

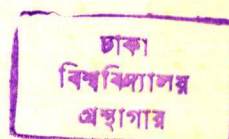
**INDUSTRIAL POLLUTION OF SOILS
CROPS SEDIMENTS AND WATER
SYSTEM AROUND DHAKA CITY**

DIGITIZED

M. NURUZZAMAN

GIFT

382453



**Ph.D. THESIS
DEPARTMENT OF SOIL SCIENCE
UNIVERSITY OF DHAKA
1995**

**INDUSTRIAL POLLUTION OF SOILS
CROPS SEDIMENTS AND WATER
SYSTEM AROUND DHAKA CITY**

DIGITIZED

**A thesis submitted for the degree of
DOCTOR OF PHILOSOPHY
in the Department
of
SOIL SCIENCE
UNIVERSITY OF DHAKA**

382453



by
M. NURUZZAMAN
B.Sc.Ag.(Hon's), M.Sc.(Soil Sc.)

March 1995

Dedicated to
my
father Md. Shamsuddin and
mother Mrs. Zennatun Nessa

382453



CERTIFICATE

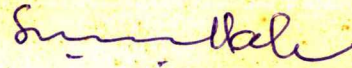
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CHAPTER 1

INTRODUCTION

CHAPTER - 1

INTRODUCTION

Soil and environment are under tremendous pressure due to industrial expansion and agricultural increased use of chemicals specially pesticides during last few decades. Very few are aware of this globally important issue. The third world countries are now in a vulnerable position. The burning issue is how to feed a ever growing human population and which demands an urgent improvement of the gross national income through industrialization.

Bangladesh has now about 30,000 industrial units of which about 24,000 are small and cottage industries. Production for all industrial groups has increased by 46 percent since 1981, with some groups such as leather products, industrial chemicals, pharmaceutical and garment products increasing by 200 to 4000 percent over the last ten years (DOE 1992). With the advent of industrialization, wastes and effluents are being discharged into the natural systems without treatment, create pollution specially of heavy metals. These are cadmium (Cd), lead (Pb), Zinc (Zn), arsenic (As), Chromium (Cr), mercury (Hg), etc. The industries like tannery, paper and pulps, textiles, carbides, pharmaceutical, insecticide and pesticides, distilleries etc. discharge their effluents and wastes containing heavy metals and organic pollutants (Table 1). The Department of environment in Bangladesh has already identified 900 polluting industrial units, most of which do not have any treatment facilities for effluents and wastes. It is generally accepted that the majority of hazardous wastes are being disposed of in low lying areas, along road sides or in the vicinity of the industrial operations.

Heavy metals like As, Cr, Cd, Pb, Hg, Cu, Zn, Ni etc. are phytotoxic and some are toxic to humans. These metals even in trace amounts, destroy

enzymes of living cells (Rahman 1992) and hence their discharge into the environment must be carefully controlled and minimized.

The data available on the impact of industrial pollution, specially of heavy metals on soils and crops and the entry into food chain are very limited in Bangladesh. No systematic research work has yet been done on heavy metal pollution of soils, crops and water system in Bangladesh. Thus the agro-based Bangladesh needs careful investigations in this important aspect.

With these views in mind, laboratory greenhouse and field experiments were performed to investigate:

- a) the effects of wastes & effluent on the physical chemical and physico-chemical properties of the soils adjacent to the industries
- b) the intensity of pollution to the soils, field crops and water bodies, by the heavy metals from the wastes and effluents of tannery, battery and pharmaceutical industries around Dhaka city
- c) the effect of addition of cowdung and waterhyacinth on availability and uptake by wheat and rice of Zn, Mn, Fe, Cu, Cr, Cd, Pb, Hg and As from soils around the factories
- d) effect of cowdung and waterhyacinth on the growth and yield of rice and wheat
- e) The possible risk, arising around the investigated industrial sites

Table 1. Some major sources of heavy metal and other hazardous substances (SCHMIDTKE, N.W., 1980)

Major source/industry	Substance								
	As	Chlorinated Hydrocarbon	Cr	Cu	Pb	Hg	Zn	Misc. organics	Cd
Battery					*	*	*		*
Tannery/leather			*					*	
Pharmaceutical	*					*		*	
Chemical manufacturing		*	*	*		*		*	
Textile			*	*				*	
Pesticide	*	*	CN		*	*	*	*	
Pulp and paper						*		*	

CHAPTER 2

REVIEW OF LITERATURE

CHAPTER - 2

REVIEW OF LITERATURE

During the last decades numerous investigations connected with trace and toxic metals in soils have been conducted in order to assess micronutrient availability and to point out the continuing pollution of soils by heavy metals. "The recognition of the associated environmental hazards either connected with trace element deficiency of living organisms or enrichment of toxic metals in the food chain and ground water is justification for many studies of the reactions of metals such as Mn, Cu, Zn, Cr, Cd, Hg and Pb with soils or different soil components and model substances thought to behave like soil materials" (Kabata-Pendias, 1984; Brümmer, 1986).

The term "heavy metals" is a physical one and refers to the specific gravity. Those metals which show a specific gravity $> 4.5 \text{ g/cm}^3$ are called heavy metals (Markert, 1993). Heavy metals as used in this text are referred to trace elements, trace metals, microelements or trace inorganics.

Practically, there are two major routes for input of trace elements into agro-ecosystem: aerial (aerosols, particulate matter, resuspended, airborne dusts etc.) and applications (fertilizers, pesticides, industrial wastes and effluents, and other soil amendments). The output pathways can be represented primarily by losses through plant tissue removal for food, feed-stuff, fiber, and by leaching and erosion (Andriano, 1986).

Heavy metals in soil are either retained by the solid phase or exist as free ions in the soil solution, as adsorbed on the soil colloids or as soluble organometallic complexes. The environmental effects and transport of heavy metals in a soil, as well as their uptake by plants,

are governed by their mobility (Cottenie, 1980). The movement of a particular metal is determined by concentration and form of the metal, physical and chemical properties, and the composition of soils and water solution with which the metal is associated. An aerobic environment increases the solubility and mobility of metals (Fuller, 1980); or decreases the solubility of metals (Page and Pratt, 1975), depending on the absence or presence of sulfides and other redox-active components in the system (Gambrell et al., 1980; Khalid et al., 1981). The adsorption and coprecipitation of trace and toxic metals with colloid hydrous oxides are important processes in decreasing metal availability in some soils (Amacher et al., 1988).

2.1. Effects of organic matter, soil pH, cation exchange capacity, clay content and plant species on the availability of metal ions:

Among the numbers of interacting soil and plant factors, affecting metal retention / release and transport in soil and plant the soil pH which increases the mobility of Cd, Cr, Cu, Hg, Ni, Pb and Zn in case of acidity while in alkaline condition, the reverse phenomenon takes place (Herms und Brummer, 1980); the absorption capacity of above mentioned heavy metals increase with the increase of cation exchange capacity (Geneveni et al., 1989); retention of Zn, Pb, Ni, Hg, Cu, Cr and Cd are more favoured in clayey soils while in sandy soils the opposite takes place (Lichtfuss, 1989); the high organic matter content in soils decreases the availability of Cd, Cr, Cu, Hg, Ni, Pb and Zn ions (Krosshavn et al., 1993). Sometimes plant itself can be used as an extracting agent and in this case heavy metal uptake is a direct indicator of the availability of metals in the soil (Bjerre et al., 1985). However in general the fixation capacity of soil for most trace elements is increased with increasing pH (Adriano, 1986).

2.2. Effects of industrial wastes and effluents :

The municipal wastewaters usually have high concentration of several heavy metals such as Pb, Ni, Cd and Cr (Larson et al., 1975; Arora et al., 1985). Their continuous use for irrigation of agricultural land may result in metal accumulation in the surface soil (Gupto et al., 1986). Higher concentrations of these metals in soils may lead to an excessive accumulation of metal, reaching levels toxic to plants, and create animal and human health problems. The disposal of such wastewaters on agricultural land beyond a certain level may convert the productive land to waste lands. Schirado et al. (1986) reported that the concentrations of Cd, Co, Cu, Mn, Ni and Zn were increased from 6 to 18, 5 to 13, 440 to 591, 140 to 502, 50 to 142 and 290 to 474 ppm, respectively in untreated municipal wastewater. Waste and effluents from the tannery industries are also of important environmental concern in many countries in the world. Tanning industry represents one of the manufacturing fields heavily involved in fresh water and soil pollution because of the highly toxic nature of wastewater coming from hide-processing. Although various treatment procedures for disposing tannery by-products have been suggested, sludge from tannery wastewater purification is still an environmental problem (Vallini et al., 1989). Duval et al. (1980) reported that the tannery industries are discharging not only Cr which is inherent to the tanning process, but also significant amounts of Ag, Cd, Cu, Pb and Zn as well. Moon et al., (1991) carried out an investigation on Pb, Cd, Zn and Cu levels in topsoils of an industrial complex, comprising of many types of polluting industries. The analysis of the samples showed (Appendix A.7), that these metals contributed significantly towards environmental contamination, albeit in localized areas, resulting from industrial activities.

Metals are the only hazardous constituents that can not be destroyed or altered by chemical or thermal methods (Connor, 1990).

They must either be treated or converted into the most insoluble form possible to prevent their reentry into the environment (Lakshmanan et al., 1993). Arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), manganese (Mn), lead (Pb) and zinc (Zn) are the concerned heavy metals in this regard.

2.3 Chromium

Chromium is omnipresent in the environment, found in varying concentration in air, soil, water, and all biological matter. Chromium is abundant in the earth's crust (NAS, 1974). It ranks 21 st among the elements in crustal abundance (Kranskopf, 1979). Between the two forms found in nature, the trivalent form is relatively benign, and the hexavalent form is relatively toxic. Uptake occurs easiest as hexavalent chromate (CrO_4^{2-}), which however is rapidly reduced to Cr^{3+} in all soils. The latter is usually precipitated in soils. It is mobile only in very acid environments. The trivalent form is absorbed little by roots (Bodek et al., 1988; Taiz and Zeiger, 1991; Markert, 1991). Cary et al. (1977) indicated that Cr from both trivalent and hexavalent sources can be taken up by plants more in alkaline than in acid soils, although this was contradicted by Ramachandran et al. (1980) who observed that the uptake of Cr^{3+} by bean shoots decreased as the pH of the nutrient solution increased. Bloomfield and Pruden (1980) found that Cr^{6+} was extensively reduced in soils of near neutral pH under anaerobic conditions, particularly when the soil contained organic matter. Amacher (1981), concluded that Cr from organic sources was not oxidized in soil and remained associated with the soil organic matter while it was resistant to oxidation.

Extractable Cr, just like any extractable trace element, is the form most commonly used to indicate Cr availability to plants. In extracting several heavy metals from polluted soil Schueneman (1974) found that

among four extractants (distilled water, 1N NH_4OAC , 0.005M DTPA, and 0.1N HCl), toxicity symptoms in several crop species became more evident as 1N NH_4OAC extractable Cr increased.

Connor et.al., (1957) reported that chromium distribution appears to be inconsistent in profile. Some soil profiles displayed accumulations of Cr in the surface horizons and depletion with depth, while other soils tend to exhibit a more uniform distribution in the soil profiles of Ontario, Canada, (Whitby et al., 1978). The mobility of Cr in the soil profile studied addressed by Lund et al. (1976) and they found metal enrichment to depths as great as 3m under some sewage sludge disposal ponds. The authors hypothesized that the metals moved as soluble metal-organic complexes. Thus, Cr could be complexed in hexavalent form and it can move even deeper in soil profiles.

Stomberg (1984), investigating the effect of tannery waste in Sweet corn, found that leaf and kernel Cu and Cr concentration did not increase significantly but total Cr and extractable Cu, Mn and Zn concentrations of soils increased with waste application. He further noticed that tannery waste could provide significant amounts of N and lime for crops, but application at high rates might be limited by salt content, heavy metal accumulation, or potential movement of $\text{NO}_3\text{-N}$ into ground water.

James et al. (1984) studied the plant-soil interaction of Cr with tannery effluent and tannery sewage sludge and found that the levels of Cr in bean tops were not increased but root levels were increased significantly. In contrast, Banasova (1978), measured high levels of Cr in plants growing in asbestos contaminated soil with 1 to 2 ppm extractable Cr. Further more, indirect effects on plant growth have been observed as subtoxic levels of Cr. Yamaguchi and Aso (1977), reported decreased root elongation of rice and wheat growing in soils amended

with 200 ppm Cr^{3+} (III); Austenfeld (1979) reported that CrO_4^{2-} decreased net photosynthesis of *Phaseolus vulgaris* L. leaves. Mukherji and Roy (1977), found that 10 to 1000 μM $\text{K}_2\text{Cr}_2\text{O}_7$ affected all the physiological functions studied in potato tubers and rice seedlings. Water loss and permeability changes worsened with increased exposure times.

Soni, et. al., (1981) experimented the mortality and reproduction in earthworms *pheretima posthuma* exposed to Cr^{6+} . The results indicate that attempts to use tannery effluents for irrigation will be harmful to the soil environment even if the effluents are diluted seven times before use.

NRCC (1976) reported that Cr can originate from the paper products; leather tanning, and finishing; chemicals; fertilizers; basic steel works; motor vehicles; aircraft-plating, finishing; cement; asbestos products; textile products and power plants.

Summarising the above observations it can be concluded that Cr has a distinct detrimental effect in soil-plant system and also has a harmful effect on human health.

2.4. Cadmium

Cadmium has no known essential biological function and is potentially toxic to both plants and animals (Bowen, 1979). It is a relatively rare element and, as such, is usually present in environment media at low concentrations. He further estimated a mean Cd concentration of $0.1 \mu\text{g g}^{-1}$ in the earth crust. Typical concentrations for uncontaminated soils are $1 \mu\text{g g}^{-1}$; however concentrations may be significantly increased by some human activities. The mean Cd concentration of agricultural soils lies in the range 0.10 to $1.00 \mu\text{g g}^{-1}$ (Jackson and Alloway, 1992). The source of input in agricultural soils

considered atmospheric deposition, the application of phosphatic fertilizers (Appendix A.8), and the application of sewage sludges or other organic wastes and effluents from the industries and output from the agricultural soils via plant uptake and leaching (Jackson and Alloway, 1992).

Cadmium is highly labile in the soil-plant system, its relative availability to plant is greater than that of other potentially harmful metal contaminant, such as lead (Alloway and Morgan, 1986; Wierma et al. 1986). Adsorption to mineral surfaces and organic matter is thought to be an important process regulating the levels of soluble and plant available Cd in soils. Most of this form is thought to be adsorbed in a more or less exchangeable form but a significant non-exchangeable specific adsorption also exists (Eriksson, 1988). The Cd level ($< 1\text{ppm}$) is generally uniform throughout the profile, and apparent mobilization also occurred in very poorly drained profiles (Adriano, 1986).

Eriksson (1988), and Krosshavn et al., (1993) observed that organic matter has a greater ability to adsorb Cd in an unavailable form and thereby reduce plant uptake. This effect is explained by the high CEC of organic matter and its ability to form chelate complexes with Cd. Alloway et al., (1990) observed that a wide variety of physico-chemical soil parameters were related to the uptake of Cd from soils. These include pH (Gerriste and van Driel, 1984; soil temperature (Siriratpuriya et al., 1985), soil sorptive capacity (Jarvis and Jone, 1980), concentrations of particular organic acids (Tyler and McBride, 1982), antagonistic, synergistic or additive reactions between elements (Elliot et al., 1986; Chammugathas and Bollag, 1987).

Numerous studies demonstrate the ability of plants to accumulate Cd. Radish tops can accumulate 5 ppm of Cd when grown on soil containing 0.6 ppm Cd. Leafy plants such as lettuce, spinach, turnip etc.

have a tendency to accumulate much Cd in the green parts. Values for the accumulation of Cd in the harvested crop tend to be low when compared with total mass of Cd in the plough layer (Jackson, and Alloway 1991).

Cadmium exposure through the diet is predominantly a chronic problem. The principal feature of its toxic action is the very long body retention time, implying that the concentration of Cd in target organs will increase with time. Cadmium is therefore classed as a cumulative toxin. The kidney, or more specially the renal cortex, is the main target human organ in which Cd has a mean residence time of 30 or more years (Hutton, 1982). It has a relatively high soil-plant concentration ratio and therefore, the variables controlling its bio-availability are of paramount importance in determining the concentration of Cd in food crops. The residence time for Cd in soil is estimated to be upto hundred or possibly more than a thousand years (Jackson and Alloway,1992).

2.5. Zinc

As Cammarota (1980) and NCR (1979) reported that most of the Zn produced in the world comes from ores containing Zn sulfide minerals. The higher concentration lies in ZnO (80.3 %) and ZnS (67.0 %). Zinc ranks forth among metals of the world in annual consumption. It is used in the manufacture of dry cell batteries, parchment papers, glass, automobile tiers, television screens, printing and dyeing of textiles, as a flux in metallurgical operations, wood preservatives, agricultural micronutrient fertilizers, insecticides etc.

Zinc is the 24th most abundant element in the earth's crust, with the average value quoted as 70 ppm (Krauskopf, 1979). Domingo and Kyuma (1983) reported 66 ppm for tropical Asia and 68 ppm for

Bangladesh. Berrow and Reaves (1984), reported a mean content of total Zn of 40 ppm for world soils.

About the Zn distribution in soil profile it can be generalized that extractable Zn decreased with depth, while total Zn was somewhat uniformly distributed throughout the profile, although there were exceptions (Nakos 1983). Zinc uptake occurs readily as hydrated Zn^{2+} , organic chelates and also adsorbed on Fe and Mn oxides. It is rather soluble in soil solutions and very mobile in acid soils. Uptake is promoted with decreasing soil pH and increasing acidity restrained by high clay content, high phosphate concentration, and high cation exchange capacity. It is easily distributed to various plant parts (Bodek et al., 1988; Taiz and Zeiger, 1991; Markert, 1991).

Occurrence of Zn toxicity has been associated with Zn smelting production practices and these add extremely large quantities of Zn to the soil (Lee and Page, 1967). For rice, a 10 % reduction in yield occurred when extractable (0.1 N HCl) Zn was 460 ppm in paddy soils in Hokkaido, Japan (Chino 1981). Ichikura et al. (1970) reported that from 250 to 1000 ppm of total Zn in soil was harmful to rice plant. Chino (1981), summarized the Zn toxic levels for rice tops as 100 to 300 ppm, and rice roots as 500 to 1000 ppm. Takkar and Mann (1978) found that soil level of 7 ppm Zn (DTPA extractable) was toxic to wheat and 11 ppm Zn toxic to maize. Van Eysinga et al. (1978) found that NH_4OAC extractant produced the best correlation between the soil and crop contents of Zn. Kabata Pendias et al. (1993) reported that an increased metal uptake was commonly observed when certain trigger levels of metals in the growth medium were exceeded. This is related mainly to Zn, Cd and Ni. They also mentioned, that legumes were more promising for indicating soil pollution with metals than monocotyledonous plants, particularly cereals. However, under more polluted soil conditions also all parts of cereal plants, including grains,

will also respond to metal levels in the growth media. Lübben and Sauerbeck (1991), with their experiment of spring wheat, manured with sewage sludge for 18 years, found that Zn content of the grain was appreciably lower than those of straw, but in the unpolluted control grain was enriched in Zn. This distribution was explained by the known Zn enrichment in the bran (Brondi et al., 1984). Higher Zn concentrations also affect the microbial population, specially actinomycetes and bacteria decreased significantly with increasing Zn content (Hiroki 1992). Moon et al. (1991) observed that Zn concentration is enhanced from the effluents of machinery, chemicals and metal molding industries (Appendix A-7), and that Zn concentration changed with the summer monsoon rain (Appendix B-10).

Zinc is, thus an essential element in human and animal nutrition but its accumulation in amounts higher than normal in soils and plants cause harmful and also an environmental concern.

2.6. Lead

Lead is a well-known environmental pollutant and has been extensively studied in the past few years.

Lead can exist in both inorganic form as Pb^{2+} and in organic form in soil upto 4 Pb-C bonds (Jaworski 1979, Forsyth et al. 1984). Hutton et al (1987) observed that the prime medium for Pb transport was air because of fine particulates ($< 1\mu m$ diameter). Most of the Pb particles deposited on soil are retained and eventually become mixed into the surface layer or deeper in the case of cultivated soils. Lead accumulated at the soil surface may be taken up directly by grazing animals and soil micro-organisms. This enter terrestrial food chains, or bypass food chains completely as in the case of children consuming dust and dirt during normal hand-to-mouth activity (Jaworski et al., 1984).

Lead uptake is passive (Bodek et al., 1988; Taiz and Zeiger, 1991; Markert, 1991). The translocation from roots to other plant parts is low. Aerial deposition and foliar uptake contribute significantly to leafy concentrations. Uptake is promoted by anaerobic conditions (e.g. by flooding), low pH and low phosphate concentrations. In soils, this metal is largely immobile with a long half-life time due to adsorption to soil clays, phosphates, sulfates, carbonates, hydroxides, and organic matter. High soil concentrations may inhibit microbial processes and reduce decomposition processes. Mesmar et al. (1991) reported that excess Pb in *Triticum sativum* and *Lens esculanta* alters several physiological and biochemical processes in both species. They further reported that Pb inhibits the growth of both plant species but root growth inhibition was more pronounced than shoot growth inhibition, inhibition percentage increased with higher Pb content, total chlorophyll content was decreased.

Lead can reach man through air, water and foodstuffs. Lead levels vary from one kind of food to another and from sample to sample reaching man via food by a variety of routes. These include plants, animals and aquatic organisms. Some species of mushrooms have well-known capacity for accumulating this metal (Stegnar et al., 1973; Kuusi et al., 1981; Zurera et al., 1986). Chen et al. (1991) showed that the rice seed germination rate and the amount of chlorophyll decreased remarkably with increasing Pb concentration. The root extension was restrained obviously by the presence of Pb. The uptake of Cu, Zn, Fe and Mn by wetland rice was also markedly affected by the additions of Pb.

Intake of relatively low doses of Pb over a long period can lead to malfunction of organs and chronic toxicity (Wierma et al., 1986). They also mentioned this toxic trace element is partly ingested with the edible parts of agricultural and horticultural crops or derived products.

2.7. Manganese

Like other trace elements, Mn is not only important for plant, animal, and human nutrition, but it also plays an important role in the chemistry of the terrestrial ecosystem. Its deficiency in calcareous soils and toxicity in acidic and waterlogged soils have been reported all over the world. In general, the adsorption of Mn by soils increases as the pH, clay, and organic matter content of the soil increase (Khattak et al., 1992).

Manganese is a ubiquitous metal in the earth's crust and is the 12 th most abundant element (Krauskopf, 1979). Adriano et al. (1980) reported that normal soils contain an average Mn concentration of 850 ppm (range 100-4000 ppm). Manganese uptake is in ionic form from soil solution. It is easily transported to different plant parts. Only the reduced form Mn^{2+} is taken up by plant. Uptake is promoted by anaerobic conditions and low pH (Islam and Ullah, 1973; Bodek et al., 1988; Taiz and Zeiger, 1991; Markert, 1991).

Manganese toxicity in plants could occur in acid soils and it is the most important growth-limiting factors in many acid soils (Foy and Campbell, 1984). Sillanpää (1982) observed that the Mn content of wheat, on very acid soils is about 10 times higher than that of wheat grown on highly alkaline soils. Manganese toxicity can be associated with Mn concentrations in plant tissues exceeding 500 ppm in general (NAS, 1974). Levels of Mn in potato foliage in excess of 250 ppm Mn may cause toxicity. In rice plants, the toxicity levels are reported at 300-1000 ppm in tops and 200 to 600 ppm in roots (Chino, 1981).

2.8. Mercury

Soil, air and water contaminated with Hg as a result of industrial pollution represent a potential risk to the environmental and human health. The associated risk is related to the suggested exposure pathways between soil Hg and humans (WHO, 1976). Exposure pathways include Hg contamination of aquatic organisms, edible crops, drinking water, and air. Human exposure may occur as a result of direct ingestion of contaminated soil (Ford and Gruba, 1984). Soils may be considered normal if their Hg contents are < 100 ppb level (Adriano et al., 1980). Most natural waters (ground water, river water, sea water etc.) contain < 2 ppb Hg (Gavis and Ferguson, 1972). This element is retained in soils as slightly mobile organo-complexes. The concentrations can be built up in the soil. Reduction to elemental form results in toxic mercury vapor. Uptake is almost totally in the form of this elemental vapor (Bodek et al., 1988; Taiz and Zeiger, 1991; Markert, 1991)

The uptake is also influenced by several soil quality factors including soil type, pH, organic matter and ion exchange capacity (Lodenius, 1990). It was also mentioned that Hg was strongly bound on soil organic matter and soil fine particles. Mercury is fairly mobile in the soil profile but tend to accumulate in the surface horizons (Poelstra et al., 1974). The various extractants used for available Hg are (CaCl_2 , NH_4OAc , EDTA and various HCl solutions) (Gracey and Steward, 1974).

The major sources of Hg to water, air and soil are from the industries of pulp and paper, chlor-alkali, base metal, batteries, lamps, thermometers, chemicals, fossil fuels, and other raw materials; municipal and industrial wastes also contain variable amounts of Hg (Lodenius, 1985).

Beauford et al. (1977) observed that 5 ppm of Hg, as HgCl_2 , in solution culture inhibited growth of higher plants and affected both physiological and biochemical processes in the plants. Gracey and Stewart (1974) recorded higher Hg levels for the straw than for the grain or seed of cereal and oil seed crops with normal soils containing < 40 ppb Hg.

Most of the Hg in water in general is strongly bound to humic substances and particles. Change in pH and Cl content have only slight effects on the binding of Hg on aquatic humus (Lodenius et al., 1985). Very little information on Hg accumulation in other than fish is available. The use of Hg caused a significantly increased level of Hg in fish in several years. The highest concentrations ever were measured in Finland (6.9 mg/kg) in 1975 contaminated from the pulp and paper factory (Lodenius, 1988). He further reported that fish eating birds and mammals might accumulate considerable amounts of Hg and may even cause death. The increased concentrations of Hg might cause risks for the human health, especially among fish consumers.

2.9. Copper

Hiroki, (1991) stated that Cu can prevent biological processes in ecosystems. Since soil pollution problems due to this heavy metal is becoming increasingly serious, it is important to assess its deleterious effects on the soil ecosystems.

The average crustal abundance of Cu range from 24 to 55 ppm (Cox, 1979). For normal agricultural soils, total Cu is expected to range from 1 to 50 ppm and available Cu may range from 0.1 to 10 ppm, depending on the kind of extractant used (Baker, 1974). Domingo and Kyuma (1983) found 27 ppm (mean) Cu for Bangladesh soil.

The major sources of Cu are from Cu compounds and Cu chelates in agriculture smelting for Cu, iron and steel production and coal combustion from the industries (Duce and Windom, 1976).

Copper in soil can occur in several forms but from the standpoint of plant nutrition, the dissolved and exchangeable forms are of special importance (McLaren and Crawford, 1973). It is one of the least mobile of the trace elements, thereby rendering it uniformly distributed in many soil profiles (Baker, 1974). In agricultural soils, Cu may be expected to accumulate in the surface from fungicide applications, soil amendments, and by accumulation from crop residues (Thornton, 1979). However considerable leaching of Cu in the soil profile can occur in exceptional cases (Mathur et al., 1984).

Accumulation rates of Cu by plant roots are among the lowest for the essential elements (Graham, 1981), 5 to 20 ppm in plant tissue is adequate for normal growth (Jones, 1972), but phytotoxic effects of Cu ions are widely reported (Woolhouse, 1983), more than 20 ppm is considered toxic (Gupta, 1979). Phytotoxicity of Cu could be predicted by Cu ion concentrations in soils either on total or extractable basis. Bjerre and Schierup (1985) found that Cu transfer from soil to plant was greatest in sandy soil. Shuman (1988) observed that increasing organic matter did not affect Cu mobility significantly in soil.

Lübben and Sauerbeck (1991) observed higher concentrations of Cu in the grain than in straw and chaff in spring wheat, roots were enriched in Cu, as compared with the soil, however sewage sludge treatment induced a significant drop of the Cu content rather than an increase. Sarkunan et al. (1989) reported that rice plants receiving the highest levels of Cu were stunted in growth and the leaves were dark green similar to phosphorous deficiency.

Zinc application decreased Cu content in straw while Cu addition enhanced Zn content indicating that both antagonistic and synergistic interactions occur on the metal accumulation in rice (Chaudhry et al., 1973)

Schirado et al. (1986) found that application of untreated municipal wastewater led to elevated extractable Cu in the cultivated layer and an increase of total Cu with depth.

The role of Cu on the growth of crops is unquestionable but amounts exceeding normal limits in soils and crops cause environmental hazard in nature.

2.10. Arsenic

Arsenic is the only element which is considerably higher in soils and shales than in the earth crust, indicating its accumulation during weathering and translocation in colloid fractions (Shibuya 1979). Arsenic levels in uncontaminated, nontreated soils seldom exceed 10 ppm. Arsenic residues can accumulate to very high levels in agricultural areas where As pesticides or defoliants were repeatedly used. It is apparent that their agricultural uses can cause surface soil accumulation of 600 ppm or more (Walsh and Keeney, 1975). Arsenic can move downward with leaching water, especially in coarse-textured soil profile (Steevens et al., 1972) and in submerged soils.

Major sources of arsenic contamination in the environment are from coal combustion, copper smelting, pesticide use, agricultural chemicals, agricultural burning, food additives, cotton desiccants, herbicide and arsenic chemicals used for wood treatment (Grant and Dobbs, 1977; Woolson, 1983). Arsenic is translocated to many parts of the plants, most is found in old leaves and roots. It forms soluble salts of both

As^{3+} and As^{5+} . Uptake seems to be promoted by reduction processes. It is strongly adsorbed by clays and organic matter. Microbial reactions release volatile forms from soil (Bodek et al., 1988; Taiz and Zeiger, 1991; Markert, 1991).

There is no evidence that As is essential for plant growth but it has phytotoxic effects on different crops, the yield-limiting As concentrations in plant tissue are 4 - 5 ppm in cotton and 1 ppm in soybeans. In rice, the critical level in tops ranges from 20 to 100 ppm As; and in roots 1000 ppm. Tillering is also severely depressed with high concentration of As (Chino, 1981). Wetland rice is known to be very susceptible to As toxicity as compared to upland rice, since As^{3+} would be more prevalent under reducing conditions (Maeta and Teshirogi, 1957). In practice, ordinary crop plants do not accumulate enough As to be toxic to man. Instead, growth reductions and crop failure are the main consequences.

Chaney, (1984) concluded that because of the so-called soil/ plant barrier effect, increased arsenic concentrations in soils may well reduce crop production substantially before enhanced food chain accumulation occurs. Moreover, the food chain can be affected directly through ingestion and inhalation significantly for occupational exposure. In contrast to several other potentially toxic elements, local health effects are apparent in areas naturally enriched with arsenic as well as areas contaminated by industrial activities (Havas et al., 1987).

2.11. Examples for heavy metal interactions:

The interaction effects on Zn, Cu and Ni in barley showed that Cu had little effect on Zn and Ni (Beckett and Davis, 1978). Zinc uptake increased in the presence of Ni. Sarkunan et al. (1989) mentioned that Zn-Cu is well reflected in yield as well as metal contents in grain and

straw in rice. It is also reported that the relative phytotoxicities of Cu, Ni and Zn compared for grain yield of rice that Cu and Ni relative to Zn are about 6.4 and 8.8 more toxic respectively. LÜbben and Sauerbeck (1991) reported that generally the more mobile elements Cd, Zn and Ni show a pronounced rise in the grain of wheat at increasing soil contents. Bjerre and Schierup (1985) found that addition of Cd to the soils resulted in higher Cd ion concentrations in all plant parts but concentrations of Pb, Zn, Cu, Mn and Fe were lower.

Addition of Cd to the soils resulted in higher Cd concentrations in all plant parts, but lower concentrations of Pb, Zn, Cu, Mn, and Fe, and the accumulation indexes of these metals were also lower when Cd was added to the soil (Bjerre and Schierup, 1985). Addition of Cd plus Pb, Zn, and Cu resulted in higher Cd concentrations in leaves and straw of oat plants grown in sandy loam and sandy soil. Conversely addition of Cd, Pb, Zn and Cu decreases Mn concentrations in leaves and straw more than when Cd is added separately, and addition of Pb, Zn, and Cu together with Cd has shown to decrease Cd adsorption in sandy loam and sandy soil (Bjeree and Schierup, 1985).

The antagonism between Mn and Fe is a well documented interaction in higher plants. The high amounts of Mn may an antagonistic effect on Zn uptake (Sajwan and Lindsay, 1986). Excess Cu is known to depress P concentrations in plants (Adriano et al., 1971). Iqbal et al. (1992) found that nitrate uptake in the roots of seven day old wheat was decreased with the CuSO_4 salt treatment. The level of inhibition was more at higher concentration of the heavy metal salts.

CHAPTER 3

MATERIALS AND METHODS

CHAPTER - 3

MATERIALS AND METHODS

3.1. Sampling sites

Three sampling sites were selected around Dhaka city. One is located in the Hazaribagh tannery area. The other two sites are in the Tongi industrial area.

3.1.1. Hazaribagh

3.1.1.1. Location

The Hazaribagh tannery complex is situated in Dhaka Municipality area (WSW of the city). The tannery factories are located inside the greater Dhaka flood protection embankment (Figure 11).

The embankment was built in the year 1989. There are about 145 tannery factories in Hazaribagh residential area (DOE, 1992). The study area was a 4 km section of Hazaribagh from the main disposal point of wastes and effluents. The spot 8 is the main disposal point (Figure 11).

3.1.1.2. Agricultural practices

Farmers fields are located outside the embankment, these are mostly situated at low lying areas. These areas remain under water throughout the year except from December to April in the dry season. But the tidal water mixed with tannery effluents submerge the farmers field even in dry season. The common agricultural practice in this area is Boro rice cultivation. This rice is generally transplanted in the month of December and harvested in April. Some winter vegetables are occasionally cultivated inside the embankment area.

3.1.1.3. General Observations

Rice plants at the maximum tillering and mature stages outside the embankment in Hazaribagh area were very dark green in colour. Tillering was also normal, but more than 60% grain was unfilled.

3.1.1.4. Soil

The soil series (around Hazaribagh) belongs to Khaler Char and comprises seasonally flooded, up to 120 - 150 cm deep for more than 6 months. They are poorly to very poorly drained soils, developed in mainly medium textured Brahmaputra alluvium in permanently wet channels or depressions on the old and young Brahmaputra, Meghna and Jamuna floodplains. Their profiles show little sign of development. The general soil type is non-calcareous alluvium, Fluvaquent. The area inside the embankment is composed of organic wastes, on Jamuna alluvium, permanently wet by the effluents of the tannery factories (Figure 11).

3.1.1.5. Origin of wastes

As a general practice the majority of solid wastes are deposited along road beds, low lying lands or in the vicinity of the tannery factories that produce the material. The effluents without treatment are directly discharged to the open street drains. The open channels originate from the residential area. Lastly, the effluents and some solid wastes are deposited in a big channel inside the embankment. The mean channel width is about 15m. Effluents mixed with high concentrations of suspended solids ultimately flow to the river Brahmaputra, passes the farmers rice fields. Some earthen protection are also made inside the embankment, with small gully/opening. This is done by the slums living on the embankment. These earth walls create a great hindrance to smooth passage of the wastes and effluents quickly. At present, there exists only one sluice gate to release the huge quantity of waste water. During the rainy season, the wastes and effluents discharged are swept away by the high waters with un-quantified effects

on ecology. In the dry, season the effluents may easily percolate to the alluvium of the floodplains. Tanneries have been operating in this area over the last 30 years. It was estimated recently that about 40 tons of solid wastes are produced in the area (DOE, 1992). Out of which, about 50% is hazardous due to its high chromium content. The highly insoluble chromium is ubiquitous throughout the area, in particular in the river floodplains that receives the effluents discharged from the tanneries.

Of the main tanning methods, chemical tannage is mainly practiced in Hazaribagh tannery area. Soaking, fleshing, pickling, re-tanning, and finished products are the steps usually followed.

Caustic soda, common salt, sulphides, and calcium hydroxides are used in soaking step for sharpening and unhairing the hides and skins. Fleshing is done by hand or machines. Ammonium bi-sulphate, sodium bi-sulphate, and ammonium chloride are used for this purpose. Pre-tanning and tanning are done in pickling stage. Common salt, sodium chlorate and sulfuric acid are thoroughly mixed with hides and skins, which release huge quantities of effluents. In the same bath, tanning is done with chromium-sulphate powder. Some phenolic derivatives, fungicides, and sulphides are used in re-tanning step. Tannins and phenolic derivatives play a key role in promoting phytotoxicity and allelopathy phenomena in soil (Wang et al. 1967, and Swain 1979). Various coloured substances with acids and soda are used for dyeing purpose in leather. Leather dusts are also released at the time of buffering.

The effluents contain excess fat, hair, grease, sulfides, caustic soda, calcium hydroxide, sulfuric acid, coloured pigments, chromium sulphate, oils, dyes, phenolic derivatives and varying amounts of heavy metals.

3.1.2. Tongi Industrial area

3.1.2.1. Location

The Tongi Industrial area is located within the greater Dhaka city. It is about 18 km in the north from the capital. It is one of the largest industrial complexes in Bangladesh. Surrounding industrial area is about 16 sq. km. This area contains diverse industries. Residential area and market places are also existing in between the industries. This region is also thickly populated.

Sampling is carried out in Ashupara, Tongi. This is located in the north-west of the industrial area. The experimental area, about 4 sq. km. is bounded in the east, north and south by industrial complexes and west by agricultural fields (Figure-12). This particular site is influenced mainly by the industries of battery and pharmaceutical. Other industries like ceramic, steel works are also located there, but these are far off from the present sampling areas. Some samples were also collected from a location where all wastes and effluents converge together and this location is designed by confluence zone (spot 6). The battery industry was established around 1962 and is in operation till today. It is one of the largest battery factories in our country. There are two large pharmaceutical industries in this sampling region. They are functioning since 1982. One of them produces raw materials for antibiotics.

3.1.2.2. Agricultural practices

Farmers fields are located just in front of the industries. The area is about 40.5 hectares of agricultural land. Previously farmers used to cultivate rice, wheat and vegetables. At present, only two rice are grown (Aman and Boro). Aman and Boro. Aman paddy is transplanted in July-August and harvested in December-January. The Boro is transplanted in December-January and harvested in April. Along with high yielding varieties of rice, local vegetables are also grown occasionally following the Aman paddy.

3.1.2.3. General observations

Abnormal growth of rice in this area was noticed. Rice plants were severely stunted and poorly tillered near the battery industry. Burning of leaves and stem were also noticed. These symptoms occurred with both Aman and Boro paddy growth. However, the number of filled-grain was less severely affected compared to other parts of the crop. The number of filled grain was 75%.

The rice plants at the mature stage near the pharmaceutical industry showed severe burning. Initially, the plants grew well, looked very bushy and, tillering was normal, but about thirty to forty percent of grains, remained unfilled in that area.

3.1.2.4. Soil

Samples from two soil series namely Kalma and Khilgaon were collected for this study. Both series comprise seasonally flooded, poorly drained soils. The Kalma series was developed in pale coloured, highly porous, silty weathering products of Madhupur clay in narrow valleys dissecting the Madhupur tract (spot No. 4,5 in Figure-12). They are mainly shallowly flooded (90cm) for 3-4 months, and gently sloping. The Khilgaon series developed in heavy Madhupur clays occupying on mainly deep valleys within the Madhupur tract. They have dark grey colour, firm to very firm, rich in clay with moderate to strong blocky structure in the B horizon (spot No. 1,2,3,6,7 in Figure-12). They remain flooded (90cm) for 3-4 months. The detail classification of the soils is presented in figure 12.

3.1.2.5. Origin of wastes

The battery factory has been operating since the last 30 years. The majority of solid wastes are deposited just outside the boundary wall of the factory building. An open drain was found outside the factory wall, and this leads to the

farmers fields. Effluents thus are directly discharged to the fields through the drain, and cover nearby fields locally. An earthen drain also exists to release the effluents to the nearby river, Turag.

The pharmaceutical industries have been operating since the last twelve years. These industries do not discharge any solid wastes but effluents. Farmers fields are located just in front of the industries. These industries directly discharge effluents to a earthen drain, which passes through the farmers rice fields. This drain also leads to the nearby river, Turag. Farmers fields are located at both sides of the drain. Most of the time, the effluents reach the nearby fields especially in the dry season. During the rainy season, the discharged effluents can easily be swept away with waters.

Battery industry in this present investigation has been using a number of raw materials for its production of dry cell batteries. These are manganese-dioxide, ammonium chloride, zinc oxide, mercuric chloride, carbon black, graphite, zinc-calcite and carbon rod. They are also using bitumen as a sealing compound. The effluents contain a mixture of those chemicals. Important heavy metals are mainly manganese, zinc, lead, cadmium and mercury..

One of the pharmaceutical industry of our sampling site is producing anti-biotic mostly Ampicillin trihydrate and Amoxycillin trihydrate. In the production process of ampicillin trihydrate, the industry has been using a solution 6-Amino penicillanic acid in methyl chloride, triethylamine and urea. D-alpha phenyl glycine chloride hydrochloride is then added in the solution. This is step one. Then for hydrolysis aqueous ammonia solution is added at step one. After hydrolysis two layers of organic and aqueous are separated. Organic layer contains methylene chloride and is distilled to recover the solvent. The pH of aqueous layer is adjusted, when ampicillin is precipitated out leaving behind triethylamine and hydrochloric acid in solution. These are the principle by product released to the drain. In the manufacture of amoxycillin trihydrate, almost the same procedure is followed. Chemical used are 6-amino penicillanic acid, methylene chloride,

triethylamine, hexanoic acid, Dane salt, N-N dimethyl acetamide, 2-6-Lutidine (catalyst) and piraloyl chloride. The aqueous layer or the effluents discharged contain triethylamine, N-N-dimethyl acetamide and a part of 2,6 lutidine and hydrochloric acid.

3.1.2.6. Sampling from experimental sites (Hazaribagh and Tongi)

Soil, plant, effluents and waste-water samples were collected (three times in the first year, and two times in the second year) from January 1992 to January 1994. Paddy grain and effluent samples were also collected in between the years. January-February, April-May and October-November were the general sampling periods. The normal sampling frequency (1,4,3,2) were changed in case of plants sampling. Soil samples were collected from different horizons of a soil profile in the first year. Generally sampling was done down to 120cm. In the second year only top soil(0-15cm) were collected. In addition, a bulk samples (0-15cm) and one composite soil sample(0-15) from all sampling sites were also collected. Root, whole tops and grain samples of paddy were collected. For other aquatic plants, whole tops and root samples were also collected. Spots 1,2 and 3 were selected for sampling near pharmaceutical industry and spots 4 and 5 near battery factory. Spots 6 and 7 were fixed as confluence zone (Figure 12). Spots 8 to 13 were marked as sampling sites from Hazaribagh Tannery area (Figure 11).

3.1.3. Pot Experiment

Pot experiments were conducted in the green house of the Department of Soil Science, Dhaka University, Dhaka. With contaminated soils from tannery, battery and pharmaceutical industries. Wheat (Kanchan) and paddy (BR-1) were the test crops. The objective of the experiments were to study the effects of different heavy metals (already present), on the growth and yield of wheat and rice. Addition of cowdung and waterhyacinth as remedial measures was also tried.

Three bulk soils were air-dried, ground and passed through 5mm sieve. Six kilogram of soil was taken in each plastic pot for conducting the experiments. The treatments were 20 and 40 tons /ha of cowdung (CD) and waterhyacinth (WH) combined with control pots. The treatments were replicated three times. These treatments were applied in case of soils of battery and pharmaceutical industries. Paddy was grown after wheat experiment in this same pots. The pots were arranged in a completely randomized block design.

Eight wheat grains were sown in each pot in the early part of December. The seedling were allowed to grow two weeks and six wheat plants were kept in each pot to maturity. Roots, shoots, and grain samples were separated. After wheat harvest four healthy and uniform rice seedlings (26 days old) were transplanted in each pot. As with the case of wheat, rice plants were harvested at maturity. Roots, shoots, and grain samples were also separated. These were then oven-dried at 70°C for 72 hours and dry weights were measured. Samples were then ground and preserved in bottles for chemical analyses. Physical characteristics upto mature stage were observed carefully and noted down.

3.2. Chemical Methods

The soil samples were air dried for several days in a clean room avoiding direct sun rays and dust. The samples were ground with wooden roller and screened through a 2mm sieve. Soil samples were properly preserved for physical and chemical analyses.

The collected field plant samples were cleaned with running tap water then with distilled water. The samples were air dried in a dust free room and then oven dried at 70°C for 72 hours. Dry weights were taken samples was ground and properly preserved for chemical analyses.

The soil and plant samples were analysed in the laboratories of Soil Science Department of Dhaka university, Dhaka; Institute of Post graduation Studies in

Agriculture, Gazipur; Department of Environmental Engineering University of Engineering and Technology of Bangladesh and Soil Science laboratory of Forschungszentrum Seibersdorf, Austria.

3.2.1. Determination of physical properties

3.2.1.1. Hygroscopic moisture

Moisture content of air-dried sample was done by oven drying at 105°C for overnight.

3.2.1.2. Texture

The mechanical analysis of soil was conducted by pipette method (Kilmier and Alexander, 1949) and the textural classes were determined by marshall's Triangular Co-ordinates.

3.2.2. Physico-chemical properties

3.2.2.1. Soil pH

Field pH was determined at the time of sample collection using helling-Truog test-kit. Soil pH (air dry) with water (1:2.5) and soil-0.01M CaCl_2 (1:2.5) suspension was measured with glass electrode pH-meter. This was also used for measurement of effluents and wastewater pH.

3.2.2.2. Electrical conductivity (EC).

Electrical conductivity was determined in saturation extract of soils, effluents and wastewater using an EC-meter.

3.2.2.3. Chloride (Cl)

Chloride was measured from the hot water (60°C) extract for soil samples using expandable ion analyzer 940 ORION, USA. The same instrument was used for effluents and wastewater.

3.2.2.4. Organic Carbon

The organic carbon was determined volumetrically by wet- oxidation method (Walkly and Black, 1934). The organic matter percentage was calculated by multiplying the percentage of organic carbon by the factor 1.724.

3.2.2.5. Cation exchange capacity (CEC)

The cation exchange capacity of soils was determined by 1N NH_4OAC (pH=7.0) method (Schollenberger C.J. and Simon, R.H., 1945).

3.2.2.6. Exchangeable cations (Na, K, Ca and Mg)

Calcium and Mg in NH_4OAC extract were determined by using an atomic absorption spectrophotometer (PYE UNICUM SP-9 series). Na and K were determined by Gallenkamp flame photometer (Black et al., 1965).

3.2.2.7. Available nitrogen (Av-N)

Available N from soils in 1N KCl, soluble nitrogen in effluents and wastewater were determined by semi micro Kjeldahl's method, P and K in Aqua-regia were measured in ICP-AES.

3.2.2.8. Total nitrogen

Total N for soil and plant samples were determined by Kjeldahl's method as outlined by Jackson (1973).

3.2.2.9. Available heavy metals with 1.0M NH_4 -Acetate

Ammonium acetate extracts the exchangeable ions of the soil, which includes especially the adsorbed ions on the surface of the clay minerals and the organically or oxide bound ions (Scheffer and Schachtschabel, 1989). This extracts also the plant available heavy metals (Horak. et.al, 1994).

3.2.2.10. Total heavy metals from soil and plant samples with Aqua regia and $\text{HNO}_3\text{-HClO}_4$.

Aqua regia decomposes nearly almost all complex forming soil particles (clay minerals, organic substance, oxide, etc.) through which all the ions are brought into solution and can be measured quantitatively (VDLUFA, 1975).

All the elements (total and available) were measured in the extracts mostly in the Plasma Emission Spectrophotometer (ICP-AES). Cadmium was measured in the extracts with the help of an Atomic Absorption Spectrophotometer (AAS), Model-5100 with a heated graphite-tube system (HGA), Model-5100 ZL. Mercury and Arsenic were measured in Atomic Absorption Spectrophotometer (AAS), Model-5000 with Mercury-Hydride system (MHS-20), but gold-platinum net was used in Hg determination.

3.3. Statistical analysis

The results of experiments reported in this manuscript were statistically evaluated by analysis of variance technique, Pearson correlation coefficients, standard deviation, and the LSD test. The latter was used for testing the significance of differences between mean values. The level of probability was indicated in tables needed.

Table 2 Soil sampling in Hazaribagh area

Spot No.	Horizon No.	Sampling period and depth				
		Jan. - Feb. '92 period 1 depth in cm	Apr. - May '92 period 2 depth in cm	Oct. - Nov. '92 period 3 depth in cm	Jan. - Feb. '93 period 4 depth in cm	Oct. - Nov. '93 period 5 depth in cm
8	1	0 - 15	0 - 15	0 - 15	0 - 15	0 - 15
	2	15 - 45	15 - 45			
	3	45 - 120	45 - 120			
9	1	0 - 15	0 - 15	0 - 15	0 - 15	0 - 15
	2	15 - 45	15 - 45			
	3	>45	>45			
10	1	0 - 15	0 - 15	0 - 15	0 - 15	0 - 15
	2	15 - 45	15 - 45			
	3	>45	>45			
11	1	0 - 15	0 - 15	0 - 15	0 - 15	0 - 15
12	1	0 - 15	0 - 15	0 - 15	0 - 15	0 - 15
13	1	0 - 10	0 - 10	0 - 15	0 - 15	0 - 15
	2	10 - 45	10 - 45			
	3	45 - 75	45 - 75			
	4	>75	>75			

Table 3 Plant, effluent and waste-water sample collection in Hazaribagh area

Spot No.	Sample code No.	Sampling period and samples				
		Jan. - Feb. '92 period 1 samples	Apr. - May '92 period 2 samples	Oct. - Nov. '92 period 3 samples	Apr. - May '93 period 4 samples	Oct. - Nov. '93 period 5 samples
8	1	Aquatic plant			Aquatic plant	
	2	Effluents	Effluents	Effluents	Effluents	Effluents
	3	Waste water	Waste water	Waste water	Waste water	Waste water
9	1					
	2					
	3	Waste water	Waste water	Waste water	Waste water	Waste water
10	1		Water hyacinth		Water hyacinth	
	2					
	3	Waste water	Waste water	Waste water		Waste water
11	1		Boro paddy		Boro paddy	
	2					
	3	Waste water	Waste water	Waste water		Waste water
12	1				Boro paddy	
	2				Grass	
	3	Waste water	Waste water	Waste water		Waste water
13	1		Boro paddy		Boro paddy	
	2					
	3	Waste water	Waste water	Waste water		Waste water

Table 4 . Soil sampling in Tongi industrial area

Spot No.	Horizon No.	Sampling period and depth				
		Jan. - Feb. '92 period 1 depth in cm	Apr. - May '92 period 2 depth in cm	Oct. - Nov. '92 period 3 depth in cm	Jan. - Feb. '93 period 4 depth in cm	Oct. - Nov. '93 period 5 depth in cm
1	1	0 - 6	0 - 6	0 - 15	0 - 15	0 - 15
	2	6 - 15	6 - 15			
	3	15 - 70	15 - 70			
	4	>70	>70			
2	1	0 - 6	0 - 6	0 - 15	0 - 15	0 - 15
	2	6 - 15	6 - 15			
	3	15 - 30	15 - 30			
	4	30 - 75	30 - 75			
3	1	0 - 6	0 - 6	0 - 15	0 - 15	0 - 15
	2	6 - 15	6 - 15			
	3	15 - 50	15 - 50			
	4	>50	>50			
4	1	0 - 15	0 - 15	0 - 15	0 - 15	0 - 15
	2	15 - 30	15 - 30			
	3	30 - 60	30 - 60			
5	1	0 - 6	0 - 6	0 - 15	0 - 15	0 - 15
	2	6 - 15	6 - 15			
	3	15 - 50	15 - 50			
	4	50 - 75	50 - 75			
6	1	0 - 15	0 - 15		0 - 15	0 - 15

Table 5. Plant, effluent and waste-water samples in Tongi industrial area

Grain samples were collected for both Aman and Boro paddy at mature stage.

Spot No.	Sample code No.	Sampling period and samples				
		Jan.-Feb. '92 period 1 samples	Apr.-May '92 period 2 samples	Oct.-Nov. '92 period 3 samples	Feb.-Mar. '93 period 4 samples	Oct.-Nov. '93 period 5 samples
1	1	Grass	Grass	Amon paddy	Boro paddy	Amon paddy
	2	Waste water	Waste water	grass	(tillering stage)	
	3			Waste water	Waste water	Waste water
2	1		completely dry field		Boro paddy	
	2	Waste water			(tillering stage)	
	3				Waste water	
3	1		Burnt Boro paddy	Amon paddy	Boro paddy	Amon Paddy
	2	Waste water	root, tops, Grass	Water hyacinth	(tillering stage)	Grass
	3		Waste water	Waste water	Waste water	Waste Water
4	1		Boro Paddy	Amon Paddy	Boro paddy	Amon Paddy
	2	Grass	(root,shoot,grain)		(tillering stage)	
	3	Waste Water	Grass, Waste W.	Waste Water	Waste water	
5	1	Boro Paddy	Boro Paddy		Boro paddy	
	2	tillering stage	(whole tops)		(tillering stage)	
	3	Waste Water	Waste Water		Waste water	
6	1			Water hyacinth	Boro paddy	Water hyacinth
	2			(root, shoot)	(tillering stage)	
	3			Waste water	Waste water	Waste water



Fig. 1: Main disposal point of effluents from the tannery industries in Hazaribagh (spot - 8)



Fig. 2: Waste and effluents in the middle part of the disposal channel in Hazaribagh (spot - 9)

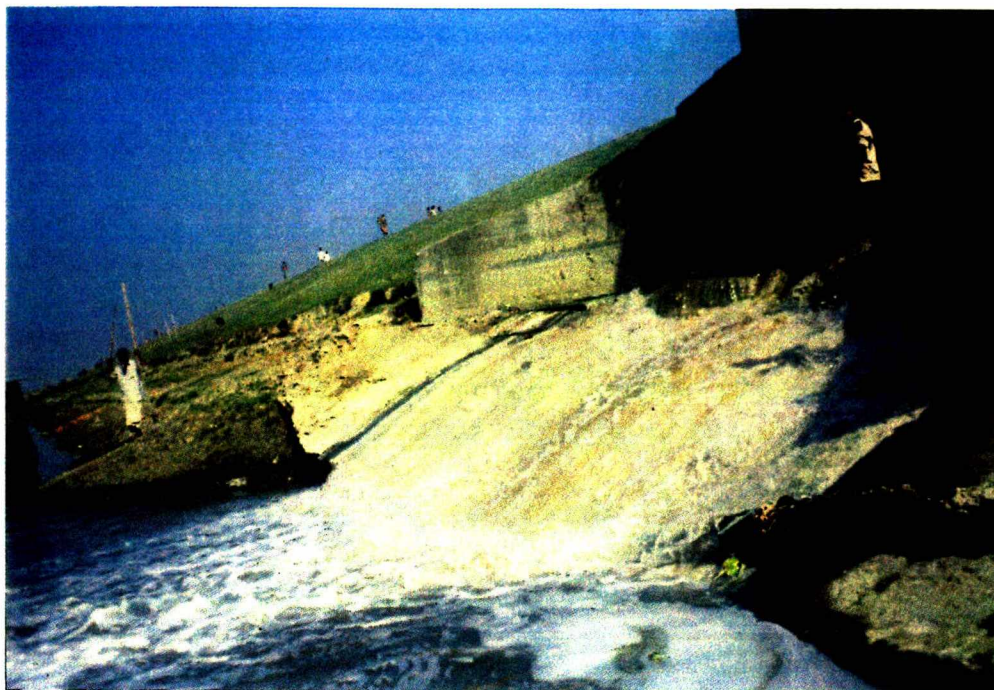


Fig. 3: The only sluice gate for the outlet effluents in Hazaribagh



Fig. 4: Farmers field outside the embankment in Hazaribagh (spot - 13)



Fig. 5: Solid wastes deposited onto low lying lands in Hazaribagh



Fig. 6: Burnt Amon paddy near pharmaceutical industries in Tongi (spot - 1)



Fig. 7: Down part of pharmaceutical area with total damage of Amon paddy (spot - 3)



Fig. 8: **Rice fields near battery factory in Tongi (spot - 4)**



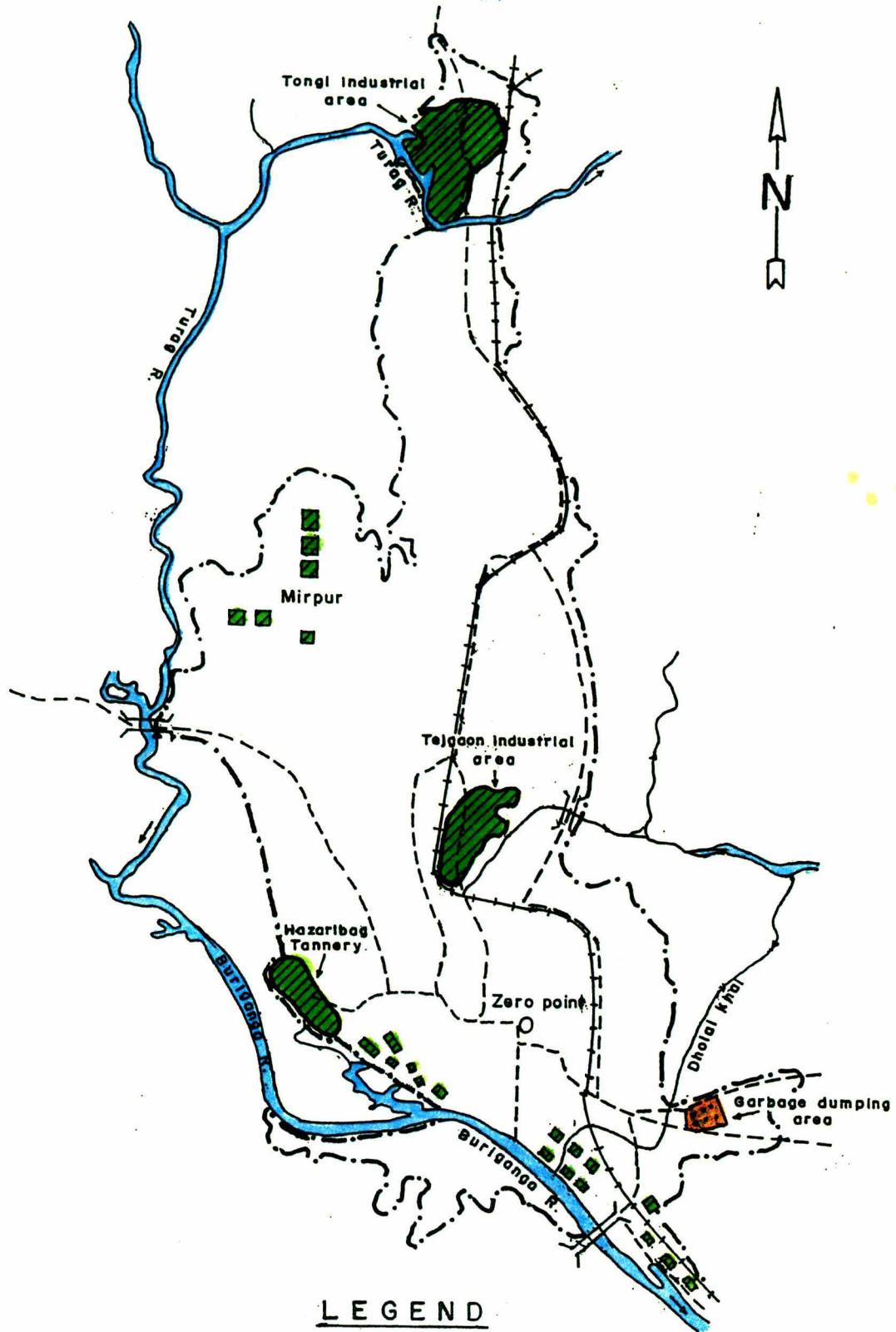
Fig. 9: **Effluents from the industries to Turag river
in Tongi (spot - 7)**

DHAKA METROPOLITAN CITY MAP

Figure 10

Scale 1:125,000

43



LEGEND

- | | |
|-------------------------|-----------------------|
| --- Dhaka city boundary | Bridge |
| River | Industrial area |
| --- Main road | Small industrial area |
| ++++ Rail line | Garbage dumping area |
| o Zero point | |

Figure 11

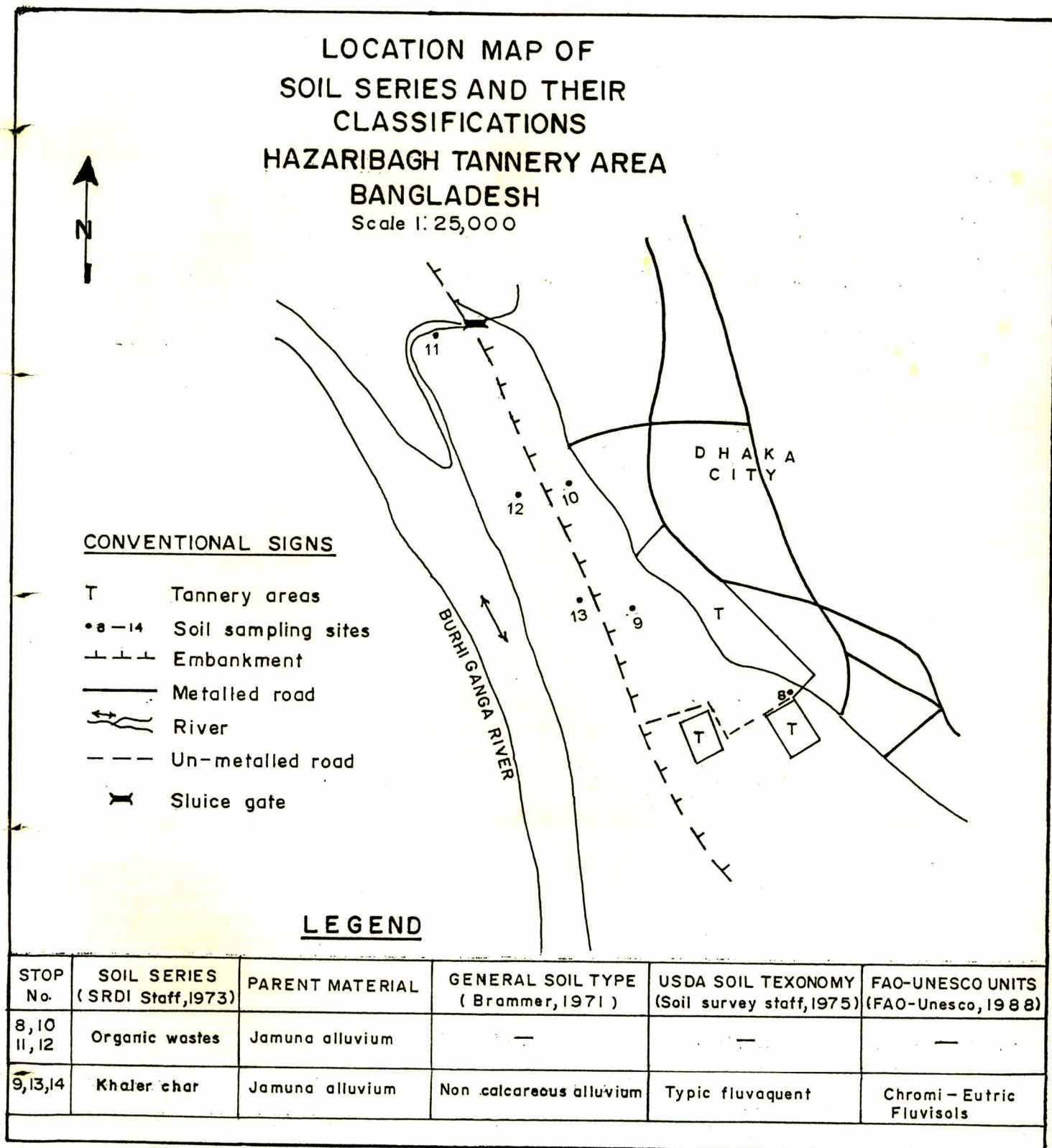


Figure 12

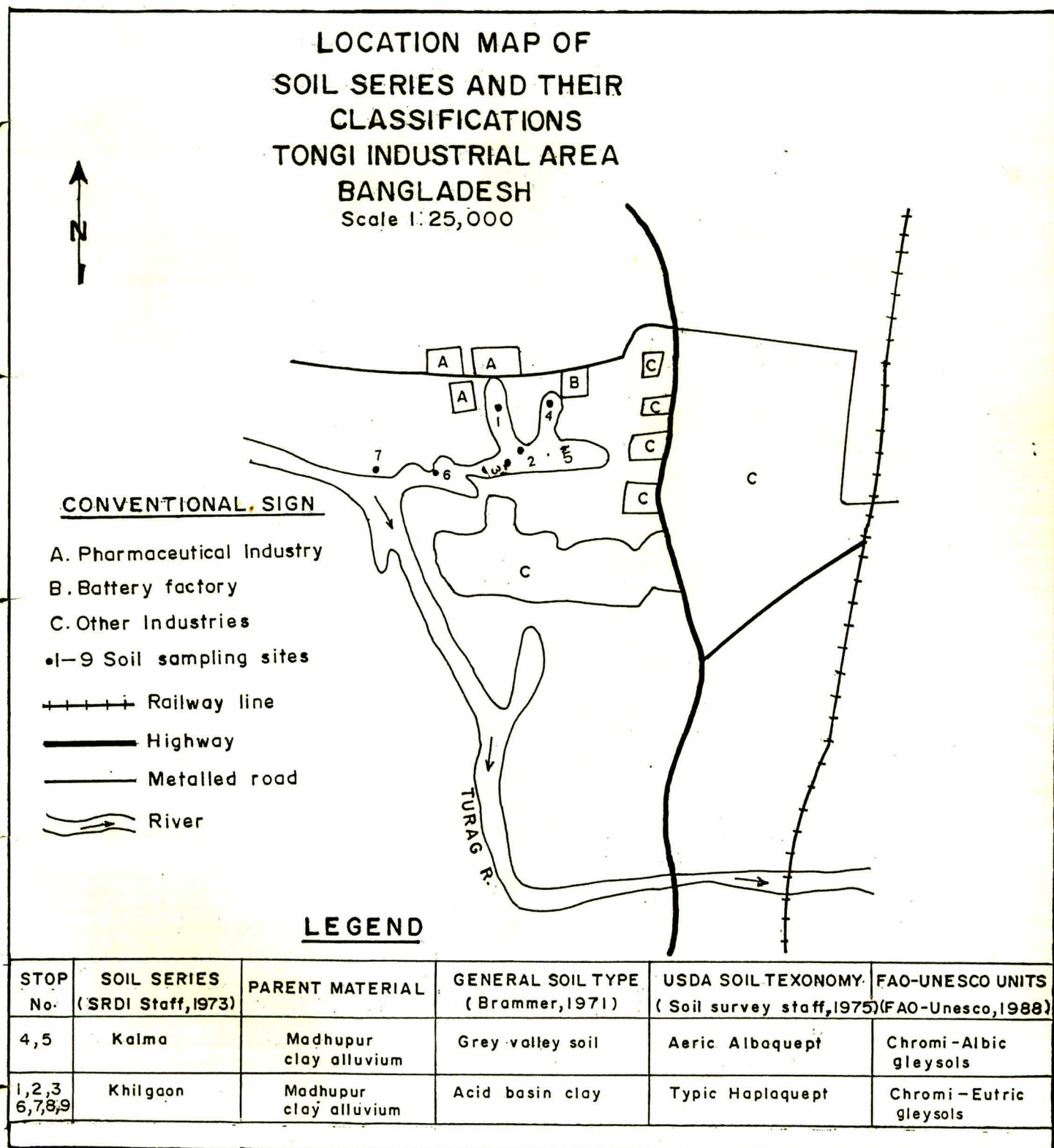
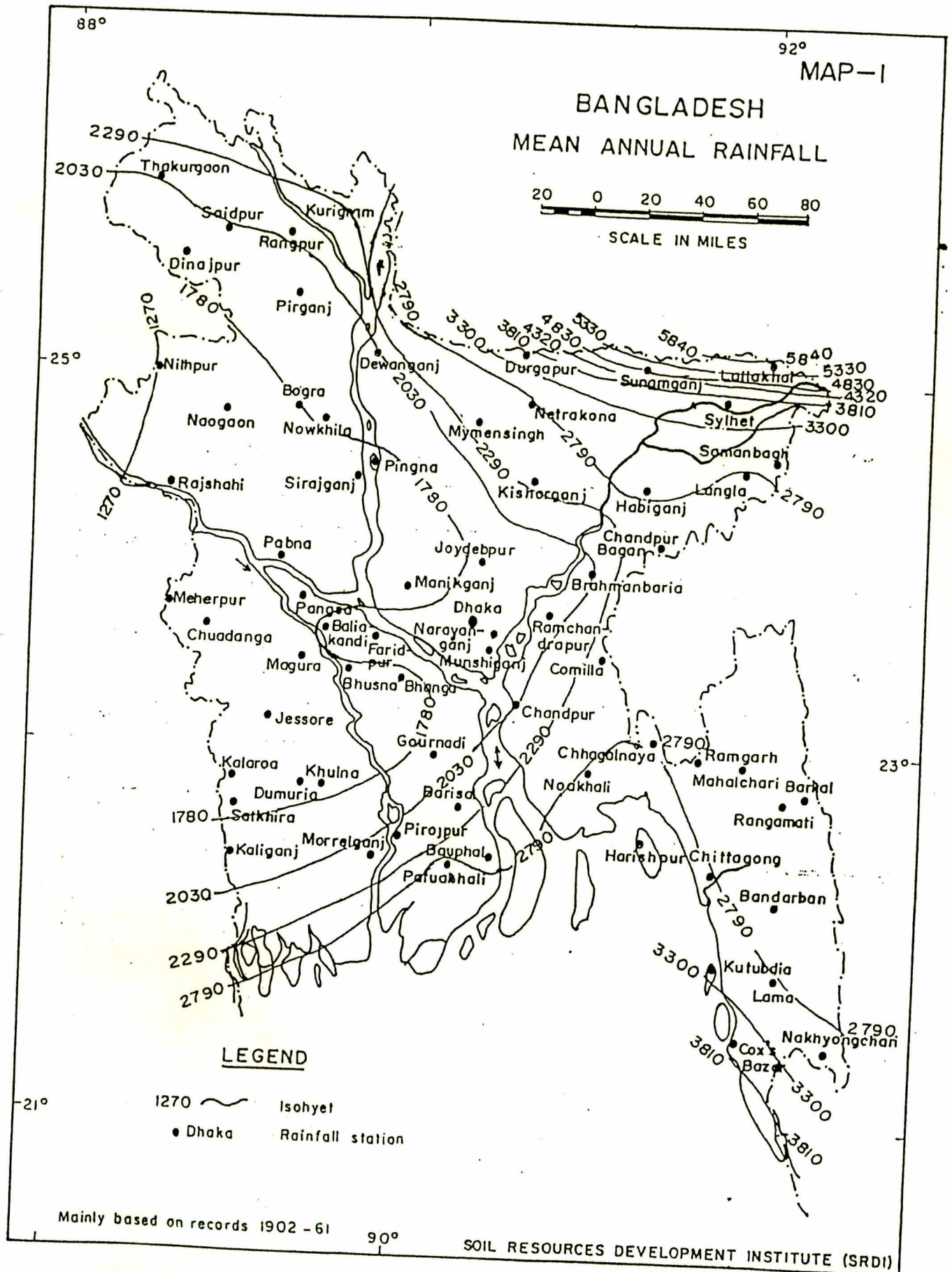


Figure 13.



CHAPTER 4

RESULTS AND DISCUSSION

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Soil samples

4.1.1. Hazaribagh tannery area

The tannery effluent contain excess fat, hair, grease, sulfides, caustic soda, calcium hydroxide, sulfuric acid, chromium sulfate, oils, dyes and varying significant amounts of heavy metals (Cr, Ag, Cd, Cu, Pb and Zn), (Duval et al. 1980). Hazaribagh tannery area is an old and the largest tannery complex in Bangladesh situated in WSW of Dhaka city. The majority of the tannery factories are discharging their effluent and solid wastes to nearby road beds, low lying lands and open street drain and channels without any pretreatment.

Five sampling were carried out (Table 2), during a period of two years. Spot 8 was considered the main point of discharge from the tanneries (Figure 11).

Soil characteristics of Hazaribagh tannery area are presented in table 6. Spot 8, 9 and 10 were inside the embankment and 13 was outside the embankment (Figure 11). Within these two sites, two spots were chosen to examine the textural class. Particle size distribution analysis of these sites showed the texture classes loam inside the embankment (spot 8) and silt loam

outside the embankment (spot 13). Soils of these two sites were developed on Jamuna (river) alluvium, the textural class was in agreement with reconnaissance soil survey report, 1966-1977, Department of Soil Survey, Dhaka. Wastes and effluent from tannery industries did not affect soil pH distinctly. The soil:water (saturation extract) pH was found to be neutral to slightly alkaline in all spots (Table 6 and appendix A-1). The pH in saturation extract was not significantly different among the spots except spot 13 but pH in CaCl_2 showed significant differences between the spots, ranging from 6.6 to 7.1 (Table 6). The highest pH value was recorded in spot 8 and the lowest in spot 13 both in saturation extract and in CaCl_2 . Although the tannery effluent and wastewater exhibit a wide range of pH values (7.2 to 12.0), they did not affect soil pH, distinctly. This may be due to buffering capacity of these soils containing amounts of organic matter.

Soil organic matter was significantly increased by tannery wastes and the maximum accumulation observed at spot 8. The organic matter ranged from 0.5 to 10.3 percent. Organic matter contents of 10.3%, 1.5%, 1.2% and 0.5% were found in the top soil of spots 8, 9, 10 and 13, respectively (Table 6 and appendix A-1).

Deposition and decomposition of huge quantities of tannery effluent and solid wastes are mainly responsible for the organic matter enhancement in spot 8 and progressively decreasing levels were found downstream and outside the embankment.

Electrical conductivity ranged from 0.4 to 4.3 EC S/cm in Hazaribagh tannery area (Table 6). Within the embankment (spots 8, 9 and 10) top soils did not show any significant difference of EC but, a very small value of 0.4 S/cm EC was found in the outside, spot 13. This increase in conductance in the spots 8,9 and 10 were due to attributed to the increase in soluble salts particularly of Na, Ca and Mg from the tannery effluent (Table 6). In a normal submerged soil the peak EC is around 2-4 S/cm, but sandy soils rich in organic matter may attain values exceeding 4 S/cm, the harmful limit for rice (Ponnamperuma, 1985). Tannery waste amended soils with a higher EC 4.3 S/cm, were found to adversely affect seedling establishment (Stomberg, 1984).

The CEC of Hazaribagh tannery area soils ranged from 8.4 to 39.0 meq/100g (Table 6) The lowest of 7.0 meg/100 was obtained in spot 9 and the highest value was found with spot 8. A CEC of 29.0 meq/100g was found in the rice field outside the embankment (Table 6). The sum of exchangeable cations (Ca,Mg,K,Na) was found to be higher than the CEC in all spots inside the embankment.

In general, CEC of soils varies markedly with amounts of organic matter and variations in clay contents and types. The high organic matter content of 10.3% in the top soil of spot 8 accounted for the high CEC. The small CECs in spot 9 and 10 are related to comparatively lower organic matter contains (Table 6). The cation exchange property and the chelating ability of organic matter influenced CEC as is well reflected here.

Chloride content ranged from 6 to 505 mg/l (saturation extract) in Hazaribagh tannery area soils (Table 6). Highest level of Cl (505mg/l) was observed in spot 8 and lowest (6mg/l) in spot 13. The concentration decreased with increasing distance from the discharge point. Values were clearly influenced by tannery effluent and wastewater.

The values of available N, P and K were also found significantly higher in spot 8 and decreased with distance from the main discharge point (Table 6 and appendix A-1). Mineralization of organic matter (tannery waste) contributed to soil N ($\text{NO}_3 + \text{NH}_4$). High concentration of N was even found below 120 cm depth. This has contaminated the ground water in this area (Appendix A-1). Tannery waste increased the N_t , $\text{NH}_4\text{-N}$, and $\text{NO}_3\text{-N}$ concentrations of surface soils (Stomberg, 1984). Tannery waste could provide significant N and lime for crops, but application at high rates may be limited by salt content, heavy metal accumulation, or potential movement of NO_3 into ground water(Stomberg,1984).

The next step in the data interpretation was to compute a Pearson correlation matrix for the chemical properties, organic matter percentage and available nutrients of Hazaribagh tannery area (Table 7). Table 7 illustrates the relationship among the elements. The critical values of the correlation coefficient (r) are 0.452 ($P < 0.05$), 0.524 ($P < 0.01$) and 0.657 ($P < 0.001$). The pH (CaCl_2) showed a positive correlation with pH S/E, OM, EC, exchangeable Ca, Na, Cl, Av-N, and Av-K at ($P < 0.001$) and with exchangeable Mg, K and Av-P

at ($P < 0.01$) but no correlation could be obtained with CEC ($r = 0.37$). Organic matter percentage showed highly positive correlations significant at ($P < 0.001$) with all parameters except EC (Table 7). No significant relation was found with EC except with Cl and Av-P at the lowest significance level ($P < 0.05$). Exchangeable cations showed positive correlations at ($P < 0.01$) and ($P < 0.001$) with all parameters except EC. Available N, P and K also showed positive correlation at ($P < 0.05$), ($P < 0.01$) and ($P < 0.001$), (Table 7).

The heavy metals (Fe, Cu, Mn, Zn, As, Cr, Hg and Pb) were analysed in the top soils of Hazaribagh tannery area. The macro nutrients N, P, K and S were also determined (Table 8). From the comparison of heavy metals in top soils it is clear that tannery industries were discharging not only Cr, which is inherent to the tanning process, but also significant amounts of Zn, Mn, Cu and Pb as well.

Iron, Cu, Mn, Zn, As, Cr, Hg and Pb contents in the soil samples of spots 8 to 13 ranged from 1.15 to 4.9% Fe, 28 to 131 ppm Cu, 208 to 645 ppm Mn, 60 to 459 ppm Zn, 1.10 to 8.15 ppm As, 47 to 29402 ppm Cr, 0.02 to 0.22 ppm Hg and 11.5 to 68.5 ppm Pb, respectively (Table 8). It is evident that very high level of Cr content was found in spot 8 (22500 to 29402 ppm), the main disposal point of Hazaribagh tannery area. Most of the heavy metals investigated were also increased in spot 8 (Table 8) which serves as a settling basin. Chromium concentrations were found to be high 20

until spot 10 (1295ppm Cr) and suddenly dropped to 96ppm Cr in spot 11 and 12. In spot 13, the concentrations again were found to be high (1335ppm Cr) (Table 8). It has to be noted that before 1989, there was no embankment to protect the effluent and wastes and thus the location of spot 13, opposite to spot 9 (Figure 11) contaminated previously.

Table 6 : Particle size distribution, chemical properties, organic matter and available nutrients of top soils (0-15 cm) of Hazaribagh tannery area

Spot	Sand % 2 - 0.05	Silt % 0.05- 0.002	Clay % < 0.002	Text class	pH		OM %	EC S/cm	CEC meq/100g	Exch. cations meq/100 g			Cl mg/l	Available in ppm		
					S/E	CaCl ₂				Ca	Mg	K	Na	N	P	K
8	40.6	44.9	14.5	1	7.3	7.1	10.3	4.3	39.0	38.5	8.3	0.9	19.2	2343	5.7	285
9					7.3	6.9	1.5	4.5	7.0	8.5	1.9	0.3	3.9	280	1.1	98
10					7.3	6.8	1.2	3.9	8.4	5.8	2.1	0.4	3.0	245	3.3	145
13	30.3	51.7	18.3	sil	7.0	6.6	0.5	0.4	29.0	6.3	2.6	0.4	1.5	26	0.6	31
LSD 5%																
F-value																
					0.1	0.1	0.2	0.9	6.3	6.8	2.1	0.2	5.5	81	1.8	76
					15.5	17.3	4561	42.8	55.4	48.5	19.4	23.2	20.1	1621	14.5	17.8

Table 7: Correlation coefficient among the chemical properties, organic matter and available nutrients of top soils (0 - 15 cm) from the tannery industrial area Hazaribagh

	pH S/E	pH CaCl ₂	OM	EC	CEC	Exchangable cations			Cl	N	Available	
						Ca	Mg	K			P	K
Av-K	0.52**	0.75***	0.82***	0.58**	0.40	0.68***	0.66***	0.73***	0.83***	0.82***	0.88***	1
Av-P	0.50*	0.63**	0.75***	0.47*	0.34	0.59**	0.50*	0.62**	0.78***	0.74***	1	
Av-N	0.38	0.81***	1.00***	0.42	0.68***	0.95***	0.89***	0.91***	0.99***	1		
Cl	0.41	0.82***	1.00***	0.45*	0.65***	0.93***	0.85***	0.88***	0.89***	1		
Exch. Na	0.33	0.73***	0.89***	0.39	0.66***	0.87***	0.93***	0.89***	1			
Exch. K	0.18	0.62**	0.89***	0.22	0.77***	0.91***	0.92***	1				
Exch. Mg	0.17	0.65**	0.87***	0.18	0.79***	0.89***	1					
Exch. Ca	0.27	0.72***	0.95***	0.32	0.72***	1						
CEC	-0.28	0.37	0.69***	-0.29	1							
EC	0.87***	0.69***	0.42	1								
OM	0.38	0.82***	1									
pH CaCl ₂	0.66***	1										
pH S/E	1											

* significant at $p < 0.05$

** significant at $p < 0.01$

*** ... significant at $p < 0.001$

Table 8: Total contents of selected nutrients and heavy metals of top soils (0 - 15 cm) in Hazaribagh tannery area at different spots and periods

Spot	Period	N	P	K	S	OM	Fe	Cu	Mn	Zn	As	Cr	Hg	Pb
%														
ppm														
8	1	2.704	0.286	0.120	1.670	10.00	1.15	102.0	203	320	2.15	26900	0.17	39.5
8	2	1.889	0.272	0.125	1.036	9.95	1.85	106.5	322	365	2.55	20970	0.17	53.0
8	3	2.162	0.343	0.105	1.266	10.00	1.95	128.0	322	459	2.40	22500	0.22	68.5
8	4	2.574	0.308	0.125	1.219	10.10	1.20	131.0	208	317	1.60	29402	0.12	39.5
8	5	1.319	0.169	0.110	0.901	9.50	1.75	50.0	260	189	1.95	25300	0.15	20.5
9	1	0.175	0.084	0.135	0.178	1.50	4.00	38.5	520	105	8.10	1440	0.11	17.5
9	2	0.106	0.068	0.130	0.236	1.55	3.25	28.0	470	86	1.75	778	0.04	13.5
9	3	0.310	0.065	0.300	0.546	1.70	3.55	36.5	499	100	1.80	1358	0.03	16.5
9	4	0.644	0.110	0.170	0.579	2.70	2.95	40.0	385	132	2.00	3775	0.03	20.5
9	5	0.375	0.076	0.135	0.488	1.90	4.05	38.5	363	91	1.10	2020	0.02	15.5
10	1	0.213	0.074	0.155	0.323	1.50	3.75	36.0	379	98	3.05	1343	0.05	19.0
10	2	0.208	0.071	0.150	0.158	1.50	4.20	50.5	475	104	5.30	805	0.04	44.5
10	3	0.119	0.066	0.300	0.044	1.50	4.65	53.0	619	110	6.60	390	0.04	24.0
10	4	0.212	0.072	0.225	0.413	1.70	3.65	47.5	375	105	3.00	1295	0.05	20.0
10	5	0.189	0.070	0.220	0.138	1.40	4.40	51.0	475	98	5.45	870	0.03	44.0
11	1	0.205	0.073	0.285	0.128	1.40	4.20	35.5	413	80	3.60	91	0.02	12.0
11	2	0.071	0.083	0.310	0.006	1.50	4.90	44.5	245	94	6.60	79	0.03	15.5
11	3	0.180	0.065	0.365	0.040	1.30	4.45	45.5	507	94	3.65	75	0.03	21.5
11	4	0.166	0.070	0.290	0.092	1.60	2.85	44.0	535	96	4.45	91	0.02	16.5
11	5	0.177	0.064	0.305	0.062	1.35	3.60	40.0	516	88	3.35	69	0.03	15.5
12	1	0.102	0.056	0.295	0.030	1.60	3.90	45.0	442	82	6.65	60	0.03	18.5
12	2	0.146	0.064	0.315	0.030	1.50	4.35	32.0	394	60	4.45	47	0.03	11.5
12	3	0.072	0.080	0.295	0.027	0.55	4.05	35.5	422	76	4.45	69	0.03	15.0
12	4	0.126	0.054	0.290	0.044	0.75	3.50	45.5	481	88	8.15	72	0.03	17.5
12	5	0.102	0.063	0.285	0.024	0.60	4.45	44.0	497	85	4.30	66	0.02	18.5
13	1	0.146	0.080	0.305	0.050	1.15	4.30	46.0	609	124	5.70	1335	0.05	25.0
13	2	0.136	0.068	0.305	0.079	0.95	4.10	46.5	562	107	6.20	500	0.04	24.0
13	3	0.010	0.060	0.325	0.045	0.70	4.20	38.5	477	92	4.85	97	0.02	17.5
13	4	0.147	0.077	0.315	0.053	1.20	4.35	45.5	612	122	4.40	1260	0.05	27.5
13	5	0.123	0.059	0.300	0.030	1.05	4.60	51.5	645	116	7.70	500	0.05	26.5
	LSD 5%	0.148	0.018	0.062	0.138	0.20	0.82	21.4	109	33	1.72	610	0.03	9.9
	F- value	227.2	171.2	15.7	89.4	2328.9	13.6	13.0	10.0	71.6	11.9	1945.7	23.7	15.4

Table 9 . Correlation coefficient among the total nutrient, organic matter and heavy metal contents of top soils (0 - 15 cm) from the tannery industrial area Hazaribagh

	N	P	K	S	OM	Fe	Cu	Mn	Zn	As	Cr	Hg	Pb
Pb	0.68***	0.73***	-0.46	0.60***	0.65***	-0.46	0.83***	-0.23	-0.81***	-0.14	0.61***	0.70***	1
Hg	0.84***	0.89***	-0.65***	0.81***	0.89***	-0.73***	0.78***	-0.50*	0.90***	-0.29	0.86***	1	
Cr	0.97***	0.94***	-0.65***	0.92***	0.99***	-0.87***	0.83***	-0.67***	0.88***	-0.47	1		
As	-0.50*	-0.46	0.47	-0.61***	-0.49	0.54*	-0.25	0.50*	-0.38	1			
Zn	0.92***	0.97***	-0.58***	0.86***	0.91***	-0.77***	0.92***	-0.51***	1				
Mn	-0.66***	-0.63***	0.54***	-0.69***	-0.67***	0.56***	-0.47	1					
Cu	0.89***	0.91***	-0.45	0.78***	0.83***	-0.69***	1						
Fe	-0.86***	-0.82***	0.65***	-0.86***	-0.87***	1							
OM	0.96***	0.95***	-0.66***	0.93***	1								
S	0.95***	0.91***	-0.71***	1									
K	0.63***	-0.63***	1										
P	0.97***	1											
N	1												

* significant at $p < 0.05$

** significant at $p < 0.01$

*** ... significant at $p < 0.001$

The tannery effluent consists of liquid wastes, flocculated sludge and other solids, and these contain extreme concentrations of Cr. Klope (1980) reported that 100ppm Cr is the tolerable level in soils. Duval et al.(1980) found as high as 24000 ppm Cr in tannery sediments. The results clearly indicated that the soils are extremely polluted with Cr, even outside the embankment in spot 13.

Zinc and Cu concentrations were found above limit values (Table 34) in soils. Highest Zn and Cu concentrations were 459ppm Zn and 131ppm Cu in spot 8. Other examined heavy metals (Mn, As, Hg and Pb) in Hazaribagh tannery area (Table 8) were found above normal soil range (Table 35) but below tolerable level (Table 34). Total Fe concentration was however, found relatively low in spot 8. Heavy metal contents in spot 8 showed significant differences to other spots. Chromium level was found to be significantly decreased with distance from spot 8. Though the concentration of heavy metals were the highest in spot 8 but their values did not vary significantly between spots 9 to 13 (Table 8).

Tannery wastes and effluent released from the industries increased the total contents of N, P, K and S in soils (Table 8). The concentrations ranged from 0.01 to 2.70% N, 0.054 to 0.343% P, 0.105 to 0.365% K, and 0.006 to 1.670% S of spot 8 to 13. From spot 8 to 10 and spot 11 to 13, two different patterns of accumulation of total N, P, K and S were found in Hazaribagh tannery area. Generally high accumulations of N, P and S showed inside the

embankment (spots 8 - 10). Decreased at down stream from the disposal point was significant at 1% level. But in locations outside the embankment (spots 11-13) showed lower accumulation of N, P and S and exhibited no statistically significant differences. A reverse phenomenon was observed in case of K, which increased generally with distance. Highest accumulation of most of the nutrients were found in spot 8.

The higher N, P and S contents in top soils are associated with the presence of high organic matter contents. The highest concentrations of total sulphur and nitrogen were in hazardous levels at Hazaribagh tannery area, this is in agreement with Bremer and Bundy (1974). The total N, P, K, S and Fe contents are significantly correlated with organic matter (OM) percentage (Table 9). Organic matter percentage showed highly positive correlation at ($P < 0.001$), $r = 0.96, 0.95$ and 0.93 with total N, P and S respectively and highly negative correlations at ($P < 0.001$), $r = -0.66$ and -0.86 with K and Fe, respectively (Table 9). This relationship was more evident from the figure 14.

The accumulation of Cr, Cu and Zn were significantly correlated with the organic matter percentage at ($P < 0.001$) in Hazaribagh tannery area. Figure 15 illustrates the relationship between soil total heavy metal (Cr, Cu, Zn) and organic matter contents.

Total Cr concentrations showed a positive correlation (Table 9) at ($P < 0.001$) with Cu, Zn, Hg and Pb contents at Hazaribagh tannery area (Figure 16).

The critical values of the correlation coefficient (r) are 0.50 ($P < 0.05$) and 0.54 ($P < 0.001$) (Table 9). Organic matter, N, P, S, Hg, Cr, Cu and Pb showed positive correlations among each other and negative correlation with Fe, Mn, K and As. Iron, Mn, K and As also exhibited positive correlation with each other and negative correlation with OM, N, P, Hg, Cr, Cu and Pb with exception between K and N. From table 9 it can be deduced that these strong associations were in consistent with the conclusion that the Hazaribagh tannery area was contaminated predominantly by metals from the tannery industrial wastes and effluents.

Figure 14. Relation: Organic matter (%) - nutrient ions

(total N, S, P, K, Fe) in Hazaribagh area

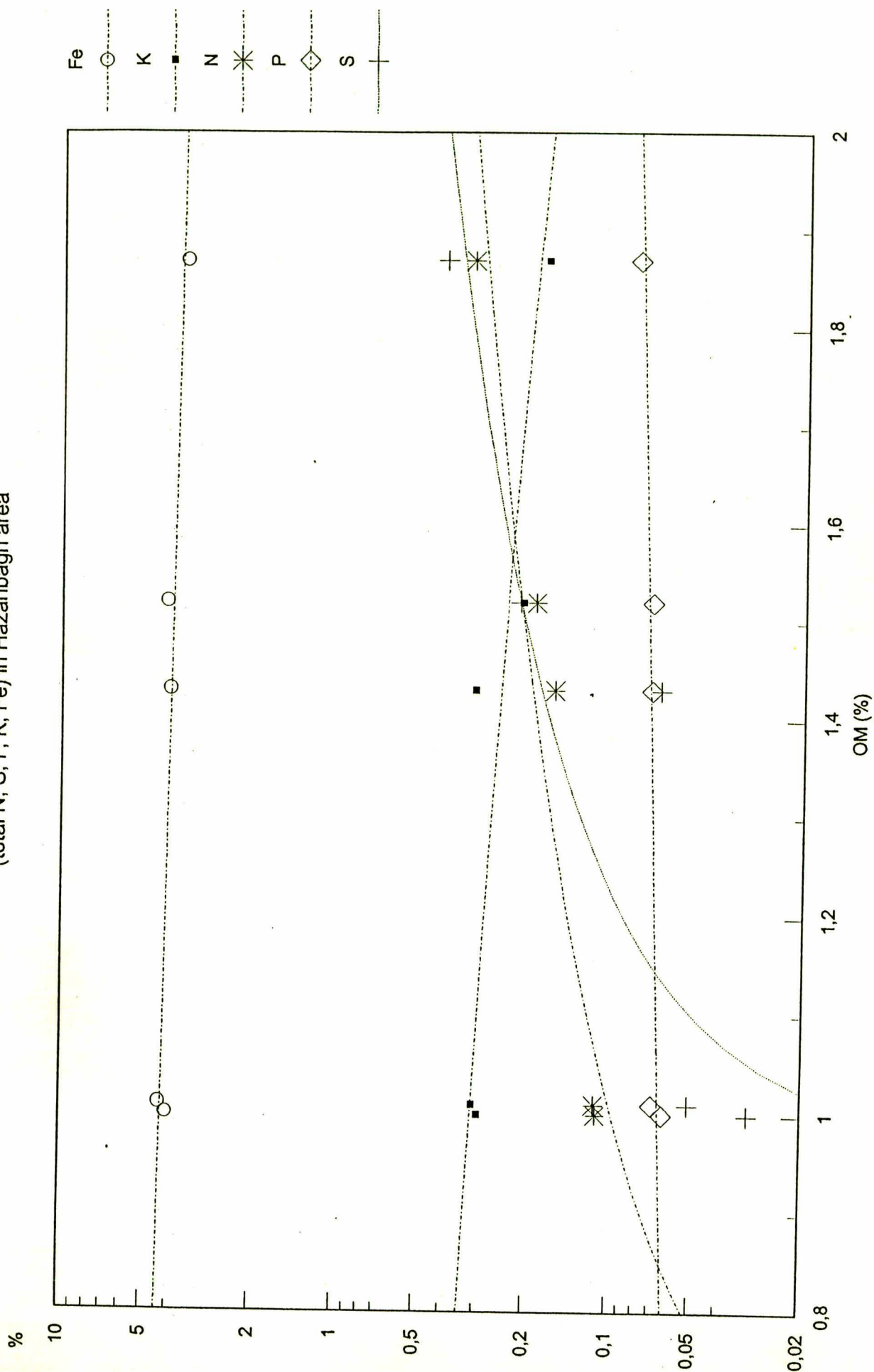


Figure 15. Correlation of total Cr, Cu and Zn with total organic matter at Hazaribagh tannery area

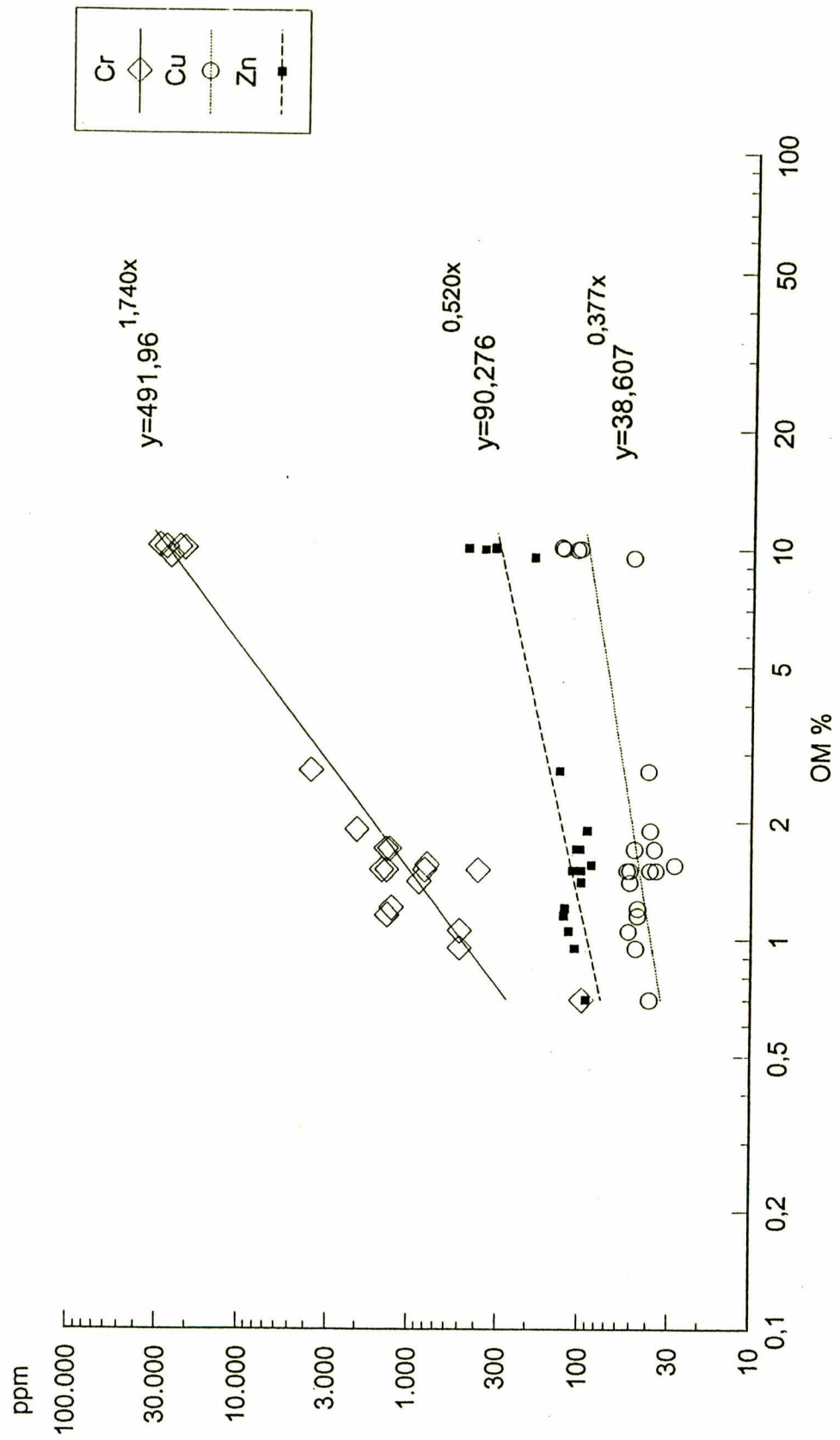
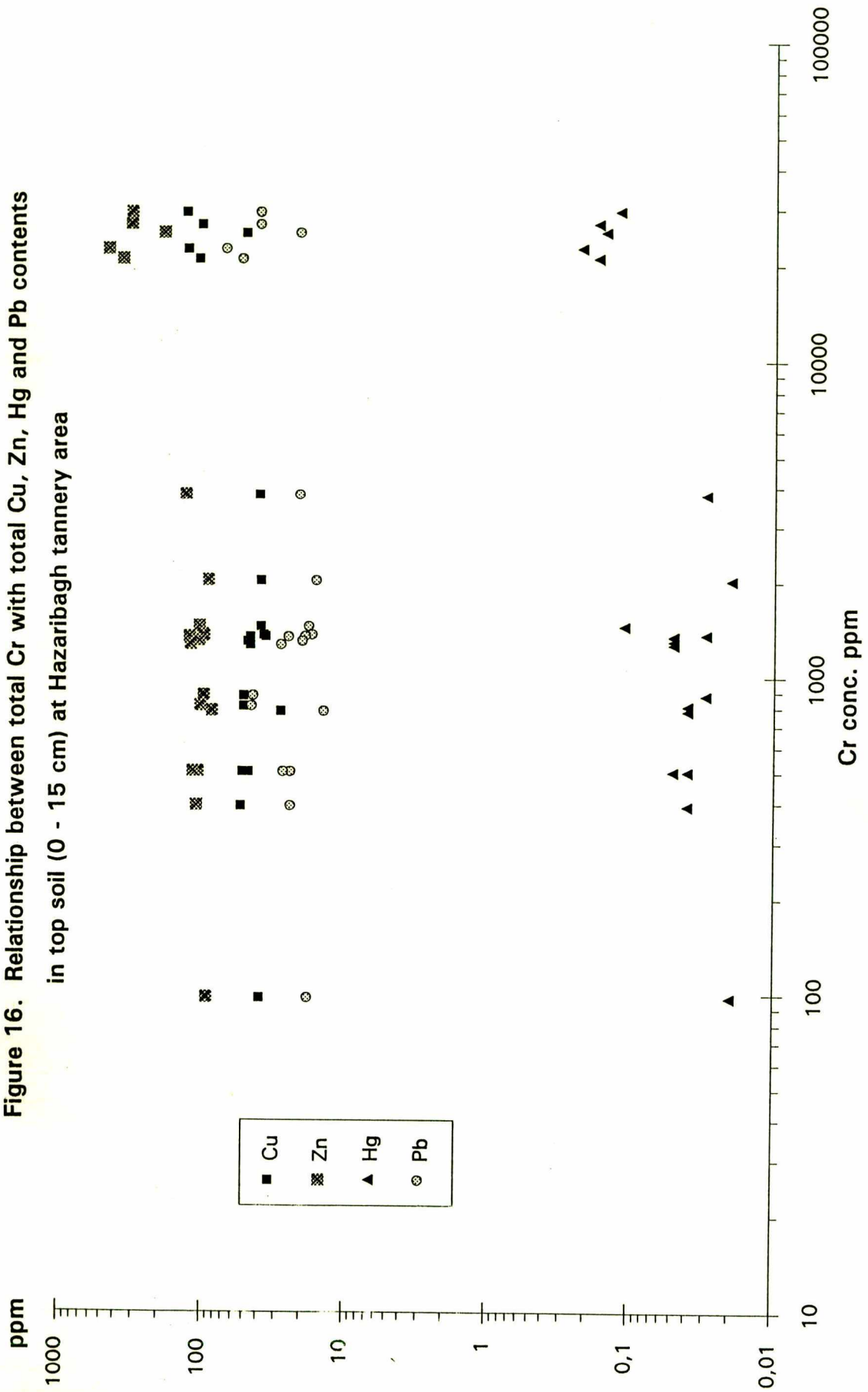


Figure 16. Relationship between total Cr with total Cu, Zn, Hg and Pb contents in top soil (0 - 15 cm) at Hazaribagh tannery area



Ammonium acetate extractable heavy metals and their percentage of total contents in top soils of Hazaribagh tannery area are presented in table 10. Iron, Cu, Mn, Zn, Cr and As contents ranged from 0.08 to 20.2ppm (Fe), 0.25 to 2.69ppm (Cu), 1.88 to 67.4ppm (Mn), 0.07 to 2.70ppm (Zn), 0.1 to 51.56ppm (Cr) and 0.002 to 0.012ppm (As) respectively. The percentage of the mobile fraction ranged from 0.0002 to 0.13 (Fe), 0.50 to 4.28 (Cu), 0.42 to 9.88 (Mn), 0.06 to 2.90 (Zn), 0.1 to 0.32 (Cr), and 0.03 to 0.56 (As) respectively.

The extractable fraction of almost all heavy metals give some indicated of their phyto-availability and mobility in soils. Soils that have the highest total contents may not have the highest amount of plant-available metals since there are numerous inherent soil factors, that affect extractability. The percentage of total mobile Cr concentrations presented in table 10, are agreed with the findings of Nakos (1982). The extractable Cr is very high in spot 8, and moderate in spot 9 and 10 but spot 13 exists in a normal range. The literature contains only limited information for comparison purposes. Banasova (1978) measured high levels of Cr in plants growing in asbestos contaminated soil with 1 to 2ppm Cr extractable. Very recent information reveal that 1 to 5 ppm Cr present in the available form in the soil solution, either Cr^{3+} or Cr^{6+} is the critical level for a number of plant species (NRCC; 1976). The extractable Mn level of 67.4 and 5.29ppm in spot 13 and 10 respectively seems to be very high for plant growth, (Liu et al. 1983). Exchangeable Fe was found to be high (20ppm) in spot 8. The studied site remains water logged/ saturated most of the time. It is assumed that under reduced conditions water soluble Fe increases.

The concentration of ammonium acetate extractable heavy metals (Table 10) of Hazaribagh tannery area correlated with the total concentration in soils (Table 9).

Table 10 Ammonium acetate extractable heavy metals from top soils (0 - 15 cm) of Hazaribagh tannery area

Spot	Fe	Cu	Mn	Zn	Cr	As
	ppm					
8	20.2 (0.13%) a	2.69 (2.60) a	2.87 (1.09%) a	2.70 (0.82%) a	51.55 (0.21%) a	0.012 (0.56%) a
9	0.79 (0.0022%)	0.78 (2.15%)	1.88 (0.42%)	0.93 (0.90%)	5.54 (0.31%)	0.008 (0.27%)
10	0.41 (0.001%)	2.04 (4.28%)	5.29 (1.14%)	2.99 (2.90%)	2.99 (0.32%)	0.006 (0.13%)
13	0.08 (0.0002%)	0.25 (0.50%)	67.41 (9.88%)	0.07 (0.06%)	0.1 (0.01%)	0.002 (0.03%)
LSD 5%	9.8	0.9	62.0	1.8	31.6	0.005
F-value	15.6	22.4	2.9	9.3	9.2	13.5

a percentage of total mobile concentration

The distribution of total Cr, Zn, Mn, As, Hg, Pb and Cu contents in soils with depth and distance from the disposal point in the Hazaribagh tannery area are illustrated in figures 17-26.

Chromium concentrations were studied in soil profiles of Hazaribagh tannery area (Figure 17). Higher concentrations of Cr (27,500-22,900) ppm were found from surface to 120 cm depth in spot 8. In spot 9, concentration ranged from 928 to 1540 ppm, in spot 10 from 151 to 1340 ppm and in spot 13 from 80 to 1370 ppm Cr. Chromium concentration gradually decreased with depth in spot 10 and 13. Agricultural soils tend to exhibit a more uniform distribution of Cr in the soil profile (Whitby et al 1978). At spots 8 and 9 the accumulation of organic wastes was high and these made the alluvium more loose and favored the movement of Cr into deeper part. Lund et al., (1976) also noticed similar phenomenon in soil.

Lund et al., (1976) hypothesized that the metals moved as soluble metal organic complexes, where Cr could be complexed or present in hexavalent form, it can move deeper in soil profiles. It can threaten ground water quality also. The present (Hazaribagh area) site has a high potential for metal movement through the subsoil. This movement can be facilitated by sandy soils and/or high level of organic and other wastes present. A second possible explanation is the different deposition rate for solids at the different spots. That means that the profile at site 8 is younger than the others and the original alluvium is not reached in 120cm depth.

Distribution of Cr with distance in Hazaribagh tannery area presents an interesting feature. The total sampling distance was about 3km. Six sampling spots were considered to study the distribution of Cr (Figure 18). The Cr concentration gradually decreased with distance but an increased Cr content was found in spot 13, the explanation was stated previously in page 60. Concentrations of Cr was the highest at spot 8, with progressively decreasing levels with distance (Figure 18) due to increasing admixtures of sludge and normal channel sediments.

Zn has been found next to Cr as heavy metal contamination in Hazaribagh tannery area (Figure 19). The distribution of Zn in the profile of spot 13 showed that Zn has accumulated in the surface (0-15 cm) and decrease with depth (Figure 19), but Zn distribution with depth in spots 8, 9 and 10 were inconsistent. Zinc contents in the profiles were found 284 to 327 ppm in spot 8, and these are above the tolerable level for soils (Table 34). The concentrations of Zn in spot 9 to 13 ranged from 81 to 119 ppm Zn, and these are threshold level of normal soil range (Table 34). Significant differences were only observed for spot 8. Zinc distribution with distance was not much appreciable influenced in Hazaribagh tannery area. From spot 9 to 12 a gradual decrease was observed (Figure 20). The data clearly indicate that the formation of stable organo-metallic complexes led to a relatively lower mobility of Zn in the downstream direction. The complexing of heavy metals with organic matter affects the distribution of metal ions between absorbed and solution phases of the soil (Ram and Verloo, 1985).

Manganese concentration in soil profiles of Hazaribagh tannery area ranged from 189 to 2268 ppm Mn. Highest concentration were observed in spot 13 and lowest in spot 8. Highest accumulations in top layers with gradual decrease downwards were observed in spots 8 and 9 but the reverse was noticed in spot 13 where the highest concentration was noticed at 45 to 120 cm depth with gradual increase upwards. Spot 10 exhibited different trend that is the highest concentration in the middle (15 to 45 cm) and more or less equal concentration in top (0 to 15 cm) and bottom (45 to 120 cm) layers (Figure 21).

The behaviour of Mn was correlated with the organic matter in Hazaribagh tannery area (Table 9). The Mn concentration in top soils tended to increased with distance from spot 8. The content of Mn in organic waste influenced spots 8 to 10 inside the embankment were found to be low. The top soil of the rice field (spots 11 to 13) exhibited high concentrations (Figure 22). The concentrations of Hg, found in soil profiles in Hazaribagh tannery area was very low, ranging from 0.02 to 0.23 ppm Hg. Arsenic concentrations determined were within the normal soil range (Table 34) in all soil profiles except in spot 13 (Figure 23). Arsenic concentrations were measured and found to be from 5.3 to 44.8 ppm As in spot 13, and these are above the tolerable limit in soil (Table 34). The particular horizon within the same profile is also very important. In spot 13, the topsoil (5.3 ppm As) and subsoil (44.8 ppm As) (Appendix table A-2) showed considerable differences in As content due to prominent migration and accumulation of As in the oxidized subsoil within the

profile. The increased As level may be due to migration from the contaminated area through shallow ground water flow (Kotuby amachar and Gambrell, 1988).

The concentration of Hg depleted with depth (Figure 23) in Hazaribagh area. In general, Pb accumulates in the soil surface, usually in topsoil and depletes with depth. Lead was found uniformly distributed in spot 8 and 10. In spot 13 (rice field), Pb concentration decreased with depth (Figure 25).

Copper concentration in all the profiles except 13 was inconsistent with respect to its distribution. Copper concentration was found to be above the critical limit in spot 8. This is important in terms of the potential for mobility and the lack of stronger immobilizing processes in the deep sandy soil of Hazaribagh tannery area. Copper is weakly retained at the top of the ground water table is relatively weakly retained in a form that can easily be displaced to become soluble, favoring its movement through the lower subsoil profile (Kotuby amacher and Gambrell, 1988).

Distribution of total Pb and Cu contents of top soils of Hazaribagh tannery area were illustrated in figure 26. Appreciable influence of the distance was observed for these two heavy metals.

Sampling periods exhibited no substantial seasonal fluctuation in the values of heavy metal contents in Hazaribagh tannery area (Table 8).

Figure 17. Depth distribution of total Cr at Hazaribagh tannery area

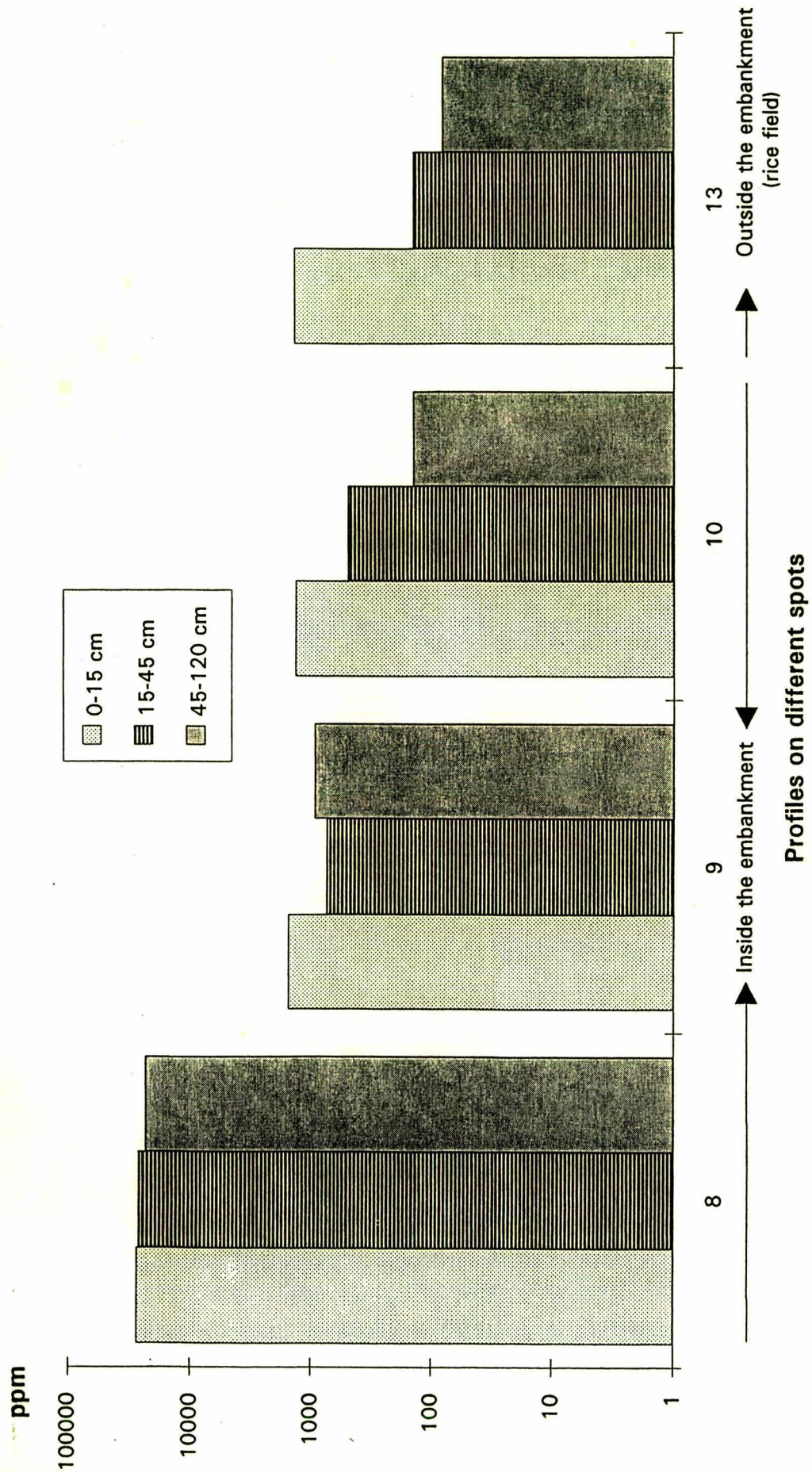


Figure 18. Distribution of total Cr at Hazaribagh tannery area (0 - 15 cm) with distance from the disposal point

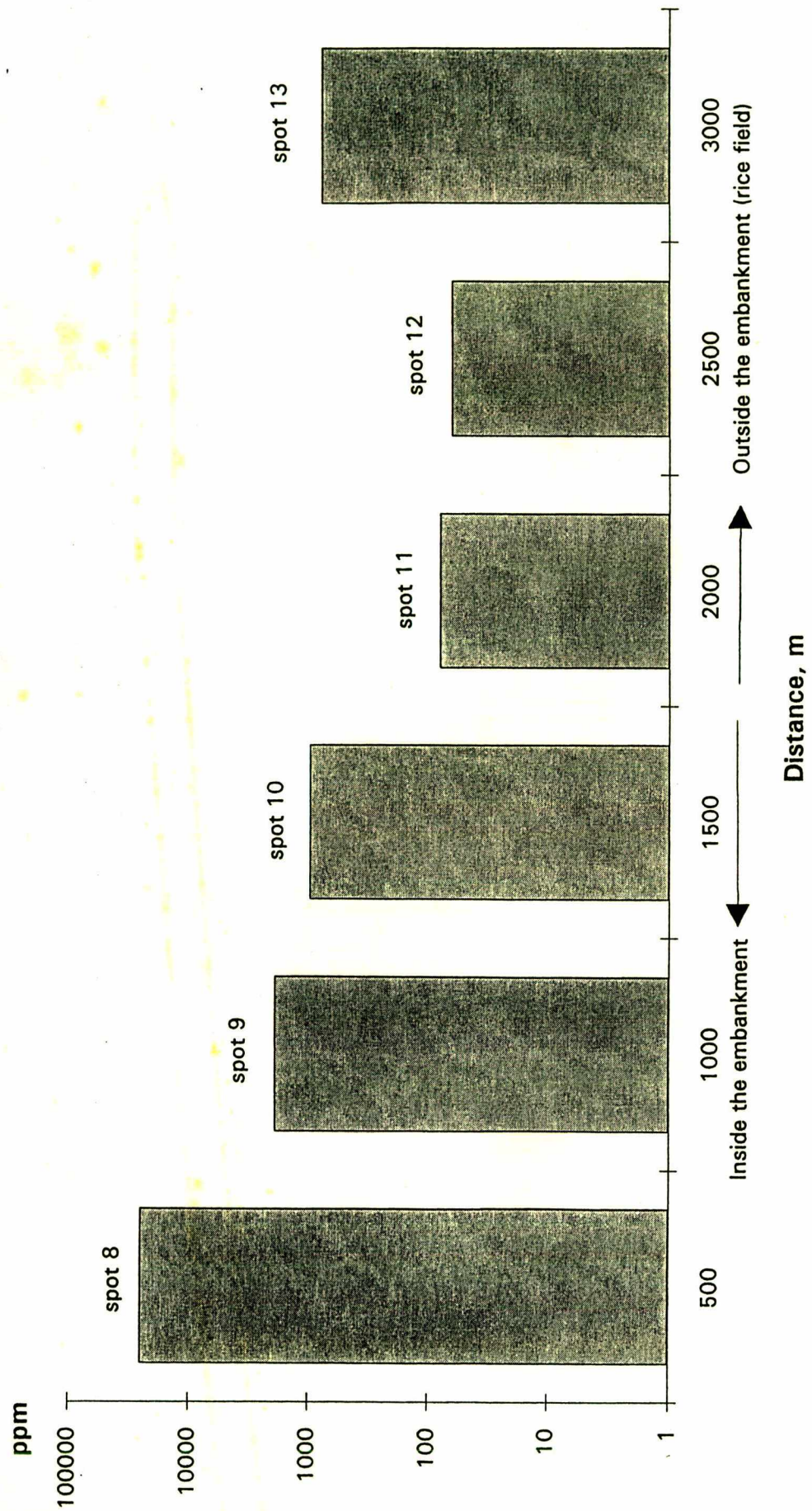


Figure 19. Depth distribution of total Zn at Hazaribagh tannery area

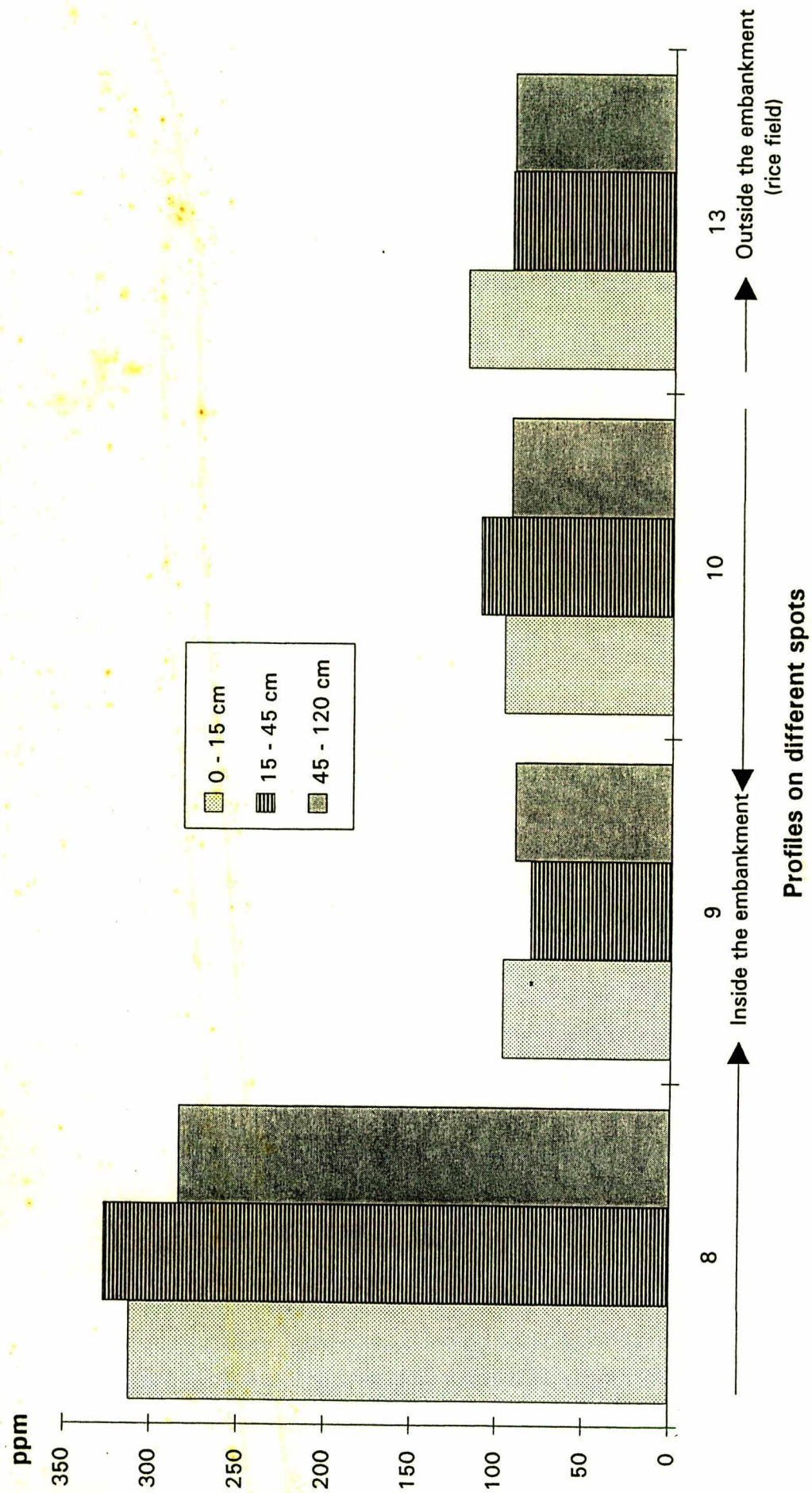


Figure 20. Distribution of total Zn at Hazaribagh tannery area (0 - 15 cm) with distance from the disposal point

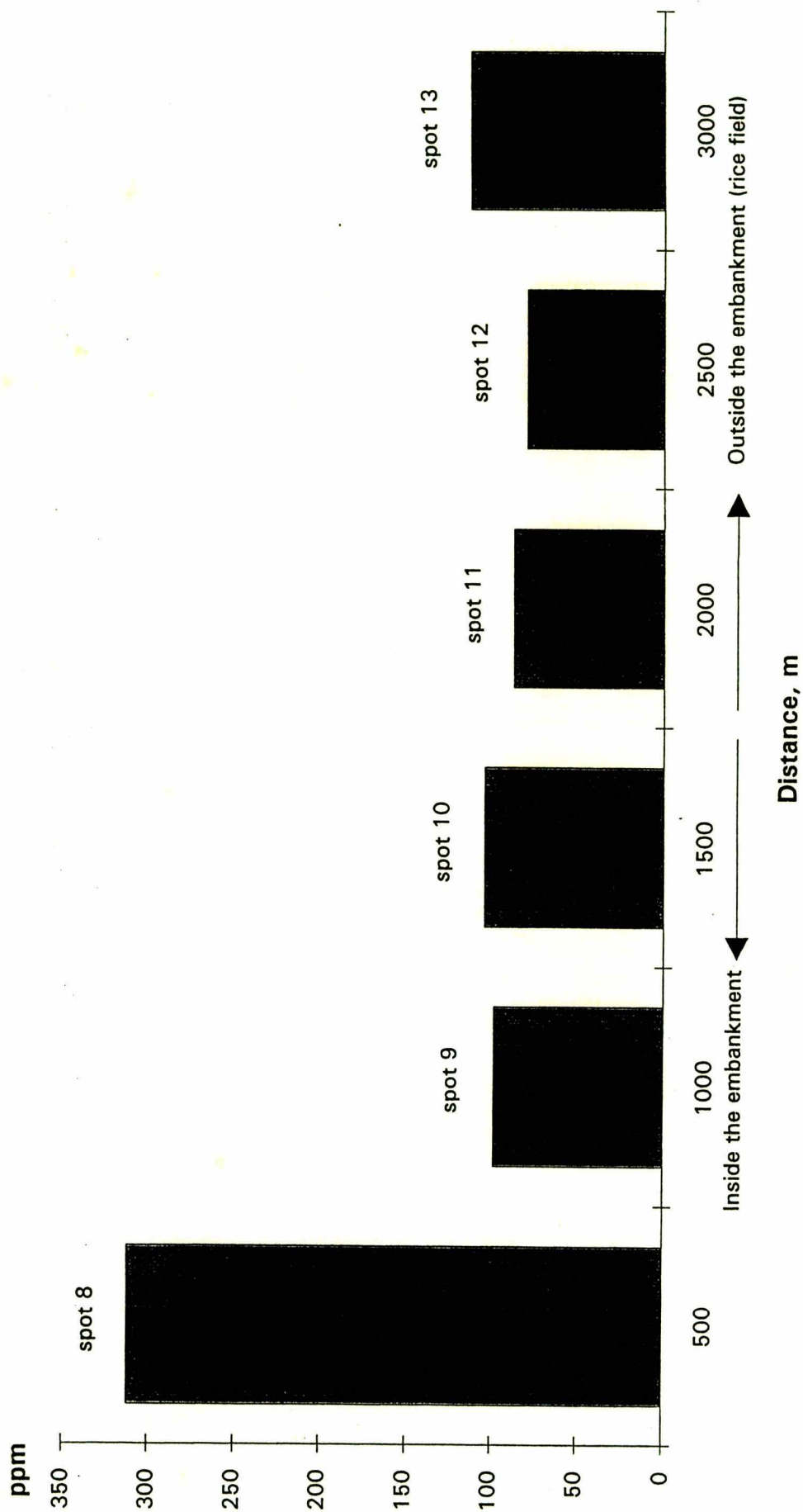


Figure 21. Depth distribution of total Mn at Hazaribagh tannery area



Figure 22. Distribution of total Mn at Hazaribagh tannery area (0 - 15 cm) with distance from the disposal point

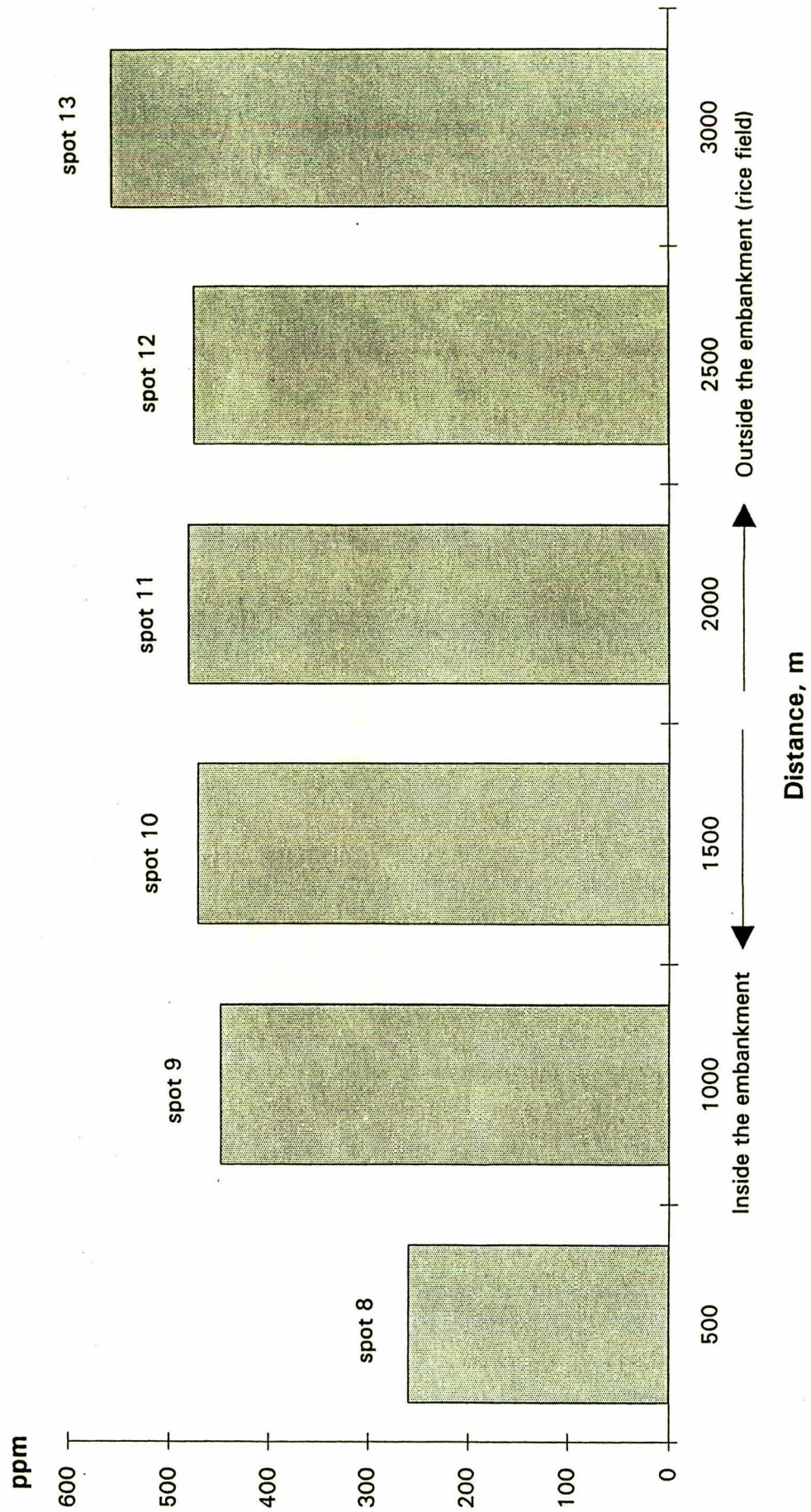


Figure 23. Depth distribution of total As and Hg at Hazaribagh tannery area

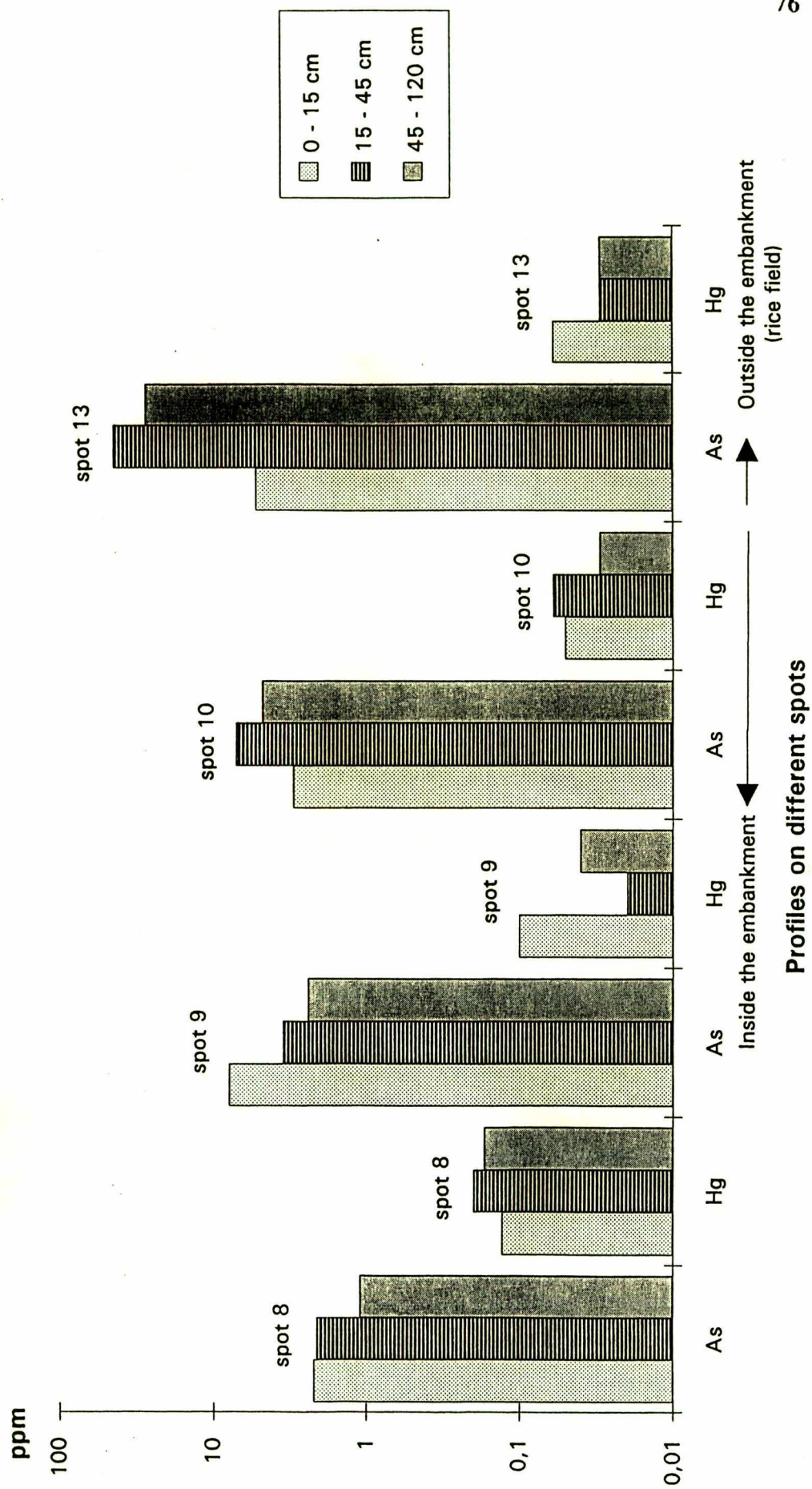


Figure 24. Distribution of total As and Hg at Hazaribagh tannery area (0 - 15 cm) with distance from the disposal point

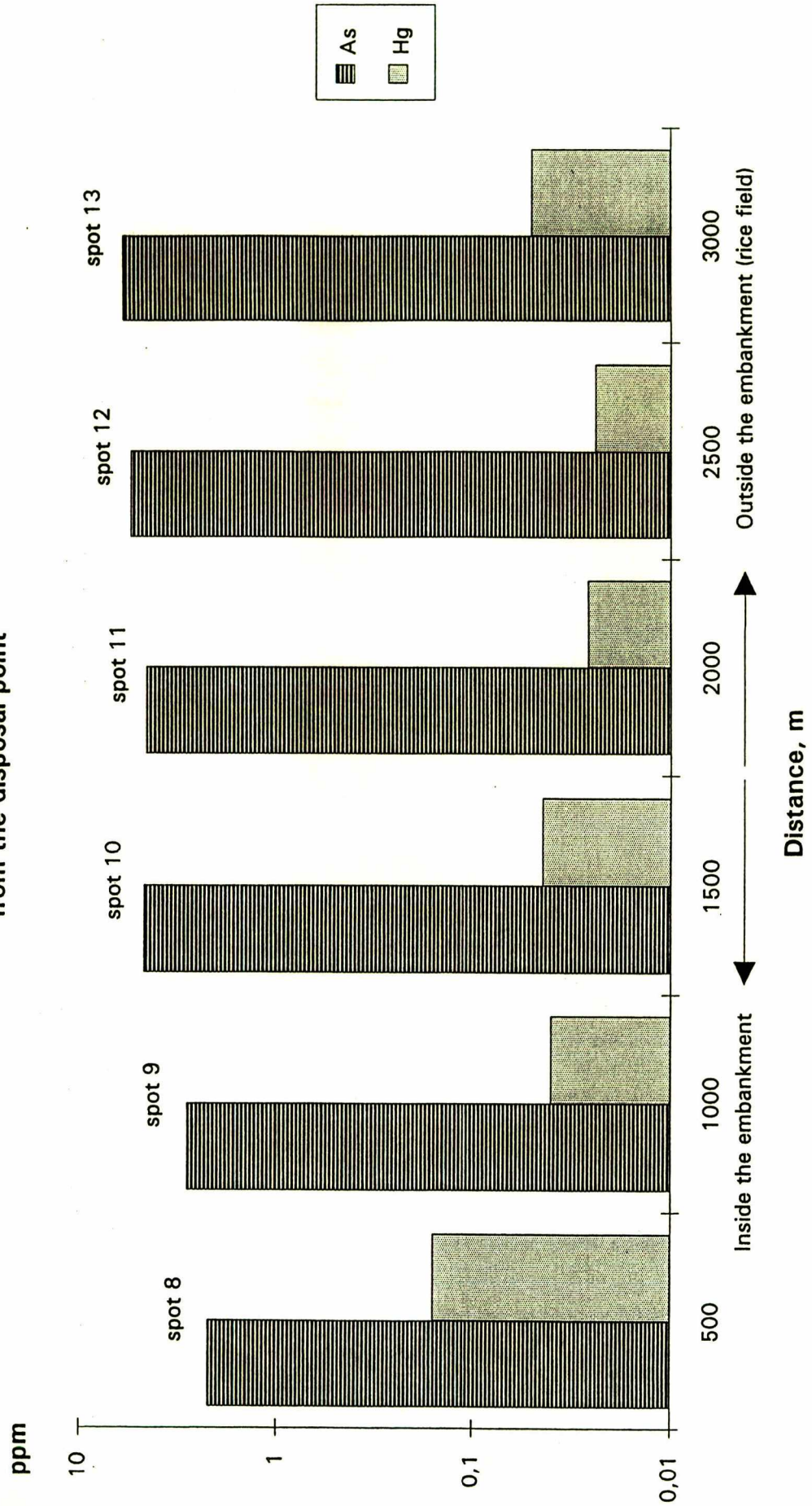


Figure 25. Depth distribution of total Pb and Cu at Hazaribagh tannery area

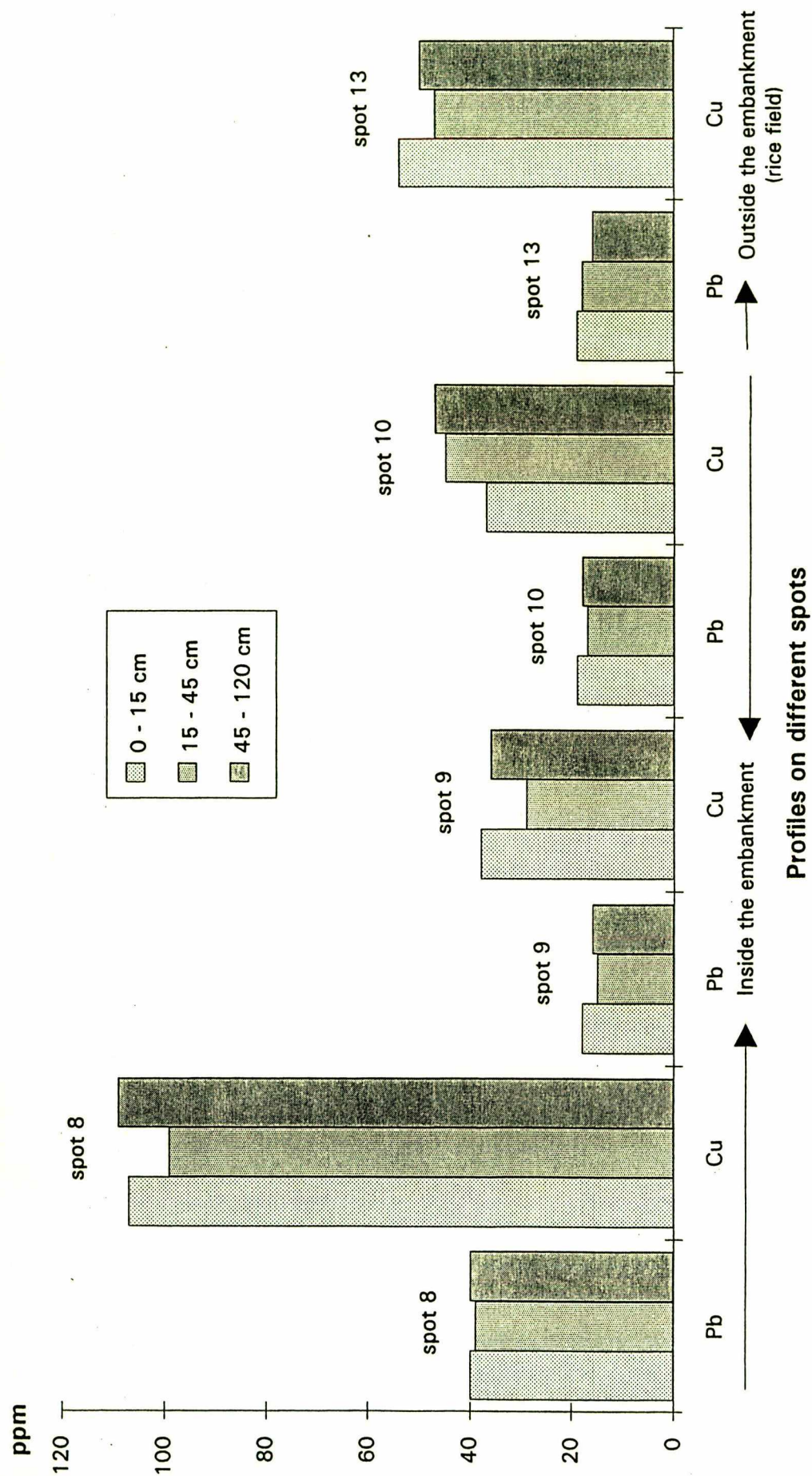
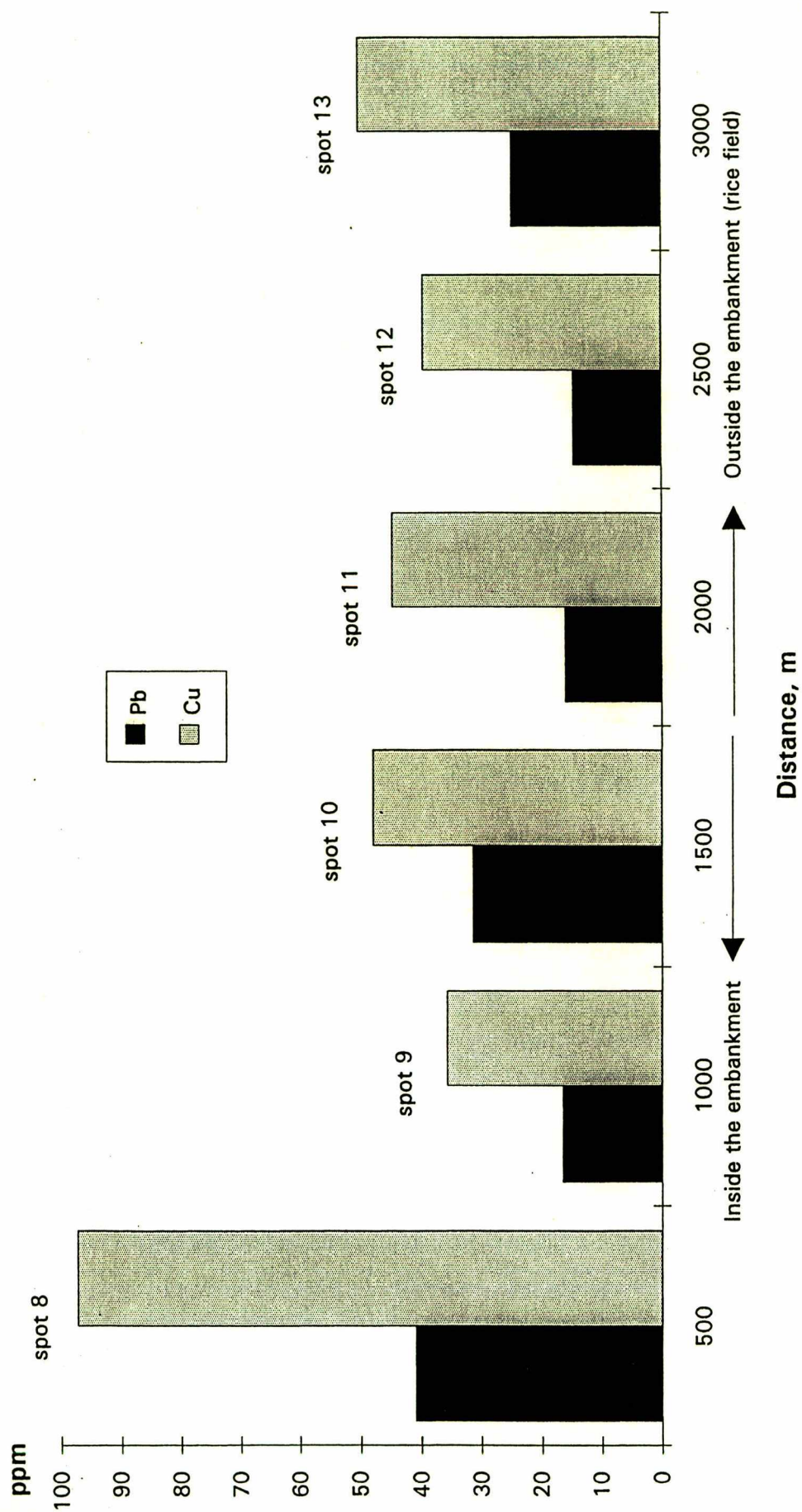


Figure 26. Distribution of total Pb and Cu at Hazaribagh tannery area (0 - 15 cm) with distance from the disposal point



4.1.2. Sampling site, Tongi

The measurements of particle size distribution, chemical properties and available nutrients of topsoils of the pharmaceutical industrial site, spot numbers 1 2 and 3 and battery industrial site, spot number 4 and 5 were carried out and the data are presented in table 11. The data represent in table 11, were the average of five sampling dates. Year and month of the sampling periods are mentioned in table 4. Correlation coefficient of soil pH, Om, EC, CEC, exchangeable cations, Cl and Av-N,P,K were presented in table 12. Particle size distribution analyses of all investigated soils showed a clayey texture except for spot number 5, which is a silty clay loam (Table 11). This is in agreement with the reconnaissance soil survey report, 1966-1977, Department of Soil Survey, Dhaka. The pH H_2O (1:2.5 soil:water) was alkaline in reaction in all spots. The pH ranged from 7.7 to 8.3 and 7.5 to 7.9 in pharmaceutical and battery industrial sites respectively. The pH in water (1:2.5) was not found significantly different within the industrial site, but the pH of battery industrial site (spot 5) was significantly lower compared with that of the pharmaceutical site. pH (Soil: $CaCl_2$ = 1:2.5) was lower than that in water (Table 11). Exchangeable Ca,K and Na concentrations are high in the top soil of the pharmaceutical site.

The organic matter contents ranged from 1.6 (spot 4) to 4.2 (spot 2) percent. Spot 2 is located in the central part of the sampling site of pharmaceutical industrial area, (Figure 12) being comparatively low and wet

compared to spot 1. The differences of organic matter contents are predominantly due to the landscape and the induced erosion and deposition process. Sampling site 4 is situated in the higher elevated part of the landscape and organic residues are washed away to the lower sites. Hiroki, (1991) stated that there may be influence of the different heavy metal accumulation through an effect on sensitive microorganisms which decrease the organic matter content.

Available K contents were found to be higher in spot 1,2 and 3 than in spot 4 and 5. Values ranged from 379 to 618 ppm K and 96 to 108 ppm K in pharmaceutical and battery industrial site respectively (Table 11). Increased contents of available K (Table 11) exchangeable K (Table 11) and total K (Table 13) were found near the pharmaceutical industry. Available and exchangeable K decreased with distance from the discharging point in pharmaceutical site. High content of K (>45ppm) was found in the effluent of pharmaceutical industry (Table 19). It is quite evident from the results, industrial effluent were responsible for high K content as well as pH values in this site.

Chloride and EC levels were found in the normal range in all spots (Table 11). Cation exchange capacity (CEC) was significantly correlated with particle size distribution in both pharmaceutical (1,2,3) and battery (4,5) industrial sites (Table 12).

Table 11 Particle size distribution, chemical properties and available nutrients of top soils (0-15 cm) of pharmaceutical (1, 2, 3) and battery industrial site, Tongi

Spot	Sand % 2 - 0.05	Silt % 0.05- 0.002	Clay % < 0.002	Text class	pH		OM %	EC S/cm	CEC meq/100g	Exch. cations meq/100 g			Cl mg/l	Available in ppm		
					S/E	CaCl ₂				Ca	Mg	K		N	P	K
1	1.7	29.0	69.3	clay	7.7	6.8	3.8	1.6	29.4	18.1	2.7	2.4	67	57	1.2	618
2	2.3	28.2	69.5	clay	8.3	6.8	4.2	1.2	31.4	13.6	2.4	1.9	31	63	0.6	421
3	3.0	35.2	61.8	clay	8.3	6.7	3.2	0.7	28.2	12.5	3.3	1.9	38	59	0.7	379
4	24.3	26.8	48.9	clay	7.9	6.6	1.6	1.4	20.2	4.6	1.7	0.6	32	128	0.9	96
5	12.8	49.7	37.5	sicl	7.5	6.5	2.9	0.7	23.8	7.3	2.8	0.5	15	16	0.5	108
LSD 5%																
F-value																
					0.5	0.1	0.4	0.2	5.4	2.9	0.8	0.4	14	27	0.7	162
					4.1	9.0	46.2	25.1	6.0	28.7	4.4	42.6	16.0	20.1	1.3	16.4

Table 12 Correlation coefficients among chemical properties and available nutrients of top soils (0 - 15 cm) from the battery industrial area Tongi

	pH S/E	pH CaCl ₂	OM	EC	CEC	Exchangeable cations			Cl	N	P	K
						Ca	Mg	K	Na			
Av-K	0.01	-0.05	0.05	-0.19	0.30	-0.03	0.07	-0.73**	0.42	0.11	0.44	1
Av-P	0.31	-0.00	-0.28	0.33	-0.23	-0.45	-0.34	-0.21	-0.14	0.27	1	
Av-N	0.42	0.78**	-0.91***	0.90**	-0.42	-0.59	-0.60	0.23	-0.71*	1		
Cl	-0.03	0.31	-0.92***	0.72**	-0.61*	-0.57*	-0.58	-0.14	-0.44	1		
Exch. Na	-0.32	-0.39	0.65*	-0.58*	0.19	0.23	0.29	-0.54	1			
Exch. K	0.10	0.20	-0.12	0.36	-0.10	0.03	-0.16	1				
Exch. Mg	-0.50	-0.48	0.73**	-0.89***	0.89***	0.96***	1					
Exch. Ca	-0.60	-0.50	0.68*	-0.82**	0.89***	1						
CEC	-0.37	-0.36	0.63*	-0.79**	1							
EC	0.44	0.51	-0.89***	1								
OM	-0.24	-0.45	1									
pH CaCl ₂	0.51	1										
pH S/E	1											

* significant at $p < 0.05$

** significant at $p < 0.01$

*** ... significant at $p < 0.001$

Detailed results of particle size distribution, chemical properties and available nutrients of soils at different spots, horizons and periods of Tongi sampling site are presented in the appendix (Table A-3). The relevant values of correlation studies between soil parameters and available nutrients of Tongi Industrial area are presented in table 12. The significance of correlation coefficients (r) were 0.632 ($P < 0.05$) 0.799 ($P < 0.01$) and 0.907 ($P < 0.001$). The pH (S/E) did not show any correlation with elements only pH CaCl_2 showed correlation with Av-N. Organic matter content showed a negative correlation with EC, Cl, Av-N at ($P < 0.001$) and positive correlation with CEC, Each. Ca, Mg and Na at ($P < 0.05$). The EC exhibited a negative correlation with OM ($r = -0.89$), Exch. Ca ($r = -0.82$), Mg ($r = -0.89$), Na ($r = -0.58$) and a positive with Cl ($r = 0.72$), Av-N ($r = 0.90$). The CEC was positively correlated with OM ($r = 0.63$), Exch. Ca ($r = 0.89$), Mg ($r = 0.89$), and negatively correlated with Cl ($r = -0.61$).

Results of selected total nutrients and heavy metal contents of top soils from pharmaceutical and battery industrial site are presented in table 13 with LSD and F-values. Iron, Cu, Mn, Zn, As, Cr, Hg, Pb and Cd contents in the soil samples from spot number 4 and 5 of battery industrial site ranged from 2.35 to 4.0% Fe, 16 to 34.5 ppm Cu, 265 to 767 ppm Mn, 885 to 4979 ppm Zn, 1.40 to 2.95 ppm As, 31.5 to 58 ppm Cr, 0.19 to 4.99 ppm Hg, 10.5 to 22.5 ppm Pb and 0.09 to 0.785 ppm Cd. It is evident from table 13 that the highest level of Zn (1510-4979 ppm) was found in spot 4. This spot is at 500 m distance from the industry. The values are significantly different from that of spot 5. This

spot is located another 500m apart. The highest Zn concentration in top soil of spot 5 was 1400 ppm Zn. Kloeke (1980) mentioned 300 ppm Zn to be the tolerable limit in soils. Thus the concentration of Zn in spot 5 was still in a hazardous magnitude with respect to effects on the soil ecosystems. Concentrations of ammonium acetate extractable Zn in spot 4 and 5 were 463 ppm and 138 ppm respectively. The percentage of the mobile fraction of Zn was 15.9 and 12.3 in spot 4 and 5 respectively (Table 16). The concentration of Hg was also observed to be very high in top soil of the battery industrial site (Table 13). In spot 4 and 5 the Hg contents were 4.90 and 0.44 ppm, respectively. The values were found to be significantly different between spots within the sites. A positive correlation (Table 15) between Hg and Zn was observed ($r = 0.94$). Arsenic, Cr, Cu, Pb, Cd, and Mn were found in a normal range (Table 34). There was no significant difference in concentrations of As, Cr, Cu and Pb between the sampling dates in battery industrial site. However, a positive correlation ($r = 0.82$ to 0.95) between the contents of Cr, Cu and Pb were found (Table 15).

Sampling periods showed a substantial seasonal fluctuation in the values of Zn, Mn, Hg and Cd contents in spot 4 and 5. In general Zn, Hg, Cd and Mn contents showed a depletion after the summer rain, a large reduction being observed in Zn concentration. In contrast higher metal contents were found in periods 1 and 4 (Jan - Feb) and lower contents in periods 3 and 5 (Oct), (Table 13). A small increasing trend of accumulation was found in the 2nd year, (period 5) compared to period 3 in the first year sampling. This suggests that

the surface wash off aided by monsoon rain was the principle cause for the reduction in the levels of heavy metals on the surface of the industrial area. Similar findings were also observed by Moon et al, (1991). The increased concentrations of Zn and Hg in the soil were the direct consequences of the effluent of battery industry. As mentioned earlier the effluent content manganese-dioxide, ammonium chloride, zinc oxide, mercuric chloride carbon black, graphite, zinc-calomite and carbon rod.

Heavy metal contents in pharmaceutical industrial site in spot 1, 2, and 3 (Table 13) were found to be in normal soil range as defined by Klok, (1980). Copper, Mn, Zn, As, Cr, Hg, and Pb ranged from 32.5 to 47.5, 197 to 383, 98 to 193, 2.75 to 4.15, 54 to 73, 0.04 to 0.29 and 20.5 to 26.0 ppm, respectively. Correlation coefficient among the total nutrient and heavy metal contents of top soils from pharmaceutical industrial area, Tongi were presented in table 14. Heavy metals did not show significant relationship except Hg and Cu with Zn.

A Pearson correlation matrix for some selected parameters of top soils from the battery industrial site are presented in table 15. The critical values of the correlation coefficient (r) are 0.505 ($P < 0.05$), 0.520 ($P < 0.01$) and 0.667 ($P < 0.001$). Table 15 illustrates the relationship among the soil total heavy metal and the total N, P, K, S and OM contents. Organic matter content showed negative correlation with Zn, Hg and Cd contents at $P < 0.01$. Significant relationships clearly indicated that the battery industrial site was contaminated by metals from the industrial waste and effluent. From correlation coefficient

(Table 15) analyses it indicates that Zn had a significant relationship with Mn, Hg and Cd contents in top soils of battery industrial site, ($r = 0.667$, $P < 0.001$). Figure 27 as well reflected the interdependent relationship with the concentration of Zn.

Results of ammonium acetate extractable heavy metals and their percentage of total concentrations of top soils of battery industrial site (spot 4,5) are presented in table 16. Iron, Cu, Mn, Zn, Pb, Cd, and As contents ranged from 0.04 to 0.05 ppm Fe, 0.10 to 0.11 ppm Cu, 143 to 165 ppm Mn, 138 to 463 ppm Zn, < 0.5 ppm Pb, < 0.05 to 0.06 ppm Cd and 0.006 to 0.02 ppm As. The mobile percentage ranged from 0.00013 to 0.0002% (Fe), 0.36 to 0.41% (Cu), 26.6 to 39.8%(Mn), 12.3 to 15.9%(Zn), 12.1%(Cd) and 0.27 to 1.01%(As). Highest concentrations of extractable Zn (463ppm) and Mn (143ppm) were found in spot 4. Mercury content was found below the detection limit in ammonium acetate extraction. Except Zn, all other elements were statistically not significantly different in spot 4 and 5.

Total contents of Fe, Cu, Mn, Zn, As, Cr, Hg, and Pb of top soils of pharmaceutical industrial site were presented in table 13. Values of total nutrients were found in a normal range with exception of slightly higher K values.

Values of heavy metal measurements of spot 6 (confluence zone) were presented in table 13. Spots 6 is about 1.5 km away from both the industrial

sites. Measured total nutrient and heavy metal contents were found to be in a normal range. Cadmium was below detection limit in spot 6. Sampling periods did not show any significant difference in spot 1,2,3, and 6 (Table 13).

The results of simple correlation analyses of pharmaceutical site showed a poor relationship between total heavy metal contents and total nutrients. Although in some cases statistically significant correlations were present at $P < 0.01$ and $P < 0.001$, but they had no conclusive affect on each other (Table 14). Data of ammonium acetate extractable heavy metals (Table 16) of pharmaceutical site with the total contents (Table 13) represents a similar indication.

Table 13 Total contents of selected nutrients and heavy metals of top soils (0 - 15 cm) from pharmaceutical (1, 2, 3) and battery (4, 5) industrial site Tongi at different spots and periods

Spot	Period	N	P	K	S	OM	Fe	Cu	Mn	Zn	As	Cr	Hg	Pb	Cd
%															
ppm															
1	1	0.195	0.058	0.255	0.065	3.65	3.95	38.5	302	118	3.66	73.0	0.08	24.5	*
1	2	0.141	0.045	0.260	0.042	3.80	4.15	36.0	292	98	3.75	64.5	0.06	22.5	*
1	3	0.274	0.061	0.240	0.081	3.65	2.95	34.5	279	108	3.10	61.5	0.21	21.0	*
1	4	0.310	0.074	0.270	0.091	4.00	2.90	47.5	197	193	3.75	64.5	0.29	25.5	*
1	5	0.329	0.063	0.260	0.062	3.95	3.25	33.5	360	112	3.65	59.5	0.15	22.0	*
2	1	0.192	0.040	0.265	0.063	3.15	4.15	35.5	320	110	3.80	68.5	0.06	25.0	*
2	2	0.149	0.040	0.270	0.050	4.20	3.95	35.5	322	98	3.80	66.5	0.05	22.5	*
2	3	0.377	0.049	0.260	0.082	3.25	3.85	36.0	347	120	3.20	63.5	0.10	24.0	*
2	4	0.215	0.038	0.255	0.076	3.05	3.65	36.0	244	113	3.65	69.0	0.04	22.5	*
2	5	0.383	0.081	0.275	0.068	3.45	2.95	32.5	273	112	2.75	56.5	0.12	25.5	*
3	1	0.193	0.038	0.255	0.060	2.80	4.75	37.0	383	134	4.15	72.0	0.07	26.0	*
3	2	0.183	0.040	0.260	0.055	3.45	3.55	35.5	322	98	3.30	63.5	0.07	22.0	*
3	3	0.251	0.036	0.275	0.084	3.35	3.45	37.5	313	118	3.65	65.5	0.10	23.0	*
3	4	0.277	0.043	0.270	0.079	3.65	2.95	36.5	283	160	3.85	65.5	0.09	24.5	*
3	5	0.407	0.091	0.255	0.086	4.35	2.85	36.0	201	138	2.95	54.0	0.23	20.5	*
4	1	0.164	0.051	0.130	0.041	1.65	2.80	27.5	767	4979	1.40	44.5	4.90	16.0	0.770
4	2	0.118	0.019	0.140	0.024	1.20	2.35	16.0	333	2450	1.45	31.5	3.15	10.5	0.325
4	3	0.161	0.030	0.135	0.038	1.25	4.00	25.0	366	1510	2.95	45.0	0.55	19.5	0.280
4	4	0.131	0.035	0.125	0.035	1.15	3.10	29.0	736	3776	2.35	49.5	3.90	16.0	0.785
4	5	0.110	0.022	0.145	0.026	1.20	2.40	23.0	483	1810	1.75	43.0	1.25	17.5	0.325
5	1	0.213	0.026	0.145	0.035	2.75	2.80	26.5	457	1320	2.35	47.5	0.44	16.0	0.135
5	2	0.089	0.019	0.135	0.027	2.35	3.45	26.0	653	885	2.30	49.0	0.28	19.0	0.090
5	3	0.344	0.023	0.110	0.054	2.25	3.00	34.5	298	1400	2.10	58.0	0.42	22.5	0.110
5	4	0.263	0.027	0.130	0.048	2.55	3.05	32.0	402	1215	2.45	57.0	0.40	20.5	0.220
5	5	0.317	0.021	0.125	0.052	2.60	2.90	33.0	265	911	2.05	58.0	0.19	22.0	0.155
6**	1	0.256	0.034	0.315	0.077	3.25	4.25	37.0	299	159	3.90	69.0	0.10	25.5	*
6	2	0.163	0.031	0.250	0.038	2.90	3.85	30.0	313	104	3.80	48.5	0.03	21.5	*
6	3	0.182	0.030	0.190	0.037	3.20	3.30	22.0	269	79	3.60	41.0	0.03	17.5	*
6	4	0.275	0.038	0.275	0.067	3.30	5.05	34.5	300	138	3.75	63.5	0.03	24.5	*
6	5	0.219	0.037	0.205	0.052	3.00	4.00	31.5	274	102	3.80	45.0	0.02	25.5	*
LSD 5%		0.078	0.014	0.049	0.024	0.49	0.88	6.8	137	568	0.69	14.2	0.27	4.7	0.090
F-value		10.3	12.8	14.1	5.5	29.0	4.7	6.8	8.5	36.1	11.4	4.6	169.4	5.1	80.5

* not determined

** common spot

Table 14 Correlation coefficient among the total nutrient and heavy metal contents of top soils (0 - 15 cm) from the pharmaceutical industrial area Tongi

	N	P	K	S	OM	Fe	Cu	Mn	Zn	As	Cr	Hg	Pb
Pb	0.08	-0.12	0.07	-0.14	-0.29	0.31	0.34	0.16	0.27	0.29	0.37	-0.09	1
Hg	0.62***	0.87***	-0.06	0.58***	0.49	-0.61***	0.39	-0.50**	0.56***	-0.32	-0.38	1	
Cr	-0.55***	-0.56***	-0.13	-0.14	-0.44	0.56***	0.38	0.38	0.13	0.72***	1		
As	-0.57***	-0.58***	0.09	-0.17	-0.21	0.54**	0.36	0.30	0.25	1			
Zn	0.31	0.30	0.11	0.61***	0.11	-0.38	0.71***	-0.38	1				
Mn	-0.31	-0.53**	0.02	-0.44	-0.40	0.53**	-0.38	1					
Cu	-0.04	0.08	-0.08	0.35	0.12	-0.08	1						
Fe	0.53**	-0.58***	0.01	-0.54***	-0.44	1							
OM	0.23	0.55***	-0.01	0.07	1								
S	0.53**	0.40	-0.04	1									
K	0.12	-0.01	1										
P	0.71***	1											
N	1												

* significant at $p < 0.05$

** significant at $p < 0.01$

*** ... significant at $p < 0.001$

Table 15 Correlation coefficient among the total nutrient and heavy metal contents of top soils (0 - 15 cm) from the battery industrial area Tongi

	N	P	K	S	OM	Fe	Cu	Mn	Zn	As	Cr	Hg	Pb	Cd
Cd	-0.38	0.65**	-0.02	-0.13	-0.60**	-0.13	-0.09	0.68***	0.92***	-0.27	-0.25	0.90***	-0.40	1
Pb	0.66***	-0.01	-0.60**	0.73***	0.56**	0.45	0.82***	-0.23	-0.45	0.34	0.85***	-0.59**	1	
Hg	-0.34	0.55**	-0.03	-0.21	-0.58**	-0.28	-0.30	0.57**	0.94***	-0.47	-0.46	1		
Cr	0.73***	0.10	-0.51*	0.77***	0.68***	0.34	0.95***	-0.12	-0.33	0.34	1			
As	0.17	-0.15	-0.06	0.12	0.17	0.74***	0.29	-0.20	-0.44	1				
Zn	-0.31	0.75***	-0.06	-0.07	-0.51*	-0.27	-0.14	0.67***	1					
Mn	-0.54**	0.55**	0.14	-0.28	-0.27	0.03	-0.03	1						
Cu	0.78***	0.29	-0.64**	0.85***	0.59**	0.30	1							
Fe	0.10	-0.01	-0.20	0.21	0.10	1								
OM	0.63**	-0.14	-0.23	0.52**	1									
S	0.89***	0.36	-0.71***	1										
K	-0.59**	-0.19	1											
P	0.03	1												
N	1													

* significant at $p < 0.05$

** significant at $p < 0.01$

*** ... significant at $p < 0.001$

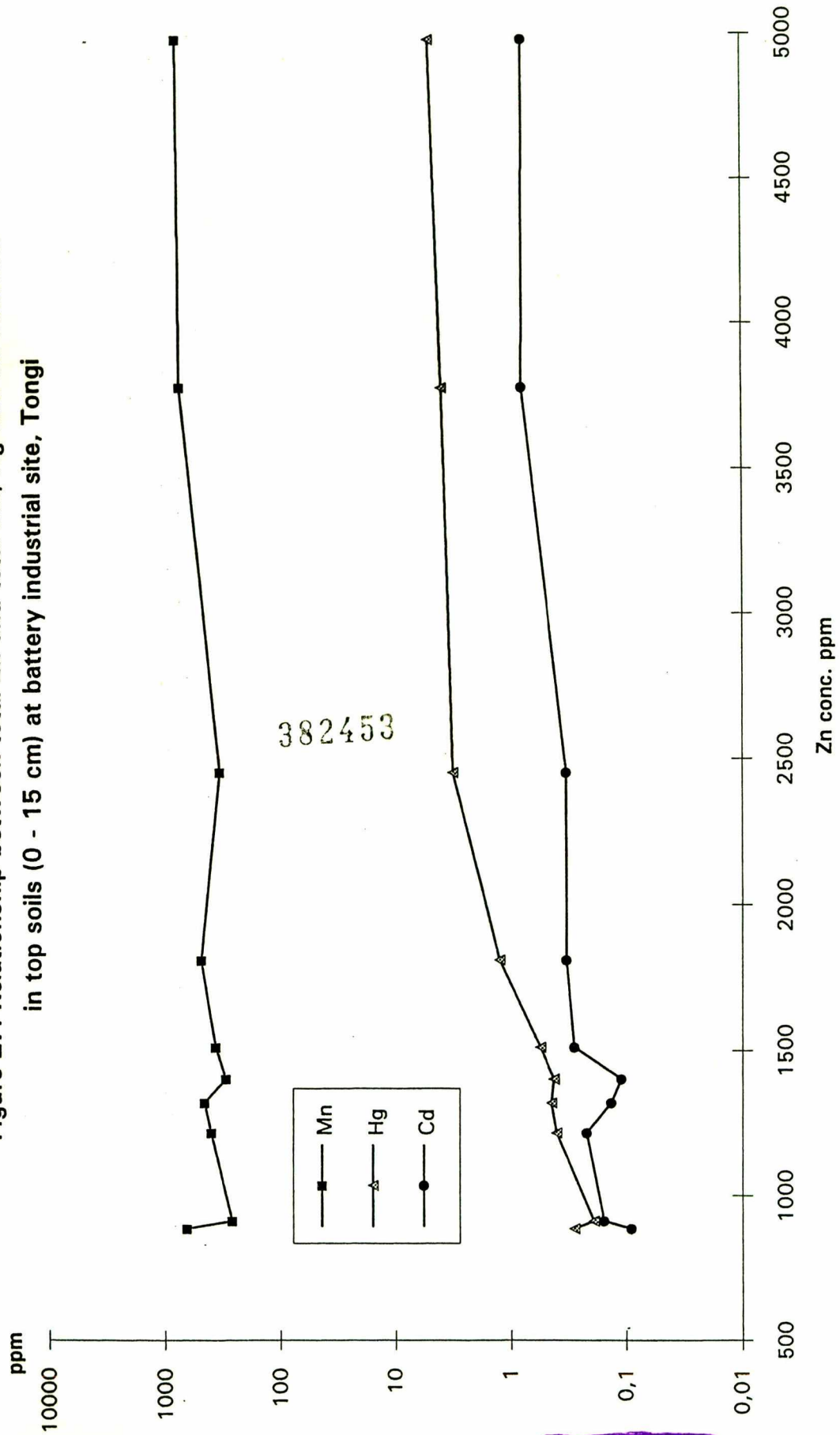
Table 16 Ammonium acetate extractable heavy metals from top soils (0 - 15 cm) of pharmaceutical (1, 2, 3) and battery (4, 5) industrial site Tongi

Spot	Fe	Cu	Mn	Zn	Pb	Cd	As
	ppm						
1	0.04 (0.00011%) a	0.09 (0.24%) a	45 (15.7%) a	0.73 (0.58%) a	*	*	*
2	0.09 (0.00024%)	0.20 (0.57%)	6 (1.99%)	0.75 (0.68%)	*	*	*
3	0.05 (0.00014%)	0.09 (0.25%)	36.2 (12.05%)	0.63 (0.49%)	*	*	*
LSD 5%	0.05	0.02	10.5	0.20	*	*	*
F-value	1.4	88.9	45.3	2.0	*	*	*
4	0.05 (0.0002%)	0.10 (0.41%)	143 (26.63%)	463 (15.94%)	≤0.5	0.06 (12.07%)	0.02 (1.01%)
5	0.04 (0.00013%)	0.11 (0.36%)	165 (39.76%)	138 (12.34%)	≤0.5	≤0.05	0.006 (0.27%)
LSD 5%	0.02	0.04	42	318	*	*	0.01
F-value	0.3	0.03	1.6	6.2	*	*	7.74

* not determined

a percentage of total mobile concentration

Figure 27. Relationship between total Zn and total Mn, Hg and Cd contents in top soils (0 - 15 cm) at battery industrial site, Tongi



Although almost all metals occur naturally in soil and participate in the nutritional chain from soil to plant and animals, they can be regarded as pollutants and become dangerous and toxic to plants and animals when they accumulate at high levels.

The Zn, Mn, Pb, Cu, As and Hg distribution with depth and distance from the disposal point, for soils in Tongi industrial area were illustrated in Figures 28 - 33.

The Zn vertical distribution showed a gradual decrease in spots 1 and 3 and uniform distribution up to 30 cm in spot 2 (Figure 28). 4360 ppm Zn was found in spot 4 at 0-15 cm, 194 ppm at 15-30 cm and 123 ppm Zn at 30-60 cm depth. Zn (1210-1390 ppm) was almost uniformly distributed up to 50 cm depth down the profile in spot 5 and then decreased to 233 ppm between 50-75 cm. Calculation of total Zn showed that 54%, 51%, 58%, 7%, and 50% Zn migrated from the top soil to the subsoil in spots 1, 2, 3, 4, and 5 respectively (Figure 28). This is in agreement with findings of Yediler et al (1994). Exceptionally high accumulation of Zn was observed in spot 4 due to the industrial discharge. From figure 28, it is evident that the Mn concentrations in all soil profiles were in normal ranges. As described by Adriano (1980). Mn accumulation in the subsoil horizons were found prominent in almost all profiles with some exception of uniform distribution. Soil texture and pH account for the distribution of Mn in the profiles in the Tongi industrial area.

The average distribution of total Zn and Mn (0-15 cm depth) with distance from the disposal point in Tongi industrial site were illustrated in figure 29. Concentration of Zn sharply decreased with the distance upto to spot 6 from battery industrial site. No appreciable difference with the distance was observed in pharmaceutical site, 125.8, 110.6 and 130.0 ppm Zn were the concentrations of the three spots. Spot 6 (confluence zone) showed normal concentrations (116.4 ppm Zn). The study revealed that locally high Zn concentrations within the battery industrial site were principally caused by the industrial influence. The same trend of distribution with distance was found in this area for total Mn ,but its concentration was higher than that of Zn in pharmaceutical areas (Figure 29).

Lead and Cu concentrations within the profiles (spots 1-5) ranged from 8 to 29 ppm Pb and 11 to 39 ppm Cu in all sampling sites of Tongi industrial area (Figure 30). These indicated that the level of Pb and Cu contents in soil profiles are in normal range. Lead and Cu concentrations showed generally a successive decrease in soil profiles with depth. Copper and Pb showed almost similar mobility patterns at all sites and statistically significant correlations ($P < 0.001$) were found in battery industrial site (Table 15) but not in pharmaceutical site.

The average concentrations of Pb and Cu (0-15 cm) with distance from the disposal point in Tongi industrial site was not significantly different (Figure 31). Spot 1 and spot 4 were considered the disposal point of

pharmaceutical and battery industrial site respectively. A higher concentration of Cu (35.1-38ppm) was observed in pharmaceutical site as compared to battery industrial site (24.1 to 30.4 ppm Cu). 31 ppm Cu was determined in top soil of spot 6. Lead exhibited also higher values in the pharmaceutical area than that of battery industrial site. Lead gradually increased upto spot 6 from the battery industrial site. Increased Cu was due to the industrial influence. Increased concentration of Pb may also arise both from motor vehicles and industrial discharge (Moon et al, 1991, appendix A-7). Both sites did not show much significant difference with the distance.

The highest Hg level (5.10 ppm Hg) was recorded in top soil of spot 4, followed by the top soil (0.45 ppm Hg) of spot 5. Conversely, the concentration of Hg ranged from 0.12 to 0.20 ppm in spots 1,2 and 3 (Figure 32). Normal soils are expected to have Hg levels between 0.01 and 0.5 ppm (Sauerbeck, 1985) and not to exceeding 2 ppm (Kloke, 1980). Thus, in top soil of spot 4 showed above permissible level of Hg. Spot 5 which is about 1 km down from the battery industrial site accumulated 0.45 ppm Hg in the top soil. This value has almost reached equal to the upper most permissible level. From the high level accumulation of Hg it could be concluded that the battery industrial area examined was affected by Hg along with Zn pollution.

The distribution of total As with depth was shown in figure 32. The concentrations ranged from 1 to 5.2 ppm and 0.9 to 4.2 ppm As in pharmaceutical and battery industrial area respectively. Arsenic levels in

uncontaminated, nontreated soils seldom exceed 10 ppm (Walsh and Keeney, 1975). Arsenic was almost uniformly distributed in all soil profiles (Figure 32) and also found to be in the normal soil range.

The average distribution of total As and Hg (0-15cm depth) with distance from the disposal point in Tongi industrial site is given in figure 33. Mercury and As showed a reverse relationship with the concentration from the disposal point of battery industry (spot 4). Hg concentrations clearly decreased with distance except for spot 3. Spot 3 is comparatively low lying area among the three spots of pharmaceutical industry. This particular location of spot 3 accounts for the higher accumulation of Hg compared to spot 2.

Arsenic showed a high positive correlation with Fe (Table 15) in Tongi industrial site.

The As contents were 3.72, 3.68 and 3.44 ppm As at spots 1, 2, and 3 respectively. At spot 4 ,5 , and 6 it was 2.15, 2.72 and 3.34 ppm As, respectively (Figure 33). Arsenic concentration sharply increased with the distance in pharmaceutical and battery industrial site. The clearly higher As contents in soil profiles of the pharmaceutical site indicate an influence of the pharmaceutical wastewaters on the As distribution with distance.

Figure 28. Depth distribution of total Zn and Mn at Tongi industrial area

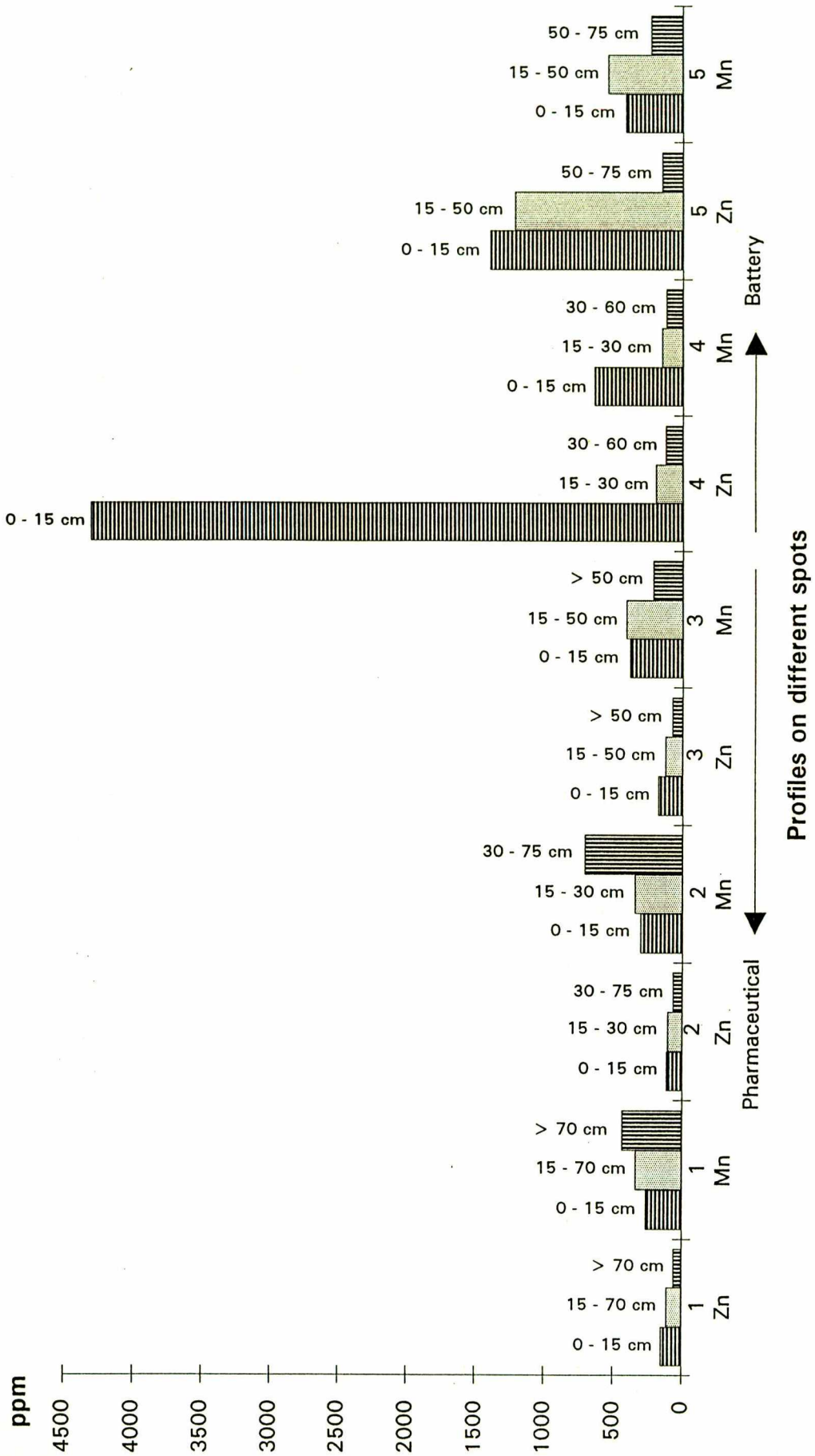


Figure 29. Distribution of total Zn and Mn at Tongi industrial area (0 - 15 cm) with distance from the disposal point

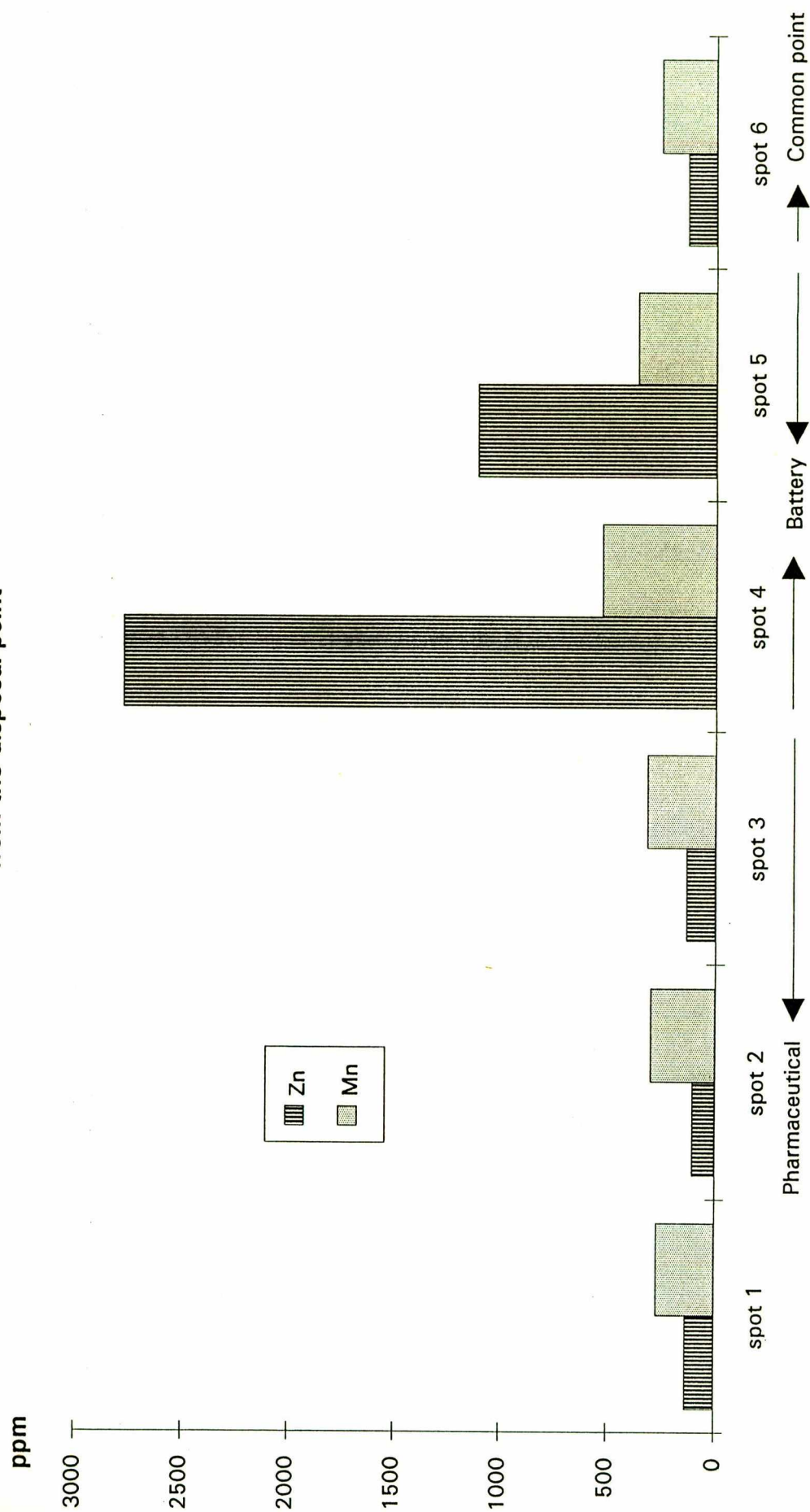


Figure 30. Depth distribution of total Pb and Cu at Tongi industrial area

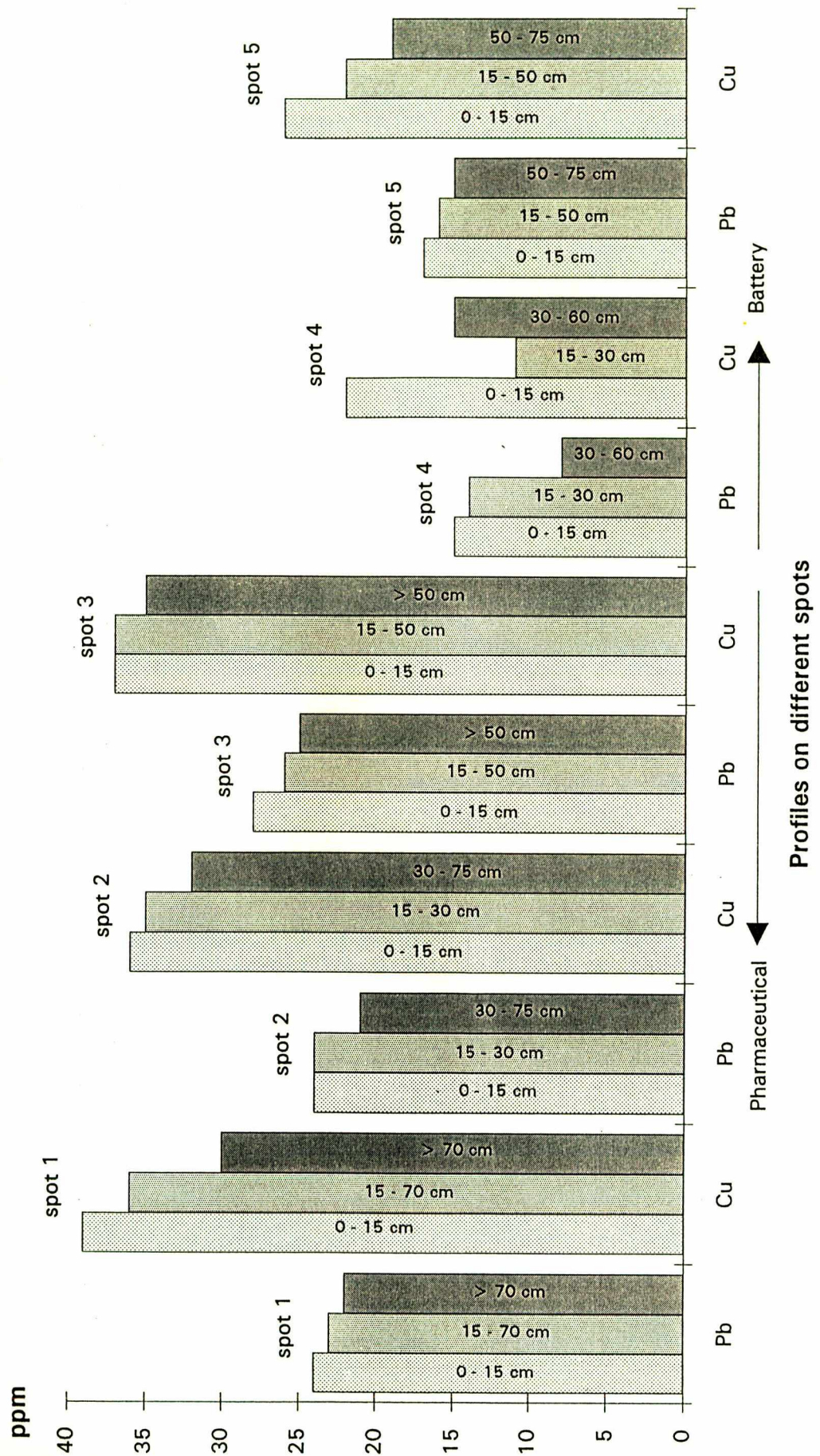


Figure 31. Distribution of total Pb and Cu at Tongi industrial area (0 - 15 cm) with distance from the disposal point

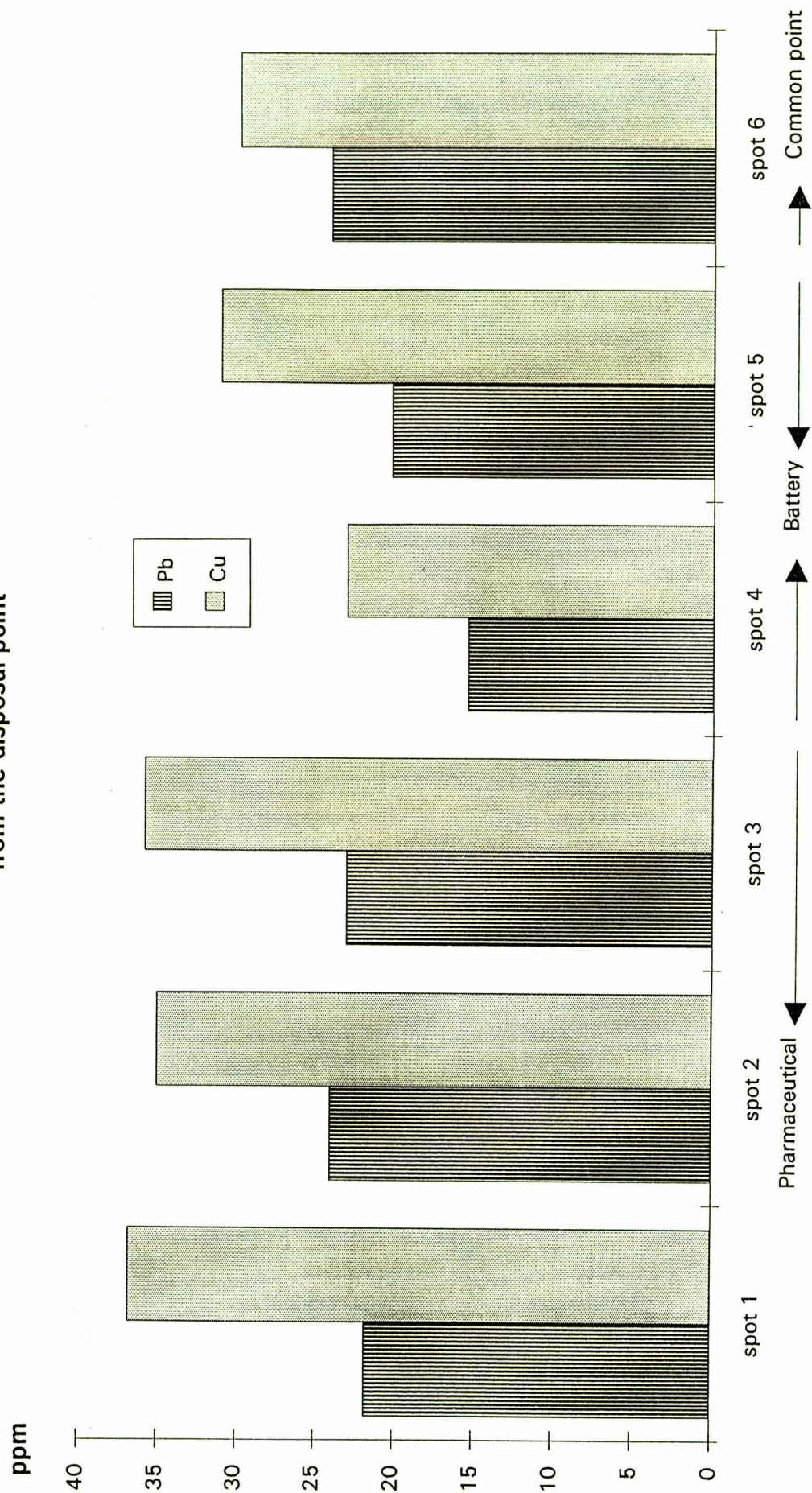


Figure 32. Depth distribution of total As and Hg at Tongi industrial area

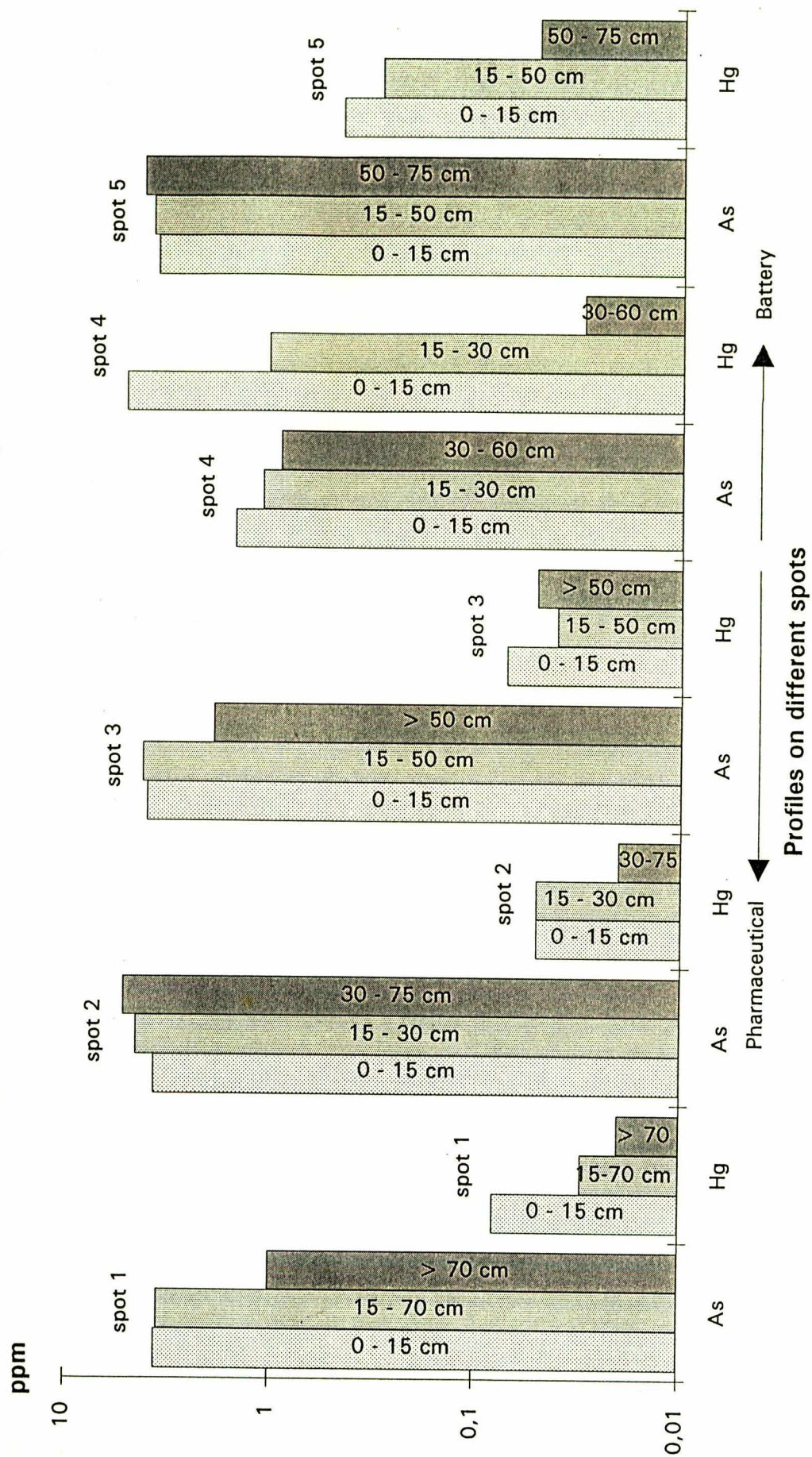
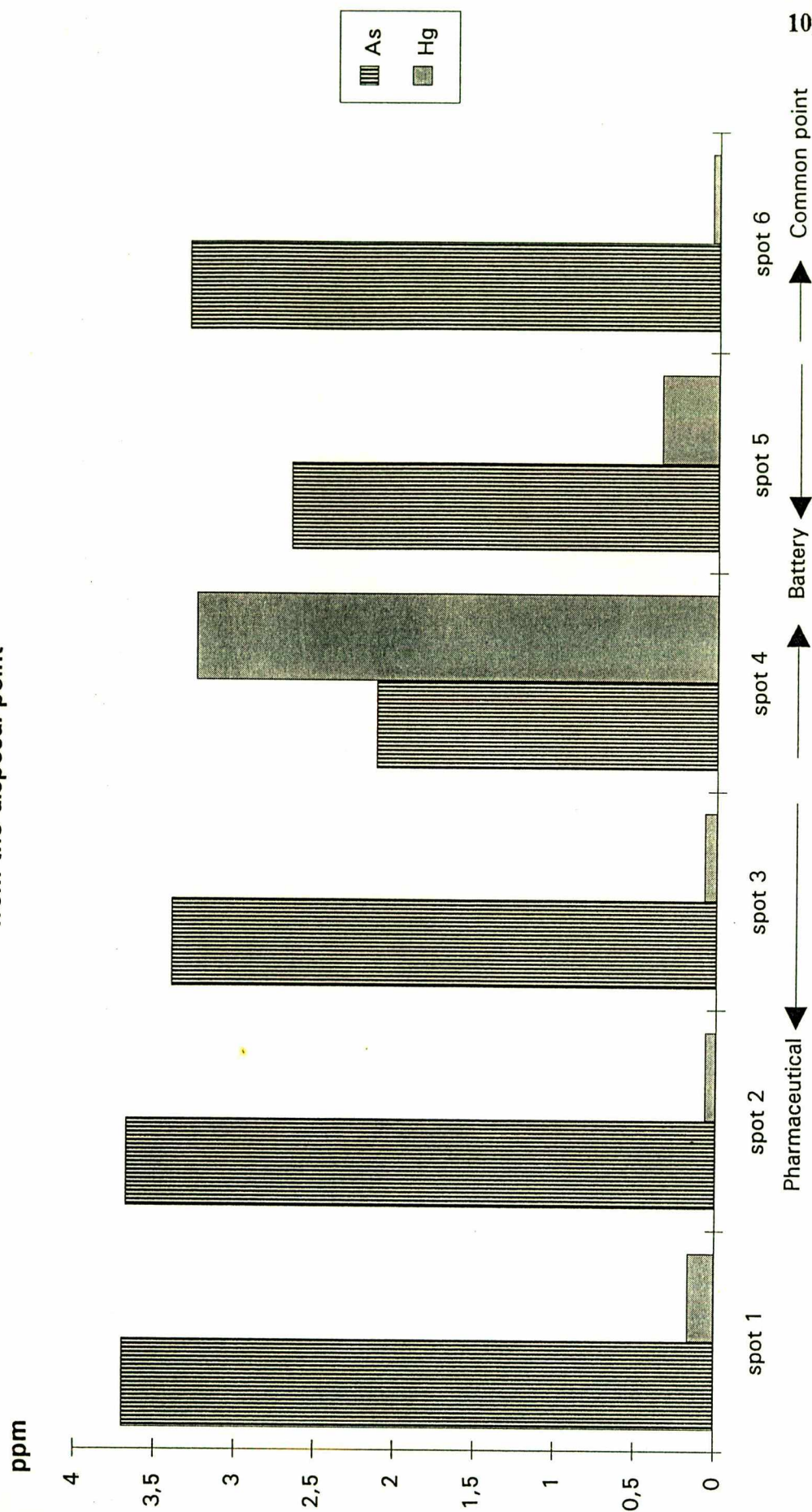


Figure 33. Distribution of total As and Hg at Tongi industrial area (0 - 15 cm) with distance from the disposal point



4.2. Water and sediment samples

4.2.1. Hazaribagh tannery area

Effluent and wastewater samples were collected at five periods in the year 1992 and 1993. The summarized values are presented in table 17. The pH, EC, Cl, Av - N, TOC, PO_4 , SO_4 , phenol and hydro carbon were the investigated parameters among the physical and chemical properties. The heavy metals Fe, Mn; Cu, Zn, Cr, Cd and Pb were determined as well (Table 18). Industrial effluents could only be collected from the disposal point that is the first spot (spot 8) of the tannery industrial site.

The pH ranged from 7.2 to 12.0 and 7.3 to 9.9 in tannery effluents and wastewater respectively (Table 17). The highest pH was recorded at spot 8 and gradually decreased with distance.

Various tanning and colouring materials used in tannery industries are responsible for the wide range of pH variation. For instance the pH of quebracho and gambier extracts varied from straw colour with a pH of 3.0 to a very deep red with a pH of 12 (Wilson and Kern). On the other hand mimosa and chestnut extract have pH values of 4.8 and 3.9, respectively (Henry, Dalton and Tomlinson, 1970). These pH values may be compared with Chowdhury (1989). Extreme pH values or rapid pH changes can exert stress conditions or destroy aquatic life outright. Dead fish, associated algal blooms, and foul

stenches are aesthetic liabilities of any waterway. Even moderate changes from acceptable criteria limits of pH are deleterious to some species. The relative toxicity to aquatic life of many materials is increased by changes in the water pH. Ammonia is more lethal with a higher pH (EPA, 1974).

Electrical conductivity of effluents and wastewater was severely affected and ranged from 3.4 to 20 and 0.72 to 7.4 s/cm in effluents and wastewater, respectively. The highest conductivity level was observed in spot 8. Chowdhury (1989) found 1.8-53.0 s/cm EC in wastewater. The EC in wastewater decreased with distance (Table 17). The higher EC is attributed to the increase in soluble salts from the tannery effluents. Standard values for the EC parameter are 0.5 s/cm in recreational, 0.8 - 1 s/cm in fishing and 0.75 s/cm in irrigation water (DOE, 1991). Values obtained in the present investigation are distinctly above the permissible limits (Table 17). The extremely high salt content carried with tannery effluents and wastewater could spread out around the water bodies and create environmental problems.

Chloride concentration ranged from 1445 to 18330 and 109 to 2470 mg/l Cl in tannery effluents and wastewater, respectively, in Hazaribagh (Table 17). Very high concentration of Cl was observed in spot 8 and gradually decreased in spots 9, 10, and 13, respectively. 175 to 18000 mg Cl/l was also observed in tannery wastewater (Chowdhury, 1989). Chloride is mainly released from liming and pre-tanning processes in the leather industry. Indian standards institute (ISI) recommended 600 mgCl/l as limit value in public sewers and also

for inland surface water when used as raw water for public water supplies and bathing. World health organization (1971) defined 200 - 600 Cl mg/l as standard value for drinking water. The values in the present investigation are very high in context to environmental aspects

Av - N was also found to be high both in effluents and wastewater in conformity with high values of N_t in Hazaribagh tannery area . The Av - N ranged from 521 to 1089 and 23 to 261 ppm in effluents and wastewater respectively (Table 17). Concentrations decreased with distance from the disposal point. Av - N ($NH_4 - N + NO_3 - N$), is an important measure of the potential environmental impact of tannery wastewater. Extreme concentration were found in the effluents and a higher level was observed also in wastewater inside the embankment. The values were found to be above limit value (ÖNORM,1991). ISI mentioned 50 ppm $NH_4 - N$ and 10 ppm $NO_3 - N$ are acceptable standard for the effluents of various industries.

Table 17 Physical and chemical properties of wastewater and effluents of Hazaribagh tannery area

Spot	wastewater									effluents								
	pH	EC S/cm	ppm							pH	EC S/cm	ppm						
			Cl	Av-N	TOC	PO4	SO4	phenol	hydro- carbon			Cl	Av-N	TOC	PO4	SO4	phenol	hydro- carbon
8	9.9	7.4	2470	261	850	30	78- 595	6.92	0.42	7.2- 12.0	3.4- 20.0	1445- 18330	521- 1089	520- 1050	74	250- 1040	9.26	0.22
9	8.0	5.1	1293	253	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
10	7.3	2.7	501	116	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
13	7.3	0.72	109	23	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

nd not determined

Concentrations of total organic carbon, PO_4 and SO_4 were found to be 850, 30 and 78 to 595 ppm in wastewater and 520 to 1050 (TOC) 74 (PO_4) and 250 to 1040 ppm (SO_4) in tannery effluents (Table 17).

The total organic carbon, PO_4 and SO_4 contained in effluents and wastewater were high in Hazaribagh tannery area. The report on environmental quality standards for Bangladesh mentioned 6 and 10 ppm PO_4 , and 400 and 1000 ppm SO_4 are allowable concentrations for drinking and irrigation water respectively (DOE, 1991). An official order for waste water emissions to main drain channel in Austria (1991) reported 25 mg/l total organic carbon as a limit value. The excessive enrichment of essential nutrients and total organic carbon cause eutrophication and create artificial oxygen demand problem respectively (Tan, 1994). A significant portion of alkaline sulfides contained in tannery wastewater might be converted to hydrogen sulfide at a pH below 8.5 to 9.0. This gas is odorous and can result in property damage through paint discoloration and at a higher concentration this gas can be lethal (EPA, 1974).

Phenols and hydrocarbons are considered common environmental pollutants, even in low concentrations. Tannery effluents and wastewater discharged to the nearby lands and water bodies contained appreciable amounts of phenols and hydrocarbons (Table 17). The contents of phenol and hydrocarbons in wastewater and effluents were found to be 6.92 and 9.26 ppm phenol, and 0.42 and 0.22 ppm hydrocarbons, respectively.

Wastewater derived from tannery sludge is extremely coloured due to the physico- chemical treatments employed during processing and still contains considerable quantities of tannins and their phenolic derivatives (Vallini et al, 1989). Phenolic derivatives play a key role in promoting phytotoxicity and allelopathy phenomena in soil (Wang et al, 1967; Swain, 1979). ISI, recommended 1.0, 5.0 and 0.005 ppm phenolic compounds for inland surface water, public sewers and for inland surface water when used as raw water for public water supplies. World health organization (1971) set limits of 0.001 to 0.002 ppm phenolic substances for drinking water. From the reports about the standard values of phenolic substances and the results of the present investigation it can be deduced that the concentration of phenol is alarming by high in Hazaribagh tannery area. If considered a similar dilution of phenolic compounds like for Cl (23) or Av-N (11) between spot 8 and 13 one has to be aware that the concentration of phenolic substances in the water of spot 13 may exceed the WHO limit for drinking water by a factor of 300 to 630. Among the heavy metals Fe, Mn, Cu, Zn, Cr, Cd and Pb were determined in wastewater and effluents samples of Hazaribagh tannery area (Table 18). Chromium was found in concentrations from 0.34 to 1.3 ppm, in effluents and between 0.11 and 0.28 ppm in wastewater within the embankment. These were above the tolerable limit. The rest of the investigated elements were below the tolerable limit (Saxena, 1990). Few data regarding toxic limits of tannery wastewater and effluents are available. A general report on wastewater disposal mentions 0.5 ppm Cr as limit value (ÖNORM, 1991). The US-EPA (1974) set a standard of 0.05 ppm for drinking water and 0.1 ppm for fresh water and aquatic life.

Table 18 Heavy metal concentrations of wastewater and effluents of Hazaribagh tannery area

Spot	wastewater							effluents						
	ppm							ppm						
	Fe	Mn	Cu	Zn	Cr	Cd	Pb	Fe	Mn	Cu	Zn	Cr	Cd	Pb
8	0.14	0.014	≤0.02	0.12	0.28	*	*	0.05	≤0.005	0.02	0.66-2.4	0.34-1.3	*	*
9	0.16	0.010	≤0.02	0.21	0.14	*	*	nd	nd	nd	nd	nd	nd	nd
10	0.05	*	≤0.02	0.12	0.11	*	*	nd	nd	nd	nd	nd	nd	nd
13	*	*	≤0.02	0.06	0.02	*	*	nd	nd	nd	nd	nd	nd	nd

nd not determined

* not detected

4.2.2. Tongi industrial site

Wastewater and effluents samples were collected five times in the years 1992 and 1993. The summarized values are presented in table 19. The pH, EC, Cl, Av - N, TOC, Av-K, Av-SO₄ and phenol and hydrocarbons were measured to represent the physical and chemical properties (Table 19). Iron, Mn, Cu, Zn, Cr, Cd, and Pb were measured (Table 20). Spots 1 and 4 (Figure 12) were considered the first spots of pharmaceutical and battery industrial site, respectively in Tongi industrial area. Industrial effluents could only be collected from these two spots.

The pH ranged from 6.6 to 7.2 and was 6.1 in wastewater and effluents of pharmaceutical industrial site, respectively. In the battery industrial site pH ranged from 6.8 to 7.3 and was 5.7 in wastewater and effluents, respectively. The pH of the wastewater samples of both pharmaceutical and battery industrial site, were nearly neutral, but in the effluents it was acidic (Table 19). Probably the effluents containing triethylamine with hydrochloric acid, chloride, heavy metal compounds of pharmaceutical and battery industrial effluents decreased pH. Waters with a pH below 6.0 are corrosive to water work structures, distribution lines, and house hold plumbing fixtures and can thus add such constituents to drinking water as Fe, Cu, Zn, Cd, and Pb (EPA; 1974).

The EC, Cl and SO₄ contents were in normal ranges in pharmaceutical and battery waste water and effluents (Table 19). Their critical values were

described in chapter 4.2. The total organic content (2507 ppm) and K (45.5 ppm) were found very high level in pharmaceutical effluents, but Av-N concentration was lower than that of wastewater. For potassium 0.5 to 5 ppm are considered as toxic level for the industrial wastewater.

The effluents discharged from the pharmaceutical industry were rich in N, K and in total organic carbon (Table 11, 13 & 19). K was possibly released from the Dane/potassium salt (used as raw material), N from 6 - amino penicillanic acid and triethylamine, and TOC from dissolved organic compounds to those pharmaceutical effluents. They create a pollution hazard when disposed improperly on land and in water bodies. The excessive enrichment of the above mentioned plant elements causes eutrophication (Tan, 1994). The dissolved organic compounds reduced the oxygen content of soil, stream and lake water because of increase in the so called oxygen demand. Part of the dissolved organic compound is sometime referred to as dissolved organic carbon . Microbial decomposition of these organic compounds consumed most of the dissolved oxygen, and might cause aquatic organisms to suffocate in polluted streams and lakes. As soon as the amount of dissolved oxygen is depleted, organic contaminants start to accumulate, decreasing the quality of soil water(Tan,1994). It is , thus, obvious that the pharmaceutical site has created some problem with organics in soil and waterbodies.

Phenol and hydrocarbons were estimated in a higher concentration in effluents of pharmaceutical site (Table 19) as recommended by standard values

mentioned in chapter 4.2. Wastewater and effluents of battery industrial site possessed higher amounts of Av-N only which pose pollution hazard (Table 19).

Iron, Mn, Cu,Zn, Cr, Cd and Pb were analysed in wastewater and effluent samples of pharmaceutical and battery industrial site (Table 20). At the pharmaceutical site (1, 2, 3) no appreciable contents of heavy metals were observed. At battery industrial site (4, 5) the concentrations of Zn, Mn, and Cd in wastewater ranged from 0.56 to 1.90 ppm Zn, 0.1 to 0.72 ppm Mn, and 0.01 ppm Cd and in effluents 5.8 ppm Zn, 4.1 ppm Mn, 0.021 ppm Cd (Table 20). Chromium and Pb were found below detection limit, Cu and Fe concentrations were also very low.

The US-EPA (1976) published a limit of 5 mg/l of Zn for domestic water supplies, 0.05mg Mn/l in drinking water and 0.01 ppm Cd in drinking and irrigation water. NAS (1973) found 0 - 0.185 ppm Mn in river water. Matching the present values obtained with those of NAS (1973) and US-EPA (1976) Mn and Zn are above the allowable limits at the battery industrial site. Available and total values of these elements were statistically correlated (Table 13 & 16).

Table 19 Physical and chemical properties of wastewater and effluents of pharmaceutical (1, 2, 3) and battery (4, 5) industrial site Tongi

wastewater										effluents								
Spot	pH	EC S/cm	ppm							pH	EC S/cm	ppm						
			Cl	Av-N	TOC	K	SO4	phenol	hydro- carbon			Cl	Av-N	TOC	K	SO4	phenol	hydro- carbon
1	7.0	1.3	381	113	343	5.0	6	0.002	0.36	6.1	0.84	476	90	2507	45.5	28	0.71	0.42
2	6.6	1.4	398	47	nd	5.6	nd	nd	nd	*	nd	nd	nd	nd	nd	nd	nd	nd
3	7.2	1.6	418	172	nd	3.3	nd	nd	nd	*	nd	nd	nd	nd	nd	nd	nd	nd
4	6.8	1.1	443	136	16.6	nd	*	nd	nd	5.7	0.65	440	25	24	nd	6	nd	nd
5	7.3	0.54	127	185	nd	nd	*	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

nd not determined

* not detected

Table 20 Heavy metal concentrations of wastewater and effluents of pharmaceutical (1, 2, 3) and battery (4, 5) industrial site Tongi

Spot	wastewater							effluents						
	ppm							ppm						
	Fe	Mn	Cu	Zn	Cr	Cd	Pb	Fe	Mn	Cu	Zn	Cr	Cd	Pb
1	0.03	≤0.005	≤0.02	0.05	*	*	*	1.36	0.17	≤0.02	0.03	*	*	*
2	≤0.02	≤0.005	≤0.02	0.03	*	*	*	nd	nd	nd	nd	nd	nd	nd
3	0.04	0.05	≤0.02	0.06	*	*	*	nd	nd	nd	nd	nd	nd	nd
4	*	0.72	≤0.02	1.90	*	0.01	*	*	4.1	≤0.02	5.8	*	0.021	*
5	*	0.10	≤0.02	0.56	*	*	*	nd	nd	nd	nd	nd	nd	nd

nd not determined

* not detected

4.2.3. Sediment samples.

Sediment samples were collected only from the main earthen drain of battery industrial site, Tongi. Zinc, Mn, Hg, Cd, Cr, Cu, and Pb were analysed (Table 21).

Extremely high contents of Zn, Mn and Hg were observed in the sediment samples. Cadmium was found below the allowable limit (Table 34) but above normal soil level (Table 35). Concentration of Zn, Mn, Hg and Cd were 6.6, 8.4, 17.6 and 2.6 times higher in sediments than those of the total heavy metal contents of top soils (spot 4) at battery industries site. Extractable Zn, Mn, Cd and Cu concentrations exceeded the respective values in top soils by a factor of 5 to 20.

Table 21. Total and extractable heavy metal contents in sediment samples of battery industrial site (in ppm).

	Zn	Mn	Gh	Cd	Cr	Cu	Pb
Total	13300	4019	27,2	0,84	58	57	18
Extracta:	1280	503	N.D	0,36	<0,1	2,2	<0.5

N.D : not determined

4.3. Plant samples

4.3.1. Field samples

The plant itself can be used as an extracting agent and in this case heavy metal uptake is a direct indicator of the availability of metals in soil. Availability of heavy metals in soil and their uptake in plants depend not only on the total metal content in soil but also on a variety of interacting soil and plant factors (Bjere and Schierup, 1985). For the determination of the availability of trace metals to existing field crops and aquatic plants, sampling was carried out for five times in the year 1992 and 1993.

4.3.1.1. Hazaribagh tannery area

Waterhyacinth (aquatic plant) and grass samples were collected from inside the embankment and paddy samples from outside the embankment. Waterhyacinth and grass inside the embankment accumulated higher amounts of N,P,K and S, but lower quantity of Fe. The absorption of S was abnormally high (Table 22).

High content of total S and N in tannery wastes (Table 8) account for their higher absorption could partly be translocated to the plant tissue. Metals forming insoluble precipitates with S or P which enter the soil in soluble forms, might be expected to be rapidly insolubilized, especially at the nearly neutral pH (Jenne, 1968). Certain elements (e.g. Fe), may form precipitate with S or

P (Keeney and Wildung, 1972). May be this phenomenon occurred with the tannery waste rich in S and P (Table 8). Excess Cr may also interfere with Fe (Anderson et al 1973).

Copper, Mn, Zn, Hg, As and Cr were analysed in plant samples of Hazaribagh tannery area (Table 23). Plant extractable Cu, Mn, As, Hg, As and Cr correlated with soil values (Table 13 & 23). Grass (*Echinochloa crus-galli*) accumulated more Cr than that of waterhyacinth and paddy rice (Table 23). Grass accumulated lower Zn, than that of waterhyacinth. The highest amounts of Cu and Mn were found higher in rice followed by grass and waterhyacinth. Chromium was mostly concentrated in roots of the plants, but was below detection limit in grains of rice collected from outside the embankment.

The heavy metal concentration gradient with distance from spot 8 (Table 8) was also reflected in the accumulation of heavy metals in aquatic plant samples (Table 23).

The general toxic concentration level for Cr, Cu and Zn are 1 to 2ppm, 15 to 20ppm and 150 to 200ppm, respectively (Table 36). Referring to Chino (1981) the toxic level in tops for Cu, Cr, Mn and Zn are 20-30, 30-100, 300-1000 and 100-300ppm, respectively. Thus, tissue concentrations exceeded toxic limits. It should be mentioned that the high accumulation of Cr in grass samples may be threatening to the animals grazing in the vicinity.

Table 22 Nutrient contents in field plant samples of Hazaribagh tannery area

Spot	Plants	N			P			K			S			Fe		
		%														
		plant parts			plant parts			plant parts			plant parts			plant parts		
		root	shoot	grain	root	shoot	grain	root	shoot	grain	root	shoot	grain	root	shoot	grain
8	w.h.	*	2.50		0.26	0.28		0.43	1.02		1.78	0.73		0.26	0.07	
	grass		2.35			0.20			0.99			1.41			0.18	
10	w.h.	*	2.90		0.45	0.52		0.76	2.14		2.78	1.01		0.38	0.06	
13	rice	*	2.95	1.73	0.11	0.17	0.24	0.93	2.49	0.81	0.44	0.28	0.16	0.57	0.14	0.04
Std.dev.	rice		0.31		0.05	0.08	0.01	0.54	0.86	0.04	0.04	0.02	0.02	0.19	0.02	0.001

* not determined
w.h. ... waterhyacinth

Table 23 Heavy metal concentrations in field plant samples of Hazaribagh tannery area

Spot	Plants	Cu		Mn		Zn		Hg		As		Cr		
		ppm												
		plant parts			plant parts			plant parts			plant parts			
		r	sh	gr	r	sh	gr	r	sh	gr	r	sh	gr	
8	w.h.	5.9	2.3		44	61		94	202		1.07	0.42	288	34.4
	grass		16.7			118			158			1.50		595
10	w.h.	10.4	2.4		164	199		206	55		0.02		154	16.0
13	rice	113	20.4	8.4	216	650	250	157	100	64	*	5.30	0.60	1.9
Std.dev.	rice	44.0	1.34	1.32	120	92	100	35.2	27.0	7.5		0.47	0.12	0.07
												9.07	0.36	

* not determined
w.h. ... waterhyacinth

r root
sh ... shoot
gr ... grain

4.3.1.2. Tongi industrial area

Rice, vegetables, grass and waterhyacinth samples were collected from pharmaceutical and battery industrial sites, Tongi. Nitrogen, P, K, S and Fe were analysed in the plant tissue (Table 24). The values of nutrient elements in plants of pharmaceutical industrial area contained slightly higher amounts than respective values of crops grown in either battery or confluence zones. The pharmaceutical effluent contains higher amounts of total organic carbon and K, than those of battery industrial site (Table 24).

Plant types behaved differently in their uptake of nutrients. Rice absorbed more nitrogen than vegetables, grass or waterhyacinth (Table 24), while vegetables (5.81%) and waterhyacinth (5.20) absorbed more K than all other crops. Waterhyacinth (0.44%) and vegetables (0.53%) absorbed significantly higher amounts of P than rice or grass (Table 24).

Zinc, Hg, Mn, Cu, As, Pb and Cd were determined in the field plant samples of pharmaceutical and battery industrial site, Tongi (Table 25). Extreme concentration of Zn were accumulated in all parts of rice, 4630, 4000 and 101 ppm were found in roots, shoot and in rice grain respectively (spot 4). Gerzabek and Ullah (1989 & 1991) in an experiment with nutrient solution culture also reported a higher accumulation of Zn and Cu in roots than the shoots, while Lubben and Sauerbeck (1991) found an appreciably lower concentration of Zn in grains of wheat than those of straw. At the same spot

2321ppm Zn was found in grass tops. Mercury Zn, Mn and Cu were also found in higher amounts in the same site (Table 25). The distribution of Hg in different plant parts of rice was 2.50, 1.55 and 0.01 ppm Hg for root, shoot and grain, respectively. In spot 5, which was about 500m away from spot 4, Hg contents of 0.54, 0.33 and 0.01 ppm Hg were observed in roots, shoot, and grain respectively. Manganese concentration in paddy samples (spot 4) were 628, 820 and 89ppm Mn in roots, shoot and grain. Cadmium and Pb were <1.0ppm and <5.0ppm in shoot and grain samples of all battery industrial sites. The highest concentration of Cu were also found in roots than in shoots. Rice shoot had in general lower concentration of Cu than other plants (Table 25).

Total heavy metal contents in soil (Table 13), ammonium acetate extractable heavy metal (Table 16) and analysis of wastewater and effluents (Table 20) were well reflected in the plant accumulation of heavy metals at the battery industrial site. Data clearly indicated that the field plant samples were contaminated with Zn, Hg, Mn and Cu. Data presented by Chino (1981) substantiates this observation.

The total and available content of heavy metals in soil of pharmaceutical industrial area well reflected by the content of translocation heavy metals in the plant tissue (Table 25). Vegetable grown in spot 1 absorbed Zn (206 ppm) above toxic levels (Table 35) and the rest were found in the normal ranges.

Table 25 Heavy metal concentrations in field plant samples of pharmaceutical (1, 2, 3) and battery (4, 5) industrial site Tongi

Spot	Plants	Cu			Mn			Zn			Pb			Cd			Hg			As				
		ppm																						
		plant parts			plant parts			plant parts			plant parts			plant parts			plant parts			plant parts				
r	sh	gr	r	sh	gr	r	sh	gr	r	sh	gr	r	sh	gr	r	sh	gr	r	sh	gr	r	sh	gr	
1	rice	31.7	9.6	4.8	126	138	51	234	57	30	*	*	*	*	*	*	*	*	*	*	*	11.1	1.4	0.7
	grass		25.5			123			83													10.3		
	veg.		18.4			80			206													0.4		
2	rice	12.0	3.6	3.2	183	260	81	160	36	23	*	*	*	*	*	*	*	*	*	*	6.3	0.4	0.2	
3	rice	67.6	14.5	3.4	258	137	58	147	85	28	*	*	*	*	*	*	*	0.02	0.01	nd	15.2	1.4	0.2	
	grass		16.2			100			121													2.4		
	w.h.		19.1			550			163															
LSD 5%	rice	3.45	3.69	1.03	39.2	24.7	17.9	152	20.4	5.95											5.16	0.63	0.31	
F-value	rice	799	30.8	8.40	33.7	85.8	9.41	0.99	6.51	5.39											8.81	10.2	8.12	
4	rice	22.0	13.7	4.2	628	820	89	4630	4000	101	14.7	≤5.0	≤5.0	≤1.0	≤1.0	≤1.0	2.50	1.55	0.01	11.7	1.1	0.2		
	grass		12.0			298			2321			10.7	≤5.0									2.6		
5	rice	13.8	5.9	6.0	256	434	82	551	91	36	6.4	≤5.0	≤5.0	≤1.0	≤1.0	≤1.0	0.54	0.33	0.01	14.3	1.1	0.1		
6	rice	23.1	7.8	5.8	82	209	76	128	43	26	*	≤5.0	≤5.0	≤1.0	≤1.0	≤1.0	*	*	*	14.0	1.0	0.2		
LSD 5%	rice	4.97	7.26	1.18	109	213	16.7	1470	684	6.86							2.65	0.85	0.03	4.24	0.74	0.03		
F-value	rice	12.9	3.70	9.00	78.4	25.2	1.74	34.2	132	424							5.38	15.7	0.00	1.36	0.04	12.4		

* not determined
 nd not detected
 w.h. ... waterhyacinth

r root
 sh ... shoot
 gr ... grain

4.3.2. Pot Experiments

4.3.2.1. Hazaribagh tannery area soils

Bulk soil samples (0-15cm) with high contents of Cr from Hazaribagh tannery area (spot 8) were used for pot experiments in order to determine the heavy metal distribution and possible toxicities in spring wheat and rice. Dry matter yields; N, P, K, S, Fe, Cu, Mn, Zn, As, and Cr concentrations were analysed in roots, shoot and grain of wheat and rice plants (Table 26 & 27). Particle size distribution, chemical properties, organic matter content, available nutrients (Table 6), total N, P, K, S, and total heavy metal contents (Table 8), ammonium acetate extractable heavy metals (Table 10) were also measured before the initiation of the pot experiment of the original soil.

Delayed maturity and stunting of growth in wheat crop were observed in soil of spot 8. Chromium possibly decreased net photosynthesis and affected physiological functions in the rice seedlings. Plant N and S correlated well with total soil N and S, respectively (Table 8 & 26).

The EC of soils at planting date was on average 4.3 S/cm (Table 6). This was sufficiently high to adversely affect the seedling establishment. Sufficient mineralization occurred to provide adequate N and induce delayed maturation with high levels of tannery waste application (Stomberg, 1984),

The heavy metal contents in different plant parts of wheat are shown in table 27. Zinc content in grain was higher than in the straw. More than 67% of the absorbed Zn was found in the grain. This distribution can be explained by the known Zn enrichment in the bran also observed Zn enrichment in the wheat bran Brondi et al., 1984). The Cr contents in grain (<5.0) and shoot (5.4ppm Cr) were extremely low in comparison to total content in soil. Tannery waste application increased total Cr levels of soil dramatically, but did not increased in significantly in Cr concentration of wheat grain. A considerable part of the absorbed Cu (>69%) was translocated to the grain. The Cu content of the grain is generally higher than that of the shoot (Lübben and Sauerbeck, 1991). Enrichment of Cu by plant from the soil roots was relatively low. The Mn content of the grain was also higher than that of shoot and relatively low in the root (Table 27). Additional Zn, Mn and Cu provided with organic wastes formed chelate and readily absorbed by crops (Narwal et al., 1992).

Rice was the subsequent crop in the same pots. Late flowering and maturity with dark green colour were observed in rice plants. Number of tillering was 5-6 and the % of filled grain was about 68. The high percentage of organic matter and the extreme N content (Table 6 & 8), are responsible for this physiological disorders in the rice plants.

The heavy metal contents in different plant parts of rice are shown in table 27. Zinc, Mn, Cu concentrations increased in the following order: roots > shoot > grain. The Cr contents in root was higher (4702ppm Cr) than in the

shoot (112ppm Cr). Cr accumulation in grain was lower than 5.0ppm Cr. The general toxic limit for Cr is 1 to 2 ppm, Sauerbeck (1992) and the limits were presented in table 36 and also referring to Chino (1981) the toxic limit is 30 to 100 ppm in the rice tops.

Table 26 Nutrient contents of wheat and rice in pot experiment on contaminated soil of Hazaribagh tannery area (spot 8)

Crop	DM/pot (g)	N			P			K			S			Fe				
		%																
		plant parts			plant parts			plant parts			plant parts			plant parts				
	root	shoot	grain	root	shoot	grain	root	shoot	grain	root	shoot	grain	root	shoot	grain	root	shoot	grain
wheat	0.45 3.79 3.97	*	0.78	2.70	0.05	0.02	0.29	0.60	2.90	0.43	0.24	0.27	0.20	0.08	0.03	0.04		
Std.dev.	0.08 0.33 0.90	*	0.10	0.08	0.01	0.01	0.01	0.04	0.32	0.01	0.01	0.02	0.01	0.02	0.01	0.01		
rice	3.20 20.7 7.25	*	1.40	1.60	0.19	0.17	0.27	0.45	2.40	0.41	0.53	0.21	0.14	1.58	0.06	0.03		
Std.dev.	1.24 0.98 2.29		0.05	0.08	0.02	0.01	0.01	0.05	0.19	0.01	0.04	0.01	0.01	0.20	0.01	0.01		

Table 27 Heavy metal contents of wheat and rice in pot experiment on contaminated soil of Hazaribagh tannery area (spot 8)

Crop	DM/pot (g)	Cu			Mn			Zn			As			Cr				
		ppm																
		plant parts			plant parts			plant parts			plant parts			plant parts				
		root	shoot	grain	root	shoot	grain	root	shoot	grain	root	shoot	grain	root	shoot	grain		
wheat	0.45	3.79	3.97	9.87	4.20	9.70	19	10	15	129	57	118	0.15	0.14	0.05	376	5.4	≤ 5
Std.dev.	0.08	0.33	0.90	0.42	0.42	0.16	1.47	0.84	1.21	5.09	13.7	5.19	0.02	0.02	0.01	43.3	0.37	
rice	3.20	20.7	7.25	40	6.3	4.3	161	125	34	276	121	35	6.0	0.38	0.11	4702	112	≤ 5
Std.dev.	1.24	0.98	2.29	8.80	0.51	0.33	25.9	25.9	3.16	75.4	1.87	0.82	0.88	0.05	0.01	1749	5.87	

* not determined

4.3.2.2. Tongi industrial soils (battery site)

To study the ameliorative effect of cowdung and waterhyacinth manure, the bulk surface soil (0-15cm) was used from spot 4 for pot experiments. Wheat and rice were used as test crops in the green house. The deleterious effect of excessive heavy metals, particularly Zn, Hg and Mn were serious problem in this site. Dry matter yields, N, P, K, S, Fe, Cu, Mn, Zn, As, Hg, Pb and Cd concentrations were measured in roots, shoot and grain samples of wheat and rice (Table 28 & 29). Particle size distribution, chemical properties, organic matter content, available nutrients (Table 11), total N, P, K, S and total heavy metal contents (Table 11), ammonium acetate extractable heavy metals (Table 16) in soil were also measured before the pot experiment started.

Wheat crop even with treatments fail to grow satisfactorily. 0.45, 0.60 and 1.22 g shoot/pot yields were produced in control, CD 20 and CD 40 treatments, respectively and in waterhyacinth treatments 0, WH 20 and WH 40 gave 0.45, 0.99 and 1.81 g shoot/pot, (Figure 34, wheat shoot). Rice crop showed a better performance with the cowdung as compared to waterhyacinth treatments with respect to dry matter yields (Figure 34, rice grain and shoot). The regression values for rice grain with cowdung (CD) and waterhyacinth (WH) manure are $r^2=0.88$ and $r^2=0.84$, respectively and for rice shoot the r^2 values are 0.92 and 0.56 with CD and WH (Figure 34). Except P all other (N, K, S, Fe) elements exhibited not statistically significant (Table 28) with CD treatment in wheat. The application of WH reduced all the values of N, P, K, S and Fe as compared to control (Table 28). It was also observed that almost all rice grain turned black to dark brownish in colour at maturity. The

accumulation of Zn and Mn contents in different plant parts of wheat decreased with the increasing rate of cowdung and waterhyacinth (Table 29). With the application of cowdung (40 mt/ha), Zn content was reduced to 1665 from 2018 ppm in wheat (shoot), 3102 from 4025 ppm in roots; Mn to 239 from 526 ppm in wheat (shoot) and 1496 from 2970 ppm Mn in wheat (root) (Table 29). With the application of waterhyacinth (40 mt/ha), Zn content was reduced to 1402 from 2018 ppm in wheat (shoot), 3307 from 4025 ppm in roots; Mn to 154 from 526 in wheat (shoot) and 2177 from 2970 ppm Mn in roots (Table 29). Lead content was to <5.0 from 5.2 ppm in wheat (shoot) with cowdung treatment (40mt /ha) and due to the waterhyacinth application dropped below detection limit. Due to insufficient wheat yields Hg was not analysed. Concentration of Cd value was below (<1.0ppm the sensitivity limits of the atomic absorption equipment. Copper and As contents in wheat did not show any significant differences between the treatments in wheat (Table 29).

Zinc contents were reduced to 1125 from 1671 ppm in rice (shoot), 4325 from 5556 ppm in roots and in grain 87 from 97 ppm and with the application of 40 mt/ha WH, Zn contents were reduced to 959 from 1671 ppm Zn in rice (shoot), 3712 from 5556 ppm in roots and 85 from 97 ppm in grain (Figure 35). Mn to 545 from 625 ppm in rice (shoot), 841 from 1107 ppm in roots by 40 mt/ha cowdung (Table 29). With the application of 40 mt/ha waterhyacinth Mn contents increased 722 from 625 ppm Mn in rice (shoot). Mercury content decreased to 0.09 from 0.62 ppm in rice (shoot) and 1.66 from 3.86 ppm Hg in roots and 0.01 from 0.02 in grain by cowdung treatment. The application of waterhyacinth (40 mt/ha) reduced Hg contents to 0.16 from 0.62 ppm in rice (shoot) and 0.48 from 3.86 ppm Hg in roots (Figure 36). Lead content was

found below 5.0ppm (shoot) in all the treatments (Table 29). Zinc and Mn contents in rice grain did not show any significant difference with the control. Narwal et al (1992) reported that in carrot, the concentration of all micronutrients decreased significantly ($P < 0.05$) with increasing application of farmyard manure. In wheat grain the Zn, Mn and Cu concentrations remained unaffected (Table 29) and the Fe content decreased with increasing application of cowdung. The most interesting observation of the present study is that the application of cowdung and waterhyacinth significantly (Table 29) decreased the toxic metal Hg concentration. The decrease in toxic metal (Hg) in plants may be ascribed to the possible complexation with added organic matter (Haghir, 1974). On the other hand the utilization of organic wastes could reduce potential toxicity of native or applied metals such as Mn, Zn or Cu. Chino (1981), mentioned the following toxicity levels in tops (ppm) of rice plants: Cu, 20-30; Fe, 500-1000; Mn, 300-1000; Zn, 100-300; As, 20-100; and roots (ppm): Cu, 100-300; Mn, 200-600; Zn, 500-1000. Sauerbeck (1982) reported 0.5 to 1ppm Hg as toxic level in plants in general. Application of CD and WH reduced the uptake of Mn and Hg appreciably but, the values in the tissue were above toxic level. These amendments reduce the concentration of Zn slightly.

It is, therefore, concluded that the application of manures were not sufficient in counteracting the adverse effect of toxic metals on plant growth in a extremely Zn, Mn and partly Hg, Cd polluted soil in battery industrial site.

Table. 28 Nutrient contents of wheat and rice in pot experiment on contaminated soil of battery industrial site Tongi (spot 4)

Crop	CD/WH m. ton/ha	DM/pot (g)		N			P			K			S			Fe		
				plant parts			plant parts			plant parts			plant parts			plant parts		
				root	shoot	grain	root	shoot	grain	root	shoot	grain	root	shoot	grain	root	shoot	grain
wheat	control	root	shoot	grain	-	-	0.09	0.45	-	0.12	0.11	-	0.6	1.2	-	0.15	0.17	-
	CD: 20	root	shoot	grain	-	-	*	0.7	-	0.10	0.08	-	0.4	0.9	-	0.17	0.15	-
	CD: 40	root	shoot	grain	-	-	*	0.8	-	0.11	0.12	-	0.5	1.1	-	0.14	0.16	-
	LSD 5%	root	shoot	grain	-	-	0.14	0.83	-	0.01	0.01	-	0.13	0.2	-	0.03	0.02	-
	F-value	root	shoot	grain	-	-	3.42	2.96	-	5.60	18.6	-	4.75	7.00	-	4.41	3.55	-
wheat	control	root	shoot	grain	-	-	*	0.9	-	0.12	0.11	-	0.6	1.2	-	0.15	0.17	-
	WH: 20	root	shoot	grain	-	-	*	0.8	-	0.10	0.07	-	0.3	1.2	-	0.14	0.16	-
	WH: 40	root	shoot	grain	-	-	*	0.7	-	0.10	0.04	-	0.4	1.3	-	0.12	0.14	-
	LSD 5%	root	shoot	grain	-	-	0.23	0.69	-	0.01	0.02	-	0.15	0.2	-	0.03	0.01	-
	F-value	root	shoot	grain	-	-	5.09	12.1	-	12.3	43.0	-	15.8	0.75	-	3.43	20.3	-
rice	control	root	shoot	grain	-	-	*	1.1	1.7	0.22	0.26	0.33	1.3	3.6	0.50	0.45	0.29	0.17
	CD: 20	root	shoot	grain	-	-	*	1.2	1.8	0.23	0.23	0.36	1.5	3.8	0.65	0.50	0.30	0.18
	CD: 40	root	shoot	grain	-	-	*	1.1	1.8	0.24	0.25	0.37	1.5	3.4	0.65	0.54	0.22	0.17
	LSD 5%	root	shoot	grain	-	-	0.53	3.96	1.13	0.13	0.08	0.01	0.47	0.42	0.06	0.10	0.05	0.03
	F-value	root	shoot	grain	-	-	8.61	14.7	6.31	1.75	6.33	9.24	0.63	2.73	27.9	2.96	8.37	1.24
rice	control	root	shoot	grain	-	-	*	1.1	1.7	0.22	0.23	0.33	1.3	3.6	0.50	0.45	0.29	0.17
	WH: 20	root	shoot	grain	-	-	*	1.0	1.6	0.20	0.22	0.34	1.4	2.7	0.59	0.59	0.22	0.16
	WH: 40	root	shoot	grain	-	-	*	1.2	1.9	0.20	0.20	0.36	1.7	3.4	0.58	0.52	0.26	0.17
	LSD 5%	root	shoot	grain	-	-	0.60	4.70	1.95	0.13	0.06	0.03	0.22	0.27	0.08	0.09	0.03	0.01
	F-value	root	shoot	grain	-	-	2.23	3.04	0.41	4.75	5.04	3.05	13.4	36.7	4.28	6.32	17.4	3.00

* not determined

CD coudung

WH waterhyacinth

- grain was not formed

Table 29 Heavy metal contents of wheat and rice in pot experiment on contaminated soil of battery industrial site Tongi (spot 4)

Crop	CD/WH m. ton/ha	DM/pot (g)		Cu			Mn			Zn			As			Hg			Pb		
				ppm			ppm			ppm			ppm			ppm			ppm		
				r	sh	gr	r	sh	gr	r	sh	gr	r	sh	gr	r	sh	gr	r	sh	gr
wheat	control	0.09	0.45	-	5.6	4.4	-	2970	526	-	4025	2018	-	0.21	0.13	-	*	-	21	6.3	-
	CD: 20	0.18	0.60	-	5.4	4.3	-	2866	298	-	3757	1898	-	0.19	0.14	-	*	-	18	5.2	-
	CD: 40	0.24	1.22	-	5.8	3.9	-	1496	239	-	3102	1665	-	0.16	0.17	-	*	-	6.2	≤ 5	-
wheat	LSD 5%	0.14	0.83	-	1.6	0.34	-	214	72	-	261	420	-	0.03	0.04	-	-	-	2.21	-	-
	F-value	3.42	2.96	-	0.13	7.73	-	178	52.4	-	40.7	2.19	-	12.1	3.25	-	-	-	145	-	-
	control	0.09	0.45	-	5.6	4.4	-	2970	526	-	4025	2018	-	0.21	0.13	-	*	-	21	6.3	-
rice	WH: 20	0.18	0.60	-	7.2	3.1	-	4389	244	-	4115	1550	-	0.17	0.19	-	*	-	8.0	≤ 5	-
	WH: 40	0.24	1.22	-	8.2	2.4	-	2177	154	-	3307	1402	-	0.44	0.10	-	*	-	5.9	≤ 5	-
	LSD 5%	0.23	0.69	-	1.54	0.48	-	482	86	-	240	398	-	0.08	0.04	-	-	-	1.60	-	-
rice	F-value	5.09	12.1	-	8.83	55.4	-	64.6	61.2	-	41.1	7.82	-	39.2	12.3	-	-	-	302	-	-
	control	0.89	9.06	7.44	32	11.8	8.6	1107	625	87	5556	1671	97	3.1	0.21	0.12	3.86	0.62	15.1	≤ 5	≤ 5
	CD: 20	1.46	15.47	7.72	35	16.0	9.6	924	636	107	4844	1798	96	5.6	0.29	0.12	2.44	0.12	11.5	≤ 5	≤ 5
rice	CD: 40	1.45	17.46	8.98	29	11.5	8.3	841	545	102	4325	1125	87	3.0	0.25	0.13	1.66	0.09	7.9	≤ 5	≤ 5
	LSD 5%	0.53	3.96	1.13	2.58	2.43	0.51	187	107	5.84	1473	339	12.7	1.25	0.04	0.02	1.10	0.17	3.0	-	-
	F-value	8.61	14.7	6.31	21.1	9.92	19.3	6.37	2.60	37.0	2.11	13.3	2.18	16.7	9.33	1.60	12.5	35.6	17.3	-	-
rice	control	0.89	9.06	7.44	32	11.8	8.6	1107	625	87	5556	1671	97	3.1	0.21	0.12	3.86	0.62	15.1	≤ 5	≤ 5
	WH: 20	1.19	13.54	7.52	32	17.7	9.5	1067	593	112	4152	1235	88	2.3	0.26	0.12	1.30	0.14	8.2	≤ 5	≤ 5
	WH: 40	1.41	12.60	8.10	27	13.5	8.5	875	722	99	3712	959	85	2.0	0.36	0.12	0.48	0.16	6.1	≤ 5	≤ 5
rice	LSD 5%	0.60	4.70	1.95	4.81	6.23	0.95	179	147	7.08	1456	515	10.1	0.97	0.06	0.02	1.06	0.18	0.01	1.4	-
	F-value	2.23	3.04	0.41	3.57	0.34	4.01	5.71	2.47	37.4	5.24	4.97	4.97	4.07	22.4	0.14	34.8	29.2	2.00	129	-

* not determined

CD cowdung

WH waterhyacinth

- grain was not formed

Figure 34. Effect of cowdung (CD) and waterhyacinth (WH) on yield of wheat and rice in soils of battery industrial site

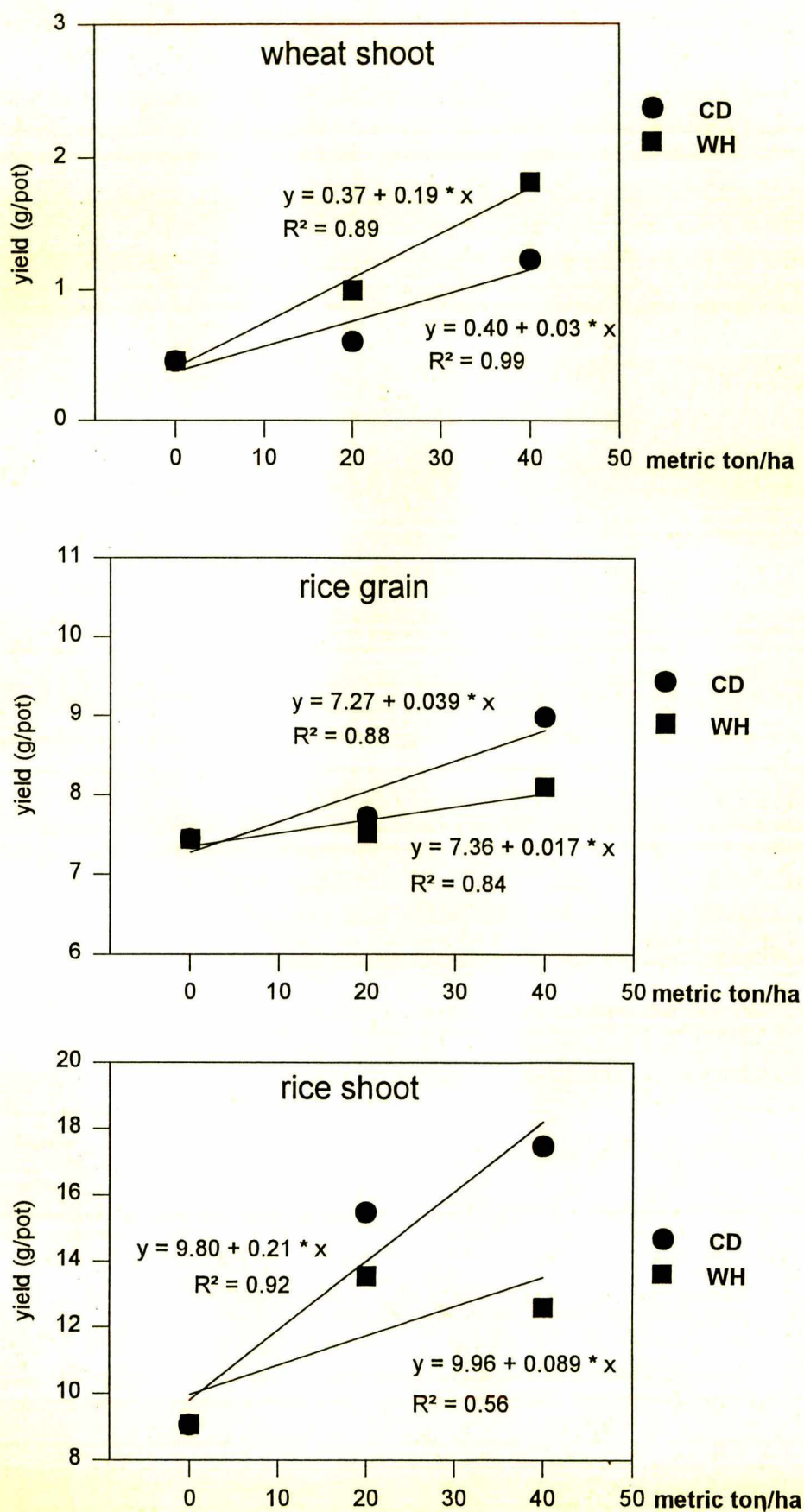


Figure 35. Effects of cowdung (CD) and waterhyacinth (WH) to zinc uptake of rice in soils of battery industrial site Tongi

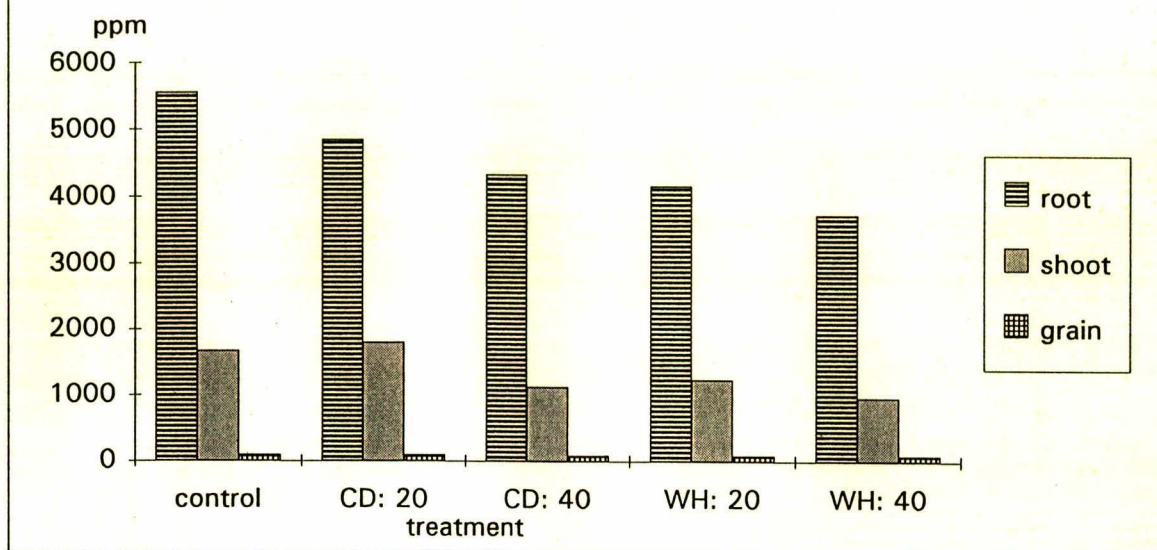
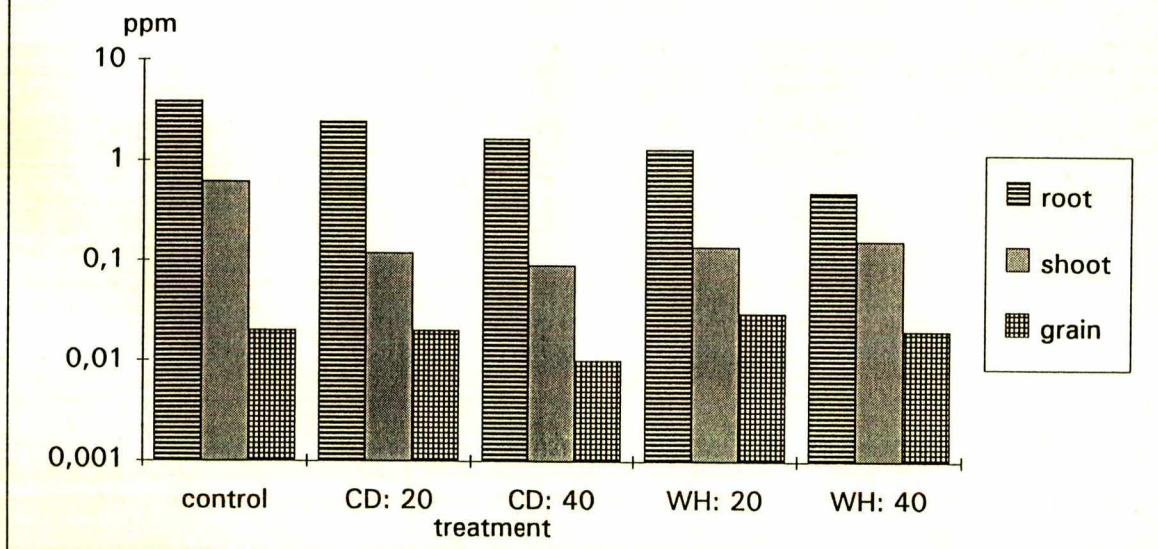


Figure 36. Effects of cowdung (CD) and waterhyacinth (WH) to Hg uptake of rice in soils of battery industrial site Tongi



4.3.2.3. Tongi industrial soil (pharmaceutical site)

Pharmaceutical industrial site, Tongi was found less contaminated with heavy metals but was appreciably polluted with organic compounds (in chapter 4.2.2.). Though effluents from the pharmaceutical industry caused death to the existing field crops (spot 1), but it is interesting that the same soils around spot 1 gave better performance when used after two months in greenhouse. Effluent and wastewater contained excessive amount of organic carbon (Table 19) which reduced the oxygen content of the soils. Microbial decomposition of these organic compounds possibly consumed most of the dissolved oxygen, which caused aquatic organisms to suffocate, as soon as the amount of dissolved oxygen is depleted. Organic contaminant accumulate dissolved oxygen and decrease the quality of soil water (Tan, 1994). Within two months organic pollutants were partly decomposed by microorganisms and thus produced favourable environment for good plant growth in pot experiments.

Dry matter yields, N, P, K, S, Fe, Cu, Mn, Zn and As concentrations were measured in roots, shoot and grain samples of wheat and rice (Table 30 & 31). The dry matter yield of wheat shoot and grain increased by 33% and 52% in the 40 mt cowdung/ha and 23% and 41% in the 40 mt/ha waterhyacinth treatments (Figure 37). The dry matter yields are statistically significant (Table 30). Better performance was observed in cowdung treatments (Table 30). The

dry matter yield of rice shoot and grain increased by 25% and 27% 40 mt/ha cowdung and 24% grain yield reduced with 40 mt/ha waterhyacinth and 35% shoot increased from those with control (Figure 38). However, there was no difference between the two treatments. Effects of waterhyacinth on wheat and rice were statistically insignificant as compared with control (Table 30).

Application of cowdung in the polluted soil has increased slightly N, P and K content of all crops (rice, wheat) but, the effect was not significant. The treatments with the waterhyacinth did not show any difference (Table 30). As was found in the pot experiment, Zn concentrations in wheat grain was higher than that in the shoot. Manganese showed the same trend as Zn with respect to grain/shoot concentration ratio. A considerable part of the absorbed Cu was translocated to the grain, Cu enrichment by plant roots was relatively low. Similar results were found by Lübben and Sauerbeck (1991) for wheat.

Table 30 Nutrient contents of wheat and rice in pot experiment on contaminated soil of pharmaceutical industrial site Tongi (spot 1)

Crop	CD/WH m. ton/ha	DM/pot (g)	N			P			K			S			Fe		
			plant parts			plant parts			plant parts			plant parts			plant parts		
			root	shoot	grain	root	shoot	grain	root	shoot	grain	root	shoot	grain	root	shoot	grain
wheat	control	root shoot grain 0.51 5.46 5.07	*	0.62	3.0	0.06	0.02	0.28	1.28	3.0	0.46	0.13	0.17	0.21	0.08	0.06	0.02
	CD: 20	0.67 7.70 8.59	*	0.62	2.8	0.05	0.02	0.34	0.94	3.6	0.45	0.15	0.22	0.18	0.11	0.05	0.03
	CD: 40	0.93 8.15 10.51	*	0.76	2.9	0.07	0.03	0.38	1.33	3.7	0.46	0.18	0.26	0.20	0.14	0.03	0.03
LSD 5%				0.19	0.28	0.01	0.01	0.05	0.28	0.36	0.04	0.03	0.03	0.01	0.05	0.01	0.01
F-value				2.33	1.72	2.40	14.4	10.7	5.85	11.6	0.09	9.39	26.9	14.3	4.26	9.80	1.00
wheat	control	0.51 5.46 5.07	*	0.62	3.0	0.06	0.02	0.28	1.28	3.0	0.46	0.13	0.17	0.21	0.08	0.06	0.02
	WH: 20	0.55 6.01 6.83	*	0.58	2.5	0.10	0.02	0.27	1.05	3.2	0.43	0.15	0.18	0.22	0.10	0.03	0.02
	WH: 40	0.57 7.16 8.61	*	0.55	2.9	0.06	0.01	0.27	0.87	3.1	0.46	0.13	0.16	0.21	0.10	0.02	0.02
LSD 5%				0.13	0.63	0.05	0.01	0.06	0.26	0.71	0.03	0.01	0.05	0.01	0.03	0.01	0.01
F-value				0.99	1.48	0.32	1.75	0.08	14.6	0.19	5.72	12.0	1.02	6.33	2.26	25.8	1.33
rice	control	2.20 15.37 7.53	*	1.09	1.6	0.13	0.17	0.34	1.03	2.5	0.42	0.44	0.15	0.14	1.71	0.05	0.02
	CD: 20	2.64 20.00 10.27	*	1.06	1.5	0.14	0.12	0.31	1.16	2.3	0.46	0.45	0.14	0.14	1.19	0.06	0.01
	CD: 40	2.58 20.74 10.31	*	1.50	1.7	0.16	0.19	0.35	1.49	2.5	0.49	0.43	0.17	0.14	1.19	0.05	0.01
LSD 5%				0.38	0.12	0.03	0.03	0.04	0.59	0.40	0.04	0.04	0.03	0.01	0.47	0.01	0.01
F-value				5.01	6.33	3.75	15.8	5.08	5.81	1.00	7.40	0.61	2.82	0.60	4.82	3.50	0.33
rice	control	2.20 15.37 7.53	*	1.09	1.6	0.13	0.17	0.34	1.03	2.5	0.42	0.44	0.15	0.14	1.71	0.05	0.02
	WH: 20	1.98 14.26 8.72	*	1.10	1.6	0.12	0.14	0.34	1.18	2.3	0.48	0.44	0.15	0.14	1.20	0.06	0.01
	WH: 40	1.87 15.93 5.72	*	1.20	1.7	0.17	0.20	0.37	1.10	2.7	0.48	0.52	0.19	0.15	1.82	0.05	0.02
LSD 5%				0.27	0.15	0.02	0.03	0.03	0.35	0.36	0.04	0.06	0.03	0.02	0.57	0.01	0.01
F-value				1.05	3.20	28.5	10.4	2.46	0.47	4.93	11.7	8.22	6.05	0.17	3.93	3.50	7.00

* not determined

CD cowdung

WH waterhyacinth

Table 31 Heavy metal contents of wheat and rice in pot experiment on contaminated soil of pharmaceutical industrial site Tongi (spot 1)

Crop	CD/WH m. ton/ha	DM/pot (g)	Cu			Mn			Zn			As		
			ppm			ppm			ppm			ppm		
			plant parts			plant parts			plant parts			plant parts		
		root shoot grain	root	shoot	grain	root	shoot	grain	root	shoot	grain	root	shoot	grain
wheat	control	0.51 5.46 5.07	4.4	3.2	7.3	37	49	55	113	79	100	0.18	0.09	0.03
	CD: 20	0.67 7.70 8.59	4.1	3.4	7.2	32	28	46	112	74	91	0.18	0.06	0.04
	CD: 40	0.93 8.15 10.51	4.8	3.7	6.9	39	40	52	130	72	97	0.28	0.13	0.03
LSD 5%		0.37 2.83 1.75	1.03	0.13	1.02	3.8	15.2	12.2	17.1	18.3	19.7	0.05	0.03	0.01
F-value		3.97 3.27 29.8	1.56	48.3	0.50	13.4	5.53	1.70	4.27	0.49	0.64	14.6	17.9	3.00
wheat	control	0.51 5.46 5.07	4.4	3.2	7.3	37	49	55	113	79	100	0.18	0.09	0.03
	WH: 20	0.55 6.01 6.83	5.1	3.7	8.1	38	39	44	108	69	93	0.15	0.11	0.02
	WH: 40	0.57 7.16 8.61	4.1	2.6	7.0	30	18	49	84	51	89	0.22	0.03	0.03
LSD 5%		0.23 2.44 1.92	1.09	0.44	0.48	10.7	13.4	11.9	17.2	18.1	11.8	0.04	0.03	0.03
F-value		0.25 1.52 10.2	2.55	17.5	16.6	1.41	16.5	2.42	10.1	7.32	2.82	8.47	25.3	2.33
rice	control	2.20 15.37 7.53	67.6	8.3	6.7	464	541	102	446	105	41	15.2	0.50	0.17
	CD: 20	2.64 20.00 10.27	55.4	5.8	5.7	327	406	75	481	121	32	9.8	0.48	0.16
	CD: 40	2.58 20.74 10.31	47.9	5.7	5.1	297	386	63	496	125	36	7.0	0.43	0.17
LSD 5%		0.99 5.87 2.70	9.75	0.82	0.39	50.1	79.7	11.1	108	35.3	1.88	5.01	0.14	0.02
F-value		0.69 2.95 4.17	12.4	37.8	47.9	38.1	13.3	38.7	0.66	1.08	63.9	8.28	0.72	1.09
rice	control	2.20 15.37 7.53	67.6	8.3	6.7	464	541	102	446	105	41	15.2	0.50	0.17
	WH: 20	1.98 14.26 8.72	68.2	8.2	7.8	389	532	77	583	123	38	9.2	0.41	0.16
	WH: 40	1.87 15.93 5.72	63.3	10.1	8.0	590	666	98	471	120	40	12.1	0.47	0.16
LSD 5%		0.93 6.24 2.69	8.66	0.79	0.83	47.2	87.4	10.2	72.0	29.0	5.88	4.95	0.18	0.01
F-value		0.39 0.22 6.97	0.83	22.9	12.4	55.8	8.79	20.0	12.2	1.38	0.55	4.41	0.85	2.33

* not determined

CD cowdung

WH waterhyacinth

Figure 37. Effect of cowdung (CD) and waterhyacinth(WH) on yield of wheat in soils of pharmaceutical site

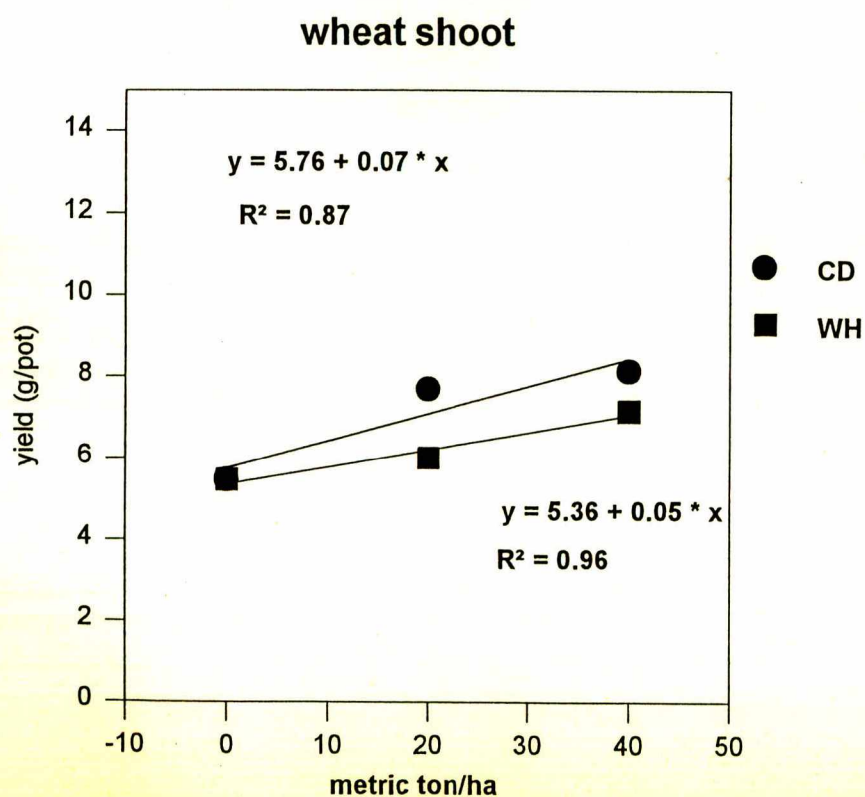
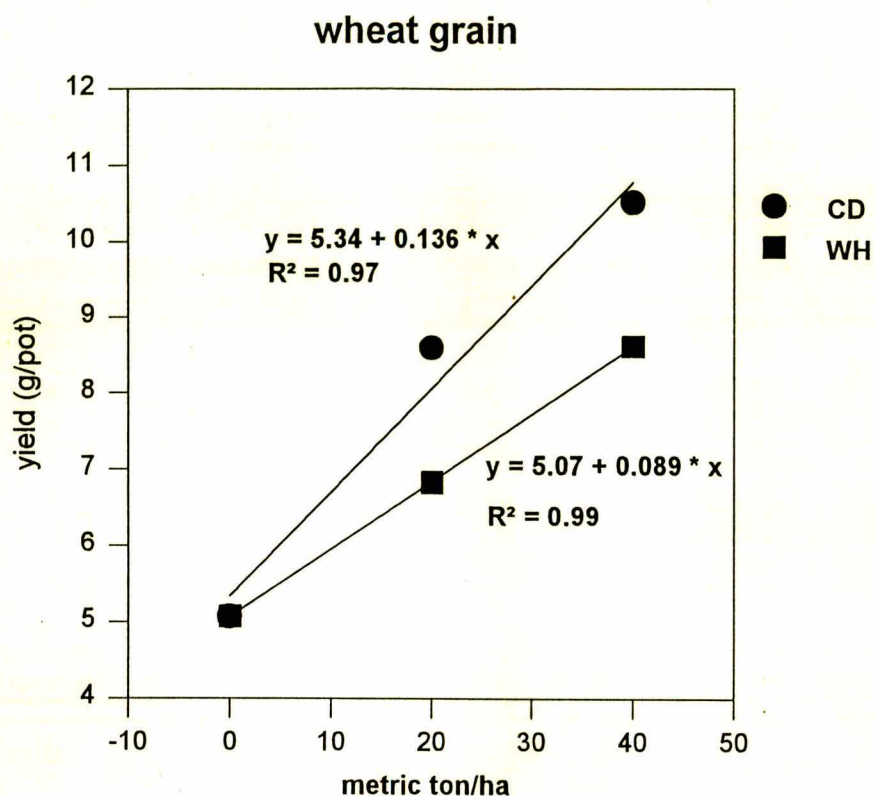
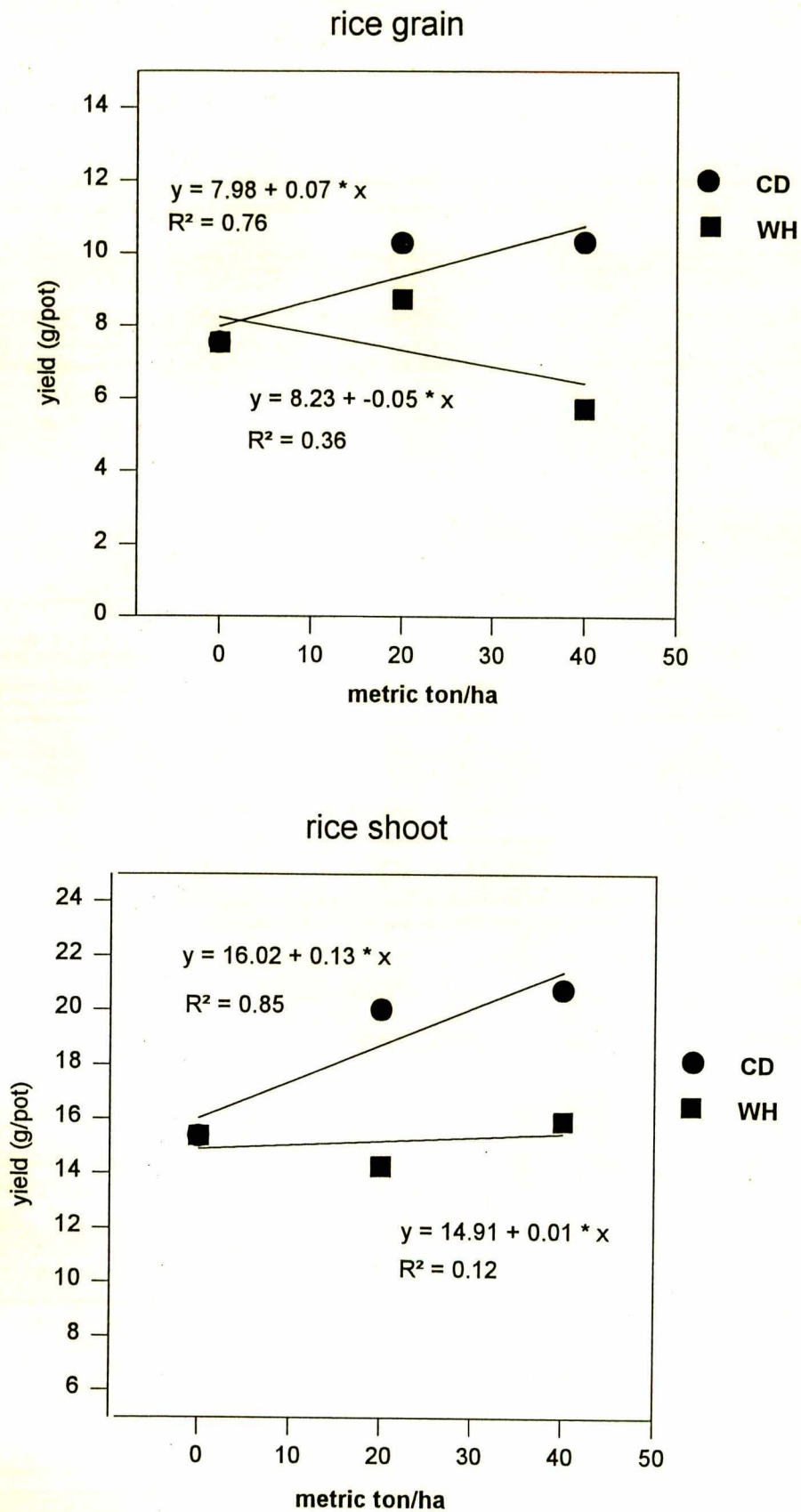


Figure 38. Effect of cowdung (CD) and waterhyacinth (WH) on yield of rice in soils of pharmaceutical site



4.4 Heavy metal soil to plant transfer

4.4.1 Field samples

4.4.1.1 Transfer coefficient soil-plant in Hazaribagh and Tongi industrial site

Rice, waterhyacinth and grass were collected from Hazaribagh and Tongi industrial area in the year 1992 and 1993. Average transfer coefficient of these field plants were determined. The heavy metals included are Cr, Zn, Cu, Mn, Hg and Cd (Figure 39 & 40). Transfer coefficients of Zn, Cu and Mn to rice plants were higher than those of grass and waterhyacinth in Hazaribagh tannery area. Chromium transfer was high in grass and low in rice and waterhyacinth (Figure 39). It is worthwhile mentioning that in all cases the soil to plant transfer of heavy metals into waterhyacinth was the lowest as compared to rice and grass. It is thus, evident that waterhyacinth is able to exclude heavy metals from uptake or has other detoxifying mechanism. The heavy metal transfer pattern into rice plant at the battery industrial site, Tongi, showed the following decreasing trend:

$$\text{Cd} > \text{Mn} > \text{Zn} > \text{Cu} > \text{Hg}.$$

Hg and Cu transfer into rice plant in battery industrial site, exceeded the published values in the literature (Schreinlechner et al., 1991). This is probably due to a relatively large mobile fraction which is continuously led through the

discharge of soluble heavy metals in the wastewater. The detailed transfer coefficient values of Hazaribagh and Tongi are presented in table A-5 (Appendix).

4.4.1.2 Correlation of mobile heavy metal fractions with plant uptake

Battery industrial site, Tongi exhibited extreme Zn concentration in soil (Table 13). Extractable heavy metal fractions particularly Zn and Mn correlated with the total contents in soil (Table 16). The accumulation of Zn by plant also showed a significant non linear correlation (Figure 41) with the mobile fractions. The slope gradient is less steep for rice grains, and this shows the ability of cereal grains to exclude Zn and to decrease shoot-grain translocation rates under toxic conditions.

Figure 39. Transfer coefficient soil-plant Hazaribagh tannery area

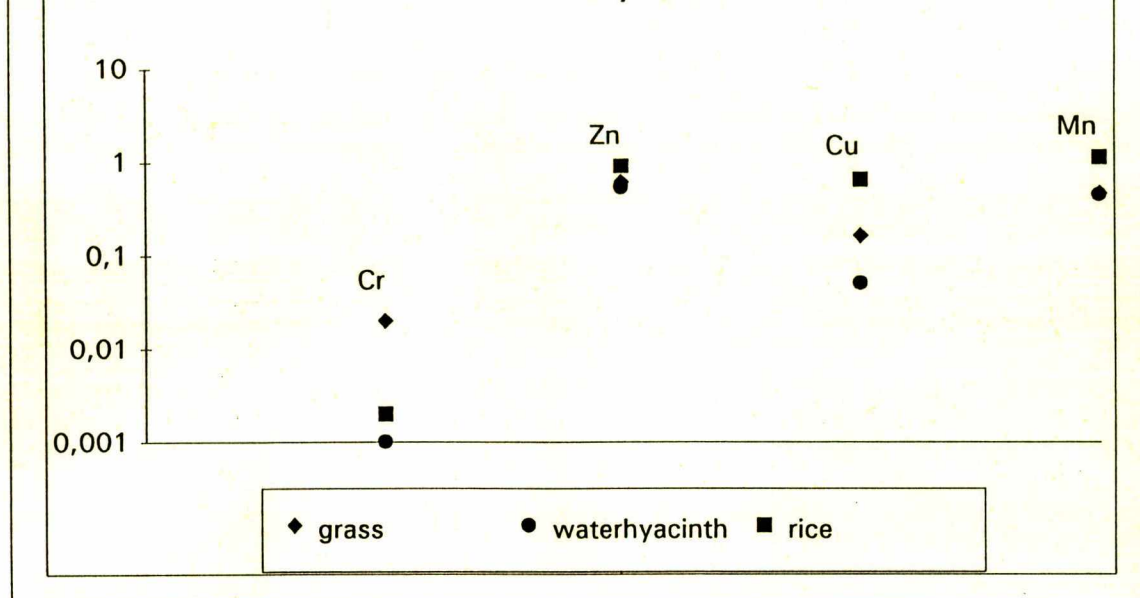
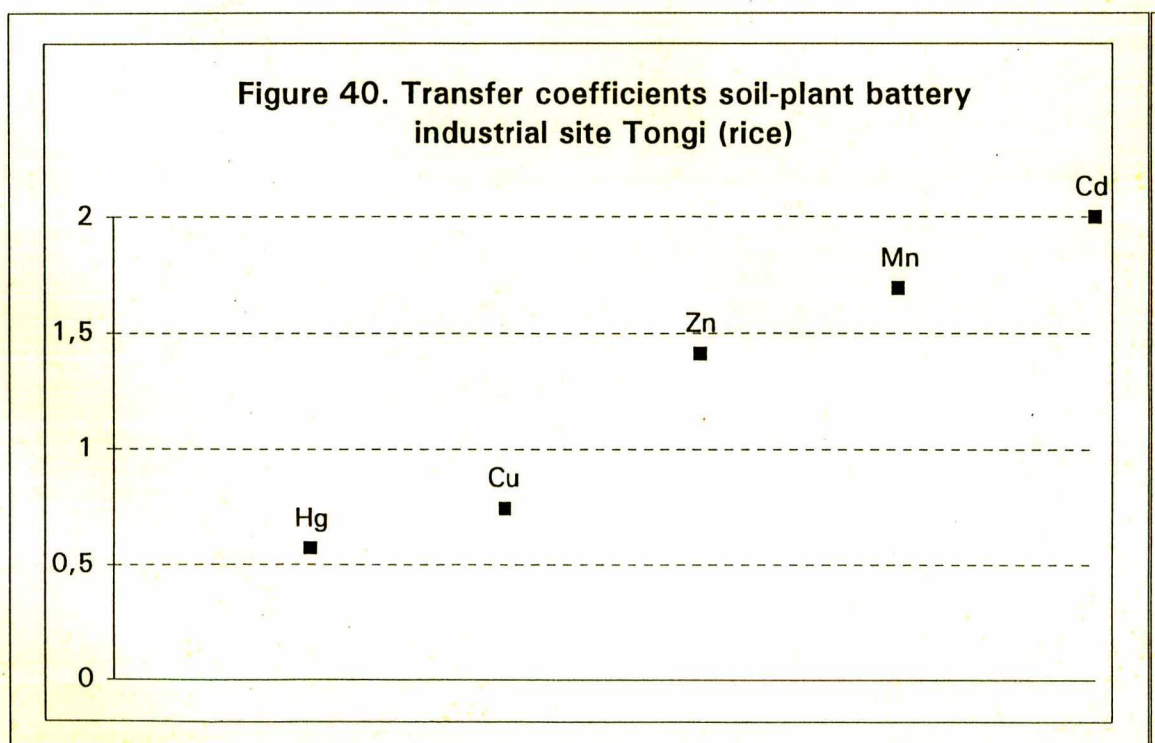


Figure 40. Transfer coefficients soil-plant battery industrial site Tongi (rice)



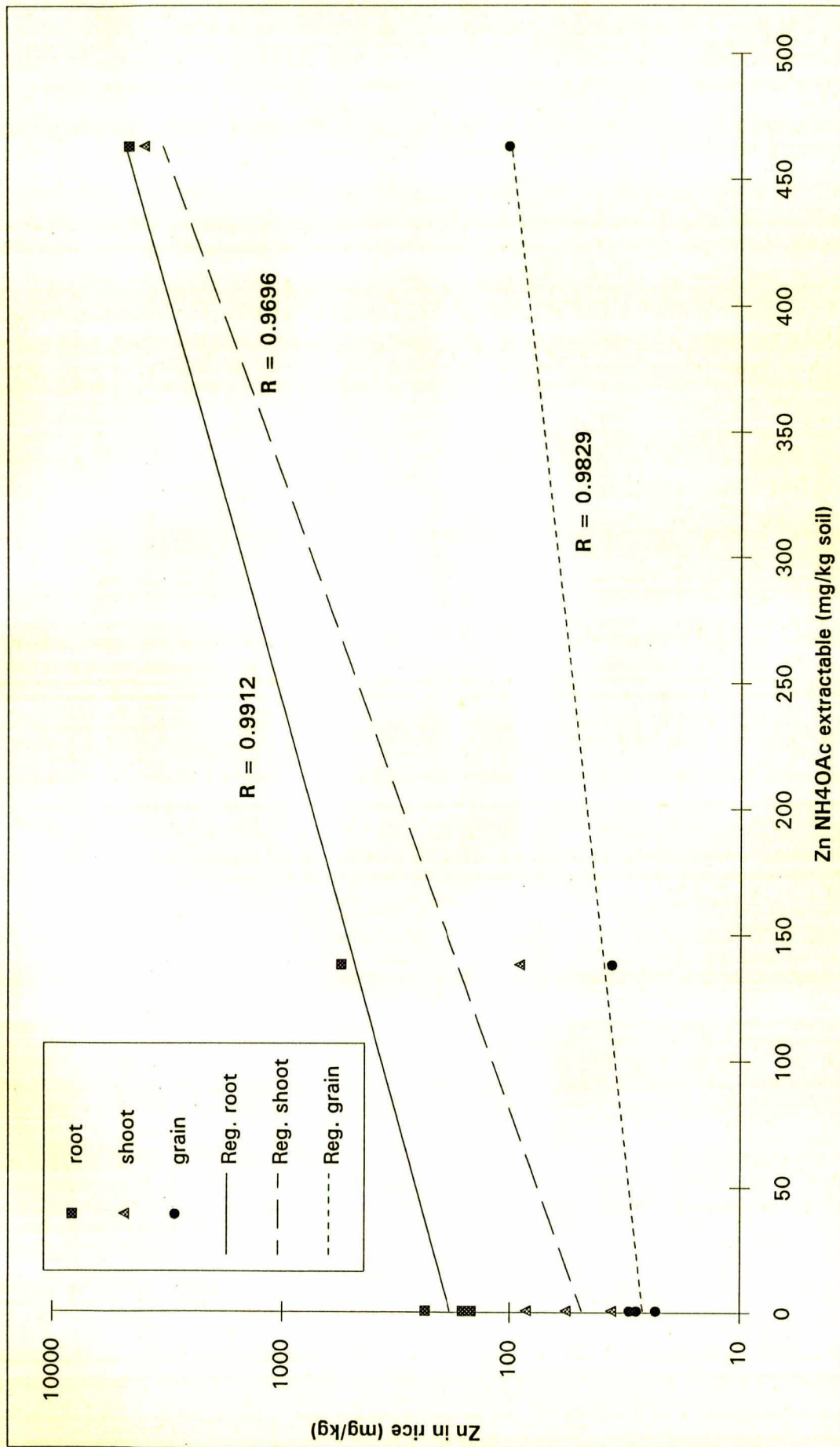


Figure 41: Zinc content of root, shoot and grain of rice as a function of its concentration of NH₄OAc extract. at Tongji industrial area

Table 32 Detection limits of the instruments used for heavy m and essential nutrients determination:

- i. ICP - AES
- ii. AAS Model 5000 with heated graphit-tube system (HGA)
- iii. AAS Model 5000 with Mercury-Hydride system (MHS-20 with gold platinum net

Element	Detection limit $\mu\text{g/L}$ -1	
As	0,2(AAS)	iii
Cu	20 (ICP)	i
Cr	50 (ICP)	i
Cr	0,5 (AAS)	ii
Cd	0,2 (AAS)	ii
Pb	0,1 (ICP)	i
Zn	20 (ICP)	i
Hg	0,2 (AAS)	iii
Mn	10 (ICP)	i
Fe	20 (ICP)	i
K	1000 (ICP)	i
P	1000 (ICP)	i
S	2000 (ICP)	i

Table 33 Common heavy metal concentrations in soils (mg/kg)

Scheffer, F. and Schachtschabel, P., 1989: Lehrbuch der Bodenkunde. Ferdinand Enke Verlag,

Element	Conc. in soil
Cd	< 0,5 - 3
Cr	5 - 100
Cu	2 - 40
Hg	0,02 - 0,5
Ni	5 - 50
Pb	2 - 60
Zn	10 - 80
As	2 - 20
Be	0,1 - 5
Co	1 - 10
Ga	0,1 - 10
Mo	0,2 - 5
Sb	0,01 - 0,5
Se	0,01 - 1
Sn	1 - 20
Ti	10 - 5000
Tl	< 0,5
U	< 0,5
V	10 - 100
Zr	1 - 300

Table 34 Tolerable total heavy metal concentrations in soils by Klokke (1980)

Element	mg/kg soil	Element	mg/kg soil
Zn	300	Cr	100
Cu	100	As	20
Cd	3	Sb	5
Ni	50	Be	10
Pb	100	B	25
Hg	2	Mo	5
Co	50	Se	10

Table 35 Common heavy metal concentration in plants, "Average" Transfer Coefficients Soil to Plant and Common heavy metal concentration in soils

Sauerbeck (1985)

Element	Conc. in plant mg/kg dw.	Trans.Coeff.	Conc. in soil mg/kg dw.
Zn	20 - 100	0,5 - 2	3 - 100
Cu	3 - 100	0,6 - 0,5	1 - 40
Cd	0,05 - 0,5	0,5 - 2	0,01 - 0,7
Ni	0,2 - 2	0,01 - 0,2	2 - 50
V	0,2 - 1	0,002 - 0,02	not mentioned
Mo	0,1 - 4	0,2 - 4	not mentioned
Pb	0,1 - 2	0,003 - 0,05	0,1 - 20
Hg	0,005 - 0,05	0,01 - 0,1	0,01 - 0,5
Co	0,02 - 0,5	0,005 - 0,1	1 - 10
Cr	0,1 - 0,5	0,002 - 0,02	2 - 50
Mn	not mentioned	0,02 - 2	20 - 3000
As	0,1 - 0,5	not mentioned	not mentioned
Th	< 0,005 - 0,05	0,05 - 0,5	not mentioned

Table 36 Critical levels for heavy metals in plants (toxic conc. level)

Element	Plants general (Ref.1)	young barley (Ref.2)
Cd	5 - 10	6 - 10
Co	10 - 20	3 - 9
Cr	1 - 2	5 - 20
Cu	15 - 20	14 - 25
Hg	0,5 - 1	2 - 5
Ni	20 - 30	11 - 13
Pb	10 - 20	20 - 35
Tl	20 - 30	11 - 45
Zn	150 - 200	120 - 220

Ref.1: Sauerbeck (1982)

Ref.2: Beckett and Davis (1977)

CHAPTER 5

SUMMARY AND CONCLUSIONS

CHAPTER - 5

SUMMARY AND CONCLUSIONS

Industrial wastes and effluent contain environmental hazardous pollutants including heavy metals. These are detrimental to agricultural production, human health and thus overall environmental ecosystems. The situation is getting worse with the rapid increasing industrialization. Bangladesh is not apart from this globally important issue. Scanty data are available regarding industrial pollution particularly by heavy metals in Bangladesh.

To investigate the intensity of pollution to the soils, crops and water bodies by heavy metals and with other organic pollutants, categorically samples (polluted soils, rice, aquatic plants, wastewater, and effluent) were collected in the years 1992 and 1993 from Hazaribagh tannery and Tongi industrial area (battery and pharmaceutical site) in the vicinity of Dhaka city.

Chromium, Cu, Cd, Zn, Mn, Fe, As, Pb and Hg were determined among the heavy metals. pH, texture, organic matter, EC, CEC, exchangeable cations, Cl and available N,P,K were also determined in soils.

The texture of the Hazaribagh tannery area was loam inside the embankment and silt loam outside the embankment. The soil: water pH was found to be neutral to

slightly alkaline in all spots in Hazaribagh. Deposition and decomposition of huge quantities of tannery effluent and solid wastes increased soil organic matter significantly (10.3% in spot 8) and progressively decreasing levels were measured downstreams. The soluble salts particularly of Ca and Mg from the tannery effluent enhanced the soil EC (3.9 to 4.3S/cm). The high EC adversely affect the seedling establishment. The CEC of Hazaribagh tannery area soils ranged from 8.4 to 39 meq/100g. The high organic matter content caused the high CEC. Highest level of Cl was observed at the wastes disposal point and the concentration decreased with increasing distance. Tannery waste significantly increased total and available nitrogen, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, P and S concentrations of surface soils. Even in 120 cm depth high accumulation of N was observed. Extreme concentrations of total sulphur and nitrogen were as hazardous elements in Hazaribagh tannery area.

The results obtained with heavy metals (Fe, Cu, Mn, Zn, As, Cr, Hg and Pb) indicated that the tannery industries are discharging not only Cr, which is inherent to the tanning process but, significant amounts of Zn, Mn, Cu and Pb as well. High levels of Cr (29402 ppm) including Zn, Cu and Pb were observed in the main wastes disposal point, exceeded the toxic level in soils. The extractable fraction heavy metals (Cr, Zn, Cu and Mn) give some indication of their phytoavailability and mobility in soils in Hazaribagh area.

Texture of the Tongi industrial site showed clayey except for spot 5, which is a silty clay loam. The soil pH was alkaline in reaction in all spots. The organic matter contents ranged from 1.6 to 4.2 percent. The soil EC and CEC were in normal ranges. Available K contents were found to be higher in pharmaceutical site (379 to 618 ppm K) than that of battery industrial site. Soil pH and K were enhanced by the industrial effluent.

High concentrations of Zn (4979ppm), Hg (4.99 ppm), Cd (0.785 ppm) and Mn (767 ppm) were observed in battery industrial site (spot 4). These heavy metals in battery industrial site are in extremely high magnitude with respect to effects on the soil ecosystems. NH_4OAC extractable Zn (463 ppm) and the mobile fraction of Zn (15.9% total) also exhibited detrimental values. The concentration of Hg was also high in the top soil of battery industrial site. The concentrations of Cu, Mn, Zn, As, Cr, Hg and Pb pharmaceutical industrial site were found in normal soil ranges.

Sampling dates showed a substantial seasonal fluctuation in the concentrations of Zn, Mn, Hg and Cd contents at battery industrial site. A large reduction being observed after the summer rain.

The pH, EC, Cl, Av-N, TOC, PO_4 , SO_4 , phenol and hydrocarbon were measured in effluent and wastewater samples from Hazaribagh and Tongi industrial area. The heavy metals Fe, Mn, Cu, Zn, Cr, Cd and Pb were also determined as well.

The pH ranged from 7.2 to 12 and 7.3 to 9.9 in tannery effluents and wastewater, respectively; pH 6.6 to 7.2 and was 6.1 in wastewater and effluents of battery industrial site, respectively and in pharmaceutical industrial site pH ranged from 6.8 to 7.3 and was 5.7 in wastewaters and effluents, respectively. Various tanning and colouring materials used in tannery industries are responsible for the wide range of pH variation and the effluents containing triethylamine with HCl, Cl and heavy metal compounds of pharmaceutical and battery industrial effluents decreased pH.

Electrical conductivity in effluents (3.4 to 20 S/cm) and wastewater (0.7-7.4 S/cm) severely affected by Hazaribagh tannery area, but it was found normal in Tongi sampling sites. Chloride concentrations exhibited extremely high values (1445 to 18330mg/l) in tannery area, Tongi area showed no severe enhancement. Liming and pre-tanning processes in the leather industry enhanced the Cl concentration.

The Av-N was also found to be increased both in effluents (521-1089 ppm) and wastewater (23-261ppm) in Hazaribagh tannery area. Av-N ($\text{NH}_4\text{-N} + \text{NO}_3\text{-N}$) is an important measure of the potential environmental impact. The effluents produced from the pharmaceutical industry specially producing raw materials for antibiotics are rich in inorganic nutrients such as N, K and very rich in total organic carbon (2507 ppm). The excessive enrichment of the elements create eutrophication and decrease the quality of soil water. The pharmaceutical site has created some problems with organics in soil

and water bodies. Values of total organic carbon were found 850 and 520 - 1050 ppm in tannery wastewater and effluents, respectively. These were above limit values.

The PO_4 and SO_4 contents in effluents and wastewater showed above toxic limit, even after 1.5 km down stream from the main disposal point of Hazaribagh tannery area.

Phenol and hydrocarbons were observed in a higher concentration at the pharmaceutical and tannery industrial sites. They are considered to be common environmental pollutants, even in a low concentration. The concentration of phenolic substances in the water of spot 13 has exceeded the WHO - limit by a factor of 300 to 630 in Hazaribagh tannery area (outside the embankment).

Matching the present values obtained with those of NAS (1993), US-EPA (1976) and USSR, Mn and Zn are above the allowable limits at battery industrial site, Tongi. Chromium concentration in wastewater and effluents were found above toxic limit in Hazaribagh area.

Sediments of battery industrial site Tongi possessed extremely high contents of Zn, Mn and Hg. Extractable Zn, Mn, Cd and Cu concentration exceeded the respective values in top soil samples by a factor of 5 to 20.

For the determination of the availability of trace metals to existing field crops and aquatic plants, five sampling were carried out in the years 1992 and 1993. N, P, K, S, Fe, Cu, Mn, Zn, Hg, As, Cr, Cd and Pb were measured in plant samples from Hazaribagh and Tongi industrial areas. The concentrations of all these heavy metals are correlated with the total concentrations in soils in all sites. Grass accumulated higher amounts of Cr than that of paddy and waterhyacinth samples in Hazaribagh, and exceeded the toxic limits. Extreme concentrations of Zn were accumulated in all parts of rice, 4630ppm, 4000ppm and 101ppm in roots, shoot and grain samples, respectively in battery industrial site. High accumulation of Zn was also observed in grass samples. Hg and Mn concentrations slightly exceeded toxic limits in battery industrial site. Pharmaceutical industrial site was not affected by heavy metal contamination.

Tannery wastes application in the pot experiment delayed maturity and caused stunting in wheat. Late flowering and maturity with dark green colour were observed a subsequent crop rice. The high level of EC (4.3 S/cm), adversely affected the rice seedling establishment at the date of planting. Tannery waste increased Zn, Mn and Cu contents in wheat grain higher than those of shoots but the Cr content was below 5ppm in both wheat and rice grain. Zn, Mn, and Cu concentrations increased in rice plants in the following order roots > shoots > grain. The Cr concentrations in roots were extremely higher (4702 ppm Cr) than those of shoots (112 ppm Cr) of rice.

Battery industrial site had turned nearly barren due to excessive deposition of industrial effluents, containing high concentration of Zn, Hg and partly Cd and Mn. To study the ameliorative effect of cowdung and waterhyacinth manure, the bulk surface soil from spot 4 was used for pot experiments, wheat and rice were used as test crops. Dry matter yields, N, P, K, S, Fe; Cu; Mn, Zn, As, Hg, Pb and Cd concentrations were measured in roots, shoot and grain samples of wheat and rice.

Wheat crop even with treatments fail to grow satisfactorily. Rice showed better performance with cowdung treatments. The accumulation of Zn and Mn content in different plant parts of wheat slightly decreased with the increasing rate of cowdung and waterhyacinth, but Zn and Mn contents in rice grain were not affected with treatments. The concentrations of Zn, and Mn particularly Zn contents still exhibited extreme concentration in wheat and rice tops. The application of cowdung and waterhyacinth significantly decreased the toxic metal Hg concentration in rice. Application of cowdung and waterhyacinth manures reduced the uptake of Mn and Hg appreciably but, the values in the tissue were above toxic level. These amendments reduce the concentration of Zn slightly.

Pharmaceutical industrial site Tongi was found less contaminated with heavy metals but, was appreciably polluted with organic compounds. Though effluents from the pharmaceutical industry caused death to the existing field crops (spot 1), but it is

interesting that the same soils around spot 1 gave better performance when used after two months in greenhouse.

A pot experiment was carried out with top soils of pharmaceutical site and the test crops were wheat and rice. Dry matter yields, N, P, K, S, Fe, Cu, Mn, Zn, and As concentrations were measured in roots, shoots and grain samples of wheat and rice. Better performance was observed in cowdung treatments and dry matter yields were significantly increased. Application of cowdung in the polluted soil increased N, P, and K contents of all crops to slightly but in the case of waterhyacinth application there were no significant differences.

Transfer coefficients into rice, waterhyacinth and grass samples from Hazaribagh and Tongi industrial site were calculated. Zn, Cu, and Mn showed higher coefficients in rice plant than that of grass and waterhyacinth. Cr transfer was higher into grass than that of rice. The heavy metal transfer pattern in rice at battery industrial site exhibited the following order :Cd > Mn > Zn > Cu > Hg.

Extractable Zn and Mn correlated with the total contents in soil and plant uptake in battery industrial site, Tongi.

Conclusions:

The results of the present investigation showed some site specific indications:

Hazaribagh tannery area

The long lasting Cr-emissions from this old tannery complex led to severe contaminations of soils in the closer vicinity. The more or less uniform Cr distribution within the soil profile down to 120cm suggests a considerable deposition of solids together with Cr and the other heavy metals observed in increased concentrations. Cu, Zn and Mn were also noticed in appreciable concentrations down to 120 cm depth. The transport of metals to the ground water below hazardous wastes in this site may be of severe environmental concern.

Phenol, hydrocarbons, Av-N (NH_4^+NO_3) Cl, SO_4 , TOC and EC parameters exceeded the critical limits both in soils and partly in surrounding water bodies.

Battery industrial site

The wastewater emissions of the battery factory increased concentrations of hazardous heavy metals (Zn, Hg & Cd) in soils considerably. Especially the mobile Zn-fraction was extremely increased and is the main cause of plant toxicity. Organic

manure treatments fail to control the deleterious affects of excessive amount of heavy metal concentrations in rice and wheat grown in pot experiments.

Pharmaceutical site

The emission of toxic organic substances was observed (TOC 2507 ppm). Hydrocarbons were observed in the surrounding top soils and water bodies. However, it seems that soil microorganisms are able to cope with that problem, if further emissions are avoided. Abnormal inputs of nitrogen and potassium led to nutrient imbalances in agricultural crops. Definite conclusions at this site could not be drawn at present, because all other parameters regarding organic pollution were not measured.

Although the present study should be regarded as a starting point of further investigations on industrial pollution of Dhaka city and other industrial sites in Bangladesh a preliminary recommendation can be made. The most important action, which should be taken in order to remedial the contaminated sites is to sharply decrease further emissions. Simple wastewater treatment systems like sewage treatment plants and e.g.a precipitation treatment for the tannery and pharmaceutical site and the battery site should be considered, respectively. From the present experiences immediate further studies on environmental pollution of industrial sites in Bangladesh have to be strongly recommended.

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Table A-1. Particle size distribution, chemical properties and available nutrients of soils at Hazaribagh industrial area from different spots, horizons and periods

Spot	Horizon	Period	Sand % 2 - 0.05	Silt % 0.05- 0.002	Clay % <0.002	Text class	pH		OM %	EC S/cm	CEC meq/100g	Exch. cations meq/100 g			Cl mg/l	Available in ppm			
							S/E	CaCl ₂				Ca	Mg	K		Na	N	P	K
8	1	1	40.6	44.9	14.5	1	7.3	7.1	10.0	4.6	43.4	37.4	9.7	1.0	29.9	512	2390	5.8	375
8	2	1					7.3	7.0	9.9	3.6	30.3	33.6	11.0	1.0	17.3	494	4196	8.3	311
8	3	1					6.9	7.0	9.4	5.4	23.1	21.1	8.6	0.4	38.0	652	694	1.3	71
8	1	2					7.4	7.1	10.1	4.8	28.4	27.4	3.2	0.6	8.9	531	2150	8.6	295
8	1	3					7.2	7.0	10.2	3.8	41.0	54.7	8.4	1.0	17.3	497	2391	4.1	184
8	1	4					7.3	7.1	10.6	4.5	42.4	36.0	10.0	1.0	24.0	513	2441	6.2	377
8	1	5					7.4	7.2	10.4	3.9	41.1	37.0	10.0	0.9	16.0	472	2343	3.7	193
9	1	1					7.4	6.8	1.4	4.9	6.4	7.2	1.2	0.3	3.5	51	299	1.5	122
9	2	1					7.3	6.9	1.5	4.8	6.4	13.4	0.9	0.3	3.7	59	286	0.9	87
9	3	1					7.2	7.0	1.0	2.8	10.0	12.5	1.8	0.4	3.0	91	93	0.3	97
9	1	2					7.3	6.9	1.6	4.7	6.7	7.5	1.3	0.3	3.0	55	210	1.7	119
9	1	3					7.1	6.8	1.5	4.3	6.8	6.5	2.0	0.5	2.5	58	307	1.1	63
9	1	4					7.4	6.8	1.5	4.5	7.6	9.9	1.3	0.3	3.7	58	305	0.2	98
9	1	5					7.4	6.9	1.4	4.3	6.8	11.5	3.5	0.3	7.0	96	280	1.2	87
10	1	1					7.3	6.9	1.4	5.0	8.8	5.3	1.6	0.2	3.5	78	248	5.2	185
10	2	1					7.3	6.8	1.5	4.3	7.7	4.5	2.0	0.3	4.0	52	27	4.7	195
10	3	1					7.3	7.1	1.0	2.7	6.5	4.0	2.3	1.3	3.0	47	22	2.1	81
10	1	2					7.3	6.9	1.3	4.3	8.6	5.3	1.7	0.3	2.5	81	238	1.7	133
10	1	3					7.2	6.5	1.0	2.9	8.7	6.2	2.5	0.5	3.0	53	246	2.2	109
10	1	4					7.3	6.5	1.1	2.3	7.9	6.1	2.2	0.5	2.9	55	251	5.3	198
10	1	5					7.4	6.8	1.3	4.9	6.9	6.1	2.3	0.3	3.0	80	241	2.1	99
13	1	1	30.0	51.7	18.3	sil	6.9	6.6	0.6	0.3	33.9	7.2	2.3	0.4	1.3	6	25	0.6	101
13	2	1					6.9	6.6	0.4	0.3	18.4	6.7	2.6	0.5	1.3	4	30	0.8	15
13	3	1					6.8	6.8	0.4	0.4	14.8	8.6	3.7	0.1	1.7	5	20	0.0	12
13	4	1					7.0	6.6	0.3	0.2	11.2	6.7	3.1	0.1	2.0	4	20	0.2	10
13	1	2					7.0	6.6	0.6	0.5	37.0	5.7	2.4	0.5	1.3	7	30	0.8	15
13	1	3					7.0	6.7	0.5	0.4	24.0	6.2	2.8	0.3	1.7	5	25	0.5	13
13	1	4					6.9	6.5	0.4	0.3	20.0	6.0	2.6	0.2	1.4	4	20	0.4	12
13	1	5					7.1	6.7	0.5	0.3	28.0	6.4	3.0	0.4	2.0	6	30	0.6	14

Table A-2. Total contents of selected nutrients and heavy metals of soils in Hazaribagh tannery area at different spots, horizons and periods

Spot	Horizon	Period	%					ppm								
			N	P	K	S	OM	Fe	Cu	Mn	Zn	As	Cr	Hg	Pb	Cd
8	1	1	2.738	0.299	0.12	1.785	10.00	1.2	107	206	312	2.2	27500	0.13	40	*
8	2	1	2.671	0.274	*	1.056	*	1.1	99	191	327	2.1	26300	0.20	39	*
8	3	1	2.471	0.292	*	2.855	*	1.1	109	189	284	1.1	22900	0.17	40	*
8	1	2	1.638	0.262	0.11	0.916	9.95	1.9	75	309	333	2.4	20400	0.17	38	*
8	1	3	2.123	0.348	0.10	1.212	10.00	2.0	127	308	465	2.9	22900	0.23	69	*
8	1	4	2.538	0.303	0.13	1.167	10.10	1.2	130	207	307	1.7	29700	0.11	38	*
8	1	5	1.269	0.164	0.11	0.852	9.50	1.8	49	268	143	2.0	25900	0.14	20	*
9	1	1	0.139	0.082	0.14	0.156	1.50	4.1	38	535	97	7.7	1540	0.10	18	*
9	2	1	0.109	0.069	*	0.222	*	3.4	29	481	81	2.4	740	0.02	15	*
9	3	1	0.768	0.081	*	0.130	*	3.9	36	489	90	3.5	928	0.04	16	*
9	1	2	0.101	0.065	0.13	0.232	1.55	3.3	29	465	81	1.6	780	0.02	12	*
9	1	3	0.311	0.066	0.31	0.522	1.70	3.9	36	503	97	1.8	1350	0.02	16	*
9	1	4	0.646	0.105	0.17	0.539	2.70	3.0	39	369	136	2.0	3800	0.03	22	*
9	1	5	0.375	0.076	0.14	0.625	1.90	4.1	39	368	90	1.1	1940	0.02	15	*
10	1	1	0.214	0.074	0.15	0.426	1.50	3.8	37	379	97	3.0	1340	0.05	19	*
10	2	1	0.126	0.067	0.31	0.038	*	4.7	55	619	111	7.1	490	0.06	27	*
10	3	1	0.006	0.071	*	0.009	*	5.5	47	400	93	4.7	151	0.03	18	*
10	1	2	0.215	0.071	0.15	0.156	1.50	4.2	50	479	109	5.2	830	0.03	46	*
10	1	3	0.126	0.067	0.31	0.038	1.55	4.7	55	619	111	7.1	490	0.06	27	*
10	1	4	0.214	0.074	0.15	0.426	1.70	3.8	37	379	97	3.0	1340	0.05	19	*
10	1	5	0.215	0.071	0.15	0.156	1.40	4.2	50	479	109	5.2	830	0.03	46	*

* not determined

Table A-2. continued

Spot	Horizon	Period	%				ppm									
			N	P	K	S	OM	Fe	Cu	Mn	Zn	As	Cr	Hg	Pb	Cd
11	1	1	0.215	0.075	0.26	0.115	1.40	4.2	35	430	74	3.3	93	0.02	11	*
11	1	2	0.006	0.086	0.32	0.004	1.50	5.0	50	268	96	7.6	80	0.03	16	*
11	1	3	0.184	0.065	0.38	0.039	1.30	4.6	46	504	90	3.5	72	0.03	20	*
11	1	4	0.136	0.070	0.28	0.053	1.60	1.6	53	674	98	5.1	93	0.03	21	*
11	1	5	0.184	0.064	0.31	0.086	1.35	3.5	40	526	83	3.4	64	0.02	13	*
12	1	1	0.112	0.061	0.28	0.039	1.60	3.6	40	491	82	6.1	62	0.02	18	*
12	1	2	0.168	0.077	0.31	0.030	1.50	4.3	24	427	58	2.8	44	0.04	10	*
12	1	3	0.080	0.059	0.31	0.018	0.55	4.3	43	474	80	4.4	69	0.02	18	*
12	1	4	0.136	0.045	0.30	0.046	0.75	3.4	47	467	89	9.8	78	0.02	15	*
12	1	5	0.120	0.068	0.26	0.033	0.60	4.6	44	515	86	4.4	67	0.02	15	*
13	1	1	0.151	0.079	0.31	0.055	1.15	4.4	54	538	119	5.3	1370	0.06	29	*
13	2	1	0.007	0.071	*	0.009	*	5.5	47	1100	93	44.8	141	0.03	18	*
13	3	1	0.006	0.086	0.32	0.004	*	5.0	50	2268	96	27.6	80	0.03	16	*
13	4	1	*	0.069	*	0.006	*	5.4	48	884	92	18.0	69	0.02	14	*
13	1	2	0.126	0.067	0.31	0.038	0.90	4.7	55	619	111	7.1	490	0.06	27	*
13	1	3	0.136	0.062	0.34	0.076	0.70	4.1	33	466	99	5.5	128	0.01	14	*
13	1	4	0.151	0.079	0.31	0.056	1.20	4.4	54	538	119	5.3	1375	0.06	29	*
13	1	5	0.126	0.067	0.31	0.038	1.05	4.7	55	619	111	7.1	490	0.06	27	*

* not determined

Table A-3. Particle size distribution, chemical properties, organic matter and available nutrients of soils from pharmaceutical (1, 2, 3) and battery (4, 5) industrial site Tongi, at different spots, horizons and periods

Spot	Horizon	Period	Sand % 2 - 0.05	Silt % 0.05- 0.002	Clay % < 0.002	Text class	S/E	pH	OM %	EC S/cm	CEC meq/100g	Ca	Mg	K	Na	Cl mg/l	Available in ppm N P K
1	1	1	1.7	29.0	69.3	clay	7.9	6.9	3.8	1.7	29.9	20.6	3.6	2.7	2.8	78	58 1.3 704
1	2	1	1.8	31.0	67.2	clay	8.4	6.5	2.7	0.8	35.0	10.6	1.5	1.8	2.0	35	62 0.6 412
1	3	1					8.4	6.7	1.5	0.7	30.3	7.7	3.8	1.2	1.7	11	22 0.3 210
1	4	1					8.4	6.7	0.3	0.5	23.1	10.1	5.5	0.3	1.5	4	7 1.6 600
1	1	2					7.1	6.6	3.6	1.7	27.0	12.0	2.5	2.3	2.0	55	61 1.5 690
1	2	2					7.3	6.7	2.1	0.2	31.5	7.3	3.0	0.6	1.3	44	* * *
1	1	3					7.9	6.9	4.0	1.3	29.0	20.0	2.2	2.6	2.8	60	45 0.7 502
1	1	4					7.6	6.7	3.7	2.0	31.0	19.0	2.9	2.6	2.2	79	62 1.4 704
1	1	5					7.8	6.8	3.9	1.3	30.0	19.0	2.3	1.6	3.0	63	* 1.2 490
2	1	1	2.3	28.2	69.5	clay	8.8	6.8	3.5	1.2	36.3	13.4	2.1	2.0	1.7	25	55 0.7 485
2	2	1	2.0	27.4	70.6	clay	8.7	6.6	2.4	0.7	21.0	13.0	5.4	1.3	2.0	18	20 0.3 211
2	3	1					8.4	6.9	1.1	0.5	20.0	8.7	4.6	0.6	1.9	8	13 0.3 209
2	4	1					8.2	6.9	0.7	0.5	19.0	5.8	3.2	0.5	1.9	7	11 0.1 85
2	1	2					8.5	6.7	4.5	1.2	28.0	13.4	3.0	1.6	1.5	30	82 0.7 490
2	2	2					8.1	6.2	*	0.3	31.5	5.4	4.2	0.9	0.9	7	14 * *
2	1	3					7.9	6.8	4.5	1.2	37.0	14.0	2.1	2.0	1.7	31	48 0.3 212
2	1	4					8.2	6.7	4.2	1.2	20.0	14.4	2.7	1.7	2.0	32	68 0.9 603
2	1	5					7.9	6.8	4.1	1.1	36.0	13.0	2.1	2.0	1.8	38	* 0.5 315
3	1	1	3.0	35.2	61.8	clay	8.4	6.8	3.0	0.8	26.0	10.6	2.7	2.0	1.9	41	44 0.6 470
3	2	1	1.9	31.3	66.8	clay	8.4	6.7	2.1	0.8	35.0	9.6	3.6	1.5	1.9	47	43 0.2 315
3	3	1					8.3	6.6	0.2	0.4	16.0	5.8	4.2	0.6	1.7	11	13 0.3 190
3	4	1					8.5	6.0	1.4	0.4	21.0	7.2	4.0	0.8	1.7	8	8 0.1 83
3	1	2					8.1	6.6	3.6	0.6	27.0	12.5	4.4	2.0	1.5	51	70 0.7 480
3	2	2					8.2	6.5	2.0	0.4	26.0	9.1	3.9	0.6	1.4	18	11 * *
3	1	3					8.3	6.8	3.1	0.7	32.0	11.5	3.0	1.6	2.0	20	26 0.6 421
3	1	4					8.1	6.7	3.4	0.8	25.0	15.8	3.2	2.3	2.4	53	95 0.7 490
3	1	5					8.2	6.6	3.0	0.7	31.0	12.0	3.0	1.5	3.0	23	* 0.6 375

* not determined

Table A-3. continued

Spot	Horizon	Period	Sand % 2 - 0.05	Silt % 0.05- 0.002	Clay % <0.002	Text class	S/E	pH	OM %	EC S/cm	CEC meq/100g	Ca	Exch. cations meq/100 g Mg K	Na	Cl mg/l	Available in ppm N P K
4	1	1	24.3	26.8	48.9	clay	8.4	6.7	1.6	1.5	21.0	3.8	1.4	0.6	1.3	149 0.2 118
4	2	1	19.2	35.7	45.1	clay	7.9	6.8	0.5	1.0	22.0	6.0	1.5	0.5	1.1	83 0.3 53
4	3	1					7.7	6.8	0.6	0.6	24.3	8.6	2.6	0.3	1.1	7 16 0.0 17
4	1	2					7.7	6.6	1.1	1.3	20.0	4.6	2.1	0.3	1.3	136 0.9 111
4	1	3					7.6	6.7	2.0	1.4	19.0	5.3	1.8	0.9	1.3	108 0.2 62
4	1	4					7.9	6.5	1.6	1.5	21.0	3.7	1.5	0.6	1.3	118 2.8 124
4	1	5					7.8	6.4	1.8	1.4	19.5	5.7	1.9	0.8	1.2	* 0.2 66
5	1	1	12.8	49.7	37.5	sicl	8.2	6.5	3.0	0.8	21.2	5.3	2.3	0.5	1.5	12 0.7 88
5	2	1					7.7	6.5	2.0	0.5	18.4	5.0	2.5	0.4	1.5	7 7 0.6 62
5	3	1					7.1	6.6	1.2	0.7	13.6	4.2	4.0	0.5	1.4	7 10 0.6 62
5	4	1					7.2	6.9	0.6	0.6	26.7	7.7	4.0	0.3	2.6	8 0.1 27
5	1	2					6.9	6.4	2.3	1.0	20.0	5.8	2.0	0.4	1.9	32 16 0.2 111
5	2	2					6.8	6.3	1.6	0.5	21.0	5.6	2.4	0.5	2.1	8 * *
5	1	3					7.2	6.4	3.2	0.5	29.0	11.5	4.2	0.6	1.5	13 0.0 101
5	1	4					8.0	6.5	3.1	0.9	21.0	5.3	2.4	0.4	2.0	25 1.1 117
5	1	5					7.4	6.5	3.1	0.5	28.0	8.8	3.2	0.5	1.7	* 0.3 120

* not determined

Table A-4. Total contents of selected nutrients and heavy metals of soils from pharmaceutical (1, 2, 3) and battery (4, 5) industrial site Tongi at different spots, horizons and periods

Spot	Horizon	Period	%					ppm										Cd
			N	P	K	S	OM	Fe	Cu	Mn	Zn	As	Cr	Hg	Pb			
1	1	1	0.246	0.066	0.26	0.083	3.65	4.1	39	260	150	3.5	74	0.11	23	*		
1	2	1	0.132	0.051	*	0.047	*	3.6	36	335	106	3.7	73	0.06	24	*		
1	3	1	0.120	0.039	*	0.026	*	4.9	34	295	87	3.8	72	0.03	23	*		
1	4	1	0.025	0.005	*	0.007	*	3.4	30	572	58	1.0	54	0.01	22	*		
1	1	2	0.189	0.059	0.26	0.058	3.80	3.8	36	289	113	3.4	62	0.07	23	*		
1	2	2	0.057	0.029	*	0.017	*	4.7	34	309	74	4.1	66	0.03	21	*		
1	1	3	0.271	0.057	0.25	0.084	3.65	3.0	31	259	110	3.2	56	0.20	20	*		
1	1	4	0.277	0.084	0.27	0.117	4.00	2.9	48	198	205	3.9	67	0.31	22	*		
1	1	5	0.343	0.065	0.27	0.065	3.95	3.2	30	359	5	3.6	54	0.14	21	*		
2	1	1	0.202	0.041	0.27	0.063	3.15	3.9	35	301	104	3.7	73	0.05	24	*		
2	2	1	0.126	0.037	*	0.032	*	4.5	36	341	110	4.5	69	0.05	24	*		
2	4	1	0.050	0.011	*	0.016	*	4.0	32	707	66	5.2	56	0.02	21	*		
2	1	2	0.176	0.043	0.26	0.065	4.20	3.2	37	312	98	3.5	61	0.04	25	*		
2	2	2	0.107	0.036	*	0.032	*	4.4	35	371	84	4.2	70	0.03	21	*		
2	1	3	0.383	0.047	0.27	0.079	3.25	4.1	35	407	133	3.4	66	0.09	26	*		
2	1	4	0.221	0.040	*	0.075	3.05	3.6	34	242	107	3.6	71	0.04	22	*		
2	1	5	0.391	0.081	0.29	0.064	3.45	2.9	32	274	111	2.5	55	0.11	23	*		
3	1	1	0.195	0.038	0.25	0.061	2.80	4.6	37	379	145	4.0	73	0.07	26	*		
3	2	1	0.164	0.033	*	0.051	*	4.9	35	406	122	4.2	71	0.04	26	*		
3	4	1	0.164	0.016	*	0.021	*	4.3	37	213	75	1.9	77	0.05	28	*		
3	1	2	0.158	0.039	0.24	0.057	3.45	3.4	37	315	94	3.1	60	0.04	24	*		
3	1	3	0.207	0.038	0.28	0.079	3.35	3.2	34	330	101	3.2	57	0.09	20	*		
3	1	4	0.227	0.039	0.26	0.084	3.65	2.2	37	319	183	3.9	69	0.09	23	*		
3	1	5	0.455	0.100	0.26	0.083	4.35	3.0	34	236	128	2.8	56	0.29	22	*		

* not determined

Table A-4. continued

Spot	Horizon	Period	%					ppm									
			N	P	K	S	OM	Fe	Cu	Mn	Zn	As	Cr	Hg	Pb	Cd	
4	1	1	0.139	0.030	0.13	0.031	1.65	3.0	22	638	4360	1.5	38	5.10	15	0.72	
4	2	1	0.050	0.006	*	0.004	*	4.6	11	119	194	1.1	19	1.03	8	0.36	
4	3	1	0.019	0.006	*	0.003	*	4.2	15	150	123	0.9	42	0.03	15	0.01	
4	1	2	0.063	0.018	0.14	0.017	1.20	1.7	15	310	2400	1.1	30	3.00	10	0.82	
4	1	3	0.176	0.031	0.14	0.038	1.25	4.1	26	366	1540	3.5	48	0.53	20	0.36	
4	1	4	0.120	0.029	0.13	0.029	1.15	3.6	31	722	3000	2.9	54	3.60	16	0.37	
4	1	5	0.069	0.015	0.16	0.016	1.20	2.3	21	601	2100	1.6	41	1.00	16	0.26	
5	1	1	0.214	0.026	0.14	0.033	2.75	2.8	26	409	1390	3.6	48	0.45	17	0.11	
5	2	1	0.120	0.020	*	0.025	*	2.1	22	538	1210	3.8	40	0.29	16	0.09	
5	3	1	0.069	0.013	*	0.018	*	3.1	19	229	233	4.2	32	0.05	15	0.05	
5	4	1	0.063	0.007	*	0.006	*	3.1	27	736	65	4.4	52	0.02	18	0.05	
5	1	2	0.095	0.019	0.14	0.025	2.35	3.3	25	519	920	3.7	47	0.29	16	0.13	
5	1	3	0.346	0.026	0.11	0.054	2.25	3.0	34	300	1480	1.9	60	0.43	23	0.22	
5	1	4	0.311	0.029	0.12	0.059	2.55	3.3	38	353	1080	2.4	67	0.35	24	0.15	
5	1	5	0.311	0.019	0.14	0.050	2.60	2.8	32	239	671	1.7	61	0.01	21	0.14	
6	1	1	0.263	0.038	0.31	0.078	3.25	4.3	37	296	196	4.1	70	0.10	25	*	
6	1	2	0.160	0.030	0.24	0.036	2.90	3.6	25	310	106	3.8	46	0.03	21	*	
6	1	4	0.271	0.036	0.28	0.052	3.30	4.7	33	243	118	3.7	60	0.03	24	*	
6	1	5	0.279	0.037	0.27	0.054	3.00	4.7	32	276	103	3.9	61	0.02	24	*	

* not determined

Table A-5. Transfer coefficient soil to plant in Hazaribagh and Tongi industrial area

Industrial site	Crop	Element	Trans. Coeff.
Battery	Rice	Zn	1.41
		Hg	0.57
		Cd	2.0
		Mn	1.69
		Cu	0.56
Tannery	Grass	Cr	0.02
	Waterhyacinth	Cr	0.001
	Rice	Cr	0.002
	Grass	Zn	0.61
	Waterhyacinth	Zn	0.53
	Rice	Zn	0.89
	Grass	Cu	0.16
	Waterhyacinth	Cu	0.05
	Rice	Cu	0.63
	Grass	Mn	0.45
	Waterhyacinth	Mn	0.43
	Rice	Mn	1.1

Table A-6

Orientation data for heavy metal contamination limits in agricultural soils

Element	Netherlands *1 C = % Clay H = % Humus	Italy *2		Switzerland *3 Extracted with 0,1 M-NaNO ₃	Germany *4		*Ref. 1			*Ref. 2		
		CEC: <5 or pH<6	>15		light	heavy	PH 5	PH 6	PH 7	Sandy	Silty	Clay
Cd	0,4 + 0,007 (C+3H)	0,5	1,0	0,03	1,0	1,5	0,3	0,5	2,5	1,0	1,5	2,0
Cr	50 + 2C	25	50	..	..	100	..	..	..	100	150	200
Cu	15 + 0,6 (C+H)	25	75	0,7	..	60	40	70	100	100	150	200
Hg	0,2 + 0,0017 (2C+H)	0,5	1,0	..	..	1,0	..	..	..	1,0	2,0	2,0
Ni	10 + C	15	50	0,2	..	50	<50	50	50	50	75	100
Pb	50 + C + H	25	50	1,0	..	100	200	200	200	100	200	300
Zn	50 + 1,5 (2C+H)	75	150	0,5	150	200	40	100	150	300	350	400

*1: BAVINCK, H.F. (1989): The Dutch Reference Values for Soil Quality. In: BEHRENS, D., WIESNER, J.; Edts. (1989): Beurteilung von Schwermetallkontaminationen im Boden. Dechema Fachgespräche Umweltschutz; AG "Bewertung von Gefährdungspotentialen im Bodenschutz" 21.-22. Januar 1988, 87-95, Dechema, Frankfurt a.M.

*2: GENEVENI, P.L., ZACCHEO, P., MANSTRETTA, M. (1989): The Presence of Organic and Inorganic Pollutants in Compost. Proc. Int. Symp.: Compost Production and Use. S. Michele all'Adige, 20.-23. June 1989.

*3: HÄNLI, H. (1989): Die Richtwerte für Fluor und Schwermet. in der Schweizerischen Verordnung über Schadstoffe im Boden. In: As *1

*4: Novelle zur deutschen Klärschlammverordnung (ANONYM 1991): Novelle zur Klärschlammverordnung - AbfKlärV. Zur Begutachtung 14.8.1991; Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit in der BRD.

*Ref. 1: HERMS, U. und G. BRÜMMER (1980): Einfluß der Bodenreaktion auf Löslichkeit und tolerierbare Gesamtgehalte an Nickel, Kupfer, Zink, Cadmium und Blei in Böden und kompostierten Siedlungsabfällen. Landw. Forsch., 33, 4, 408-423

*Ref. 2: LICHTFUSS, R. (1989): Geogene, pedogene und anthropogene Schwermetallgehalte in Böden. In: As *1.

Table A-7 Pb, Cd, Zn and Cu concentrations in topsoil (0-3 cm) and road dust in survey sites (Jan. 1989)

Sample No.	Mean metal contents ($\mu\text{g/g}$)				Industrial activity
	Pb	Cd	Zn	Cu	
IC-1	84	1.0	81	17	Textile
IC-2	60	1.5	142	22	Tiles
IC-3	143	1.5	82	13	Electrical
IC-4	84	1.4	69	16	Food
IC-5	283	1.6	426	47	Machinery
IC-6	211	1.9	273	45	Machinery
IC-7	109	1.4	150	53	Agricultural Chemical
IC-8	99	1.9	167	259	Cable wiring
IC-9	105	1.5	310	93	Chemicals
IC-10	288	1.6	215	40	Ferrous materials
IC-11	59	1.5	148	16	Animal feed
IC-12	111	1.4	184	30	Metal materials
IC-13	58	1.5	117	21	Precision machine
IC-14	54	1.3	147	26	Rubber
IC-15	58	2.0	82	32	Paper manufacturing
IC-16	61	1.6	73	28	Textile
IC-17	1413	1.2	115	25	Waste dump
IC-18	746	1.5	64	36	Metals
IC-19	234	1.4	164	30	Boiler manufacturing
IC-20	236	1.7	170	60	Chemicals
IC-21	83	1.5	106	28	Food
IC-22	356	1.7	130	99	Ferrous materials
IC-23	191	1.4	541	54	Metal molding
IC-24	79	1.5	55	28	Building materials
IC-25	147	1.7	43	25	Waste treatment
CA-1	31	0.2	57	14	Agricultural land
CA-2	39	0.4	59	16	Agricultural land
RD-1	69	1.7	121	40	Road junction
RD-2	118	1.6	186	39	Main traffic road

(IC = Industrial Complex, RD = Road Dust, CA = Control Area)

Table A-8 | Concentrations of Cd In Rock
Phosphate Imported Into the U.K.

Source Country	Concentration (mg kg ⁻¹)
U.S.	6.5
Senegal	71.0
Morocco	18.0
Tunisia	18.0
From Hutton, M. and C. Symon. <i>Sci. Total Environ.</i> 57:129-150 (1986).	

Figure B-1. Distribution of total Cr at Hazaribagh tannery area (0 - 15 cm) with periods

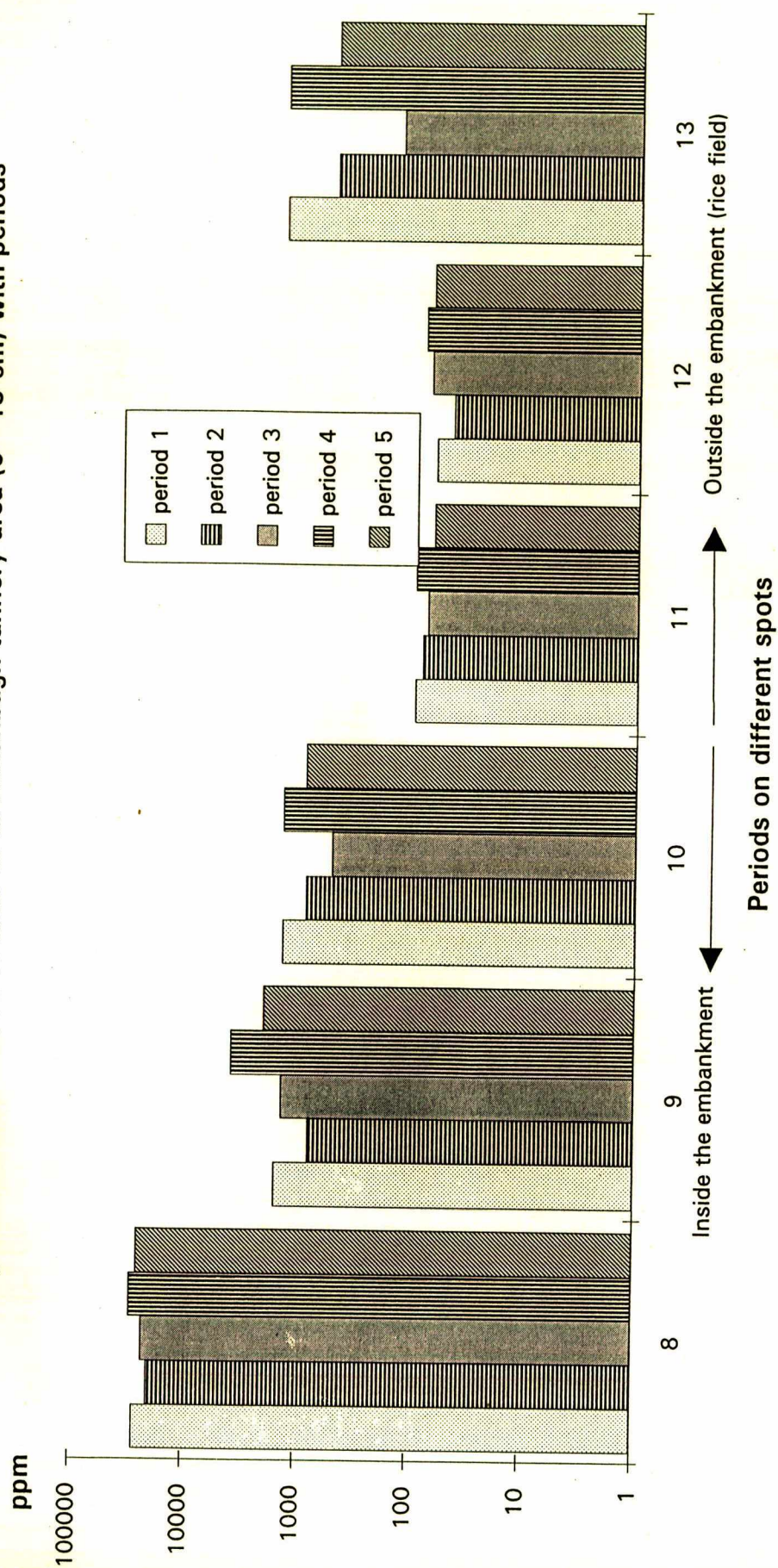


Figure B-2. Distribution of total Zn at Hazaribagh tannery area (0 - 15 cm) with periods

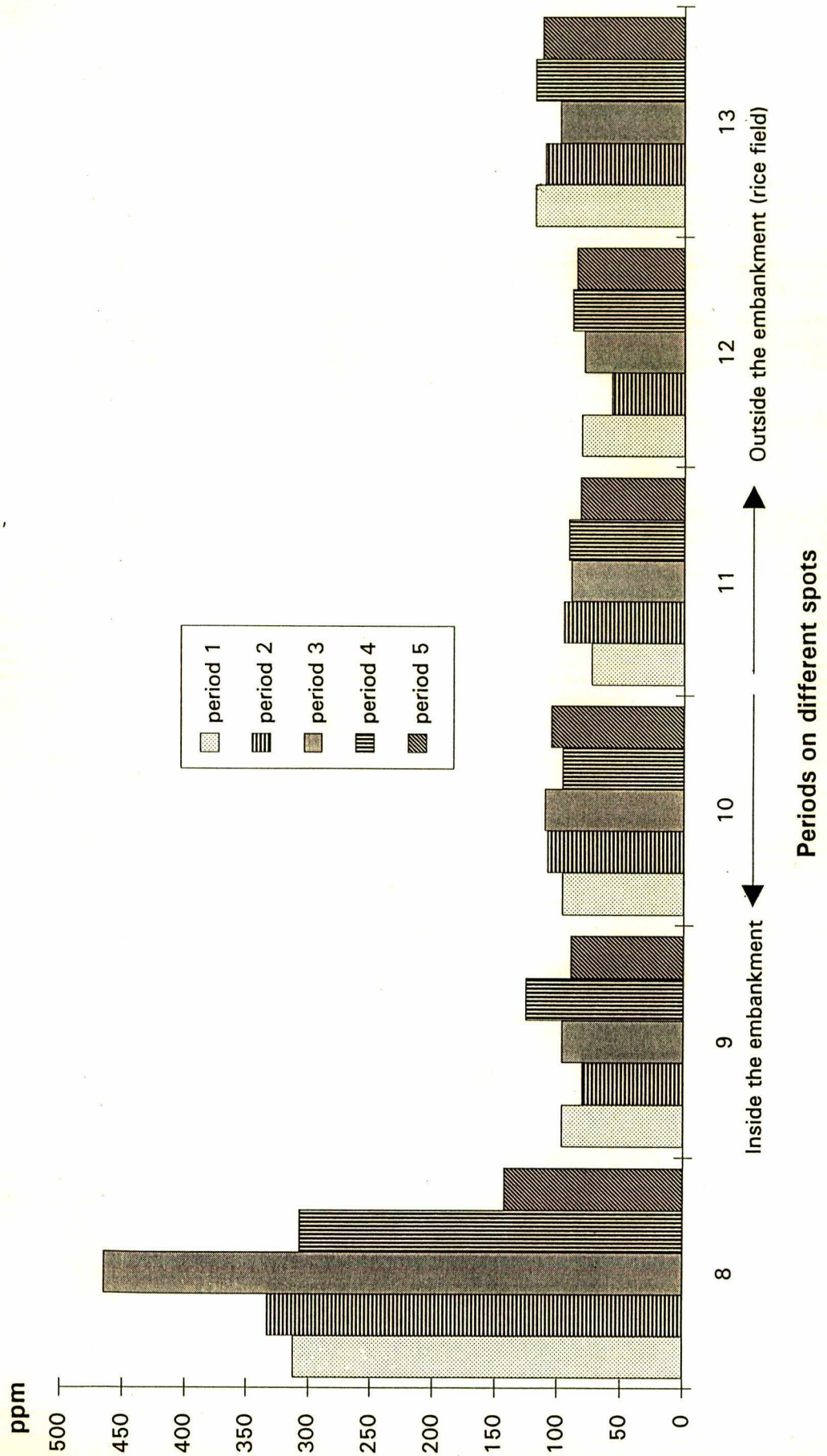


Figure B-3. Distribution of total Mn at Hazaribagh tannery area (0 - 15 cm) with periods

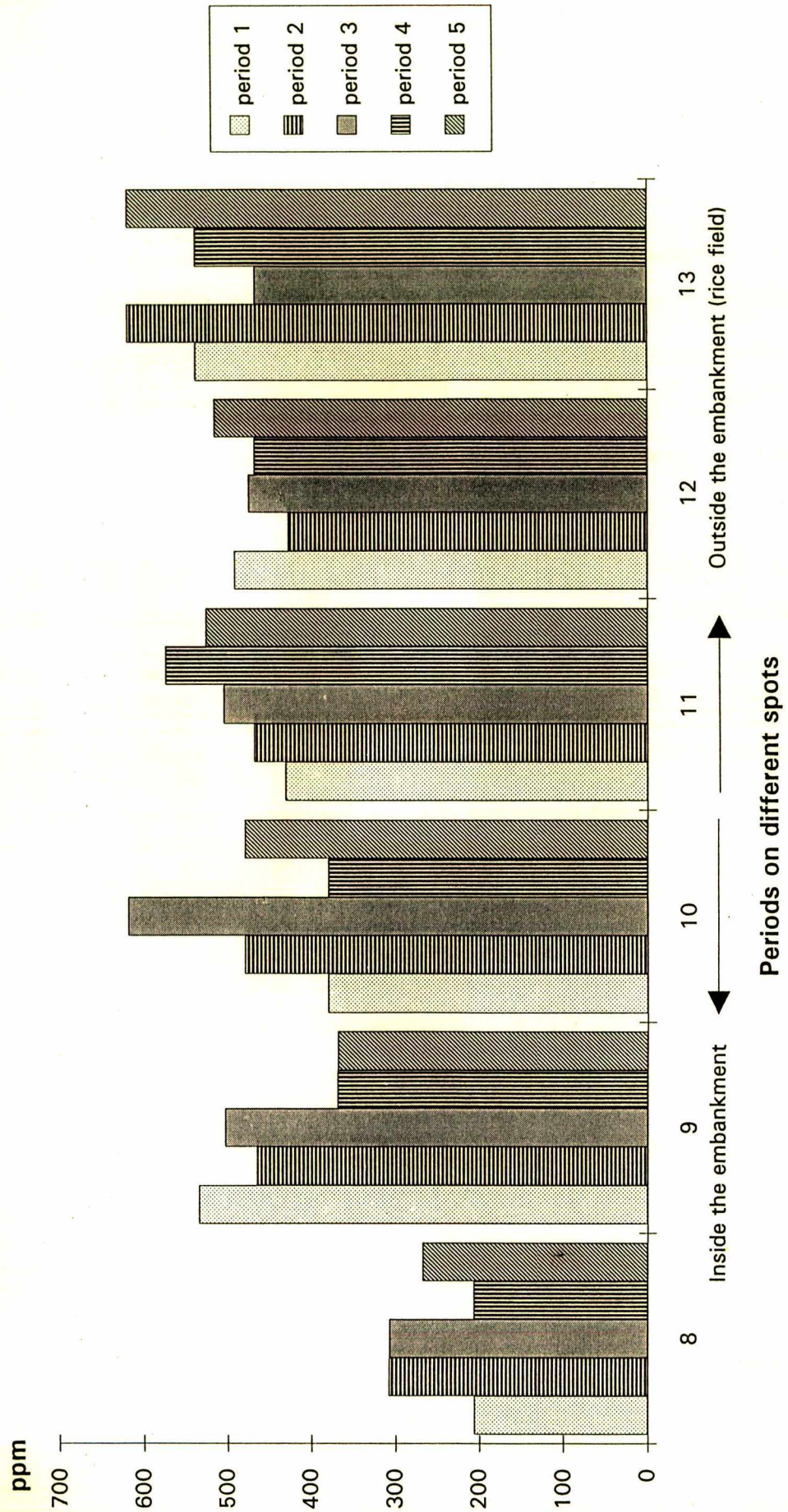


Figure B-4. Distribution of total As and Hg at Hazaribagh tannery area (0 - 15 cm) with periods

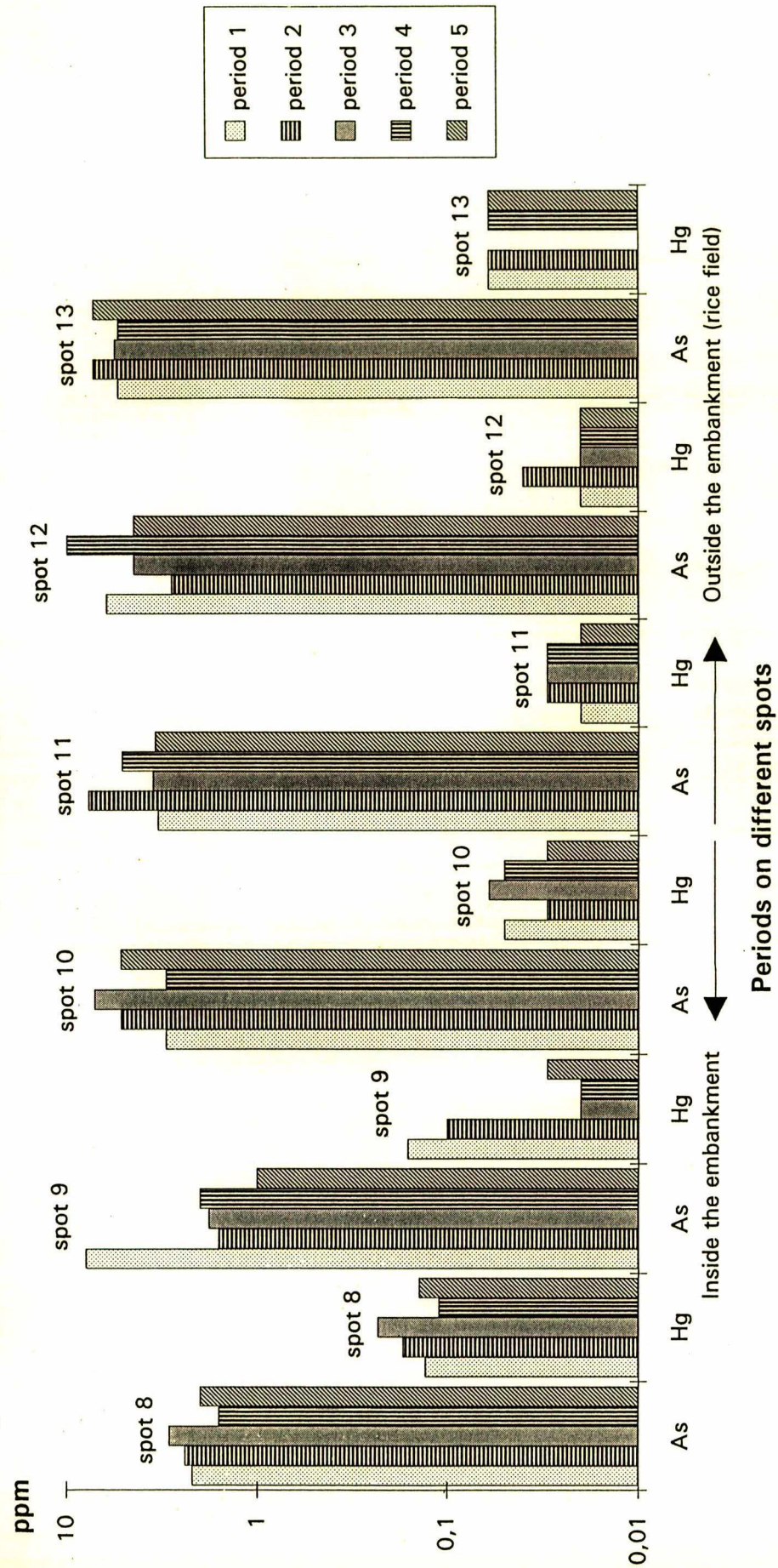


Figure B-5. Distribution of total Pb and Cu at Hazaribagh tannery area (0 - 15 cm) with periods

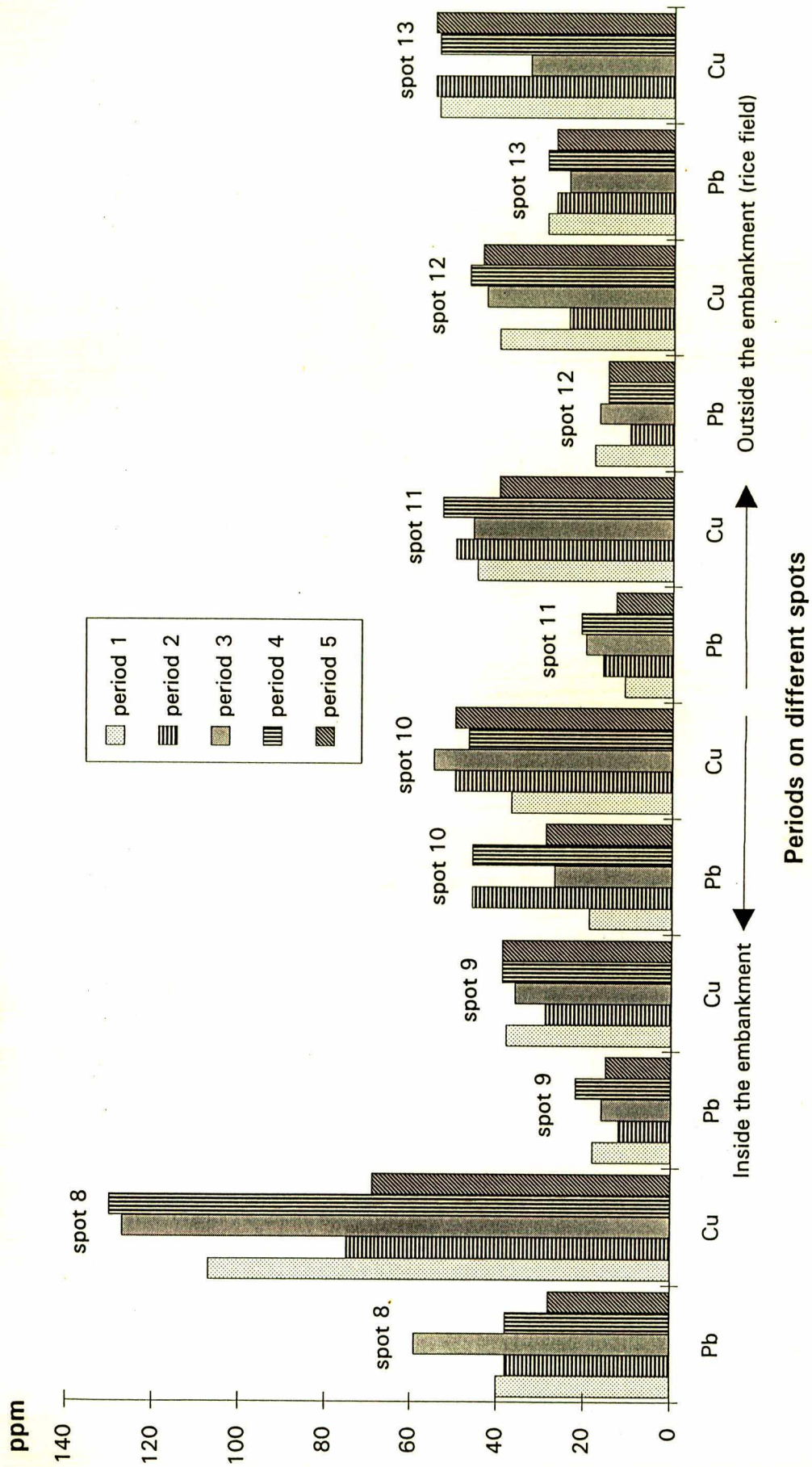


Figure B-6. Distribution of total Zn and Mn at Tongi industrial area (0 - 15 cm) with periods

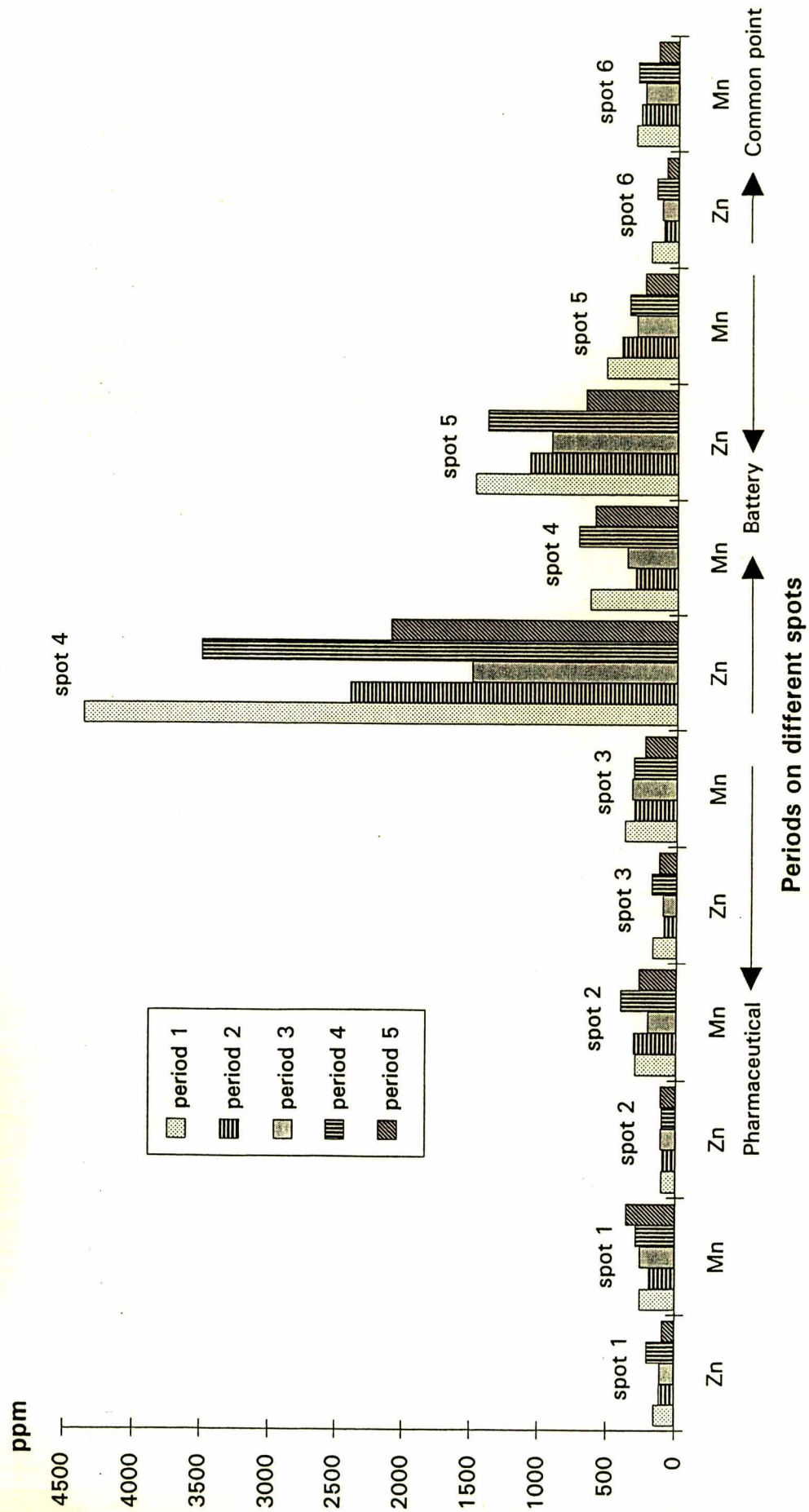


Figure B-7. Distribution of total Pb and Cu at Tongi industrial area (0 - 15 cm) with periods

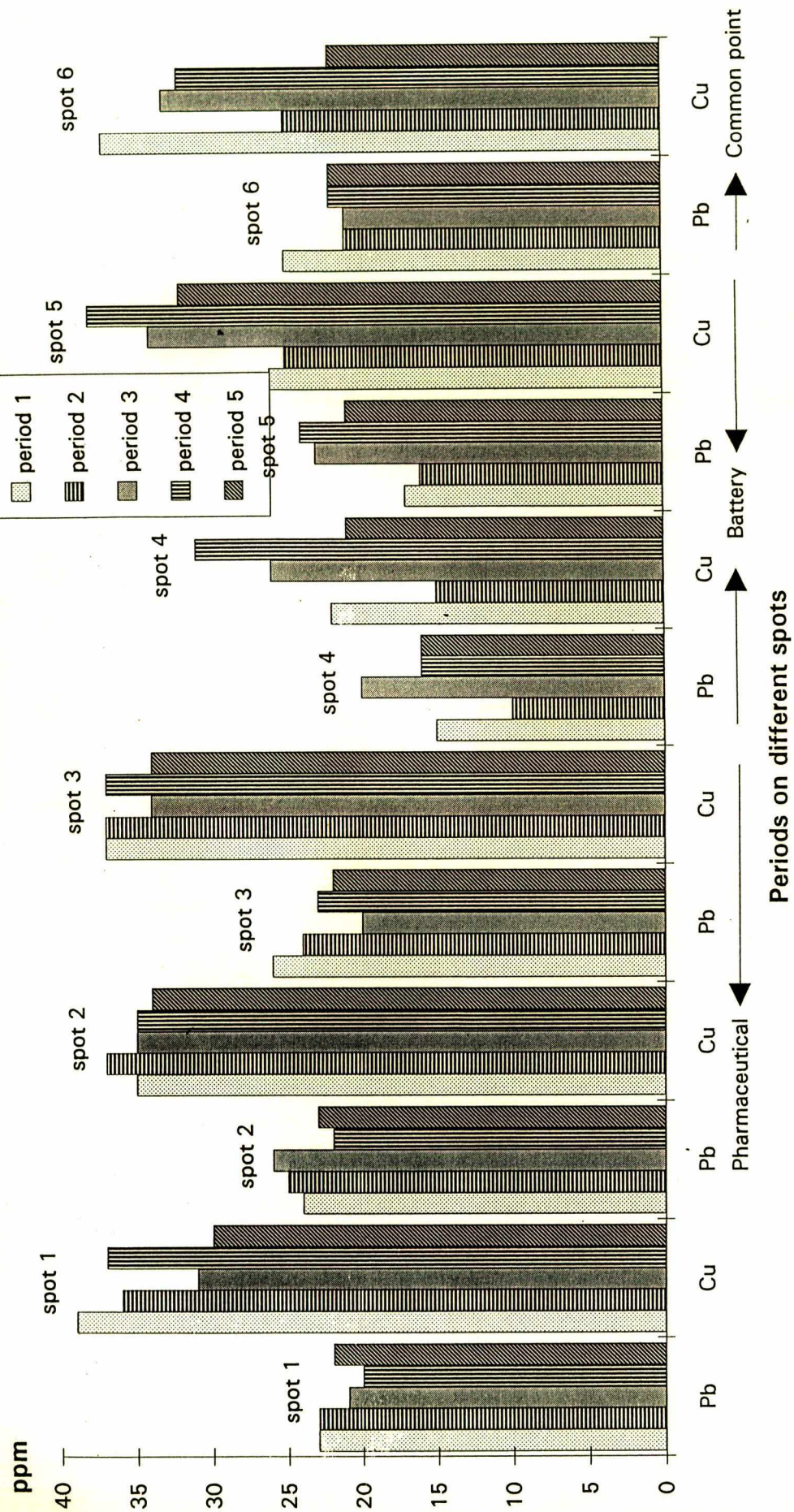


Figure B-8. Distribution of total As and Hg at Tongi industrial area (0 - 15 cm) with periods

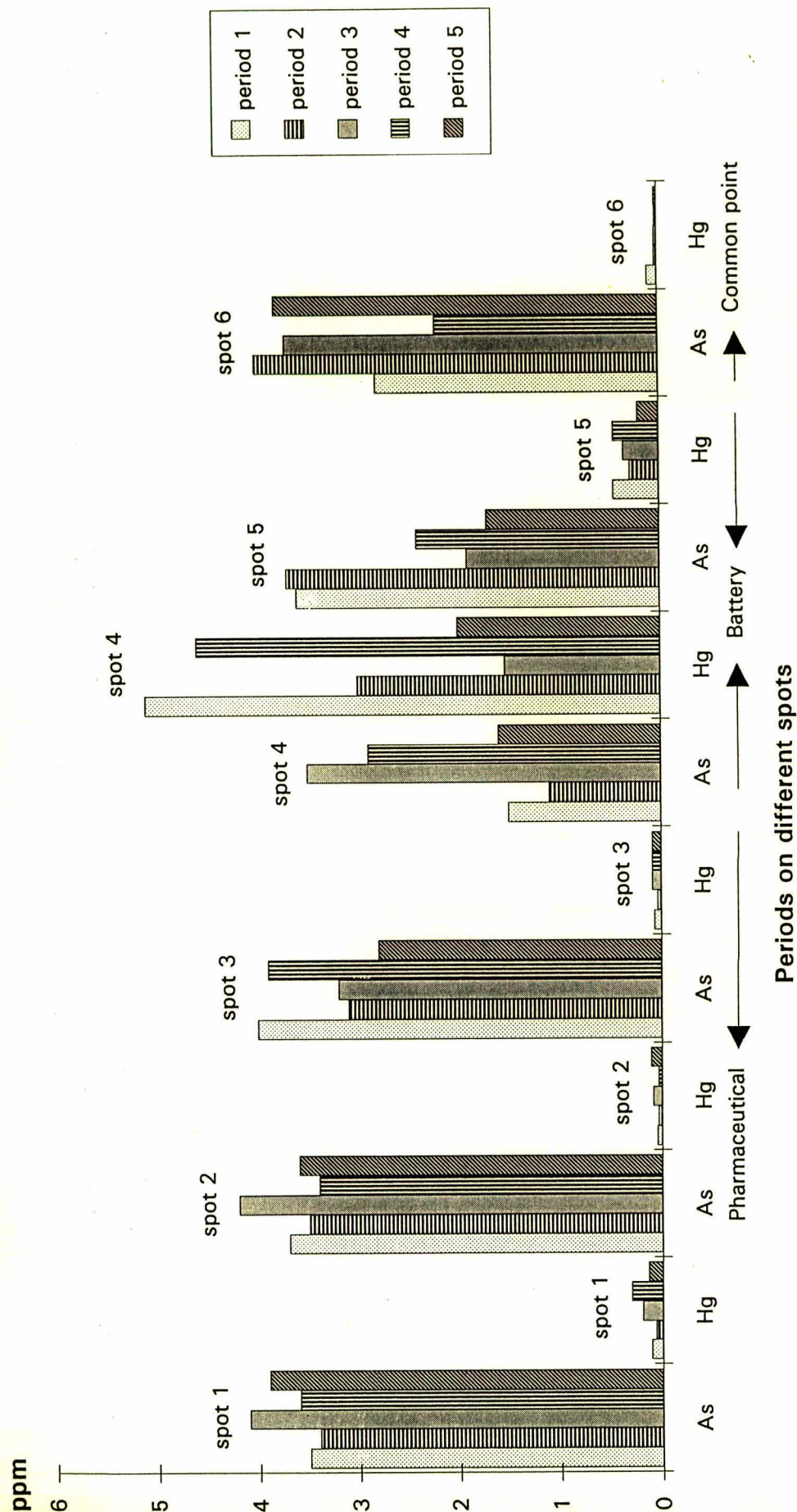


Figure B-9. Comparison of total Zn, Hg and Cd contents in top soil (0 - 15 cm) at Tongi battery site

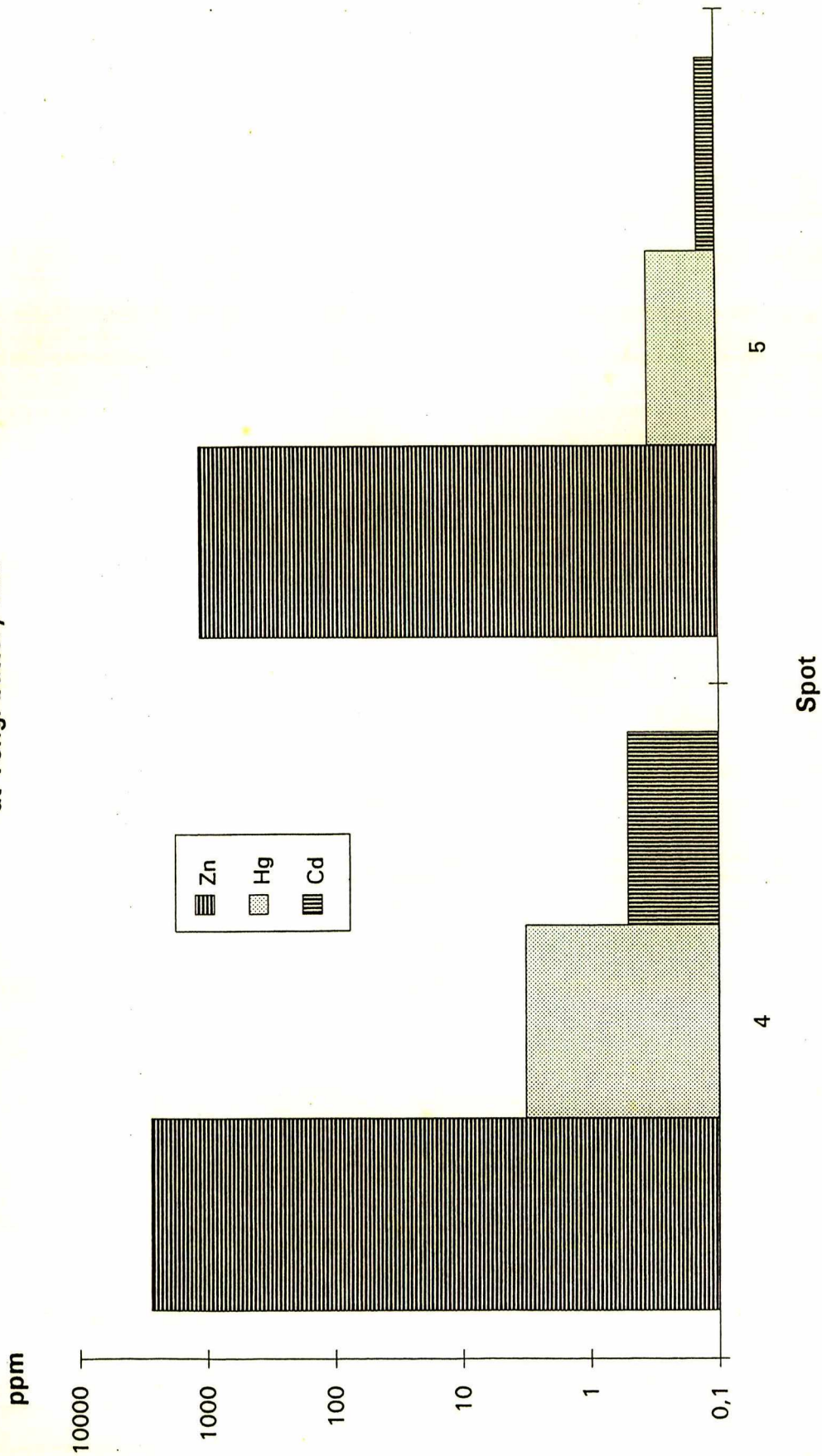


Figure B-10 Seasonal variation of Zn concentration**(Moon et al. 1991)**