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THE ENVIRONMENTAL GEOCHEMISTRY OF TRACE-METAL CONTAMINANTS IN THE URBAN AREA OF GLASGOW

Thesis submitted in accordance with the
requirements of the University of Glasgow
for the degree of Doctor of Philosophy
by Martin John Gibson.

Department of Forensic Medicine and Science.

January, 1984.

DEDICATION

To Mary -

Teacher, tender comrade, wife,
A fellow-farer true through life

A Child's Garden of Verses (1885)

Ad majorem Dei gloriam

ACKNOWLEDGEMENTS

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SUMMARY

This study is primarily concerned with the chemical speciation and partitioning of trace-metal contaminants in a typical urban environment. In particular, major emphasis has been placed on the gaseous organic and particulate inorganic compounds of lead in the atmosphere and on the chemical associations of lead, zinc, copper and cadmium in the soils and street dirt of Glasgow, the largest city in Scotland. At the same time, a systematic city-wide survey of trace-metal contamination in Glasgow soil and street dirt has been carried out. When viewed as a whole, the separate features of this investigation enable an assessment of the significance of current trace-metal levels, forms and behaviour with respect to the environmental exposure to - and possible uptake of - potentially deleterious materials by the inhabitants of UK cities.

As the establishment of total metal concentrations was a fundamental component of the partitioning study and formed the basis of the soil/street dirt pollution surveys, an analytical method for the measurement of total levels of major, minor and trace elements in siliceous materials, based on atomic absorption spectrometric analysis of aqua regia/hydrofluoric acid/boric acid digests, was initially developed and verified on a variety of appropriate standard reference materials.

In a comprehensive survey of trace-metal contamination in over 400 Glasgow surface soils, total concentrations ranged up to 1900μg/g lead, 1840μg/g zinc, 925μg/g copper and 4.1μg/g cadmium, with 66%, 37%, 90% and 1%, respectively, of samples above the levels expected in an uncontaminated environment. Only about 5% of samples exceeded the existing government guidelines for the limitation of lead contamination of soil. Without data on chemical partitioning, however, this sort of approach provides only limited information on the true significance of enhanced urban trace-metal levels.

The importance of distinguishing chemical form in assessing the mobility and biological significance of trace-metal contaminants was demonstrated in a corresponding investigation of exchangeable trace-metal levels in all soils and in a subsequent six-step sequential leaching study performed on 90 samples. The six fractions defined by the selected chemical leaching agents were exchangeable (1M ammonium acetate, pH7), carbonate-bound (1M sodium acetate, pH5), easily-reducible (0.1M hydroxylamine hydrochloride/0.01M nitric acid), moderately-reducible (1M hydroxylamine hydrochloride/25% acetic acid), organic (30% hydrogen peroxide/0.02M nitric acid) and residual (aqua regia/hydrofluoric acid/boric acid). The greater ease of release and availability of cadmium, relative to lead, zinc and copper, were evident in both studies: the exchangeable fraction, averaging 29% of the total cadmium for all samples, was more significant, by a factor of about 10, for cadmium than for the other three elements; and the first three fractions contained 35% of total cadmium (>0.6μg/g) in contrast to 13%, 15% and 4% for lead, zinc and copper respectively. Lead (51%) was strongly associated with the moderately-reducible fraction and zinc (29%) and copper (41%) with the organic phase while the residual fraction retained 40-45% of zinc, copper and cadmium. For cadmium and zinc, summation of the exchangeable and carbonate-bound fractions, corresponding to 'maximum availability', revealed that 80% and 13% respectively of samples exceeded levels regarded as phytotoxic.

In a similar study of trace-element partitioning in Glasgow street dirt, the release and mobility of trace metals were shown to be markedly greater than in soils, the sum of the more readily mobilised exchangeable, carbonate-bound and easily-reducible fractions accounting for 46%, 39%, 18% and 50% respectively, of lead, zinc, copper and cadmium. The street-dirt partitioning data are probably of more relevance to the quality of the receiving waters, biota and bottom sediments of adjacent aquatic systems than to plant life in the terrestrial biosphere. There the greatest immediate significance perhaps lies in the exposure of young urban children to toxic metals, especially lead, via ingestion of dust. Using dilute hydrochloric acid to simulate human stomach acidity, it was found that an average 41% of total lead in Glasgow street dirt (<500µm) is solubilised and available for absorption by the body. Street dirt was further shown to be at least comparable to normal dietary sources in contributing to the body lead burden of young children, a matter for continuing concern in view of the harmful effects of lead on childhood intelligence and behaviour.

Additional information on the speciation of lead in the urban environment was obtained through measurement of gaseous tetraalkyl lead (TAL) and particulate inorganic lead in the atmosphere. The volatile species, added to petrol as a liquid anti-knock agent, is emitted to the atmosphere via evaporation from car petrol tanks and, along with particulate lead, via car exhausts. It was found that TAL accounted typically for 5.7% of total daily atmospheric lead in central Glasgow but could vary considerably in concentration with time of day, altitude and geographical location. The intriguing possibility that natural environmental methylation of lead may occur was not, in general, supported by the TAL data for a comparatively remote rural site, adjacent to an inorganic-lead-contaminated coastal environment, to the north-west of Glasgow. Nevertheless, the observation of an occasional elevated rural TAL/total lead ratio endorses the importance of adopting approaches based on analytical speciation in studies of environmental and human responses to trace-metal contamination.

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CHAPTER 1 - INTRODUCTION

Over the last few millennia and most notably since the onset of the Industrial Revolution, man has mobilised, extracted, used and ultimately released increasing quantities of chemical elements from a variety of crustal materials to the air, water and soil of his natural environment. Many of these elements occur naturally in only trace amounts. The known biological consequences of this large-scale elemental redistribution have sometimes been very serious, in specific cases, but much remains to be learned about the relationships and interactions between trace element contaminants and biological systems. In assessing the environmental impact of trace element contamination, however, it is first necessary to place in perspective the natural levels, sources, geochemical pathways, distribution and roles, beneficial and otherwise, of trace elements in the physical environment and in the biota, including humans. As most human beings in the western world live in heavily-populated, industrialised cities and towns, thus constituting a significant exposure group, it is particularly important to relate the above factors to the context of the urban environment.

1.1 CHEMICAL ELEMENTS IN THE ENVIRONMENT

In the solar system the chemical elements were derived from initial fusion of the lightest element, hydrogen, and subsequent nuclear processes (Burbridge et al, 1957), largely accounting for the general inverse relationship between cosmic abundance and atomic number of the elements as shown in Figure 1.1 (Hamilton, 1979a). When the earth was formed ca. 4.5 billion years ago, it seems likely that the elements were fairly evenly distributed but, following separation and evolution into an iron-rich core and outer mantle and a comparatively thin outer crust (10-60km), they became segregated according to

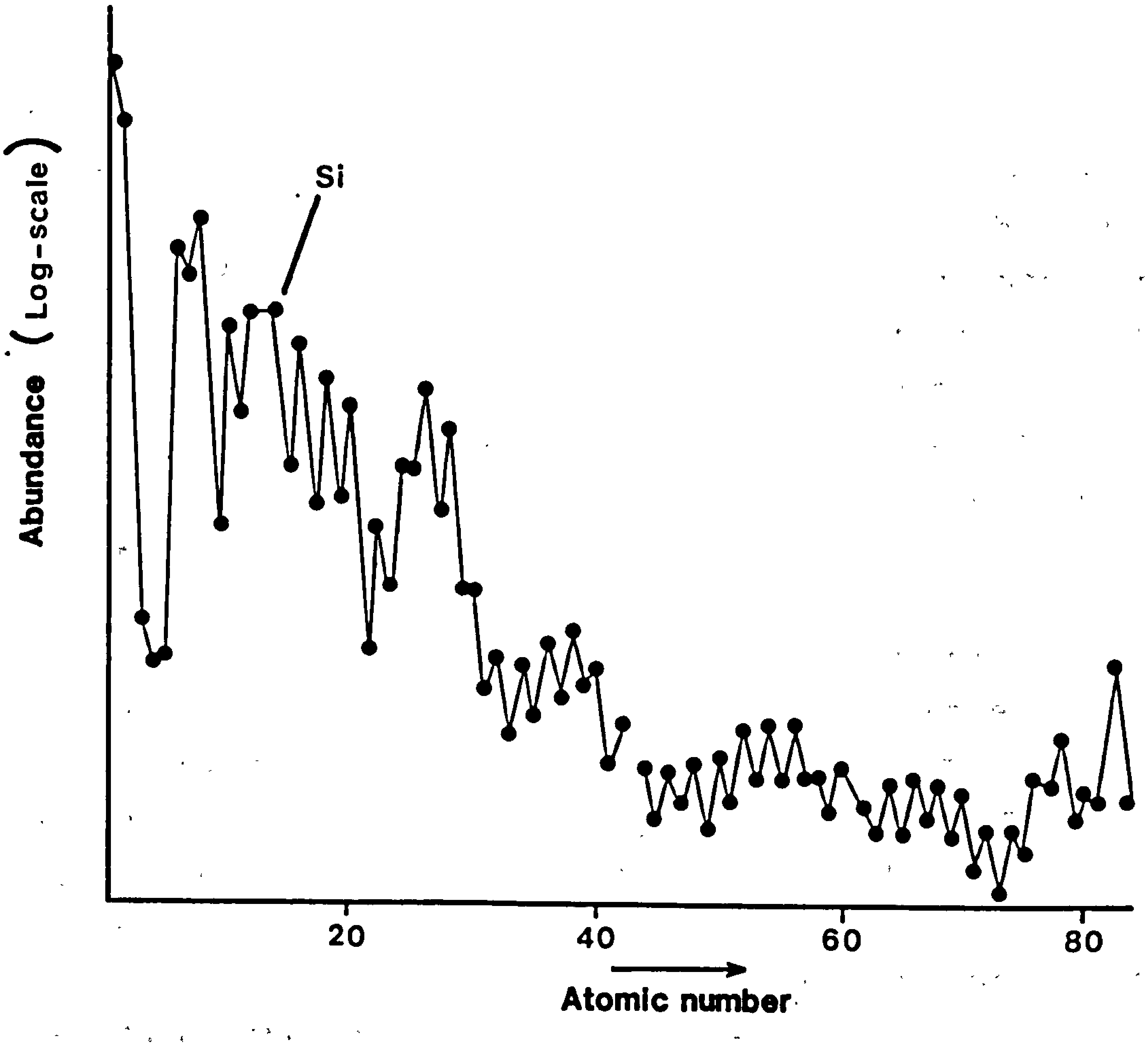


FIGURE 1.1 THE COSMIC ABUNDANCE OF THE CHEMICAL ELEMENTS (ATOMIC CONCENTRATIONS RELATIVE TO Si = 10^6) [Hamilton, 1979a]

their physical and chemical properties, yielding a series of mineral phases - predominantly silicates, oxides and sulphides - in the continental masses (Hamilton, 1979b). Intervening geological events and geochemical and pedochemical weathering processes have altered the crustal distribution of the elements (and also strongly influenced elemental composition of the oceans and atmosphere) which may exhibit wide geographical variations in concentration. The average crustal abundance of the elements is shown in Figure 1.2.

As all living organisms have evolved against this background it is reasonable to anticipate that their chemical composition would largely reflect that of their environment (soil, water etc), although internal biochemical processes may discriminate against certain elements. Hamilton (1979b) has demonstrated a strong resemblance between the relative abundances of elements in crustal rocks, seawater and human blood, indicative of a link between the inert and the living, although some elements (e.g. aluminium, silicon) are found preferentially in rocks and minerals and others (e.g. carbon, hydrogen, nitrogen) in living matter. Those elements most abundant in nature (atomic number <20, e.g. hydrogen, oxygen, carbon, nitrogen, calcium etc.) almost exclusively constitute the bulk of living matter. The remaining elements of the periodic table occur in much lower concentrations but, in appropriate chemical forms, can exert effects out of all proportion to their abundance (Mertz, 1981a).

1.2 THE NATURE AND BIOSIGNIFICANCE OF TRACE ELEMENTS

The majority of mineral elements occur in nature in such small concentrations (<100μg/g) that they are frequently referred to as trace elements (Irving et al, 1978). These trace elements can be classified as essential for health

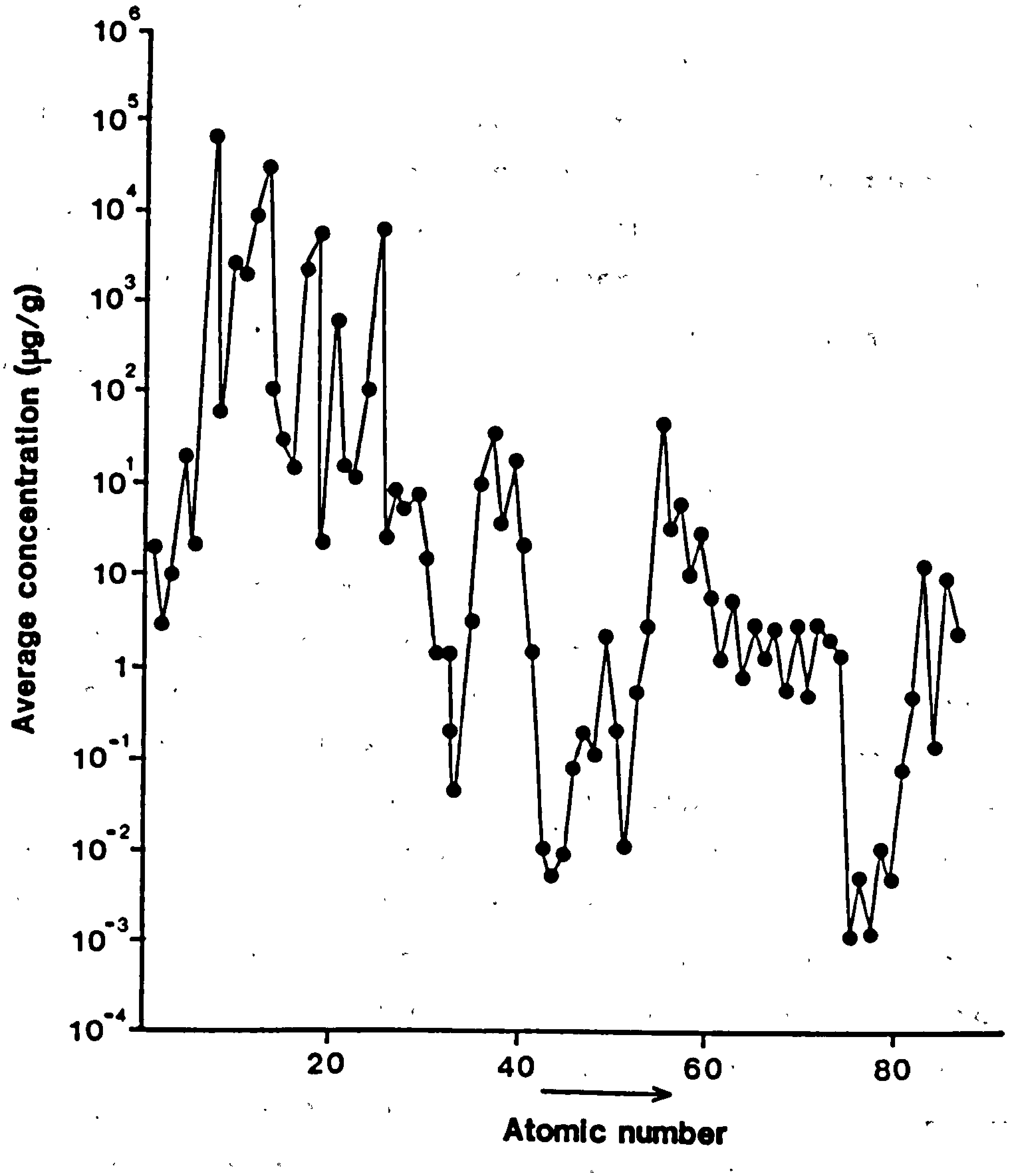


FIGURE 1.2 THE AVERAGE CONCENTRATIONS (µg/g) OF ELEMENTS IN CRUSTAL ROCKS (Hamilton,1979b)

and growth of living organisms, with deficiency symptoms appearing where the element supply is restricted, or functional (often classed as essential) in as much as they exhibit beneficial effects on growth or yield, or non-essential in that no evidence of essentiality exists. All known essential and functional trace elements are structural or catalytic components of, or interact with, larger molecules such as enzymes or hormones (which need the trace elements to express their activity) that, in turn, regulate much larger masses of substrate. Their effects are absolutely specific which suggests that, on entry to the organism, 'carrier substances', e.g. plasma proteins, recognise the element immediately and deliver it to its own specific site of action (Hamilton, 1979a; Mertz, 1981b).

Although it is possible that most elements in the periodic table have some function or influence in biological systems (West, 1979), it appears that the evolutionary processes have selected certain elements for the essential functioning of living organisms while rejecting the others. Including the constitutional and major elements (Table 1.1), 25 elements, of which 14 are present in trace amounts, have been demonstrated as necessary for efficient human and animal metabolism (Mertz, 1981a) while in man approximately 40 more are present in detectable quantities (Schroeder, 1974). The essential and functional trace elements described, for humans, in Table 1.2, include several - molybdenum, selenium, chromium, nickel, vanadium, silicon and arsenic - whose significance has only been established over the last 25 years due to the development of an ultraclean experimental environment and to the spectacular improvements in analytical instrument sensitivity. This suggests that additional elements, particularly gallium, germanium and bromine, with atomic numbers adjacent to the majority of the recognised biosignificant elements

TABLE 1.1 ELEMENTS OF BIOSIGNIFICANCE TO HUMANS AND ANIMALS (Mertz, 1981a)

	Essential		Functional
Constitutional	Major	Trace	
C	Ca Cl	Co Cu	As
H	K	Fe	Cr
O	Mg	Mn Mo	F
	N Na	Zn	I
	P		Ni
	S		Se Si
			V

TABLE 1.2 CLASSIFICATION OF THE ESSENTIAL AND FUNCTIONAL TRACE ELEMENTS FOR HUMANS (Mertz, 1981a)

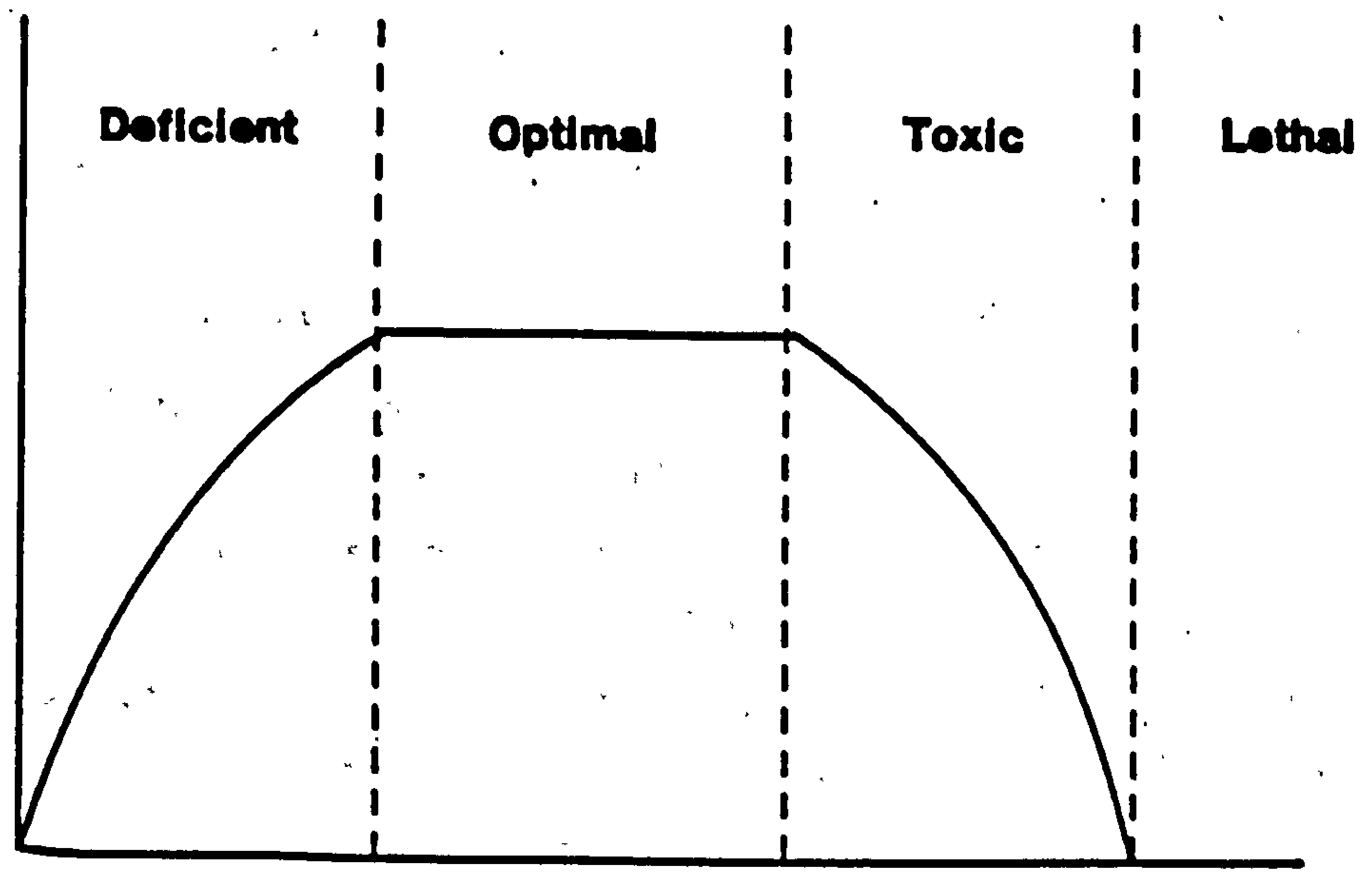
Element	Function	Deficiency signs	Occurrence of imbalances
Fluorine	Structure of teeth, possibly of bones; possibly growth effect	Increased incidence of caries; possibly risk factor for osteoporosis	Deficiency and excess known
Silicon	Calcification; possibly function in connective tissue	Not known	Not known
Vanadium	Not known	Not known	Not known
Chromium	Potentiation of insulin	Relative insulin resistance, impaired glucose tolerance, elevated serum lipids	Deficiency known in malnutrition, aging, total parenteral alimentation
Manganese	Mucopolysaccharides metabolism superoxide dismutase	Not known	Deficiency not known; toxicity by inhalation
Iron	Oxygen, electron transport	Anaemia	Deficiencies widespread; excesses dangerous in hemochromatosis; acute poisoning
Cobalt	As part of vitamin B_{12}	Only as vitamin B_{12} deficiency	Inability to absorb vitamin B_{12}; low B_{12} intake from vegetarian diets
Nickel	Interaction with iron absorption	Not known	Not known
Copper	Oxidative enzymes; interaction with iron; cross-linking of elastin	Anaemia, changes of ossification; possibly elevated serum cholesterol	Deficiencies in malnutrition, total parental alimentation
Zinc	Numerous enzymes involved in energy metabolism and in transcription and translation	Growth depression, sexual immaturity, skin lesions, depression of immuno-competence, change of taste acuity	Deficiencies in Iran, Egypt, in total parental nutrition, genetic diseases, traumatic stress
Arsenic	Not known	Not known	Not known
Selenium	Glutathione peroxidase; interaction with heavy metals	Endemic cardiomyopathy (Keshan disease) conditioned by selenium deficiency	Deficiency and excess in areas of China; one case resulting from total parenteral alimentation
Molybdenum	Xanthine, aldehyde, sulphide oxidases	Not known	Excessive exposure in parts of Soviet Union associated with goutlike syndrome
Iodine	Constituent of thyroid hormones	Goiter, depression of thyroid function cretinism	Deficiencies widespread; excessive intakes may lead to thyrotoxicosis

(Underwood, 1977), could be proven essential or functional by future research (Mertz, 1981a). The non-essential elements are believed to be acquired by biological systems as environmental contaminants, sometimes accumulating to levels greater than the essential trace elements, and as such reflect the exposure of the organism to these elements.

The biological significance of some trace elements (e.g. cadmium, mercury, lead) is so far confined to their toxic or potentially toxic properties at relatively low concentrations. The designation of these elements as toxic has limited value because all trace elements are toxic if biological exposure is sufficiently great. Moreover, the recent confirmation of the essentiality of arsenic (Anke et al, 1978), generally regarded as a toxic element, illustrates that no trace element is inherently toxic or beneficial. This phenomenon was recognised as long ago as the early years of this century by Bertrand who formulated the dose-dependence hypothesis (Bertrand's Law) which states that, for essential trace elements, both deficiency and excess can produce detrimental effects (Bertrand, 1906). This can be represented diagrammatically in a dose-response curve (Figure 1.3a). The plateau region reflects concentrations for optimum growth and health, a wide region indicating an element of low inherent toxicity. Although the shape of the dose response curve is unique to each element, every element has a range of safe and adequate exposure concentrations within which optimal biological conditions are realised, and a level beyond which it is potentially toxic.

Conversely, the non-essential elements, e.g. lead and cadmium, which are potentially hazardous at low exposure levels, exhibit a so-called tolerable concentration region in the dose response curve (Figure 1.3b). This however, may merely reflect the current inability to detect harmful effects at very low concentrations.

(a) Essential (e.g. zinc, copper)



(b) Non-essential (e.g. lead, cadmium)

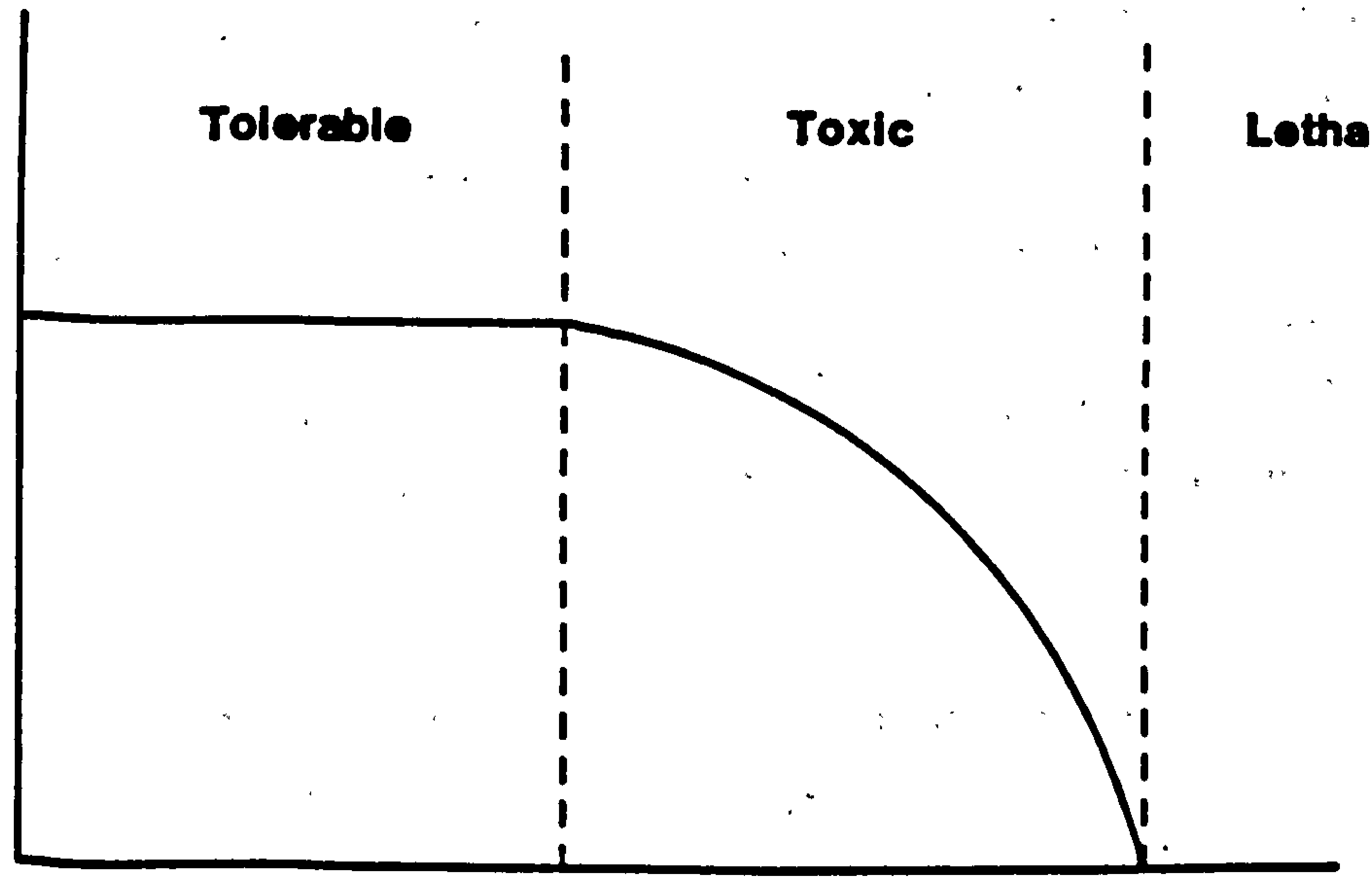


FIGURE 1.3 DOSE-RESPONSE CURVES IN TERMS OF DEFICIENCY AND OVERSUPPLY OF ESSENTIAL AND NON-ESSENTIAL TRACE ELEMENTS (Bertrand, 1906)

1.3 ENVIRONMENTAL TRACE-ELEMENT CONTAMINATION

1.3.1 EVIDENCE OF CONTAMINATION

Contamination of the environment has been described as 'the dispersion of some substance in it at concentrations which may produce undesirable effects - when the undesirable effects are evident, the contamination amounts to environmental pollution' (Purves, 1977). Environmental contaminants cover a wide range and diversity of materials generally categorised on the basis of their chemical nature, e.g. inorganic elements, oil, organic pesticides etc. In contrast with those chemical pollutants which are biodegradable, inorganic elements tend to accumulate with time, producing long-term hazards. To determine the extent of trace-element contamination it is necessary to formulate historical perspectives of elemental deposition in terms of temporal trends, geographical variations and magnitude relative to the scale of natural mobilisation and redistribution (Patterson, 1965; Bowen, 1977; Nriagu, 1979a). Historical records of trace-element contamination are preserved in a variety of natural systems in which the rate of accumulation of undisturbed and unmodified deposited matter can be determined by radiometric (e.g. ^{14}C, ^{210}Pb) or stratigraphic techniques (Robbins, 1978; Muller, 1981).

Global contamination is recorded in remote areas such as the permanent snow of the polar ice-caps where the localised influence of man is minimal. Analysis of the snow/ice strata of Greenland reveals a >200 fold increase in lead pollution during the past 3000 years (Murozumi et al, 1969; Ng and Patterson, 1981), a 2-10 fold increase in cadmium deposition in the past 300 years, a 3-6 fold increase in zinc between 1900-1966 and a similar increase in copper over the same period (Weiss et al, 1975).

Contamination on a more regional scale, often more directly influenced by industrial and human domestic activities, is preserved in sedimentary cores from shallow marine coastal areas (Bruland et al, 1974; Goldberg et al, 1977) and freshwater lakes (Forstner, 1976). Heavily polluted sediments such as in Lake Erie in Canada show increased trace metal levels of 80-600% in modern times (Nriagu et al, 1979). In Scotland, increasing anthropogenic pollution from the densely-populated industrial belt of the west central region is reflected by the 10-fold enhancement of lead and zinc in sedimentary profiles from Loch Lomond, 30km to the north-west of Glasgow, over the last 130 years, primarily as a consequence of atmospheric deposition (Farmer et al, 1980).

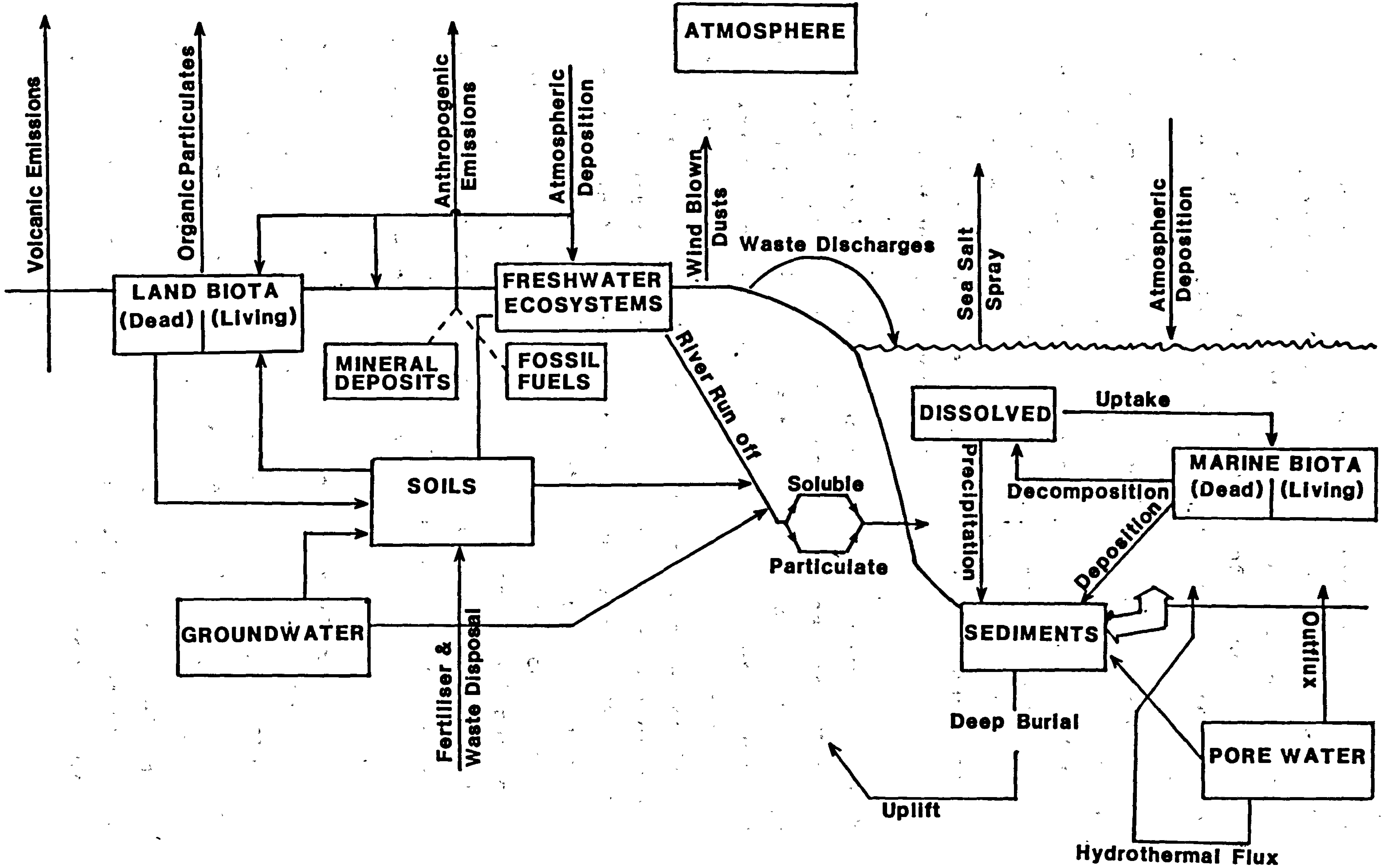
In the case of soils, historical trends of trace-element contamination are usually obscured. Nevertheless, on account of their close proximity to emission sources, urban soils are useful indicators of localised pollution and can provide an integrated expression of past and present deposition. Their widespread occurrence enables their employment in a reconnaissance capacity to determine the geographical distribution and extent of trace element pollution in urban and industrialised areas and indicate variations in environmental quality relative to adjacent rural areas (Parry et al, 1981). Several studies of UK urban soils (Farmer and Lyon, 1977; Purves, 1977; Davies, 1978; 1983b) have shown considerable enhancement of lead, zinc, copper and cadmium over background levels observed in rural soil and stream sediment surveys. The latter can supply information on both typical low background levels and the anomalously high metal concentrations of natural mineralised areas (Mitchell, 1971; Webb et al, 1978; Webb and Howarth, 1979).

Further evidence of trace-element contamination since the onset of human civilisation is preserved in skeletal remains and provided by comparison of present-day environmental levels with estimates of those which prevailed in the precivilisational period. Settle and Patterson (1980) have shown that the bones of present-day Americans contain 500 times more lead than those of an isolated Peruvian community of ca. 200A.D. They also deduced that dietary lead intakes of late 20th century Americans are 100 times greater than prehistoric dietary levels. Similarly, atmospheric lead levels are believed to have increased from $0.00004 \mu g/m^3$ (Settle and Patterson, 1980) to typical urban levels today of $>0.5 \mu g/m^3$ (DeJonghe and Adams, 1982) while surface seawater shows a 10-fold increase in lead over the same period (Settle and Patterson, 1980; Schaule and Patterson, 1981).

1.3.2 TRACE ELEMENT CYCLING AND SOURCES OF CONTAMINATION

The environmental distribution of trace-element contaminants is governed by the responses of natural cycles to inputs from the perturbatory sources of contamination. A typical model of the global cycle, incorporating the principal reservoirs and transport pathways, is shown in Figure 1.4. Most global models assume that the total system is in a stationary state but anthropogenic activity has displaced the dynamic equilibrium balance of the natural biogeochemical cycle to the extent that there is a net transfer of elements from the lithosphere to the surface of the land and to the hydrosphere. There are considerable differences in the elemental inventories of the reservoirs. Although the total atmospheric inventories are usually small relative to the other reservoirs, the atmosphere is of great importance in element transport, notably with respect to the dispersal and deposition of airborne pollutants leading to surface contamination in the urban environment.

FIGURE 1.4 THE BIOGEOCYCLE OF THE ELEMENTS (Nriagu, 1979b)


ATMOSPHERE
Volcanic Emissions
Organic Particulates
Anthropogenic Emissions
Atmospheric Deposition
Wind Blown Dusts
Waste Discharges
Sea Salt Spray
Atmospheric Deposition
LAND BIOTA
(Dead)
(Living)
FRESHWATER ECOSYSTEMS
MINERAL DEPOSITS
FOSSIL FUELS
River Run off
DISSOLVED
Uptake
MARINE BIOTA
(Dead)
(Living)
Precipitation
Decomposition
Deposition
SOILS
Soluble
Particulate
GROUNDWATER
Fertiliser & Waste Disposal
SEDIMENTS
Outflux
Deep Burial
Uplift
PORE WATER
Hydrothermal Flux

Atmospheric residence time of particulate pollutants depends on particle size. Particle sizes range from <0.01 ->100μm in diameter but due to coagulation of small particles and rapid sedimentation of larger particles most are in the 0.1-15μm range. Most aerosols are removed by precipitation in rainfall, gravitational fallout impaction or Brownian diffusion returning to earth after 7-10 days, but aerosols which reach the stratosphere, usually particles <1μm, are distributed worldwide (Cawse, 1974). In contrast, the residence times of elements in the lithosphere, where mobilisation and transportation are considerably slower, are in the order of hundreds to thousands of years (Bowen, 1977).

Elemental contamination originates from a variety of both natural sources and technogenic emissions. Natural mobilisation of the elements occurs principally through the weathering, erosion and uplift of mineral deposits and through gaseous emissions from the substrata during volcanic activity. Natural emissions can be estimated from current environmental data and from models of their biogeochemical cycles (Settle and Patterson, 1980). The estimated annual quantities of lead, zinc, copper and cadmium released by the major natural sources into the atmosphere are listed in Table 1.3. Eroded soil particles generally account for ca. 60-80% of natural lead, zinc and copper while volcanic emissions constitute ca. 60% of natural cadmium (Nriagu, 1979a).

Significant anthropogenic release of elements to the environment began in ancient times (5000 - 6000B.C.) with the development of metal smelting technology. Elements such as gold, copper, iron, lead, silver and zinc were widely used until the demise of the Roman Empire some 1600 years ago. Subsequently, as is illustrated in the classic diagram for lead (Figure 1.5), the general trend in metal production and use and, consequently,

TABLE 1.3 GLOBAL EMISSIONS OF TRACE METALS FROM NATURAL SOURCES (Nriagu, 1979a).

SOURCE	EMISSION ($x10^9$g/yr except* x 10^6g/yr)			
	Pb	Zn	Cu	Cd*
Windblown dusts	16	25	12.0	100
Forests fires	0.5	2.1	0.3	12
Volcanogenic particles	6.4	7.0	3.6	520
Vegetation	1.6	9.4	2.5	210
Seasalt sprays	0.02	0.01	0.08	1.0
TOTAL	24.5	43.5	18.5	843

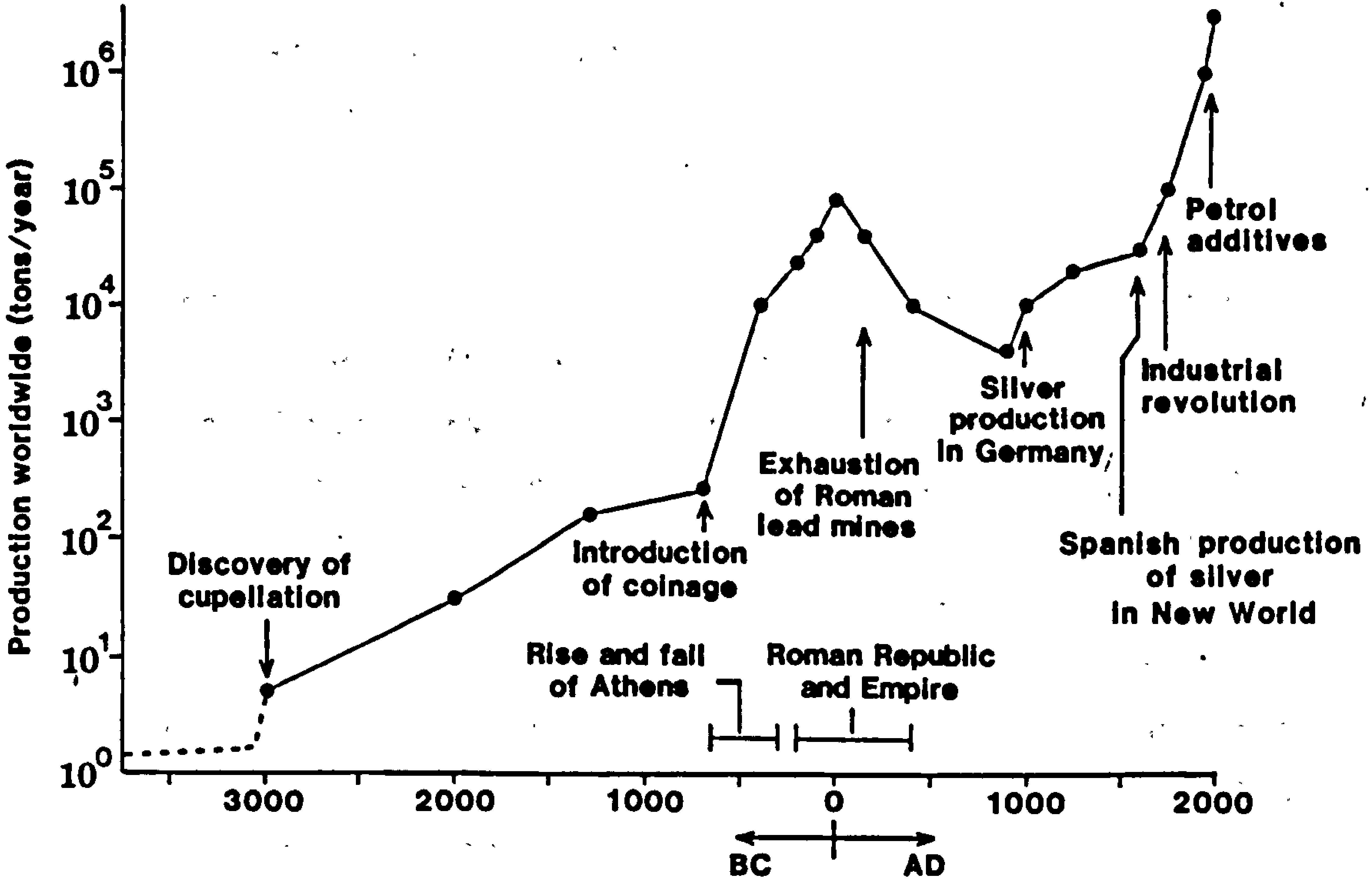


FIGURE 1.5 HISTORICAL PRODUCTION AND CONSUMPTION OF LEAD (Settle and Patterson, 1980)

dispersion, has been upwards, with a dramatic increase since the onset of the Industrial Revolution (1750A.D.). During the 20th century, metal emissions to the atmosphere have also risen with the combustion of exponentially-increasing quantities of fossil fuels. In recent years, environmental attention has focussed on four metals with potentially serious ecological consequences - lead, zinc, copper and cadmium. Details of the release of these elements to the environment are summarised below along with a brief discussion of their uses and biological roles and effects.

(i) Lead

Lead is an extremely versatile element with a considerable number of uses as a result of its physical (softness, malleability, density), chemical (resistance to corrosion) and electrical properties. Its metallic uses range from sheet for roofing to pipes and shielding from radioactive emissions. It is also used in electric battery manufacture, in solders and bearings for internal combustion engines, while its compounds are widely employed in paints (lead oxides and lead naphthenates), insecticides (lead arsenates) and most notably, petrol additives (lead alkyls). Lead alkyls, mainly tetramethyl and tetraethyl lead, are added to petrol as anti-knock agents to produce the high-octane fuel required by high-compression internal combustion automobile engines.

The total annual flux of lead to the atmosphere is estimated to be ~457 x 10^6 kg/year of which 96% is from technogenic sources, predominantly (90%) in the northern hemisphere (Settle and Patterson, 1980), and 30% is deposited in the oceans (Nriagu, 1978). Leaded petrol, while constituting only 12% of total lead consumed per annum, is the single most important source of lead to the atmosphere, accounting for 60% of the global atmospheric burden (Nriagu, 1979a) and 90% of the atmospheric lead burden in UK cities (Royal Commission, 1983). Consequently, it is primarily responsible for widespread environmental lead contamination. Other important global sources of lead emissions are iron and steel production, primary and secondary non-ferrous metal production and coal combustion (Table 1.4).

As lead has no known beneficial function in human or animal metabolism, interest has centred principally on its role as a highly toxic cumulative poison. Although instances of acute poisoning are now relatively rare, there is general concern over the insidious sub-clinical health effects of long-term exposure to elevated levels of lead in highly urbanised environments. Lead poisoning damages the central nervous system - causing lead encephalopathy and neuropathy - and produces renal tubular dysfunction and anaemia (Moore et al, 1977). In children, who are particularly susceptible, sub-clinical lead poisoning may cause brain damage, the symptoms including behavioural abnormality, intelligence deficits and hyperactivity (Needleman et al, 1979).

The principal indicator of lead exposure in humans is lead in blood (whole blood) expressed as µg/100ml or µmol/l (80µg/100ml = 3.86µmol/l). Blood lead levels of workers occupationally exposed in the lead industry sometimes reach 70-80µg/100ml while people in urban areas have levels in the 10-20µg/100ml range (Royal Commission, 1983). Because tolerance to lead is influenced by so many factors such as age, diet composition, forms and sources (Underwood, 1977), there is considerable debate over the blood levels at which adverse effects occur and, consequently, what is considered to be an acceptable level for the general population. Blood lead levels and some related health effects are shown in Table 1.5. Biochemical effects are observed as low as 10µg lead/100ml with the heme synthetic pathway affected at

TABLE 1.4 WORLDWIDE ANTHROPOGENIC EMISSIONS OF TRACE METALS DURING 1975 (Nriagu, 1979a)

	Trace metal emissions ($x10^6$kg/yr)			
	Pb	Zn	Cu	Cd
Mining, non-ferrous metals	8.2	1.6	0.8	0.002
Primary non-ferrous metal production				
Cd				0.11
Cu	27	6.6	19.7	1.6
Pb	31	0.44	0.29	0.20
Zn	16	99	0.78	2.8
Secondary non-ferrous metal production	0.77	9.5	0.33	0.60
Iron and steel production	50	35	5.9	0.07
Industrial applications	7.4	26	4.9	0.05
Coal combustion	14	15	4.7	0.06
Oil (including gasoline) combustion	273	0.07	0.74	0.003
Wood combustion	4.5	75	12	0.2
Waste incineration	8.9	37	5.3	1.4
Manufacture, phosphate fertilisers	0.05	1.8	0.6	0.21
Miscellaneous	5.9	6.7	-	-
TOTAL	449	314	56	7.3

TABLE 1.5 BLOOD LEAD LEVELS AND RELATED HEALTH EFFECTS

cited in Fergusson (1982)

Whole Blood Lead Level (μg/100ml)	Health Effect
10	Delta - ALAD inhibition
15-20	Erythrocyte protoporphyrin elevation
40	Increased delta-ALA in urine Anaemia Coprotoporphyrin elevation in urine
50-60	Effect on central nervous system Peripheral neuropathics
>80	Encephalopathic (Brain) symptoms

less than typical urban levels (<20µg/100ml). Recently, a European Community Directive (1977), on reference levels for lead in blood, defined blood lead objectives for three specific population groups: (i) urban inhabitants, (ii) groups exposed to significant sources and (iii) critical groups at special risk (excluding occupationally exposed). The directive stated that blood lead levels should be <35, <30 and <20µg/100ml for 98%, 95% and 50%, respectively, of individuals in all three groups. Typical levels in Western Europe, although generally less than 20µg lead/100ml (Royal Commission, 1983), are significantly greater than blood levels observed in populations living in remote areas of the Earth such as Papua, New Guinea - 5µg/100ml (Poole et al, 1980) - and the Himalayan foothills - 3µg/100ml (Piomelli et al, 1980). This information strengthens the argument of some workers, like Patterson's group, who believe that ancient blood lead levels could have been far lower than this reflecting their contention that the average concentration of lead in the American diet in prehistoric times was <2ng/g compared with ~200ng/g today (Settle and Patterson, 1980).

(ii) Zinc

Zinc is an important industrial metal with a wide range of uses and applications. In its metallic form, zinc is an integral part of brass and other alloys with notable use as a constituent of many car components. Zinc is also used in paint and rubber while its high reactivity enables its employment as a protective coating on iron and steel products. Zinc sheets are also utilised for building purposes. Zinc salts are astringent, corrosive in action and mildly antiseptic with some uses in medicine.

The total annual flux of zinc to the atmosphere is ca. 353 x 10^6kg (Nriagu and Davidson, 1980) with around 90% (314 x 10^6kg) derived from anthropogenic sources. The major emission source is the production of zinc metal (99 x 10^6kg) but as zinc is a natural component of many materials significant amounts are also released via wood and coal combustion, waste incineration, iron and steel production and industrial applications (Table 1.4).

Although the essential nature of zinc for animals has been known for some time (Todd et al, 1934), its essential role in human metabolism was only recognised in the early sixties (Prasad et al, 1961). Subsequently more than 80 zinc-containing proteins and enzymes, mainly peptidases and anhydrases, have been identified, including carbonic anhydrase, an enzyme involved in the transport of CO_2 in the blood, alkaline phosphatase and alcohol dehydrogenase while a number of zinc enzymes are catalysts for RNA and DNA metabolism. Zinc also influences growth rate and bone development, the integrity of the skin and the development and function of the reproductive organs.

Zinc is relatively non-toxic to man and animals with dietary sources unlikely to produce chronic toxicity, particularly in the western world where the diet may be deficient in zinc (Lyon et al, 1979). Most species exhibit considerable tolerance to high zinc intakes but this is dependent on dietary levels of other elements, e.g. calcium, copper, iron, cadmium, with which it is antagonistic in absorption and utilisation. Toxic effects can arise where zinc salts or compounds are given orally in large amounts (>150 mg/day) over prolonged periods e.g. in the treatment of illness or disease; concomitant deficiencies of copper and iron may be induced where dietary intake of these elements is already low. Lethal doses are in the order of 6g/day.

(iii) Copper

Copper is also an important industrial metal, rating third in the annual global consumption of metals. The distinctive properties of ductility and conductivity of electricity and heat have led to its use in piping, casting, alloys (notably brass), cooking utensils, chemical and pharmaceutical equipment, coins (copper-nickel alloy) and in all gauges of wire, circuitry, coil and armature windings. Certain copper salts, toxic to microbial life forms, are used as pesticides, e.g. the insecticide copper fluorarsenate and the fungicide copper sulphate.

The total annual flux of copper to the atmosphere has been estimated to be 75 x 10^6kg/year (Nriagu, 1979b) of which 75% (56 x 10^6kg/year) is from anthropogenic sources and 80% (of total) is deposited on land, predominantly in the vicinity of point sources. The most significant copper emission source is the production of copper metal, accounting for 19.7 x 10^6kg/year, while other important environmental releases derive from wood and coal combustion, waste incineration, iron and steel production and industrial applications (Table 1.4).

Copper is an essential element present in all living organisms and many copper-containing enzymes have been identified, including tyrosinase, ascorbic acid oxidase and cytochrome oxidase. Chronic copper poisoning may occur in animals as a consequence of excessive copper intake, e.g. under natural grazing conditions, but, as with most trace elements, the variety of different chemical forms and combinations affects copper's availability to the animal. Several other elements present in the diet, e.g. calcium, cadmium, iron, lead, zinc, markedly affect copper absorption, retention and distribution within the body (Underwood, 1977). While it is not certain that chronic poisoning can occur in humans, copper synergistically affects the metabolic cycles of more toxic elements, e.g. cadmium, lead, mercury and silver, as well as essential elements, e.g. iron, molybdenum, magnesium, nickel, selenium and zinc (Kirchgessner et al, 1979) and an imbalance in zinc/copper metabolism may contribute to the risk of coronary heart disease (Klevay, 1973). Acute poisoning by copper salts does occur, with ~1g of copper sulphate causing toxic reactions, but this may be partially due to a corrosive rather than a biochemical reaction (Cross et al, 1976).

(iv) Cadmium

Cadmium, obtained wholly as a by-product in zinc and lead production, and its compounds are used in numerous and varied industrial processes. Electroplating, through sacrificial corrosion, is the major use of the metal itself, while it is a constituent of fusible alloys and aluminium solder. Also, as an impurity in zinc, significant amounts of cadmium are present in galvanised metals. Other metallic uses include amalgam in dentistry and nickel-cadmium storage batteries. Cadmium formulations, e.g. cadmium-barium-(zinc)-epoxyorganophosphites, are extensively used as plastic stabilisers, e.g. PVC, and cadmium sulphide, a pigment fast to light, colours glass, ceramics, plastics and printing inks. Cadmium oxide is utilised in glass manufacture, cadmium bromide and iodide are used in photography while cadmium acetate is employed for producing iridescent effects on pottery and porcelain.

The annual total emission of cadmium to the atmosphere is ca. 80 x 10^5kg (Nriagu, 1980) with primary (notably zinc and copper) and secondary non-ferrous metal production and waste incineration the major contributory sources (Table 1.4). In addition, the main uses of cadmium, in contrast to lead, zinc and copper, are almost completely dissipative, though not to the atmosphere, with <5% of the metal being recycled for commercial purposes.

Cadmium has no known function in biological systems and is recognised as a potent toxin to man and other organisms in virtually all of its chemical forms. It is an inhibitor of sulphydryl enzymes, has an affinity for other ligands in cells, e.g. hydroxyl, carboxyl and phosphatyl side chains of proteins, purines and porphyrin, and can disrupt pathways of oxidative phosphorylation. Cadmium also interacts or competes with other elements such as zinc and copper. Poisoning can result from inhalation of fumes, or dust, or ingestion of heavily contaminated food or water, the main target organs being the lung and kidney. Lethal doses are >350mg (Yasumura et al, 1980). The most notorious case of cadmium poisoning is that of Itai-Itai disease which occurred in Japan through the consumption of rice grown on heavily contaminated soil and was exacerbated by a nutritional deficiency of calcium and vitamin D (Kobayashi, 1971). The more insidious effects of low-level environmental exposure, however, are not so obvious but, as cadmium is a cumulative poison, may cause illness or possibly death (Yasumura et al, 1980).

1.4 THE URBAN ENVIRONMENT

1.4.1 SURVEYS

Although trace-metal contamination of the environment is global (Section 1.3), it is much more pronounced in the atmosphere, dust, soil, vegetation and waters of the urban environment. This is due to the presence of large numbers of polluting sources such as industry, housing, traffic, and to the physical and climatic conditions (e.g. street-canyon effects) which prevent much of the emitted material from being widely dispersed

(Fergusson, 1982). The cities and towns are also the major centres of population with, in the UK, 81% of the population residing in urban conurbations (Beaujeu-Garnier, 1978). Consequently, there is considerable concern over the environmental exposure of city-dwellers to enhanced, potentially highly elevated, levels of trace metals in urban areas, and more generally, about current overall environmental quality. There is clearly an important need to investigate and monitor urban trace-metal contamination not only with reference to implications for humans such as intake via inhalation, consumption of locally-grown produce and direct ingestion of soil and dust, but also with respect to plant/vegetation uptake and the contamination of adjacent waterways. Contamination of the soil is particularly important with respect to the possibility of long-term human exposure.

There have been many measurements made of trace metal levels in the atmosphere, soil and street dirt of the urban environment, lead being the most frequently studied element (Solomon and Hartford, 1976; Harrison, 1979; Fergusson et al, 1980; JURUE, 1980; Jeffries and Synder, 1981; Parry et al, 1981; Durando and Aragon, 1982; Culbard et al, 1983). In soils, levels of lead and cadmium of up to 13,680µg/g and 40µg/g, respectively, have been measured (Culbard et al, 1983) while concentrations of zinc and copper in an urban area noted for its non-ferrous metal industry, ranged up to 7843µg/g and 4574µg/g respectively (JURUE, 1980). Dust levels of ca. 50,000µg/g lead have been reported at highly polluted urban sites such as car parks and garage forecourts (Harrison, 1979). In Glasgow, a heavily industrialised complex with a diverse and changing pattern of industry, several air, soil and dust studies have been performed (Dale et al, 1973; Farmer and Lyon, 1977; Apling et al, 1979; MacDonald and Duncan, 1979) with concentrations of lead up to 9800µg/g recorded in street dirt (Farmer and Lyon, 1977).

Despite the large number of surveys, however, many urban studies of trace-metal contamination have been deficient in certain important areas and aspects of the work:-

(i) With respect to planning, many studies have been unsystematic with little emphasis placed on the adoption of a grid sampling strategy.

(ii) Sampling density has often been low with the result that some reports are insufficiently detailed and comprehensive.

(iii) Many studies have been single-element (lead) so that information on other environmentally important trace elements tends to be limited.

In marked contrast, a comprehensive approach has been adopted in some rural studies such as the stream sediment reconnaissance surveys which, although they excluded cities, have formed the basis of the Wolfson Geochemical Atlas of England and Wales (Webb et al, 1978; Webb and Howarth, 1979). Additional deficiencies in previous urban studies are discussed in Section 1.4.2.

1.4.2 CHEMICAL SPECIATION AND PARTITIONING

Trace elements are present in the environment in many different chemical forms, reflecting the natural diversity of chemical species, the influence of transformation processes, often biologically mediated, and, especially in urban areas, the great variety of emissions. The chemical forms (classified as inorganic compounds, simple and inorganic complexed ions and metal organic compounds [Cantillo and Segar, 1975]) determine the environmental mobility of an element - whether and for how long the element will stay in a particular 'sink' or be removed to another, the bioavailability - the ability of a biological organism to take up the element, and consequently the potential human (and animal) intake, digestion, absorption, metabolism and effect (Wood, 1975; Wood et al, 1978; Goldwater and Stopford, 1977; Iverson and Brinckman, 1978). For example: volatile organo-element species, such as methyl mercury and tetra-alkyl lead (TAL) follow different environmental and metabolic pathways and are often considerably more toxic than their corresponding inorganic forms (Brinckman and Bellama, 1978; Grandjean and Nielsen, 1979); the toxic potential of certain elements, notably arsenic and chromium, depends on their oxidation state with As (III) > As (V) and Cr (VI) > Cr (III) while within a certain class of compounds, e.g. inorganic arsenic (III) species (arsines, arsenite $[As^{III}O_3]^{3-}$), there are appreciable differences in environmental behaviour and toxic potential, arsines for instance, are significantly more toxic than arsenite.

Therefore, it is quite apparent that information on the chemical speciation and form of a trace metal, especially in more than one environmental reservoir, is required for an assessment of its biological impact and mobility and, in general, for an understanding of the long-term fate of metal contaminants in the environment. This is particularly relevant to lead which is present in the atmosphere not only in inorganic forms but also as the highly toxic organic species (TAL) [DeJonghe and Adams, 1982].

Unambiguous identification of chemical species in atmospheric gaseous samples is readily achieved using combinations of chromatography and atomic absorption spectrometry (AAS) [Van Loon, 1981; Ebdon et al, 1982] or specific chemical trapping techniques and AAS (Birch et al, 1980; DeJonghe and Adams 1980, 1982). In contrast, identification of specific chemical species in soils and street dirt e.g. by X-ray diffraction (Biggins and

Harrison, 1980) is difficult or inappropriate. Information on the chemical form of trace metals in this type of sample, as studies in agricultural chemistry (McLaren and Crawford, 1973; Mitchell and Burridge, 1979; West, 1979) and on aquatic sediments (Tessier et al, 1979; Salomons and Förstner, 1980) have shown, is obtained through studies of geochemical partitioning using selective chemical leaching techniques. In the above respects, many urban studies have suffered from the following weaknesses:

(i) In the chemical analysis of samples, there has been a lack of standardisation of methods. In particular, the use of different one-step chemical procedures has prevented valid comparison of data from independent studies. This is illustrated by the measurement of 'total' metal concentration, the most common appraisal of contamination, where complete digestion of the material is not always achieved, so that the total metal content may be underestimated.

(ii) The reliance of most studies on 'total' metal concentrations has led to neglect of the geochemical partitioning of trace metals in urban soils. This is in marked contrast to agricultural studies in rural/agricultural environments where, despite the absence of a common approach on the choice of chemical leaching agents, there is at least some attempt to measure the availability of trace metals to plants, for instance (Jackson, 1958; Mitchell, 1971; Mitchell and Burridge, 1979; West, 1979). The value of even more detailed, multi-step sequential leaching procedures has been demonstrated in recent studies of the chemical partitioning of trace elements in aquatic sediments which have yielded useful information on the geochemical behaviour and fate of trace metals (Presley et al, 1972; Gupta and Chen, 1975; Engler et al, 1977; Tessier et al, 1979; Wilber and Hunter 1979; Salomons and Förstner, 1980). Also, in the field of environmental health, it can be rather more important to assess potential metal uptake, e.g. from street dirt by young children, by the use of appropriate chemical leaching techniques than to measure 'total' levels.

(iii) With respect to lead in the atmosphere, attention has been directed almost exclusively to inorganic particulate lead. One important species - tetraalkyl lead - has been comparatively ignored despite its significance, as the source material, to the overall atmospheric burden.

These points, in conjunction with those of Section 1.4.1, serve to illustrate deficiency areas of many previous urban studies which should now be important considerations of subsequent appraisals of trace-metal contamination and related health implications. Although some information may be obtained from analogous situations, such as natural mineralised rural areas with comparably elevated trace metal levels, e.g. Shipham (Thornton et al, 1980; Moorcroft et al, 1982), Derbyshire (Colbourn and Thornton, 1978), where it is perhaps easier to delineate health effects, many of the conclusions may not be applicable in an urban context. Trace metal inputs and subsequent geochemical processes can be completely different or vary widely in importance between urban areas and mineralised zones.

1.5 PROJECT AIMS

The central theme of this work was a fundamental and representative study of urban environmental trace-element geochemistry, within the framework of a comprehensive survey of trace-metal contamination in a typical large industrial city (Glasgow), to assess the environmental behaviour, mobility and bioavailability of the elements along with the potential implications for human health.

In particular, this involved the identification of specific chemical forms and associations of the trace-metal contaminants using appropriate chemical partitioning, speciation and digestion techniques, focussing on lead, zinc, copper and cadmium in urban soils and street dirts, and on tetraalkyl lead and inorganic lead in the atmosphere. Accordingly, specific aims were as follows:

(i) Development of an appropriate analytical method, based on flame and graphite furnace AAS, for the determination of total levels of trace metals in siliceous materials.

(ii) Measurement of bioavailable and total metal levels, in a number of soil land-use categories over a comprehensive sampling grid of Glasgow.

(iii) Determination of bioavailable/readily mobilised metal levels in street dirt throughout Glasgow.

(iv) Development and application of a multi-step sequential leaching procedure to determine the geochemical assocations of lead, zinc, copper and cadmium, over a wide total-metal concentration range, in urban soils and street dirt.

(v) Assessment of potential uptake of metals from street dirt by target groups such as young children.

(vi) Investigation and measurement of gaseous tetraalkyl lead and particulate inorganic lead in the urban atmosphere of Glasgow.

CHAPTER 2 - INSTRUMENTATION AND ANALYTICAL METHODOLOGY

As a large proportion of this study was concerned with the generation of elemental data, reported in Chapters 3, 4 and 5, it is particularly appropriate in this experimental chapter to describe in some detail the major analytical technique employed - Atomic Absorption Spectrometry (AAS) (Sections 2.1 - 2.5) and subsequently to illustrate the theoretical and practical aspects of the technique in the method development of Section 2.6.

2.1 HISTORICAL DEVELOPMENT OF ATOMIC SPECTROSCOPY

Newton's discovery of the visible spectrum (430-750 nm) in 1666 by separating white light into its component colours, using a prism, marks the beginning of spectroscopy. Early spectroscopists directed their attention to the sun discovering, in 1800, the infra red (0.75-500 µm), and, later, the ultraviolet (160-430 nm) portions of the electromagnetic spectrum. In 1802, Wollaston reported the presence of dark lines in the continuum emission spectrum of the sun. Later, in 1823, following his introduction of the diffraction grating, Fraunhofer, using a basic spectroscope, was able to measure the wavelength of these lines - Fraunhofer lines. Similar lines were observed in the coloured diffusion flame of metallic salts but it was not until 1859 that Bunsen realised that these Fraunhofer emission line spectra were characteristic of specific elements and could be used in element identification. Kirchoff, with the assistance of Bunsen, was able to relate the emission and absorption spectra to form the basis of a new and highly specific method of spectrochemical analysis - atomic spectroscopy.

However, analytical developments were restricted to emission spectrochemical techniques, initially in arc and spark spectrography and, later, through the work of

Lunegardh, in flame (air-acetylene) emission, possibly because emission spectra were easier to observe and, at that time, to measure. Flame photometry, the measurement of light emitted from flames by chemical species after the absorption of radiant energy, was particularly useful in the analysis of the alkali metals. By 1950, developments in emission instrumentation enabled the rapid determination of 20-30 elements in one sample.

The potential of atomic absorption as an analytical tool was not realised until the introduction of a line source capable of providing the very high resolution necessary for quantitative measurements. The analytical method was published independently by Walsh (1955) and Alkemade and Milatz (1955 a and b) in the mid 1950's but the theoretical background is credited almost entirely to Walsh. Although AAS offered certain advantages over emission techniques, it was neglected outside Australia and did not gain acceptance until certain instrumental difficulties were overcome, allowing the advent of commercial equipment in the early 1960's.

During those early years there was an exponential growth in the use of AAS and many practical problems were resolved: reliable sources of resonance radiation and electrical detection systems were introduced; readily controllable flames for routine analysis and hotter flames for refractory elements became available and methods such as background correction for overcoming interferences were developed. The potential of the technique was greatly extended with the development of electrothermal (non-flame) atomisers by L'vov (1959) and Massmann (1968), hydride generation systems (Hatch and Ott, 1968; Holak, 1969) and, latterly, sophisticated instrumentation including the introduction of microprocessor-controlled equipment.

Atomic absorption spectrometry remains one of the most popular forms of elemental analysis despite the upsurge of a new generation of more costly emission systems such as inductively-coupled and direct-current plasmas. It is widely employed in many fields, e.g. agricultural chemistry, soil science, geochemistry, environmental chemistry, biochemistry, nutrition and toxicology, for a variety of sample types such as atmospheric particulates, soils, sediments, plant materials, human tissues, water (dissolved and suspended material) and biological fluids. Its wide application results from its high sensitivity, high precision and the number, ca. 70, of elements that can be determined (Figure 2.5). Operating procedures are simple and fast with sample preparation in many cases requiring only a minimum of chemical manipulation. Interferences, which present severe problems in emission analysis, are largely understood and controllable.

These factors, along with the comparatively low cost of equipment, make atomic absorption an extremely viable and reliable analytical technique.

2.2 THEORY OF ATOMIC SPECTROSCOPY

For the purposes of understanding the basic principles of atomic spectroscopy, the atom can be viewed as consisting of a positively charged nucleus and negatively charged electrons which travel in fixed orbitals around the nucleus. When the electrons occupy orbitals with the lowest energy, the atom is in the ground state (energy level E_0). When an atom becomes excited, the valence electron moves to a higher energy level (energy level E). The energy difference between the two levels is called the energy of excitation and is equal to E-Eo or ΔE. Therefore, when an electron of an atom in its lowest energy state, the ground state, absorbs a quantum of energy equal to ΔE (i.e. $+\Delta E$), it undergoes transition to a low-lying excited state. Emission occurs when this quantum of energy is released ($-\Delta E$) and the electron returns to the ground state. Emission and absorption are related as shown in Figure 2.1. A transition between the states, as illustrated, is called a resonance transition. Resonance lines are the most useful in AAS because they are the easiest to excite and consequently are the strongest.

The (absorbed or emitted) energy is quantised according to Planck's equation:

$$E = h\nu$$

where E = the energy difference between the two energy levels in the atom

h = Planck's constant

ν = the frequency of radiation

The frequency of radiation is related to the wavelength (λ) by the formula:

$$\nu = \frac{c}{\lambda}$$

where c = the speed of light.

Thus electronic transitions can be discussed in terms of frequency ν, energy E and wavelength λ. The latter is most frequently used in atomic spectroscopy. The parameters ΔE, λ and ν have unique values for a given electronic transition. An element can undergo many electronic transitions generating a series of sharp lines - a spectrum - which is uniquely characteristic of that element.

Techniques covered by the general term of atomic spectroscopy include atomic emission (AES), atomic absorption (AAS) and atomic fluorescence spectroscopy (AFS). These involve electronic transitions generated by energy transfers, yielding radiation with discrete wavelengths in the UV-visible region of the spectrum.

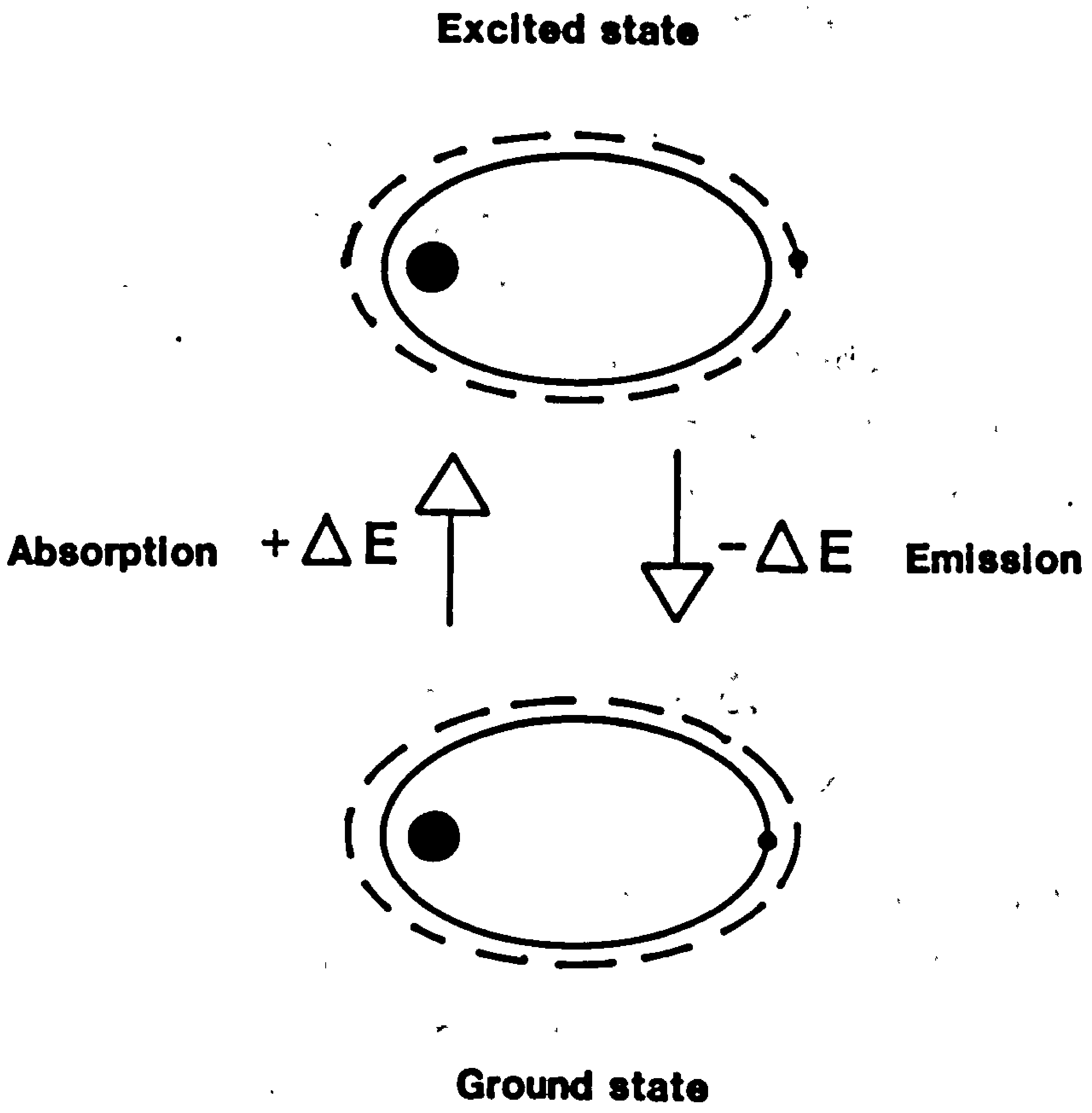


FIGURE 2.1 RELATIONSHIP BETWEEN EMISSION AND ABSORPTION OF ENERGY BY A VALENCE ELECTRON

In emission spectroscopy, thermally or electrically excited atoms transfer their energy by means of collision processes. The amount of energy transferred may vary considerably from atom to atom resulting in a number of different excitation states throughout the population. The subsequent emission of these different quantums of energy involves many energy levels in addition to the ground state. This results in radiation of a number of different frequencies and hence the emission spectrum of any given element may be highly complex.

Conversely, in AAS, light of any of these given frequencies will be absorbed (generating excited atoms) when passed through a vapour containing the atom of interest. It is the free, uncombined, unionised ground state atoms that are important. The proportion of excited to ground state atoms in a population at a given temperature is defined by Boltzmann's Law:

$$\frac{Nm}{Nn} = \frac{gm}{gn} \exp\left(-\frac{\Delta E}{kT}\right)$$

where N = the number of atoms in the excited state (m) and ground state (n) respectively,

g = the quantum-number-related statistical weight for a particular state

k = the Boltzmann constant.

T = °K

At equilibrium, the number of ground state atoms vastly exceeds the number of excited state atoms, particularly at temperatures around 1700 - 2700°C (Walsh, 1955), so that absorption of radiation other than that originating from a transition involving a ground state would be very small. Consequently, the absorption spectra under these temperature conditions are extremely simple with little possibility of line overlap so that spectral intereferences are rare.

Atoms excited by absorption of resonance radiation also re-emit the absorbed energy. This process is called atomic fluorescence. The re-emitted energy, however, may be of the same or longer wavelength than the absorbed energy, indicating that an intermediate state is also involved with the partial loss of energy in some other form. The fluorescence spectrum of a given element, when excitation is by absorption of resonance radiation, is even simpler than the absorption spectrum, consisting of only a small number of lines.

The three types of spectroscopy are summarised diagramatically in Figure 2.2. As production of atomic vapours always results in the production of heat, all three processes occur simultaneously to some extent, though they can be observed and measured separately by appropriate choice of experimental conditions. Figure 2.3 illustrates the basic instrumentation for each technique. Free atoms are produced in the atom cell which also acts as an excitation source for AES. With AAS and AFS, an external light source is used to excite the ground state atoms. In AAS, the source is viewed directly and the attenuation of radiation measured, in contrast to AFS where the re-emitted radiation is measured. The particular spectral line of interest is isolated from the transmitted light by the monochromator which directs the radiation into the detector where an electrical signal is generated and subsequently converted to a 'read-out'.

In AAS, the amount of source radiation absorbed by the sample atoms is defined by:

$$Io - I$$

where Io is the intensity of radiation measured without the sample in the atom cell and I the intensity measured with the sample in the atom cell ($I<Io$ due to atomic absorption).

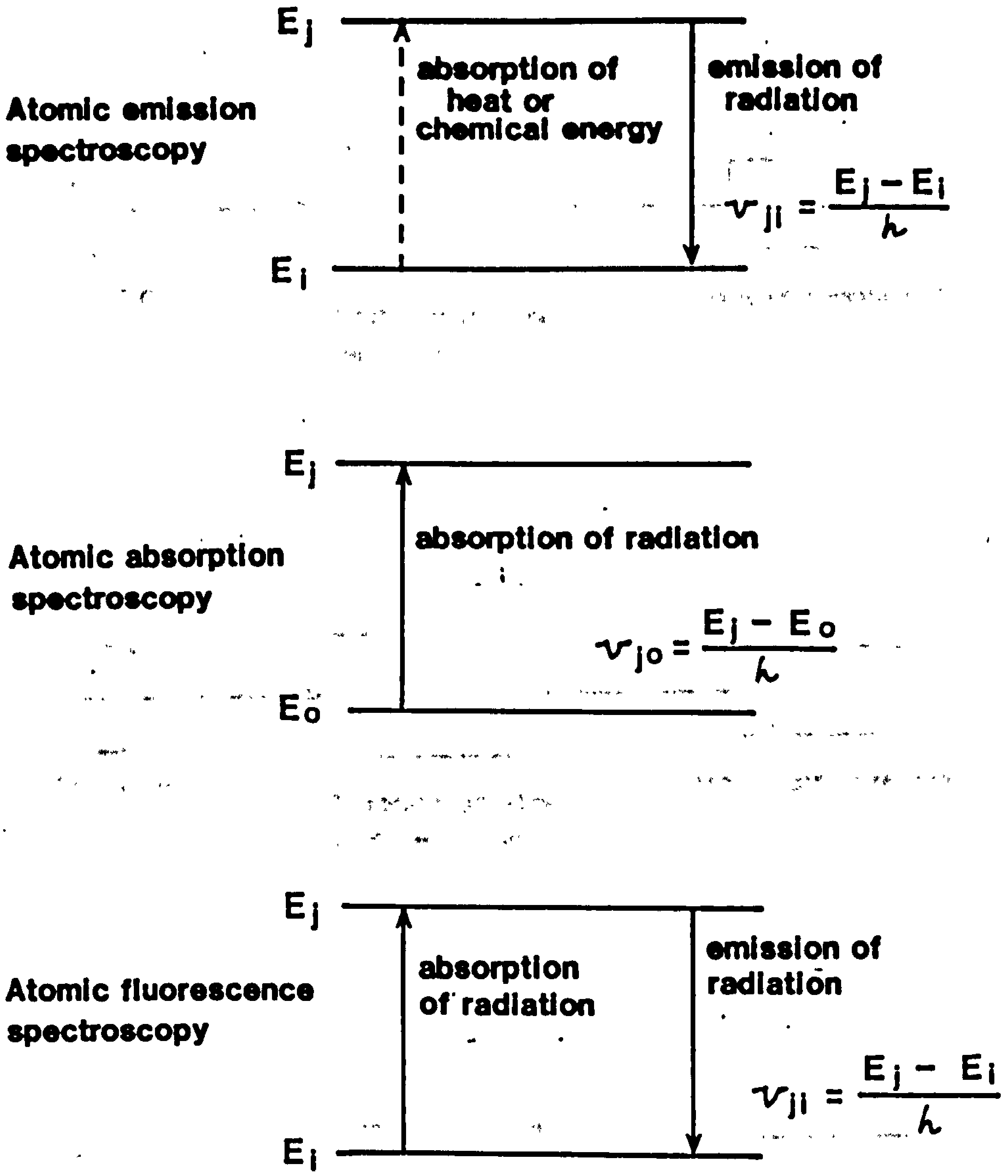
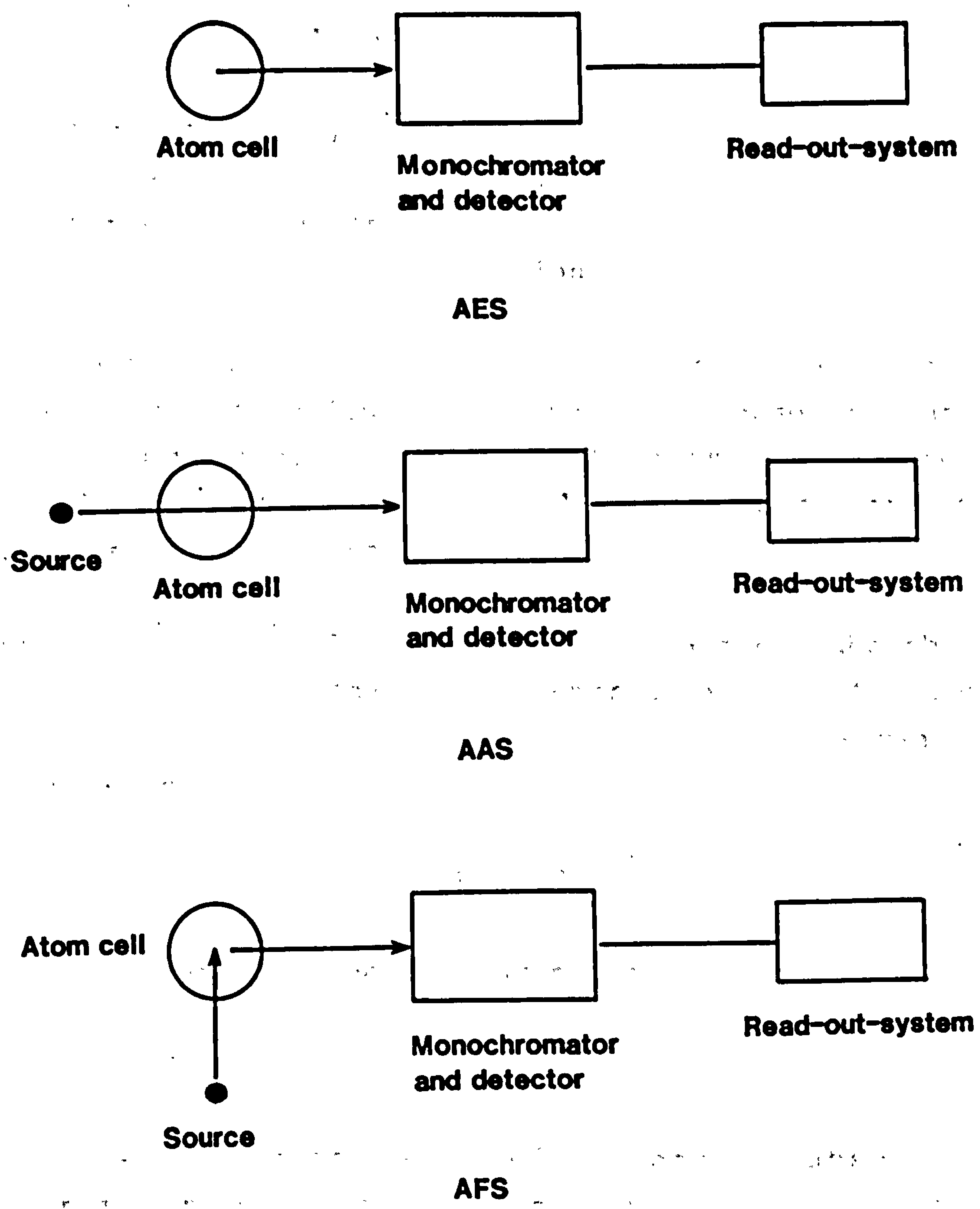


FIGURE 2.2 SUMMARY OF AES, AAS AND AFS

E_o is the lowest energy level, the ground state, whereas E_i and E_j refer to higher energy levels with $E_j > E_i$. A solid vertical line indicates a transition involving the absorption or emission of energy as radiation with the dotted line referring to a non-radiative transition.



AES

AAS

AFS

FIGURE 2.3 BASIC INSTRUMENTAL SYSTEMS USED IN ANALYTICAL ATOMIC SPECTROSCOPY

The quantitative relationship between absorption and sample atom concentration is derived from the Beer-Lambert Law:

$$A = a.b\,c$$

where A = absorbance,
a = absorptivity constant,
b = cell path length
c = the sample concentration.

This states that the amount of light that is absorbed by a sample is a function of the number of absorbing atoms in the light path. The number of atoms is, therefore, controlled by the sample cell path length and the concentration of the sample.

Since the sample cell (atom cell) is constant, absorbance is directly proportional to concentration. In AAS, the % absorption obtained is converted to absorbance via the relationship

$$A = \log_{10} \frac{Io}{I}$$

and then related to sample concentration.

2.3 INSTRUMENTATION

The essential components of an atomic absorption spectrometer are outlined in Figure 2.3. In most commercial instrumentation the radiation source is a hollow cathode lamp (HCL), the atom cell is a flame or electrothermal device, the monochromator is a diffraction grating and the detector is a photomultiplier. The monochromator and detector are constituent parts of the optical system. Although the general instrumental set-up described in this section is common to most AAS systems, specific mention is made of the Perkin-Elmer model 306

(PE-306) and electrothermal atomiser HGA-74 which were employed in this study.

2.3.1 RADIATION SOURCES

The primary radiation source must emit a sharp resonance line (typically <0.001 nm) which is narrower than the absorption profile of the atoms in the flame. It should be of high intensity, stable in output and be free of impurity interference lines. The most common radiation source in AAS is the hollow cathode atomic spectral lamp, although electrodeless discharge lamps (EDL) are often employed for certain elements.

2.3.1.1 HOLLOW CATHODE LAMPS

The HCL, illustrated in Figure 2.4, consists of a hollow cylindrical cathode, lined with the metal of interest, and an anode enclosed in a gas-tight envelope. The gas is normally argon or neon at 1-5 Torr. A high potential (500 mV) is applied across the electrodes creating a low pressure discharge which concentrates in the hollow cathode. Typical currents of 2-30mA are used. Subsequent electron impact ionises the carrier gas atoms which are attracted to the cathode and accelerated by the electrical gradient. The bombardment of the cathode cavity by these positive ions causes metal ions to sputter out of the cathode. Further collisions with gas ions and slowed-down electrons excite the metal atoms to emission and a simple, intense, characteristic spectrum of the metal is produced. Shielding and insulation prevent discharge outside the cathode thus decreasing self-absorption and the possibility of ion lines.

2.3.1.2 ELECTRODELESS DISCHARGE LAMPS

Electrodelss discharge lamps are considerably more intense than HCLs but lack the equivalent stability. For

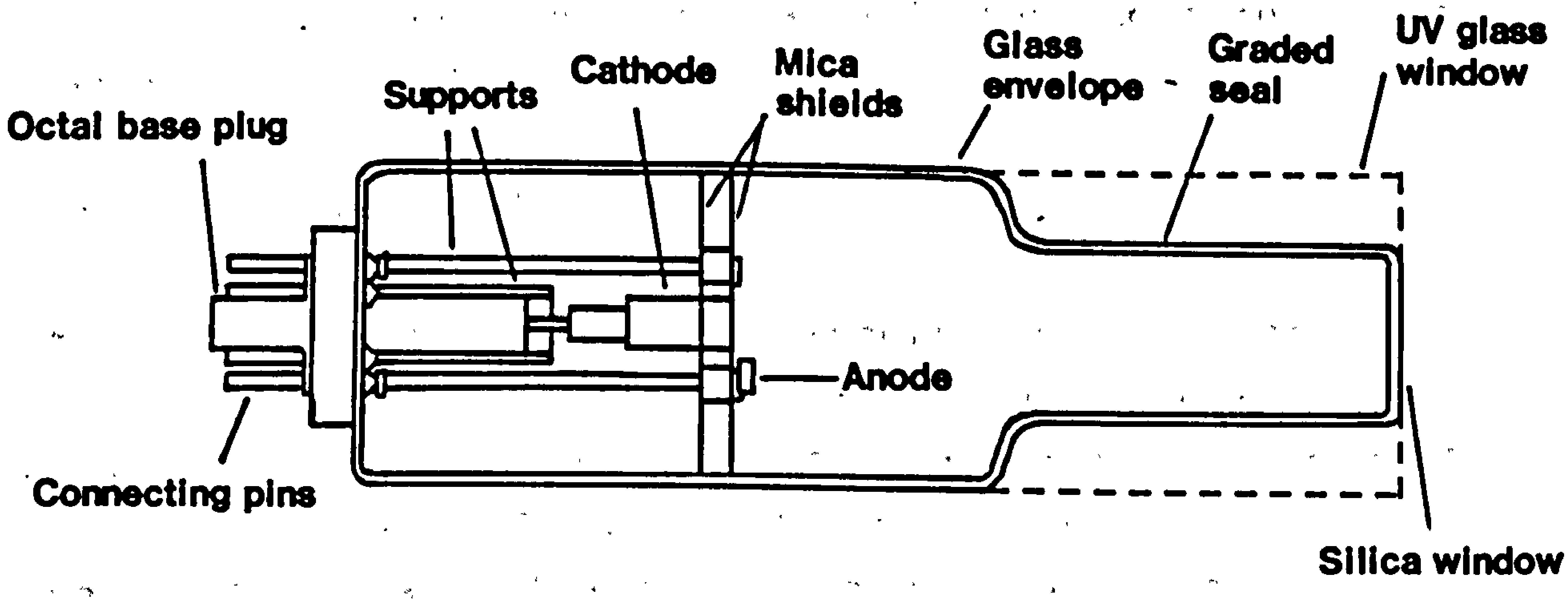


FIGURE 2.4 SCHEMATIC DIAGRAM OF SHIELDED-TYPE HOLLOW-CATHODE LAMP

certain elements which produce unstable, short-lived, dim HCLs, the EDL is preferred.

The EDL consists of a sealed quartz tube, of up to 8cm in length and around 1cm in diameter, that contains a few milligrams of the metal or volatile metal salt (usually the iodide) in an inert low-pressure atmosphere of a filler gas such as neon or argon. The excitation energy is provided by a radio- or microwave frequency electromagnetic field through a wave guide cavity or coil. Radio-frequency lamps use a frequency of 27 MHz for excitation. Their light intensity is somewhat less than the microwave EDL but their stability is significantly greater. Radio-frequency lamps are recommended for arsenic, selenium, antimony, tellurium and phosphorus and are also available for about ten other elements.

2.3.2 ATOMISATION SYSTEMS

Atomic absorption spectrometry requires the production of free ground state atoms of the element of interest. The production of free atoms (atomisation) occurs in the atom cell or atomiser. A variety of commercial atomisers are available for AAS, the most common of which are flames and furnaces, but modified systems exist for the hydride-forming elements.

2.3.2.1 FLAME ATOMISATION

The combustion flame is the most convenient, stable, economic and popular source of converting a solution into an atomic vapour. A wide range of chemical substances may be used to generate a flame but in practice only a few have been utilised:

FUELS: hydrogen, coal gas, propane, acetylene, butane
OXIDANTS: air, oxygen, nitrous oxide

Some characteristics of the two most popular premixed flames used in FAAS are given in Table 2.1. The air-acetylene flame (air/C_2H_2) is the most routinely employed; its ease of handling, stability, reproducibility, low signal and acoustic noise levels produce sufficient atomisation to enable good sensitivity and freedom from interferences for around 35 elements (Figure 2.5). Flame mixtures can be varied from oxidising to reducing to assist atomisation, but some elements with high M-O bond dissociation energies (>5eV), e.g. aluminium, have low sensitivity in air/C_2H_2 flames.

The hotter nitrous oxide-acetylene flame (N_2O/C_2H_2) eliminates many chemical interferences associated with the air/C_2H_2 flame and thus extends the scope of flame AAS analysis to include the refractory elements (Willis, 1965). Its characteristic red, inter-conal zone, obtained under slightly fuel rich conditions, is due to emission by the cyanogen radical. The radical's efficient scavenging for oxygen, together with the higher temperature, promotes dissociation.

Other fuel mixtures that have been employed include air-hydrogen (for the alkali metals) and air-propane, which was extensively used in the early days of AAS for elements that are easily atomised, e.g. alkali metals, cadmium, copper, lead, silver and zinc. Both these flames generate low temperatures (1900-2000^{o}C) relative to air/C_2H_2.

The chemical reactions that occur in the flame are not well understood. Flames are not uniform in composition, length or cross section. Figure 2.6 indicates the three zones identifiable in pre-mix flames: the primary combustion, interconal and secondary combustion zones. The primary combustion zone is not often used for absorption work as strong reducing conditions prevent

TABLE 2.1 SOME CHARACTERISTICS OF THE TWO MOST POPULAR PRE-MIXED FLAMES USED IN FAAS

		Flow Rates (l/min)			
Oxidant	Fuel	Oxidant	Fuel	Max. burn velocity cm/s	Approx. Temp.°C
Air	Acetylene	8	1.2 - 1.5	160	2300
Nitrous Oxide	Acetylene	10	3.5 - 4.5	285	2900

I	IIa	IIIa	IVa	Va	VIa	VIIa	VIII			Ib	IIb	IIIb	IVb	Vb	VIb	VIIb
Li	*Be*											*B*				
Na	Mg											*Al*	*Si*	P		
K	Ca	*Sc*	*Ti*	*V*	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	
Rb	Sr	*Y*	*Zr*	*Nb*	Mo		Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Cs	Ba	*La**	*Hf*	*Ta*	*W*	*Re*	*Os*	Ir	Pt	Au	Hg	Tl	Pb	Bi		
			Th		*U*											

* *Ce* *Pr* *Nd* Pm *Sm* *Eu* *Gd* *Dy* *Ho* *Er* *Tm* *Yb* *Lu*

FIGURE 2.5 ELEMENTS DETERMINED BY AAS

Elements underlined require N_2O/C_2H_2 flame while others are determinable in air/C_2H_2 flame

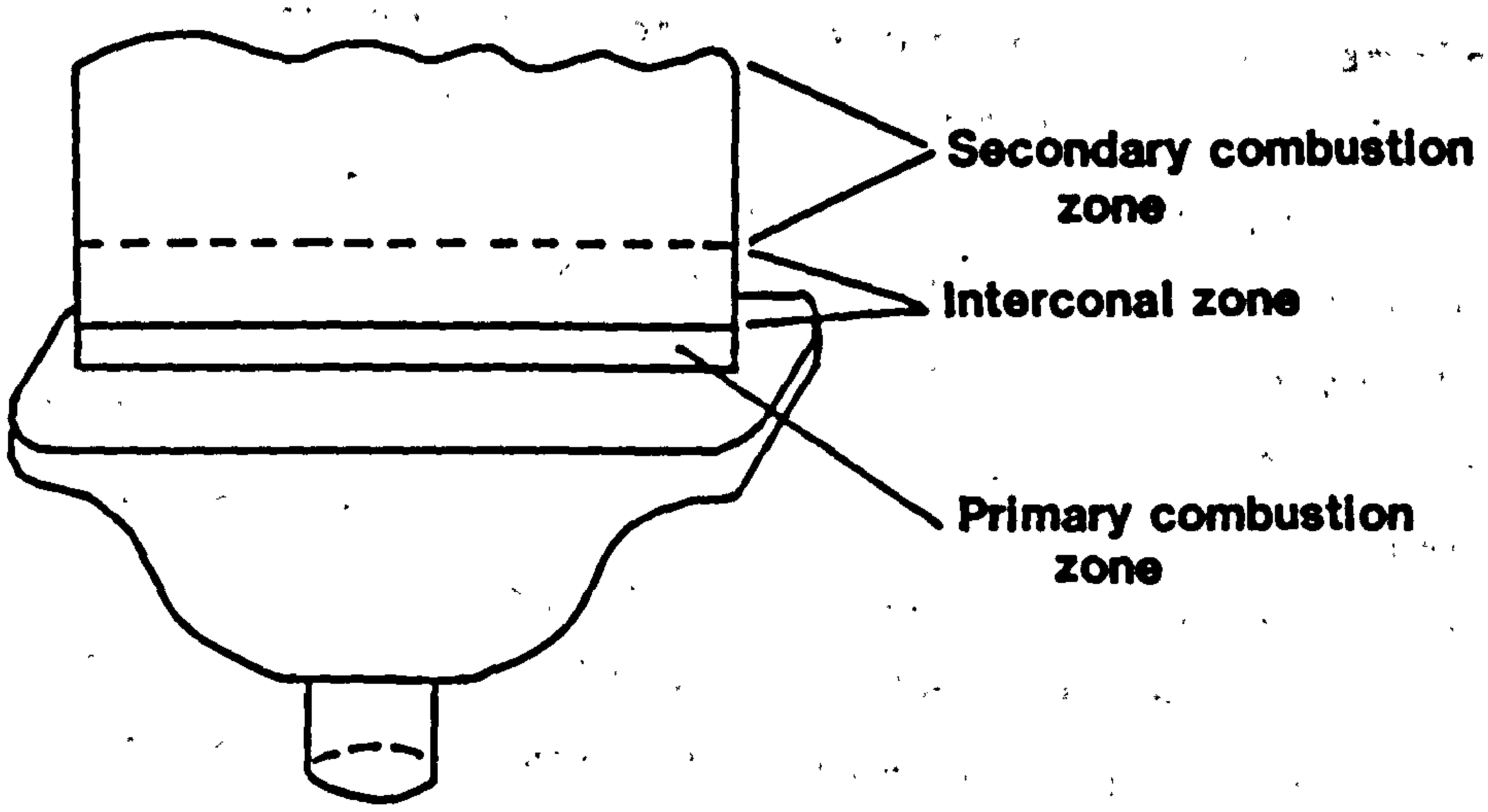


FIGURE 2.6 ZONES OF A FLAME BURNING ON A PREMIX BURNER

thermodynamic equilibrium and emission is very intense. In the interconal zone, which separates the primary and secondary combustion zones, thermodynamic equilibrium is obtained making this area very useful for absorption measurements. In the secondary combustion zone the main reaction is

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$

This area of the flame is cooler and more oxidising than the interconal zone and is less suitable for atomic absorption.

2.3.2.2 ELECTROTHERMAL ATOMISATION

Electrothermal atomisation is an alternative method to the flame for production of atomic vapour when the sample volume is limited or more frequently when the analyte concentration is extremely low. Thus it generally complements existing flame techniques. A discrete aliquot of the analyte solution is electrically heated, up to ca. 2700°C, normally in a graphite furnace or on a carbon rod, generating the ground state atoms. The atomisation process involves several distinct temperature-controlled steps in which the matrix solution is selectively removed allowing the production of atomic vapour in an uncomplicated environment. Electrothermal atomisers are more complex than flames and suffer from less well understood interferences, particularly non-specific absorption.

2.3.2.3 ATOMISERS FOR HYDRIDE-FORMING ELEMENTS

Special methods can be employed to separate some elements from the main sample matrix in a form suitable for subsequent atomisation upon introduction into the spectrometer. The elements which form volatile hydrides quite readily include antimony, arsenic, bismuth, germanium, selenium, tellurium, tin and lead. The hydride is generated by chemical reduction of the sample, usually with sodium borohydride, and then is decomposed by heat to form the atomic vapour. Atomisation occurs at much lower temperatures (<1000°C) by direct introduction into a cool flame, e.g. argon-hydrogen where argon has replaced the normal oxidant (Fleming and Taylor, 1978), or into a silica tube, co-axial with the resonance beam, which is heated by an air/C_2H_2 flame supported on a multi-slot or other wide-path burner (Thompson and Thomerson, 1974).

2.3.3 OPTICAL AND DETECTION SYSTEM

The optical system (Figure 2.7) refers to the constituent parts (excluding the atom cell) of the spectrometer which influence and direct the resonance beam to the detector.

2.3.3.1 MIRRORS AND LENSES

A complex array of mirrors and lenses focusses first the source radiation (and, where deployed, the background correction signal) in the centre of the atomiser and then the transmitted light at the entrance slit of the monochromator.

2.3.3.2 DOUBLE-BEAM SYSTEMS

Atomic absorption spectrometers can be single or double beam instruments. In double beam systems the light from the source is split into two beams using a rotating half-silvered mirror or a beam splitter (a 50% transmitting mirror) so that a reference beam by-passes the flame and is recombined with the sample-beam at a point where both beam distances from source are identical (Figure 2.7). Their ratio is then electronically compared and variation in the sample-beam compensated

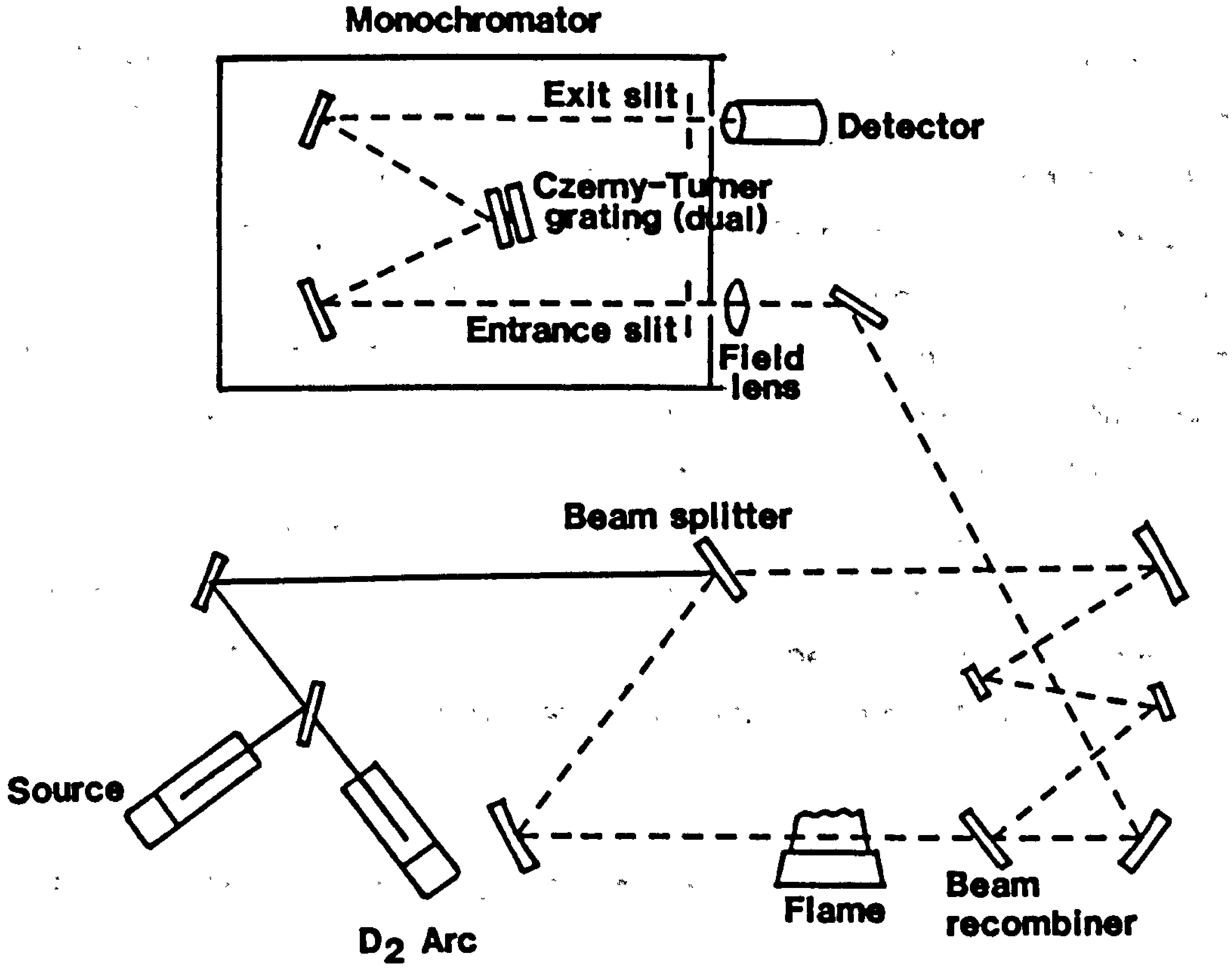


FIGURE 2.7 SCHEMATIC DIAGRAM OF THE DOUBLE-BEAM OPTICAL SYSTEM OF PE-306

for, thus correcting source drift, warm up and source noise but not flame noise. Double beam systems can lead to improvements in precision and in the detection limit but they require a more complex optical system which results in a reduced signal strength.

2.3.3.3 MODULATION

The signal received by the detector consists of the resonance radiation, modified by absorption in the atomiser, and emission from the atomiser. Flame emission may include both resonance emission of the wavelength at which absorption is being measured, and molecular band emission and scatter from particles in the flame. These problems are accentuated with electrothermal atomisers. Only the resonance radiation originating from the source lamp is wanted. Other radiation falling on the detector diminishes the value of absorbance that can be recorded. The lamp output is therefore modulated using an AC supply current or by positioning a synchronous chopper, normally a rotating sector, in the beam before the atomiser and employing a detector which only amplifies alternating current.

2.3.3.4 BACKGROUND CORRECTION

Non-specific molecular absorption or light scattering effects, due to salt or smoke particles, attenuate the light beam during atomisation, particularly at shorter wavelengths and in electrothermal atomisers, giving an apparent increased absorption signal. The enhanced absorption must be corrected by subtracting the 'background'. In the PE-306 system, background correction is achieved by employing a second beam of continuum radiation, e.g. a D_2 arc, aligned in an identical optical path to that of the primary source, from which there is negligible atomic absorption but the same amount of non-specific absorption. This secondary signal is subtracted from the primary. Continuum sources are efficient over the region 190-280 nm but can normally be employed at wavelengths up to 330 nm. Background correction using a continuum source is covered by Hendrikx-Jongerius and de Galan (1976).

2.3.3.5 MONOCHROMATOR

With the ultimate resolution of the system depending on the spectral band width of the resonance line emitted by the primary radiation source, the function of the monochromator is to isolate that single resonance line from non-absorbing lines situated close to it in the source spectrum.

Most AAS systems employ a grating monochromator to achieve the dispersion and control the amount of radiant energy reaching the detector. This can isolate a narrow range of wavelengths (e.g. 1-0.01 nm) anywhere in a comparatively wide spectral range (190-900 nm). The slit width selected is generally a compromise between the width needed for high energy and the narrowness to resolve the resonance line. Mechanical slit width in the PE-306 varies from 10um to 2mm corresponding to a spectral band width adjustment of <0.05 nm to around 5 nm. Elements with uncomplicated emission spectra, e.g. the alkali metals, arsenic, calcium, lead, selenium and zinc, permit the use of wide slits and it is a disadvantage to operate the monochromator at a resolution setting which is narrower than required.

The internal optics of the monochromator may be arranged in several ways, notably the Ebert, Czerny-Turner and Littrow designs which are all effective. The PE-306 employs a Czerny-Turner grating mounting, illustrated in Figure 2.7, which uses two small symmetrically mounted mirrors to collimate and focus the beam. The specific wavelength leaving the exit slit is controlled by simple rotation of the grating about its vertical axis to which is attached a scale calibrated in nm.

2.3.3.6 DETECTOR

The changes in spectral radiation from the source must be converted into an electrical signal for amplification and measurement by the read-out system.

A photomultiplier tube, sensitive to radiation over the wavelength range 198-800 nm, is generally used. The photomultiplier is a current source with the intensity of the current produced proportional to the signal strength. The tube consists of a photo-emissive cathode and a series of dynodes at successively more positive potentials, culminating in an anode all enclosed in a vacuum. When photons strike the cathode, electrons are ejected which subsequently are accelerated down the dynode chain. Each electron impacting upon the first dynode releases a number of secondary electrons which are focussed onto the next dynode and the process repeats itself. In this way, four secondary electrons generated from the first dynode in a chain of 12 dynodes, would produce 17 million electrons per photon. For a typical duration of 5 ns, this would produce an anode current of around 1mA.

2.3.4 READ-OUT SYSTEM

The electrical signal produced by the photomultiplier is, after conversion to a voltage and suitable amplification, converted to a readable value. Common read-out devices include electronic digital displays, print-outs and strip chart recorders.

The lamp, electronics and flicker of the flame all contribute to short-term signal fluctuations. Readability, however, can be improved by electronically increasing the time constant, using damping or by statistically evaluating the result using integration. Longer-term fluctuations in the electronics, together with unsteady lamp output, produce baseline drift which can be compensated for by autozeroing. In addition, most instruments offer scale expansion facilities which electrically expand the signal improving detection limits and precision, but the expansion is accompanied by a proportional increase in noise.

2.4 FLAME ATOMIC ABSORPTION SPECTROMETRY

2.4.1 INTRODUCTION

Flame atomic absorption spectrometry (FAAS) is extensively employed for the determination of the majority of metallic elements and metalloids (Figure 2.5). It has a unique advantage over other analytical methods in that the form of the original sample is not important provided it can be brought into solution. Its high specificity means that the analyte element can be determined in the presence of others, thus reducing to a minimum the need for chemical preparation which is common to other forms of wet analysis. Indeed separations are only required to remove an interferent or to concentrate the sample.

2.4.2 SAMPLE INTRODUCTION/NEBULISATION/BURNER SYSTEM

The quantitative application of FAAS rests on the efficient transfer of the sample to the flame. This is achieved by nebulisation which results in liquid samples being directed into the burner as a fine aerosol mist. The PE-306 nebuliser-premix chamber-burner assembly is illustrated in Figure 2.8.

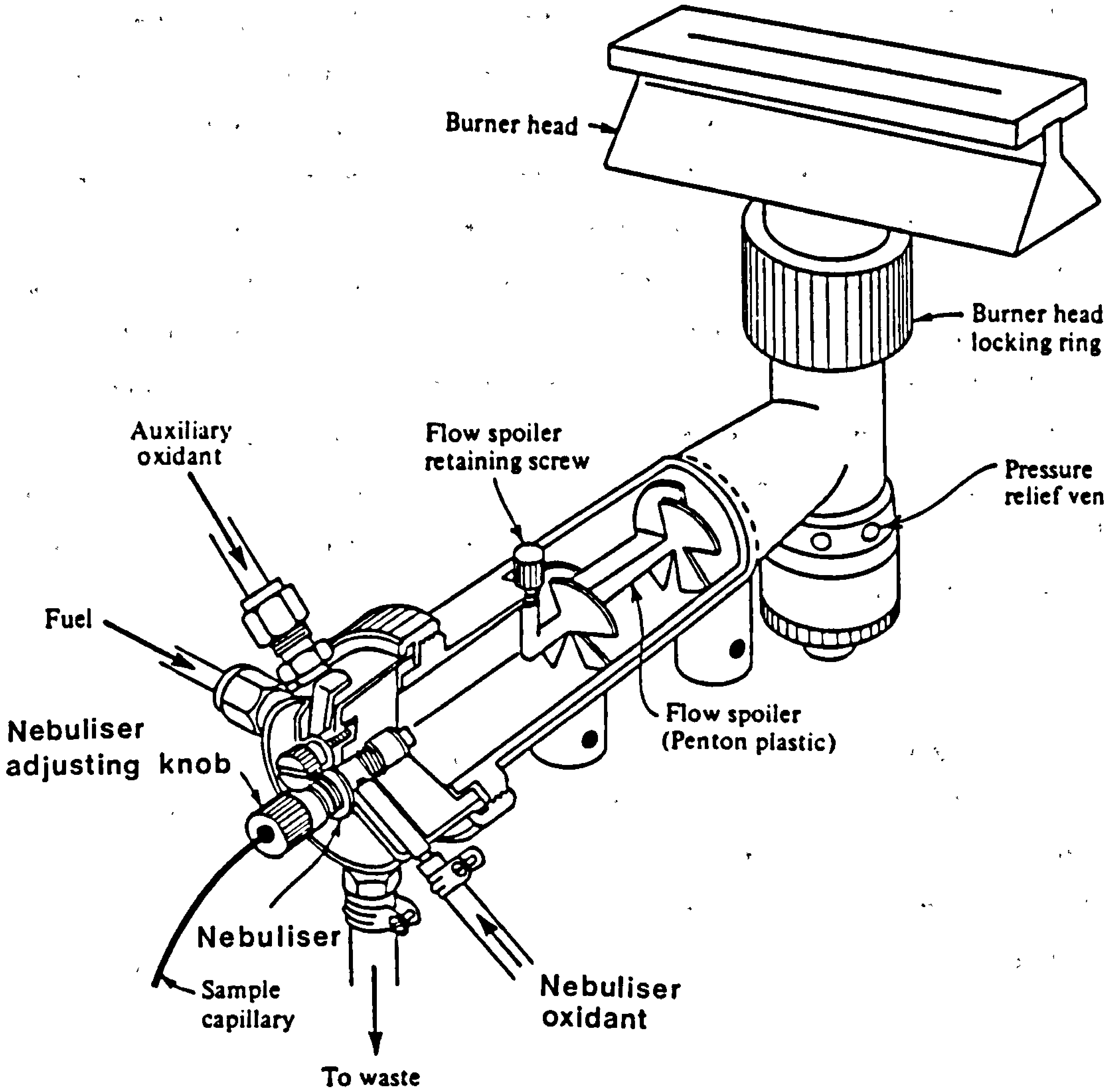


FIGURE 2.8 SLOT BURNER AND EXPANSION CHAMBER OF PE-306

The sample is drawn via a capillary tube into the nebuliser by a pressure drop where it is 'shattered' into very tiny droplets by the 'venturi effect' of the oxidant gas. Sample uptake and drop size may be optimised by adjusting a screw thread at the nebuliser/capillary junction. Alternatively or additionally, an impact bead placed in the path of the initial aerosol provides secondary fragmentation to improve the efficiency of nebulisation. The plastic capillary leads to a platinum-iridium alloy (9:1) capillary which enters the expansion chamber. Further separation of the aerosol into coarse and fine droplets is achieved in the chamber with the larger droplets condensing on the walls before flowing down the drain tube. This must be sealed (e.g. by a 'U' tube) to create a back pressure for the flame. To ensure that only the smallest particles reach the flame, baffles (or spoilers) are placed in the chamber. Rejection of the larger droplets helps minimise light-scattering effects in the flame. Baffles are also responsible for adequate mixing of the gases and smooth delivery to the flame.

This premixing arrangement of the fuel, oxidant and sample, although only utilising ca. 10% of sample, achieves homogenous combustion and produces a quieter, stable flame. It has replaced the direction injection procedure in which samples and gases were supplied separately to the burner.

The burner head consists of a slot at which the flame burns (Figure 2.8). The elongated style of the slot is to permit the maximum number of analyte atoms in the light path. Air/C_2H_2 flame burner slots are typically 100mm long, but due to the higher burning velocity of the N_2O/C_2H_2 flame, a shorter length (50mm) is safer. The width of the slot, its length and the conductivity of the metal used (commonly titanium) are important, narrower slots achieving rapid cooling and greater stability.

2.4.3 ATOMISATION

The formation of free metal atoms from the sample in the flame is a complex process involving several distinct steps. These are illustrated in Figure 2.9.

(i) Desolvation

The removal of solvent, the initial step, begins in the spray chamber and continues into the primary combustion zone of the flame. For efficient vaporisation in the interconal zone, desolvation must be completed very quickly but is dependent on a number of factors such as drop size, chemical nature of the solvent, flame temperature and solvent flow rate.

(ii) Evaporation

Following desolvation, the mist of salt clotlets agglomerate and vaporise. This depends on the size and number of the particles, their composition and the flame composition.

(iii) Decomposition

As the molecules pass into the hotter regions of the flame, they dissociate into atoms. Most vapours break down spontaneously to atoms in the flame but others, particularly diatomic species such as metal oxides (e.g. alkaline earth and rare earth oxides), are more refractory so that flame conditions are very important with high temperatures and reducing environments aiding dissociation [see Section 2.2.3 (i)].

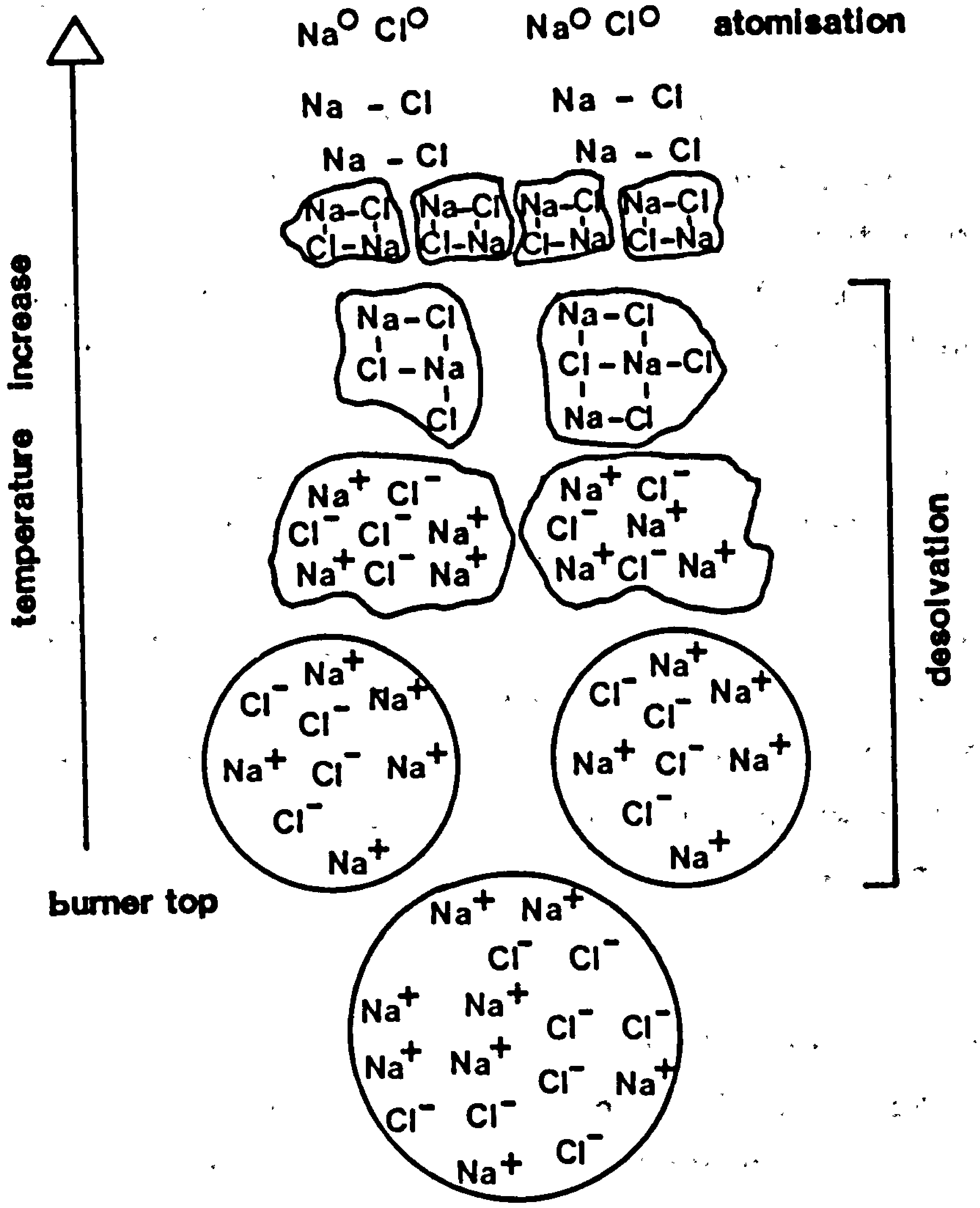


FIGURE 2.9 ATOMISATION PROCESSES RESULTING WHEN LIQUID MIST IS INTRODUCED INTO A FLAME

2.4.4 INSTRUMENT OPERATION AND OPTIMISATION (PE-306)

Operating conditions are described in the manufacturer's manual but generally require fine adjustment to ensure optimisation of the instrument.

(i) Source: the lamp source and D_2 lamp require 'warm-up' periods to stabilise output and allow matching of lamp signals.

(ii) Wavelength: the analytical line and monochromator slit width are recommended by the manufacturer; the intensity of the incident light on the detector is optimised using the x, y facility of lamp holder and the fine adjustment of the wavelength selector.

(iii) Flame Ignition: gas flow rates, set prior to ignition, often require a fine adjustment of the fuel/oxidant ratio to achieve maximum sensitivity; ignition of the air/C_2H_2 flame is obtained by sparking the oxidant and fuel gases; the N_2O/C_2H_2 flame requires the air/C_2H_2 flame to be lit first and made fuel rich before the air is switched to N_2O by a two-way valve; the flame is extinguished by the reverse procedure.

(iv) Nebuliser: nebulisation is optimised using a suitable standard solution and may require adjustment when the solvent is changed.

(v) Burner: the alignment of the incident beam in the flame is critical to produce maximum sensitivity or, in more concentrated solutions, the sensitivity that is required; this is achieved by varying the position of the burner relative to the light beam, usually by rotation, while aspirating a standard.

(vi) Calibration: the relationship between the absorption indicated by the instrument and the concentration of the element that produces it, is established in the calibration procedure; a calibration curve is constructed by plotting the absorbance produced by several standards of varying analyte content; from this relationship, illustrated in Figure 2.10, the unknown concentration of the sample can be derived. The ideal calibration curve, Figure 2.10(1), is rarely obtained; more common is the curve illustrated in Figure 2.10(2) where the curve bends at higher concentrations due to stray or unabsorbable light being detected. Consequently, the precision in the non-linear portion of the curve is reduced and measurements are normally made in the linear part termed the working curve. In practice, this linear region should lie between 0.1 and 0.5 absorbance units with the concentration of the standards bracketing the expected concentration of the sample.

2.4.5 INTERFERENCES

Interference is defined as 'an effect causing a systematic deviation in the measure of the signal when the sample is nebulised as compared with the measure that would be obtained for a solution of equal analyte concentration in the same solvent, but in the absence of concomitants' (Ebdon, 1982). There are several kinds of interferences which, if uncorrected, can lead to significant errors in analytical measurement by atomic absorption.

(i) Spectral Interferences

Spectral interferences are rarely encountered in AAS. With the resolving power of modern monochromators, a

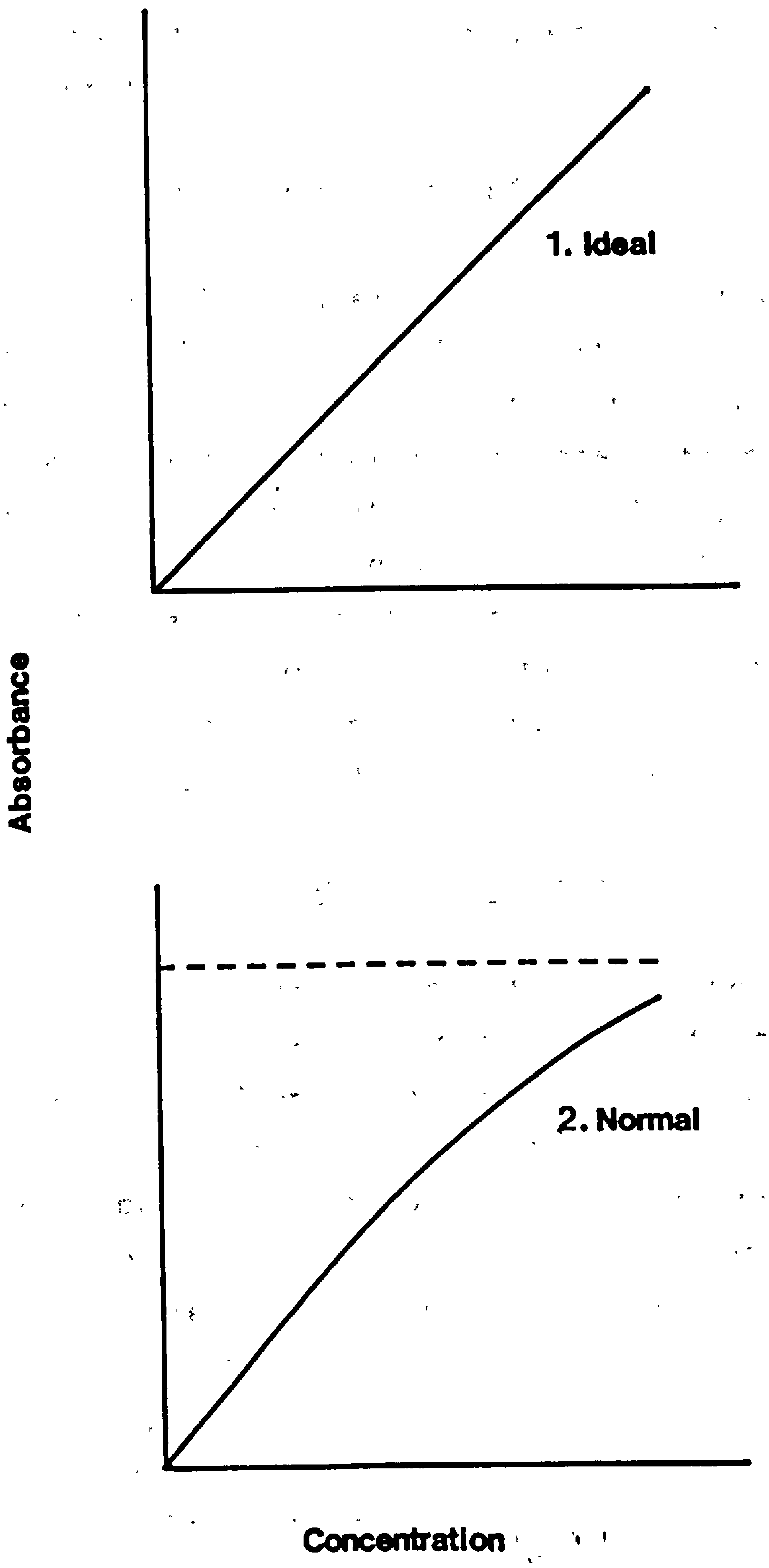


FIGURE 2.10 IDEAL AND NORMAL CALIBRATION CURVES

spectral interference only occurs where two or more elements overlap each other's spectral profile. Only one 'real' case, that of copper (324.754 nm) and europium (324.753 nm), was indicated by West (1974) in his review of all reported spectral interferences in AAS. This type of interference can be overcome by using an alternative absorption line.

(ii) Non-Specific Interferences

Non-specific interference is attributable to molecular absorption or light scattering in the atomiser. Molecular absorption occurs when a molecular species in the atomiser produces an absorption profile over a wide range of wavelengths, e.g. 100 nm, that overlaps that of the analyte element. Light scattering occurs when solid particles cause a deflection of some of the source radiation away from the detector resulting in a pseudo-absorption effect. Correction for non-specific interference is described in Section 2.3.3.4.

(iii) Ionisation Interference

The neutral atom population of the flame can be reduced when the flame temperature is sufficiently high to remove electrons from free atoms. The positively-charged ions produced absorb radiation at a different wavelength from the parent atoms, thereby depressing sensitivity. Elements with low ionisation potentials, i.e. alkali and alkaline earth metals, are most susceptible and ionisation interferences are more common in hotter flames, e.g. N_2O/C_2H_2. In trace analysis, an ionisation buffer, consisting of a large excess of an easily ionisable element, e.g. potassium, is added to the sample solution. The excess potassium ionises in the flame suppressing ionisation of the analyte atom by a mass action effect (Rantala and Loring, 1975; Price and Whiteside, 1977).

(iv) Chemical Interferences

Chemical interferences, which constitute a major source of problems in AAS, occur when the analyte element combines with some other cation or anion in solution to form a compound that influences the degree of reduction to neutral atoms in the flame, e.g. the formation of aluminates, silicates and phosphates by magnesium, calcium, strontium, barium. This decreases the analyte's sensitivity and consequently is responsible for the erroneous results obtained when the sample concentration is calibrated against an interferent-free standard.

This type of interference can be controlled in two ways: use of a higher temperature flame to break down the compound formed, or the addition of a releasing agent to the sample (and standard) solution. The releasing agent preferentially reacts with the analyte element or the inteferent, thereby overcoming the interference. A common example of this is the addition of lanthanum or EDTA to calcium solutions to overcome the effect of phosphate.

(v) Matrix Interferences

Matrix interferences, which alter the slope of the calibration curve, result from differences in the physical characteristics (e.g. viscosity, surface tension) of the sample and standard solutions, generally occurring when the sample solution contains a high concentration of dissolved salts or acids.

This particular problem can often be eliminated by matching the concentration of major constituents in sample and standard solutions or by using the technique of standard additions (Beukelman and Lord, 1960) or dilutions. In this approach, known amounts of the analyte are added to aliquots of the sample. Typically three aliquots are taken: the first is left untreated while 1x and 2x the apparent analyte concentration is added to the second and third aliquots, usually in a minimum volume so that the sample volume is virtually unchanged. The results are plotted on an absorbance/concentration graph (Figure 2.11). The curve is extrapolated to the point of intersection on the x-axis which corresponds to the concentration of the unknown. A standard addition curve parallel to the calibration curve is indicative of the absence of interference.

2.4.6 ACCURACY, PRECISION, DETECTION LIMIT AND SENSITIVITY

The accuracy of a determination is a measure of how close the value obtained is to the 'true' value. Unfortunately, the true value of a chemical constituent cannot be known absolutely so that an assessment of accuracy is to a large extent subjective. However, 'relative accuracy' can be assessed using standard reference materials to which 'accepted' values have been assigned, as indicated in Section 2.6.

The precision (degree of variation) of an analytical procedure is derived from the replicate analysis (normally 10-20 individuals) of the parent material by expressing the standard deviation on the mean as a percentage of the mean. This is distinguishable from the precision of an atomic absorption measurement where several aspirations of one sample solution are performed.

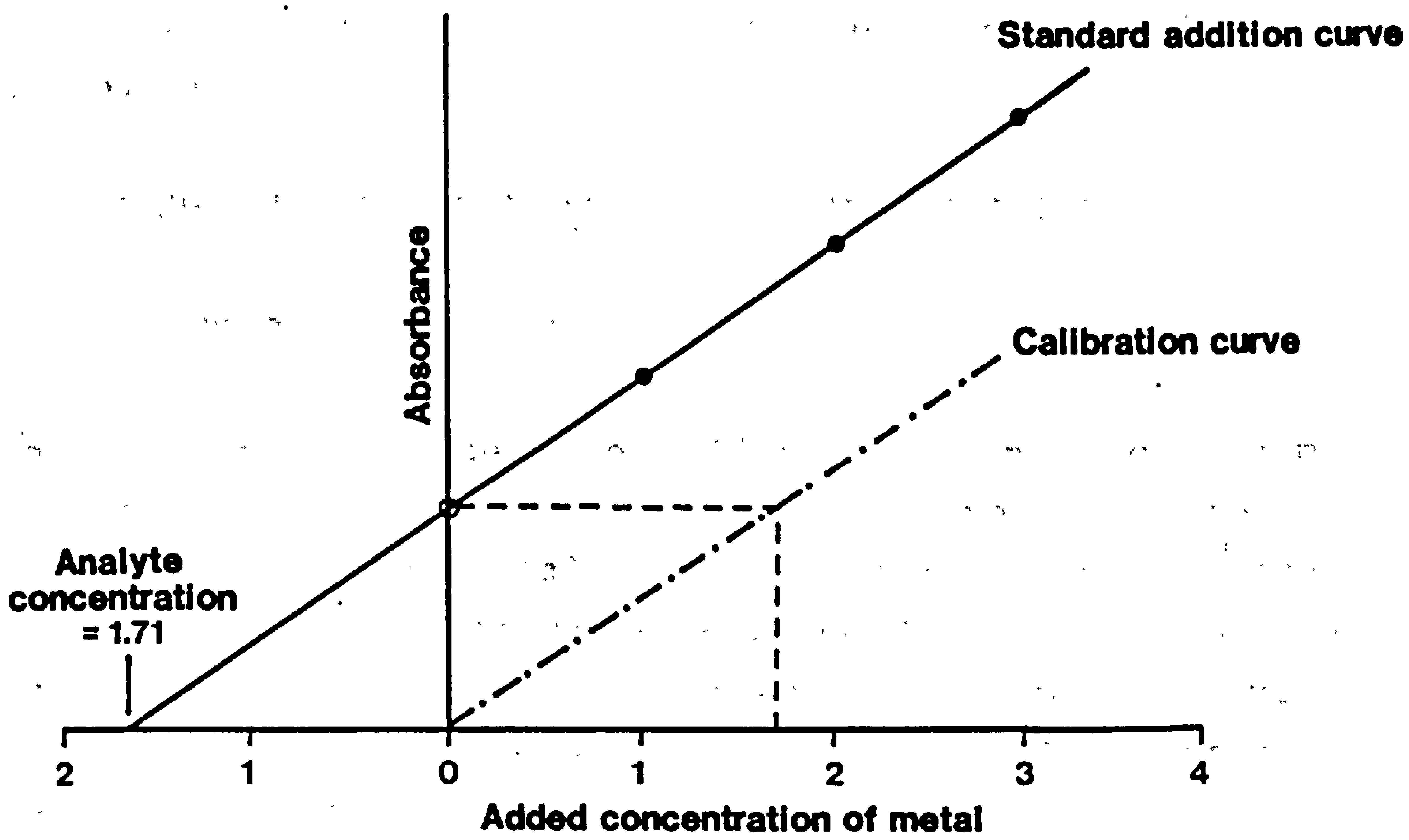


FIGURE 2.11 PLOT FOR THE METHOD OF STANDARD ADDITIONS

The power of detection in AAS is expressed as the lower limit of detection of the analyte. This limit of detection is derived from the smallest measure x which can be accepted with confidence as genuine. The detection limit is usually defined as that concentration of an element which gives a signal equal to twice the standard deviation of the chemical blank (reagents taken through the entire analytical procedure) and is dependent on the signal/noise ratio (Van Loon and Parissis, 1969).

Sensitivity is defined as the concentration of an element which will absorb 1% of the incidence radiation, i.e. it produces an absorbance of 0.0044. In AAS, as concentration is proportional to absorbance (Section 2.2), the sensitivity figure is a measure of the slope of the calibration graph.

2.5 GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

2.5.1 HISTORICAL INTRODUCTION

Electrothermal atomisers were first used in spectroscopy by King in 1908 to obtain the emission spectra of elements using electrical heat. King employed a carbon furnace developed from an arc-heated furnace, heated to 3000°C to investigate these elemental spectra. However, it was not until the work of L'vov (1959) that a graphite furnace was used to generate atoms as an absorbing medium in analytical AAS. The atomiser, based on the principle of King's original device, achieved the atomisation temperature by arcing (d.c.) an auxillary electrode between the sample electrode and the graphite furnace tube. In subsequent models the sample was atomised using resistive heating for the electrode and furnace, by passing an alternating current through the narrowed section of the electrode to the furnace tube.

In 1967 Massmann designed an atomiser, a much simplified and compact version of the resistively heated King furnace, that could be used routinely as an analytical tool (Massmann, 1968). In this furnace, the graphite tube was supported by water-cooled steel end cones which were electrically connected to a low voltage supply. The whole device was held in an inert atmosphere within a metal casing to prevent oxidation of the tube during operation.

Although several other electrothermal atomisers had been developed by the late 1960's (Woodriff and Ramelow, 1968; West and Williams, 1969), only the carbon filament atomiser of West and Williams, further developed as the carbon rod atomiser, commercially competed with the 'Massmann' furnace. While both atomisers contain carbon tubes, the surrounding inert atmospheres differ in direction of movement: with the graphite furnace, the purge gas travels axially through centre of the tube in contrast to the carbon rod, where the gas encircles the rod assembly.

Electrothermal atomisers offer advantages over flames in two main areas: a much smaller sample volume (5-100 µl) is required compared with typical minimum volumes of 0.5-1.0 ml for the flame; sensitivity for the majority of elements is about three orders of magnitude better than in the flame, giving detection limits in the range 10^{-11} - 10^{-13} g for some elements. This has been achieved by the direct introduction of a fixed quantity of sample <u>into</u> the atomiser thereby circumventing the inefficient nebulisation system, and avoiding the large dilution of the atomic population in the flame gases.

2.5.2 HGA-74 GRAPHITE FURNACE

The graphite furnace unit, HGA-74, which is directly interchangeable with the burner assembly of the PE-306 spectrometer, is illustrated in Figure 2.12.

The sample is introduced to the optically aligned graphite tube, the site of atomisation, using an automated micropipette system, AS-1. This autosampling system can transfer 10 or 20 µl of sample aliquots into the graphite tube from each of 30 plastic containers mounted on a circular table. The pipette is automatically rinsed between samples. Automated injection enables high precision and reduces the possibility of contamination. The tube itself is an open-ended cylinder of graphite typically 25-30mm long and 5-10mm in diameter with a central hole for sample injection. It is held between graphite rings which provide electrical contact to the tube. When the voltage (10V) is applied, the current (up to 300A) flows, causing the tube, which operates like a resistor in an electrical circuit, to increase rapidly in temperature (2000°C/sec) thereby inducing atomisation of the sample.

The furnace is sheathed with an inert gas stream (argon or nitrogen) subdivided into an external protective gas stream around the graphite tube and an internal purging gas stream through the graphite tube. The external gas stream flows continuously around the furnace through holes in the contact rings acting as a buffer zone to prevent oxidation by the air. The internal gas enters the tube at both ends and escapes via the sample introduction hole, carrying vapours produced during the early steps of the atomisation process and, in so doing, reduces background absorption and matrix interferences. In addition, the purge gas flow rate affects sensitivity. Reducing or, more commonly, interrupting the flow rate

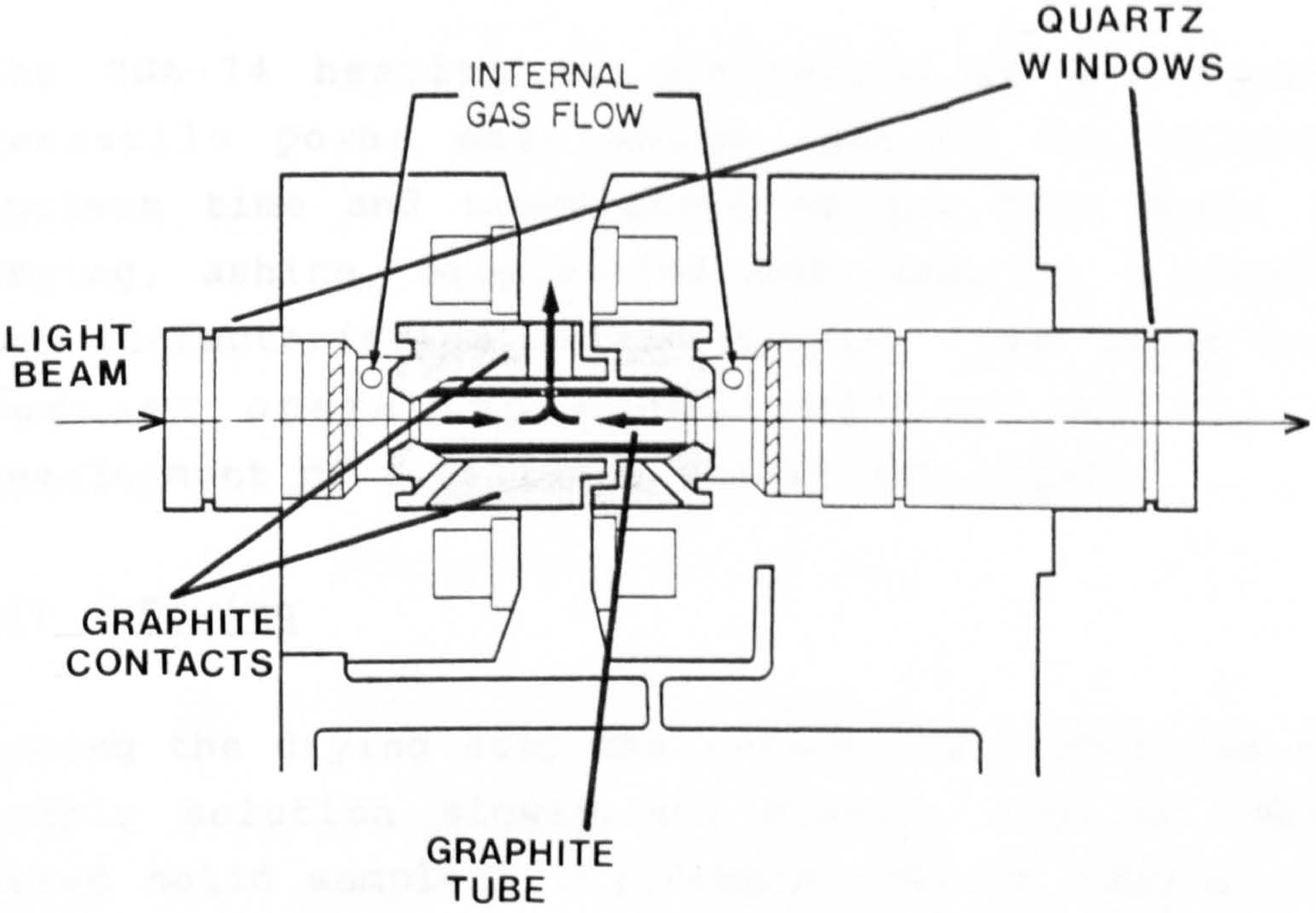


FIGURE 2.12 CROSS-SECTION OF PE GRAPHITE FURNACE HGA-74

during atomisation increases the atom residence time and has the effect of increasing sensitivity. Conversely, exclusion of the gas stop facility permits the determination of higher concentrations of analyte in the linear range of the working curve. At the end of the programme cycle the rapid decrease of furnace temperatures is effected by a water cooling system incorporated into the metal housing.

2.5.3 TEMPERATURE PROGRAMMING

The HGA-74 heating is controlled by a programmable, versatile power unit which enables the selection of optimum time and temperature of the four basic steps - drying, ashing, atomisation and clean up - according to the characteristics of the sample. The optimisation of furnace operating conditions is central to the development of a reliable analytical method.

(i) Drying

During the drying step the solvent is evaporated from the sample solution slowly and evenly, leaving behind the dried solid sample. Over-rapid solvent removal from the injected droplet can cause spitting and loss of sample. The temperature selected is normally around 105°C with a drying time of 20 - 30 secs.

(ii) Ashing

The ashing step is conducted at a predetermined intermediate temperature, sufficient to volatilise the organic and low boiling point inorganic compounds of the matrix. The cycle often converts the analyte into a different chemical state. A temperature that is too high or is maintained for too long can result in loss of analyte, especially for the more volatile elements like arsenic, cadmium, lead and mercury. Therefore, the highest temperature not resulting in loss of analyte is generally selected. This is derived experimentally for individual elements and matrix solutions by constructing ash/atomise curves. The time employed depends on the matrix but is usually similar to that in the drying stage.

(iii) Atomisation

The appropriate power is applied to raise the furnace unit to the required atomisaton temperature which is both element- and matrix-dependent and is determined experimentally. The lowest temperature which produces atomisation is selected as it maximises tube life expectancy, improves precision of results and, in many cases, reduces emission interference (Price 1979). The time selected is that taken for complete atomisation as indicated by the return of the response signal to zero.

(iv) Determination of Ash/Atomise Conditions

The conditions sought are the highest ashing temperature which does not cause the premature loss of analyte and the lowest temperature at which complete atomisation takes place. The best method to determine the limits of these temperatures is the construction of ash/atomise curves for the elements and matrices involved. Experimentally this involves the measurement of absorption when:

(a) The atomisation temperature is increased step-wise with the ashing temperature control set at zero (i.e. room temperature).

(b) The ashing temperature is increased step-wise with the predetermined atomisation temperature constant.

By plotting absorbance against temperature the optimum conditions can be derived. This is illustrated in an ideal situation in Figure 2.13. The maximum ash temperature is typically taken as 100°C below loss of analyte (shown as a rapid fall in absorbance) while the atomisation temperature selected is where absorbance reaches a plateau (Figure 2.13).

(v) 'Clean-up' or 'Burn-out'

The maximum temperature (2700°C) of the unit is applied for a few seconds (5-10 secs) to remove the last traces of the sample matrix in the graphite tube, thus eliminating any memory effects.

(vi) The Atomisation Process

Although the atomisation processes are not well understood, certain reactions have been postulated and investigated thermodynamically and through kinetic modelling (Fuller, 1977). The main reactions can be summarised as follows: the metal salts, unstable after drying, are decomposed to metal oxides prior to atomisation. Some metal oxides (those with high vapour pressure, e.g. silicon dioxide) may be lost but most are dissociated:-

$$MO \longrightarrow M + 1/2\ O_2$$

or reduced (by carbon or the metal from the atomiser, e.g. tantalum) to the free metal:-

$$MO_{(s/l)} + C_{(s)} \longrightarrow M_{(g)}\downarrow + CO_{(g)}\downarrow$$

or to the carbide:-

$$MO + 2C \longrightarrow MC + CO$$

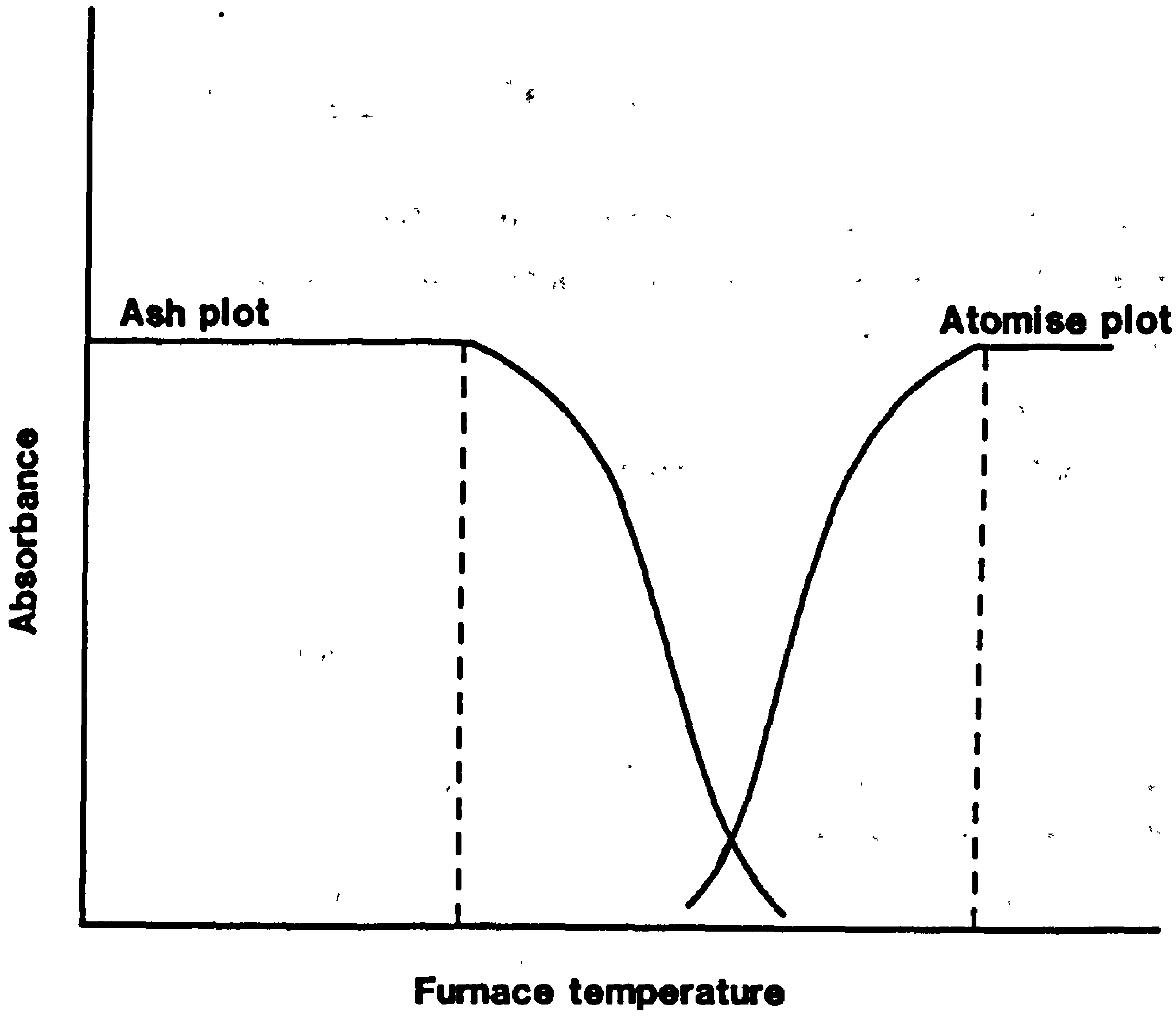


FIGURE 2.13 PLOT OF AN IDEAL ASH/ATOMISATION CURVE

2.5.4 INTERFERENCES

Graphite furnace AAS is generally regarded as being more prone to interferences than FAAS. The most important are discussed below:

(i) Physical

The steep temperature gradient means that variation in the sample position (e.g. due to pipetting, surface tension or viscosity) or size will affect the response signal. Automatic pipetting (Slavin, 1978) and the use of peak area integration significantly improves reproducibility.

(ii) Non-Specific Interference

Although described in Section 2.4.5 (ii), it is particularly common in GFAAS due to the volatilisation of large amounts of matrix in a confined space. However, removal of the matrix during the ashing stage and employment of background correction can usually eliminate or control this problem.

(iii) Memory Effects

The incomplete atomisation of some elements, e.g. those forming stable refractory oxides, vanadium, molybdenum, tungsten may produce an enhancement of the subsequent signal. The inclusion of a cleaning step can help to overcome this problem.

(iv) Chemical Interferences

(a) Losses due to Volatility of Analyte

The chemical form of the analyte may promote volatilisation before atomisation, i.e. in ashing or the early stages of atomisation. It is particularly common with halides, e.g. chlorides. Volatility can be reduced by converting the halide to a less volatile form, e.g. nitrate or sulphate, prior to the ashing step; or by the addition of stabilising ions such as nickel to arsenic (Ediger, 1975), permitting the use of higher ashing temperatures.

(b) Cation Interferences

The presence of large quantities of cations can suppress the response signal of the analyte, e.g. as in the influence of aluminium, calcium and iron on lead (Fuller, 1977). This type of interference is complex and is not well understood but it can be minimised by close matching of standards to samples or by standard additions.

(c) Carbide Formation

The slow atomisation in GFAAS of some elements is often attributed to carbide formation, e.g. in the cases of barium, boron, beryllium and vanadium. This can be reduced by ensuring a reproducible surface, e.g. via pyrolytic or lanthanum coating, or by employment of a rapid temperature gradient.

(d) Condensation

When the atomic vapour reaches cooler areas of the tube, condensation occurs. This vapour-phase effect leads to occlusion of analyte within matrix particles. This type of interference may be reduced by the use of a L`vov-type platform (Fernandez et al, 1981), or of a reactive purge gas, e.g. hydrogen.

2.6 APPLICATION OF FAAS AND GFAAS IN THE DIRECT DETERMINATION OF MAJOR, MINOR AND TRACE ELEMENTS IN SILICEOUS MATERIALS

2.6.1 INTRODUCTION

This section, in addition to describing the development of a method for the total decomposition of siliceous materials which forms the underlying basis of the analytical methodology of Chapters 3 and 4, serves to illustrate the suitability and versatility of AAS for the accurate determination of major, minor and trace elements.

Siliceous materials such as soils, street dirt and sediments, generate certain problems in AAS analysis: the presence of aluminosilicates makes total dissolution rather difficult and even after successful dissolution there may be severe matrix or inter-element interferences (Berrow and Ure, 1981). While several mineral acids, e.g. perchloric, nitric, hydrochloric, sulphuric, have been employed in classical soil chemical analysis (Jackson, 1958; Black, 1965; Hesse, 1971), hydrofluoric acid, notable among mineral acids in its ability to dissolve silica, is frequently used, often in conjunction with other acids, to digest rocks, soils and sediments. In particular, the addition of aqua regia (HNO_3/HCl in ratio 1:3) makes the dissolution considerbly easier (Bernas, 1968), especially at raised temperatures (90-100°C). Several workers have improved this method (aqua regia/HF) by adding boric acid, followed by a second heating step, to complex the excess fluoride (forming soluble fluoborate) and to dissolve precipitated fluoride salts (Price and Whiteside, 1977), and by conducting the full decomposition procedure in a sealed polypropylene bottle to eliminate volatilisation losses. This allows the analysis to be extended to elements which form more volatile fluorides, e.g. silicon, and significantly reduces potential contamination (Buckley and Cranston, 1971). In addition, employment of the N_2O/C_2H_2 flame removes most inter-element interferences, particularly the chemical suppression by elements such as aluminium and silicon of calcium and magnesium, and eliminates the need for releasing agents, e.g. lanthanum, and for complex matching of standards to sample composition (Buckley and Cranston, 1971; Rantala and Loring, 1975; Price and Whiteside, 1977). The overall method enables the determination of a wide range of major and minor elements using FAAS (Bernas, 1968; Langmyhr and Paus, 1968; Buckley and Cranston,, 1971; French and Adams, 1973; Gill and Kronberg, 1975; Rantala and Loring, 1975; Price and Whiteside, 1977; Price, 1978).

It has recently been suggested that the same fluoboric acid solution matrix may be suitable for the analysis of trace elements, at concentrations close to or below flame detection limits, by GFAAS (Whiteside, 1977; Silberman and Fisher, 1979). If such a GFAAS method were viable, it would clearly extend the potential of the 'fluoboric acid' method to a wider range of major, minor and trace elements. Sections 2.6.2 - 2.6.5 describe the full development of the dissolution method and the application of FAAS and GFAAS in the direct determination of major and minor elements (aluminium, calcium, iron, magnesium, manganese, silicon) and, in particular, of trace elements lead, zinc, copper, cadmium and chromium in siliceous materials. The validity of the method is demonstrated by the accurate analysis of several appropriate international standard reference materials of soil, sediment, street dirt and atmospheric particulate matter.

2.6.2 ANALYTICAL PROCEDURE

(i) Reagents

All reagents were Aristar grade unless stated. Water was purified (10-18MΩ) using a Milli-Q Water Purification System, incorporating ion-exchange reverse-osmosis and activated charcoal filters, preceded by an Elgacan ion-exchanger connected to the laboratory water supply. Analyses were performed on IAEA Soil-5 samples.

Nitric and hydrochloric acid: concentrated
Hydrofluoric acid: 40%
Boric Acid (H_3BO_3): saturated aqueous solution of Analar H_3BO_3.
Potassium Chloride (KCl): 2% (w/v) aqueous solution of Analar KCl.

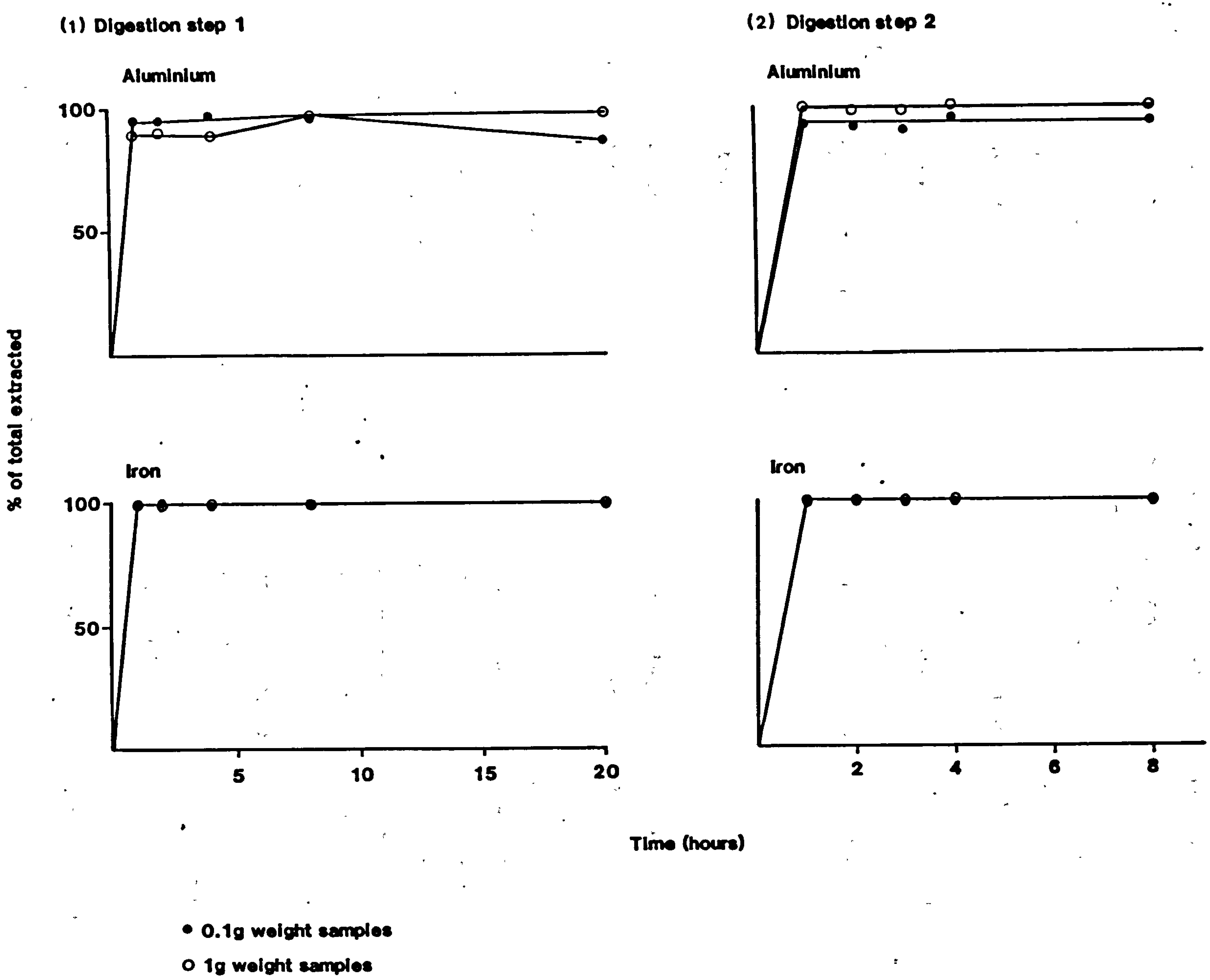
(ii) Optimisation of Digestion Procedure

Aqua regia: Samples with (1 ml) and without aqua regia were dissolved using 7ml HF at 90°C. Direct observation indicated that the presence of aqua regia was necessary for dissolution.

Hydrofluoric acid: 7-10 ml HF was required for total dissolution of 0.1 - 1.0g samples (Farmer et al, 1980).

Heating times: Optimum times for both heating stages were determined using major elements aluminium and iron as indicators. Total decomposition was complete after one hour periods in both stages for 0.1g and 1.0g samples (Figure 2.14).

FIGURE 2.14 DETERMINATION OF OPTIMUM CONDITIONS FOR TOTAL DIGESTION OF SILICEOUS MATERIALS USING IAEA SOIL-5


(1) Digestion step 1
Aluminium
Iron
(2) Digestion step 2
Aluminium
Iron
% of total extracted
100
50
100
50
5
10
15
20
2
4
6
8
Time (hours)
● 0.1g weight samples
o 1g weight samples

(iii) Adopted Dissolution Procedure

For 0.1g samples the procedure consists of two parts: (a) the decomposition of moistened sample using 1 ml aqua regia and 7 ml HF in a capped 125 ml polypropylene container at 90°C on a water bath, and (b) the addition of 50 ml of a filtered, saturated solution of H_3BO_3 and further heating at 90-100°C. While successive heating times of one hour (a) and one hour (b) are adequate, in practice, for 0.1g, 20 hours (a) and 4 hours (b) were employed to ensure complete dissolution and to fit in with laboratory schedules. After complete dissolution, 5 ml 2% KCl is added as an ionisation buffer for the N_2O/C_2H_2 flame and the final volume adjusted to 100 ml with water via monitoring of solution weight (102g).

(iv) Standard Solutions

A range of single-element working standard solutions of up to 0.02 µg/ml cadmium, 0.15 µg/ml chromium, 0.2 µg/ml copper and 0.2 µg/ml lead were prepared in a reagent matrix of aqua regia/HF/H_3BO_3/KCl, identical to that of the samples, from successive dilutions of stock 1000 µg/ml BDH AA spectroscopy standards using an adjustable Gilson automatic pipette. Composite multi-element standards of major and minor elements were also prepared in the reagent matrix: standard solution A contained; 10 µg/ml aluminium, 3 µg/ml calcium, 10 µg/ml iron, 2 µg/ml magnesium, 1 µg/ml manganese, 1 µg/ml sodium, 30 µg/ml silicon and 1 µg/ml zinc, while standard solution B contained; 100 µg/ml aluminium, 30 µg/ml calcium, 100 µg/ml iron, 30 µg/ml magnesium, 5 µg/ml manganese, 10 µg/ml sodium, 300 µg/ml silicon and 2 µg/ml zinc. Silicon concentrations were obtained by dilution of a 5650 µg/ml stock solution.

(v) Determination of Graphite Furnace Operating Conditions

Using the procedure described in Section 2.5.3 (iv) ash/atomise curves were constructed for cadmium, chromium, copper, lead (and zinc) in fluoboric acid solution (aqua regia/HF/H_3BO_3/KCl) and compared with similar curves for the elements in aqueous solution (1% HNO_3). Cadmium and lead curves are shown in Figures 2.15 and 2.16 respectively. From these plots optimum furnace operating conditions were derived as listed in Table 2.2. No significant differences in temperature settings were found for the reagent matrix relative to 1% HNO_3, but mean reductions in sensitivity of 5-10% for cadmium, chromium and copper and 20% for lead were recorded.

(vi) Instrumentation and Operating Conditions

The Perkin-Elmer PE-306/HGA-74/AS-1 GFAAS system, outlined in Section 2.5, was used for cadmium, chromium, copper and lead analyses. Sample volumes of 20 µl were injected. Ordinary graphite tubes were used with argon as inert sheathing gas. Peak heights were recorded on a Kipp and Zonen BD8 chart recorder. The temperature programmes listed for fluorboric acid solutions in Table 2.2 were employed. Detailed instrumental settings are presented in Table 2.3.

The elements aluminium, calcium, iron, magnesium, manganese, silicon and zinc were determined in a N_2O/C_2H_2 flame using instrumental settings indicated in Table 2.3. Burner rotation was employed, where necessary, to reduce sensitivity.

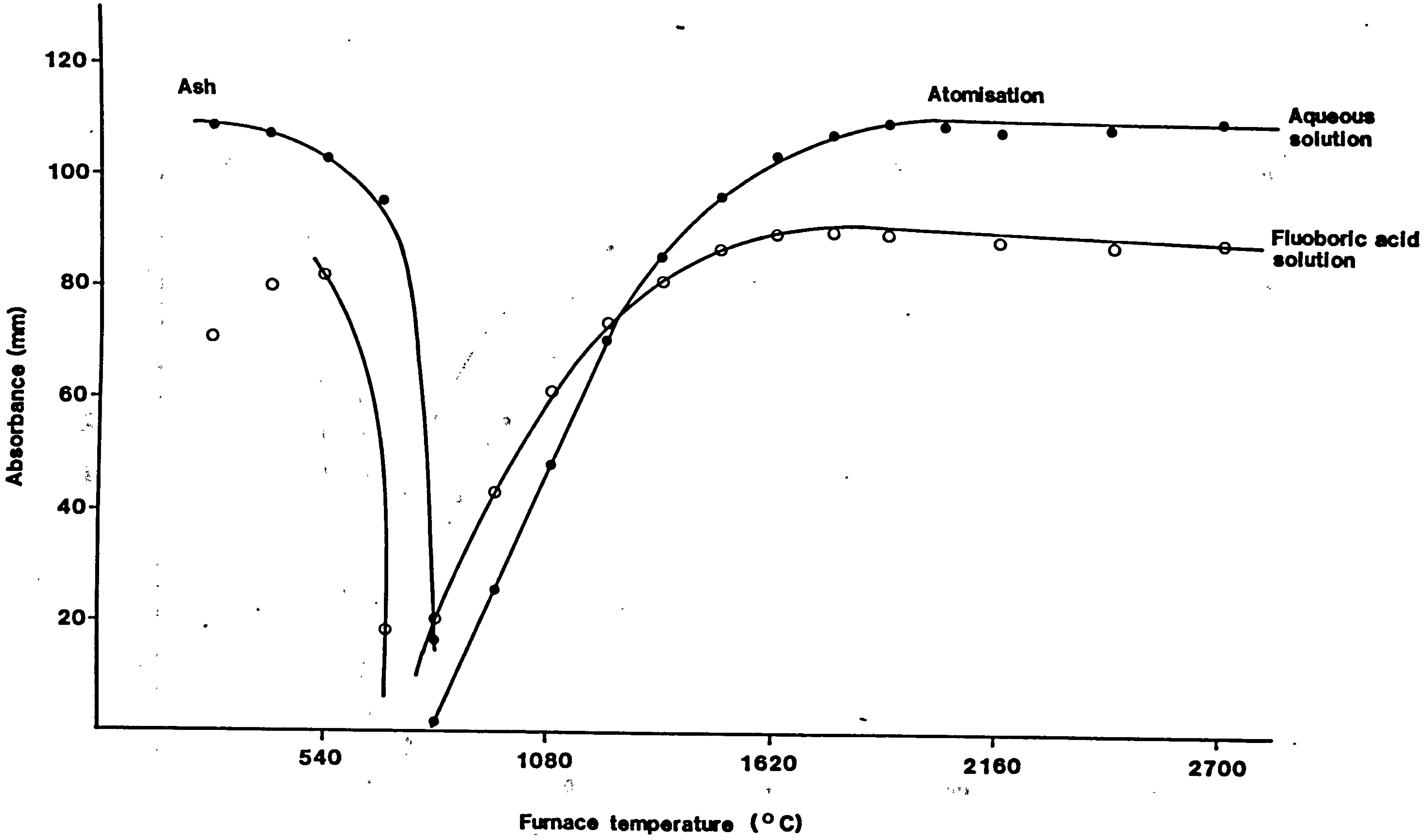


FIGURE 2.16 DETERMINATION OF ASH/ATOMISATION CURVES FOR LEAD: (100ng/ml) IN AQUEOUS AND FLUOBORIC ACID SOLUTIONS

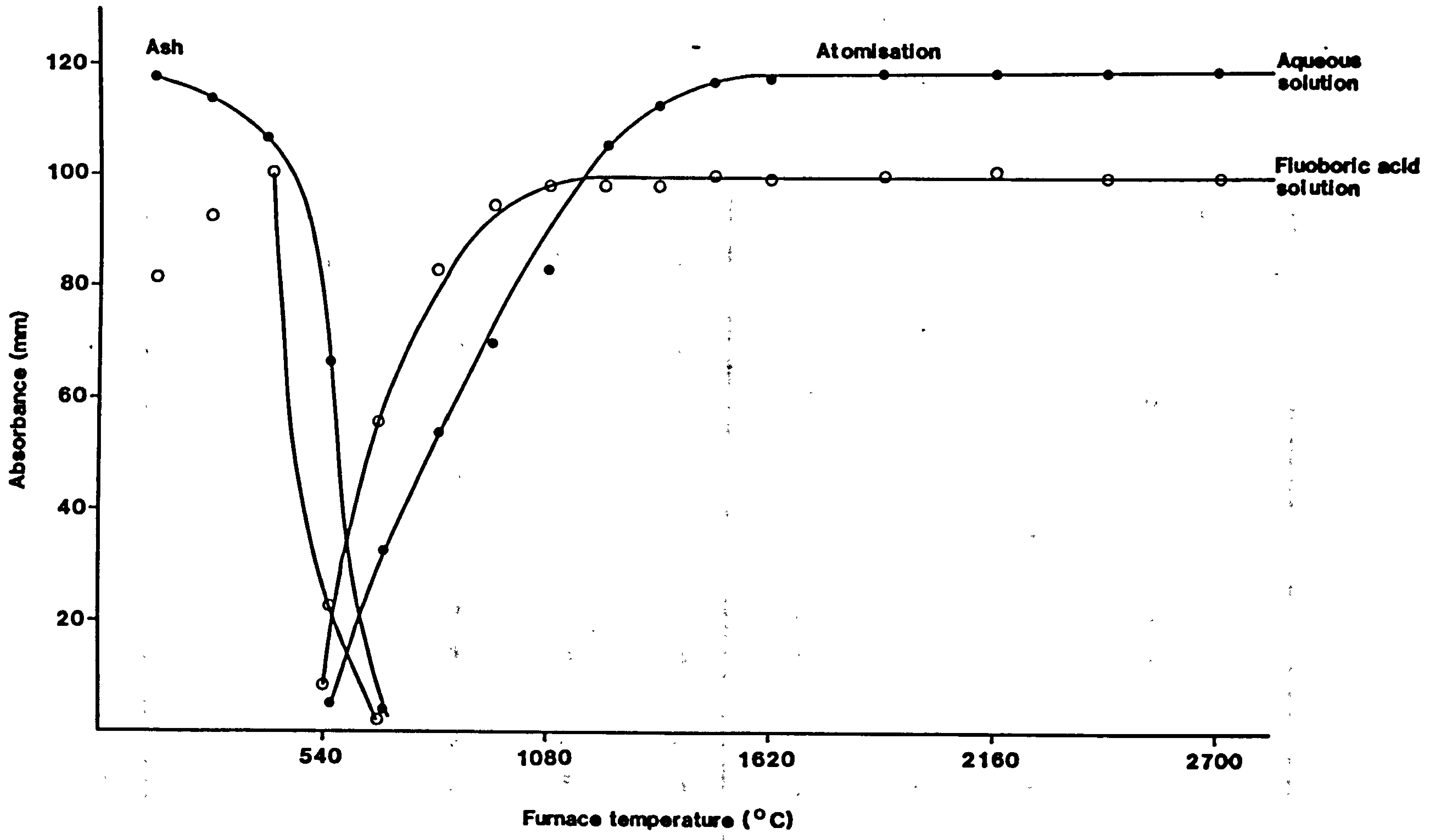


FIGURE 2.15 DETERMINATION OF ASH/ATOMISATION CURVES FOR CADMIUM (10ng/ml) IN AQUEOUS AND FLUOBORIC ACID SOLUTIONS

TABLE 2.2 FURNACE TEMPERATURE SETTINGS FOR CADMIUM, CHROMIUM, COPPER, LEAD AND ZINC IN AQUEOUS (1% HNO_3) AND FLUOBORIC ACID SOLUTIONS

		AQUEOUS SOLUTION					FLUOBORIC ACID SOLUTION				
		Cd	Cr	Cu	Pb	Zn	Cd	Cr	Cu	Pb	Zn
Dry	°C	105	105	105	105	105	105	105	105	105	105
	Sec	30	30	30	30	30	30	30	30	30	30
Ash	°C	270	810	405	405	340	300	920	600	480	540
	Sec	30	30	30	30	30	40	40	40	40	40
Atomise	°C	1500	2700	2700	1900	2500	1200	2700	2700	1620	2570
	Sec	8	12	8	8	8	8	12	10	8	8
Burn-out	°C	2700	2700	2700	2700	2700	2700	2700	2700	2700	2700
	Sec	5	8	5	5	5	5	8	5	5	5

TABLE 2.3 AAS INSTRUMENTAL SETTINGS FOR ELEMENTAL ANALYSIS

	TRACE ELEMENTS					MAJOR ELEMENTS					
	Cd	Cr	Cu	Pb	Zn	Al	Ca	Fe	Mg	Mn	Si
λ (nm)	228.8	357.9	324.8	283.3	213.9	309.3	422.7	248.3	285.2	279.5	251.6
Lamp* Current (mA)	7	25	5	8	8	15	10	10	10	10	25
Slit Width (nm)	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.2	0.7	0.2	0.2
Background Correction	✓			✓	✓			✓	✓	✓	✓

* All radiation sources were hollow cathode lamps

(vii) Standard Reference Material

Four standard reference materials were analysed - NBS River Sediment SRM 1645, NBS Urban Particulate Matter SRM 1648, IAEA Soil-5 and IAEA Lake Sediment SL-1. For each reference material several 0.1g aliquots (0.025g for NBS SRM 1648) were dissolved.

All sample solutions were injected undiluted into the furnace except in the measurement of lead in NBS SRM 1645 and 1648 where dilution with reagent blank was necessary. Chromium in NBS SRM 1645 was determined in the N_2O/C_2H_2 flame. The gas-stop facility was employed in all furnace analyses of cadmium, chromium, copper and lead except for cadmium in NBS SRM 1645 and 1648. Precision on duplicate injections was usually better than 1% (± 1σ) at concentrations of 0.002 μg/ml cadmium and 0.1 μg/ml chromium, copper and lead. Reagent blanks were typically 0.0003 μg/ml cadmium, 0.001 μg/ml chromium, 0.01 μg/ml copper and 0.005 μg/ml lead.

2.6.3 RESULTS

The measured levels of cadmium, chromium, copper and lead in the reference materials are compared with certified values in Table 2.4, while Table 2.5 lists the corresponding data for aluminium, calcium, iron, magnesium, manganese, silicon and zinc. The associated analytical errors on the results represents the standard deviation (± 1σ) of the mean of 8-12 separate analyses which are listed in Appendix 1.

IAEA certified values are classified as (a) 'recommended with a relatively high degree of confidence' (aluminium, copper, zinc in Soil-5; iron, manganese, zinc in SL-1) or (b) 'recommended with a reasonable degree of confidence' (chromium, iron, manganese, lead in Soil-5; cadmium, chromium, copper and lead in SL-1). In some cases, where

TABLE 2.4 DETERMINATION OF CADMIUM, CHROMIUM, COPPER AND LEAD (μg/g) in NBS and IAEA STANDARD REFERENCE MATERIALS BY GFAAS

		NBS SRM 1645 River Sediment	NBS SRM 1648 Urban Particulate Matter	IAEA Soil-5 Soil	IAEA SL-1 Lake Sediment
Cd	Cert.	10.2 ± 1.5	75 ± 7	(1.5)	0.26 ± 0.05
	Meas.	9.2 ± 0.5	69 ± 4	1.41 ± 0.11	0.28 ± 0.05
Cr	Cert.	2.96±0.28*	403 ± 12	28.9 ± 2.8	104 ± 9
	Meas.	3.18±0.08*	173 ± 27	26.1 ± 1.5	103 ± 5
Cu	Cert.	109 ± 19	609 ± 27	77.1 ± 4.7	30.0 ± 5.6
	Meas.	111 ± 7	586 ± 22	78.3 ± 4.8	29.4 ± 3.5
Pb	Cert.	714 ± 28	6550 ± 80	129 ± 26	37.7 ± 7.4
	Meas.	683 ± 29	6210 ± 85	149 ± 6	40.5 ± 5.8

* per cent, determined by flame AA.

TABLE 2.5 DETERMINATION OF ALUMINIUM, CALCIUM, IRON, MAGNESIUM, MANGANESE, SILICON AND ZINC IN NBS AND IAEA STANDARD REFERENCE MATERIALS BY FAAS

		NBS SRM 1645 River Sediment	NBS SRM 1648 Urban Particulate Matter	IAEA Soil-5 Soil	IEAE SL-1 Lake Sediment
Al	Cert.	(2.12)	(3.3)	8.19 ± 0.28	(8.9)
(%)	Meas.	2.42 ± 0.12	3.3 ± 0.45	7.93 ± 0.09	10.0 ± 0.2
Ca	Cert.	(2.86)	-	(2.2)	(0.25)
(%)	Meas.	2.90 ± 0.13	6.8 ± 0.23	2.38 ± 0.04	0.30 ± 0.01
Fe	Cert.	11.3 ± 1.2	3.91 ± 0.10	4.45 ± 0.19	6.74 ± 0.17
(%)	Meas.	10.6 ± 0.3	4.50 ± 0.23	4.63 ± 0.13	6.56 ± 0.17
Mg	Cert.	(2.4)	(0.8)	(1.5)	(2.9)
(%)	Meas.	0.75 ± 0.02	0.76 ± 0.04	1.28 ± 0.05	0.67 ± 0.02
Mn	Cert.	785 ± 97	(860)	852 ± 37	3460 ± 160
(μg/g)	Meas.	750 ± 90	810 ± 60	970 ± 85	3560 ± 110
Si	Cert.	(23.8)	-	(33)	-
(%)	Meas.	23.6 ± 1.2	13.3 ± 0.8	26.4 ± 1.4	23.1 ± 1.1
Zn	Cert.	1720 ± 169	4760 ± 140	368 ± 8.2	223 ± 10
(μg/g)	Meas.	1640 ± 40	4580 ± 160	354 ± 41	216 ± 28

certificated values are not available, concentrations classified as non-certified or 'information only' by NBS and IAEA are included inside brackets in Tables 2.4 and 2.5. Additional to the tabulated data, Greenberg (1979), has reported levels for NBS Urban Particulate Matter of 3.5 ± 0.1% aluminium, 5.8 ± 0.5% calcium, 0.83 ± 0.08% magnesium and 790 ± 20 µg/g manganese; Nadkarni and Morrison (1978) obtained 10.4 ± 0.5% for aluminium in IAEA SL-1.

2.6.4 DISCUSSION

In some cases after the aqua regia/HF/H_3BO_3 treatment, certain samples yielded an insoluble black residue which Buckley and Cranston (1971) also observed in samples with high carbon concentrations and concluded was probably unoxidised carbon. Total decomposition of the inorganic matrix was demonstrated, however, by the agreement between measured levels of the major constituent elements (e.g. aluminium, iron) and certified values. Thus, release of trace metals held in the crystal lattices of the materials was achieved, yielding excellent agreement between certified values and those obtained via direct determination in the fluoboric acid matrix by GFAAS. One notable exception was chromium in NBS Urban Particulate Matter (Table 2.4). Filtration of the resultant insoluble black residue and subsequent digestion with HNO_3/$HClO_4$ yielded a further 60 µg/g chromium suggesting that a substantial fraction of this reference material is incorporated in the carbonaceous matrix resistant to decomposition by aqua regia/HF/H_3BO_3. Recently, a low recovery of chromium from the same material was reported by Lum et al (1982), who attributed it to volatilisation of chromyl chloride and/or fluoride during acid digestion.

The data listed (Tables 2.4-2.5) are based on direct analyses of the sample solutions. Calibrations of the method by standard additions and, where appropriate, standard dilutions confirmed the validity of using cadmium, chromium, copper and lead standards in a fluoboric acid matrix and also the absence of major interferences for these elements, substantiating the findings of Rantala and Loring (1980) for cadmium. With the analytical procedure described here, the trace elements of interest in this study can be measured at levels as low as 0.25 µg/g for cadmium and about 5 µg/g for chromium, copper and lead, subject to reagent blank concentrations, for 0.1g samples.

2.6.5 SUMMARY OF USEFULNESS OF METHOD

The analytical method described here is suitable for determination of total metal contents (major, minor and trace) in a wide range of siliceous materials. It is particularly appropriate for geochemical and environmental studies on soil, sediment, street dirt, atmospheric particulates etc, complementing investigations of speciation and partitioning of individual elements among various chemical and mineralogical phases by chemical leaching techniques (Farmer, 1981). Thus, not only it is useful in the measurement of total trace element concentrations in the original sample but also, after sequential leaching steps, of the content of intermediate residues (and hence, by difference, the levels previously removed) and of the final resistant clay mineral lattice residue of soils, street dirts, and sediments (Farmer et al, 1980; Farmer, 1983).

Consequently, the method was employed in these capacities (total and residual sample digestion), forming an integral part of the environmental/geochemical study undertaken in Chapters 3 and 4.

CHAPTER 3 - A SURVEY OF TRACE-METAL CONTAMINATION AND CHEMICAL PARTITIONING IN GLASGOW URBAN SOILS AND STREET DIRT: PART A: SAMPLING, METHOD DEVELOPMENT AND ANALYSIS

3.1 INTRODUCTION

As discussed in Chapter 1, the underlying objective of this study was to conduct a comprehensive survey of trace metal contamination in Glasgow soils and street dirt, while, at the same time, pursuing a detailed investigation of fundamental urban trace-metal geochemistry and relating this information to the long-term fate of metal contaminants in the urban environment and to potential environmental and health effects. The credibility of this type of study depends to a large extent, like sediment analysis (Farmer, 1981), on the integrity of the samples collected, as no amount of sophisticated instrumentation or data processing can eliminate errors introduced in faulty or unrepresentative sampling.

Logistically, therefore, the study required (i) the formulation of an elaborate systematic sampling strategy, based on a grid pattern (Section 3.2.2); (ii) the careful establishment of criteria for collection (bearing in mind the wide range of sample types such as open space, garden, parkland etc.) of sufficient numbers of representative samples of soils and street dirt (Section 3.2.3); and (iii) the development of a carefully designed sequential chemical leaching scheme to identify the chemical forms and associations of trace metals in these materials (Section 3.3).

The chemical leaching approach is derived from agricultural chemistry, where selective chemical extraction has been employed to assess the soil's ability to supply various individual elements of particular importance to crop and livestock nutrition (Scott et al, 1971; Mitchell and Burridge, 1979; West, 1979; Davies et al, 1980; MAFF, 1980). Similarly, single-step leaching techniques have been utilised to determine the geochemical associations of trace metals in aquatic sediments (Chester and Hughes, 1967; Chao, 1972).

In these studies, a diverse range of single leaching agents has emerged somewhat arbitrarily, with little consistency of methodology. However, more emphasis is now being placed on the standardisation and selectivity of procedure and on the design of <u>multi-step</u> sequential leaching techniques whereby individual leaching agents, applied in order of increasing power of extraction, remove trace metals associated with defined geochemical phases. The main types of metal associations in soil/street dirt/sediments are listed in Table 3.1. Several schemes have recently been devised and deployed in studies of contaminated aquatic sediments (Gupta and Chen, 1975; Engler et al, 1977; Tessier et al, 1979; Salomons and Förstner, 1980) and soils (Harrison et al, 1981) but, in general, there has been a noticeable lack of application to urban soils and street dirts.

3.2 SAMPLING

3.2.1 THE STUDY AREA

The city of Glasgow is situated in the centre of the densely-populated industrial belt of west central Scotland (Figure 3.1). The population of the region is ca. 2.5 million, of which 1.71m reside in the Clydeside conurbation with 0.71m located in Glasgow (HMSO, 1981). The city comprises a land area of approximately 16,000 hectares divided by the River Clyde which runs westwards

TABLE 3.1 MECHANISMS OF TRACE METAL BONDING IN SEDIMENTS, SOILS AND STREET DIRT (Förstner and Wittmann, 1979)

Minerals of natural rock debris eg. heavy minerals		Metal bonding predominantly in inert positions
Heavy metal - hydroxides - carbonates - sulphides		Precipitation as a result of exceeding the solubility product in the area of the water course
Hydroxides and oxides of Fe/Mn	pH-dependent	Physico-sorption Chemical sorption (exchange of H^+ in fixed positions) Coprecipitation as a result of exceeding the solubility product
Bitumen, lipids Humic substances Residual organics	pH-dependent	Physico-sorption Chemical sorption (exchange of H^+ in COOH-, OH-groups) Complexes
Calcium carbonate	pH-dependent	Physico-sorption Pseudomorphosis (dependent on supply and time) Coprecipitation (incorporation by exceeding the solubility product)

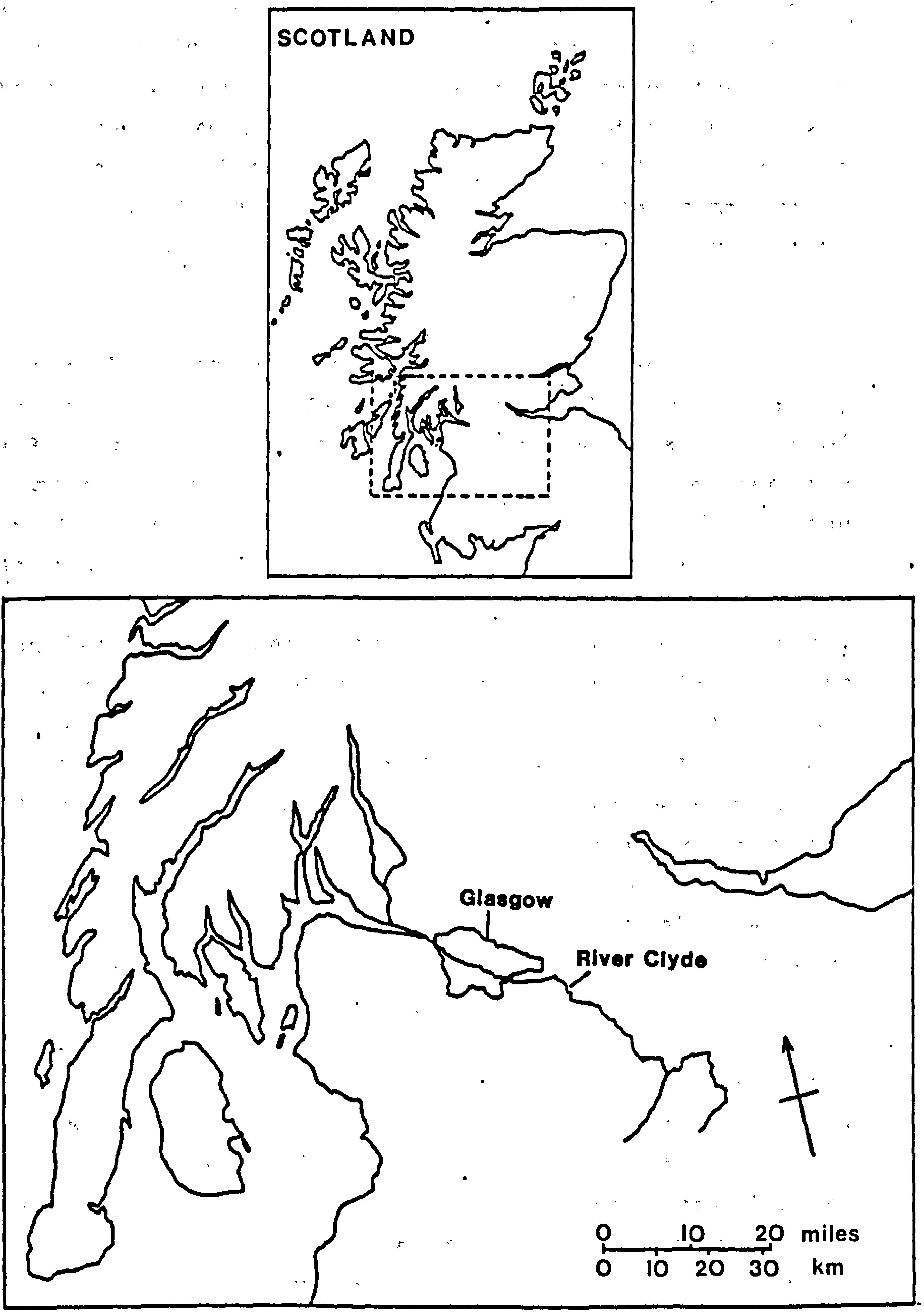


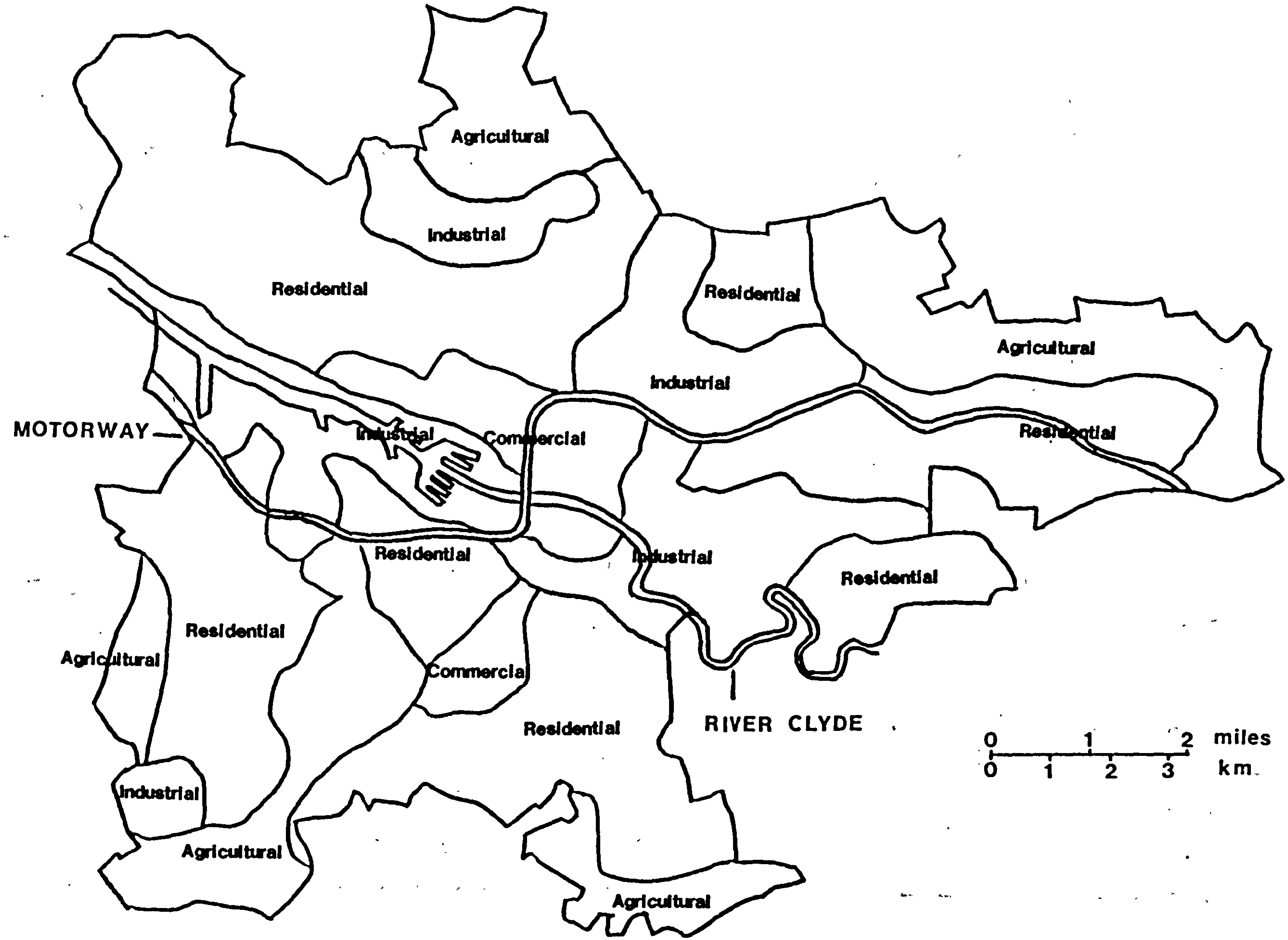
FIGURE 3.1 LOCATION OF GLASGOW

through the city (Figure 3.2) and discharges into the adjacent Clyde Sea Area, the subject of a recent metal pollution study by Farmer (1983). The river and the geology of the region have strongly influenced the manner of human settlement and the nature of industrial growth in the area. Figure 3.2 indicates the current distribution of land area in terms of the commercial, industrial, residential and agricultural/parkland regions.

Geologically Glasgow lies on the Coal Measures in the heart of the Midland Valley of Scotland, a major rift, some 80km wide, in which relatively young rocks mainly of the Upper Palaeozoic age, are down-faulted between the Lower Palaeozoic rocks of the Southern Uplands to the south and of the Highlands to the north (Black, 1973). The underlying rocks on which most of the city stands are carboniferous sediments, mainly sandstone and limestone, with overlying beds of boulder clay and drift deposits (Melvyn-Howe, 1972). The soils in the region, like most Scottish soils, have developed on glacial till laid down 12,000 years ago and, where they have not been obscured by property, are predominantly acid-brown earths and gleyed soils (Melvyn-Howe, 1972) with a trace metal content, due to the prevailing conditions of temperate weathering, largely reflecting the nature of the parent material (Berrow and Mitchell, 1980).

The industrial basis of the city was founded on coal mining which commenced in the 15th and 16th centuries. The foundation of the chemical industry in the mid-17th century and the establishment of the iron works around 1750 were responsible for the development of Glasgow into a large industrial complex during the late-18th and early 19th centuries (Oakley, 1975; Slavin, 1975). Further rapid growth in industrialisation, particularly in shipbuilding, heavy machinery and textiles, was accompanied by substantial increases in population until

FIGURE 3.2 MAIN FORMS AND LOCATION OF LAND TYPES IN GLASGOW

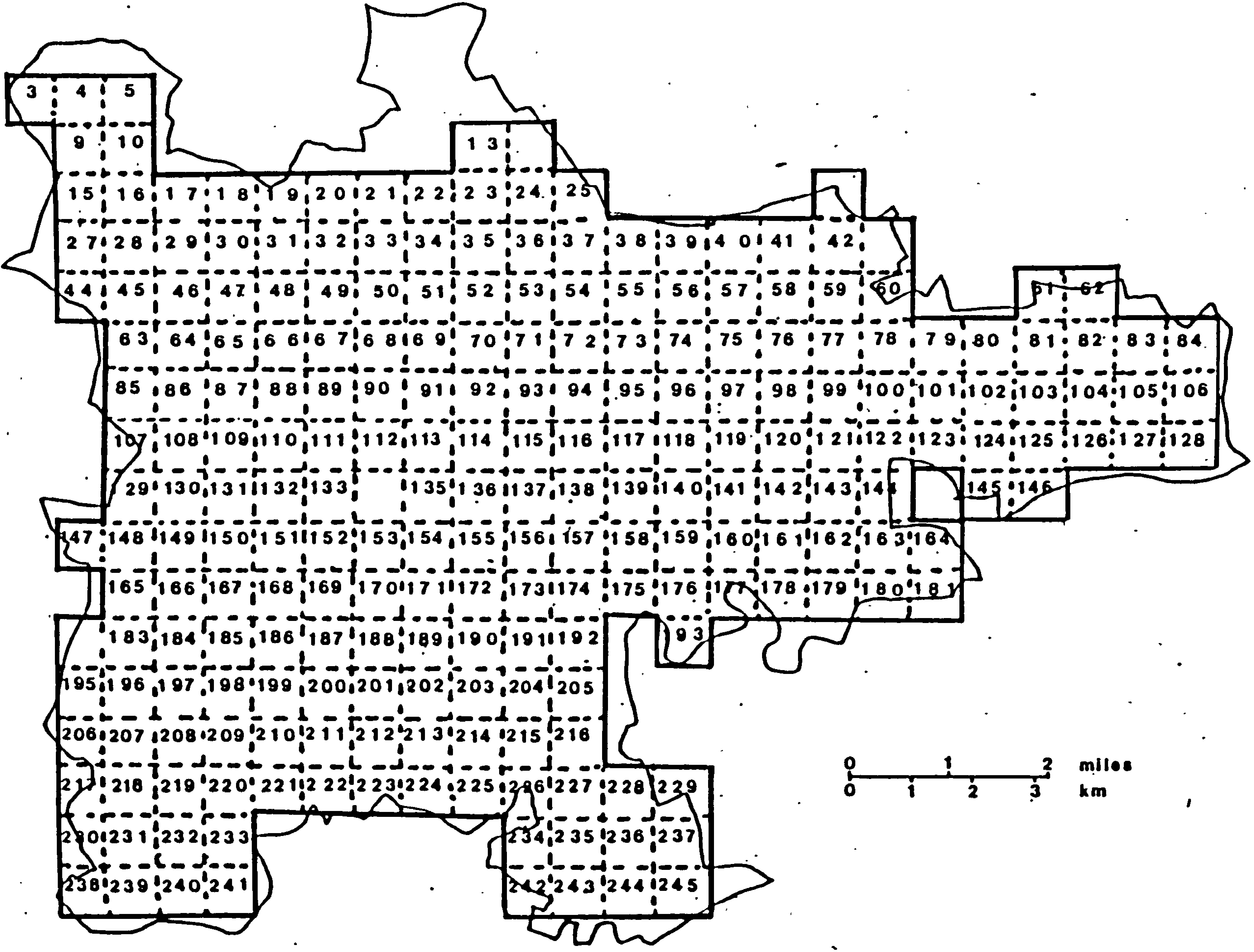

Agricultural
Industrial
Residential
Residential
Agricultural
Industrial
MOTORWAY
Industrial
Commercial
Residential
Residential
Industrial
Residential
Residential
Agricultural
Commercia
Residential
RIVER CLYDE
Industrial
Agricultural
Agricultural
0 1 2 miles
0 1 2 3 km

the early years of the 20th century. Recent years, however, have seen the decline of the traditional heavy industries, a considerable expansion of the commercial centre of the city and a redistribution of population to new towns. Meanwhile, automobile traffic has significantly increased with the establishment of a major road network including an urban motorway system (Figure 3.2). Consequently, like most major UK cities, this rapid growth in industrialisation, transportation and population has resulted in the general pollution of the Glasgow environment (Oakley, 1975; Wilson, 1976) with elevated metal levels in the atmosphere (McDonald and Duncan, 1979, Apling et al, 1979), parkland soils and street dirt (Farmer and Lyon, 1977) and the surrounding marine and lacustrine sediments (Farmer et al, 1980; Farmer, 1983).

3.2.2 SAMPLING STRATEGY

Using a detailed grid system, based on unit squares of 0.8km x 0.8km, similar to systems employed in several recent studies of trace metal contamination in UK urban soils (Parry et al, 1981; JURUE, 1982), samples were systematically collected from inside the municipal area of Glasgow. Peripheral units were established to be grid squares with more than 50% of the land inside the municipal boundary (Figure 3.3). In total, 231 grid squares were sampled with typically three samples, two soil and one street dirt, collected per unit square. When samples of a particular type were occasionally unobtainable, e.g. soil in some central Glasgow districts and street dirt in more rural agricultural areas which lacked a true road network, a constant sampling density was maintained, in most cases, by collecting substitute samples, i.e. street dirts in place of soils or vice versa. Consequently, 452 soil and 234 street dirt samples were collected (Table 3.2). Soil samples were generally selected on the basis of the predominant type(s) of

FIGURE 3.3 GRID SYSTEM EMPLOYED IN SAMPLING STRATEGY


3 4 5
9 10
13
15 16 17 18 19 20 21 22 23 24 25
27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42
44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62
63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84
85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100 101 102 103 104 105 106
107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128
129 130 131 132 133 135 136 137 138 139 140 141 142 143 144 145 146
147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164
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0 1 2 miles
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TABLE 3.2 SUMMARY OF SAMPLE NUMBERS IN RELATION TO LAND-USE CATEGORIES AND REGIONS

	Residential	Commercial	Industrial	Agricultural/ Parkland	Total
No. of sample squares	115	16	55	45	231
Open Spaces	99	11	53	19	182
Garden Soils	60	3	26	5	94
Parkland Soils	63	11	25	21	120
Agricultural	5	0	1	50	56
Total no. of soil samples collected	227	25	105	95	452
No. of street dirt samples collected	116	22	58	38	234

land-use categories (defined in Table 3.3) found in individual grid squares. The number of samples collected in each land-use category (open spaces, garden soils etc) and regions (residential, commercial, etc) are summarised in Table 3.2. (Details of all the sample sites in relation to the sampling grid and distance from the nearest road are given in Appendix 2).

3.2.3 SAMPLING PROTOCOL

Sampling was performed from April to October 1981, predominantly during the long dry spell of April to June. Surface soil samples (0-5cm), which reflect maximum trace-metal enhancement (Lagerwerff and Specht, 1970; Farmer and Lyon, 1977; Byrd et al, 1983), were collected using a 4.5cm diameter polypropylene corer and placed into a precleaned polypropylene storage jar using a plastic plunger. Typical sample weight was 40-60g (wet weight). Street dirts (10-20g wet weight) were gently scraped from the road or kerbside with a plastic spatula into a storage jar. Subsequently, all samples were air-dried for 3-4 days at 25-30°C to remove moisture, without the loss of volatile elements such as cadmium, and then stored at room temperature.

Before chemical treatment, soils were lightly ground using a mortar and pestle to allow separation of vegetative material, to achieve homogeneity and, by disaggregation, to facilitate passage through a 500µm (the predominant size range of metal particulates [Revitt and Ellis, 1980]) mesh nylon sieve, thereby reducing dilution (elemental concentration decreases with increasing particle size) and improving reproducibility. Street dirts, which usually did not require grinding, were also sieved. Sieved material was accurately weighed into the appropriate treatment flask for chemical analysis.

TABLE 3.3 LAND-USE DEFINITION OF SOIL CATEGORIES COLLECTED IN GLASGOW

Soil Category	Land-use definition
Open spaces	Grass covered public open space
Garden soils	Garden soils without grass cover
Parkland soils	Parkland or landscaped area soils
Agricultural soils	Agricultural land soil

3.3 DEVELOPMENT OF CHEMICAL LEACHING PROCEDURES

3.3.1 TOTAL METAL CONTENT

Total metal determinations were performed using the digestion procedure and atomic absorption analysis outlined in Section 2.6. Approximately 0.1g samples of soil were dissolved using aqua regia/HF (4-hours) followed by H_3BO_3 (4 hours). The resulting solution was analysed for lead, zinc, copper and cadmium using GFAAS and FAAS (zinc) with furnace operating conditions and instrumental settings as previously described (Tables 2.2 and 2.3 respectively).

3.3.2 MULTI-STEP SEQUENTIAL LEACHING SCHEME

Trace elements in soils and street dirt are partitioned among geochemical phases from which they are released under certain environmental conditions. The main geochemical phases, identified and defined by leaching studies on soils (McLaren and Crawford, 1973; Harrison et al, 1981) and aquatic sediments (Chester and Hughes, 1967; Chao, 1972; Gupta and Chen, 1975; Engler et al, 1977; Tessier et al, 1979; Salomons and Förstner, 1980; Förstner et al, 1981), are listed in approximate order of trace metal release in Table 3.4 along with the corresponding modes of chemical attack. Examples from the wide range of chemical leaching agents deployed in this capacity are shown in Table 3.5, illustrating the arbitrary choice of reagents and the absence of a universally-agreed standard procedure.

3.3.2.1 EXCHANGEABLE

The importance of the exchangeable fraction, particularly in soils, has been recognised for a long time. Cations which are adsorbed, through electrostatic attraction, on the negatively charged surfaces of clay minerals and

TABLE 3.4 THE MAIN GEOCHEMICAL PHASES OF SOILS AND STREET DIRT AS DEFINED BY CHEMICAL EXTRACTION TECHNIQUES FOR THE RELEASE OF TRACE METALS

Phase	Extraction technique
Exchangeable	Exchange with excess cations
Carbonate-bound	Release by mild acid
Easily-reducible	Reduction
Moderately-reducible	Reduction
Organic	Oxidation
Residual	Digestion with strong acid

TABLE 3.5 RANGE OF CHEMICAL EXTRACTANTS USED IN SELECTIVE LEACHING OF TRACE METALS FROM SOILS, STREET DIRTS AND SEDIMENTS (Davies et al, 1980; Salomons and Förstner, 1980; Farmer and Gibson, 1981)

Exchangeble	$BaCl_2$,$MgCl_2$, NH_4OAc,EDTA
Carbonate	HOAc,NaOAc/HOAc
Manganese and iron phases (easily- and moderately-reducible)	Acidified $NH_2OH.HCl$, acid ammonium oxalate, $NH_2OH.HCl$/HOAc, $Na_2S_2O_4$/ Na-citrate
Organic	H_2O_2,H_2O_2-NH_4OAc,NaOH,EDTA
Residual	HCl/HNO_3/HF/H_3BO_3,HF,HNO_3/$HClO_4$

organic matter can be replaced by the process of ion-exchange. The negative charges are of two types: permanent and pH-dependent. Permanent charges, common in silicate clays, result from the isomorphous replacement of a structural cation by a less positive cation of similar size within the clay structure and are most pronounced in the clays with the largest surface areas, e.g. montmorillonite. The pH-dependent charges are directly related to variation in the soil pH. At low pH the charge and number of exchange sites are low but increase as pH rises. Both mineral and organic materials have pH-dependent charges. In mineral matter the charge is thought to be due to SiOH and AlOH groups at broken edges and surfaces of clay minerals, while in organic matter carboxyl (-COOH) and phenol (-OH) groups contain covalently-bonded hydrogen atoms which can dissociate as positive ions at high pH values leaving behind negatively charged species.

Exchangeable cations constitute the immediate nutrient reservoir for the soil solution, which provides the vital link between the solid phase of the soil and the plant root. The exchangeable fraction is available to plants during the growing season. As the exchangeable pool is depleted, the intermediate supply of trace metals (i.e. those held more strongly on other phases) can replenish the exchangeable fraction within a short time (West, 1981), so that the levels remain fairly constant. The estimation of trace metals in the exchangeable fraction is considered by many to be a more valid approach than the measurement of total concentration in the assessment of the environmental exposure of plants to these elements.

The ideal solution for extracting exchangeable metals would simulate the behaviour of plant roots in soil but this is impossible to achieve due to varying soil types and plant species. In practice, many chemical reagents have been employed to liberate metals held in exchangeable sites (Tessier et al, 1979; Salomons and Förstner, 1980; Davies et al, 1980) but without consensus as to which is the most selective or effective. Typical extractants used in such studies are weak acids, chelating agents and neutral salts. The Agricultural Development and Advisory Service (ADAS) recommends the use of acetic acid (0.5M) for estimating available cadmium, cobalt, nickel, lead and zinc (ADAS, 1981a). Although weak acid easily dissolves the exchangeable metals, it may also release some metals located in other phases (Swaine and Mitchell, 1960) and is therefore likely to overestimate the fraction available to crops and plants. Ethylene diamine tetra acetic acid (0.05M) is frequently used by ADAS to measure plant available copper (ADAS, 1981a) and has recently been employed to extract cadmium, nickel, lead and zinc (ADAS, 1981b). Such chelating agents remove the exchangeable fraction but can also extract chelated ions held in organic or organomineral complexes (Berrow and Mitchell, 1980). Neutral salts such as ammonium acetate (1M) and magnesium chloride (1M) have been employed in many studies to release exchangeable metals (Gupta and Chen, 1975; Engler et al, 1977; Wilber and Hunter, 1979; Tessier et al, 1979; Salomons and Förstner, 1980; Harrison et al, 1981). Ammonium acetate is recommended by ADAS for the measurement of the cation exchange capacity (CEC - total number of cation exchange sites in a soil) of agricultural soils (ADAS, 1981a) and has been extensively used in soil and sediment analysis. Magnesium chloride is also an effective releasing agent for desorbing specifically adsorbed trace metals (O'Connor and Kester, 1975) and simulates the effect de-icing salt has on soils in winter (Harrison et al, 1981). It has been suggested, however, that the adsorption-desorption processes of specifically adsorbed cations is pH-dependent so that neutral salts may not fully extract exchangeable metals (Tessier et al, 1979). Nevertheless, neutral salts are more specific in their mode of attack than acetic acid or EDTA and therefore lend themselves better to the selective release of exchangeable trace metals. For this reason acetic acid and EDTA were excluded from the study. Some consider ammonium acetate to be more efficient (Badri and Aston, 1981), but this may be attributable to partial attack on the carbonate fraction (Tessier et al, 1979); magnesium chloride, however, has been found to release higher concentrations of some elements than ammonium acetate by virtue of metal-chloride complex formation in solution (Salomons and Förstner, 1980). Recently, Salomons and Förstner (1980) and Förstner et al (1981), following extraction studies on a wide range of sediment types, recommended the use of ammonium acetate in preference to magnesium chloride. Therefore, ammonium acetate was selected for this study with a leaching period of 4 hours to allow adequate time for saturation and exchange, particularly on coarse materials (<500μm).

3.3.2.2 CARBONATE

Carbonates of calcium and magnesium, notably calcium, are widely distributed in soils and sediment, occurring either separately or in association with soluble salts. Calcite ($CaCO_3$), occurs as a massive structure or as deposits on the surface of rock fragments and detrital grains, and has been identified, by X-ray diffraction, as a crystalline component of soils and street dirt (Harrison et al, 1981). Carbonates have sufficient surface energy to adsorb trace metals (Suess, 1973) and carbonate-metal coprecipitation has been implied as an important mechanism in lake sediments (Deurer et al, 1978) especially when the concentrations of trace metals are high enough to saturate other geochemical phases (Jenne, 1976).

Not all sequential extraction schemes have employed a separate carbonate extraction step. However, some recent evidence suggests that the carbonate phase may be an appreciable reservoir for a number of elements in soils (Harrison et al, 1981) and sediments (Tessier et al, 1979).

Selective dissolution of the carbonate fraction is usually achieved by leaching with sodium acetate and/or acetic acid at acidic pH values (Gupta and Chen, 1975; Tessier et al, 1979; Harrison et al, 1981). The reagent chosen in this study, 1M sodium acetate adjusted to pH5 with acetic acid, releases little organic carbon and free iron in non-calcareous soils (Grossman and Millet, 1961). Carbonate dissolution time depends on particle size, the percentage and type of carbonate present and sample size, but, for most samples, extraction is generally complete after 5 hours (Tessier et al, 1979).

3.3.2.3 HYDROUS METAL OXIDES

It is widely recognised that secondary iron and manganese oxides act as an important reservoir for heavy metals in soils and sediments (Jenne, 1968). They are extensively distributed in street dirt, soils and sediments, occurring as coatings on mineral surfaces, 'cement' between particles and as fine discrete particles in clusters and aggregates of colloidal dimensions. This general mode of occurrence allows these oxides to exert chemical influence over other mineral species far out of proportion to their concentration (Jenne, 1968).

In normal aerated soils and sediments, manganese and iron exist as oxides and hydroxides (Mitchell, 1964; Page, 1964). Under reducing conditions, however, as in water logging in gully pots or in the anaerobic environment of the sediment column, the metals are solubilised (Russell,

1977) and in the sediment migrate upwards through the pore water to be reoxidised and fixed in the aerobic surface layers (Price, 1976).

The main iron oxides present in soils are hematite (Fe_2O_3), goethite (FeOOH), magnetite (Fe_3O_4) and hydrated amorphous ferric hydroxide ($Fe(OH)_3$: nH_2O) [Oades, 1963; Chao and Theobald, 1976]. Amorphous and crystalline forms can be differentiated through chemical extraction to only a limited extent as transition from amorphous ⟶ cryptocrystalline ⟶ crystalline is not clearly defined. Soils usually contain greater amounts of iron oxides than of manganese oxides but the latter exhibit a more complex mineralogy and are more reactive (Ponnamperuma et al, 1969). For example, manganese can exist in several oxidation states and around 36 oxidic manganese minerals are known (Ponnamperuma et al, 1969). Manganese and iron oxides, however, exhibit a marked tendency to form coprecipitates or mixed oxides.

This frequent association of iron and manganese oxides in soils and sediments has led to the simultaneous extraction of these phases. The most efficient method generally combines the action of a reducing agent, releasing divalent ferrous and manganous ions, with a reagent capable of keeping the liberated metals in solution. In this study, it was decided to separate the easily-reducible manganese oxide phase from the moderately-reducible iron oxide phase. Chao (1972) selectively dissolved the manganese oxides, without excessive concomitant attack on the iron oxides, using a weak acid reducing agent - 0.1M hydroxylamine hydrochloride in 0.01M nitric acid (NH_2OH. HCl/HNO_3). The common reagent mixtures used to remove the iron oxide fraction are acid ammonium oxalate (Schwertmann, 1964), sodium dithionite/citrate (Gupta and Chen, 1975) and hydroxylamine hydrochloride/acetic acid (Chester and

Hughes, 1967; Tessier et al, 1979; Wilber and Hunter, 1979; Farmer et al, 1980; Farmer, 1983). Acid ammonium oxalate is a milder reagent than the others (Salomons and Förstner, 1980) and the use of dithionite/citrate is fraught with analytical problems such as metal sulphide formation, zinc contamination and burner clogging in AA analysis (Tessier et al, 1979). For these reasons it was decided that $NH_2OH.HCl/HOAc$ would be employed in the sequential leaching scheme following extraction with $NH_2OH.HCl/HNO_3$.

Optimum times and solution concentrations for the selective removal of the easily reducible and moderately reducible fractions were determined experimentally using aluminium, iron and manganese as indicators. Elemental analyses were performed using FAAS (N_2O/C_2H_2 flame for aluminium; air/C_2H_2 flame for iron and manganese), with operating conditions and instrumental settings described in Section 2.6. Standards were prepared in the leaching solutions and reagent blanks were taken through the entire extraction procedure.

(i) Easily-Reducible Fraction

One gram samples of soil (grid numbers 59/1 and 135/3) were placed in 50ml polypropylene centrifuge tubes and 20ml $NH_2OH.HCl$ (0.04, 0.1, 0.5 and 1.0M)/ 0.01M HNO_3 added. Capped tubes were mechanically shaken for 30 mins, and centrifuged before the solutions were filtered into Sterilin containers. The procedure was repeated with 0.1M $NH_2OH.HCl$/0.01M HNO_3 for various shaking times (15, 30 and 60 mins). The solutions were analysed for aluminium, iron and manganese and the results plotted as shown in Figures 3.4 and 3.5 respectively.

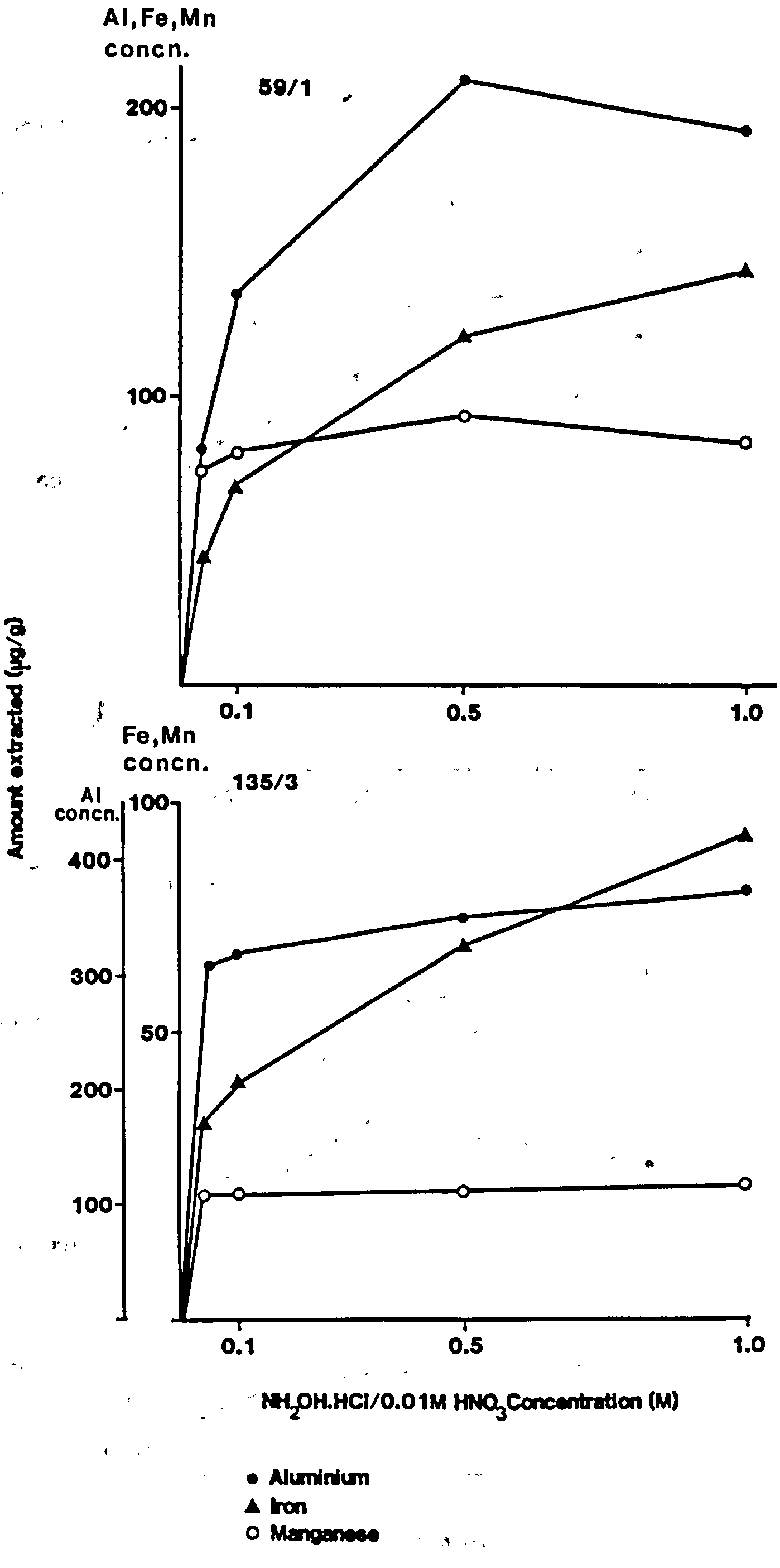


FIGURE 3.4 EFFECT OF REAGENT CONCENTRATION ($NH_2OH.HCl$/ 0.01M HNO_3) ON EXTRACTION EFFICIENCY OF EASILY REDUCIBLE FRACTION

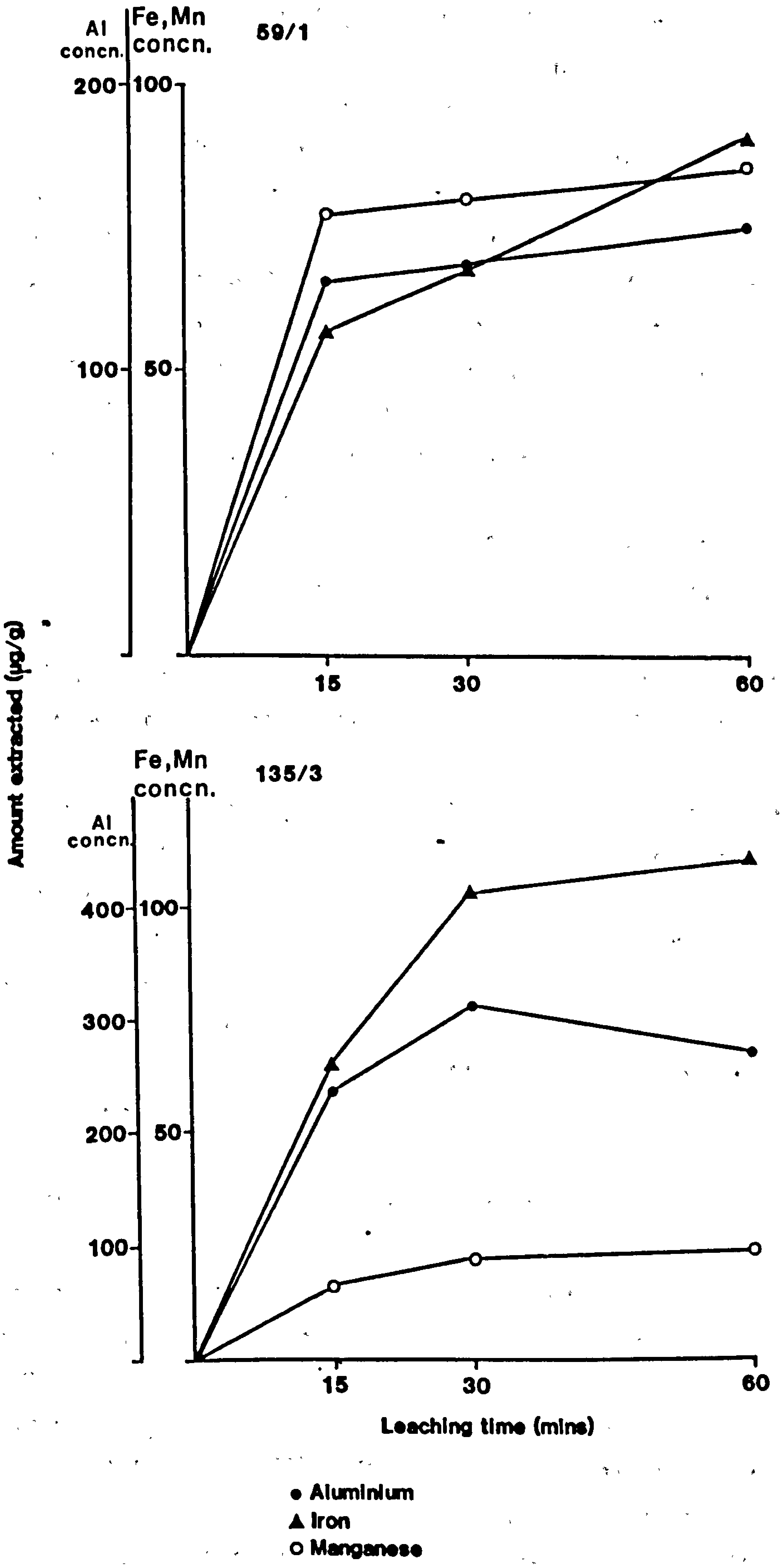


FIGURE 3.5 EFFECT OF LEACHING TIME ON 0.1M $NH_2OH.HCl$/ 0.01M HNO_3 EXTRACTION OF EASILY REDUCIBLE FRACTION

Easily-reducible manganese is quantitatively released using 0.1M $NH_2OH.HCl$/0.01M HNO_3 for 30 mins (Figures 3.4 and 3.5). This has also been confirmed by Lovell and Farmer (1983) in the leaching of manganese from manganese-rich (percent levels) Loch Lomond surface sediment. Extracted iron tends to increase with increasing $NH_2OH.HCl$ concentration and with time of extraction. Lovell and Farmer also found only slight removal of iron from Loch Lomond sediments by the 0.1M $NH_2OH.HCl$/0.01M HNO_3 solution. Therefore, it can be concluded, in agreement with Chao (1972), that the selective dissolution of amorphous and, possibly, pseudo-crystalline manganese oxides from soils and street dirts can be achieved using 0.1M $NH_2OH.HCl$/0.01M HNO_3 (pH2) over an equilibration time of 30 mins.

Under these conditions, the more readily soluble manganese oxides will be released with little dissolution of the crystalline forms or of iron oxides (except the very reactive amorphous oxides which constitute only a minor proportion of total iron). Apparent variations in removal of aluminium may be attributable to the fact that only a very small amount of aluminium, relative to the total matrix aluminium, is extracted. It should be noted that any trace metals released are prevented by the pH of this solution (pH2) from forming insoluble hydroxides or basic salts.

(ii) Moderately-Reducible Fraction

The procedure is similar to that employed for the easily reducible fraction except that 20ml $NH_2OH.HCl$ (0.5, 1.0 and 2.0M) in 25% (v/v) acetic acid was used with a shaking period of 4 hours. The procedure was repeated using 1M $NH_2OH.HCl$/25% HOAc for different shaking times (2, 4, 8 and 24 hours). The results, presented in Figures 3.6 and 3.7 respectively, indicate that progressively

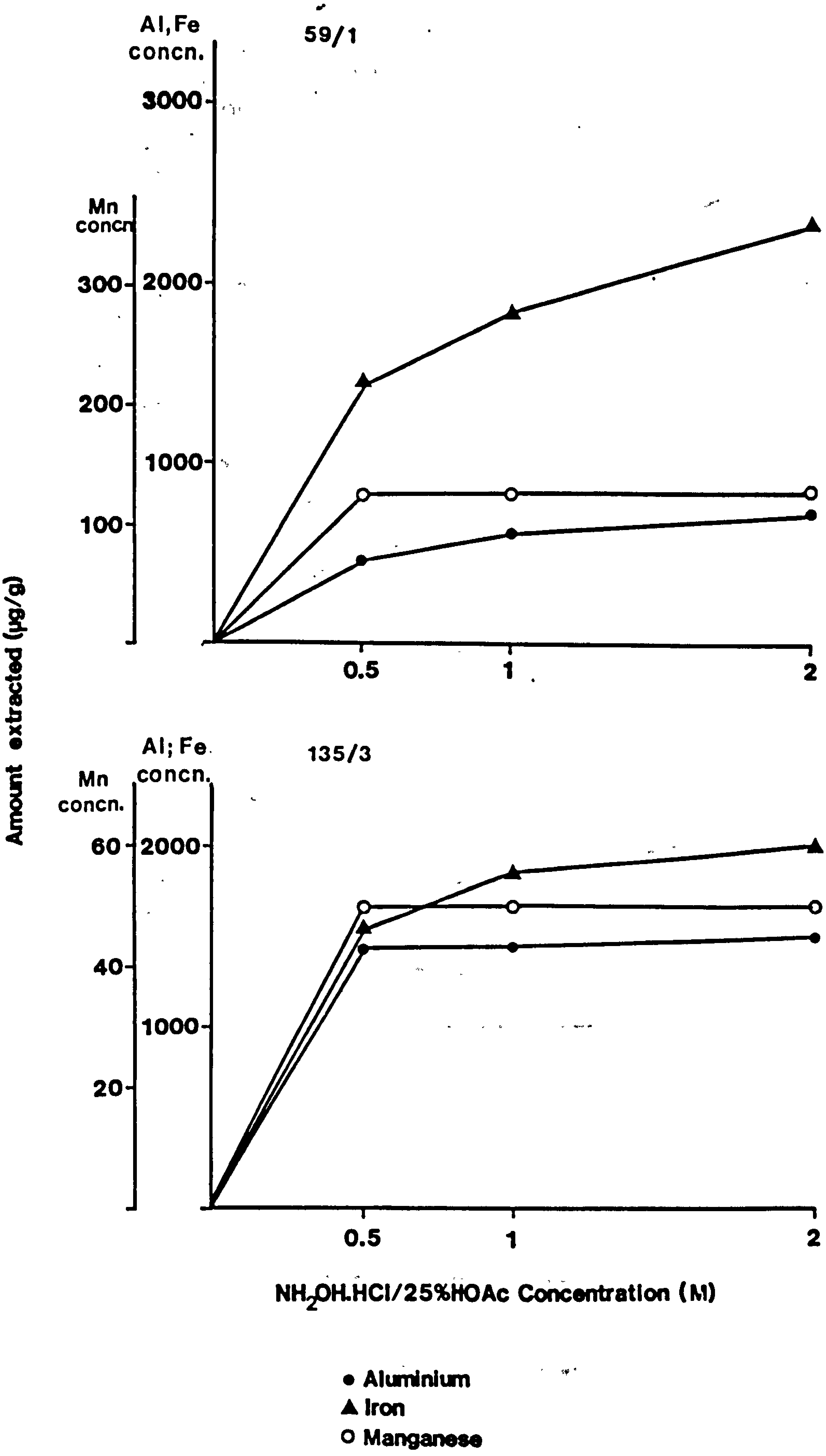


FIGURE 3.6 EFFECT OF REAGENT CONCENTRATION ($NH_2OH.HCl$/25% HOAc) ON EXTRACTION OF MODERATELY REDUCIBLE FRACTION

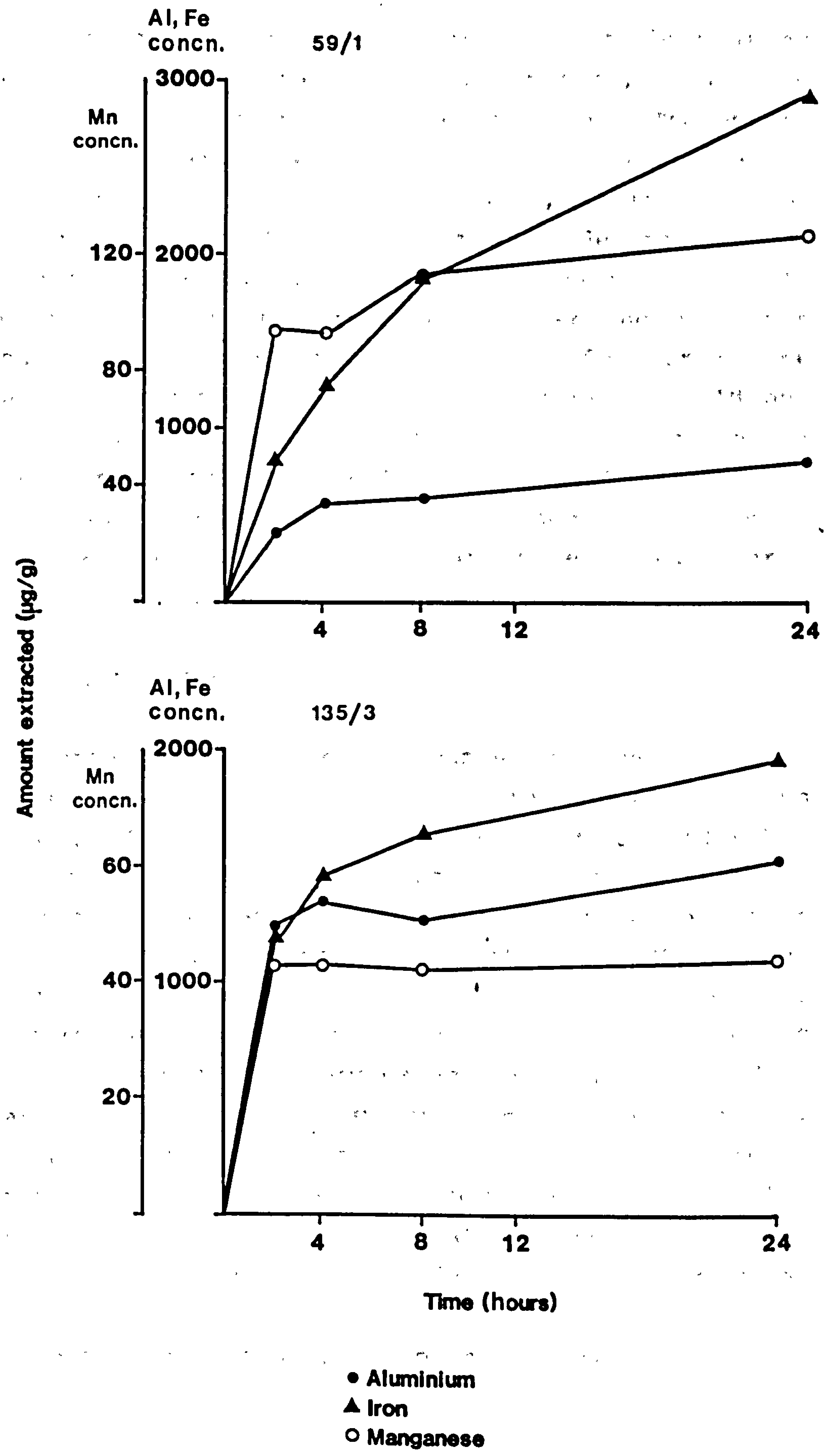


FIGURE 3.7 EFFECT OF LEACHING TIME ON EXTRACTION OF MODERATELY REDUCIBLE FRACTION

more aluminium and iron are removed with increasing solution concentration and equilibration time, suggesting some attack on the crystal lattice structure. The amount of manganese released appears independent of solution concentration but was slightly elevated, in the case of 59/1, over longer shaking periods. The delineation of fractions is evidently more distinct for easily-reducible manganese oxides than for moderately-reducible iron oxides. However, extraction curves for iron are noticeably less steep at solution concentrations >1M and after 4 hours. Therefore, to ensure minimal attack on the residual fraction, 1M $NH_2OH.HCl$/25% HOAc with an equilibration time of 4 hours was chosen to release moderately-reducible iron and manganese (i.e. poorly crystalline forms).

3.3.2.4 ORGANIC MATTER

Organic matter in the form of humus, can be found in almost all terrestrial and aquatic environments (Schnitzer, 1978). It is known to exert considerable control over trace metal reactions and plays an important role in the cycling and accumulation of trace metals in soils and sediments (Bloomfield et al, 1976; Nissenbaum and Swaine 1976; Cheshire et al, 1977). Natural organic matter makes a significant contribution to the soil's cation exchange capacity (Davies and Davies, 1965) and is involved in trace-metal complexation and peptisation. Divalent and trivalent cations are bound by humus through the formation of very stable complexes, especially chelates. When discarded organic matter decomposes in the upper horizons of soil, through microbial action under aerobic conditions, complexed trace metals are released, becoming potentially available to the biota.

It has been estimated that between 70-80% of organic matter in predominantly inorganic soils consists of humic materials, i.e. humic acid, fulvic acid and humin, with the remainder composed of polysaccharides and protein-like substances (Schnitzer, 1978). Humic substances derive from the biological degradation of plant and animal residues and from synthetic activities of microorganisms (Schnitzer, 1978). Characteristically, humic materials have a relatively high content of oxygen-containing functional groups (CO_2H, phenolic and alcoholic OH, ketonic and quinonoid $C = O$) (Kerndorff and Schnitzer, 1980). It is through the functional groups that these materials are thought to interact with metal ions, metal oxides, metal hydroxides and minerals to form metal-organic associations of widely differing chemical and biological stabilities and characteristics (Kerndorff and Schnitzer, 1980). Schnitzer (1978) reported that on average, over a wide range of soils, fulvic acid is composed of lower molecular weight compounds and is usually more acidic, containing more functional groups. However, humic acid, because of its greater abundance, is more important in trace metal binding than fulvic acid, e.g. Nriagu reported substantially greater amounts of trace elements in association with the humic acid fraction in lacustrine sediments (Nriagu and Coker, 1980).

Although humic components can be selectively extracted using sodium hydroxide (Schnitzer and Khan, 1972), the usual procedure for the degradation of organic matter, releasing complexed trace metals, is based on chemical oxidation. Acidified hydrogen peroxide combines strong oxidation power with selectivity and has been frequently employed (Gupta and Chen, 1975; Tessier et al, 1979; Farmer et al, 1980; Salomons and Förstner, 1980; Harrison et al, 1981; Farmer, 1983). However, certain forms of organic matter are not completely broken down, e.g.

paraffin-like material and resistant structural (non-humified) organic matter residues (Jackson, 1958). While these can be degraded using stronger oxidising agents such as nitric acid, either alone or in combination with hydrochloric or perchloric acids, some non-organic material will also be dissolved (Tessier et al, 1979). Consequently, in this study, hydrogen peroxide was selected to remove organically-bound trace metals. The adopted procedure incorporated a second shaking step using ammonium acetate to prevent readsorption of extracted metals onto oxidised material (Gupta and Chen, 1975).

3.3.2.5 RESIDUAL

The residual material remaining after selective sequential extraction consists mainly of detrital aluminosilicate materials (primary and secondary), resistant sulphides and some refractory organic material (Tessier et al, 1979). Aluminosilicates often contain substantial amounts of trace metals selectively occluded in the crystal lattice during rock formation (West, 1981). The majority of trace metals held in this way are unavailable and would only be released through weathering over long, possibly geological, time periods.

Procedures for dissolving siliceous materials usually involve attack with strong mineral acids such as hydrofluoric acid in combination with nitric or perchloric acid (Section 2.6.1). However, in this study, total dissolution of aluminosilicates was effected using the aqua regia/HF/H_3BO_3 decomposition procedure described in Section 2.6 although, occasionally, certain refractory carbonaceous materials may be resistant (Farmer and Gibson, 1981).

3.3.3 DILUTE HYDROCHLORIC ACID-SOLUBLE

Street dirts and dusts are recognised as potential sources of excessive amounts of harmful trace metals, such as lead, to young children, particularly in urban areas, through inadvertent ingestion (Duggan, 1980; 1983a; Royal Commission, 1983). The intake of such metals is extremely difficult to measure (Royal Commission, 1983). In this study the objective was to estimate the intake and the possible uptake of trace metals from street dirt by simulating human stomach acidity (pH1), using a dilute solution of hydrochloric acid (0.07M) which is crudely representative of stomach conditions (Pencils and Graphic Instruments [Safety] Regulations, 1974; Duggan and Williams, 1977; Day et al,1979; Harrison, 1979).

Leaching time and extraction temperature were determined experimentally: 1g samples of street dirt (samples 74/3, 218/2) were shaken with 20ml of 0.07M hydrochloric acid in Erlenmeyer flasks partially immersed in a water bath for 1 hour at varying temperatures (20, 30, 37°C). Samples were also mechanically shaken in centrifuge tubes for different time intervals (0.5, 1, 2 and 4 hours) at room temperature (20°C). All samples were centrifuged, filtered and analysed for lead and zinc using FAAS.

The results (Figure 3.8) indicate that the trace metal concentrations of the hydrochloric acid extracts are essentially unaltered within this temperature range and after a leaching period of 1 hour. An extraction period of 1 hour, at room temperature, was therefore adopted for this study.

3.3.4 SUMMARY OF LEACHING METHODS ADOPTED

On the basis of the literature studies and the preliminary experimental work descirbed in Sections 3.3.2 and 3.3.3, the following extraction methods and

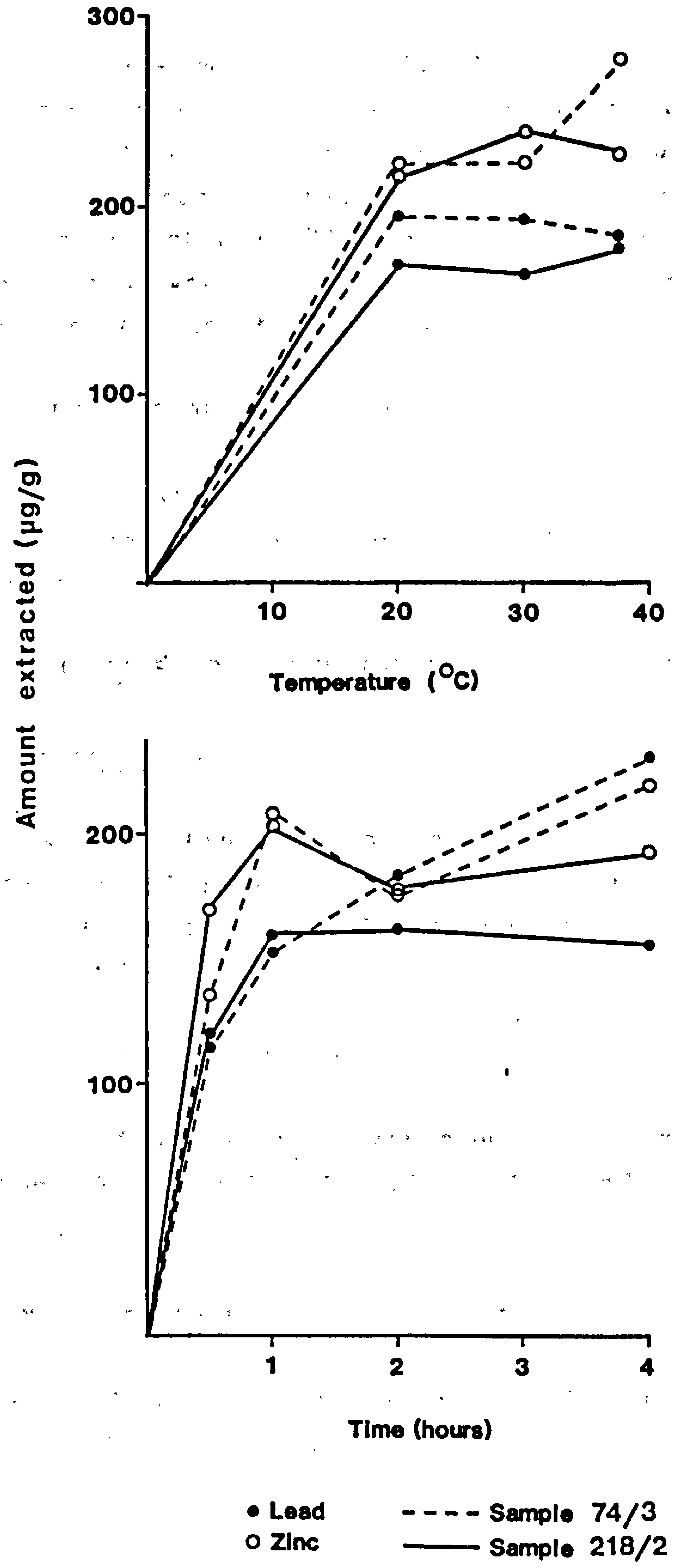


FIGURE 3.8 EFFECT OF TEMPERATURE AND LEACHING TIME ON EXTRACTION OF TRACE METALS FROM STREET DIRT USING DILUTE HYDROCHLORIC ACID

procedures were adopted (3.3.4.1 - 3.3.4.3). Reagent volumes correspond to sample weights of 1g except in the sequential scheme, (Figure 3.9), where 1g was used for the initial extraction and resulting residues were used for subsequent steps; all sample solutions, except for the residual, were centrifuged and filtered through Whatman's 40 Ashless filter paper.

3.3.4.1 EXCHANGEABLE FRACTION

Samples were extracted at 20°C for 4 hours with 25ml ammonium acetate solution (1MNH_4OAc, pH7.0) with continuous shaking. The volume was made up to 50ml.

3.3.4.2 MULTI-STEP SEQUENTIAL LEACHING SCHEME

(i) Carbonate Bound

Samples were continuously agitated at 20°C for 5 hours with 15ml 1M sodium acetate (NaOAc) adjusted to pH5 with acetic acid (HOAc). The solution was acidified with 1ml concentrated HNO_3.

(ii) Easily-Reducible Fraction

The residue from (i) was extracted for 30 mins at 20°C with 20ml 0.1M $NH_2OH.HCl$/0.01M HNO_3 under continuous agitation.

(iii) Moderately-Reducible Fraction

The residue from (ii) was shaken for 4 hours at 20°C with 20ml 1M $NH_2OH.HCl$/25% (v/v) HOAc.

(iv) Organic Matter

To the residue from (iii) was added 3ml 0.02M HNO_3 and 5ml 30% H_2O_2 adjusted to pH2 with concentrated HNO_3, and the solution was heated to 85°C in a water bath with occasional agitation. After 2 hours the temperature was reduced to 40-50°C and a further 3ml of the H_2O_2 solution added. The mixture was again heated at 85°C with occasional agitation for 3 hours or until the solution had completely evaporated. After cooling, 5ml 3.2M NH_4OAc in 20% (v/v) HNO_3were added and the sample continuously shaken for a further 30 mins at 20°C. The sample was washed with 5ml water which was combined with the original solution and the volume made up to 25ml.

(v) Residual

The residue from (iv) was air-dried at 25-30°C for 12 hours. A subsample (0.1g) was totally dissolved using the procedure described for total digestion of silicous material in Section 3.3.1.

3.3.4.3 DILUTE HYDROCHLORIC ACID-SOLUBLE

Street dirt samples were continuously agitated at 20°C for 1 hour with 20ml HCl (0.07M, pH ~1).

3.4 APPLICATION OF CHEMICAL PROCEDURES

Exchangeable lead, zinc, copper and cadmium were determined in most soil (ca. 440) and street dirt (ca. 220) samples. In addition, exchangeable lead was measured in 8 soils collected from a natural lead mineralised area (Leadhills, Lanarkshire) for comparison. Results were obtained using FAAS (air/C_2H_2) for lead, copper and zinc, and GFAAS for cadmium, with instrumental settings as listed in Table 2.3 and furnace conditions for cadmium, obtained experimentally, as described for aqueous solutions in Table 2.2.

Total lead, zinc, copper and cadmium were measured in ca. 390 soil samples from which a subset (90 samples), representative of different concentration ranges and sample categories, was selected for a more detailed investigation using the six-step sequential chemical leaching procedure (Figure 3.9). The same scheme was applied to 60 street dirt samples chosen to reflect the exchangeable concentration ranges. Total and residual concentrations were determined using GFAAS while FAAS (air/C_2H_2) was employed for the other fractions. Iron and manganese, were also measured in the six-fraction study, using FAAS (air/C_2H_2 with the exception of N_2O/C_2H_2 for the residual fraction).

Finally, dilute hydrochloric acid-soluble lead, zinc, copper and cadmium were determined using FAAS in most street dirts (ca. 220).

3.5 RESULTS

Individual soil exchangeable and total, six-fraction study and street dirt exchangeable and hydrochloric acid-soluble results are listed in Appendices 2, 3 and 4 respectively. The summarised data are presented in Chapter 4 as follows: Section 4.1-soil results (total, exchangeable, two-fraction and six-fraction studies); Section 4.2-street dirt results (exchangeable, hydrochloric acid-soluble and six-fraction study).

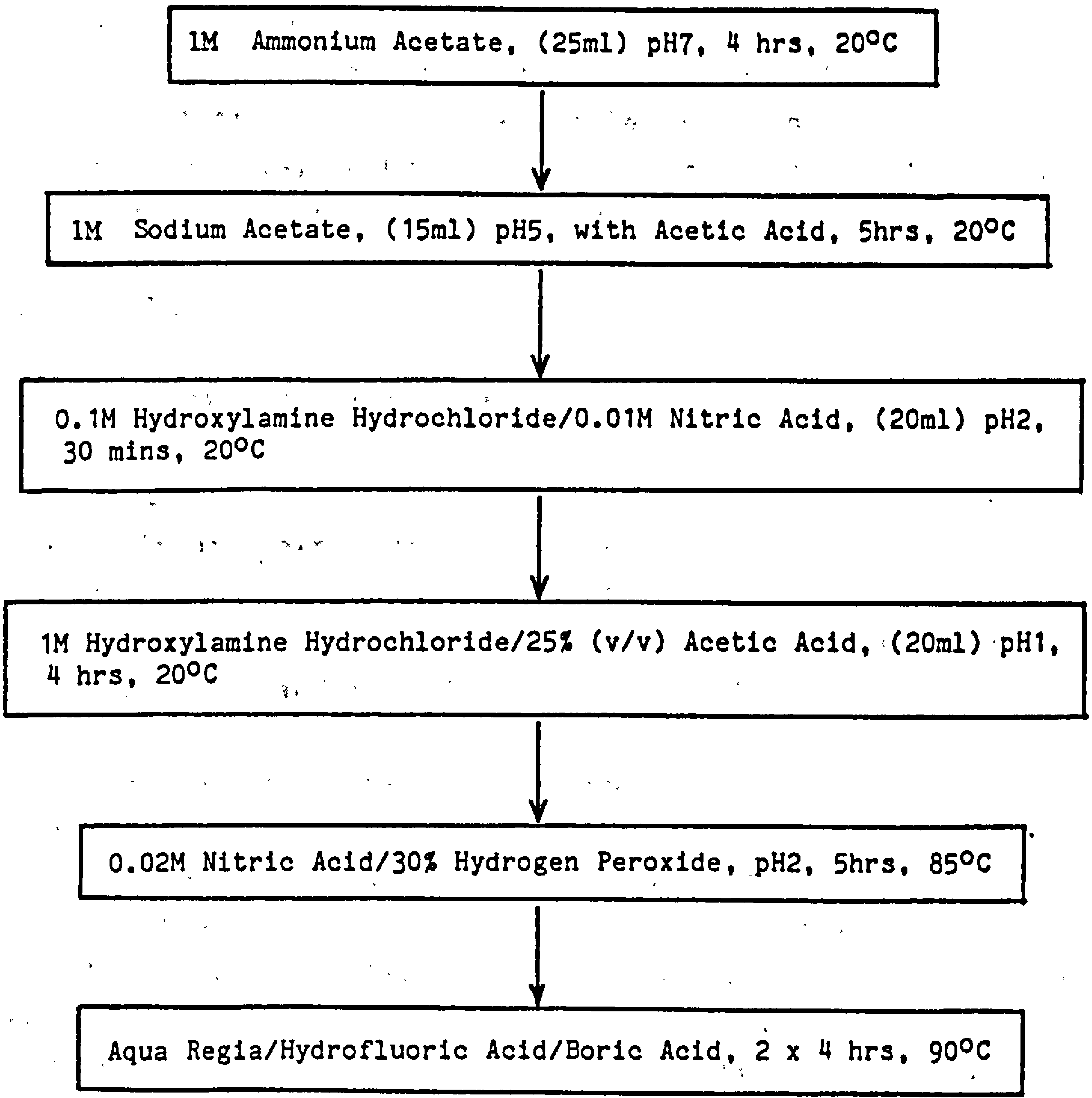


FIGURE 3.9 SCHEMATIC REPRESENTATION OF THE SIX-FRACTION SEQUENTIAL LEACHING SCHEME

CHAPTER 4 - A SURVEY OF TRACE METAL CONTAMINATION AND CHEMICAL PARTITIONING IN GLASGOW URBAN SOILS AND STREET DIRT: PART B: RESULTS AND INTERPRETATION

The data generated by the procedures of Chapter 3 and listed in Appendices 2-4 are summarised and reviewed in the Tables, Figures and text of Sections 4.1 and 4.2 of this chapter. This enables relevant discussion of the major findings, with respect to the study objectives (Section 1.5), to follow in Section 4.3.

4.1 SOILS

4.1.1 TOTAL CONCENTRATIONS

The ranges of total concentrations of lead, zinc, copper and cadmium, expressed in μg/g dry weight, in Glasgow soils are summarised in Table 4.1. Results are reported for individual land-use categories (garden soils, parkland etc) and for all samples combined.

The trace-element data are presented as class frequency distributions in Figures 4.1-4.4. Distribution patterns for all elements in all soil categories are strongly skewed towards the higher concentrations, producing similar shaped 'all-soils' curves, but the majority of results are <350μg/g lead (84%), <300μg/g zinc (84%), <140μg/g copper (83%) and <0.8μg/g cadmium (82%). This skewed frequency distribution pattern, often found in contaminated systems (Davies, 1980b), is suggestive of a log-normal distribution. Plotting the logs of the data as cumulative percentage frequencies on arithmetic probability paper produces a straight line for each element (Figures 4.5-4.8) confirming the log-normal distributions (Davies, 1983a). The data, therefore, must first be converted to their common logarithms if the statistical treatment of normal (Gaussian) distributions

TABLE 4.1 TRACE METAL CONTENT OF GLASGOW SOILS (0-5cm), 1981

		Gardens	Open Spaces	Parks	Agricultural	All
	No. of Samples	80	169	103	45	397
	Maximum	1310	1900	1260	749	1900
	Minimum	37	23	22	24	22
	Mean	244	219	226	136	216
LEAD	Std. devn.	191	244	190	122	211
(µg/g)	Median	190	140	141	106	145
	Geom. mean	196	157	168	107	160
	Upper 95%	722	714	795	400	714
	Lower 95%	53	35	36	29	36
	No. of Samples	80	168	102	44	394
	Maximum	1170	1840	630	384	1840
	Minimum	40	18	39	30	18
	Mean	240	213	193	157	207
ZINC	Std. devn.	173	204	119	91	170
(µg/g)	Median	194	158	158	122	165
	Geom. mean	203	169	163	131	169
	Upper 95%	608	608	520	474	580
	Lower 95%	68	47	51	36	49
	No. of Samples	77	166	99	46	388
	Maximum	426	925	443	305	925
	Minimum	15	4.1	14	3.4	3.4
	Mean	102	105	98	56	97
COPPER	Std. devn.	80	121	78	48	98
(µg/g)	Median	72	65	79	47	69
	Geom. mean	80	73	75	42	70
	Upper 95%	317	369	338	215	343
	Lower 95%	20	14	17	8	14
	No. of Samples	77	162	93	44	376
	Maximum	4.07	2.75	1.5	1.05	4.07
	Minimum	0.1	0.1	0.1	0.13	0.1
	Mean	0.69	0.51	0.49	0.43	0.53
CADMIUM	Std. devn.	0.60	0.40	0.32	0.23	0.43
(µg/g)	Median	0.45	0.38	0.36	0.37	0.39
	Geom. mean	0.53	0.42	0.41	0.37	0.43
	Upper 95%	2.24	1.46	1.31	1.12	1.54
	Lower 95%	0.12	0.03	0.13	0.12	0.12

Upper and lower 95% probability ranges were calculated from logarithm transformed values.

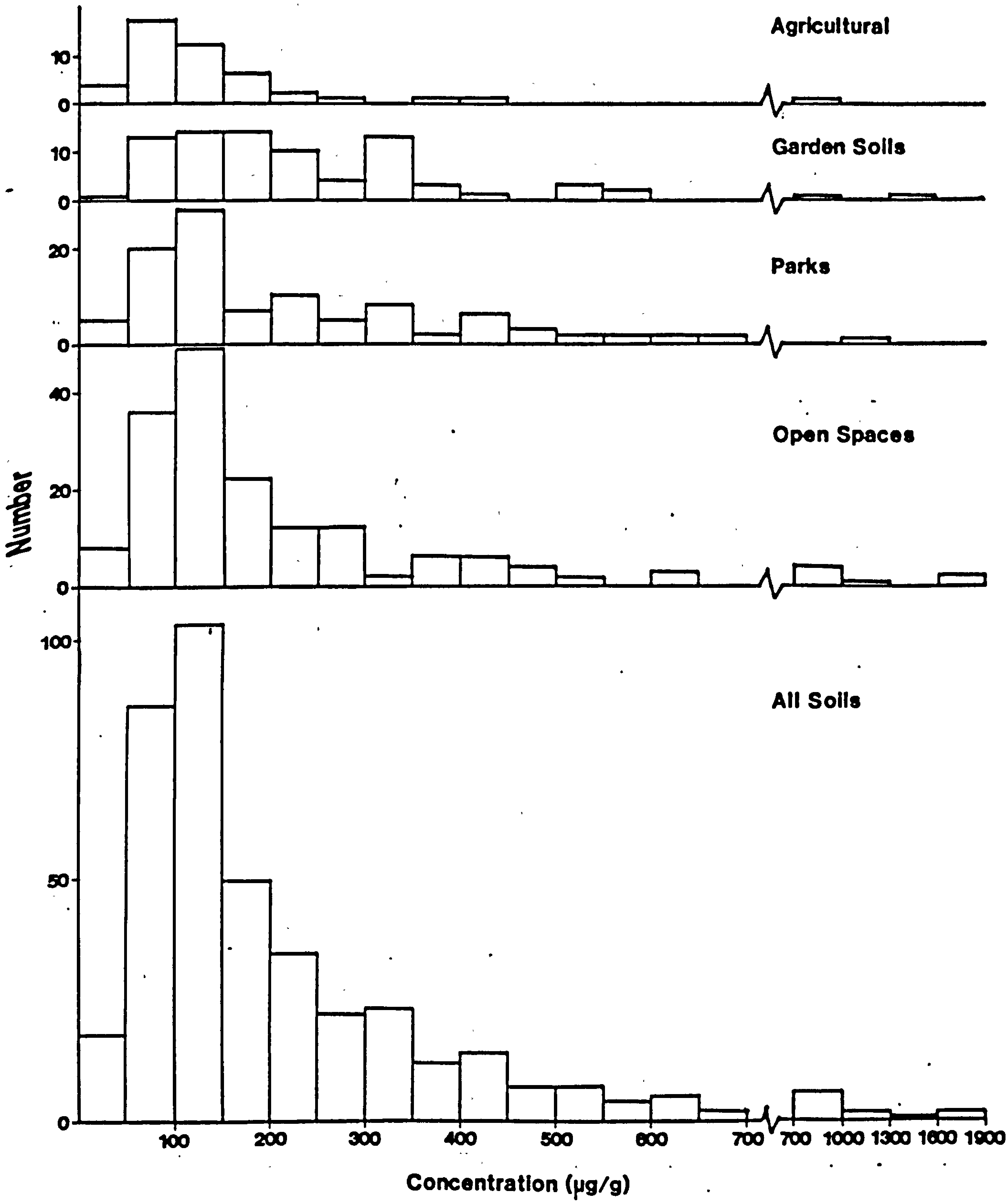


FIGURE 4.1 FREQUENCY DISTRIBUTION OF SOIL TOTAL LEAD

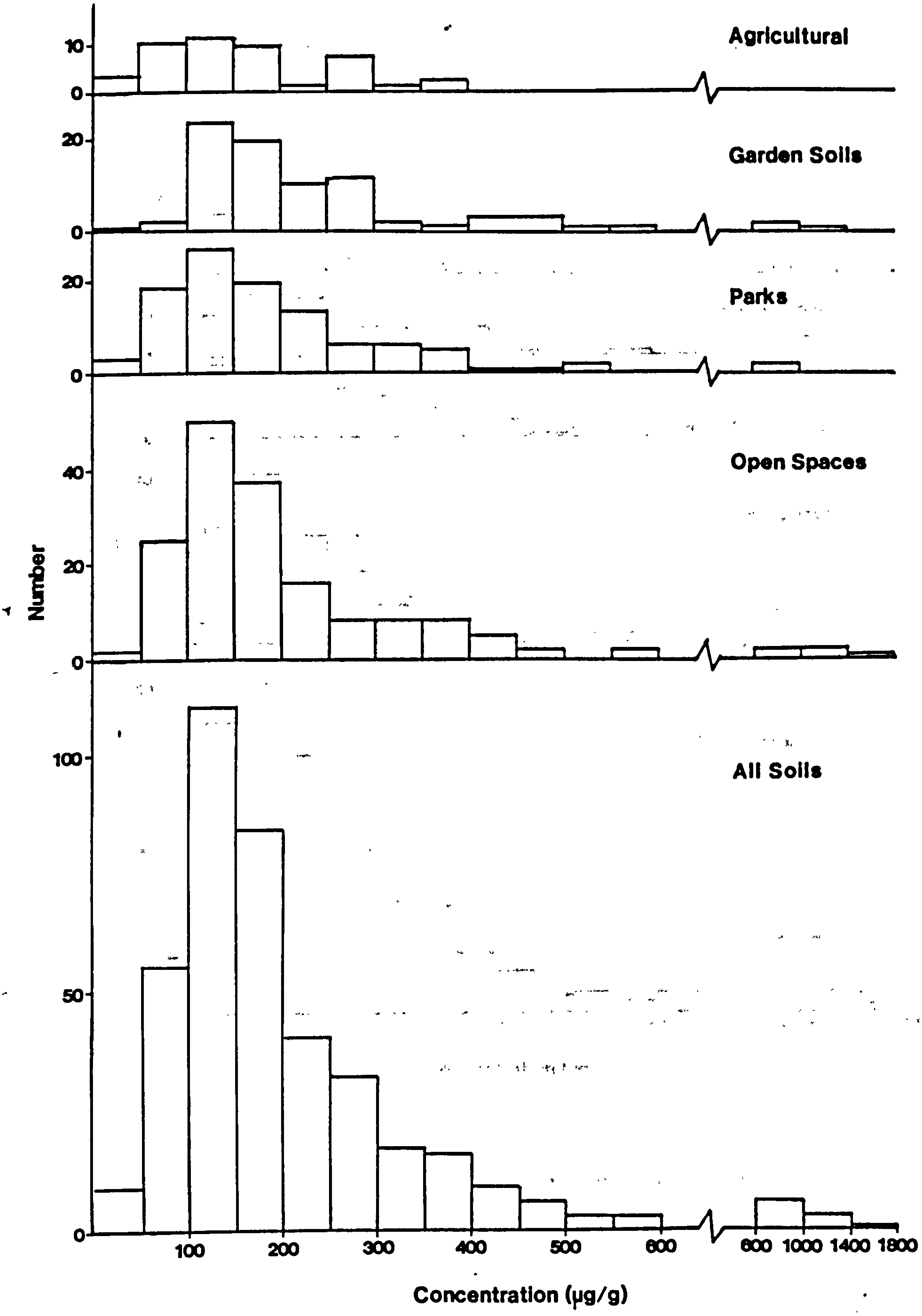


FIGURE 4.2 FREQUENCY DISTRIBUTION OF SOIL TOTAL ZINC

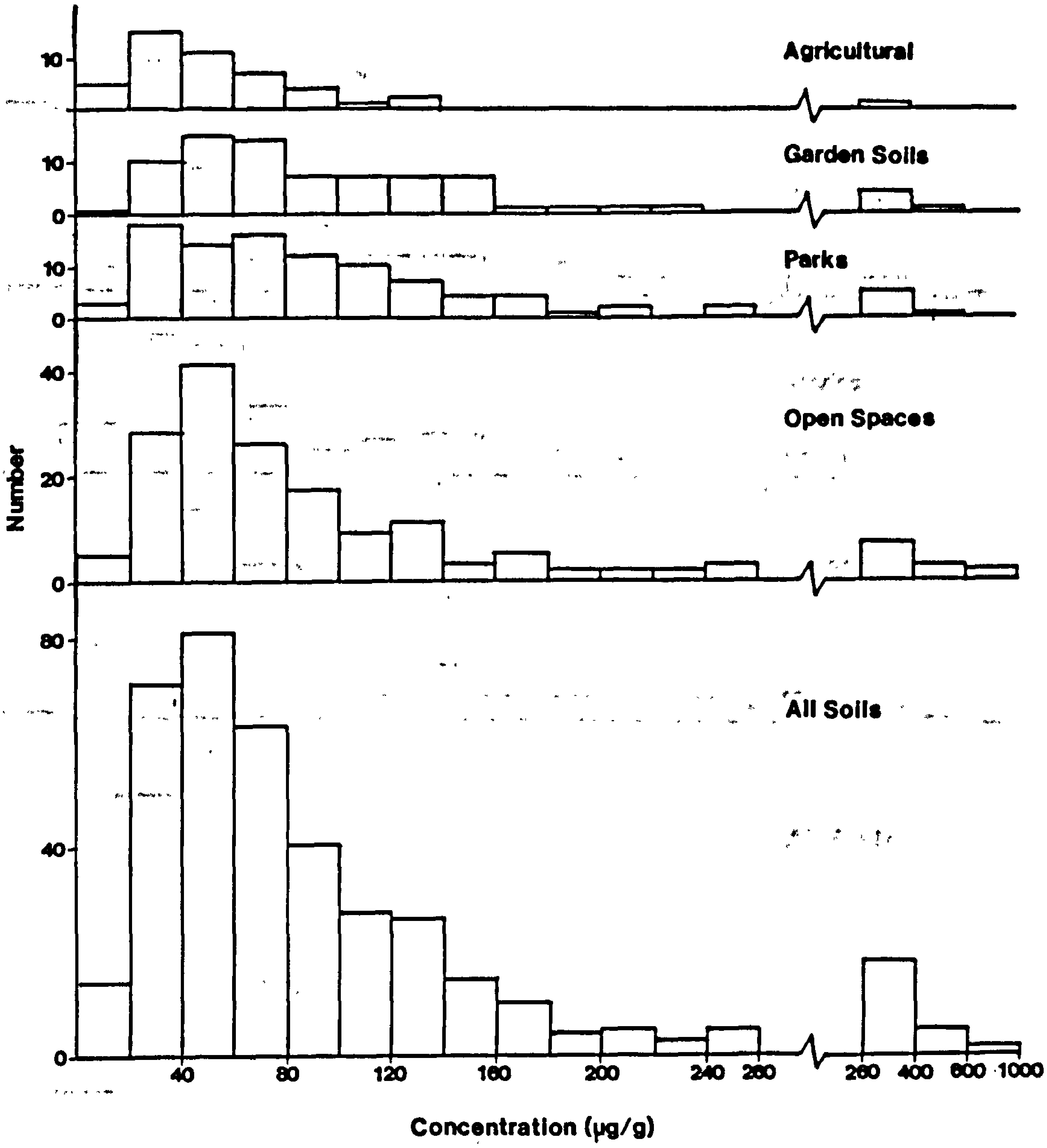


FIGURE 4.3 FREQUENCY DISTRIBUTION OF SOIL TOTAL COPPER

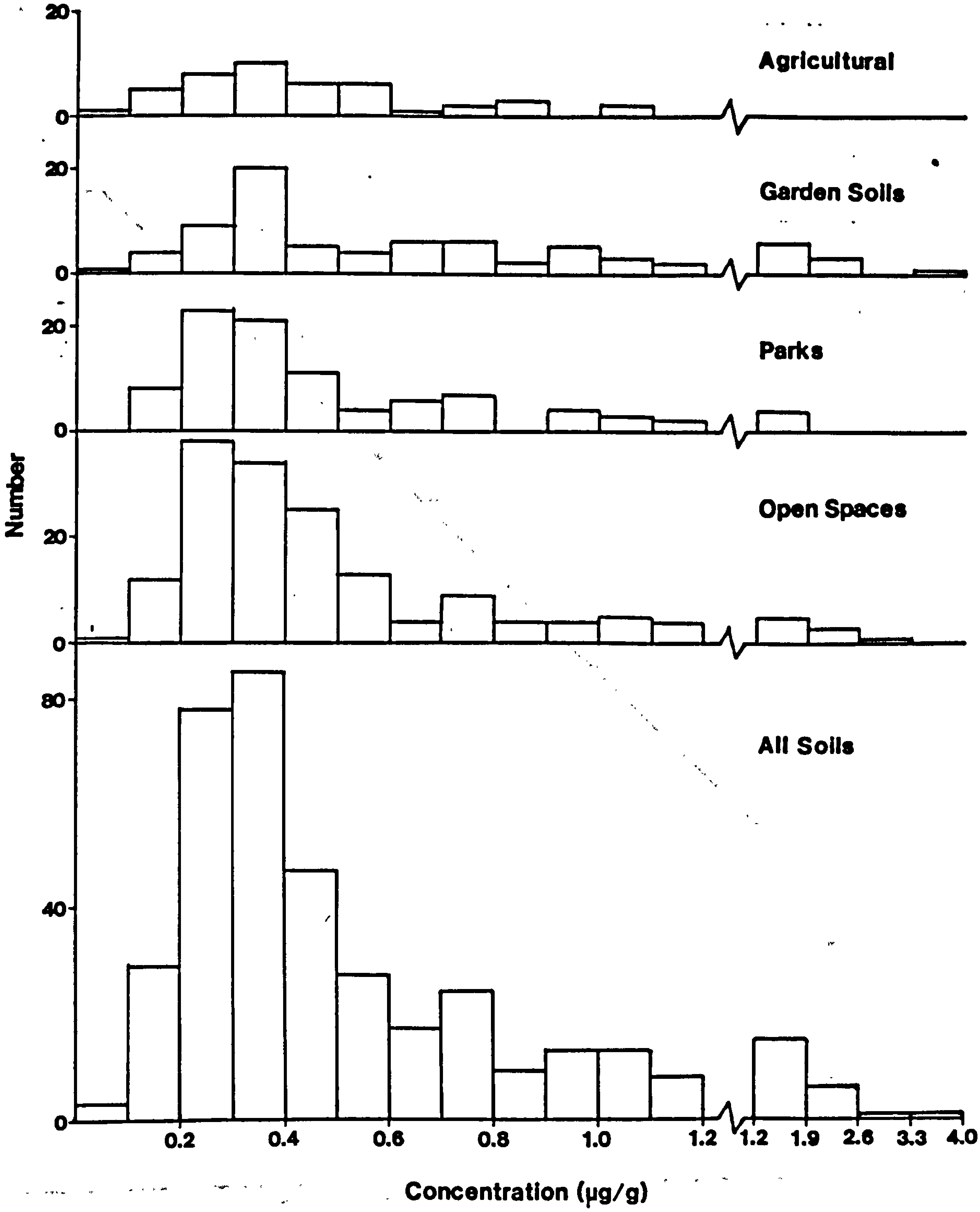
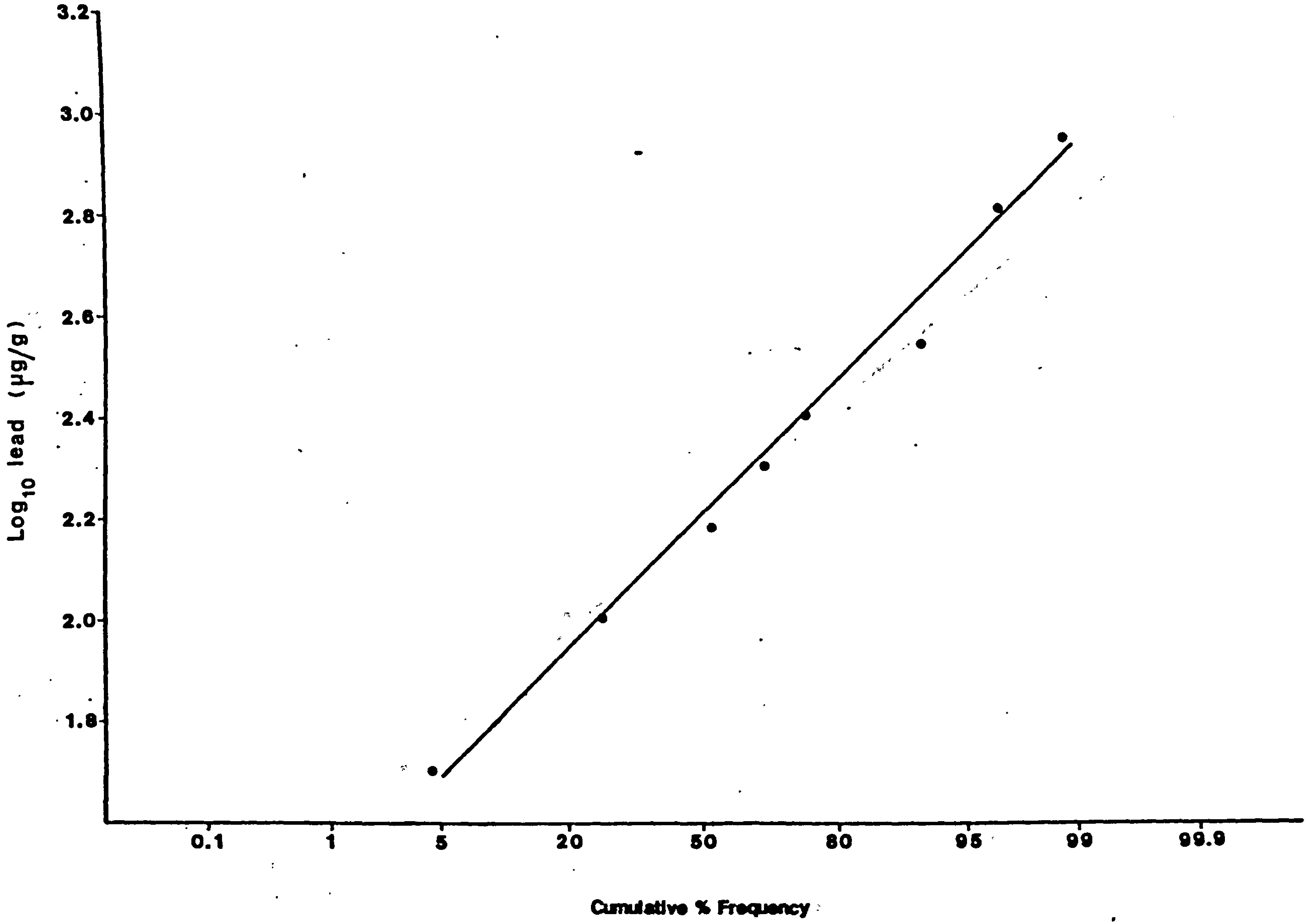


FIGURE 4.4 FREQUENCY DISTRIBUTION OF SOIL TOTAL CADMIUM



<u>FIGURE 4.5</u> CUMULATIVE PERCENTAGE FREQUENCY PLOT OF SOIL TOTAL LEAD

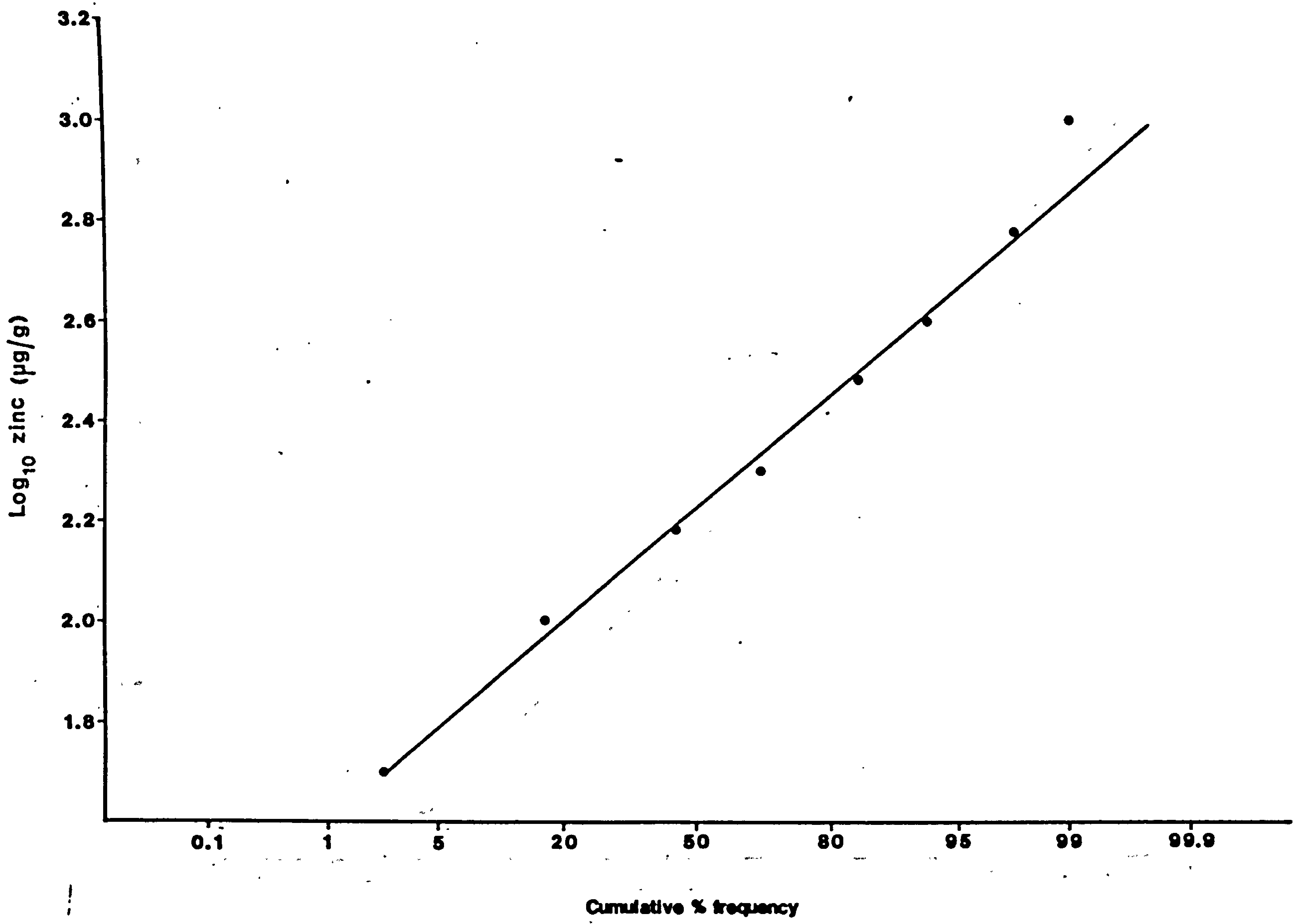


FIGURE 4.6 CUMULATIVE PERCENTAGE FREQUENCY PLOT OF SOIL TOTAL ZINC

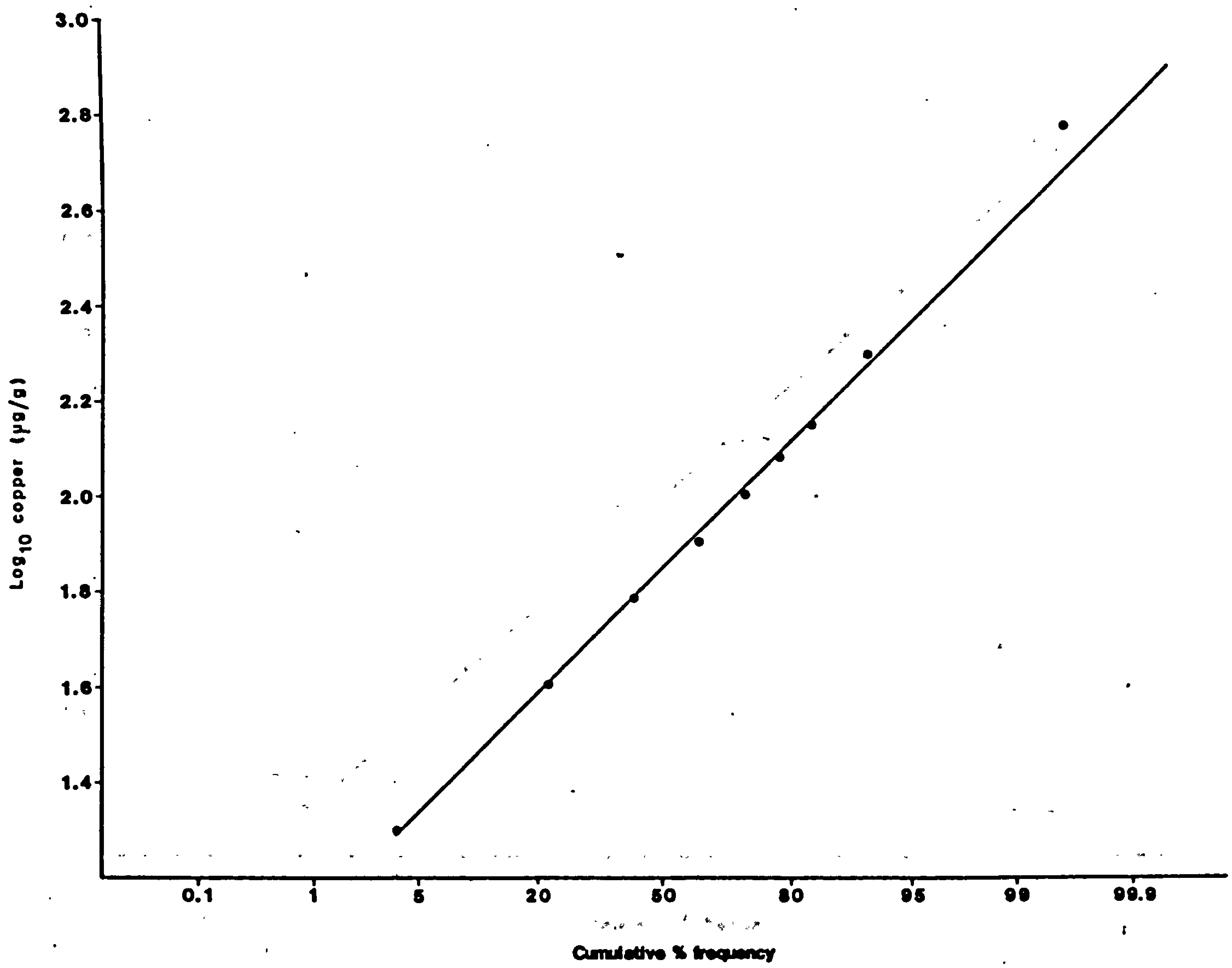


FIGURE 4.7 CUMULATIVE PERCENTAGE FREQUENCY PLOT OF SOIL TOTAL COPPER

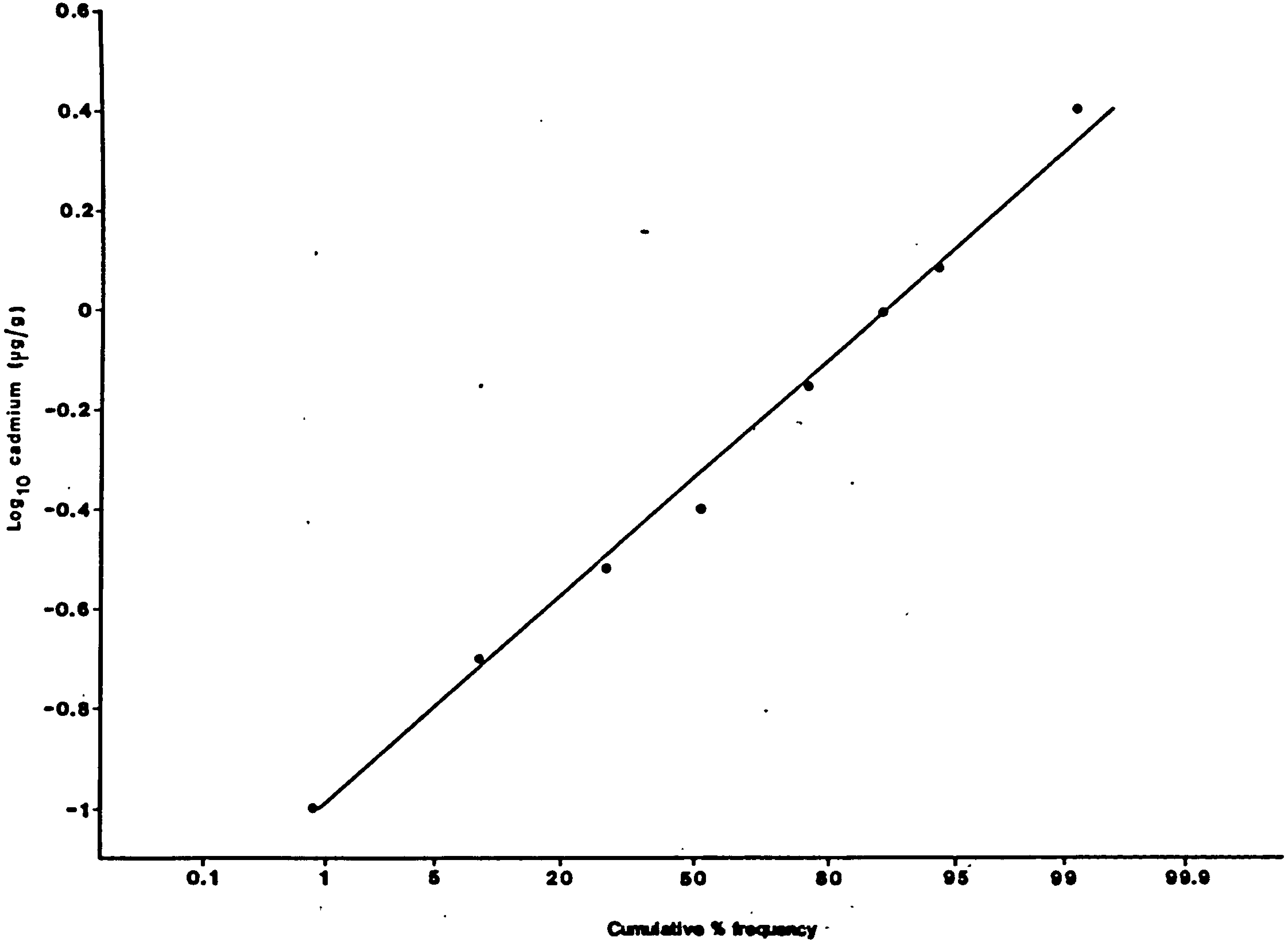


FIGURE 4.8 CUMULATIVE PERCENTAGE FREQUENCY PLOT OF SOIL TOTAL CADMIUM

__FIGURE 4.9__ GEOGRAPHICAL DISTRIBUTION OF SOIL TOTAL LEAD

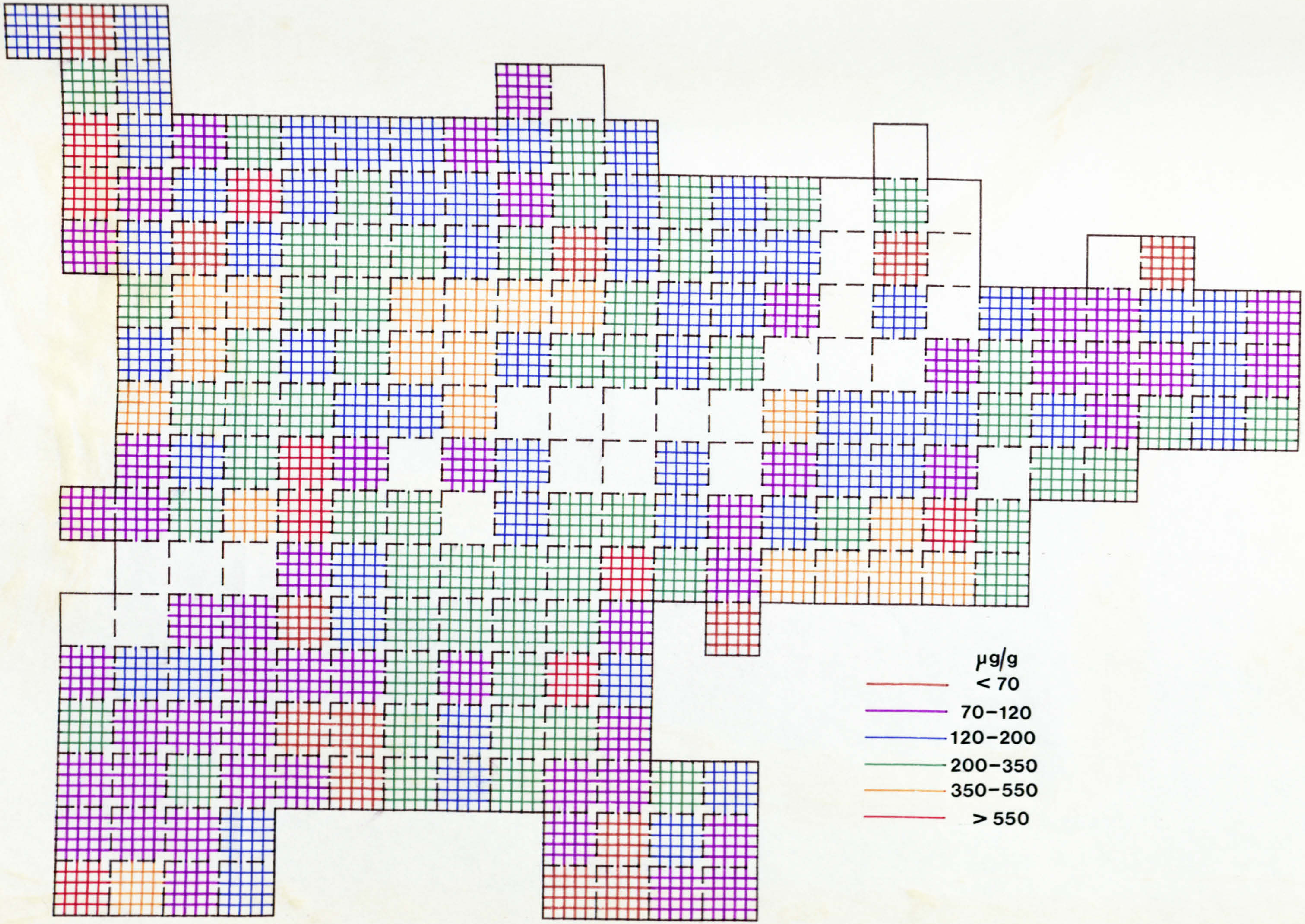

μg/g
< 70
70–120
120–200
200–350
350–550
> 550

FIGURE 4.10 GEOGRAPHICAL DISTRIBUTION OF SOIL TOTAL ZINC

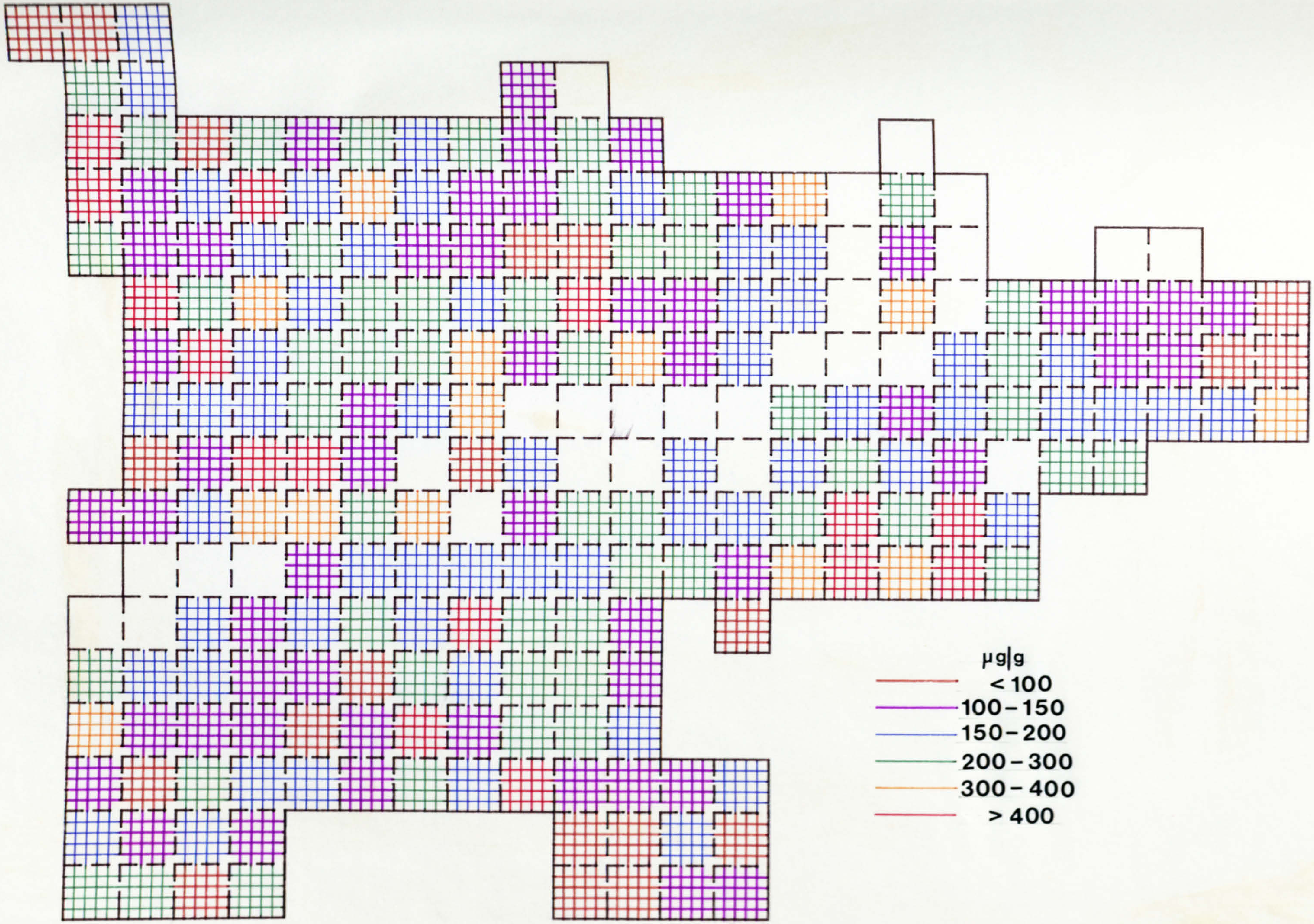

µg|g
< 100
100 – 150
150 – 200
200 – 300
300 – 400
> 400

FIGURE 4.11 GEOGRAPHICAL DISTRIBUTION OF SOIL TOTAL COPPER

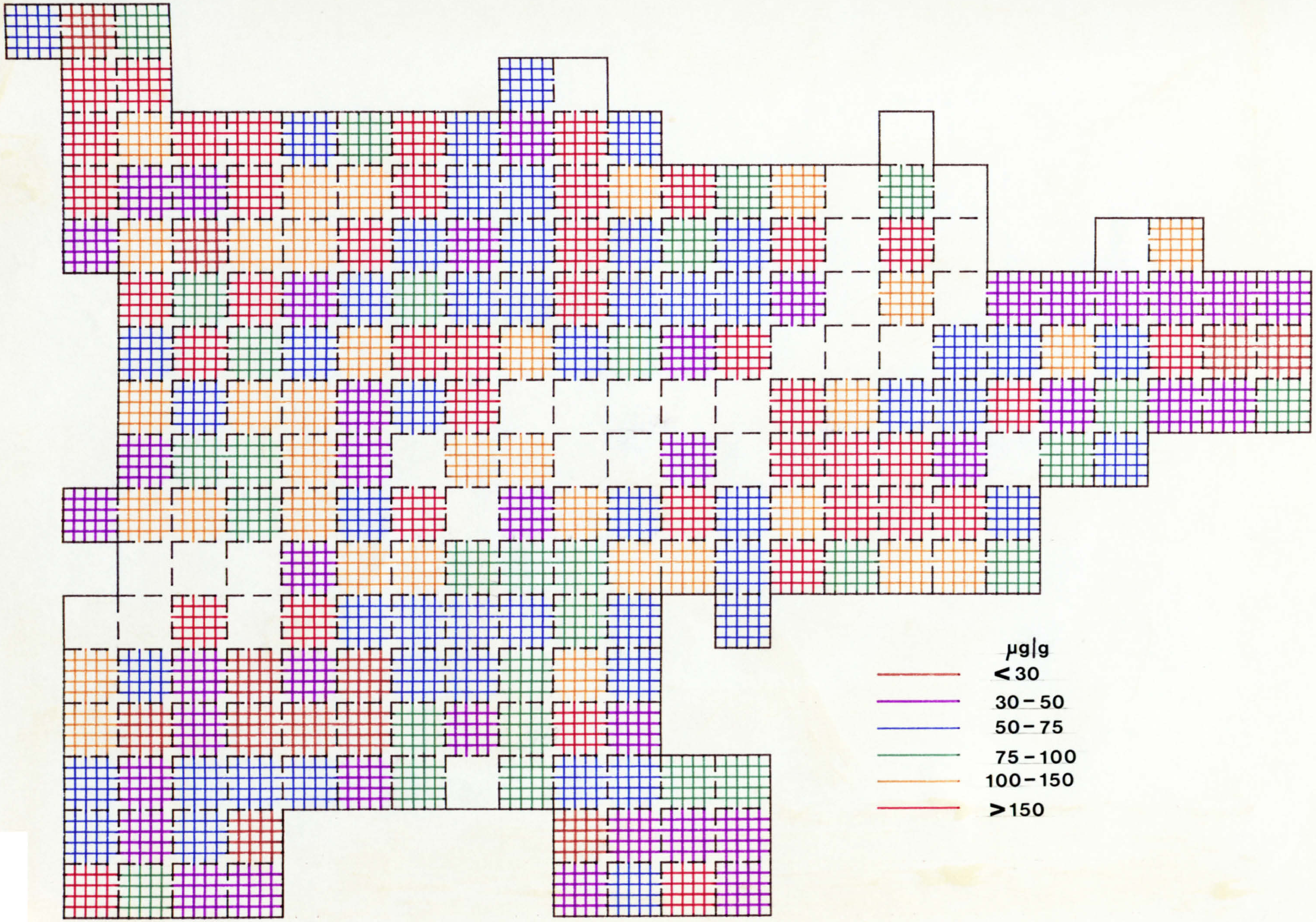
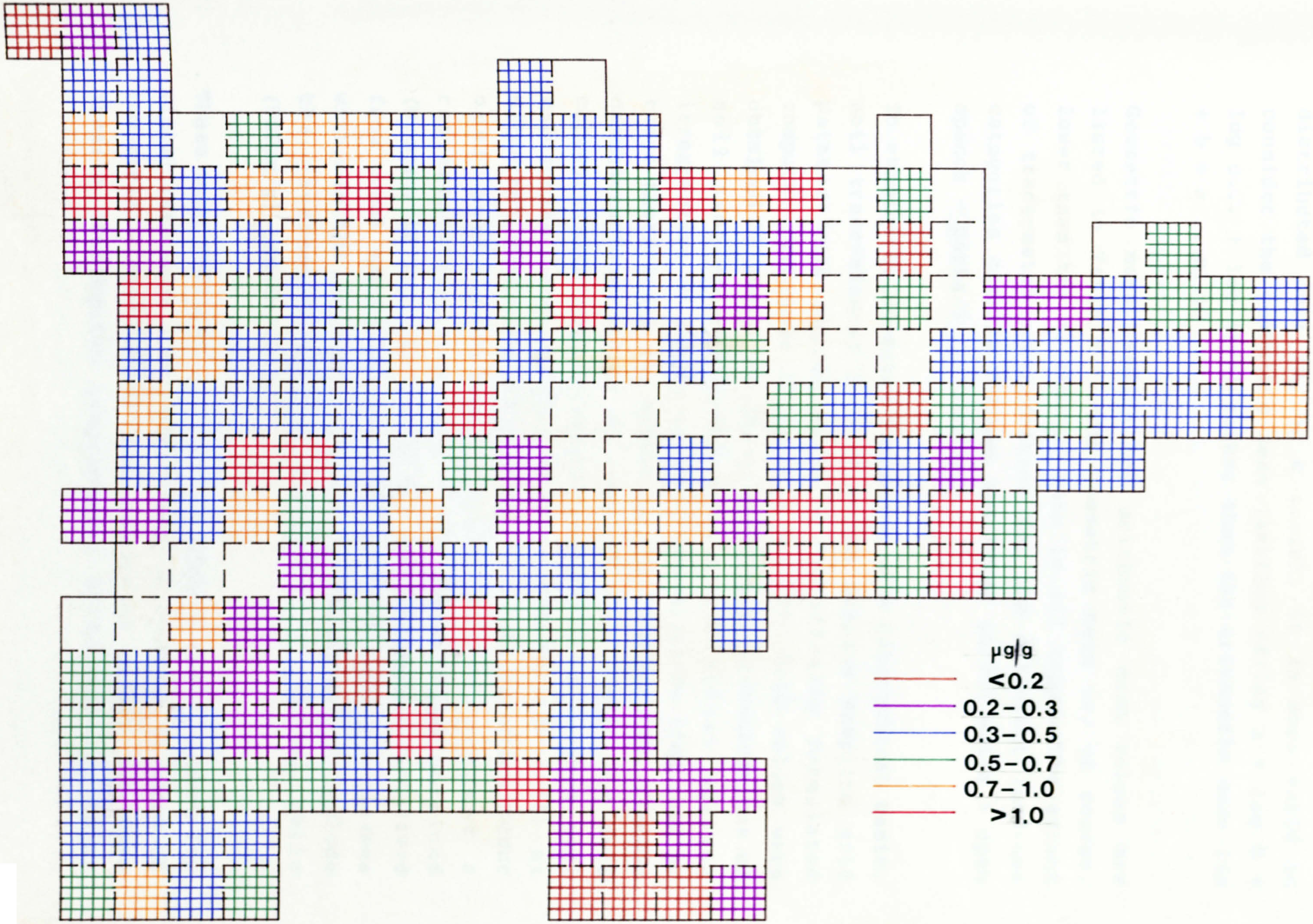

µg|g
<30
30 – 50
50 – 75
75 – 100
100 – 150
>150

FIGURE 4.12 GEOGRAPHICAL DISTRIBUTION OF SOIL TOTAL CADMIUM

μg/g
<0.2
0.2 – 0.3
0.3 – 0.5
0.5 – 0.7
0.7 – 1.0
>1.0

is to be employed. Thus, in evaluating log-normally distributed data (a, b, c ....n), it is more valid to consider the geometric mean [antilog of(log a + log b + log c... + log n)/n] rather than the arithmetic mean [(a + b + c...n)/n].

Geometric mean, median and arithmetic mean values are listed in Table 4.1. The geometric mean is, of course, lower than the arithmetic mean in all cases. The extent of trace-metal contamination for the different land-use categories clearly follows the trend garden soils > open spaces ~ parks > agricultural.

To examine trace-metal variation on a geographical basis, soil trace-element data from the Glasgow sampling grid pattern were mapped using a specifically formulated computer programme (Figures 4.9-4.12). Grid values were obtained by averaging the trace-element concentrations of soil samples collected within individual squares irrespective of sample category and distance from road as these factors did not appear to bias the results. (Indeed concentrations tended to vary as much within one soil category with same distance from road as between soil categories [e.g. garden soil - agricultural soil] at different distances from road). Variations which occur over quite short distances do not prevent a representative figure for the area being obtained (Duggan, 1983c). The ranges for the mappings were derived from equal apportionment of the results into six classes with, in the case of lead, slight adjustment to include the government guideline figure for garden soils (550μg/g) [Smith, 1981].

These maps (Figures 4.9-4.12) provide a useful format for visual reference particularly when considered in terms of industrial, residential and commercial areas. The maps clearly distinguish geographical differences in total metal concentrations in Glasgow, revealing a general reduction in metal levels towards the peripheral areas of the city, a distribution pattern that has been observed in other polluted urban environments (Davies, 1983b). Certain regions of the city, e.g. part of the 'east-end', are shown to be elevated in all four elements. With respect to lead, several areas are identifiable where concentrations exceed the government guidelines for lead in garden soils (550µg/g) [Figure 4.9].

4.1.2 EXCHANGEABLE CONCENTRATIONS

The exchangeable levels of lead, zinc, copper and cadmium (µg/g) in Glasgow soils are summarised in Table 4.2. For lead, zinc and copper some results were below the detection limit of FAAS preventing a complete statistical analysis. Average concentrations therefore are reported in terms of the median values.

As with total metal concentrations (Table 4.1), differences are observed in exchangeable levels among land-use categories. Typical exchangeable levels in agricultural land are noticeably lower than in other soil types with median levels for zinc and copper around 50% of those of the non-agricultural categories.

Exchangeable levels of lead in the naturally-mineralised Leadhills area are listed and summarised in Table 4.3. The median value, 1243µg/g, reflects the influence of the parent material in the trace-metal composition of these soils.

Histograms of the exchangeable Glasgow metal concentrations are shown in Figures 4.13-4.16 while corresponding geographical mappings of the data are presented in Figures 4.17-4.20. As with total metal data, frequency curves for exchangeable concentrations are skewed with a tail of values at higher concentrations,

TABLE 4.2 EXCHANGEABLE TRACE METAL CONTENT OF GLASGOW SOILS (0-5cm), 1981

		Gardens	Open Spaces	Parks	Agricultural	All
	No. of Samples	91	177	115	51	434
	Maximum	67.3	211	68.9	32.3	211
LEAD	Minimum	1.1	<0.5	0.5	<0.5	<0.5
(µg/g)	Median	2.0	1.9	2.0	1.6	2.0
	No. of Samples	91	181	120	48	440
	Maximum	52.4	56.8	54.3	60.0	60.0
ZINC	Minimum	<0.2	<0.2	<0.4	<0.2	<0.2
(µg/g)	Median	4.8	3.8	4.8	2.3	4.0
	No. of Samples	91	181	120	51	443
	Maximum	5.1	10.4	10.9	10.1	10.9
COPPER	Minimum	0.3	0.1	0.3	<0.1	<0.1
(µg/g)	Median	1.3	0.8	1.2	0.6	1.0
	No. of Samples	90	173	112	49	424
	Maximum	0.37	0.63	0.31	0.43	0.63
CADMIUM	Minimum	0.03	0.03	0.03	0.02	0.02
(µg/g)	Median	0.12	0.11	0.12	0.09	0.12

TABLE 4.3 EXCHANGEABLE LEAD CONTENT OF A NATURAL MINERALISED SOIL (LEADHILLS)

	Lead (µg/g)
Individual Results:	
	846
	1270
	1210
	2990
	832
	2284
	144
	4790
	498
	1760

Summary:

Number of samples	10
Maximum	4790
Minimum	144
Median	1243

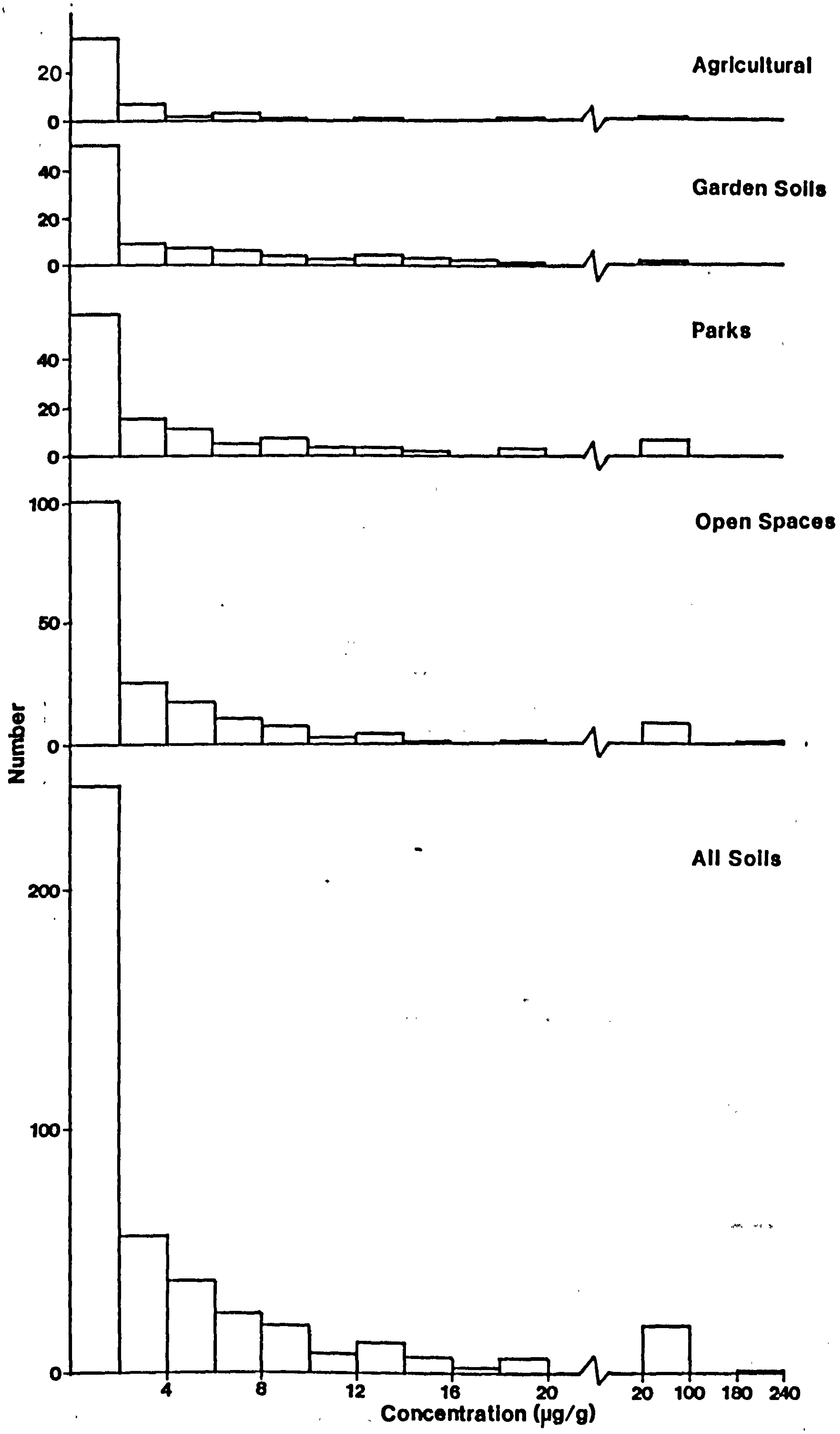


FIGURE 4.13 FREQUENCY DISTRIBUTION OF SOIL EXCHANGEABALE LEAD

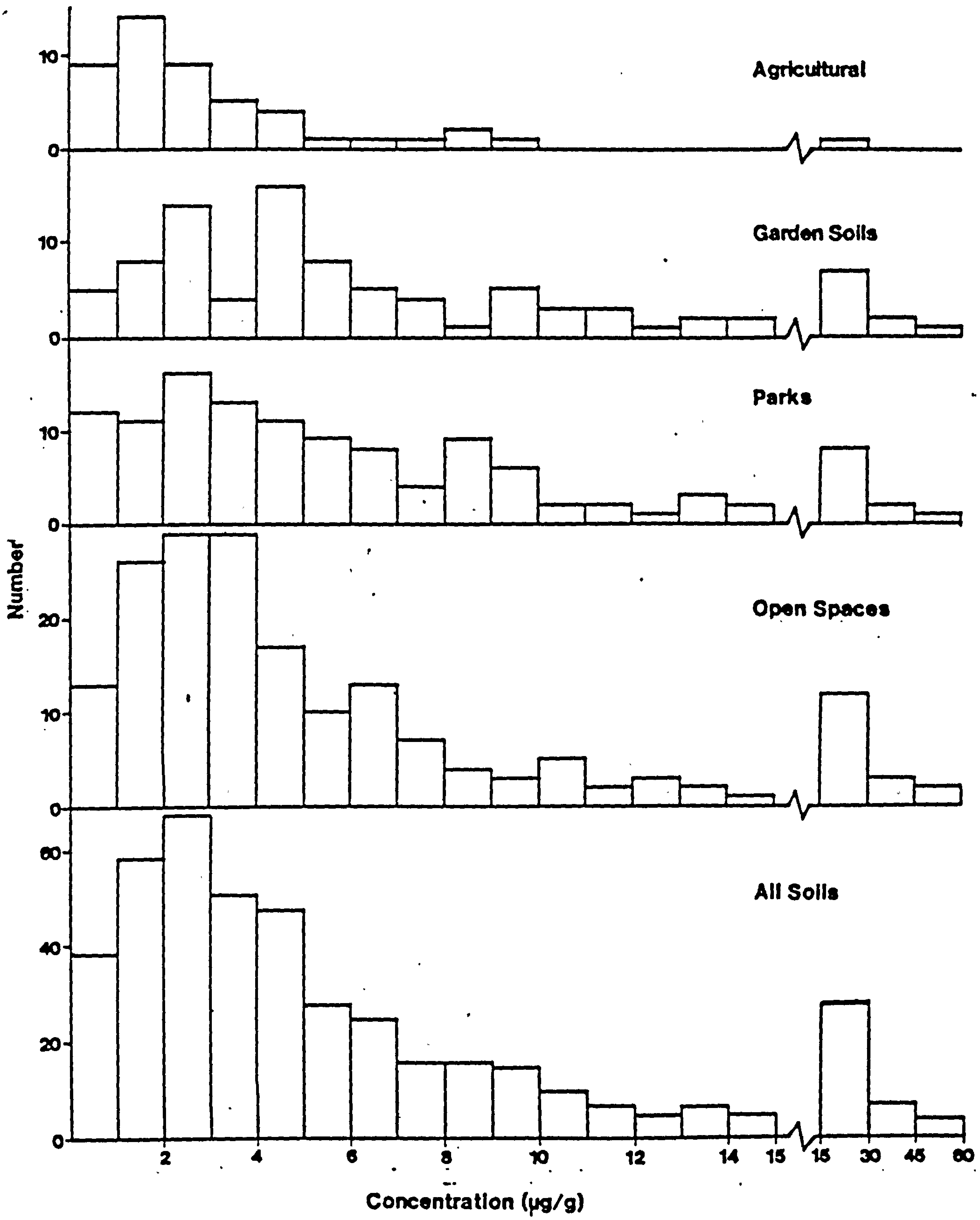


FIGURE 4.14 FREQUENCY DISTRIBUTION OF SOIL EXCHANGEABLE ZINC

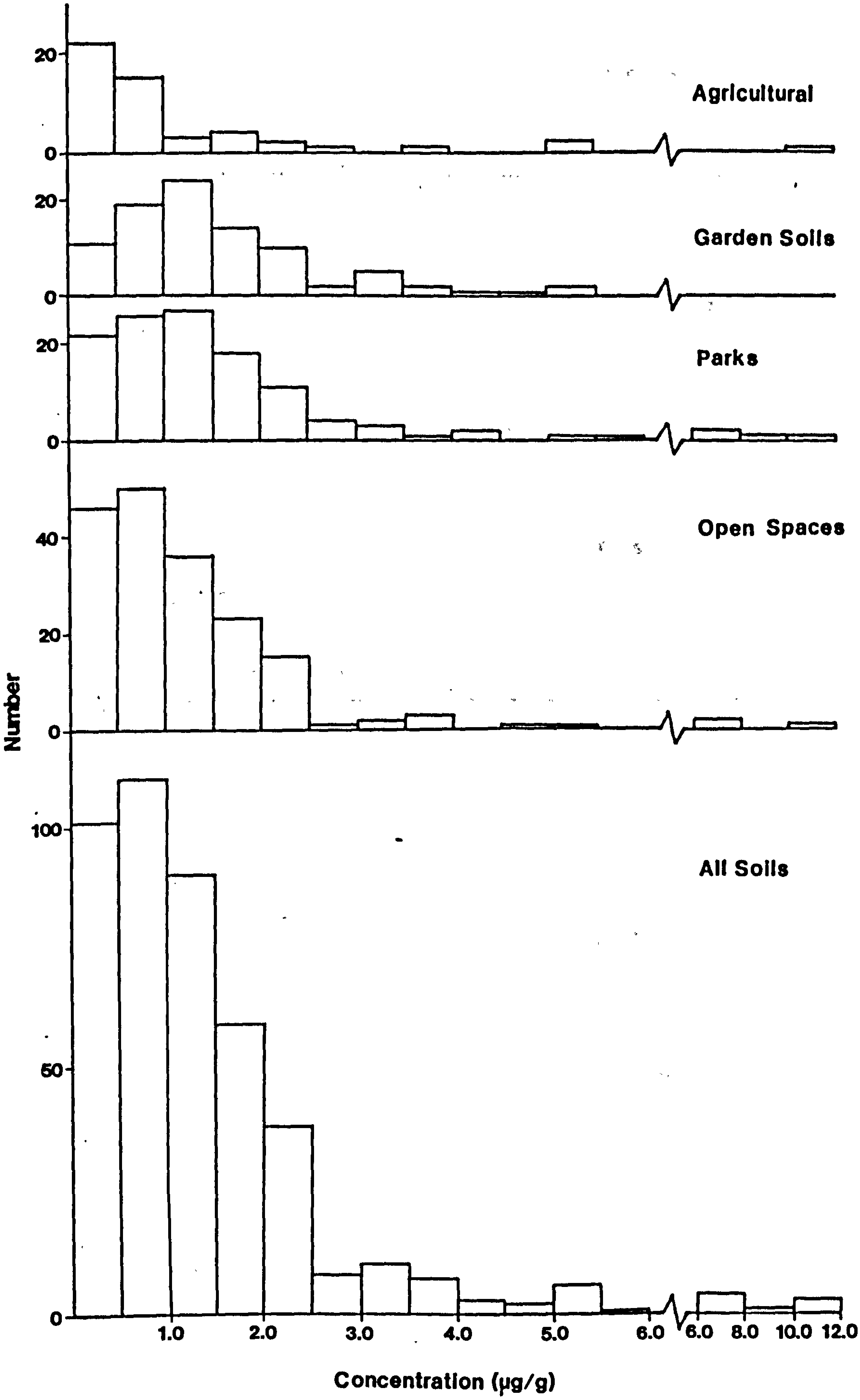


FIGURE 4.15 FREQUENCY DISTRIBUTION OF SOIL EXCHANGEABLE COPPER

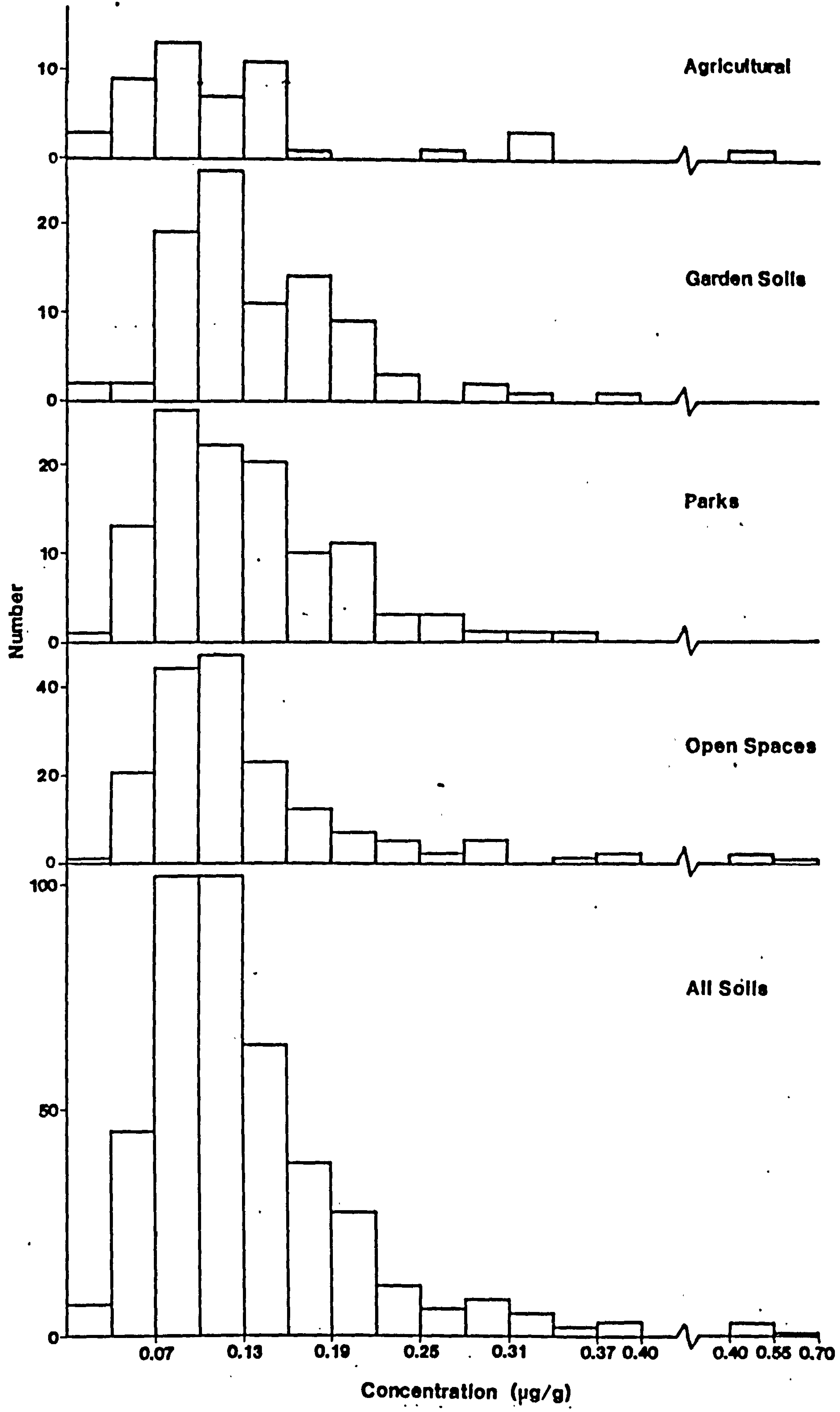


FIGURE 4.16 FREQUENCY DISTRIBUTION OF SOIL EXCHANGEABLE CADMIUM

<u>FIGURE 4.17</u> GEOGRAPHICAL DISTRIBUTION OF SOIL EXCHANGEABLE LEAD

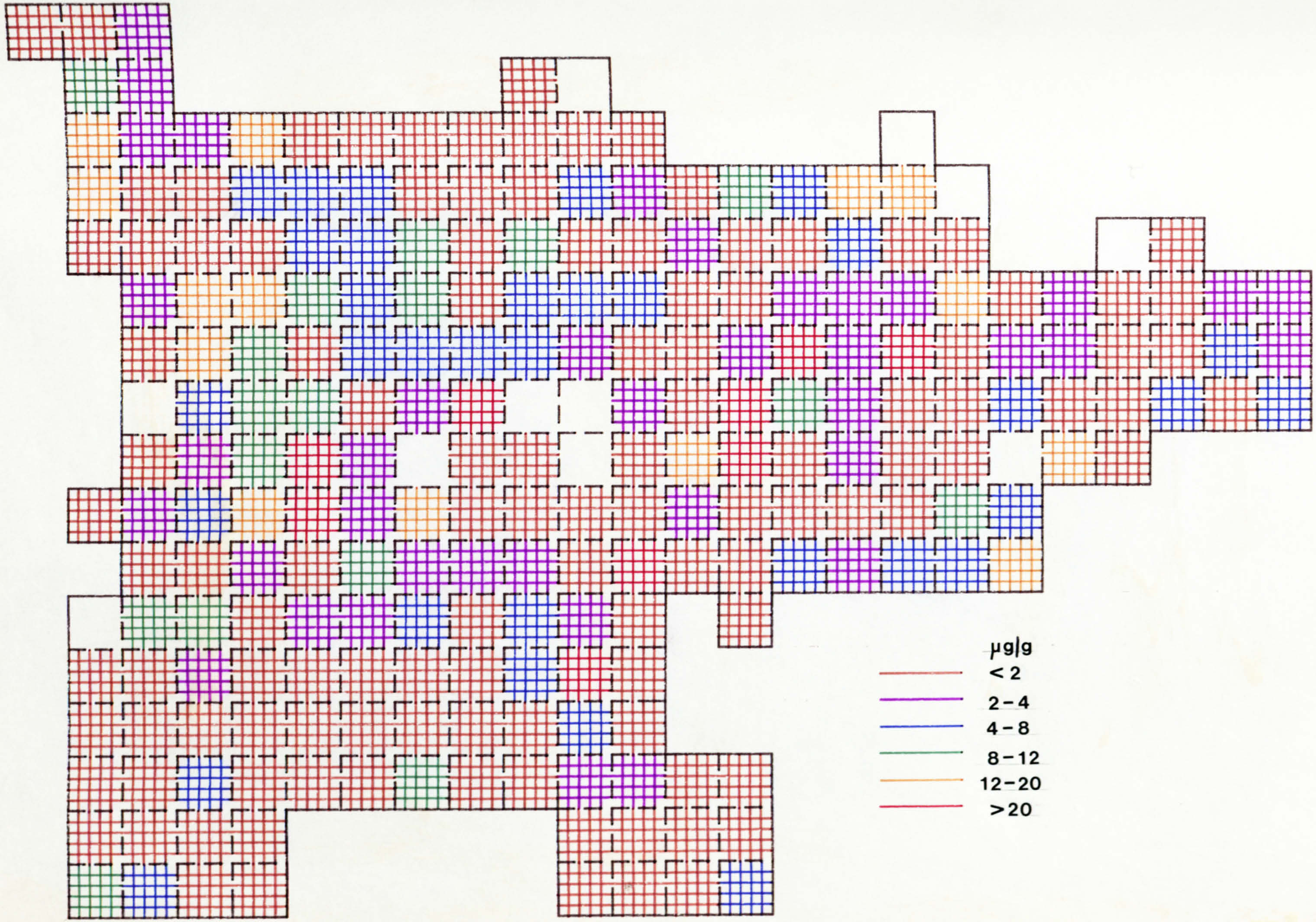

μg/g
< 2
2 − 4
4 − 8
8 − 12
12 − 20
> 20

FIGURE 4.18 GEOGRAPHICAL DISTRIBUTION OF SOIL EXCHANGEABLE ZINC

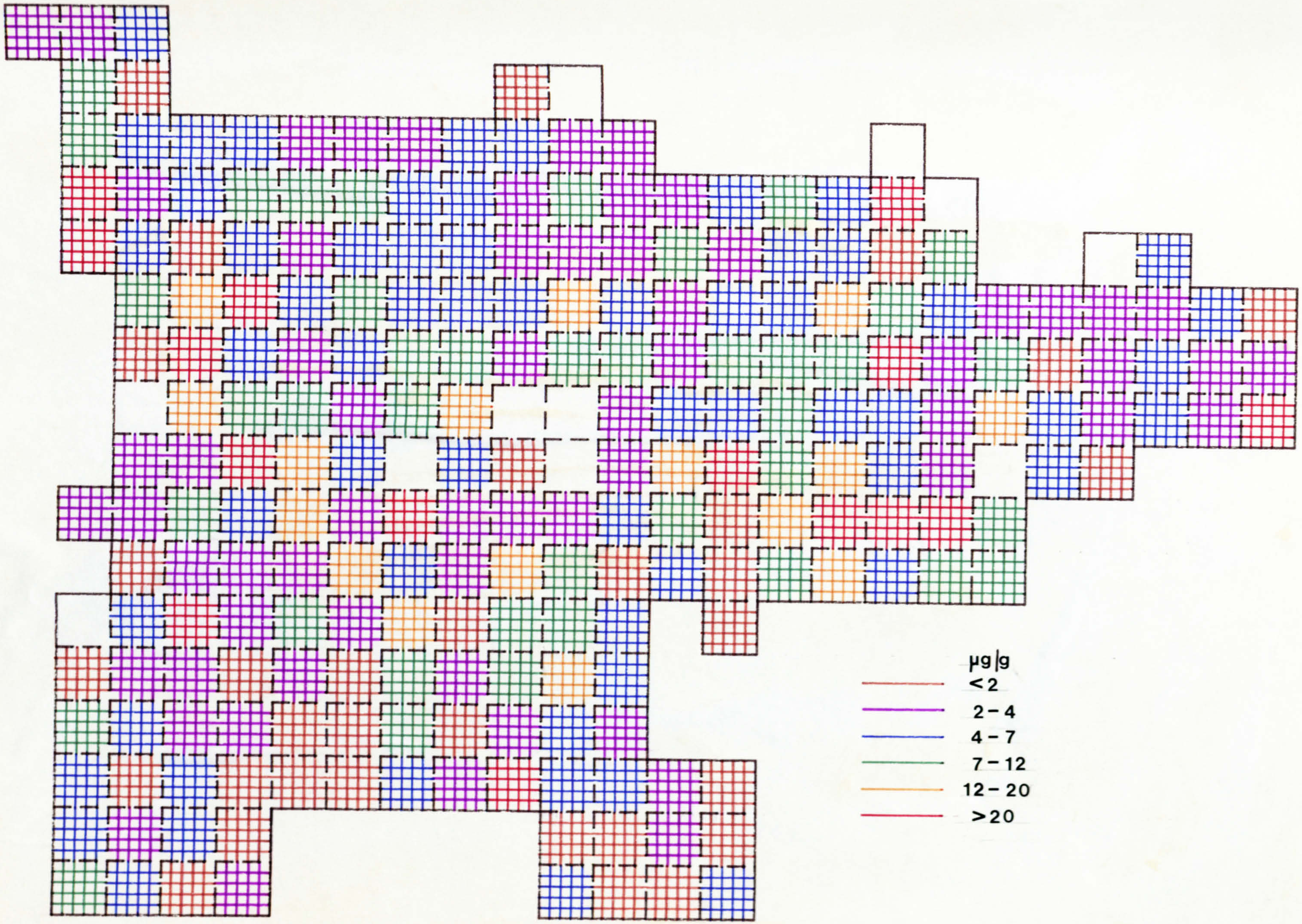

µg/g
<2
2 – 4
4 – 7
7 – 12
12 – 20
>20

FIGURE 4.19 GEOGRAPHICAL DISTRIBUTION OF SOIL EXCHANGEABLE COPPER

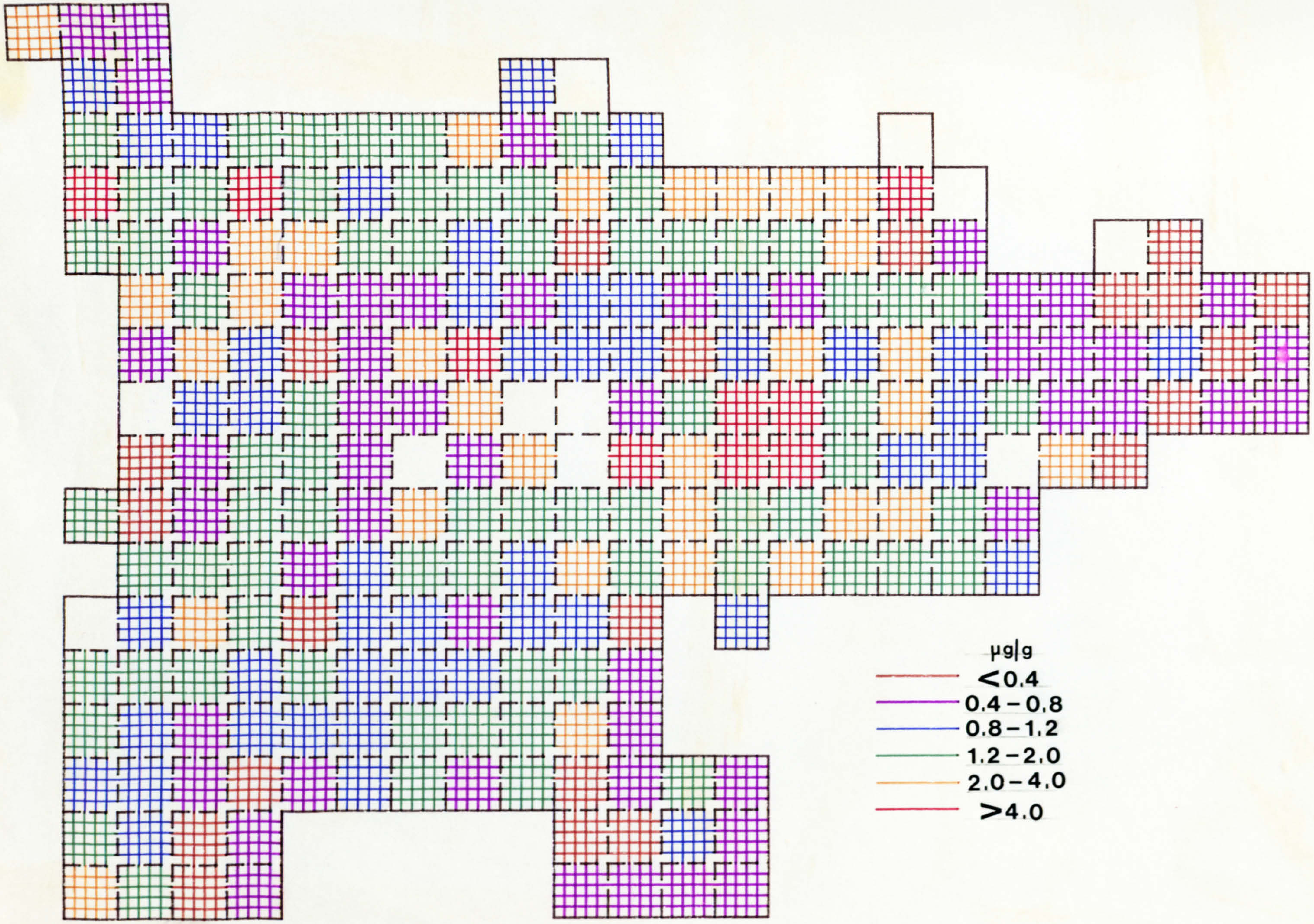
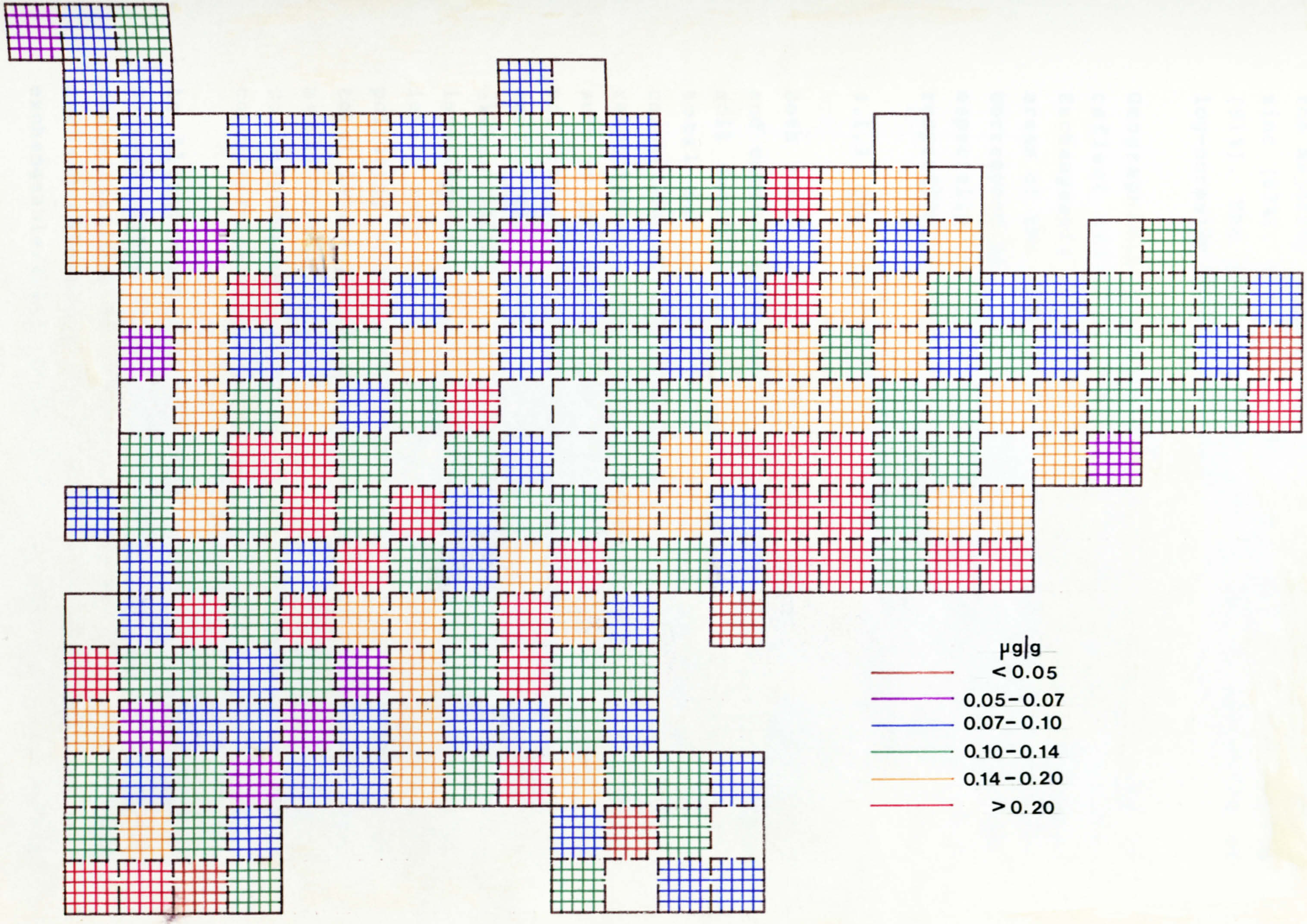

µg/g
<0.4
0.4 – 0.8
0.8 – 1.2
1.2 – 2.0
2.0 – 4.0
>4.0

FIGURE 4.20 GEOGRAPHICAL DISTRIBUTION OF SOIL EXCHANGEABLE CADMIUM

µg/g
< 0.05
0.05 – 0.07
0.07 – 0.10
0.10 – 0.14
0.14 – 0.20
> 0.20

the majority of results being <10µg/g lead (88%), <10µg/g zinc (83%), <2.5µg/g copper (90%) and <0.22µg/g cadmium (91%). The positive skewness is again indicative of log-normally distributed data.

Geographically, exchangeable concentrations tend to reflect total concentration distribution patterns. Exchangeable metal levels decrease towards peripheral areas of the city, while certain identifiable 'hot-spots' correspond to those of the total concentration mappings, especially for zinc and cadmium (Figures 4.10 and 4.12 respectively).

4.1.3 TWO-FRACTION STUDY

Both total and exchangeable data for lead, zinc, copper and cadmium were available for approximately 400 Glasgow soil samples. The relationship between exchangeable and total metal concentration, loosely apparent in a comparison of mappings (Figures 4.17-4.20 and 4.9-4.12 respectively), is dependent on chemical characteristics such as pH, number of exchange sites and the proportions of clay and organic matter, as well as on elemental source and degree of natural leaching. The ratio of exchangeable to total metal content is particularly important in contaminated urban soils where the total levels vary widely with high input fluxes of metals from polluting sources. The relationship of exchangeable to total levels can be demonstrated in a histogram of total metal concentration on which are superimposed corresponding exchangeable levels for each total concentration subgroup (Figures 4.21-4.24).

As illustrated for all four elements, exchangeable concentrations tended to increase with increasing total concentrations but differences among elements in the exchangeable/total ratio were observed. Whereas the exchangeable/total ratio for lead and zinc was fairly

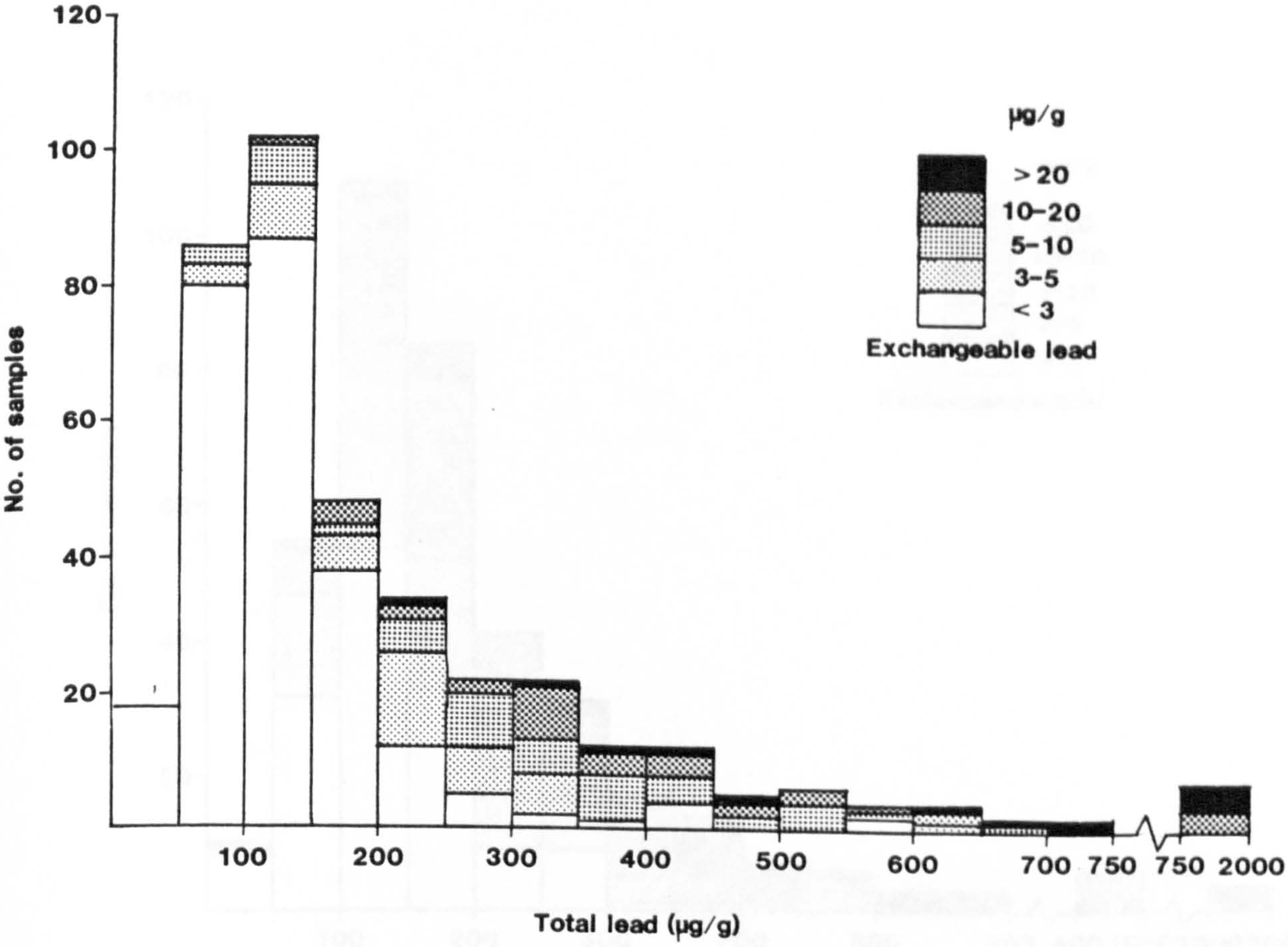


FIGURE 4.21 FREQUENCY DISTRIBUTION OF SOIL TOTAL LEAD WITH THE LEVELS OF EXCHANGEABLE LEAD FOR EACH TOTAL CONCENTRATION SUBGROUP SUPERIMPOSED

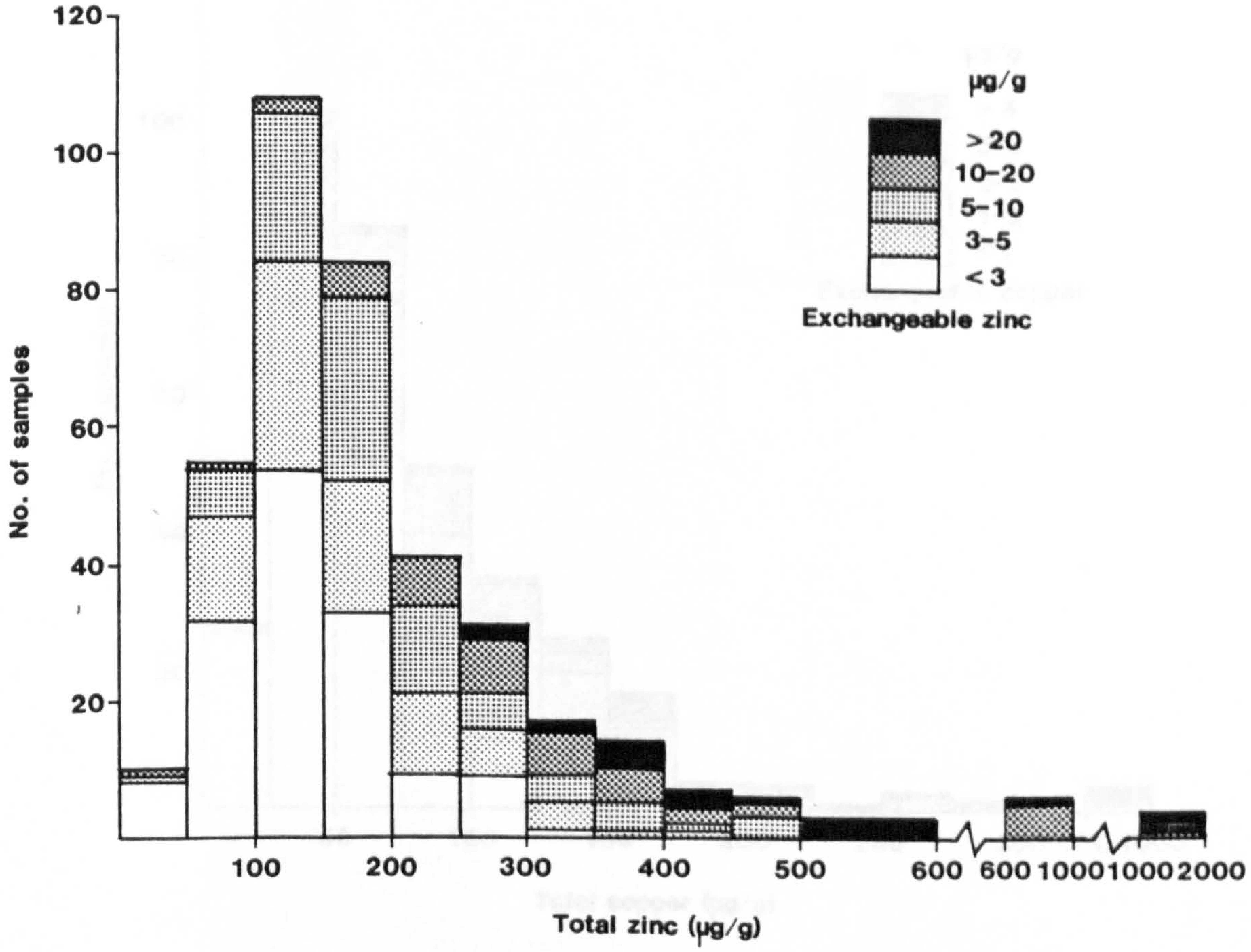


FIGURE 4.22 FREQUENCY DISTRIBUTION OF SOIL TOTAL ZINC WITH THE LEVELS OF EXCHANGEABLE ZINC FOR EACH TOTAL CONCENTRATION SUBGROUP SUPERIMPOSED

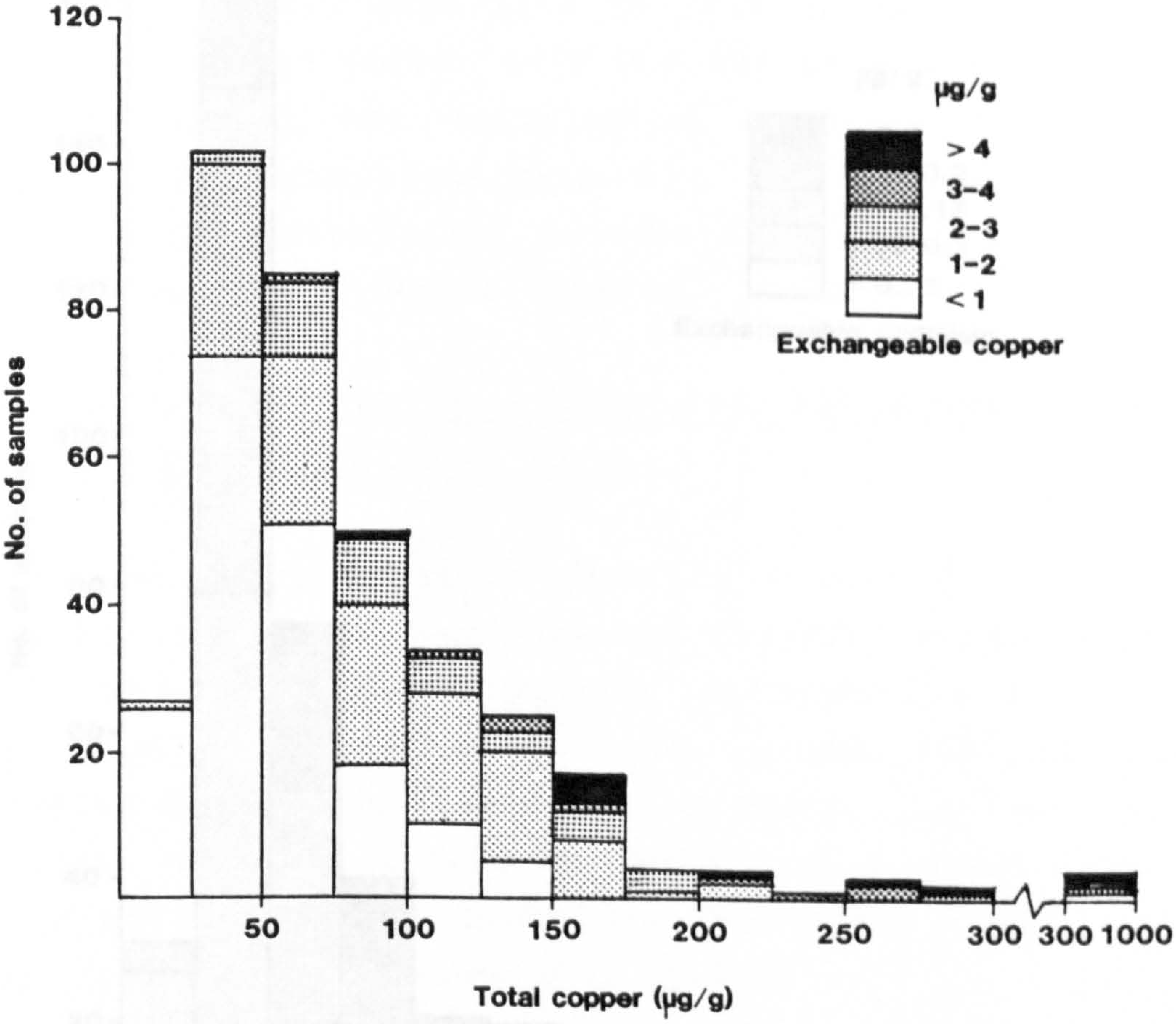


FIGURE 4.23 FREQUENCY DISTRIBUTION OF SOIL TOTAL COPPER WITH THE LEVELS OF EXCHANGEABLE COPPER FOR EACH TOTAL CONCENTRATION SUBGROUP SUPERIMPOSED

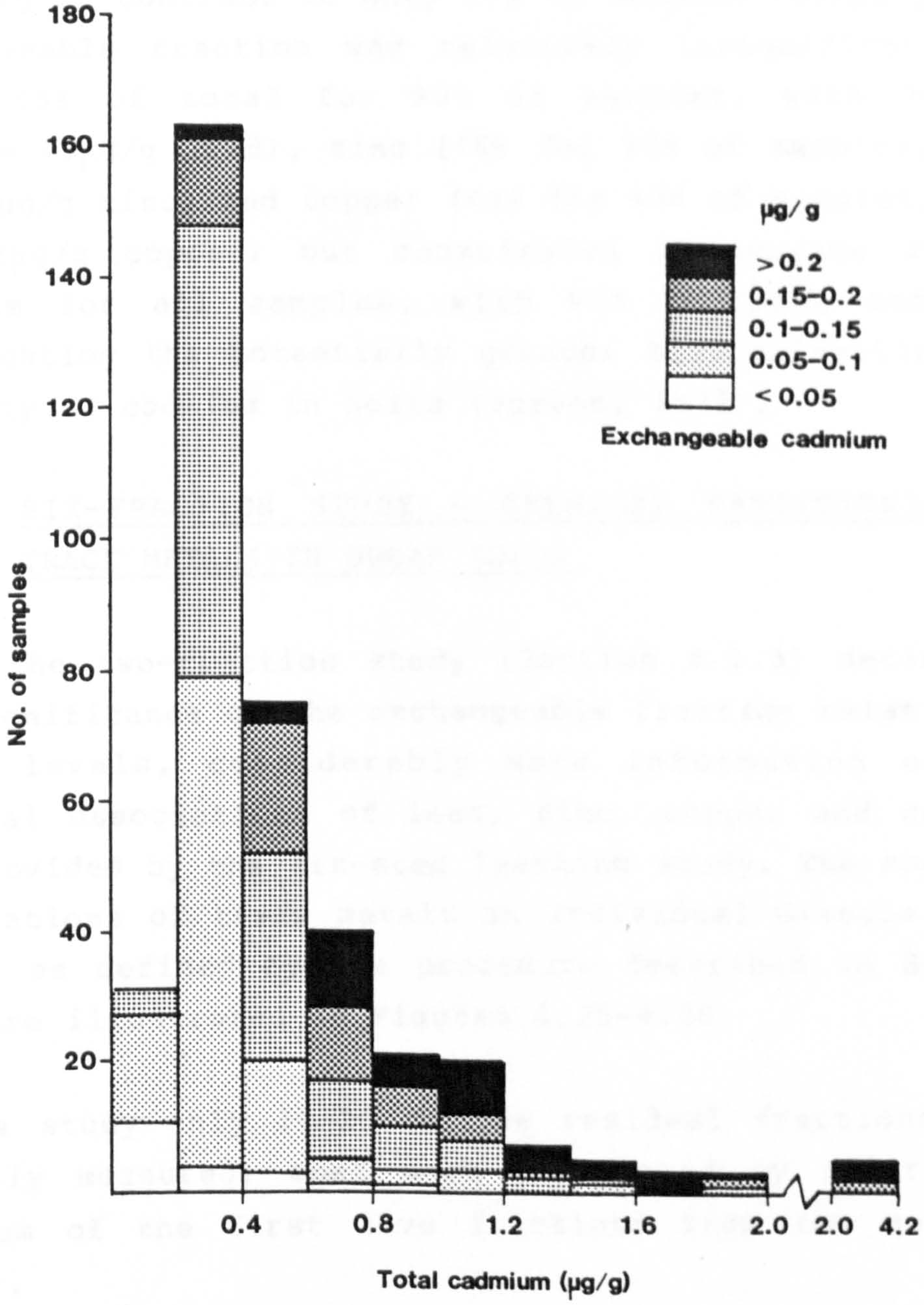


FIGURE 4.24 FREQUENCY DISTRIBUTION OF SOIL TOTAL CADMIUM WITH THE LEVELS OF EXCHANGEABLE CADMIUM FOR EACH TOTAL CONCENTRATION SUBGROUP SUPERIMPOSED

constant over the whole concentration range, there was a slight tendency with copper for the ratio to fall at very high concentrations and a pronounced decline in the case of cadmium, where the ratio was >30% for 53% of samples <0.6µg/g in contrast to only 17% of samples >0.6µg/g. The exchangeable fraction was relatively insignificant for lead (<5% of total for 90% of samples, with 76% of samples <5µg/g lead), zinc (<6% for 90% of samples, with 61% <5µg/g zinc) and copper (<4% for 95% of samples, with 84% <2µg/g copper) but constituted an average 29% of cadmium for all samples, with 62% >0.1µg/g cadmium, highlighting the potentially greater bioavailability and mobility of cadmium in soils (Purves, 1977).

4.1.4 SIX-FRACTION STUDY - CHEMICAL PARTITIONING OF TRACE METALS IN URBAN SOILS

While the two-fraction study (Section 4.1.3) determined the significance of the exchangeable fraction relative to total levels, considerably more information on the chemical associations of lead, zinc, copper and cadmium was provided by the six-step leaching study. The chemical associations of trace metals in individual Glasgow urban soils, as defined by the procedure described in Section 3.4, are illustrated in Figures 4.25-4.28.

In the study only 10-20 of the residual fractions were actually measured; most were calculated by subtracting the sum of the first five fractions from the measured total[1].

[1] Calculated residuals were used in Figures 4.25-4.28 except where very occasionally, a negative value was obtained. In such cases a theoretical residual was worked out on the basis of a mean measured residual and a mean calculated residual for the appropriate total concentration range. The theoretical residual was added to the sum of the first five fractions and the total adjusted accordingly (solely for the purposes of the six-fraction study). Where the calculated residual was negative and a measured residual was available, the measured residual was used.

KEY TO SIX-FRACTION STUDY

□ Exchangeable

░ Carbonate

░ Easily-Reducible

▒ Moderately-Reducible

▓ Organic

■ Residual

__FIGURE 4.25__ THE CHEMICAL PARTITIONING OF LEAD IN INDIVIDUAL GLASGOW SOILS AS DISCLOSED BY THE SIX-FRACTION LEACHING STUDY

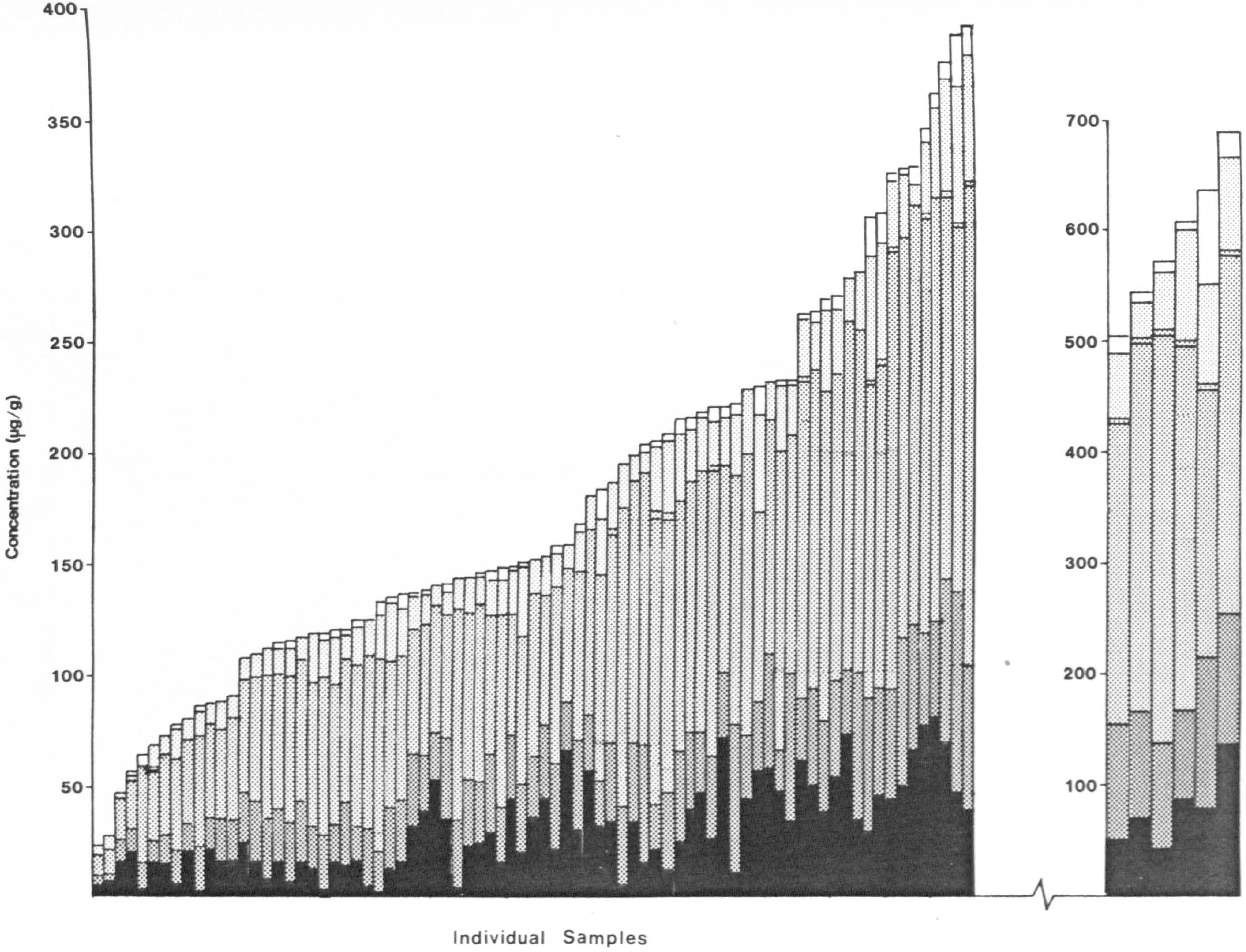
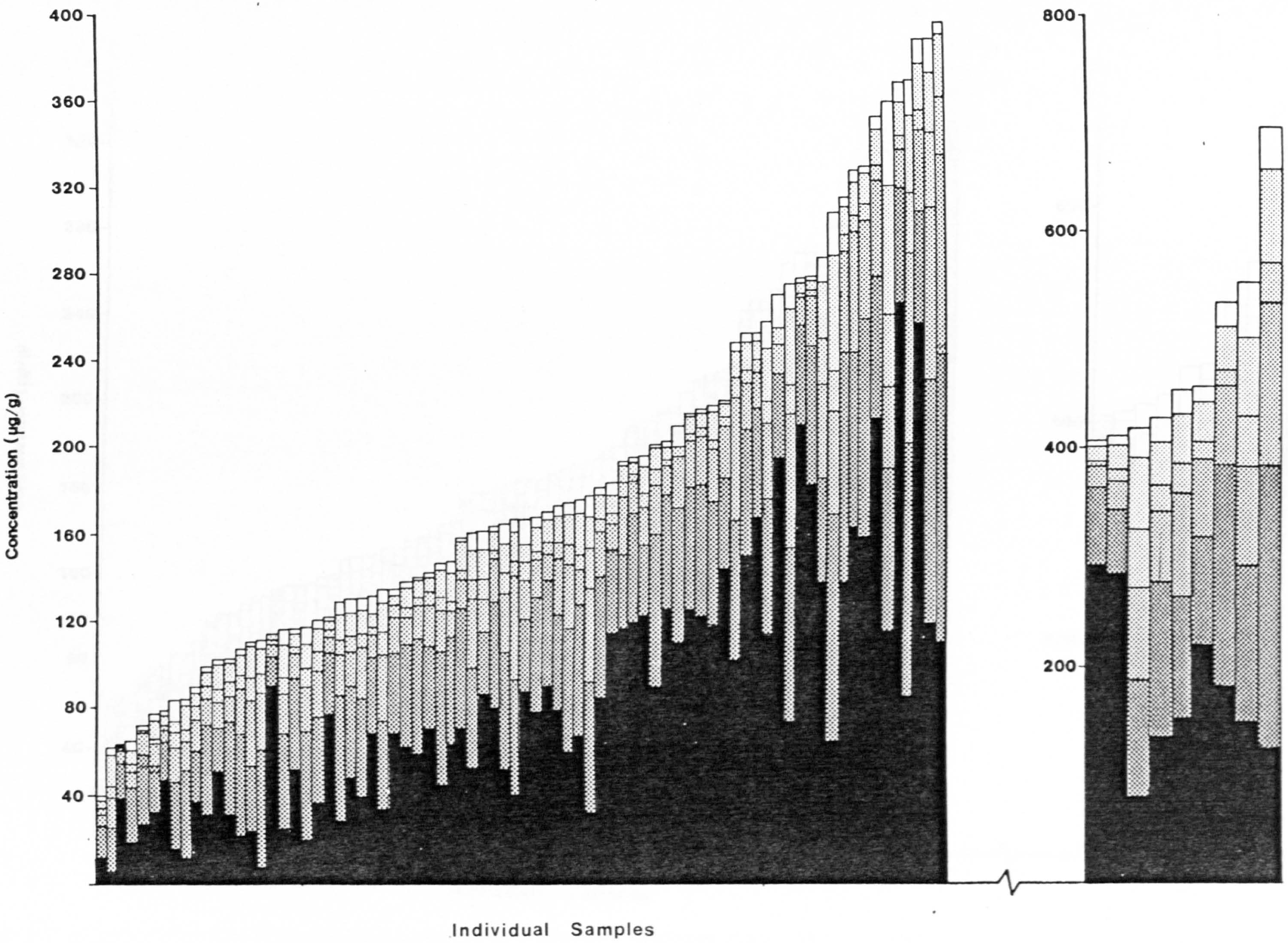
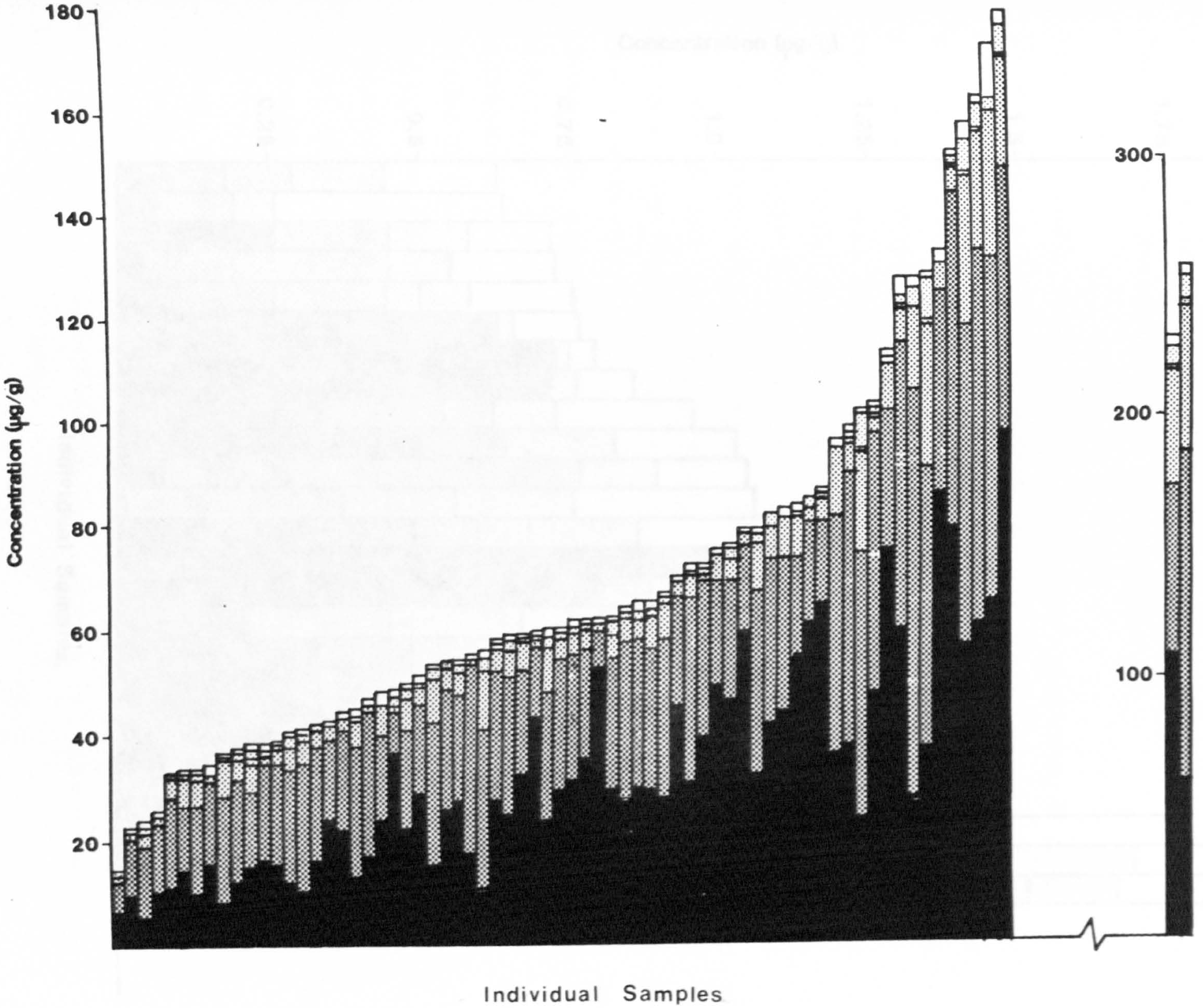

400
350
300
250
200
150
100
50
Concentration (µg/g)
Individual Samples
700
600
500
400
300
200
100

__FIGURE 4.26__ THE CHEMICAL PARTITIONING OF ZINC IN INDIVIDUAL GLASGOW SOILS AS DISCLOSED BY THE SIX-FRACTION LEACHING STUDY



400
360
320
280
240
200
160
120
80
40
Concentration (µg/g)
800
600
400
200
Individual Samples

FIGURE 4.27 THE CHEMICAL PARTITIONING OF COPPER IN INDIVIDUAL GLASGOW SOILS AS DISCLOSED BY THE SIX-FRACTION LEACHING STUDY


Concentration (µg/g)
180
160
140
120
100
80
60
40
20
300
200
100
Individual Samples

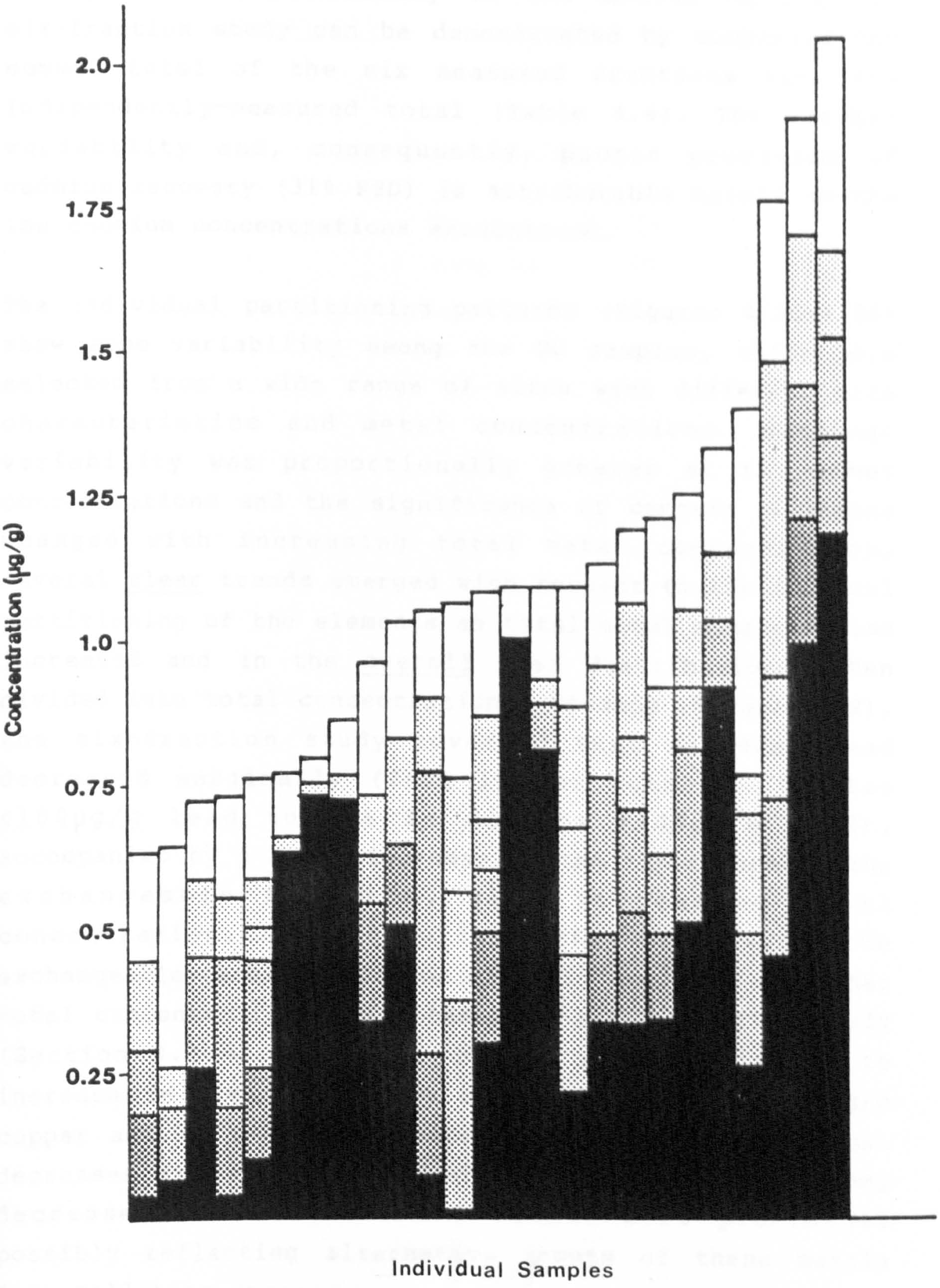


FIGURE 4.28 THE CHEMICAL PARTITIONING OF CADMIUM IN INDIVIDUAL GLASGOW SOILS AS DISCLOSED BY THE SIX-FRACTION LEACHING STUDY

The quantitative recovery of the metals during the six-fraction study can be demonstrated by comparing the summed total of the six measured fractions with the independently-measured total (Table 4.4). The greater variability and, consequently, poorer precision of cadmium recovery (31% RSD) is attributable mainly to the low cadmium concentrations encountered.

The individual partitioning patterns (Figures 4.25-4.28) show some variability among the 90 samples, which were selected from a wide range of sites with different site characteristics and metal concentrations. Although variability was proportionally greater at the lower concentrations and the significance of certain fractions changed with increasing total metal concentration, several *clear* trends emerged with respect to the chemical partitioning of the elements as total metal concentration increased and in the *overall* mean distributions. When divided into total concentration subgroups (Figure 4.29), the six-fraction study revealed that residual lead decreased marginally (from 19% of total in samples <100µg/g lead to 13% in samples >400µg/g lead), accompanied by a small increase in the importance of the exchangeable fraction, with increasing total concentration. Conversely, the significance of the exchangeable cadmium fraction markedly declined at higher total concentrations, as noted in the two-fraction study (Section 4.1.3). Residual copper and zinc tended to increase in significance up to total levels of 100µg/g copper and 300µg/g zinc, respectively, with proportional decreases in the organic fraction, but thereafter they decreased as fractions 1-4 became more prominent, possibly reflecting alternative inputs of these metals from polluting sources.

TABLE 4.4 RECOVERY EFFICIENCY OF SEQUENTIAL LEACHING SCHEME COMPARED WITH DIRECTLY MEASURED TOTAL CONCENTRATIONS

Element	Mean Percentage recovery	No. of Samples	Relative Std. Deviation (RSD) %
Pb	104 ± 13	15	13
Zn	107 ± 19	15	18
Cu	103 ± 21	9	20
Cd	97 ± 30	10	31
Mn	99 ± 12	17	12
Fe	104 ± 13	15	13

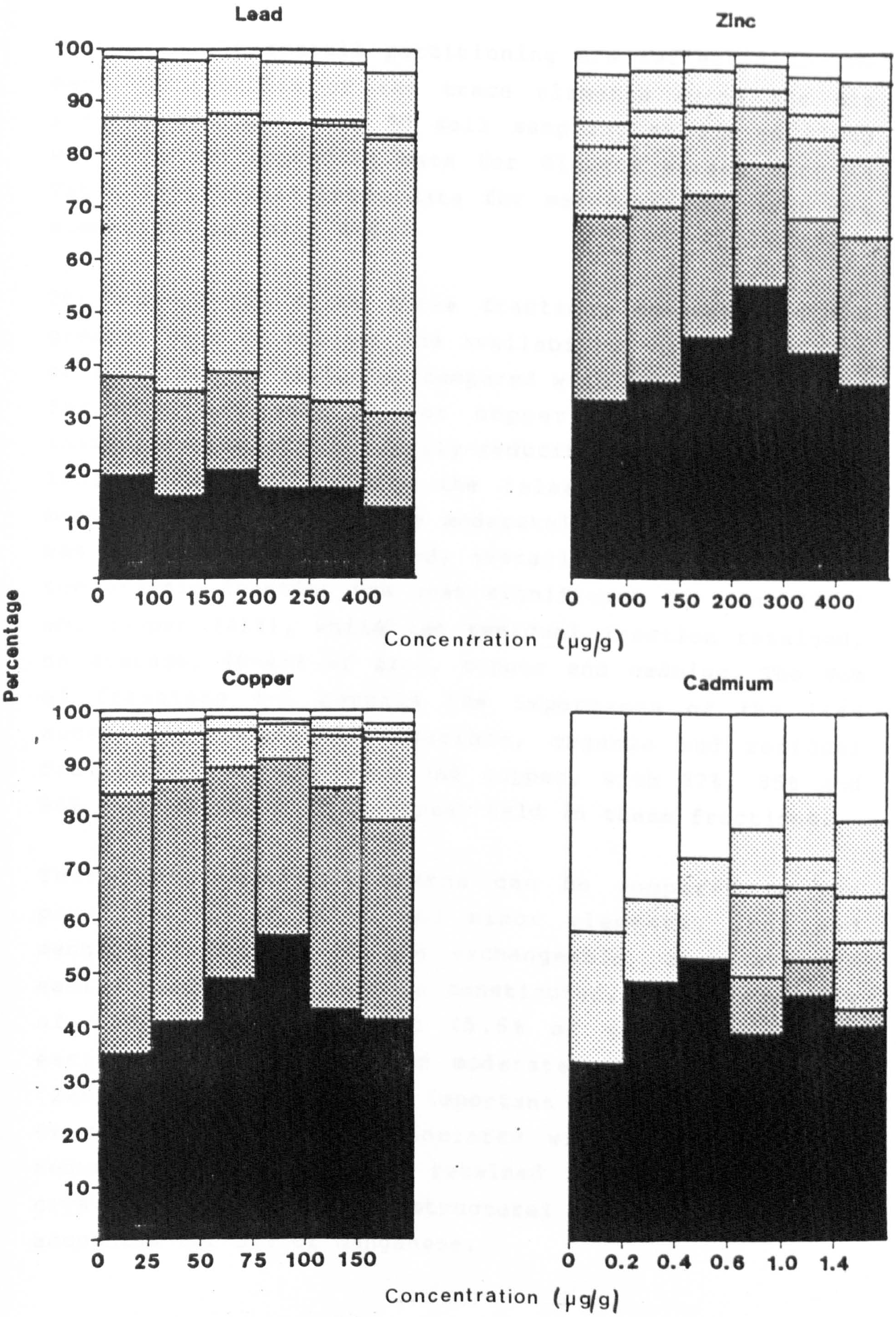


FIGURE 4.29 THE CHEMICAL PARTITIONING OF TRACE-METAL CONTAMINANTS (PERCENT OF TOTAL) OVER TOTAL CONCENTRATION SUBGROUPS IN GLASGOW SOILS

Trends in the overall partitioning are reflected in the mean distribution of the trace elements among the six phases, averaged over 90 soil samples, as listed along with the corresponding data for Glasgow street dirt in Table 4.5. Partitioning data for manganese and iron are summarised in Table 4.6.

The sum of the first three fractions demonstrated the greater ease of release and availability of cadmium (36% of total for Cd >0.6µg/g) compared with 13% for lead, 15% for zinc and only 4% for copper, and the relative insignificance of the easily-reducible fraction (0% for lead and copper) despite the release of 25% of total manganese (Table 4.6). The moderately-reducible fraction was very important for lead, averaging 51% of the total, the organic fraction was most significant for zinc (29%) and copper (41%), while the residual fraction retained, on average, 40-45% of zinc, copper and cadmium. The sum of fractions 4-6 reveals the importance of the less accessible moderately-reducible, organic and residual fractions for lead, zinc and copper, with 87%, 85% and 96% respectively, of the total held in these fractions.

These distribution patterns can be compared to the partitioning of major and minor elements, iron and manganese. The sum of the exchangeable, carbonate and easily-reducible components constituted, on average, 36% of total manganese, but <0.6% of total iron. The easily-reducible (25%) and moderately-reducible phases (22%) were almost equally important for manganese. Only 6% of total iron was associated with the moderately-reducible phase, 80% being retained in the more immobile crystalline forms of the structural lattice, which also accounted for 31% of manganese.

TABLE 4.5 MEAN CHEMICAL PARTITIONING (PERCENT OF TOTAL) OF TRACE METAL CONTAMINANTS IN GLASGOW SOIL AND STREET DIRT

	LEAD		ZINC		COPPER		CADMIUM	
	Soil	St.Dirt	Soil	St.Dirt	Soil	St.Dirt	Soil*	St.Dirt**
Exchangeable	2	13	3	10	2	11	19	27
Carbonate-bound	11	28	7	23	2	4	13	19
Easily reducible	0	5	4	6	0	3	4	4
Moderately reducible	51	27	13	19	9	8	15	12
Organic	19	14	29	16	41	43	7	22
Residual	17	13	43	26	46	31	42	16

* for samples >0.6µg/g
** for samples >1µg/g

TABLE 4.6 MEAN CHEMICAL PARTITIONING (PERCENT OF TOTAL) OF MANGANESE AND IRON IN GLASGOW SOIL AND STREET DIRT

	Manganese		Iron	
	Soil	St.Dirt	Soil	St.Dirt
Exchangeable	5	3	0	0
Carbonate-bound	6	7	0	0
Easily reducible	25	8	0	0
Moderately reducible	22	15	6	3
Organic	11	8	15	3
Residual	31	60	80	94

4.2 STREET DIRT

4.2.1 EXCHANGEABLE CONCENTRATIONS (cf. 4.1.2)

The exchangeable concentrations of lead, zinc, copper and cadmium, expressed in μg/g dry weight, in Glasgow street dirt are summarised in Table 4.7.

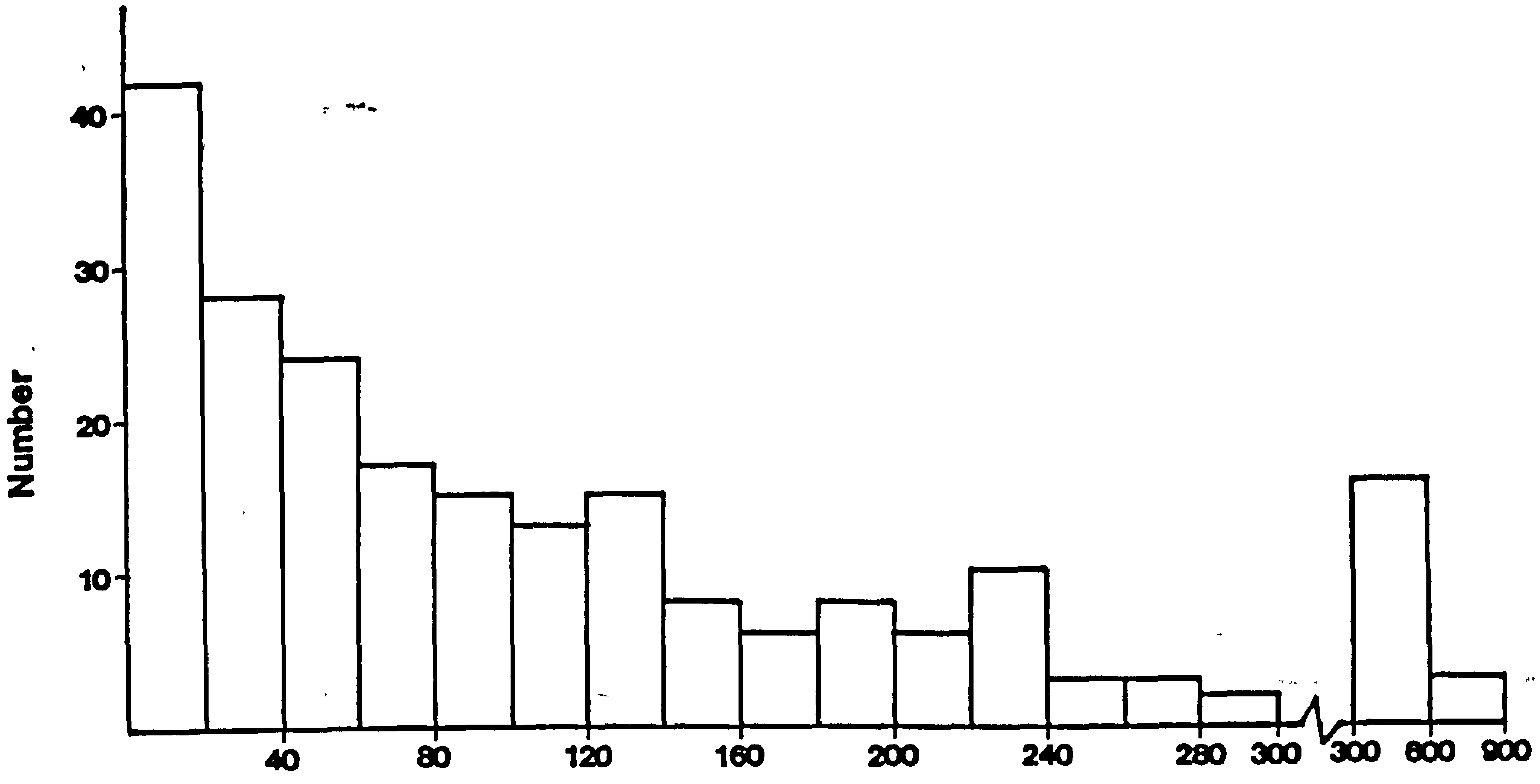
The results are presented as class frequency histograms in Figures 4.30-4.33. Elemental distribution patterns are strongly positively skewed, showing a close resemblance to the corresponding exchangeable-metal curves for soil and suggestive of log-normal distributions. Statistical analysis of the logarithm-transformed values (Table 4.7) indicates that geometric mean values approach or exceed average total metal concentrations in normal uncontaminated soils. For example, the typical natural total level of lead in soil is usually quoted as 20-40μg/g lead (Berrow and Burridge, 1980; Davies, 1983a). While trace-metal exchangeable levels in street dirt are clearly of less obvious significance with respect to trace metal uptake by plants, they do reflect concentration differences between street dirt and soil which are attributable to variations in physical, e.g. grain size (Ellis and Revitt, 1982), and chemical characteristics as well as in distance from sources of contamination e.g. vehicular traffic. Thus median street-dirt exchangeable levels of 75μg/g lead, 40μg/g zinc, 12μg/g copper and 0.36μg/g cadmium (Table 4.7) greatly exceeded corresponding values of 2μg/g lead, 4μg/g zinc, 1μg/g copper and 0.12μg/g cadmium for soils (Table 4.2). Moreover, the six-fraction study (Section 4.2.2) revealed that the exchangeable phase contained, on average, 12% of total lead, 10% of total zinc and 10% of total copper in street dirt, proportions which were greater than in soil (Section 4.1.3): lead-<5% for 90% of samples, zinc-<6% for 90% of samples and copper-<4% for 95% of samples.

TABLE 4.7 EXCHANGEABLE TRACE METAL CONTENT OF GLASGOW STREET DIRT, 1981

	Lead	Zinc	Copper	Cadmium
		µg/g		
No. of Samples	219	219	219	221
Maximum	937	327	64	3.58
Minimum	<1.5	1	<0.3	0.04
Mean	121	54	15	0.49
Std. devn.	137	43	13	0.47
Median	75	40	12	0.36
Geom. mean	65	39	10	0.37
Upper 95%	833	229	77	1.58
Lower 95%	5	7	1.3	0.09

Upper and lower 95% probability ranges were calculated from logarithm transformed values.

(1) Exchangeable lead



(2) Hydrochloric acid-soluble lead

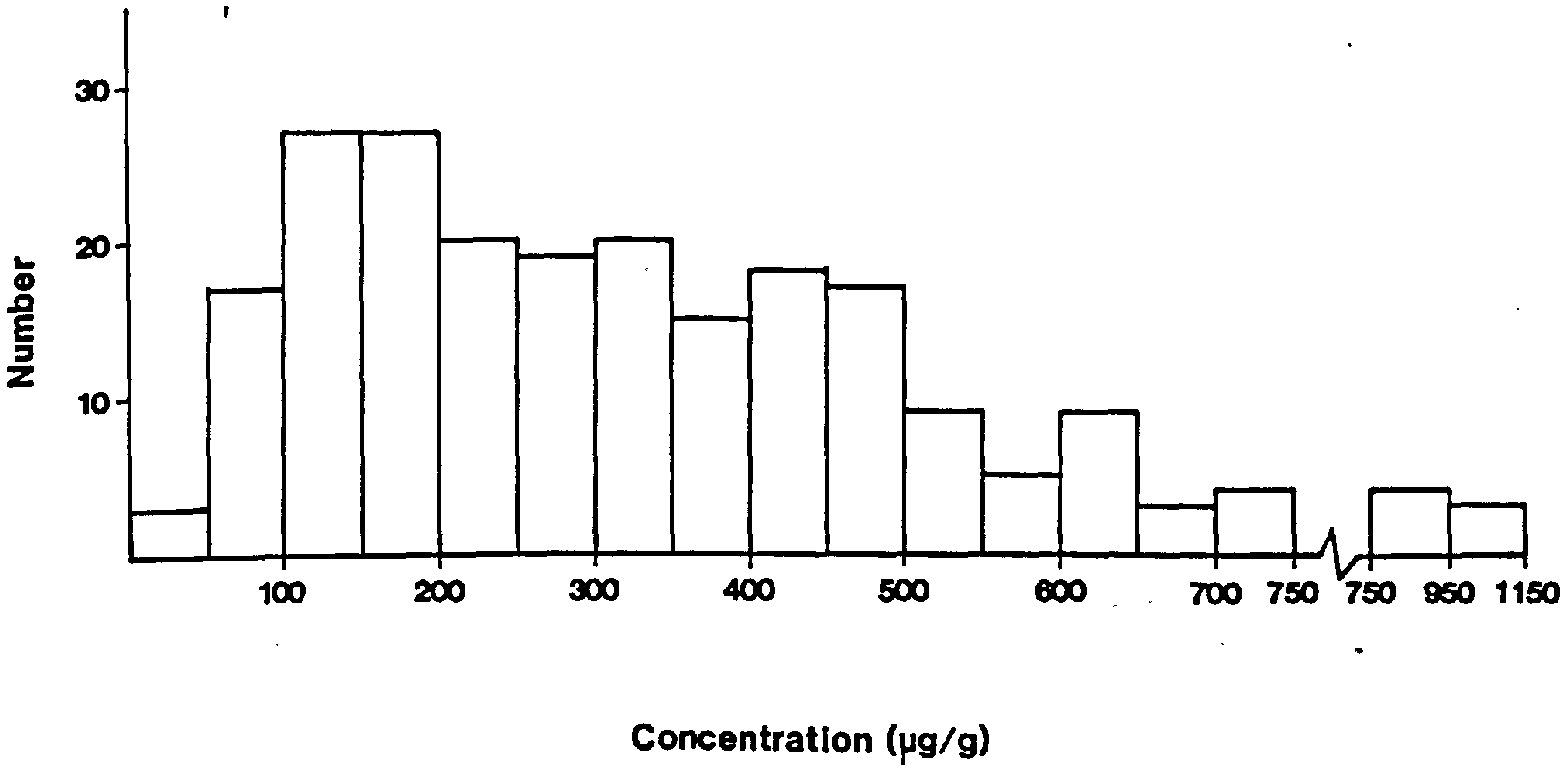
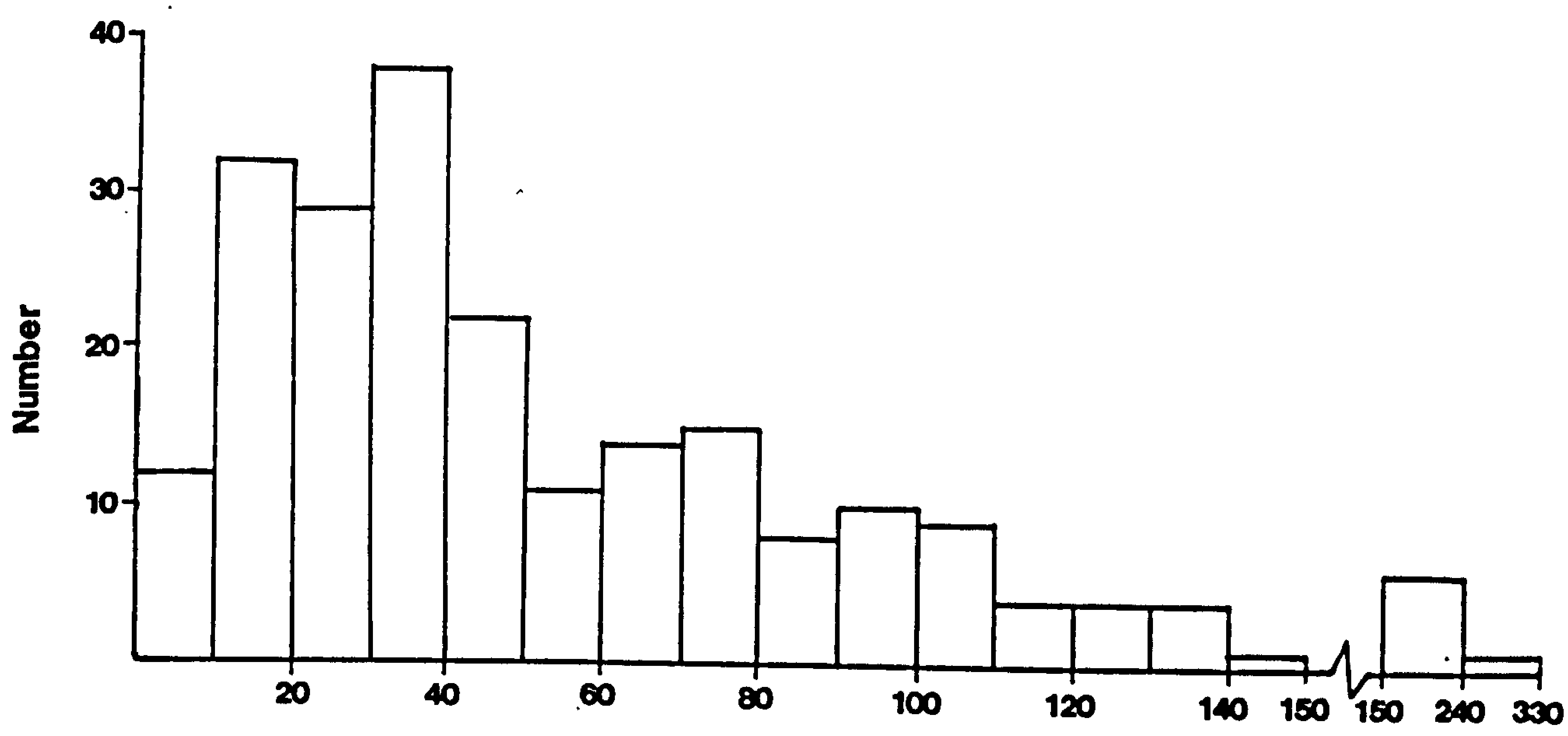


FIGURE 4.30 FREQUENCY DISTRIBUTION OF STREET DIRT (1) EXCHANGEABLE LEAD (2) HYDROCHLORIC ACID-SOLUBLE LEAD

(1) Exchangeable zinc



(2) Hydrochloric acid-soluble zinc

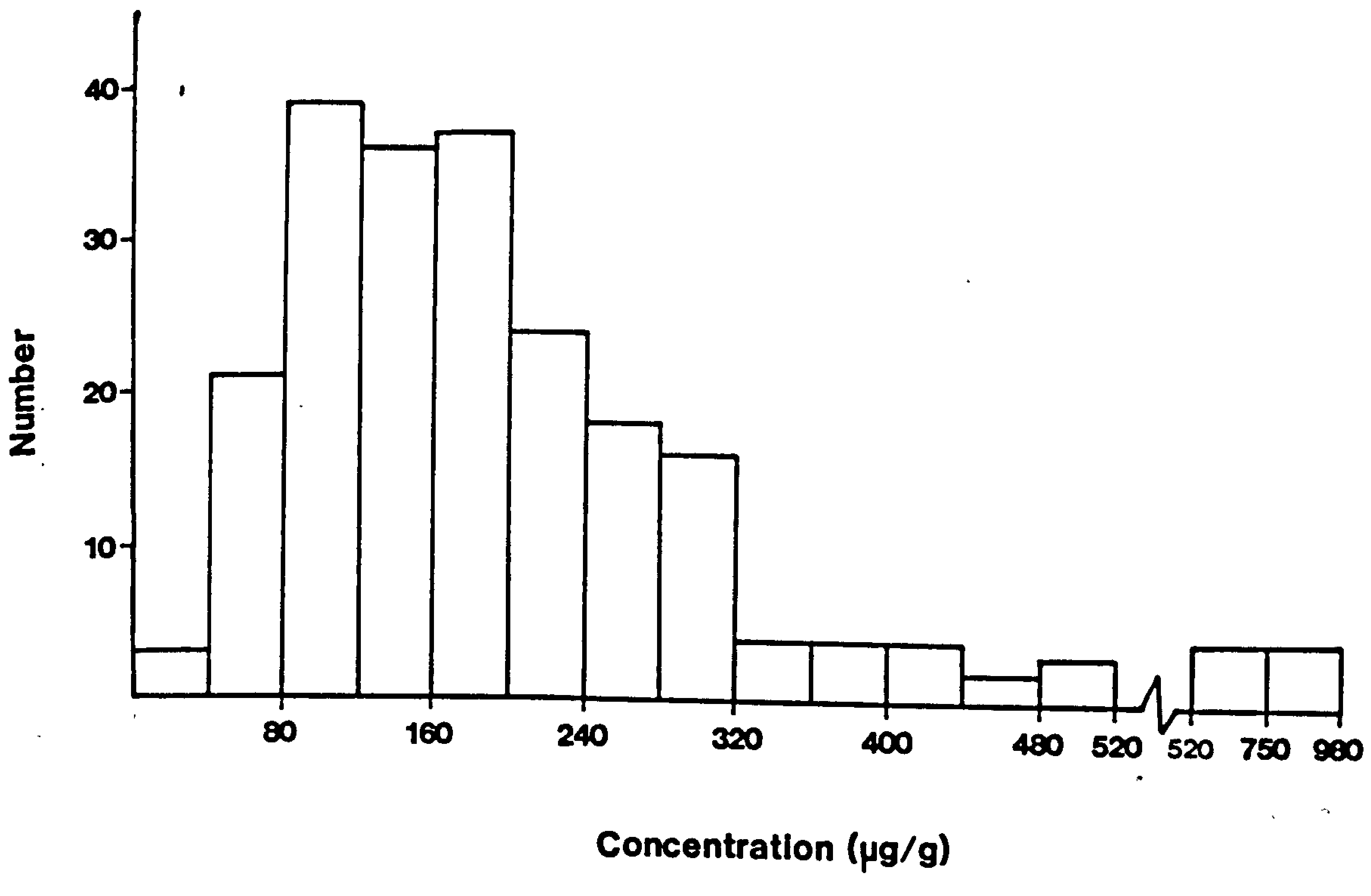
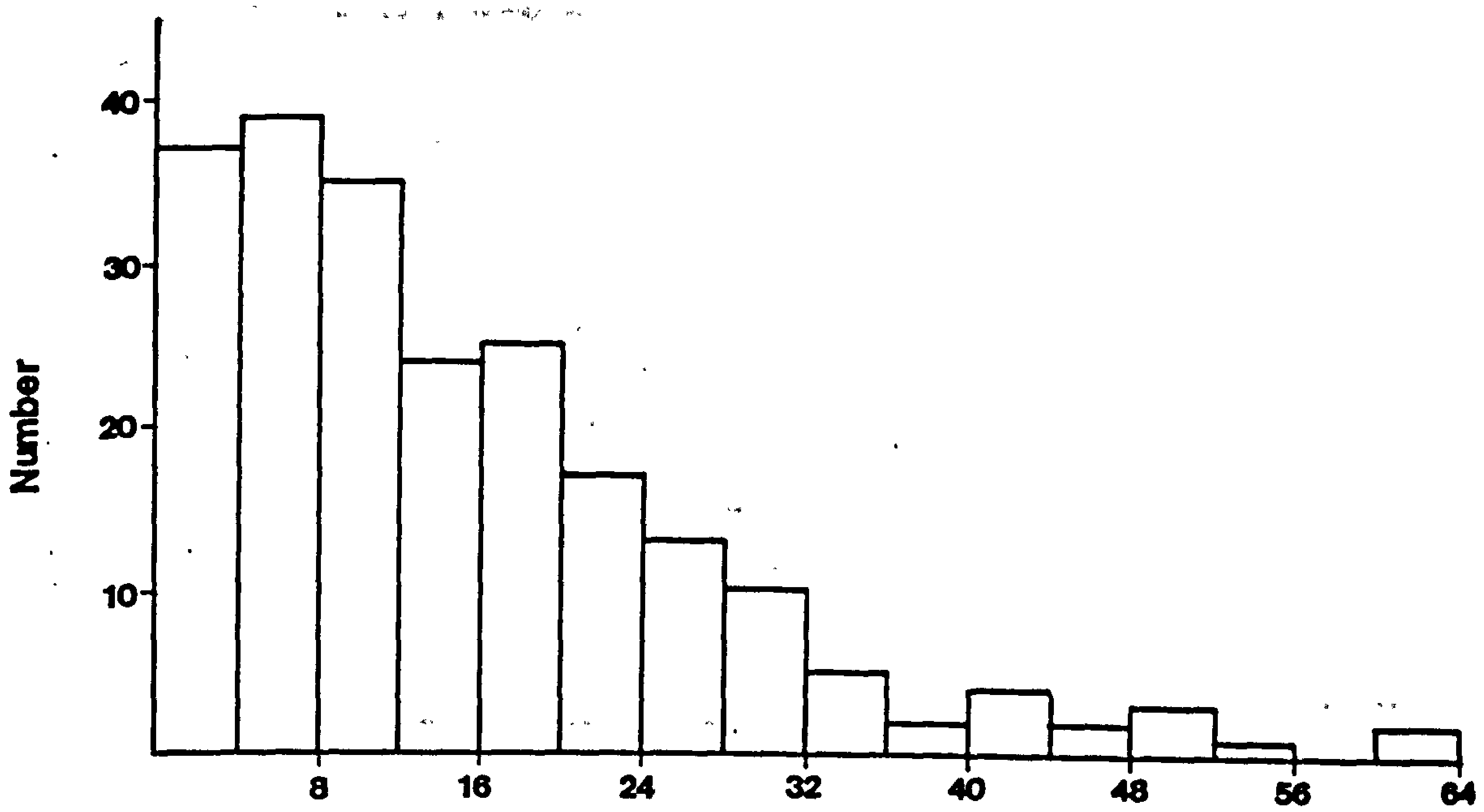


FIGURE 4.31 FREQUENCY DISTRIBUTION OF STREET DIRT (1) EXCHANGEABLE ZINC (2) HYDROCHLORIC ACID-SOLUBLE ZINC

(1) Exchangeable copper



(2) Hydrochloric acid-soluble copper

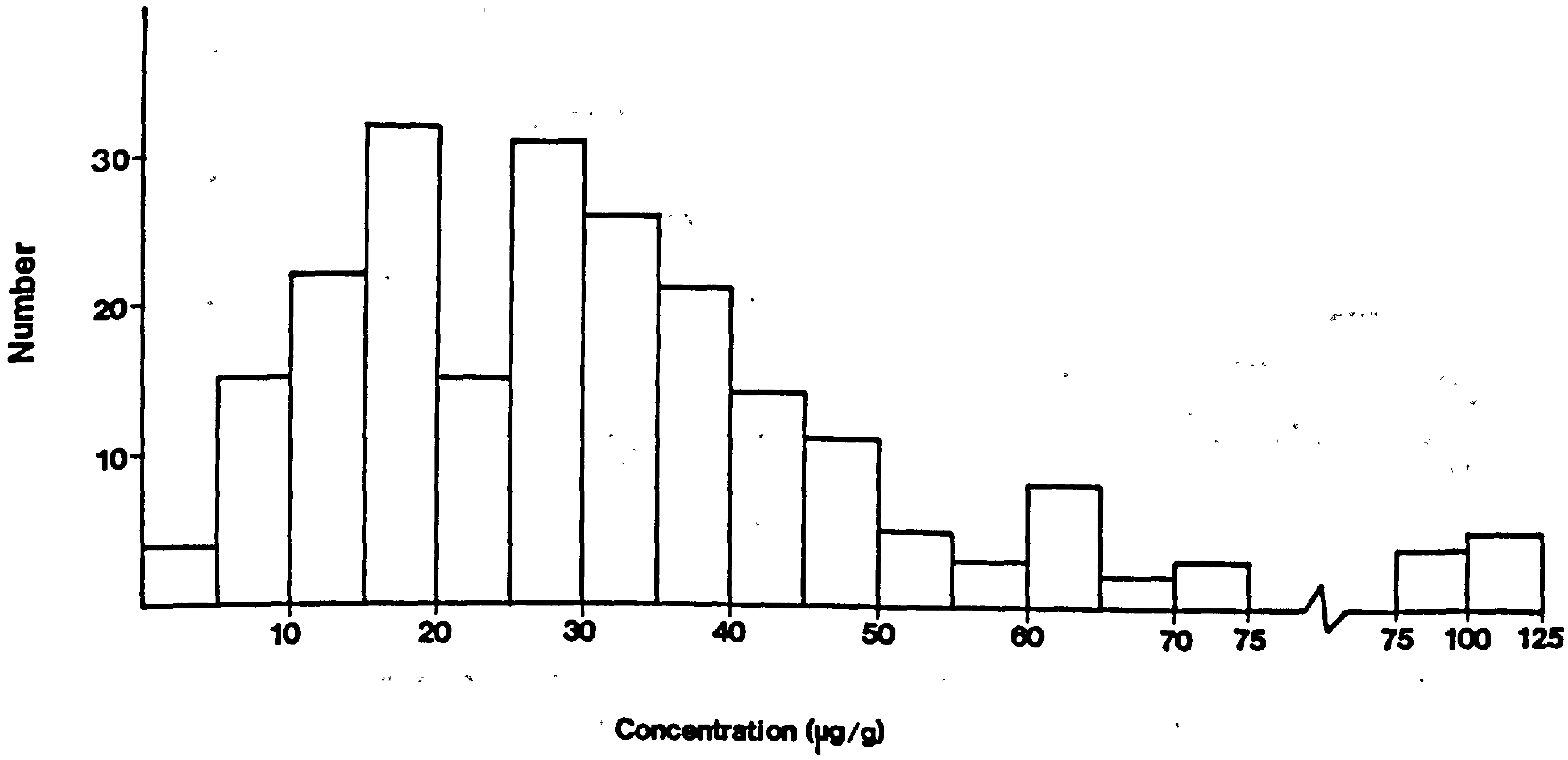
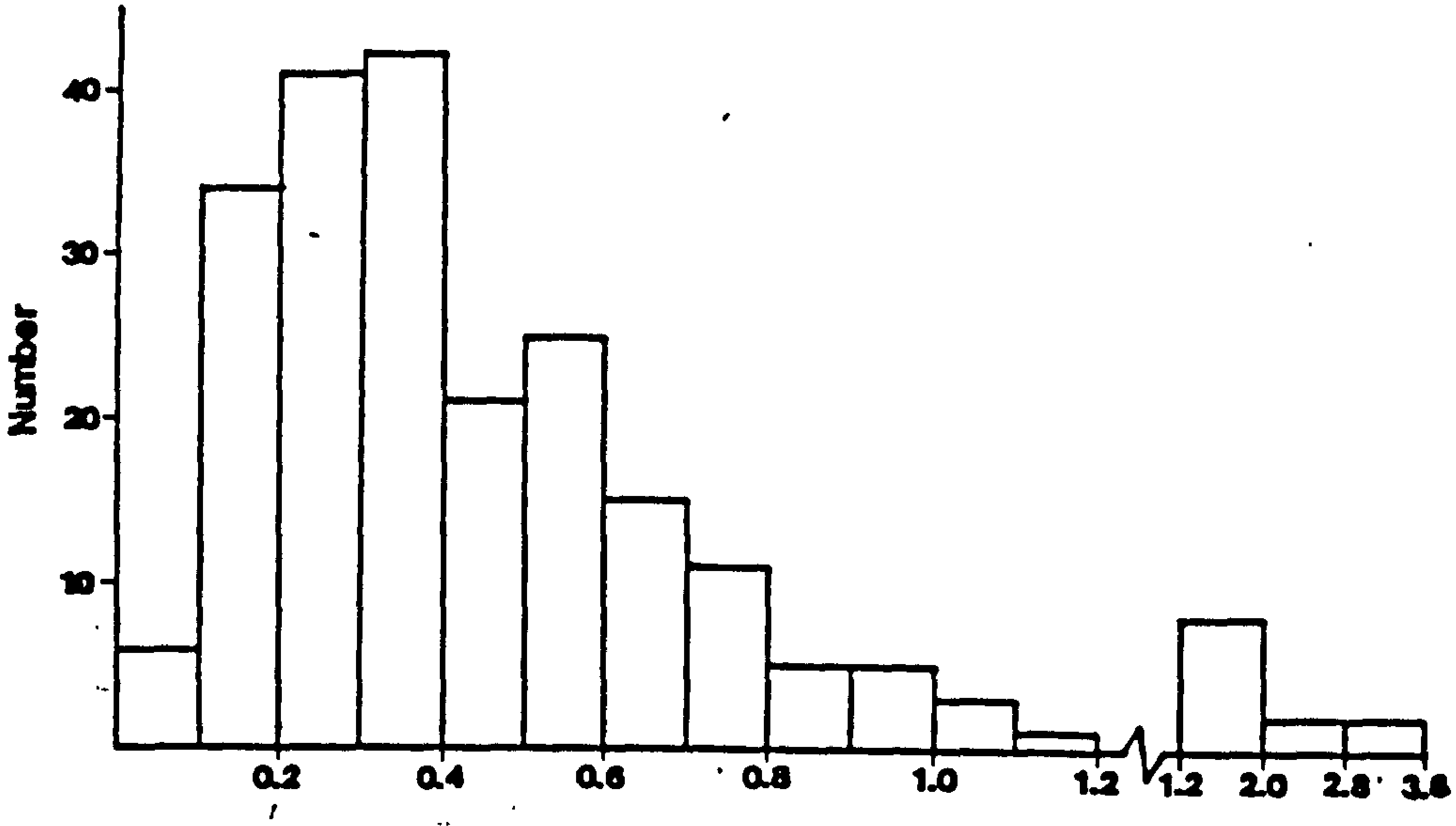


FIGURE 4.32 FREQUENCY DISTRIBUTION OF STREET DIRT (1) EXCHANGEABLE COPPER (2) HYDROCHLORIC ACID-SOLUBLE COPPER

(1) Exchangeable cadmium



(2) Hydrochloric acid-soluble cadmium

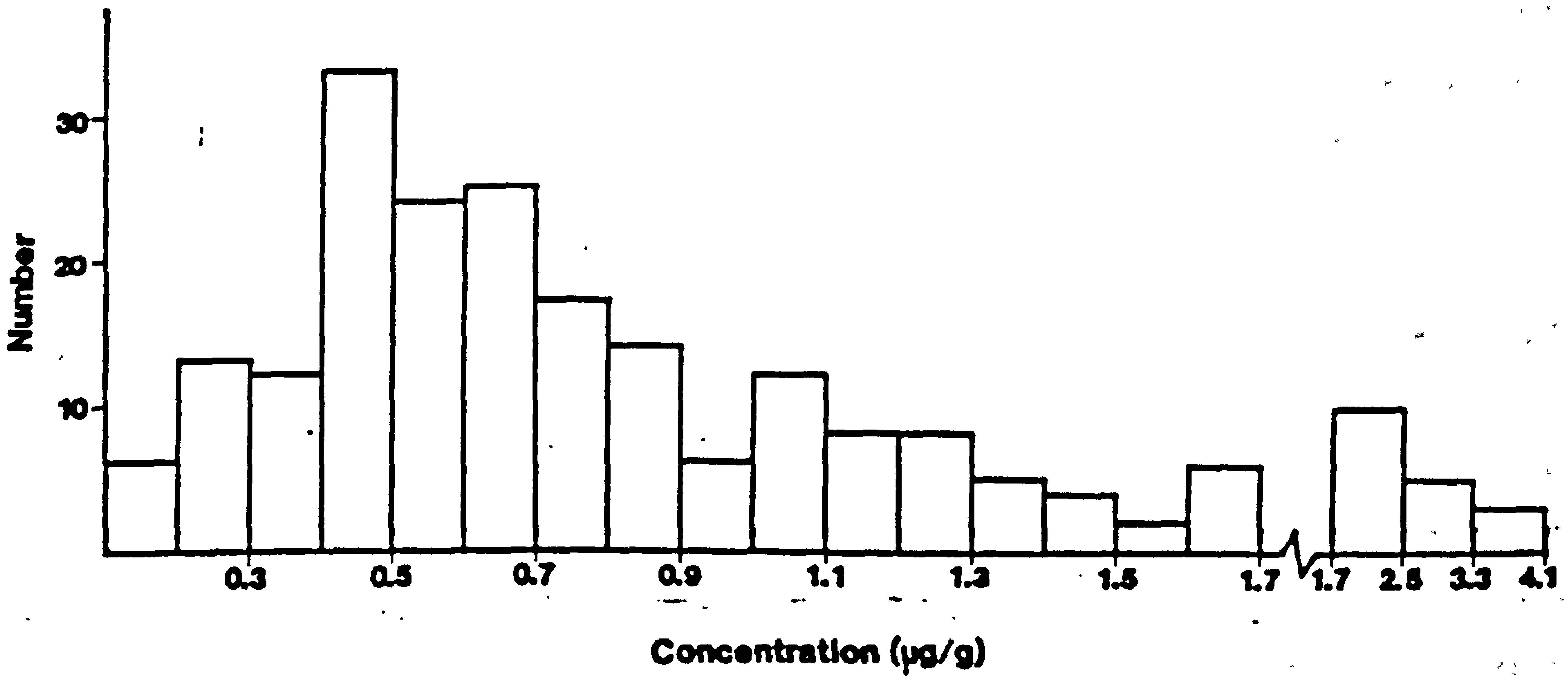


FIGURE 4.33 FREQUENCY DISTRIBUTION OF STREET DIRT (1) EXCHANGEABLE CADMIUM (2) HYDROCHLORIC ACID-SOLUBLE CADMIUM

Exchangeable cadmium, however, represented, on average, 29% of total cadmium in street dirt, identical to the corresponding ratio in soils.

Geographical mappings of the street-dirt exchangeable metal data are presented in Figures 4.34-4.37. Maps were constructed generally from one sample result per grid square although occasionally the average of two sample results was used. The maps reveal that substantial areas of the city are enhanced with respect to exchangeable metal levels, with around 16% of Glasgow exceeding 200μg/g lead (Figure 4.34). For all four metals, the highest levels occur in central Glasgow with a reduction towards suburban areas as previously observed for total and exchangeable metals in soils (Figures 4.9-4.12 and 4.17-4.20 respectively).

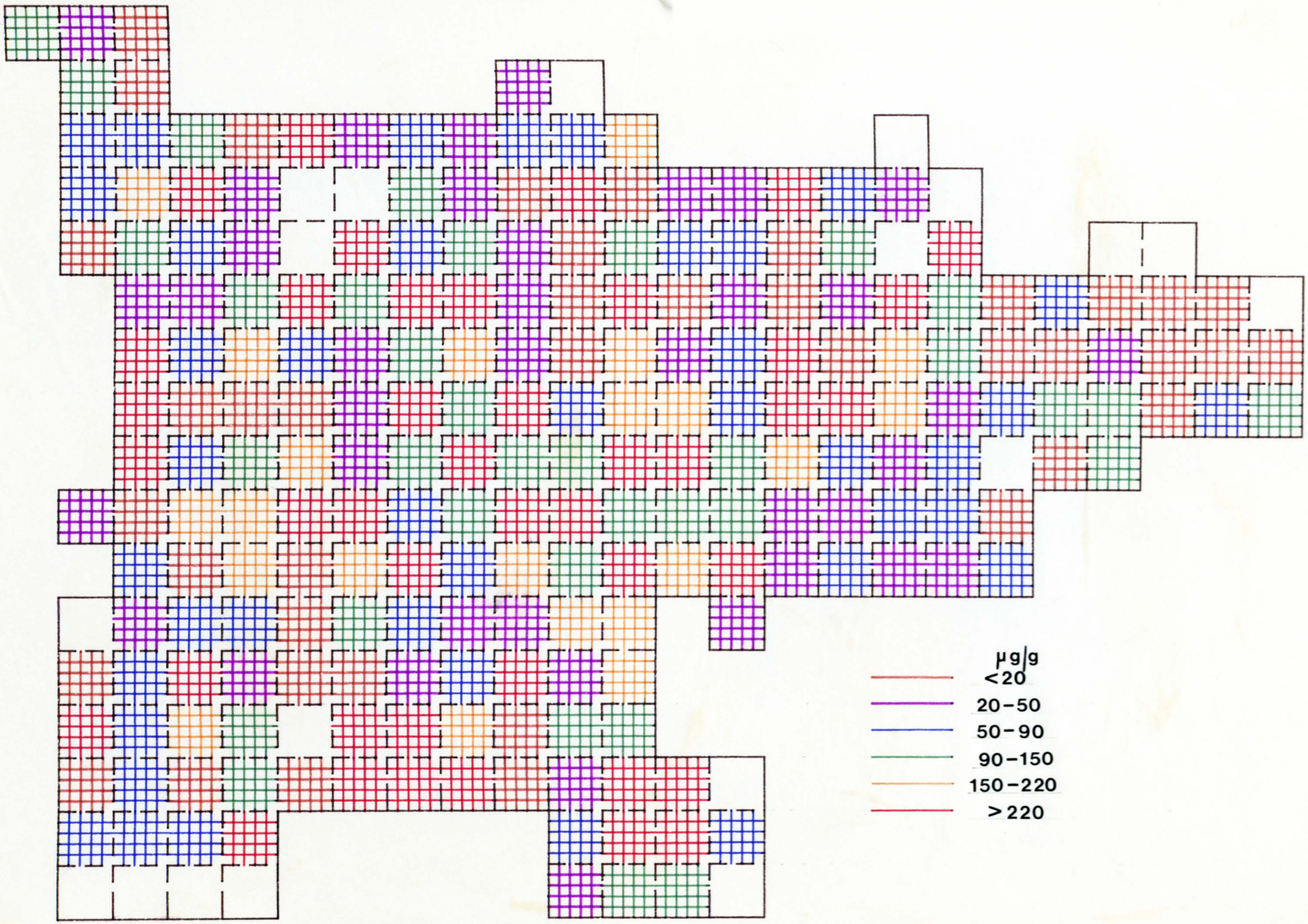
4.2.2 SIX-FRACTION STUDY - CHEMICAL PARTITIONING OF TRACE METALS IN STREET DIRT

As with soils, the six-fraction sequential leaching procedure, described in Section 3.4, provided detailed information on the chemical associations of lead, zinc, copper and cadmium in Glasgow street dirt.

In contrast to soils, street-dirt total metal concentrations were not measured directly, but were obtained by summing the individual concentrations of the six fractions. The mean total-metal values for the 60 samples investigated were 793μg/g lead (range 35.2-2280μg/g), 477μg/g zinc (range 99.8-2030μg/g), 118μg/g copper (range 16.7-466μg/g) and 1.9μg/g cadmium (range 0.06-8.7μg/g).

Although, as illustrated in Figures 4.38-4.41, some variability was observed in partitioning between individual samples, the data sets generated for the large

FIGURE 4.34 GEOGRAPHICAL DISTRIBUTION OF STREET DIRT EXCHANGEABLE LEAD


μg/g
<20
20−50
50−90
90−150
150−220
>220

<u>FIGURE 4.35</u> GEOGRAPHICAL DISTRIBUTION OF STREET DIRT EXCHANGEABLE ZINC

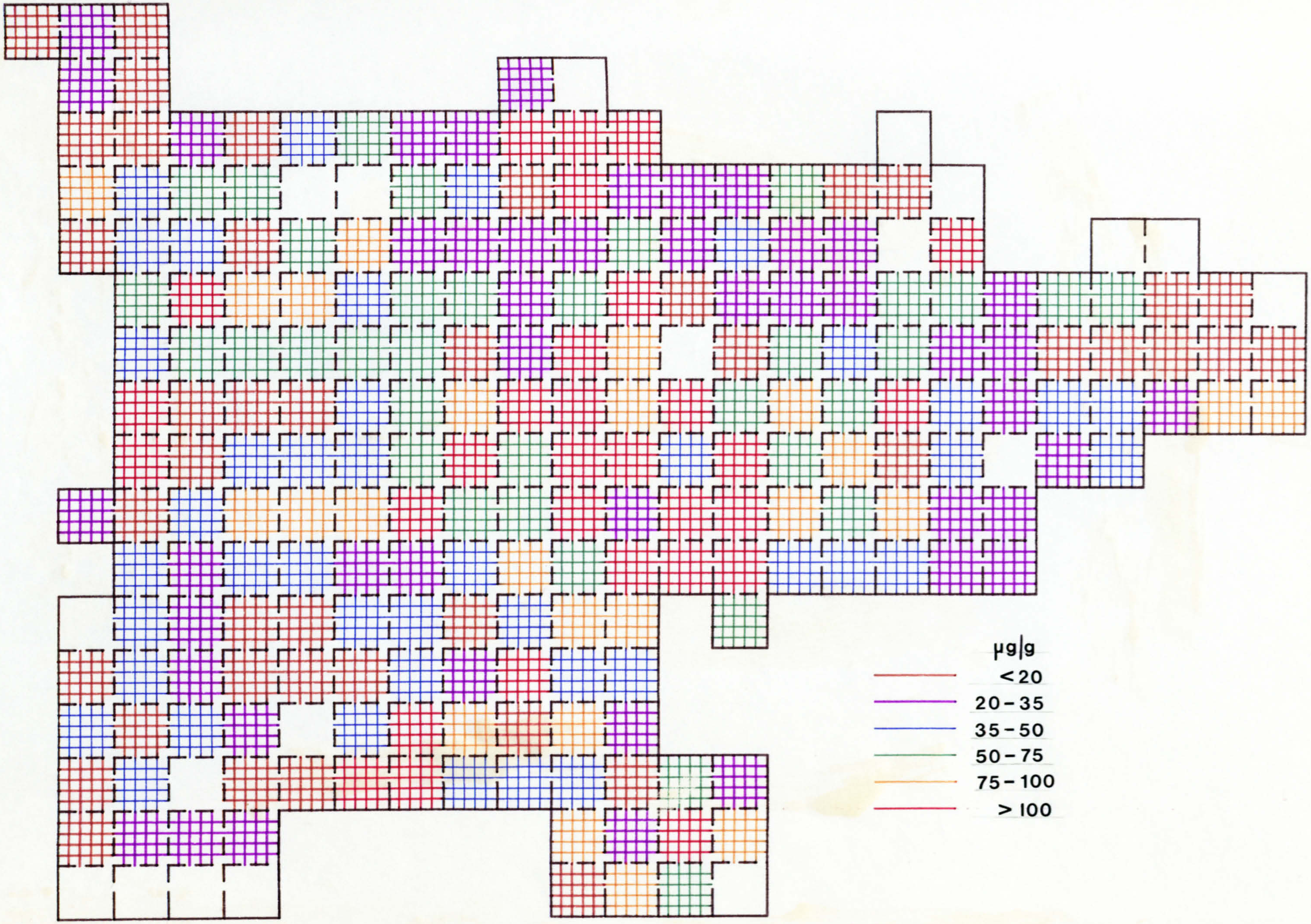

µg/g
< 20
20 – 35
35 – 50
50 – 75
75 – 100
> 100

FIGURE 4.36 GEOGRAPHICAL DISTRIBUTION OF STREET DIRT EXCHANGEABLE COPPER

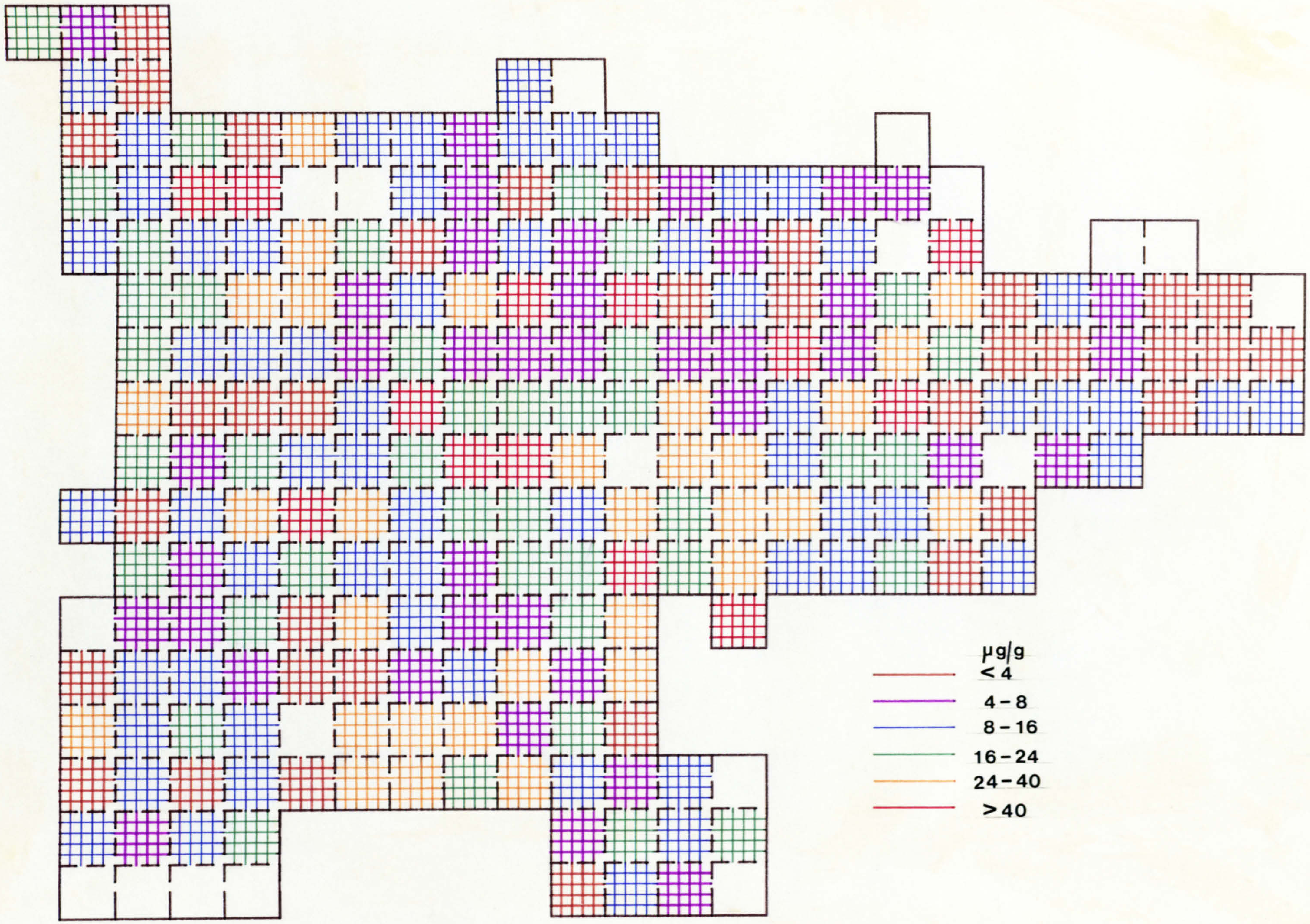
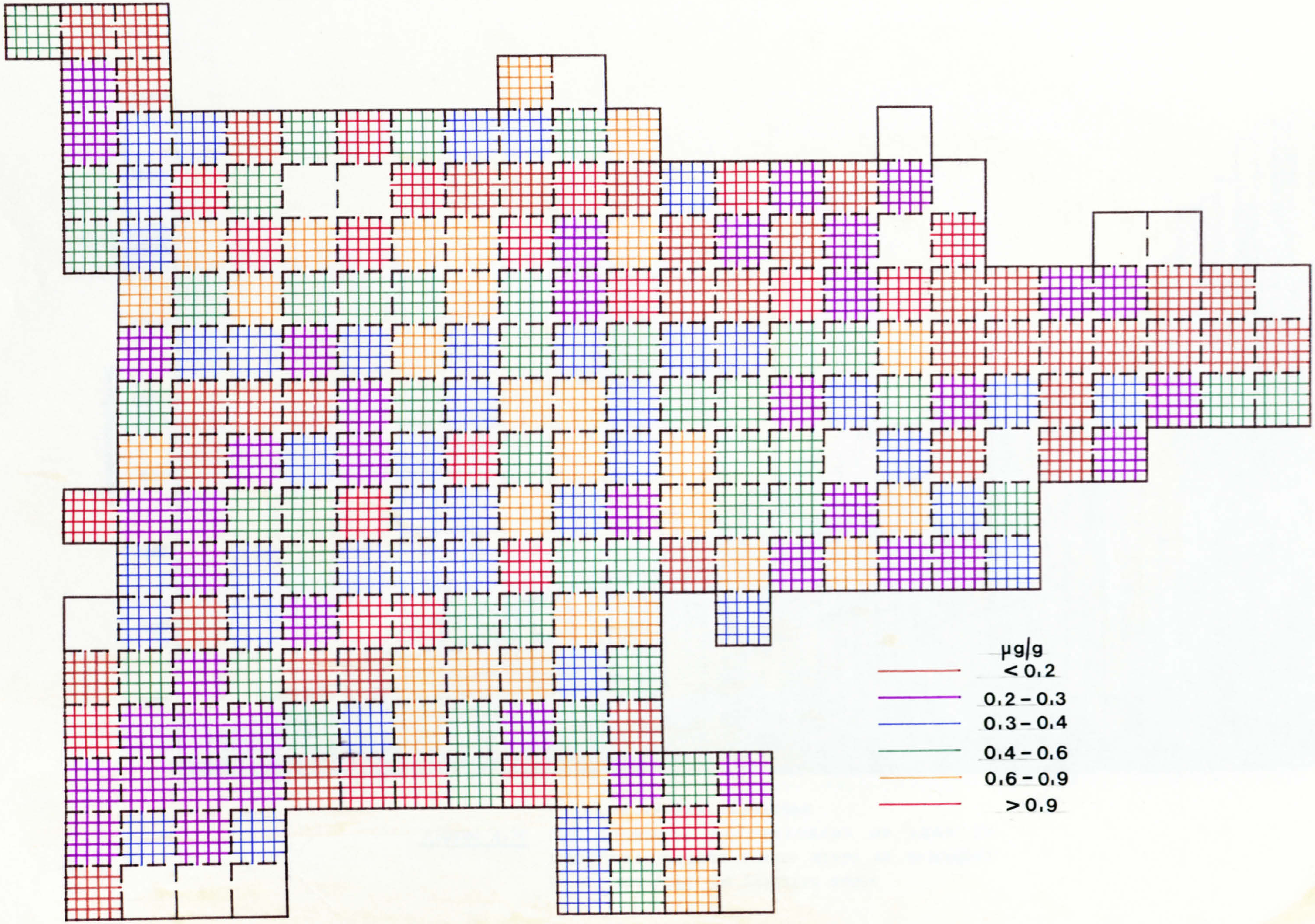

μg/g
< 4
4 – 8
8 – 16
16 – 24
24 – 40
> 40

FIGURE 4.37 GEOGRAPHICAL DISTRIBUTION OF STREET DIRT EXCHANGEABLE CADMIUM


μg/g
< 0,2
0,2 – 0,3
0,3 – 0,4
0,4 – 0,6
0,6 – 0,9
> 0,9

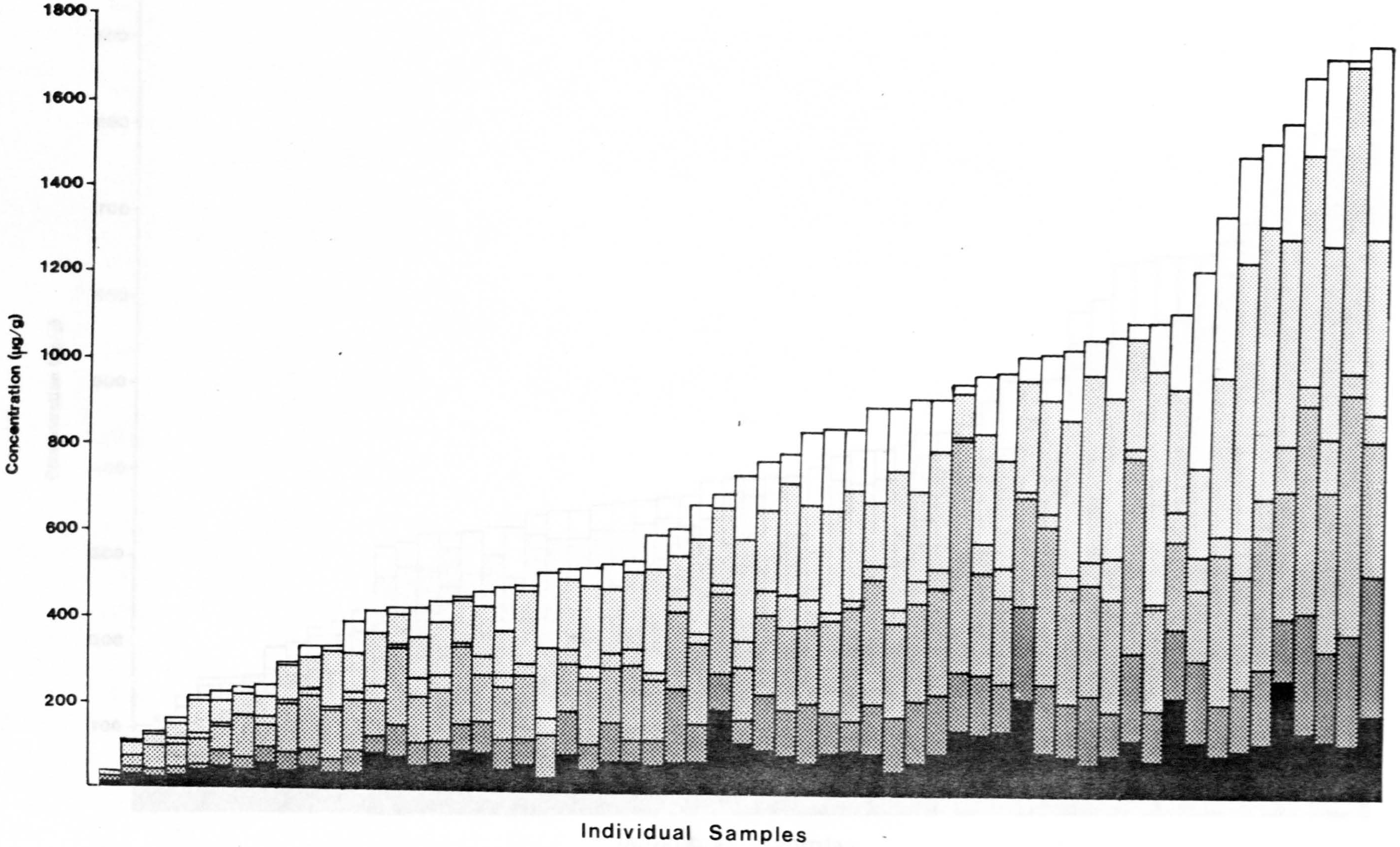


FIGURE 4.38 THE CHEMICAL PARTITIONING OF LEAD IN INDIVIDUAL GLASGOW STREET DIRTS AS DISCLOSED BY THE SIX-FRACTION LEACHING STUDY

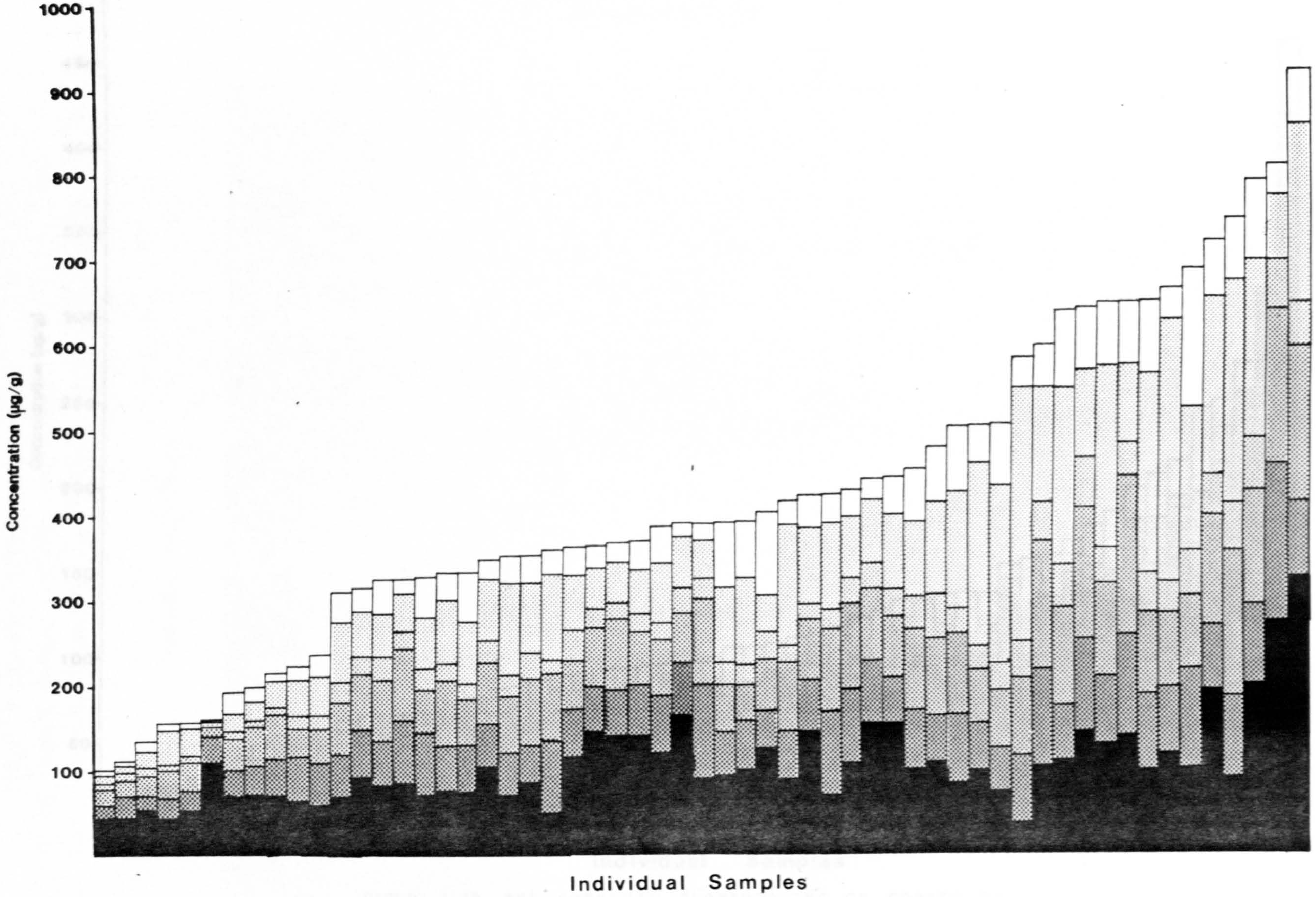


FIGURE 4.39 THE CHEMICAL PARTITIONING OF ZINC IN INDIVIDUAL GLASGOW STREET DIRTS AS DISCLOSED BY THE SIX-FRACTION LEACHING STUDY

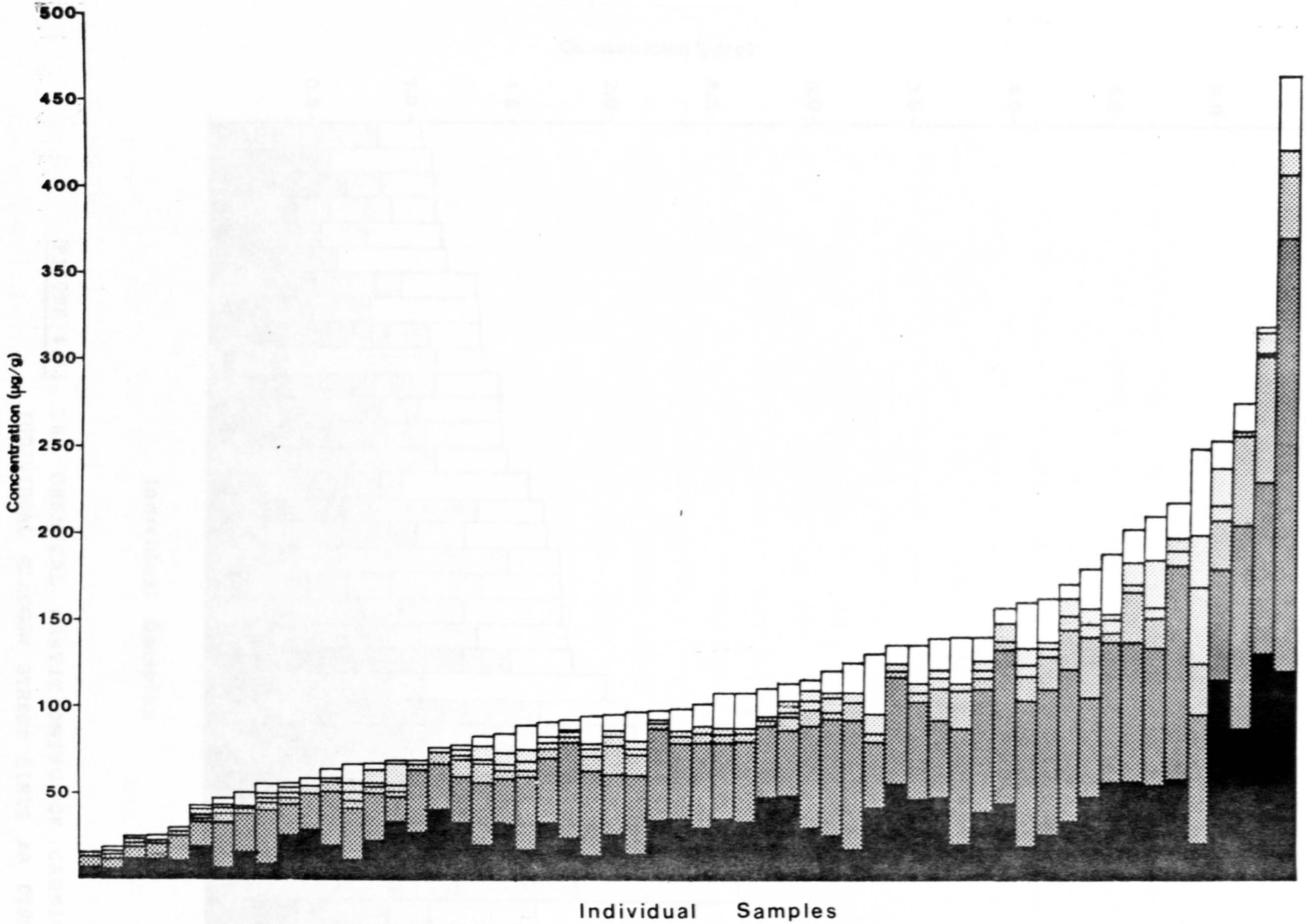


FIGURE 4.40 THE CHEMICAL PARTITIONING OF COPPER IN INDIVIDUAL GLASGOW STREET DIRTS AS DISCLOSED BY THE SIX-FRACTION LEACHING STUDY

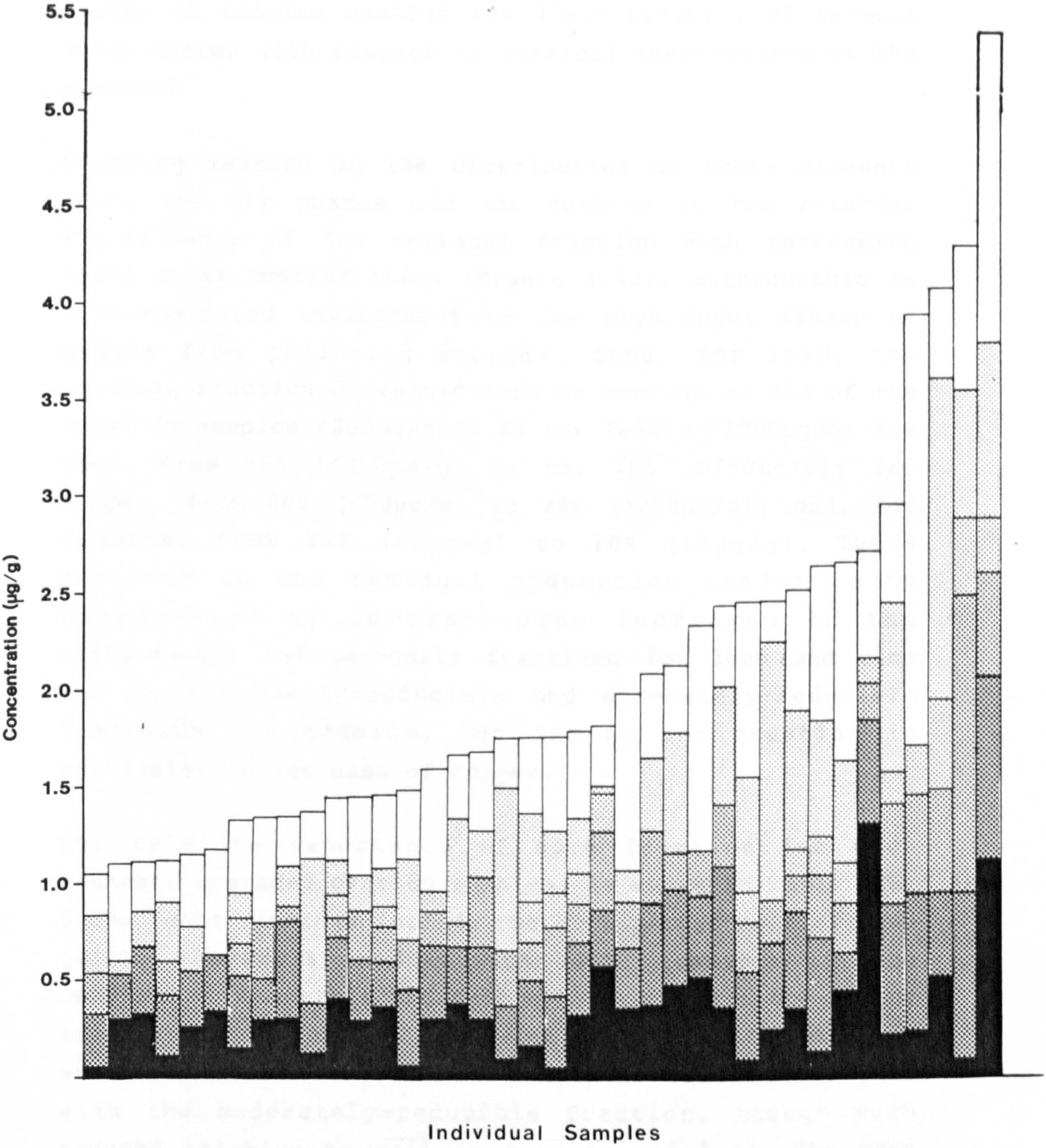


FIGURE 4.41 THE CHEMICAL PARTITIONING OF CADMIUM IN INDIVIDUAL GLASGOW STREET DIRTS AS DISCLOSED BY THE SIX-FRACTION LEACHING STUDY

number of samples enabled the identification of several clear trends with respect to chemical associations of the elements.

A common feature in the distribution of trace elements among the six phases was the decline in the relative significance of the residual fraction with increasing total metal concentration (Figure 4.42), attributable in a contaminated environment to the high input fluxes of metals from polluting sources. Thus, for lead, the residual fraction decreased from an average of 20% of the total in samples <200µg/g to 9% for levels >1200µg/g; for zinc, from 36% (<250µg/g) to ca. 20% (>750µg/g); for copper, from 40% (<30µg/g) to 29% (>200µg/g); and, for cadmium, from 32% (<1µg/g) to 10% (>3µg/g). These deficits in the residual proportion tended to be compensated by corresponding increases in the exchangeable and carbonate fractions for lead and zinc and in the easily-reducible and moderately-reducible fractions for cadmium, but for no one fraction in particular in the case of copper.

The relative importance of each fraction for each element, averaged over 60 samples, is shown in Table 4.5. Significant findings include the high percentages of lead (41%), zinc (33%) and cadmium (46%) contained in the combined exchangeable and carbonate fractions, the strong association of copper (43%) with organic matter and the association of a substantial component of lead and zinc with the moderately-reducible fraction, though much reduced relative to soil in the case of lead. The most noticeable difference between street dirt and soil is the greater importance of the combined exchangeable and carbonate fractions in the former for all four elements (Table 4.5). In addition, the relative significance of the residual fraction is much reduced for street dirt compared with soil, reflecting a general tendency for

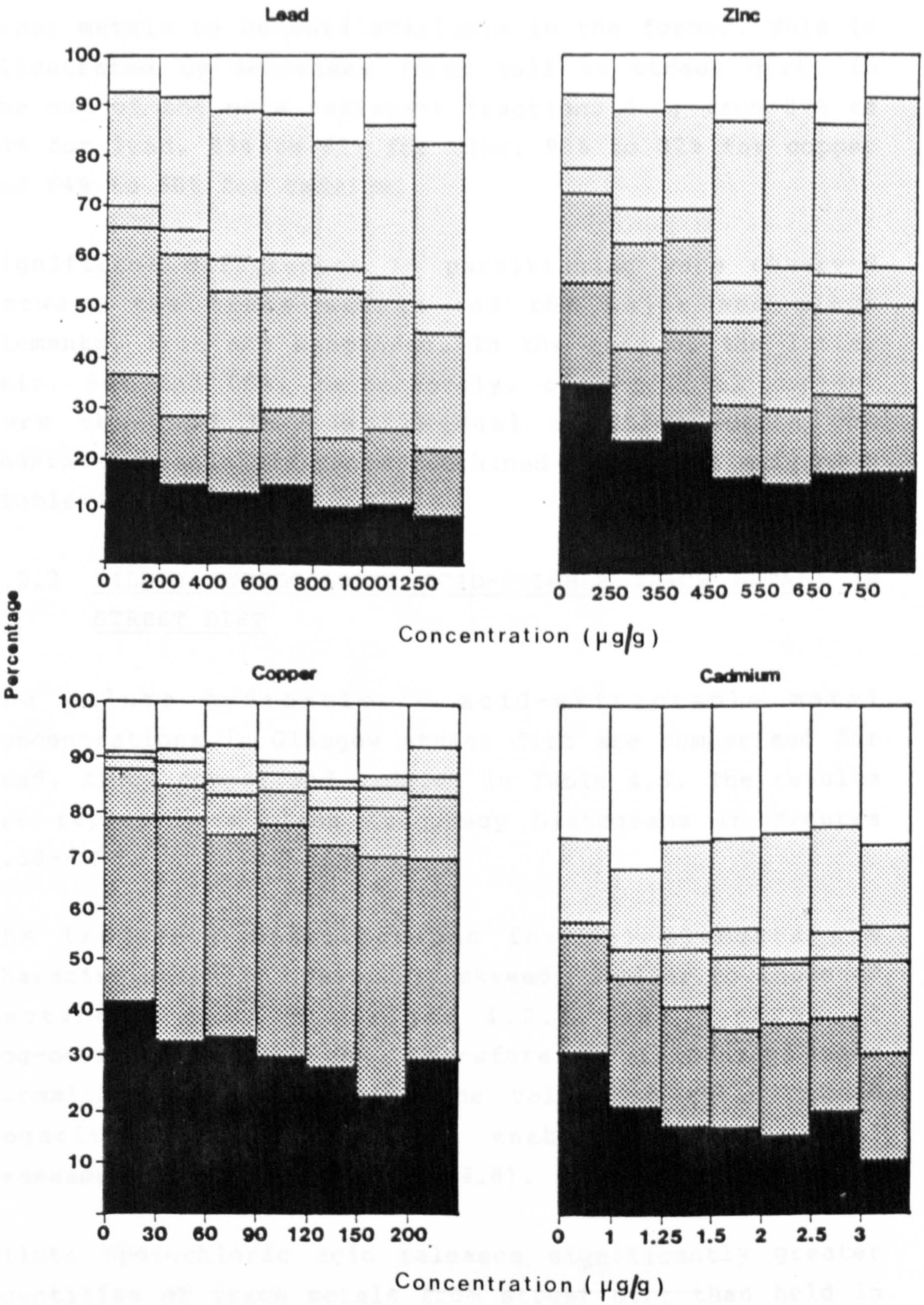


FIGURE 4.42 THE CHEMICAL PARTITIONING OF TRACE-METAL CONTAMINANTS (PERCENT OF TOTAL) OVER TOTAL CONCENTRATION SUBGROUPS IN GLASGOW STREET DIRT

trace metals to be more available in the former. This is illustrated by decreases (from soil to street dirt) in the sum of the more resistant fractions 4-6, from 87% to 54% for lead, 85% to 61% for zinc, 96% to 82% for copper and 64% to 50% for cadmium.

Significant differences in partitioning were observed between the trace metals and the major and minor elements, iron and manganese. In the case of the latter pair, 94% and 60%, respectively, of the total content were retained in the residual fraction while the moderately-reducible phase contained 15% of the manganese (Table 4.6).

4.2.3 DILUTE HYDROCHLORIC ACID-SOLUBLE TRACE METALS IN STREET DIRT

The dilute hydrochloric acid-extractable metal concentrations in Glasgow street dirt are summarised for lead, zinc, copper and cadmium in Table 4.8. The results are reported as class frequency histograms in Figures 4.30-4.33.

The frequency distributions for all elements are characteristically positively skewed, similar to those of Sections 4.1.1, 4.1.2 and 4.2.1, and typical of log-normal distributions. Therefore, distributions were normalised by transforming the values to their common logarithms (Section 4.1.1), enabling a statistical assessment of the data (Table 4.8).

Dilute hydrochloric acid releases significantly greater quantities of trace metals from street dirt than held in exchangeable form, measuring, on average (g. mean), 260µg/g lead, 166µg/g zinc, 26µg/g copper and 0.70µg/g cadmium. Corresponding exchangeable levels (g. mean) are 65µg/g lead, 39µg/g zinc, 10µg/g copper and 0.37µg/g cadmium.

TABLE 4.8 DILUTE (0.07M) HYDROCHLORIC ACID - SOLUBLE TRACE METAL CONTENT OF GLASGOW STREET DIRT, 1981

	Lead	Zinc	Copper	Cadmium
		μg/g		
No. of samples	220	220	221	213
Maximum	1170	970	131	4.1
Minimum	8	13	2	0.06
Mean	327	220	32	0.86
Std. devn.	208	136	22	0.64
Median	284	169	28	0.67
Geom. mean	260	166	26	0.70
Upper 95%	1155	575	105	2.6
Lower 95%	59	48	6	0.19

Upper and lower 95% probability ranges were calculated from logarithm transformed values.

Leaching of the 60 samples selected for the six-fraction study with 0.07M hydrochloric acid revealed a considerable range in the extractability of lead (18-66%), zinc (22-66%), copper (13-56%) and cadmium (>1µg/g; 7-76%) from individual samples but a fairly uniform mean percentage of the total over the concentration range sub-groups studied (Table 4.9). On average, 0.07M hydrochloric acid released 41% of lead, 44% of zinc, 28% of copper and 47% of cadmium.

When the hydrochloric acid-soluble trace-metal data are considered with respect to the findings of the six-fraction study, it can be seen that the release of trace-metals from street dirts by dilute hydrochloric acid reflects the detailed chemical partitioning pattern.

In the lower total concentration ranges for lead (0-400µg/g), zinc (0-450µg/g) and cadmium (1-2µg/g), 0.07M hydrochloric acid extracted some 15-25% more of each metal than was contained in the sum of exchangeable, carbonate and easily reducible fractions (Figure 4.43). This proportion decreased with increasing total metal concentration, particularly for lead and cadmium, so that over the full concentration range, relative to the sum of the first three fractions, 0.07M hydrochloric acid released an average 98% of lead, 120% of zinc and 101% of cadmium (Figure 4.44). This demonstrates that lead, zinc and cadmium associated with the first three fractions are quantitatively released by dilute hydrochloric acid with some additional zinc being removed from the fourth fraction. With respect to the sum of the first four fractions, i.e. after inclusion of the moderately-reducible phase, the amount extracted by dilute hydrochloric acid fell to 77% of zinc (Figure 4.44). For copper, where the organic and residual fractions are both major phases, 117% of the sum of the first four fractions (194% of the first three) were released by the dilute

TABLE 4.9 HYDROCHLORIC ACID-SOLUBLE TRACE METAL CONTENT OF GLASGOW STREET DIRT AS PERCENT OF TOTAL OVER TOTAL CONCENTRATION SUB-GROUPS

LEAD			ZINC			COPPER			CADMIUM		
Range (µg/g)	No.	Mean* (%)	Range (µg/g)	No.	Mean* (%)	Range (µg/g)	No.	Mean (%)	Range (µg/g)	No.	Mean* (%)
0–200	3	40.5±19.5	0–250	10	37.0±11.9	0–30	5	29.3±8.4	1–1.25	7	53.1±12.7
200–400	7	43.8+12.7	250–350	8	44.6±10.3	30–60	6	27.7+11.6	1.25–1.5	7	50.5±12.3
400–600	14	40.5±12.3	350–450	19	43.3±11.0	60–90	9	30.2±12.3	1.5–2	8	52.7±14.5
600–800	6	41.3±15.3	>450	19	46.1±9.3	90–120	14	28.3±10.3	2–2.5	5	38.9±14.7
800–1000	10	42.5±8.5				120–150	6	30.6±12.5	2.5–3	5	43.4±15.4
1000–1250	9	37.7±10.4				>150	14	25.3±7.2	>3	6	34.8±21.7
<1250	8	39.7±8.6									
$\overline{X}$	57	40.8±11.3	$\overline{X}$	56	43.7±9.8	$\overline{X}$	54	28.1±9.9	$\overline{X}$	38	46.5±15.9

* Arithmetic mean.

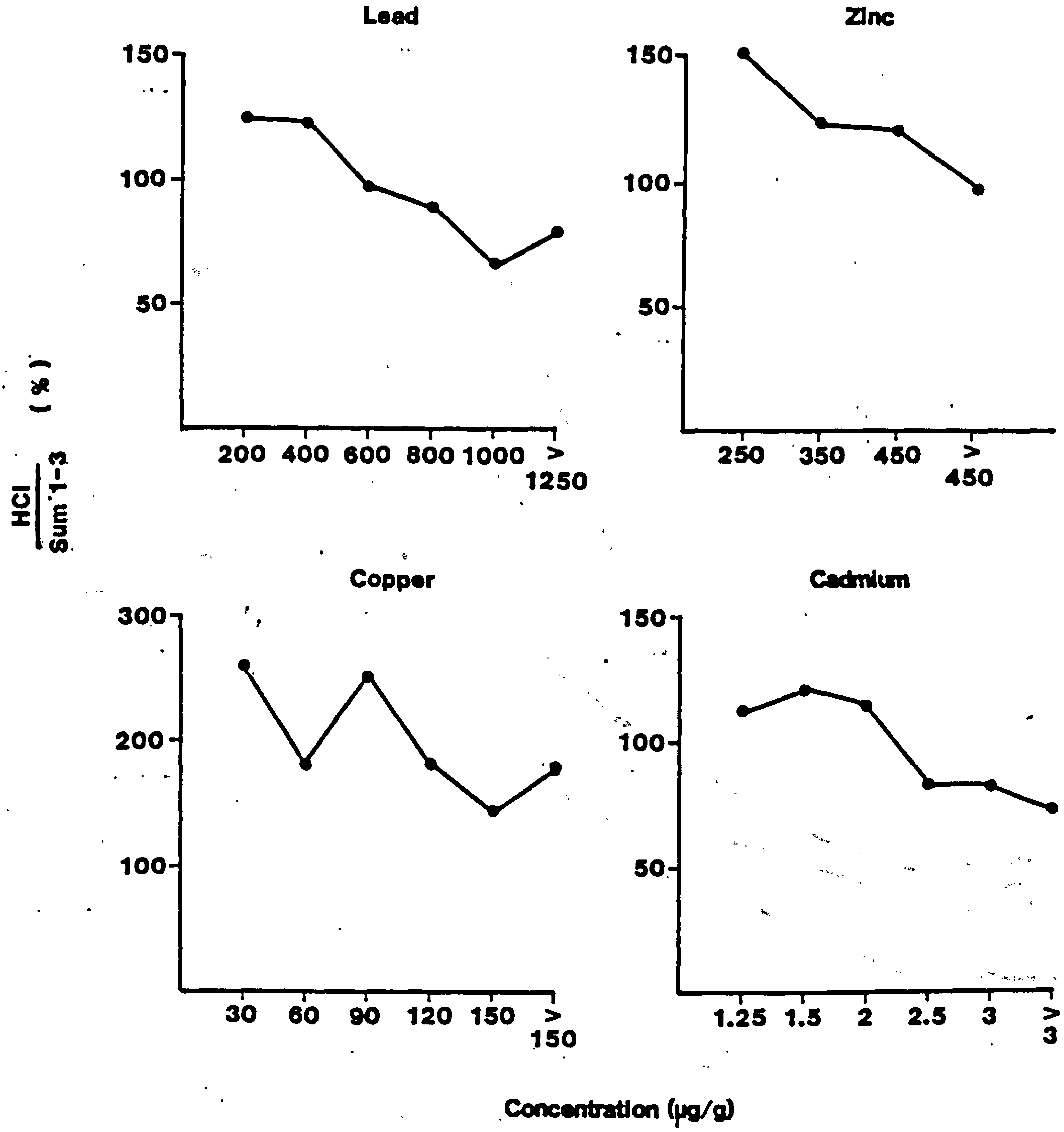


FIGURE 4.43 HYDROCHLORIC ACID EXTRACTABLE TRACE METALS RELATIVE TO THE SUM OF EXCHANGEABLE, CARBONATE AND EASILY REDUCIBLE FRACTIONS (%) OVER TOTAL CONCENTRATION METAL SUBGROUPS

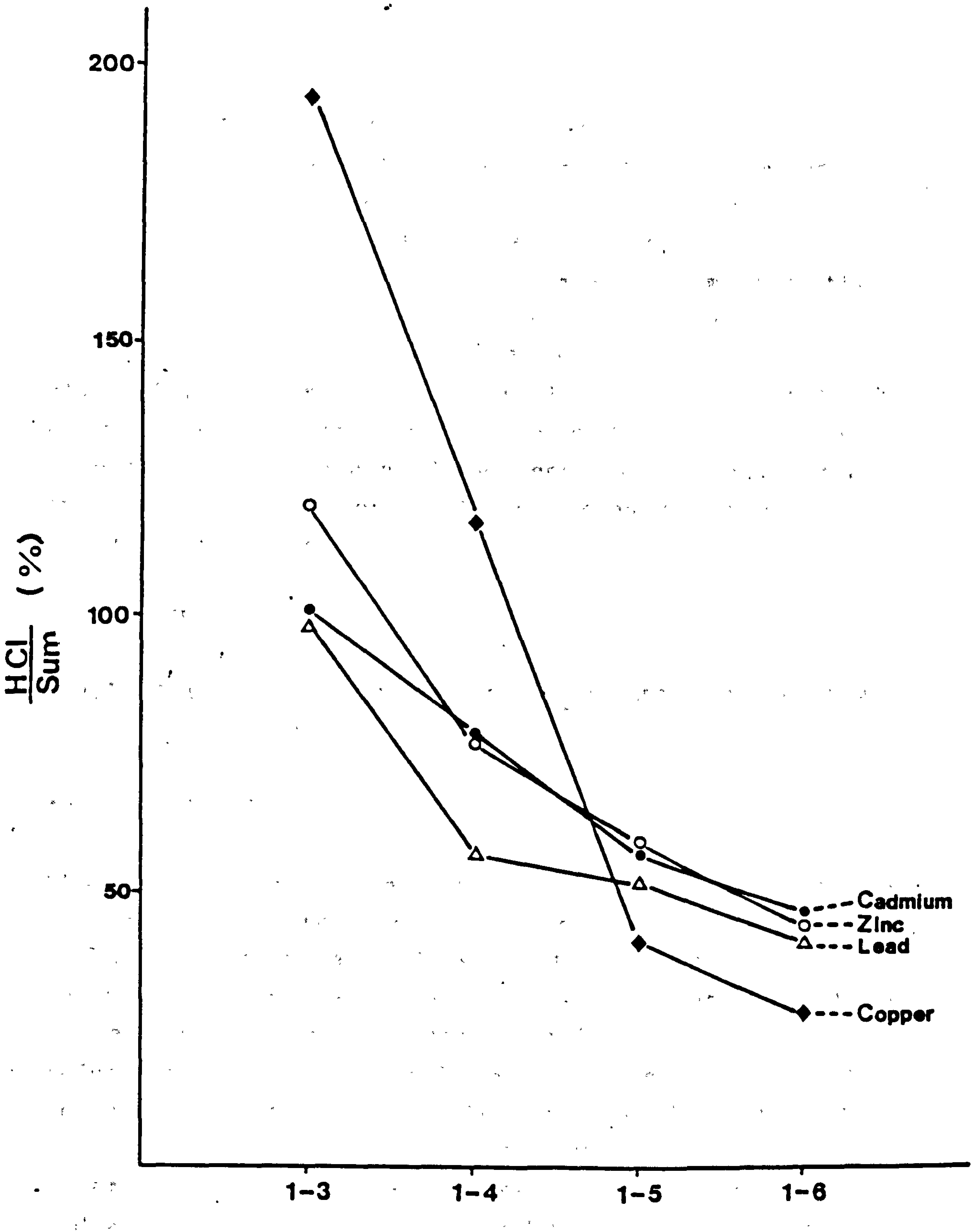


FIGURE 4.44 HYDROCHLORIC ACID EXTRACTABLE TRACE METALS RELATIVE TO THE SUM OF FRACTIONS OF THE SIX-FRACTION STUDY (%)

mineral acid (Figure 4.44). This fell to 41% of the first five or 50% of the first four combined with the residual fraction. In all, the amount of copper solubilised by 0.07M hydrochloric acid exceeded the sum of the first four fractions in 61% of the samples, mainly those <120µg/g (total). In view of the resistance of organic matter to attack by dilute hydrochloric acid (Kitano et al, 1980), however, the quantitative apportionment of the excess between organic and residual fractions is uncertain, but when considered separately, the excess, on average, is equivalent to 20% of organic copper and 28% of residual copper.

4.3 DISCUSSION

4.3.1 TRACE-METAL CONTAMINATION IN GLASGOW SOILS AND STREET DIRT

4.3.1.1 SOILS

The total metal content of a soil reflects the environmental factors and conditions during and after its formation. Assessment of the extent of contamination, which may be considered as a positive deviation from the normal trace-metal content (Section 1.3.1), requires information on the typical metal concentrations present in uncontaminated soils. Although normal levels in UK uncontaminated soils can vary widely depending on parameters such as parent material, soil type, location and weathering (Mitchell, 1964; West, 1981), the range of concentrations listed in Table 4.10 are considered typical. Furthermore, Davies (1978; 1980a; 1983a), on the basis of statistical treatment of data from soil pollution studies in England and Wales, has derived the maximum concentrations of trace metals likely in an uncontaminated agricultural environment (Table 4.10).

TABLE 4.10 **NORMAL LEVELS OF TRACE METALS IN UNCONTAMINATED SOILS**

	Lead	Zinc	Copper	Cadmium
		(μg/g)		
Typical concentrations[1]	20-40	50-100	10-20	0.5-1.0
Maximum concentration[2]	110	195	29	2.0

[1] Davies, 1980; Berrow and Mitchell, 1980.

[2] Davies, 1978; 1980; 1983.

Relative to the ranges found in uncontaminated soils (Table 4.10), the total concentration ranges in Glasgow soils were large, typically covering two orders of magnitude, e.g. lead, 22-1900µg/g; zinc, 18-1840µg/g; copper, 3.4-925µg/g and cadmium, 0.1-4.07µg/g. For all soils a small percentage of lead, zinc and copper results were within the anticipated UK normal concentration ranges, with ca. 5% of samples <40µg/g lead, 16% <100µg/g zinc and 4% <20µg/g copper (Figures 4.1-4.3 respectively). Nevertheless, Glasgow soils frequently exceeded the maximum levels expected in an uncontaminated environment with 66% of samples >110µg/g lead, 37% >195µg/g zinc and 90% >29µg/g copper. Highest concentrations were 9-32 times greater than the maximum natural levels. Cadmium displays the least contamination, with 11% of soils exceeding the 'typical' range (0.5-1.0µg/g cadmium) but only 1% of soils greater than 2µg/g. These results show that most urban land in Glasgow is elevated, with respect to uncontaminated soils, in lead, zinc and copper.

Although there is a general lack of <u>urban</u> soil data, two recent large-scale comprehensive studies from England provide useful data for comparison with the Glasgow results. In similar systematic surveys of trace metal contamination, total levels of lead, zinc, copper and cadmium were measured in the whole West Midlands Metropolitan County area (WMMC) [JURUE, 1980; 1981] and in Walsall (JURUE, 1982). The results of the former are summarised in Table 4.11 while, in Walsall, lead concentrations ranged from 0.5-2575µg/g and cadmium from 0.1-53.2µg/g. Like trace metal concentrations in Glasgow, distribution patterns tended to be lognormal in character. For lead, 58% of samples in the WMMC exceeded 100µg/g while in Walsall 47% of samples were greater than 100µg/g, results which are similar to the Glasgow study. Levels of lead were generally enhanced throughout the

TABLE 4.11 TRACE METAL LEVELS IN THE WEST MIDLANDS METROPOLITAN COUNTY AREA[1]

	Lead	Zinc	Copper	Cadmium
		(µg/g)		
Range	5-2232	10-7483	4-4574	0.1-30.3
Mean[2]	167	442	130	1.51
Std. Devn.	97	349	124	1.08

[1] JURUE 1980, 1981

[2] Mean of cited means

survey areas with the highest levels observed in the most heavily urbanised and industrialised zones, due to motor vehicle emissions and, to a lesser extent, industrial smokes and domestic coal ash. In contrast to the similarity in lead concentration between Glasgow and the English surveys, probably reflecting similar sources, both English studies are considerably enhanced in zinc, copper and cadmium (25% of samples >2µg/g cadmium in Walsall) relative to the Glasgow results (Table 4.1). Elevations of this magnitude were attributed to certain industrial activities in areas, such as the Black Country, which have a long history of metal smelting, refining and finishing.

Within Glasgow soil types (e.g. garden soils, open spaces etc.), garden soils were clearly the most contaminated for all four elements (Table 4.1). For example, with respect to lead, 83% of garden soils exceeded the upper 'natural limit' - 110µg/g - (Davies, 1983a) compared with 74%, 76% and 53% of open spaces, parkland and agricultural soils respectively. In a study of soil contamination in Manchester, Davies et al (1978) noted that garden soils were generally enriched in lead, zinc and copper when compared with unpolluted rural soils, with concentrations (g.mean) of 171µg/g lead, 152µg/g zinc, and 33µg/g copper, broadly similar to those observed in Glasgow (196µg/g, 203µg/g and 82µg/g respectively). Both Glasgow and Manchester appear to be considerably less contaminated with lead than the conurbations reported in a recent 10-town survey where garden soils averaged 671µg/g lead (median 436µg/g, range 21-12,420µg/g) and in a London Borough survey where mean lead was 956µg/g with median 704µg/g (range 1-13,680µg/g) [Culbard et al, 1983] (Table 4.12). Severe contamination of this nature may result from <u>major</u> lead emission sources, such as lead works, specific to very localised areas - as was noted for one garden soil in Manchester, collected adjacent to a lead battery scrapworks, which

TABLE 4.12 SUMMARY OF LEAD CONCENTRATIONS MEASURED IN UK URBAN GARDEN SOILS

	Lead Concentration (µg/g)
Manchester[1]	
Range	34 - 3270
g. mean	171
mean	381
median	215
10-town survey[2]	
Range	21 - 12,420
Average	671
Median	436
London[2]	
Range	1 - 13,680
Average	956
Median	704

[1] Davies, 1978

[2] Culbard et al, 1983

contained an exceptionally high lead concentration of 3270µg/g (Davies et al, 1978). In general, however, metal levels in garden soils tend to be greater than in surrounding agricultural areas (Purves, 1977; Parry et al, 1981; Royal Commission, 1983) due to the close proximity of polluting sources such as vehicular emissions, eroded paint and burning of vegetative material, timber and coal. Not surprisingly, therefore, in view of their peripheral urban locations, Glasgow agricultural soils were the least contaminated with respect to all four elements (Table 4.1). Only 44% of the agricultural soils, as compared with 69% of the rest, were above the 110µg/g upper limit for lead (Davies, 1983a). This does show, however, that peripheral Glasgow urban soils are contaminated with trace metals and suggests that the contamination may extend far beyond the city boundary into the adjacent rural land, as observed in studies of other areas (Davies, 1983b).

Geographically, while trace-element contamination tends to increase towards central Glasgow, certain specific areas can be identified, mainly adjacent to the River Clyde and in the north/northwest of the city, where levels are most enhanced (Figures 4.9 - 4.12). These 'hot-spots' are derived from active and former components of Glasgow's industrial framework: iron and steelworks to the north and along the banks of the Clyde in the 'east end' of the city, the activities (metal plating, welding, etc.) associated with shipbuilding beside the river in the city's 'west end' and the emissions of a local leadworks.

This demonstrates that soil mapping of trace metals within urban areas is capable of distinguishing between general enhancement and additional contamination by particular industrial processes.

As most vehicular-emitted lead is deposited on or close to the road, the lead concentration of roadside soil rapidly declines with increasing distance from the road (Farmer and Lyon, 1977; Royal Commission, 1983). However, this trend may not be clearly reflected in the data of an urban survey unless the project is deliberately designed to show it. Nevertheless, this commonly-observed influence is illustrated in the present study by a drop in garden and open space lead from averages of 199µg/g and 167µg/g (g.mean) respectively at <10m from roads to 183µg/g at 10-50m in the former and to 99.3µg/g at >50m in the latter (Table 4.13). When all soil types are averaged (g.mean), lead levels decline from 177µg/g at <10m to 156µg/g at 10-50m and eventually to 129µg/g at >50m (Table 4.13).

4.3.1.2 STREET DIRT

Glasgow street dirt contains trace metals at levels representative of the typical range of total concentrations reported for urban/residential street-dirt (Table 4.14). Mean Glasgow street dirt concentrations are significantly higher than corresponding metal levels in Glasgow soils, in line with similar urban soil-street-dirt studies (Harrison et al, 1981). Street-dirt metal loadings differ from soil deposits as a result of their closer proximity to the source of contamination, particularly cars, the absence of a protective covering (e.g. grass) and their impervious nature. While vehicular emissions are the main source of lead (Table 1.4), levels are not necessarily directly related to traffic density or driving mode, but may in part reflect the composition of the road surface e.g. concrete surfaces yield, through abrasion, higher levels of lead (and zinc) than asphalt surfaces (Shaheen, 1975).

TABLE 4.13 INFLUENCE OF DISTANCE FROM ROAD ON SOIL LEAD CONCENTRATIONS

	Lead Concentration[1] (μg/g)		
Distance from road (m)	<10	10-50	>50
Garden Soils	199	183	-
Open Spaces	167	147	99.3
Parks	151	179	158
Agricultural	-	90.4	114
All Soils	177	156	129

[1] geometric mean

TABLE 4.14 COMPARISON OF GLASGOW STREET DIRT TRACE METAL CONTENT WITH OTHER REPORTED UK DATA

	Lead	Zinc	Copper	Cadmium
			(μg/g)	
Glasgow street dirt				
Range[1]	35.2-2280	99.8-2030	16.7-466	0.06-8.7
Mean[1]	793	477	118	1.9
Range[2]	19.5-2853	29.7-2224	7.1-466	0.13-8.8
Mean[2]	798	503	114	1.8
Median[2]	696	387	99.6	1.5
UK-10-town survey[3]				
Range	140-7720			<1-210
Mean	1188			5.1
Median	914			2.7
London[3]				
Range	172-9664			<1-280
Mean	1764			12.0
Median	1450			4.0
Lancaster[4]				
Range	920-3560	200-940	57-312	1.3-10.1
Mean	1880	534	143	4.6

1 Derived from six-fraction study.
2 Derived from HCl-soluble results.
3 Culbard et al, 1983.
4 Harrison, 1979.

Environmental pathways and effects of street-dirt metals are influenced by particle grain size and both chemical forms and concentration of the metals. Municipal cleaning is efficient in the removal of particulate matter >250µm but, as many metals have a strong affinity for smaller particle sizes (>50% by mass, of lead, zinc, copper and cadmium are associated with particles <250µm [Ellis and Revitt, 1982]), substantial quantities of these metals will remain. Street dirt metals are also removed in urban stormwater through chemical leaching and suspension of particulate matter. Metals removed in this way are eventually deposited in local receiving waters. Fine-grained particulates (<63µm) are readily suspended and transported in urban rainwater (Ellis and Revitt, 1982; Harrop et al, 1983) with levels of trace metals of up to 8500µg/g lead, 8000µg/g zinc, 1600µg/g copper and 670µg/g cadmium being reported in stormwater suspended sediments (Revitt et al, 1982). The extent of chemical leaching depends on the physico-chemical form of the metal, weakly-bound exchangeable metals equilibrating rapidly in water (Patrick et al, 1977). As street dirt represents both recent and longer-term accumulations of atmospheric particulates and dust particles, its chemical composition is highly variable e.g. certain elements, such as lead, are present in their primary weathered form ($PbSO_4 . (NH_4)_2 SO_4$) as well as in subsequent weathered states ($PbSO_4$) [Biggins and Harrison, 1980]. The six-fraction study indicates that trace metals in street dirts are notably more labile than in soils, with 18-50% of total lead, zinc, copper and cadmium present in the exchangeable, carbonate and easily-reducible fractions (Table 4.5). The weakly-bound exchangeable fraction contains 10-29% of total metal concentration illustrating that appreciable amounts of street-dirt metals are chemically mobile and readily transported in highway run-off. Further, these exchangeable results relate to pH7, the pH of natural waters, whereas rainwater in urbanised/industrialised areas is invariably acidic and therefore more effective in metal removal (Day et al, 1979). Heavily contaminated highway run-off has an immediate impact on the quality of receiving waters and ultimately leads to the contamination of the biota and bottom sediments (Laxen and Harrison, 1977; Wilber and Hunter, 1979; Revitt and Ellis, 1980). In the west of Scotland, contamination of Clyde Sea Area sea-loch sediments is due, in part, to the removal of trace metals in urban run-off (Farmer, 1983).

4.3.2 CHEMICAL PARTITIONING

The geochemical nature of trace metals in Glasgow urban soils (pH range 4.3-7.1, mean 5.7 [Appendix 5]) and street dirts (pH range 4.5-7.5, mean 7.0 [Appendix 5]) has been disclosed using a detailed sequential extraction procedure (Table 4.5, Sections 4.1.4 and 4.2.2). The scheme employed reflects the ease of release of metals into solution under various environmental conditions.

While the exchangeable trace metal level in soils represents the most easily mobilised and biologically available fraction, readily liberated from ion-exchange sites of the soil matrix (Wilber and Hunter, 1979; MAFF, 1980; Harrison et al, 1981), the levels in street dirt are clearly of less importance with respect to uptake by plants, but they do represent levels which may be released through changes in the ionic composition of stormwater (Hamilton et al, 1983). Differences in metal partitioning between soil and street dirt (the street dirt exchangeable fraction is of greater significance for all four elements [Table 4.5]) are attributable to variations in chemical and physical (e.g. grain size [Ellis and Revitt, 1982]) characteristics which increase the number and abundance of exchange sites in the latter. Therefore, whereas exchangeable lead, zinc and copper constitute only a minor proportion (<3%) of the total metal concentration in soil, they represent a more significant fraction (11-13%) in street dirt. However, the strong association of cadmium with the exchangeable fraction in soils (19% of total in soils >0.6µg/g) and street dirt (27% of total in street dirt >1µg/g), highlights the potentially greater bioavailability and mobility of this element. These results are consistent with laboratory-based experiments on stormwater leaching of street dirts where cadmium was the most readily-extracted element (Ellis and Revitt, 1982). There have been several reports of the significant mobility of cadmium in street dirt and roadside soils (Harrison et al, 1981; Hamilton et al, 1983) and in some aquatic sediments (Gupta and Chen, 1975; Förstner and Salomons, 1980). However, there is some evidence suggesting that the apparent significance of the exchangeable fraction for cadmium in aquatic sediments may be due to partial release of the carbonate phase (Tessier et al, 1979), especially when using acetate extractants (Rapin and Förstner, 1983).

The carbonate phase contains metals which are easily to moderately available for release and are very susceptible to changes in pH. This has significant implications for the urban environment where stormwater pH may be mildly acidic, (pH 5-6). Appreciable amounts of lead, zinc and cadmium, especially in street dirt (19-28%), are present in this fraction, enhancing the overall ease of removal of these elements, e.g. 32% and 46% of total cadmium in soil and street dirt, respectively, is present in the combined exchangeable/carbonate fraction. The greater significance of the carbonate fraction for all four metals in street dirt relative to soil was also observed in Lancaster by Harrison et al (1981), who attributed the greater proportion of metal in the carbonate phase of street dirt to the higher amounts of calcite present.

Further, the large proportion of calcium carbonate present in aquatic sediments (sometimes >50%) may account for the observed importance of this phase in trace-metal partitioning (Gupta and Chen, 1975; Tessier et al, 1979; Salomons and Förstner, 1980).

Manganese and iron oxides are widely acknowledged to be efficient scavengers for trace metals. They are, however, thermodynamically unstable under the anoxic conditions which prevail during waterlogging in soils (Russel, 1977) and in street-dirt accumulations in gullypots (Hamilton et al, 1983). The easily-reducible fraction (mainly manganese oxides), which is released under weak reducing conditions, is of minor importance for all four elements in Glasgow soils and street dirts (<6% of total) despite the fact that 8-25% of manganese is solubilised. Salomons and Förstner (1980) extracted the easily-reducible fraction of aquatic sediments and noted that substantial amounts of zinc and cadmium (23-49%) but small amounts of lead and copper (3-6%) were associated with this phase. Chao (1972) observed large differences in the solubility of manganese oxides between soils and sediments with those present in the latter being more easily released (85% of total compared with 50%). This was confirmed by Wilber and Hunter (1979) who found that only 18% of manganese in street dust sweepings and stormwater solids, compared with 65% of manganese in river sediments, was released in the easily-reducible phase along with, on average, 11% and 14% respectively of trace metals (lead, zinc, copper). The easily-reducible manganese oxides therefore appear to be considerably less important in the trace-metal geochemistry of soils and street dirt than in aquatic sediments. This, however, would not be apparent when only one reducing step is employed, e.g. as in the leaching schemes of Harrison et al (1981) and Hamilton et al (1983).

Conversely, the moderately-reducible phase is of major significance for lead (51% and 27% of total in soil and street dirt respectively) and moderately important for zinc (13% and 19% of total) and cadmium (15% and 12% of total) [Table 4.5]. However, with regard to availability under typical environmental conditions, the trace metals contained in this fraction would only be weakly available. Close association with the moderately reducible/iron-manganese oxide phases has been reported for lead and zinc in soil and street dirt (Harrison et al, 1981; Hamilton et al, 1983) and also in sediments (Wilber and Hunter, 1979; Tessier et al, 1979; Salomons and Förstner, 1980; Farmer et al, 1980; Farmer, 1983). As with manganese oxides, iron oxides in surface sediments tend to be more concentrated and of a more amorphous, secondary nature than those in soils and street dirt, with typically >50% of the total released using 1M $NH_2OH.HCl$/25% HOAc (Chao, 1972; Wilber and Hunter, 1979).

Copper geochemistry differs greatly from that of lead, zinc and cadmium as illustrated by the strong association copper has with the organic fraction of soil and street dirt (Table 4.5). The preference of copper for this phase has been demonstrated in numerous studies on aquatic sediments (Förstner and Wittman, 1979) and soils and street dirt (McLaren and Crawford, 1973; Harrison et al, 1981; Hamilton et al, 1983). The humic acid and fulvic acid fractions are responsible for soil organic matter complexing metallic ions from solution (Lewis and Broadbent, 1961; Mitchell, 1964). In the fulvic acid chelation of copper, there is some evidence that the -SH, -COOH and $-NH_2$ groups may be involved (Mitchell, 1964) and that soil pH is important, with optimum complex formation at pH6 for fulvic acid and pH 2.5-3.5 for humic acid (Mitchell, 1964). The formation of copper-organic complexes also appears to depend on the form of copper, with the free form (Cu^{2+}) tending to complex with phenolic groups whereas hydroxylated forms ($CuOH^{+}$) combine with carboxyl groups (Lewis and Broadbent, 1961)

The organic fraction is, in general, of moderate significance for lead, zinc and cadmium in soil (7-29%) and street dirt (14-22%), the latter range being broadly in agreement with that (13-27%) reported by Hamilton et al (1983). The results of Harrison et al (1981), however, with the organic fraction accounting for <12% of total lead, zinc and cadmium in soils and <8% in street dusts, are somewhat lower than those of the Glasgow study.

The order of extraction employed in most sequential leaching schemes conveys the impression that trace metals associated with the organic fraction are generally unavailable. However, under conditions of high microbial activity, as in humus soils or as found in street surface run-off, the less resistant forms of organic matter are degraded, releasing associated trace metals. In addition, the solubility of metal-organic complexes may change with pH. Consequently, the contribution of the organically-bound forms to the pool of plant-available soil copper may be greater than the exchangeable phase alone e.g. some humic acid-copper complexes from peat are available to oat plants (Mitchell, 1964). For this reason EDTA is sometimes employed as a predictive soil extractant for copper (and zinc) [ADAS, 1981a].

Metals associated with the residual phase are considered to be held firmly within the mineral crystal lattice and are thus immobile and unavailable. The residual component is the predominant geochemical phase for zinc, copper and cadmium in soils (42-46% of the total [Table 4.5]) which reflects, to some extent, even in a contaminated environment, the influence of the parent material in determining the trace metal composition of soils. In street dirt, the metal-residual associations are noticeably less important (13-31%), compared with soils, illustrating the general tendency for the residual fraction to decrease in significance with increasing total metal concentration (Förstner et al, 1981; Harrison et al, 1981). This reflects the high input fluxes of metals from polluting sources in a contaminated environment. The residual component of Glasgow street dirt, however, is somewhat higher for zinc, copper and cadmium than the residual proportions of Lancaster (4.5-12% of total) [Harrison et al, 1981] and London (4-18% of total) [Hamilton et al, 1983] street dirt.

In summary, the chemical associations of trace metals in Glasgow soils and street dirt in the pH groups studied reveal that the order of overall environmental mobility is cadmium >> lead ⪢ zinc > copper. These trace metals are considerably more mobile in street dirt than in soils.

The usefulness of the chemical leaching approach has been criticised on the grounds of readsorption of released metals (Rendell et al, 1980) and lack of selectivity of extractants (Oakley et al, 1981; Luoma and Bryan, 1981). Readsorption is as likely to occur in the environment during dissolution of a metal as it is during a laboratory extraction procedure (Harrison et al, 1981). More importantly, although selectivity for a specific geochemical phase in a strictly thermodynamic sense cannot be achieved (Rapin and Förstner, 1983), the type of extraction scheme employed in this study, based on examination of well-defined mineral phases and optimised for selectivity (Sections 3.3.2.3 (i) and (ii)), is rather specific (Rapin and Förstner, 1983) and, at the very least, enables the broad identification of the physico-chemical associations of trace metals in Glasgow soils and street dirt (Sections 4.1.4 and 4.2.2).

It may be concluded from the work described here and in the literature that sequential leaching techniques are applicable in the investigation of a wide range of environmental samples such as soils, street dirts, sediments and atmospheric and suspended particulates, which differ in chemical and physical characteristics. Through the provision of information on trace-metal availability and mobility, chemical partitioning is of particular importance in the consideration of environmental health and ecological effects and in the construction of guidelines for control of environmental trace-metal contamination (Sections 4.3.3-4.3.4).

4.3.3 POTENTIAL UPTAKE OF TRACE METALS FROM STREET DIRT BY HUMANS

Although humans are exposed to significant amounts of trace metals in air, water, food and soil, the possible health hazard represented by elevated metal concentrations in street dirt has hitherto received insufficient attention (Culbard et al, 1983). Despite evidence suggesting that oral ingestion of lead from dust via fingers is at least comparable to intake levels obtained through dietary routes (Duggan and Williams, 1977; Charney et al, 1980; Royal Commission, 1983), the importance of street dust and housedust as a major source of lead for young children is still disputed. One ground for this opposition is the closeness claimed between the blood-lead ratios (ca. 1.3) of child/mother and adult male/female pairs, implying the absence of a separate important pathway for child lead uptake (Chamberlain et al, 1978). However, recent evidence indicates that the child/adult blood-lead ratio is enhanced in high lead contaminated areas relative to low-lead areas and that the probable route is via dust (Duggan, 1983b).

Some assessment of the potential lead uptake by young pre-school children, from the sucking of dirty fingers and contaminated objects, can be made by leaching the dust with dilute hydrochloric acid, simulating the digestive juices of the human gastrointestinal tract (Table 4.8) [Duggan and Williams, 1977; Day et al, 1979; Harrison, 1979].

It has been estimated that young children ingest about 100mg dust per day in this manner (Duggan and Williams, 1977; Royal Commission, 1983). The percentage of ingested lead which is absorbed into the bloodstream depends on the physical and chemical form of the lead, the other contents of the gut and the main constituents of the diet (Heard and Chamberlain, 1982; Royal Commission, 1983). Estimates of lead absorption by children, including a factor for lead solubilisation, range up to 53% (Alexander et al, 1973; Royal Commission, 1983).

In a highly contaminated environment such as Glasgow, where pollutant trace element concentrations are log-normally distributed, it is more valid, e.g. when evaluating the health implications of the data, to consider the geometric mean - 260µg/g for 0.07M hydrochloric acid-soluble lead. Comparison with the six-fraction study lead data demonstrates that lead released from street dirt by dilute hydrochloric acid is broadly related to the combined exchangeable, carbonate and easily-reducible fractions and constitutes 41% of total lead. This suggests that an average 41% of ingested lead is solubilised and available for absorption. If this were completely absorbed, then daily ingestion of 260µg/g (Table 4.8) would yield an uptake of 26µg lead per day. Although this value would be reduced by less effective absorption, it may well underestimate lead uptake as some workers believe the effective concentration of lead in street dust is probably about twice the value determined from coarsely-sieved (<500μm) dust, through retention of smaller particles on hands (Duggan and Williams, 1977).

In April 1983, the Ninth Report of the Royal Commission on Environmental Pollution (Royal Commission, 1983) estimated (Appendix 4, Table 1) that the typical daily lead intake of a 2-year-old child in an inner-city environment from ingestion of dust was 140μg (0.1g dust of lead content 1400μg/g) which, at 53% absorption, corresponded to a daily uptake of 74μg lead. This was equivalent to 70% of the total daily lead uptake via lungs and gut of 105μg, of which inhalation accounted for only 3%. Dietary intake (food and solder) contributed 47μg lead, equivalent to an uptake of 25μg lead per day.

In general, bearing in mind the wide range of lead concentrations in dust and uncertainties about the quantities of dust ingested and lead absorption factors, this study on the solubilisation and bioavailability of lead in street dirt endorses the Royal Commission's conclusions and concern about the ingestion of street dusts as a major route of lead uptake. Increments of up to 5μg/100ml in the blood-lead level concentration of young children per 1000μg/g lead in dust have been inferred (Duggan, 1980; Duggan, 1983a), a worrying correlation in view of the deleterious effects of lead on childhood intelligence and behaviour (Needleman et al, 1979; Rutter and Jones, 1983).

The average amounts of bioavailable zinc (17μg), copper (2.6μg) and cadmium (0.07μg) resulting from the daily ingestion of 100mg street dirt are negligible relative to dietary intakes of ca. 15mg, 2.0-3.0mg and 50-150μg, respectively, per day (Underwood, 1977; Mertz, 1981a).

4.3.4 GUIDELINES FOR THE LIMITATION OF ENVIRONMENTAL TRACE-METAL CONTAMINATION

In an effort to reduce community exposure to heavy metals, several authorities have set standards or guidelines for airborne concentrations (European Community Directive, 1982), domestic water supplies (European Community Directive, 1980), food (Lead in Food Regulations, 1979; Food Additives and Contaminants Committee, 1983) and certain paints (Pencils and Graphic Instruments [Safety] Regulations, 1974). As a significant proportion of daily human intake of certain metals may be derived from soil and dust, either directly or indirectly, some people consider that similar attention should be directed to the establishment of standards for these materials (Duggan, 1980; 1983b), particularly as many areas of former industrial land are being redeveloped for more sensitive uses e.g. housing and recreation. However, despite the monitoring of urban dust by local authorities (GLC, 1980), several studies on metal contamination of household and street dust (Day et al, 1975; Duggan and Williams, 1977; Harrison, 1979; Fergusson et al, 1980) and the recent 10-town survey by the Department of the Environment (DOE) [Culbard et al, 1983], there are no government guidelines for metal levels in urban dust. The Greater London Council recommends a safety limit for lead in dust of 500µg/g [GLC, 1981]. Using the current GLC guideline, 66% of Glasgow street dirt samples (particle size <500µm) exceed the recommended limit although no samples were found to exceed the previous limit of 5000µg/g lead.

With respect to trace metal contamination of soils there have, until recently, been few detailed systematic studies in major UK cities to provide adequate data-bases for necessary policy formulation (Parry et al, 1981; JURUE, 1980; 1981; 1982; Davies, 1983b). Nonetheless, tentative steps have been taken by the DOE towards the construction of guidelines for the limitation of soil contamination in urban areas (Smith, 1981). Guideline concentrations, which also include provision for phytotoxicity, have been fixed according to the land-use category - a measure of the degree of possible human exposure. Where new development or redevelopment is taking place, DOE guidelines for acceptable concentrations of total lead have been set at 550µg/g for small gardens, large gardens and allotments and at 2000µg/g for open spaces, including parkland (Smith, 1981). In Glasgow, only about 5% of garden soils (and of all samples) exceeded 550µg/g lead and no sample contained more than 1900µg/g lead. In a corresponding survey in Walsall (JURUE, 1982) soil lead levels were similar to Glasgow concentrations, with 5% of all samples >550µg/g and 0.25% >2000µg/g. In contrast, Davies (1983b), deriving total lead concentrations from EDTA-extractable levels (on the basis that EDTA-extractable corresponds to 75% of total), concluded that 40% of all land in central or inner London surpassed the lower guideline, 550µg/g, while in outer rural areas (20-50km from city centre) only 3% of land exceeded 550µg/g lead.

For cadmium, the corresponding DOE guidelines are set at 5µg/g (small gardens), 3µg/g (large gardens and allotments) and 15µg/g (open spaces and parkland). Relative to these guidelines, Glasgow soils are uncontaminated - with only one sample, a garden soil, exceeding 3µg/g - and are noticeably lower in cadmium than the soils of Walsall where 13% of samples were >3µg/g and 1.5% >15µg/g.

Department of Environment guideline figures for zinc and copper are reported as available concentrations (280µg/g and 140µg/g respectively) using the standard ADAS (acetic acid) extraction method (Smith, 1981). Acetic-acid-extractable metal levels are regarded as an estimate of maximum availability (Berrow and Mitchell, 1980). A broadly comparable estimate of maximum availability in this work is obtained by summing the exchangeable and carbonate phases of the six-fraction study (Table 4.5). All Glasgow maximum available zinc and copper levels, averaging 24µg/g and 3µg/g respectively, are considerably below the proposed DOE guidelines but it is worth noting that these guidelines are substantially higher than the experimentally obtained undesirable available metal concentrations of Purves (1977) [Table 4.15].

While total metal concentrations are obviously of some significance in constructing guidelines for limitation of environmental contamination, they do not necessarily relate to the environmental behaviour of the elements which, as shown in the two-fraction study for soils and the six-fraction study for soils and street dirt, can be quite variable (Figures 4.21-4.24, 4.25-4.28 and 4.38-4.41). In the case of lead, similar guidelines have been advocated, admittedly by different groups, for lead in garden soils (550µg/g) and lead in street dust (500µg/g), despite the considerable differences between soil and street dirt with respect to mobility and bioavailability of lead (Table 4.5). The effectiveness of the chemical partitioning approach for assessment of bioavailability has been recognised in agricultural studies in the identification of potentially nutrient-deficient areas (Mitchell, 1971) and recently in the construction of soil contamination guidelines for zinc and copper (Smith, 1981). Therefore, in the future formulation of environmental health guidelines, it would be advisable, particularly with regard to the more toxic elements such as lead and cadmium, to take into account chemical speciation and partitioning of the elements. More realistic assessments of potential exposure and associated health effects should ensue.

TABLE 4.15 MAXIMUM AVAILABILITY OF TRACE METALS IN GLASGOW SOILS

	Lead	Zinc (μg/g)	Copper	Cadmium
Maximum available concentration[1]				
Range	1.6-176	1.9-126	0.5-12.9	0.03-0.83
Mean	28.9	23.8	3.02	0.23
Std. Devn.	26.7	24.3	2.68	0.14
'Undesirable' level[2] (Acetic acid extractable)	N.D.	60	15-30	0.13
Percent of Glasgow soils exceeding undesirable level	-	13	0	80

1 Sum of exchangeable and carbonate fractions disclosed by the six-fraction study

2 Purves, 1977

N.D. Not determined

4.3.5 CONTAMINATION OF THE BIOTA

Plants and vegetables receive most of their metal requirements from the soil although a small proportion is directly absorbed through leaf surfaces after aerial deposition. Metal uptake is controlled by the chemical and physical conditions of the soil (John, 1972) and synergistic and antagonistic interactions with other nutrients (Davies, 1980b). Uptake also varies considerably from species to species, for different varieties of a single species and is dependent on rate of growth (Davies, 1980b). However, the most important factor in regulating plant uptake from soil is the chemical form of the metal (John, 1972).

The two- and six-fraction studies not only reveal differences in bioavailability among elements but also show that a considerable proportion of the total amount of each element in the soil is in a form that is not readily available. In comparison with other metals, the availability of cadmium in soil is high, so that the element may be phytotoxic even in the absence of marked soil enhancement. By contrast, the low availability of lead, zinc and copper suggests that, even where soil levels are elevated, plant levels may still be unaffected or only slightly increased, with little affect on growth.

Although there is no simple relationship between plant uptake and soil metal concentration, the two-fraction study (Figures 4.21-4.24) demonstrates that as soil metal concentration increases, a greater amount of lead, zinc, copper and cadmium is available and consequently the uptake by plants is likely to be higher. This has been confirmed in both naturally and anthropogenically metal-enriched soils, where plant metal levels are enhanced (Purves, 1972; 1977; Davies, 1978; Davies et al, 1978; Davies and White, 1981; Khan, 1980).

In grossly-polluted land, soils may be completely devoid of plant life, so that special treatment measures are needed to restore it for reasons of amenity or agricultural/ horticultural use. More usually, polluted land supports active plant growth and the problem of its use becomes one of assessing whether soil available levels are phytotoxic or whether crops are absorbing harmful trace metals at a level likely to constitute a hazard for animals and man.

Purves (1977) derived phytotoxic/human-animal undesirable metal levels, based on pot experiments with food crops, using acetic acid. Comparable maximum available levels in the Glasgow work are obtained by summing the results of the exchangeable and carbonate phases of the six-fraction study (Table 4.15).

In Glasgow soil, the maximum availability of trace metals is significantly greater than exchangeable content alone, particularly for lead and zinc, reflecting the importance of the carbonate phase for these elements. Although zinc is essential to plants and animals, it is extremely phytotoxic at higher concentrations with inhibition of plant growth occurring at an acetic acid-extractable level of 60µg/g zinc (Purves, 1977), a value exceeded in terms of maximum availability by 13% of Glasgow soils. Maximum-available cadmium, on average, is twice the undesirable level, with 80% of samples >0.13µg/g cadmium, emphasising the greater mobility and bioavailability of this element in the environment. Cadmium, and also lead, are considered to be non-phytotoxic at low concentrations with the result that accumulation in plant tissue may go unobserved, rendering apparently healthy crops unsafe for human or animal consumption. The maximum permitted level of lead in vegetables in the UK is 1µg/g lead fresh weight (Lead in Food Regulations, 1979). Although phytotoxic concentrations for lead have not been quantified, MacLean et al (1969) observed a correlation between plant lead uptake and ammonium acetate-extractable lead in soil but noted that extractable lead was reduced with increasing organic matter, lime and phosphate. The maximum available copper levels found in the Glasgow study (maximum 12.9µg/g, mean 3.02 ± 2.68µg/g) are well below the undesirable guidelines (15-30µg/g) [Table 4.15].

4.3.6 THE ROLE OF SOIL IN THE URBAN CYCLE OF TRACE METALS

While soils receive trace metals from many sources, e.g. agricultural application, degradation of organic matter, industrial emissions etc, the most important route in urban areas is atmospheric deposition. This is influenced by a number of factors such as meteorological conditions (precipitation, wind speed and direction) and land topography, as well as proximity to point source and particle size, and therefore depends, to a large extent, on local conditions. The ranges and median quantities of trace metals annually deposited in the UK have been summarised by Jeffries and Snyder (1981) [Table 4.16]. No results are available for cadmium in urban/industrial or rural areas of the UK but the corresponding cadmium data for rural areas in Europe are reported. Using a deposition rate twice that of rural areas (based on the results obtained in North America [Jeffries and Snyder, 1981]) an annual deposition of cadmium in Glasgow can be estimated. Using these figures and assuming a constant deposition rate throughout Glasgow (total area ~16,000ha), the quantities of trace metals deposited annually on the city can be estimated (Table 4.17). Of these, around 40-50% is directly deposited on soil or grass/plant cover. The total amount of lead estimated to be deposited in the UK in 1981 was 3,700tonnes (Royal Commission, 1983).

TABLE 4.17 ESTIMATE OF ANNUAL TOTAL DEPOSITION OF TRACE METALS IN GLASGOW

	Total Deposition per year (tonnes)	
	Range	Median
Lead	28.8 - 102	64
Zinc	83.2 - 184	102
Copper	12.8 - 80	54.4
Cadmium	-	1.28[1]

[1] Based on estimate of deposition rate (Table 4.16)

TABLE 4.16 ANNUAL DEPOSITION RATE OF TRACE METALS IN THE UK

		Deposition Rate (kg/ha/yr) Range	Deposition Rate (kg/ha/yr) Median
Lead	Urban/industrial	1.8 - 6.4	4.0
	Rural	1.6 - 5.5	2.6
Zinc	Urban/industrial	5.2 - 11.5	6.4
	Rural	4.0 - 12.0	6.0
Copper	Urban/industrial	0.8 - 5.0	3.4
	Rural	1.3 - 3.9	1.7
Cadmium	Urban/industrial	-	0.08[2]
	Rural[1]	0.02 - 0.13	0.04

[1] Annual European deposition rate

[2] Estimated on basis of twice the rural deposition rate

Trace metals are deposited on the soil surface. Depletion from the surface occurs through wind erosion (as dust to be redeposited elsewhere) and leaching down the soil profile. Removal by the biota (plants, animals and microorganisms) is only temporary as this fraction is eventually returned. Leaching from the soil depends on the level of precipitation and on the chemical forms of the metals. The chemical associations of the metals, in the mildly acidic Glasgow soils (pH5.8) indicate that the overall mobility is cadmium >>lead ⩾zinc >copper [Section 4.3.2]. Although the mobility is susceptible to changes in environmental conditions (pH, reduction, oxidation), the chemical associations illustrate that for all elements, particularly lead, zinc and copper, the greatest proportions are in non-readily available forms with only limited circulation within the environment (Table 4.5).

Estimates for the residence time of lead in surface soil range from several hundred to several thousand years (Doner, 1979; Khan, 1980) while Purves (1972) infers that contamination of the soil with lead, zinc and copper is virtually irreversible. According to the six-fraction study (Table 4.5), cadmium mobility in soil is an order of magnitude greater than that of lead, indicating a much shorter residence time. Tyler (1978), investigating leaching rates of heavy metal ions from the upper layers of moorland soil, estimated the residence time of cadmium to be 6-20 years compared with 70-200 years for lead, in accord with the implications of this chemical partitioning work.

Nevertheless, although the residence time of cadmium in soil is shorter than those of the other elements, trace metals, in general, do not move readily through the soil to other environmental locations. Redistribution of trace metals from the lithosphere, in contrast to the atmosphere and hydrosphere, occurs over decades and centuries (Purves, 1977; Davies, 1980b). Therefore, as further anthropogenic release appears inevitable, soils will play an increasingly important role in the biogeochemical cycle of trace metals in the urban environment and, consequently in the long-term exposure of major sections of the population to trace-metal contaminants.

CHAPTER 5 - TETRAALKYL LEAD IN THE URBAN ATMOSPHERE OF GLASGOW

5.1 INTRODUCTION

As the atmosphere plays a significant role in the movement and redistribution of trace elements within the environment (Section 4.3.6; Jeffries and Snyder, 1981), identification and measurement of the chemical species present is extremely important in elucidating the processes which control trace element interconversions and influence transfer between environmental phases. More generally, knowledge of speciation leads to greater understanding of the biogeochemical cycle of the elements (Farmer et al, 1983). One class of trace-element-containing compounds for which knowledge of chemical speciation is particularly important is that of volatile organo-element species e.g. methyl mercury, tetraalkyl lead. The entirely different physico-chemical and toxic properties of these organo-metallic compounds, relative to their corresponding inorganic forms, results in widely varying environmental and metabolic pathways (Wood, 1975; Goldwater and Stopford, 1977; Iverson and Brinckman, 1978; Brinckman and Bellama, 1978; Grandjean and Nielsen, 1979).

Most environmental research on atmospheric lead levels has concentrated on particulate inorganic lead despite the fact that organic lead constitutes the predominant primary source. However, several recent studies have shown that gaseous organo-lead, in the form of tetraalkyl lead (TAL), contributes typically 1-15% of the total lead burden of urban air (Harrison and Perry, 1977; Reamer et al, 1978; Birch et al, 1980; Rohbock et al, 1980; DeJonghe and Adams, 1980; DeJonghe et al, 1981; Nielsen et al, 1981) which, in view of its greater toxicity, has potentially serious ecological implications (Grandjean and Nielsen, 1979).

5.1.1 USE OF TAL

Liquid TAL compounds, primarily tetramethyl lead (TML) and tetraethyl lead (TEL), but also mixed ethyl-methyl derivatives, have been added to petrol since 1923 to improve the octane rating[1], without the need for further refining, for use in high-compression internal combustion engines. The existing UK maximum permitted level is 0.4g (as lead) per litre of petrol but the current controversy over the health effects of lead (Needleman et al, 1979; Needleman and Landrigan, 1981; Settle and Patterson, 1980; Gloag, 1980; Bryce-Smith and Stephens, 1981) has prompted a reduction to 0.15g/l by 1985 and eventual removal by 1990.

In the combustion chamber of the engine, petrol is burnt from the spark plug to the cylinder corner. Because the mixture in this corner (end-gas zone) is heated and compressed the longest, an abnormal state of partial oxidation develops, producing spontaneous rapid ignition (knocking). Higher octane petrol, i.e. RON 90-98.5, delays the state of partial oxidation so that more 'efficient' burning of the fuel is achieved at a given compression ratio.

The combustion products of lead alkyls, mainly lead oxides, are effectively removed from the engine by 'scavenger compounds' ethylene dichloride and dibromide, which are other petrol additives. These convert the non-volatile lead oxides into the more volatile chlorides and bromides which are readily exhausted from the combustion chamber. Subsequently, the lead halide salts

---

[1] The octane number (called Research Octane Number, RON) of a fuel measures its resistance to explosive combustion ('pinking' or 'knocking') in a spark ignition internal combustion engine. It is defined as the percentage of 'iso-octane' (2,2,4-trimethyl pentane) in the 'equivalent fuel' formed by mixing iso-octane (octane number 100) with n-heptane (octane number 0).

are emitted as, or attached to, fine particulates, mostly of submicron diameter (Little and Wiffen, 1978), in the exhaust gases. The resulting correlation between lead and bromine in air and soil may serve, to a limited extent, as a secondary indicator of vehicular-emitted lead (Farmer and Cross, 1978; Khandekar et al, 1982; Harrison and Sturges, 1983).

5.1.2 OCCURRENCE AND FATE OF TAL IN THE ENVIRONMENT

Although most of the TAL is decomposed during petrol ignition and released as inorganic lead, incomplete combustion, especially during cold start with choke and town driving, may result in considerable gaseous emissions of undissociated TAL. In addition, due to its relatively high vapour pressure, TAL is easily vaporised from spillages of leaded petrol, notably in garages, and, to a lesser extent, from fuel tanks and carburettors (Harrison and Perry, 1977; Grandjean and Nielsen, 1979). There is also the possibility of natural biosynthesis of TAL, via microorganism-controlled methylation, in inorganic-lead-polluted sediments, such as coastal/ estuarine intertidal mudflats, as suggested by the unusually high atmospheric TAL concentrations reported in rural locations in north-west England (Harrison and Laxen, 1978a).

Although the fate of organo-lead compounds in the environment is not fully understood, the probable main pathways have been postulated as shown in the biogeochemical cycle of lead (Figure 5.1) [Röderer, 1981]. Tetramethyl lead, thermally and photolytically more stable than TEL, is the predominant compound in the atmosphere with a mean lifetime in the order of several days. In this gaseous form TAL can easily be inhaled or

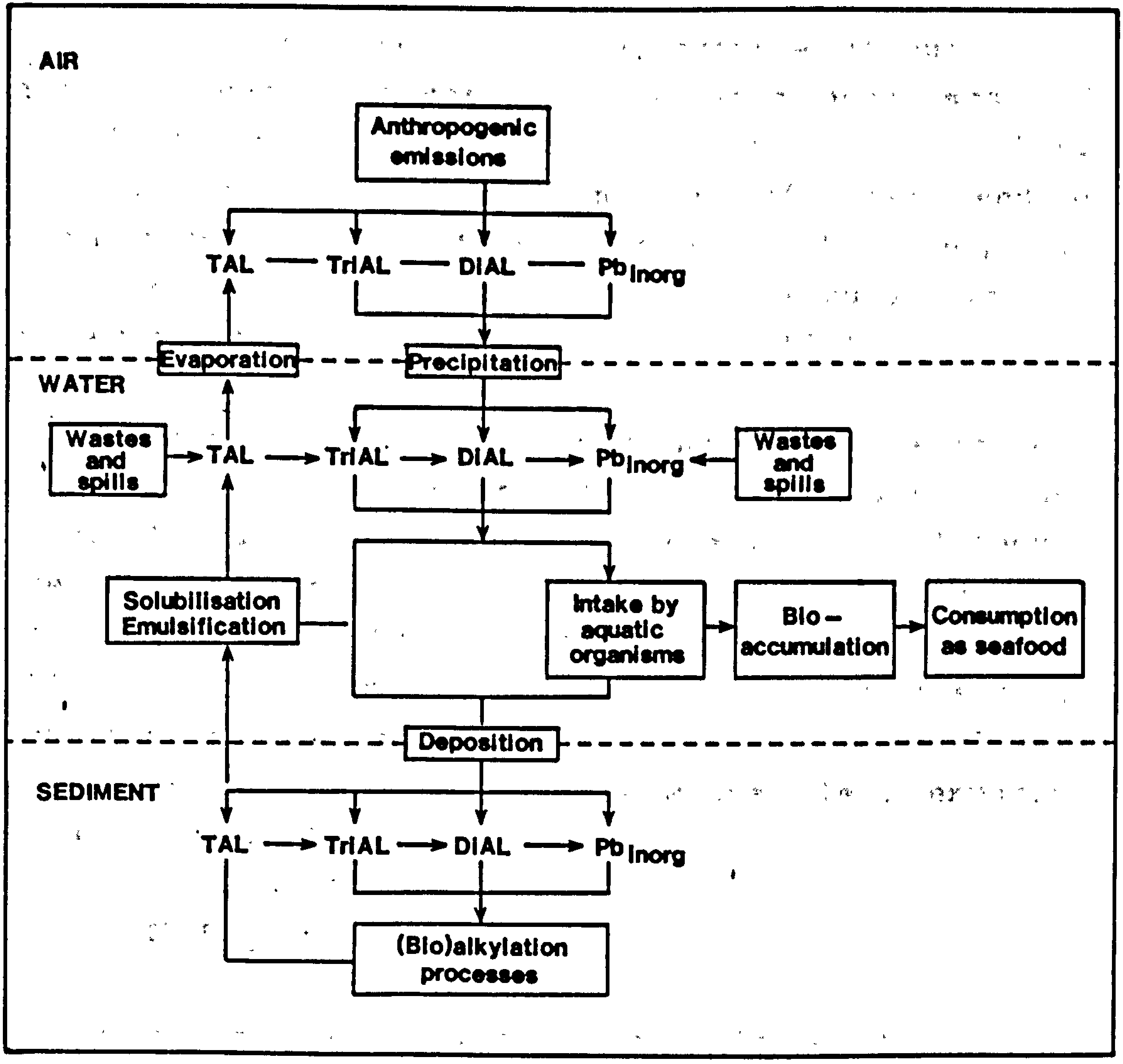


FIGURE 5.1 SIMPLIFIED BIOGEOCHEMICAL CYCLE FOR TAL COMPOUNDS IN THE ENVIRONMENT (Röderer, 1981)

absorbed through human tissue. Both compounds, however, are eventually decomposed to inorganic lead via tri-and dialkyl lead (triAL and diAL) salts through attack by hydroxy radicals and photolytic decay during daylight hours (Harrison and Laxen, 1978a, b). On removal from the atmosphere, via both wet and dry precipitation, these soluble salts may enter the hydrosphere (Figure 5.1) where they can be absorbed by aquatic organisms and accumulate in the food chain (Chau et al, 1979). Recently, the death of large numbers of river feeding dunlin birds in the Mersey estuary, England, was attributed to triAL poisoning from bioaccumulation in invertebrate marine animals (Bull et al, 1983).

In the human body TAL compounds appear to be rapidly oxidised in the liver to trialkyl derivatives, which are responsible for toxic effects (Röderer, 1981). Although highest concentrations of triAL are present in the liver with smaller amounts in other organs, e.g. kidney, muscle, heart, the critical organ appears to be the brain (Grandjean and Nielsen, 1979) with triAL levels closely related to the degree of environmental lead exposure (Nielsen et al, 1978).

5.1.3 METHODS FOR TAL COLLECTION

The aim of this study was to investigate the levels, distribution and behaviour of gaseous TAL in the urban area of Glasgow using a technique sufficiently sensitive to enable the detection of TAL at less polluted rural sites for comparison purposes.

It is only in the last few years that the acquisition of reliable atmospheric TAL data has been made possible by the development of appropriate satisfactory sampling and analytical techniques (Harrison and Perry, 1977; DeJonghe and Adams, 1982). Most procedures used for the determination of organic lead in the atmosphere separate the organic from inorganic lead by filtration. Particulate matter, containing the majority of inorganic lead, is quantitatively impacted on a filter while gaseous organo-lead passes through to be collected separately. Two analytical approaches to organo-lead trapping have been employed: (i) the TAL content of the non-filterable fraction of the air-particulate system is collected chemically by converting the volatile compounds into non-volatile lead salts (Harrison and Laxen, 1978a; DeJonghe and Adams, 1979; 1980; Birch et al, 1980); (ii) an alternative approach in which volatile organo-lead compounds are trapped physically on a packed column at low temperature (<-100°C) (Harrison et al, 1974; Rohbock et al, 1980; DeJonghe et al, 1980a), allowing subsequent chemical manipulation, using chromatographic techniques (e.g. gas-liquid chromatography) interfaced with a specific detector, to separate and identify individual organo-lead species (Reamer et al, 1978; Radziuk et al, 1979; DeJonghe et al, 1981; Nielsen et al, 1981).

The collection method employed here, based on the first approach, involved the chemical trapping of TAL in iodine monochloride solution (Moss and Browett, 1966; Hancock and Slater, 1975) after initial removal of particulate lead on a filter. The procedure is suitable for the collection of air samples over periods of up to 48 hours and has been successfully adopted and applied by several other workers (Harrison and Laxen, 1978a; DeJonghe and Adams, 1979; 1980; Birch et al, 1980).

5.2 METHODOLOGY

5.2.1 SAMPLING SITES

Air samples were collected at a variety of sites in Glasgow from July 1980 to October 1981. These included two sites in a narrow city centre street (Hope Street), with steep buildings on either side and heavy, slow-moving traffic, where samples were taken over 24-hour periods and at different heights above street level over 7-hour daytime (1000-1700) periods. Twenty-four-hour samples were collected on a regular basis about 0.5km distant at another central Glasgow site (West Graham Street), 7.5m above street level, where daytime (0800-1800) and overnight (1800-0800) concentrations were also investigated. Additional 24-hour samples were obtained at three sites in quieter areas of the city as well as at a rural hill farm between Loch Long and Gareloch, some 40km north-west of Glasgow (Figure 5.2). A few samples were also collected from a Glasgow petrol station forecourt where high TAL levels were anticipated.

With the inclusion of daytime/overnight combinations, 65 of the total 128 samples covered 24 hour sampling periods. Duplicates were collected on 25% of the sampling occasions.

5.2.2 SAMPLING AND ANALYTICAL PROCEDURES

(i) REAGENTS

All reagents were Analar grade unless otherwise stated. Water was purified as described in Section 2.6.2 (i).

Potassium iodide (25% w/v): 250g of potassium iodide (KI) were dissolved in ca. 500ml water and then ammonia solution (sp.gr.0.88) was added dropwise until the solution became slightly alkaline. Contaminant lead was removed by shaking with successive portions of a carbon tetrachloride solution of dithizone until the green colour of the latter remained unchanged. After separation of the organic phase, the solution was acidified with dilute nitric acid (HNO_3) and washed with chloroform to extract dissolved dithizone. The volume was made up to 1000ml with water.

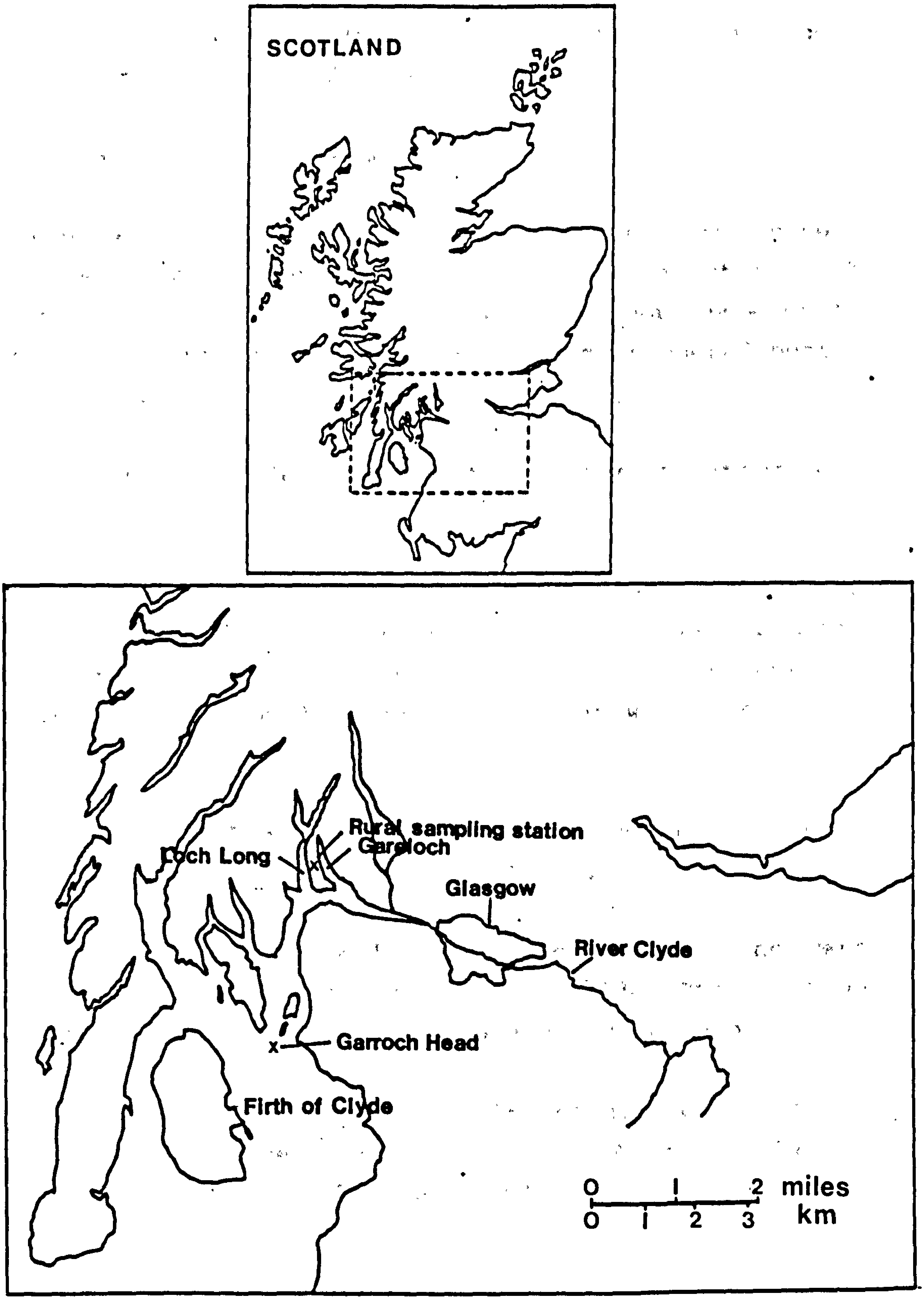


FIGURE 5.2 LOCATION OF THE RURAL SAMPLING SITE 40km NORTH-WEST OF GLASGOW

Iodine monochloride stock solution (1.0M): iodine monochloride solution (ICl) is prepared by combining KI and excess potassium iodate (KIO_3) in hydrochloric acid (HCl) according to the following reaction:

$$KIO_3 + 2KI + 6HCl \longrightarrow 3\ ICl + 3\ KCl + 3H_2O$$

To prepare a 1.0M solution, 37.5g of KIO_3 were slowly dissolved (several hours) in 222.5ml of KI solution with 222.5ml of Aristar HCl added. The volume was made up to 500ml and the solution stored in a glass stoppered bottle in darkness.

Iodine monochloride (0.1M): the stock solution was diluted with water.

Buffer: 8g of citric acid monohydrate and 40g of hydrated sodium sulphite were dissolved in 340ml of water. After the addition of 160ml of ammonia solution the volume was made up to 1000ml with water. The buffer was stored in a glass container.

EDTA (0.1M): 3.72g of disodium dihydrogen EDTA were dissolved in water and diluted to 100ml.

Dithizone solution (8×10^{-5}M): 10mg of dithizone were dissolved in 500ml of carbon tetrachloride. The solution was kept refrigerated in a darkened glass container.

Acid solution (1% H_2O_2/1% HNO_3): 5ml of hydrogen peroxide (30%, 100-volume) were added to 5ml of Aristar HNO_3 and the volume made up to 500ml with water.

(ii) SAMPLING ASSEMBLY

Figure 5.3 shows schematically the experimental set-up for the collection of gaseous organic and particulate inorganic lead. Air was drawn by means of a vacuum pump (Millipore XX60 220 50 or Charles Austin Capex 2D) through a sampling assembly consisting of a 0.45µm membrane filter (Millipore MHWP 037 AO) in a stainless steel filter folder connected by teflon tubing first to a darkened gas bubbler, containing 40-70ml of 0.1M ICl, and then to a U-tube containing activated charcoal to protect the pump from ICl vapour. The flow rate was regulated, typically to 2-3 l/min, by a valve placed between the U-tube and the pump. The collection efficiency of TML and TEL from ambient air at this flow rate is extremely high, being generally greater than 96.5% (Birch et al, 1980). Airborne particulate lead was removed by the filter while gaseous TAL was quantitatively converted to the corresponding dialkyl lead dichloride through a series of reactions with ICl: $PbR_4 \rightarrow PbR_3^+ \rightarrow PbR_2^{+2}$ (Moss and Browett, 1966). The total air volume sampled, typically 3-3.5m^3 for a 24-hour period, was calculated from measurements of flow rate at the beginning and end of each sampling session using a GEC-Elliott 1100 rotameter.

(iii) ANALYTICAL PROCEDURE

Organic lead was extracted from the buffered ICl with 2 x 2 min shakings of 5ml dithizone solution, after addition of several drops of 0.1M EDTA to mask any inorganic lead present. Addition of the ammoniacal buffer solution reduces the ICl, preventing any further reaction with the organo-lead, and provides the appropriate conditions (pH~9-11) for the conversion of the dialkyl lead halide to the lead dithizonate. Dithizonates are formed according to the reaction:

$$M^{n+} + nH_2D_z \longrightarrow M\ (HD_z)n + nH^+$$

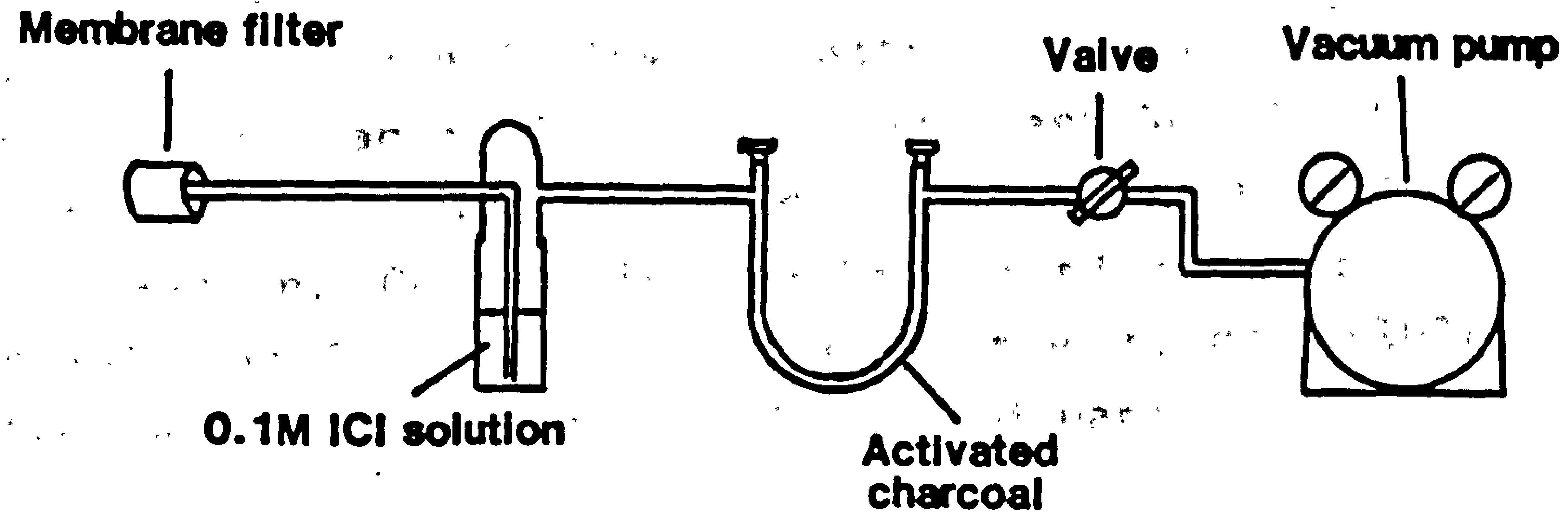


FIGURE 5.3 SCHEMATIC REPRESENTATION OF ATMOSPHERIC LEAD SAMPLING ASSEMBLY

The combined dithizone extracts were then back-extracted with 2ml of the oxidising acid solution (1% H_2O_2/1% HNO_3), converting all organo-lead to inorganic lead in a nitrate matrix suitable for analysis by GFAAS. This extraction method is extremely efficient for organo-lead compounds retained in ICl solution with recovery generally exceeding 95% (Birch et al, 1980). Particulate lead on the membrane filter was dissolved by shaking with 20ml of 10% HNO_3 in an ultrasonic bath for 20 mins. Quantitative removal of particulate lead, confirmed by total digestion of the remaining filter using aqua regia/HF/H_3BO_3, was obtained. In each sampling session duplicate reagent blanks for both procedures were taken through the entire method.

Lead analyses were performed at wavelength 283.3nm (slit 0.7nm) on the Perkin-Elmer PE-306/HGA-74/AS-1 graphite furnace atomic absorption system, employing background correction, using the following instrumental settings for the graphite furnace:- dry-105°C (30s); ash-500°C (30°S); atomisation-2100°C (8s, gas stop); burn-out-2700°C (5s); purge gas-argon. Calibration against lead standards of appropriate acid concentration over the range 0-100ng (lead)/ml enabled calculation of TAL and particulate lead data.

It was observed that, with consistent use of the sampling apparatus and glassware, the reagent blank for the TAL analysis was usually about 6ng lead. The detection limit for TAL over a 24-hour sampling period was 0.8ng (lead)/m^3. The overall precision of the method, based on duplicate determinations of TAL and particulate lead concentrations greater than 10ng/m^3, was ±12% for TAL (n = 18) and ±11% for particulate lead (n = 20) with ±10% for the TAL/total lead ratio (n = 14) and ±9% for the TAL/particulate lead ratio (n = 14).

5.3 RESULTS

Individual TAL and particulate lead results are listed in Appendix 6 along with calculated TAL/total lead and TAL/particulate lead ratios. Conventionally TAL is presented as a fraction of the total lead concentration, where total lead is the sum of gaseous TAL and particulate inorganic lead, as this ratio is less dependent than the TAL concentration itself on variables such as total lead use at particular locations, sampling site topography and meteorology (Harrison and Perry, 1977). Although the total lead concentration is not strictly known, the excluded forms (gaseous inorganic lead, non-filterable particulate lead, organo-lead present in particulate matter) probably only constitute a small percentage of the overall total (Liu and Lee, 1976; Harrison and Perry, 1977; Harrison and Laxen, 1977), with the result that the TAL/'total' lead ratio approximates to the true ratio. Nevertheless, Rohbock et al (1980) and, subsequently, DeJonghe and Adams (1982) suggested that the ratio of non-filterable organo-lead to filterable particulate lead is more appropriate. However, as most reported TAL data are expressed as a proportion of total lead, as defined above, omission of this ratio would preclude direct comparisons with other studies. Consequently, TAL results are reported here as a percentage of both total lead and particulate lead.

Individual TAL results are plotted against corresponding particulate lead values at all sampling locations in Figure 5.4. This data along with the corresponding TAL/total lead and TAL/particulate lead ratios are summarised in Table 5.1 while the ranges and mean values of TAL and particulate lead at different locations are presented diagrammatically in Figures 5.5 and 5.6 respectively. The frequency distributions of TAL, TAL/total lead ratio and particulate lead at 24-hour urban and rural sites are illustrated in Figures 5.7-5.9

FIGURE 5.4 PLOT OF INDIVIDUAL TAL RESULTS AGAINST CORRESPONDING PARTICULATE LEAD RESULTS AT ALL SAMPLING LOCATIONS

24-hour sites		7-hour sites	
× West Graham St		▲ Hope St. Stn. 1	
○ Hope St. Stn.	2-7m	◆ ″	2-3m
∧ ″	2-12m	◊ ″	2-12m
● Other urban		⌶ Garage	
△ Rural			

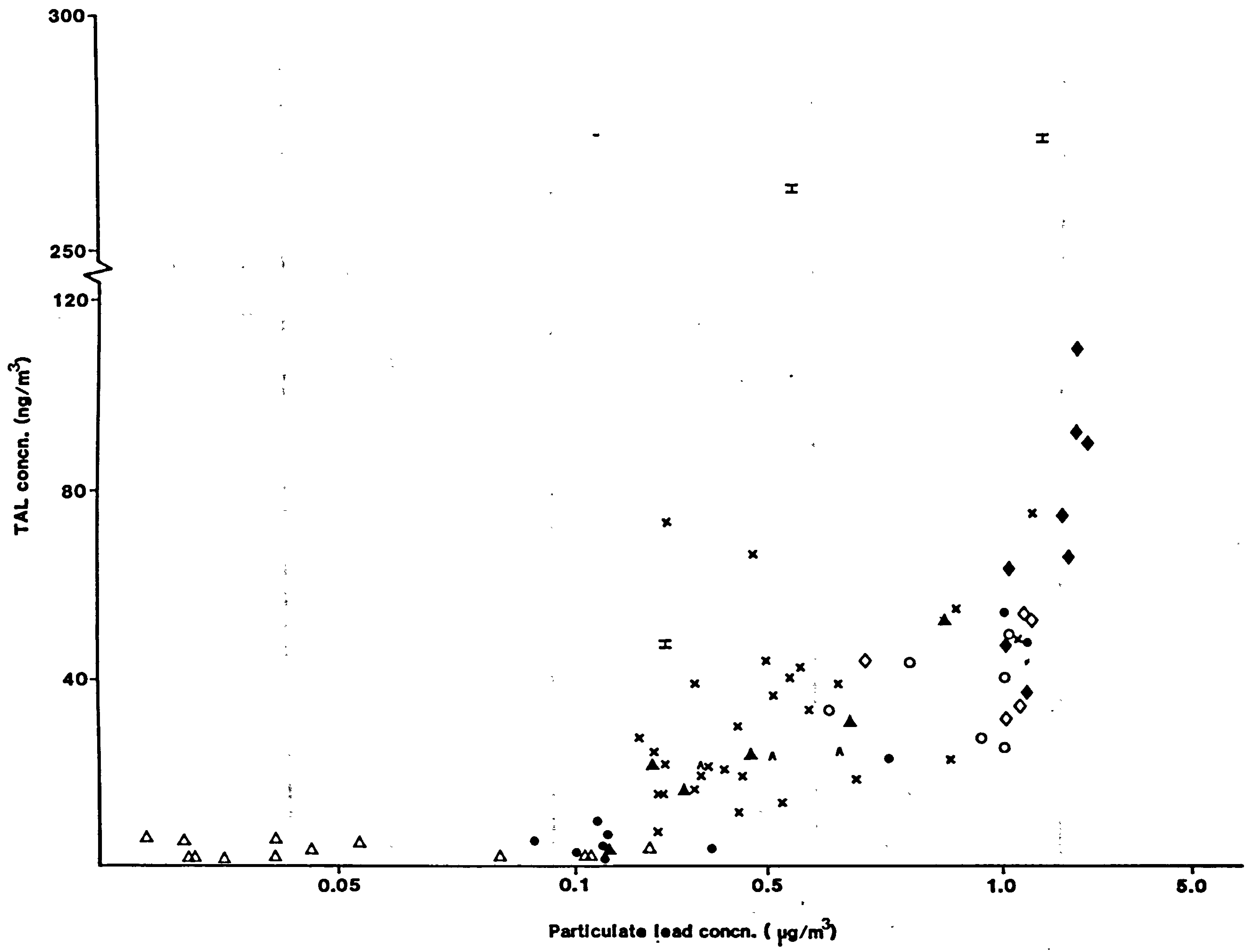

300
250
120
80
40
TAL concn. (ng/m3)
0.05
0.1
0.5
1.0
5.0
Particulate lead concn. (µg/m3)

TABLE 5.1

SUMMARY OF TAL AND PARTICULATE LEAD DATA FOR GLASGOW AIR

		TAL (ng/m^3)		Particulate Lead (ng/m^3)		TAL/Total Lead (%)		TAL/Particulate Lead (%)	
24 Hour sites	n	Range	Mean	Range	Mean	Range	Mean	Range	Mean
WGS (7.5m)	28	7.2-77	32.0±18	232-1620	531±314	2.4-20	6.3±3.7	2.5-25.3	6.9±4.6
HS (Stn.1)(0.3m)	1	96	96	880	880	9.9	9.9	10.9	10.9
HS (Stn.2)(7 and 12m)	9	1.5-54	31.4±10.1	365-1140	783±261	2.4-5.4	4.1±1.0	2.4-5.7	4.2±1.1
Other Urban (7-30m)	10	1.5-54	16.0±19	104-1460	528±480	0.9-6.3	2.9±1.9	0.9-6.6	3.5±1.8
Rural (2m)	17	<0.8-6.5	1.9[2]	<5-308	66±88	1.5-39[1]	4.8[2]	1.5-64.2[1]	5.1[2]
WGS (7.5m) Overnight (1800-0800)	5	2.7-30	11±12	120-715	385±222	0.8-4.0	2.4±1.3	0.9-4.2	2.5±1.3
Daytime (0800-1800)	5	21-144	53±51	695-2880	1300±900	2.2-6.0	3.8±1.6	2.3-6.3	3.9±1.7
7 Hour sites (1000-1700)									
HS (Stn.1)(5-30m)	6	2.9-52	24±17	166-875	462±271	1.7-7.5	4.7±1.9	1.7-8.1	5.0±2.1
HS (Stn.2)(3m)	8	37-110	73±24	1020-2850	2020±710	2.4-5.9	3.6±1.1	2.5-6.2	3.8±1.2
HS (Stn.2)(12m)	5	31-53	43±10	705-1605	1270±370	2.4-5.7	3.4±1.3	2.4-6.1	3.6±1.5
Garage	3	47-274	195±128	295-1840	895±830	13-32	20±11	15-48	26±19

[1] excluding 'less than' results

[2] median

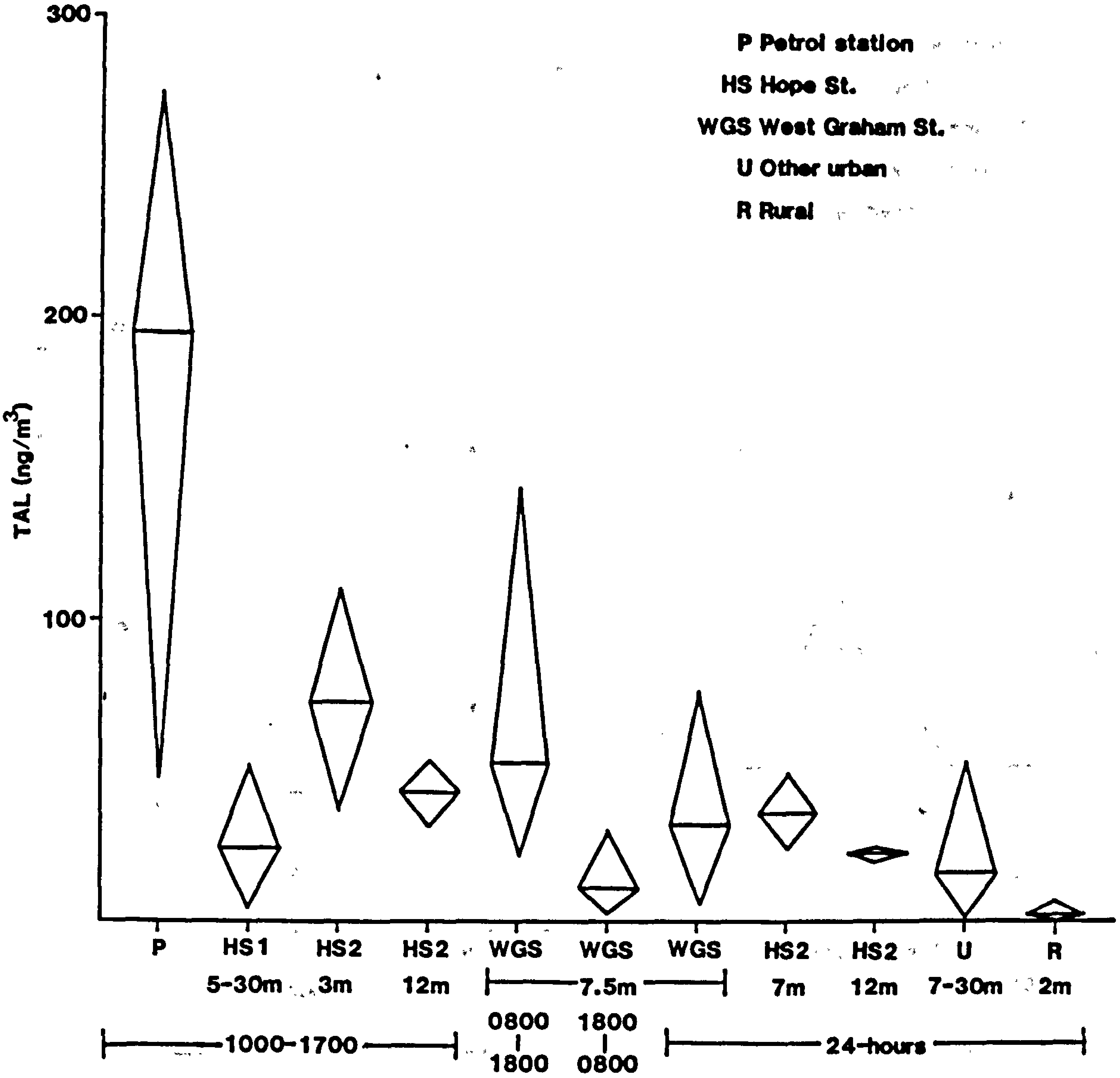


FIGURE 5.5 SUMMARY OF THE RANGE AND MEAN CONCENTRATION OF TAL IN THE ATMOSPHERE AT SEVERAL HEIGHTS OVER VARIOUS TIME INTERVALS AT LOCATIONS IN URBAN GLASGOW AND AT THE RURAL SAMPLING SITE

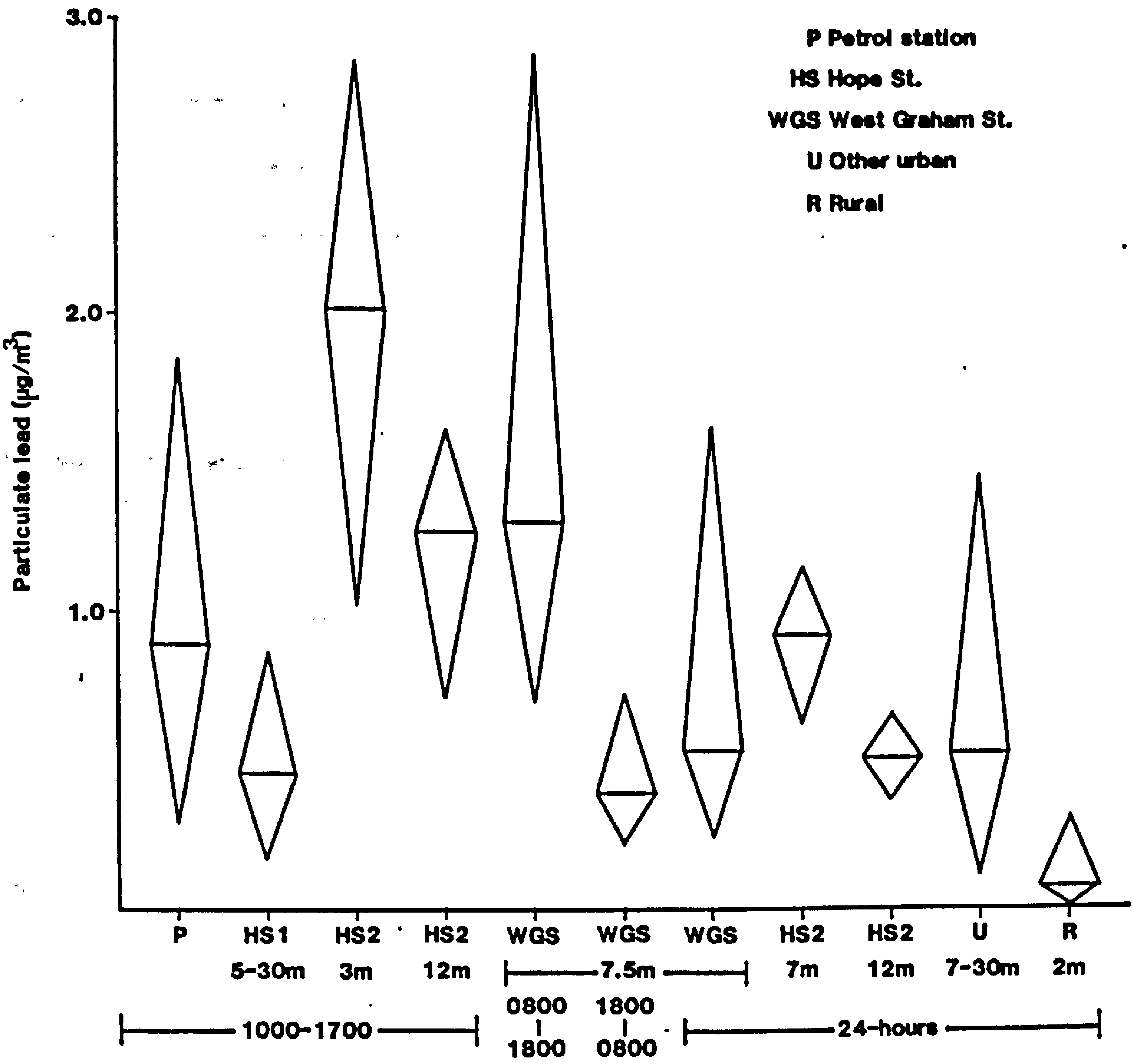
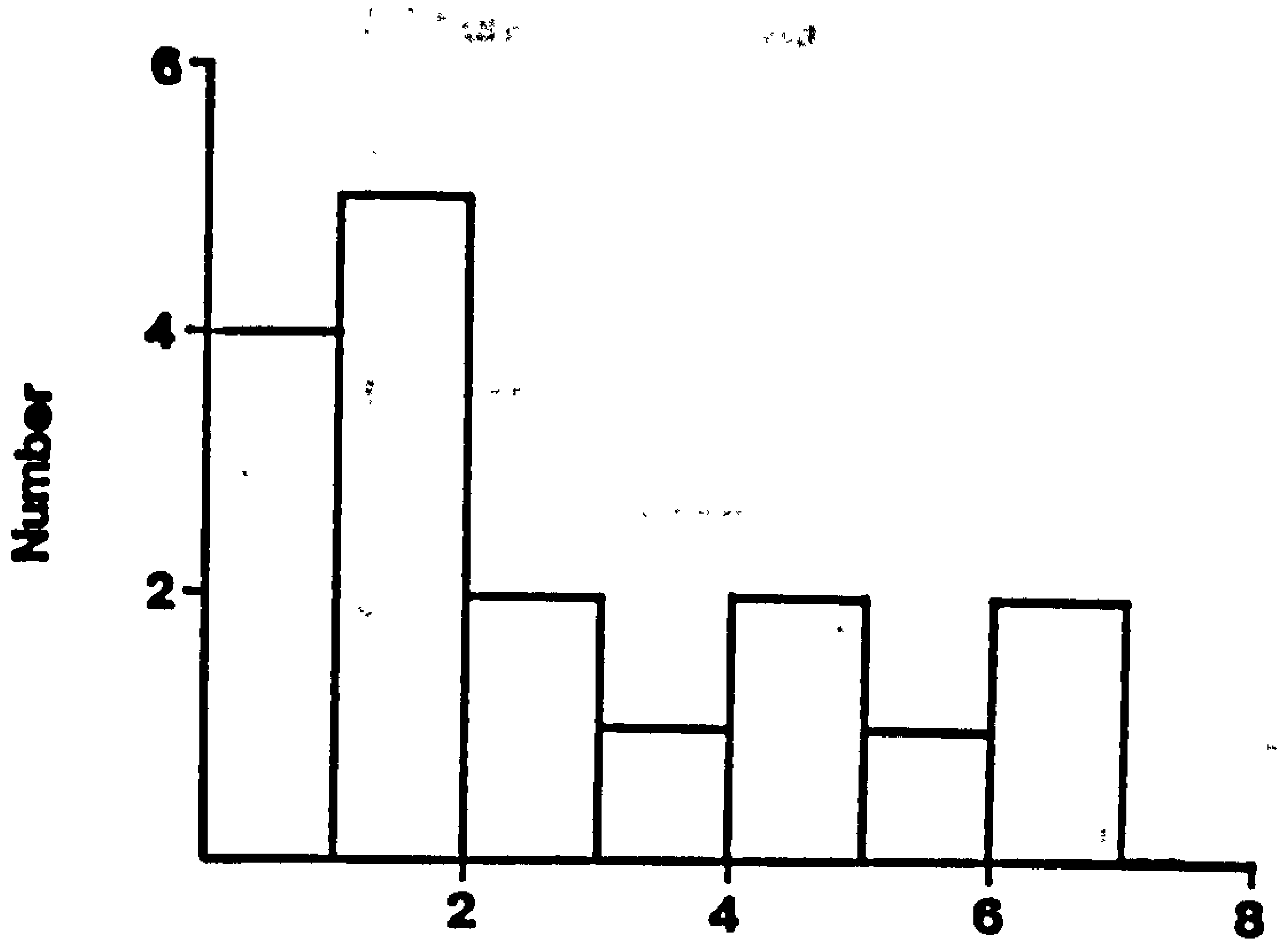


FIGURE 5.6 SUMMARY OF THE RANGE AND MEAN CONCENTRATION OF PARTICULATE LEAD IN THE ATMOSPHERE AT SEVERAL HEIGHTS OVER VARIOUS TIME INTERVALS AT LOCATIONS IN URBAN GLASGOW AND AT THE RURAL SAMPLING SITE

(2) Rural 24-hour site



(1) Urban 24-hour sites

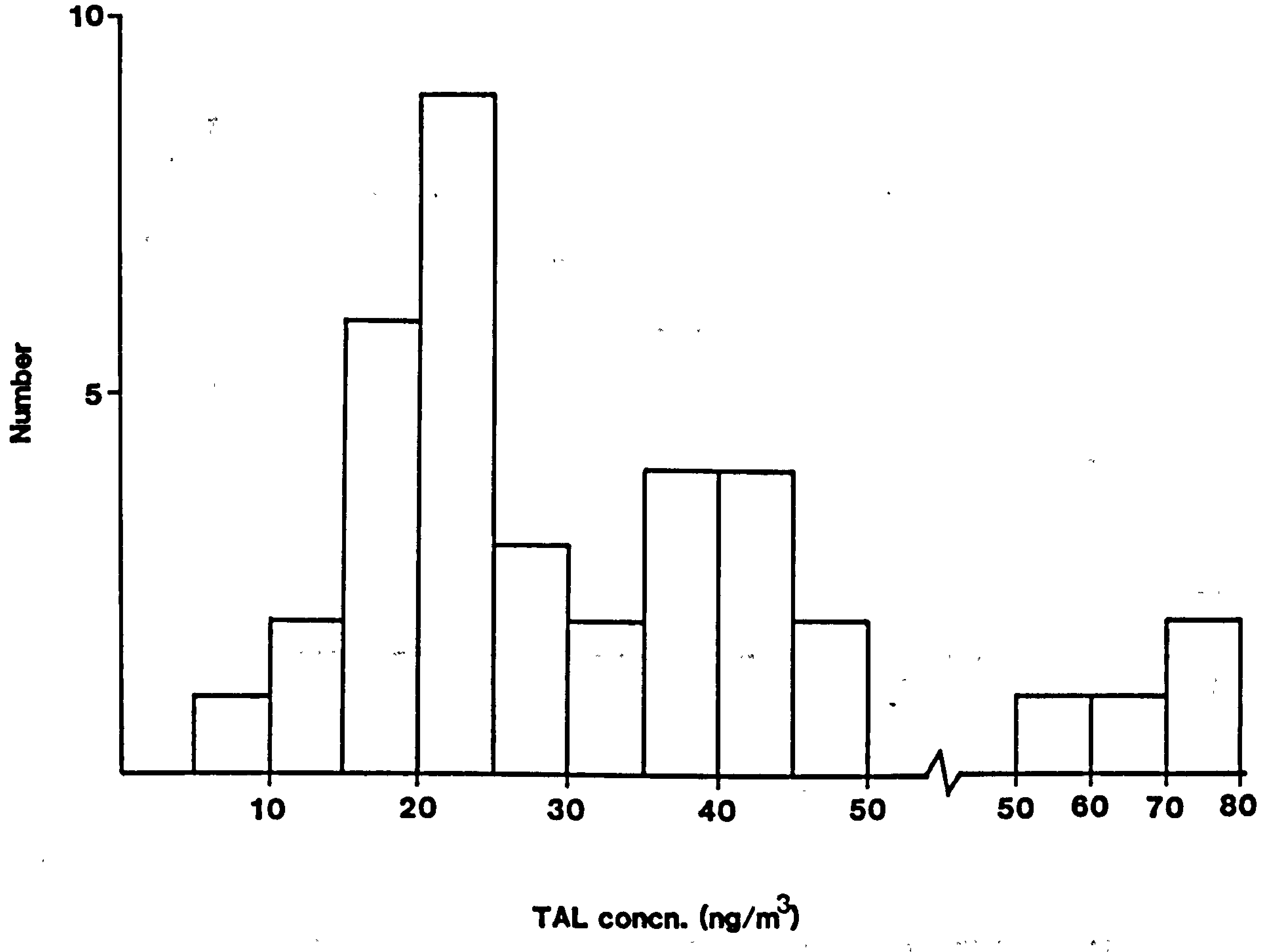
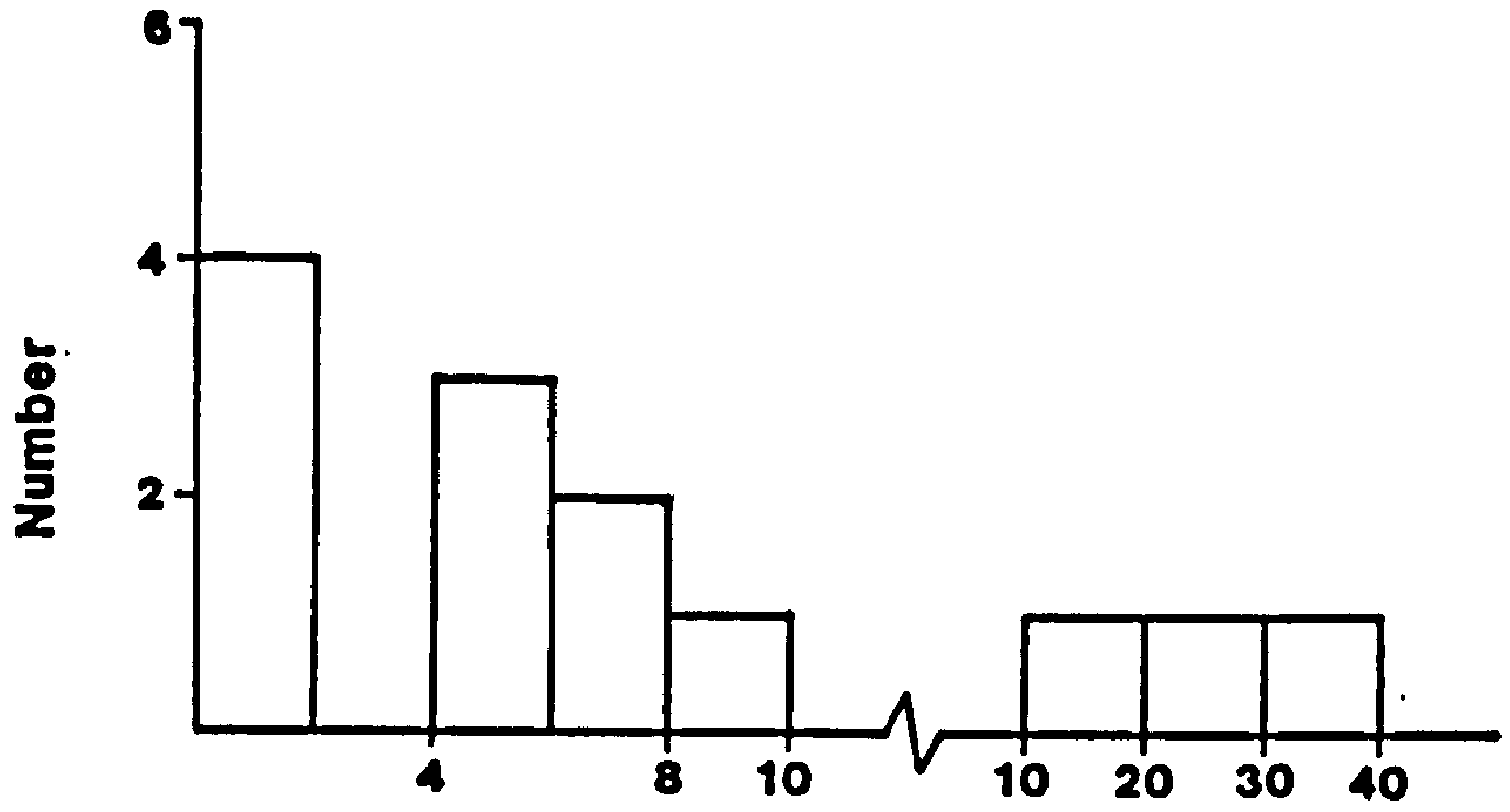


FIGURE 5.7 FREQUENCY DISTRIBUTION OF TAL CONCENTRATIONS AT (1) URBAN 24-HOUR SITES (2) RURAL 24-HOUR SITE

(2) Rural 24-hour site



(1) Urban 24-hour sites

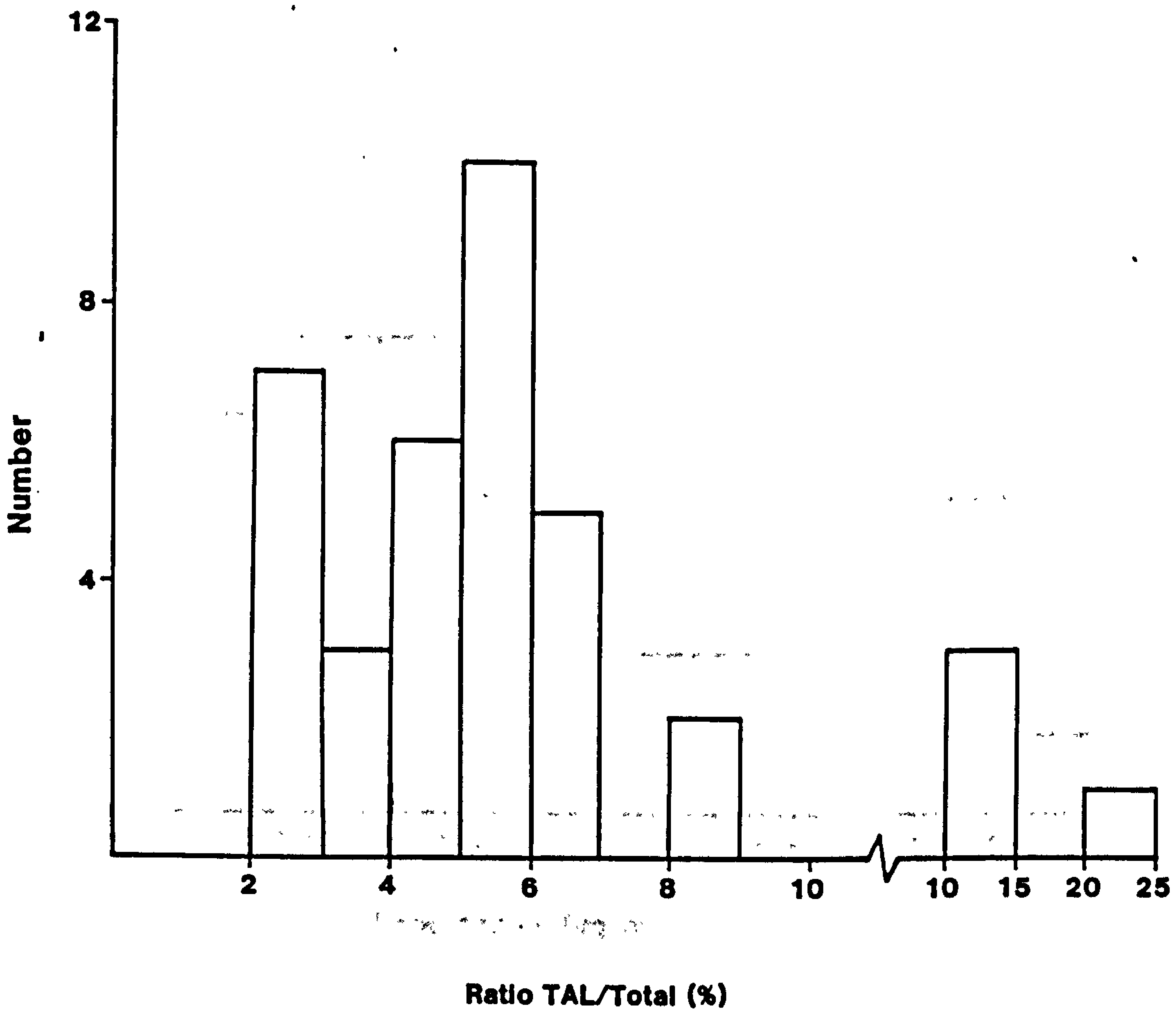


FIGURE 5.8 FREQUENCY DISTRIBUTION OF TAL/TOTAL LEAD RATIO AT (1) URBAN 24-HOUR SITES (2) RURAL 24-HOUR SITE

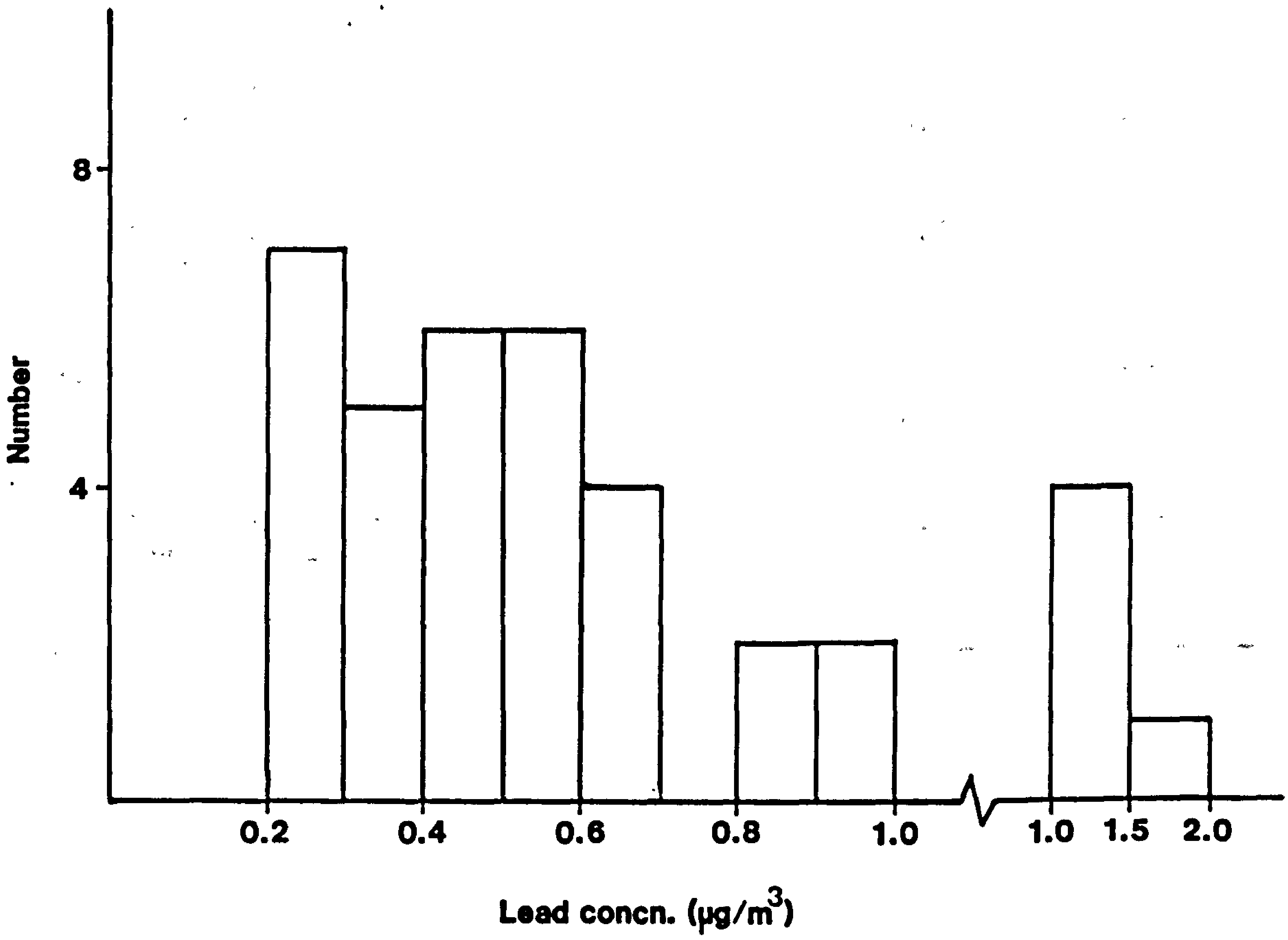


FIGURE 5.9 FREQUENCY DISTRIBUTION OF PARTICULATE LEAD AT URBAN 24-HOUR SITES

TABLE 5.2 DIURNAL VARIATIONS IN TAL AND PARTICULATE LEAD CONCENTRATIONS IN GLASGOW URBAN AIR - WEST GRAHAM St. SITE (7.5m)

Date	Sampling Interval	TAL (ng/m^3)	Particulate Lead (ng/m^3)	TAL / Total Lead (%)	TAL / Particulate Lead (%)
19-20	1800-0800	30	715	4.0	4.2
Jan.1981	0800-1800	144	2880	4.8	5.0
2-3	1800-0800	4.4	300	1.4	1.5
Feb.1981	0800-1800	44	695	6.0	6.3
16-17	1800-0800	14	475	2.9	2.9
Feb.1981	0800-1800	27	1160	2.3	2.3
2-3	1800-0800	3.4	120	2.7	2.8
Mar.1981	0800-1800	21	890	2.3	2.4
16-17	1800-0800	2.7	315	0.8	0.9
Mar.1981	0800-1800	31	885	3.4	3.5

TABLE 5.3 CONCENTRATIONS OF TAL AND PARTICULATE LEAD IN AIR COLLECTED SIMULTANEOUSLY FROM 1000-1700 AT HEIGHTS OF 3m AND 12m ABOVE HOPE St. (Stn. 2) IN CENTRAL GLASGOW

Date	Sampling Height (m)	TAL (ng/m^3)	Particulate Lead (ng/m^3)	TAL/ Total Lead (%)	TAL/ Particulate Lead (%)
21 Jan.1981	3	90	2850	3.1	3.2
	12	52	1610	3.1	3.2
4 Feb.1981	3	75	2260	3.2	3.3
	12	53	1530	3.3	3.5
18 Feb.1981	3	37	1480	2.4	2.5
	12	31	1100	2.7	2.8
4 Mar.1981	3	66	2370	2.7	2.8
	12	34	1390	2.4	2.4
18 Mar.1981	3	48	1090	4.2	4.4
	12	43	705	5.7	6.1
Mean ± S.D.	3	63±21	2010±710	3.1±0.7	3.2±0.7
	12	43±10	1270±370	3.4±1.3	3.6±1.5

respectively. Detailed data for five successive day-time/overnight sampling sessions at West Graham Street and for vertical height (3m and 12m) distribution studies at Hope Street (Stn.2) are given in Tables 5.2 and 5.3 respectively.

5.4 DISCUSSION

5.4.1 URBAN 24-HOUR TAL LEVELS

At the West Graham Street site where 24-hour samples were collected routinely, the mean and maximum TAL concentrations were 32ng/m^3 and 77ng/m^3 respectively (Table 5.1, Figure 5.5), with 75% of the values under 40ng/m^3. The mean TAL 24-hour level at the city centre site (Stn.2) was 31ng/m^3 (77% < 40ng/m^3) while in all central urban 24-hour sites (West Graham Street and Hope Street Stn. 2) 74% of samples were <40ng/m^3 (Figure 5.7(1)). The average TAL concentration at quieter city locations was 16ng/m^3. Hope Street Stn.2 samples were taken at two heights, 7m and 12m. The mean at 7m (6 samples) was 36 ± 9 ng/m^3 compared with 22 ± 2 ng/m^3 at 12m (3 samples).

In comparing the TAL content of Glasgow urban air with reported values for other cities, it must be borne in mind that sampling sites, viable for 24-hour collection periods, may not be strictly comparable. For example, the one 24-hour TAL concentration of 96ng/m^3 available for the Hope Street Stn.1 site exceeded all 28 and 9 values recorded at West Graham Street and Hope Street Stn.2 sites respectively, not unexpectedly in view of the greater traffic density and lower sampling height at Hope Street Stn.1. Nonetheless, the Glasgow 24-hour data are similar to Frankfurt-Main city-station mean TAL concentrations of 45 ± 34 ng/m3 (3.5m) and 20 ± 27 ng/m3 (20m) with a residential area mean of 24 ± 29 ng/m^3 (Rochbock et al, 1980) and are broadly comparable with, albeit lower than, mean TAL levels of 94 ± 64 ng/m^3 (4.9m) and 65 ± 45 ng/m^3 (14m) observed in a busy central London street (Birch et al, 1980).

The mean central urban Glasgow 24 hour TAL/total lead ratio (West Graham Street and Hope Street Stn.2) of 5.7 ± 3.4% (2.9 ± 1.9% in the more residential areas [Table 5.1]) is very similar to the 6.2 ± 2.4% (4.9m) and 6.7 ± 3.0% (14m) found in London (Birch et al, 1980) and to the 6.6 ± 0.5% (winter) and 7 ± 1% (summer) observed for Stockholm urban air (Nielsen et al, 1981), but noticeably lower than the daytime (1100-1700) average of 16.8 ± 3.4% reported for Antwerp (DeJonghe and Adams, 1980). The corresponding data of Rohbock et al (1980) for Frankfurt were presented as TAL/particulate lead ratios of 7.1 ± 3.7% (3.5m) and 9.0 ± 8.5% (20m) which closely relate to the mean urban Glasgow TAL/particulate lead ratio of 6.2 ± 4.2%. Although the Glasgow values support the typical range of Western European TAL/particulate lead ratios (5-15%), as derived from available urban TAL/total lead data by DeJonghe and Adams (1982), they are more in line with Harrison et al's (Harrison et al, 1979; Harrison and Laxen, 1981) derivation of 1-6% (TAL/total lead) as 84% of the TAL/total lead ratios at the West Graham Street and Hope Street Stn.2 sites were less than 7% (Figure 5.8(1)). The ratios TAL/total and TAL/particulate lead, however, are quite variable depending on such parameters as vehicle driving mode, source-to -site distance and the relative abundance of TML to TEL in petrol, the former being more volatile and also of greater thermal stability and atmospheric residence time (Birch et al, 1980). Also, wind speed can affect the degree of dispersion of both TAL and particulate lead but no consistent influence of wind speed on either ratio was evident in this study.

5.4.2 OVERNIGHT/DAYTIME TAL LEVELS

The five pairs of overnight (1800-0800)/daytime (0800-1800) data (Table 5.2) yielded distinct differences in mean TAL concentration (11ng/m^3 v 53ng/m^3), maximum TAL level (30ng/m^3 v 44ng/m^3) and mean TAL/total lead ratios (2.4 ± 1.3% v 3.8 ± 1.6%). The latter were very similar to the TAL/particulate lead ratios (2.5 ± 1.3% v 3.9 ± 1.7%). The significant daytime enhancements are consistent with higher traffic density, slower-moving traffic and greater TAL evaporation during the day.

The average daytime (1000-1700) TAL levels at Hope Street Stn.2 of 73 ± 24ng/m^3 (3m) and 43 ± 10ng/m^3 (12m), with a maximum recorded value of 110ng/m^3 (3m), may be compared with a mean of 137 ± 78 ng/m^3 (range 78-262ng/m^3) observed for the period 1100-1700 in central Antwerp (DeJonghe and Adams, 1980) and a mean TML level of 61ng/m^3 (range 47-77ng/m^3) found over 10-hour daytime periods in a busy Stockholm street (Nielsen et al, 1981). As noted elsewhere (Rohbock et al, 1980), TAL is variable over shorter sampling intervals particularly during the day. Concentrations of 18, 15 and 30ng/m^3 with associated ratios of 11.1, 5.8 and 7.9% (TAL/total lead) and 12.6, 6.2 and 8.6% (TAL/particulate lead) were obtained for successive 2.3 hour intervals from 1000 to 1700 at Hope Street Stn.1 on 10/12/80. Although these concentrations are noticeably lower than the mean concentration of 83 ± 19ng/m^3 (range 49-109 ng/m^3) reported by DeJonghe et al (1981) in a busy central Antwerp street for one hour sampling periods at different times during the day, the mean (7.9 ± 2.7%) and range (4.6-12.7%) of the TAL/particulate lead ratios are very similar.

5.4.3 VERTICAL DISTRIBUTION OF TAL

In the study of TAL variation with vertical height above street level at Hope Street Stn.2 (Table 5.3), the TAL and particulate lead concentrations were greater at 3m than at 12m in all five simultaneous sampling sessions. On going from a height of 3m to 12m, TAL and particulate lead levels declined on average by 29 ± 16% and 36 ± 7% respectively, decreases remarkably similar to those observed, 31 ± 9% and 35 ± 8%, by Birch et al (1980) between 4.9m and 14m above a London Street. The limited nature of these reductions is probably due to the poor vertical dispersion commonly associated with narrow 'street canyons'. In Frankfurt, Rohbock et al (1980) also found decreasing TAL concentrations with increasing altitude. Further, they considered that particulate lead decreased more rapidly with height and attributed this to the higher diffusivity of the gaseous lead compounds relative to particulate lead. In Glasgow, the TAL/total lead ratio showed an insignificant mean increase from 3.1 ± 0.7% (3m) to 3.4 ± 1.3% (12m) in line with the minor enhancement from 6.2 ± 2.4% (4.9m) to 6.7 ± 3.0% (14m) in London (Birch et al, 1980).

5.4.4 RURAL 24-HOUR TAL LEVELS

At the rural site the atmospheric TAL content was markedly lower than at urban sites (Figure 5.7), with four samples below the detection limit (0.8ng/m^3) and a maximum concentration of only 6.5ng/m^3 (Table 5.1). The median value of 1.9ng/m^3 is similar to the mean TAL level of 1.5ng/m^3, maximum 2.5ng/m^3, in a Danish rural area (Nielsen et al, 1981) and the mean TAL content of 3 ± 2 ng/m^3, maximum 5ng/m^3, found by Rohbock et al (1980) in a mountain resort area 30km from Frankfurt. DeJonghe and Adams (1980) reported TAL at less than 8ng/m^3 in all rural samples collected outside Antwerp.

The presence of TAL at rural sites has generally been attributed to advection from urban areas, the atmospheric persistence of TAL compounds enabling urban-range TAL/total lead (Figure 5.8) [or TAL/particulate lead] ratios in rural areas through atmospheric transport of TAL accompanied by particulate lead (Harrison and Laxen, 1978a). A suggested alternative mechanism (Rohbock et al, 1980), desorption of TAL from particulate matter, seems less likely (Harrison and Laxen, 1981) as any sorbed organic lead is believed to contribute no more than 1% of the total particulate atmospheric lead (Harrison and Laxen, 1977) and is probably not present as TAL (Harrison and Laxen, 1978a).

At the remote hill farm site in this Glasgow study, 14 of the 17 TAL/total lead ratios were <8% (Figure 5.8(2)) and thus lay within the typical urban range. The two elevated ratios of 28% and 39% were associated with particularly low particulate lead levels of 17ng/m^3 and 9ng/m^3 respectively, perhaps indicative of a clean maritime air mass, rather than with any marked enhancement in TAL content. Harrison and Laxen (1978a) found rural TAL levels of up to 230ng/m^3 (mean 19ng/m^3) [Birch et al, 1980] in north-west England, where 7 out of 28 samples had TAL/total lead ratios greater than 15%. Natural environmental methylation of lead in adjacent coastal/estuarine intertidal mud-flats and subsequent release of TAL to the atmosphere were invoked to account for the unusually high concentrations and fractions of TAL. Although the two elevated TAL/total lead ratios at the rural site in this west of Scotland study may reflect a small maritime source of environmental methylation, this seems unlikely, in view of the absence of enhanced TAL levels, despite the proximity of inorganic lead-contaminated sediments in the upper sea lochs of the Clyde Sea Area (Figure 5.2), [Farmer, 1983].

5.4.5 ENVIRONMENTAL EXPOSURE TO TAL

It has been claimed (Nielsen et al, 1978) that the brains of deceased humans who formerly resided in the lower floors of urban multi-storey buildings contained significantly higher quantities of the triAL metabolic derivatives of TAL than those of corresponding urban upper-floor and rural dwellers. On the basis of the extent of TAL variation with vertical height above street level (Table 5.3) and the relative magnitude of urban and rural TAL levels (Table 5.1), it might be expected that urban upper- and lower-floor dwellers would experience similar environmental exposure to TAL while rural dwellers would constitute a distinctly separate low-exposure group. This is in accord with the findings of Birch et al (1980). Nevertheless, the observation of TAL metabolites in the critical organ-the brain-of members of the general public at concentrations possibly sufficient to inhibit enzyme action (Nielsen, 1978; Grandjean and Nielsen, 1979) suggests that potentially deleterious health effects may not be confined merely to the occupationally-exposed. The latter group may include petrol-station and underground car-park attendants. The highest TAL concentrations in this study - mean 195ng/m^3, maximum 274ng/m^3 - were obtained in a petrol station forecourt where the high 13-32% and 15-48% ranges for TAL/total and TAL/particulate lead ratios, respectively, resulted predominantly from evaporation of TAL.

5.4.6 PARTICULATE LEAD

Although certain factors peculiar to the release and atmospheric chemistry of TAL may influence the proportion of TAL to total and particulate lead levels, trends in particulate lead concentrations were generally similar to those of TAL (Figure 5.4). For example, although all 8 daytime (1000-1700) samples at Hope Street Stn.2 exceeded 1μg/m^3, with 5 greater than 2μg/m^3, only 3 out of 6 24-hour samples at 7m exceeded 1μg/m^3, while at 12m all 3 24-hour samples were less than 0.65μg/m^3 (Figure 5.6).

The corresponding figures for the 5 daytime (0800-1800) West Graham Street samples were 2 (>1μg/m^3) and 1 (>2μg/m^3) while, over 24-hours, only 2 out of 28 samples (and 5 out of 37 samples - including Hope Street Stn. 2 24-hour results [Figure 5.9]) exceeded 1μg/m^3, with 17 less than 0.5μg/m^3. In the Department of Industry 5 towns Survey of Kerbside Air Pollution (Apling et al, 1979), annual daily means from 1974-1977 at a Hope Street site, 0.5m from the kerb and 2.5m above street level, averaged 1.7-2.5μg/m^3. The 'Lawther Report' (DHSS, 1980) has recommended that 'measures should be taken to keep the annual mean concentration of lead in air to less than 2μg/m^3 in places where people are liable to be continuously exposed'. The UK government has recently introduced proposals to reduce the lead (as TAL) content of petrol from 0.4g/l to 0.15g/l by 1985 and remove it completely by 1990. These measures should result in a significant fall in atmospheric particulate lead levels as observed in Germany (Jost and Sartorius, 1979) where a reduction to 0.15g/l from 0.4g/l was enforced in 1976.

Somewhat paradoxically, Rohbock et al (1980) concluded that German gaseous lead (TAL) concentrations had shown no significant decrease, a viewpoint since challenged by Harrison and Laxen (1981) partially on the grounds of insufficient reliable pre-1976 TAL data for a valid comparison to be made. Careful monitoring of atmospheric TAL levels in the UK over the next few years should resolve this question as well as provide valuable information with respect to human exposure to environmental organo-lead compounds and the occurrence, or otherwise, of environmental methylation of inorganic lead. The latter unresolved question highlights the potentially significant role that identification of chemical species plays in environmental studies, particularly in aiding our understanding of the environment's capacity for transformation of trace-element contaminants. In the case of lead, natural methylation, which has been postulated by a number of workers (Chau and Wong, 1979; Wood, 1979; Craig, 1980; Thompson and Crerar, 1980), but disputed by others (Reisinger et al, 1981; Jarvie et al, 1983), could produce elevated TML levels and inflate the TAL/(total or particulate) lead ratio in apparently uncontaminated atmospheric environments. Consequently, the application of a combined chromatographic - specific detector speciation method (Reamer et al, 1978; Radziuk et al, 1979; Rohbock et al, 1980; DeJonghe et al, 1980a and b, 1981; Chakraborti et al, 1981; Messman and Rains, 1981; Nielsen et al, 1981) capable of identifying and measuring individual TAL species would be particularly useful in such studies.

APPENDIX 1

INDIVIDUAL ELEMENT CONCENTRATIONS OF STANDARD REFERENCE MATERIALS

MAJOR AND MINOR ELEMENTS

	Aluminium (%)				Calcium (%)			
	River[1] Sediment	Urban[2] Particulate	Soil-5[3]	Lake[4] Sediment	River Sediment	Urban Particulate	Soil-5	Lake Sediment
	2.36	2.70	7.86	10.30	2.92	6.08	2.36	0.30
	2.16	3.49	7.82	9.95	3.15	6.55	2.40	0.30
	2.44	4.07	7.90	9.98	2.82	6.21	2.34	0.30
	2.43	3.19	7.80	9.54	2.90	6.21	2.30	0.29
	2.38	3.23	8.00	9.98	2.94	6.38	2.35	0.30
	2.41	3.08	7.89	9.80	2.82	6.27	2.34	0.30
	2.55	3.54	8.04	10.35	2.95	5.95	2.44	0.30
	2.42	3.39	7.89	9.94	2.99	6.00	2.35	0.31
	2.31	3.32	7.95	10.05	2.75	5.79	2.39	0.31
	2.55	2.74	7.99	9.84	2.63	6.04	2.35	0.30
	2.43	2.80	8.13	10.24	2.99	6.09	2.41	0.32
	2.61	4.05	7.92	10.10	2.95	6.55	2.37	0.30
Mean	2.42	3.30	7.93	10.0	2.90	6.18	2.38	0.30
Std.Devn.	0.12	0.45	0.09	0.2	0.13	0.23	0.04	0.01

	Iron (%)				Magnesium (%)			
	River Sediment	Urban Particulate	Soil-5	Lake Sediment	River Sediment	Urban Particulate	Soil-5	Lake Sediment
	10.5	4.46	4.55	6.46	0.73	0.75	1.22	0.65
	11.0	4.87	4.50	6.48	0.72	0.83	1.26	0.68
	10.6	4.65	4.73	6.26	0.75	0.77	1.29	0.65
	10.7	4.68	4.67	6.48	0.75	0.74	1.30	0.66
	10.5	4.59	4.60	6.50	0.73	0.75	1.28	0.66
	10.4	4.37	4.38	6.48	0.75	0.75	1.19	0.64
	10.9	4.18	4.54	6.47	0.78	0.75	1.30	0.69
	10.8	4.64	4.89	6.54	0.76	0.77	1.32	0.69
	10.9	4.09	4.70	7.00	0.72	0.69	1.30	0.64
	10.0	4.51	4.56	6.49	0.77	0.77	1.28	0.68
	10.8	4.43	4.69	6.71	0.78	0.75	1.31	0.67
	10.3		4.63	6.60	0.77	0.83	1.33	0.67
Mean	10.6	4.50	4.63	6.56	0.75	0.76	1.28	0.67
Std.Devn.	0.3	0.23	0.13	0.17	0.02	0.04	0.05	0.02

[1] River Sediment SRM 1645

[2] Urban Particulate Matter SRM 1648

[3] Soil-5 IAEA

[4] Lake Sediment IAEA SL-1

MAJOR AND MINOR ELEMENTS

	Manganese (µg/g)				Zinc (µg/g)			
	River Sediment	Urban Particulate	Soil-5	Lake Sediment	River Sediment	Urban Particulate	Soil-5	Lake Sediment
	719	1130	994	3730	1610	4850	293	191
	890	871	991	3550	1670	4580	338	239
	775	655	986	3560	1630	4610	330	227
	691	827	917	3520	1660	4580	319	175
	883	966	944	3550	1620	4400	352	257
	771	840	1030	3650	1590	4480	401	224
	723	942	966	3800	1670	4510	416	240
	765	558	1010	3800	1560	4440	347	216
	605	756	1040	3650	1670	4470	349	234
	722	745		3580	1690	4860	311	176
	670	607		3580	1640		371	194
	671			3690			415	
Mean	740	810	986	3640	1640	4580	354	216
Std.Devn.	80	170	40	100	40	160	41	28

Silicon (%)

	River Sediment	Urban Particulate	Soil-5	Lake Sediment
	21.7	13.1	29.2	24.2
	23.2	13.8	25.8	22.4
	22.9	12.8	24.9	21.7
	25.6	12.5	26.1	21.4
	24.7	13.4	26.3	23.1
	24.3	12.8	25.0	22.4
	22.5	13.4	29.1	22.6
	23.0	15.0	27.0	25.2
	24.4	12.3	25.6	24.0
		13.7	25.7	23.2
		12.6	25.9	23.0
		14.6	26.2	23.3
Mean	23.6	13.3	26.4	23.1
Std.Devn.	1.2	0.8	1.4	1.1

TRACE ELEMENTS

	Cadmium (µg/g)				Chromium (µg/g)			
	River Sediment	Urban Particulate	Soil-5	Lake Sediment	River* Sediment	Urban Particulate	Soil-5	Lake Sediment
	9.9	64	1.72	0.34	3.12	144	27.1	101
	8.7	70	1.35	0.34	3.27	157	26.0	98
	9.0	65	1.33	0.25	3.19	200	25.8	97
	8.95	69	1.47	0.24	3.25	144	24.8	96
	8.6	69	1.29	0.22	3.11	149	25.4	98
	8.75	65	1.36	0.26	3.03	137	25.6	106
	10.0	69	1.48		3.19	185	24.5	106
	9.6	77	1.37		3.28	182	26.6	109
	9.05	65	1.39		3.10	195	25.9	109
	8.8	70	1.41		3.10	206	30.4	105
	9.35	66	1.39		3.23	200	25.4	107
	9.3	76	1.41		3.23		26.1	107
Mean	9.2	69	1.41	0.28		173	26.1	103
Std.Devn.	0.5	4	0.11	0.05		27	1.5	5

	Copper (µg/g)				Lead (µg/g)			
	River Sediment	Urban Particulate	Soil-5	Lake Sediment	River Sediment	Urban Particulate	Soil-5	Lake Sediment
	111	585	72	31	726	6144	150	34.5
	112	615	78	32	672	6328	145	44.7
	114	591	78	31	663	6193	143	42.1
	116	601	84	31	671	6180	142	42.2
	98	540	80	31			143	42.0
	102	601	77	28			141	46.7
	111	563	72	22			159	47.0
	121	589	85				153	40.3
		592					146	39.7
							154	33.9
							153	31.5
							158	37.8
Mean	111	586	78.3	29.4	683	6210	149	40.5
Std.Devn.	7	22	4.8	3.5	29	80	6	5.8

* Concentration in %

APPENDIX 2

INDIVIDUAL SOIL EXCHANGEABLE AND TOTAL METAL CONCENTRATIONS

All concentrations in µg/g

OPEN SPACES

Sample	Sample Distance from Road(m)	Lead		Zinc		Copper		Cadmium	
		Exch.	Total	Exch.	Total	Exch.	Total	Exch.	Total
3/3	>50	<1.5	108	3.7	136	4.9	98.0		
4/2	<10	2.6	84.4	5.7	56.9	0.7	30.7	0.12	0.31
4/3	10-50	<0.5	52.4	<0.2	69.1	<0.4	17.1	0.03	0.12
5/1	<10	3.2	163	3.2	229	1.1	56.7	0.11	0.42
9/1	10-50	<0.6	101	0.6	151	0.8	197	0.09	0.29
9/2	10-50	20.4	429	22.7	385	1.4	77.8	0.19	0.52
10/3	<10	5.5	289	3.1	223	0.4	84.9	0.10	0.43
15/1	<10	20.2	1000	10.6	639	0.7	258	0.11	0.84
15/2	<10	9.9	640	9.0	482	1.7	143	0.18	1.14
16/2	10-50	7.7	323	6.4	285	1.8	116	0.09	0.42
17/1	<10	<1.6	35.0	4.8	181	0.6	16.6		
18/2	10-50	25.0	207	4.0	149	1.9	71.0	0.07	0.56
20/1	<10	1.2	157	0.4	199	1.2	65.8	0.07	0.45
21/3	<10	<1.5	96.5	1.2	126	1.4	133	0.07	0.21
23/2	<10	<1.2	70.3	6.1	102	0.7	23.2	0.16	0.31
24/1	10-50	<1.7	403	4.4	440	2.0	733	0.13	0.54
24/3	<10	<1.2	103	2.0	144	0.6	434	0.09	0.17
25/2	<10	<1.7	134	1.3	113	0.9	29.2	0.09	0.31
27/1	10-50	34.9	1900	37.6	1380	6.7	925	0.23	1.90
28/1	10-50	<1.7	107	2.8	138	2.0	50.9		
28/2	<10	<1.6	94.8	3.2	122	0.4	29.7	0.07	0.14
31/2	<10	8.3	226	13.2	232	1.4		0.20	1.17
31/3	<10	6.2	131	6.2	143	1.6	109	0.09	0.43
33/2	10-50	<2.0	133	4.4	203	1.1	45.6	0.17	0.94
34/1	10-50	<1.7	189	5.7	150	1.3	59.3	0.11	0.29
36/3	<10	12.1	459	10.2	354	3.2	423	0.21	0.71
37/2	10-50	2.9	163	3.8	136	1.4	138	0.12	0.26
38/2	<10	1.8	257	4.0	220	2.2	314	0.14	1.01
38/3	<10	1.9	218	2.6	217	2.0	83.0	0.12	1.39
39/1	<10	3.9	157	6.6	166	2.4	97.5	0.12	0.89
44/3	<10	2.4	98.4	41.1	361	1.5		0.14	0.25
45/3	10-50	<2.0	119	9.0	162	1.2	76.2	0.14	0.21
49/1	10-50	<2.3	278	4.3	248	1.0	380	0.20	1.25
51/1	<10	2.2	205	5.8	135	0.3	33.8	0.12	0.46
51/3	<10	<1.3	85.8	3.4	66.1	1.5	51.5	0.09	0.27
53/1	<10	<1.0	76.0	2.3	140	0.3	38.8	0.07	0.38
53/3	<10	<1.5	34.0	2.1	50.7	<0.7	261	0.09	0.24
54/1	<10	4.1	188	2.6	128	2.0	67.0	0.08	0.47
54/3	<10	<2.0	181	2.0	278	1.5	65.0	0.10	0.37
56/2	<10	2.4	300	4.8	207	1.5	60.9	0.17	0.71
57/1	<10	2.1	180	4.7	229	1.6	362	0.12	0.41
57/2	<10	<1.9	73.3	3.6	104	1.0	48.5	0.06	0.13
59/1	>50	<1.5	53.4	1.2	103	0.2	280	0.04	0.10
59/2	>50							0.09	
60/1	<10	<1.8		2.8		<0.8		0.09	
67/1	<10	7.0	269	13.0	390	0.3	72.0	0.38	0.64
67/3	<10	5.8	220	6.1	174	1.1	66.7	0.15	0.44
68/3	<10	6.7	362	2.7	108	<0.4	54.4	0.04	0.13

OPEN SPACES

Sample	Sample Distance from Road(m)	Lead		Zinc		Copper		Cadmium	
		Exch.	Total	Exch.	Total	Exch.	Total	Exch.	Total
69/1	<10		899	8.5	198	1.2	90.3	0.22	0.51
69/2	>50	<1.0	106	1.4	178	0.5	33.1	0.07	0.21
70/1	<10	1.4	350	5.3	187	0.3	42.1	0.06	0.37
70/2	<10	7.6	520	6.4	397	0.5	63.8	0.13	0.71
71/1	<10	<1.1	140	2.6	143	<0.3	42.8	0.04	0.29
71/2	<10	12.5	849	23.8	1010	2.1	388	0.13	1.97
72/1	<10	8.2	281	10.4	153	1.5	81.3	0.18	0.41
73/1	<10	1.0	124	3.5	122	0.3	35.6	0.08	0.38
74/1	<10	1.9	119	7.2	72.9	1.0	45.7	0.08	0.27
74/2	<10	1.3	149	2.1	271	0.8	58.8	0.10	0.25
75/1	<10	<1.1	67.9	1.0	125	<0.3	40.8	0.04	0.23
75/2	<10	4.9	148	10.3	178	<0.5	33.5	0.63	1.40
76/1	10-50	4.9		23.5		3.6		0.19	
76/2	<10	<2.0		2.8		<0.8		0.09	
77/1	<10	7.1		16.7		1.1		0.23	
80/2	10-50	1.2	99.0	3.0	126	0.4	46.9	0.08	0.22
80/3	>50	2.8	127	1.6	99.9	0.4	38.6	0.08	0.25
85/1	10-50	<1.5	135	1.4	137	0.5	50.6	0.05	0.38
88/1	<10	<1.0	152	2.3	218	0.3	57.9	0.09	0.33
89/1	<10	<1.5	148	3.5	338	0.3	95.7	0.08	0.27
89/2	<10	9.4	372	6.9	198	0.9	112	0.13	0.57
91/1	<10		635	10.2	370	1.9	152	0.20	1.03
91/2	<10	7.0	271	11.7	412	10.4	172	0.13	0.38
92/1	10-50	<0.8	108	2.0	131	0.4	95.4	0.06	0.27
93/1	<10	6.0	395	11.2	279	1.5	106	0.11	0.61
93/3	<10	<1.0	121	3.2	172	0.5	38.0	0.11	0.47
94/1	10-50	<1.0	97.0	5.3	101	0.3	32.9	0.12	0.44
95/1	<10	<1.1	73.6	4.6	66.1	<0.3	30.6	0.05	0.23
95/2	<10	<1.1	183	2.1	224	0.5	51.7	0.09	0.50
96/3	10-50	1.3	142	4.3	64.9	0.6	49.8	0.08	0.32
97/3	<10	5.8		6.9		2.0		0.12	
100/1	<10	<1.4	75.1	2.4	232	0.8	64.6	0.11	0.47
101/1	10-50	3.0	158	19.5	309	0.7	61.6	0.13	0.53
101/2	<10	4.1	241	2.3	135	<0.6	70.9	0.07	0.44
102/1	<10	2.5	109	2.5	177	0.4	94.6	0.06	0.36
102/3	<10	1.8	110	1.2	191	0.5	129	0.07	0.43
103/1	>50	2.0	117	3.0	157	0.7	44.0	0.11	0.44
104/1	<10	1.4	138	4.0	220	0.4	278	0.09	0.37
105/2	10-50	11.2	247	3.3	81.7	0.2	46.8	0.07	0.23
107/2	<10		469				129		0.71
109/1	10-50	11.4	443	12.2	287	1.2	96.5	0.15	0.57
111/3	10-50	<0.7	83.3	1.9	79.7	0.8	35.5	0.07	0.32
112/1	<10	2.7	184	18.2	211	0.5	81.8	0.11	0.43
112/2	10-50	1.4	156	1.7	141	0.4	49.6	0.10	0.26
113/2	<10		549		330		98.9		1.12
113/3	<10	31.4	493	12.4	309	2.2	338	0.28	0.89
116/1	<10	4.0		5.5		<0.8		0.16	
123/1	<10	<1.5	132	5.0	179	0.7		0.15	1.15

OPEN SPACES

Sample	Sample Distance from Road(m)	Lead		Zinc		Copper		Cadmium	
		Exch.	Total	Exch.	Total	Exch.	Total	Exch.	Total
123/2	10-50	9.1	446	22.2	310	1.7	154	0.13	0.58
124/1	<10	3.1	254	8.2	243	0.8	52.1	0.25	0.72
124/2	10-50	<0.5	74.6	0.8	106	<0.4	31.8	0.06	0.27
125/2	<10	<1.3	95.3	1.3	171	0.4	125	0.09	0.37
125/3	<10	2.8	119	6.1	129	0.6	37.1	0.12	0.39
126/1	<10	<1.1	103	7.1	220	<0.5	45.9	0.12	0.44
126/2	<10	12.4	375	6.4	153	0.4	41.9	0.10	0.38
129/2	<10	4.3	95.5	3.2	77.4	0.1	43.2		
130/1	10-50	2.6	136	3.9	139	0.8	133	0.13	0.34
130/3	10-50	5.2	165	3.9	142	0.5	59.9	0.12	0.38
132/2	<10	40.9	623	24.8	569	2.1	115	0.36	1.04
132/3	<10		778	14.1	435	1.8	174	0.30	0.79
133/1	<10	2.7	96.3	3.8	83.3	0.5	33.8	0.11	0.25
135/3	<10	<1.5	78.0	6.5	80.1	0.4	110	0.10	0.62
138/1	<10	<1.5		3.8		1.9		0.14	
139/3	<10	12.8	183	12.0	167	2.2	48.3	0.16	0.43
142/1	<10	5.0	256	16.9	371	1.9	206	0.30	1.06
142/2	10-50	1.5	134	8.3	188	2.0	160	0.15	0.99
144/3	10-50	<1.6	143	4.3	188	1.2	54.5	0.12	0.38
145/1	10-50	3.3	115	5.7	131	1.1	70.1	0.12	0.31
145/3	10-50	23.5	388	5.3	407	3.5	127	0.22	0.52
146/1	<10	<1.1	444	1.5	381	<0.6	90.3	0.04	0.50
146/3	<10	<0.9	68.7	1.3	111	0.5	21.7	0.08	0.31
147/1	<10	<0.6	69.3	1.9	103	0.9	33.2	0.08	0.24
148/1	10-50	1.9	98.2	3.5	147	0.5	235	0.10	0.29
148/3	10-50	5.2	92.4	3.1	84.4	<0.7	38.5		
149/3	<10	2.5	134	8.2	128	0.7	136	0.17	0.26
150/2	<10	4.7	235	6.0	186	1.2	74.0	0.10	0.46
150/3	<10	29.1	704	7.1	452	1.4	103	0.16	0.93
152/3	10-50	<0.9	114	0.4	347	0.5	43.5	0.07	0.29
153/1	<10	15.1	406	56.8	567	3.3	256	0.39	1.45
154/2	<10	<1.5		2.7		1.1		0.07	
154/3	<10	<1.5		2.1		1.3		0.06	
155/2	<10	<2.6	158	2.1	135	1.6	34.5	0.08	0.21
155/3	<10	<1.5		4.9		1.0		0.18	
156/1	<10	<2.4	281	3.3	330	1.9	137	0.18	0.73
156/2	<10	<1.5	128	0.6	178	0.7	92.3	0.06	1.05
157/3	<10	<2.0	166	3.8	191	1.5	52.7	0.19	0.79
158/2	<10	1.8	78.0	3.2	62.2	1.1	59.6	0.11	0.29
159/1	<10	<1.7	103	1.2	187	1.5	82.2	0.09	0.26
160/2	10-50	3.7	209	26.1	418	1.3	128	0.28	1.76
161/2	<10	3.7		39.5	1840	3.6	558	0.29	2.75
163/1	<10	3.5	125	9.3	165	0.6	54.4	0.11	0.27
166/1	10-50	<1.5		4.2		1.5		0.10	
169/1	<10	9.6	254	23.7	264	1.4	167	0.26	0.38
169/3	<10	6.6	133	7.5	118	0.6	55.5	0.14	0.31
173/2	<10	<1.3	216	7.4	169	2.5	94.6	0.22	0.39
174/1	<10	211	1710	1.6	199	1.2	75.6	0.13	0.95

OPEN SPACES

Sample	Sample Distance from Road(m)	Lead		Zinc		Copper		Cadmium	
		Exch.	Total	Exch.	Total	Exch.	Total	Exch.	Total
174/3	<10	<1.5	158	1.8	264	1.6	163		
175/1	10-50	<1.9	163	1.9	205	2.0	76.5	0.11	0.36
176/2	<10	<1.9	181	1.6	192	2.2	59.4	0.10	0.38
177/3	10-50	8.9	299	4.0	305	5.3		0.18	0.87
180/1	<10	4.4	220	7.7	161	0.6	62.0	0.17	0.50
180/3	<10	6.4	484	16.0	664	2.1	199	0.45	2.10
184/1	<10	<1.5	97.9	3.9	173	0.8	266	0.10	0.71
184/3	<10	18.3		63.2		6.7		0.41	
185/1	<10	<1.5	92.1	0.8	120	1.7		0.06	0.26
186/2	<10	1.3	60.5	1.6	65.4	<0.5	206		
187/3	10-50	3.9	168	4.3	171	0.7	41.5	0.14	0.32
192/2	<10	<1.2	112	1.7	100	0.5	68.9	0.09	0.36
196/1	>50	<2.1	144	2.4	151	1.4	40.4	0.10	0.20
205/1	10-50	<1.1	98.8	3.3	115	0.6	72.6	0.09	0.31
205/2	<10	1.2	154	4.9	149	0.5	62.6	0.14	0.50
208/1	10-50	<1.9	147	2.2	195	1.1	59.2	0.08	0.34
211/1	<10	5.2	111	2.3	158	1.3	49.7	0.10	0.66
211/3	<10	<1.5	22.8	0.4	64.3	0.5	4.1	0.05	0.17
215/3	<10	4.3	261	3.1	251	<0.6	116	0.12	0.45
217/3	<10			6.8		1.0	80.6	0.11	0.47
218/1	10-50	1.4	100	1.5	72.5	0.7	25.6	0.09	0.21
218/3	<10	<1.0	67.6	0.9	94.5	0.8	44.9	0.09	0.19
219/3	<10	<1.5	39.2	4.8	122	0.6	72.4	0.11	0.28
222/2	<10	<2.0	33.4	2.0	75.7	1.4	22.2	0.10	0.36
226/1	10-50	5.9	107	7.1	148	<0.7	84.6	0.15	0.24
228/1	<10	1.2	126	1.6	140	1.1	128	0.10	0.32
228/2	<10	<1.5	144	3.4	147	1.2	44.7	0.12	0.26
229/3	10-50	<1.8	105	0.8	120	0.5	114	0.06	0.20
231/2	<10	<1.7	117	3.5	139	1.0	41.1	0.14	0.25
232/3	10-50	<0.6	83.8	2.3	93.4	<0.5	60.7	0.07	0.42
233/2	10-50	<0.5	45.4	1.2	99.8	<0.5	16.2	0.11	0.34
233/3	>50	1.8	203	1.2	135	<0.5	33.6	0.04	0.44
234/2	10-50	<1.4	112	2.8	164	<0.4	42.5	0.09	0.45
234/3	>50	<0.9	35.9	0.4	31.5	0.5	12.5	0.04	0.09
235/1	10-50	2.2	84.7	0.4	120	0.3	53.5	0.04	0.19
235/2	10-50	<1.0	46.8	0.6	72.1	<0.5	22.7	0.04	0.14
236/2	<10	<1.4	103	2.0	141	1.1	38.3	0.10	0.17
237/2	<10	<1.6	67.3	1.4	89.9	0.6	65.2		
242/2	<10	1.0	55.0	3.9		0.5	21.4	0.10	0.15
242/3	10-50	2.6	73.4	5.2	57.0	0.5	50.4		

GARDEN SOILS

Sample	Sample Distance from Road (m)	Lead		Zinc		Copper		Cadmium	
		Exch.	Total	Exch.	Total	Exch.	Total	Exch.	Total
5/2	<10	1.1	98.2	9.4	149	<0.6	124	0.10	0.24
16/1	<10	<1.6	70.6	3.8	137	<0.5	114	0.07	0.24
18/1	<10	8.5	412	5.1	293	1.3	293	0.10	0.52
19/1	10-50	<1.8	92.9	0.4	117	1.6	41.2	0.03	0.15
19/2	<10	<2.0	154	3.8	137	1.4	76.6	0.10	1.25
21/2	<10	1.7	179	4.1	215	1.8	181	0.11	0.45
22/1	<10	<1.5	89.1	2.9	131	1.5	39.2	0.12	1.00
22/2	10-50	2.1	94.4	9.5	271	3.0	62.2	0.13	0.77
23/1	<10	<1.4	157	2.2	163	0.7	69.3	0.08	0.37
27/3	<10	1.9	274	3.5	191	1.2	135	0.10	0.30
29/3	10-50	<1.8	190	8.0	242	1.0		0.11	0.40
30/1	<10	3.4	236	5.4	178	4.6	157	0.10	0.24
30/2	10-50	11.8	933	11.0	847	5.1	293	0.28	1.74
32/1	<10	15.6	349	9.7	349	1.3	126	0.20	1.73
32/3	<10	<1.5		6.9		0.6		0.17	
33/1	<10	<2.1	192	4.8	176	2.0	281	0.16	0.34
34/2	<10	<2.1	128	4.6	148	2.2	68.2	0.10	0.34
35/2	<10	<1.6	87.0	2.9	100	0.7	22.3	0.07	0.15
37/1	<10	1.7	232	2.9	194	0.9	86.7	0.10	0.86
44/1	<10	<1.7	63.6	7.5	117	1.0	39.4		
45/2	<10	<1.5	138	4.0	115	1.8	144	0.09	0.36
46/2	<10	<1.8	90.6	1.2	222	0.7	26.2	0.08	0.34
46/3	<10	<1.4	37.3	1.0	40.0	<0.5	15.1	0.03	<0.10
47/1	<10	2.8	138	4.1	194	1.6	103	0.12	0.42
47/2	<10	<1.6	229	4.7	196	4.1	159	0.12	0.38
48/1	<10	7.1	376	3.8	252	2.8	178	0.16	1.09
48/3	<10	2.0	137	2.2	195	1.7	51.5	0.11	0.77
49/3	<10	9.1	323	6.6	141	1.3	68.5	0.11	0.24
50/1	<10	13.9	184	6.3	130	2.0	65.0	0.17	0.37
50/3	<10	7.1	236	6.5	140	1.3	71.8	0.16	0.39
55/3	<10	<1.9	186	2.4	203	1.5	45.1	0.09	0.39
60/2	<10	1.2		11.8		1.4		0.21	
63/2	<10	6.6	346	14.2	456	3.9	230	0.19	1.90
64/2	<10	15.6	570	7.3	135	0.3	52.1	0.11	0.31
64/3	<10	9.0	329	20.6	453	3.3	110	0.18	1.33
66/1	<10	11.0	348	4.9	198	0.5	54.5	0.09	0.29
66/2	10-50	7.0	150	5.5	139	0.8	42.2	0.10	0.30
86/2	<10	12.6	522	28.0	505	2.4	155	0.20	0.99
86/3	<10	14.7	503	23.9	428	3.4	157	0.18	0.76
87/1	10-50	12.1	381	10.2	205	1.5	116	0.09	0.39
96/1	10-50	4.5	281	9.6	300	0.9	397	0.16	0.69
98/3	<10	2.6		9.7		<0.8		0.12	
99/1	<10	3.9		4.7		1.4		0.10	
111/1	<10	<1.5	164	4.0	214	<0.5	48.7	0.11	0.60
118/1	<10	67.3		4.4		5.1		0.12	
118/3	<10	18.3		6.5		3.4		0.18	
121/2	<10	1.5	171	4.4	102	2.2	71.1	0.11	0.18
131/1	<10	3.6	282	10.1	358	0.7	94.7	0.19	0.91
131/2	<10	13.1	392	52.4	553	1.7	102	0.37	2.04

GARDEN SOILS

Sample	Sample Distance from Road(m)	Lead		Zinc		Copper		Cadmium	
		Exch.	Total	Exch.	Total	Exch.	Total	Exch.	Total
139/1	<10	11.5		13.7		3.3		0.13	
140/3	<10			37.6		3.9		0.24	
141/1	<10	<1.7	105	18.0	228	2.2	70.8	0.31	0.57
143/1	<10	<1.5	90.2	2.0	162	0.7		0.07	0.30
157/1	<10	<2.2	242	4.5	275	2.3	65.4	0.18	0.74
160/3	<10	<1.6	118	5.0	160	1.1	83.8	0.14	0.39
161/1	<10	<1.8	231	13.0	276	2.0	98.7	0.18	0.60
163/3	<10	16.7	1310	14.1	1170	2.8	426	0.16	2.02
164/1	<10	6.7	281	7.0	199	<0.5	59.0	0.13	0.66
165/2	<10	<1.5		2.1		1.7		0.11	
167/1	<10	4.9		5.7		0.9		0.13	
170/1	<10	4.6	219	4.3	195	1.1	121	0.07	0.22
171/1	<10	<1.5		2.7		0.7		0.09	
172/1	<10	4.9	306	16.5	186	0.5	67.2	0.19	0.50
177/2	<10	5.2	531	11.3	468	1.6	157	0.23	1.31
178/1	10-50	3.7	328	21.1	428	1.1	94.0	0.24	0.71
179/2	<10	1.9	552	5.0	265	1.1	135	0.15	0.58
181/2	<10	4.2	232	10.5	213	<0.5	64.4	0.19	0.45
183/1	<10	21.1						0.07	
183/3	<10	<1.5		5.1		1.0		0.09	
188/2	<10	8.1	304	21.1	281	1.4	87.3	0.21	0.68
189/3	<10		343		402		65.9	0.15	4.07
197/1	<10	6.1	128	2.6	148	0.8	31.7	0.10	0.28
197/2	<10	<2.5	159	4.5	172	2.2	40.7		
198/1	<10	<1.5	112	0.5	130	1.1	28.3	0.07	0.30
201/1	<10	<1.7	234	2.1	251	1.3	102	0.17	0.76
202/1	<10	<2.1	118	4.1	149	1.0	48.2	0.14	1.03
203/1	<10	4.2	326	12.1	288	1.8	61.5	0.19	0.63
207/2	<10	<1.5	68.7	0.9	96.1	0.7	26.3	0.05	0.26
213/1	<10	1.3	197	2.9	172	1.5	46.7	0.09	1.10
213/2	<10	<1.6	136	0.8	108	0.9	41.1	0.06	0.88
214/1	<10	<1.7	132	1.9	189	1.3	105	0.07	0.34
214/2	<10	<2.0	347	4.5	285	1.2	80.2	0.11	1.18
222/1	<10	<1.5	59.1	<0.2	125	0.4	36.9	0.07	0.45
223/2	<10	<1.8	219	1.6	276	1.7	125	0.13	0.97
223/3	<10	16.0	301	7.4	158	1.3	39.9	0.17	0.36
224/1	<10	<1.5	189	5.4	200	0.4		0.14	0.96
225/2	<10	<1.7	164	2.5	117	0.6	46.6	0.14	0.97
225/3	<10	3.1	328	38.1	696	2.1	127	0.29	1.21
229/1	10-50	<1.7	143	1.6	202	0.9	58.5	0.12	0.38
236/1	<10	<1.8	148	2.7	182	1.1	38.8	0.11	0.33
237/3	10-50	<1.8	83.3	1.4	76.1	0.7	27.3		
244/2	<10	<1.6	109	1.6	113	1.0	218	0.08	0.23
244/3	10-50	<1.8	80.7	1.5	114	<0.4	149	0.07	0.12

PARKLAND SOILS

Sample	Sample Distance from Road (m)	Lead Exch.	Lead Total	Zinc Exch.	Zinc Total	Copper Exch.	Copper Total	Cadmium Exch.	Cadmium Total
3/1	>50	<1.6	37.3	0.8	59.0	<0.5	20.1	0.06	0.16
10/1	10-50	0.8	74.9	0.7	147	0.4	269	0.07	0.31
17/3	10-50	5.0	135	3.5		1.0	315		
20/3	>50	1.5	137	5.4	205	1.5	131	0.31	1.44
25/1	10-50	<1.5	246	6.4	89.3	0.9	108		
29/1	>50	<1.9	78.2	4.0	82.9	1.9	35.1		
35/1	10-50	<1.5	124	4.1	145	1.6	88.7		
36/1	<10	1.6	141	3.9	158	1.1	62.8	0.10	0.22
39/3	10-50	13.4	230	1.4	78.9	2.1	83.6	0.09	1.09
40/1	10-50	10.4	307	8.5	354	2.9	123	0.36	1.39
52/1	>50	1.6	126	2.2	77.3	1.0	38.8	0.05	0.19
52/2	>50	19.0	312	3.8	115	1.4	78.5	0.06	0.28
55/1	10-50	7.8	263	14.4	320	2.3	116	0.19	0.47
56/3	10-50	<1.7	81.2	2.5	122	2.1		0.08	0.25
63/3	<10	<1.5		6.3		0.9		0.11	
65/1	10-50	12.4	314	18.5	237	1.7	301	0.19	0.39
65/3	10-50	19.2	411	33.8	544	5.2	258	0.28	0.71
68/1	10-50	9.6	572	5.3	328	0.9	103	0.14	0.72
72/2	>50	<0.9	140	2.6	75.1	0.3	29.8	0.05	0.29
73/2	>50	2.7	140	3.6	84.6	0.4	75.8	0.07	0.42
77/3	10-50	<2.1	195	4.1	316	2.2	132	0.11	0.57
78/1	>50	32.1		9.6		1.7		0.16	
78/3	10-50	1.3		0.9		1.3		0.05	
87/2	10-50	5.3	83.0	1.2	141	0.7	33.8	0.04	0.23
90/1	>50	6.2	215	4.7	168	0.9	71.7	0.13	0.49
90/3	10-50	9.6	545	16.0	390	3.6	257	0.21	1.09
92/2	10-50	11.9	275	5.7	123	1.8	110	0.13	0.56
94/2	>50	2.8	574	13.1	630	1.8	138	0.13	1.10
97/1	>50	43.0		10.2		4.0		0.18	
98/2	10-50	4.1		6.4		1.9		0.12	
99/3	<10	42.0		40.7		6.0		0.25	
100/2	10-50	<1.9	91.5	4.4	124	1.0	35.3	0.08	0.21
108/1	10-50	2.3	86.5	10.0	84.2	0.9	24.1	0.09	0.23
108/2	<10	9.3	402	17.2	258	1.0	90.1	0.23	0.68
109/2	10-50	5.6	142	4.9	96.6	1.8	135	0.11	0.20
110/1	10-50	2.1	232	7.8	89.6	1.1	112	0.14	0.36
110/2	>50	18.1	306	8.5	132	1.5	105	0.16	0.24
116/2	>50	<1.5		0.7		1.0		0.08	
117/1	10-50			8.4		1.2		0.15	
117/3	10-50	<1.5		3.1		1.8		0.09	
119/2	<10	8.2	616	13.7	334	2.2	182	0.19	0.58
119/3	>50		415	6.3	207	5.9	154	0.19	0.55
120/1	10-50	2.5	135	6.3	176	1.6	123	0.17	0.49
122/1	10-50	<1.5	169	2.3	198	0.8	74.1	0.09	0.94
122/2	10-50	<2.0	129	3.5	135	0.7	53.8	0.12	0.28
127/1	>50	<1.1	140	1.6	152	0.5	45.5	0.12	0.48
127/2	10-50	1.5	136	4.9	178	0.7	51.6	0.12	0.34
129/1	10-50	<1.6	106	4.2	86.9		42.4	0.10	0.31

PARKLAND SOILS

Sample	Sample Distance from Road(m)	Lead		Zinc		Copper		Cadmium	
		Exch.	Total	Exch.	Total	Exch.	Total	Exch.	Total
133/2	10-50	2.8	124	6.5	149	0.4	44.1	0.12	0.35
136/3	<10	<1.5	146	1.3	179	2.2	103	0.07	0.26
138/2	<10					10.9		0.06	
140/1	10-50	466.6		11.0		9.8		0.18	
141/3	10-50	<2.1	65.4	2.4	111	7.1	300	0.12	0.26
143/2	10-50	2.0	159	9.2	171	1.3	167	0.14	0.38
144/1	<10	<2.1	60.9	3.1	63.5	0.5	33.5	0.11	0.20
147/2	>50	<0.8	74.3	2.5	110	1.7	40.1	0.11	0.32
149/1	10-50	9.5	520	7.9	227	0.4	102	0.19	0.42
151/1	10-50	20.6	688	24.5	534	1.5	162	0.21	0.63
151/2	>50		485	9.3	222	2.2	75.8		
152/1	10-50	7.0	363	6.6	204	0.5	91.0	0.13	0.38
153/3	10-50	12.6	283	9.5	231	2.0	120	0.12	0.33
158/3	>50	4.4	264	19.9	250	3.1	443	0.20	1.16
159/3	10-50	1.7	82.0	0.8	125	1.3	41.9	0.06	0.32
162/1	>50	<0.7	422	2.8	172	2.6	142	0.11	0.31
162/2	>50		425	54.3	300	3.3	209		
164/2	10-50	3.5	120	16.7	130	0.8	72.0	0.15	0.37
165/3	>50	<1.5		1.2		1.5		0.07	
166/3	<10	<1.5		2.0		1.1		0.11	
167/2	10-50	<1.5		0.7		2.0		0.08	
168/2	10-50	3.1	101	4.8	85.7	<0.5	65.0	0.08	0.16
168/3	>50	0.5	95.4	2.3	155	<0.5	27.5	0.10	0.28
170/3	10-50	<1.5		5.5		1.6		0.13	
171/2	<10	5.0	206	5.0	159	2.4	92.3	0.10	0.32
172/2	<10	2.3	222	8.8	193	1.1	114	0.15	0.45
175/2	10-50	4.5	318	7.8	350	3.1	141	0.13	0.94
176/3	10-50	<1.9	27.7	1.0	38.8	1.0		0.04	0.79
178/3	>50	3.2	636	6.1	450	1.6	98.0	0.19	0.73
179/1	10-50	7.7	476	8.2	388	1.4	141	0.08	0.60
181/3	10-50	23.3	346	8.1	194	1.8	106	0.21	0.77
185/2	10-50	<1.5		3.3		1.3		0.15	
186/3	>50	4.9	222	13.4	259	0.4	313	0.23	0.60
187/2	10-50	1.5	169	2.0	234	0.8	59.6	0.14	0.70
188/1	10-50	<1.5	98.2	5.6	99.7	0.3	14.0	0.08	0.27
189/1	<10	<1.5		0.8		0.4		0.08	
190/2	<10	8.5	371	11.0	224	0.6	66.0	0.24	0.61
190/3	>50	3.2	161	8.7	196	1.2	63.2	0.18	0.46
191/2	10-50	4.2	215	5.6	175	1.4	79.1	0.15	0.37
191/3	<10	1.7	191	14.2	282	0.5	84.6	0.17	0.69
192/3	>50	1.8	114	7.1	137	<0.6	30.9	0.09	0.34
193/2	<10	<1.2	28.0	0.4	82.4	1.1	31.0	0.03	0.42
193/3	10-50	<1.5	21.9	0.4	115	0.6	83.6	0.05	0.33
195/1	<10	<1.5		0.2		1.3		0.27	
198/3	<10	<1.5	82.8	1.7	132	0.9	24.6	0.07	0.24
200/1	>50	<3.1	89.2	2.4	32.1	<1.3	17.7	0.06	0.16
200/2	>50	<1.7	91.6	<0.4	91.5	<0.7	17.5	0.04	0.19
201/2	<10	3.4	206	2.1	307	0.7	42.0	0.17	0.42

PARKLAND SOILS

Sample	Sample Distance from Road(m)	Lead		Zinc		Copper		Cadmium	
		Exch.	Total	Exch.	Total	Exch.	Total	Exch.	Total
202/2	10-50	<2.1	114	3.2	210	1.0	90.0	0.12	0.33
203/3	10-50	4.9	306	4.4	292	1.2	97.3	0.21	1.07
204/1	10-50	68.9	1260	2.4	152	<0.3	30.9	0.12	0.33
204/2	10-50	14.9	321	28.9	383	2.6	170		
206/1	10-50	5.1	663	15.4	618	2.5	172	0.27	0.97
207/1	10-50	<1.9	100	12.7	178	1.3		0.07	1.50
208/3	<10	<1.6	46.8	1.7	72.4	<0.7	22.1	0.08	0.29
209/1	<10	<2.0	140	3.6	145	2.1	50.3	0.13	0.26
212/1	10-50		274		416		87.6	0.14	1.44
212/3	10-50	<1.5		8.0		1.3		0.16	
215/2	10-50	8.0	246	8.2	215	4.2	218	0.14	0.40
216/1	>50	1.5	85.6	2.5	137	0.3	20.4	0.08	0.16
216/2	>50		100	5.0	214	0.4	48.8	0.09	0.27
219/1	10-50	11.9	471	5.4	305	0.4	70.7	0.09	0.76
221/1	>50	<0.6	113	0.3	169	0.5	55.3	0.04	0.93
221/2	10-50	<1.5	101	2.4	173	0.6	51.3	0.10	0.24
224/2	10-50	<1.5	105	1.7	145	0.9		0.10	0.29
226/2	10-50	1.2	128	3.8	123	0.5	57.6	0.13	0.19
227/1	>50	2.0	66.1	2.8	89.8	<0.6	29.1	0.09	0.15
227/2	10-50	2.7	104	9.3	121	<0.4	73.5	0.16	0.29
231/1	10-50	<1.1	81.1	4.3	135	1.0	40.7	0.15	0.36
238/1	10-50	<1.5	412	3.8	213	0.7	71.2	0.09	0.33
243/3	10-50	<1.9	59.3	1.1	48.2	0.5	97.6		
245/1	>50	<2.2	64.8	1.6	124	<0.6	19.7	0.09	0.24
245/2	>50	7.1	101	3.6	101	0.8	26.3		
245/3	>50	14.8	154	9.0	120	1.2	71.2		

AGRICULTURAL SOILS

Sample	Sample Distance from Road (m)	Lead		Zinc		Copper		Cadmium	
		Exch.	Total	Exch.	Total	Exch.	Total	Exch.	Total
13/1	10-50	<1.7	82.7	1.4	112	0.8	25.4	0.09	0.20
13/2	10-50	<1.6	132	1.7	175	0.9	93.4	0.09	0.49
41/1	>50	8.2		4.3		2.0		0.13	
41/2	>50	19.4				5.3		0.26	
42/2	>50	32.3				10.1		0.31	
42/3	10-50	3.7	263	1.5	279	2.1	96.1	0.08	0.52
58/2	>50	13.1		8.3		3.6		0.14	
58/3	>50	<1.5		1.3		1.4		0.14	
62/2	>50	<1.5		7.5		<0.1		0.15	
62/3	>50	<1.5	56.8	0.6		0.1	130	0.07	0.57
79/1	>50	<1.0	85.0	1.0	296	<0.5	31.9	0.06	0.18
79/2	>50	3.6	233	4.7	260	<0.5	55.9	0.08	0.29
81/1	>50	<1.0	88.0	2.9	103	<0.5	35.4	0.11	0.37
81/2	>50	<1.5	113	2.4	134	0.6	37.2	0.10	0.35
82/1	>50	<1.2	112	3.5	162	0.4	41.7	0.09	0.66
82/2	>50	<1.1	157	4.2	112	<0.3	47.2	0.14	0.54
83/1	>50	3.7	204	6.2	167	<0.7	55.5	0.15	1.05
83/2	>50	1.5	146	2.5	99.7	<0.5	32.1	0.11	0.32
84/1	>50	7.6	82.7	1.4		0.8	13.4	0.07	0.28
84/2	>50	1.9	120	2.3	104	<0.5	79.1	0.06	0.31
84/3	>50	<1.0	92.2	1.3	79.6	<0.5	28.8	0.09	0.32
103/2	>50	<1.3	106	3.0	129	0.7	70.5	0.09	0.45
104/2	>50	1.2	92.5	4.1	69.3	1.2	28.1	0.12	0.40
105/1	>50	1.8	63.6	1.3	29.8	<0.3	11.9	0.07	0.22
106/1	>50	1.1	96.1	<0.3	69.7	<0.5	29.7	0.02	0.19
106/2	>50	3.1	93.1	<0.3	31.4	<0.5	26.3	0.03	0.16
128/1	>50		178		361		75.0		0.82
128/2	>50	7.6	419		384	0.7	121	0.31	0.83
195/2	10-50	<2.1	108	2.7	252	1.8	109	0.15	0.51
196/2	10-50	<2.0	153	2.5	159	1.4	60.3	0.15	0.40
199/1	>50	<2.2	49.3	1.9	70.7	<0.9	16.7	0.08	0.27
199/2	>50	<2.0	121	3.7	185	2.6	68.2	0.17	0.40
206/2	>50	<0.5	33.2	<0.2	60.8	<0.5	34.0	0.05	0.08
209/3	10-50	2.2	23.9	1.7	58.3	<0.7	3.4	0.06	0.13
210/1	>50	<1.5	27.5	<0.2	34.7	0.8	8.3	0.04	0.19
210/2	10-50	3.1	52.7	2.0	70.8	0.7	4.1	0.08	0.35
217/1	>50	<0.7	95.5	1.8	135	0.9	48.2	0.12	0.26
220/1	10-50	0.4	106	1.8	122	<0.4	31.9	0.06	0.52
220/3	10-50	<0.5	91.2	1.8	259	0.6	75.2	0.06	0.77
230/1	10-50	<1.0	54.5	2.7	117	0.5	53.6	0.10	0.32
230/2	10-50	4.8	147	5.3	184	1.8	60.1		
232/1	>50	1.3	77.6	9.9	274	0.6	56.3	0.14	0.27
238/3	>50	23.6	749	19.4	313	5.2	305	0.43	0.85
239/1	>50	4.2		8.8	235	1.8	99.2	0.31	1.01
239/2	>50	7.7	372	3.0	186	1.5	81.1	0.13	0.41
240/1	>50	2.1	57.4	<0.2	63.2	<0.5	61.7	0.02	0.37
240/2	>50	1.8	160	0.8	90.5	0.4	30.0	0.06	0.29
240/3	>50	1.2	141	0.7	122	0.5	41.9	0.05	0.38
241/1	>50	<1.5	152	2.6	181	0.9	28.7	0.10	0.71
241/2	>50	<1.0	153	3.5	292	0.6	46.8	0.09	0.33
241/3	>50	<0.6	105	1.4	167	<0.5	34.1	0.14	0.52
243/2	10-50	<1.7	64.0	0.7	125	0.4	50.3		

APPENDIX 3

INDIVIDUAL RESULTS OF SIX-FRACTION SEQUENTIAL LEACHING STUDY

The six fractions are defined as follows:

FRACTION 1:	Exchangeable
FRACTION 2:	Carbonate-bound
FRACTION 3:	Easily-reducible
FRACTION 4:	Moderately-reducible
FRACTION 5:	Organic
FRACTION 6:	Residual

All results are in µg/g except residual and total iron (%).

LEAD - SOILS

Fraction

Sample	1	2	3	4	5	6	Total
193/3	<1.5	3.2	<1.0	7.8	4.9	6.0	21.9
176/3	<1.9	5.8	<1.0	10.3	3.8	7.8	27.7
46/3	<1.4	10.4	1.5	31.2	10.3	-	37.3
235/2	<1.0	1.6	<1.0	18.0	10.0	17.2	46.8
230/1	<1.0	12.9	<1.0	40.0	19.5	-	54.5
240/1	2.1	2.2	<1.0	21.5	11.2	11.1*	57.4
44/1	<1.7	9.2	<1.0	42.7	14.0	22.0*	63.6
141/3	<2.1	5.8	<1.0	43.1	12.3	4.2	65.4
57/2	<1.9	6.5	<1.0	35.9	13.4	15.6	73.3
158/2	1.8	13.5	<1.0	42.2	14.4	6.1	78.0
56/3	<1.7	10.3	<1.0	38.0	12.0	20.9	81.2
236/2	<1.4	11.0	<1.0	56.3	26.7	-	86.3
108/1	2.3	11.7	<1.0	49.7	20.3	2.5	86.5
46/2	<1.8	10.0	<1.0	45.8	18.3	26.5*	90.6
133/1	2.7	11.5	<1.0	60.3	23.9	-	96.3
44/3	2.4	21.9	<1.0	62.9	16.8	-	98.4
226/1	5.9	21.6	<1.0	64.6	27.8	-	107
195/2	<2.1	10.3	<1.0	50.4	21.9	25.4	108
234/2	<1.4	12.7	<1.0	64.7	27.0	7.6	112
145/1	3.3	12.2	<1.0	66.0	26.7	6.8	115
231/2	<1.7	9.3	<1.0	64.7	27.0	16.0	117
45/3	<2.0	22.0	1.0	64.0	20.0	12.0	119
125/3	2.8	16.8	<1.0	71.8	26.0	1.6	119
84/2	1.9	11.3	<1.0	63.9	29.2	13.7	120
163/1	3.5	17.1	1.0	71.2	15.7	16.5	125
236/1	<1.8	16.2	<1.0	78.5	25.7	4.6	125
52/1	1.6	31.4	<1.0	65.9	31.0	20.1*	126
169/3	6.6	18.5	<1.0	86.9	20.5	-	133
120/1	2.5	26.5	<1.0	65.5	27.2	13.3	135
48/3	2.0	14.7	<1.0	55.1	33.3	31.9	137
104/1	1.4	13.8	<1.0	58.5	25.9	38.4	138
71/1	<1.1	9.4	<1.0	56.1	21.1	53.4	140
73/2	2.7	10.7	<1.0	54.9	36.8	34.9	140
229/1	<1.7	13.4	<1.0	95.0	31.6	3.0	143
228/2	<1.5	16.1	<1.0	75.0	29.8	23.1	144
83/2	1.5	12.9	<1.0	80.0	27.5	24.1	146
230/2	4.8	15.9	<1.0	62.9	34.7	30.7*	147
75/2	4.9	16.4	<1.0	86.3	24.5	21.6*	148
74/2	1.3	20.8	<1.0	53.3	29.3	44.3	149
88/1	<1.0	15.2	<1.0	73.2	27.5	36.1	152
196/2	<2.0	17.4	<1.0	58.6	32.9	44.1	153
82/2	<1.1	11.1	<1.0	117	36.0	-	157
101/1	3.0	15.2	<1.0	79.8	38.1	21.9	158
155/2	<2.6	9.8	<1.0	60.1	21.9	63.6	158
187/3	3.9	17.3	<1.0	75.5	40.8	30.5	168
54/3	<2.0	15.6	<1.0	80.5	27.5	33.8*	181
139/3	12.8	25.1	<1.0	93.1	19.8	32.2	183
50/1	13.9	52.1	2.5	144	49.0	46.0*	184
112/1	2.7	21.6	<1.0	107	66.9	-	184
55/3	<1.9	21.5	1.0	93.6	36.4	29.5*	186

LEAD - SOILS

	Fraction						
Sample	1	2	3	4	5	6	Total
77/3	<2.1	19.9	<1.0	131	39.2	4.9	195
83/1	3.7	9.5	<1.0	122	54.2	29.8*	204
51/1	2.2	30.4	1.8	129	20.4	21.2	205
160/2	3.7	33.0	1.9	123	35.5	11.9	209
90/1	6.2	30.6	<1.0	112	41.2	25.0	215
191/2	4.2	24.4	<1.0	111	35.7	39.7	215
38/3	1.9	23.8	<1.0	117	28.3	47.0	218
67/3	5.8	21.4	1.0	128	37.5	26.3	220
180/1	4.4	21.4	<1.0	93.1	28.6	72.5	220
186/3	4.9	28.1	<1.0	111	67.1	10.9	222
47/2	<1.6	29.8	<1.0	126	28.4	44.8	229
39/3	13.4	43.4	<1.0	85.3	31.2	56.7	230
161/1	<1.8	16.4	<1.0	105	51.6	58.0	231
37/1	1.7	30.2	<1.0	133	19.0	48.1	232
40/3	2.9	27.3	0.9	142	28.3	61.6	263
42/3	3.7	22.2	<1.0	143	43.0	55.8*	263
67/1	7.0	34.3	<1.0	148	41.3	38.4	269
91/2	7.0	29.1	<1.0	137	44.1	53.8	271
49/1	<2.3	18.7	<1.0	157	28.1	74.2	278
156/1	<2.4	26.0	<1.0	154	65.6	35.4	281
110/2	18.1	57.1	1.0	140	60.0	29.8	306
203/1	4.2	29.6	2.0	196	50.4	28.8*	326
225/3	3.1	27.9	<1.0	180	66.3	50.7	328
64/3	9.0	8.6	<1.0	188	57.3	66.1	329
63/2	6.6	32.6	1.6	186	40.8	78.4	346
68/3	6.7	40.4	<1.0	190	44.1	80.8	362
48/1	7.1	51.7	3.0	171	73.1	70.1	376
145/3	23.5	62.6	1.0	164	89.7	47.2	388
131/2	13.1	57.0	1.7	216	65.2	39.0	392
86/3	14.7	58.1	3.9	272	104	50.3	503
70/2	7.6	102	3.3	329	78.4	87.2*	520
90/3	9.6	32.5	4.0	332	97.6	69.3	545
68/1	9.6	54.8	2.7	367	95.6	76.5*	572
91/1	85.1	90.9	2.2	242	136	78.8	635
151/1	20.6	88.4	2.1	323	116	105*	688

* measured residual

LEAD - STREET DIRT

Sample	Fraction 1	2	3	4	5	6	Total
108/3	4.5	10.8	2.3	5.8	4.2	7.6	35.2
10/2	3.0	29.0	0.9	20.9	19.5	28.7	102
199/3	4.0	23.9	1.0	50.4	21.9	24.2	125
18/3	17.0	32.6	11.8	48.0	25.0	25.2	160
82/3	8.9	77.5	12.9	54.9	17.2	36.7	208
148/2	17.9	49.6	15.9	51.0	34.6	51.1	220
106/3	8.8	48.3	<1.0	97.9	33.2	39.1	227
189/2	22.7	45.6	14.8	50.8	41.4	56.9	232
145/2	8.3	81.3	4.8	112	48.2	35.7	290
53/2	19.9	79.5	10.2	124	45.9	47.0	327
105/3	7.2	131	9.5	112	31.6	35.4	327
232/2	80.0	87.0	22.2	115	53.4	34.4	392
4/1	49.5	125	32.6	81.6	40.8	82.7	412
164/3	11.0	69.6	3.4	179	81.1	72.6	417
130/2	63.1	96.9	43.7	106	53.5	55.2	418
70/3	48.2	124	35.6	113	54.2	61.3	436
166/2	6.6	102	11.4	175	62.5	90.5	448
122/3	32.6	125	38.0	106	76.1	84.6	462
244/1	105	105	29.5	118	68.4	50.5	476
44/2	17.8	164	33.7	141	59.5	63.5	480
141/2	178	169	30.0	108	13.0	14.1	512
25/3	25.5	159	37.4	108	103	82.9	516
74/3	42.1	187	29.6	146	68.3	44.6	518
218/2	53.8	145	38.0	133	85.7	69.6	525
63/1	22.3	182	36.4	178	43.8	70.6	533
80/1	80.1	238	21.2	138	53.0	64.9	595
184/2	61.3	104	31.2	177	168	71.5	613
86/1	74.9	219	25.7	182	92.4	70.2	664
20/2	33.1	183	23.0	179	86.4	191	696
157/2	143	242	54.5	124	55.3	115	734
176/1	109	191	56.4	187	125	103	771
23/3	73.0	260	71.8	192	109	85.0	791
87/3	166	226	55.8	184	138	70.5	840
205/3	188	237	18.5	214	96.4	92.5	846
9/3	140	257	19.7	255	74.8	101	848
169/2	218	145	34.0	288	122	87.7	895
17/2	147	321	34.0	219	130	49.4	900
150/1	214	209	55.4	221	145	73.9	918
51/2	117	276	44.2	250	140	92.7	920
95/3	20.8	105	5.3	533	141	151	956
215/1	132	254	64.7	239	146	137	973
28/3	197	252	73.9	195	113	148	979
118/2	55.6	258	6.7	258	220	223	1021
3/2	101	261	35.5	370	164	95.2	1027
208/2	160	361	28.8	274	125	88.2	1037
196/3	88.8	427	53.9	260	163	70.5	1063
33/3	137	372	98.2	263	106	90.3	1067
64/1	36.3	256	19.8	453	204	130	1099

LEAD - STREET DIRT

Sample	Fraction 1	2	3	4	5	6	Total
78/2	115	544	17.6	230	116	81.6	1104
172/3	169	280	77.0	204	161	229	1120
211/2	456	208	73.8	164	195	124	1221
206/3	364	376	34.4	355	124	94.2	1348
19/2	247	636	95.2	260	147	105	1490
116/3	195	630	86.4	313	178	121	1523
97/2	270	476	107	295	151	270	1569
99/2	180	533	41.6	492	278	148	1673
29/2	436	450	116	376	215	128	1721
225/1	18.9	713	46.6	561	260	121	1721
224/3	447	412	63.6	315	326	188	1752
114/3	385	568	105	546	588	92.0	2284

ZINC - SOILS

	Fraction						
Sample	1	2	3	4	5	6	Total
176/3	1.0	4.1	2.1	5.3	14.8	11.5	38.8
46/3	1.0	7.3	7.1	13.6	24.0	-	40.0
158/2	3.2	15.2	5.2	12.8	21.3	4.5	62.2
240/1	<0.2	2.1	1.1	5.1	15.5	55.0*	63.2
96/3	4.3	6.9	2.9	6.9	24.6	19.3	64.9
235/2	0.6	1.3	1.7	9.5	32.4	26.6	72.1
52/1	2.2	9.2	2.8	7.8	22.9	47.0*	77.3
39/3	1.4	5.6	2.1	4.9	18.1	46.8	78.9
133/1	3.8	10.4	8.6	21.1	40.1	-	83.3
108/1	10.0	5.4	7.0	16.0	29.9	15.9	84.2
73/2	3.6	11.0	4.7	13.1	41.6	10.6	84.6
83/2	2.5	5.7	5.2	12.4	42.7	31.2	99.7
57/2	3.6	11.0	5.2	13.1	19.4	51.7	104
84/2	2.3	9.1	6.9	11.3	43.3	27.2*	104
68/3	2.7	9.5	5.7	22.1	47.1	20.9	108
141/3	2.4	14.1	10.2	28.9	31.0	24.4	111
82/2	4.2	11.9	7.9	26.9	53.8	7.3	112
193/3	0.4	2.4	3.1	4.6	13.1	91.4	115
44/1	7.5	14.8	7.2	17.5	44.7	46.7*	117
230/1	2.7	5.6	2.8	10.8	41.9	53.2	117
169/3	7.5	11.8	7.4	21.6	49.9	19.8	118
56/3	2.5	2.9	3.7	7.4	27.0	78.5	122
125/3	6.1	11.6	5.6	18.9	58.5	28.3	129
50/1	6.3	11.0	5.4	16.1	42.5	119*	130
145/1	5.7	9.7	6.2	24.0	46.1	39.3	132
110/2	8.5	5.0	4.4	10.0	35.6	68.5	132
51/1	5.8	13.8	10.1	30.0	41.5	33.8	135
155/2	2.1	4.9	5.2	18.0	35.4	69.4	135
231/2	3.5	9.2	3.6	13.5	45.7	63.5	139
236/2	2.0	7.3	3.6	15.2	53.5	59.4	141
71/1	2.6	6.4	5.8	18.7	38.5	71.0	143
228/2	3.4	12.1	5.2	19.6	61.6	45.1	147
226/1	7.1	11.4	4.0	11.5	50.3	63.7	148
196/2	2.5	12.6	4.0	13.5	55.7	70.7	159
180/1	7.7	15.1	7.2	32.0	45.9	53.1	161
45/3	9.0	13.1	7.9	15.7	29.3	87.0	162
234/2	2.8	8.0	4.1	19.1	49.7	80.3	164
163/1	9.3	13.0	9.0	27.5	53.6	52.6	165
83/1	6.2	12.6	4.6	49.7	53.1	145*	167
139/3	12.0	7.9	7.6	17.4	34.5	87.6	167
90/1	4.7	11.2	4.0	17.0	52.8	78.3	168
187/3	4.3	10.4	4.1	13.6	47.6	91.0	171
67/3	6.1	12.1	6.2	25.7	44.3	79.6	174
191/2	5.6	13.7	9.0	29.4	56.9	60.4	175
120/1	6.3	19.0	6.4	16.4	60.4	67.5	176
75/2	10.3	14.8	15.7	44.4	61.9	70.5	178
236/1	2.7	11.7	5.9	20.4	56.4	84.9	182
230/2	5.3	8.5	4.1	12.4	38.7	102	184
37/1	2.7	7.6	4.5	27.5	34.6	117	194

ZINC - SOILS

	Fraction						
Sample	1	2	3	4	5	6	Total
48/3	2.2	5.6	2.4	14.0	50.8	120	195
47/2	4.7	13.1	5.4	17.1	32.7	123	196
229/1	1.6	10.5	6.5	23.1	70.8	89.5	202
55/3	2.4	6.1	2.5	12.8	52.8	86.5*	203
112/1	11.0	0.2	4.4	22.1	63.1	110	211
38/3	2.6	7.4	3.0	21.5	56.1	126	217
88/1	2.3	7.0	3.2	22.6	60.8	122	218
104/1	4.0	11.7	4.3	24.5	57.4	118	220
46/2	1.2	6.3	3.6	24.8	42.1	105*	222
49/1	4.3	11.5	8.8	56.9	64.6	102	248
48/1	3.8	12.3	5.8	20.5	58.4	151	252
195/2	2.7	9.9	5.2	15.7	51.0	168	252
186/3	13.4	23.8	9.7	34.8	63.1	114	259
74/2	2.1	14.2	6.9	13.6	39.6	195	271
161/1	13.0	34.0	13.8	60.2	81.0	74.0	276
54/3	2.0	3.7	3.2	12.2	45.7	79.8	278
42/3	1.5	3.8	2.8	23.0	64.5	164*	279
203/1	12.1	25.7	21.1	43.1	48.1	68.7	288
101/1	19.5	55.0	17.2	48.1	104	65.2	309
77/3	4.1	13.3	5.8	48.5	106	138	316
68/1	5.3	15.4	7.1	55.5	81.3	240	328
156/1	3.3	14.7	7.4	46.0	100	159	330
40/3	5.9	17.2	7.0	44.5	66.0	213	354
44/3	41.1	58.7	34.7	35.3	75.3	116	361
91/1	10.2	16.0	4.8	18.9	54.9	265	370
142/1	16.9	36.5	27.7	88.0	116	85.9	371
67/1	13.0	22.0	6.6	39.1	51.3	258	390
90/3	16.0	27.3	34.0	80.2	112	179	390
70/2	6.4	29.6	24.3	93.8	132	248	397
145/3	5.3	14.7	5.4	16.2	73.4	292	407
91/2	11.7	20.5	9.2	26.1	60.8	284	412
160/2	26.1	65.3	52.8	86.2	108	79.6	418
86/3	23.9	38.9	21.6	66.7	143	134	428
64/3	20.6	46.4	24.5	95.3	115	151	453
63/2	14.2	34.5	17.2	71.1	98.7	220	456
151/1	24.5	37.2	16.4	71.1	205	307*	534
131/2	52.4	73.6	45.6	89.3	144	148	553
225/3	38.1	87.9	37.1	149	262	192*	696

* measured residual

ZINC - STREET DIRT

	Fraction						
Sample	1	2	3	4	5	6	Total
108/3	5.9	9.7	6.4	16.4	18.2	43.2	99.8
18/3	4.6	9.8	7.4	17.6	28.5	43.9	112
148/2	12.5	18.6	7.8	22.8	17.2	55.2	134
189/2	7.1	39.4	8.8	31.4	23.8	43.9	154
10/2	6.1	29.6	9.3	31.0	26.8	52.5	155
199/3	1.8	2.9	2.2	12.0	32.8	109	161
232/2	23.6	21.1	11.0	33.8	33.7	68.7	192
82/3	16.6	19.5	9.7	43.8	35.7	72.0	197
106/3	11.4	28.8	9.6	51.6	42.8	70.9	215
105/3	13.9	42.2	16.5	32.1	51.6	64.6	221
4/1	25.6	46.4	16.2	40.2	49.2	59.4	237
70/3	33.8	72.2	20.2	63.2	50.2	68.1	308
169/2	25.9	52.5	20.7	65.1	59.2	89.1	313
28/3	40.8	49.4	26.9	71.8	52.8	82.3	324
44/2	15.9	42.9	20.5	85.2	74.5	84.5	324
80/1	48.7	60.3	25.0	49.0	71.8	72.2	327
74/3	30.3	74.7	20.0	75.7	55.4	75.0	331
78/2	58.9	69.1	18.0	54.9	55.9	74.6	331
166/2	23.3	73.2	22.1	74.8	47.8	106	347
145/2	29.5	111	22.7	66.9	52.2	69.6	352
51/2	32.3	80.7	31.0	78.6	45.2	85.1	353
9/3	30.1	101	16.9	77.6	82.9	52.3	361
122/3	35.7	64.0	35.3	57.3	57.3	115	365
17/2	28.4	49.1	19.8	70.6	54.4	144	366
53/2	23.0	49.0	16.5	82.9	53.2	143	368
224/3	35.1	52.0	20.2	62.7	61.0	140	371
205/3	45.1	70.9	16.8	65.7	67.8	122	388
130/2	14.1	60.8	27.0	60.2	62.3	165	389
3/2	18.8	46.4	24.2	97.4	113	90.1	390
215/1	77.7	90.3	20.9	61.1	50.6	92.7	393
141/2	68.5	104	17.8	43.3	62.9	98.0	395
25/3	96.7	45.3	30.8	61.4	42.9	127	404
157/2	30.7	143	20.0	78.9	60.1	86.9	420
211/2	39.3	87.7	19.7	68.8	63.1	145	424
206/3	25.7	102	24.2	94.1	100	70.1	426
184/2	30.1	72.9	29.1	103	86.6	108	430
164/3	24.8	74.2	27.0	89.5	71.3	157	444
218/2	45.8	89.2	33.2	69.2	51.9	158	447
87/3	61.4	90.6	36.8	95.0	72.9	99.1	456
33/3	65.2	108	52.1	88	57.1	109	479
150/1	75.6	141	28.5	93.5	80.2	86.2	505
19/3	45.3	217	26.1	65.6	55.4	98.0	507
244/1	73.9	209	31.7	66.8	51.7	74.1	507
208/2	36.3	298	38.4	96.0	78.7	38.0	585
225/1	49.1	137	42.3	153	112	106	600
116/3	90.2	208	49.4	115	66.5	109	638
63/1	73.8	103	58.9	154	111	144	645
97/2	74.6	217	34.6	114	79.4	129	649

ZINC - STREET DIRT

	Fraction						
Sample	1	2	3	4	5	6	Total
86/1	73.1	94.9	37.2	187	119	141	652
176/1	88.5	232	42.8	102	88.4	99.8	654
196/3	38.7	309	33.9	88.2	82.1	117	669
114/3	164	170	49.5	90.2	116	102	692
118/2	65.8	211	42.7	132	79.4	193	724
29/2	74.0	261	56.8	171	101	86.5	750
172/3	91.4	212	60.4	136	93.1	201	794
20/2	66.6	211	49.4	182	88.9	328	926
99/2	65.9	592	99.0	197	133	132	1219
23/3	103	543	106	243	136	108	1239
64/1	113	352	132	607	444	384	2030

COPPER - SOILS

Sample	1	2	3	4	5	6	Total
46/3	<0.5	0.7	0.2	1.5	6.2	6.5	15.1
235/2	<0.5	0.9	<0.2	1.2	10.8	9.8	22.7
108/1	0.9	0.5	0.2	3.5	13.6	5.4	24.1
46/2	0.7	0.8	<0.2	0.9	13.3	10.5	26.2
83/2	<0.5	0.6	<0.2	2.8	13.4		32.1
75/2	<0.5	0.9	0.2	3.8	17.7	5.0*	33.5
51/1	0.3	1.2	<0.2	5.5	12.2	14.6	33.8
133/1	0.5	1.4	0.2	4.8	17.1	9.8	33.8
155/2	1.6	-	<0.2	2.1	14.8	16.0	34.5
125/3	0.6	1.5	<0.2	6.6	20.5	7.9	37.1
236/2	1.1	1.4	<0.2	3.7	20.4	11.7	38.3
52/1	1.0	2.8	<0.2	5.4	14.4	8.6*	38.8
236/1	1.1	0.3	<0.2	2.6	18.3	16.5	38.8
44/1	1.0	0.4	<0.2	3.3	19.0	13.4*	39.4
231/2	1.0	2.3	<0.2	4.3	21.6	11.9	41.1
187/3	0.7	1.9	<0.2	3.9	24.7	10.3	41.5
234/2	<0.4	1.8	<0.2	2.7	22.3	15.7	42.5
71/1	<0.3	0.8	<0.2	2.6	15.7	23.7	42.8
228/2	1.2	-	<0.2	2.2	19.2	22.1	44.7
55/3	1.5	0.5	<0.2	5.4	24.7	13.0	45.1
82/2	<0.3	0.8	<0.2	1.7	27.6	17.1	47.2
139/3	2.2	-	<0.2	5.9	16.1	24.1	48.3
57/2	1.0	1.4	<0.2	1.1	8.0	37.0	48.5
96/3	0.6	2.3	<0.2	5.4	19.0	22.5	49.8
48/3	1.7	0.6	<0.2	2.9	16.9	29.4	51.5
230/1	0.5	2.7	<0.2	7.8	27.8	14.8	53.6
68/3	<0.4	1.8	0.2	3.6	22.6	26.2	54.4
163/1	0.6	1.3	0.2	4.1	20.2	28.0	54.4
83/1	<0.7	0.8	<0.2	0.8	36.4	17.5	55.5
169/3	0.6	2.7	0.3	11.1	30.7	10.1	55.5
88/1	0.3	1.8	<0.2	4.0	24.7	27.1	57.9
229/1	0.9	2.3	<0.2	4.9	26.3	24.1	58.5
74/2	0.8	1.2	<0.2	5.1	19.7	32.0	58.8
158/2	1.1	0.3	<0.2	1.9	13.0	43.3	59.6
230/2	1.8	2.0	<0.2	8.5	24.9	40.3*	60.1
196/2	1.4	0.5	<0.2	4.2	25.3	28.9	60.3
203/1	1.8	0.6	0.2	3.8	24.3	59.0*	61.5
101/1	0.7	1.4	<0.2	3.4	20.9	35.2	61.6
240/1	<0.5	0.5	<0.2	2.0	6.7	52.5	61.7
180/1	0.6	2.9	<0.2	4.2	25.2	30.1	62.0
70/2	0.5	0.9	<0.2	4.9	29.9	27.6	63.8
50/1	2.0	1.8	<0.2	3.1	28.6	25.9*	65.0
54/3	1.5	1.6	<0.2	6.0	26.3	29.6	65.0
67/3	1.1	0.8	<0.2	7.0	29.8	28.0	66.7
145/1	1.1	0.3	<0.2	2.5	21.4	44.8	70.1
90/1	0.9	1.5	<0.2	4.9	33.9	30.5	71.7
67/1	0.3	1.7	<0.2	1.2	30.2	38.6	72.0
45/3	1.2	1.0	<0.2	4.2	20.0	48.8	75.2
73/2	0.4	2.0	0.2	3.4	23.9	45.9	75.8
84/2	<0.5	1.0	<0.2	2.5	16.8	58.8	79.1
191/2	1.4	1.3	<0.2	9.5	35.0	31.9	79.1

COPPER - SOILS

	Fraction						
Sample	1	2	3	4	5	6	Total
112/1	0.5	2.2	<0.2	6.1	31.4	41.6	81.8
38/3	2.0	0.1	<0.2	7.6	29.3	44.0	83.0
39/3	2.1	-	0.2	7.7	19.2	54.4	83.6
226/1	<0.7	1.9	<0.2	2.2	19.7	60.8	84.6
37/1	0.9	0.5	<0.2	4.9	16.4	64.0	86.7
42/3	2.1	-	<0.2	12.3	46.3	35.4	96.1
161/1	2.0	0.6	0.2	6.0	52.4	37.5	98.7
131/2	1.7	6.0	0.4	19.7	51.1	23.1	102
68/1	0.9	1.3	0.2	3.5	49.7	47.4	103
40/3	1.6	1.3	<0.2	8.5	26.7	74.9	113
145/3	3.5	1.8	0.6	6.8	54.8	59.5	127
225/3	2.1	3.6	<0.2	15.5	78.5	33.9*	127
160/2	1.3	8.0	1.0	27.1	53.6	37.0	128
77/3	2.2	-	<0.2	5.3	39.3	85.2	132
91/1	1.9	1.5	0.4	4.8	64.4	79.0	152
86/3	3.4	6.4	0.5	29.0	61.1	56.6	157
151/1	1.5	4.9	0.2	22.7	72.2	50.0*	162
91/2	10.4	2.5	0.4	28.0	65.7	65.0	172
48/1	2.8	5.6	0.4	20.5	51.2	97.5	178
63/2	3.9	7.3	0.5	45.5	63.5	109	230
90/3	3.6	8.6	2.7	54.5	126	52.2*	257

* measured residual

COPPER - STREET DIRT

	Fraction						
Sample	1	2	3	4	5	6	TOTAL
10/2	<0.5	1.4	<0.2	1.6	6.1	7.6	16.7
108/3	2.3	0.6	0.8	2.9	6.7	5.7	19.0
18/3	3.1	-	0.6	3.2	6.5	12.2	25.6
189/2	4.4	-	0.6	1.6	8.2	11.8	26.6
199/3	1.3	0.1	<0.2	1.9	16.0	10.3	29.6
148/2	1.4	4.4	2.2	1.4	15.4	18.0	42.6
4/1	4.3	0.6	4.3	3.5	28.1	6.2	47.0
25/3	7.6	-	1.5	1.9	22.2	16.1	49.3
244/1	6.6	1.3	2.1	4.9	32.1	8.0	55.0
122/3	3.0	2.5	2.3	4.4	18.2	25.2	55.6
53/2	4.5	-	0.4	3.3	21.5	28.0	57.7
145/2	6.8	0.7	0.4	5.0	32.5	18.2	63.6
74/3	10.3	6.0	3.1	5.4	30.5	11.0	66.3
166/2	4.8	6.1	1.2	5.2	27.3	22.3	66.9
82/3	2.5	12.9	2.5	2.4	14.9	33.4	68.6
164/3	1.2	1.5	<0.2	2.5	36.9	26.7	68.8
106/3	1.4	2.3	<0.2	5.5	27.0	39.6	75.8
105/3	1.5	5.6	0.8	9.9	26.8	32.4	77.0
51/2	6.5	7.3	1.5	11.3	36.0	19.4	82.0
232/2	11.6	6.2	3.7	4.6	26.3	31.7	84.1
28/3	14.3	7.1	5.9	2.2	43.7	16.1	89.3
44/2	8.2	2.9	2.8	6.0	37.2	32.9	90.0
184/2	7.5	0.7	2.1	2.9	55.9	23.2	92.3
9/3	15.9	4.5	1.9	9.3	49.3	13.5	94.4
33/3	9.2	3.7	5.4	17.2	34.2	25.0	94.7
208/2	17.5	5.2	2.0	13.1	44.9	14.1	96.8
118/2	5.1	1.5	0.4	2.6	53.1	34.4	97.1
218/2	12.4	-	3.2	3.6	44.4	34.0	97.6
87/3	12.6	0.2	4.1	5.2	49.9	29.0	101
215/1	19.4	-	4.1	4.2	44.3	34.7	107
224/3	21.1	-	2.2	3.7	46.9	33.4	107
17/2	16.9	-	1.1	2.3	42.7	47.1	110
169/2	10.7	6.3	2.0	7.8	37.5	48.7	113
130/2	5.7	6.3	5.0	8.7	58.5	30.8	115
23/3	12.2	1.8	8.7	4.1	66.1	26.1	119
114/3	17.8	-	5.9	9.8	75.1	17.0	126
19/3	34.8	-	11.5	3.8	38.9	40.9	130
20/2	11.7	-	2.7	3.8	61.7	55.4	135
172/3	21.6	-	5.4	4.6	56.8	46.5	135
63/1	18.4	4.3	5.9	18.6	45.5	46.9	140
78/2	28.7	-	1.8	23.7	66.6	20.4	141
86/1	15.7	4.8	4.4	5.3	72.6	38.6	141
176/1	9.3	-	9.6	4.9	88.8	44.2	157
150/1	25.1	11.3	6.1	13.0	86.0	18.3	160
225/1	25.7	3.8	3.7	19.0	85.2	25.4	163
141/2	8.3	10.9	6.6	23.2	87.8	34.3	171
99/2	24.4	9.0	6.2	35.0	59.5	46.1	180
157/2	37.4	1.5	9.2	4.1	81.0	56.1	189
3/2	18.1	14.9	3.7	28.8	80.5	56.6	203

COPPER - STREET DIRT

	Fraction						
Sample	1	2	3	4	5	6	TOTAL
205/3	26.2	28.0	4.6	17.7	80.0	53.7	210
116/3	20.7	-	6.9	8.3	124	58.7	218
196/3	15.7	21.5	7.1	30.5	63.0	116	254
64/1	16.8	-	2.6	51.5	118	87.3	276
95/3	4.0	11.9	0.8	72.9	99.4	131	320
29/2	43.3	-	13.7	37.6	250	121	466

CADMIUM - SOILS

Sample	Fraction 1	2	3	4	5	6	Total
46/3	0.03	<0.03	<0.06	<0.06	<0.10	0.07	<0.10
57/2	0.06	0.02	<0.06	<0.06	<0.10	0.05	0.13
68/3	0.04	0.03	<0.06	<0.06	<0.10	0.06	0.13
44/1	0.11	0.03	<0.06	<0.06	<0.10	0.15*	0.15
235/2	0.04	<0.03	<0.06	<0.06	<0.10	0.11	0.15
236/2	0.10	0.13	<0.06	<0.06	<0.10	-	0.17
52/1	0.05	0.04	<0.06	<0.06	<0.10	0.02*	0.19
45/3	0.14	<0.03	<0.06	<0.06	<0.10	0.07	0.21
155/2	0.08	0.08	<0.06	<0.06	<0.10	0.05	0.21
108/1	0.09	<0.03	<0.06	<0.06	<0.10	0.14	0.23
110/2	0.16	<0.03	<0.06	<0.06	<0.10	0.08	0.24
44/3	0.14	<0.03	<0.06	<0.06	<0.10	0.11	0.25
56/3	0.08	<0.03	<0.06	<0.06	<0.10	0.17	0.25
74/2	0.10	0.02	<0.06	<0.06	<0.10	0.13	0.25
133/1	0.11	0.11	<0.06	<0.06	<0.10	0.03	0.25
141/3	0.12	0.04	<0.06	<0.06	<0.10	0.10	0.26
163/1	0.11	0.08	<0.06	0.16	<0.10	-	0.27
226/1	0.15	<0.03	<0.06	<0.06	<0.10	0.13	0.28
230/2	0.19	<0.03	<0.06	<0.06	<0.10	0.09	0.28
71/1	0.04	0.06	<0.06	<0.06	<0.10	0.19	0.29
148/1	0.10	0.04	<0.06	<0.06	<0.10	0.15	0.29
158/2	0.11	0.12	<0.06	<0.06	<0.10	0.06	0.29
228/2	0.12	<0.03	<0.06	<0.06	<0.10	0.17	0.29
231/2	0.14	<0.03	<0.06	<0.06	<0.10	0.16	0.30
84/2	0.06	0.09	<0.06	<0.06	<0.10	0.16	0.31
145/1	0.12	0.06	<0.06	<0.06	<0.10	0.13	0.31
169/3	0.14	0.05	<0.06	<0.06	<0.10	0.12	0.31
83/2	0.11	0.06	<0.06	<0.06	<0.10	0.30*	0.32
96/3	0.08	0.06	<0.06	<0.06	<0.10	0.18	0.32
187/3	0.14	0.07	<0.06	<0.06	<0.10	0.11	0.32
230/1	0.10	<0.03	<0.06	<0.06	<0.10	0.22	0.32
88/1	0.09	0.13	<0.06	<0.06	<0.10	0.11	0.33
193/3	0.05	0.03	<0.06	<0.06	<0.10	0.25	0.33
236/1	0.11	0.15	<0.06	<0.06	<0.10	0.07	0.33
46/2	0.08	0.07	<0.06	<0.06	<0.10	0.28*	0.34
50/1	0.17	0.08	<0.06	<0.06	<0.10	0.18*	0.37
54/3	0.10	<0.03	<0.06	<0.06	<0.10	0.27*	0.37
104/1	0.09	0.07	<0.06	<0.06	<0.10	0.21	0.37
191/2	0.15	0.01	<0.06	<0.06	<0.10	0.21	0.37
240/1	0.02	0.05	<0.06	<0.06	<0.10	0.02*	0.37
47/2	0.12	0.05	<0.06	<0.06	<0.10	0.21	0.38
91/2	0.13	0.11	<0.06	<0.06	<0.10	0.14	0.38
229/1	0.12	0.07	<0.06	<0.06	<0.10	0.19	0.38
55/3	0.09	0.03	<0.06	<0.06	<0.10	0.27*	0.39
125/3	0.12	0.11	<0.06	<0.06	<0.10	0.16	0.39
196/2	0.15	0.13	<0.06	<0.06	<0.10	0.12	0.40
73/2	0.07	0.05	<0.06	<0.06	<0.10	0.30	0.42
112/1	0.11	0.11	<0.06	<0.06	<0.10	0.21	0.43
139/3	0.16	0.04	<0.06	<0.06	<0.10	0.23	0.43

CADMIUM - SOILS

	Fraction						
Sample	1	2	3	4	5	6	Total
67/3	0.15	0.04	<0.06	0.18	<0.10	0.07	0.44
234/2	0.09	0.02	<0.06	<0.06	<0.10	0.34	0.45
51/1	0.12	0.08	<0.06	<0.06	<0.10	0.26	0.46
40/3	0.12	0.03	<0.06	<0.06	<0.10	0.34	0.49
90/1	0.13	0.10	<0.06	<0.06	<0.10	0.26	0.49
120/1	0.17	0.12	<0.06	<0.06	<0.10	0.20	0.49
180/1	0.17	0.15	<0.06	<0.06	<0.10	0.18	0.50
195/2	0.15	0.10	<0.06	<0.06	<0.10	0.26	0.51
42/3	0.08	0.09	<0.06	<0.06	<0.10	<0.02	0.52
145/3	0.22	0.11	<0.06	0.08	<0.10	0.13	0.52
101/1	0.13	0.10	<0.06	<0.06	<0.10	0.30	0.53
82/2	0.14	0.18	<0.06	<0.06	<0.10	0.22	0.54
77/3	0.11	0.12	<0.06	0.18	<0.10	0.16	0.57
161/1	0.18	0.19	<0.06	0.27	0.16	-	0.60
186/3	0.23	0.11	<0.06	0.08	0.21	-	0.60
151/1	0.21	0.18	0.09	0.11	0.19	0.30*	0.63
203/1	0.19	0.15	<0.06	0.11	0.14	0.04	0.63
67/1	0.38	0.07	<0.06	0.12	<0.10	0.07	0.64
70/2	0.13	0.23	0.12	0.18	0.20	0.49*	0.71
68/1	0.14	0.13	<0.06	0.18	<0.10	0.06	0.72
156/1	0.18	0.10	<0.06	0.26	0.15	0.04	0.73
86/3	0.18	0.08	0.06	0.18	0.16	0.10	0.76
48/3	0.11	0.03	<0.06	<0.06	<0.10	0.63	0.77
176/3	0.04	0.02	<0.06	<0.06	<0.10	0.73	0.79
37/1	0.10	0.04	<0.06	<0.06	<0.10	0.72	0.86
91/1	0.20	0.19	<0.06	<0.06	0.14	0.50	1.03
83/1	0.15	0.13	<0.06	0.49	0.21	0.03*	1.05
142/1	0.30	0.20	0.19	0.36	<0.10	0.01	1.06
39/3	0.09	<0.03	<0.06	<0.06	<0.10	1.00	1.09
48/1	0.16	0.04	<0.06	0.08	<0.10	0.81	1.09
90/3	0.21	0.21	0.22	0.24	<0.10	0.23*	1.09
225/3	0.29	0.29	<0.06	0.14	0.15	0.47*	1.21
49/1	0.20	0.13	0.11	0.30	<0.10	0.51	1.25
64/3	0.18	0.12	<0.06	0.11	<0.10	0.92	1.33
75/2	0.63	0.07	0.21	0.23	<0.10	0.27*	1.40
160/2	0.28	0.55	0.21	0.27	<0.10	0.45	1.76
63/2	0.20	0.26	<0.06	0.23	0.22	0.99	1.90
131/2	0.37	0.15	0.17	0.17	<0.10	1.18	2.04

CADMIUM - STREET DIRT

	Fraction						
Sample	1	2	3	4	5	6	Total
108/3	0.04	<0.03	<0.06	<0.06	<0.09	0.02	0.06
199/3	0.09	0.01	<0.06	<0.06	<0.09	0.06	0.16
232/2	0.20	<0.03	<0.06	<0.06	<0.09	0.06	0.26
10/2	0.09	0.07	<0.06	<0.06	<0.09	0.20	0.49
82/3	0.11	0.03	<0.06	<0.06	<0.09	0.35	0.49
18/3	0.15	<0.03	<0.06	<0.06	0.15	0.23	0.53
106/3	0.18	0.10	<0.06	<0.06	<0.09	0.26	0.54
145/2	0.19	0.13	<0.06	0.08	0.15	0.13	0.60
130/2	0.17	0.17	<0.06	<0.06	0.16	0.13	0.63
184/2	0.17	0.08	<0.06	<0.06	0.29	0.09	0.63
74/3	0.16	0.22	<0.06	<0.06	0.25	0.04	0.67
4/1	0.18	0.08	<0.06	<0.06	0.20	0.29	0.75
105/3	0.18	0.09	<0.06	<0.06	0.21	0.33	0.81
122/3	0.27	0.12	<0.06	0.13	0.26	0.09	0.87
78/2	0.16	0.27	<0.06	<0.06	0.12	0.34	0.89
9/3	0.21	0.30	<0.06	0.20	0.27	0.06	1.04
141/2	0.52	0.06	<0.06	<0.06	0.23	0.30	1.11
157/2	0.27	0.18	<0.06	<0.06	0.35	0.32	1.12
166/2	0.23	0.29	<0.06	0.18	0.32	0.10	1.12
211/2	0.37	0.22	<0.06	<0.06	0.29	0.26	1.14
44/2	0.55	<0.03	<0.06	<0.06	0.30	0.33	1.18
28/3	0.38	0.13	0.12	0.17	0.38	0.14	1.33
189/2	0.55	<0.03	<0.06	0.28	0.22	0.29	1.34
80/1	0.26	0.21	<0.06	0.07	0.51	0.30	1.35
218/2	0.26	0.74	<0.06	<0.06	0.26	0.12	1.38
17/2	0.33	0.18	0.11	0.11	0.33	0.39	1.45
205/3	0.42	0.18	<0.06	0.24	0.33	0.29	1.46
23/3	0.39	0.20	0.10	0.18	0.24	0.36	1.47
87/3	0.36	0.42	<0.06	0.25	0.40	0.06	1.49
25/3	0.65	<0.03	0.09	0.19	0.37	0.31	1.61
169/2	0.34	0.54	<0.06	0.12	0.30	0.38	1.68
118/2	0.41	0.24	<0.06	0.36	0.37	0.31	1.69
53/2	0.26	0.85	<0.06	0.29	0.28	0.09	1.77
97/2	0.40	0.46	0.20	0.20	0.35	0.16	1.77
164/3	0.50	0.33	0.17	0.36	0.37	0.05	1.78
3/2	0.47	0.28	0.15	0.21	0.37	0.33	1.81
95/3	0.33	0.03	0.20	0.40	0.30	0.58	1.84
29/2	0.91	0.17	<0.06	0.24	0.31	0.36	1.99
70/3	0.43	0.39	<0.06	0.38	0.52	0.38	2.10
86/1	0.34	0.63	<0.06	0.20	0.49	0.48	2.14
206/3	1.17	-	<0.06	0.23	0.42	0.53	2.35
215/1	0.43	0.60	<0.06	0.32	0.73	0.37	2.45
114/3	0.91	0.60	0.15	0.26	0.46	0.09	2.47
208/2	0.22	1.33	<0.06	0.23	0.44	0.25	2.47
63/1	0.62	0.73	0.12	0.20	0.51	0.35	2.53
51/2	0.80	0.60	0.19	0.33	0.60	0.13	2.65
33/3	1.03	0.54	0.20	0.25	0.20	0.45	2.67
224/3	0.56	-	0.13	0.18	0.54	1.32	2.73
64/1	0.51	0.88	0.16	0.52	0.67	0.23	2.97
225/1	2.24	-	0.25	0.52	0.71	0.24	3.96
196/3	0.47	1.66	0.45	0.55	0.44	0.52	4.09
99/2	0.75	0.67	0.40	1.53	0.87	0.09	4.31
172/3	1.63	0.91	0.27	0.54	0.96	1.12	5.43
244/1	0.67	-	0.40	1.92	3.45	0.10	6.54
20/2	3.58	1.97	0.40	1.02	0.65	1.09	8.71

MANGANESE - SOILS

	Fraction						
Sample	1	2	3	4	5	6	Total
39/3	4.2	1.1	1.3	1.8	10.3	154*	173
52/1	27.7	24.1	10.3	6.1	21.8	60.6*	176
110/2	26.4	-	7.5	3.6	22.5	117	177
108/1	20.8	6.0	21.8	38.5	24.6	79.3	191
57/2	18.5	34.8	67.3	44.6	24.8	26.0	216
46/3	2.7	13.5	52.3	31.1	16.2	109	225
169/3	14.9	19.9	76.0	88.2	38.0	42.0	279
91/1	12.8	11.9	5.8	11.5	48.5	214	304
64/3	3.1	8.3	46.4	84.3	27.1	140	309
145/3	22.6	56.6	17.6	25.1	81.8	112	316
73/2	29.1	18.7	48.5	53.9	93.2	80.6	324
44/3	22.2	24.0	41.3	53.2	36.2	153	330
158/2	18.1	35.5	139	94.9	42.0	21.5	351
133/1	45.6	12.3	37.6	57.2	30.0	172	355
131/2	24.1	20.1	64.8	65.7	37.4	144	356
56/3	41.5	35.2	73.2	67.2	37.6	103	358
42/3	6.3	13.8	72.5	9.6	42.8	113*	363
230/2	106	30.0	24.2	15.3	45.5	65.5*	363
230/1	26.8	23.2	37.2	77.8	56.4	143	364
96/3	35.2	47.1	83.7	62.6	33.5	104	366
176/3	15.3	25.7	78.6	74.9	42.5	141	378
88/1	13.5	29.3	69.0	71.4	44.4	165	393
75/2	16.6	27.1	123	79.2	46.9	130*	400
70/2	7.1	31.3	88.8	64.5	37.3	202*	408
77/3	13.9	26.1	76.0	96.2	56.4	139	408
37/1	9.6	13.6	79.8	96.5	28.8	186	414
55/3	35.9	49.0	144	113	62.4	195*	422
196/2	22.3	16.8	43.9	54.3	63.3	227	428
125/3	30.0	40.8	91.8	136	47.2	87.2	433
44/1	22.3	26.9	99.2	112	46.7	120*	436
139/3	19.7	20.0	76.1	87.1	27.9	231	437
90/1	16.5	25.3	85.6	91.1	50.7	170	439
104/1	10.9	35.6	102	108	54.9	142	453
38/3	23.3	15.2	88.4	143	39.9	149	459
191/2	16.9	22.3	76.6	96.9	52.6	195	460
160/2	10.6	40.5	200	169	58.6	-	464
45/3	31.3	17.3	76.1	72.6	24.6	251	473
112/1	21.4	37.1	88.3	74.6	78.1	175	474
236/2	35.7	62.5	171	110	75.3	25.5	480
120/1	40.2	60.8	89.1	95.5	70.4	134	490
148/1	72.6	21.6	102	98.8	51.2	145	491
203/1	17.4	21.0	167	113	52.7	177*	515
234/2	23.8	46.2	131	109	63.7	144	518
54/3	23.8	27.7	90.9	103	41.9	235*	523
51/1	8.6	38.3	163	135	23.7	159	528
161/1	18.8	12.1	47.8	101	73.0	253	536
91/2	15.7	35.7	103	141	63.7	178	537
240/1	8.2	46.1	239	99.3	57.8	85.1*	550
155/2	20.2	23.2	132	93.9	80.2	215	564

MANGANESE - SOILS

	Fraction						
Sample	1	2	3	4	5	6	Total
74/2	19.6	57.3	131	63.7	53.2	240	565
151/1	15.7	22.4	101	116	59.0	335*	568
235/2	16.5	56.4	218	123	72.5	82.6	569
228/2	21.9	31.5	156	119	97.6	144	570
68/3	32.6	43.0	190	169	73.1	76.0	584
48/3	21.4	16.8	39.9	61.3	48.4	401	589
145/1	19.5	25.1	170	129	63.2	187	594
180/1	12.8	13.0	77.1	148	49.2	301	601
40/3	31.3	32.0	127	155	65.8	203	614
186/3	11.8	18.6	83.6	129	90.0	293	626
71/1	12.0	40.0	120	62.8	49.1	347	631
67/1	27.8	33.8	79.9	112	45.1	344	643
50/1	23.1	33.0	159	141	54.1	368*	650
156/1	17.4	43.1	174	141	86.8	210	672
141/3	26.9	41.0	180	135	58.0	251	692
68/1	31.2	30.0	130	199	78.7	278*	696
90/3	18.7	23.1	168	148	81.0	259*	697
236/1	13.2	47.7	187	143	72.5	234	697
101/1	29.6	53.1	192	132	68.3	231	706
48/1	10.4	18.6	71.1	231	73.1	306	710
193/3	21.3	51.8	425	97.0	58.2	56.7	710
187/3	105	62.0	155	126	150	116	714
231/2	112	34.0	185	178	82.0	123	714
46/2	24.2	52.4	129	145	58.6	243*	722
225/3	6.3	30.9	171	131	80.3	330*	725
63/2	16.3	0.6	87.5	185	43.8	401	734
86/3	10.2	16.9	168	157	50.0	373	775
142/1	22.6	23.6	213	162	73.8	290	785
67/3	51.1	24.4	116	228	90.0	279	788
229/1	29.3	57.7	282	141	75.9	231	817
47/2	55.6	43.5	184	277	85.5	174	820
226/1	81.9	40.1	195	232	136	211	896
83/1	30.4	48.6	175	375	84.9	136*	900
49/1	17.9	47.0	340	357	67.5	231	1060
84/2	36.1	76.9	682	237	125	105*	1180
195/2	106	68.0	448	219	184	405	1430
82/2	51.8	166	1310	797	127	-	2200

* measured residual

MANGANESE - STREET DIRT

	Fraction						
Sample	1	2	3	4	5	6	Total
108/3	14.1	18.0	17.9	21.6	28.4	250	350
18/3	11.5	23.4	61.6	78.0	47.9	283	505
33/3	24.3	46.0	50.0	105	59.2	281	566
199/3	22.6	5.9	26.0	78.9	76.5	409	619
99/2	27.0	58.2	39.7	89.6	76.8	340	631
148/2	16.7	59.5	61.1	114	42.8	342	636
116/3	23.6	66.7	49.9	129	64.7	322	656
105/3	19.0	55.3	94.1	73.0	49.6	389	680
114/3	23.4	49.9	38.2	108	58.2	403	681
189/2	21.9	119	49.5	147	72.4	283	693
150/1	20.9	74.7	37.5	86.1	64.5	413	697
87/3	23.2	62.3	43.0	107	60.6	415	711
23/3	21.5	40.4	40.8	114	55.9	447	720
232/2	24.6	50.6	64.4	95.2	75.8	414	725
70/3	21.3	44.9	43.4	99.9	53.7	468	731
169/2	33.8	54.4	87.0	108	77.1	377	737
10/2	21.4	87.6	67.5	92.4	62.6	406	738
208/2	21.4	73.2	33.2	80.9	85.3	452	746
196/3	40.6	49.5	34.2	73.1	65.9	484	747
141/2	73.6	37.4	18.9	38.8	44.9	556	770
225/1	25.8	49.9	49.9	132	77.3	436	771
106/3	43.1	76.9	110	106	63.8	396	796
3/2	12.8	32.3	101	152	97.5	407	803
19/3	18.1	48.9	56.7	91.1	57.1	533	805
218/2	28.1	66.7	63.4	119	66.3	463	807
28/3	15.7	46.7	75.5	127	56.5	495	816
20/2	31.3	72.7	57.1	183	55.1	422	821
29/2	26.5	55.3	28.0	96.8	65.6	558	830
44/2	19.6	41.4	58.1	112	57.0	545	833
82/3	17.6	47.2	49.0	115	46.9	557	833
176/1	27.5	72.5	44.8	132	78.9	486	842
211/2	25.6	42.4	29.2	94.4	60.5	592	844
25/3	22.8	63.8	79.3	212	89.0	382	849
145/2	19.3	81.7	84.1	167	81.8	419	853
53/2	14.1	86.9	53.2	133	66.3	521	875
215/1	20.8	100	37.8	128	55.6	538	880
4/1	13.8	34.1	38.1	100	56.0	643	885
130/2	19.0	30.7	54.1	96.5	59.8	637	897
224/3	15.1	30.2	32.3	102	51.9	692	924
95/3	16.8	42.1	277	201	83.5	327	947
122/3	18.3	31.1	52.8	93.6	60.5	700	956
184/2	23.8	53.9	99.5	147	80.6	556	961
157/2	18.5	108	38.4	133	54.0	620	972
86/1	27.3	83.7	50.9	220	70.2	545	997
51/2	19.6	65.7	60.5	107	87.4	658	998
172/3	22.4	67.4	50.5	129	68.2	666	1000
206/3	30.8	79.2	43.8	136	87.5	632	1010
78/2	34.6	139	91.1	18.4	106	632	1020
205/3	22.3	79.7	47.1	112	75.4	687	1020

MANGANESE - STREET DIRT

Sample	Fraction 1	2	3	4	5	6	Total
118/2	48.4	78.6	85.4	191	87.0	557	1050
244/1	28.1	47.3	62.7	116	71.0	737	1060
64/1	26.9	61.2	55.3	152	97.6	680	1070
80/1	20.6	54.4	81.5	102	65.2	745	1070
17/2	25.2	48.5	94.6	216	113	687	1180
97/2	25.1	45.3	53.1	179	74.4	844	1220
9/3	19.0	107	57.8	224	109	742	1260
164/3	43.0	99.0	220	279	147	599	1390
63/1	44.0	130	149	396	184	931	1830
166/2	44.9	383	319	902	346	2000	3990

IRON - SOILS

	Fraction						
Sample	1	2	3	4	5	6	Total
46/3	<1	17.3	63.4	546	1730	1.21	1.45
57/2	4.1	35.2	82.3	1240	4250	0.94	1.50
39/3	15.6	263	176	2440	1390	1.16	1.59
108/1	4.8	45.9	87.3	2420	4090	1.00	1.66
83/1	9.8	22.3	57.7	2420	7020	1.05*	1.92
82/2	3.7	21.3	134	2440	6120	1.09	1.96
158/2	4.3	44.6	79.2	1190	2850	1.55	1.97
133/1	4.4	39.9	95.0	2320	3940	1.40	2.04
110/2	36.2	359	367	2530	3850	1.34	2.05
169/3	2.1	29.7	75.8	2370	4340	1.44	2.12
83/2	2.5	16.7	132	1560	3890	1.58	2.14
75/2	4.0	11.4	74.1	1850	4190	2.22*	2.26
145/1	3.8	5.9	35.0	757	3890	1.82	2.29
44/3	9.9	133	191	2600	3050	1.87	2.47
139/3	9.2	136	143	2190	2520	1.97	2.47
45/3	12.2	57.6	120	1340	2420	2.10	2.49
73/2	7.5	74.9	143	1480	4960	1.82	2.49
70/2	2.1	8.9	54.9	1280	3280	2.06	2.52
84/2	1.6	16.4	136	1040	7250	1.77*	2.55
52/1	7.3	378	269	3520	3970	1.33*	2.56
51/1	2.1	74.1	170	3310	1930	2.04	2.59
176/3	<1	8.3	28.8	859	3980	2.18	2.59
56/3	5.3	82.5	146	3200	4000	1.87	2.61
193/3	<1	9.7	75.0	695	3390	2.22	2.64
88/1	<1	14.8	49.5	1700	4120	2.07	2.66
44/1	3.1	35.5	85.0	1370	3860	2.84*	2.82
120/1	9.3	60.7	96.8	1210	7240	1.97	2.83
191/2	2.8	14.4	55.4	1430	3500	2.34	2.84
40/3	<1	12.9	39.0	2230	4330	2.31	2.97
228/2	2.9	14.3	58.6	1320	7010	2.13	2.97
96/3	3.2	107	153	2410	3980	2.31	2.98
131/2	2.1	21.8	61.6	2360	4710	2.26	2.98
77/3	<1	19.6	62.7	2410	4400	2.32	3.01
203/1	3.8	5.0	42.1	866	3050	2.14*	3.01
230/2	13.1	174	211	2430	5690	2.73*	3.02
91/1	25.2	86.8	102	1420	4200	2.45	3.03
234/2	<1	18.8	60.6	1450	5930	2.28	3.03
90/1	3.9	24.7	58.6	1260	4120	2.49	3.04
68/3	2.0	17.6	54.9	2040	6250	2.22	3.06
148/1	4.4	13.5	47.0	1440	5300	2.40	3.08
230/1	1.8	41.5	87.4	1810	3850	2.54	3.12
125/3	4.2	59.3	119	2130	7120	2.19	3.13
160/2	2.0	33.7	84.1	2240	3920	2.52	3.15
64/3	<1	14.9	51.9	1590	4010	2.63	3.20
55/3	<1	80.6	143	2180	5530	2.67*	3.21
71/1	2.6	6.7	43.4	873	3690	2.76	3.22
155/2	<1	10.9	45.0	1140	2470	2.87	3.24
236/2	<1	15.5	134	2590	5780	2.43	3.28
37/1	<1	16.6	49.0	2150	2080	2.89	3.31

IRON - SOILS

	Fraction						
Sample	1	2	3	4	5	6	Total
91/2	3.8	21.9	85.9	2040	3800	2.72	3.32
235/2	<1	7.5	43.8	959	7970	2.44	3.34
38/3	2.8	23.1	53.6	2800	3860	2.69	3.36
141/3	<1	26.9	118	1810	2980	2.89	3.38
104/1	2.2	26.8	55.0	1440	6070	2.63	3.39
236/1	<1	16.4	67.5	1610	5570	2.68	3.41
112/1	<1	17.2	82.3	1780	6820	2.56	3.43
101/1	2.5	34.2	106	1930	6170	2.63	3.45
180/1	2.4	15.8	49.4	1290	2690	3.05	3.45
42/3	<1	22.7	102	3170	4120	3.29*	3.51
187/3	2.8	27.7	71.0	1070	7170	2.71	3.54
142/1	4.0	12.7	77.9	1760	3960	2.97	3.55
50/1	9.7	130	148	1960	4540	2.90*	3.60
74/2	<1	50.3	98.8	810	4240	3.09	3.61
54/3	<1	64.1	99.9	2060	4040	3.33*	3.63
186/3	9.7	41.7	94.8	1430	6140	2.86	3.63
90/3	2.4	12.7	96.3	4320	5910	2.31*	3.74
231/2	5.4	47.2	112	2530	6550	2.84	3.76
67/1	2.7	14.0	26.5	1000	4620	3.24	3.81
68/1	2.0	11.5	20.2	1560	4500	3.23	3.84
161/1	11.8	2.3	37.1	1040	6140	3.15	3.87
240/1	<1	12.3	71.6	1250	6350	3.30*	3.88
63/2	<1	17.4	56.4	2270	3260	3.36	3.92
229/1	<1	24.9	92.4	1960	4590	3.38	4.05
67/3	2.8	17.1	61.9	1980	4190	3.61	4.24
226/1	11.7	59.0	92.9	1590	7970	3.28	4.25
156/1	<1	11.1	45.5	1590	6320	3.48	4.28
47/2	3.1	61.2	98.2	2440	3330	3.70	4.29
225/3	4.9	20.5	99.9	2730	6940	3.36*	4.45
46/2	2.0	7.2	30.7	1060	4010	3.91*	4.51
86/3	<1	56.7	108	1900	3410	4.01	4.56
49/1	<1	8.2	38.6	2420	2822	4.04	4.57
48/1	<1	83.7	124	2220	4590	3.88	4.58
48/3	5.8	41.6	74.1	1900	2970	4.55	5.05
145/3	59.3	339	281	3340	10600	3.77	5.23
151/1	2.1	36.5	106	2440	7220	4.26	5.24
196/2	7.7	60.4	131	2190	7320	4.49	5.54
195/2	4.1	108	196	3430	9090	5.10	6.38

* measured residual

IRON - STREET DIRT

Fraction

Sample	1	2	3	4	5	6	Total
108/3	<1	72.7	166	468	1080	1.66	1.84
189/2	<1	56.6	79.1	585	249	2.77	2.87
148/2	<1	34.2	63.1	614	170	2.88	2.97
18/3	<1	22.4	103	570	1440	3.29	3.50
106/3	<1	37.6	63.2	1640	1790	3.31	3.66
70/3	<1	79.0	139	1260	891	3.67	3.91
105/3	<1	37.9	82.3	992	2300	3.60	3.94
157/2	<1	237	192	1970	479	3.88	4.17
145/2	<1	83.9	110	1570	2070	3.81	4.19
199/3	<1	33.8	72.5	1520	3720	3.68	4.21
25/3	<1	42.1	113	1080	564	4.04	4.22
33/3	<1	76.2	170	1670	2120	3.85	4.25
78/2	<1	229	103	1340	1360	4.02	4.32
164/3	<1	13.1	70.7	1560	1030	4.07	4.34
82/3	<1	52.6	101	890	663	4.19	4.36
20/2	<1	82.9	105	1690	523	4.17	4.41
53/2	<1	48.9	63.1	1540	1710	4.07	4.41
3/2	<1	43.2	74.7	1440	2220	4.04	4.42
169/2	<1	56.1	112	1500	2330	4.07	4.47
208/2	<1	136	111	1600	2560	4.09	4.53
232/2	<1	64.5	73.9	923	1750	4.35	4.63
118/2	3.8	35.9	69.9	1460	769	4.41	4.64
87/3	<1	114	214	1370	1730	4.41	4.75
218/2	<1	76.0	153	1080	993	4.57	4.80
116/3	<1	169	263	1720	1890	4.41	4.81
150/1	<1	147	134	1480	1740	4.46	4.81
28/3	<1	69.1	152	934	513	4.74	4.91
99/2	<1	122	149	1670	3630	4.35	4.91
29/2	<1	209	149	1660	1740	4.53	4.91
114/3	5.5	111	272	1790	1720	4.54	4.93
74/3	<1	72.5	102	1330	1030	4.74	4.99
184/2	<1	40.3	70.7	1090	1130	4.81	5.04
4/1	<1	45.7	126	809	1520	4.81	5.06
10/2	<1	58.5	80.7	1040	1510	4.79	5.06
225/1	<1	79.9	93.1	1860	1610	4.73	5.09
206/3	<1	120	64.3	1770	1920	4.76	5.15
176/1	<1	401	397	1810	807	4.83	5.17
23/3	<1	81.3	190	1650	1650	4.87	5.23
122/3	2.2	29.2	206	904	1310	4.99	5.24
95/3	<1	22.7	98.9	2660	4290	4.57	5.28
224/1	<1	163	213	1090	2450	4.91	5.30
215/1	<1	192	180	1260	626	5.15	5.38
63/1	<1	171	355	2270	2010	4.91	5.39
17/2	<1	45.9	125	1010	553	5.25	5.42
51/2	2.5	58.3	149	1380	1810	5.09	5.43
196/3	<1	33.8	72.5	1520	3720	3.68	5.54
130/2	<1	35.1	182	1150	964	5.32	5.55
44/2	<1	65.2	134	1740	1440	5.23	5.57

IRON - STREET DIRT

Sample	Fraction 1	2	3	4	5	6	Total
141/2	<1	260	145	1120	1170	5.32	5.59
80/1	<1	85.5	133	1250	1560	5.46	5.76
19/3	<1	86.0	174	1290	1120	5.51	5.78
211/2	<1	113	137	1300	791	5.57	5.80
166/2	5.6	128	159	3480	1590	5.32	5.86
205/3	<1	99.2	70.0	1390	1310	5.63	5.92
172/3	<1	115	250	1450	683	5.93	6.18
86/1	<1	370	378	2360	939	5.81	6.21
9/3	<1	181	96.3	2010	1480	6.15	6.53
224/3	<1	35.6	67.6	858	559	6.40	6.55
64/1	<1	280	387	5470	2540	6.51	7.38
97/2	<1	119	196	1800	786	8.00	8.29

APPENDIX 4

INDIVIDUAL STREET DIRT EXCHANGEABLE AND HYDROCHLORIC ACID-SOLUBLE METAL CONCENTRATIONS

All concentrations in µg/g

STREET DIRT

Sample	Lead		Zinc		Copper		Cadmium	
	Exch.	HCl	Exch.	HCl	Exch.	HCl	Exch.	HCl
3/2	101	602	18.8	172	18.1	63.1	0.47	1.15
4/1	49.5	139	25.6	105	4.3	13.2	0.18	
5/3	4.5	64.2	16.3	103	2.3	4.5	0.16	0.47
9/3	140	399	30.1	200	15.9	47.5	0.21	0.71
10/2	3.0	56.9	6.1	68.6	<0.5	5.2	0.09	0.24
13/3	49.6	172	22.7	118	10.4	32.3	0.75	1.24
15/3	52.0	225	17.2	93.3	3.3	19.6	0.24	0.57
16/3	80.1	358	11.5	125	9.6	34.0	0.34	0.99
17/2	147	472	28.4	159	16.9	18.5	0.33	0.69
18/3	17.0	75.5	4.6	35.4	3.1	7.1	0.15	0.27
19/3	247	703	45.3	183	34.8	60.8	0.55	0.62
20/2	33.1	253	66.6	477	11.7	25.6	3.58	2.50
21/1	83.9	430	32.9	169	12.5	27.7	0.49	0.51
22/3	21.1	178	28.3	166	6.2	14.9	0.30	0.68
23/3	73.0	431	103	757	12.2	31.9	0.39	0.77
24/2	57.6	443	102	295	11.5	30.2	0.52	0.77
25/3		192		242		12.2		0.63
27/2	87.1	301	77.0	238	23.7	44.6	0.44	0.83
28/3	197	371	40.8	115	14.3	19.0	0.38	0.56
29/2	436	935	74.0	480	43.3	76.3	0.91	1.29
30/3	23.9	315	58.2	179	42.5	27.7	0.48	0.64
33/3	137	453	65.2	244	9.2	27.7	1.03	0.87
34/3	28.5	90.7	48.4	106	6.5	3.6	0.16	0.25
35/3	17.8	156	13.0	88.1	2.0	6.3	0.19	0.42
36/2	242	478	124	474	16.5	43.8	1.04	1.56
37/3	2.7	83.1	21.3	95.9	3.0	10.4	0.11	0.25
38/1	27.5	146	22.8	133	6.1	20.2	0.34	0.31
39/2	38.6	234	33.5	206	8.9	20.9	1.58	2.00
40/2	512	907	50.5	161	14.3	35.5	0.26	0.51
41/3	51.8	375	14.6	135	4.8	33.7	0.16	0.41
42/1	45.1	284	19.5	141	4.0	33.6	0.20	0.40
44/2	17.8	285	15.9	134	8.2	43.0	0.55	0.74
45/1	106	327	40.9	154	17.8	43.7	0.33	0.64
46/1	72.8	420	47.1	207	8.3	39.2	0.60	1.11
47/3	34.1	268	17.0	113	9.6	18.0	3.29	0.75
48/2		988	70.2	171	35.1	51.3	0.83	0.94
49/2	248	301	75.3	194	19.3	25.6	1.67	1.91
50/2	52.0	336	30.3	181	3.4	13.2	0.82	1.43
51/2	117	425	32.3	189	6.5	30.5	0.88	1.62
52/3	45.0	232	26.6	190	12.9	19.4	1.67	0.79
53/2	19.9	81.4	23.0	108	4.5	7.2	0.26	0.53
54/2	121	462	53.2	204	21.7	29.9	0.69	0.83
55/2	62.9	234	24.6	99.4	10.9	16.9	0.17	0.27
56/1	84.7	154	39.3	121	5.6	14.2	0.27	0.77
57/3	14.9	108	20.7	101	1.7	7.1	0.17	0.37
58/1	138	530	28.4	121	10.6	26.6	0.25	2.65
60/3		374		555		94.5		2.56
63/1	22.3	267	73.8	341	18.4	63.5	0.62	1.15
64/1	36.3	494	113	970	16.8	74.0	0.51	1.61

STREET DIRT

Sample	Lead		Zinc		Copper		Cadmium	
	Exch.	HCl	Exch.	HCl	Exch.	HCl	Exch.	HCl
65/2	127	727	75.9	458	28.3	129	0.75	1.35
66/3	592	1170	97.4	204	24.0	105	0.59	
67/2	112	353	37.5	190	7.5	20.3	0.52	1.32
68/2	265	621	63.4	194	15.0	34.7	0.48	1.33
69/3	361	638	67.8	238	38.0	41.6	0.60	3.08
70/3	48.2	210	33.8	181	50.9	86.4	0.43	0.80
71/3	16.8	247	51.0	296	4.7	27.2	0.27	1.62
72/3		548		238		44.1		2.62
73/3	<1.5	8.4	8.4	51.6	2.7	1.8	0.10	0.19
74/3	42.1	206	30.3	152	10.3	37.3	0.16	
75/3	13.6	100	28.1	131	2.0	10.6	1.00	
76/3	47.3	376	28.6	185	7.8	36.7	0.24	0.76
77/2	231	825	59.1	295	18.0	57.6	0.91	2.19
78/2	115	374	58.9	196	28.7	39.5	0.16	
79/3	8.5	78.0	23.2	79.7	1.4	7.9	0.11	0.16
80/1	80.1	249	51.1	120	12.8	38.0	0.26	1.02
81/3	13.4	124	57.1	150	7.6	35.6	0.21	0.54
82/3	8.9	88.9	16.6	70.6	2.5	16.7	0.11	0.19
83/3	7.3	107	13.1	89.1	<0.3	19.2	0.10	0.32
85/2	238	535	48.1	190	22.7	43.0	0.26	0.68
86/1	74.9	230	73.1	229	15.7	26.9	0.34	0.76
87/3	166	385	61.4	228	12.6	26.1	0.36	0.60
88/2	160	375	105	293	16.7	24.8	0.44	1.63
88/3	4.1		2.4		<0.5		0.09	
89/3	37.1	379	69.8	237	6.6	33.7	0.31	0.63
90/2	127	406	67.6	231	16.6	31.0	0.63	2.11
91/3	175	266	17.8	79.9	6.8	16.7	0.38	0.52
92/3	42.2	248	33.4	162	7.5	17.9	0.42	0.74
93/2	19.4	110	101	281	4.7	11.9	0.35	0.62
94/3	218	463	88.1	289	19.6	51.9	0.51	0.77
95/3	20.8	455		303	4.0	119	0.33	1.23
96/2	85.8	228	17.8	110	6.3	15.0	0.31	0.45
97/2	270	585	74.6	218	63.9	131	0.40	
98/1	19.7	325	44.4	249	7.7	27.5	0.46	1.02
99/2	180	736	65.9	818	24.4	61.9	0.75	2.36
100/3	124	335	20.1	163	16.8	27.4	0.17	0.57
101/3	9.7	103	25.0	54.8	3.5	18.5	0.17	0.22
102/2	7.5	161	15.7	69.2	3.0	17.0	0.11	0.25
103/3	37.9	113	15.3	100	6.2	19.6	0.11	0.25
104/3	12.2	149	11.3	94.7	1.7	15.3	0.13	0.41
105/3	7.2	123	13.9	114	1.5	17.9	0.18	0.46
106/3	8.8	94.7	11.4	77.4	1.4	19.8	0.18	0.42
107/1		258		211		39.8		0.43
108/3	4.5	48.5	5.9	40.4	2.3	7.8	0.04	0.06
109/3	13.8	123	13.5	103	1.9	10.1	0.19	0.46
110/3	10.5	88.2	14.6	86.8	2.1	11.3	0.13	0.41
111/2	33.3	242	43.9	258	9.9	28.6	0.23	0.56
112/3	282	515	72.3	337	52.0	89.2	0.45	1.39

STREET DIRT

Sample	Lead		Zinc		Copper		Cadmium	
	Exch.	HCl	Exch.	HCl	Exch.	HCl	Exch.	HCl
113/1	144	525	76.3	295	19.6	42.1	0.35	0.86
114/1	90.0	703	327	805	24.0	43.4	0.75	4.14
114/3	385		164		17.8		0.91	
115/1	112	475	135	388	21.3	31.3	0.74	1.02
115/2	59.8		89.7		23.0		0.35	
115/3	93.0		145		22.4		0.70	
116/3	195	402	90.2	279	20.7	36.9	0.34	1.15
117/2	184	491	114	313	26.4	38.0	0.58	1.05
118/2	55.6	316	65.8	328	5.1	19.8	0.41	0.85
119/1	228	498	92.2	252	11.6	28.3	0.21	0.65
120/2	234	319	61.9	184	27.6	45.1	0.33	0.59
121/1	219	623	176	586	47.5	101	0.45	0.93
122/3	32.6	306	35.7	158	3.0	25.9	0.27	0.54
123/3	55.7	435	34.4	136	15.3	31.6	0.33	0.55
124/3	128	216	40.1	107	14.0	41.2	0.19	0.50
125/1	136	288	45.3	156	15.1	29.3	0.36	0.54
126/3	18.1	86.7	33.8	113	2.3	11.0	0.23	0.48
127/3	52.3	189	82.0	257	8.0	35.0	0.49	0.90
128/3		109		76.5		11.8		0.45
129/3		430		179		26.9		0.74
130/2	63.1	153	14.1	84.0	5.7	26.4	0.17	0.42
131/3	92.6	194	35.6	125	18.0	16.5	0.29	0.52
132/1	160	354	39.7	225	12.3	37.3	0.32	0.76
133/3	26.2	185	39.8	273	11.9	26.3	0.23	0.60
135/1	<1.5		1.0		2.3		0.08	
135/2	232	519	135	265	42.3	73.6	0.59	1.20
136/1		568		384		60.1		1.01
136/2	107		62.5		40.6		0.52	
137/1	149	506	174	332	19.1	28.3	0.59	0.92
137/2	120		154		19.5		0.72	
137/3	105		128		50.5			
138/3	227	679	105	399		45.3	0.38	1.82
139/2	225	849	38.8	207	24.5	58.1	0.63	1.79
140/2	144	352	109	285	28.0	30.4	0.41	0.81
141/2	178	117	68.5	217	8.3	33.0	0.52	0.65
142/3	68.6	342	99.2	357	23.8	62.8		1.29
143/3	34.2	268	16.6	117	16.6	36.9	0.35	0.51
144/2	71.5	444	40.7	167	7.8	35.8	0.18	0.37
145/2	8.3	190	29.5	196	6.8	26.6	0.19	0.40
146/2	98.2	264	35.3	151	12.0	34.8	0.28	0.54
147/3	44.8	423	34.0	184	11.3	68.9	0.99	2.06
148/2	17.9	117	12.5	59.5	1.4	8.9	0.21	0.38
149/2	185	365	41.1	113	15.8	31.7	0.27	0.53
150/1	214	424	75.6	262	25.1	45.8	0.50	1.02
151/3	501	599	99.1	302	44.0	67.4	0.42	1.13
152/2	381	601	85.8	256	31.8	37.5	1.60	1.20
153/2	83.8	259	104	135	10.4	14.6	0.38	0.36
154/1	116	493	71.7	283	23.3	25.8	0.37	1.05

STREET DIRT

Sample	Lead		Zinc		Copper		Cadmium	
	Exch.	HCl	Exch.	HCl	Exch.	HCl	Exch.	HCl
155/1	263	575	52.4	246	22.8	36.7	0.62	0.65
156/3	224	420	105	273	15.4	31.3	0.39	0.83
157/2	143	479	30.7	254	37.4	48.2	0.27	0.48
158/1	136	468	180	619	16.5	43.0	0.68	1.10
159/2	115	328	117	307	33.0	39.2	0.50	0.62
160/1	34.7	333	99.6	426	30.1	61.6	0.52	3.82
161/3	38.1	94.3	50.2	133	11.0	1.9	0.27	0.37
162/3	69.6	126	86.8	187	11.4	26.6	0.64	0.50
163/2	58.9	200	31.7	99.7	25.7	20.8	0.35	0.70
164/3	11.0	159	24.8	167	1.2	14.1	0.50	1.15
165/1	69.9	178	38.1	122	18.3	30.5	0.33	0.40
166/2	6.6	111	23.3	110	4.6	14.4	0.23	0.45
167/3	208	491	44.4	253	12.0	33.5	0.36	0.76
168/1	4.6	416	47.9	208	22.9	55.8	0.59	1.23
169/2	218	404	25.9	149	10.7	35.0	0.34	0.69
170/2	231	639	25.8	99.4	9.9	22.3	0.32	1.56
171/3	60.6	283	38.1	161	4.5	25.7	0.35	0.69
172/3	169	347	91.4	288	21.6	34.1	1.63	3.31
173/1	134	281	89.8	223	14.8	31.0	0.64	1.34
173/3	120		50.8		28.8		0.51	
174/2	624	432	138	252	48.2	32.5	0.51	0.68
175/3	154	311	155	392	20.8	33.9	0.17	1.75
176/1		236		345		33.8		0.64
177/1	26.1	123	39.2	148	9.2	17.0	0.21	0.47
178/2	73.4	180	38.7	143	10.8	19.2	0.69	0.80
179/3	20.7	166	38.9	150	22.2	32.6	0.23	0.44
180/2	34.9	131	21.3	104	2.4	12.8	0.21	0.33
181/1	87.1	337	24.4	126	14.7	40.4	0.38	0.73
183/2	25.4	153	37.5	140	5.4	21.3	0.31	0.84
184/2	61.3	160	30.1	183	7.5	15.2	0.17	0.47
185/3	53.7	196	18.4	104	21.4	45.8	0.30	0.56
186/1	10.8	161	11.3	89.2	2.1	17.3	0.25	0.49
187/1	143	280	46.5	165	33.8	51.3	0.95	1.00
188/3	60.4	419	46.5	200	11.1	48.3	1.75	1.26
189/2	22.7	96.1	7.1	52.0	4.4	7.7	0.55	0.56
190/1	28.4	339	40.7	195	7.7	21.8	0.55	1.04
191/1	194	276	80.8	215	16.0	17.6	0.77	1.04
192/1	209	640	93.7	305	26.6	47.6	0.63	1.41
193/1	42.6	127	61.0	187	62.9	60.1	0.31	0.56
195/3	11.1	88.5	5.5	48.9	2.4	13.8	0.13	0.29
196/3	88.8	460	38.7	232	15.7	37.5	0.47	0.63
197/3	221	332	27.0	142	11.7	29.1	0.25	0.80
198/2	31.6	155	11.0	67.9	4.8	9.7	0.57	0.65
199/3	4.0	23.1	1.8	12.5	1.3	5.2	0.09	0.18
200/3	3.1	115	3.9	43.2	<0.7	15.9	0.16	0.37
201/3	46.9	266	48.5	211	5.3	23.9	0.72	0.86
202/3	72.8	214	31.6	130	10.3	24.1	0.88	1.45
203/2	559	629	108	303	31.0	45.1	0.75	2.13
204/3	35.0	167	44.7	114	7.8	27.5	0.39	0.45

STREET DIRT

Sample	Lead		Zinc		Copper		Cadmium	
	Exch.	HCl	Exch.	HCl	Exch.	HCl	Exch.	HCl
205/3	188	272	45.1	124	26.2	50.9	0.42	0.79
206/3	364	520	35.7	149	28.7	49.3	1.17	1.42
207/3	50.3	137	19.2	91.1	9.3	26.9	0.23	0.40
208/2	160	294	36.3	255	17.5	22.0	0.22	0.48
209/2	101	226	25.5	105	15.3	36.0	0.24	0.45
210/3		331		125		49.3	0.48	0.84
211/2	456	318	39.3	161	31.0	23.7	0.37	0.42
212/2	689	691	126	423	24.1	34.5	0.82	1.62
213/3	191	360	81.2	196	29.7	28.5	0.56	0.89
214/3	18.3	156	8.8	59.5	6.9	19.0	0.28	0.65
215/1	132	238	77.7	169	19.4	25.5	0.43	1.01
216/3	108	119	31.7	73.6	2.1	5.9	0.17	0.31
217/2	7.8	106	10.8	80.2	2.4	18.7	0.29	0.67
218/2	53.8	148	45.8	146	12.4	24.2	0.26	
219/2	12.8	76.6		269	2.2	7.5	0.23	0.42
220/2	135	205	19.8	85.7	11.1	26.9	0.21	0.42
221/3	7.8	152	2.9	59.0	0.5	9.9	0.09	0.23
222/3	424	680	128		24.0	71.4	2.53	1.17
223/1	937	1090	115	339	30.3	53.0	1.75	
224/3	447	629	35.1	127	21.1	40.0	0.56	0.64
225/1	18.9	578	49.9	191	25.7	36.4	2.24	1.68
226/3	42.7	189	39.8	142	10.8	12.5	0.65	1.08
227/3	305	215	17.8	70.4	5.0	16.9	0.23	0.32
228/3	340	487	61.5	225	14.9	25.3	0.57	0.53
229/2		54.9	27.2	69.7		10.1	0.23	0.22
230/3	65.9	197	16.4	104	10.9	43.2	0.20	0.24
231/3	60.8	71.8	27.0	53.1	5.2	24.6	0.32	0.94
232/2	80.0		23.6		11.6		0.20	
233/1	428	549	31.8	82.0	23.0	16.9	0.35	0.48
234/1	67.6	254	99.8	136	7.7	15.3	0.39	0.29
235/3	329	448	26.2	92.9	18.9	16.7	0.73	0.56
236/3	291	479	131	356	11.2	24.6	1.80	0.60
237/1	89.2	113	76.8	189	17.6	13.1	0.68	0.43
238/2		10.4		30.0		8.4	0.18	0.19
242/1	24.1	116	17.0	97.6	2.1	14.4	0.37	0.41
243/1	134	153	94.3	168	11.7	11.2	0.49	0.37
244/1	105	189	73.9	252	6.6	18.5	0.67	0.43

APPENDIX 5

pH RESULTS OF SOILS AND STREET DIRTS USED IN THE SIX-FRACTION STUDY

SOIL				STREET DIRT	
Sample	pH	Sample	pH	Sample	pH
37/1	5.8	108/1	5.9	3/2	7.0
38/3	5.6	110/2	4.6	4/1	7.4
39/3	4.5	112/1	6.2	9/3	7.2
40/3	5.8	120/1	4.7	10/2	7.2
42/3	6.1	125/3	5.3	17/2	7.0
44/1	5.3	131/2	5.7	19/3	7.2
44/3	5.1	133/1	5.9	20/2	6.6
45/3	5.4	139/3	5.0	23/3	7.2
46/2	6.4	141/3	7.1	28/3	7.0
46/3	6.2	142/1	6.0	33/3	7.0
47/2	5.2	145/1	6.2	44/2	7.0
48/1	5.0	145/3	4.3	51/2	7.4
48/3	5.1	148/1	5.3	53/2	7.1
49/1	6.2	151/1	5.8	63/1	6.9
50/1	5.2	155/2	6.0	70/3	6.7
51/1	6.0	156/1	6.1	74/3	7.2
52/1	4.7	158/2	5.6	78/2	6.7
54/3	5.3	160/2	5.6	80/1	7.0
55/3	5.3	161/1	5.5	82/3	7.3
56/3	5.3	163/1	6.1	87/3	6.6
57/2	5.3	169/1	5.5	105/3	6.8
63/2	6.4	176/3	5.8	106/3	6.8
64/3	6.1	180/1	5.8	108/3	7.5
67/1	5.8	186/3	5.3	114/3	7.1
67/3	5.8	187/3	5.0	116/3	6.8
68/1	6.4	191/2	5.6	130/2	7.0
68/3	5.7	193/3	6.0	141/2	4.5
70/2	7.0	195/2	5.0	145/2	7.0
71/1	6.2	196/2	4.8	148/2	7.2
73/2	4.8	203/1	5.7	150/1	6.7
74/2	6.0	225/3	5.9	157/2	7.0
75/2	6.1	226/1	5.1	166/2	7.3
77/3	6.6	228/2	5.5	169/2	7.0
82/2	5.5	229/1	6.8	184/2	6.5
83/1	6.0	230/2	5.8	189/2	6.7
83/2	5.8	230/1	5.7	205/3	7.2
84/2	5.5	231/2	5.5	206/3	6.9
86/3	5.5	234/2	6.6	208/2	6.8
88/1	5.9	235/2	6.5	211/2	7.0
90/1	5.6	236/1	5.3	215/1	7.4
90/3	6.2	236/2	5.4	218/2	7.0
91/1	N.D.	240/1	5.6	225/1	7.0
91/2	6.3			232/2	7.5
96/3	5.2				
101/1	5.5				
104/1	5.4				

N.D. = Not determined

APPENDIX 6

INDIVIDUAL TAL, PARTICULATE LEAD, TAL/TOTAL AND TAL/PARTICULATE LEAD RESULTS

24-HOUR SITES

Date	TAL ng/m^3	Particulate Lead ng/m^3	TAL/Total Lead (%)	TAL/Particulate Lead (%)
West Graham St. (7.5m)				
4-5/8/80	39.1	349	10.1	11.2
7-8/8/80	7.2	271	2.6	2.7
11-12/8/80	15.1	279	5.1	5.4
12-13/8/80	29.8	435	6.4	6.9
14-15/8/80	66.4	469	12.4	14.2
18-19/8/80	72.5	286	20.2	25.3
19-20/8/80	26.7	232	10.3	11.5
20-21/8/80	24.0	259	8.5	9.3
25-26/8/80	54.9	906	5.7	6.1
26-27/8/80	22.3	884	2.4	2.5
27-28/8/80	16.5	342	4.6	4.8
1-2/9/80	15.1	266	5.4	5.7
2-3/9/80	21.0	285	6.9	7.4
3-4/9/80	21.5	378	5.4	5.7
8-9/9/80	19.5	362	5.1	5.4
9-10/9/80	20.4	404	4.8	5.0
10-11/9/80	39.7	548	6.8	7.2
15-16/9/80	42.2	567	6.9	7.4
16-17/9/80	39.4	651	5.7	6.1
17-18/9/80	36.1	511	6.6	7.1
21-22/10/80	43.5	499	8.0	8.7
18-19-11/80	47.7	1280	3.5	3.7
1-2/12/80	33.0	587	5.4	5.6
19-20/1/81	75.2	1577	4.6	4.8
2-3/2/81	19.2	446	4.1	4.3
16-17/2/81	18.4	694	2.6	2.7
2-3/3/81	10.8	439	2.4	2.5
16-17/3/81	13.4	531	2.5	2.6

Date	TAL ng/m^3	Particulate Lead ng/m^3	TAL/Total Lead (%)	TAL/Particulate Lead (%)
Hope St (Stn.1) (0.3m)				
23-24/10/80	96.3	880	9.9	10.9
Hope St. (Stn.2) (7m)				
26-27/8/81	27.3	950	2.8	2.9
27-28/8/81	24.5	1004	2.4	2.4
23-24/9/81	32.6	627	5.0	5.2
24-25/9/81	40.0	1004	3.8	4.0
27-28/10/81	42.7	800	5.1	5.3
29-30/10/81	48.8	1140	4.1	4.3
Hope St. (Stn.2) (12m)				
22-23/6/81	22.7	513	4.3	4.4
23-24/6/81	23.7	645	3.6	3.7
24-25/6/81	20.7	365	5.4	5.7
Other Urban (7-30m)				
5-6/8/80	3.1	104	2.9	3.0
20-21/10/80	53.7	1017	5.0	5.3
27-28/10/80	9.6	145	6.3	6.6
28-29/10/80	1.5	159	0.9	0.9
3-4/11/80	47.5	1458	3.2	3.3
10-11/11/80	3.9	156	2.4	2.5
11-12/11/80	22.5	757	2.9	3.0
17-18/11/80	6.8	167	4.0	4.1
24-25/11/80	4.5	913	4.7	4.9
25-26/11/80	3.6	384	0.9	0.9
Rural (2m)				
16-17/7/80	6.5	16.8	27.9	38.7
12-13/10/80	1.9	126	1.5	1.5
2-3/11/80	4.4	255	1.7	1.7
23-24/11/80	1.6	19	7.7	8.4

Date	TAL ng/m^3	Particulate Lead ng/m^3	TAL/Total Lead (%)	TAL/Particulate Lead (%)
18-19/1/81	6.1	9.5	39.1	64.2
31/1-1/2/81	4.7	54.2	8.0	8.7
15-16/2/81	2.4	126	1.9	1.9
1-2/3/81	3.6	43.5	7.6	8.3
22-23/8/81	0.8	5.5	-	-
23-24/8/81	2.2	36.3	5.7	6.1
24-25/8/81	0.8	7.9	-	-
3-4/10/81	1.3	25.3	4.9	5.1
4-5/10/81	5.5	36.5	13.1	15.1
5-6/10/81	1.4	83.4	1.7	1.7
24-25/10/81	0.8	5.0	-	-
25-26/10/81	1.0	18.1	5.2	5.5
26-27/10/81	0.8	308	-	-

	Date	TAL ng/m^3	Particulate Lead ng/m^3	TAL/Total Lead (%)	TAL/Particulate Lead (%)
7-HOUR SITES					
Hope St. (Stn.1) (5-30m)					
	3/12/80	52.3	876	5.6	6.0
	4/12/80	29.9	682	4.2	4.4
	8/12/80	22.8	462	4.7	4.9
	8/12/80	15.6	326	4.6	4.8
	9/12/80	2.9	166	1.7	1.7
	10/12/80	20.8	258	7.5	8.1
Hope St. (Stn.2) (3m)					
	30/10/80	92.6	2582	3.5	3.6
	6/11/80	63.5	1021	5.9	6.2
	13/11/80	110.0	2472	4.2	4.4
	21/1/81	90.0	2847	3.1	3.2
	4/2/81	75.4	2260	3.2	3.3
	18/2/81	36.6	1481	2.4	2.5
	4/3/81	65.9	2372	2.7	2.8
	18/3/81	48.3	1093	4.2	4.4
Hope St. (Stn.2) (12m)					
	21/1/81	51.9	1606	3.1	3.2
	4/2/81	52.6	1526	3.3	3.4
	18/2/81	30.8	1103	2.7	2.8
	4/3/81	34.1	1386	2.4	2.5
	18/3/81	42.8	705	5.7	6.1
Garage	27/11/80	46.7	294	13.7	15.9
	27/1/81	274.0	1841	13.7	14.9
	5/2/81	263.0	551	32.3	47.7
2-3 HOUR SITES					
	10/12/80	18.4	146	11.1	12.6
	10/12/80	15.0	243	5.8	6.2
	10/12/80	30.0	350	7.9	8.6

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