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HEAVY METAL DISTRIBUTION IN MASSACHUSETTS SOILS

A Thesis Presented

by

JUDITH A. BARTOS

Submitted to the Graduate School of the
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Dedicated to the memory of my good friends, Kathy and Dick

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Words are our common means of expression, yet often the richness
of experience lies beyond their reach.
-Edward Hill-

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ABSTRACT

HEAVY METAL DISTRIBUTION IN MASSACHUSETTS SOILS

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Considerable variation exists within normal ranges of heavy metals in Massachusetts soils. This study provides a comprehensive data set of background levels of heavy metals in a statewide evaluation. Total and Toxicity Characteristic Leaching Procedure (TCLP)-extractable Pb, Cu, Ni, Cr, Mo, Zn and Cd were measured in sixty Massachusetts soils taken from four parent materials: glacial outwash, glacial till, glacio-lacustrine and floodplain. Individual soils were sampled at three depths generally corresponding to the A, B, and C horizons. Median total metal concentrations ($N=180$) were: Cu, 79 mg/kg; Pb, 46 mg/kg; Zn, 41 mg/kg; Cr, 40 mg/kg; Ni, 14 mg/kg; and Cd, 0.9 mg/kg. Mo concentrations approached method detections limits at a median value of 0.08 mg/kg. Metal abundances fell into different groups according to parent material ($N=45$), following a hierarchy of outwash<till<lacustrine<floodplain with all metals except for Mo. No trends were observed when the soils were grouped by horizon ($N=60$). Results of a two-way ANOVA on transformed log-normal data showed that parent material was statistically significant at the .01 level with all metals except for Mo ($p<.05$). The most distinctive trends with depth ($N=15$) occurred in the well-sorted materials, ie: metals increased with depth in lacustrine soils, decreased with depth in floodplains and were highest in the B horizons of outwash soils. Multiple stepwise regressions of all metals on measured chemical and physical soil properties yielded results of low significance. However, lacustrine soils resulted in the highest r^2 with respect to total metals, ranging between .50 and .80. Soil properties in themselves cannot explain a substantial amount of chemical variability at the selected scale of a statewide evaluation. This suggests that possibly the mineralogy of the parent material may contribute to the observed variation. Furthermore, the geogenic depositional environment of minerals containing heavy metals within these parent materials may have been selective. Low levels of TCLP extractable metals were often near method detection limits, and substantiates the inability of this procedure to extract metals present in uncontaminated soils.

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CHAPTER 1

INTRODUCTION

Heavy metals in unpolluted soils generally exist in trace amounts (Alloway, 1990) although common ranges for heavy metals up to 1,000 mg/kg can be found in soils. Lindsay (1979) reports the following ranges of metals: Cd (0.01-0.70 mg/kg); Cr (1-1,000 mg/kg); Cu (2-100 mg/kg); Mo (0.2-5 mg/kg); Ni (5-500 mg/kg); Pb (2-200 mg/kg); and Zn (10-300 mg/kg). Considerable variation exists within these normal ranges. The mineralogical and elemental composition of rock types and surficial deposits promote local concentration differences between soils as well (Plant and Raiswell, 1983). The availability of these metals is further modified by weathering, geochemical, and pedogenic processes occurring in the soil profile. As soil chemical conditions change, so does the speciation and subsequent release or retention of the metals (Sposito, 1983).

Anthropogenic sources, namely from industry, mining and smelting operations, and atmospheric emissions have contributed greatly to metal loading into the environment (Singh and Subramanian, 1984). It therefore becomes important to differentiate between naturally occurring and anthropogenic sources in light of regulatory concerns. Due to the expansive natural variability of metals in soils, background levels in soils need to be established so that these levels may be used to ascertain concentration limits at contaminated sites (Superfund Advisory Committee, 1990a). These quantitative data also expedite the site investigation process in assessing the impact of soil contaminants in soil and groundwater (USEPA, 1989).

In 1989, as part of the Massachusetts Code of Regulations, the Massachusetts Contingency Plan (MCP) was released, providing the public with a regulatory approach to deal with remediation of oil and hazardous materials (OHM). After three years, it was found that the efforts of remedial activities were actually hindered rather than enhanced through this process, mainly due to improper prioritization, disparate attentions, and lack of supportive staffing and finances (Hazardous Waste Committee, 1990). Effort was also made to require potentially responsible parties (PRP) into accepting more responsibility in cleanup (USEPA, 1990). The MCP has currently undergone an update, to streamline the risk assessment process by incorporating and clarifying additional site notification regulations and cleanup standards (Superfund Advisory Committee, 1990b).

The study described herein provides the regulatory and private sector with a comprehensive data set of information regarding background levels of selected metals in Massachusetts soils based primarily on differences in parent material. This study also addresses metal variability in relation to selected soil properties. Total metal concentrations were determined for Al, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, and Zn. Extraction of these metals also was performed using the Toxicity Characteristics Leachate Procedure (TCLP). Further investigations included analysis of selected soil properties that affect the speciation and available labile metals.

1.1 Objectives

The objective of this study was to establish baseline heavy metal levels through the determination of surface and subsurface concentrations in selected Massachusetts soils. An attempt was made to relate differences in concentrations to parent material and corresponding soil properties.

Specific Objectives are:

1) To determine total heavy metal concentrations by using a standard acid dissolution procedure.

2) To establish background levels from the data generated in this study to facilitate creation of a data base of heavy metal concentrations in 60 Massachusetts soils with regards to parent material.

3) To determine extractable heavy metal concentrations using the Toxicity Characteristic Leaching Procedure (TCLP).

4) To measure soil properties including pH, Fe and Al oxides, organic carbon, base cations, extractable acidity, CEC, and particle size, and

5) To perform multivariate analysis and analysis of variance to correlate heavy metal levels with selected soil properties. Those properties that may have predictive significance will be used in multiple stepwise regression.

CHAPTER 2

LITERATURE REVIEW OF REGULATIONS

2.1 Legislative Overview

Regulatory issues involving hazardous waste materials and management undergo periodic policy assessment in an attempt to modify applications of the regulation. Since the National Environmental Policy Act set up the Environmental Protection Agency in 1970, provisions of major laws have been enacted to remediate the threat of hazardous materials to public health. In the early seventies these laws had a general scope aimed at controlling the amount of toxic materials that were emitted into the environment. Since then, previous laws have been re-evaluated which specify quality standards of specific chemicals that are likely to damage health and environment. Additional legislation implements regulatory programs that are concerned with the complete chemical lifecycle in order to exert greater control in safe disposal (Worobec and Ordway, 1989). The following discussion will give a brief overview of the major laws concerning hazardous waste management: the term hazardous waste will be used in a generic sense, with heavy metals in mind.

2.1.1 Resource Conservation and Recovery Act

The Resource Conservation and Recovery Act (RCRA) became law in 1976. It was initially created with safe disposal and recycling of refuse in mind but it presently emphasizes regulations on hazardous waste (Subtitle C "Hazardous Waste Management"). RCRA began in 1965 as the Solid Waste Disposal Act. Prompted by Love Canal, new amendments in 1984 came into effect and further defined how these materials were to be treated, transported, stored and disposed of (Worobec and Ordway, 1989).

2.1.2 Subtitle C of RCRA, Title 40 CFR, Part 260, 261

RCRA mandates that EPA devise a list of materials that it considers to be hazardous. Chemical control provisions include Section 3001-3008 plus Subtitle 1. Crucial to Subtitle C is Section 3001. It directs EPA to list and provide identification, and characterize hazardous wastes needing management. According to regulations promulgated by EPA (40 CFR 260, 261) criteria for listing a hazardous waste are as follows:

If any (of these) material exhibits one or more of the following four characteristics it is considered a hazardous waste:

1. Ignitability (Section 261.21)
2. Corrosivity (Section 261.22)
3. Reactivity (Section 261.23)
4. EP Toxicity (261.24)

The first three characteristics broadly include physical and chemical criteria such as pH, flash point, compressed gas, oxidizing ability, susceptibility to violent reactions with water or other agents, and generation of toxic gases.

"A solid waste exhibits the characteristics of EP Toxicity if using the (EP Toxicity Test) methods used in Appendix 2 or equivalent methods... if the extract from a representative sample of the waste contains any of the contaminants listed in Table 2.1 at a concentration equal to or greater than the value given in that table" (40 CFR 261). RCRA defines material as "hazardous" when this material possesses characteristics that would be harmful to health or environment if improperly managed. A dichotomous approach is taken in Section 3001 when describing a hazardous waste where *i)* identification of a waste is made from established lists, or *ii)* by means of a characteristic (USEPA 51 FR 21650, 1986). The former devises lists after toxic compounds are identified as being primary constituents in the waste being studied. The latter approach analyzes chemical and physical properties of the material that can potentially cause harm. This does not imply that materials lacking a characteristic are not hazardous nor safe for disposal even if concentrations are within regulatory levels (USEPA 51 FR 21650, 1986).

Maximum regulatory threshold levels are usually determined using a groundwater transport model addressing dilution/attenuation factors for specific compounds (USEPA, 1989). Specifically, chronic toxicity levels are initially declared as they pertain to acceptable levels in drinking water. These values are then combined with a transport equation that estimates the amount of attenuation and dilution that would occur as a function of distance (USEPA 51 FR 21650, 1986). The standard test procedures, EP Toxicity and TCLP, are leachate extraction tests initially designed as pass-fail extraction tests used on solid waste to determine concentrations of hazardous materials. They are also often used (RCRA-EPA) to establish soil cleanup levels at Superfund sites under the National Contingency Plan. Both procedures can help determine the amount of soluble material that might potentially leach down to the groundwater at contaminated sites. Listed in 40 CFR Part 261.24 are maximum concentration values for eight metals, four pesticides and two herbicides (Table 2.1). Through an ordinance by Congress, EPA developed the TCLP to expand the amount of hazardous materials listed in 40 CFR 261.24 from 14 to 52 (USEPA, 1989). The expanded list (Table 2.2) is composed of additional contaminants that include 20 volatile organics, 16 semi-volatile organics and two pesticides. Drinking water quality standards use a generic application of a 100 x dilution of EP Toxicity values (Table 2.3).

The conceptual and methodological differences between TCLP and the EP Toxicity procedures are slight. One difference is that a zero headspace extraction vessel is used with the TCLP in order to facilitate analysis of volatile organics. For this study, either procedure would be an appropriate method for heavy metal analysis. The TCLP was employed since it is now the conventional standard used by EPA.

2.1.3 Comprehensive Environmental Response, Compensation, and Liability Act

In response to releases of hazardous wastes into the environment, the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) was enacted with major amendments in the Superfund Amendments Reauthorization Act (SARA) made in 1986. CERCLA responds to authorized cleanup and identification of hazardous substances released while also establishing a trust fund to cover some

Table 2.1 Maximum concentration of contaminants for characteristic of EP Toxicity (40 CFR 261.24).

EPA Hazardous Waste Number	Contaminant	Regulatory Level (mg/L)
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0
D012	Endrin	0.02
D013	Lindane	0.4
D014	Methoxychlor	10.0
D015	Toxaphene	0.5
D016	2,4-D	10.0
D017	2,4,5-TP	1.0

Table 2.2 Extended EPA list for TCLP contaminants (51 FR 21648).

EPA Hazardous Waste Number	Contaminant	Regulatory Levels (mg/L)
D018	Acrylonitrile	5.0
D004	Arsenic	5.0
D005	Barium	100.0
D019	Benzene	0.07
D020	Bis (2-chloroethyl) ether	0.05
D006	Cadmium	1.0
D021	Carbon disulfide	14.4
D022	Carbon tetrachloride	0.07
D023	Chlordane	0.03
D024	Chlorobenzene	1.4
D025	Chloroform	0.07
D007	Chromium	5.0
D026	o-Cresol	10.0
D027	m-Cresol	10.0
D028	p-Cresol	10.0
D016	2,4-D	1.4
D029	1,2-Dichlorobenzene	4.3
D030	1,4-Dichlorobenzene	10.8
D031	1,2-Dichloroethane	0.40
D032	1,1-Dichloroethylene	0.1
D033	2,4-Dinitrotoluene	0.13
D012	Endrin	0.003
D034	Heptachlor (and hydroxide)	0.001
D035	Hexachlorobenzene	0.13
D036	Hexachlorobutadiene	0.72
D037	Hexachloroethane	4.3
D038	Isobutanol	36.0
D008	Lead	5.0
D013	Lindane	0.06
D009	Mercury	0.2
D014	Methoxychlor	1.4
D039	Methylene chloride	8.6
D040	Methyl ethyl ketone	7.2
D041	Nitrobenzene	0.13
D042	Pentachlorophenol	3.6
D043	Phenol	14.4
D044	Pyridine	5.0
D010	Selenium	1.0
D011	Silver	5.0
D045	1,1,1,2-Tetrachloroethane	10.0
D046	1,1,2,2-Tetrachloroethane	1.3
D047	Tetrachloroethane	0.1
D048	2,3,4,6-Tetrachlorophenol	1.5
D049	Toluene	14.4
D015	Toxaphene	0.07
D050	1,1,1-Trichloroethane	30.0
D051	1,1,2-Trichloroethane	1.2
D052	Trichloroethylene	0.07
D053	2,4,5-Trichlorophenol	5.8
D054	2,4,6-Trichlorophenol	0.3
D017	2,4,5-TP(Silvex)	0.14
D055	Vinyl chloride	0.05

Table 2.3 Groundwater quality criteria (314 CMR 6.06).

Contaminant	Maximum Contaminant Level (mg/L)
Arsenic	0.05
Barium	1.0
Cadmium	0.01
Chromium	0.05
Copper	1.0
Fluoride	2.4
Iron	0.3
Lead	0.05
Manganese	0.05
Mercury	0.002
Nitrate	10.0
Total trihalomethanes	0.1
Selenium	0.01
Silver	0.05
Sulfate	250.0
Zinc	5.0
Endrin	0.0002
Lindane	0.004
Methoxychlor	0.1
Toxaphene	0.005
Chlorophenoxys	0.1

costs of cleanup. EPA is also given authority to impose cost recovery to those responsible for the contamination.

The National Contingency Plan is a major provision under the Superfund law that offers a prototype for the federal government to respond to various types of discharge into the environment. Policy in 40 CFR, 300 formulates regulations pertaining to discharges into waters and old abandoned waste sites. Three types of responses exist for those sites put on the National Priorities List by EPA: immediate removal, planned removal, and remedial action. Sites put on this list are eligible for Superfund monies.

2.1.4 Massachusetts Contingency Plan

Massachusetts Contingency Plan (MCP) regulations are promulgated by DEP according to Massachusetts General Laws (MGL) chapter 21E. It describes roles and responsibilities of DEP pertaining to the discovery, release, threats of release of oil and hazardous materials (OHM) and strategies to protect the health of the general public, complementing the National Contingency Plan. The MCP provides a list of OHM, procedures and regulations for notifying DEP of a release and assessing the extent of a release, procedures and regulations for involvement of potentially responsible people and procedures for recovery costs incurred by DEP in response to releases. DEP has full authorization regarding response actions. Subpart C of the MCP includes Notification Regulations for Releases of OHM, and Identification and Listings of OHM. The criteria for listing OHM and determining their characteristics parallel the federal plan (Jessup, 1988).

Parts of this study may be used to establish Reportable Concentrations (RC). The state, based on previous work generated out of the UMass Soil Characterization Laboratory (Veneman, 1985), has established background levels for Ni, Pb, Zn, and Cr using 33 datapoints. These levels are taken across all parent materials at all depths at which background is determined at the 95th percentile along a cumulative frequency curve. The study reported herein refined the 1985 data by grouping different surficial deposits with depth (A, B, and C horizons). In RC derivation, background levels are only one part of the final RC value. The flowchart in Fig. 2.1 explains that there are four components. The first component, *Health-based Soil Concentration*, is a value that combines such parameters as soil ingestion rates, average daily soil dermal contact rate, oral cancer potency factor, soil ingestion rate normalized to body weight, and relative absorption factors. The second component, *Upper Concentration Limit*, is a value based on experience and best professional judgement with large scale releases in mind. The *Quantitation Limit* is the lowest analytical concentration that can be reliably measured, usually just above detection limits. This study contributes to the fourth component, *Soil Background Concentrations*. These RC's are risk-based concentration values below which adverse impacts or health risks are unlikely. RC's are used early in the *risk assessment* process. They can provide a point for analytical data; if any environmental concentration exceeds the RC, then notification is required. The MCP has recently been revised to streamline the risk assessment process. The lack of finances and cohesive effort towards the common goals of site remediation has shown a deterioration in the present system. One of the major concerns is that the policy allows for the inclusion of even the most minimally contaminated sites that pose little risk (Hazardous Waste Committee, 1990).

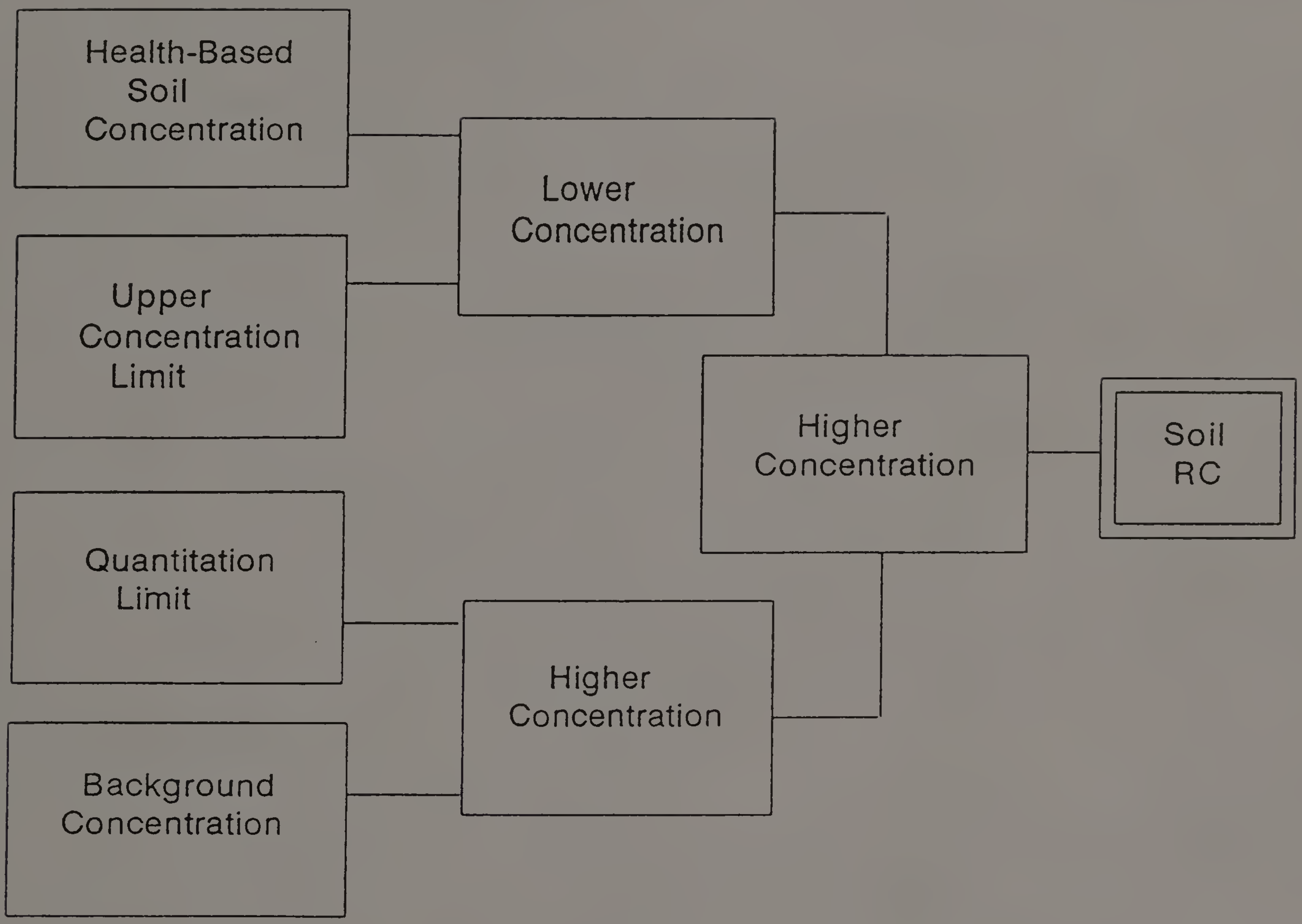


Figure 2.1 Flowchart of RC derivation.

These improperly prioritized sites become involved in the entire four phase plan leading to a misuse of time and money. DEP is also concerned with the burden imposed upon the agency in regards to cleanup responsibility. DEP has attempted to divert much of the responsibility to potentially responsible parties in the private sector in order to remove superfluous cost and effort on the part of the state (Waste Site Cleanup Program Advisory Committee, 1991).

Some specific changes to the MCP include a 2- tier classification system which consists of a numerical ranking system characterizing sites based on potential threat and complexity. This is also an attempt for DEP to pass on responsibility to the private sector and lessening the need for oversight, eliminating backlog and minimizing sites that get involved in the whole MCP process. Tier I sites require some oversight for response actions. These sites pose more health risks and are more complicated than the Tier II sites, which do not require any oversight by DEP (except by audit). Classification is site-specific and incorporates soil, groundwater, surface water and air as environmental media. A Compliance Audit Program has also been initiated to ensure the public and DEP that MCP and 21E compliances are met and that cleanups are appropriately addressed without DEP oversight. This program requires that DEP audit 25% of all sites per year with an annual compliance assurance fee. A combined random and target approach is used in selecting sites and response actions to be audited. Non-compliance is enforced by penalties or referrals to the Attorney General. Critical to these new amendments is the Licensed Site Professional (LSP), who oversees and manages the initial classification of sites and also coordinates response actions. The LSP expedites assessment and cleanup to enable the private sector to deal with more sites in a timely fashion while also holding them accountable for the quality of the work involved with the response action. The LSP also ensures that adequate cleanup is occurring and that it is relevant to the site and not the PRP budget.

CHAPTER 3

LITERATURE REVIEW OF HEAVY METALS AND SOIL PROPERTIES

3.1 Trace Metal Distribution and Their Natural Occurrence in Geologic Material

Heavy metal distribution in geologic material varies substantially with respect to mineralogical differences in rock types. Initially, during crystallization of igneous rock, these trace metals coalesce by isomorphic substitution into the ionic structure of primary minerals where they later become available through geochemical and pedogenic alterations (Alloway, 1990). When isomorphic substitution takes place, usually an ion of the same size will exchange with another in the crystal structure. Plant and Raiswell (1983) indicate that electronegativity and crystal field stabilization energies are also influential during substitution such that Cr, Co, Ni, Cu, and Zn will replace Mg and Fe, and Pb will replace K. The availability of these trace metals in igneous rock further depends on the stability of the existing minerals. For example Co, Cu, Mn, Ni, and Zn will be released in easily weathered minerals such as olivines and hornblendes. Sedimentary rock consists of weathered and re-transported primary minerals as well as secondarily formed minerals of aluminosilicates, carbonates and oxides of iron and manganese all having undergone lithification. Alloway (1990) states that 75% of exposed surface rocks are sedimentary which are an important source for soil parent material. The abundance of heavy metals is dependent upon the matrix of sedimentary (and metamorphic) rock. Shales, and schists inherently have high amounts of trace metals since these rocks are formed along with a substantial percentage of organic matter that will sorb metal ions (Singh and Subramanian, 1984). This organic matter also provides a substrate for microorganisms that reduce existing sulfates. Metals will then precipitate and complex with available sulfides. Generally, basic, ultrabasic igneous and fine-grained sedimentary rock contain the highest amounts of heavy metals and these metals often occur in associations (Haque and Subramanian, 1982; Plant and Raiswell, 1983). Sandstones are low in heavy metals since the mineralogy consists of inert quartz that weathers slowly. Acid igneous rocks and carbonates are naturally deficient in metals (Alloway, 1990).

Concentrations of naturally occurring trace metals found in soils then, are highly dependent upon the parent material derived from the pre-existing rock types. In Massachusetts, most parent materials are only transported over short distances (Bodine, 1986), and one may assume most soils have the same general composition as the parent materials (Haque and Subramanian, 1982). If the natural concentration levels remain low in parent material, then the soils will most likely contain low amounts as well. However, metal distribution within a local area can vary substantially. Several studies involving till deposits and glacier movement indicate that dispersal patterns of metals do occur. Rencz and Shilts (1980) found that high nickel concentrations occurred up-ice and gradually became diluted with distance. These dispersal trains often cover an area that includes several drainage basins. Shilts (1973) also investigated trace element dispersal in tills of southeastern Quebec to characterize glacial flow and found distinct southeasterly bands of high metal concentrations that had moved from an initial ultrabasic rock source. Rencz and Shilts (1980) additionally found that unlikely metal associations (such as chromium-uranium-zinc) exist in till since the glacier may erode several different outcrops that include a variety of acid and ultrabasic rocks. Distribution and concentrations of metals in alluvial soils even within the profile can be extremely varied since deposition occurs in short time intervals with apparent source changes (as opposed to slower continuous deposition of lacustrine environments). Alluvium happens to be extremely susceptible to point source metal pollution due to the expeditious aquatic avenue and can be used to provide contaminant records (Mueller *et al.*, 1989).

3.2 Geochemical and Pedogenic Influences on Metal Availability

Although the mineralogy inherent in soil parent material dictates relative abundance, the labile pool of heavy metals is created by certain geochemical processes that further modify the reactive constituents of the soil and existing rock fragments. As environmental factors controlling soil chemical conditions change, so does metal speciation and their subsequent release or retention. Much attention is focused on soil properties and their effect on metal retention (Forstner, 1981; Sposito, 1983; McGrath and Smith, 1990, Davies, 1990). Most investigations of metal transport in soils and possible groundwater contamination is directed towards understanding adsorption processes that are controlled mainly by redox and pH conditions, organic matter, Fe/Mn oxides, and clay constituents.

3.3 Organic Matter and pH

Although pH is highly influential in dissolution and precipitation reactions of metal species it also critical in controlling adsorption mechanisms. Elliot *et al.* (1986) investigated the effects of organic matter and pH-dependent adsorption. Their study concluded that noticeable trends occur with changing pH conditions but that adsorption differs substantially with each metal. Hierarchal sorption orders among the metals were established. Other studies have reinforced this phenomenon (Biddapa *et al.*, 1981; King, 1988), while some are contrary (Berish and Ragsdale, 1986). It appears that qualitative adsorption sequences may vary due to soil constituents possessing specific sorbing qualities. Adsorption processes are also dependent on ambient concentrations of competing metals as well as particulate and colloidal organic matter (Jenne, 1968). Elliot *et al.* (1986) concluded that adsorption of metals was enhanced by an affinity for organic ligands rather than a cationic exchange of organic matter or clays. It is found that fulvic acids have high stability constants when associated with metals. King (1988) studied the effects of pH, clay, Fe and Mn oxides, CEC, and organic matter on sorbed and nonexchangeable metals in the southwestern U.S. Although pH and organic matter was important in the amount of metals sorbed at particular depths, he concluded that Fe oxides and clay content were the critical properties. He also concluded that the calcium carbonate prevalent in southwestern soils controlled pH effects more than its ability to sorb. Miller *et al.* (1983) performed laboratory experiments on sandy soils in Indiana. These soils were highly permeable with little clay. They observed little leaching of added metals indicating that organic matter within the upper few centimeters was responsible for most of the sorption.

Additionally, under controlled neutral pH conditions a majority of the metals existed as co-precipitates with hydroxides and carbonates. A decrease in pH did not appear to substantially affect metal redistribution within the profile. On the other hand, Anderson and Christensen (1988) performed batch adsorption experiments on 38 different soils and found that pH was the prevailing agent in controlling the distribution of metals providing that concentrations remained low. Tyler (1978) claimed that metal solubility did not become significant until a pH of 3 was reached.

3.4 Soil Redox Conditions

Soil redox conditions highly influence chemical reactions taking place in the soil profile. Redox potential is the thermodynamic equilibrium of free-electron activity in aqueous solutions and is commonly represented as *i)* pE: the ability to accept or donate electrons calculated as the negative log of electron activity, or *ii)* Eh: the electrical potential difference when measured between a platinum and standard hydrogen electrode. If the soil is highly reduced, donation of electrons increase and activity is large and so pE/Eh values will be low. High pE/Eh values indicate oxidizing conditions with comparatively smaller electron activity. Since pH is the negative log of hydrogen activity (protons) it then conversely relates to redox conditions in the soil. Stumm and Morgan (1981) give an excellent review of the relationship between Eh and pH. Redox reactions remain relatively slow and they are catalyzed by the presence of organic matter where microbial activity increases electron activity by reduction of the organic matter (Ponnamperuma, 1972). Sposito (1983) describes two ways in which metal chemistry is affected by redox status: the change in oxidation state of only the metal or by a ligand complex that may bond with a metal. Many analytical determinations of metals consider total concentrations. These data need to be interpreted cautiously since total metals do not necessarily indicate toxicity or availability in themselves. Sposito (1983) claims that the chemical form and species of the metal is of primary importance in determining availability as compared to total concentrations. This fact is reiterated through several studies and that redox status is a primary influence (Jenne, 1968; Clevenger, 1990).

3.5 Soil Texture - The Clay Fraction

Particle size distribution and the reactive clay fraction are extremely important in metal concentration determination, especially when establishing natural background levels (Shilts, 1973; Forstner, 1983). The presence of clays tends to bias those sediments that have a wide range in particle size. The transport of colloidal clays that migrate through surface and subsurface systems would then be critical. Forstner (1983) described a high preference of metals for the clay fraction over the coarse grains in Rhine River alluvium. He proposed a method of correction to reduce the effects of smaller grain size on samples by separation and employing an extrapolation method. Specific surface of grains in some instances, was also taken into consideration. Esser *et al.* (1991) calculated an enrichment factor with respect to particle-size distribution to correct for possible concentration bias in the smaller size fraction. Pitt *et al.* (1986) and Clevenger (1990) characterized overburden/spoil materials and mine tailings, respectively. Their results showed that fine-grained fractions were responsible for elevated concentrations. Different metals had different preferences for the clays in the various environments.

3.6 Hydrous Iron and Manganese Oxides

Alloway (1990), Forstner (1983), Haque and Subramanian (1982) and Jenne (1968) all recognized the significance of iron and manganese oxides and hydroxides as complexing agents of heavy metals. Iron and manganese when in thermodynamically unstable forms, will form insoluble compounds of oxides and hydroxides in aqueous soil solutions. Stumm and Morgan (1981) state that hydroxides have the greatest attraction to Fe (III) over most other elements. In a classic paper, Jenne (1968) postulates that Fe and Mn oxides are the predominant factor in metal fixation. These oxides are pervasive in soil systems and form by *i)* precipitating out of an existing grain, or *ii)* surrounding a nucleus of a negatively charged clay mineral, and can exist as amorphous or well-crystalline coatings. System pH (and thus Eh) as well as the zero point of charge will affect Fe/Mn oxide chemistry such that positively charged species occur in acid conditions, negatively charged in alkaline solutions, and anionic or cationic behavior near neutral conditions. Likewise, the surface charge will be negative and positive when solution pH is above or below the mineral zero point of charge, respectively. The low solubility of these oxides in combination with their large specific surface area (up to 300 m^2/g) makes them extremely influential in metal sorption (Singh and Subramanian, 1984).

Hickey and Kittrick (1984) partitioned heavy metals to find which soil property dominated the sorbing process in soils. They found that half of the analyzed trace metals were predominantly associated with the Fe/Mn oxide fraction. This oxide fraction still contributed greatly to sorbing other metals although not as significant. Sediment chemistry has been investigated by several researchers. Martin and Whitfield (1981) found that the majority of heavy metals were associated with the sediment in alluvial systems rather than in the dissolved state. This further indicates sediments are not only a major sink for metals but that metal species exist in the solid phase during transport. Subramanian (1976) and Murty *et al.* (1980) found proportional relationships between the amount of iron and manganese and heavy metals in marine and alluvial sediments. Sediments in aquatic systems can be used as a pollution index (Mueller *et al.* 1989). Robinson (1981), Chao and Theobold (1976), and Aston and Chester (1973) further stressed the importance of hydrous oxides of iron and manganese in trace metal adsorption.

3.7 Sorption Mechanisms and Transport Phenomena

The context in which sorption will be described in this study will focus on partitioning of ions from the liquid phase to a solid surface with emphasis on metal cations but is also relevant to any lyophobic or hydrophilic substance.

3.7.1 Types of Sorption

Ion exchange mechanisms depend on establishing electroneutrality between negative surface charges on anionic minerals, and colloids and cationic metals. The diffuse double layer keeps additional cations near this region at a particular distance, and so controls the amount of cations that can be held by electrostatic bonds (Bohn *et al.*, 1979). Desorption can also take place and in this sense competition exists that is dependent on cation concentration. Usually, valency and degree of hydration will determine selectivity at the exchange site: cations with a higher valency and small hydration sphere are exchanged more easily. The exchange fraction then, will include metals that are weakly sorbed, mostly through van der Waals forces.

Specific adsorption is characterized by covalent bonding of metals to organic and mineral ligands, and hydroxide complexation with iron, aluminum, and manganese (Alloway, 1990). Therefore, with Fe and Mn oxides in mind, this mechanism is very dependent on acid or alkaline conditions. The pK values of hydrolysis reactions remain critical to metal behavior. Lower pK values increase specific adsorption phenomena. In some cases, metals can actually diffuse into the lattice structure of some minerals and Al/Mn oxides. Specific adsorption possesses a range in bonding strengths from high energy chemical adsorption to low energy physical adsorption occurring at low temperatures (Weber, 1972).

Co-precipitation is described as being the concurrent precipitation of metals or elements resulting in a mixed solid. Any mechanism may be involved. Replacement of elements or compounds may occur at the surface of solids where, for example, Cd may replace Ca in calcite in supersaturated conditions. Or, simultaneous precipitation can occur when a metal sorbs to precipitating Fe/Mn oxides from soil water. Co-precipitation would also include the incorporation of metal compounds into other minerals (i.e. CuS inclusion within silicates).

Metals may also chelate with organic ligands, specifically forming coordination complexes with reactive carboxyl groups that are prevalent in humic and fulvic compounds. Metal transition ions have high stability constants with organic ligands since they are better able to configure their electrons than other elements (Forstner, 1983).

3.8 Distribution Coefficients and Sorption Isotherms

Heavy metals can be dissolved, complexed with organic ligands, and sorbed or occluded into primary minerals and secondary structures such as aluminosilicates or carbonates. Sequential extraction can establish an association of metals with sorption mechanisms on solid surfaces and thus enumerate which soil constituents control sorption. But which phase actually controls metal distribution? The mobility of metals can be further quantified by obtaining partition coefficients (Kd). High Kd values mean that the metal is preferentially retained on the particle surface while low Kd's indicate greater concentration of metal in solution, thus an increase in transport capabilities. Some sorption studies found nonlinear relationships with the Langmuir model (Harter, 1984) that are most likely due to variable bonding energies associated with sorbing sites (Benjamin and Lecke, 1981). Critical to sorption isotherms is the use of low concentrations during equilibration of soil and solution (Hendrickson and Corey, 1981; Anderson and Christensen, 1988). It was found that excessive competition for sites exist and unreliable results are obtained when high concentrations are used.

Extensive research has been directed towards understanding and obtaining sorption information and partitioning between solutes and soil particles. Much of the information gained from distribution coefficients is used in fate and transport models for remedial actions in hazardous waste cleanup sites to determine potential migration of contaminants in soil systems (USEPA, 1989). Some work has been done in Massachusetts in regards to this. Tirsch (1976) studied the partitioning of Cu and Cd in six Massachusetts soils with a special emphasis on land applications of wastewater. He investigated Cu and Cd removal from solution by changing ionic strengths and varying pH. The soils studied were variations of floodplain soils (Hadley, Winooski, and Limerick), and an outwash (Windsor) and till (Cheshire) soil. A very comprehensive study was made by Tirsch and Jennings (1978) on attenuation type breakthrough curves and characterization of numerous chemical constituents found in leachate at a landfill in Barre, MA. Two soils were used for the breakthrough curves, a clay and a sand that were representative of the soil at the landfill site (series never recognized). The only heavy metals characterized by this study were Cu and Zn.

3.9 Anthropogenic Effects: Point and Non-Point Sources

Many of the metal concentrations found in soil probably can be attributed to anthropogenic sources (Haque and Subramanian, 1982; Forstner, 1983; Friedland and Johnson, 1985; Ramade, 1989). Point and non-point sources of contaminants are introduced into soil and water systems as waste generated by industry, through atmospheric deposition, and by mining and smelting operations (Davies, 1983; Alloway, 1990). Davies (1983) states that many mined metals subsequently become part of the labile fraction after they have been exposed to the surface. Usually, during the mining process, the untreated mine tailings are left as exposed spoil heaps subject to weathering and dissolution (Clevenger, 1990). This does not necessarily mean that mine tailings will always give rise to rapid rates of environmental contamination. Clevenger (1990) found that the metals in Pb-Zn mine tailings were in an unavailable form, mainly as PbS or residuals. He concluded that there was still a high potential for contamination if these spoil heaps interacted with microbes or low pH solutions. A study by Pitt *et al.* (1986) assessed the ability of mine spoils to release trace metals into the environment. They found that the mining operation in this area (Texas) did not show any adverse effects of metal contamination, and that concentrations of the spoil material were similar to the native soil. They felt that mixing of spoil with overburden material would not be potentially hazardous. However, it should be noted that the spoil material analyzed in this study was relatively young and that chemical changes are likely to occur (Pitt *et al.*, 1986).

Several attempts have been made to quantify the extent of anthropogenic inputs of metals. Input rates of metals into the environment, especially from atmospheric emissions usually supersede the effects of natural weathering (Alloway, 1990). Friedland and Johnson (1985) studied the effects of atmospheric lead in forest soils of northern Vermont. Distinctively higher concentrations of lead were found between a depth of 2 and 6 cm with lower concentrations at increasing depths. The mineral soil at lower depths were found to have comparable lead concentrations as reported by Nriagu (1978) with little variability. Friedland and Johnson (1985) further concluded that lead was accumulating by 3.3% per year and by calculating the flux, estimated an average residence time of 500 yr.

Steinnes *et al.* (1989) observed spatial trends of metal contamination of soils (As, Zn, Cu, Ni, and Pb) across southern Norway and attributed the pollution to long range atmospheric deposition rather than any local point sources. They found high correlations of metal concentrations with geographical distance with high concentrations emphasized in the upper soil surface. Estimation of increased metal concentration per year was 1%.

Esser *et al.* (1991) assessed anthropogenic influences of trace element fallout in soils of Indiana. Their study showed increased concentrations of metals in surface soils (Mn, Zn, As, Cs, Se, Fe, and Cr). Some migration of these metals was detected in lower horizons, especially closer to the pollution source yet this could also be attributed to a greater degree of weathering. They found that abundance of organic matter influenced metal retention; surface horizons were deficient of any accumulated metals within 17 cm.

3.10 Heavy Metal Species Common in Soils

Ions not included in crystalline mineral structures exist as colloidal suspensions in the soil solution and are affiliated with some sorption or precipitation mechanism. Speciation of metals remain the most critical factor in realizing the extent of contamination at any given site. If species can be identified, then the operative behavior of metals in the system can be predicted (Alloway, 1990). One expedient method in assessing metal species is through the use of computer trace equilibrium models such as GEOCHEM (Mattigod and Sposito, 1979) where species predictions can be made using thermodynamic information specific to paired metals and ligands. A brief synopsis of metal chemistry relevant to the acidic soils found in Massachusetts follows. Table 3.1 summarizes the principal species in acid and alkaline conditions.

Cadmium is similar to Zn in ionic structure and electronegativity. Cd may be quite high in topsoils influenced by atmospheric deposition and subsequent organic matter complexation but ordinarily is found in relatively low amounts in areas without anthropogenic effects (Alloway 1990). Cd sorption is inhibited by the presence of Co, Cr, Cu, Ni and Pb even though sorption mechanisms appear to control the distribution of Cd phases rather than precipitation. As pH increases, sorption increases where organic matter complexation and specific sorption with hydrous oxides prevail

Table 3.1 Predominant metal species in soil solutions in oxidizing conditions (Adapted from Alloway (1990). OC refers to organically bound metals.

Metal	Acid Soils	Alkaline Soils
Cd	Cd^{2+}, $CdSO_4$, $CdCl^+$	Cd^{2+}, $CdSO_4$, $CdCl^+$, $CdHCO_3{}^+$
Cr	$CrOH_2{}^+$, $CrO_4{}^{2+}$	$CrO_4{}^{2-}$, $Cr(OH)_4{}^-$
Cu	OC, Cu^{2+}	$CuCO_3$, OC, $CuB(OH)_4{}^+$, $Cu(B(OH)_4)_2$
Mo	H_2MoO_4, $HMoO_4{}^-$	$HMoO_4{}^-$, $MoO_4{}^{2-}$
Ni	Ni^{2+}, $NiSO_4$, $NiHCO_3{}^+$, OC	$NiCO_3$, Ni^{2+}, $NiHCO_3{}^+$, $NiB(OH)_4{}^+$
Pb	Pb^{2+}, OC, $PbSO_4$, $PbHCO_3{}^+$	$PbCO_3$, $PbHCO_3{}^+$, $Pb(CO_3)_2{}^{2-}$, $PbOH^+$
Zn	Zn^{2+}, $ZnSO_4$	$ZnHCO_3{}^+$, $ZnCO_3$, Zn^{2+}, $ZnB(OH)_4{}^+$

over sorption with 2:1 clays. Less metal is sorbed in low pH conditions because H^+ is bound. Reduced soils will have lower sorption capacities for Cd due to the lack of Fe/Al oxides. GEOCHEM speciation models predict that Cd(II), $CdSO_4$, and $CdCl^+$ are prevalent in acid soils.

The most stable and common forms of *Chromium* are Cr (III) and Cr(IV). The behavior of these two species are equivocal in nature. Cr(IV) exists as an anion and is more mobile than Cr (III) which sorbs strongly to the solid phase. Cr (III) will precipitate above pH 5.5 and is still relatively insoluble around pH 4. Cr (IV) is a strongly oxidizing species and if present will most likely be quickly reduced to Cr (III) in the presence of organic matter because of a high positive reduction potential. The Cr (III) in these conditions are present as hydrated oxides or are associated with Fe oxides.

Nickel chemistry is based on Ni^{2+} where the predominant species in acid soils are Ni^{2+}, $NiSO_4$, $NiHCO_3^+$, and organic complexes. Ni is very soluble in acid soils and mobility will increase as pH and CEC decrease to the point where soil acidification may contribute to significant translocation of Ni. Over 50% of Ni is associated with the residual fraction (HF and $HClO_4$ soluble) while 20% is associated with iron and aluminum oxides. The remaining fraction is associated with organic complexes and exchange sites. However, clay appears to have the most influence in controlling sorption while Fe oxides are secondary.

Molybdenum exists as an anion in soils and increases in solubility with increasing pH. It is mainly associated with Fe and Al oxides and with organic matter. Mo can exist at oxidation states ranging from Mo^{3+} to Mo^{6+} in reducing conditions, and as Mo^{4+} to Mo^{6+} in oxidizing conditions. The primary Mo mineral is molybdenite (MoS_2). The lithophilic nature of Mo allows substitution of Mo^{4+} for Al^{3+} in micas and feldspars. Molybdate is highly pH-dependent with anionic availability increasing at higher pH due to hydroxyl ion displacement on adsorption sites. Poorly drained soils frequently have high levels of Mo. These soils are often high in pH and organic matter favoring the mobilization of anions.

Copper occurs mainly as the Cu^{2+} ion in acid soils. It is generally occluded in aluminosilicates or organically complexed. Most Cu minerals are too soluble to control the very low activities of Cu^{2+} in soil solution, therefore precipitation of $Cu(OH)_2$, CuO, or $Cu_2(OH)_2CO_3$ compounds are not usually responsible for sorption. In soils with normal levels of organic matter, most of the Cu not in the minerals is bound by organic matter due to the high stability constants associated with organic complexes. A fractionation study indicated that over 50% Cu is held in the lattice of minerals, 30% was bound by organic matter, and 15% was adsorbed by hydrous oxides of Fe and Al.

Lead will accumulate and remain stable in the soil because of the low solubility of lead compounds and exemption from microbial degradation. Pb^{2+} is the prevalent oxidation state found in the environment and remains in a stable cationic form with organic complexes in acidic soils. Lead appears to accumulate naturally in surface horizons, and is rarely lost from soil profiles by leaching.

Below a pH of 7.7 *zinc* predominates as Zn^{2+} however $ZnSO_4$ may also contribute to total Zn (in solution). The colloidal phases of the soil, namely clay minerals, organic matter and hydrated metal oxides contribute to the sorption of Zn from soil solution. The sorption of Zn by clays and organic matter is quite substantial and is dichotomized by two different mechanisms occurring in acid or alkaline conditions. It appears that cation exchange controls Zn sorption in acid soils. Organic ligands are responsible for sorption in alkaline soils. Therefore in acidic conditions, as Zn^{2+} is sorbed by negatively charged sites, a simultaneous desorption of other cations will occur. Zn will be reversibly sorbed by ion exchange and irreversibly sorbed if incorporated in clays. Humic and fulvic substances play an important role when Zn is associated with soil organic matter. Fulvic acids will form chelates with Zn ions over a wide pH range. Thus the solubility and mobility of Zn is enhanced since fulvic acids are soluble in both acid and alkaline medium. In alkaline conditions Zn fulvates show only slight colloidal properties. In this respect, fulvic acids act to mobilize other metals as well. Humic acids are soluble in alkaline media and dissolve gradually as pH increases. Interactions between Zn and humic acids react inversely to pH. In acid conditions most of the Zn is soluble while humic acids are not.

CHAPTER 4

METHODS AND MATERIALS

4.1 Sampling Protocol

Soils overlying the following parent materials were investigated:

a. alluvium

b. glacial outwash

c. marine and glacio-lacustrine silts and clays

d. non-calcareous glacial till

Data published by Veneman (1985) were used for an initial evaluation of existing data. This information was heavily biased towards a few geographic areas within the state. Thirty-three soils in the present soil characterization laboratory database come from Hampshire County in West-central Massachusetts. The study reported herein augments the existing database *i)* by increasing the number of datapoints from 33 to 80, and *ii)* by enhancing the geographical distribution to include representative soils from most counties. In this study, fifteen of the original 33 soils were retained for the expanded metal analysis and 45 new sites were added (Figure 4.1). Specific site locations and series designations can be found in Appendix A.

Soil pits were dug 4 to 6 feet deep at sixty locations; fifteen at each of the four parent material groups. Standard soil profile descriptions were made at each site

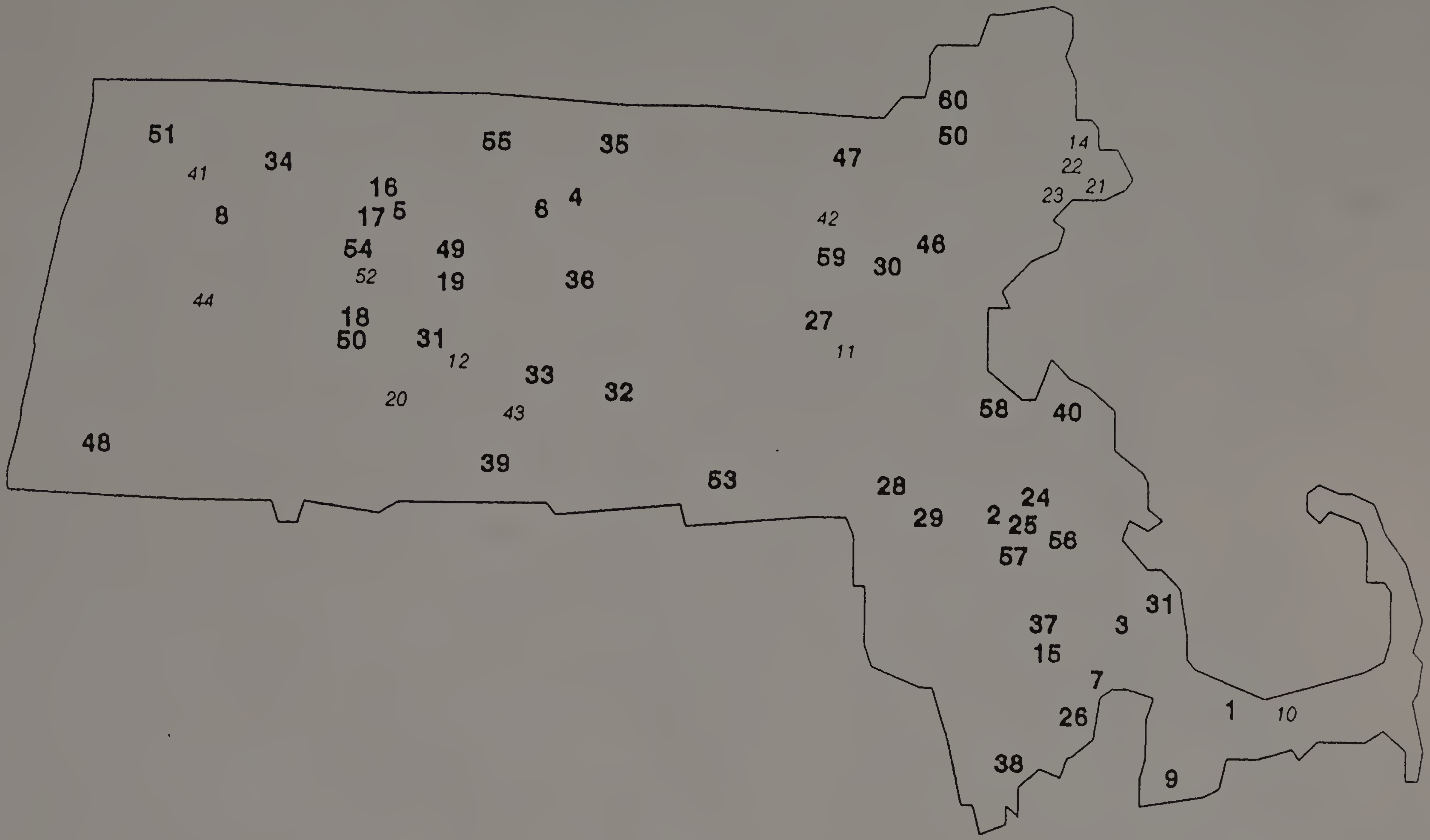


Figure 4.1 Location of study sites. Numbers in small italicized font indicate sites from the 1985 study (Veneman, 1985).

(Soil Survey Staff, 1962). Three samples from different depths at each location were collected to relate the data to morphology and soil development. These samples were not collected at specific depth ranges but represent the A, B, and C horizons whenever possible. At sites without distinct horizonation samples were taken at depths of 6, 20, and 36 inches, respectively. A total of 180 soil samples were analyzed for heavy metals in addition to standard chemical and physical soil characterization.

4.2 Analytical Methods

4.2.1 Sample Preparation

Prior to analysis, samples were air-dried and passed through a 2-mm Teflon sieve to remove coarse fragments. All analysis were performed on the <2-mm size fraction unless otherwise noted in the procedure. Soils were mechanically ground with a Model #8510 Spex Pulverizer for 5 minutes for those procedures that required ground samples. To reduce contamination from alloy metals, tungsten carbide grinding containers were used.

4.2.2 Reagents and Standards

All acids used in the heavy metal analysis were trace metal grade. Primary standards were made from dissolution of pure metals or their salts, and acidified. Spex Plasma grade Fe and Al was used in determining background corrections. All other reagents were reagent grade or ACS Certified.

4.2.3 Heavy Metal Analysis - Total Dissolution

Heavy metals were determined by a total dissolution procedure using 10 ml nitric acid (70%), 10 ml hydrofluoric (49%) and 5 ml perchloric (70%) to 1 gram ground soil (Veneman, 1985). Samples were digested on a hotplate in open Teflon beakers to near dryness following a volatilization scheme of nitric-hydrofluoric-perchloric. If needed, 5 ml of additional hydrofluoric acid was added and evaporated to near dryness. After cooling, 10 ml hydrochloric acid (38%) was added and the supernatant was transferred to 100-ml volumetric flasks and raised to volume with deionized distilled water. Additions of boric acid were not needed to neutralize the HF for ICP analysis. Observation of thick white perchloric acid fumes assured volatilization of HF precluding any subsequent attack on the quartz torch of the ICP instrument.

4.2.4 Semi-Total Heavy Metal Analysis - Nitric/Perchloric Acid Digestion

Five milliliters of concentrated nitric acid (70%) and 3 ml perchloric acid (70%) were added to 1g ground soil and digested in macro Kjeldahl test tubes using a Tecator #1015 Digestion Block with a #1012 Autostep Controller. Temperatures, ramp time and plateau time are preset and automatically controlled during the digestion. Different combinations of controlled times were investigated to find the most enhanced and rapid digestion without allowing samples to go dry. The reflux fronts for both acids were observed and recorded to ensure that each acid reached its boiling point. An acid scrubber system was set up using a water vacuum to remove the perchloric acid fumes by combining with water into the waste drain. The digestion procedure employed two steps:

Step 1

Temperature = 150°
Ramp time = 10 min.
Plateau time = 10 min.

Step 2

Temperature = 200°
Ramp time = 5 min.
Plateau time = 10 min.

The observed reflux fronts for nitric and perchloric acid were 150° and 185°, respectively. After the final plateau time was attained, the system automatically shut down and samples were allowed to cool. The samples were then transferred to 100-ml volumetrics and raised to volume with deionized distilled water. Many of the soil grains still remained upon application of this procedure.

4.2.5 Heavy Metals - Toxicity Characteristics Leaching Procedure (TCLP)

Extractable metals were determined using the Toxicity Characteristic Leaching Procedure (without the volatile fraction), as cited in 40 CFR Part 268, Appendix I.

An initial determination of pH was performed to choose the appropriate extraction fluid according to section 7.4 (USEPA, 1986). Five grams of unground soil passing a 2.0-mm sieve were weighed to a 150-ml glass bottle. One hundred milliliter of sodium acetate, pH 4.9, was added if the initial pH was less than 5.0; or acetic acid with pH of 2.8 was added when the sample pH was greater than 5.0 according to the following equation where:

weight of extraction fluid = 20 x weight of soil

The bottle was sealed and shaken for 18 hours in an EPA approved TCLP end-over-end rotating apparatus at 30 rpm (ASTM 3987). After agitation, the soil/solution was vacuum-filtered through acid washed 0.6 to 0.8- μm borosilicate glass fiber filters. Zero headspace extraction vessels were not used since only non-volatile inorganic metals were analyzed in this study. After filtration using suction flasks with Buchner funnels, the TCLP extract was immediately preserved with nitric acid to a pH less than two and refrigerated.

The TCLP procedure specifies that extracts analyzed for metals undergo acid digestion according to SW-846 Test Methods for Evaluating Solid Waste, Physical and Chemical Methods (USEPA, 1982). Method 3010A was employed prior to spectroscopic analysis to digest organic and colloidal constituents remaining in the extract. A 90-ml aliquot was transferred to a 150-ml Griffin beaker and 3 ml of nitric acid was added. Samples were covered with a watch glass and evaporated slowly on a hot plate to approximately 5 ml. Three more ml of nitric acid was added and the samples were refluxed to 3 ml by increasing the temperature until a clear or light color resulted. The samples were cooled and 2.5 ml HCl (10% by volume) was added, followed by refluxing for 15 minutes to dissolve any precipitates. Samples were cooled and raised to 25 ml volume with deionized distilled water.

4.3 ICP-AES Instrumentation for Heavy Metal Analysis (HF Procedure)

A Jarrell-Ash Model 955 ICP-AES was used to analyze for total Al, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, and Zn. After assessing reductions in line intensity, the frequency currents-incident power, mass flow controllers for argon and sample, nebulizer efficiency, and plasma conditions were optimally set to provide the highest signal to background ratio for the least sensitive element as follows:

Monochromator: Ruled Differential Grating
RF Power: 1.0 kW
Ar Coolant: 15-20 l/min
Ar Sample Carrier: 0.3 l/min
Peristaltic Pump: 3 ml/min
Nebulizer: Babington-type
Integration: 5 sec.
Observation Height: 17 mm
Profiling Solution: 10 ppm Cu
Interfaced with: Thermospec Software/DOS

Several interferences known to occur in emission spectroscopy were addressed. Incomplete dissociation of refractory elements for ICP are negligible since the plasma reaches temperatures of around 6000^{o} K. Ionization is usually not a problem either. The most significant interferences were *i)* matrix interferences (viscosity differences) due to the acids used in the digestion, and *ii)* interelemental spectral interferences/line overlap caused by high concentrations of Al and Fe. The former was remedied by means of a peristaltic pump. The latter issue required attention as these interfering elements are the main constituents of soil. Since the software that was interfaced with the ICP did not provide for background correction, separate Fe and Al standards made of 100, 200, 300, 500, 700, and 1000 μg/ml were run with each analytical batch. Conveniently, this response was linear and regression equations were developed of Fe and Al with the other 8 measured metals for a total of 16 equations. The background correction derived for Fe and Al were summed and applied to each (subtracted from) of the metal values obtained for a complete background noise correction. Table 4.2 lists the derived regression equations.

4.3.1 Analytical Quality Assurance

The following minimum quality control measures were routinely employed during chemical analysis:

1. Control of blank variability to obtain accurate low-level trace determinations since many sources of contamination may occur. Even deionized water can have organically bound metals. Blank corrections therefore, become increasingly important when approaching detection limits. One blank was used for every ten samples to detect any drifting of the instrument and for recalibration. Restandardization occurred every ten samples as well.

2. A matrix spike of known concentration for each analytical batch to monitor methodology and to detect any matrix interferences.

3. Rinse blanks to eradicate memory interferences.

Table 4.1 Regression equations for Fe and Al background corrections in a 10% HCl matrix using a Thermal Jarrell Ash ICP-AES 955.*

Equation	r^2
Pb-Fe $y = 0.05336(x) - 0.4838$	0.99
Pb-Al $y = 0.1929(x) - 2.686$	0.99
Cu-Fe $y = 0.00646(x) - 0.2788$	0.98
Cu-Al not needed for correction	
Ni-Fe $y = 0.1177(x) + 0.5036$	0.98
Ni-Al $y = 0.00087(x) + 0.06367$	0.81
Cr-Fe $y = 0.00568(x) + 0.1075$	0.98
Cr-Al not needed for correction	
Mn-Fe $y = 0.02763(x) + 1.053$	0.98
Mn-Al $y = 0.02843(x) - 0.07995$	0.99
Mo-Fe $y = 0.00867(x) + 0.4859$	0.98
Mo-Al $y = 0.06531(x) + 0.03396$	0.99
Zn-Fe $y = 0.01157(x) + 1.457$	0.98
Zn-Al $y = 0.00713(x) + 0.5541$	0.95
Cd-Fe $y = 0.00467(x) + 0.1693$	0.97
Cd-Al $y = 0.00049(x) + 0.2437$	0.99

*The concentrations of Fe and Al were designated as "x" to obtain background correction "y" in the following regression equations for each individual sample. The two values of "y" were summed and then subtracted from the uncorrected value of the appropriate metal analytically measured on the ICP to obtain the final corrected concentration.

4.4 Soil Characterization

4.4.1 pH

The pH of soil samples was measured with three different reagents using a 1:1 soil-solution ratio (Soil Survey Investigations Staff, 1991). Twenty grams of soil were weighed to which 20 ml of deionized distilled water was added (Method 8C1a). Samples were stirred and left for one half to one hour before this pH-H_2O measurement. The pH-$CaCl_2$ used to mask the effects of salts present from fertilizers or liming, was determined by adding 20 ml of 0.01 M $CaCl_2$ to 20 grams of soil (Method 8C1e). To determine how much aluminum could be attributed to soil acidity, the pH in a 1N KCl solution was measured (Method 8C1c). A Fisher Accumet #805 pH meter with glass pH and calomel reference electrodes was used in the analysis.

4.4.2 Base Cations

Exchangeable base cations (Ca, Mg, K, Na) were extracted using 1 N ammonium acetate buffered at pH 7.0 (Method #5Aa; Soil Survey Investigations Staff, 1991). Twenty-five grams of soil were weighed to which 50 ml of the extracting solution was added. Samples were shaken overnight and filtered under vacuum using #42 Whatman filter paper in Buchner funnels. The extractant was analyzed for the cations using an Instrumentation Laboratory #551 atomic absorption spectrophotometer in a lean-blue oxidizing air/acetylene flame. Na and K were analyzed by emission spectrometry generally using a straight extract with no dilution. Ca and Mg were analyzed using absorption spectrometry with supplied source radiation. Concentrations of these two elements required dilution between 5x and 25x. Lanthanum was added for a total of 1% in solution to prevent depression of absorbance caused by aluminum and silicon.

4.4.3 Extractable Acidity

Extractable acidity (H, Al) was determined using 100 ml of 0.5 N $BaCl_2$-0.055 N Triethanolamine buffered to pH 8.2, to 10 grams of soil (Peech *et al.*, 1964). The soil and reagent was shaken overnight and filtered under vacuum using #42 Whatman filter paper in a Buchner funnel. The extractant was titrated to a pink endpoint using 0.2 N HCl. The HCl titrant was standardized with Tris Hydroxymethyl Aminomethane four times and the average taken to obtain the normality of the HCl.

4.4.4 Cation Exchange Capacity (CEC)

CEC was calculated in $cmol^+/kg$ by summing total cations, using the quantitative information obtained from measurement of the four basic cations and the extractable acidity.

4.4.5 Organic Carbon

Organic carbon was quantified using a modified Mebius wet oxidation method (#29-3.5.3) described by Nelson and Sommers (1982). Between 0.25 and 1.0 gram ground soil was used depending on the amount of organic matter present in the sample. The organic fraction was then oxidized by heating a mixture of 10 ml of 0.5 N potassium dichromate and 15 ml concentrated sulfuric acid for one-half hour. Eight milliliter of deionized distilled water was added to prevent decomposition of the dichromate. Any unreduced chromate was back-titrated to a blue-green endpoint with 0.2 N ferrous sulfate. The titrant was standardized daily by titrating a boiled and an unboiled blank.

4.4.6 Particle-Size Distribution

Particle-size was determined using the pipet method of Gee and Bauder (1986). Twenty-five grams of < 2-mm soil were weighed and, when necessary, pretreated with 30% hydrogen peroxide to oxidize organic material (Method 15-4.2.1.2). Bicarbonate-buffered sodium dithionite/citrate for iron oxide removal was used only in those horizons that were iron rich. Upon pretreatment, 50 ml of 5% Calgon was added with approximately 200 ml distilled water and shaken overnight (Method 15.2.1.5.1). The sample was wet-sieved through a 50-μm sieve to determine the sand fraction. The sand fraction (by weight) was oven-dried and passed through a nest of sieves corresponding to USDA delineated very coarse sand, coarse sand, medium sand, fine sand, and very fine sand (Method 15-4.2.2). The silt and clay fractions were transferred to sedimentation cylinders and brought to volume with distilled water. Twenty-five milliliter aliquots were taken at prescribed times as calculated from Stokes Law. After the last aliquot was taken, approximately 40 ml of suspension was removed and centrifuged. Another 25-ml aliquot was pipetted to be used as a correction factor for a blank and any dissolved mineral matter. These aliquots were dried at 105°C and weighed to 3 decimal places to determine the various fractions. Textural classification was determined using USDA specifications (Soil Survey Staff, 1962).

4.4.7 Fe and Al Oxides

Concentrations of Fe and Al oxides were determined using a Jarrell-Ash Inductively Coupled Plasma (ICP-AES) Model # 955 and an Instrumentation Laboratory #551 Atomic Absorption (AA) spectrophotometer. Sodium pyrophosphate (0.1 N; pH 10) and sodium citrate-sodium dithionite (pH 7) were used to preferentially extract different forms of the Fe and Al (Soil Survey Investigations Staff 1991, Method #6C5 and #6C2, respectively). For Na-pyrophosphate Fe and Al, 50 ml of extracting solution was added to 0.5 grams of ground soil and shaken overnight. The samples were brought to 100 ml volume with the pyrophosphate solution, transferred to 40-ml centrifuge tubes, and centrifuged for 30 minutes at 10,000 rpm. The supernatant was refrigerated until analysis. Citrate-dithionite extractable Fe and Al were determined by adding 2 grams of Na-dithionite, 20 grams of Na-citrate, and 125 ml of deionized-distilled water to 2 grams of ground soil. The samples were shaken overnight, brought to 250 ml volume with water, and transferred and centrifuged in the same manner as the pyrophosphate extracts. The supernatant was refrigerated until analysis. Iron was measured on the AA by absorption in an air/acetylene flame, usually requiring 50x dilutions. Aluminum was measured by emission using a nitrous oxide/acetylene flame. Samples were mostly 10x dilutions. Potassium was added in the form of 5% KNO_3

to prevent ionization of the Al. ICP analysis replicated that of the heavy metal analysis and required no dilutions.

4.5 Statistical Quality Control Measures

Since this project dealt with a great number of chemical samples, a systematic approach to quality control in the initial phase of the study was undertaken to ensure proper statistical control.

Concentration estimates with initial measurements and evaluation of quality assurance in the early phase of the study was done prior to the first two analytical runs on the ICP. The ICP was a dedicated instrument for soil testing so no ruggedness testing was performed. Instrument detection limits were assessed through published data and by available information from other analysis performed in this laboratory. Method detection limits and percent recoveries for TCLP and HF total dissolution procedures were determined for each of the metals analyzed. A range of values likely to be expected was obtained from previous work (Veneman, 1985).

To achieve consistency in the proposed methods and to assess analytical precision, control charts for blanks and spiked matrices (for each element) were constructed to document statistical control, any affiliated uncertainty, and to identify any inconsistencies. In the first couple of analytical sessions the following was implemented:

a. ten separate analytical blanks (method blanks) were made containing the same reagents and undergoing the same digestion as the actual samples. RSD's, CV's and precision of the blanks were assessed for each metal separately. Control charts were made by taking the mean of measurements and setting upper and lower limits (X+3s, X-3s). Much of the literature recommended at least seven replicate measurements with 6 df (Taylor, 1987).

b. seven spiked samples were made containing the same reagents and undergoing the same digestion as the actual samples. The concentration of the spiked samples was 2-3 times higher than the estimated detection limit. This resulted in an estimate of the method detection limit (MDL) which is 3 times the standard deviation of these measurements. This information was applied to each metal separately. Method Detection Limits (MDL) were obtained using *Definition and Procedure for the Determination of the Method Detection Limit* (USEPA 51 FR 23703, 1986). Blanks did not exceed the MDL.

c. Additional spiked samples at different and higher concentrations were made and digested and recoveries were calculated for each element individually.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Experimental Design

Copper, Cd, Cr, Mo, Ni, Pb, and Zn were determined in 180 soil samples. Iron, Mn and Al were also measured but were not treated as trace metals in the final statistical analysis. The 180 samples were comprised of four parent materials resulting in 45 samples per parent material (N=45). Within each parent material group there were 15 sites (N=15) with 3 horizons per site. Emphasis will be placed on analysis of the sample population as a whole, scaling down to concentrations across parent materials or horizons, and finally to an analysis of individual horizons within each parent material. In this way, general trends of metals in soil can be noticed through the initial broad spectrum approach. More detailed levels magnify differences in surficial deposits across the landscape or with depth, while allowing an assessment of possible anthropogenic effects. Systat software was used in the statistical analysis.

5.2 Heavy Metals - Total Dissolution

5.2.1 Assumption Diagnostics

Regression analysis presumes that the distribution of residuals are normal, and the values are independent, linear, and have constant variance. The normality of the subpopulation of dependent variables is not assumed with regression, however, non-normal distribution or unequal variance could heavily influence the outcome of the regression as well as in the ANOVA. An initial evaluation of the data was made to assess its distribution by performing applicable statistical tests. Figure 5.1 represents a simple histogram of a few selected metals using all data points (N=180). The normal curve, observed with all metals, fits the distributions quite poorly with kurtosis and positive skewness. The means in this data set in fact, would not be good descriptors for this non-normal distribution. Even when a subset of the data is chosen, for example till (N=45) and the B horizons within the till (N=15), the fit of the curve (Figure 5.2 - 5.3) still appears non-normal even though the medians are closer to the means and skewness and kurtosis approach zero when N=15 (values< +/-0.6, one value -0.9). It is reasonable to assume that when all data points are considered (N=180), the distribution is non-normal since sub-populations of parent material (and even horizons) exist within this data set. It is critical then, to determine if the data are really non-normal or have normal distribution with outliers. Tests for normality with probability plots were made for each parent material using Cu, Ni, Cr, and Zn as representative metals. The plots yielded no straight lines confirming that the data is non-normal.

There are two approaches to deal with non-normal distribution. One would be to transform the data by taking the logarithm or square root of individual values while the other option would be to use distribution-free statistics to describe the data. Transformations are not necessarily a superficial statistical maneuver that would

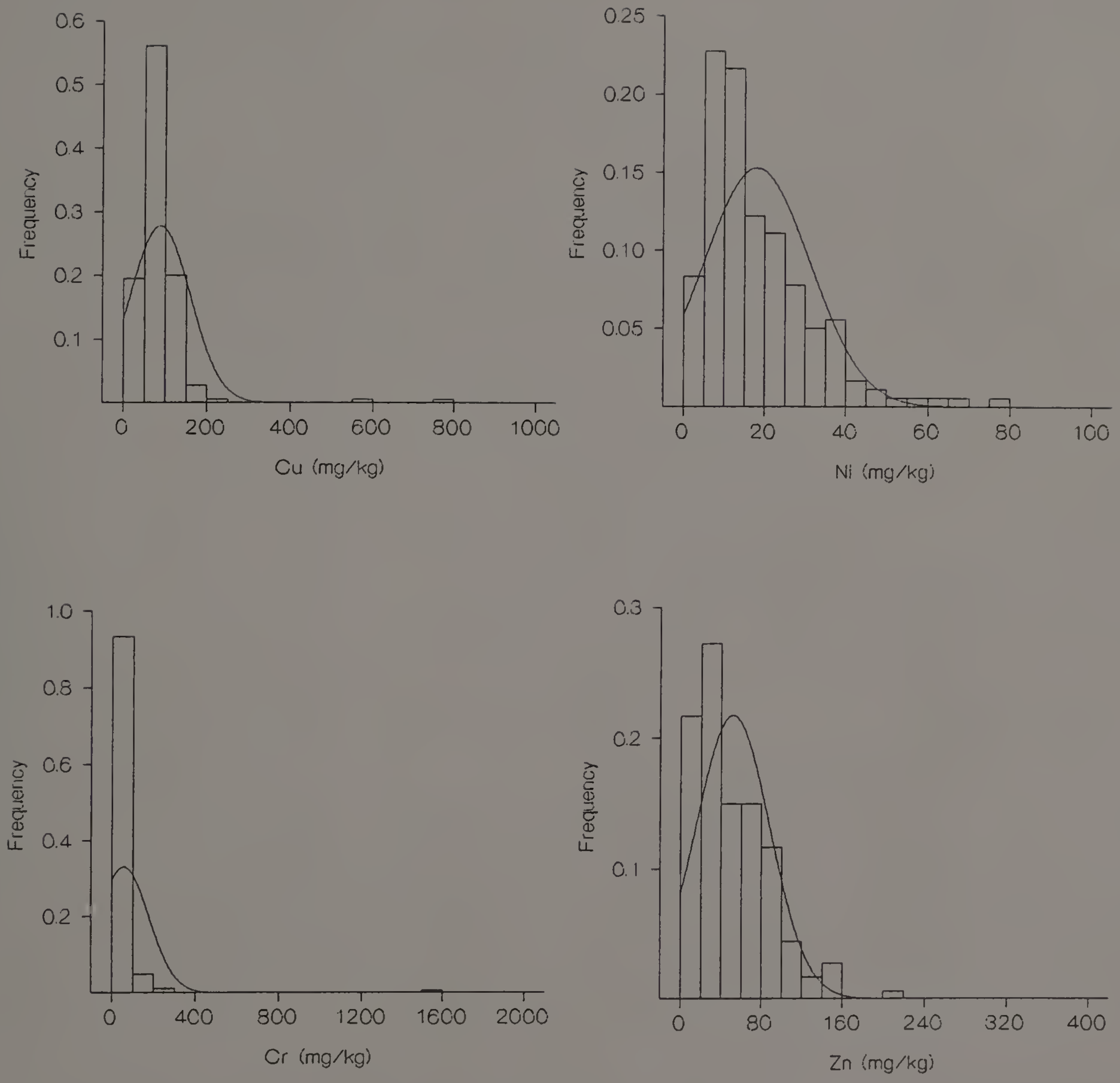


Figure 5.1 Depiction of non-normal distribution for selected metals using all samples (N = 180).

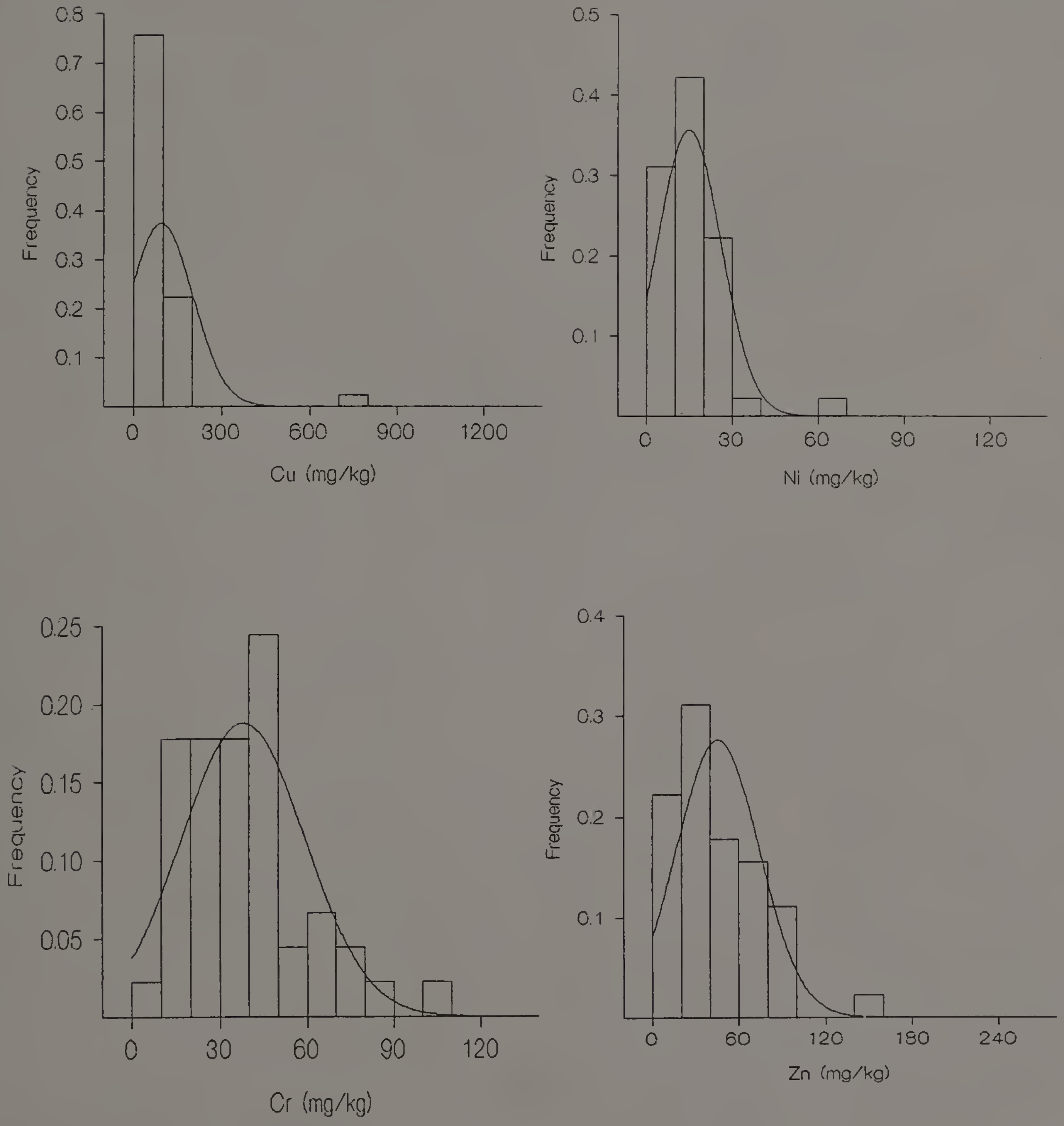


Figure 5.2 Distributions of selected metals in till (N=45)

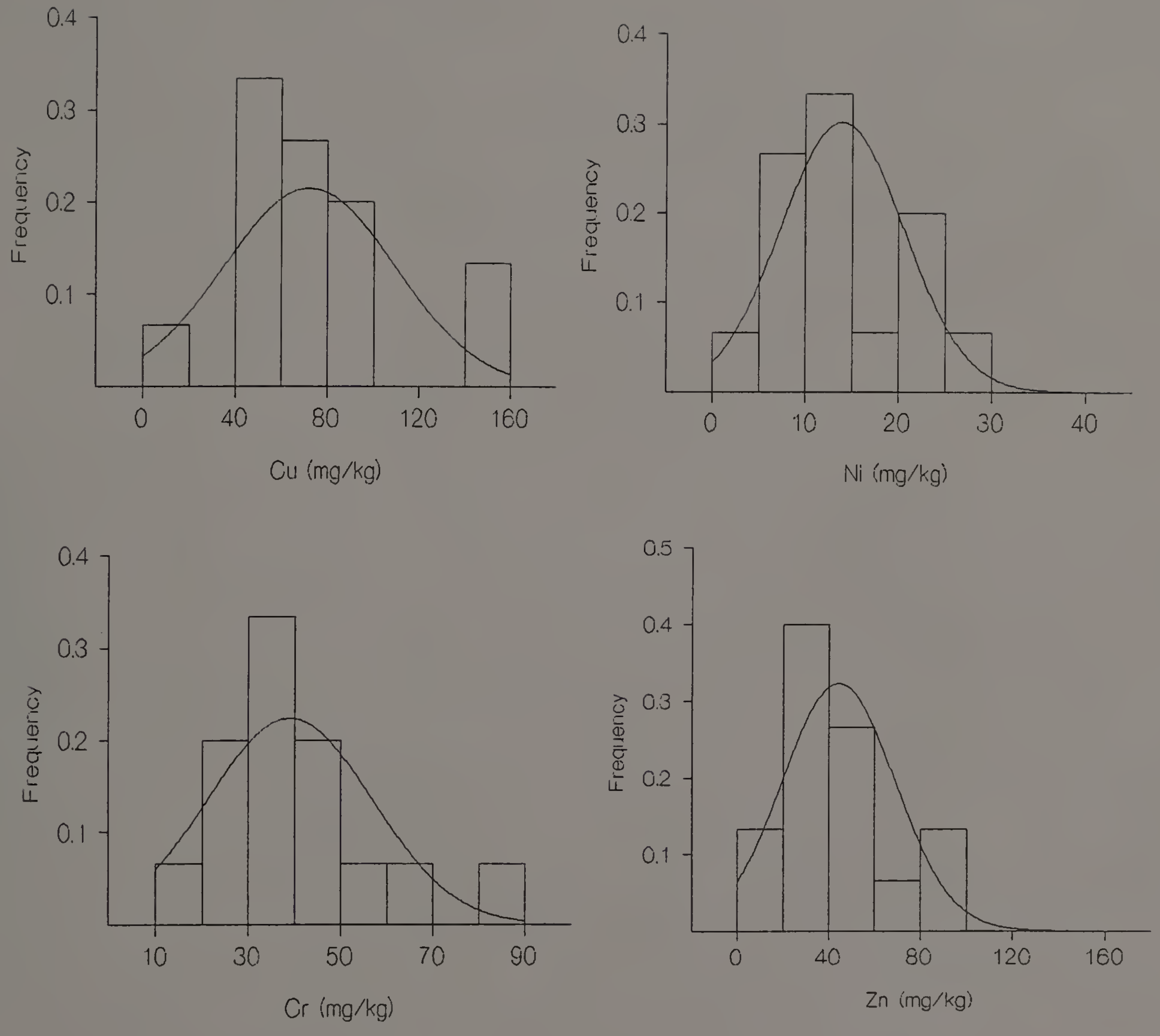


Figure 5.3 Distribution of selected metals in B horizons of till parent materials (N = 15).

obscure observations, but allow any unremoved (and possibly naturally occurring) outliers to effectively have less weight. A log transformation in this instance would remove the positive skew which occurred and pull in extreme values while expanding the significance of lower values. Figure 5.4 shows non-normal plots of selected metals using untransformed data, while Figure 5.5 depicts the transformed data. The normality probability plots yield relatively straight diagonal lines indicating that the correct transformation was chosen to produce normal distribution. Homogeneity of variance however, may be of even greater importance in regression analysis. Preliminary multiple regressions were made using Cu as the dependent variable. Y estimates were plotted against studentized residuals to test for homogeneity of variance. Figure 5.6 indicates a violation of this assumption with the untransformed data while Figure 5.7 shows constant variance using the log transformed data. Based on the results of these preliminary statistical diagnostics, transformed log-normal data for ANOVA and multiple stepwise regression were used with an occasional non-parametric analysis for comparison. Distribution-free statistics will be used when presenting summary data.

The fact that the distribution is log-normal is important since presently the Massachusetts Department of Environmental Protection (DEP) has used parts of the 1985 data set (Veneman, 1985) in establishing background levels for Pb, Cr, Ni and Zn. Figures 5.8 - 5.11 show how background levels were determined by the DEP using the older data set. The 36 soils used to generate the graphs were from all types of landforms and drainage classes but they are all topsoil samples giving a consistency in their depth. The DEP opted to use the information in the correct manner by

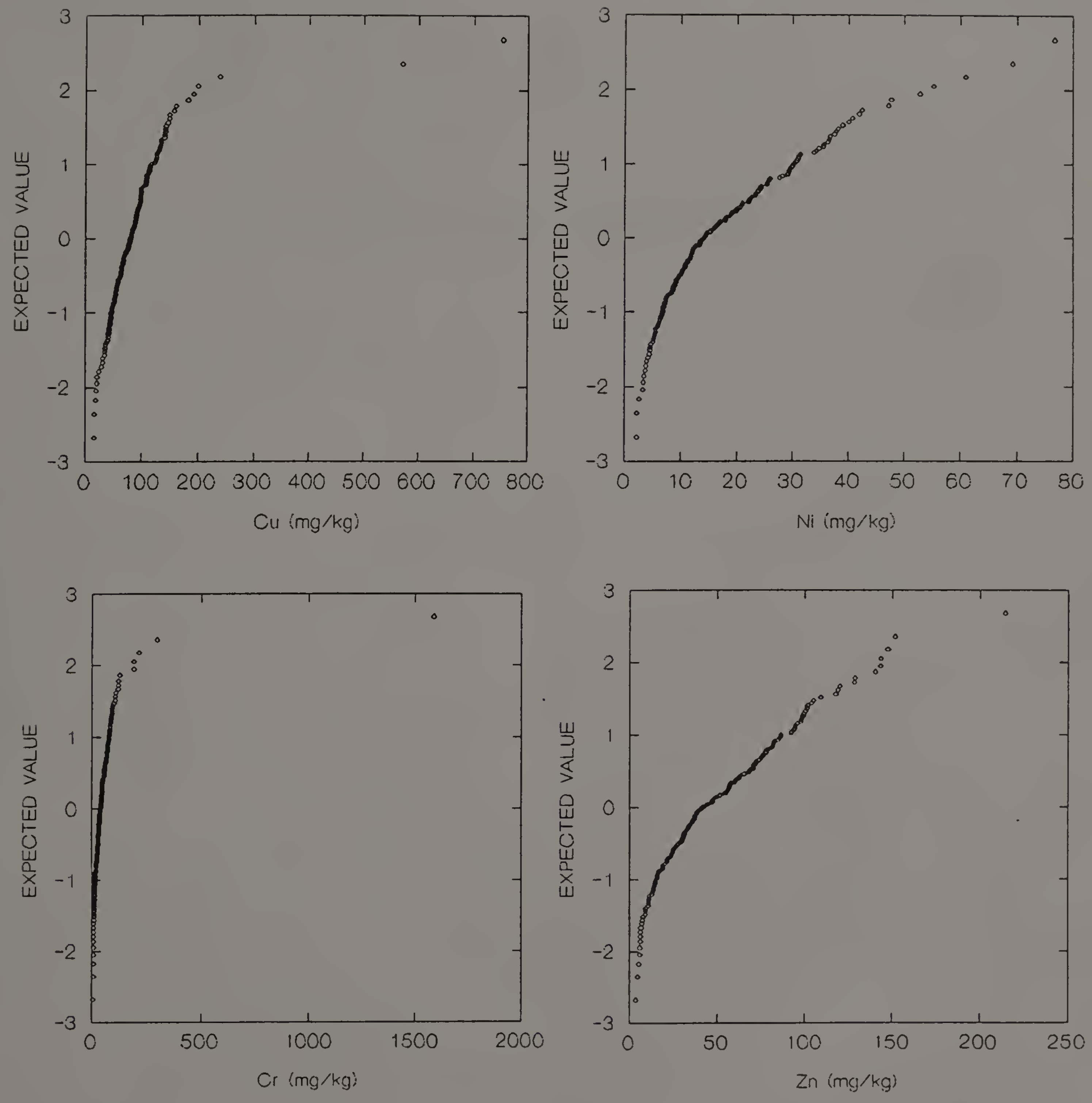


Figure 5.4 Normality probability plots for untransformed data. Curvature shows violation of normality assumption.

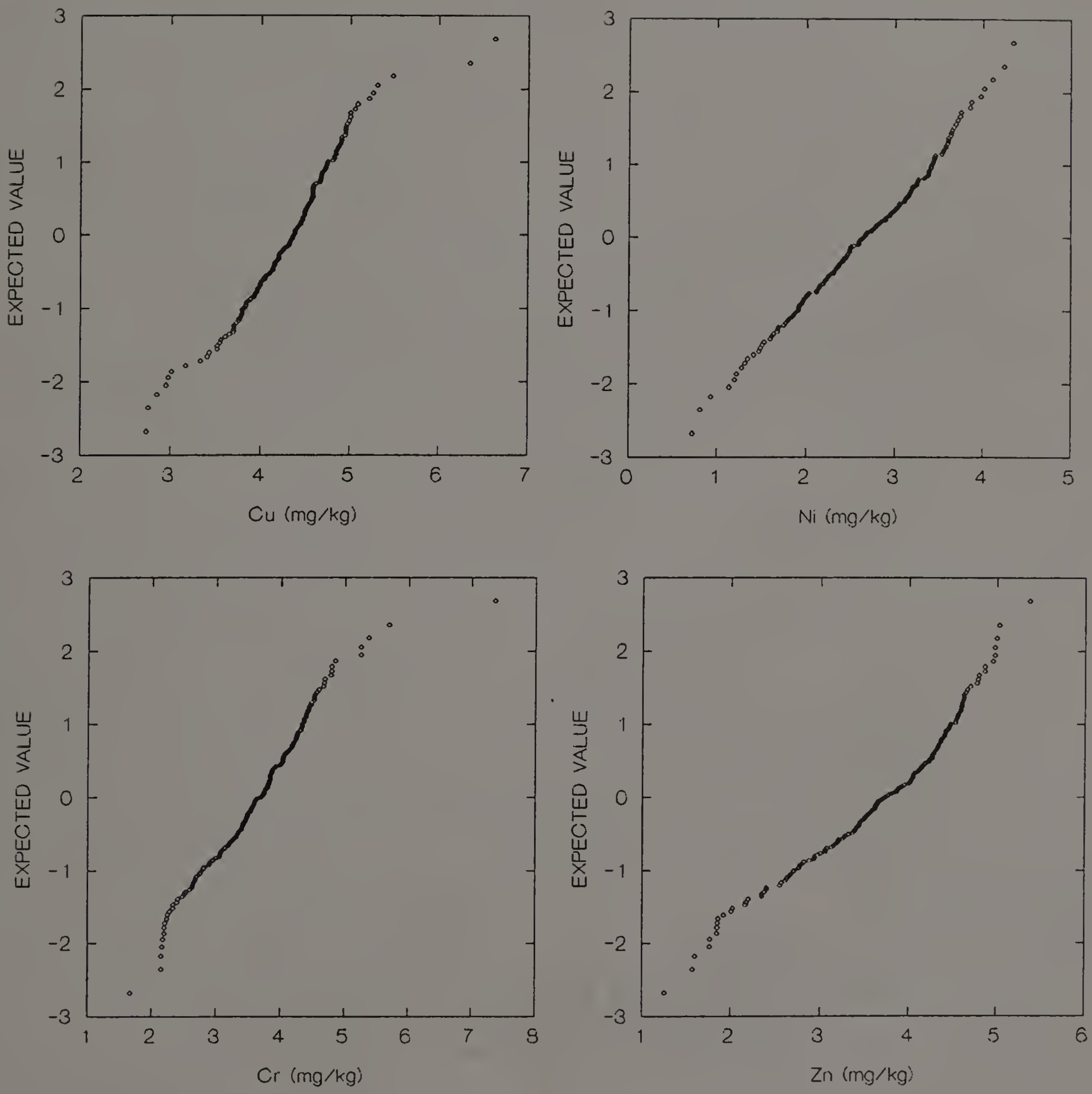


Figure 5.5 Normality probability plots for transformed log-normal data.

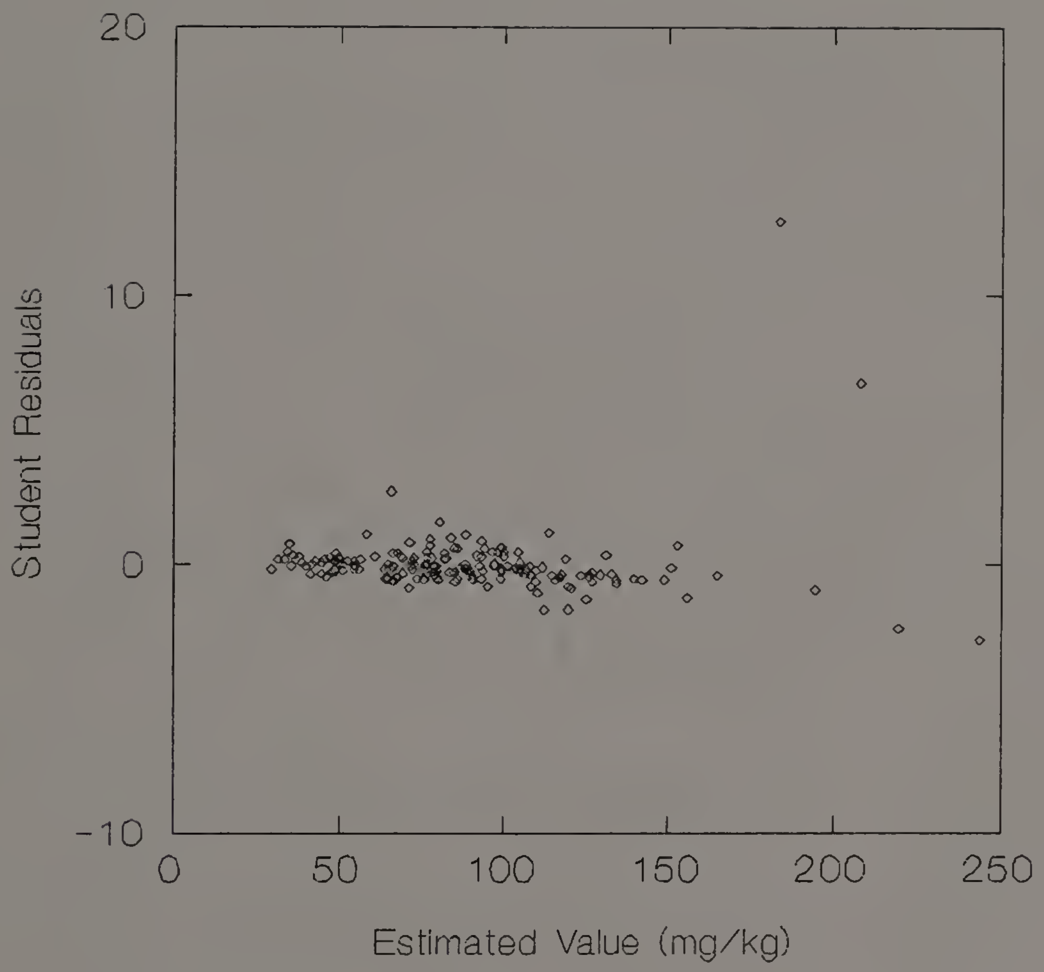


Figure 5.6 Test for homogeneity of variance for Cu. Studentized residuals are plotted against estimated values. Any curvature or trends suggests a violation of this assumption.

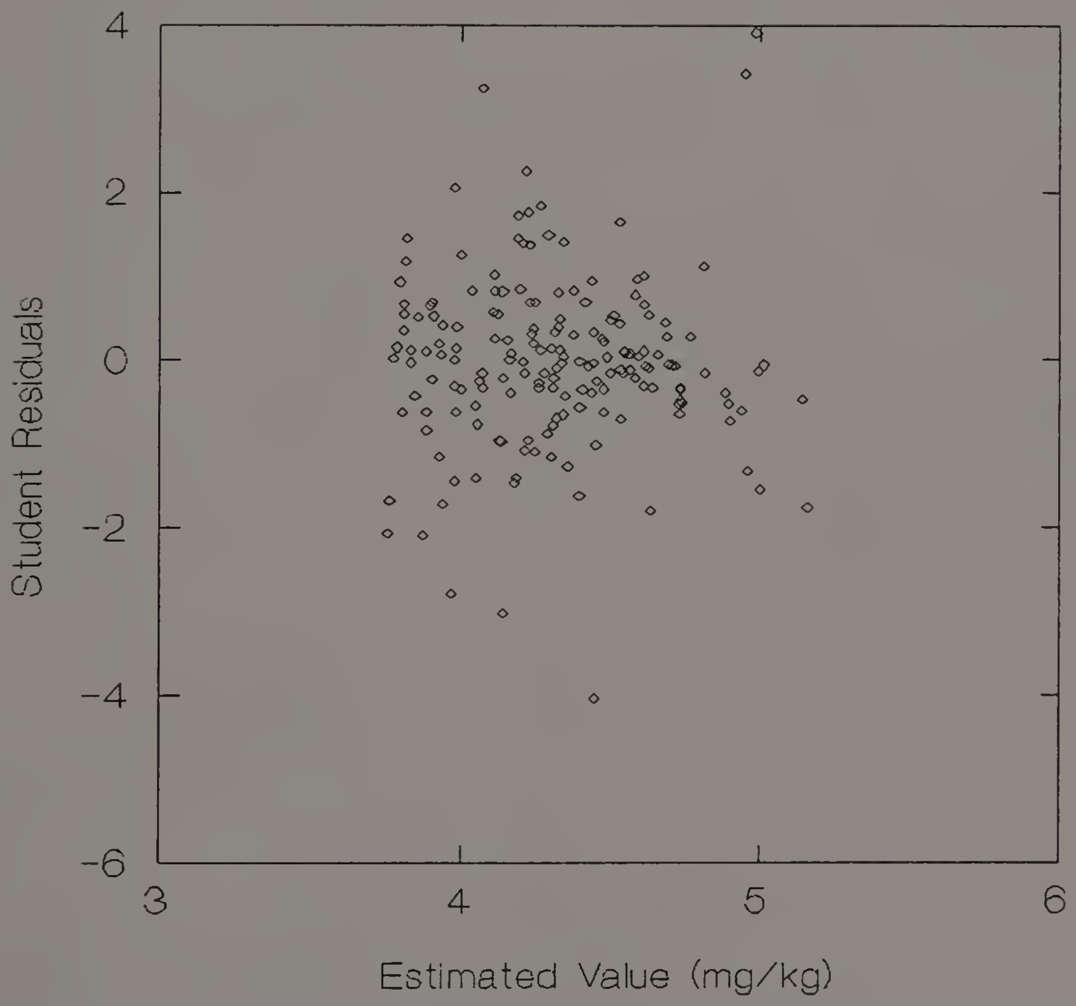


Figure 5.7 Test for homogeneity of variance for Cu. Studentized residuals are plotted against estimated values. The relatively random scatter of points indicate constant variance.

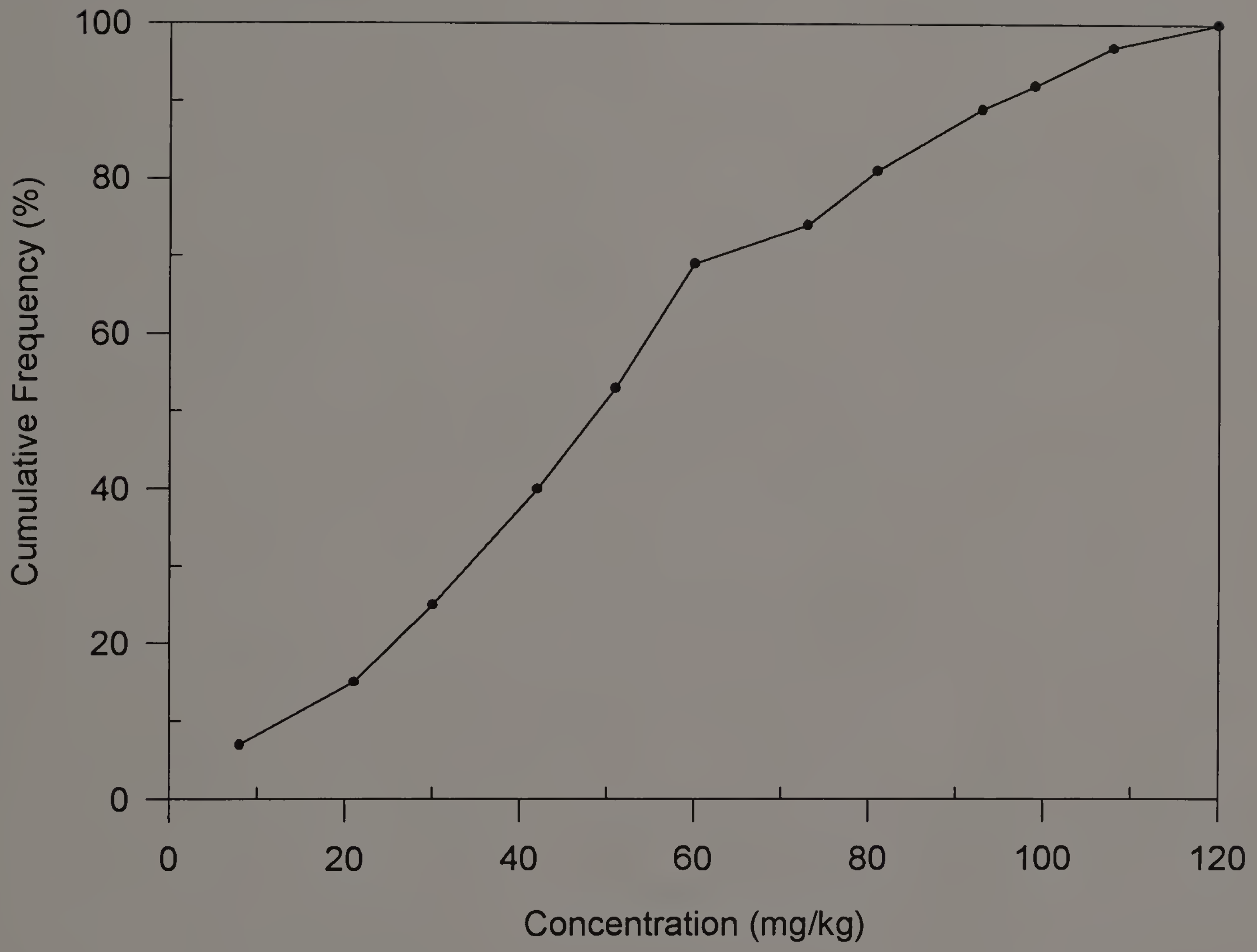


Figure 5.8 Cumulative frequency of chromium based on 36 Massachusetts soils (after Veneman, 1985)

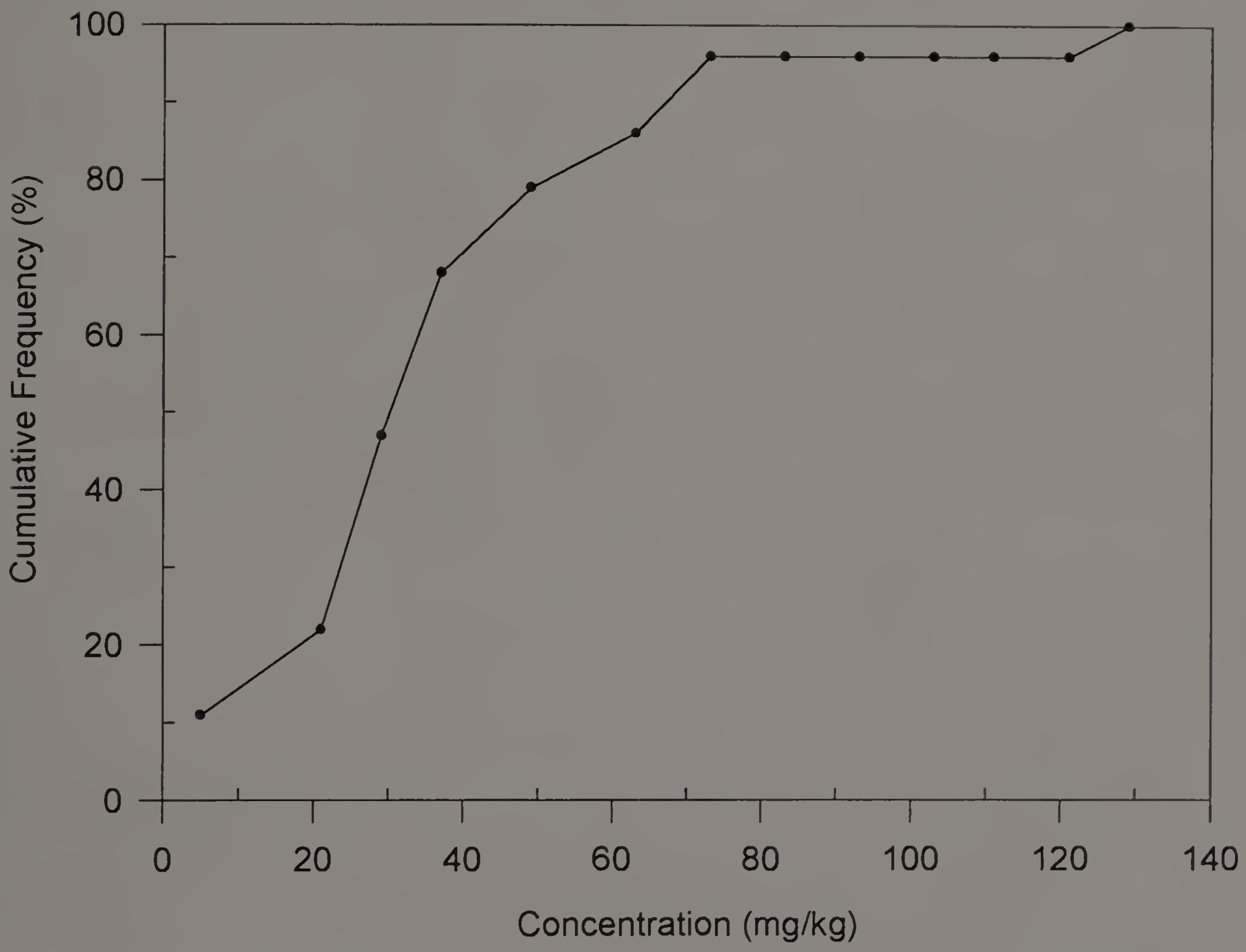


Figure 5.9 Cumulative frequency of lead based on 28 Massachusetts soils (after Veneman, 1985)

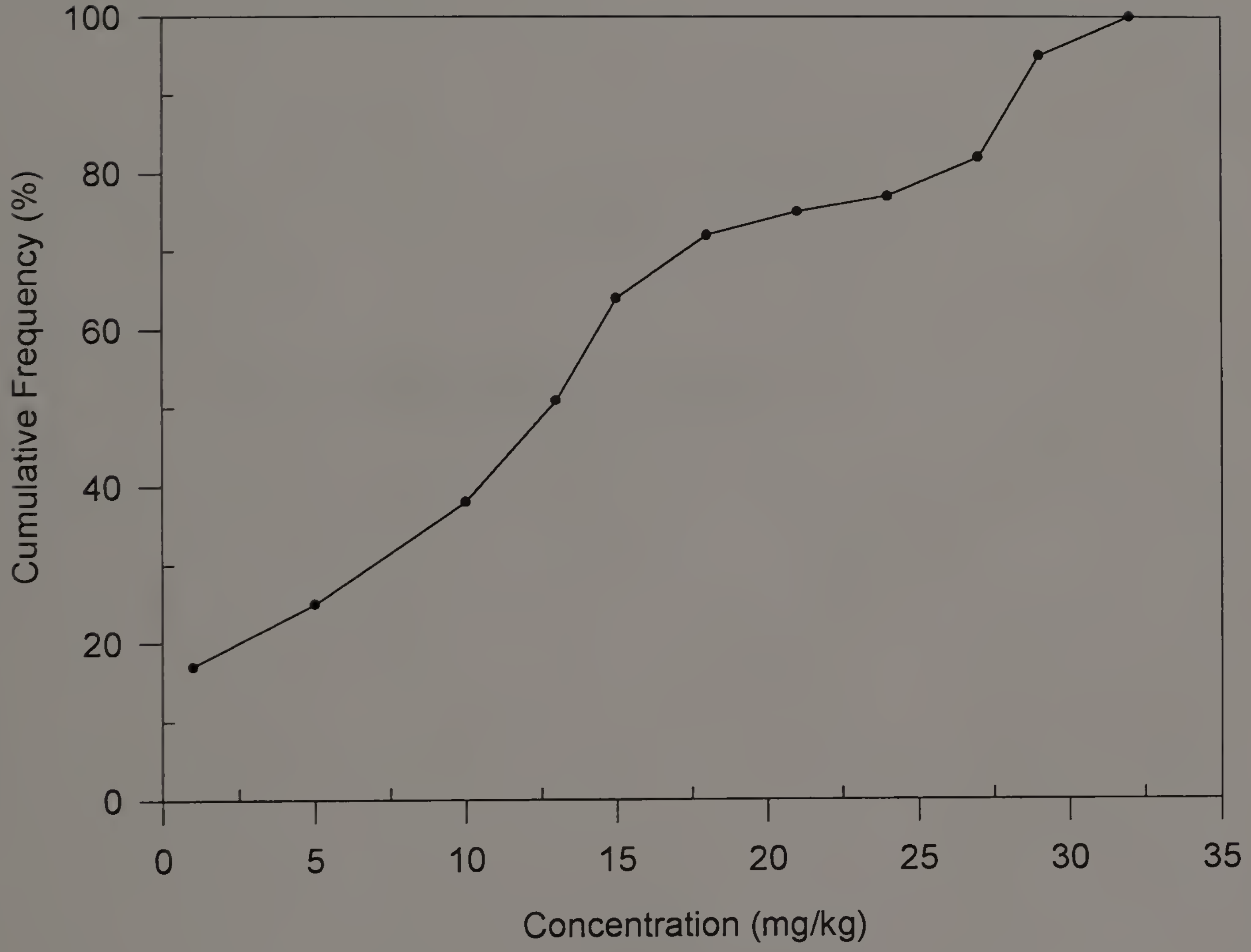


Figure 5.11 Cumulative frequency of nickel based on 36 Massachusetts soils (after Veneman, 1985).

designing cumulative frequency curves and graphically obtaining background levels at the 95th percentile. Their reasoning stands that 95% of the samples represents non-contaminated samples. Percentiles are a valid analysis and cumulative frequency is probably the safest way to display non-normal data. The approach of using the 95th percentile is somewhat arbitrary. It is quite possible that only one or two samples are present in the remaining 5% making a weak case for statistical significance. A complete set of distribution curves of all metals within soils of each parent material analyzed in this study is in Appendix B.

5.2.2 Summary Statistics - Observable Trends in Metals (N = 180).

Means and standard deviations are only useful when describing data that have a normal distribution, therefore in this section only medians are used when describing summary statistics and observable trends. Figure 5.12 depicts median values showing concentrations of 39 mg/kg or more for Cu, Pb, Cr and Zn. The median for Ni is 14.0 while Cd and Mo in soils are negligible with 0.9 and 0.08 mg/kg respectively. A large range is associated with these values which is probably quite representative of a natural system such as soil. The data reflect ambient soil concentrations expected across different soils in the state, ranging from 0.9 to 78.9 mg/kg. The values of Mo need to be interpreted cautiously. Mo concentrations are generally close to the detection limits of the method (Table 5.1), except in the second horizon of the sandy outwash and poorly-sorted till. Although median values indicate that greater than 50% of measured values are near zero, several are between 1.0 and 4.0 mg/kg. Refer to Appendix B for the full distribution of sample values. Of all metals analyzed, only

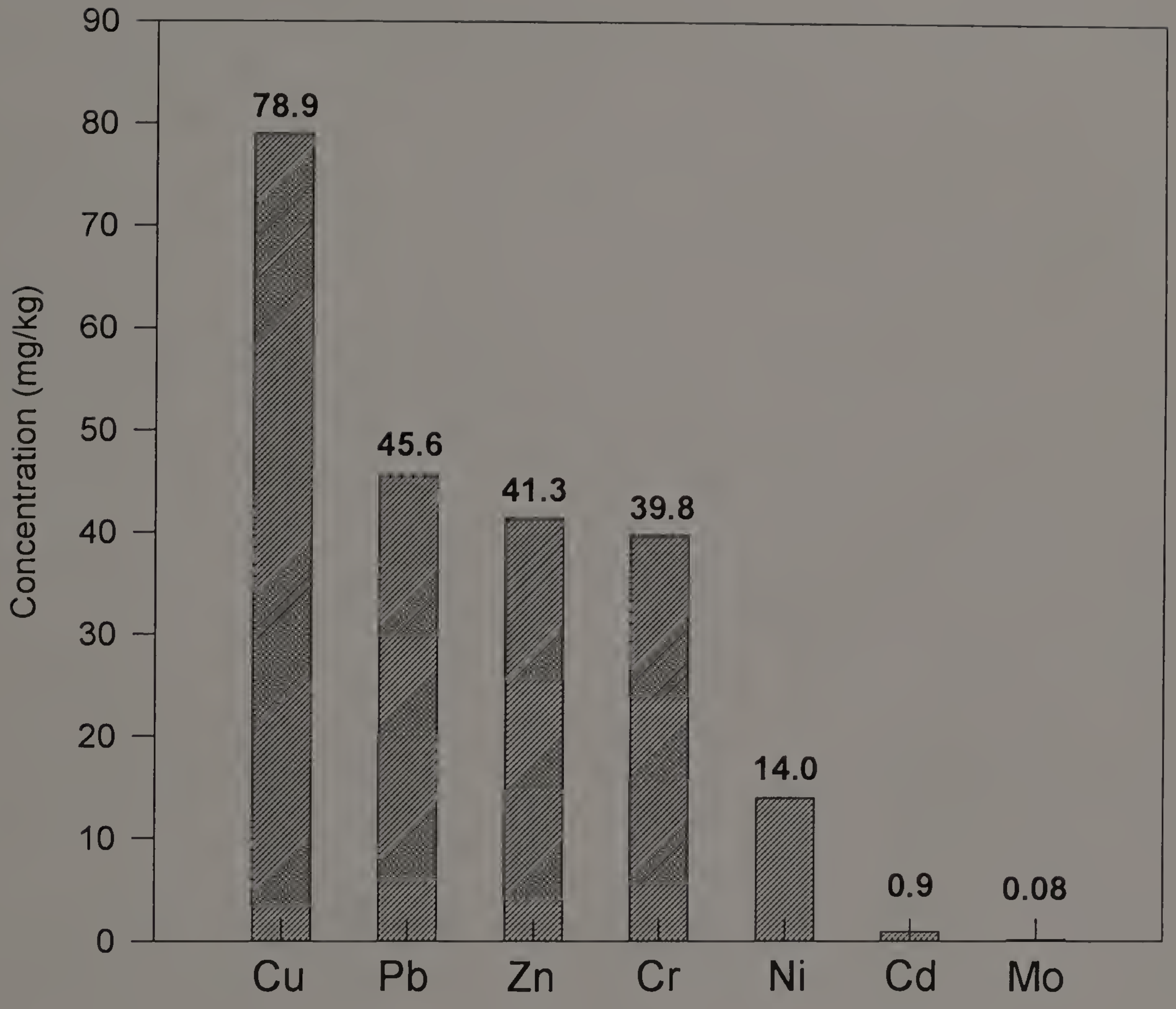


Figure 5.12 Median values (mg/kg) for heavy metals in Massachusetts soils (N = 180).

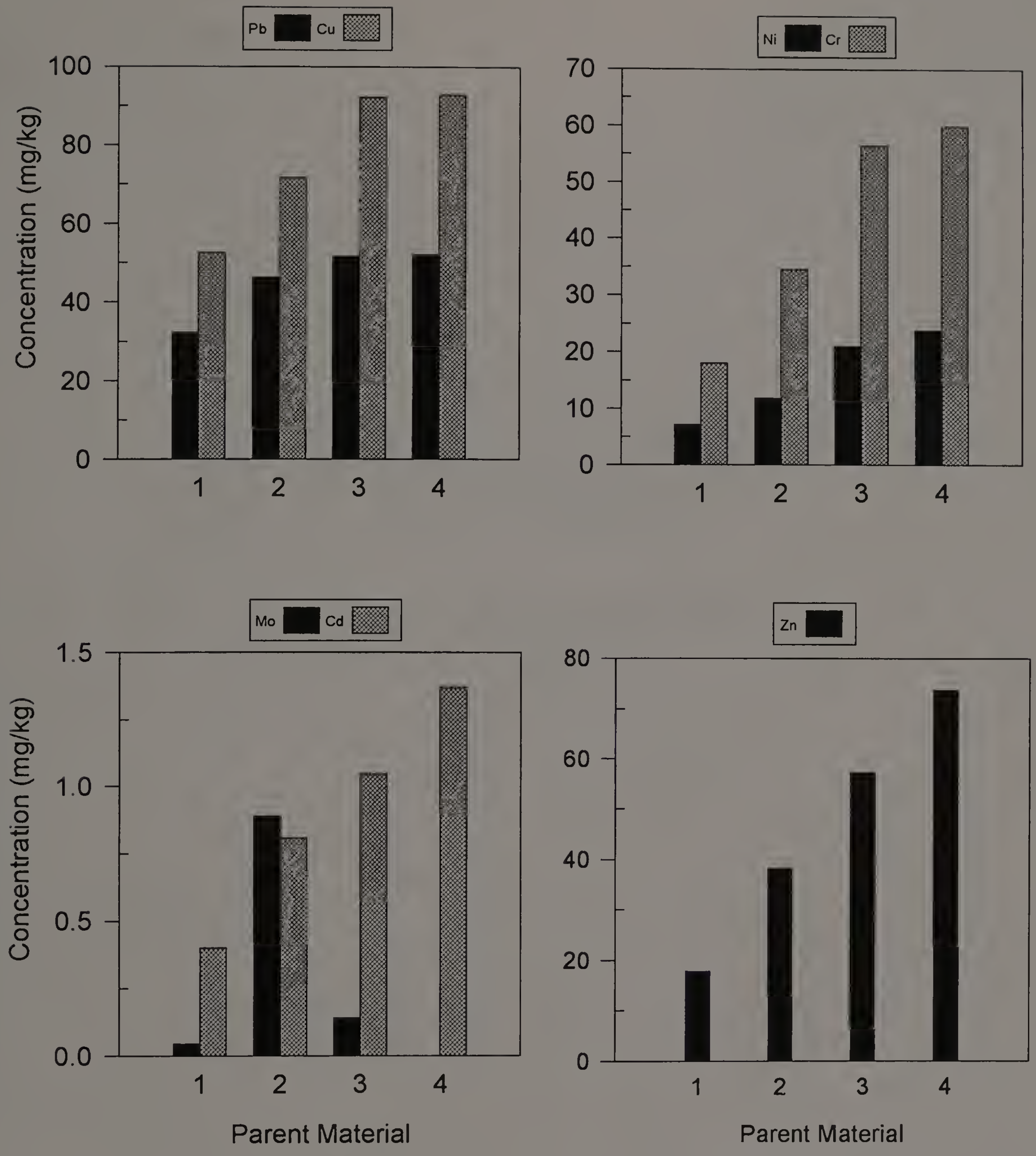
Mo exists as an anion and either the predominant Mo mineral (Molybdenite) is not prevalent in lacustrine and floodplain soils or leaching has ocurred resulting in very low concentrations. Based on these observations, Mo will not be included in the following discussion of observable trends but will still be included in the graphs.

Table 5.1 Method Detection limit (MDL) and percent recovery for the HF total dissolution method. Analysis reflect seven replicate samples.

	Pb	*Cu*	*Ni*	*Cr*	*Mo*	*Zn*	*Cd*
MDL (mg/kg)	0.05	0.11	0.05	0.44	0.04	0.06	0.03
% Recovery	115	99	94	94	101	101	101

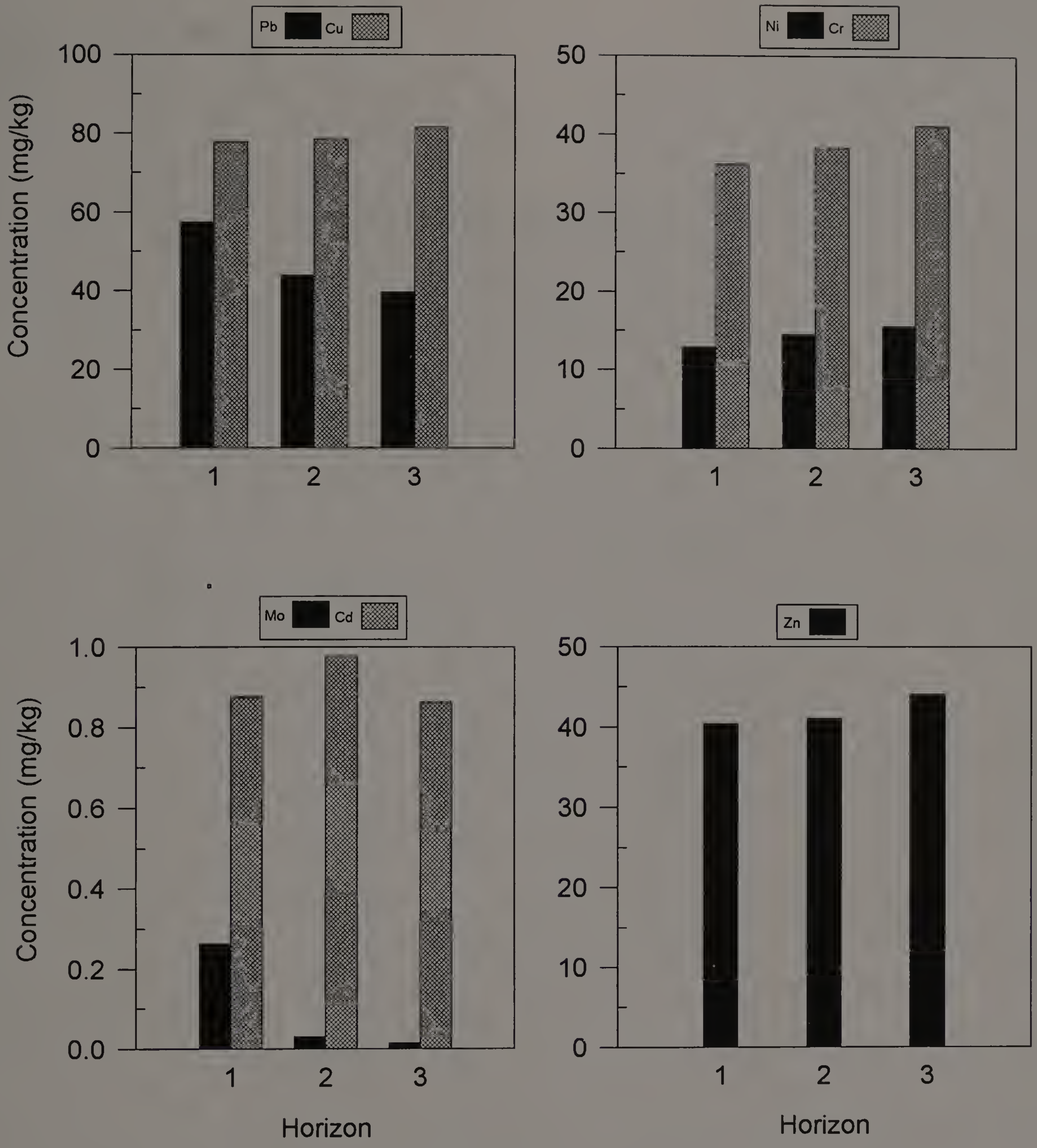
5.2.3 Summary Statistics - Observable Trends in Metals (N=45 and N=60).

Median concentrations grouped by parent material across all horizons (N=45) and by horizon across all parent materials (N=60) are presented in Figure 5.13 and 5.14 respectively. The influence of physical and chemical properties of soil is apparent by the groupings. A distinct increase in concentrations occurs from the coarse sandy outwash materials (parent material 1), grading to finer silty-clay/silt loam lacustrine (parent material 3) to the highest values in the floodplain soils (parent material 4). The hierarchy outwash<till<lacustrine appears to follow a logical order of fertility and reactivity with the increase of fines. However, the floodplain soils in this study are not necessarily finer than the lacustrine materials, ranging from silt loams to very



1 = outwash   2 = till   3 = lacustrine   4 = floodplain

Figure 5.13 Median values of heavy metals across all horizons, grouped by parent material (N = 45 per parent material).



1 = A, E, or C horizon 2 = Ab, B, or C horizon 3 = Ab or C horizon

Figure 5.14 Median values of heavy metals across parent material, grouped by horizon (N = 60 per horizon).

fine/fine sands. The trends clearly suggest either a selective sedimentation process favoring the stratification of minerals containing heavy metals or the influence of anthropogenic effects in the floodplain environment. Some floodplain soils may fine upwards potentially increasing CEC, or have higher organics which would cause them to contain more metals in the upper part. Additionally, the lacustrine soils in Massachusetts are not as clayey as the word lacustrine usually indicates. Many of the former glacial lakes sampled for this study were small shallow lakes where wind effects created turbulence closer to lake bottom disallowing the settling of clays or were influenced by meltwater stream deposits. These lakes have a greater ratio of silts to clay than deeper quieter lakes. This may possibly explain why lacustrine soils do not deviate wildly from either till or floodplain. Except for Cd, trends occur in one direction or another. Cu, Ni, Cr and Zn all behave similarly and increase slightly with depth. Cd values are the same in the 1st and 3rd horizon but are higher in horizon 2. Of all metals, Pb has the most dramatic difference in concentration with depth. Very high concentrations exist in horizon 1 as compared to horizon 2 and 3. This is due to strong bonding with organic matter. These metallo-organic compounds may reside in the soil for great lengths of time and the lead probably has anthropogenic origins. Some of these trends may be masked by horizonation within the profiles. As Figure 5.14 indicates, horizon 1 can be either an A, E, or C horizon. Horizon 2 can be an Ab, B, or C horizon and horizon 3 can be either an Ab or C. Due to the nature of the study and the natural differences in morphology across the Massachusetts landscape it was difficult to always obtain a profile with consistent A, B, C horizonation, especially in floodplains soils. Figure 5.14 shows concentration differences with depth but references to soil morphology cannot be made. Figure 5.15 shows the median values

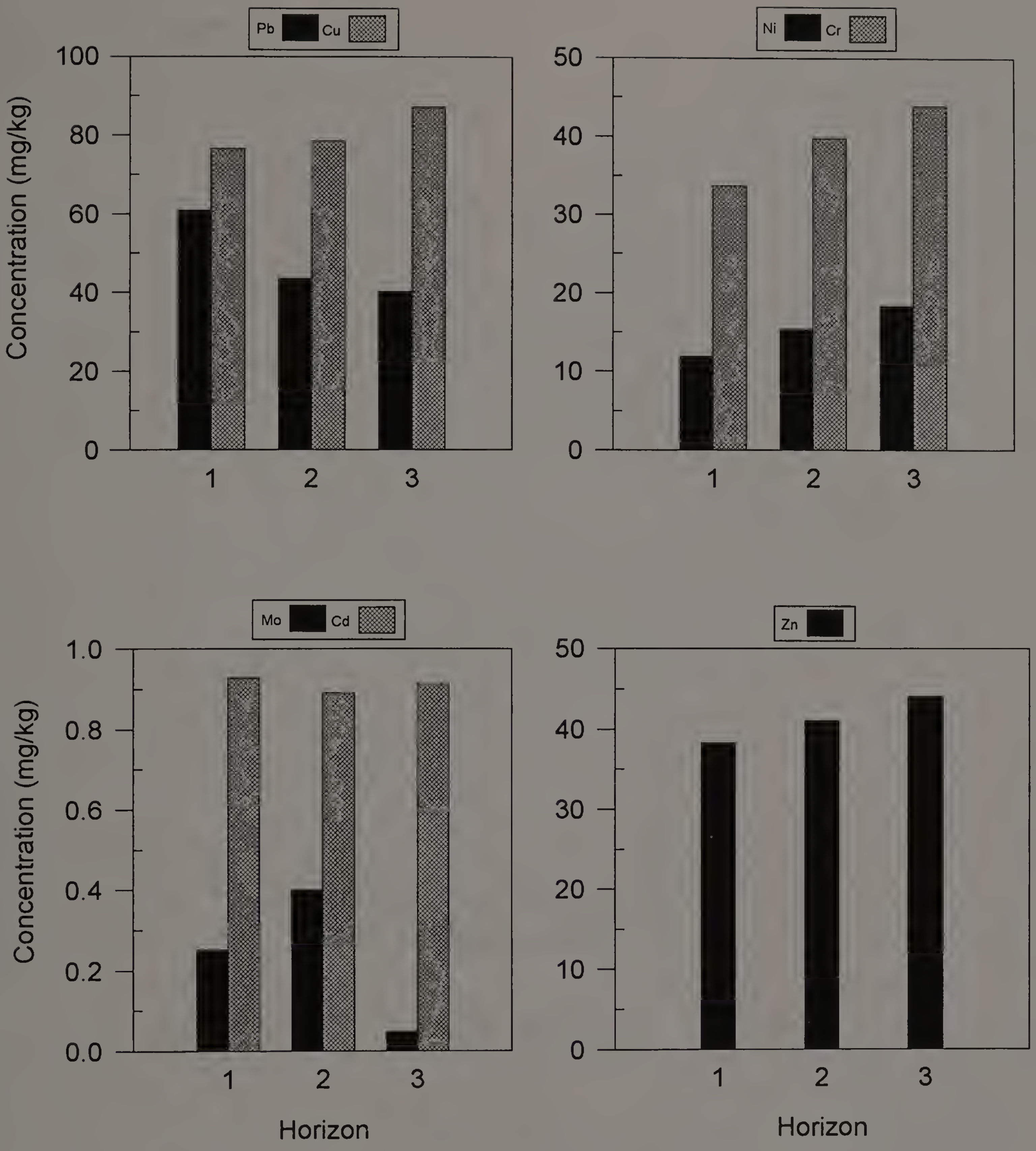


Figure 5.15 Median values of heavy metals with depth across all parent materials with typical A, B, C, horizonation (N = 114).

of heavy metals in soils which had an A, B, and C horizon sequence. This represented 38 out of the 60 sampling locations. Most of the soils that failed to have the normal A, B, and C horizon sequence were floodplain soils. Outwash, tills, and lacustrine soils tend to be represented in Figure 5.15 and show the same trends as Figure 5.14 except for Cd. Cd shows a decreasing trend in the B horizon and then increasing again in the C. One may argue that this data set is statistically more reliable since horizonation was kept consistent. However, the data for Pb, Cu, Cr, Ni and Zn reflect similar trends, inferring that pedogenic horizonation may not be influential on the metal distribution in the soil profile by depth.

5.2.4 Summary Statistics - Observable Trends in Metals (N=15).

The most distinctive trends with depth occur in lacustrine, floodplain, and outwash soils (Figures 5.16 - 5.18). Cu, Cr, Ni Cd and Zn increase successively from horizon 1, 2, and 3 with lacustrine samples. Pb peaks in horizon 1 but then drops off in the second and third horizon. Conversely, all metals decrease with depth between horizon 1 and 3 in floodplain soils. Outwash soils appear to rise in metal concentration in the middle horizon for Cd, Cr, Mo, Ni, and Zn. Cu does drop off in horizon 3 while Pb decreases with depth. Till soils appear to show no consistent trends, with most metals behaving in a dissimilar manner although Cu and Cr increase with depth (Figure 5.19). Ni and Zn concentrations are nearly constant throughout the profile and Cd decreases slightly from horizon 1 to horizon 3. Again, Pb decreases with depth.

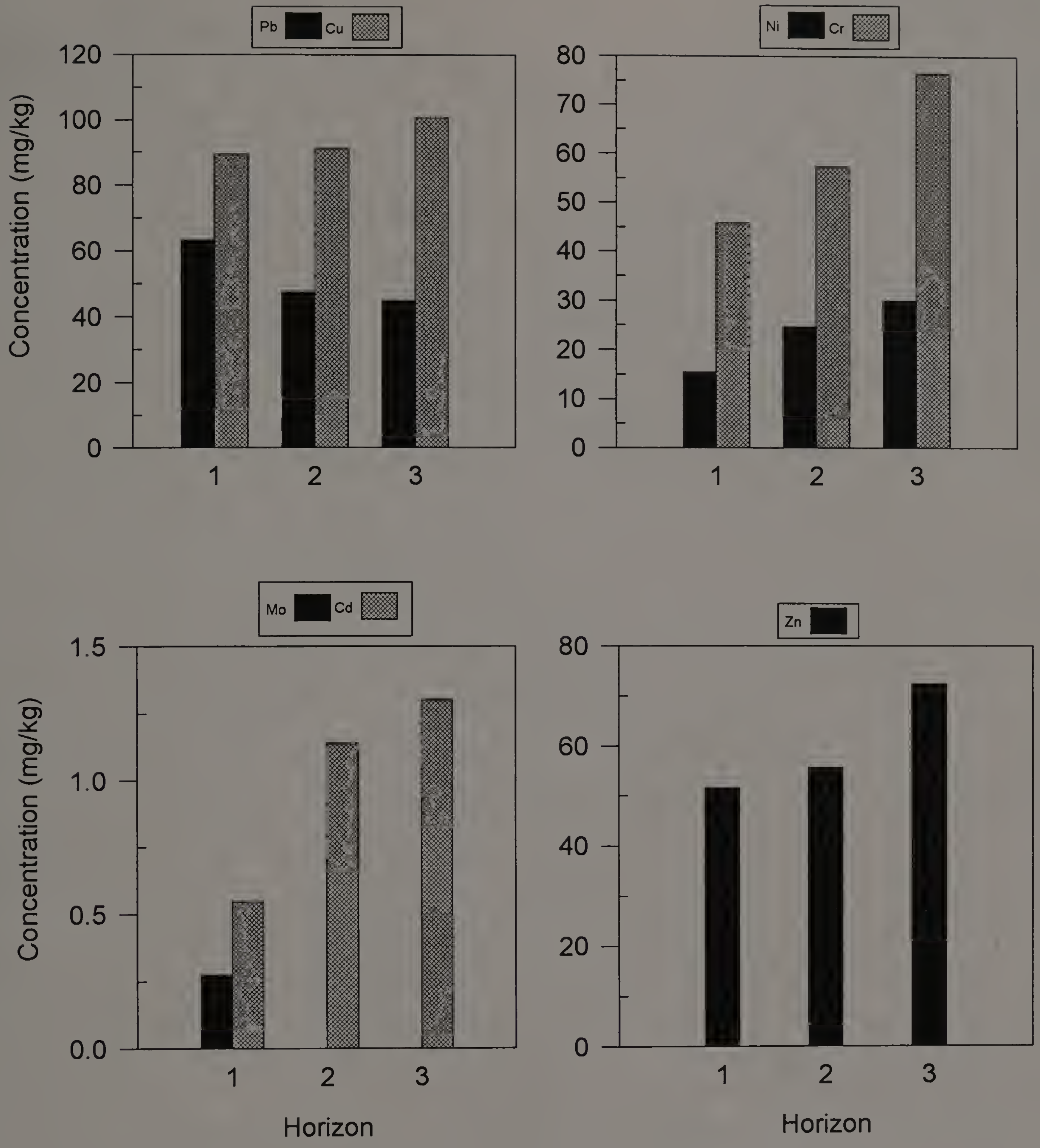


Figure 5.16. Median values of heavy metals with depth in lacustrine soils.

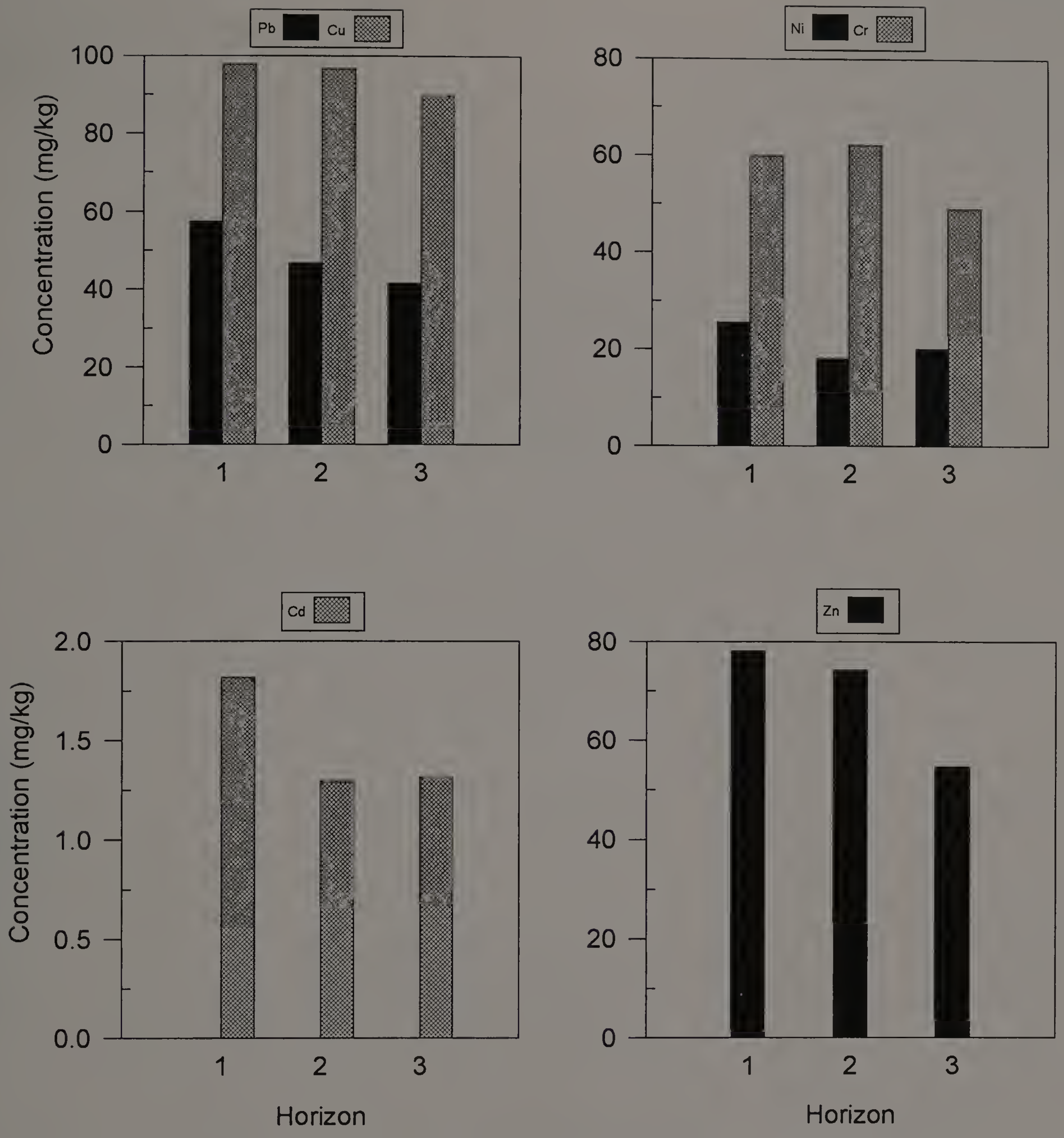


Figure 5.17. Median values of heavy metals with depth in floodplain soils.

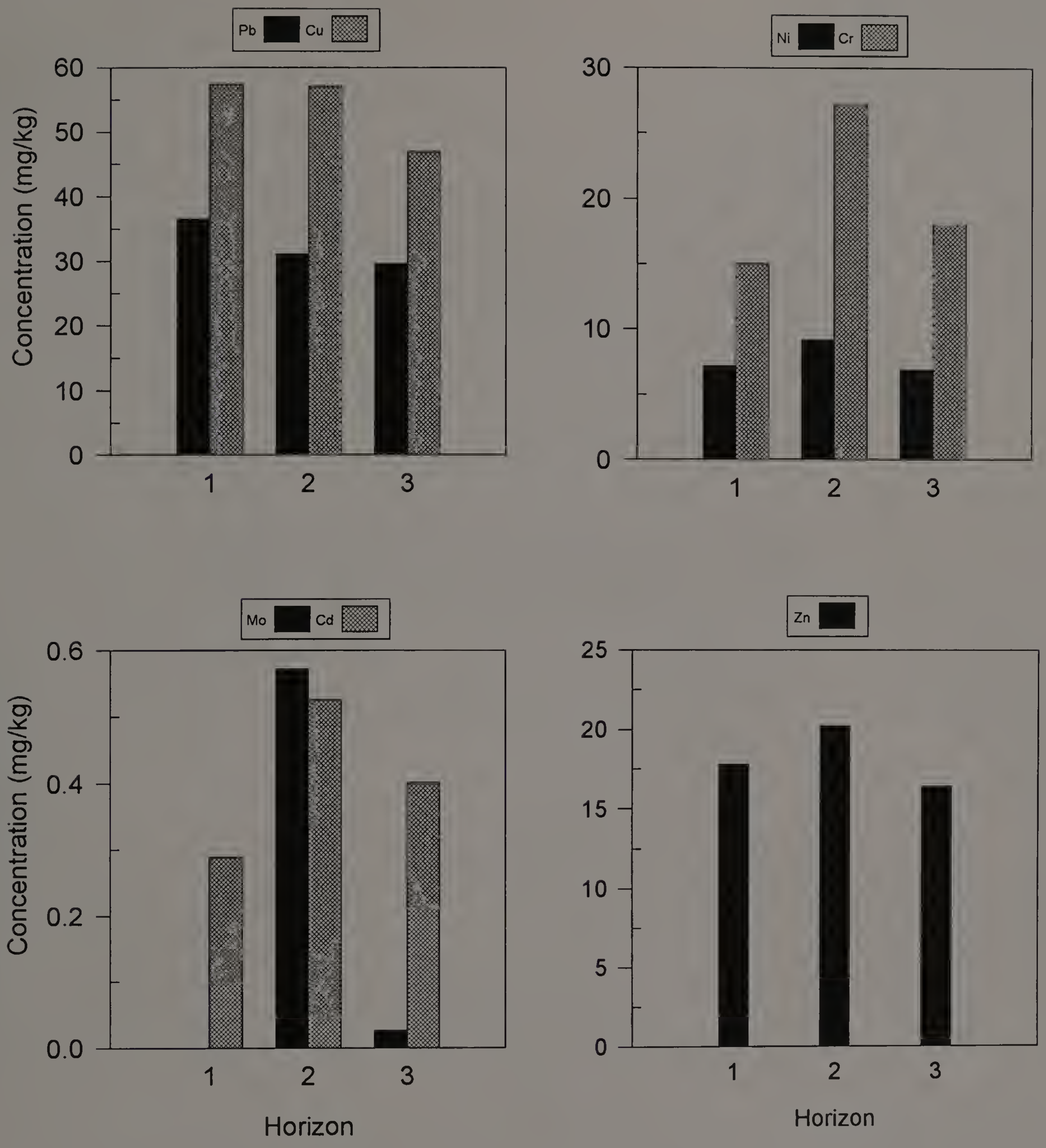


Figure 5.18 Median values of heavy metals with depth in outwash soils.

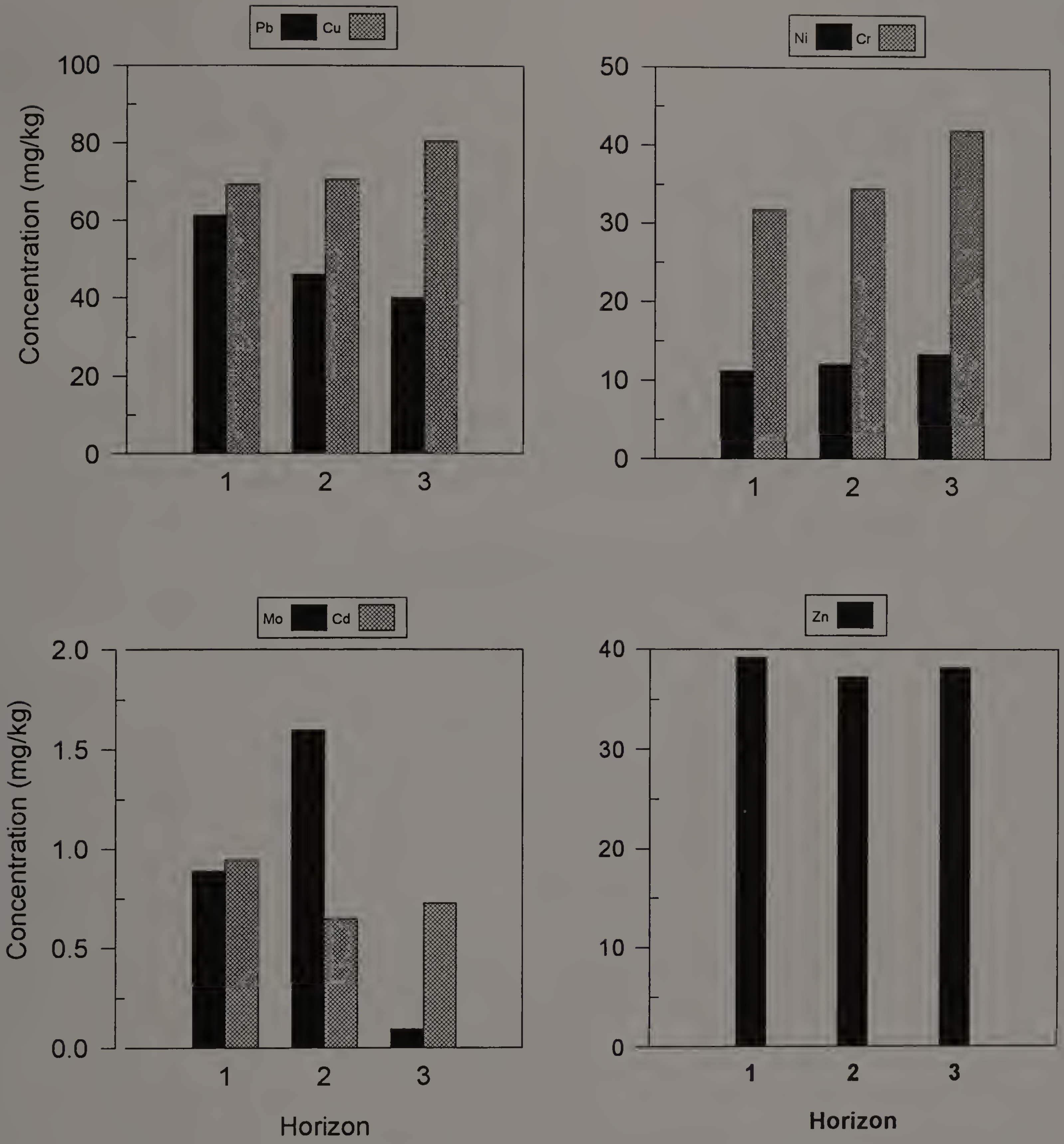


Figure 5.19 Median values of heavy metals with depth in till soils.

5.2.5 Discussion of Metals in Bedrock and Depositional Environments

With an understanding that a large range between minimum and maximum values exists, the data indicate distinct trends in the well-sorted parent materials. The grouping of soils by parent material was in part due to the nature of the present classification system where the Soil Conservation Service (SCS) delineates mapping units based on landforms and parent materials. The conventional philosophy of Soil Taxonomy is that mineralogy is included when classifying soils. A plausible interpretation of the observed trends in lacustrine or floodplain soil precludes parent materials in the context of classification, and asserts that the geogenic depositional environment of minerals containing heavy metals within these parent materials may have been selective.

Heavy metals originate from isomorphous substitution during the formation of rocks and are especially prevalent in secondary silicate minerals (Holmgren *et al.*, 1993). The predominant factor in substitution is that a metal cation may replace a constituent ion if the ionic radii are within 15% of each other and charges do not differ more than one unit. For example Ni may replace Fe and Mg but is unlikely to substitute for Na (Bohn *et al.*, 1985). Table 5.2 shows the ionic radii of metals vs. common ions in minerals.

Table 5.2 Crystal ionic radii for heavy metals and constituent ions. (Handbook of Chemistry and Physics, 1984)

Heavy Metals	Crystal Ionic Radius in A	Constituent Ions	Crystal Ionic Radius in A
Cd^{2+}	0.97	Ca^{2+}	0.99
Cr^{3+}, Cr^{6+}	0.63, 0.52	Mg^{2+}	0.66
Cu^{2+}	0.72	K^{+}	1.33
Mo^{4+}	0.70	Fe^{2+}, Fe^{3+}	0.74, 0.64
Ni^{2+}	0.69	Al^{3+}	0.51
Pb^{2+}	1.20	Si^{4+}	0.42
Zn^{2+}	0.74	Na^{+}	0.97

Motts and O'Brien (1981) described predominant bedrock types within specific regions in Massachusetts. Included with this information are ranges of heavy metals that can be found in the different rock types (Table 5.3) and minerals (Table 5.4). Differences in regional distribution of metals may be addressed by considering the location of the sampling sites. For example, soils in the central highlands of Massachusetts may have the lowest amounts of metals if most of the sites are comprised of till. Lacustrine environments enhance the deposition of finer silicate minerals possibly containing higher concentrations of heavy metals. Floodplain soils contain fine sands, silts and clays with a range of different minerals containing heavy metals. These sediments, however, also reflect a wide geographic range of approximately 350 miles representing many watersheds over a diversity of geologic deposits even as far as Canada. Some former lacustrine environments (eg. Glacial Lake Hitchcock and Glacial Lake Taunton) covered vast areas as well. Differences between the central and marginal lake-bottom materials will be more evident in lakes that are

Table 5.3 Bedrock types in Massachusetts separated by physiographic regions with corresponding averages of metal concentrations for typical rocks.

Heavy Metal Concentration in Typical Rocks - Averages and Ranges in mg/kg							
	Cd	Cr	Cu	Mo	Ni	Pb	Zn
Igneous							
Granite	0.20	20	15	1.0	8	18	40
Basalt	0.13	220	90	1.4	140	6	100
Sedimentary							
Shale, Clay	.017-11	120	50	--	68	20	80-120
Black Shale	.30-219	100	70	70	50	30	--
Sandstone, Cong.	.019-.4	35	2-40	2	2	12	30
Carbonates	.065	10	5-20	--	20	9	10

Region	Bedrock Type
WESTERN HIGHLAND	Schist Gneiss Quartzite
CONN R. VALLEY LOWLAND	Sandstone Conglomerate
CENTRAL UPLAND	Gneiss Granite Schist
EASTERN PLATEAU	Ultra Mafic Gneiss Granodiorite
SEABOARD LOWLAND	Shale Sandstone Conglomerate
COASTAL LOWLAND	Few Exposures
BOSTON-SUDBURY LOWLAND	Conglomerate Sandstone Granodiorite

Metal concentrations adapted from Alloway (1990). Bedrock types from Motts and O'Brien (1981).

Table 5.4 Heavy metal constituents in common minerals of Massachusetts. (Adapted from Alloway (1990).

Mineral	Heavy Metal	Susceptibility to weathering
Olivine	Ni, Co, Li, Zn, Cu, Mo	Easily weathered
Hornblende	Ni, Co, Li, Zn, Cu, V, Ga	
Augite	Ni, Co, Li, Zn, Cu, V, Ga, Pb,	
Biotite	Ni, Co, Li, Zn, Cu, V, Ga, Ba	
Oligoclase	Cu, Ga	Moderately stable
Orthoclase	Cu, Ga, Ba	
Muscovite	Cu, Ga, V, Ba	
Magnetite	Ni, Co, Cr, Zn, V	
Quartz	-------	Very resistant

several miles wide (Brodzikowski and van Loon, 1991). Tills (along with some smaller lake environments) possibly reflect a much more limited geographical range in parent material. Proglacial (lateral) and ice-contact (deeply-incised) outwash deposits inheriting the till mineralogy are fluvial but may not move as far as the other water-sorted materials. Outwash facies are diverse, resulting in deposits that vary tremendously in grain size with short distances but typically consist of very resistant quartz with rare associations of heavy metals. Any finer heavy metal-rich silicate minerals have been washed out due to the permeable qualities of the deposit. Sources for till and outwash probably reflect mostly local conditions with respect to mineralogy. Minerals bearing heavy metals must be present, yet New England tills are quite sandy and the dilution effect of the quartz dominated sand probably prevents these soils from exhibiting higher heavy metal concentrations than lacustrine or floodplain sediments. Metals within parent materials were usually significantly correlated with either sand, silt, or clay. These particle-size groups were further separated and a correlation matrix was established (Table 5.5-5.8). An inverse relationship existed between the particle extremes. Negative correlations occurred with the sand fraction while the most significant positive correlations were associated with the finer fractions. Cd had no significant correlation with various size fractions except in lacustrine soils. Mo was not correlated with any size fraction regardless of parent material. Significant p values may merely reflect the percentage of the size fraction in some cases.

Table 5.5 Matrix of probabilities for outwash soils (USDA size delineation). Asterisk signifies a negative correlation.

Size Fraction	Pb	Cu	Ni	Cr	Mo	Zn	Cd
Silt	0.005	0.007	0.026	0.007	0.191*	0.024	0.347*
Clay	0.005	0.319	0.288	0.377	0.805*	0.405	0.462*
V. Coarse Sand	0.758*	0.775*	0.372	0.435	0.117	0.136	0.157
Coarse Sand	0.367*	0.000*	0.318 *	0.055*	0.078	0.291*	0.767
Medium Sand	0.228*	0.000*	0.710 *	0.140*	0.108	0.158*	0.919*
Fine Sand	0.366*	0.502	0.145 *	0.268*	0.748	0.134*	0.938
V. Fine Sand	0.802*	0.000	0.826 *	0.381	0.100*	0.543*	0.959

Table 5.6 Matrix of probabilities for till soils (USDA size delineation). Asterisk signifies a negative correlation.

Size Fraction	Pb	Cu	Ni	Cr	Mo	Zn	Cd
Silt	0.735	0.503	0.211	0.140	0.378*	0.084	0.669
Clay	0.060	0.137	0.102	0.205	0.328	0.069	0.221*
V. Coarse Sand	0.895*	0.544*	0.261	0.546	0.428	0.914*	0.653
Coarse Sand	0.323	0.298*	0.177*	0.106*	0.673	0.070*	0.541
Medium Sand	0.193	0.175*	0.003*	0.005*	1.000	0.006*	0.630*
Fine Sand	0.004*	0.295*	0.942*	0.868*	0.412	0.559*	0.805
V. Fine Sand	0.497*	0.710*	0.810*	0.878	0.688*	0.798	0.933

Table 5.7 Matrix of probabilities for lacustrine soils (USDA size delineation). Asterisk signifies a negative correlation.

Size Fraction	Pb	Cu	Ni	Cr	Mo	Zn	Cd
Silt	0.258	0.030	0.796	0.278	0.287	0.807*	0.452*
Clay	0.059	0.000	0.000	0.000	0.251	0.000	0.000
V. Coarse Sand	0.574	0.917	0.995*	0.798*	0.609*	0.490	0.812*
Coarse Sand	0.927	0.032*	0.126*	0.030*	0.314*	0.519*	0.051*
Medium Sand	0.551*	0.001*	0.057*	0.011*	0.327*	0.354*	0.081*
Fine Sand	0.002*	0.000*	0.003*	0.000*	0.152*	0.017*	0.041*
V. Fine Sand	0.047*	0.000*	0.001*	0.000*	0.050*	0.002*	0.036*

Table 5.8 Matrix of probabilities for floodplain soils (USDA size delineation). Asterisk signifies a negative correlation.

Size Fraction	Pb	Cu	Ni	Cr	Mo	Zn	Cd
Silt	0.831	0.220	0.000	0.002	0.602	0.017	0.717*
Clay	0.795*	0.049*	0.689*	0.675	0.812	0.357*	0.107*
V. Coarse Sand	0.784*	0.982*	0.188	0.513	0.743	0.166	0.514
Coarse Sand	0.899*	0.940*	0.452	0.608	0.856*	0.291	0.626
Medium Sand	0.515	0.736	0.002*	0.092*	0.421*	0.244*	0.218
Fine Sand	0.940*	0.269*	0.000*	0.002*	0.775*	0.057*	0.584
V. Fine Sand	0.730*	0.138	0.549	0.985*	0.589*	0.932*	0.581

Although heavy metals predominate in rock fragments and silicate structures, mineralogy may not necessarily be a factor in the actual concentrations obtained. A true assessment of metals in the crystal lattice vs. exchangeable or available cannot be made unless other extraction techniques are employed. Many studies such as this one, consider only total metal concentrations without regard to their chemical nature. This assumes that potential contamination to soil systems and groundwater can be impacted by all labile metals with similar ability. Sequential extraction of metals has been used to assess soil contamination (Kuo *et al.* 1983; Miller and McFee, 1983) and to determine background levels (Tessier *et al.* 1980). These methods do not permit species determination but allow for geochemical distinctions that represent different sorption mechanisms elucidating mobility and transport modes. Five distinct geochemical fractions are grouped and related to common sorption mechanisms. The exchangeable fraction (1) is considered to be specifically sorbed and ion exchangeable. Desorption can be accomplished by increasing the ionic strength of the solution by addition of excess ions. The metal fraction bound to carbonates (2) is precipitated or co-precipitated and released by mild acids. The Fe and Mn oxide fractions (3) are considered to be specifically sorbed. They are unstable in low Eh conditions and can be released by reduction. The fraction bound to organic matter (4) is considered to be complexed (specifically forming coordination complexes with reactive carboxyl groups) and ion exchangeable and can be released by oxidation. The residual fraction (5) is assumed to contain the concentration of metals that are held in the lattice structure of the minerals. These metals are not a part of the labile pool that would be released by changing environmental conditions so metals can only become available by digestion with acids. In sequential extraction the least soluble item is extracted last and each fraction provides an index of availability in the soil system (Clevenger, 1990).

Although total concentrations are represented and a legitimate approximation of available metals cannot be made based on this type of data, much of the sequential extraction literature suggests that anywhere from 50 to 80% of heavy metals is found in the residual fraction of soils. This may allow one to infer that the concentrations of metals found in soils of Massachusetts may also reside in the crystal structure of minerals. Tessier *et al*. (1979) found that Co, Ni, and Zn found in the residual fraction accounted for more than 50% of the total metal concentration in sediment samples. Clevenger (1990) found that 61-69% of Pb, 69-86% Zn, 61-76% Cu, and 62-89% Cd was associated with the residual fraction in mine tailings. Alloway (1990) also states that over 50% of Ni and Cu is in the residual fraction. These ambient concentrations locked in crystal lattices are unavailable posing little threat to the environment.

5.2.6 Analysis of Variance

ANOVAS were performed on the data to test the significance of the variation in parent material, horizon, and parent material*horizon for each metal. The initial objective and main question posed in this study is to determine if there are any differences in heavy metal concentration due to parent material. A secondary consideration is to look at the effects of horizon by depth. A two-way ANOVA with each metal was applied to the log-normal transformed data and is depicted in Table 5.9. For comparison, the Kruskal-Wallis, a non-parametric equivalent to a one-way ANOVA was used on the untransformed data and showed similar results. Only one difference appeared where Mo was statistically significant at the .05 level with parent material using the non-parametric test.

Results of the two-way ANOVA on the transformed data indicate that parent material was statistically significant with all metals at the .01 level except for Mo ($p < .05$). Horizon showed no statistical differences except in the case of Pb ($p < .01$). The crossing of parent*horizon showed no interaction with any of the metals. In summary, parent material has enough variation to effectively cause differences in what metal concentrations will be found in soil across the landscape. However, horizonation does not appear to promote any differences in metal levels found with depth except for Pb.

Table 5.9 ANOVA of all metals using log-normal transformed data.

Pb	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
Parent	8.080	3	2.693	8.458	0.000
Horizon	5.267	2	2.634	8.271	0.000
Parent *Horizon	0.586	6	0.098	0.307	0.933
Error	53.495	168	0.318		
Cu					
Parent	12.711	3	4.237	24.136	0.000
Horizon	0.233	2	0.117	0.664	0.516
Parent *Horizon	1.159	6	0.193	1.101	0.364
Error	29.140	166	0.176		
Ni					
Parent	29.141	3	9.714	26.414	0.000
Horizon	1.344	2	0.672	1.827	0.164
Parent *Horizon	2.914	6	0.486	1.320	0.251
Error	61.781	168	0.368		
Cr					
Parent	36.646	3	12.215	36.634	0.000
Horizon	1.284	2	0.642	1.925	0.149
Parent *Horizon	2.637	6	0.439	1.318	0.252
Error	55.685	167	0.333		
Mo					
Parent	4.872	3	1.624	0.788	0.504
Horizon	0.086	2	0.043	0.021	0.979
Parent *Horizon	11.153	6	1.859	0.902	0.497
Error	179.212	87	2.060		
Zn					
Parent	46.450	3	15.483	32.270	0.000
Horizon	0.083	2	0.041	0.086	0.917
Parent *Horizon	1.994	6	0.332	0.693	0.656
Error	80.608	168	0.480		
Cd					
Parent	24.006	3	8.002	11.180	0.000
Horizon	0.928	2	0.464	0.648	0.525
Parent *Horizon	2.986	6	0.498	0.695	0.654
Error	100.203	140	0.716		

5.2.7 Multiple Stepwise Regression

To assess which physical and chemical soil properties are correlated with metal occurrence, a number of chemical and physical measurements were made. The transformed log-normal dependent variables (metals) were regressed on untransformed independent variables (soil properties) for this analysis. Not all measured soil properties were included since some of the parameters were interrelated. For instance the exchangeable cations (Ca, Mg, K and Na) were excluded but their indirect indicator of base saturation was kept in the statistical manipulation. The pH of soil was measured using H_2O, $CaCl_2$, and KCl but only pH-H_2O was used since the trends between the three were the same and significant covariance could be expected. The five separated sand fractions were combined into one sand fraction. The remaining independent variables included: sand, silt, clay, pH-H_2O , extractable acidity, CEC, base saturation, organic carbon, Fe and Al from citrate/dithionite and pyrophosphate extractions respectively, resulting in a total of 12 independent variables. CEC was later excluded as well since it is a combination of acidity and the bases and its inclusion produced severe collinearity problems. Since parent material was the only variable that resulted in statistical significance, the regression analysis was performed separately on each of the four parent materials with each of the metals. Interactive mode was used for the final regression models where the variables were chosen based on the appropriate F-statistic and what was rational for this particular environmental scenario. In the exploratory phase of the analysis, certain screening guidelines were employed to initially determine which variables should be included in the model. First, a model was fit using all predictor variables. Then, stepwise backwards elimination was used after evaluating the statistical output where the variable was only included if the t value was well above 2.0 and tolerance was greater than 0.1. Each of the models were further adjusted by the reselection or removal of variables until the best r^2 resulted. Variables that were intercorrelated were also addressed. The predictor variables indicated collinearity when the t values were near zero or some standard errors were quite high in the initial model. Tolerance can also be an indicator of collinearity since it equals 1 minus the variance proportion of the other predictors so these predictors begin to have a linear relationship to each other when tolerances approach zero. Systat software provided an additional output of Eigenvalues, condition indices and variance proportions to help determine intercorrelated variables. Condition indices compare the ratios of the Eigenvalues to each other. These were evaluated closely. A value of 15 suggested potential collinearity but if indices were greater than 30 collinearity was assumed. Variance proportions were also examined. This output explained the amount of proportionally produced variance by each Eigenvalue. A variance proportion of 0.5 or greater was arbitrarily chosen to distinguish high variance proportions of the coefficients. This essentially indicates that greater than 50% of the variance of a particular coefficient is attributed by the collinear relation. Subsequently then, those Eigenvalues (variables) that produced a high condition index and contributed greatly to the variance of several other variables were examined and the model was re-evaluated.

An alpha of 0.05-to-remove was chosen, meaning that a variable that was associated with a high F statistic (p value < 0.05) remained in the equation.

This multiple regression analysis approach correlates several soil properties to each metal and determines how they are related (eg. in a linear fashion) and the strength of the relationship. Often, in regression analysis a correlation matrix is established *prior* to choosing significant variables. This study established a correlation matrix with the model variables after the equations were finalized. Knowledge of basic soil science determined which variables were initially included. Oftentimes models that could explain the same amount of variance had different subset variables. Silt and sand were frequently among these variables. In this instance, the variable with a positive correlation was chosen (refer to Tables 5.5-5.8). Overall, the models are poor predictors of heavy metal content and indicate that the measured soil properties cannot explain a substantial amount of variability of metals in parent materials. One form of statistical measure would be to use the categorical variable of parent material as a dummy variable to assess the significance of any unmeasured parameters. This was not pursued due to the limitations of the software. Further pursuits towards unmeasured parameters might include mineralogical analysis by x-ray diffraction techniques to assess specific minerals within residual fractions. Even total cations such as Ca, Na, or K or their ratios could be used an indirect indicator of existing mineralogy (i.e. plagioclase vs. orthoclase, etc.).

Table 5.10-5.13 shows the predictive equations of each metal within each parent material group. Soil properties can only explain 51% of the variation for Pb, and 9-27% for all other metals in outwash soils. Several of the model coefficients are negligible, especially pertaining to the soil separates but their removal resulted in a

Table 5.10 Predictive models using multiple stepwise regression of heavy metals for outwash soils.* Alpha-to-remove = 0.05.

Metal	Model Coefficient	Variable	Correlation Coefficient†	r^2	Significance
Pb	4.313	Constant		0.51	$p < .001$
	-0.009	Sand	-0.438		
	0.080	OC	0.437		
	-2.381	Fe_{py}	-0.308		
	0.664	Al_{py}	-0.167		
Cu	3.778	Constant		0.17	$p < .007$
	0.016	Silt	0.369		
	-0.354	Fe_{cd}	-0.196		
Ni	1.971	Constant		0.18	$p < .006$
	0.014	Silt	-0.331		
	-1.501	Fe_{py}	-0.313		
Cr	2.666	Constant		0.27	$p < .001$
	0.019	Silt	0.396		
	0.358	H_2O - pH	0.296		
Zn	2.577	Constant		0.09	$p < .024$
	0.017	Silt	0.336		
Cd	-0.583	Constant		0.16	$p < .05$
	-0.085	Acidity	-0.017		
	0.291	OC	0.157		
	2.218	Al_{py}	0.077		

* OC = organic carbon, Fe_{py} = Na-pyrophosphate extractable Fe, Al_{py} = Na pyrophosphate extractable Al, Fe_{cd} = Na-citrate/Na-dithionite extractable Fe, Al_{cd} = Na-citrate/Na-dithionite extractable Al, CEC = cation exchange capacity, Acidity = extractable acidity.

† Correlation coefficients reflect Pearson values as a single independent component against the dependent variable and are not partial coefficients.

Table 5.11 Predictive models using multiple stepwise regression of heavy metals for till soils.* Alpha-to -remove = 0.05.

Metal	Model Coefficient	Variable	Correlation Coefficient†	r^2	Significance
Pb	3.277	Constant		0.29	$p<.001$
	0.025	CEC	0.392		
	-0.713	Fe_{cd}	0.118		
	-0.759	Al_{cd}	0.152		
	-1.152	Fe_{py}	-0.038		
Cu	3.650	Constant		0.43	$p<.001$
	1.209	Fe_{cd}	0.364		
	-1.419	Fe_{py}	0.095		
Ni	1.783	Constant		0.38	$p<.001$
	0.015	Bases	0.380		
	1.040	Fe_{cd}	0.268		
	-1.334	Fe_{py}	0.011		
Cr	2.777	Constant		0.42	$p<.001$
	0.015	Bases	0.386		
	0.996	Fe_{cd}	0.332		
	-1.190	Fe_{py}	0.076		
Zn	1.573	Constant		0.54	$p<.001$
	0.239	H_2O - pH	0.330		
	1.520	Fe_{cd}	0.470		
	-1.712	Fe_{py}	0.138		
Cd	-4.890	Constant		0.30	$p<.002$
	0.796	H_2O - pH	0.396		
	0.081	Acidity	-0.094		
	-0.245	OC	-0.264		

* OC = organic carbon, Fe_{py} = Na-pyrophosphate extractable Fe, Al_{py} = Na pyrophosphate extractable Al, Fe_{cd} = Na-citrate/Na-dithionite extractable Fe, Al_{cd} = Na-citrate/Na-dithionite extractable Al, CEC = cation exchange capacity, Acidity = extractable acidity.

† Correlation coefficients reflect Pearson values as a single independent component against the dependent variable and are not partial coefficients.

Table 5.12 Predictive models using multiple stepwise regression of heavy metals for lacustrine soils.* Alpha-to-remove = 0.05.

Metal	Model Coefficient	Variable	Correlation Coefficient†	r^2	Significance
Pb	3.619	Constant		0.35	$p<.001$
	0.009	Clay	0.283		
	0.041	CEC	0.375		
	-0.006	Bases	-0.282		
	-0.111	OC	0.083		
Cu	3.843	Constant		0.66	$p<.001$
	0.008	Silt	0.323		
	0.007	Clay	0.500		
	-0.026	OC	-0.399		
	0.257	Fe_{cd}	0.545		
Ni	1.210	Constant		0.64	$p<.001$
	0.013	Clay	0.646		
	0.241	H_2O - pH	0.609		
	0.427	Fe_{cd}	0.608		
Cr	3.859	Constant		0.80	$p<.001$
	-0.010	Sand	-0.653		
	0.011	Clay	0.697		
	-0.053	OC	-0.438		
	0.300	Fe_{cd}	0.601		
	1.404	Al_{py}	-0.096		
Zn	2.564	Constant		0.68	$p<.001$
	0.013	Clay	0.587		
	0.152	H_2O - pH	0.480		
	-0.074	OC	-0.481		
	0.433	Fe_{cd}	0.650		
	2.393	Fe_{py}	0.072		
Cd	-0.220	Constant	0.56		$p<.001$
	0.040	Clay	0.624		
	0.065	Acidity	0.006		
	-0.493	Fe_{cd}	0.181		
	-4.935	Fe_{py}	-0.211		

* OC = organic carbon, Fe_{py} = Na-pyrophosphate extractable Fe, Al_{py} = Na pyrophosphate extractable Al, Fe_{cd} = Na-citrate/Na-dithionite extractable Fe, Al_{cd} = Na-citrate/Na-dithionite extractable Al, CEC = cation exchange capacity, Acidity = extractable acidity.

† Correlation coefficients reflect Pearson values as a single independent component against the dependent variable and are not partial coefficients.

Table 5.13 Predictive models using multiple stepwise regression of heavy metals for floodplain soils.* Alpha-to-remove = 0.05.

Metal	Model Coefficient	Variable	Correlation Coefficient†	r^2	Significance
Pb	4.969	Constant		0.53	$p<.001$
	-0.320	H_2O - pH	-0.390		
	0.148	OC	0.514		
	0.883	Fe_{cd}	0.421		
Cu	3.973	Constant		0.65	$p<.001$
	-0.021	Clay	-0.313		
	0.067	OC	0.140		
	0.550	Fe_{cd}	0.523		
	0.780	Al_{cd}	0.492		
Ni	0.961	Constant		0.59	$p<.001$
	0.008	Silt	0.608		
	0.273	H_2O - pH	0.659		
	0.289	Fe_{cd}	0.479		
Cr	2.851	Constant		0.56	$p<.001$
	0.008	Silt	0.484		
	0.176	OC	0.347		
	0.858	Fe_{cd}	0.531		
Zn	3.647	Constant		0.51	$p<.001$
	0.815	Fe_{cd}	0.718		
Cd	-0.499	Constant		0.30	$p<.001$
	0.006	Sand	0.108		
	0.827	Fe_{cd}	0.525		

* OC = organic carbon, Fe_{py} = Na-pyrophosphate extractable Fe, Al_{py} = Na pyrophosphate extractable Al, Fe_{cd} = Na-citrate/Na-dithionite extractable Fe, Al_{cd} = Na-citrate/Na-dithionite extractable Al, CEC = cation exchange capacity, Acidity = extractable acidity.

† Correlation coefficients reflect Pearson values as a single independent component against the dependent variable and are not partial coefficients.

substantial lowering of the r^2. In outwash the removal of fines results in an inert soil by comparison and perhaps may explain the poor relation among variables and low multiple coefficients of determination. Organically bound (Fe_{py}, Al_{py}) and oxides (Fe_{cd}, Al_{cd}) of Fe and Al were often negatively correlated with Pb, Cu, and Ni. The r^2 values for till soils were only slightly better, ranging from 0.29 to 0.38 for Pb, Ni, and Cd. The r^2 for Cu, Cr, and Zn are 0.43, 0.42 and 0.54 respectively. These regression equations do not indicate a strong relationship between soil properties and total metals in tills. The correlation coefficients are quite low, not exceeding 0.4 but reveal that most correlations are positive. As with outwash, till soils favored the selection of organically bound and oxides of Fe and Al. Occasionally H_2O- pH or bases remained in the regression equation. Soil properties in lacustrine soils by far show the best potential in explaining the variability of total metals. Eighty percent of the variability is explained with Cr, 68% with Zn, 66% with, 64% with Ni, and 56% and 35% for Cd and Pb respectively. Many of the same variables appear in these equations as in the first two sets but with much higher correlation coefficients generally ranging from 0.4 to 0.6. Fe_{cd} is always positively correlated, however OC appears quite frequently but is mostly negatively correlated. Clay appears in all of the equations and is always positive and highly correlated. Soil properties in floodplain soils do not explain quite as much variation, generally between 50 and 60%, but with 65% for Cu and 30% with Cd. Fe_{cd} appears in all equations and is positive and highly correlated. Other positive correlations are quite high, between 0.4 and 0.6.

It appears that predicting total metals based on soil physical and chemical properties is inappropriate at the selected scale. These statistical results are premised on a statewide evaluation. In some cases, there may not be enough variability. For instance, organic carbon values may not vary enough to have a significant correlation with metal content and distribution. Humic and fulvic acids are known to form strong complexes with metals. Even conventional statistics with a large, representative data set may not illustrate what is known empirically about natural systems. Models using selected soil properties may be more efficacious in explaining the variability of specific phenomenon, such as a sorption mechanism.

Selection of the final model is a tradeoff between prejudice and variance. By decreasing the number of variables in the model, the stability increases because the variance decreases. Conversely, favoritism towards decreasing these variables or choosing only a select few known to perform well may result in a loss of the most appropriate model. Dimensionality or the number of variables to include, becomes an issue. Many soil properties have to be included to improve the prediction however collinearity was a large problem and many variables needed to be removed thereby substantially lowering the r^2. Once the dimensionality was determined, several models of equal performance resulted. Knowledge of soil science and what a variable communicates were criteria in the final selection.

5.3 Heavy Metals - Toxicity Characteristics Leaching Procedure (TCLP)

Several methods exist for measuring cations and metals. Conventional ammonium acetate methods are used to determine the exchangeable fraction of major soil cations such as Ca, Mg and K in cation exchange phenomena. Inundation with neutral salts is not effective in measuring quantities of trace metals in soils. Acetic acid or sodium acetate has been used specifically as a soil extraction of uncontaminated soils (eg. The Morgan's Soil Testing System for soil nutrients) based on an understanding of chemical reactivity at the soil solid-solution interface. This extraction method employs a predominant weakly ionized organic acid buffered with its sodium salt. The TCLP is a method that was originally designed to estimate potential leachability of solid waste. A 0.1 N acetic acid solution is used to simulate low molecular weight carboxylic acids present in municipal landfills and is generally 5 to 10 times weaker than conventional acetic acid extractants. Although the original intent is to use the results for prediction or modelling of contaminant migration when combining industrial with municipal waste, it is often used as a soil extraction test to assess cleanup levels of soils at contaminated sites. However the validity of this test as a soil extraction method for uncontaminated soils is unclear.

The TCLP was used in this study for three reasons. It is *the* extraction procedure most widely used in Massachusetts to assess heavy metal content in contaminated soils. Secondly, it's efficacy as a soil extraction on uncontaminated soils has not been evaluated, and thirdly, it would identify any inadvertently contaminated soils in a study originally designed to evaluate ambient concentrations. Twenty-two sub-samples out of the original 180 soils were initially chosen for TCLP analysis. Ten samples were randomly selected while 12 were chosen based on high concentrations of metals found in the total analysis. Table 5.14 shows mean TCLP concentrations indicating few TCLP extractable metals in these soils. One floodplain soil had more Pb than the regulatory level permits and was removed from the data set. Cr in this same soil was also high and near the regulatory limits indicating that this site may have been contaminated. Zinc is consistently high compared to the other metals in the data set indicating that contamination may have occurred during sample preparation. Because of low TCLP extractable levels in this sample set, the TCLP extraction of the remaining soils was discontinued.

Table 5.14 Means, Method Detection Limits (MDL), and percent recoveries for TCLP analysis. Mean values represent 22 samples. MDL and recoveries reflect seven replicate analyses.

	Pb	***Cu***	***Ni***	***Cr***	***Mo***	***Zn***	***Cd***
Mean TCLP (mg/kg)	0.08	0.16	0.03	0.05	0.01	1.68	0.07
MDL (mg/kg)	0.07	0.08	0.07	0.11	0.04	0.08	0.06
% Recovery	90	99	83	87	90	93	98

MDL's and percent recovery are presented in Table 5.14. Published values of the MDL on the TCLP are only available for Cd, Cr, and Pb and are 0.01, 0.01, and 0.08 mg/kg respectively, reinforcing the MDL's obtained in this study. Regulatory limits have only been set for Cd, Cr and Pb.

The low levels of TCLP extractable metals are somewhat questionable since the concentrations are at or below the detection limits of the method. These results substantiate the ineffectiveness of this procedure to assess the level of extractable metals under natural conditions (i.e. uncontaminated) unless the normality of the solution is increased. This would simulate more aggressive conditions that may exist in some situations. A 0.1 N solution may be quite suitable for contaminated soils with extremely excessive amounts of metals since it estimates the most highly bioavailable metals bound loosely to the solid phase. However, the use of an acetic acid solution as an extracting agent may result in discrepancies in assessments of bioavailability in some cases. Acetic acid-soluble chromium for example, is often near detection limits because insoluble hydrated oxides of Cr (III) are occluded in Fe oxides under acidic conditions (Alloway, 1990). This exemplifies the inability of a single extractant to target specific metal phases commonly found in soils. Additionally, the extractant used to analyze metals at trace levels may even change the speciation.

There are several perspectives involving the use of the TCLP procedure in the remediation of contaminated sites. If it is used as a leachate extraction in determining soluble contaminants, one approach could be to set cleanup levels at concentrations lower than the maximum allowed values established by EPA. This assumes that the soils have been cleaned to an acceptable level while in fact there still may be enough contamination left to migrate down to the groundwater, producing concentrations higher than designated drinking water quality standards. It also assumes that contaminant concentrations leaching from soil are similar to the concentrations found in the lab. Since the TCLP test was not designed as an analytical method for soil extraction there are limitations if the test is to be used in this manner. Only water soluble contaminants in the aqueous phase are measured. Any hydrophobic organic materials sorbed on soil particles are lost in the filtering step of this test although some colloidal material may pass through the filter. Some contaminants that were not made soluble may still be sorbed onto particles. Studies indicate that natural systems may easily sorb and desorb chemical compounds, while desorption may not actually take place using this extraction procedure (USEPA 1989). The natural variability found in the chemical and physical properties of soils is another limitation. Water transport and solubility phenomena are also overlooked. Although this may not pertain to heavy metals, some volatile organics or solvents that are immiscible in water do not depend on the aqueous phase for transport through the soil.

5.4 Nitric-Perchloric Acid Digestion

Twenty-one sets of samples were randomly chosen and paired for a comparison of the two digestion methods. A nitric-perchloric acid digestion was used in this study to assess the effectiveness of the hydrofluoric total dissolution procedure. The nitric-perchloric procedure can assess total concentrations in a rapid fashion. Presently, environmental labs rarely use either hydrofluoric or perchloric due to its danger in handling. The total methods concept in the environmental arena generally involves using nitric or hydrochloric acid and occasionally hydrogen peroxide as an oxidizer. The hydrofluoric acid digestion proceeds to attack silicate minerals where the fluoride ion combines with Si^{4+} to form SiF_4 which volatilizes. This mechanism is crucial to the complete dissolution of silicates and is most effective with hydrofluoric acid. The nitric-perchloric acid digestion then, is not a total dissolution in the true sense. As the TCLP method was not stringent enough to extract a high amount of metal, the nitric-perchloric digestion is not aggressive enough to dissolve all of the soil particles. In fact, approximately 20-25% of the soil grains still remain with this procedure.

The discrepancies between the terms total and background levels should be noted. Is background considered all metals within the geologic sample, or just the bioavailable fraction indicating immediate bioavailability? If much of the heavy metals are residing in the crystal structure, then it is not considered available. Using the nitric-perchloric digestion to assess total metals would still be suitable since it would simulate extreme weathering unrepresentative of typical soil conditions. Most environmental labs strive to measure bioavailable metals or those concentrations posing an immediate threat in order to address remediation technology. Using the total metals data from the hydrofluoric procedure would then give a highly liberal estimate. Table 5.15 depicts the differences between the hydrofluoric and nitric-perchloric acid digestion procedures, generally indicating that the hydrofluoric acid results are between 1.5 and 4.0 times higher than the nitric-perchloric digestion. Much of the soil matrix is comprised of silica. The data suggests that a selective extraction is taking place where nitric-perchloric acid digestion dissolves only those heavy metals not associated with silicate phases. An ANOVA was performed on the two separate methods as well. Significant differences at the .01 level occurred with Pb, Cu, Cr, and Mo. Ni, Zn, and Cd were not statistically significant. Table 5.16 shows regression equations generated where metal total metal content (M_{total}) was regressed on M_{np} (nitric-perchloric metal concentration). Ni, Cr, and Zn result in the best fitting equations with r^2 of .92, .90, and .79 respectively. Mo often approached detection limits and Cd was quite low as well. This may explain the poor fit for these elements. It should be noted that Pb technically was always a difficult element to measure using ICP instrumentation which may be reflected in the regression results.

Table 5.15 Median values for HF total dissolution vs. nitric-perchloric digestion.

Median values for HF Total Dissolution (mg/kg)						
Pb	Cu	Ni	Cr	Mo	Zn	Cd
45.6	78.9	14.0	39.8	0.08	41.3	0.9
Median values for Nitric-Perchloric Digestion (mg/kg)						
Pb	Cu	Ni	Cr	Mo	Zn	Cd
14.4	20.6	9.4	13.8	0.2	22.8	0.9
Percent Silicates (%)						
Pb	Cu	Ni	Cr	Mo	Zn	Cd
31.2	58.3	4.6	26.0	n/a	18.5	0

Table 5.16 Regression equations of two total metals methods using HF total dissolution and nitric-perchloric digestion.

Regression Equations	r^2
$Pb_t = 0.82\ (Pb_{np}) + 34.9$	0.37
$Cu_t = 1.21\ (Cu_{np}) + 53.7$	0.33
$Ni_t = 0.98\ (Ni_{np}) + 6.4$	0.93
$Cr_t = 1.33\ (Cr_{np}) + 15.8$	0.90
$Zn_t = 0.89\ (Zn_{np}) + 15.7$	0.79
$Cd_t = 0.56\ (Cd_{np}) + 0.1$	0.64

CHAPTER 6

CONCLUSIONS

This study reports concentrations of 7 heavy metals in soils at 60 sites across Massachusetts. These sites were partitioned into 4 parent materials commonly found in the state in order to evaluate variations of metal distribution between and within each surficial deposit. The reported values are based on a total dissolution method that reflects the entire geologic sample. A semi-total nitric/perchloric acid digestion and TCLP extractable metals were also analyzed to help evaluate the site occupancy of the metals and characterize the effectiveness of the extraction procedures. Standard chemical and physical characterization was additionally performed on all samples. These data were used in multiple stepwise regression analyses to generate models predicting controls on heavy metal distribution. Preliminary assumption diagnostics were executed on the data set prior to statistical analysis where the data was found to be non-normal. This issue was addressed by reporting summary statistics as median values or cumulative frequency. Transformed log-normal data were used in the analysis of variance, and as dependent variables when regressed on untransformed independent variables in the predictive models. The study concludes several points:

1) Concentrations of heavy metals in Massachusetts soils range between 0.08 and 79 mg/kg. This range is based on median values of the entire data set (N=180). Mo values are questionable since they often approached method detection limits.

2) Distinctive differences appear when separating out the parent materials. All metals increase following a hierarchy of outwash$<$till$<$lacustrine$<$floodplain (except for Mo). This reflects an increase of fine particle sizes and indicates that the geogenic depositional environment of minerals containing heavy metals (i.e. silicates) within these parent materials may have been selective. Other studies have reported that $>50\%$ of heavy metals reside in the crystal structure of minerals, suggesting that these metals would not readily be released in the environment. There were no trends observed when the soils were grouped by horizon. Results of a two-way ANOVA also showed that parent material was statistically significant at the .01 level while depth by horizon was not.

3) Depths within parent materials showed unique trends. Heavy metals increased with depth in lacustrine soils, decreased with depth in floodplains and were highest in the B horizons of outwash soils. Till soils exhibited erratic distributions of metals with depth reflecting the lack of sorting of this deposit.

4) The semi-total nitric/perchloric acid digestion results are 1.5 to 4.0 times lower than the hydrofluoric total dissolution method. This suggests that this procedure discriminates against metals associated with silicate mineral phases.

5) The efficacy of the TCLP extractable metals procedure on uncontaminated soils is poor. Most TCLP metal concentrations approached method detection limits. This procedure was originally designed to assess contaminant migration for co-disposal of

industrial and municipal waste. It was not designed as a soil extraction but is often used as such.

6) Discrepencies in the terms total and background exist. Background levels of metals in most studies consists of total concentrations. Perhaps background levels should be represented by the bioavailable fraction of soils that pose the most immediate threat. Total values are effectively governed by the chosen procedure.

7) The implications of the use of TCLP extractable metals in the regulatory sense is clear. It remains useful as a screening tool for separating occluded metals in soils from those of anthropogenic origin.

8) The models generated from this study are poor predictors of heavy metal content and distribution and indicate that soil property information cannot explain a substantial amount of variability of metals in parent materials. The characterization data used in the models reflect the products of weathering and chemistry altered by pedogenesis. Very few metals may be affiliated with the labile fraction of soils or with the chemical parameters chosen for this study. Predicting total metals based on soil property information may also be inappropriate at a statewide scale. Additionally in some cases, there may not be enough variability produced by the measured parameters.

9) Background levels obtained from this study are effective in discerning between those soils that are uncontaminated or highly contaminated. Site specific information is best in questionable situations.

APPENDIX A

SITE LOCATION AND SERIES DESIGNATION

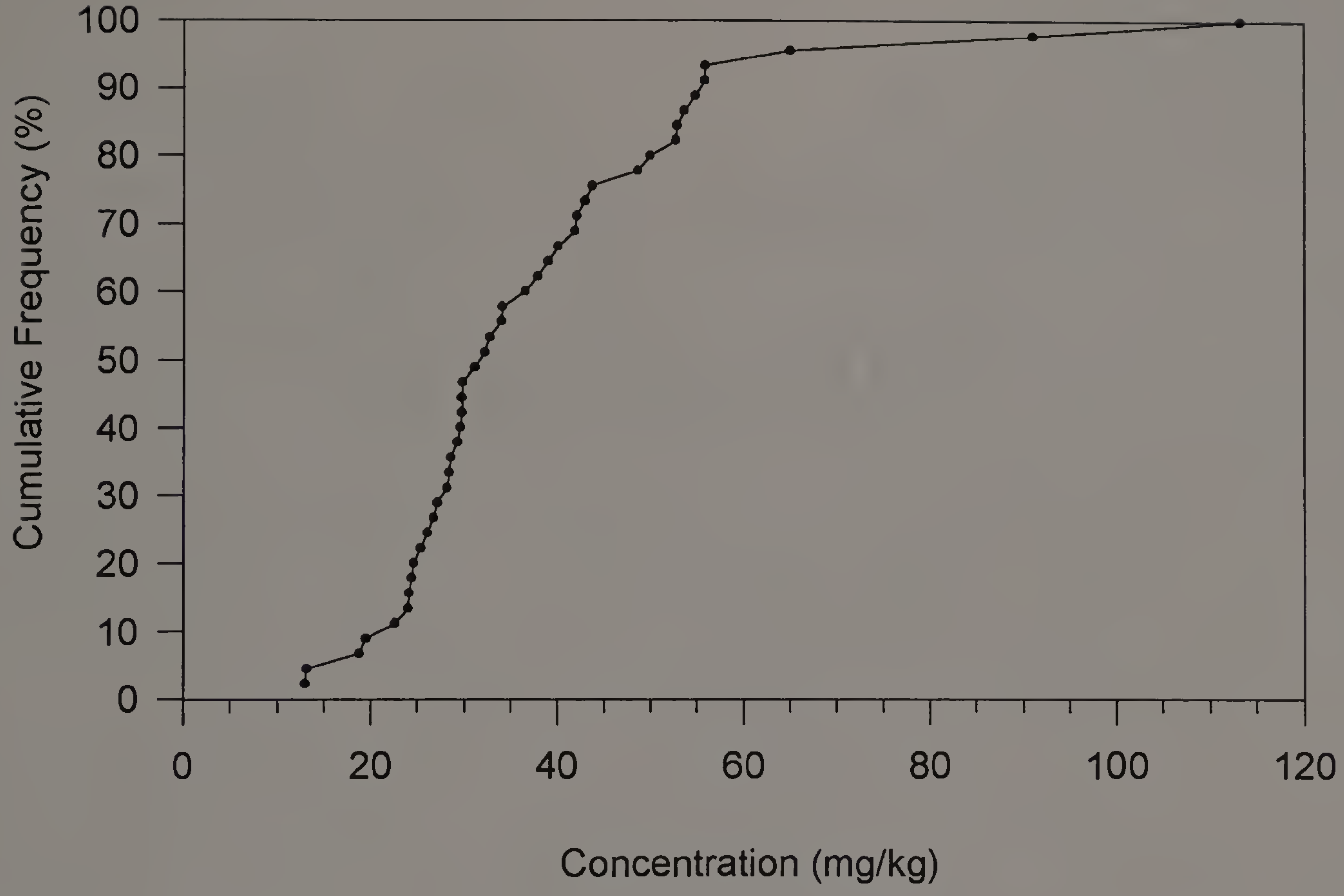
Site ID	Parent Material	Series	County	Town
1	outwash	East Chop	Barnstable	Sandwich
2	outwash	Pipestone	Plymouth	Bridgewater
3	outwash	Carver	Plymouth	Carver
4	outwash	Berryland	Worcester	Westminster
5	outwash	Berryland	Franklin	Turners Falls
6	outwash	Saugatuck	Worcester	Templeton
7	outwash	Deerfield	Plymouth	Wareham
8	outwash	Merrimac	Hampshire	Cummington
9	outwash	Saugatuck	Barnstable	Falmouth
10	outwash	Windsor	Barnstable	E. Sandwich
11	outwash	Agawam	Worcester	Northboro
12	outwash	Hinckley	Hampshire	Belchertown
13	outwash	Riverhead	Dukes	W. Tisbury
14	outwash	Sudbury	Essex	Ipswich
15	outwash	Amostown	Plymouth	Lakeville
16	lacustrine	Scio	Franklin	W. Deerfield
17	lacustrine	Scio	Franklin	W. Deerfield
18	lacustrine	Buxton Var	Hampshire	Northampton
19	lacustrine	Raynham	Hampshire	Amherst
20	lacustrine	Scitico	Hampshire	Hadley
21	lacustrine	Boxford	Essex	Essex
22	lacustrine	Boxford	Essex	Ipswich
23	lacustrine	Scitico	Essex	Danvers
24	lacustrine	Raynham	Plymouth	Bridgewater
25	lacustrine	Maybid	Plymouth	Bridgewater
26	lacustrine	Scio	Plymouth	Lakeville
27	lacustrine	Raynham	Worcester	Northboro
28	lacustrine	Raynham	Norfolk	Norfolk
29	lacustrine	Raynham	Norfolk	Dover
30	lacustrine	Scio	Middlesex	Maynard
31	till	Barnstable	Plymouth	Manomet
32	till	Paxton	Worcester	Spencer
33	till	Woodbridge	Worcester	W. Brookfield
34	till	Paxton	Franklin	Hawley
35	till	Paxton	Worcester	Winchendon
36	till	Chatfield	Worcester	Petersham
37	till	Scituate	Plymouth	Lakeville
38	till	Ridgebury	Bristol	Dartmouth
39	till	Brockton	Hampden	Monson
40	till	Pittstown	Plymouth	Hingham
41	till	Berkshire	Berkshire	Windsor
42	till	Canton	Worcester	Harvard
43	till	Scituate	Worcester	Warren
44	till	Marlow	Berkshire	Washington
45	till	Nantucket	Dukes	Gay Head

46	floodplain	Rippowam	Middlesex	Concord, Concord R.
47	floodplain	Limerick	Middlesex	Pepperell, Nashua R.
48	floodplain	Winooski	Berkshire	Sheffield, Housatoni
49	floodplain	Hadley Var	Franklin	Montague Conn R.
50	floodplain	Saco	Hampshire	Northampton, Conn R.
51	floodplain	Limerick	Berkshire	Cheshire, Hoosic R.
52	floodplain	Limerick	Hampshire	Hatfield, Conn R.
53	floodplain	Limerick	Worcester	Uxbridge, Blackstone
54	floodplain	Hadley	Franklin	Montague, Conn R.
55	floodplain	Hadley	Franklin	Northfield, Conn R.
56	floodplain	Limerick	Plymouth	E. Bridgewater, Matf
57	floodplain	Saco	Plymouth	Middleboro, Nemaskit
58	floodplain	Saco	Norfolk	Dedham, Charles R.
59	floodplain	Limerick	Worcester	Lancaster, Nashua R.
60	floodplain	Pootatuck	Middlesex	Methuen, Merrimac R.

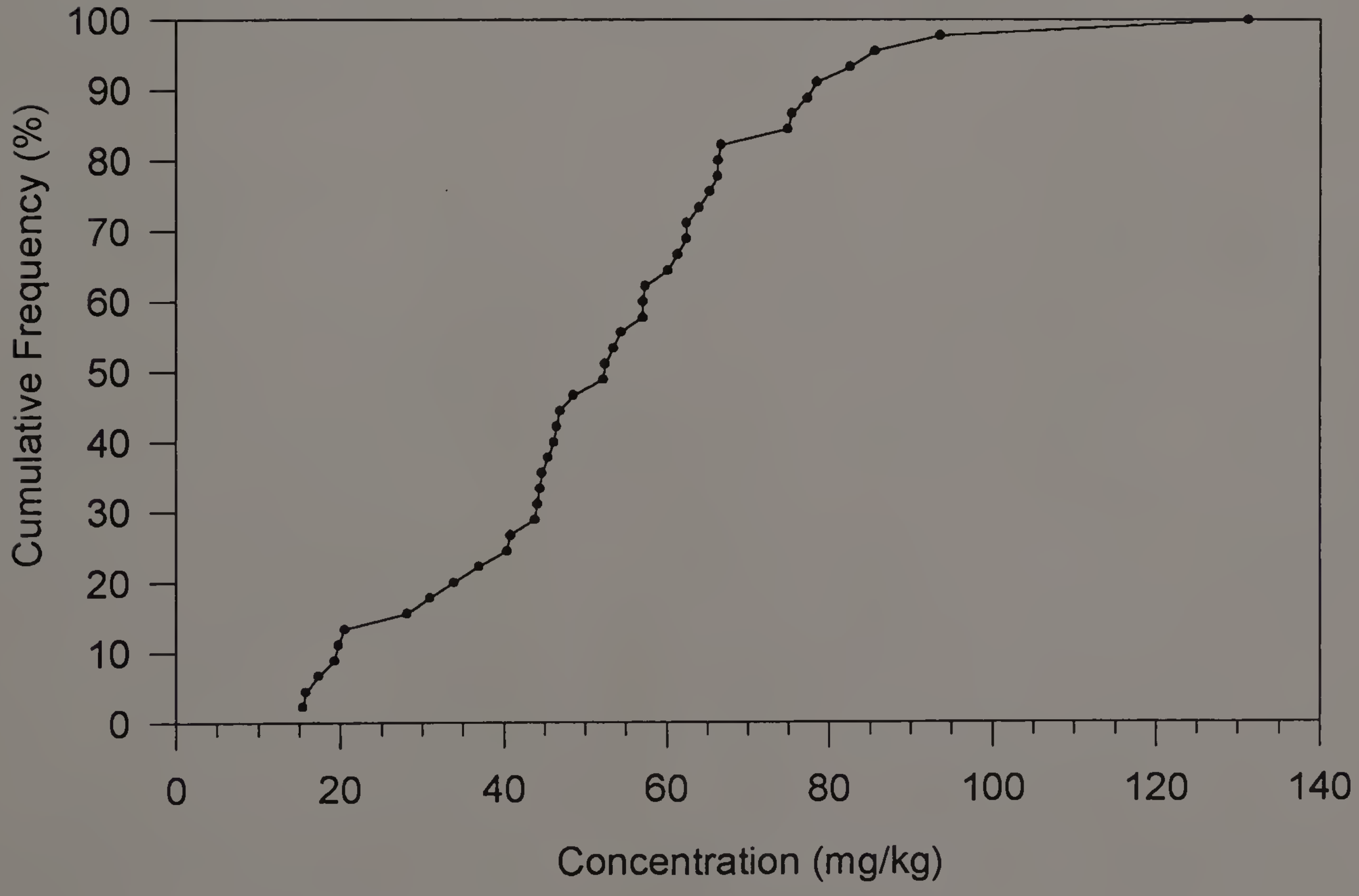
APPENDIX B

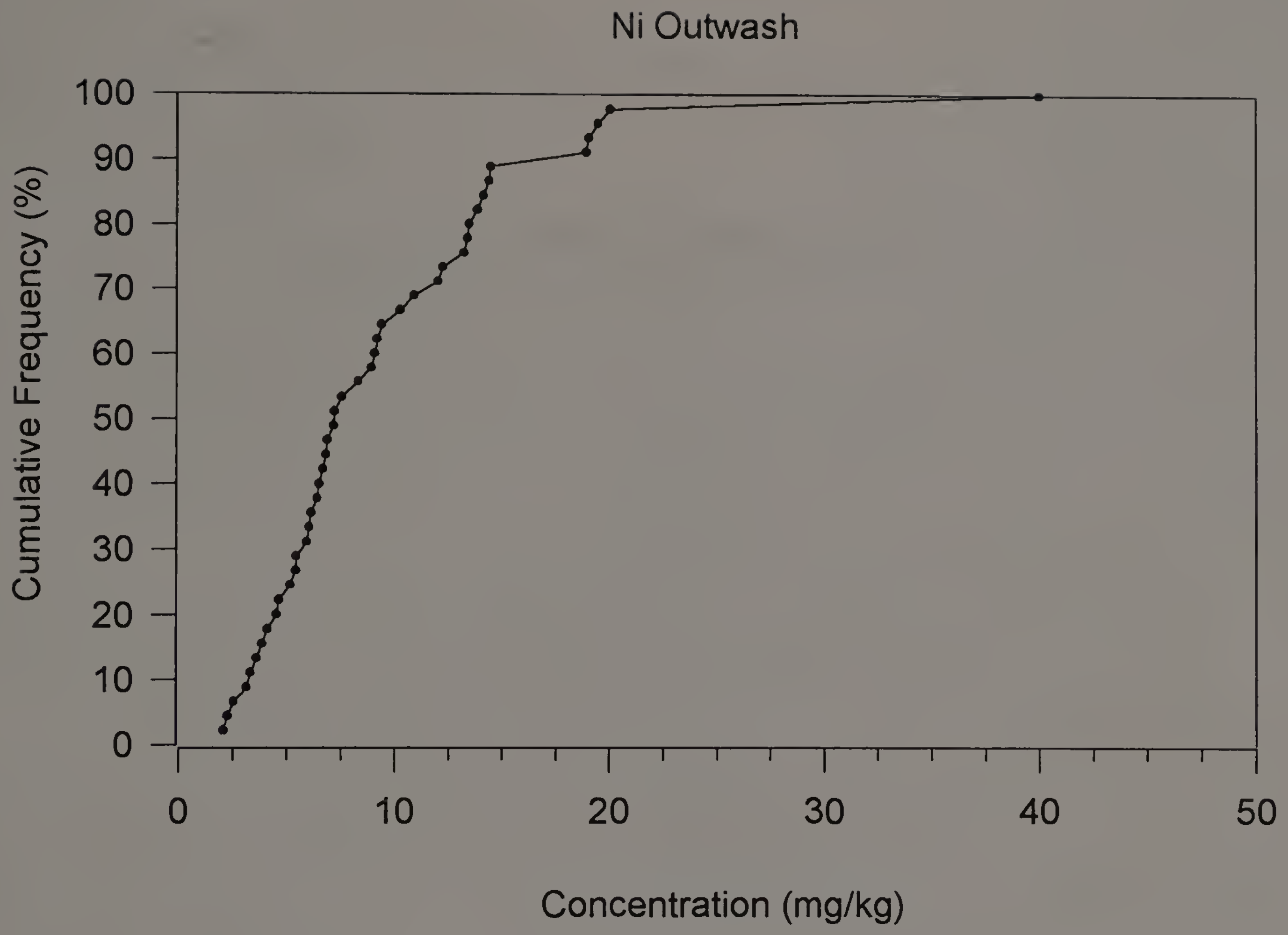
DISTRIBUTIONS OF METALS WITHIN PARENT MATERIAL

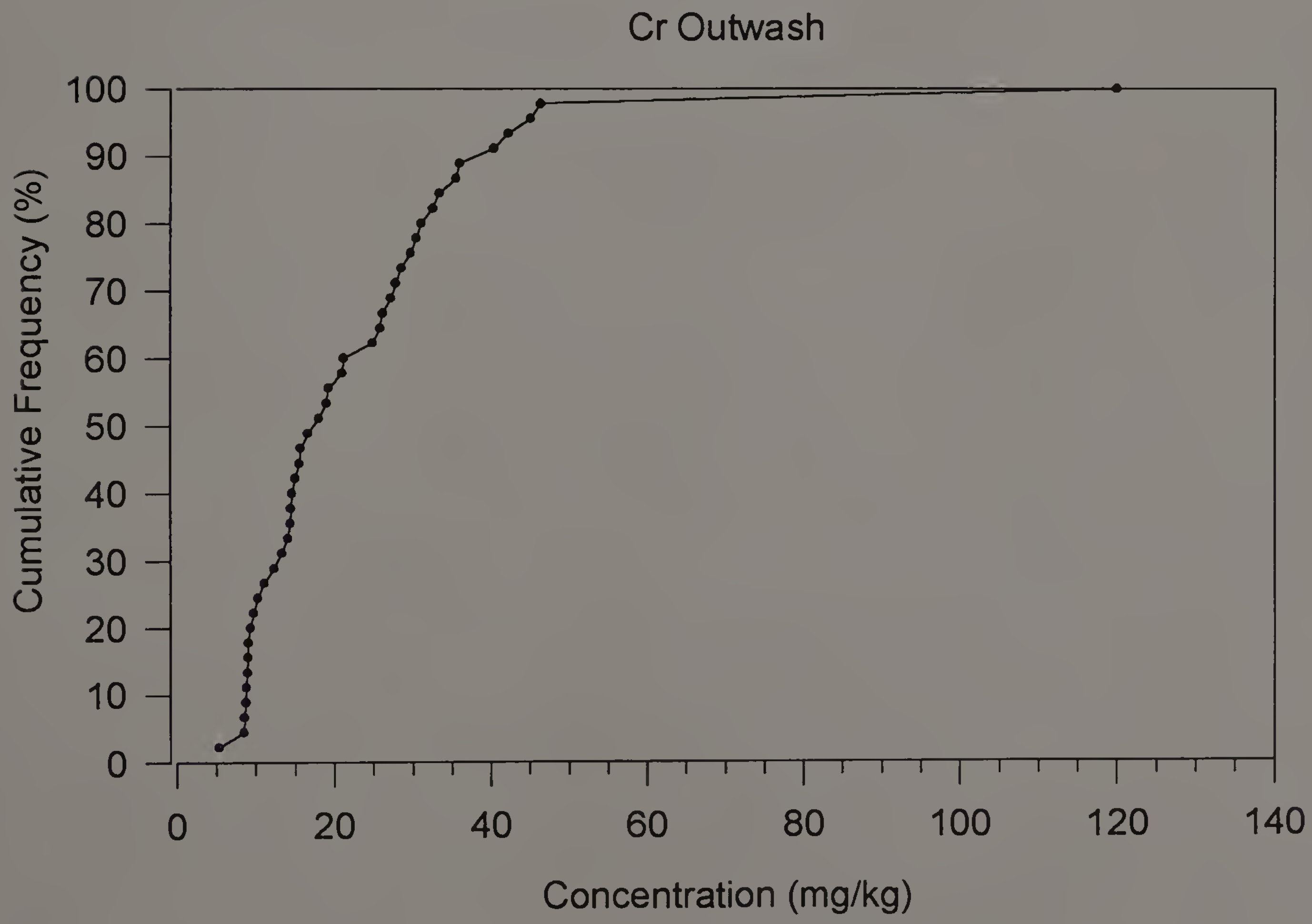
Pb Outwash

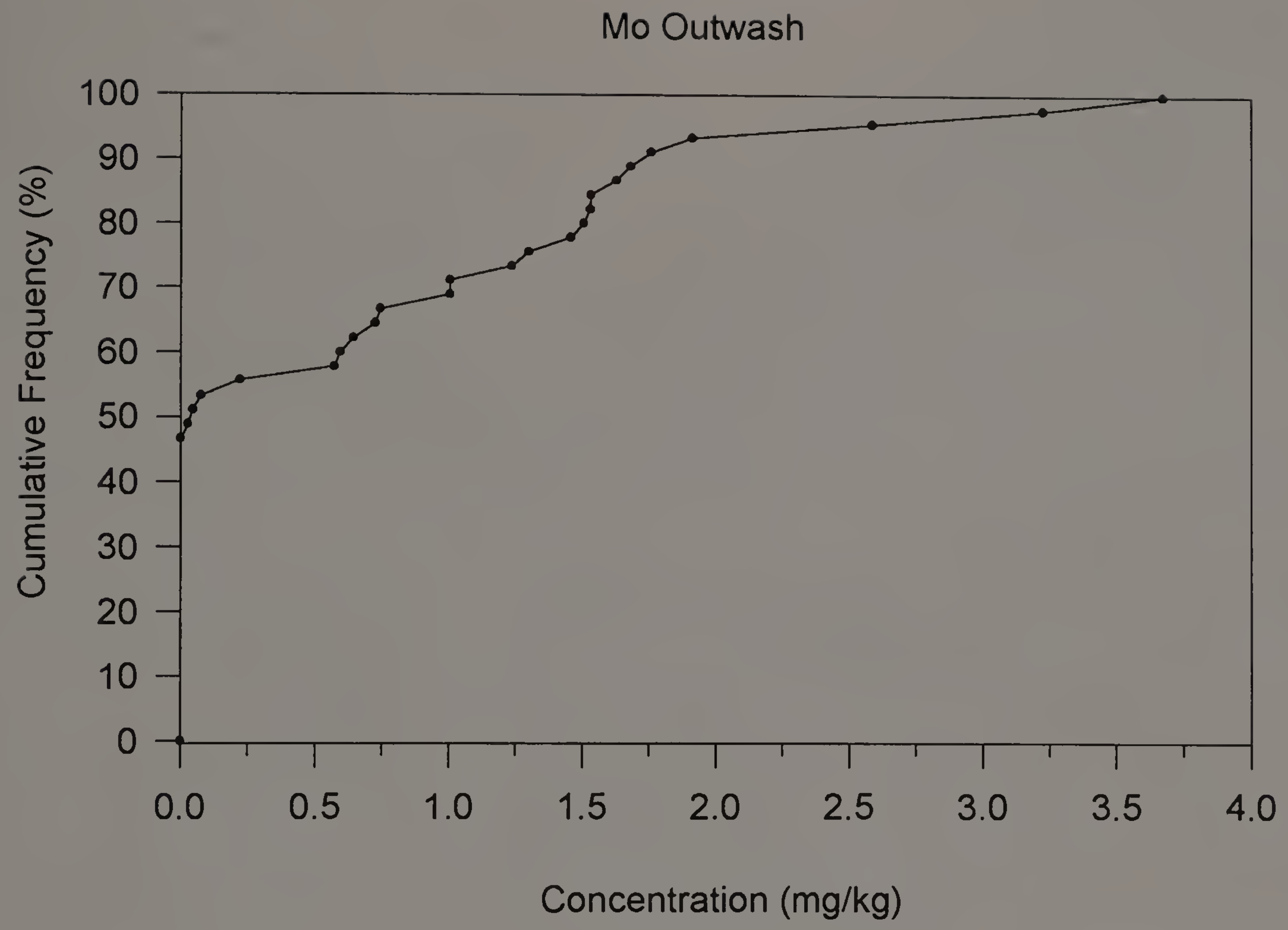


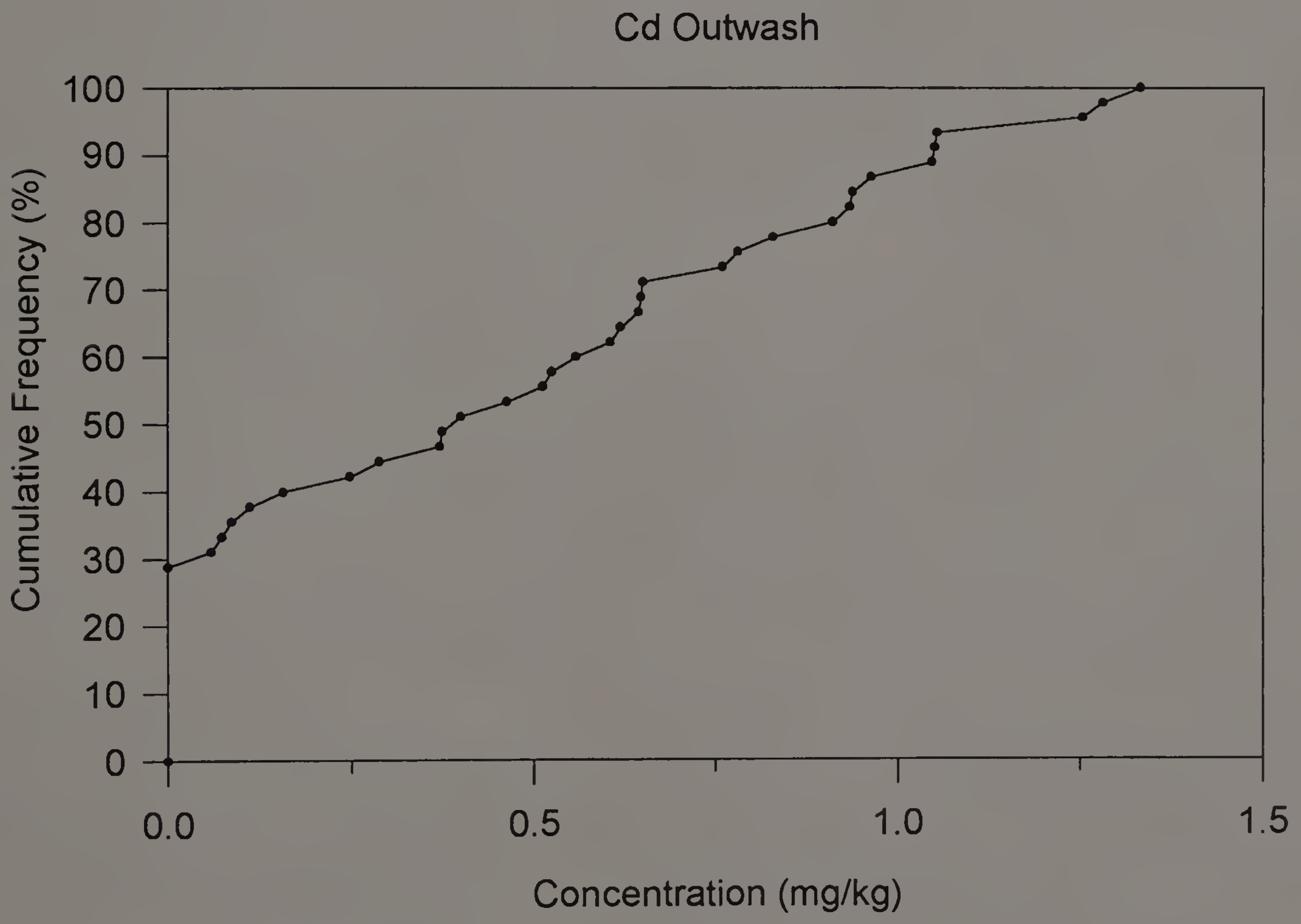
Cu Outwash




Ni Outwash
Cumulative Frequency (%)
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
Concentration (mg/kg)


Cr Outwash
Cumulative Frequency (%)
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
Concentration (mg/kg)


Mo Outwash
Cumulative Frequency (%)
100
90
80
70
60
50
40
30
20
10
0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Concentration (mg/kg)


Cd Outwash
Cumulative Frequency (%)
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90
80
70
60
50
40
30
20
10
0
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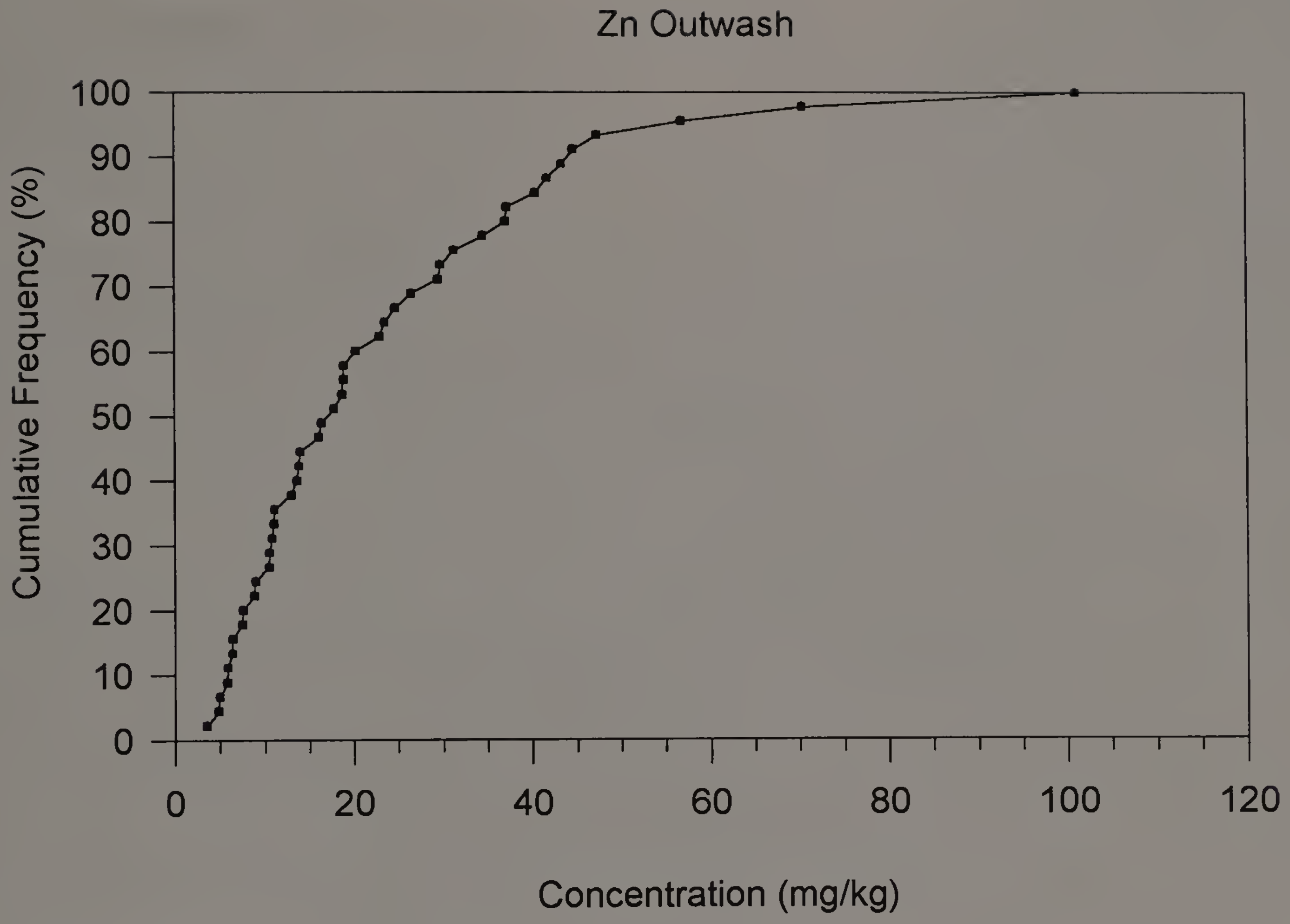
0.5
1.0
1.5
Concentration (mg/kg)


Zn Outwash
Cumulative Frequency (%)
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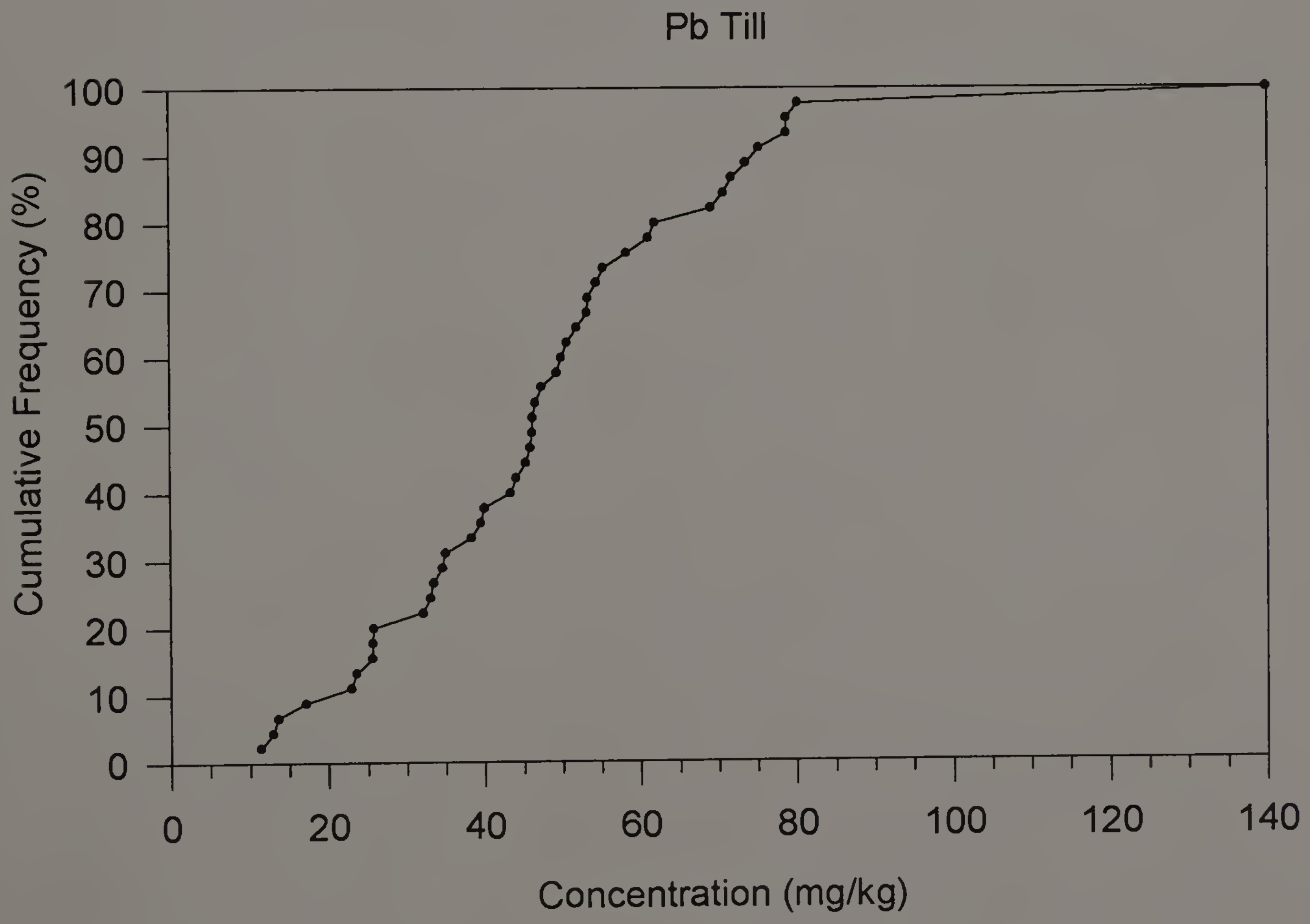
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
Concentration (mg/kg)


Pb Till
Cumulative Frequency (%)
0
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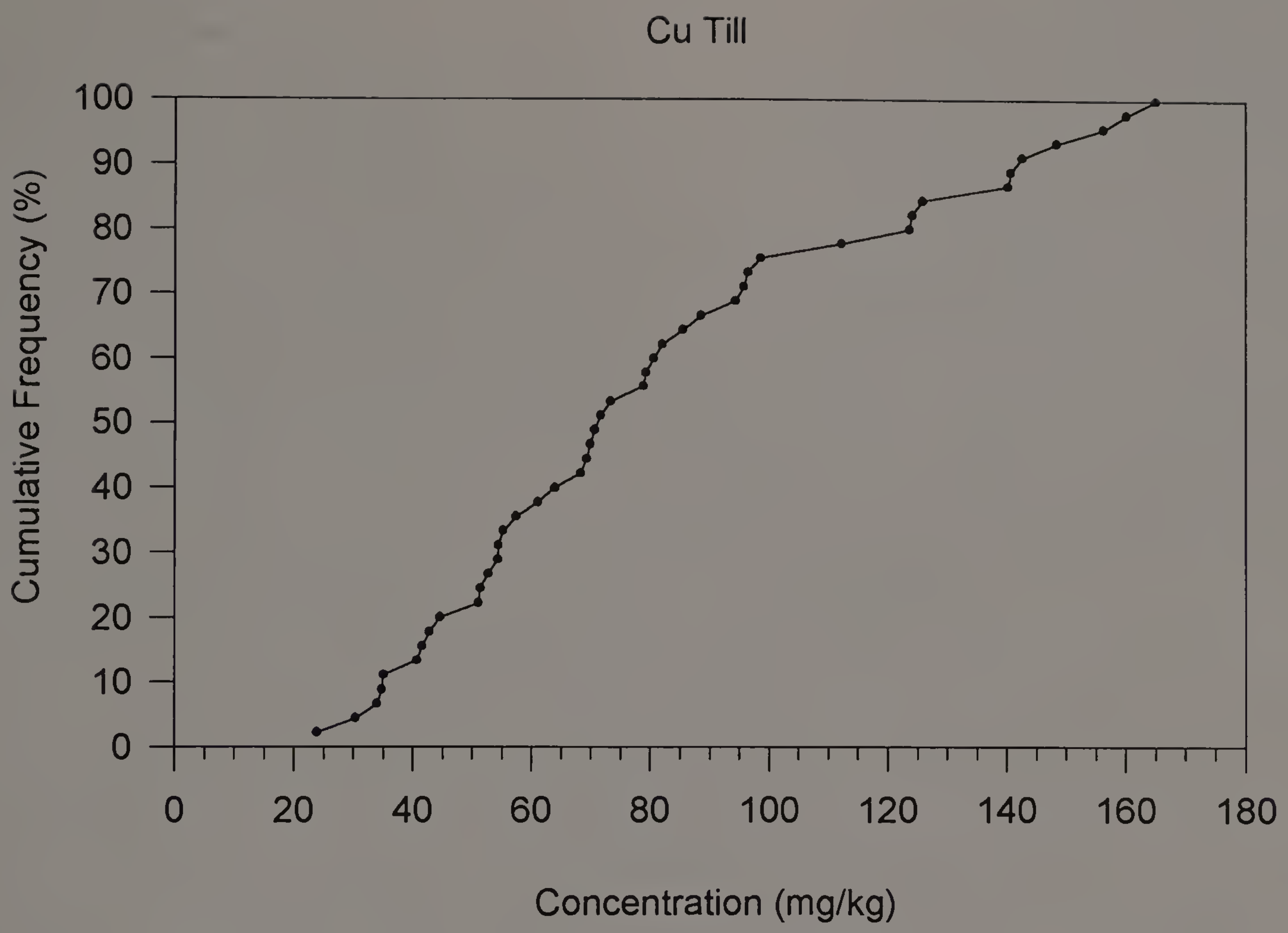
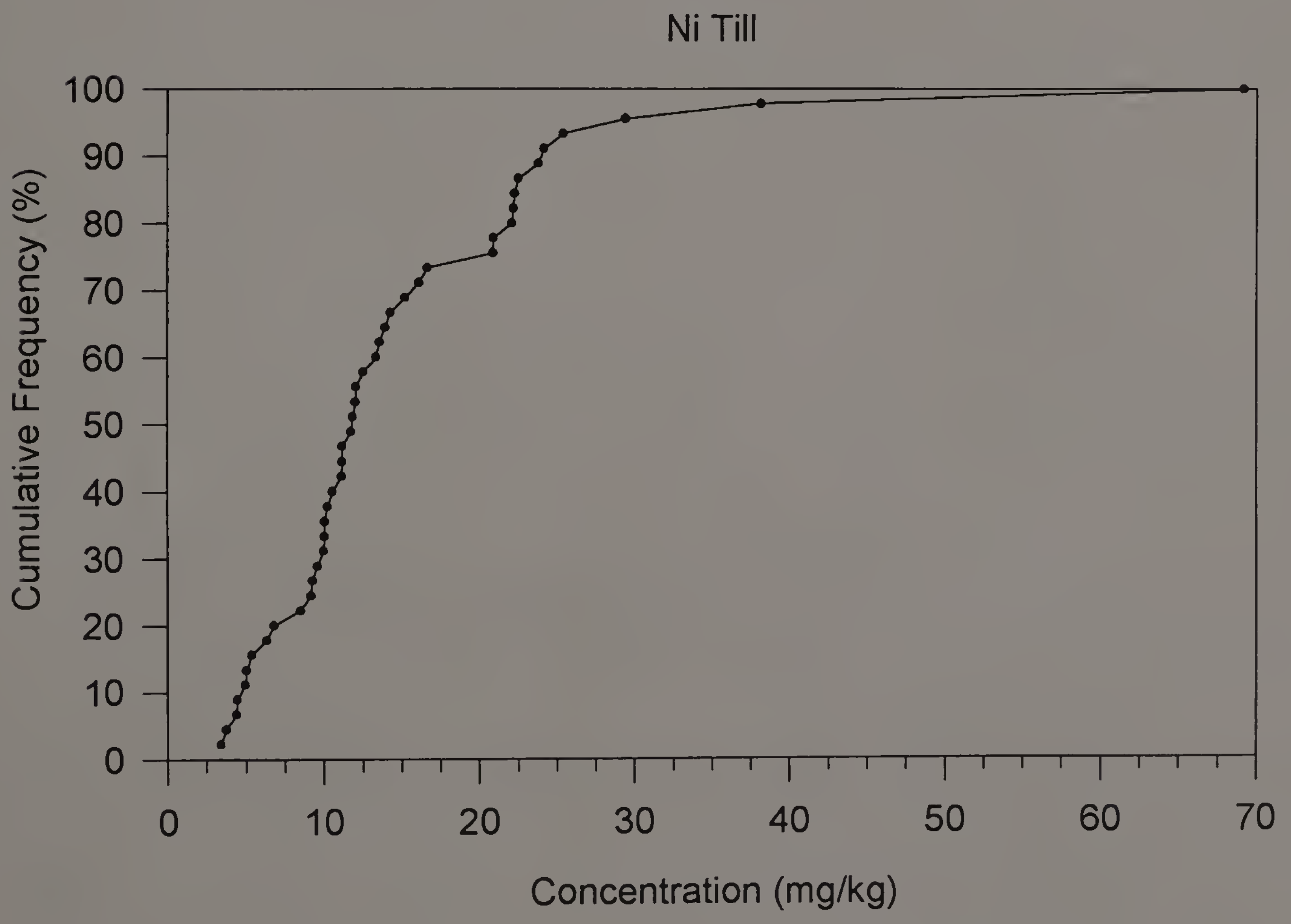
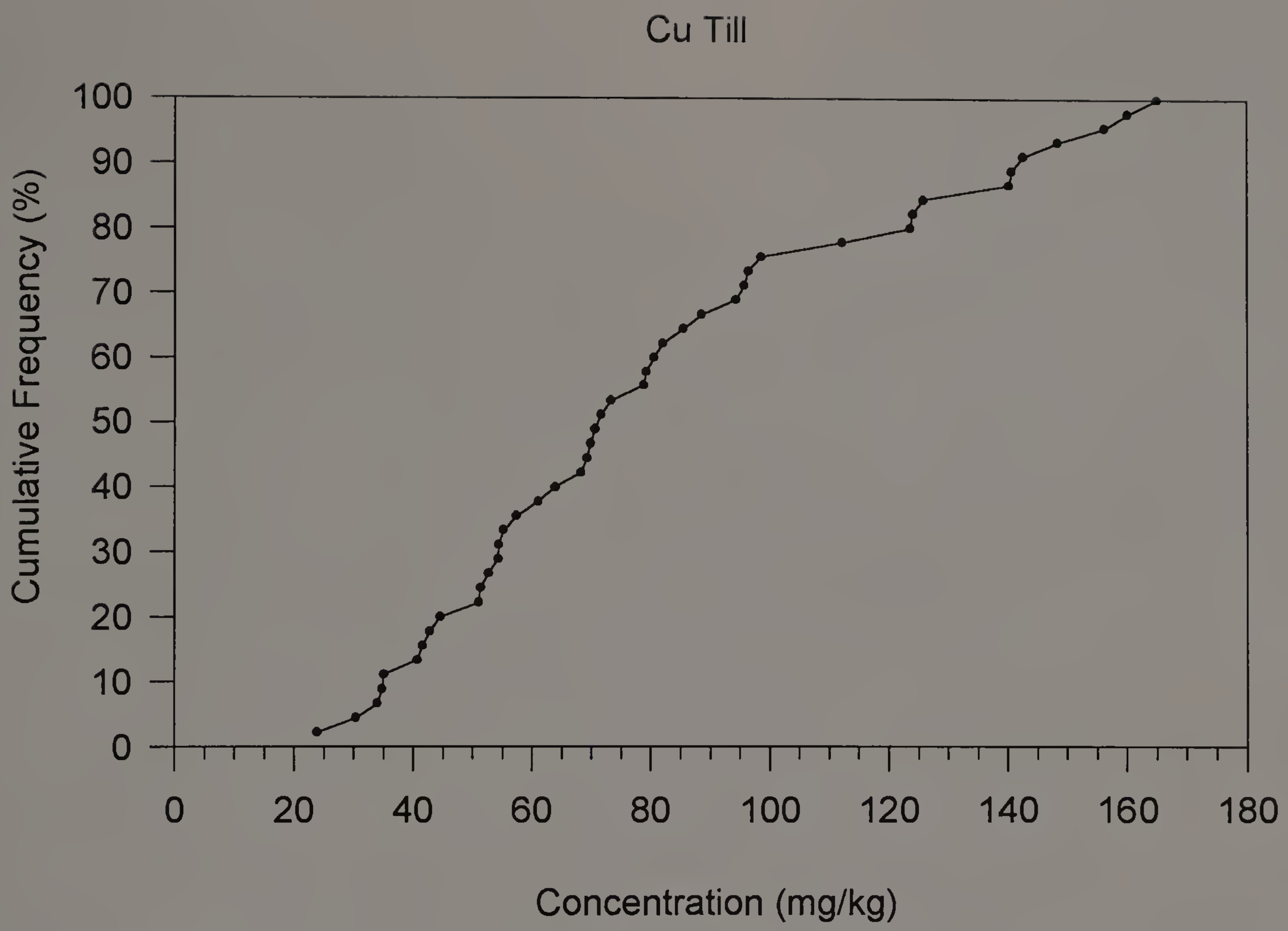
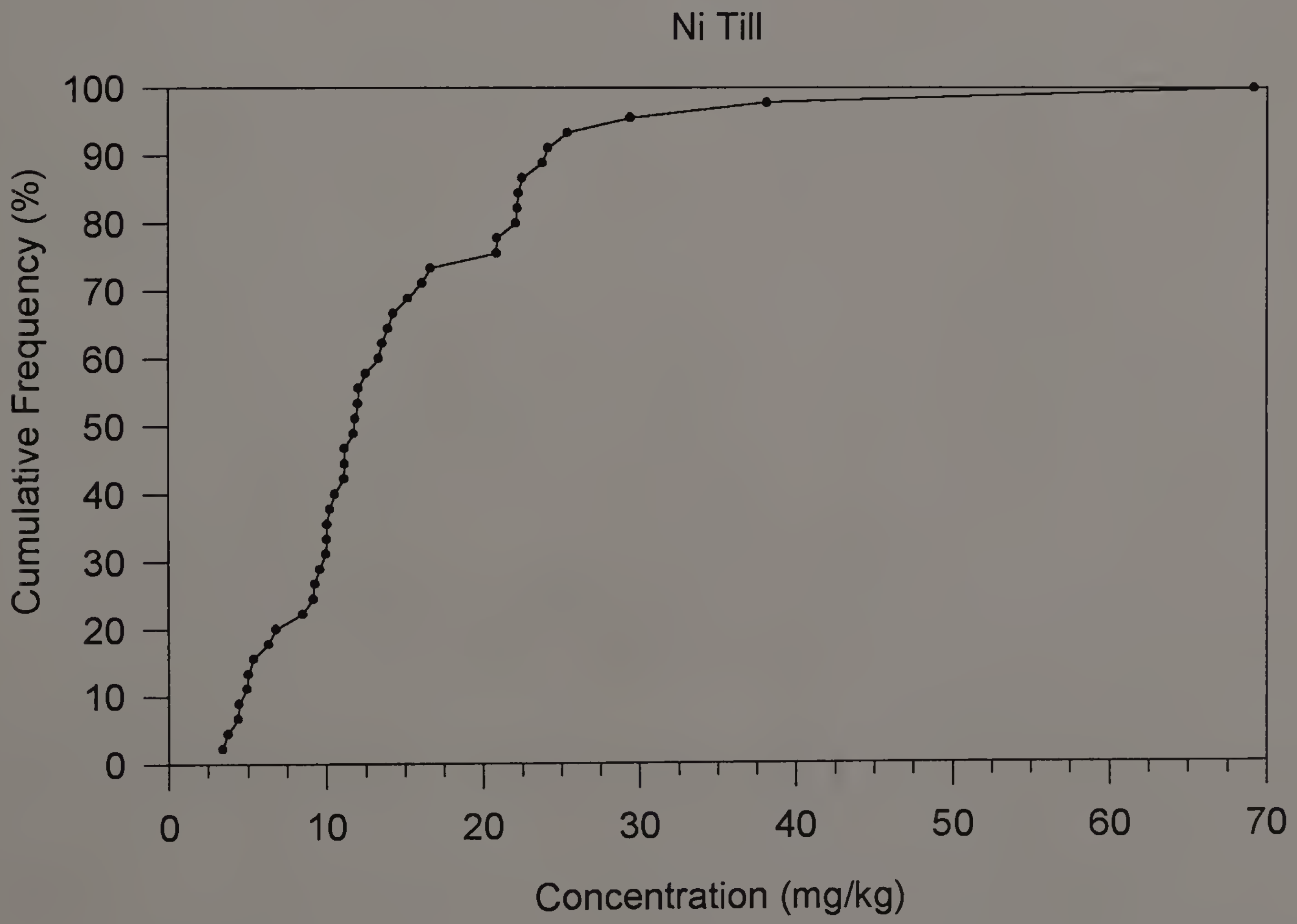
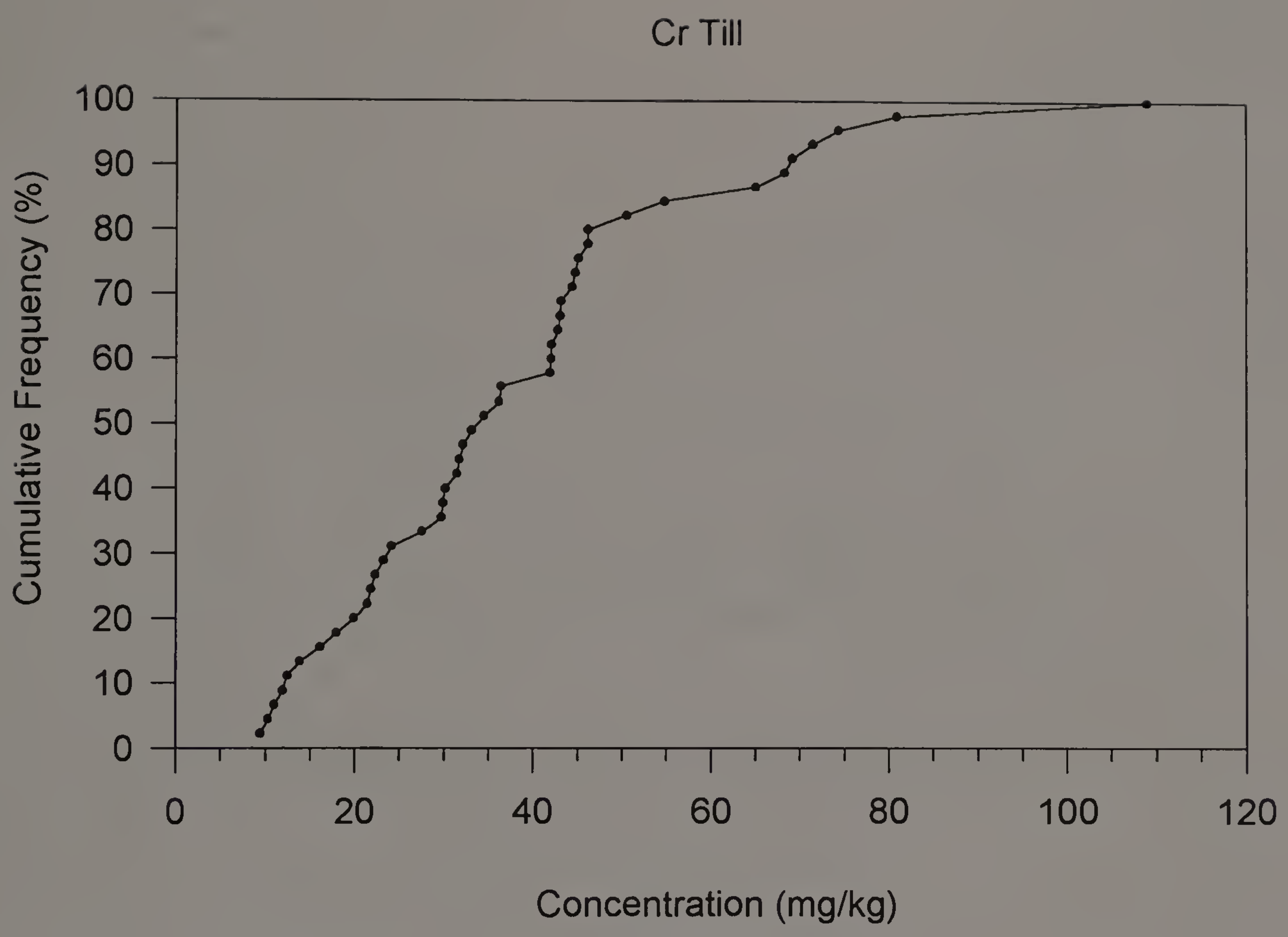
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
Concentration (mg/kg)

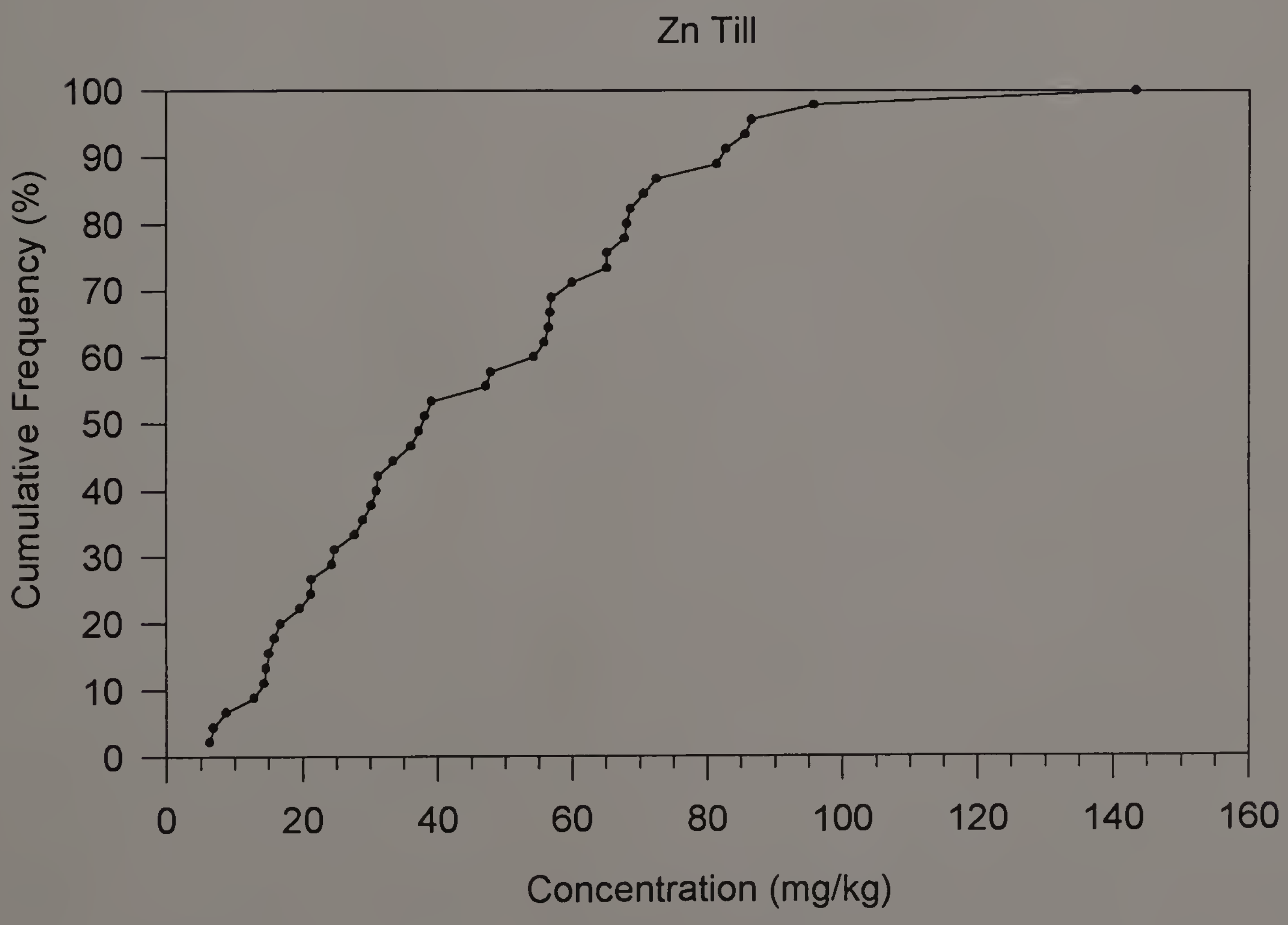

Cu Till
Cumulative Frequency (%)
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
Concentration (mg/kg)

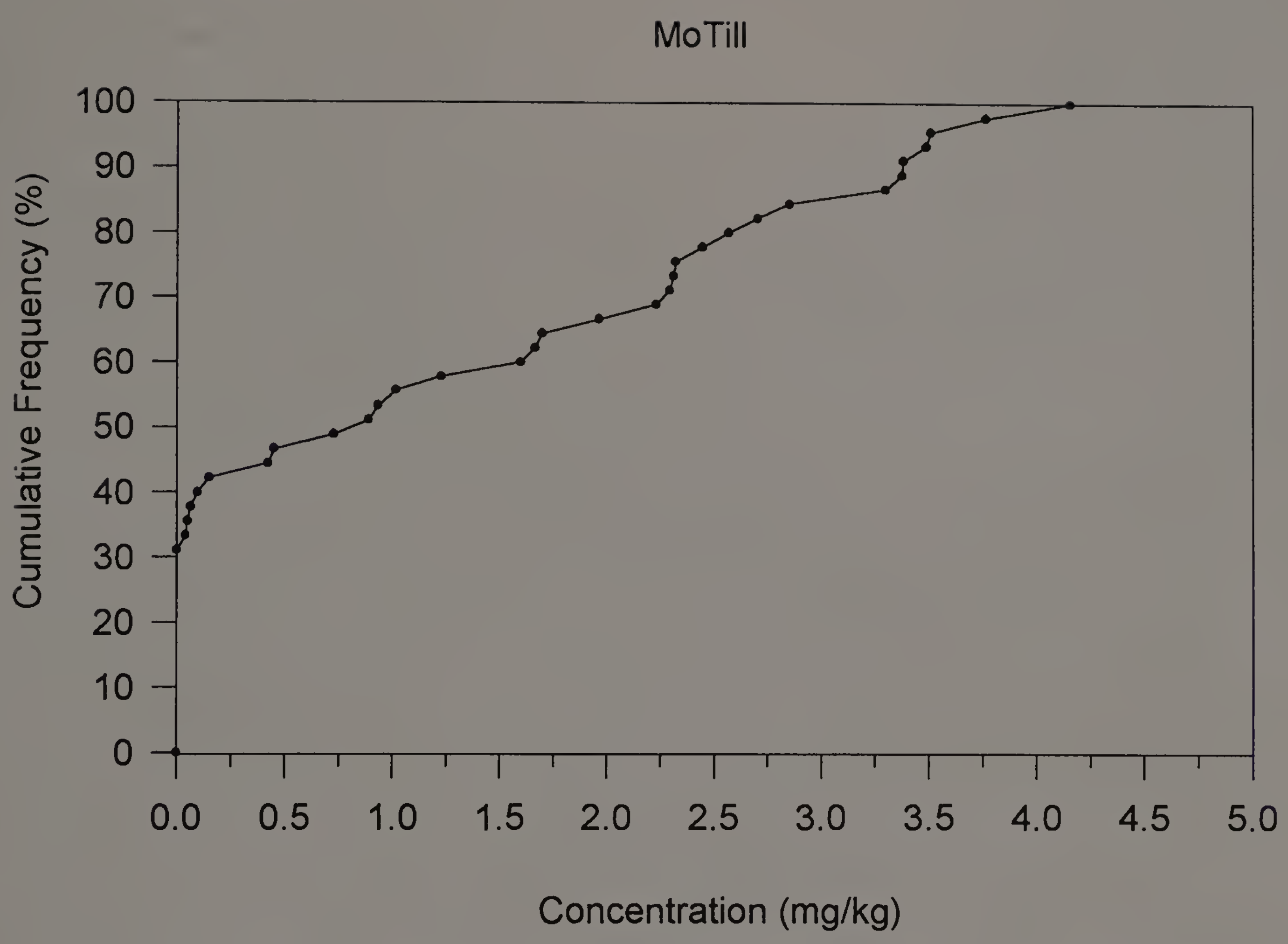

Ni Till
Cumulative Frequency (%)
0
10
20
30
40
50
60
70
80
90
100
0
10
20
30
40
50
60
70
Concentration (mg/kg)


Cu Till
Cumulative Frequency (%)
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
Concentration (mg/kg)


Ni Till
Cumulative Frequency (%)
0
10
20
30
40
50
60
70
80
90
100
0
10
20
30
40
50
60
70
Concentration (mg/kg)


Cr Till
Cumulative Frequency (%)
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
Concentration (mg/kg)


Zn Till
Cumulative Frequency (%)
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160
Concentration (mg/kg)


MoTill
Cumulative Frequency (%)
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90
80
70
60
50
40
30
20
10
0
0.0
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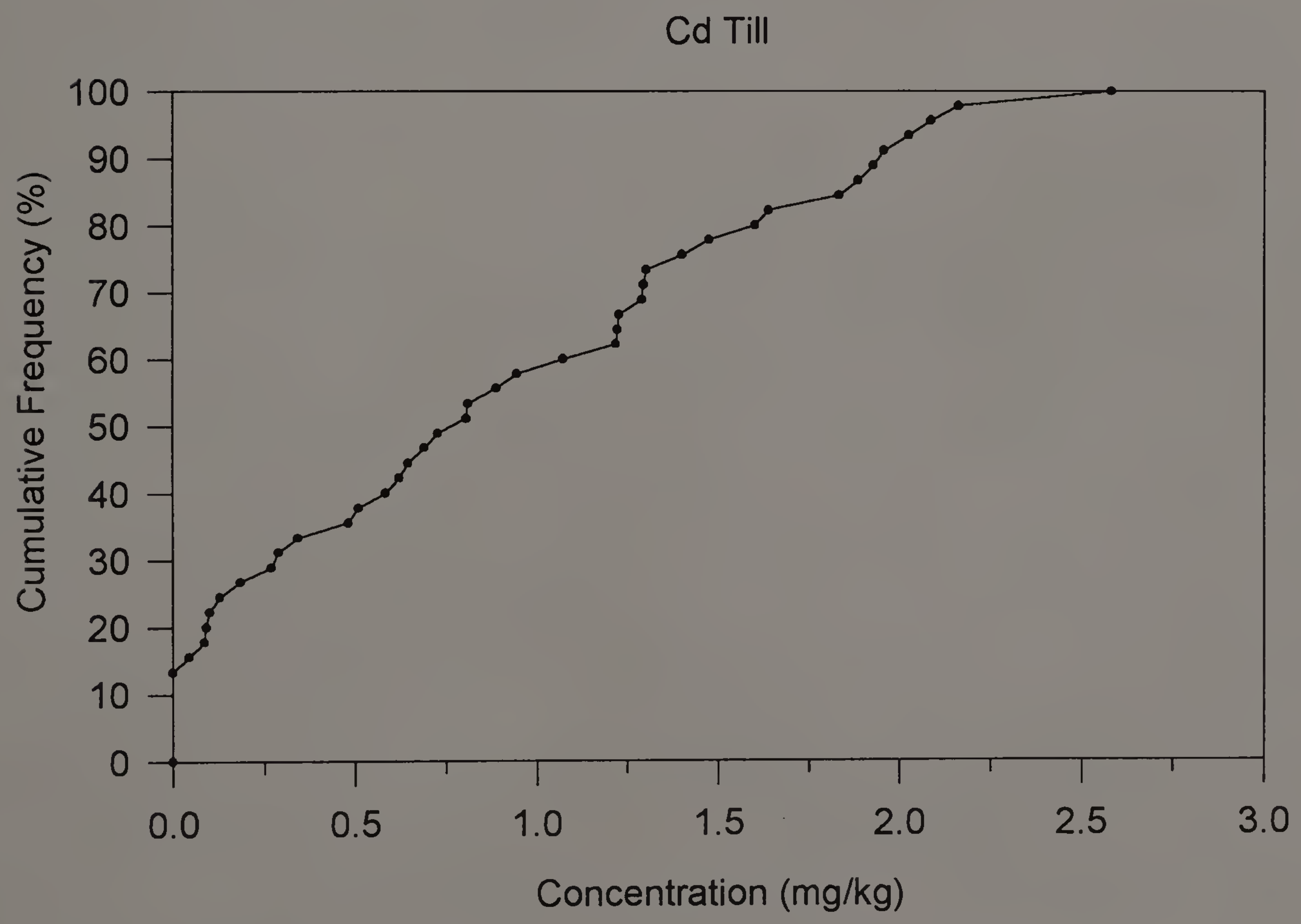
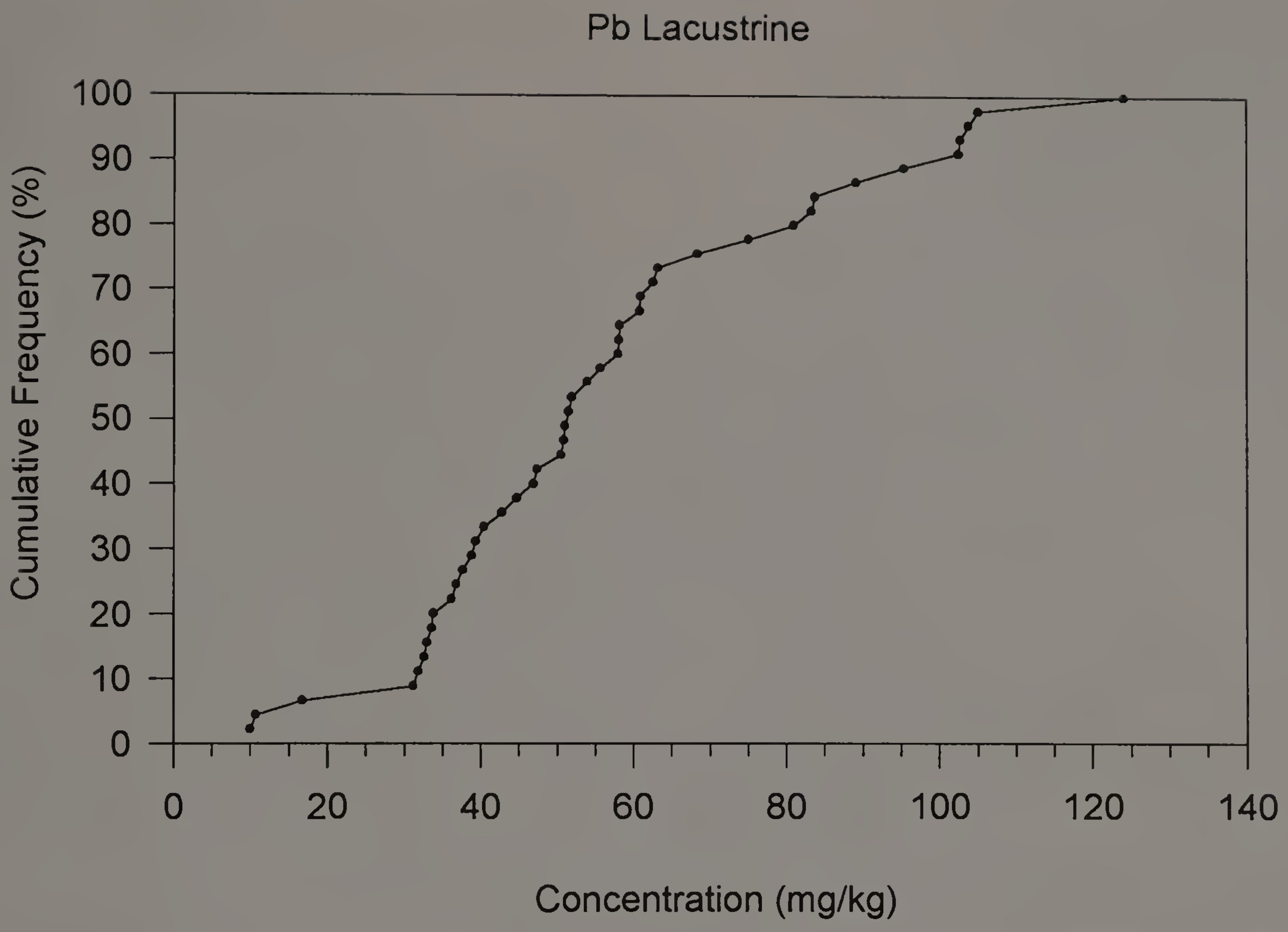
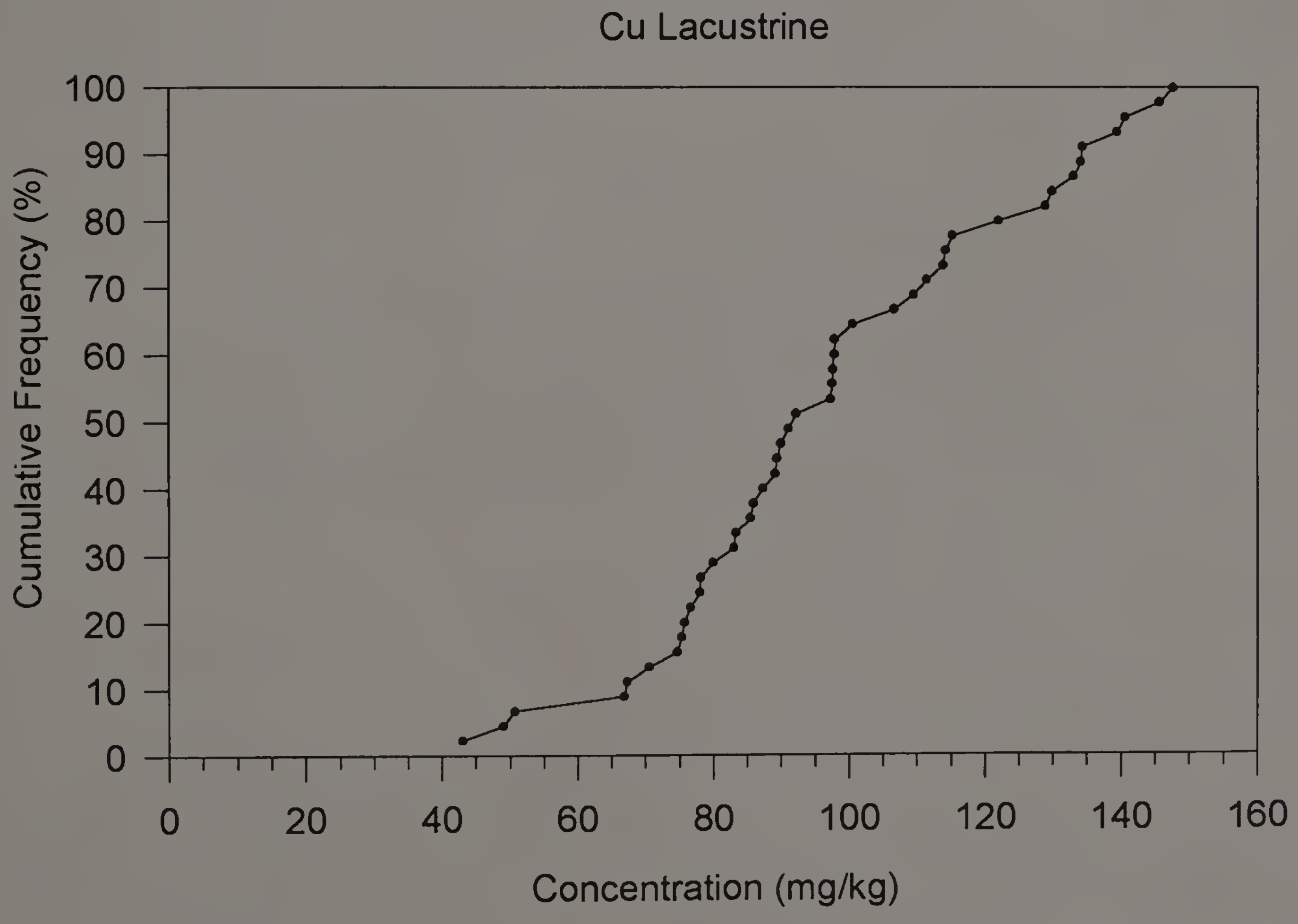
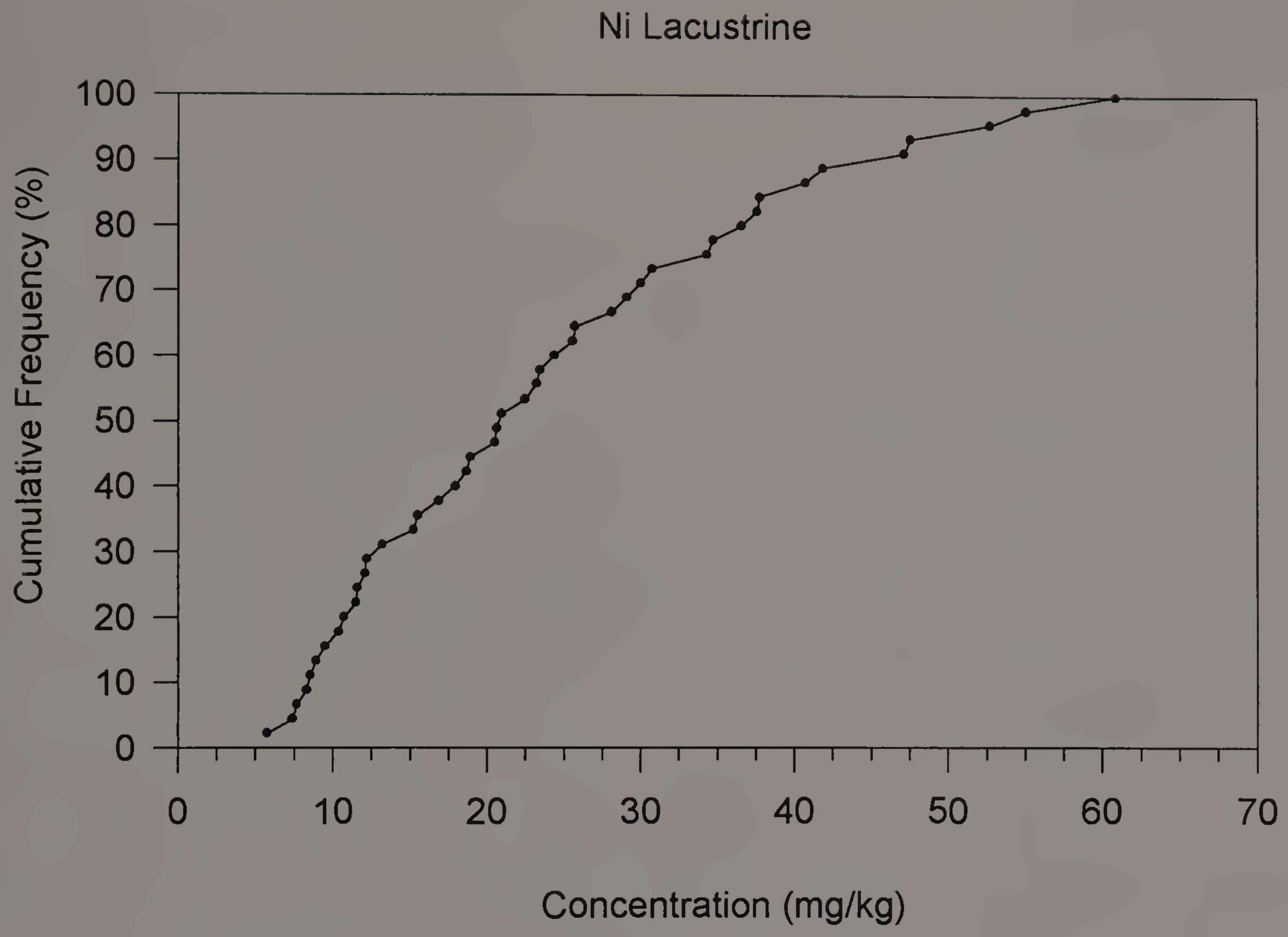
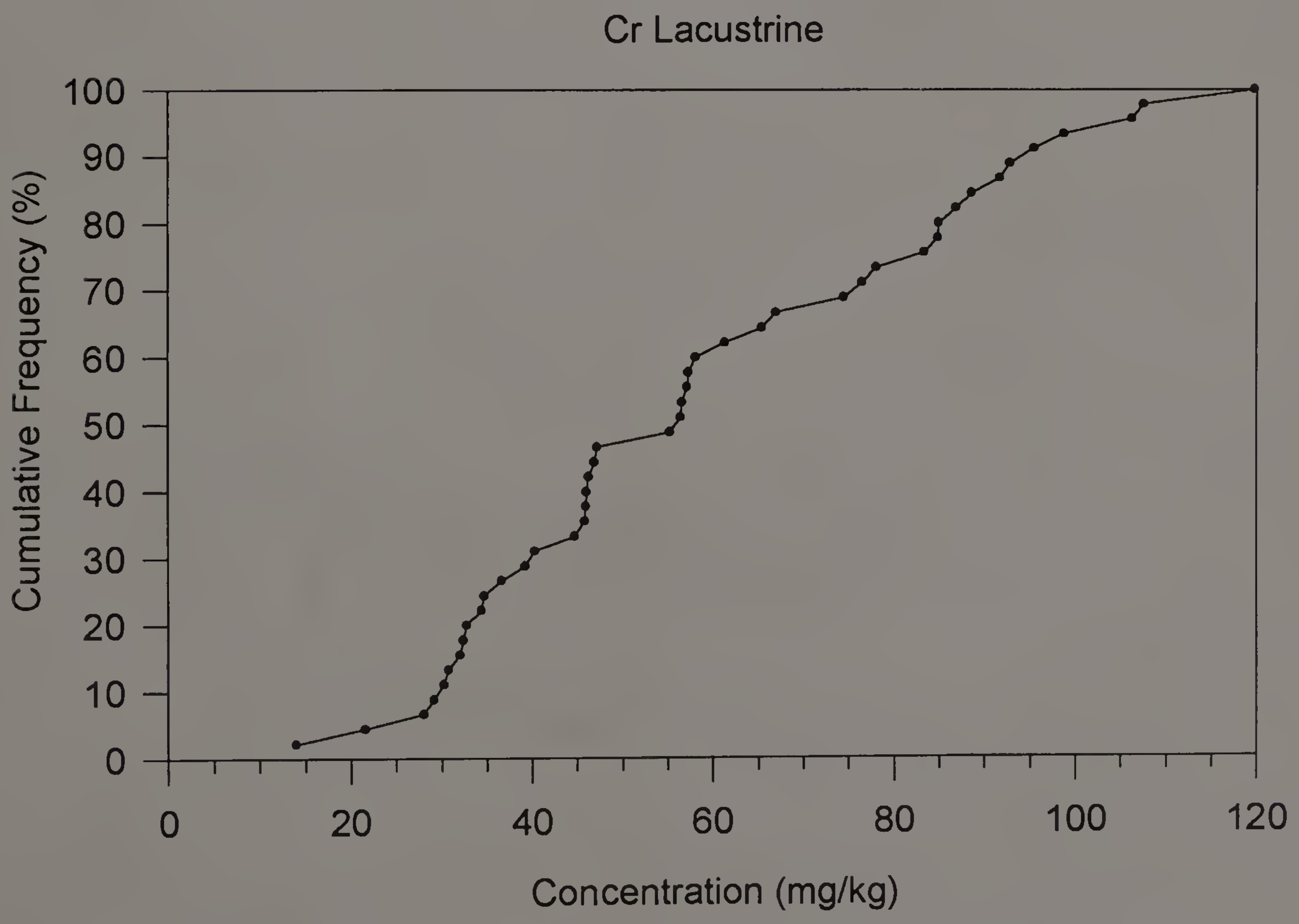
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
Concentration (mg/kg)

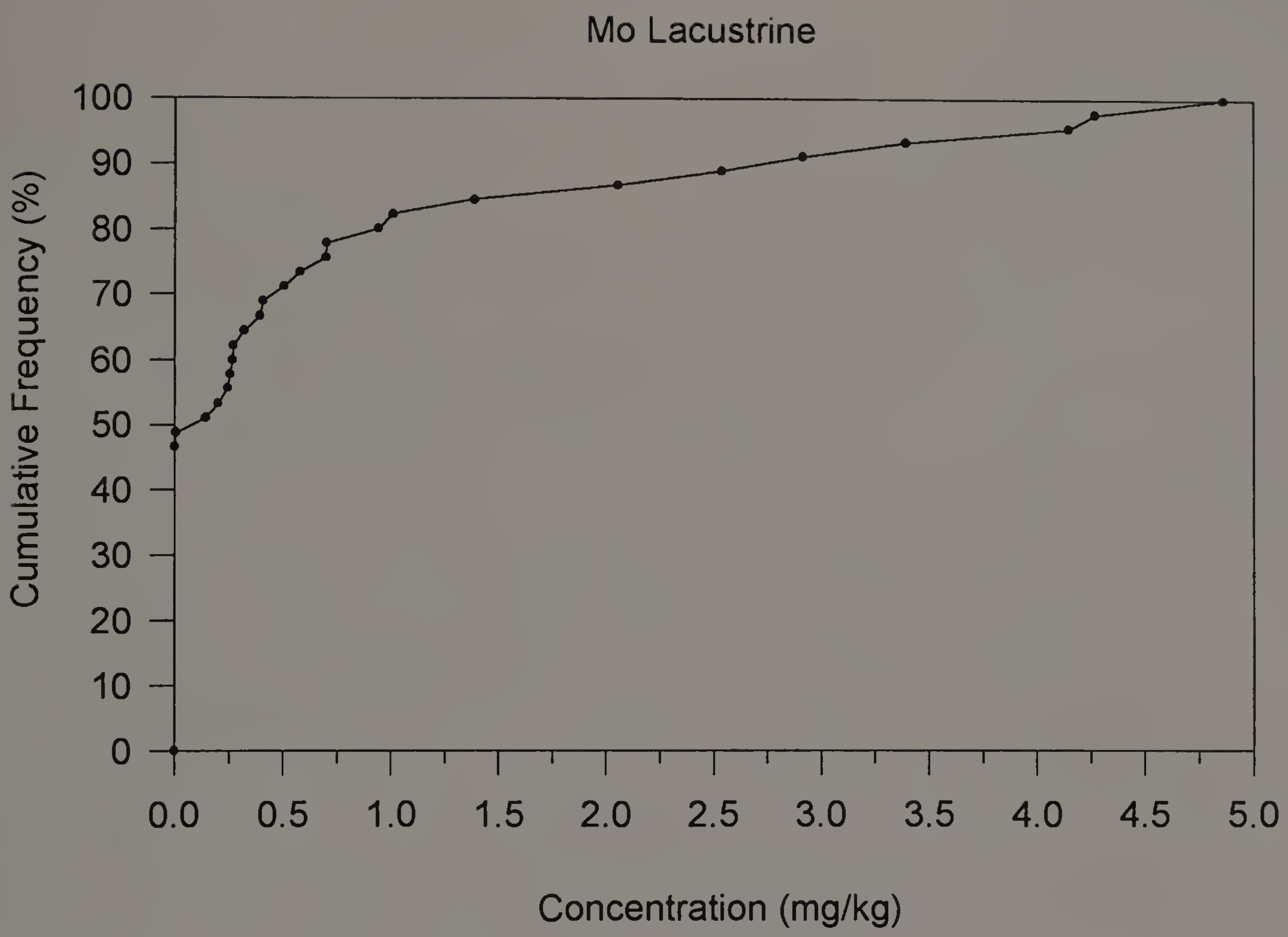

Cd Till
Cumulative Frequency (%)
100
90
80
70
60
50
40
30
20
10
0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Concentration (mg/kg)

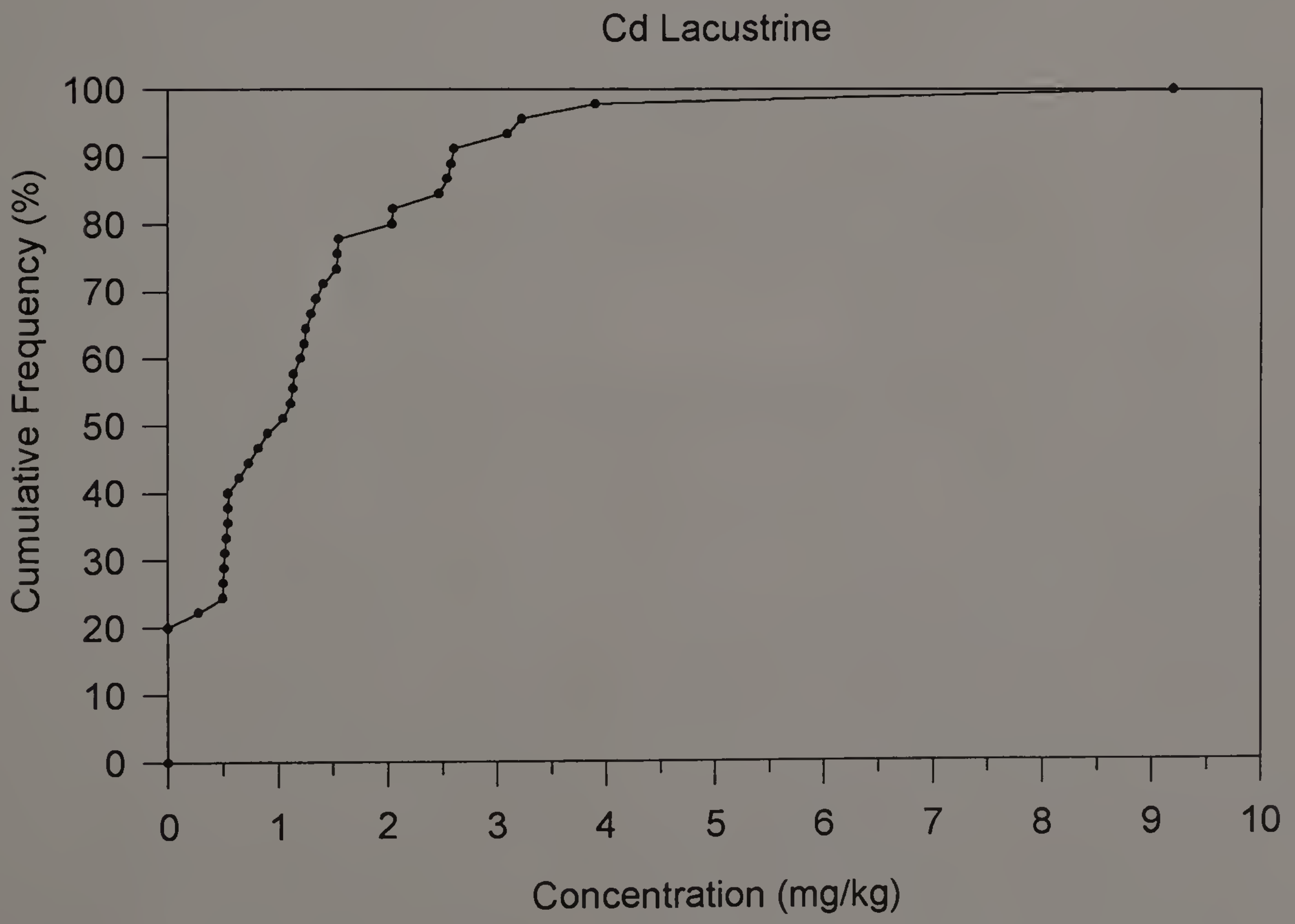

Pb Lacustrine
Cumulative Frequency (%)
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
Concentration (mg/kg)

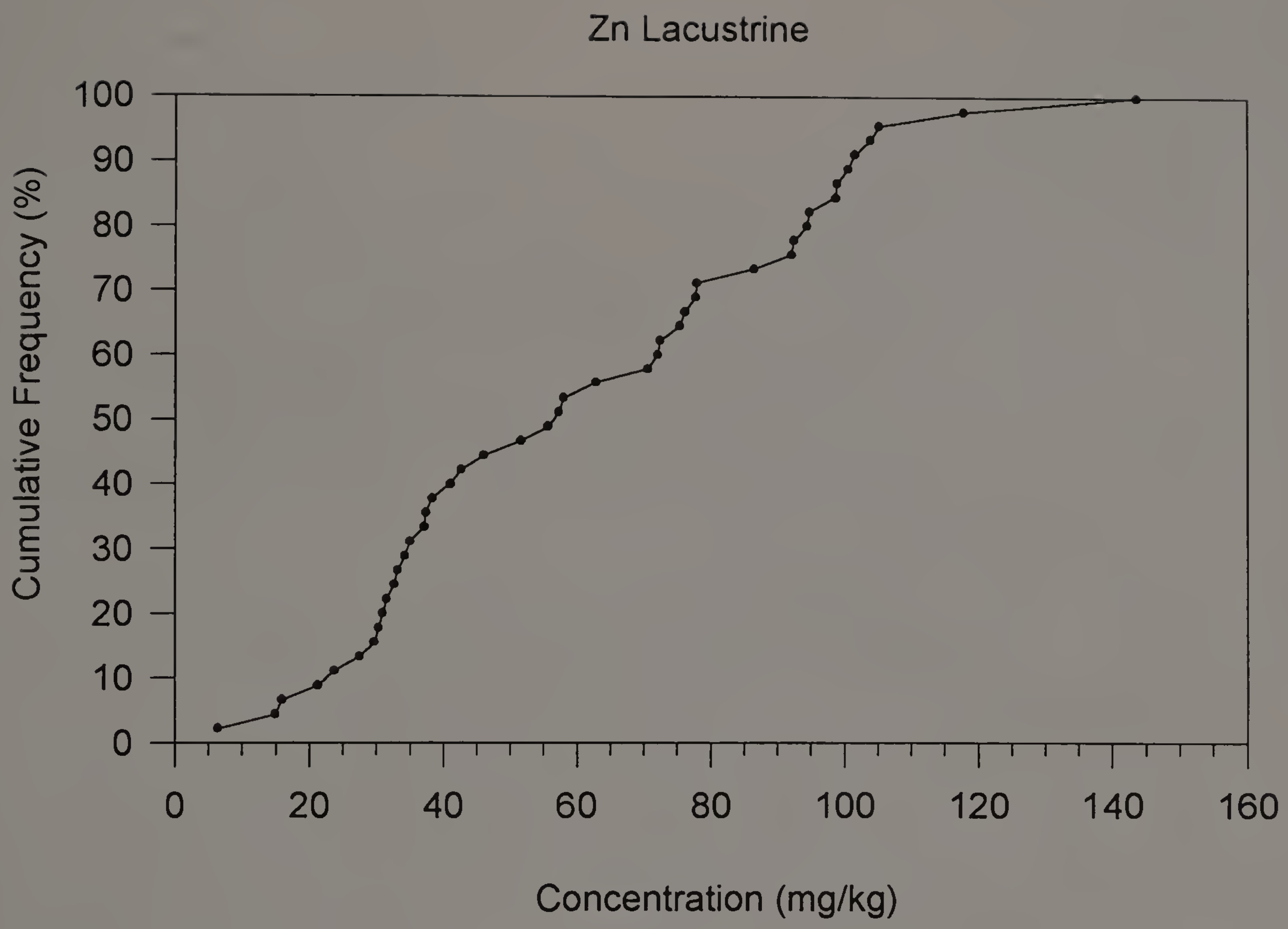

Cu Lacustrine
Cumulative Frequency (%)
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
Concentration (mg/kg)

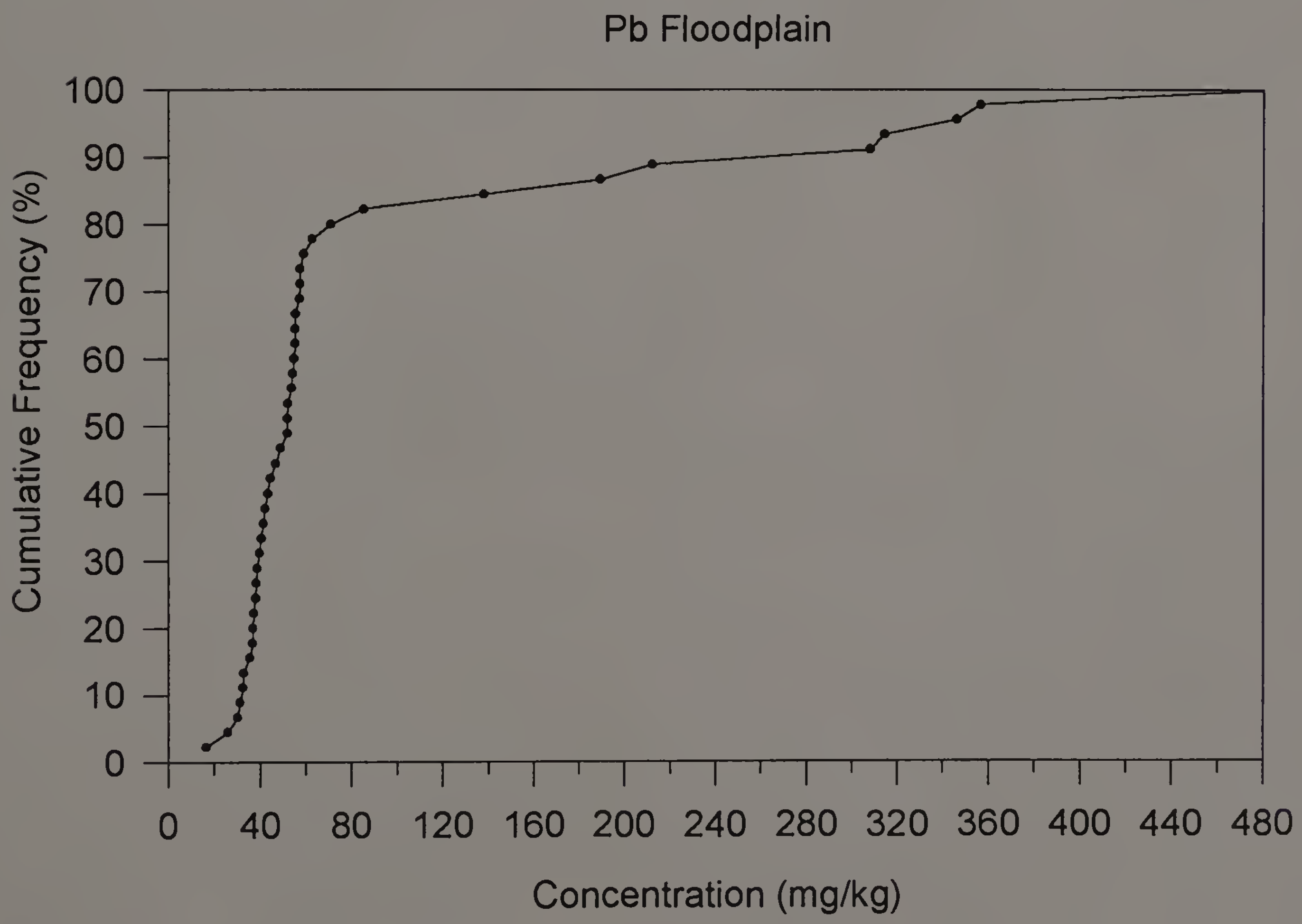

Ni Lacustrine
Cumulative Frequency (%)
0
10
20
30
40
50
60
70
80
90
100
0
10
20
30
40
50
60
70
Concentration (mg/kg)

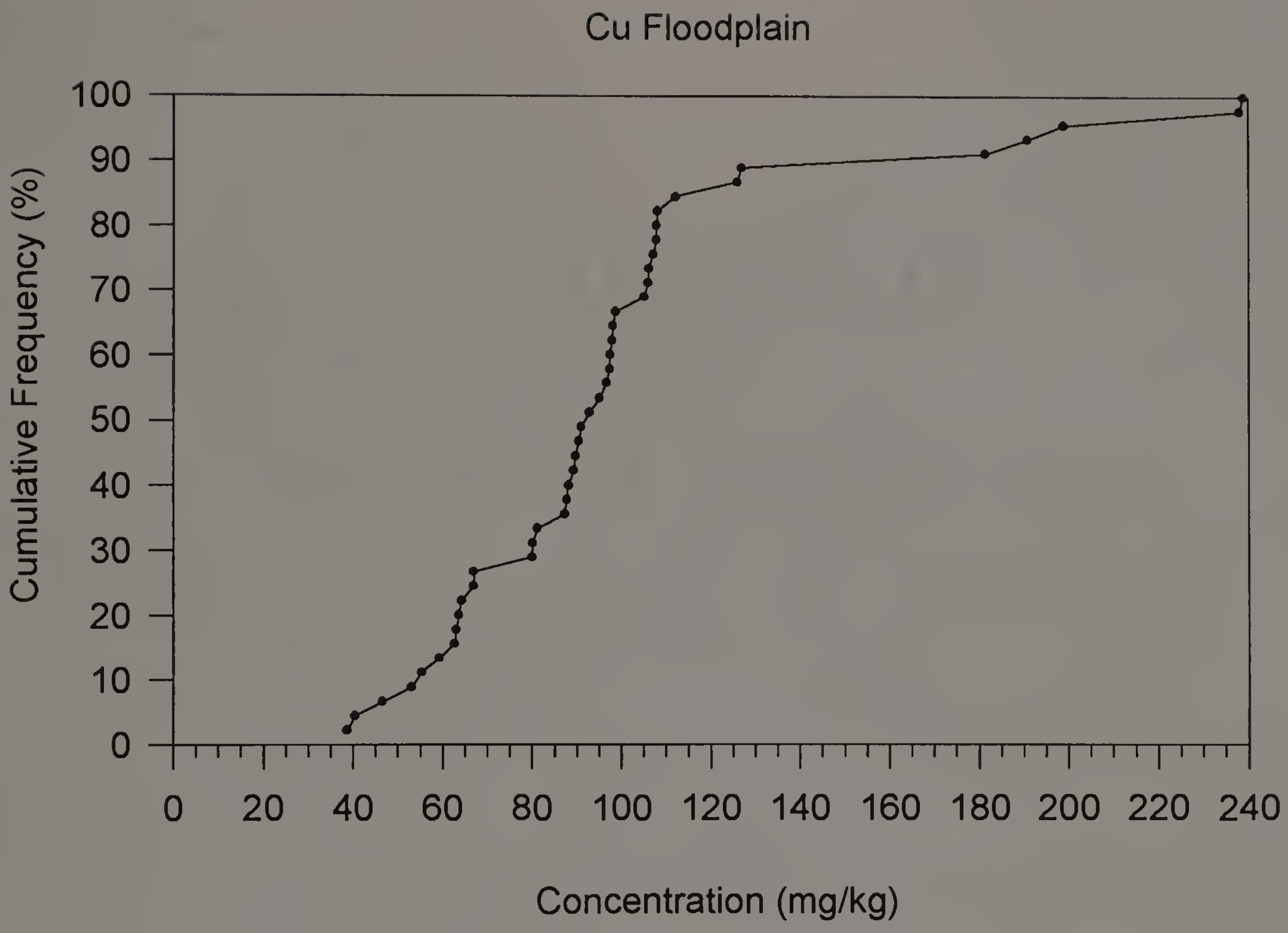

Cr Lacustrine
Cumulative Frequency (%)
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
Concentration (mg/kg)

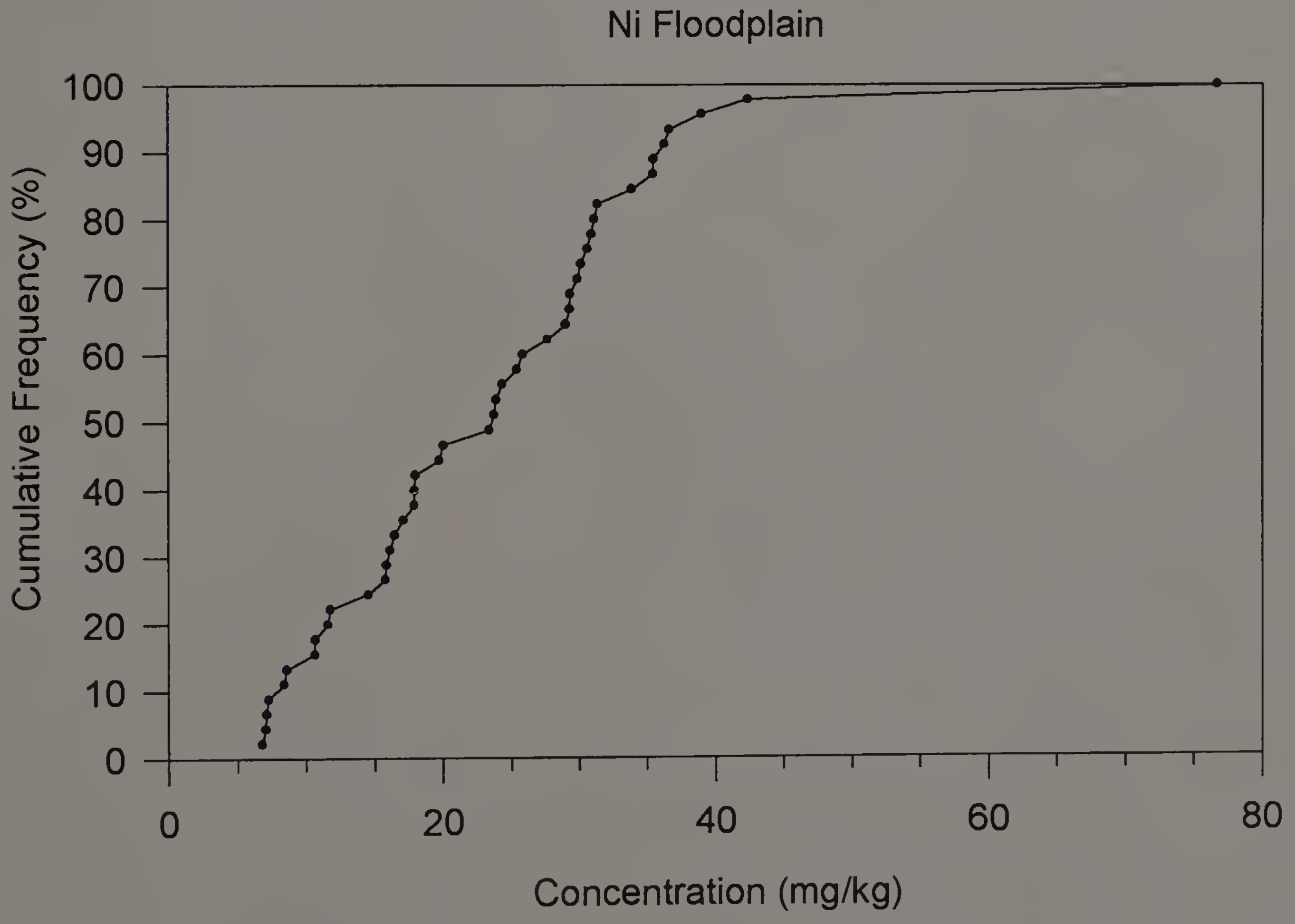

Mo Lacustrine
Cumulative Frequency (%)
0
10
20
30
40
50
60
70
80
90
100
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
Concentration (mg/kg)

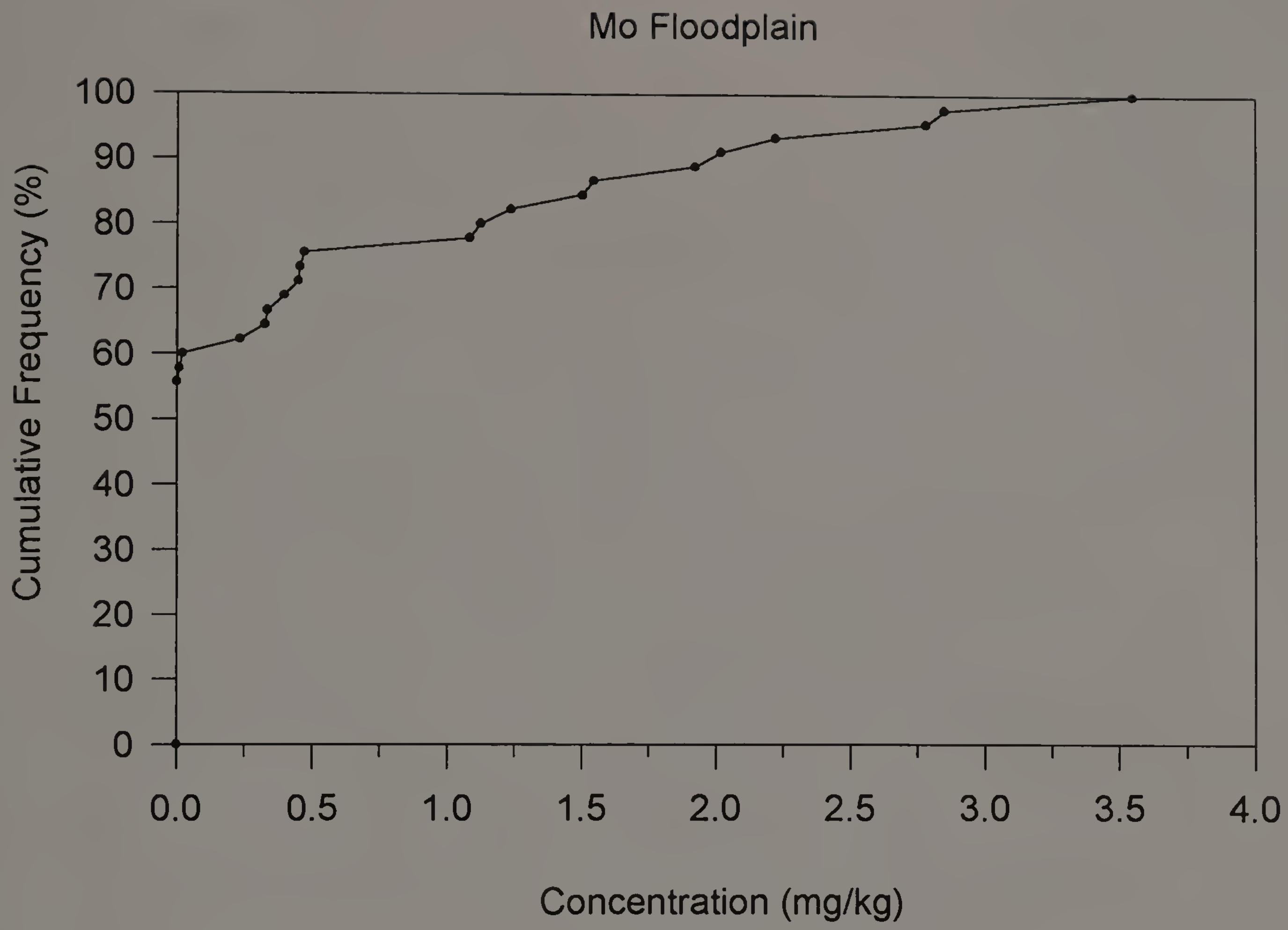

Cd Lacustrine
Cumulative Frequency (%)
0
10
20
30
40
50
60
70
80
90
100
0
1
2
3
4
5
6
7
8
9
10
Concentration (mg/kg)

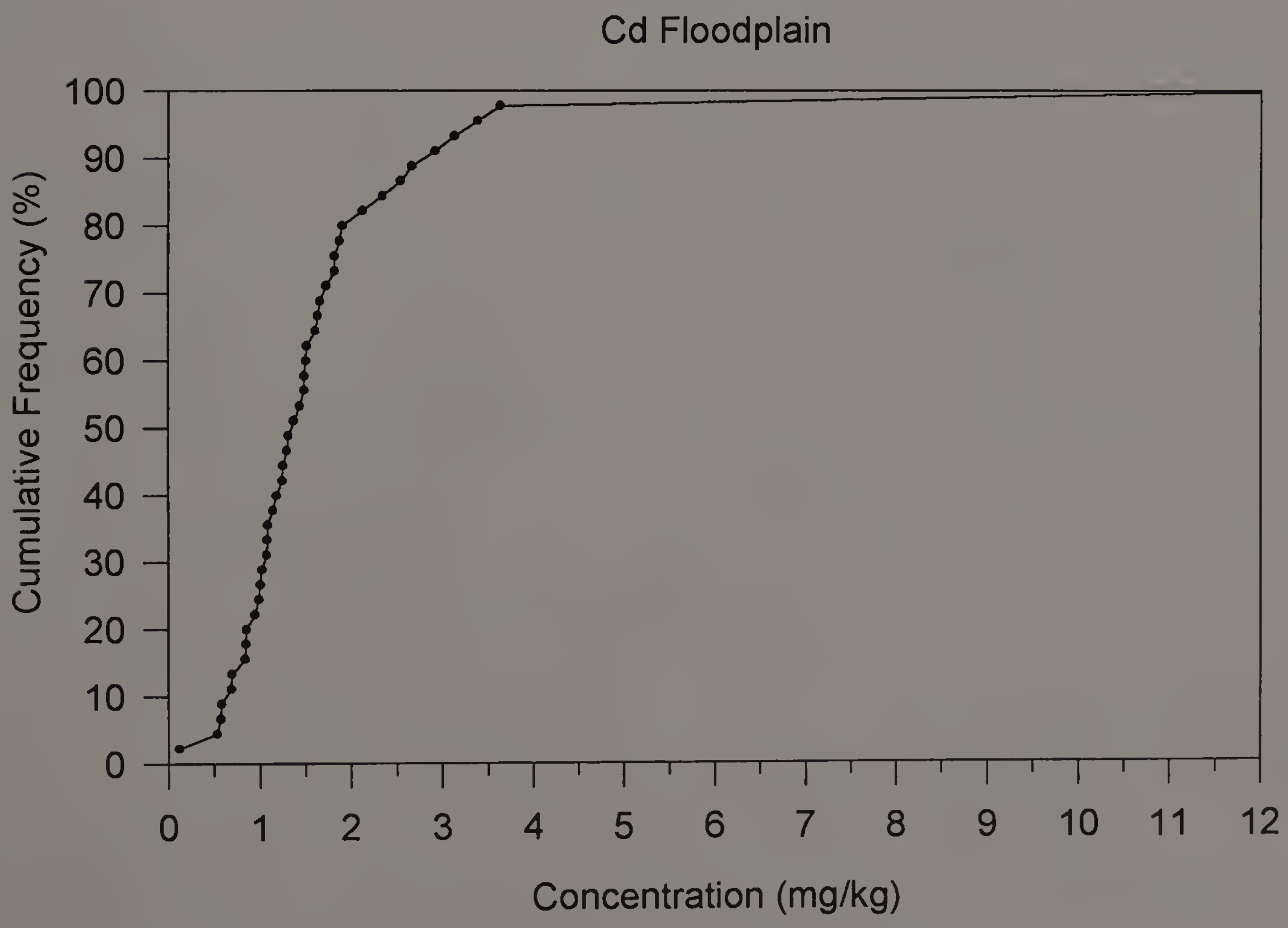

Zn Lacustrine
Cumulative Frequency (%)
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
Concentration (mg/kg)

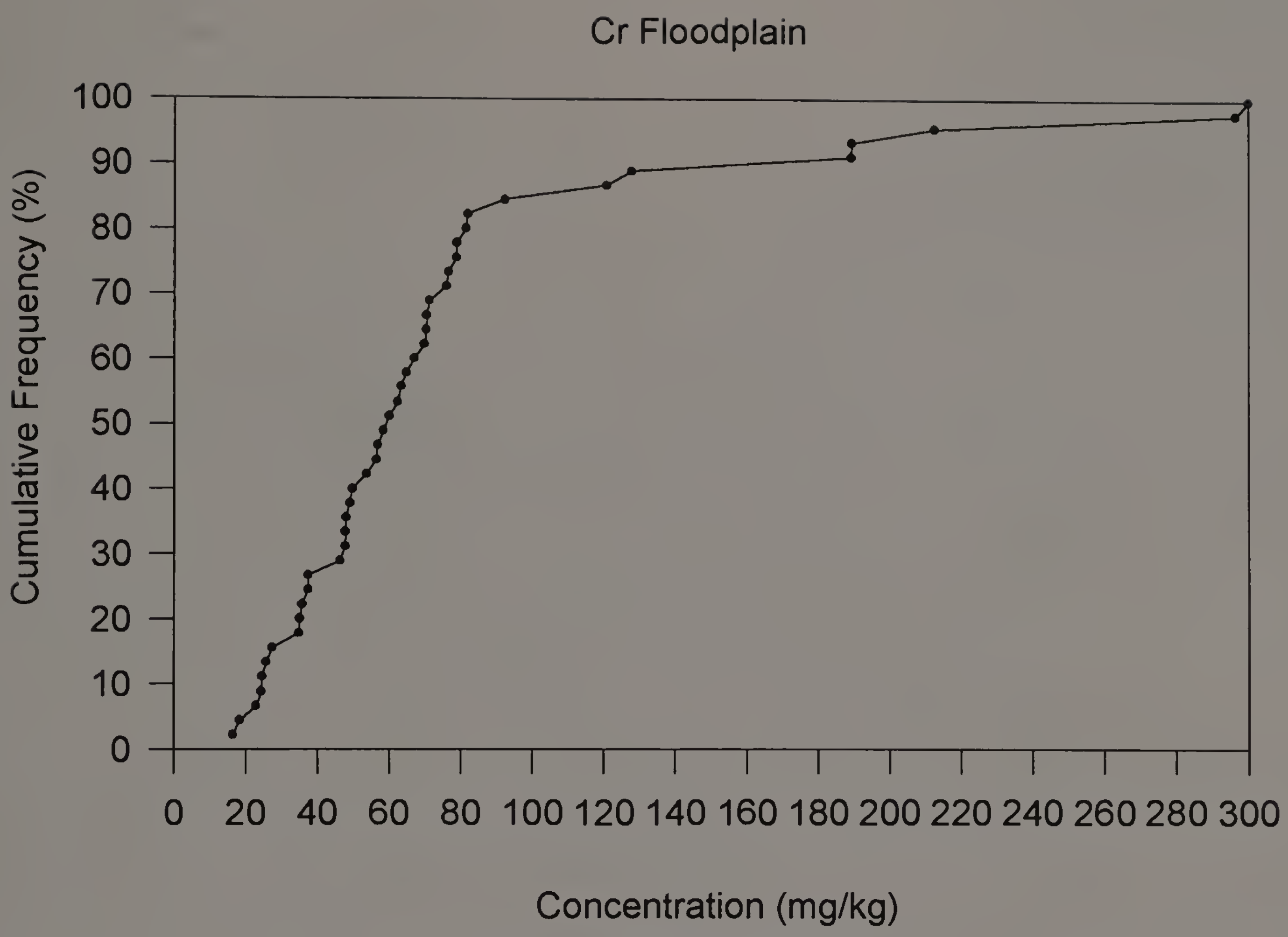

Pb Floodplain
Cumulative Frequency (%)
0
10
20
30
40
50
60
70
80
90
100
0
40
80
120
160
200
240
280
320
360
400
440
480
Concentration (mg/kg)

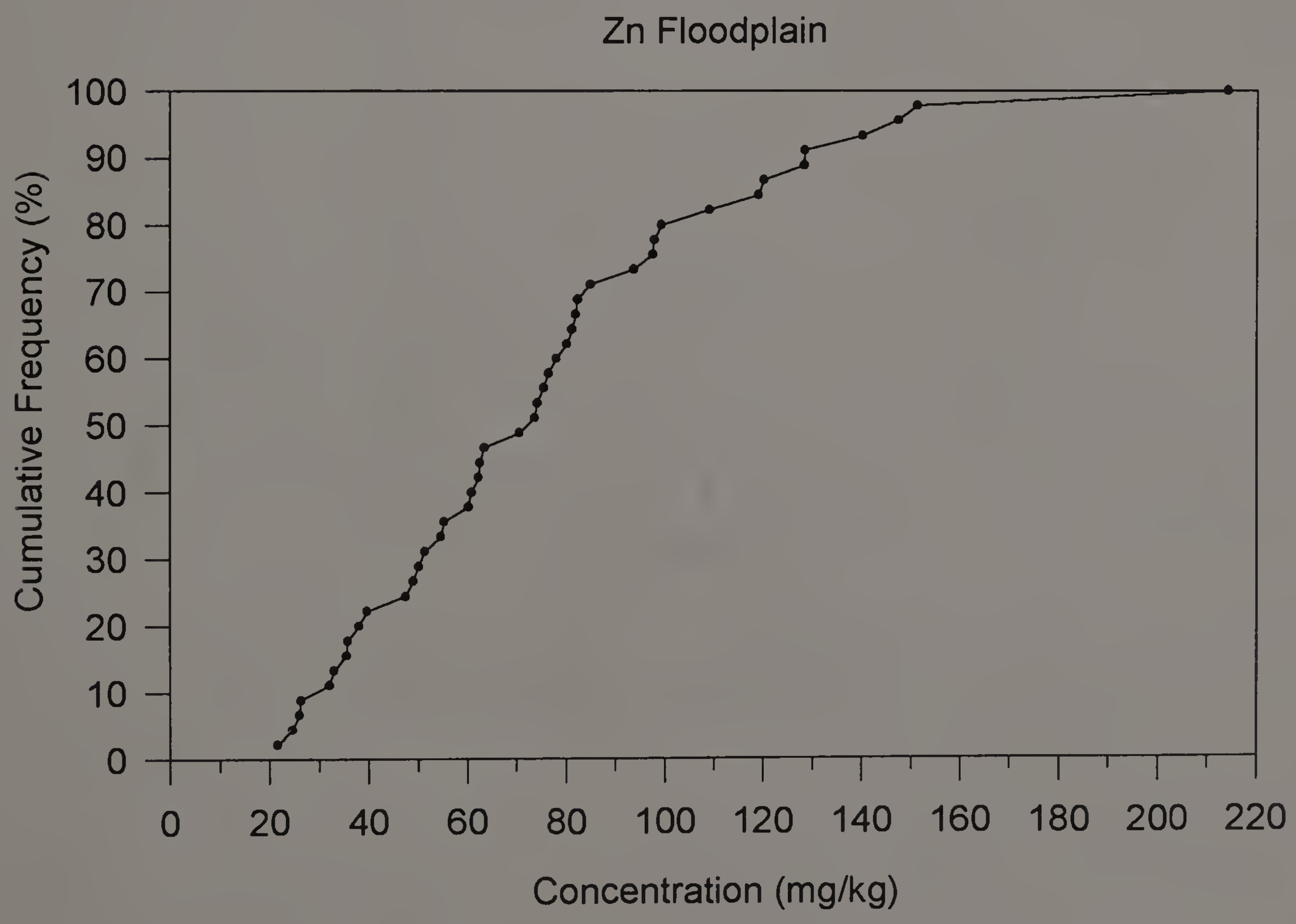

Cu Floodplain
Cumulative Frequency (%)
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240
Concentration (mg/kg)


Ni Floodplain
Cumulative Frequency (%)
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
Concentration (mg/kg)


Mo Floodplain
Cumulative Frequency (%)
0
10
20
30
40
50
60
70
80
90
100
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Concentration (mg/kg)


Cd Floodplain
Cumulative Frequency (%)
0
10
20
30
40
50
60
70
80
90
100
0
1
2
3
4
5
6
7
8
9
10
11
12
Concentration (mg/kg)


Cr Floodplain
Cumulative Frequency (%)
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
Concentration (mg/kg)


Zn Floodplain
Cumulative Frequency (%)
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
Concentration (mg/kg)

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