdl
2. BS + Pb @ 500 mg kg^{-1}	bdl	4.50	5.75	bdl	2.30	5.26
3. BS + Pb @ 1000 mg kg^{-1}	bdl	3.85	6.26	bdl	3.00	6.17
4. RS-Control	bdl	0.65	1.05	bdl	0.91	0.90
5. RS + Pb @ 500 mg kg^{-1}	bdl	3.60	5.27	bdl	3.45	4.89
6. RS + Pb @ 1000 mg kg^{-1}	bdl	4.70	6.44	bdl	3.93	5.65
SEd		0.11			0.10	
LSD (5%)		0.23			0.20	

b. Changes observed in exchangeable fractions (KNO_3-Pb) (mg kg^{-1})

Treatment	M_1			M_2		
	T_0	T_{30}	T_{60}	T_0	T_{30}	T_{60}
1. BS-Control	2.40	6.75	6.16	2.35	5.42	6.00
2. BS + Pb @ 500 mg kg^{-1}	1.25	12.73	14.50	1.68	10.65	12.47
3. BS + Pb @ 1000 mg kg^{-1}	4.46	18.62	21.20	3.93	15.44	18.34
4. RS-Control	3.50	5.24	4.76	2.68	5.06	3.29
5. RS + Pb @ 500 mg kg^{-1}	8.40	13.12	18.40	6.52	8.64	13.12
6. RS + Pb @ 1000 mg kg^{-1}	8.00	14.18	20.75	6.89	12.63	17.12
SEd		0.10			0.07	
LSD (5%)		0.21			0.14	

T_0 - Time (0 day) M_1 - Moisture I
T_{30} - 30 days M_2 - Moisture II
T_{60} - 60 days

Though not significant always, soils under field capacity moisture content (M_1) showed relatively higher concentration of H_2O-Pb than under alternate wetting and drying. This trend was observed in black and red soils both at 30 and 60 days incubation. In general, the H_2O-Pb progressively increased during 60 days incubation (Figure 15a).

4.2.2 Changes in exchangeable fractions (KNO_3-Pb)

The change in exchangeable fractions of Pb in soils as extracted in KNO_3 (KNO_3-Pb) during 60 days incubation is presented in Table XVIIb. There was a progressive increase in the concentration of KNO_3-Pb from time 0 to time 60 days. The concentration of KNO_3-Pb varied between 1.25 (BS + Pb @ 500 mg kg^{-1} + M_1 + T_0) and 21.20 (BS + Pb @ 1000 mg kg^{-1} + M_1 + T_{60}) mg kg^{-1} in black soil and between 2.68 (RS – Control + M_2 + T_0) and 20.75 (RS + Pb @ 1000 mg kg^{-1} + M_2 + T_0) mg kg^{-1} in red soil. Relatively higher values were observed in black soil than red soil at 30 and 60 days. Irrespective of soils and moisture conditions, the control soils without Pb addition recorded the lowest values at all times.

Increase in the rate of application of Pb significantly increased the exchangeable - Pb in black and red soils under both moisture conditions.

Irrespective of soils, the concentration of exchangeable-Pb was significantly higher due to field capacity moisture than alternate wetting and drying in all treatments (Figure 15b).

Figure 15. Transformation of lead (black and red soil)

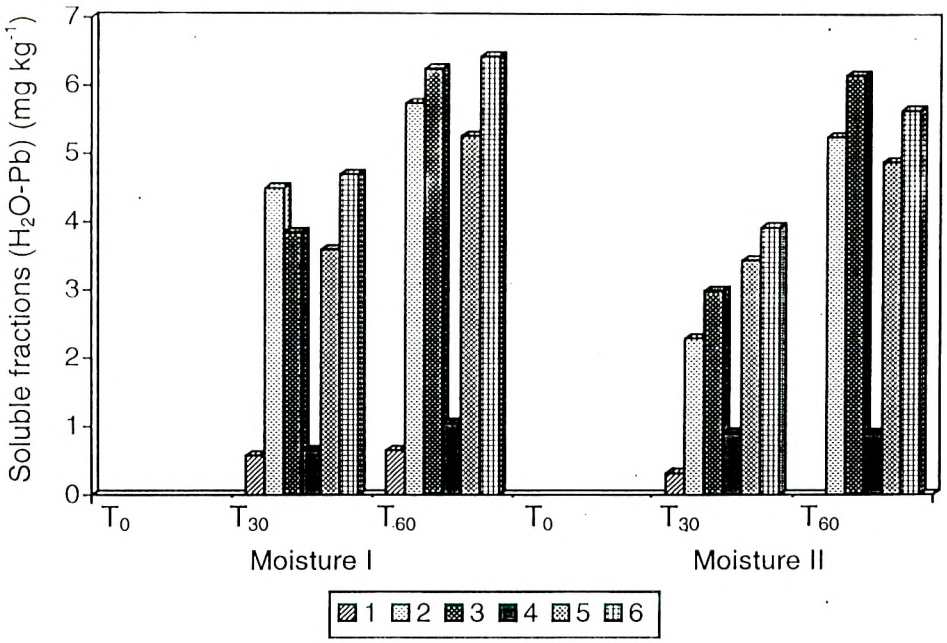
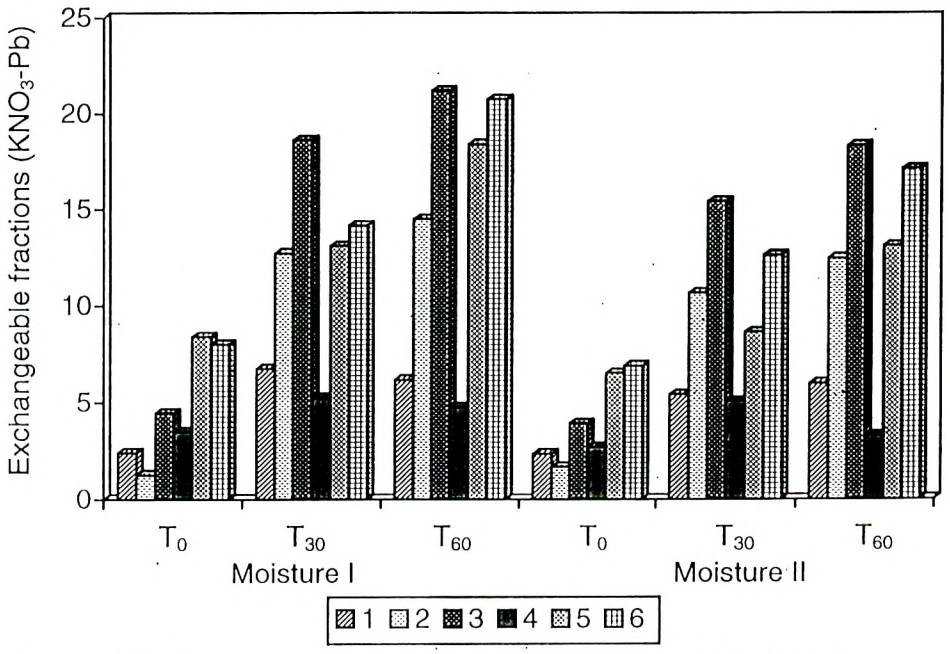


Figure 15a. Changes observed in soluble fractions (H_2O-Pb)



1	BS-Control	4	RS-Control
2	BS+Pb @ 500 mg kg^{-1}	5	RS+Pb @ 500 mg kg^{-1}
3	BS+Pb @ 1000 mg kg^{-1}	6	RS+Pb @ 1000 mg kg^{-1}

Figure 15b. Changes observed in exchangeable fractions (KNO_3-Pb)

4.2.3 Changes in organic fractions (NaOH-Pb)

Lead bound in organic form as extracted in NaOH ranged from 6.2 (BS – Control + M_2 + T_0) to 25.0 (BS + Pb @ 1000 mg kg^{-1} + M_1 + T_{60}) mg kg^{-1} in black soil and 5.0 (RS – Control + M_2 + T_0) to 24.2 (RS + Pb @ 1000 mg kg^{-1} + M_1 + T_{60}) mg kg^{-1} in red soil. Increase in the rate of Pb addition significantly had increased the concentration of NaOH-Pb under both moisture conditions at all days of incubation. The addition of Pb at a rate equivalent to 1000 mg kg^{-1} recorded the highest value 25.0 mg kg^{-1} in black soil and 24.2 mg kg^{-1} in red soil. Soils without Pb addition (control) had lower concentration of NaOH-Pb at all times.

The NaOH-Pb differed significantly with field capacity moisture content than with alternate wetting and drying. Though not always significant, black soil recorded higher values than red soil at all days of incubation. With increase in the period of incubation, the originally bound-Pb increased markedly under both moisture conditions (Table XVIIc and Figure 15c).

4.2.4 Changes in iron oxide bound fractions (EDTA-Pb)

The iron oxide bound-Pb was extracted in 0.5 M EDTA. The changes in the concentrations of EDTA as influenced by varied levels of Pb and moisture content are furnished in Table XVIId and Figure 15d. The EDTA-Pb ranged from 4.1 (BS – Control + M_2 + T_{60}) to 470.8 (BS + Pb @ 1000 mg kg^{-1} + M_1 + T_0) mg kg^{-1} in black soil and from 3.8 (RS – Control + M_2 + T_{60}) to 680.5 (RS + Pb @ 1000 mg kg^{-1} + M_1 + T_0) mg kg^{-1} in red soil. The lowest

Table XVIIc. Changes observed in organic fractions (NaOH-Pb) (mg kg^{-1})

Treatment	M_1			M_2		
	T_0	T_{30}	T_{60}	T_0	T_{30}	T_{60}
1. BS-Control	6.5	8.3	6.8	6.2	7.6	7.5
2. BS + Pb @ 500 mg kg^{-1}	9.7	19.6	16.4	8.6	14.3	13.3
3. BS + Pb @ 1000 mg kg^{-1}	10.1	24.7	25.0	9.7	19.8	20.6
4. RS-Control	5.4	7.6	8.1	5.0	7.6	10.5
5. RS + Pb @ 500 mg kg^{-1}	8.4	14.9	13.7	8.6	12.5	12.1
6. RS + Pb @ 1000 mg kg^{-1}	9.0	18.1	24.2	7.3	16.2	17.5
SEd	0.15			0.16		
LSD (5%)	0.31			0.32		

Table XVIId. Changes observed in iron oxide bound fractions (EDTA-Pb) (mg kg^{-1})

Treatment	M_1			M_2		
	T_0	T_{30}	T_{60}	T_0	T_{30}	T_{60}
1. BS-Control	5.5	4.2	5.6	5.3	4.9	4.1
2. BS + Pb @ 500 mg kg^{-1}	262.6	210.5	168.4	240.7	217.3	145.5
3. BS + Pb @ 1000 mg kg^{-1}	470.8	425.7	380.5	416.9	416.8	360.7
4. RS-Control	8.4	6.0	5.5	7.2	5.3	3.8
5. RS + Pb @ 500 mg kg^{-1}	316.7	260.7	203.9	286.5	240.5	210.8
6. RS + Pb @ 1000 mg kg^{-1}	680.5	587.6	512.3	612.4	560.0	480.5
SEd	0.18			0.19		
LSD (5%)	0.37			0.30		

T_0 - Time (0 day) M_1 - Moisture I
T_{30} - 30 days M_2 - Moisture II
T_{60} - 60 days

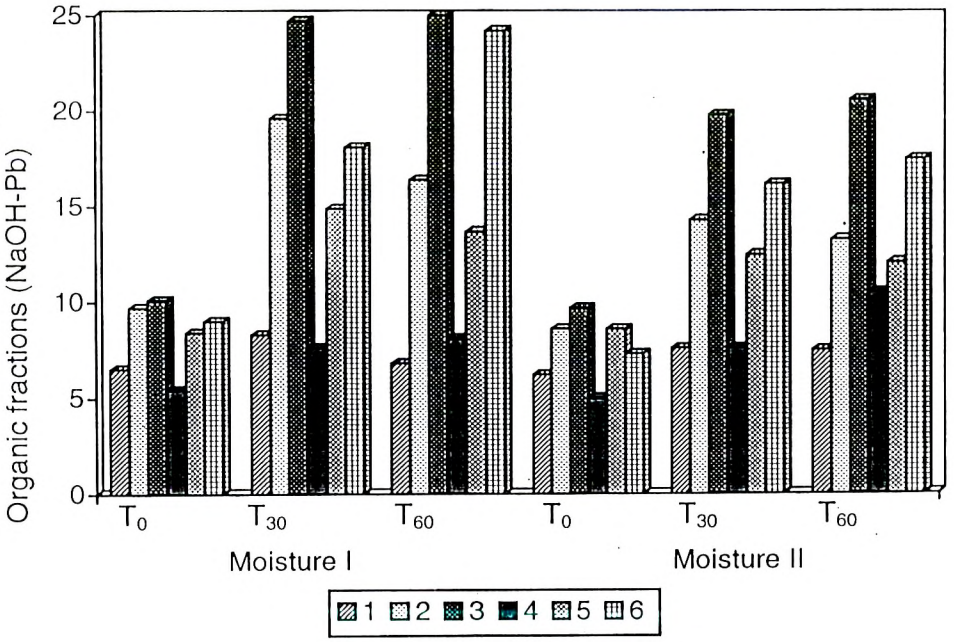
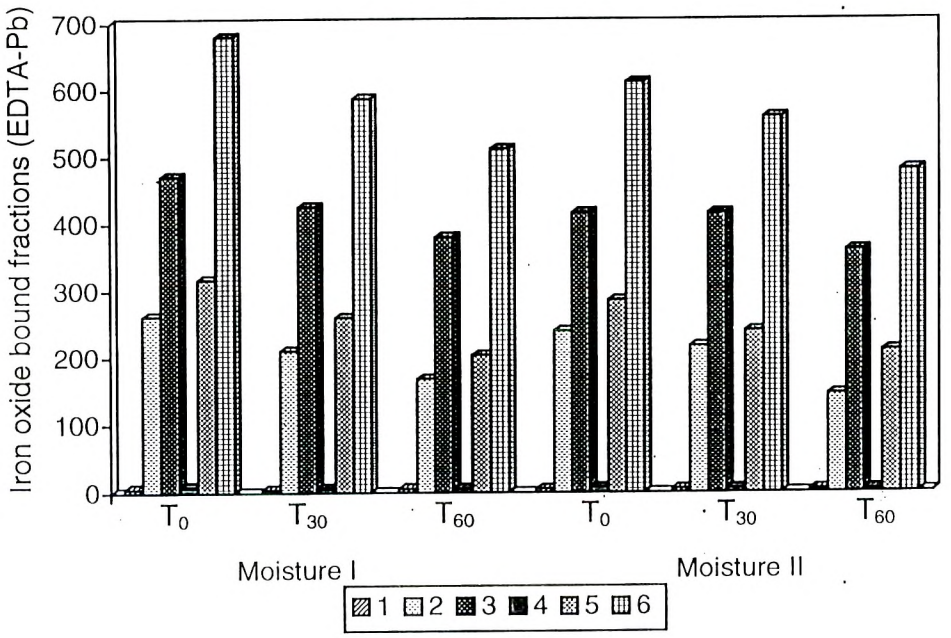


Figure 15c. Changes observed in organic fractions (NaOH-Pb)



1	BS-Control	4	RS-Control
2	BS+Pb @ 500 mg kg^{-1}	5	RS+Pb @ 500 mg kg^{-1}
3	BS+Pb @ 1000 mg kg^{-1}	6	RS+Pb @ 1000 mg kg^{-1}

Figure 15d. Changes observed in iron oxide bound fractions (EDTA-Pb)

values were observed in both black and red soils without Pb addition (control). Significantly higher values were observed in red soil than in black soil.

Increase in the rate of application of Pb progressively had increased the iron oxide bound-Pb under both moisture conditions. Similar to exchangeable and organically bound-Pb, the iron oxide bound fractions of Pb were significantly higher under field capacity moisture condition than under alternate wetting and drying. However, the EDTA-Pb progressively decreased during the incubation in all treatments, recording significantly higher values initially (T_0).

4.2.5 Changes observed in residual fractions (HNO_3-Pb)

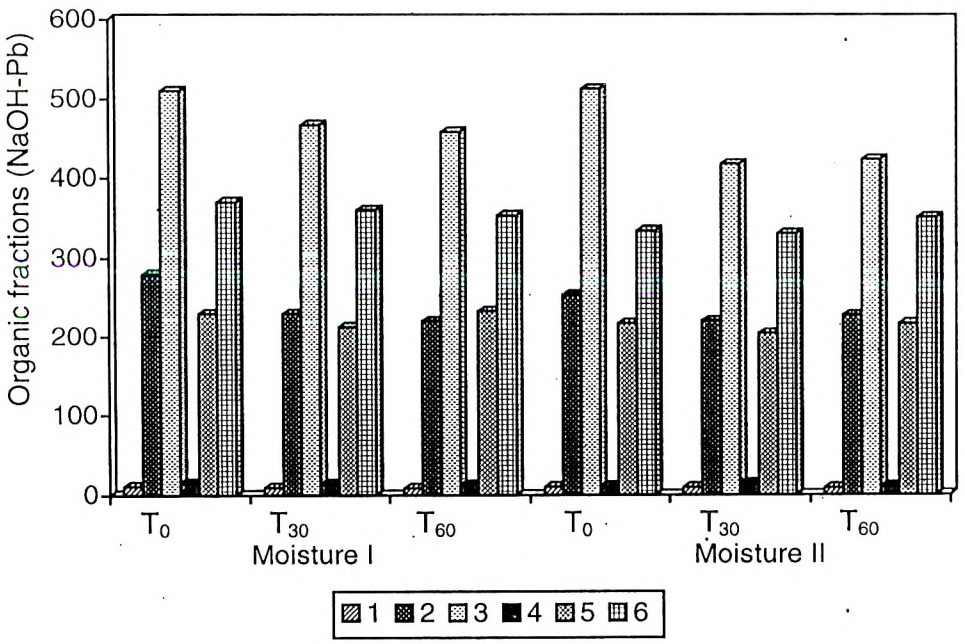
The residual fractions (HNO_3-Pb) ranged from 8.1 (BS – Control + M_2 + T_{60}) to 512.5 (BS + Pb @ 1000 mg kg^{-1} + M_2 + T_0) mg kg^{-1} (black soil) and 9.5 (RS – Control + M_2 + T_{60}) to 370.0 (RS + Pb @ 1000 mg kg^{-1} + M_1 + T_0) mg kg^{-1} (red soil). Under both moisture conditions, the concentrations were higher initially (T_0) which markedly decreased with increase in incubation period. The lowest values were observed in soils (control) without any Pb addition, and the highest values were with the Pb addition at a rate equivalent to1000 mg kg^{-1} (Table XVIIe and Figure 15e).

Similar to other fractions, the HNO_3-Pb was higher under field capacity moisture than under alternate wetting and drying at all times. Black soil showed higher values of HNO_3-Pb than red soil on all days.

Table XVIIe. Changes observed in residual fractions (HNO_3-Pb) (mg kg^{-1})

Treatment	M_1			M_2		
	T_0	T_{30}	T_{60}	T_0	T_{30}	T_{60}
1. BS-Control	10.6	9.2	8.5	10.0	9.3	8.1
2. BS + Pb @ 500 mg kg^{-1}	280.0	230.0	220.1	253.7	220.3	227.2
3. BS + Pb @ 1000 mg kg^{-1}	510.0	467.0	458.0	512.5	417.5	423.0
4. RS-Control	14.3	13.6	12.4	10.2	14.1	9.5
5. RS + Pb @ 500 mg kg^{-1}	230.0	212.5	233.0	216.8	203.9	216.7
6. RS + Pb @ 1000 mg kg^{-1}	370.0	360.0	353.0	333.7	330.0	350.0
SEd	0.29			0.26		
LSD (5%)	0.60			0.52		

T_0 - Time (0 day) M_1 - Moisture I
T_{30} - 30 days M_2 - Moisture II
T_{60} - 60 days



1	BS-Control	4	RS-Control
2	BS+Pb @ 500 mg kg^{-1}	5	RS+Pb @ 500 mg kg^{-1}
3	BS+Pb @ 1000 mg kg^{-1}	6	RS+Pb @ 1000 mg kg^{-1}

Figure 15e. Changes observed in residual fractions (HNO_3-Pb)

4.3 Adsorption of lead in urban soils

The adsorption of Pb on two different soils was examined through a batch experiment. The range of Pb concentrations added was above the optimum geochemical situation in order to examine the maximum adsorption capacity of urban soils. Two different pHs were also imposed representing extreme conditions normally encountered in soils.

In both soils, the adsorption was found increased with increase in Pb concentration (Tables XVIII and XIX). The amount of Pb adsorbed varied markedly due to the soils and pHs. In general, the adsorption was higher on red soil than black soil. The percentage of adsorption varied from 70.4 to 89.2 in pH 6 and from 70.2 to 99.1 in pH 8. In red soil the adsorption rates between 75.0 and 88.5 showed a variation in pH 6 and 85.2 and 93.6 in pH 8. Increase in soil pH 8 resulted in higher adsorption of Pb on both soils. The results showed that even at a high rate of Pb application (1000 mg Pb kg^{-1} soil) more than 90 per cent adsorption was observed in both soils particularly at pH 8 (Figures 16 and 17).

4.4 Effect of leaching on Total Pb (mg kg^{-1}) accumulation in urban soils

In black soil, the amount of Pb in soils after the leaching event is presented in Table XX and Figure 18. In black soil the Pb content ranged from 5.30 (T_1) to 28.75 mg kg^{-1} (T_5) in the surface soil and from 9.50 (T_1) to 121.50 mg kg^{-1} (T_5) in the subsurface soil. Significantly large amounts of Pb were found in subsurface soils than surface soil due to downward movement

Table XVIII. Effect of pH on lead adsorption in black soils

Treatments (mg Pb kg^{-1} soil)	Black soil					
	pH 6			pH 8		
	Equilibrium solution concentration (mg l^{-1})	Amount adsorbed (mg / kg)	% adsorbed	Equilibrium solution concentration (mg l^{-1})	Amount adsorbed (mg / kg)	% adsorbed
0	1.3	-	-	0.9	-	-
250	74.0	176.0	70.4	73.5	176.5	70.2
500	93.0	407.0	81.4	76.0	424.0	84.8
750	101.9	648.1	86.4	85.5	664.5	88.5
1000	108.0	892.0	89.2	89.0	911.0	99.1

Table XIX. Effect of pH on lead adsorption in red soils

Treatments (mg Pb kg^{-1} soil)	Black soil					
	pH 6			pH 8		
	Equilibrium solution concentration (mg l^{-1})	Amount adsorbed (mg / kg)	% adsorbed	Equilibrium solution concentration (mg l^{-1})	Amount adsorbed (mg / kg)	% adsorbed
0	0.7	-	-	0.2	-	-
250	62.5	187.5	75.0	37.0	213.0	85.2
500	64.5	435.5	87.0	63.5	454.2	90.8
750	100.5	649.5	86.5	54.6	695.2	92.7
1000	114.9	885.1	88.5	63.9	936.1	93.6

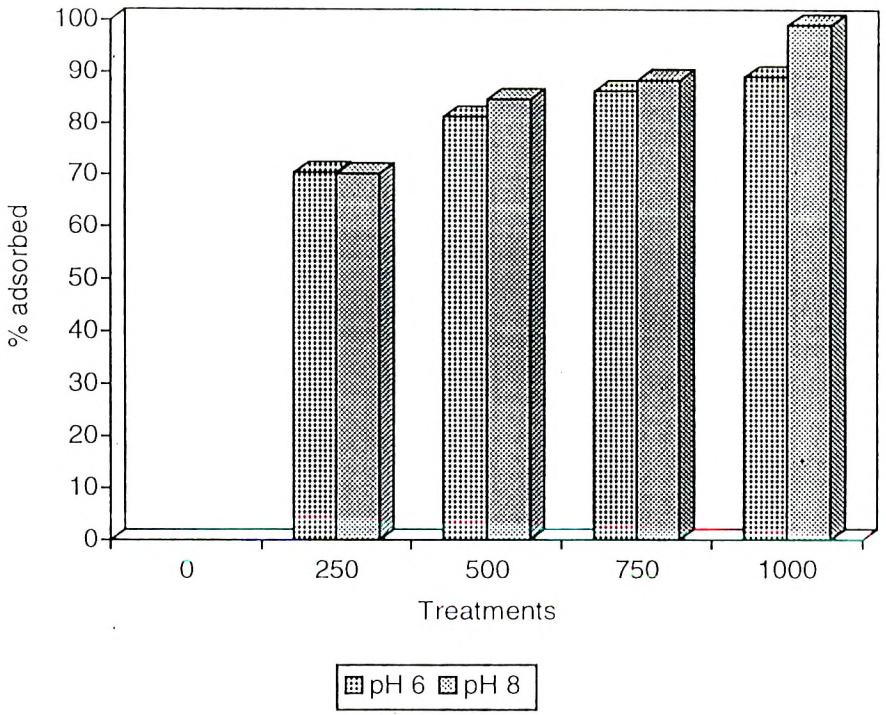


Figure 16. Adsorption of lead in black soils

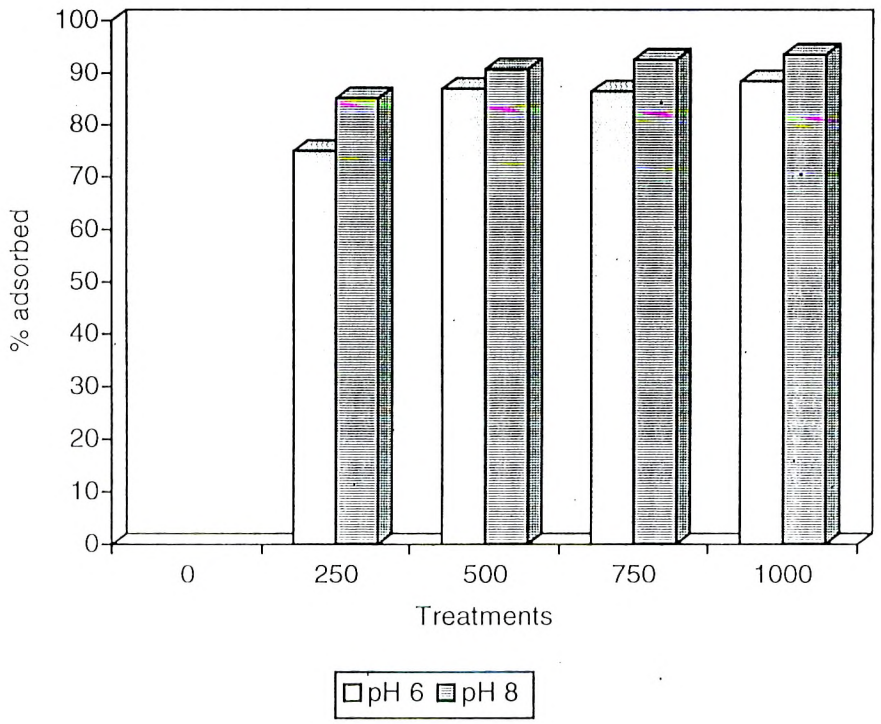
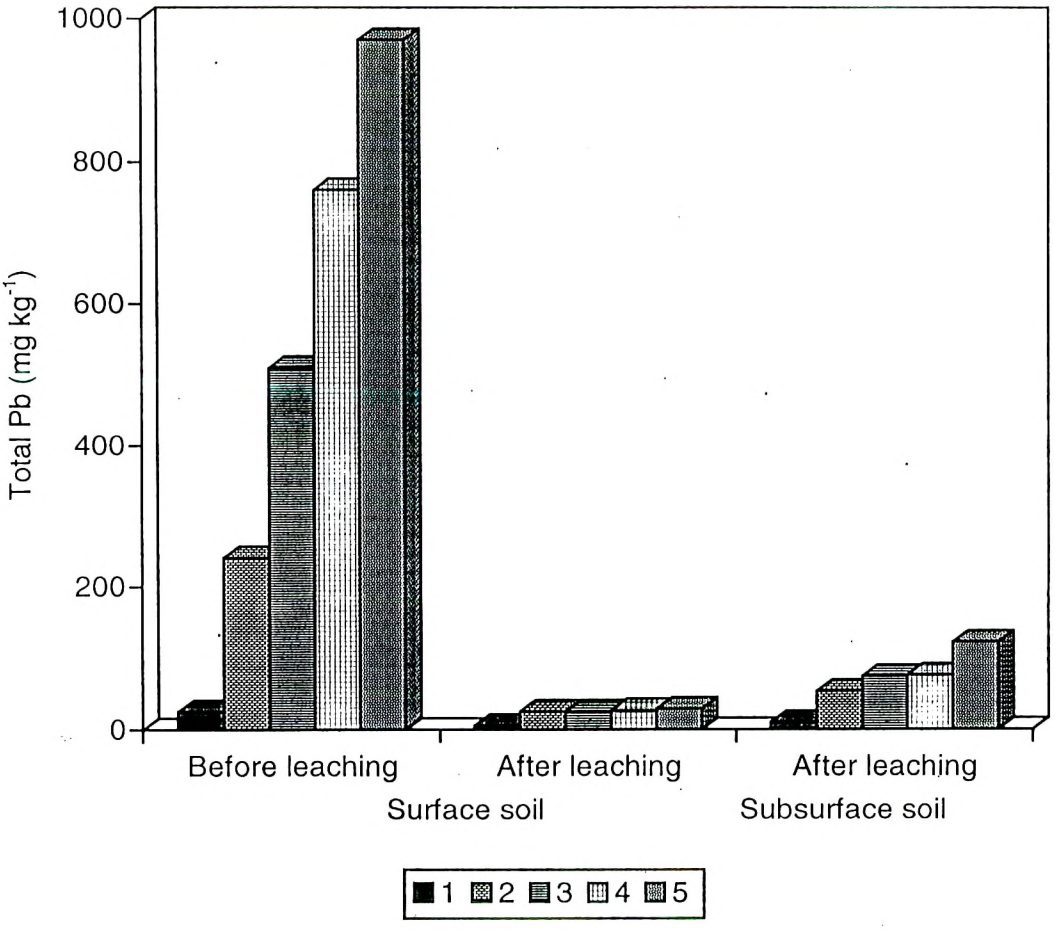


Figure 17. Adsorption of lead in red soils

Table XX. Effect of leaching on Total Pb (mg kg^{-1}) accumulation in urban (black soils)

Treatments	Surface soil		Subsurface soil
	Before leaching	After leaching	After leaching
T_1 - Soil (Control)	25.1	5.30	9.50
T_2 - Soil + 250 mg Pb kg^{-1}	240.8	25.22	52.50
T_3 - Soil + 500 mg Pb kg^{-1}	510.3	25.33	73.00
T_4 - Soil + 750 mg Pb kg^{-1}	760.7	26.33	75.50
T_5 - Soil + 1000 mg Pb kg^{-1}	970.3	28.75	121.50
SEd	0.39		0.20
LSD (5%)	0.81		0.44



1 – T_1 ; 2 – T_2 ; 3 – T_3 ; 4 – T_4 ; 5 – T_5

Figure 18. Leaching of Total Pb (black soil)

of Pb along with leaching water. After leaching the amount of Pb was found significantly higher at 1000 mg Pb kg^{-1} both in surface and subsurface soils.

In red soil the Pb content was significantly reduced due to leaching. The concentration ranged from 2.5 (T_1) to 26.2 mg kg^{-1} (T_5) in the surface soil and 5.1 (T_1) to 119.0 mg kg^{-1} (T_5) in the subsurface soil (Table XXI and Figure 19). Though not significant always, marked variations were observed due to different levels of Pb addition. The amount of Pb remaining in the soil was found relatively higher in black soil than in red soil.

4.4.1 Leaching of Pb from soils of urban environment

The leaching of Pb from urban soils amended with graded levels of Pb was examined through column experiment. The concentration of Pb in the leachate and the total amount of Pb leached from black and red soils are presented in Table XXII and in Figure 20.

In black soil, the concentration of Pb in the leachate ranged from 0.55 to 121.0 mg l^{-1}, whereas it was from 0.22 to 116.0 mg l^{-1} in red soil. Both black and red soils (control) showed the lowest concentrations of Pb in the leachate. The highest concentrations of Pb were observed when 1000 mg Pb kg^{-1} as added to black and red soils. Increase in the rate of Pb from 250 to 1000 mg kg^{-1} had significantly increased the Pb concentration in the leachate. A large amount of Pb was found leached from black soil.

Table XXI. Effect of leaching on Total Pb (mg kg^{-1}) accumulation in urban (red soil)

Treatments	Surface soil		Subsurface soil
	Before leaching	After leaching	After leaching
T_1 - Soil (Control)	32.00	2.50	5.10
T_2 - Soil + 250 mg Pb kg^{-1}	262.50	25.25	74.00
T_3 - Soil + 500 mg Pb kg^{-1}	520.10	25.89	104.17
T_4 - Soil + 750 mg Pb kg^{-1}	740.50	26.09	115.00
T_5 - Soil + 1000 mg Pb kg^{-1}	990.30	26.20	119.00
SEd	0.26		0.23
LSD (5%)	0.55		0.52

Table XXII. Leaching of Pb from soils of urban environment

Treatments	Black soil		Red soil	
	Lead concentration	Total Pb (leached) (mg l^{-1})	Lead concentration	Total Pb (leached) (mg l^{-1})
T_1 - Soil (Control)	0.55	49.50	0.22	21.34
T_2 - Soil + 250 mg Pb kg^{-1}	40.00	31.60	41.50	33.20
T_3 - Soil + 500 mg Pb kg^{-1}	53.50	46.00	58.50	52.65
T_4 - Soil + 750 mg Pb kg^{-1}	71.50	57.20	65.00	55.25
T_5 - Soil + 1000 mg Pb kg^{-1}	121.00	114.95	116.00	110.20
SEd	0.37	16.4	0.58	17.6
LSD (5%)	0.81	36.6	1.29	39.2

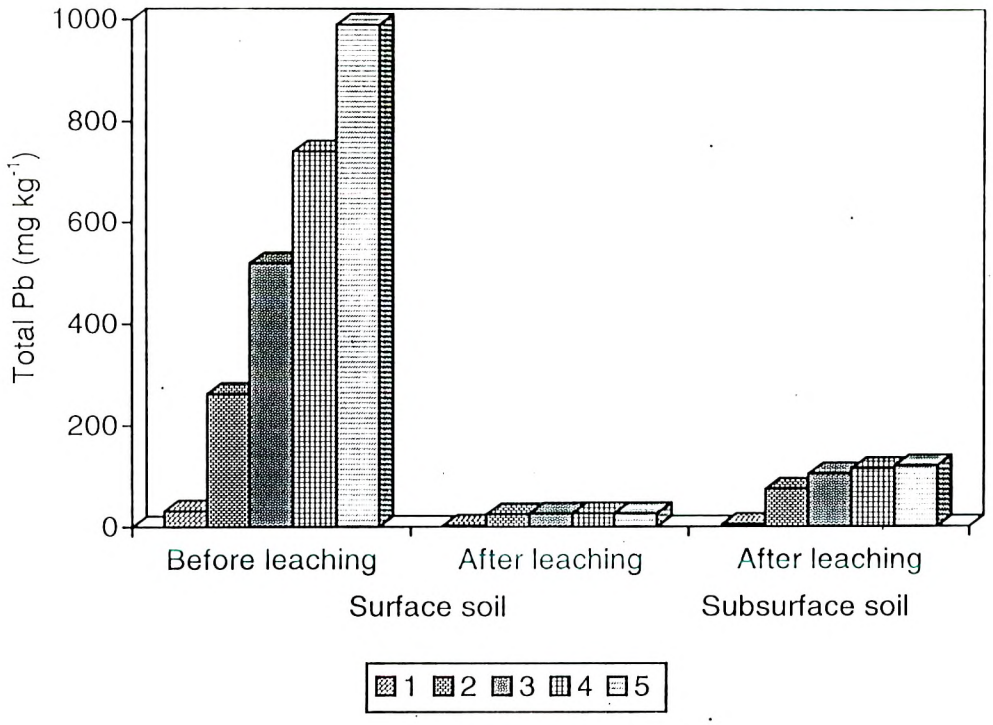


Figure 19. Leaching of Total Pb (red soil)

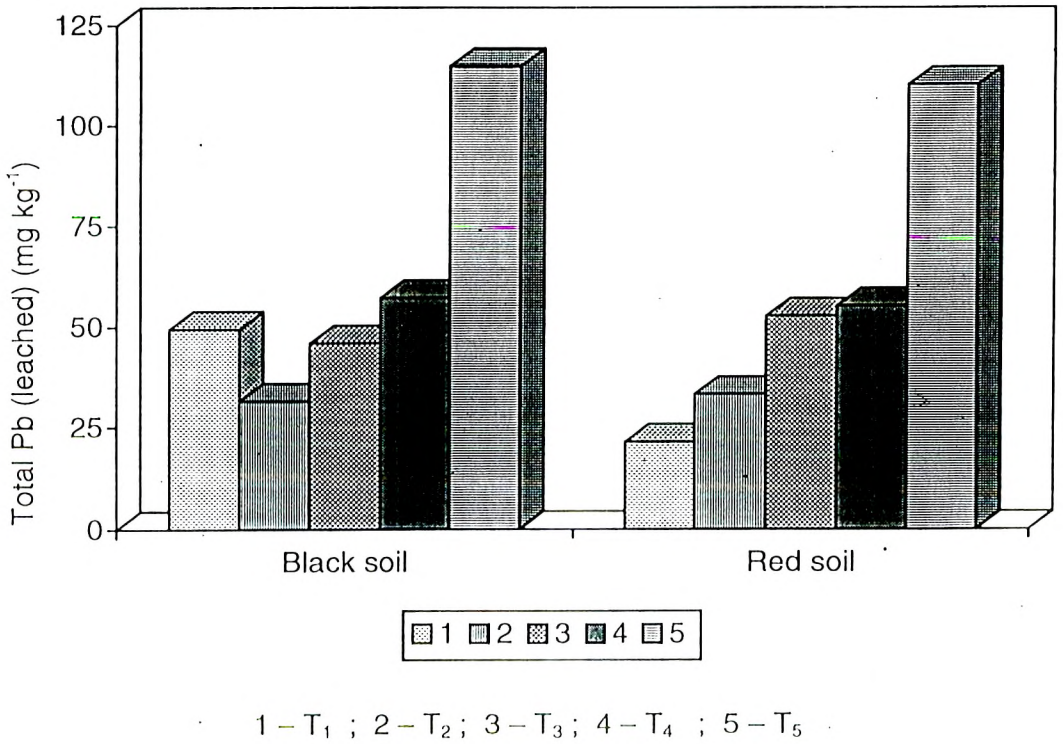


Figure 20. Leaching of Pb from soils of urban environment

The total amount of Pb leached (concentration of Pb in the leachate x total volume of leachate collected) ranged between 49.5 and 114.95 mg l^{-1} from black soil. Similar to black soil, there was a remarkable increase in the leaching of Pb as the rate of Pb addition increased in the red soil. The highest amount of Pb was observed in the black soil with 1000 mg Pb kg^{-1}.

Comparing the two soils, both the Pb concentration and the total amount leached were significantly higher in red soil than in black soil in the treatments – soil (control), soil + 250 mg Pb kg^{-1} and soil + 500 mg Pb kg^{-1} whereas, the 4^{th} and 5^{th} treatments (soil + 750 mg Pb kg^{-1} and soil + 1000 mg Pb kg^{-1}) using black soil, recorded significantly higher values than red soil. In general, it was observed that a considerable amount of Pb was found leached from both soils, which may have impact on ground water contamination.

4.4.2 Effect of leaching on soil pH

The pH of soil measured before and after leaching event is given in Table XXIII and in Figure 21. In black soil, before leaching the pH varied from 7.26 (T_5) to 7.69 (T_1). The control soil recorded the highest pH. Increase in the rate of Pb markedly reduced the pH and Pb at 1000 mg kg^{-1} recorded the lowest value. After the leaching event the pHs were found slightly increased in the surface layer (0-15 cm depth), which ranged from 7.32 (T_5) to 7.60 (T_1). The highest pH was recorded in the control soil. The pHs were found lower in subsurface soil (15-30 cm depth), which ranged from 7.17 (T_5) to 7.32 (T_2). Increasing the rate of Pb did not show any clear trend in the subsurface soil.

Table XXIII. Effect of leaching on pH of urban black soils

Treatments	Surface soil		Subsurface soil
	Before leaching	After leaching	After leaching
T_1 - Soil (Control)	7.69	7.60	7.20
T_2 - Soil + 250 mg Pb kg^{-1}	7.48	7.57	7.32
T_3 - Soil + 500 mg Pb kg^{-1}	7.40	7.45	7.25
T_4 - Soil + 750 mg Pb kg^{-1}	7.35	7.40	7.30
T_5 - Soil + 1000 mg Pb kg^{-1}	7.26	7.32	7.17
SEd	0.11		0.03
LSD (5%)	0.22		0.07

Table XXIV. Effect of leaching on pH of urban red soil

Treatments	Surface soil		Subsurface soil
	Before leaching	After leaching	After leaching
T_1 - Soil (Control)	6.32	6.30	6.40
T_2 - Soil + 250 mg Pb kg^{-1}	6.50	6.55	6.30
T_3 - Soil + 500 mg Pb kg^{-1}	6.42	6.46	6.85
T_4 - Soil + 750 mg Pb kg^{-1}	6.19	6.34	6.71
T_5 - Soil + 1000 mg Pb kg^{-1}	6.26	6.20	6.25
SEd	0.12		0.05
LSD (5%)	0.24		0.11

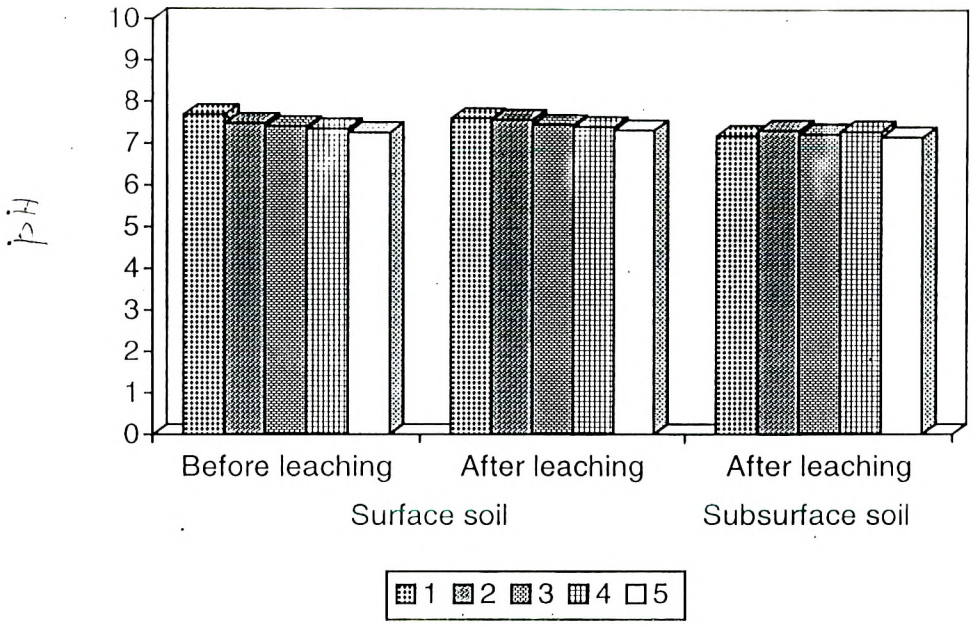
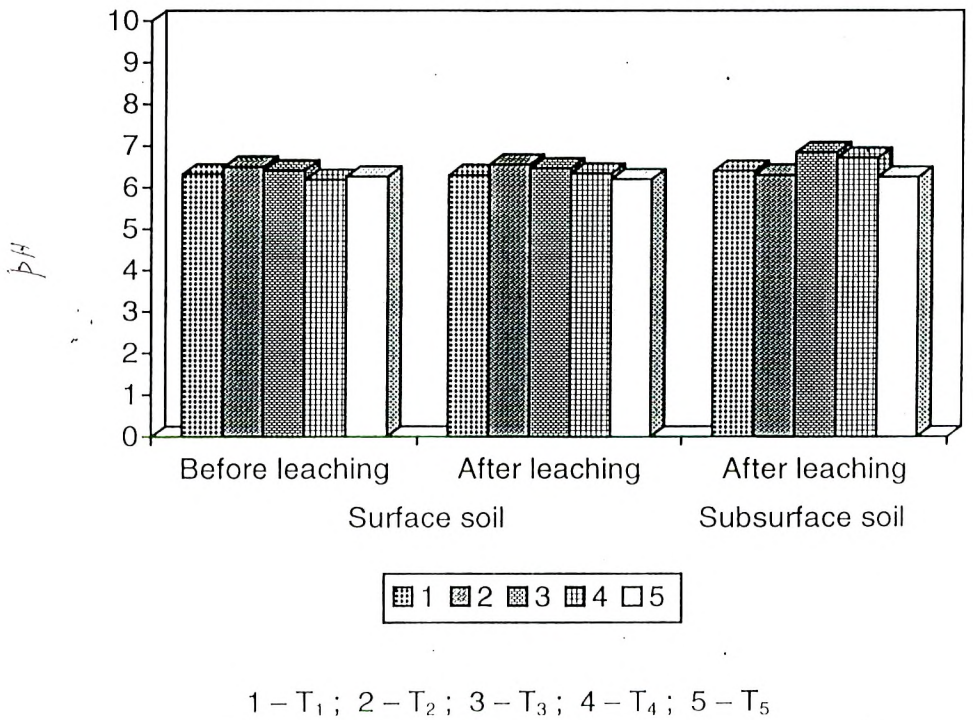


Figure 21. Effect of leaching on pH of urban black soil



1 – T_1 ; 2 – T_2 ; 3 – T_3 ; 4 – T_4 ; 5 – T_5

Figure 22. Effect of leaching on pH of urban red soils

Similar to black soil, the effect was also observed in red soil (Table XXIV and Figure 22). There was a small increase in pH of surface soil after leaching, which ranged from 6.20 (T_5) to 6.55 (T_2) and further increase was observed in (T_5) of subsurface soils which ranged from 6.25 (T_5) to 6.85 (T_3).

4.5 Effect of composted coir pith on plant available Pb (DTPA – Pb) in black soil

The change in the plant available Pb as extracted in DTPA during incubation from 0 – 60 days is given in Table XXV. The application of Pb at a rate equivalent to 1000 mg Pb kg^{-1} both in the presence and absence of composted coir pith had remarkable influence on DTPA-Pb at all days of incubation. The DTPA-Pb in black soil ranged from 2.0 to 136.2 mg kg^{-1} (Figure 23). The control soil recorded the lowest values at all days of incubation. The addition of Pb at a rate of 1000 mg kg^{-1} significantly increased the DTPA-Pb content in soil and there was a continuous increase upto 60 days. From the initial content of 3.2 mg kg^{-1}, the DTPA-Pb progressively increased to 136.2 mg kg^{-1}.

The addition of composted coir pith at a rate equivalent to 50 g kg^{-1} had decreased the plant availability of Pb as significantly lower DTPA-Pb contents were observed at all days of incubation which ranged between 2.7 and 92.7 mg kg^{-1}.

Table XXV. Effect of composted coir pith on plant available Pb (DTPA-Pb) in black soil (mg kg^{-1})

Treatments	Incubation days				
	0	15	30	45	60
1. Control (Soil alone)	2.8	2.6	3.2	3.2	2.0
2. Soil + Pb @ 1000 mg kg^{-1}	3.2	67.8	112.6	123.7	136.2
3. Soil + Pb + Composted coir pith (@ 50 g kg^{-1})	2.7	44.3	73.8	86.4	92.7
SEd	0.17				
LSD (5%)	0.35				

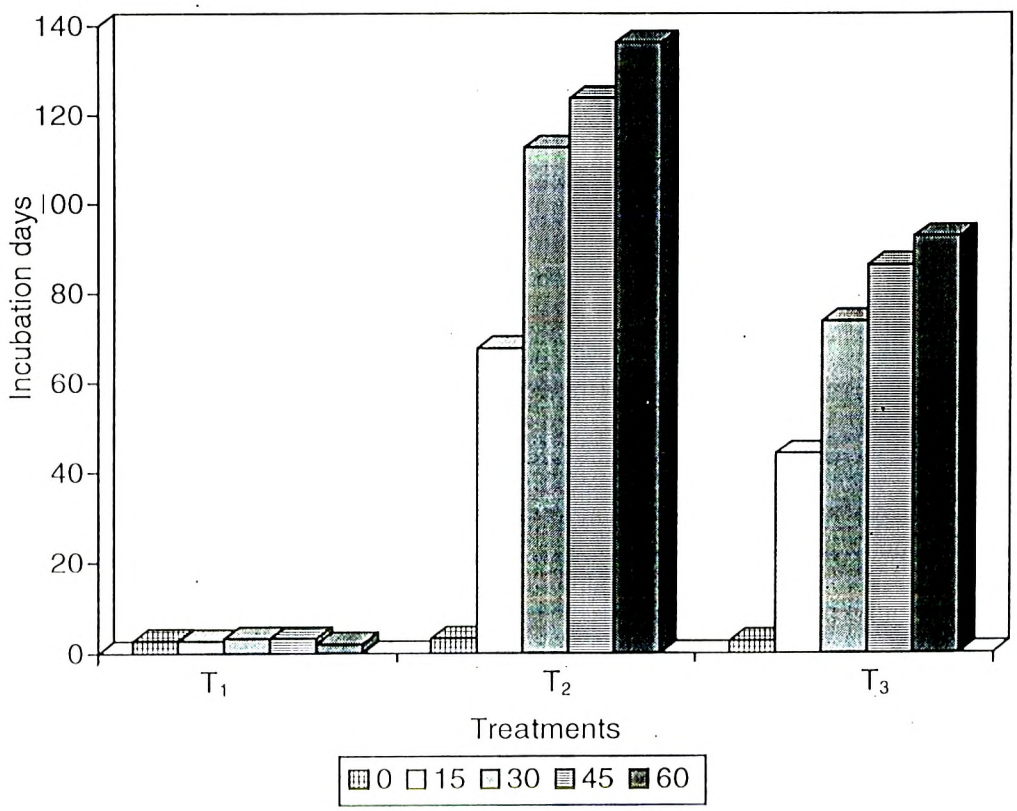


Figure 23. Effect of composted coir pith on plant available Pb (DTPA-Pb) in black soil

Irrespective of whether composted coir pith was added or not, the rate of increase in DTPA-Pb was remarkably higher upto 30 days and thereafter, showed relatively lower rate of increase.

4.6 Effect of Pb in plants

Coir pith is an organic waste produced from coconut industry (Plate 13) and it helps in reducing the Pb availability in soil.

The effect of different rates of Pb with and without composted coir pith application on plant growth and accumulation of Pb in plant parts were examined through a mini-pot experiment (Plate 14).

4.6.1 Effect of different levels of Pb with and without composted coir pith on growth parameters of castor (*Ricinus communis*) (Plate 15)

The growth of castor was examined by measuring the length of shoot and root of 45 day-old castor plants. The results are presented in Table XXVI. The length of shoots ranged from 13.3 (T_1, T_5) to 19.2 cm (T_3) only during 45 days of growth. Significantly, increase in shoot growth was observed with Pb application upto 500 mg kg^{-1} and which, thereafter, markedly decreased. At 1000 mg Pb kg^{-1} (T_5) the length of shoot was found equal to that of plants in control pot (T_1). Such a trend was also observed in the presence of composted coir pith. But Pb at 250 mg kg^{-1} along with composted coir pith (T_7) recorded the highest value (18 cm) and thereafter, the length of shoots was reduced (Figure 24).

Table XXVI. Effect of different levels of Pb with and without composted coir pith on growth parameters of castor (*Ricinus communis*) on 45 days after sowing

Treatments	Shoot length (cm)	Root length (cm)	Plant fresh weight (g)
T_1 - Soil (Control)	13.3	12.2	5.20
T_2 - Soil + 250 mg Pb kg^{-1}	15.3	17.2	5.71
T_3 - Soil + 500 mg Pb kg^{-1}	19.2	20.6	7.22
T_4 - Soil + 750 mg Pb kg^{-1}	16.2	18.3	6.47
T_5 - Soil + 1000 mg Pb kg^{-1}	13.3	16.2	6.36
T_6 - Soil + Composted coir pith	17.2	15.3	5.84
T_7 - Soil + Composted coir pith + 250 mg Pb kg^{-1}	18.0	15.5	6.97
T_8 - Soil + Composted coir pith + 500 mg Pb kg^{-1}	17.1	24.0	7.40
T_9 - Soil + Composted coir pith + 750 mg Pb kg^{-1}	17.1	20.1	6.73
T_{10} - Soil + Composted coir pith + 1000 mg Pb kg^{-1}	16.2	18.2	7.00
SEd	0.23	0.20	0.07
LSD (5%)	0.48	0.42	0.15

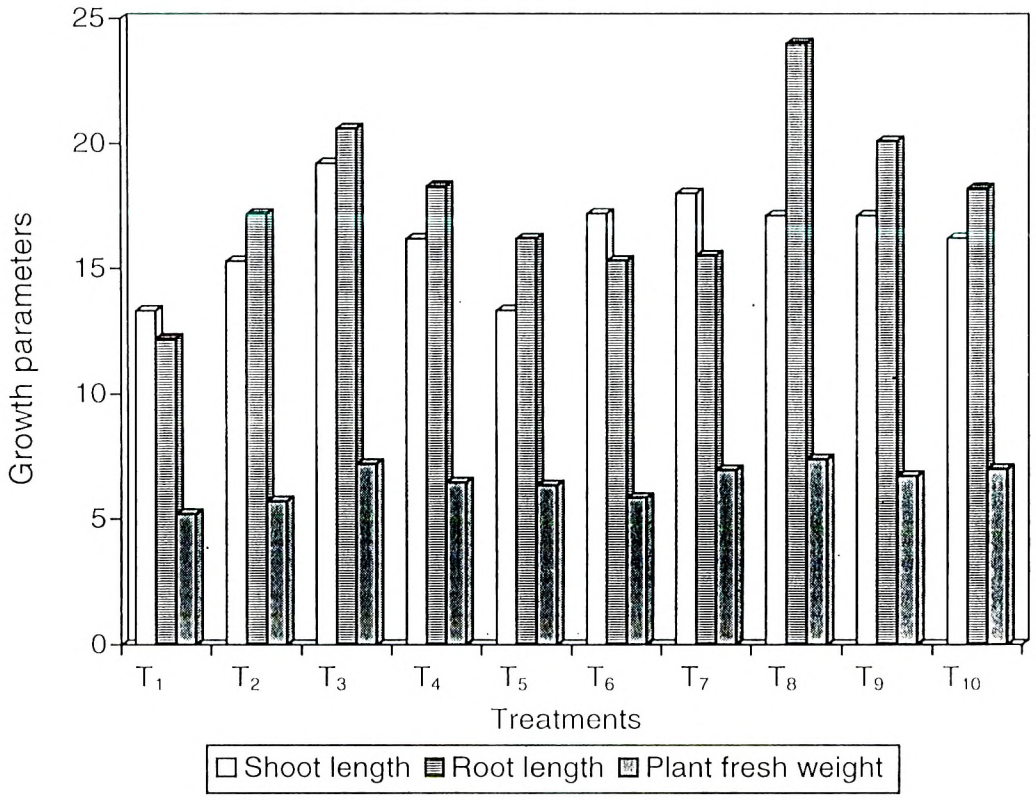


Figure 24. Effect of different levels of Pb with and without coir pith on growth parameters of castor

The root length was significantly influenced due to different levels of Pb with and without application of composted coir pith. It ranged between 12.2 (T_5) and 20.6 cm (T_3) in the absence of composted coir pith, whereas, it was between 15.3 (T_6) and 24.0 cm (T_8) in the presence of composted coir pith. Shorter roots were observed in control. Similar to shoot length, both in the presence and absence of composted coir pith, the increase in Pb significantly increased the root length only upto 500 mg Pb kg^{-1} and thereafter, declined significantly.

The biomass of castor in terms of fresh weight ranged from 5.2 (T_1) to 7.40 g (T_8). In control pots significantly lower values were observed. Increase in the rate of Pb kg^{-1} addition progressively had increased the biomass production upto 500 mg Pb kg^{-1} and thereafter, the biomass production was found decreased significantly. The highest value, 7.4 g was observed due to combined application of Pb (500 mg kg^{-1}) and composed coirpith (T_8). Further increase in the rate of Pb resulted in significant reduction in the biomass production.

4.6.2 Effect of different levels of lead with and without composted coir pith on Plant available Pb (DTPA-Pb)

The plant available Pb as measured through DTPA extractable Pb was significantly influenced by varied levels of Pb in the presence and absence of composted coir pith. In general the DTPA-Pb ranged from 2.7 (T_3) to 3.2 mg kg^{-1} (T_4, T_5, T_8) initially. Whereas, after the harvest of castor, it ranged between 3.0 (T_6) and 23.5 mg kg^{-1} (T_{10}). Increase in the level of Pb

had significantly increased the DTPA-Pb. Such an effect was more pronounced in the presence of composted coir pith. The highest value of 23.5 mg kg^{-1} was obtained with the addition of 1000 mg Pb kg^{-1} in the presence of composted coir pith. However, it did not significantly differ in the absence of composted coir pith (Table XXVII and Figure 25).

4.6.3 Lead accumulation in plant parts

The accumulation of Pb in different parts of castor as influenced by application of different rates of Pb with and without composted coir pith is furnished in Table XXVIII and in Figure 26. The Pb content ranged from 3.5 (T_1) to 22.7 mg kg^{-1} (T_5) (dry weight basis) in roots, 7.3 (T_1) to 31.0 mg kg^{-1} (T_{10}) in shoots and 3.9 (T_1) to 87.9 mg kg^{-1} (T_{10}) in leaves. Irrespective of the rates of Pb and composted coir pith addition, the Pb accumulation in castor follows the order : leaves > shoots > roots.

In roots, the increase in the rate of Pb application had significantly increased the Pb content. Though the application of composted coir pith did not result in a significant effect of Pb content in roots, these presented a significant difference at 250 and 750 mg Pb kg^{-1}.

In shoots, the Pb content ranged from 7.3 (T_1) to 31.0 mg kg^{-1} (T_{10}), the highest value being observed at 1000 mg Pb kg^{-1} (T_{10}). The control pots recorded the lowest values. Increase in the rate of Pb application significantly increased Pb content in shoots. Composted coir pith addition resulted in significantly higher Pb content at all the rates of Pb, except at 750 mg kg^{-1} (T_9).

Table XXVII. Effect of different levels of lead with and without composted coir pith on plant available Pb (DTPA – Pb) in black soils

Treatments	Initial	After harvest
Without composted coir pith		
T_1 - Soil (Control)	2.8	4.0
T_2 - Soil + 250 mg Pb kg^{-1}	3.1	9.6
T_3 - Soil + 500 mg Pb kg^{-1}	2.7	11.3
T_4 - Soil + 750 mg Pb kg^{-1}	3.2	17.1
T_5 - Soil + 1000 mg Pb kg^{-1}	3.2	23.2
With composted coir pith		
T_6 - Soil + Composted Coir pith	2.8	3.0
T_7 - Soil + Composted Coir pith + 250 mg Pb kg^{-1}	2.8	8.9
T_8 - Soil + Composted Coir pith + 500 mg Pb kg^{-1}	3.2	17.7
T_9 - Soil + Composted Coir pith + 750 mg Pb kg^{-1}	3.0	22.9
T_{10} - Soil + Composted Coir pith + 1000 mg Pb kg^{-1}	2.8	23.5
SEd	0.16	
LSD (5%)	0.32	

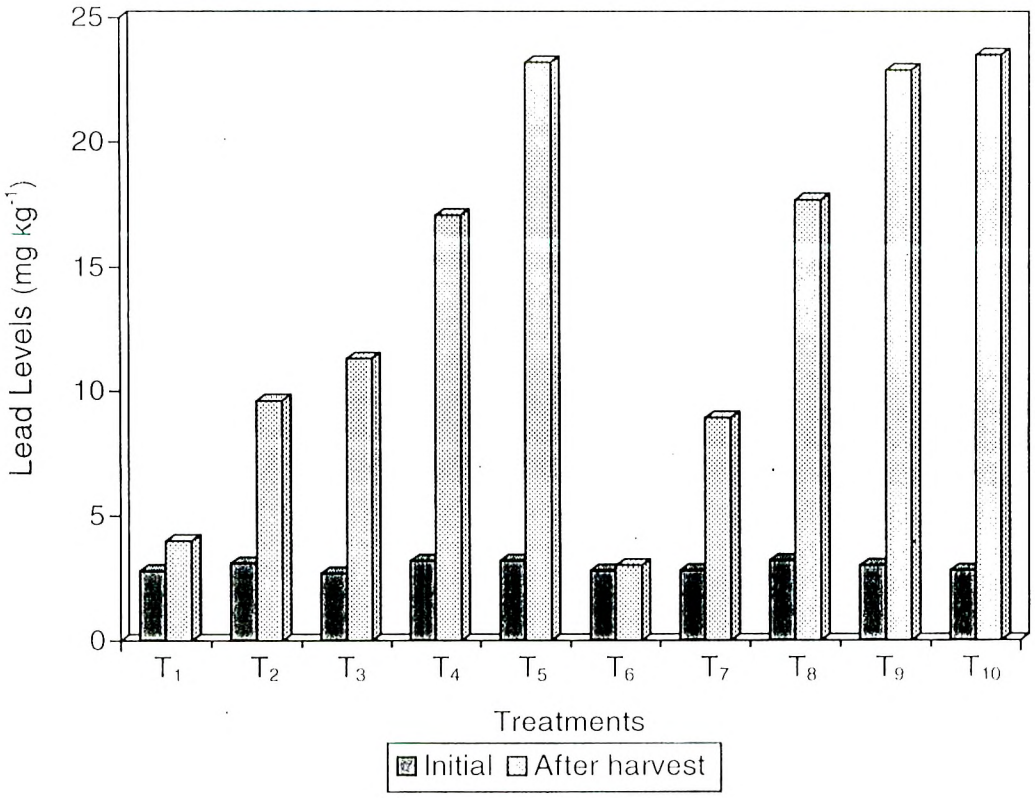


Figure 25. Effect of different levels of lead with and without composted coir pith on plant available Pb (DTPA-Pb) in black soils

Table XXVIII. Lead accumulation in different parts of castor plant as influenced by application of different levels of Pb with and without composted coir pith

Treatments	Pb (mg / kg)			
	Root	Shoot	Leaves	Total Pb uptake
Without composted coir pith				
T_1 - Soil (Control)	3.53	7.30	3.9	17.99
T_2 - Soil + 250 mg Pb kg^{-1}	16.9	17.3	41.2	48.55
T_3 - Soil + 500 mg Pb kg^{-1}	12.6	16.9	45.9	81.00
T_4 - Soil + 750 mg Pb kg^{-1}	14.7	26.0	56.8	65.15
T_5 - Soil + 1000 mg Pb kg^{-1}	22.7	29.0	54.1	99.32
With composted coir pith				
T_6 - Soil + Composted Coir pith	3.6	10.6	36.1	73.44
T_7 - Soil + Composted Coir pith + 250 mg Pb kg^{-1}	6.8	23.6	59.3	174.92
T_8 - Soil + Composted Coir pith + 500 mg Pb kg^{-1}	12.3	23.8	59.7	210.63
T_9 - Soil + Composted Coir pith + 750 mg Pb kg^{-1}	17.4	25.8	80.6	248.84
T_{10} - Soil + Composted Coir pith + 1000 mg Pb kg^{-1}	22.3	31.0	87.9	365.71
SEd	0.24	0.25	0.20	
LSD (5%)	0.51	0.52	0.43	

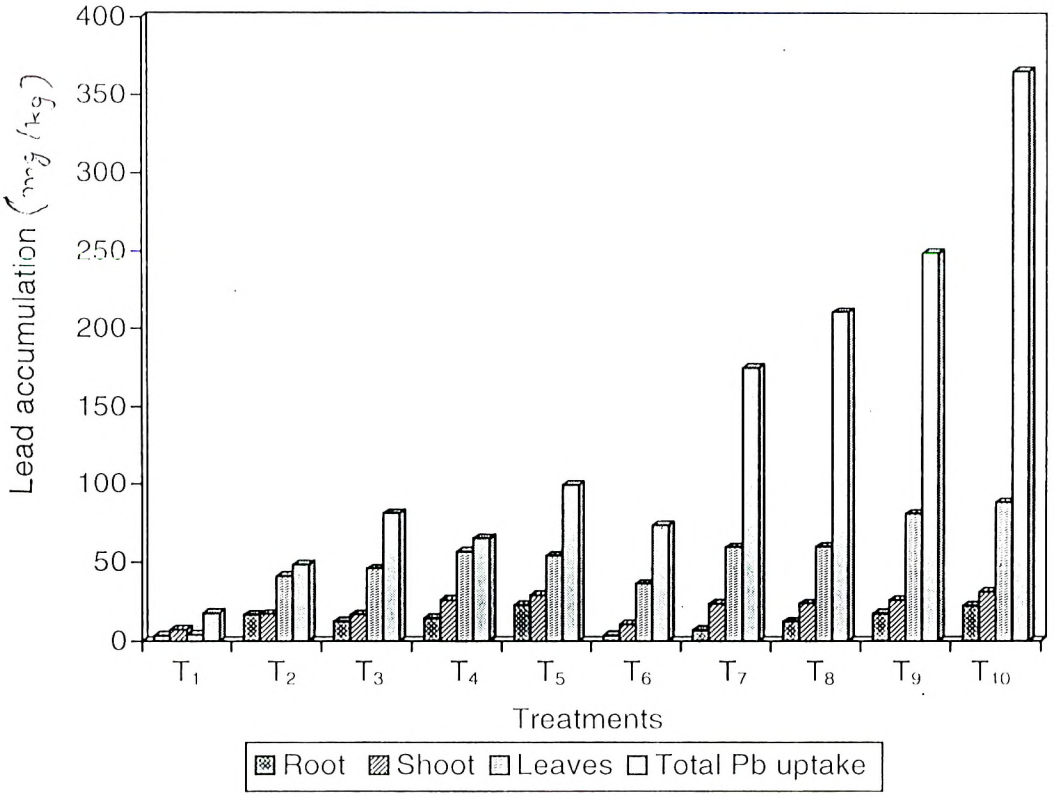


Figure 26. Lead accumulation in different parts of castor plant as influenced by application of different levels of Pb with and without composted coir pith

Leaves of castor accumulated relatively large amounts of Pb which ranged from 3.9 (T_1) to 56.8 (T_4) mg kg^{-1} in the absence of composted coir pith, whereas, it was 36.1 (T_6) to 87.9 (T_{10}) mg kg^{-1} in the presence of composted coir pith. Increase in the rate of Pb remarkably increased the Pb content and the highest value was observed at 750 mg Pb kg^{-1} and 1000 mg Pb kg^{-1}, respectively, in the absence and presence of composted coir pith.

The application of composted coir pith had very significantly influenced leaf-Pb content as significantly higher values were observed at all the rates of Pb in combination with composted coir pith.

4.6.4 Total uptake of Pb by castor

The uptake of Pb in castor as influenced by different rates of Pb is given in Table XXVIII. The uptake of Pb in castor varied from 17.99 (T_1) to 365.71 mg kg^{-1} (T_{10}) on dry weight basis. Increase in the rate of Pb addition had increased the uptake of Pb in castor. Addition of coir pith had significantly increased the uptake of Pb. Several fold increase was observed in the Pb uptake due to combined application of coir pith and Pb.

4.6.5 Effect of different levels of Pb without and with composted coir pith on soil pH

The pH of soil as influenced by different rates of Pb in combination with and without composted coir pith is given in Table XXIX and Figure 27. Initially the soil pH was 7.6 (T_1) with control, upon addition of Pb and composted coir

Table XXIX. Effect of different levels of Pb with and without composted coir pith on soil pH

Treatments	Initial	After harvest
Without composted coir pith		
T_1 - Soil (Control)	7.60	7.49
T_2 - Soil + 250 mg Pb kg^{-1}	7.51	7.40
T_3 - Soil + 500 mg Pb kg^{-1}	7.44	7.38
T_4 - Soil + 750 mg Pb kg^{-1}	7.36	7.20
T_5 - Soil + 1000 mg Pb kg^{-1}	7.22	7.12
With composted coir pith		
T_6 - Soil + Composted Coir pith	7.50	7.20
T_7 - Soil + Composted Coir pith + 250 mg Pb kg^{-1}	7.41	7.28
T_8 - Soil + Composted Coir pith + 500 mg Pb kg^{-1}	7.30	7.19
T_9 - Soil + Composted Coir pith + 750 mg Pb kg^{-1}	7.25	7.12
T_{10} - Soil + Composted Coir pith + 1000 mg Pb kg^{-1}	7.13	7.10
SEd	0.50	
LSD (5%)	0.09	

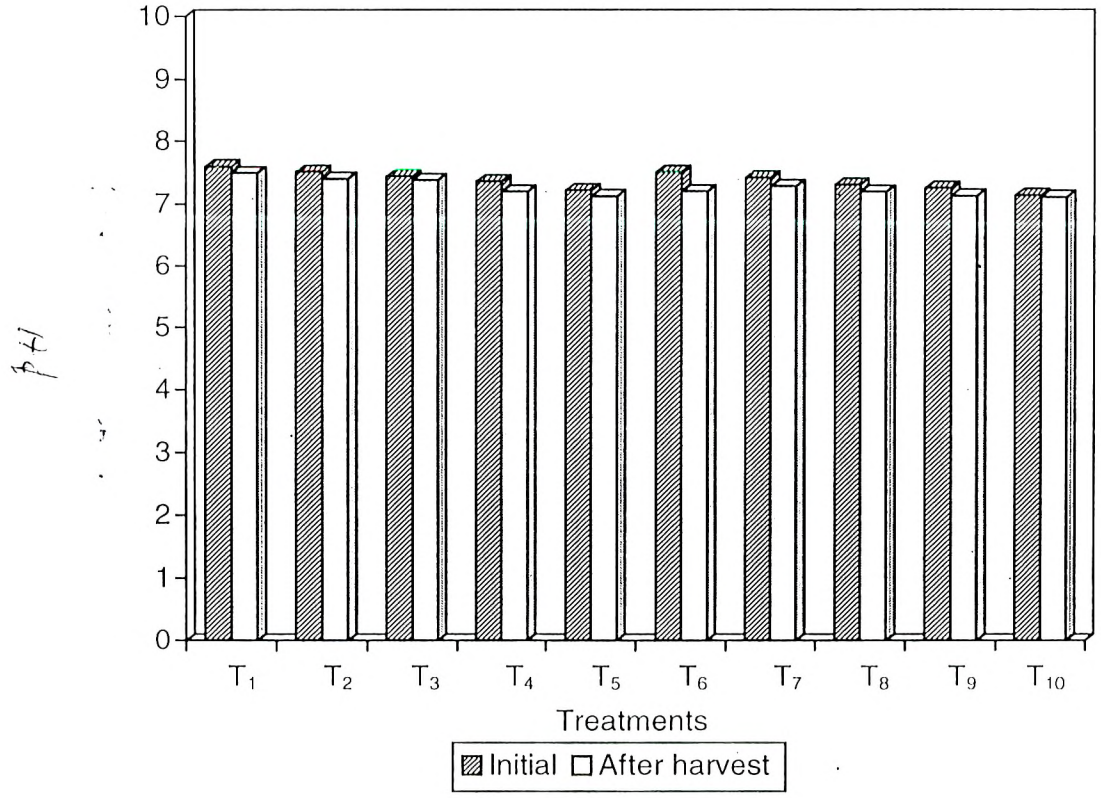


Figure 27. Effect of different levels of Pb with and without composted coir pith on soil pH

pith notable reduction in pH as low as 7.13 (T_{10}) was observed. There was a significant reduction in soil pH after the harvest of castor. Increasing the level of Pb significantly reduced the soil pH from 7.49 (T_1) to 7.12 (T_5, T_9) and the lowest value was observed at 1000 mg Pb kg^{-1}.

Application of composted coir pith had a significant effect on soil pH. In the control, the pH was reduced from 7.49 (T_1) to 7.20 (T_6), which further decreased to 7.1 due to combined application of 1000 mg Pb kg^{-1} and composted coir pith (T_{10}). There was a reduction in soil pHs at all levels of Pb due to presence of composted coir pith.

Plate 2



Soil, Water and Plant collected along National Highways 47.

Plate 3



Soil and plant collected along National Highways 47.

Plate 4



Soil and plant collected along State Highways 10

Plate 5



Water collected along State Highways 10

Plate 6



Soil collected from Coimbatore inner city - Mettupalayam Road

Plate 7



Plant and Water collected along Coimbatore inner city - Mettupalayam Road

Plate 8



Test plant along Highways (*Cyanodon dactylon*)

Plate 9



Test plant along inner city (*Boerhaavia diffusa*)

Plate 10



Collection of blood sample from automobile Personnel

Plate 11



Collection of hair sample from automobile Personnel

Plate 12



Collection of nail sample from automobile personnel

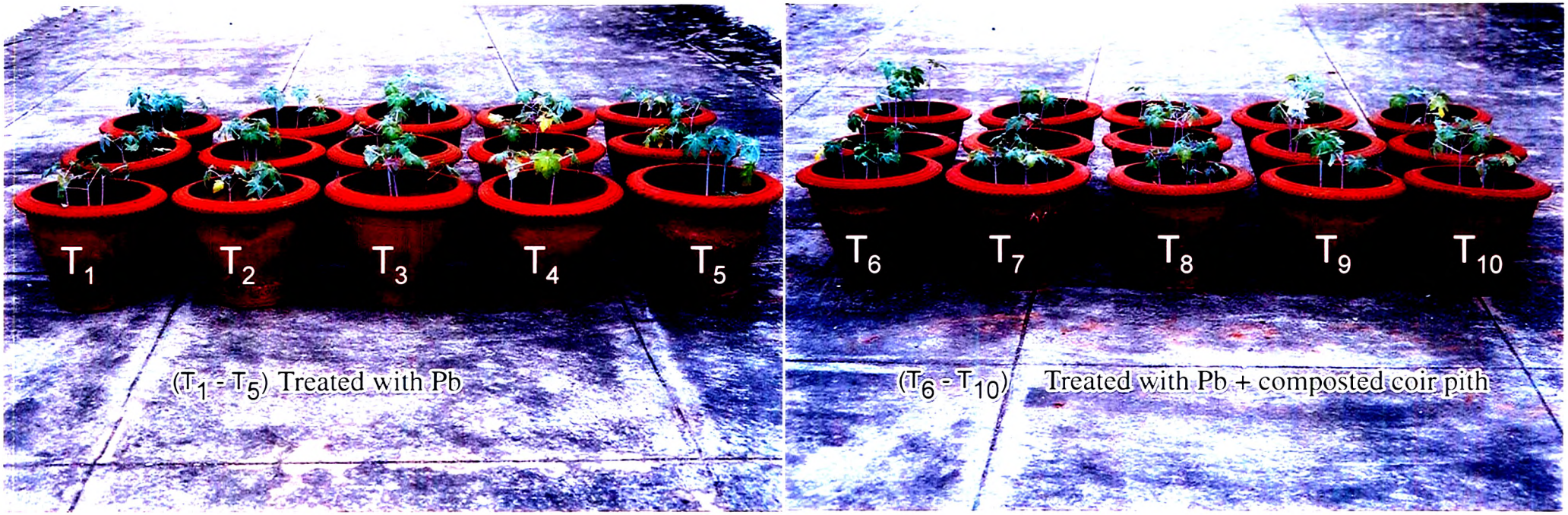
Plate 13





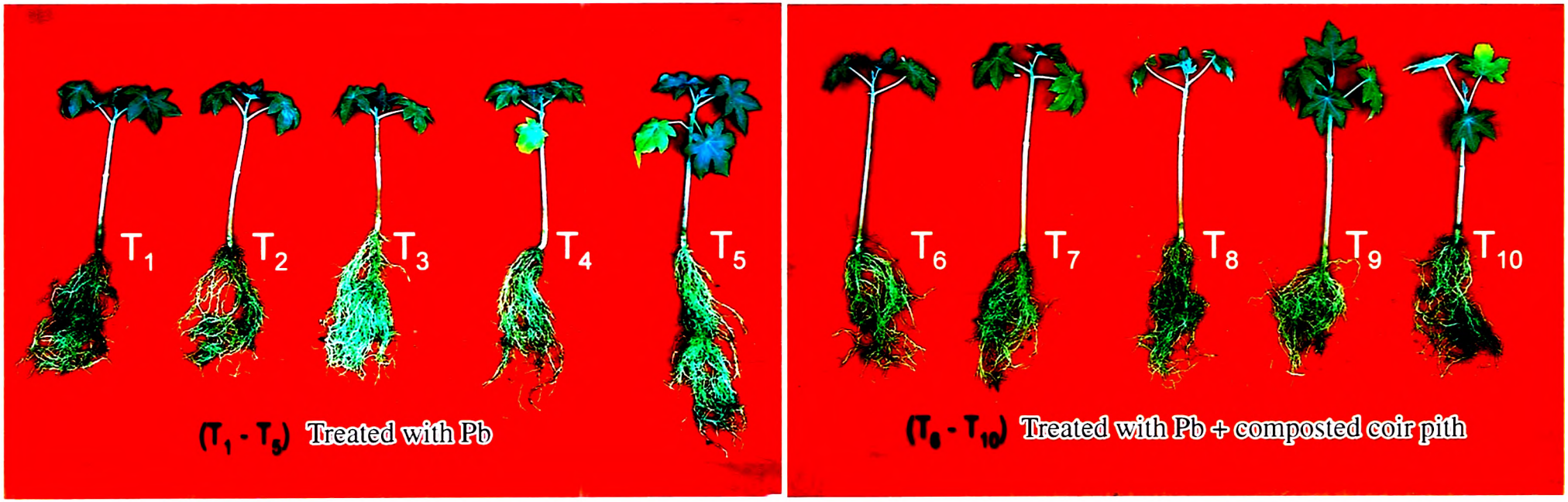
Coir pith deposition on road sides polluting the environment

Plate 14



Pot culture experiment of castor (*Ricinus communis*) with lead and composted coir pith amendment

Plate 15



Effect of Pb and Pb+ composted coir pith on the growth parameters of castor (*Ricinus communis*)

CHAPTER V

DISCUSSION

Automobile emissions are the major source of Pb pollution in the urban environment. Soil contamination can have dire consequences, such as loss of ecosystem and agriculture productivity, tainted water sources, diminished food chain quality, economic loss and human and animal illness.

5.1 LEAD CONTAMINATION IN URBAN ENVIRONMENT

The sampling location of the study includes National Highway 47 which connect Coimbatore to Palghat and State Highway 10 which connect Coimbatore to Pollachi, both of which exhibit heavy traffic.

The inner city areas selected for the study are representatives of different roads that exist in Coimbatore covering the east, west, north and south directions of the city. Town Hall road (South) is a major motorway where most of the economic activities of the city take place, whereas, Avinashi road (East) which comprises of more than 10 colleges on the same road is often packed with 2 and 3 wheelers. The road representing the west direction of the city, the Saibaba Colony road (West) comprises of the school zone and the other road selected for the study is the Mettupalayam road (North) with lower traffic density.

The traffic density of the roads followed the order :

Highways : State Highway 10 > National Highways 47

Inner city : Town Hall road (South) > Avinashi road (East) > Saibaba Colony road (West) > Mettupalayam road (North).

The quality of Pb emissions from vehicles to environment depends on various factors namely, Pb content of petrol, wind speed, quality of roads and speed of vehicles (Gajghate and Hasan, 1997). Gasoline based exhausts are the predominant source of Pb pollution in Kanpur city (Gajghate *et al.*,1998).

5.1.1 pH, Electrical Conductivity and Lead Content of Soil

The pH of the soil samples collected was generally higher in all the locations exhibiting the sodic nature of the soil. The higher pHs may be due to the predominance of cations such as Ca, Mg, Na and K in soil which tends to raise the soil pH.

The electrical conductivity as a measure of soluble salt content showed lesser content of soluble salts, though at certain locations the EC values were higher indicating higher salt accumulation in the soil.

Elevated concentrations of Pb were found in soils collected from both NH 47 (112.58 mg kg^{-1}) and SH 10 (128.93 mg kg^{-1}). Such accumulation of Pb is mainly attributed to automobile exhausts (Brown, 1986). Piron *et al.* (1992) reported Pb values ranging from 180μg/g near a road with heavy traffic density of 24,000 vehicles in Northern part of France, whereas,

Singh *et al.* (1997a) reported a concentration of only 44 µg/g near an Indian Highway with a traffic density of approximately 20,000 vehicles.

The inner city soils from heavy traffic roads exhibited higher concentrations of Pb which reflected severe Pb pollution in the urban environment due to automobile emissions. Soils from Town Hall road and Avinashi road, heavily packed with 2 and 3 wheelers had higher levels of Pb than from the soils of Saibaba Colony road and the low traffic Mettupalayam road. Roads with high traffic load had more Pb levels than residential roads (David and Babur, 1992). It has been observed that the street dust levels fall off with distance from busy roads, with traffic density and distance from central city area (Fergusson and Simmonds, 1983 ; Hamilton *et al.*, 1984 and Davies *et al.*, 1987).

The chances of Pb exposure is much greater in surface soils than in subsurface soils. The concentration of Pb in soils along Highways was generally higher in the surface soils than in the subsurface soils, though a relative increase in the Pb concentration was observed in the subsurface soils at certain locations. According to Vidic *et al.* (1997) the concentrations of Pb in soils decreased with depth and distance from the road suggesting that even though Pb is considered relatively immobile (Adriano, 1986) some migration into deeper areas occurs in polluted soil.

Surface soils showed higher content of Pb than the subsurface soils along the inner city. As Pb is immobilized by the organic component of the soil, Pb deposited from the air generally retained in the upper 2-5 cm of

undisturbed soil (EPA, 1986). A significant drop in soil-Pb concentration from 1130 μg g^{-1} in the top 0 - 2 cm to 350 μg g^{-1} in the 8-10 cm of soil profile was noted by Fergusson *et al.* (1980).

5.1.2 Pb content of water samples

Wide variation in the water-Pb concentration was observed between National and State Highways. High concentrations of Pb was also observed in inner city water samples. Urban surface water usually contains Pb from atmospheric washouts and road run-offs due to pollution from vehicular emissions. The concentrations are usually higher in areas closer to the land and in confined areas such as in harbours and channels because of additional sources of Pb from urban run-off and sewage (Bernhard,1980 ; Burnett *et al.*, 1980 ; Mart *et al.*,1980 ; Schaule and Patterson,1981 ; Smith,1986). Water samples from State Highway 10 recorded higher concentrations of Pb than from National Highway 47.

Lead concentration in water is generally influenced by the content of Pb in soils. The transformation of Pb into soluble form enhances the leaching of Pb in soil profile and eventually would contaminate the ground water. The positive correlation (r = 0.140) observed between water-Pb and soil-Pb further confirms these observations (Figure 28).

It is assumed that a significant portion of Pb in these water samples is bound to colloids, either hydrous iron oxides or organic macromolecules depending on the composition of the water. Hart and Davies (1981) found that

in the fresh water about 45 per cent of total Pb was present in particulate form. The calculated equilibrium distribution of ion-exchangeable species showed that $PbCO_3$ accounted for about 80 per cent, with smaller contributions from Pb^{2+} and Pb (OH^+).

Inner city water samples collected from Mettupalayam road showed higher concentrations of Pb which is mainly attributed to the leaching of soil-Pb to the ground waters. According to Sadiq (1992) the ability to form complexes may increase its mobility through soil profiles, which, in turn should have elevated the Pb concentrations in ground water.

The safe limit for Pb in drinking water fixed by the Ministry of Health, Government of India (1971) is 0.1 mg l^{-1}. In the present investigation most of the water samples examined in the Coimbatore urban environment exceeded the maximum permissible limit of Pb prescribed for drinking water.

5.1.3 Pb content in Plants

Plants along highways showed higher accumulation of Pb than plants from the inner city. The Pb content in plants appeared to have increased with increase in Pb content in soil. Lindberg and Harris (1981) concluded that Pb was absorbed internally by leaves or irreversibly adsorbed onto leaf surfaces. As with the soils, plants (*Cyanodon dactylon*) along State Highways (136.93 mg kg^{-1}) showed higher accumulation of Pb than from National Highways (79.93 mg kg^{-1}). Similar results were reported by Saxena *et al.* (1991). The accumulation of Pb in vegetation through aerial

deposition near highways varies with vehicular traffic density and distance from roads (Thakre and Vittal, 1985).

Higher concentration of Pb was observed in plants (*Boerhaavia diffusa*) collected along the inner city. The plants from different locations differed significantly in their Pb content. This may be due to differential uptake resulting from different levels of soil Pb. The accumulation of Pb was highest in plants along Avinashi road, whereas, the least concentration of Pb was observed in plants collected from Mettupalayam road. Lord *et al.* (1979) stated that entry of Pb in the plant system is mostly through stomatal pores.

A positive correlation (r = 0.119) was observed between soil-Pb and plant-Pb (Figure 29).

5.1.4 Lead accumulation in Biological samples (human tissues)

Vehicular exhausts have resulted severe in concentrations of Pb in soil, water and plant from where it enters the human body. The impact of Pb contamination in the urban environment was clearly exhibited on Pb accumulation in human tissues. Debbie *et al.* (1991) reported that environmental Pb levels were elevated near heavy traffic and automobile emissions, which were considered to be a major source of increased blood levels of children attending schools near heavy traffic at Cape Town.

Though blood showed normal Pb level, hair and nail samples appeared to have accumulated large amounts of Pb. Quinn and Delves (1987) reported elevated blood levels in people whose work takes them into contact with

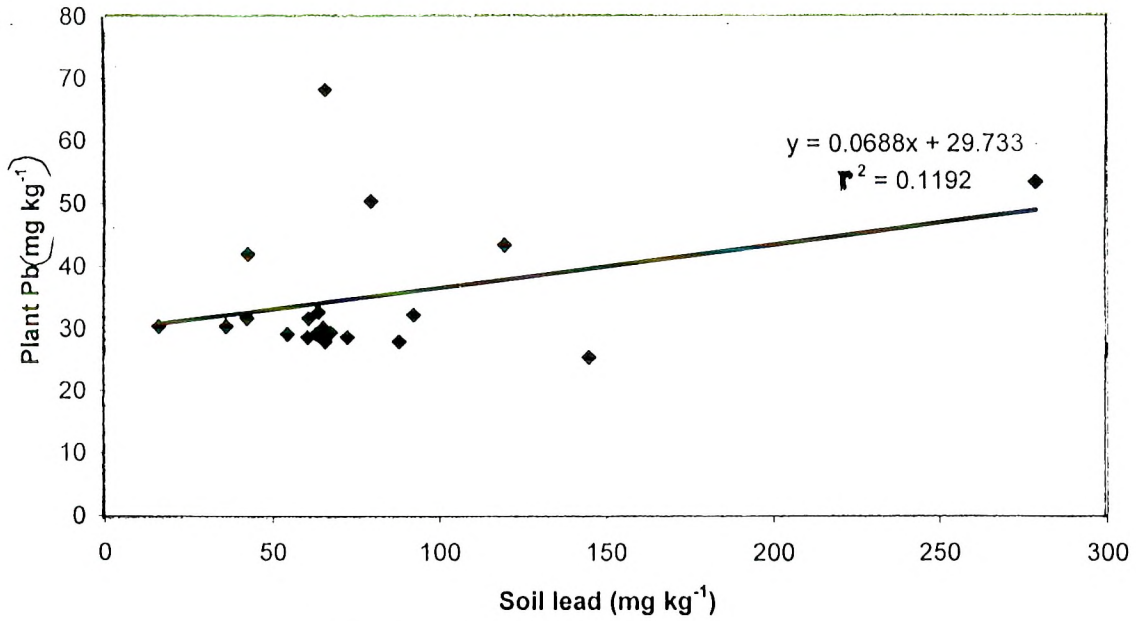


Figure 28. Correlation between soil lead and water lead along Avinashi road (East)

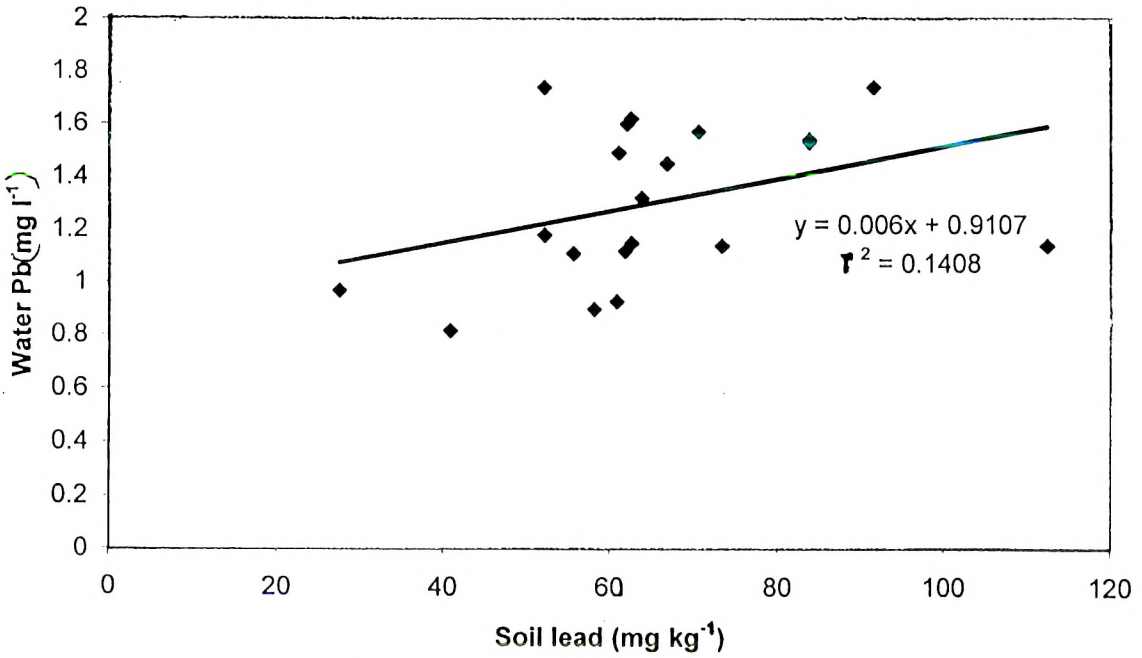


Figure 29. Correlation between soil lead and plant lead along Town Hall road (South)

petrol. e.g. petrol vendors, traffic policemen, taxi drivers and toll booth operators when compared with control groups. Multifold increase in nail-Pb content was observed in automobile personnel due to automobile exhausts. Inner city people have higher blood levels than sub urban and sub urban higher than rural (Taskenin *et al.*, 1981 ; McBride *et al.*, 1982 ; Brunekreef *et al.*, 1983 ; Elwood *et al.*, 1984 ; Schutz *et al.*, 1984 ; Skerfving *et al.*, 1986 and Heany *et al.*, 1988).

5.2 TRANSFORMATION OF LEAD IN SOILS

The chemistry and toxicity of Pb in soil are largely governed by the species (forms) of Pb and their transformation in soils. Depending upon soil and environmental factors prevailing in situ, Pb undergoes both chemical and biological transformations. Total Pb in soils includes five 'pools' classified according to their physico-chemical properties. The pools include soluble (H_2O extractable-Pb), exchangeable (KNO_3 extractable-Pb), organically bound (NaOH extractable-Pb), iron-oxide bound (EDTA extractable-Pb) and residual (HNO_3 extractable-Pb) fractions.

The results from the incubation experiment have shown that both the moisture conditions and soils play significant role on Pb-transformation in soil. The concentrations of soluble, exchangeable and organically bound-Pb were higher under field capacity moisture content (M_1) than under alternate wetting and drying (M_2). This may be due to continuous dissolution of $Pb(NO_3)_2$ in soil which would have increased the Pb concentration in soil and further facilitated chemical and microbially mediated transformations in soil. Under alternate

wetting and drying, some portion of soluble and exchangeable forms might have been strongly adsorbed by soil mineral lattice and this reduces their concentrations.

During the incubation, the increase in the rate of Pb application had significantly increased the concentration of soluble and exchangeable-Pb in both black and red soils. The soluble and exchangeable forms are of special importance, as they represent bioavailable forms, which, at high concentration become toxic.

It is likely that the increase in the concentration of soluble and exchangeable-Pb during incubation event enhances the leaching of Pb in the soil profile and contaminates the ground water. The difference between the two soils could be ascribed to the physical, chemical and biological characteristics of black and red soils used in the incubation experiment.

Both the period of incubation and moisture conditions exerted profound influence on the concentration of organically bound-Pb and iron oxide bound-Pb in both soils. With the increase in the period of incubation the organically bound-Pb markedly increased, both under field capacity moisture and alternate wetting and drying. Correspondingly, the iron oxide bound-Pb progressively decreased during incubation. This suggests that a portion of iron oxide bound-Pb is dissolved in soil solution and is made available for microbially mediated transformation (biotransformation) to organic form. As microbes are active, the biotransformation is continuously taking place and

results in the higher concentration of organically bound-Pb. Decrease in the residual fraction of Pb also provides an evidence.

The results provide evidence that in urban soils, Pb undergoes both chemical and biological transformation, resulting in a large amount of soluble, exchangeable and organic bound-Pb. It is likely that soluble-Pb (H_2O-Pb) may leach down in the soil profile and there is a risk of ground water contamination, in urban areas. Increase in soil pH (to 8.0) resulted in higher adsorption in both soils. Even at a high rate of Pb application (1000 mg Pb kg^{-1}) more than 90 per cent adsorption occurred in both soils, particularly, at pH 8.0. Change in soil pH by several units will change the adsorption capacity of soil for many metals as has been reported for minerals and soils (Duker *et al.*, 1995 and Boekhold and Vanderzee, 1991).

Irrespective of soils, the higher adsorption occurred at pH 8.0, probably because for most components with variable charge, such as organic molecules and oxide minerals, charge reversal from positive to neutral to negative occurs at this pH. A practical raising of soil pH increases Pb adsorption and thus reduces its potential toxicity to crops.

5.3 ADSORPTION OF LEAD ON SOIL

Adsorption and desorption reactions of Pb in soil are considered to be the major factors controlling the bioavailability and leaching of Pb in soil. Therefore, in this study, the adsorption of lead on urban soils was studied.

Adsorption of Pb by the soils was examined through laboratory batch experiments. Preliminary experiment (data not presented) had shown that Pb sorption by the urban soils (black and red) was rapid up to 24 hours and later on slowed down. This might be due to the diffusion of Pb into the soil aggregates. However, in both soils the adsorption continued to increase with time. The Mitscherlich function indicated that more than 90 per cent of adsorption occurred within 24 hrs and hence in order to give sufficient contact time to ensure an equilibrium system, a 24 hrs shaking time was adopted for all adsorption experiments.

In both soils the adsorption was found increased with increase in Pb concentration. Irrespective of soils, graded levels of Pb additions and soil pHs had marked influence on Pb adsorption. The red soil recorded significantly higher adsorption than the black soil. This might be due to the difference in the chemical characteristics of the original soils. The higher amount of iron and aluminium oxide present in red soil might have increased the adsorption of Pb. The organic fractions seem to be a source of sites for specific Pb adsorption as it forms inner-sphere complexes at a wide range of pH values. Conversely organic complex formation could lead to increased mobility in the soil, since Pb is known to form soluble complexes with fulvic acids. Adsorption into organic matter, clay minerals and metal oxides in soils is the main mechanism of heavy metal removal from soil solution (McBride, 1989 and Scheidegger and Sparks, 1996). Since the oxides have variable charges, the extent to which adsorption occurs, is dependent on the pH of solution (Barrow, 1987 and Bolan *et al.*, 1999). Cavallaro and McBride (1984) found

that the treatment of the clays for the removal of organics tended to either enhance or have little effect on adsorption and fixation of Zn and Cu. They suggested that oxide components of clay are more significant than the organic component in metal sorption and fixation.

The adsorption capacities of soils at varying initial equilibrium concentrations were examined using the following linearized Freundlich equation.

$$\log (X/m) = \log K + 1/n \log Ce$$

where,

X/m = Amount of Pb adsorbed per unit mass of soil mg kg^{-1}

Ce = Equilibrium concentration of Pb in solution mg l^{-1}

k = Constant related to adsorption capacity

1/n = Constant related to adsorption intensity

* $y = k\ Ce^{1/n}$

where,

k = Adsorption capacity mg kg^{-1}

Ce = Equilibrium concentration mg l^{-1}

1/n = Adsorption intensity

Table XXX. Freundlich equation obtained for Pb adsorption

Soil	Equation	r^2
pH 6.0		
Black soil	$Y = 73.04\ C^{0.45}$	0.94
Red soil	$Y = 90.46\ C^{0.64}$	0.96
pH 8.0		
Black soil	$Y = 120.45\ C^{0.86}$	0.98
Red soil	$Y = 132.13\ C^{0.97}$	0.99

The Freundlich constant (K) values increased with increasing pH in both black and red soils. The adsorption constant strongly correlated with soil pH and the r values varied from 0.94 to 0.99 (Table XXX). Higher r^2 values were associated with high soil pH.

The retention capacity was calculated on the basis of the distribution coefficient (kd') which is a function of the activity of the dissolved Pb in equilibrium with soil particles.

$$kd = \frac{\text{Pb adsorpted per kg soil}}{\text{Equilibrium concentration of Pb (mg } l^{-1})}$$

The distribution coefficients obtained for black and red soils at two different pHs are presented in Table XXXI.

Table XXXI. Distribution coefficients for black and red soils

Rate of Pb addition (mg Pb kg^{-1})	Black soil		Red soil	
	pH 6.0	pH 8.0	pH 6.0	pH 8.0
250	2.37	2.40	3.0	5.76
500	4.38	5.57	6.75	7.15
750	6.36	7.77	6.46	12.73
1000	8.26	10.23	7.70	14.65

Irrespective of soils the 'kd' value markedly increased with increasing rate of Pb addition at both pHs. The 'kd' values were higher at pH 8.0 in both soils. The red soil recorded higher values of 'kd' at high pH than black soil

indicating higher adsorption of Pb in this soil. It could be inferred that at higher pHs, soils have larger affect towards Pb adsorption.

5.4 LEACHING OF LEAD

Using disturbed soils in columns, the transport and mobility of Pb in two urban soils (black and red) was examined. The data showed that increase in the concentration of Pb (0 to 1000 mg Pb kg^{-1}) substantially increased the concentration of Pb in the leachate and therefore increased the total amount of Pb leached from both black and red soils. This may be due to continuous dissociation of Pb from Pb $(NO_3)_2$ which increased the Pb concentration and subsequently leached from soil. As explained earlier, the dissolved Pb in soil might also have transformed into soluble (H_2O-Pb), exchangeable (KNO_3-Pb) and organic (NaOH-Pb) forms of Pb. Increase in the rate of Pb addition increased the Pb concentration in the solution and resulted leaching of Pb in higher amounts. Significant difference in the Pb concentration of leachate and the total amount of Pb leached were observed between the two soils. The ability to form complexes may increase its mobility through soil profiles which in turn should have elevated the Pb concentration in ground water (Sadiq, 1992). Both the leachate concentration and the total amount of Pb leached were significantly higher with the black soil than the red soil. It could be due to the difference in physico-chemical properties of black and red soils studied. According to Alloway (1995) the retention of added heavy metals to soils is often correlated with soil organic matter.

The black soil contains relatively higher amount of organic matter and thus organic carbon. As the organic fractions seem to be a source of sites for specific adsorption of Pb it forms inner-sphere complexes at a wide range of pH values. Conversely organic complex formation could lead to increased movement in the soil, since Pb is known to form soluble complexes with fulvic acids. This might have resulted in relatively large amounts of Pb leached down from the soil column (Camobreco *et al.*, 1996). Relatively higher adsorption of Pb on metal (Fe/Al) and mineral (Kaolinite) surfaces reduce the amount of Pb leached from red soil column. Similar results were reported by Elliott *et al.* (1986) who reported that metals can bind to soil through the processes of ion exchange and chemo-sorbtion. Oxides of Fe, Al and Mn can provide chemo-sorbtion sites for metals.

In general it has been observed that a large amount of Pb was found leached from both soils occurring in the urban environment. In spite of high adsorption of Pb on these soils, the results from column experiment have shown that the increase in the concentration of Pb in soils is likely to contaminate the ground water. Therefore, there is a risk of ground water contamination due to Pb in the severely contaminated areas within the urban environment.

5.4.1 Effect of leaching on lead accumulation

Lead was found accumulated in large amounts due to application of different levels of Pb in both soils. Irrespective of soils, significantly large amounts of Pb was observed in subsurface than in surface soil mainly due to

downward movement of Pb along with leaching water. Most of the Pb in soil is insoluble precipitate or bound to soil solids. In most soil solutions only a small fraction of Pb is present as free ionic species (Pb^{2+}). Most of the soluble Pb being complexed with dissolved organic matter (Sauve *et al.*, 1997). The solubility of Pb and physico-chemical characteristics of soil influence the leaching and accumulation of Pb in soils. The pH of soils plays a major role on the fate of applied Pb in soils. Increase in the rate of Pb markedly reduced the soil's pHs after the leaching event.

5.5 REMEDIATION

PLANT AVAILABILITY OF LEAD

The dissolved and exchangeable forms of Pb in soil are of special importance in plant nutrition. Lead in soil solution, exchangeable, specifically adsorbed and organically bound-Pb are considered in equilibrium. They represent the available forms for plant uptake. Iron oxide bound and residual forms of Pb are relatively unavailable to plants.

The change in the concentration of available Pb as extracted in DTPA extract during 60 days incubation was examined. The result showed that the addition of Pb at a rate equivalent to 1000 mg Pb kg^{-1} soil markedly increased the concentration of plant available Pb in soil. The rate of increase was higher upto 30 days and slowed down afterwards. As explained earlier, the continuous dissolution of Pb $(NO_3)_2$ might have increased the availability of the Pb in soil. In soil solution Pb is present as (i) inorganic complexes of Pb, (ii) Pb complexed with soluble organic matter, and (iii) uncomplexed-Pb or

ionic-Pb. The existence of these forms is dependent on the pH of soil solution. It is likely that at low pH, a higher proportion of Pb is present as the uncomplexed ion and with increasing pH, soluble Pb-organic complexes became more significant.

Addition of composted coir pith had remarkably reduced the plant available Pb in soil at all days of incubation. This could be due to either adsorption of Pb on organic matter (coir pith) or formation of Pb-organic complex in soil. Organic matter plays a major role in the retention of Pb in soils. The organic fraction seems to be a source of specific Pb sorption sites in coir pith amended soils. Organic complex formation could lead to an increased mobility in the soil, since Pb is known to form stable complexes with fubric acid. The complexing of Pb by organics can also affect retention by mineral surfaces. This could be also attributed to the increased sorption capacity to exposed edges as well as to the presence of carboxylate and phenolic groups. The complexing of metals by carboxylate groups is commonly proposed as a mechanism of metal retention in soil (McLaren *et al.*, 1981). The results suggest that addition of organics / biological wastes like composted coir pith could be useful in reducing the phytoavailability of Pb in soil, thus biotoxicity of Pb could be minimized.

5.6 PHYTOREMEDIATION

The use of plants to remove toxic metals from soil (Phytoremediation) is emerging as a strategy for cost effective and environmentally sound remediation of contaminated soils. Phytoremediation as a soil cleanup

technology seeks to capitalize on the ability of metal accumulating plants to extract metals from the soil with their roots and to concentrate these metals in above ground plant parts.

In the present study, castor (*Ricinus communis*), a commonly grown plant in water ways and in ditches, was identified and evaluated for its potential in hyper accumulating Pb and tolerance under high Pb status in soil.

5.6.1 Effect of lead on growth of castor

The results of the mini-pot experiment showed that different rates of Pb addition had significant influence on growth of castor (*Ricinus communis*). The shoot growth was found increased upto 500 mg Pb kg^{-1} soil and thereafter, markedly reduced. Though no toxicity symptoms were observed, the growth of castor at 1000 mg Pb kg^{-1} soil was found equal to that of plants in control. A similar trend was also observed in root growth. These results corroborate with the findings of Manju *et al.* (2000) in green gram. However, Lane *et al.* (1978) reported that the presence of Pb has a marked influence on the elasticity / plasticity of the cell wall, resulting in an over-all increase in tissue walls rigidity.

Lead was reported to inflict reductions in growth. A significant correlation was observed between addition of Pb + CCP and Pb accumulation in plants. The correlation between shoot Pb Vs added Pb + CCP was higher (r = 0.88) followed by leaves Pb Vs added Pb + CCP (r = 0.72) and root Pb Vs added Pb + CCP (r = 0.61) (Figure 31). Most of the studies indicate

that Pb does bind to membranes and this binding is likely to be associated with detrimental effects (Saxena *et al.*, 1991). Lead has also been found to affect the flow of electrons in electron transfer reactions (Bittel *et al.*, 1974).

The application of composted coir pith along with graded levels of Pb had significant effect on castor. At lower level (250 mg Pb kg^{-1}) the shoot and root length were reduced in the presence of composted coir pith. Whereas, the composted coir pith notably increased the length of shoot and root at all the level of Pb application (from 500 to 1000 mg Pb kg^{-1}). A highly significant correlation was observed between Pb addition and accumulation of Pb in plants. The correlation between root Pb Vs added Pb was higher (r = 0.97) followed by leaves Pb Vs added Pb (r = 0.53) and shoot Pb Vs added Pb (r = 0.41) (Figure 30).

A similar trend was also observed with regard to biomass production. Significant improvement in the growth of castor (length of shoot and root and biomass production) was observed in the presence of composted coir pith at all levels of Pb application. This suggests that composted coir pith application was found to alleviate the toxic effect of Pb at its higher concentration. Since most of the Pb added to soils is associated with organic matter (due to composted coir pith) a large proportion of the Pb in soil might have formed organic complex and decreases the plant availability of Pb in soil. This might have favoured relatively better growth under composted coir pith application.

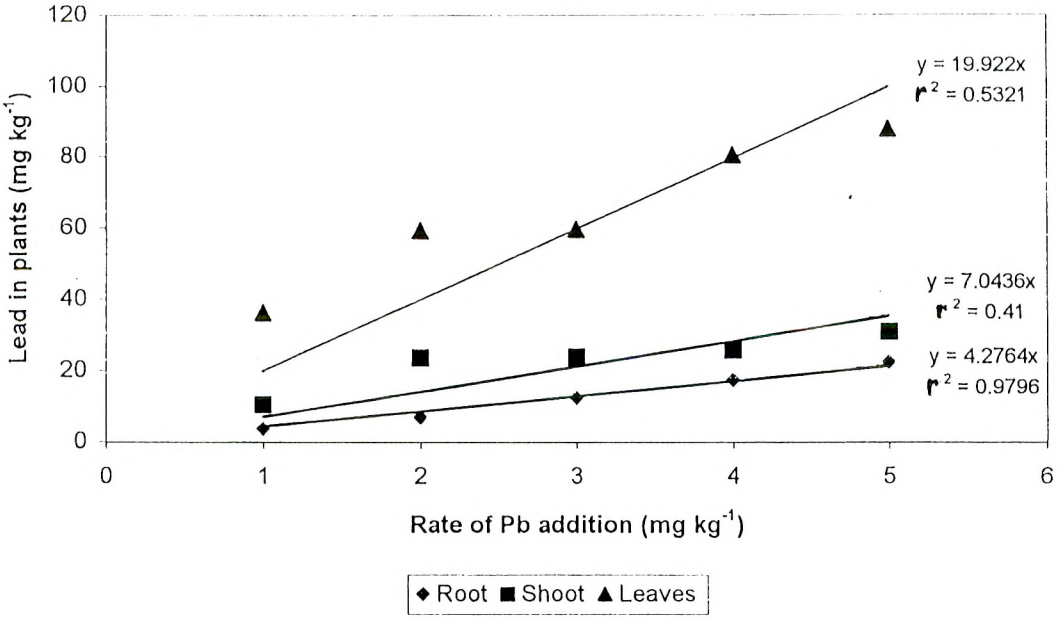


Figure 30. Correlation of root lead, shoot lead and leaf lead of castor as influenced by the different levels of lead with composted coir pith

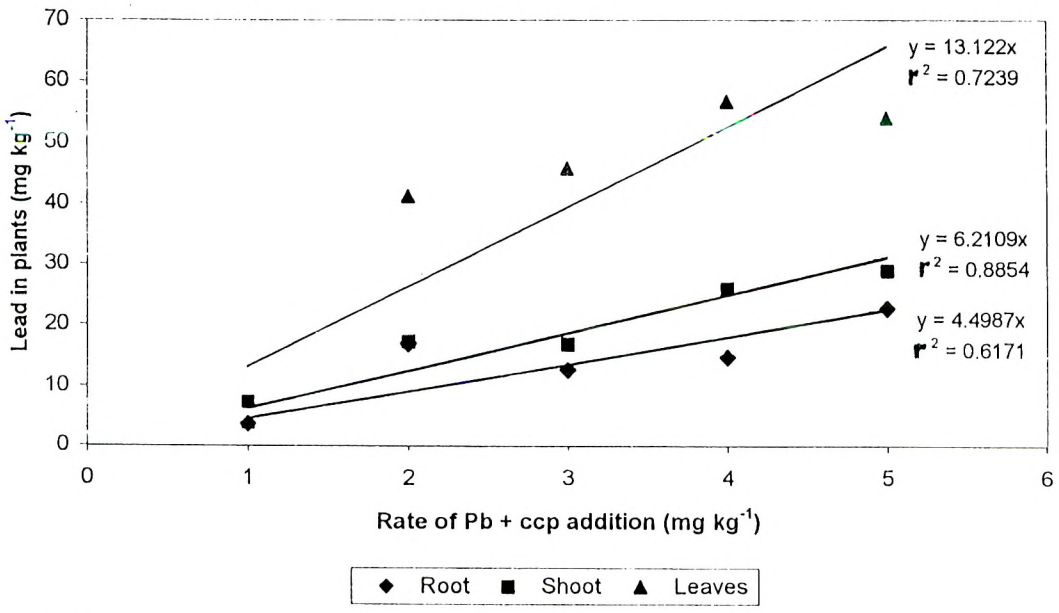


Figure 31. Correlation of root lead, shoot lead and lead of castor as influenced by the different levels of lead with composted coir pith

5.6.2 Lead accumulation in castor

In general the accumulation of Pb in castor follows : leaves > shoot > root pattern. Similar pattern in the accumulation of Pb was reported by Saxena *et al.* (1991) in sorghum, maize and wheat grown adjacent to highways. In roots, the increase in the rate of Pb application had significantly increased the Pb content. The composted coir pith application effected only a small difference in Pb content of plants.

Higher content of Pb in leaves of castor suggests that Pb is rapidly translocated within the plant system. The highest Pb content of 87 µg / g (dry weight of plant material) was observed in plants. According to Pahlsson (1989), the plant species are sensitive to Pb at a concentration ranging from 25 to 85 µg / g. This study, therefore, showed the potential of castor in tolerating higher concentration of Pb.

Increase in the rate of Pb application remarkably increased the Pb content in shoot and leaves. Leaves of castor appeared to have accumulated relatively large amounts of Pb. The highest accumulation was observed due to the combined application of composted coir pith and Pb at a rate of 1000 mg Pb kg^{-1}. A similar trend was also exhibited in total uptake of Pb by castor. Higher accumulates of heavy metals in different parts of rice plants were observed (Ray *et al.*, 1988).

It is likely that most of the Pb added to soil would be associated with organic matter (in the presence of composted coir pith). Therefore, a large

proportion of the Pb taken up by castor must have originated from soluble organic complexes. The dissociation of Pb from the organic ligand apparently must occur prior to plant uptake. The case with which the dissociation and subsequent absorption of Pb by plant takes place will, therefore, depend upon the complexing ligand and this, in turn, will depend on the soil in which the plant is growing, as well as conditions within that soil.

The decomposition of composted coir pith produces organic acid in soil resulting in decrease in soil pHs. The organic acid thus produced might have solubilized the organic Pb and increased the plant availability of Pb. The data on soil pHs and the plant available Pb as extracted in DTPA extracts after the harvest of castor plants in the mini pots further lend support to these observations.

The study has shown that use of castor and composted coir pith could be a successful remediation technology for Pb contaminated sites. However, the application of composted coir pith to the road sides along highways may not be practically possible. Therefore, growing castor may be encouraged in urban areas to minimize the Pb pollution.

SUMMARY AND CONCLUSION

CHAPTER VI

SUMMARY AND CONCLUSION

Lead (Pb), a toxic heavy metal, is being introduced into the environment by automobile emissions mostly from petrol driven vehicles. Accumulation of Pb in urban soil-water results in serious environmental threats. The level of Pb contamination in soil and its impact on water, plant and humans has not been well documented. Therefore, a study was undertaken to quantify Pb pollution due to automobile emissions in a typical urban environment. The chemistry of Pb, particularly transformation, adsorption, plant availability and transport and mobility in urban soils was examined through a series of laboratory experiments. Some of the phytoremediation and bio-remediation techniques were also evaluated through pot experiment. The results obtained from the study are summarised below.

Lead pollution in urban environment

- Elevated concentrations of Pb were found in soils collected from National Highway (NH 47) and State Highway (SH 10). Such accumulation of Pb was mainly attributed to automobile exhausts. Lead accumulation in soil was positively correlated with traffic density in the city.

- The soils collected from inner city with heavy vehicular flow exhibited higher concentration of Pb which reflects Pb pollution in the urban environment due to automobile emissions. The soils near roads that had heavy flow of two and three wheelers also had higher levels of Pb.

- In most of the locations examined, surface soils showed higher Pb content than subsurface soil as Pb is relatively immobile in soil.

- Most of the water samples examined in the Coimbatore urban environment exceeded the safe limit of Pb (0.1 mg l^{-1}) for drinking water prescribed by the Ministry of Health, Government of India.

- Plants (*Cyanodon dactylon* and *Boerhaavia diffusa*) grown profusely along Highways showed higher accumulation of Pb than plants in inner city, and a strong positive correlation was observed between plant-Pb and soil-Pb.

- The impact of Pb pollution in the urban soil-water-plant ecosystem was clearly exhibited on Pb accumulation in human tissues. Though blood samples had normal Pb level, hair and nail samples had higher accumulation of Pb.

Transformation and adsorption of lead

The transformation of Pb in urban soils was investigated through open incubation experiment, by measuring the changes in various fractions of Pb. The following are the results :

- The concentrations of soluble (H_2O-Pb), exchangeable (KNO_3-Pb) and organic (NaOH-Pb) were higher in soils under field capacity moisture than under alternate wetting and drying. The rate of application of Pb markedly increased the concentration of these fractions.

- The results provide evidence that in urban soils Pb undergoes both chemical and biological (microbial) transformation resulting in large amount of soluble, exchangeable and organic forms of Pb. It is likely that soluble-Pb may leach down in the soil profile and therefore, there is a risk for ground water contamination.

- Adsorption and desorption reactions of Pb in soil are considered to be the major phenomena controlling the bioavailability and leaching of Pb in soil. Therefore, the adsorption of lead in soil was studied through a laboratory batch experiment. The result showed that Pb adsorption by the urban soils was rapid up to 24 hours and later on slowed down due to diffusion of Pb into the soil aggregates. However, in both soils the adsorption continued to increase with time.

- Increase in soil pHs and increase in the rate of Pb application markedly enhanced Pb adsorption. Even at a high rate of Pb application (1000 mg kg^{-1}) more than 90 per cent adsorption was observed at pH 8.0 in both soils.

- The red soil (*Typic haplustalf*), having higher amount of iron and aluminium oxide exhibited significantly higher adsorption than the black soil.

- The Freundlich equation adequately described the adsorption data.

Plant availability of lead

- A 60-day laboratory incubation experiment had shown that the addition of Pb at a rate equivalent to 1000 mg kg^{-1} markedly increased the concentration of plant available Pb in soil as extracted in DTPA.

- Addition of composted coir pith significantly reduced the DTPA extractable Pb in soil due to either adsorption of Pb on organic matter or formation of Pb-organo complex in soil.

- The result suggests that addition of organics like composted coir pith could be useful in reducing the phytoavailability of Pb in soil.

Leaching of lead

Using disturbed soil column the transport and mobility of Pb in urban soils were examined. The following are the results.

- Increase in the rate of application of Pb (0 to 1000 mg) substantially had increased the Pb concentration in the leachate.

- Both the leachate concentration and the total amount of Pb leached were significantly higher in black soil than in red soil.

- In spite of high adsorption of Pb on these soils, the leaching experiment indicated that increase in the concentration of Pb in soils is likely to leach down from soil profile and contaminate the ground water.

Remediation techniques

- The results of a mini-pot experiment have shown that different rates of Pb application had significant influence on growth of castor (*Ricinus communis*). No toxicity symptoms were observed even at a rate of 1000 mg Pb kg^{-1}.

- The pattern of accumulation of Pb in castor is as follows : Leaves > shoots > roots. Higher content of Pb in leaves suggests that Pb is mobile and therefore, rapidly translocated within plant system.

- Application of composted coir pith was found to have potential in alleviating the toxic effect of Pb.

The study has shown that the use of castor plants and composted coir pith could be successful in remediating Pb contamination. However, the application of composted coir pith to the urban soils (road sides along Highways) may not be practicably feasible. Therefore, growing castor plants may be encouraged in urban areas to minimise the Pb pollution.

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