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THE DISTRIBUTION OF TEN TRACE ELEMENTS IN ROCKS, SOILS AND STREAM SEDIMENTS IN SEVEN REGIONS OF ENGLAND AND WALES.

BY

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Dedicated To My Late Dad

Collins U.M. Gardner (Sr.)

(Paa da yei)

And

To All Those Who Have Helped Me In His Absence, Especially

My Loving Wife Elizabeth

And Mum

Mary Kawanye Gardner

(Nne daalu).

This Thesis Has Been Produced By The Word Processor Facility Of

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Abstract

The distribution of trace elements (total) in soils and stream sediments derived from a range of geological parent materials in England and Wales has been studied with the aim of investigating the geochemical controls governing multi-element associations in the rock-soil-sediment system. Ten elements were determined by atomic absorption spectroscopy. These were Ca, Mg, Al, Fe, Zn, Mn, Co, Pb, Ni and Cu.

The parent material (rock) was found to exert an overriding control on the distribution and associations of elements in the soils and stream sediments. The clay units tended to have more of most of the elements determined than the sandstones and mudstones, and this was reflected in the element concentrations in the soils and stream sediments derived from them. Low levels of most elements, particularly Cu and Co in the sandstones were reflected in the associated soils and stream sediments. Lithological variation in the parent material also resulted in local variation of element concentrations in the soils and stream sediments. Other factors controlling the distribution and associations of elements were soil type and texture, drainage, organic matter, pH and dilution of the stream sediments by the precipitation of secondary calcium carbonates.

Multi-element associations were discerned by statistical means. Four main groups of associations were found. These were :-

(a) The clay mineral group (Mg, Al, Fe and Ni).
(b) The carbonate group (Ca, Pb, and Zn).
(c) The organic matter group (Pb, Cu, Zn and Ni).
(d) The hydrous oxide group (Mn, Fe, Co and Cu).

In general multi-element associations in the soils and stream sediments were broadly correlated with those in the parent material (rocks). Major reconstitution of the clay minerals in the transition from rocks to soils and stream sediments were thought to be uncommon. Higher concentrations of elements in the carbonate group in the stream sediments, often resulted in lower concentrations of other elements. This was thought to be due to the dilution of the sediments by the formation of secondary carbonates. Higher concentrations of elements in the organic matter group in the topsoils compared to the subsoils, particularly of Pb, were thought to be due to the accumulation of organic debris in the topsoils. Manganese oxides were thought to exert greater activity in the control of elements distibution, particularly Co than Fe oxide.

The findings of the present work confirmed the usefulness of stream sediments (data) in providing reconnaissance information on the distribution of trace elements in soils and their parent materials. This provides an efficient, cheap and rapid method of primary investigations with applications to geological and agricultural problems in parts of the world where technical and financial resources are scarce.

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CHAPTER 1

Introduction.

The vast amount research devoted to the study of the complex relationship between living organisms and their environments since the turn of the century has led to a better understanding of the importance of minor elements, present in trace quantities in rocks, soils, plants and humans. The studies of earlier geochemists such as Goldschmidt (1954), Rankama and Sahama (1950), Mason (1952) and Wedepohl (1969) established many of the principles governing the evolution, abundance, distribution and associations of elements in the geochemical environment. The abundance and distributions of elements in igneous rocks are now well documented (Wager and Mitchell, 1951; Wedepohl, 1969). Krauskopf (1955) noted that concentrations of trace elements in some black shales were more than a hundred times their average crustal abundance. The major elements oxygen, hydrogen, silicon, aluminium, iron, carbon, nitrogen, calcium and magnesium occur in large quantities in soils. Other elements such as copper, lead, nickel, cobalt, molybdenum only trace amounts occur in soils. The concentrations of elements in the soils vary widely, depending on the initial concentrations in the parent material and pedological modification.

In the later half of this century public concern about the chemical deterioration of the environment combined with the awareness of the role of trace elements in health and nutrition made it important to know more about trace elements; thus, in the field of

agronomy trace elements play an important role in soil fertility. The uptake of trace elements in insufficient or excessive quantities can lead to poor plant growth. This imbalance may be passed on to the animals that feed on the plants.

Webb (1964) proposed that regional geochemical reconnaissance techniques based on the analysis of stream sediments, developed for use in mineral exploration, could with slight modification provide geochemical information for agricultural, epidemiological and nutritional purposes. Since stream sediments are composite samples of eroded rocks and soils, their trace element content are to a large extent a reflection of the concentrations in the bedrocks and soils. Frequently, there is a direct relationship between the concentration of a given element in the rock and that in the soils and stream sediment derived from it. Differences between the content of an element in the rock and that of the associated soils and stream sediments are due to processes that intervene during the formation of soils and stream sediments. Such processes may be due to weathering or pedological modification (illuviation, eluviation, biogenic accumulation, adsorption or absorption). These processes influence the overall distribution patterns in the soils and stream sediments.

Webb subsequently pioneered a programme of research into trace elements in the environment in the Applied Geochemistry Research Group (A.G.R.G.), in Imperial College, and the work described in this thesis forms part of a continuous series of investigations arising from that programme.

1-2 Regional Geochemical Reconnaissance:

The systematic sampling of stream sediments to delineate concealed mineral deposits dates from the original work of Goldschmidt

in Scandinavia and Vernadsky in Russia during the 1930's. These workers demonstrated the correlation between the trace element concentrations in soils and vegetation and those in the underlying bedrock. The techniques of stream sediment and water sampling to evaluate the mineral potential of a given area (Hawkes and Webb, 1965) was later modified for use in estimating areas of potential environmental and agricultural problems(Webb, 1964). The technique developed is based on the premise that stream sediment is a composite sample of the clastic and soluble products of weathering and erosion of rocks and soils upstream within a catchment area.

The parent material (rock) contains a reserve of elements found in the derived soils and stream sediments. The relationship between the parent material and the associated soils and stream sediments is however not a direct one. Thus lithological variation in the soil parent material can give rise to contrasting concentrations of elements in the soils and stream sediments. The initial concentrations in the underlying bedrock may be influenced by subsequent covering by drift material; this influence may be less marked if the drift is locally derived and more marked if the drift has been transported over longer distance and possibly derived from a different underlying geological unit.

Frequently, particularly around urban areas, the natural element concentrations may be influenced by pollution which may be of agricultural, mining or industrial origin. The initial metal concentrations may be further influenced by the physical and chemical characteristics of the local environment. The local topography, for instance, may determine the rate of flow of the streams and hence the erosional characteristics of the streams. The presence of clays and

organic matter may restrict the mobility of elements by adsorption. The local chemical environment can also influence the overall trace element pattern. The Eh/pH of the aqueous environment is a dominant factor in determining the mobilisation or the precipitation of elements in streams. The hydrous oxides of Fe and Mn can cause the precipitation of many elements including Co, Zn and Ni. The complex relationships between the unweathered parent materials and the associated soils and stream sediments necessitates that interpretaion of stream sediment anomalies takes into account the local weathering patterns the secondary environmental characteristics, the nature of the parent material and the climate.

1-3 Background To Re search.

The use of regional geochemical techniques in helping to solve environmental and agricultural problems has been the object of many investigations in recent decades, particularly since the development of more rapid and reliable analytical techniques. Pioneer work in Great Britain has demonstrated that certain deficiency and toxicity diseases may be localised in certain regions, for example, the occurrence of molybdenum induced copper deficiency in cattle in Somerset (Ferguson et al. 1943) and the incidence of selenosis in Ireland (Fleming 1962). Fleming (1962) showed that the incidence of selenosis was related to the distribution of seleniferous vegetation which in turn was related to high selenium in the soils. This was confirmed by Webb and Atkinson (1965) who showed that the seleniferous soils were derived from marine black shales that had high concentrations of selenium.

The term "Biogeochemistry" was introduced by the Russian geochemist Vernadsky (1926) to describe the study of the relationships

between the chemical composition of plants, animals and the geochemistry of the environment. The original interpretation has been broadened by Hutchinson(1954), Bass-Becking et.al. (1960) and Vinogradov(1963) to mean the interaction between the biosphere on one hand and the atmosphere, lithosphere and hydrosphere on the other. Vinogradov (1963) extended the concept to define "Biogeochemical Provinces" in terms of regions of the earth characterised by their trace element content which may be related to certain endemic disorders (toxicity and deficiency) in the local flora and fauna. Further work in this field has been aimed at the interpretation of geochemical maps in terms of influence of the parent material and secondary environment, and the use of these geochemical maps to delineate areas of potentially toxic or deficient levels of trace elements (Webb 1964).

In Eire, low levels of Co in stream sediments in the counties of Wicklow and Carlow defined an area of high incidence of cobalt pine, a cobalt deficiency desease in sheep (Webb 1964). The area was found to contain a granite outcrop of low Co status. In county Limerick, stream sediment data revealed an association between Mo and Se in areas underlain by Namurian shales in which a high incidence of molybdenum induced copper deficiency and selenium toxicity in livestock were found . Webb et. al. (1966) demonstrated that in the Midlands, North Wales and South-West England, anomalous concentrations of Mo and Se in the stream sediments were related to soils that contained moderately anomalous concentrations of these elements. The source of these anomalous concentrations was shown to be certain marine black shale facies of the Lower Carboniferous in Staffordshire and Devon, and the Ordovician in North Wales. The results were also

consistent with the occurrence of bovine hypocuprosis in cattle grazing pasture in the Mo anomalous regions in North Wales.

In the A.G.R.G. in Imperial College, Thornton (1968) studied the inter-relationships of metal concentrations in the stream sediment, soil, plant, animal system. He demonstrated the correlation between the incidence of certain trace element induced diseases in livestock and the metal concentration in the surface drainage. Horsnail (1968) and Fletcher (1968) demonstrated the relationship between element concentrations in stream sediment, soils, underlying geology and related these to the incidence of trace element disorders in livestock and crops. Thomson (1971) showed that anomalously high levels of Mo coincided with outcrops of marine black shale. Later workers in A.G.R.G. have looked more closely at the interpretational problems encountered in the soil, stream sediment and rock relationships. Keeley (1973) investigated those environmental factors that caused soil concentrations of Co, Cu and Mn to bear little relationship to the stream sediment values. Wood (1975) investigated the variation in texture and composition of soils and stream sediments mainly derived from sandstones. Jordan (1975) looked more closely at the elements Cu and Mg and related the stream sediment, total soil, and extractable soil trace element concentrations to crop yields. Sanders (1977) investigated factors affecting the distribution of trace elements within selected soils in England and Wales.

1-4 Object Of The Present Investigation.

Previous studies have related the trace element concentrations in the stream sediments to the geology, soil type and incidence of trace element disorders. The Wolfson Geochemical Atlas

of England and Wales (1979) now makes it possible to delineate areas of potential trace element disorders in England and Wales. The present investigations set out to explore multi-element patterns in rocks, soils and stream sediments under contrasting geology and various secondary environments with the aim of exploring whether the multi-element associations evident in the stream sediments were still reflected in the soils and rocks from which they were derived. It is hoped to demonstrate that stream sediment reconnaissance technique, in addition to its use in mineral exploration and epidemiological studies is an efficient and useful means of obtaining information about element associations of geological and agricultural value in those parts of the world where the lack of resources impede extensive geological and agricultural investigations.

1-5 Presentation of the thesis:

The thesis is presented in four sections. The first section provides the introduction and background to the investigation with reviews of the range of concentrations of elements commonly found in rocks, soils and stream sediments. The methods employed in the research are also discussed in this section. The preliminary investigations in seven study areas are presented as one chapter per study area in Section 2, while in Section 3, detailed investigations in three selected areas are discussed. Finally, in Section 4, a general summary and conclusions of this study are presented.

CHAPTER 2

The concentrations and distributions of elements in different media.

2-1 Trace element distribution in rocks, soils and stream sediments:

The distribution of trace elements in igneous rocks and primary minerals are well understood, based on the principles laid down by Goldschmidt(1954) and confirmed by a number of later workers (Mason 1952; Wager and Mitchell, 1951). The chemical affinity of an element determines the rock type in which the element is concentrated, while the ionic radius governs its position in the mineral structure. The concentrations of the elements Ni, Fe, Mn, Cu and Zn tend to be enhanced in the early crystallising ultrabasic and basic rocks such as gabbro and basalts, and less concentrated in the later crystallising acidic rocks such as andesites and granites. The similarity of ionic radii may result in chemically unrelated elements occupying similar structural positions in a mineral as a result of isomorphous substitutions eg, Mg, Zn and Al in micas, and K, Ba and Pb in feldspars.

In sedimentary rocks, physico-chemical and colloidal factors are the dominant features governing the distribution and associations of elements, although isomorphous replacements may also be important. Redox potentials and ionic potential (charge/radius ratio) determines whether an element will behave as a cation and whether it will remain in solution or be precipitated. In general, trace elements tend to be more enriched in argillaceous rocks than in the arenaceous equivalents.

Processes concerned with rock weathering are mechanical, chemical and biological. Physical weathering breaks down rock material into smaller fractions to facilitate the release of minerals. Chemical weathering results in the solution and degradation of primary minerals and when the conditions are right may lead to the synthesis of new secondary minerals, such as the clay minerals. Biological influences are additional and often crucial factor in rock weathering and involve a combination of both mechanical and chemical weathering processes. Plant roots can physically split rock material, while organic acids produced by decaying plant material and carbon dioxide resulting from respiration, are powerful agents of chemical weathering. In general, minerals have varying degrees of resistance to weathering, simple salts like gypsum are lost more easily than the more resistant minerals such as quartz and rutile. The end products of weathering are:-

(a) resistant residues,

(b) weathering solutions,

(c) alteration and synthesised minerals.

The resistant residue include minerals such as quartz, zircon, rutile and magnetite which alter only very slowly particularly in the finely divided state. The weathering solutions contain basic cations with some Fe, Al and silicate ions, all of which are lost or redistributed in the soil and the drainage system. Alteration and synthesised products are principally the oxides and hydrous oxides of Fe, Al and Mn, as well as silica and the clay minerals. The various insoluble fractions constitute the regolith from which soils are formed. In the soils, trace elements released by weathering are held in one of the following fractions:

(a) adsorbed by organic matter or clay minerals,

(b) held within mineral structure such as clays,

(c) incorporated into carbonate minerals,

(d) remain in solution.

The degree of mobility of cations in the pedogenic environment is largely determined by the extent to which they are associated with these fractions and the buffering effects of soil solution which control the release of these fractions into the soil. These processes are largely influenced by the pH and Eh of the medium. Clay minerals and organic matter both possess negatively charged surfaces which are capable of adsorbing cations to varying degrees. Under suitable conditions, the clay minerals and organic matter can form organo-clay complexes by ligand exchange and polyvalent bonding. Isomorphous substituion of cations within the structure of the clay minerals is also a common feature in soil. Together, these fractions account for a significant proportion of the binding power of soil for trace elements.

The incorporation of trace elements into new minerals is essentially a secondary process in soils and stream sediments. For instance, the mobility of such elements as Cu, Zn and Pb may be restricted by the formation of secondary carbonates, while the sorption of cations by Mn and Fe oxide minerals is common and well documented (Jenne, 1968; McClaren and Crawford, 1973). Aluminium hydrous oxides may also be important.

The redistribution of elements within the soil and subsequently into the streams and rivers depends on two factors:

(a) drainage status of the soils, and,

(b) mobility of the elements.

Five classes of drainage can be recognised (Table 2-1). The ease of redistribution of elements is influenced by the drainage. Leaching and translocation also play an important role in the redistribution of elements. The principal types of translocation are :-

(a) translocation in solution,

(b) translocation in suspension,

(c) translocation due to organic activity.

Translocation in solution is accomplished by migration of soil solutions containing dissolved solutes, in response to gravity or capillary forces by moving vertically down through the soil to underground waters and ultimately to the surface drainage. As the solution moves some of the materials such as compounds of Fe, Al and Mn may be precipitated while the soluble materials such as the bicarbonates, sulphates and nitrates are lost. Swindale and Jackson (1956) have shown that in soils, where humus tends to accumulate in the surface, the movement of Al and Fe compounds is greatly accelerated. This is a result of cheluviation, a process in which organo-mineral complexes are leached down the profile. On the slopes there may be lateral movement of solution through the soils. Soluble materials are transferred laterally to enrich soils in the lower part of the slope.

Translocation in suspension involves the movement of small colloidal-sized particles from the upper horizons to the lower horizons or the redistribution of these particles between neighbouring sites. Such a process is purely mechanical.

The principal organism responsible for the movement of solid materials in the soils is the earthworm, although in tropical climates termites may be important. Many other smaller fauna may also play an

TABLE 2:1

DRAINAGE CLASSES

CLASS	PHYSICAL CHARACTERISTICS	CHEMICAL CHARACTERISTICS
EXCESSIVE	Water moves rapidly through soils unimpeded.	Bright coloured due to oxidising conditions that prevails, organic matter rapidly oxidises.
FREE	Water moves steadily with little tendency to be waterlogged.	Bright coloured due to oxidising conditions.
IMPERFECT	Moist all year often due to impermeable horizon or high precipitation.	Reducing conditions results in mottling by the reduction of ferric to ferrous state.
POOR	Wet for long periods with the tendency to be waterlogged.	Slow decomposition of organic matter. Weak organic acids are formed which dissolve sesquioxides.
VERY POOR	Saturated all year round.	Blue or grey in colour with reducing conditions dominant.

important role.

2-2 Biogeochemistry of selected trace elements.

The knowledge that certain trace elements are involved in the aetiology of certain deficiency, toxicity and malignant diseases, combined with the fact that concentrations of trace elements in soils, water supplies, plants and foodstuff are primarily derived from the parent material(rock) means that it is not unreasonable to ask if there is a particular geological formation or soil type that predisposes to certain diseases? To answer this question it is important to know the mode of occurrence and associations of these elements in the different media. In this section the distribution and mode of occurrence of selected trace elements of biological importance in the rocks, soils and stream sediments will be reviewed.

(a) Manganese:

All the rocks of the earth's crust contain Mn in concentrations generally much higher than other trace elements, being in the main, higher in basaltic and gabbroic rocks and widely varying in acidic igneous, metamorphic and sedimentary rocks. During weathering, Mn tends to separate as discreet higher valent Mn-oxide in soils. In streams where oxidising conditions tend to prevail Mn-oxides are often deposited on clays, organic matter fragments, gravels and on pebbles as coatings and nodules (Tiller, 1963; Taylor et al. 1964). The most common mineralogical forms are lithiophorite and birnessite, although the minerals hollandite, todorokite and pyrolusite have also been identified in soils (Taylor et al. 1964).

The ability of Mn oxide minerals to adsorb other trace

elements has been noted by a number of workers (Jenne, 1968; McKenzie, 1971), and despite their varied forms, the chemistry of these minerals are similar particularly in their higher content of other divalent cations such as Co and Ni. The solubility of Mn oxides in soils and stream sediments are dependent on the Eh/pH of the environment. Under acidic or waterlogged conditions the leaching of Mn oxides is an intense process(Blume and Schwertmann,1969). This is due to the reduction of the quadrivalent ion Mn^{4+} to the more soluble and mobile divalent cation.

Manganese is very important for the adequate testicular and ovarian development and function in rats (Lee,1975). It has been shown to be important in preventing poultry perosis(slipped tendon), and in Holland, Mn deficiency has been implicated in the loss of productivity in cattle (Lee,1975). Egan (1972) has provided evidence that Mn supplements in diets have sometimes led to increase in the number of lambs born to a flock of Dorset Horn ewes.

(b) Cobalt:

The average content of Co in the lithosphere is about 30ppm (Vinogradov, 1959; Turekian and Wedepohl, 1961). The highest concentrations occur in ultrabasic igneous rocks (dunites, peridotites) and the products of their metamorphism (serpentinites). The lowest concentrations occur in arenaceous sedimentary rocks, particularly coarse sands. In general, Co substitutes for Fe in ferromagnesian minerals. During weathering differentiation of Co is not common since the simple trivalent ion is unstable.

Cobalt deficiency occurs in ruminants where it results in cobalt "pine" disease, characterised by retarded growth and deficiency

of vitamin B 12 (Underwood,1971). This condition results in loss of appetite and ultimately, death.

(c) Iron:

In rocks Fe occurs in both the ferrous and ferric states in Fe bearing minerals as well as replacing Mg and Al in other minerals. Iron released from these minerals during weathering is retained in the soils mainly as amorphous hydrous ferric oxides, goethites(FeOOH) or haematites (Fe_3O_4). The more widely distributed goethites is crystalline with a reddish colour which changes to brown when hydrated. Pedological processes such as gleying, profoundly affect the state of Fe hence its mobility. Under acid and waterlogged conditions the mineral lepidocrocite tends to develop. As with Mn the higher valent states tend to be precipitated particularly in the oxidising environment of a stream bed. The studies of Taylor et al. (1964) have shown that in nodules collected from soils the Fe and Mn oxides exist as separate phases and that the Fe content of Mn minerals is not very high. Brewer et al. (1973) confirmed that the two elements usually segregate into separate phases. The presence of organic matter often accelerates the reduction of Fe ions (Tisdale and Neilson,1966). Other Fe minerals such as chromites and garnets resist weathering.

Iron is one of the biologically essential elements. In man Fe is an important component of blood as haemoglobin and transferine. Deficiency of Fe can result in anaemia. In plants both haem and non-haem iron proteins have been identified (Nicholas, 1975). These are involved in key metabolic activity such as nitrogen fixation, photosynthesis, respiration, electron transfer and hormone biosynthesis .

(d) Nickel:

The average Ni concentration in the lithosphere is about 100ppm (Vinogradov,1959; Turekian and Wedepohl,1961), with contents varying with the rock type. Thus Ni contents are higher in ultrabasic rocks than in acidic igneous rocks. In igneous rocks some Ni may occur as sulphides, but most of it like Co is contained in the ferro magnesian minerals where it replaces Fe. During weathering, Ni can combine with dissolved silica to form Ni-rich minerals such as garnierites but more often it replaces Mg in clay minerals. Le Riche and Wier (1963), and Taylor and Mckenzie (1966) have shown that part of Ni in soils may be incoporated into oxides of Fe and Mn.

Growth impairment has not been demonstrated for Ni; however, chicks fed on diets containing less than 0.4ppm of Ni, after four weeks developed increase in skin pigmentation of the legs, swelling of the hooks and thickening of the legs near the joints (Nielsen,1971). Nielsen also demonstrated the relationship between Ni and the two hormones thyroxine and epinephrine (Nielsen, 1971).

(e) Lead:

The average concentrations of Pb in the lithosphere is about 7-10ppm (Vinogradov,1959; Turekian and Wedepohl, 1961), being greater in acidic igneous rocks than in basic rocks. The concentrations in metamorphic and sedimentary rocks are about the same. Lead is commonly found in the primary mineral galena, lead sulphide. In soils Pb is bound tightly by organic matter (Swaine and Mitchell,1960). Vinogradov (1959) pointed out that some soils in the USSR particularly the Grey Forest soils showed an accumulation of Pb in the A horizon. Le Riche and Weir (1963) removed about 60% of the total Pb by extracting free Fe oxides from soils. Jenkins and Davis (1966)

observed a positive correlation between Pb and the loss on ignition in soils.

Lead has been shown to be a renal carcinogen and has been correlated positively with mortality from kidney cancer, leukaemia, stomach and ovarian cancer.

(f) Copper:

The average crustal abundance of Cu is about 100ppm (Vinogradov,1959; Turekian and Wedepohl,1961) with the contents varying according to the rock type. Basic igneous rocks contain more copper than the acidic igneous rocks. The lowest concentrations of Cu are found in arenaceous rocks, while in general the Cu contents of sedimentary and metamorphic rocks are about average. In igneous rocks Cu is present as sulphides and during weathering it tends to form hydroxy compounds and carbonates rather than entering the clay mineral structure, although clay minerals can adsorb it to a limited extent on exchangeable sites. Taylor and Mckenzie (1966) showed that Cu in soils is incorporated into Fe and Mn minerals. He found that Cu was high in soil Mn oxides but that only a small fraction of the total Cu in the soils was in this form. Fried and Broeshart (1967) have shown that Cu may be associated with organic matter in the soil and may accumulate in the surface horizon. Davies et al.(1969) have shown that Cu forms stable complexes with organic matter, and organic matter together with the oxide fraction are the main features of the distribution of Cu.

Anaemia in most mammals and the weakening of oestrus in pigs have been shown to be related to Cu deficiency. Demyelination of the central nervous system is common in lambs of Cu deficient ewe (Lee, 1975).

(g) Zinc:

Zinc in igneous rocks may be present in silicates and sulphides but most is present in silicate minerals. No pure Zn silicates occur, but in resistate minerals such as ilmenite and magnetite, the concentrations of Zn can be high. Taylor and McKenzie (1964) have shown that Zn may also accumulate in the oxide fraction in soils. Part of the Zn in the soils may be fixed by the clay minerals by adsorption or within the structure.

Zinc deficiency occurs in pigs , poultry (O'Dell et al. 1958), cattle (Legg and Sears, 1960) and in humans(Prasad et al. 1963). Underwood and Somes (1969) have shown that this may be initiated by feeding on a purified diet. The noticeable effects are male infertility, retarded growth and skin lesions.

CHAPTER 3

Sampling, Analytical Techniques And Data Analysis.

3-1 Sampling and sample preparations:

The present investigations were conducted in two phases, preliminary and detailed. A total of over two thousand samples of rocks, soils and stream sediments were collected. The sampling strategies used were different in the two phases. In the preliminary investigations the aim was to sample as rapidly and cheaply as possible, as a result most of the localities that were chosen had more than one geological exposure. Sampling of rocks was concentrated at rock exposures, stream banks and road cuttings. Soils developed from individual units were sampled at random. Stream sediments were sampled along the course of the streams which often flowed across contrasting geological beds. Care was taken to avoid contamination and few representative samples were sampled in duplicate. Implements used in the sample collection were trowel, hammer, spade and soil auger. Details of each sample, including identification number, location and field characteristics, were recorded in the field.

In the detailed investigations in addition to the random sampling, ten duplicate samples from preselected sites were collected in each medium. This ensured the hierachical sampling design necessary for the estimation of the variances associated with each level described in Section 3-4.

(a) Rock.

Grab and chip samples were collected from suitable exposures by chip sampling from stream banks, quarries and road cuttings. Representative samples of the lithologies present were sought. In areas where rock exposures were rare, the soil auger was used to obtain fresh rock samples from depths of >1.2m. The rock samples were dried and crushed to a minus 10 mesh size using the tungsten-carbide mortar. This was then coned and quartered to yield about 15gm of material which was further ground to minus 80 mesh size using a Tema agate mill.

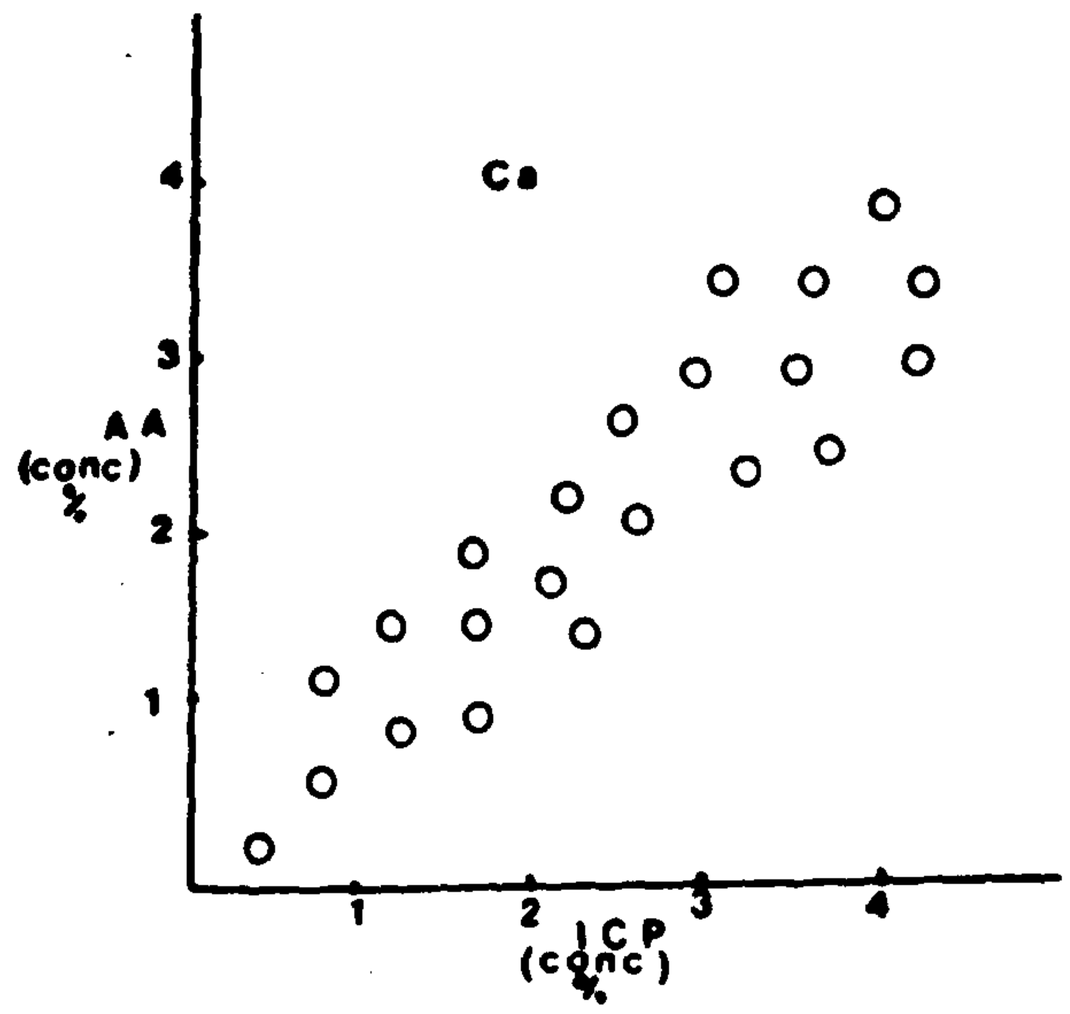
(b) Soils:

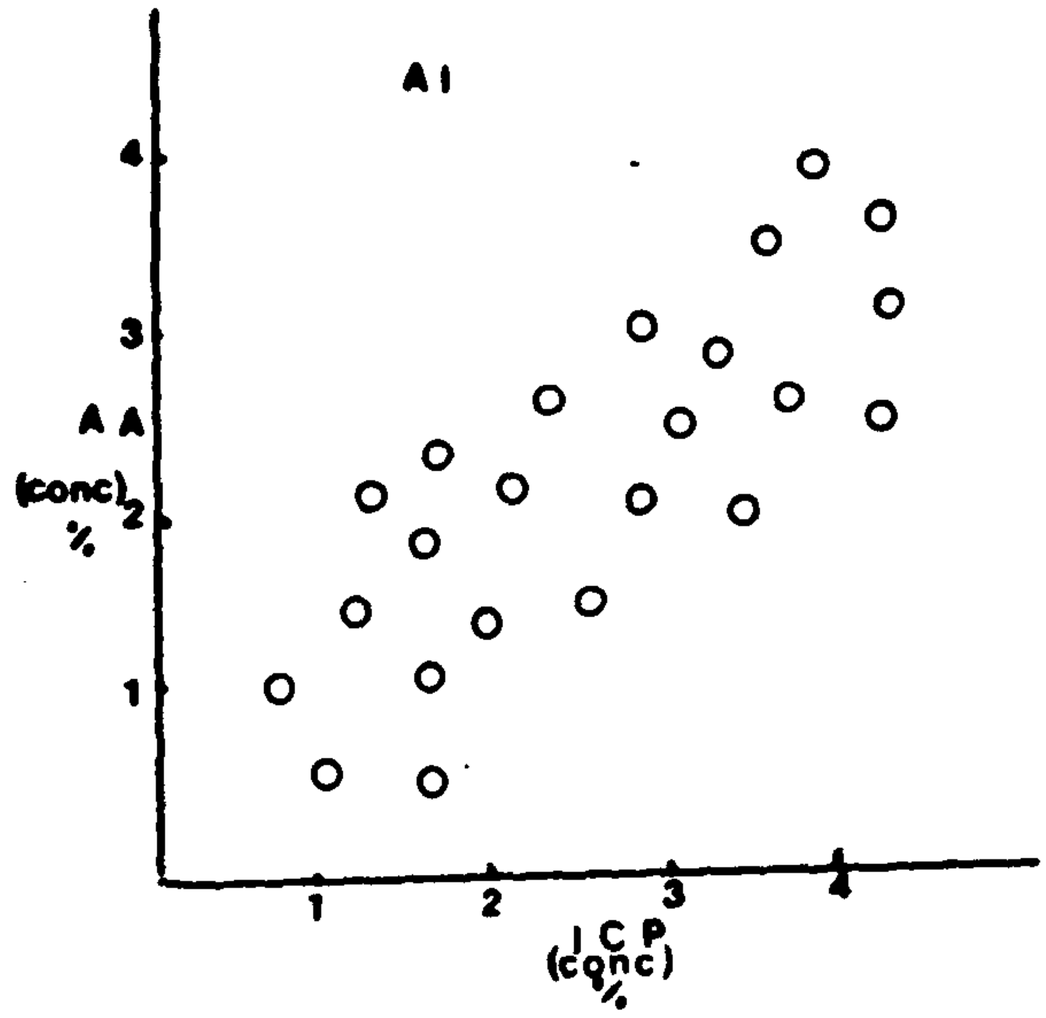
Soil samples were generally obtained using a one inch diameter screw auger. Topsoil samples were obtained from depths of 0 to 15cm, and subsoil samples from depths of 30 to 45cm. Each sample consisted of five cores taken from the corners of a square of 10m side together with one from the centre. Ordnance survey maps (at the scale of 2½ : 1mile) and soil survey maps (where available) were used to locate the site and soil series sampled. Each sample was placed in a "Kraft" paper bag in the field. In the laboratory samples were dried at 60 C and sieved through a 2mm sieve after a slight disaggregation. This was then coned and quartered into about 15gm a quarter and further sieved to pass through a minus 80 mesh sieve.

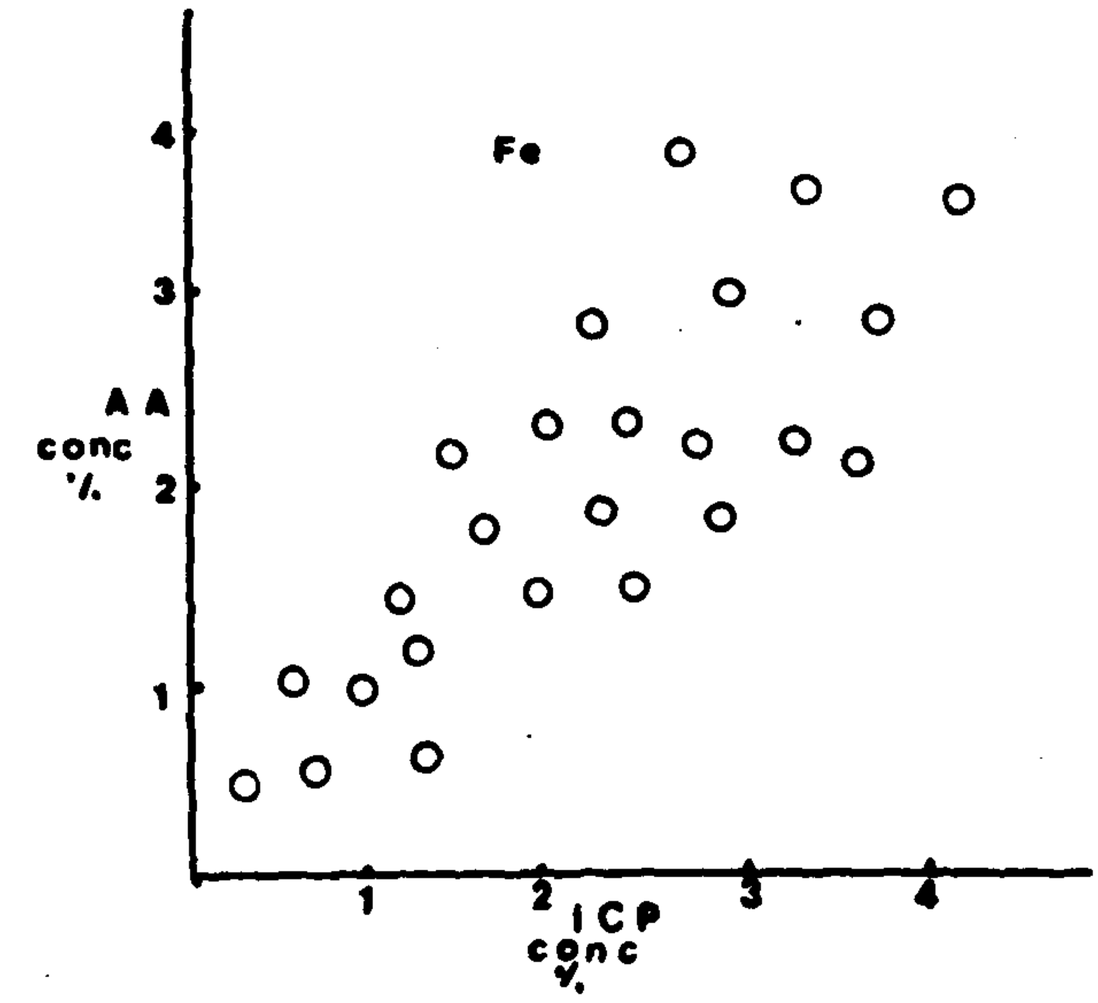
(c) Stream sediments:

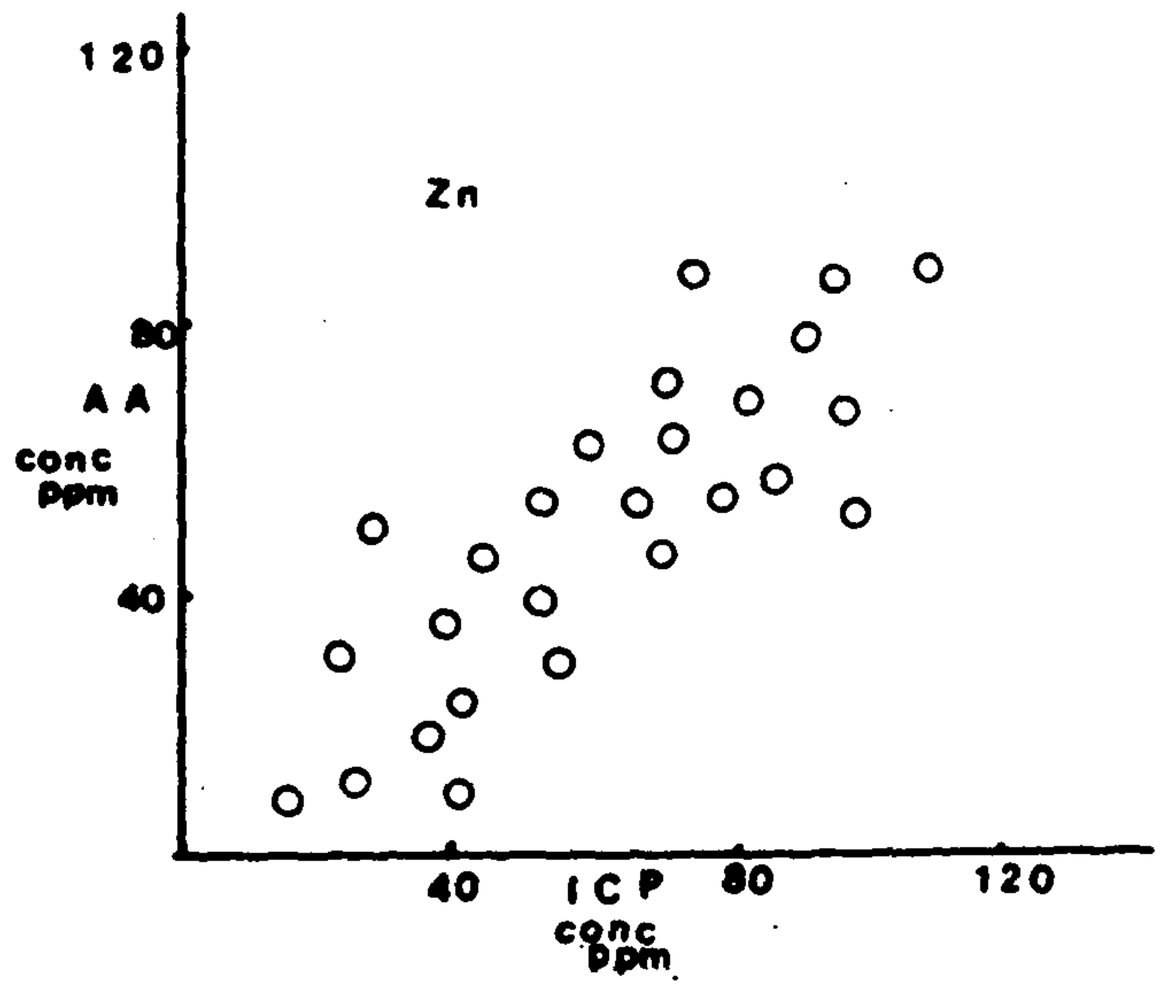
Active stream sediments were collected upstream at road/stream junctions, often with a trowel, and placed in "Kraft" bags. They were dried overnight at about 60° C and disaggregated with a porcelain mortar to pass through a minus 80 mesh sieve.

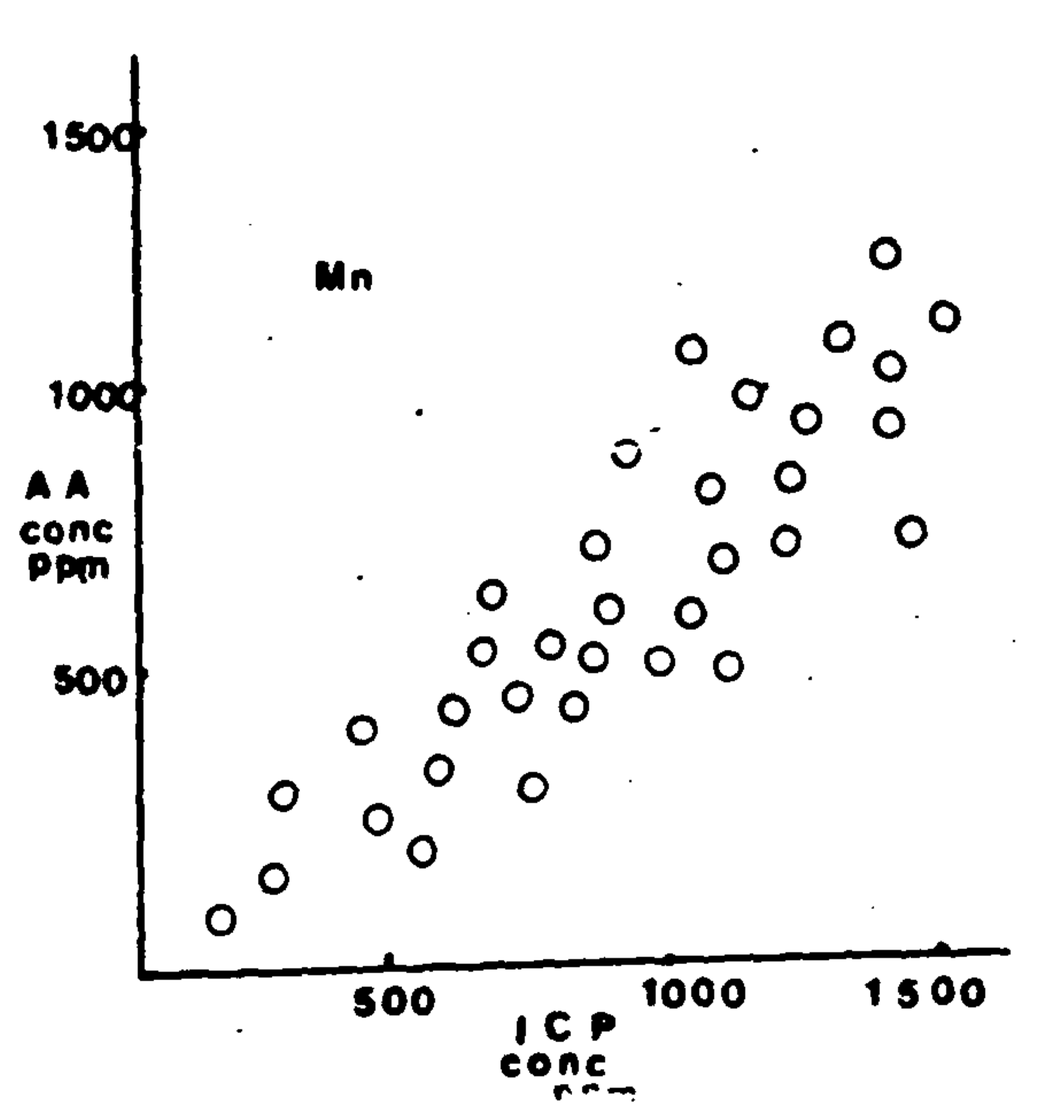
Fig. 3-1 Comparison between Atomic Absorption Spectroscopy and Inductively Coupled Plasma Emission Spectroscopy (Analysis of same samples, Nitric/Perchloric Acid DIGESTION)

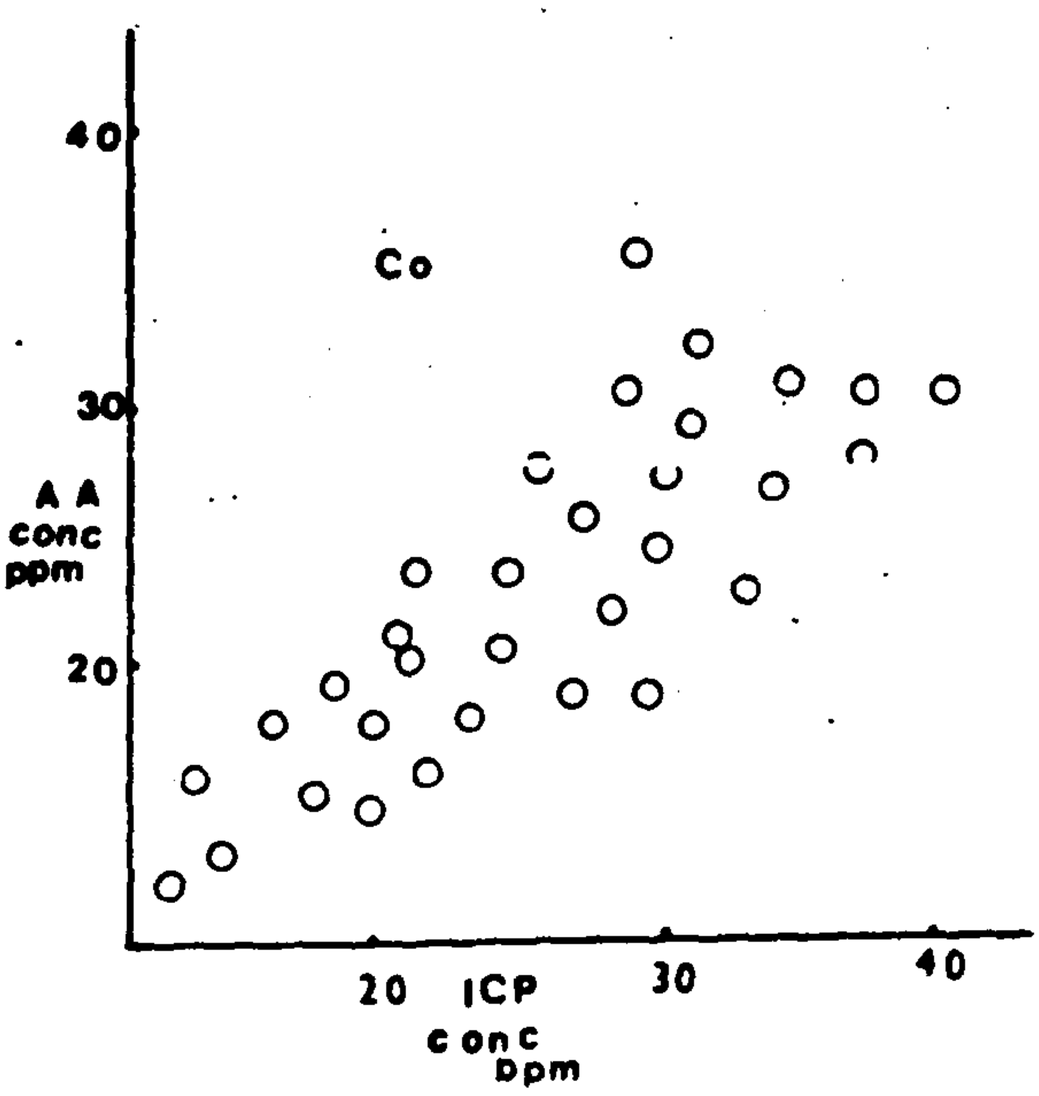












3-2 Analysis of samples:

(a) Sample digestion.

Two methods were employed in the sample digestion. These were:-

(i) Nitric acid digestion.

(ii) Nitric/perchloric acid digestion.

No significant differences were observed between the two methods in the extraction of the elements determined .

(i) Nitric acid digestion.

0.250gm of the minus 80 fraction was digested with 2ml of conc. HNO at a temperature of 80-90° C for one hour. The solution was then made up to 10ml with de-ionised water and mixed thoroughly. This was then analysed directly using the atomic absorption spectroscopic method and the inductively coupled plasma.

(ii) Nitric/perchloric acid digestion:

0.250gm of the minus 80 mesh fraction was digested with 5ml of a 4:1 mixture of conc. HNO_3 and $HCLO_4$ in test tubes heated in an aluminium block. The mixture was taken to dryness and heated with 2ml of 6M HCL in an air bath. The solution was made up to 10ml with deionised water, mixed and left to settle overnight.

(b) Instrumentation:

Elements were analysed using either the Atomic Absorption Spectrometer (AA) or the Inductively Coupled Plasma Emission Spectrometer (ICP). Figure 3-1 shows the relationship between the two methods.

(i) Atomic Absorption Spectroscopic Method (AA):

The instruments employed for AA analysis were a Perkin-Elmer 403 and a Pye Unican SP 90. After the lamp current, slit, burner and fuel flow have been set for a particular element (Table 3-1), the correct wavelength was obtained and the instrument calibrated with standards made up in 1M HCL. Ten elements were determined; Ca, Mg, Al, Fe, Zn, Mn, Co, Pb, Ni and Cu. The results were measured in micrograms per ml on the digital readout on the Perkin-Elmer 403. A correction for Ca interference was made for the elements Zn, Co, Pb, Ni and Cu and the results multiplied by the dilution factor which in the present investigation was 40x.

(ii) Inductively Coupled Plasma Emission Spectroscopic Method:

The system has been described by Greenfield et. al. (1975 a, b). The technique employs a stream of ionised argon gas as an excitation source prior to the determination of elements. Digestion methods employed were similar to those used for the AA.

(c) pH:

2g sample of the minus 2mm fraction of argillaceous rocks, soils and stream sediments were flocculated with 5ml of 0.01M $CaCl_2$ solution (Schofield and Taylor, 1955). The solution was thoroughly mixed and shaken intermittently and allowed to equilibrate for 10 minutes before measurements were taken using a pH meter and glass electrode.

(d) Loss on ignition (LOI):

The loss on ignition technique was used to assess the organic matter content of rocks, soils and stream sediments (Ball, 1964;

Table 3-1

ANALYTICAL PARAMETERS FOR ATOMIC ABSORPTION SPECTROPHOTOMETRY

Element	Wavelength nm	Sensitivity mg ml-1	Detection Limit mg ml-1
Ca	42270	±0.15	
Co	24070	0.45	±0.07
Cu	32480	0.15	0.01
Fe	37190, 24870	0.50	0.05
Mn	27950, 20150	0.10	0.05
Pb	28330	0.50	0.24
Zn	21380	0.06	0.02

Data were obtained from Miss Maktia and members of the Applied Geochemistry Research Group

Davies et. al., 1969). 2gm of minus 80 mesh size fraction was dried in a dessicator, weighed and ignited at 450° C overnight in a muffle furnace. The samples were cooled in a dessicator and reweighed. The difference in the weight was used to calculate the percent loss on ignition.

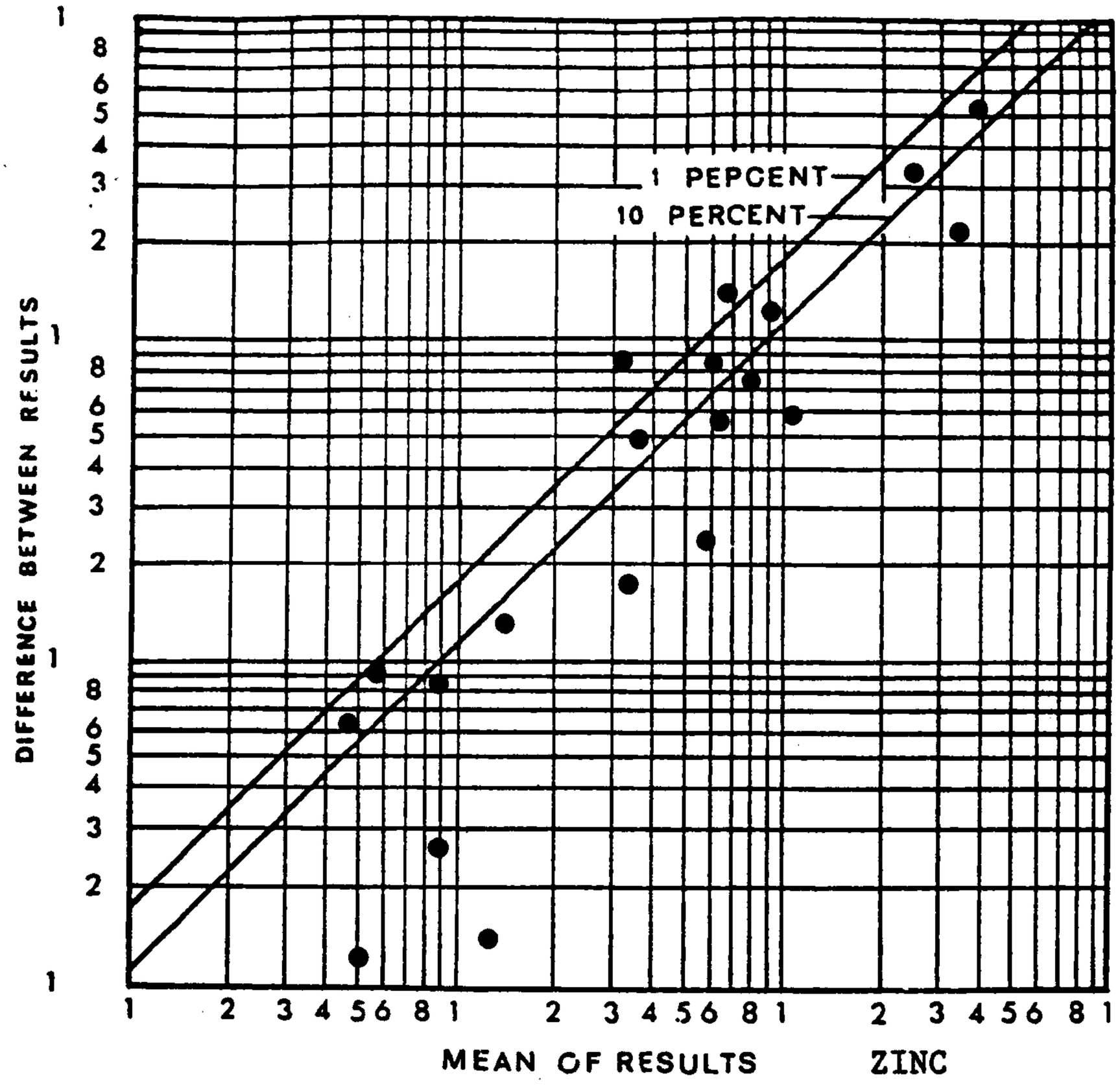
3-3 Analytical quality control:

Generally, analytical results can be influenced by a number of procedural errors resulting in overall lack of accuracy. The precision of the data is the reproducibility of the sub-sampling and analytical methods used. Analysis of samples was done in batches of between 50 and 200 and reproducibility of the analytical results was monitored by the repeated analysis of natural standards chosen to cover the range of most of the elements analysed, usually placed at intervals of ten samples. Replicate analysis of samples within batches were also monitored. The analytical precision of the natural standards was expressed in terms of the coefficient of variation (Table 3-2).

Table 3-2

Coefficient of variation of natural standards(total nitric/perchloric acid digestion).

Standard	N	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu
AA590	30	8.2	4.3	2.2	7.6	9.0	7.6	11.2	17.8	12.1	5.0
AA644	25	9.2	3.3	6.3	5.3	7.3	8.1	15.6	18.2	10.0	4.0
AA154	30	9.5	2.9	7.3	3.6	9.2	10.2	9.0	13.4	8.2	6.9
AA560	20	9.0	3.7	2.1	7.2	6.2	8.1	19.0	20.0	9.0	3.1



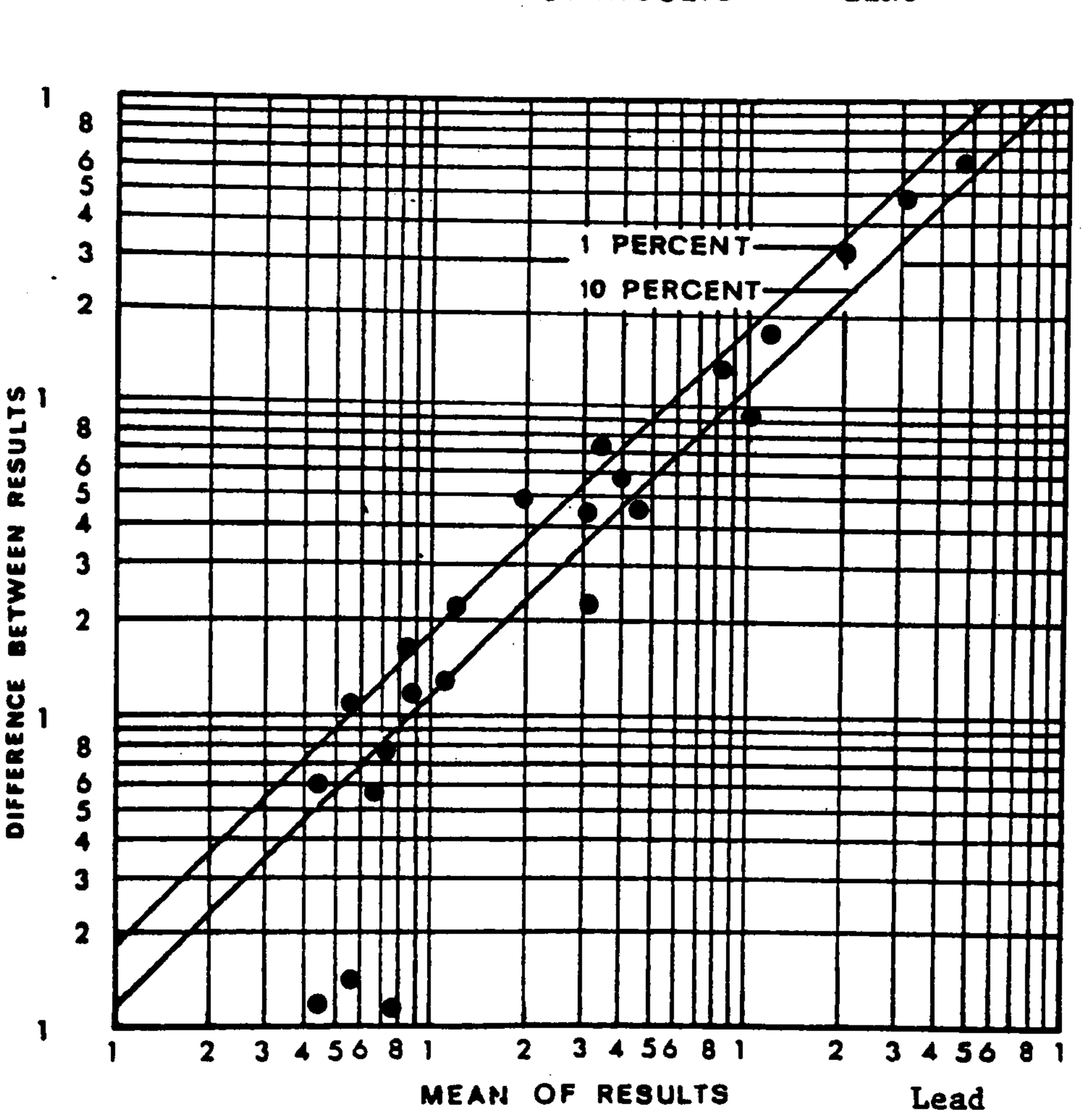


Fig. 3-2

PRECISION CONTROL CHART FOR DUPLICATE RESULTS

In a set of duplicate measurements on many samples where for each sample the precision of measurement is 10 per cent at the 95 per cent confidence limit (i.e. $\sigma/\mu = 0.05$) the indicated proportion of points will fall above the diagonals. The scale of the means must be 10 times greater than the scale of the differences.

The precision was generally reasonable. Errors arose from sub-sampling, instrumental instability and lack of sensitivity for certain elements at low concentrations (eg. Pb, Ni). A within batch precision of 10% at 95% confidence level was sought. This was done by plotting the differences between the replicate analysis of samples against the mean of the results (Fig. 3-2).

The accuracy of a set of data is an estimate of how far the determined values deviate from the true values. The most important sources of error are the contamination of a batch of samples during preparation, instrument drift and interference. An estimate of the likely true value can be obtained by a comparison of two independent methods. In the present investigations the AA and the ICP methods have been compared. The results are presented in Fig 3-1.

Contamination of samples was monitored by analysis of blank solutions of deionised water processed by similar digestion methods as the samples within a batch. In general the blank solutions yielded a constant value of < 0.5mg/ml for Zn , while Fe yielded sporadic levels of 1 - 2mg/ml. For the rest of the elements analysed contamination was not observed. The persistent Zn contamination was thought to be introduced from the deionised water, while Fe may be due to contamination from the glass materials used.

3-4 Statistical analysis of data:

The summary statistics (Appendix 1), and in the case of the detailed investigation the frequency distribution were determined for each element in each medium. The correlation matrix was calculated for each pair of constituents after making a log transformation (Ahrens, 1954). Multi-element associations were determined by factor analysis of each correlation matrix. The use of multivariate

statistics to discern element groupings offered an indirect means of identifying associations. The problem of spurious results and dilution (Chapman, 1976) which may impose significant correlations of no geochemical significance was investigated by a close examination of each data set for "wild" results, and such results were either removed from the calculations or, where appropriate, meaningful geochemical explanations sought.

(a) Factor analysis technique:

The aim of factor analysis is to simplify a multi-dimensional set of variables eg. a p-variate system with n individuals (p x n matrix) by expressing the total variance of the set by a reduced number of variables or factors. The technique assumes that each variable, x, can be expressed in the form

$$x = a_{i1} f_1 + a_{i2} f_2 + \ldots\ldots\ldots\ldots a_{im} f_m + au_i$$

where f is common factor present in each variable

ai indicates the relative importance of the common factor

ui is the unique factor peculiar to a variable.

Factor analysis proceeds either by examining the relationships between variables (R-mode), or between samples (Q-mode). Dimensional reduction is carried out by an orthogonal coordinate scheme in which uncorrelated principal components provide a reference axis for the variables which become vectors in space of a dimension determined by the number of axes (factors) extracted. The proportion of the overall magnitude or variability contained in each factor is expressed by the eigenvalues.

The initial factor matrix is obtained from a product of the

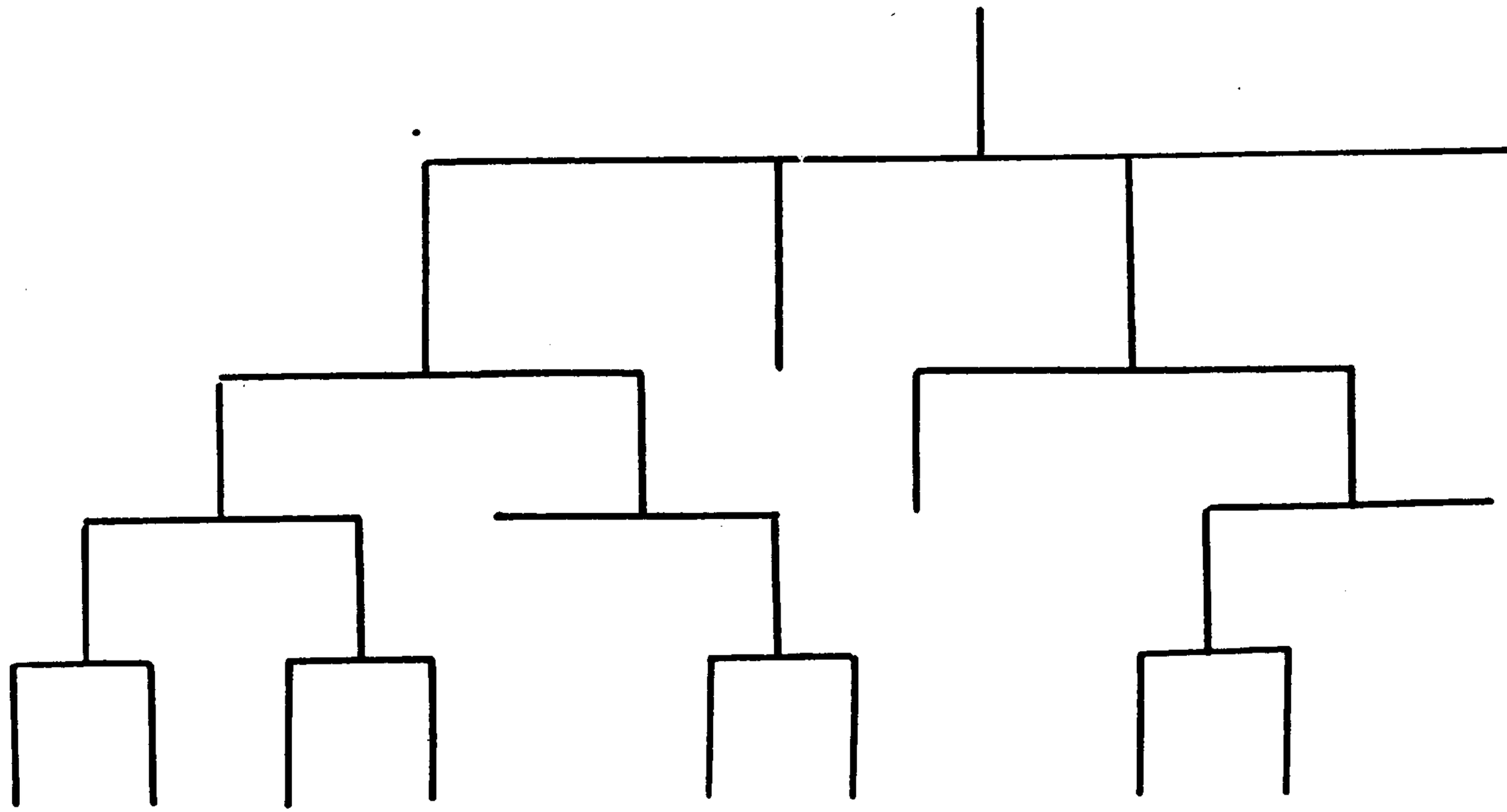
eigenvectors of the correlation matrix and the square root of the eigenvalue. In order to obtain a true factor analytic solution one needs to have a prior knowledge of the proportion of the total variability accounted for by the common factors on the one hand and the unique factor on the other. Since one does not have a means to know this figure in geological situations it is preferable to use the mathematically exact principal components solution to obtain an initial set of uncorrelated linear transforms of the original variables rather than the arbitrary factor solutions. For example p-principal components are required to account for the total variation of inherent in the original data set. However, truncation of the principal component solution after the first k- components is commonly regarded as the best approach to the ideal factor analytic solution.

Various criteria have been proposed ($1>\lambda$, scree plot, etc.), but subjetctive interpretation of the meaning of the derived element associations is generally agreed to be satisfactory (Howarth,1979). This may be combined with the percentage of the total variability accounted for, together with consideration of those components which have multiple as opposed to single element associations. The factor loadings which can be regarded as a combination between the elements and the new linear combinations of elements, are more interpretable by rotating the original principal component solution using the Kaiser's varimax criterion(Kaiser, 1958) so that the magnitude of the loadings tend towards 0 or +1 or -1. This heightens the contrast between significant and less significant loadings. The varimax rotated, truncated principal components is hereafter referred to as the "factor analysis solution".

FIG. 3-3

Hierarchical Scheme for the Three Level Nested Analysis of Variance
(Based on Webster 1977)

Number of Divisons	Stage	Comparisons	F ratio
4	Media	Between Media	F1
10 per medium	Sites	Between Sites within Medium	F2
2 per site	Sample	Between Samples within sites	F3
2 per sample	Analysis	Between Analysis	



(b) Analysis of variance technique:

If a population is divided into several classes and these are in turn divided into smaller classes a "nested" or a hierarchical classification results. The important point in such a multi-level classification is that the smaller groups occur within bigger groups. The sampling design adopted in order to compute the analysis of variance in the present studies followed such a nested design (Krumbein and Slack, 1956; Tourtelot and Miesch, 1975). Ten sites were chosen from four media, rock, topsoil, subsoil and stream sediments. Duplicate samples were collected from each site and each sample was analysed in duplicate. The design is shown in Fig 3-3.

The aim of the technique is to separate the total variance into its components or sources; hence in the model used the aim was to estimate the variances associated with each level in the hierarchical design. The mathematical computations employed are shown in Appendix 2. Various models of the technique can be constructed, for example, the equivalency of Cu determinations in samples collected from different media can be calculated by the one way analysis of variance. The null hypothesis would be

$H_o = {}_{Cu}\mu_1 = {}_{Cu}\mu_2 \ldots\ldots {}_{Cu}\mu_m$ where ${}_{Cu}\mu$ = mean of Cu in a medium

$H_1 \neq {}_{Cu}\mu_1 \neq {}_{Cu}\mu_2 \ldots\ldots {}_{Cu}\mu_m$

In the hierarchical scheme adopted in the present investigations the two way analysis of variance can be used to determine differences in the metal concentrations between sites within a medium (Fig 3-3). The present investigations utilised the three level nested analysis of variance model (Chork, 1977) on the log transformed data. The null hypothesis was given by

$$H_c^1 : \sigma_A^2 = 0$$
$$H_c^2 : \sigma_{B(A)}^2 = 0$$
$$H_c^3 : \sigma_{C(AB)}^2 = 0$$

The appropriate analysis of variance model is given by

$$Y_{ijkl} = \mu + A_i + B_{i(j)} + C_{k(ij)} + E_{i(ijk)}$$

where

i= medium;i=1,2,3,4

j= site;j=1.....10

k= sample;k=1,2

l= analysis;l=1,2.

Thus the Yijkl is the metal concentration in the l analysis of the k sample from the j site in the i medium. The calculations were calculated by the computer programme BANOVA (Chork, Imperial College).

(c) Data Storage:-

The storage of data was adapted from the scheme outlined by Rudeforth (1975). The type of medium ie. rocks, topsoils, subsoils and stream sediments were represented by numbers such as 1, 2, 3, and 4 respectively, and the drainage class was represented by numbers such as 1, 2, 3, 4, and 5 denoting excessive, free, imperfect, poor and very poor drainage. Lithology and texture of rocks and soils were similarly represented by numbers. With this scheme the following data on each sample were punched in fixed format on 80-column Hollerith cards; site number, grid reference, type of sample (rock, soils, and stream sediments), drainage, element concentrations (in mg/ml), pH and loss on ignition. The data were processed on the C.D.C. Cyber 174 Computer using standard packages (Minitab and ISIS) provided by the Imperial college computer advisory unit. Programs for the analysis of variance and factor analysis were provided by the A.G.R.G.

SECTION 2

Introduction To Preliminary Investigations.

The aim of the present investigation is to establish on a preliminary basis the concentration ranges of the elements Ca,Mg,Fe, Zn,Pb,Cu,Co and Mn in various lithological units in England and Wales as a basis of comparison with those in the associated residual soils and stream sediment derived from them. Rock, topsoil, subsoil and stream sediment derived from a range of lithologies were sampled from the following study areas:-

(a) Lincolnshire- Chalk,Kimmeridge Clay,Lower Greensand.

(b) Wiltshire- Corallian Limestone, Kimmeridge Clay, Upper Greensand

(c) Worcestershire- Keuper Marl and Lower Lias

(d) Herefordshire- Old Red Sandstone

(e) Somerset- Keuper Marl and Lower Lias

(f) North Wales- Silurian Mudstone and Dinantian Limestone

(g) Surrey- Lower Greensand.

In areas where rock exposures were sparse, particularly in the clay dominated terrain, rock samples were obtained from the same locations

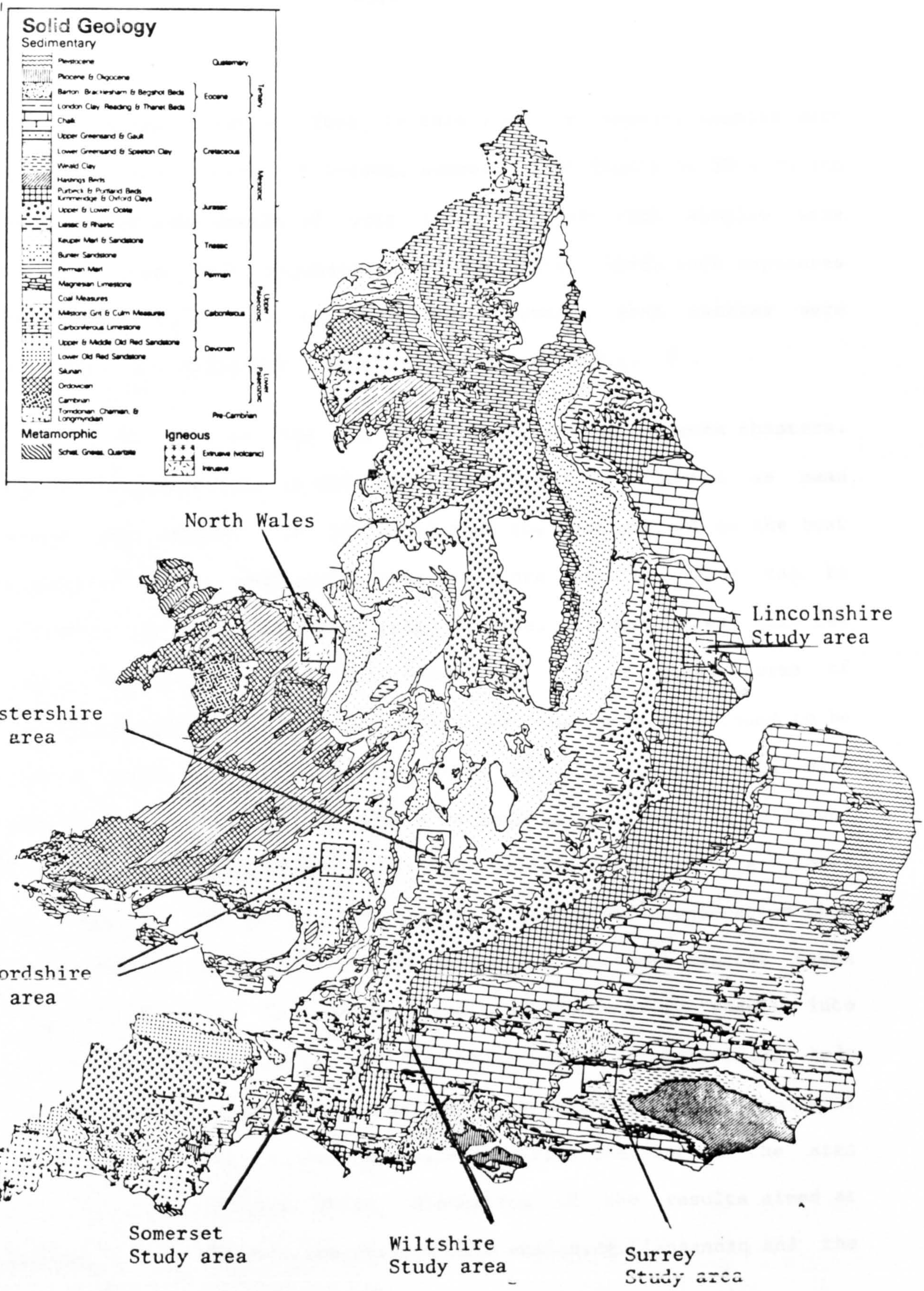


FIG. 2

LOCATION OF STUDY AREAS (IGS Map of England and Wales)

as the top and subsoils. Thus, in this instance, topsoil samples were obtained from depths of 0-15cm, subsoils from depths of 30-45cm and rock samples from depths of over 1.2m. A few rock samples were obtained from bank exposures at stream banks. Where rock exposures were common, such as in the sandstone terrain, grab samples were obtained. The different localities are shown in Fig. 2 .

The results are discussed in the following seven chapters. Element concentrations in the respective media are quoted as mean levels and ranges. It is noted that the mean may not be the best measure of central tendency in this instance as its value can be distorted in a case where the range is wide. In most cases, only few samples were collected per unit, hence the use of other forms of representations such as the median or the mode were found to be impracticable. In cases where the range were large, the data were examined more closely to enable reasonable inferences to be drawn. For example, ferruginisation within certain beds in the Lower Greensand in the Surrey study area resulted in unrepresentative mean concentrations of Fe for the combined results of rock samples taken from all the beds. This necessitated a breakdown of the results into the respective beds despite the fact that samples of individual beds were very few. Also, in the case of North Wales where the results of Zn and Pb in the Llansannan area were in marked contrast to the area east of the Clwydian Hills, discussion of the results aimed at differentiating between the western half enclosing Llansannan and the eastern half enclosing Holywell.

CHAPTER 4

Lincolnshire Study Area.

A Discussion Of The Metal Concentrations In The Rock, Soil, And Stream Sediment Derived From The Cretaceous And Jurassic Rocks.

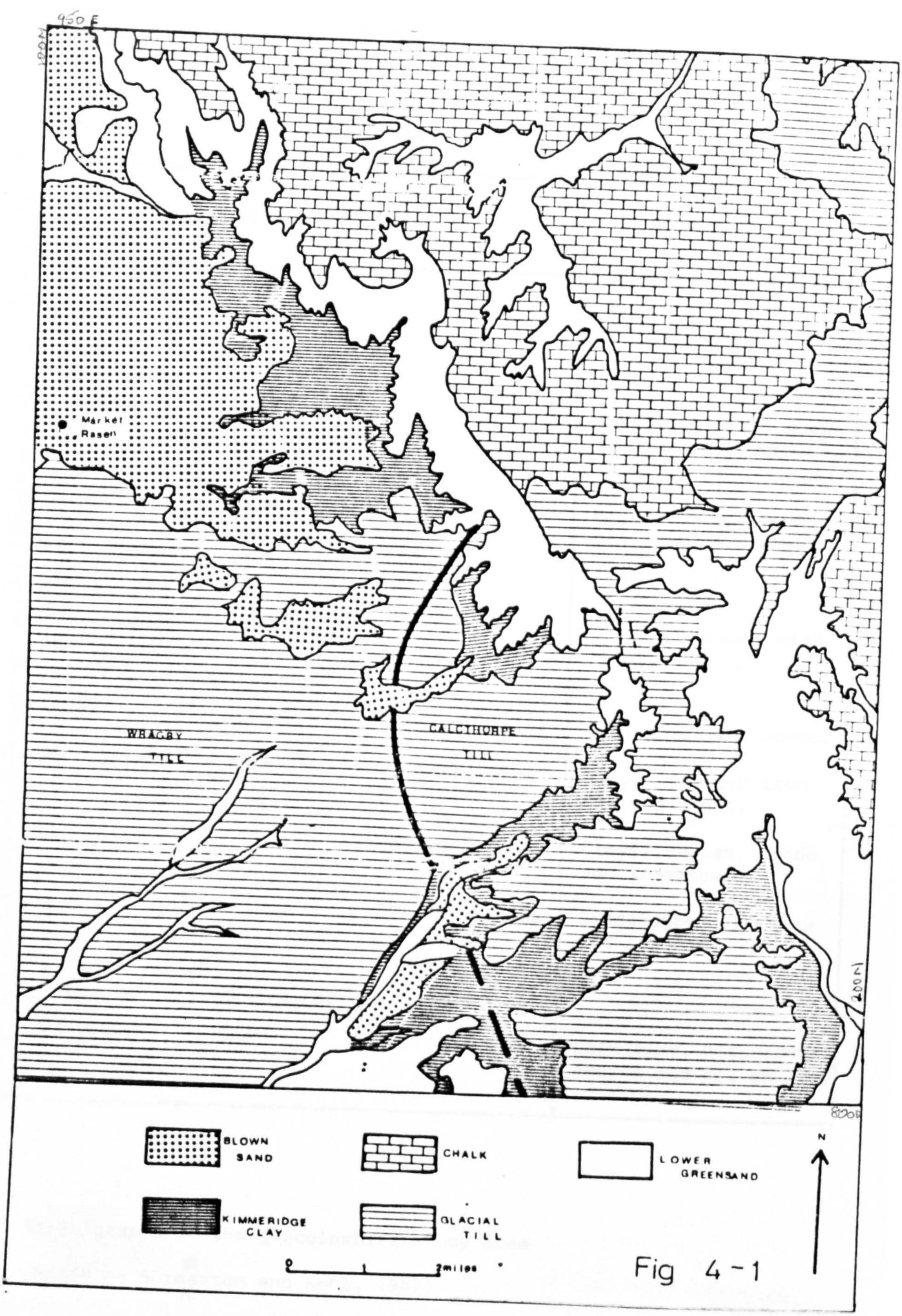
4-1 Location.

The study area is situated in the north east of Lincoln, between the Lincoln edge and the Lincolnshire Wolds.

4-2 Geology.

The Jurassic and Cretaceous rocks that occur in the study area have been reviewed by Usher et. al. (1888), and Swinnerton and Kent (1949). The Pleistocene glacial drift that occur extensively in the study area is recorded by Straw (1957, 1958). Table 4-1 outlines the succession while Fig. 4-1 shows a sketch map of the geology of the study area.

The oldest formation in the area is the Upper Jurassic Kimmeridge Clay. This consists of dark bituminous clay and oil shales throughout the entire thickness in the study area (Pringle, 1919, Arkell, 1933). This is succeeded by the Spilsby and Tealby Series of Lower Cretaceous age. The Spilsby Series consists of massive, gritty ferruginised sandstone and yellow grey unconsolidated sandstone. The Tealby series comprises clays, shales, sands and limestone. The Upper



Geology of the Lincolnshire study area

TABLE 4:1

GEOLOGICAL FORMATION			LITHOLOGY
RECENT	ALLUVIUM		Gravel, sand and silt
	BLOWN SAND		Quartzose sand, occasionally ferruginous.
PLEISTOCENE	GLACIAL DRIFTS		Boulder clay, sands, clays and gravels.
UPPER CRETACEOUS	CHALK		White limestone with flints.
LOWER	LOWER	Langton Series	Dark clays and sands.
CRETACEOUS	GREENSAND	Fulletby Beds	Clays, oolitic iron ore and sands.
		Tealby Series	Clays, shales, sands and limestones.
		Spilsby Series	Sandstones dark clay and iron ore.
UPPER JURASSIC	KIMMERIDGE CLAY		Dark clay, bituminous shales and oil shales.

Stratigraphy of the Lincolnshire study area

(Based on Swinerton and Kent, 1949)

Cretaceous Chalk consists of white limestone with flints. Drift of Quaternary age overlies much of the study area. Straw (1957, 1958) recognised the drift in this area to be divided into two main groups, the Calcethorp Till derived essentially from the Upper Cretaceous Chalk is light and creamy in colouration. This extends south westwards from Kelston and Calcethorpe into the Bain valley. West of the Calcethorpe Till, a second till, the Wragby Till is recognised by its dark grey colour. These are derived from the Kimmeridge Clay and have been described by Usher et al. (1888).

4-3 Topography.

The dominant topographic feature is the Lincolnshire Wolds which strike NNW-SSE across the north of the study area rising to a height of 104m. Locally, the topography is much subdued with rounded spurs separating branching dry valleys. Down cutting by some permanent streams has led to the exposure of some impervious clays on which the streams flow. West of the escarpments, streams rise as springs and flow ENE-WSW across the low relief.

4-4 Soils

The whole area is under intensive arable cultivation where improved drainage and ploughing have greatly modified the soil conditions. In general, heavy clay loams and sandy clay loams predominate . The impervious bed rock often results in waterlogging of the soils. In the vales, gleyed soils are common. The Blown Sands give rise to freely drained sandy loams. Over the Wolds, shallow and

TABLE 4:2

Geological Unit	Number of Samples	Ca%	Zn(ppm)	Pb(ppm)	Fe%	Mg%	Cu(ppm)	Co(ppm)	Mn(ppm)
BLOWNSAND	5	0.06 (.02-.08)	18.8 (16-34)	-	0.12 (.08-.18)	0.02 (.01-.04)	-	-	37.5 (10- 80)
CHALK	7	23.4 (10 - 32)	74.2 (25-83)	37.3 (20-45)	0.21 (.1 - .3)	0.21 (.09-.29)	25.4 (5-29)	14.6 (5-20)	245.6 (183-370)
LOWER GREENSAND	6	1.3 (.5 -2.4)	76.4 (46-100)	38.1 (17-62)	3.26 (.5 - 11)	0.17 (.02-.3)	17.8 (10-24)	16.2 (14-29)	134.0 (82-250)
WRAGBY TILL (Boulder clay)	8	6.7 (4 - 10)	78.1 (56- 97)	27.5 (20-30)	0.25 (.13-.38)	0.15 (.05-.19)	18.9 (13-23)	18.7 (10-24)	280 (135-360)
KIMMERIDGE CLAY	6	1.2 (.9 -1.5)	52.6 (34- 57)	17.8 (20-36)	0.37 (.31-.46)	0.24 (.19-.30)	34.4 (9-49)	12.1 (8-21)	137.5 (120-155)

Range and mean element concentrations in the rock samples (ground to -80 mesh) taken from the principal Geological units in the Lincolnshire study area
( ) Range of element concentrations

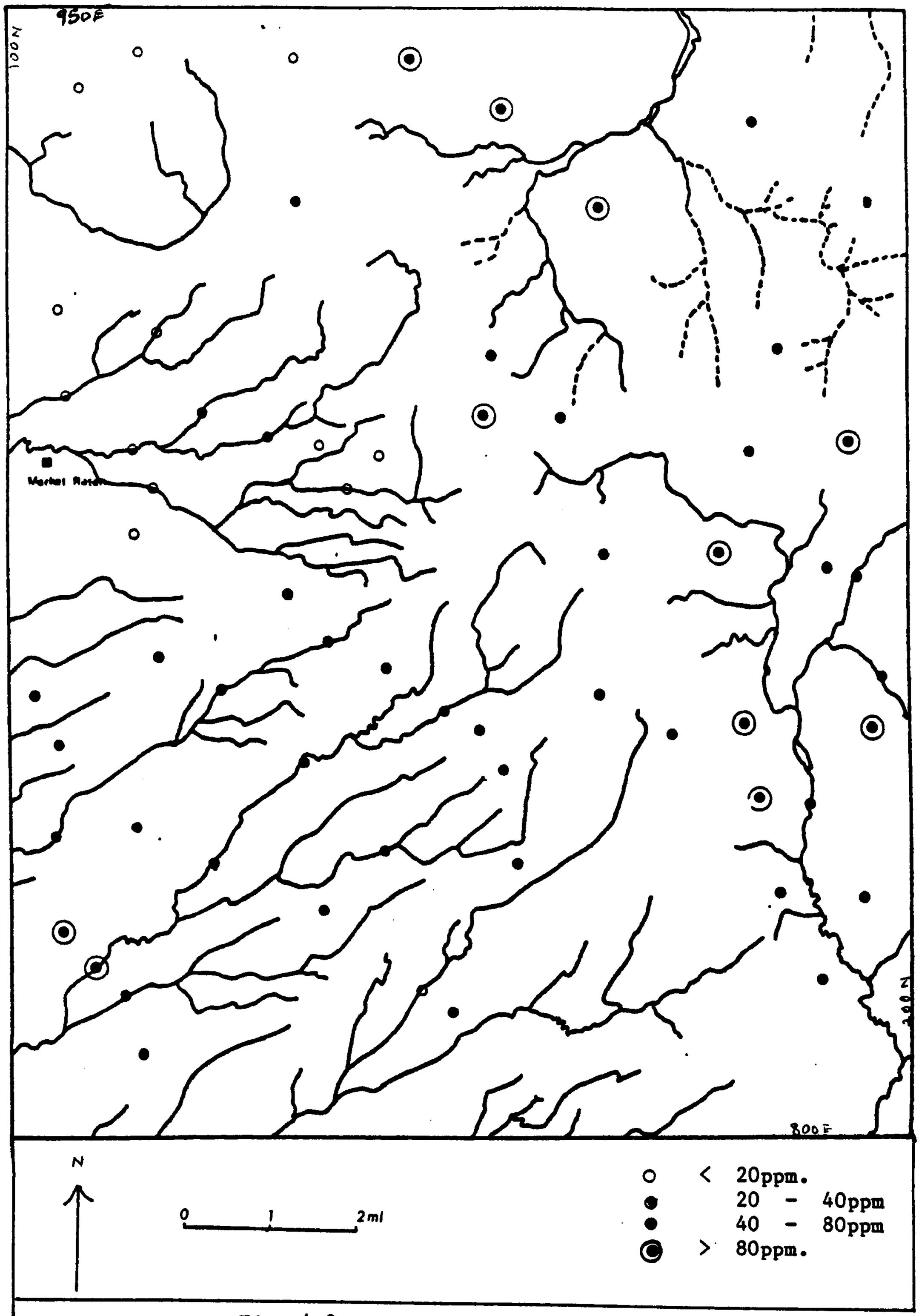


Fig 4-2

Zinc concentrations in the topsoils and stream sediments in the Lincolnshire study area.

heavy clay loams develop, usually containing numerous flints. The Lower Cretaceous rocks form sandy loams often reddish in colour with oolitic ferruginous grains found in some soils developed from the Spilsby sandstones.

4-5 Agriculture.

Around the town of Market Rasen conifer plantations are managed by the Forestry Commission while on the hillier parts of the Wolds, dairy farming and beef production are dominant. Important crops include sugar beet and winter oats.

4-6 Geochemical patterns.

Element concentrations in the rocks, soils and stream sediments are presented in Table 4-2, -3, -4. Geochemical maps of Zn, Pb, Cu and Mn are shown in Figs. 4-2 to 4-5. Figure 4-6 shows the metal concentrations in topsoils along a transect taken across the main geological units in the study area.

(a) Geochemical patterns in the rocks.

Concentrations of most elements were lower in the Blown Sand than the rest of the units in the study area (Table 4-2). Calcium concentrations were exceedingly high in the Chalk and Wragby Till with concentrations in excess of 30% and 10% Ca recorded in the Chalk and Wragby Till respectively. The maximum concentrations of Ca in the Kimmeridge Clay was below 2%. Apart from the low concentrations of Mg

TABLE 4:3

Parent Material	Medium and depth	Ca%	Zn(ppm)	Pb(ppm)	Fe%	Mg%	Cu(ppm)	Co(ppm)	Mn(ppm)
BLOWN SAND 6 *	Topsoil 0 -15cm	0.51 (.02- .6)	23.2 (7-35)	19.8 (10- 23)	0.12 (.08-.90)	0 .04 (.02- .4)	6.4 (5-8)	5.4 (- 8)	93 (36 -125)
	Subsoil 30-45cm	0.82 (.5-1.2)	18.0 (6-20)	18.5 (8-20)	0.13 (.06-.22)	0 .11 (.08-.25)	4 (-8)	6.4 (10)	176 (74 -230)
CHALK 10 *	Topsoil 0 -15cm	13.2 (10-22)	118.0 (64-189)	52.3 (31-66)	0.46 (.81-1.6)	0 .24 (.2-.8)	27.1 (5-36)	17.7 (6-25)	199.0 (88 -220)
	Subsoil 30-45cm	19.6 (9-34)	101.1 (73-174)	38.8 (14-42)	0.53 (.8-1.73)	0 .24 (.16-.54)	27.9 (5-32)	17.4 (9-25)	223.8 (170-260)
LOWER GREENSAND 15 *	Topsoil 0 -15cm	2.6 (.28-11.4)	108.4 (50-182)	62.3 (26-102)	4.37 (1.3-13)	0 .25 (.08-.35)	20.9 (7-36)	16.7 (6-25)	110.6 (69 -200)
	Subsoil 30-45cm	5.1 (.38-14)	72.11 (52-93)	51.4 (22-71)	4.8 (2 -14)	0 .32 (.2-.95)	18.5 (6-26)	23.4 (7-40)	134.7 (64- 300)
KIMMERIDGE CLAY 11 *	Topsoil 0 -15cm	1.3 (.44-2.5)	75.8 (25-90)	37.3 (15-50)	0.21 (.9-1.7)	0 .21 (.04-.27)	18.4 (5-23)	14.6 (5-18)	147.7 (80 -370)
	Subsoil 30-45cm	2.6 (.3 -3.5)	54.2 (30-68)	30.8 (18-45)	0.25 (1.3-4.3)	0 .22 (.09-.43)	15.7 (5-19)	13.9 (5-19)	245.6 (96- 360)

Range and mean element concentrations of the minus 80- mesh fraction of residual soils from the principal geological units of the Lincolnshire study area

( ) Range of elements

* Number of samples

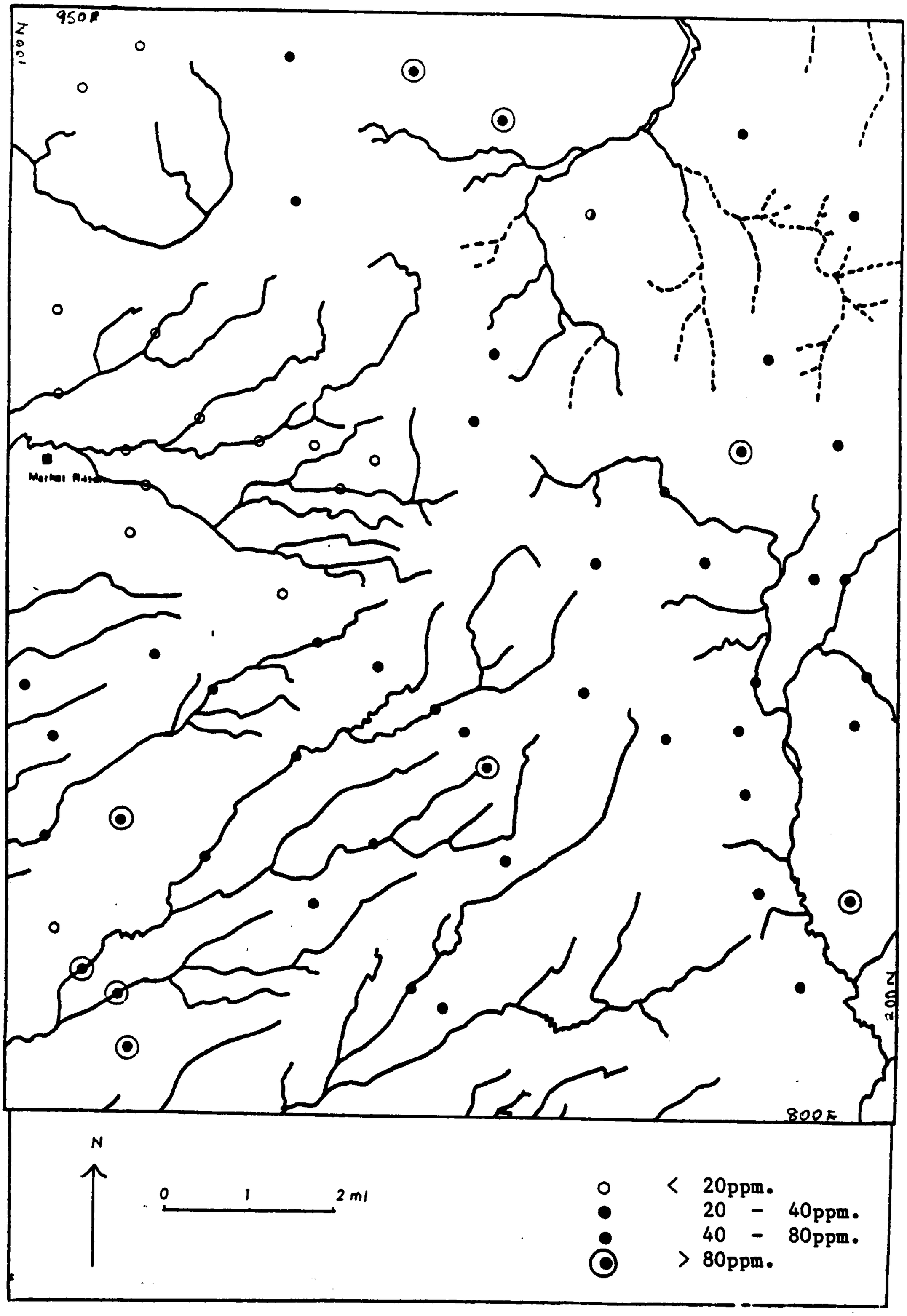


Fig 4-3

Lead concentrations in the topsoils and stream sediments in the Lincolnshire study area.

in the Blown Sand (below 0.05%) Mg did not show significant differences between the units. Zinc and lead concentrations were lower in the Kimmeridge Clay than in the Chalk and Lower Greensand. Iron concentrations were markedly enhanced in the Lower Greensand. Concentrations in excess of 10% were found in some ferruginised samples of the Lower Greensand. Copper, cobalt and manganese concentrations were low in all the units although, locally, Cu concentrations in the Kimmeridge Clay could rise to 40ppm. In the Blown Sand, Cu and Co concentrations below the detection limit (Table 3-1) and 10ppm Mn were common.

The results showed that element concentrations in the different units were controlled by their lithology. The high concentrations of Ca in the Wragby Till may be due to mixing of the drift with materials from the Chalk.

(b) Geochemical patterns in the soils.

Concentrations of Ca and Zn were higher in the soils derived from the Lower Greensand and Chalk than those derived from other units (Table 4-3). Soils derived from the Lower Greensand often had oolitic iron grains and showed very much higher concentrations of Fe than soils derived from other units. The concentrations of Co, Cu and Mn were often low, with the lowest concentrations found in the soils derived from the Blown Sand. In general, concentrations of Ca, Fe and Mn tended to be higher in the subsoils than in the topsoils. Magnesium showed only minor differences in the top and subsoil concentrations. In the Chalk the mean concentration of Mg in the topsoil was almost identical to that of the subsoil. In contrast, Zn

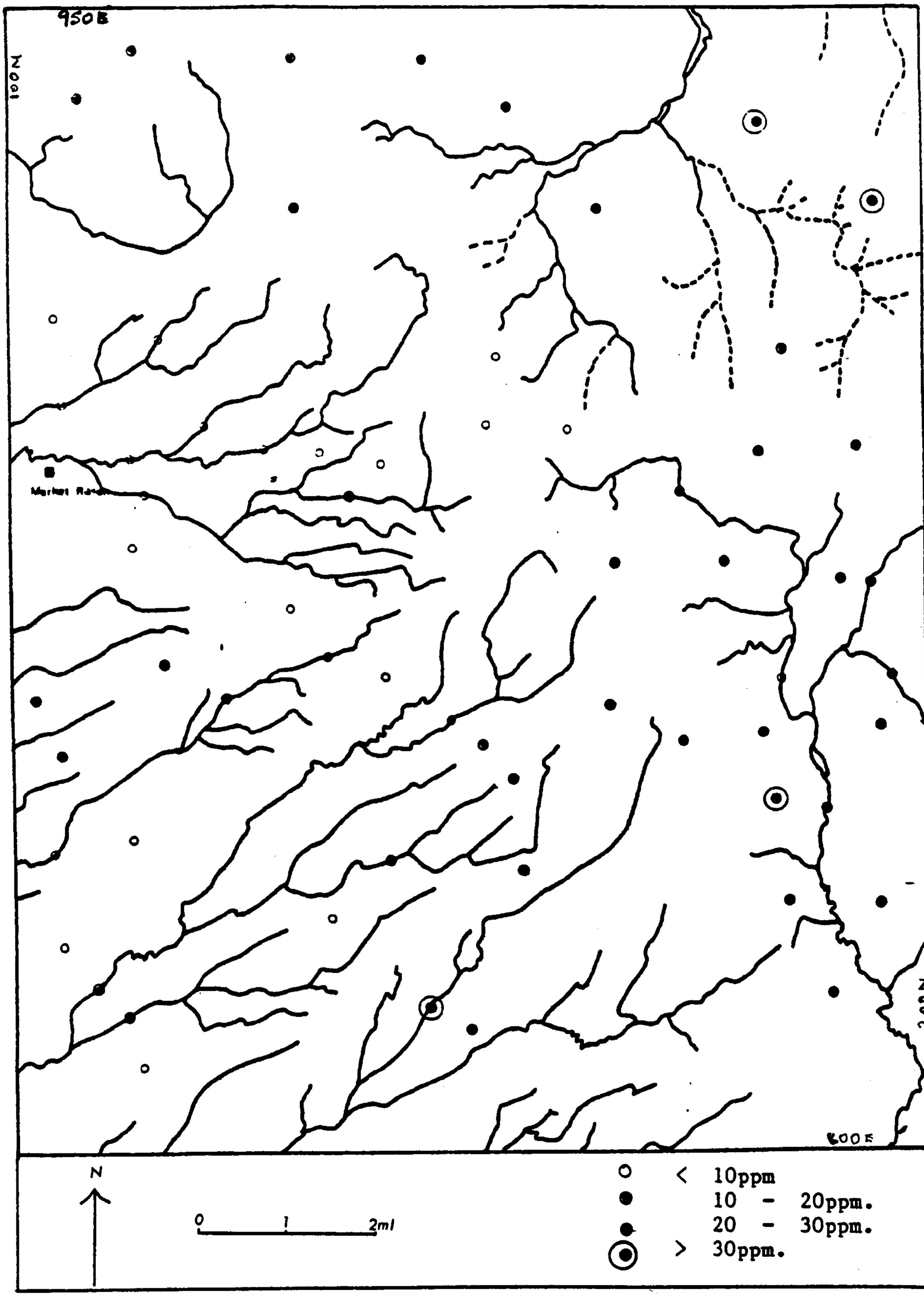
TABLE 4:4

Geological Units	Number of Samples	Ca %)	Zn(ppm)	Pb(ppm)	Fe(%)	Mg(%)	Cu(ppm)	Co(ppm)	Mn(ppm)
BLOWNSAND	5	.27 (.16-.36)	22.9 (15-34)	20.0 (16-25)	0.21 (.18- 30)	0.14 (.10-.20)	6.4 (5-12)	15.7 (11-21)	194.2 (120-300)
LOWER GREENSAND	7	4.1 (.7 - 5.4)	63.1 (55-78)	29.8 (22-39)	5.8 (4- 16)	0.10 (.03-.17)	8.6 (5-14)	12.7 (8-18)	358.3 (150-755)
KIMMERIDGE CLAY	8	2.7 (2.2-3.2)	75.4 (63-87)	30.1 (21-33)	0.49 (.11-.68)	0.15 (.11-.21)	25.8 (8-27)	19.9 (8-23)	303 (160-350)

Range and mean element concentrations of stream sediments (-80 mesh) derived from the principal geological units in the Lincolnshire study area.

( ) Range of elements

Fig 4-4



Copper concentrations in the topsoils and stream sediments in the Lincolnshire study area.

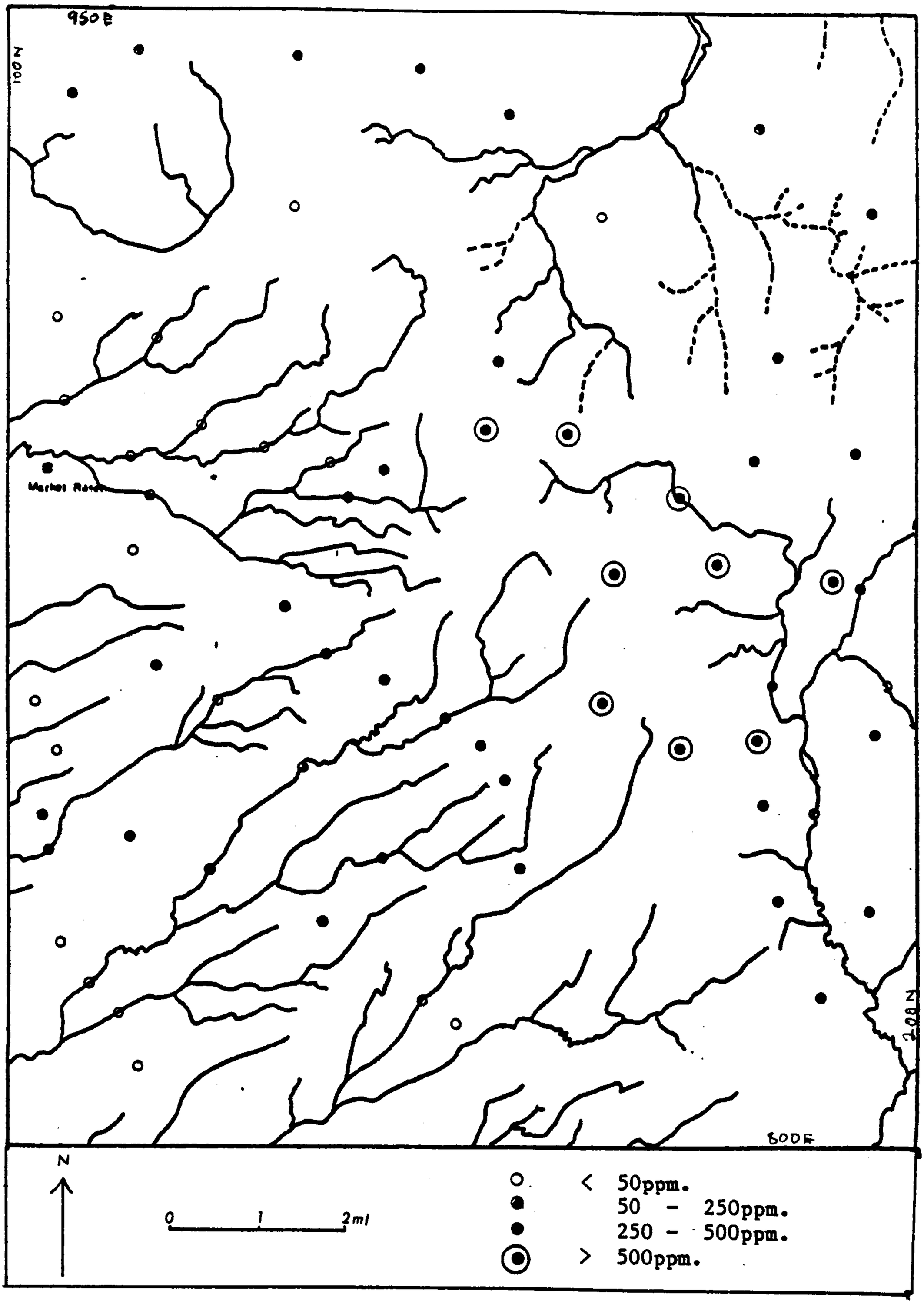
and Pb concentrations tended to be higher in the topsoils than in the subsoils. Copper and cobalt concentrations also showed very little differences between the top and subsoil concentrations over the Chalk while in the soils derived from other units Cu tended to be higher in the topsoils than in the subsoils.

The results showed that element concentrations in the soils were primarily controlled by the concentrations in the soil parent materials. The high concentrations of Ca in the soils derived from the Chalk and Fe in the soils derived from the Greensand were thought to be due to the influence of the parent material. The similarities of most element concentrations in the top and subsoils derived from the Chalk suggested that leaching and redistribution of elements in these soils were not common, although there was a decrease in the concentrations of Ca in the soils compared to the parent material (rocks). Leaching may account for the higher concentrations of Fe and Mn in the subsoils compared to the topsoils over the Lower Greensand. The gleyed and waterlogging conditions that prevail in the soils derived from the Kimmeridge Clay may be encouraging such mobilisation in the soils.

(c) Geochemical patterns in the stream sediments.

Element concentrations in the stream sediments also reflected lithological differences in the parent materials (Table 4-4). Concentrations of Ca, Fe in the stream sediments derived from the Lower Greensand were higher than in the rocks and topsoils. Over the Kimmeridge Clay, concentrations of Fe were marginally higher in the stream sediments than in the soils.

Fig 4-5



Manganese concentrations in the topsoils and stream sediments in the Lincolnshire study area.

Zinc and copper concentrations in the stream sediments derived from the Lower Greensand were lower than in the rocks and soils, while over the Blown Sand, Zn concentrations were higher in the sediments than in the soils and rocks. Lead concentrations were similar to those in the soils over the Kimmeridge Clay while over the Lower Greensand, Pb concentrations were lower in the sediments than in the soils. Apart from the Lower Greensand, concentrations of Mn and Co were higher in the sediments than in the soils and rocks. The reduced concentrations of Mn and Co in the sediments derived from the Lower Greensand followed the trend observed in the case of Zn, Pb and Cu. This was thought to be due to the dilution of the sediments by the precipitation of calcium carbonates in the stream bed.

4-7 Discussion of results.

The results showed that factors controlling the distribution of elements in the rocks, soils and stream sediments can be classified into three groups,

(a) influence of parent material

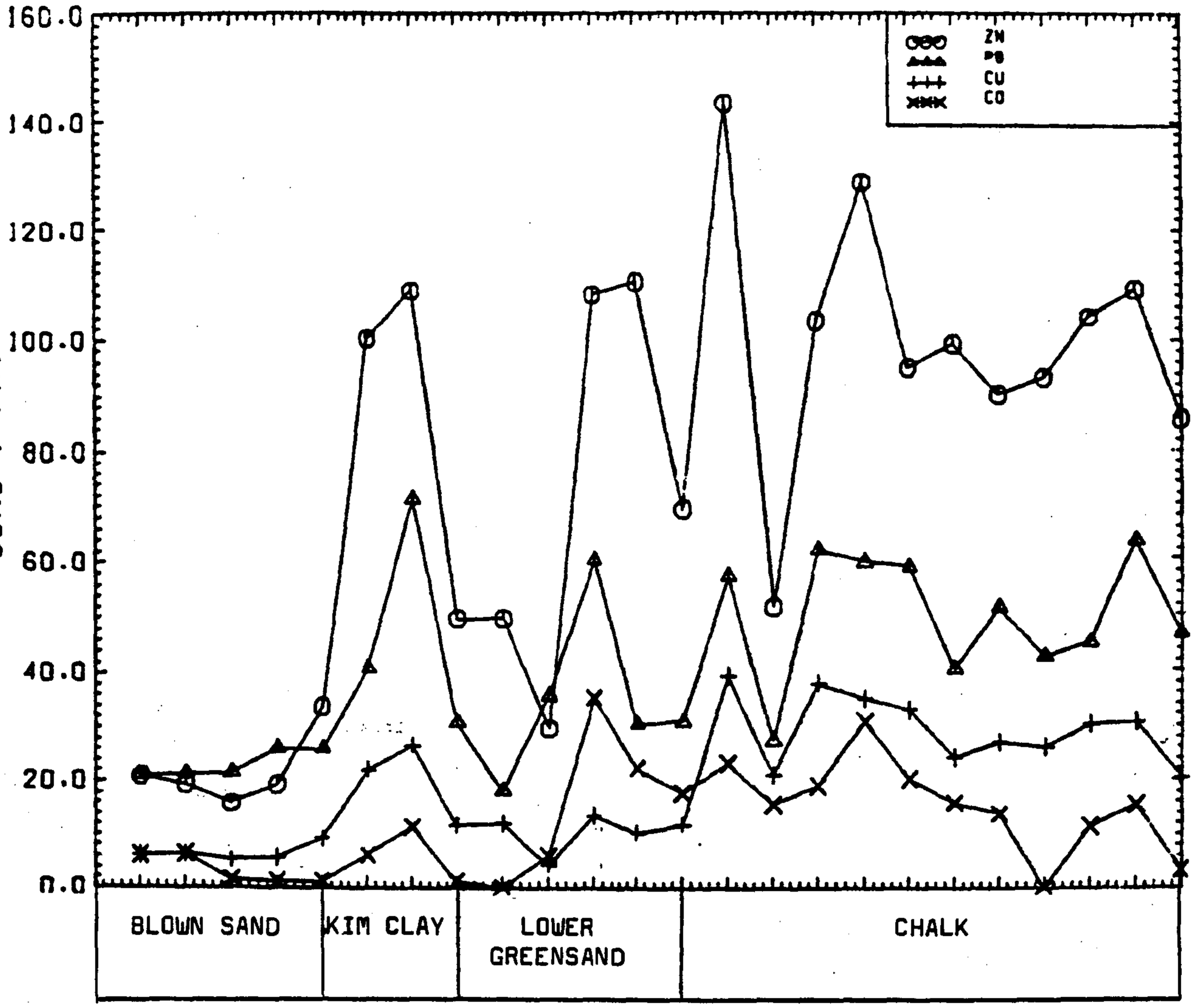
(b) modification in the soils, and

(c) influence of the secondary environment.

(a) Influence of the parent material.

The results showed that the distribution of elements in the soils and stream sediments followed the lithological variations in the study area. The high concentrations of Ca and Pb in the soils derived from the Chalk and the low concentrations of these elements in the

FIG 4-6



Topsoil metal concentrations across the main geological units in the Lincolnshire study area.

soils and stream sediments derived from the Blown Sand emphasised the dominant control of the parent material on the distribution of elements. Again, over the Lower Greensand where Fe concentrations in the rocks were high, this was reflected on the associated soils and stream sediments. The influence of the parent material is further demonstrated by Fig. 4-6 which plots element concentrations taken along a transect across the main lithological units. Lithological control was also thought to account for the variations of the topsoil and stream sediment concentrations shown in Figs. 4-2 to 4-5.

(b) Pedological modication of elements.

In general, element concentrations increased in the soils except in the case of Ca which tended to be depleted in the soils. The concentrations of Zn, Pb, Cu, Co and Mn were higher in the soils than in the rocks. Lead, zinc and copper had higher concentrations in the topsoils than in the subsoils. These were thought to be due to an association with organic matter which may form stable complexes with with these elements in the soils (Davies et al. 1969).

(c) Influence of the secondary environment.

Staining of pebbles in the streams by Fe oxides and black Mn oxide minerals were widespread in the study area. In areas underlain by Lower Greensand, iron concretions were found in the streams and in such areas Fe staining increased on the pebbles. This was thought to reflect the mobilisation of Fe and Mn in the soils and redistribution in the stream sediments. The lower concentrations of most elements in

stream sediments were thought to be due to the dilution by the precipitation of calcium carbonates.

4-8 Conclusions.

The following conclusions were made from the preceding discussion.

(a) Lithological control was the most important factor controlling the distribution of elements in the soils and stream sediments. Concentrations of most elements were lower in the soils and stream sediments derived from the Blown Sand than in those derived from other units. High concentrations of Ca in the Chalk and Fe in certain beds of the Lower Greensand were reflected in the associated soils and stream sediments.

(b) Apart from Ca which tended to be lower in the soils than in the rocks over the Chalk, the concentrations of most elements studied were higher in the soils than in the rocks over other units.

(c) Lead and zinc concentrations were higher in the topsoils than the subsoil. The reverse was true for Mn and Fe over the soils derived from the Kimmeridge Clay.

(d) Over the Lower Greensand, apart from Mn and Fe which were noticeably more in the stream sediments than rocks and soils, in general, concentrations of most elements in the stream sediments were lower than those in the rocks and soils.

(e) The stream sediments were good indicators of metal concentrations in the soils and rocks.

CHAPTER 5

Wiltshire Study Area.

A Discussion Of The Metal Concentrations In The Rock Soil And Stream Sediments Derived From The Cretaceous And Jurassic Rocks.

5-1 Location.

The study area lies to the north west of counties of Wiltshire and Somerset and includes the towns of Gillingham to the north and Shaftesbury to the south.

5-2 Geology.

The Cretaceous and Jurassic rocks in the study area have been described by Osborn White (1923), and Mottram (1961). The stratigraphy is outlined in (Table 5-1) . The oldest rocks comprise the Corallian formation of Jurassic age. The variation within the unit includes oolitic limestone, ragstones, marls and calcareous clays. The Kimmeridge Clay that succeeds the Corallian has been described as "dark grey to bituminous shelly clay" by Osborn White (1923). The scarcity of outcrops precluded any detailed observation of the lithology in the field; however, Downie and Wilson (1968) noted the similarity in the lithology of the Kimmeridge Clay in the study area to that of the bay of Kimmeridge, where bituminous shales and clays are dominant. The Lower Cretaceous Gault and Upper Greensand

TABLE 5:1

GEOLOGICAL FORMATION		LITHOLOGY
RECENT	ALLUVIUM AND COLLUVIUM	Sands, silts and clays.
PLEISTOCENE	HEAD	Unconsolidated sands and loams.
UPPER CRETACEOUS	CHALK	White limestone with flints.
	UPPER GREENSAND	Micaceous and glauconitic sands and sandstones with cherts.
LOWER CRETACEOUS	GAULT	Blue grey micaceous clay and sandy clays.
	LOWER GREENSAND	Fine ferruginous and glauconitic sands.
UPPER JURASSIC	PURBECK	Shelly limestones with calcareous clays and shales.
	PORTLAND	Limestones with chert overlying grey sands and clays.
	KIMMERIDGE CLAY	Dark bituminous shelly clays.
	C ORALLIAN	Oolitic limestones, ragstones, marls and calcareous clays.
	OXFORD CLAY	Blue grey pyritous clays, dark shales.
	KELLOWAYS BEDS	Calcareous sands and sandy clay.

Stratigraphy of the Wiltshire study area
(Based on Osborne White, 1923 and Mottram, 1961)

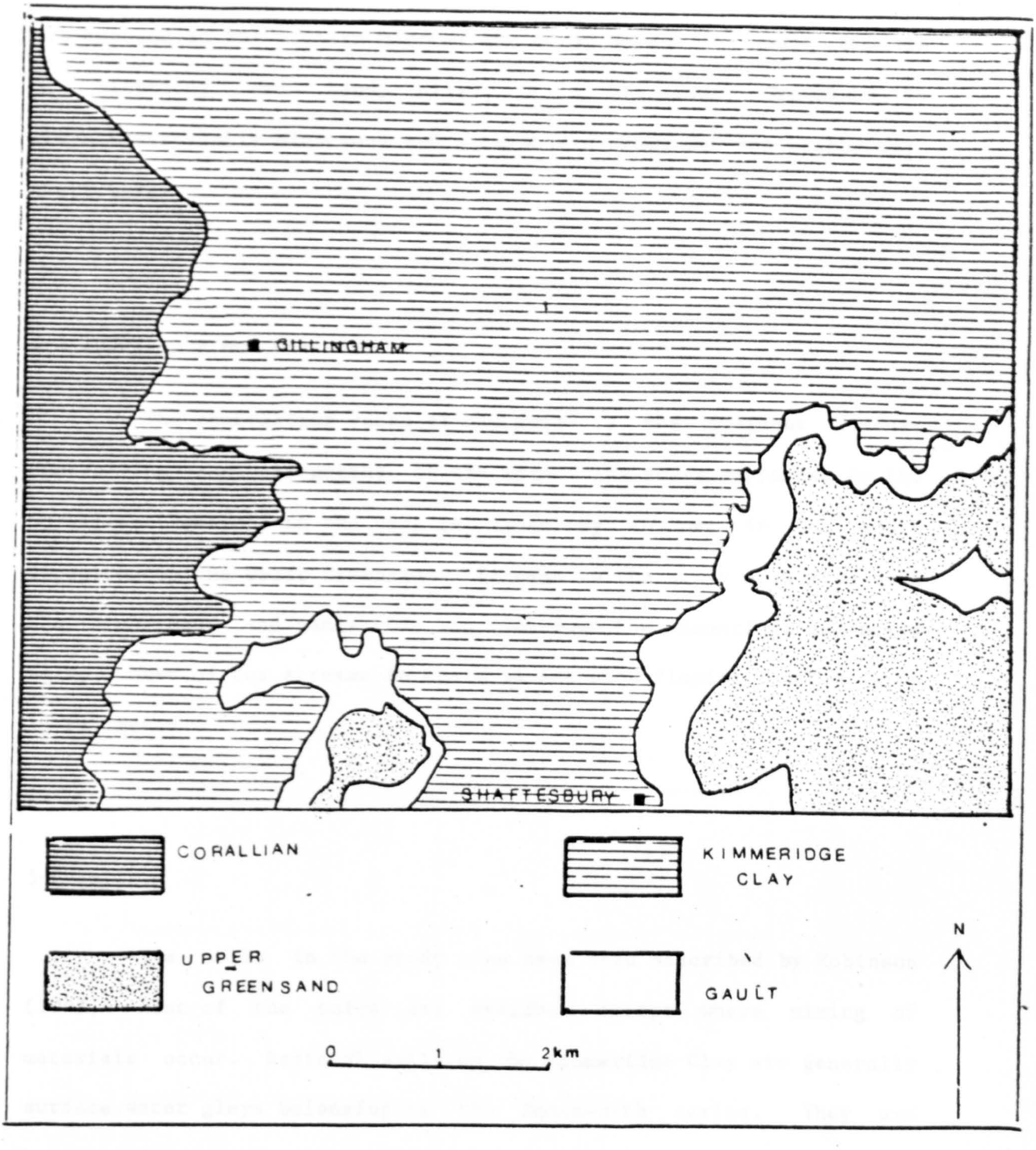


Fig. 5-1

Geological Map Of Wiltshire Study Area.

are exposed in the eastern half of the study area. The Gault consists of micaceous and sandy clays, while the Upper Greensand is characteristically micaceous and glauconitic sands and sandstones with chert beds.

5-3 Topography and drainage.

The contrasting rocks of the area is the dominant feature controlling the topography of the area. The scarp supported by the Corallian Limestone in the west is faced by another in the south supported by the Upper Greensand. Streams in the study area rise from the limestones and sandstones and flow down the Kimmeridge dominated vales. Most of the streams in the area are slow flowing, often rich in sediments.

5-4 Soils.

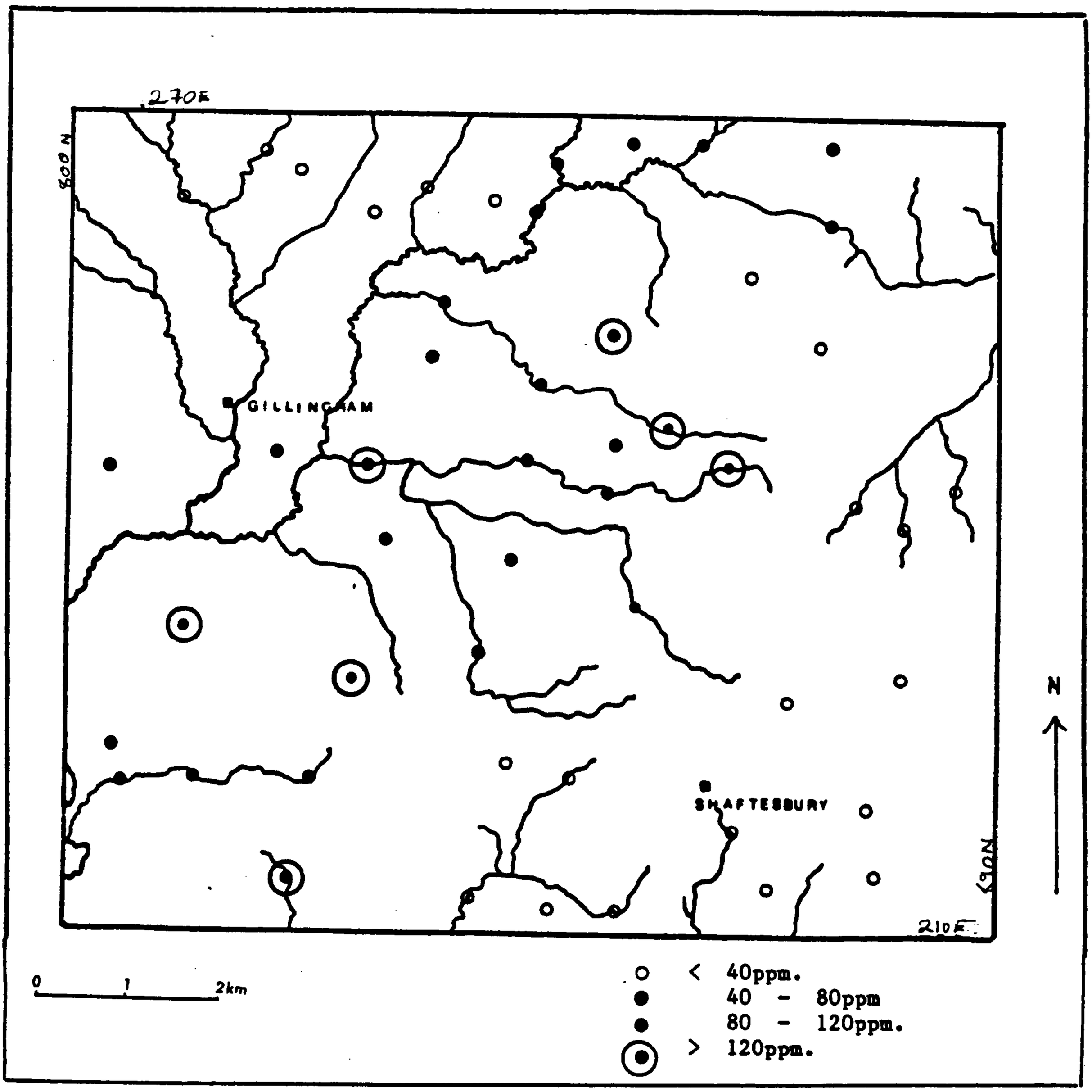
The soils in the study area have been described by Robinson (1948). Most of the soils are residual except where mixing of materials occur. Residual soils on the Kimmeridge Clay are generally surface water gleys belonging to the Denchworth series. They are heavy and non-calcareous showing evidence of periodic waterlogging. Most of the soils on the limestone terrain are shallow grey to brown loams of moderate drainage.

TABLE 5:2

Geological Units	Number of Samples	Ca%	Zn(ppm)	Pb(ppm)	Fe%	Mg%	Cu(ppm)	Co(ppm)	Mn(ppm)
UPPER GREENSAND	4	1.25 (.5-1.9)	35.9 (23-49)	12.0 (10-21)	1.4 (.7 - 2)	0.42 (.09-.85)	6.4 (5-18)	8.9 (5-12)	80.0 (6-120)
KIMMERIDGE CLAY	15	0.49 (.2- .7)	88.3 (40-210)	30.6 (28-48)	3.4 (1.8-4.5)	1.4 (0.9-1.6)	30.9 (18-43)	18.1 (15-27)	345.0 (130-400)
CORALLIAN	8	22.0 (9-36)	40.0 (15-45)	29.8 (20- 47)	3.2 (2-4.6)	0.43 (.06-1.0)	14.3 (8-16)	28.2 (16-32)	350 (200-450)

Range and mean element concentrations of the rocks of the wiltshire study area

Fig 5-2



Zinc concentration in the topsoils and stream sediments in the Wiltshire study area.

5-5 Agriculture

The geology and the associated soils govern the type of agriculture in the area. Mixed dairy and arable farming is common in the moderately drained soils of the limestone terrain, while the heavy soils of the vale carry permanent pasture which supports only dairy farming.

5-6 Geochemical Patterns

Tables 5-2, -3, -4, show the metal concentrations in the rocks, soils and stream sediments from the study area. The geochemical patterns revealed in the present investigations are discussed below. Figures 5-2 to 5-5 shows the element concentrations in the topsoils and stream sediments in the study area. Figure 5-6 shows the metal concentrations in the topsoils taken along a traverse over the main geological units in the area. Metal concentrations in selected soils derived from the the Kimmeridge Clay are presented in Table 5-5.

(a) Geochemical patterns in the rocks.

Calcium displayed a marked contrast between the rock types in the study area. Over the Corallian Limestones concentrations as high as 36% were found in the rocks while over the Kimmeridge Clay and Upper Greensand concentrations of Ca were all below 2%. Magnesium on the other hand showed higher concentrations in the Kimmeridge Clay than in the Corallian Limestone and Upper Greensand. The ranges and mean concentrations of Fe and Pb were similar in the Kimmeridge Clay and the Corallian Limestone, being twice as high as those in the Upper

TABLE 5:3

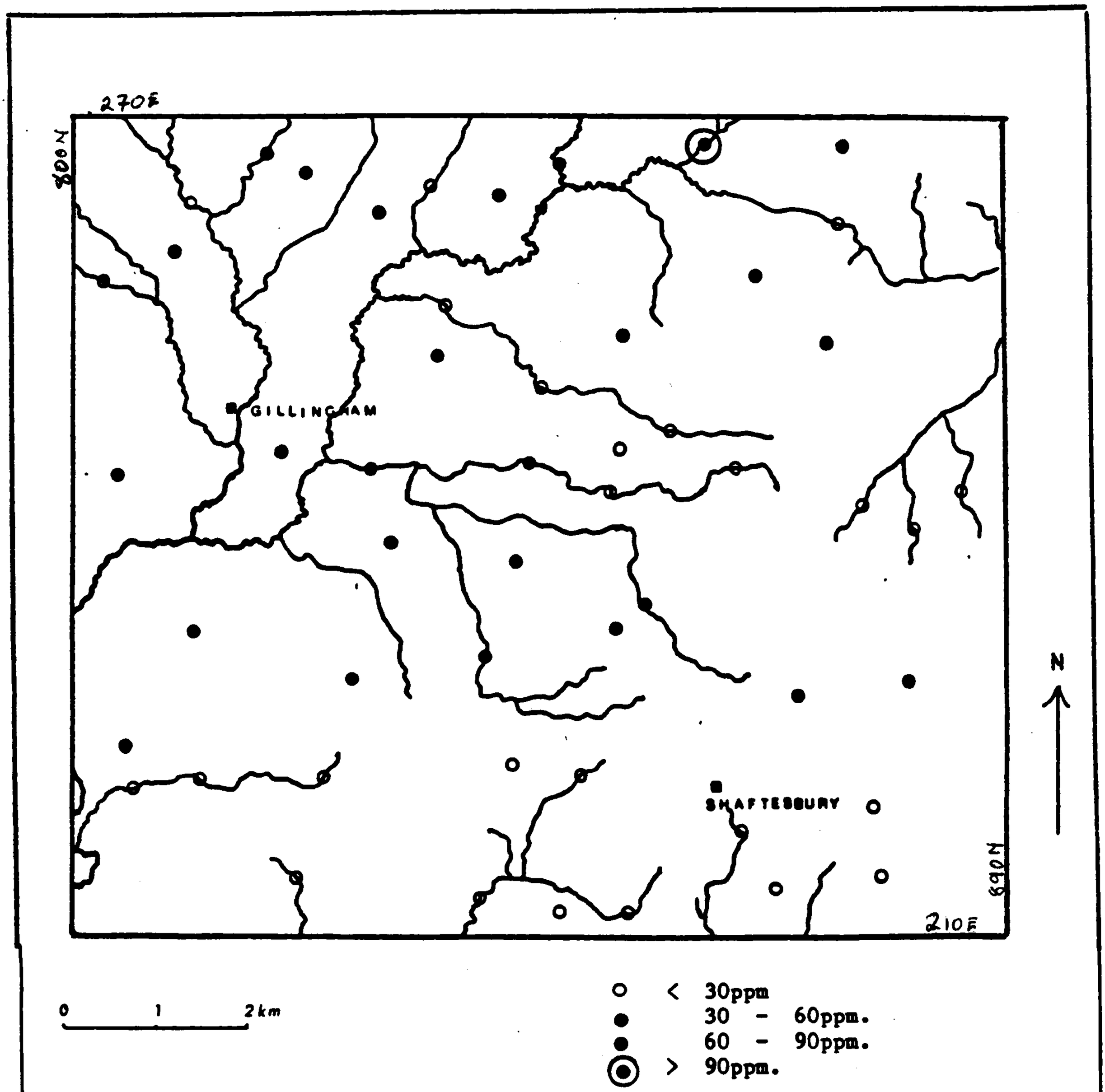
Geological Unit	Medium and Depth	Ca%	Zn(ppm)	Pb(ppm)	Fe%	Mg%	Cu(ppm)	Co(ppm)	Mn(ppm)
UPPER GREENSAND 9*	Topsoil 0 - 15cm	0.27 (.01- .4)	31.9 (15- 35)	25.0 (10- 30)	3.1 (1.5-4.0)	0.23 (.14-.56)	15.0 (6-18)	5.3 (5-11)	180.0 (50-220)
	Subsoil 30 - 45cm	0.30 (.04- .6)	29.4 (16- 33)	20.6 (11- 26)	4.0 (1.1-5.6)	0.20 (.09-.7)	10.4 (8-15)	10.4 (6-15)	200.0 (60-300)
KIMMERIDGE CLAY 20*	Topsoil 0 - 15cm	0.54 (.30-1.1)	69.9 (29-108)	30.4 (25- 70)	3.3 (2.1-5.7)	0.25 (.11-.39)	15.6 (10-36)	18.4 (10-26)	302 (150-350)
	Subsoil 30 - 45cm	0.55 (.29-1.5)	62.9 (40- 73)	19.9 (15- 46)	4.4 (2-7)	0.24 (.19-.5)	24.6 (20-30)	21.2 (18-35)	342 (142-389)
CORALLIAN 14*	Topsoil 0 - 15cm	12.6 (6-15)	79.4 (50-200)	41.9 (22-100)	4.6 (3-5)	0.17 (.10-0.89)	20.0 (8-35)	17.2 (12-38)	469 (181-550)
	Subsoil 30 - 45cm	19.0 (10-24)	73.0 (45-180)	21.5 (15- 36)	4.9 (2.5-7)	0.20 (.20-.53)	23.5 (16-38)	22 (11-39)	450 (150-600)

Range and mean element concentrations in the soils of the Wiltshire study area

( ) Range

* Number of samples

Fig 5-3



Lead concentrations in the topsoils and stream sediments in the Wiltshire study area.

Greensand (Table 5-2). The concentrations of Cu, Co and Mn were exceedingly low in the Upper Greensand. Copper and zinc concentrations were lower in the Corallian Limestone than in the Kimmeridge Clay. Manganese concentrations were higher in the Kimmeridge Clay and Corallian Limestone, being four times higher than those in the Upper Greensand.

The results showed that element concentrations in the rocks were controlled by the lithology of each unit. Concentrations of elements in sandstone unit (Upper Greensand) were generally lower than those in the clays and limestones.

(b) Geochemical patterns in the soils.

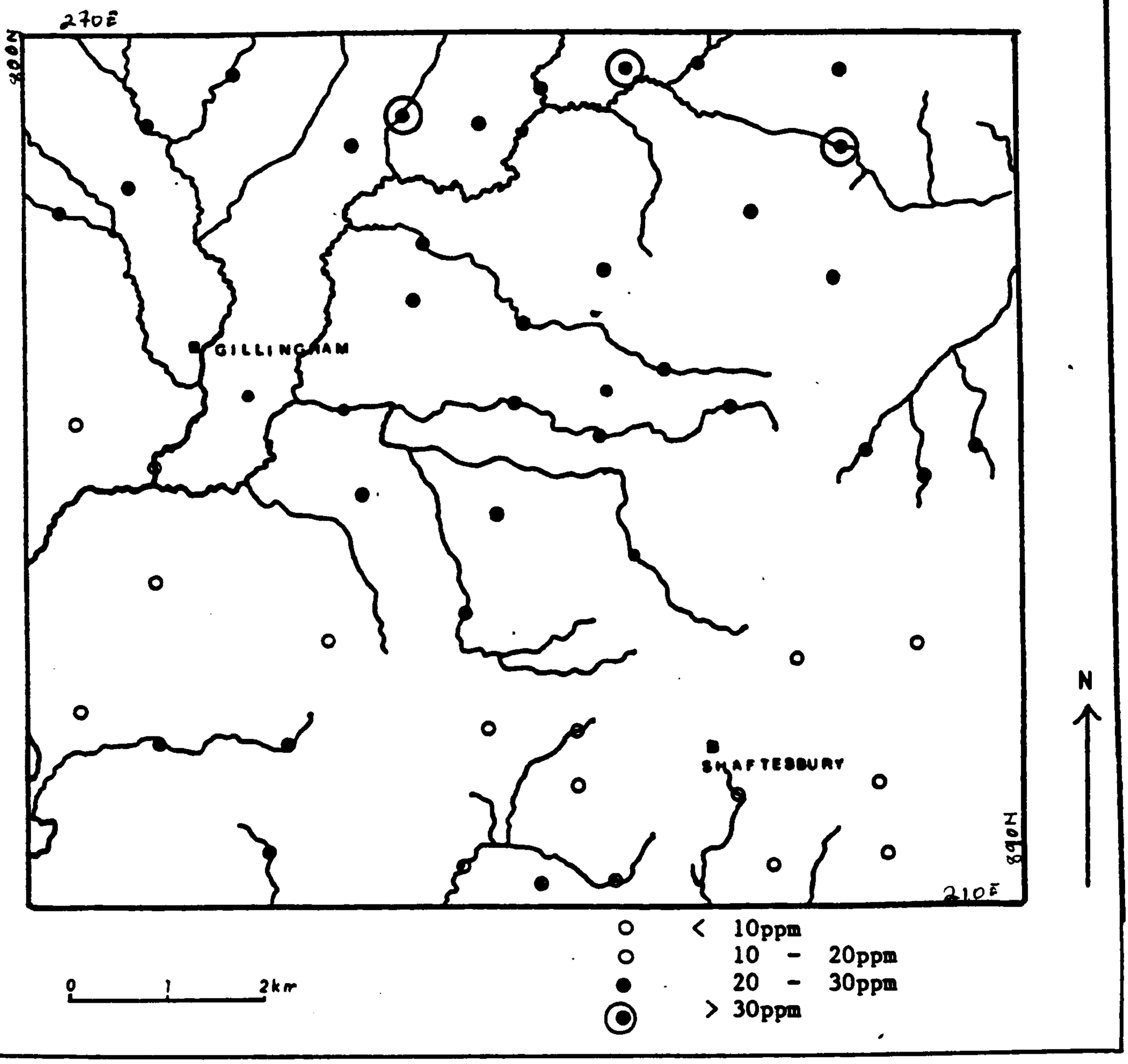
Metal concentrations in the soils generally reflected the metal concentrations of their associated parent materials (Table 5-3). Thus , apart from Mg where the concentrations in the soils were similar over the different units, soils derived from the Upper Greensand had lower concentrations of most elements than those derived from the Kimmeridge Clay and Corallian Limestones (Table 5-3). Zinc concentrations were higher in the soils derived from the Corallian Limestone than those derived from other units, with concentrations as high as 200ppm found in some topsoils. In general, the trend was towards an increase of Zn concentrations in the soils compared to the parent materials (rocks) with the higher concentrations occurring in the topsoils. A similar situation was observed in the case of Pb where topsoil concentrations were higher than those in the subsoil. Thus the mean concentrations of Pb in the topsoils derived from the Kimmeridge Clay and the Corallian Limestones were nearly twice as high as those in the subsoil. Over the Upper Greensand the enhancement of Pb in the topsoil was not as marked as was the case of soils derived

TABLE 5:4

Geological Units	Number of Samples	Ca%	Zn(ppm)	Pb(ppm)	Fe%	Mg%	Cu(ppm)	Co(ppm)	Mn(ppm)
UPPER GREENSAND	3	2.4 (1-2.9)	22.0 (15- 31)	18.7 (12-24)	2.1 (.07-2.4)	0.34 (.01-.9)	15.3 (5-19)	10.9 (5-15)	108 (80-150)
KIMMERIDGE CLAY	19	1.1 (.3-2)	97.6 (45-121)	38.0 (22-45)	2.6 (.9-3)	0.21 (.01-.7)	33.0 (12-40)	19.4 (8-22)	189 (100-850)
CORALLIAN	11	19 (10-26)	43.1 (31- 84)	26.8 (10-82)	3.9 (1.2-5)	0.20 (.01-.6)	20.0 (10-30)	19 (2-37)	269 (100-600)

Range and mean levels of metals in the stream sediments of the Wiltshire study area

Fig 5-4



Copper concentrations in the topsoils and stream sediments in the Wiltshire study area.

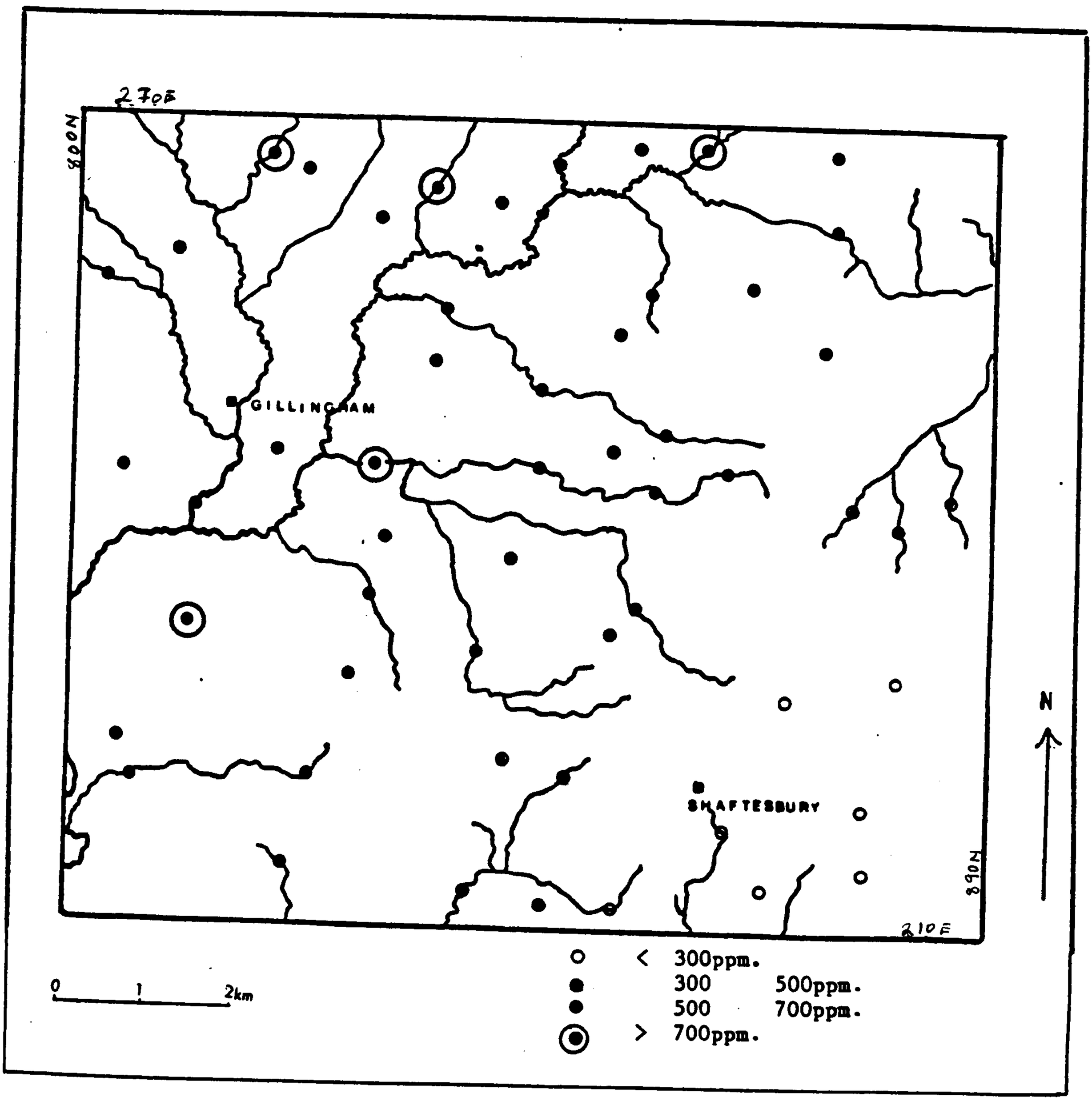
from other units. Iron concentrations were higher in the soils than the parent materials. The concentrations of Cu and Co were low in all the soils derived from the units in the study area, although locally concentrations of Cu may rise to 30ppm in the soils derived from the Kimmeridge Clay and the Corallian. There was a trend for the concentrations of the elements Fe, Cu, and Co to be increased in the subsoil than in the topsoil, except for Cu in the Upper Greensand where topsoil concentration of Cu was higher than the subsoil.

The results showed that the dominant control on the distribution of elements in the soils was the parent material. The nature of the soils developed on each parent material had varying effects on the distribution of elements. For instance, leaching in the soils may account for the higher concentrations of Ca in the subsoils over the Corallian. Again the higher concentrations of Fe, Cu and Co in the subsoils compared to the topsoil may be due to leaching from the upper horizons of the soils and redistribution in the lower horizons. This process was more common in the soils derived from the Corallian and Kimmeridge Clay where gleying and waterlogging conditions prevailed. The freely drained soils derived from the Upper Greensand did not show any evidence of leaching of elements , except in the case of Co.

(c) Geochemical patterns in the stream sediments.

As with the soils variations in metal concentrations in the stream sediments reflected element concentrations in the rocks (Table 5-4). Only three samples of stream sediments derived from the Upper Greensand were obtained hence a full assessment of the metal concentrations could not confidently be made, however, the results suggested that concentrations of most elements were lower than those

Fig 5-5



Manganese concentrations in the topsoils and stream sediments in the Wiltshire study area.

derived from other units. Calcium concentrations in the Upper Greensand seemed to be higher in the stream sediments than in the rocks. This may be due to materials washed down from the nearby Corallian Limestone which showed concentrations of Ca in excess of 20% in the streams. Lead and copper concentrations in stream sediments derived from the Kimmeridge Clay were higher than those derived from the Corallian and Upper Greensand. The mean concentration of Zn in the sediments derived from the Kimmeridge Clay was twice as high as that in the stream sediments derived from the Corallian Limestone and four times as high as that in the Upper Greensand. Higher concentrations of Fe and Mn were found in the sediments derived from the Corallian than in the Kimmeridge Clay and Upper Greensand.

5-7 Discussion of results.

Factors controlling the distribution of elements in the soils and stream sediments were thought to be due to,

(a) influence of the parent material,

(b) pedological modification,

(c) influence of the secondary environment.

(a) Influence of the parent material.

Concentrations of most elements in the soils and stream sediments reflected lithological differences in the parent material. Calcium and Mg concentrations were higher in the stream sediments derived from the Upper Greensand than those derived from the Kimmeridge Clay.This may be due to colluvial material from the nearby Corallian Limestone. In general, the concentrations of most elements

in the soils and stream sediments derived from the Upper Greensand were lower than those derived from the Kimmeridge Clay and Corallian Limestone. Figure 5-6 shows the variation of the elements Pb, Zn, Co and Cu in topsoils taken across the Kimmeridge Clay and the Corallian Limestone. The common distribution of these elements in the topsoils derived from each unit was thought to reflect variations in the bedrock. The higher concentrations of Zn and Pb found in the Corallian Limestone than in the Kimmeridge Clay were also shown by the topsoils concentrations of these elements (Fig. 5-6). The influence of the parent material was further reflected by the stream sediments (Figs. 5-2 to -5).

(b) Pedological modification.

Apart from Ca which decreased in the soils most elements were higher in the soils than in the rocks. The higher concentrations of Zn and Pb in the topsoils than in the subsoils were thought to be due to an association with the organic matter. Leaching seemed to be the reason for the enhanced concentrations of Fe, Cu and Co in the subsoils compared to the topsoils derived from the Kimmeridge Clay and the Corallian Limestone.

(c) Influence of the secondary environment.

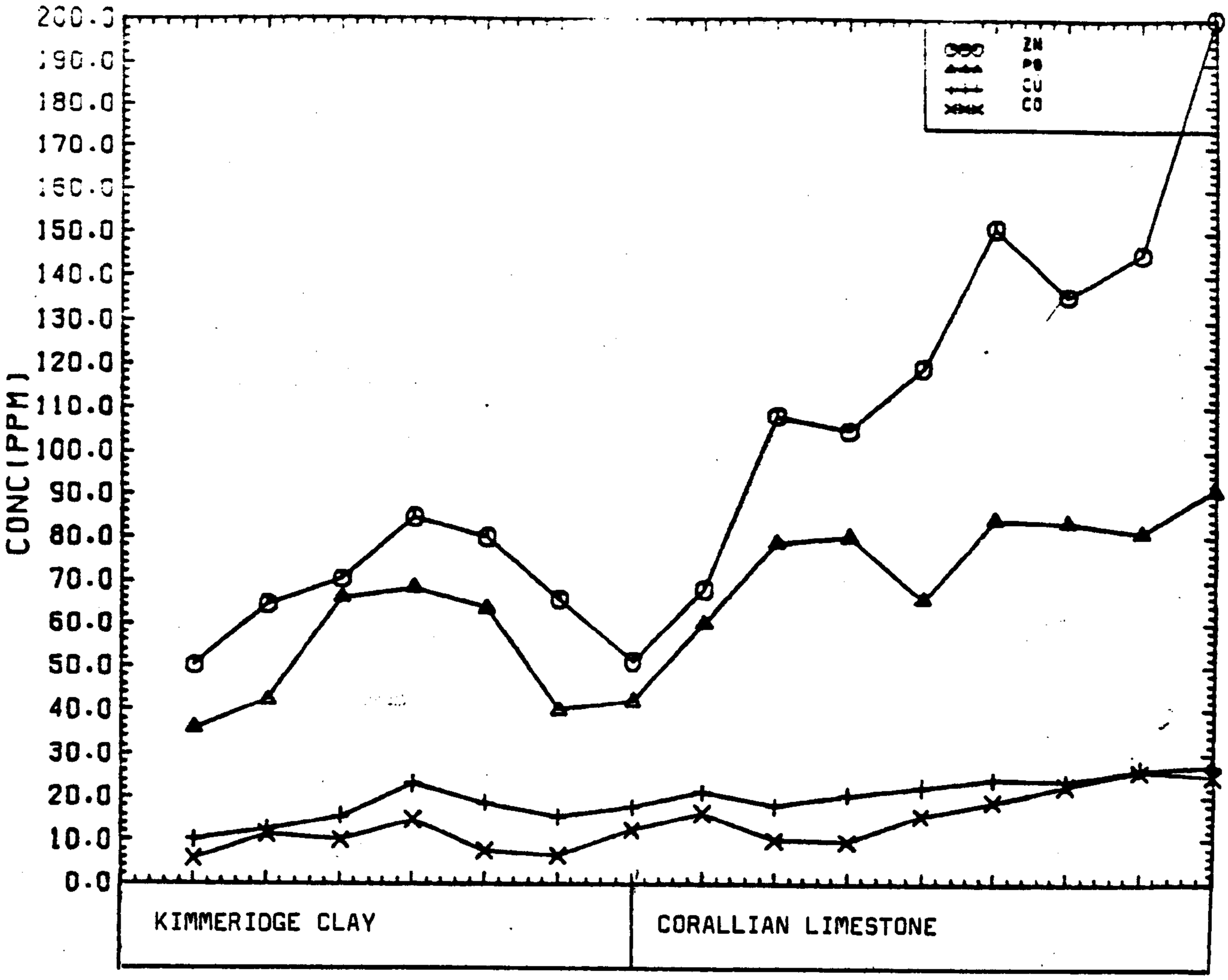
Processes operating in the secondary environment seemed to be important in influencing element distribution in the soils and stream sediments. Topography did not always influence element distribution in the same way. Table 5-5 shows element concentrations in poorly drained soils derived from the Kimmeridge Clay taken at different

TABLE 5:5

Profile, Drainage	Sample Depths (cm)	Ca%	Zn(ppm)	Pb(ppm)	Fe%	Mg%	Cu(ppm)	Co(ppm)	Mn(ppm)
VERY POORLY DRAINED AND SHALLOW (Hill Top)	0 - 15	1.0	61.3	30.5	1.8	0.11	12.7	5.6	245
	30 - 45	1.1	48.8	25.1	4.0	0.11	18.6	5.2	90
VERY POORLY DRAINED (Mid Slope)	0 - 15	0.40	64.9	31.4	1.8	0.17	14.2	6.4	225
	30 - 45	0.42	49.9	26.4	1.9	0.19	18.7	5.6	115
VERY POORLY DRAINED (Level ground near stream)	0 - 15	0.26	58.2	80.5	1.45	0.25	14.4	8.0	250
	30 - 45	0.22	36.2	42.9	2.40	0.25	25.0	7.0	400
VERY POORLY DRAINED (water logged)	0 - 15	0.19	49.0	55.0	4.8	0.18	22.0	8.5	350
	30 - 45	0.20	30.0	23.0	4.2	0.14	15.0	6.0	150

Metal content of selected residual soils over the Kimmeridge Clay in the Wiltshire study area.

FIG 5:6



Topsoil metal concentrations across the main geological units in the Wiltshire study area.

levels down a slope. Calcium and zinc concentrations decreased down the slope while Pb, Fe and Mn increased down the slope. Magnesium was unaffected by topographic changes. The higher concentrations of most elements in the topsoils than the subsoils were not a characteristic feature of the soils derived from the Kimmeridge Clay. The increased concentrations of Pb, Fe and Mn down the slope were thought to be due to redistribution by ground water while the decreased concentrations of Ca and Zn down the slope suggested that these elements were locked up in immobile forms, possibly as secondary carbonates.

5-8 Conclusions.

The following conclusions were made from the results.

(a) The parent material was the dominant factor controlling the distribution of elements in the soils and stream sediments. The lower concentrations of most elements tended to occur in the soils and stream sediments derived from the Upper Greensand while the higher concentrations tended to occur in the soils and stream sediments derived from the Kimmeridge Clay and Corallian Limestone.

(b) Concentrations of most elements except Ca, were higher in the soils than in the rocks and in the case of Pb and Zn concentrations were higher in the topsoils than in the subsoil. Copper concentrations in the topsoils derived from the Upper Greensand were similarly higher than those in the subsoil.

(c) Stream sediments reflected metal concentrations in the soils and rocks.

CHAPTER 6

Worcestershire Study Area.

Discussion of Metal Concentrations In The Rock Soil And Stream Sediment Derived From The Triassic and Jurassic Rocks.

6-1 Location.

The study area lies to the north west of Stratford-Upon-Avon.

6-2 Geology.

The area is underlain by Triassic and Jurassic rocks. The oldest unit in the study area is the Keuper Marl, of Triassic age. This is overlain by the Rhaetic which is not exposed in the study area. The Lower Lias succeeds the Rhaetic and it is extensively exposed in the study area (Fig. 6-1). The geology of the area has been described by Woodward (1886) , Wills (1976) and Davis (1967). The Keuper Series is mainly divisible into three illustrated in Table 6-1. The Keuper Sandstone is not exposed in the study area. Its presence is known from borehole information. It is pebbly and conglomeratic at its base and it is generally regarded as being erosion products from the Mercian Highlands, deposited underwater during the intermittent inundations of an arid phase. The Keuper marl is predominantly composed of unfossilferous silt and clay laid down in a subsidence phase of the Worcester basin. Lithologically, the rocks

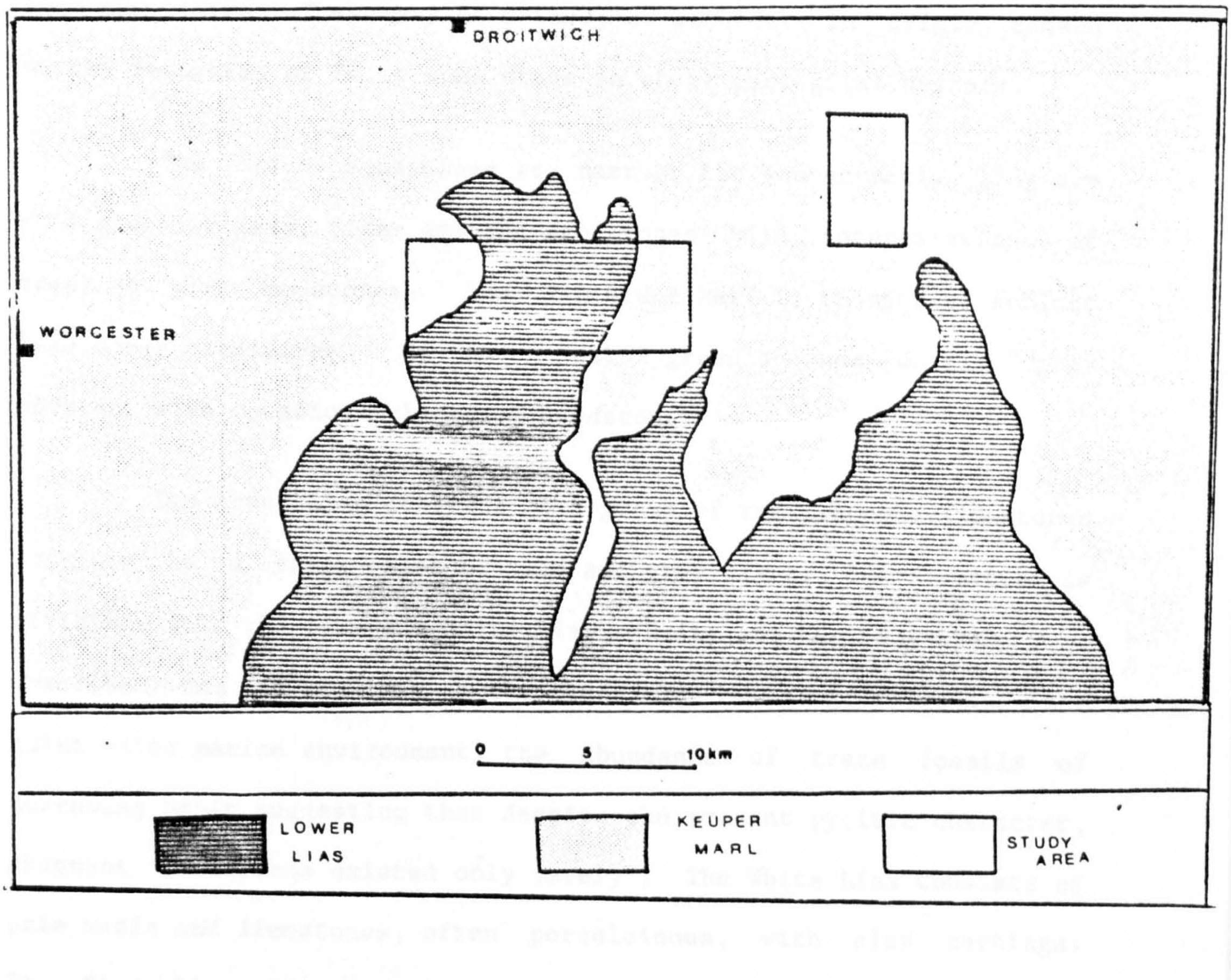
TABLE 6:1

GEOLOGICAL UNITS			LITHOLOGY
JURASSIC	LOWER LIAS	LOWER LIAS	Clay with limestones.
		BLUE LIAS	Alternation of fine grained argillaceous limestones with grey sandstones and shales.
		WHITE LIAS	White or pale grey, fine-grained limestones (calcitic mudstones) with thin clay partings.
TRIASSIC	KEUPER SERIES	TEA-GREEN MARL	Grey, green and white mudstones.
		ARDEN SANDSTONES	Grey sandstones and bluish grey shales. Cross stratified and dolomitic.
		KEUPER MARL	Reddish brown mudstones with bands of subordinate sandstones and siltstones.
		LOWER KEUPER SANDSTONES	Sandstones, conglomerates and beds of hard calcareous marl-breccia.

Stratigraphy of the Worcester study area

(Based on Hains and Horton, 1969)

Fig. 6-1



Sketch of the Geology and Location of Worcestershire study area

are reddish brown mudstone and silty mudstone associated with evaporite minerals such as gypsum and anhydrite.

The term "Marl" is a misnomer as the Keuper Marl is generally poorly or non-calcareous. The presence of evaporite deposits suggests an arid environment at the time of deposition with periods of complete evaporation. Blue and green mottles and streaks occur in the rocks at some localities. These may be primary or secondary in origin caused by the reduction of Fe at some stage in their geological history.

The Arden Sandstones are part of the Keuper Marl. They are pale greenish grey, fine- grained sandstones with intercalations of greenish grey mudstones. The Tea Green Marl is thought to reflect more humid conditions. It is a pale greenish and whitish grey mudstone with occasional bands of sandstone.

The Lower Lias consists of a group of argillaceous limestones overlain by a thick mass of blue and grey clays. The formation is divisible into the Blue and White Lias. Hains and Horton (1969) , described the Lower Lias in the study area as being "deposited in a quiet water marine environment, the abundance of trace fossils of burrowing habit suggesting that despite the present pyritic character, stagnant conditions existed only rarely". The White Lias consists of pale marls and limestones, often porcelainous, with clay partings. The Blue Lias which is dominant, consists of alternations of fine-grained argillaceous limestones with grey calcite mudstones and shales.

6-3 Climate.

The study area has a climate typical of much of Worcestershire, with mild winters and warm fairly wet summers. The months of Febuary, March and June are the driest and the months of January, July and November being the wettest. Average rainfall is in excess of 25ins, per annum.

6-4 Soils and Drainage.

The red marl which is generally non-calcareous weathers to a red silty clay which forms the parent material of the Worcester series, the main soil type over the Keuper Marl (Mackney and Burnham, 1964). It consists of medium to heavy textured, moderately drained soils of variable depths. The colour ranges from dark red to reddish grey. In general, soils of the north-western half of the study area tend to be sandy and shallow. This may be due to sandstone facies of the the Keuper Series that may contribute significantly to the soil forming material. Eastwards the soil gets deeper (60cm) and more granular in structure.

Soils developed over the Lower Lias are heavy and often imperfectly drained. The Evesham series which is widespread consists of calcareous dark grey soils having imperfect drainage. These soils are common over the flat lands often supporting arable agriculture. The Denchworth series that occurs to a limited extent in the study area consists of heavy textured non calcareous clay with very poor drainage. The whole area is drained by the River Avon which meanders northeast towards Evesham. The River Arrow is the main tributary of

TABLE 6:2

Medium	Number of Samples	Ca%	Zn(ppm)	Pb(ppm)	Fe%	Mg%	Cu(ppm)	Co(ppm)	Mn(ppm)
ROCK	10	2.5 (.6-4.8)	75.1 (37-105)	26.7 (19-40)	3.8 (1.5-5.0)	1.8 (.7-3.5)	24.5 (10-37)	12.7 (8-20)	670 (550-1000)
TOPSOIL 0 - 15cm*	22	0.51 (.24-1.5)	68.5 (37- 96)	35.6 (21-52)	2.0 (1.3-3.2)	0.79 (.34-1.4)	22.1 (11-32)	13.2 (7-21)	579.8 (350- 800)
SUBSOIL 30 - 45cm*	21	0.61 (.19-.89)	56.1 (36- 72)	23.2 (19-26)	2.2 (1.8-2.7)	1.1 (.5-2.1)	23.6 (8-30)	11.9 (9-20)	559.6 (500- 750)
STREAM SEDIMENT	10	2.1 (.85-3.9)	121.3 (50-157)	47.4 (29-96)	2.3 (1.5-3.0)	0.8 (.3 - 2)	27.6 (14-45)	11.2 (25-27)	867 (500-1100)

Range and mean of element concentrations in the rock (ground to -80 mesh), soil and stream sediments (-80 mesh), derived from the Keuper Marl in the Worcestershire study area.

( ) Range
* Depths of soil

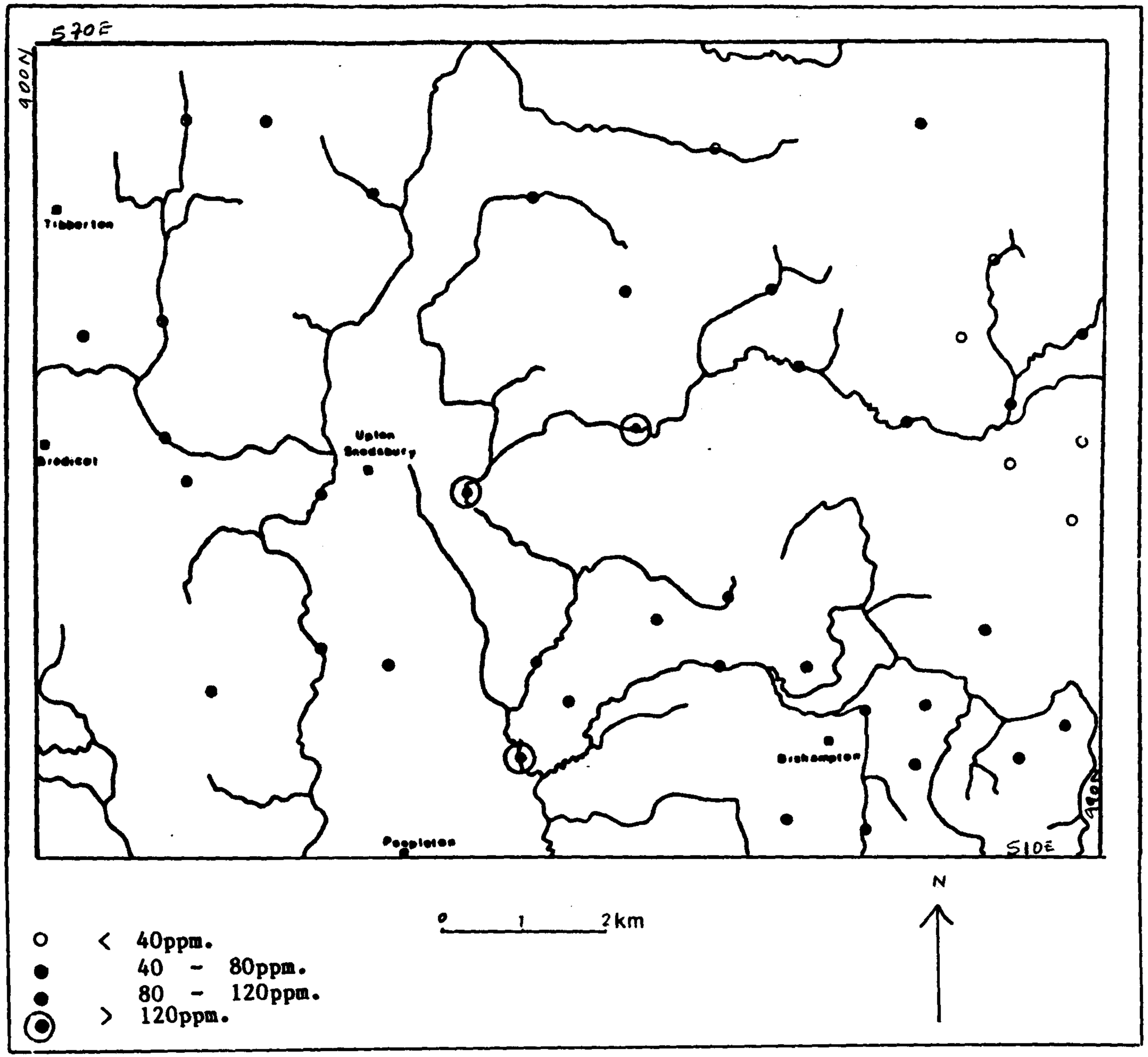


Fig 6-2

Zinc concentrations in the topsoils and stream sediments in the Worcestershire study are.

the Avon that governs the distribution of the streams and their course. The area is gently dissected with the Keuper Marl terrain forming undulating plains and the Lower Lias forming the flat lands.

6-5 Agriculture.

The imperfectly drained soils in the study area support mixed farming with emphasis on stock raising and hence a relatively high proportion of permanent grassland. Dairy cattle and sheep are the main stocks. Popular crops include oats, sugar beet and wheat. Most farms in the area are large and highly mechanised.

6-6 Geochemical patterns.

Tables 6-2, -3 summarise the metal concentrations in the rock, soils and stream sediments derived from the Keuper Marl and the Lower Lias in the Worcestershire study area. Geochemical maps showing the metal concentrations in the topsoils and stream sediments for the elements Zn, Pb, Cu and Mn are shown in Figs. 6-2, -3, -4, -5. Figure 6-6 shows topsoil concentrations taken along a traverse across the Lias and the Keuper Marl. The patterns revealed by individual elements are discussed below.

(a) Geochemical patterns in the rocks.

The distribution of Ca followed the anticipated geological units in the study area (Tables 6-2, -3). The mean concentration of Ca in the Lower Lias (6.3%) was more than twice as high as that in the

TABLE 6:3

Medium	Number of Samples	Ca%	Zn(ppm)	Pb(ppm)	Fe%	Mg%	Cu(ppm)	Co(ppm)	Mn(ppm)
ROCK	10	6.3 (2.2-10.8)	71.8 (30- 94)	24.9 (14-38)	2.4 (1.4-4 .0)	0.88 (.42-1.7)	28.7 (18-42)	15.6 (10-26)	695.6 (300-1050)
TOPSOIL 0 - 15cm*	24	2.5 (.67- 6.6)	86.2 (49-147)	42.4 (20-85)	2.8 (2.1-3.4)	0.68 (.48-1.9)	32.2 (22-41)	14.1 (8-25)	β39.6 (550-1250)
SUBSOIL 30 - 45 *	24	2.8 (.6 - 7)	57.6 (41- 68)	30.9 (22-41)	3.3 (2.5-4.3)	0.54 (.3 -.68)	30.1 (24-41)	18.9 (18-30)	1005.0 (600-1350)
SEDIMENT	12	2.2 (.9 - 5.1)	96.3 (61-147)	43.2 (19-66)	2.7 (1.3-3.5)	0.83 (.4-1.35)	35.3 (17-41)	23.9 (10-36)	1102.0 (450-1400)

Range and mean of element concentrations in the rock (ground to -80 mesh), soil and stream sediment (-80 mesh) derived from the Lower Lias in the Worcestershire study area.

( ) Range
* Depths of soil

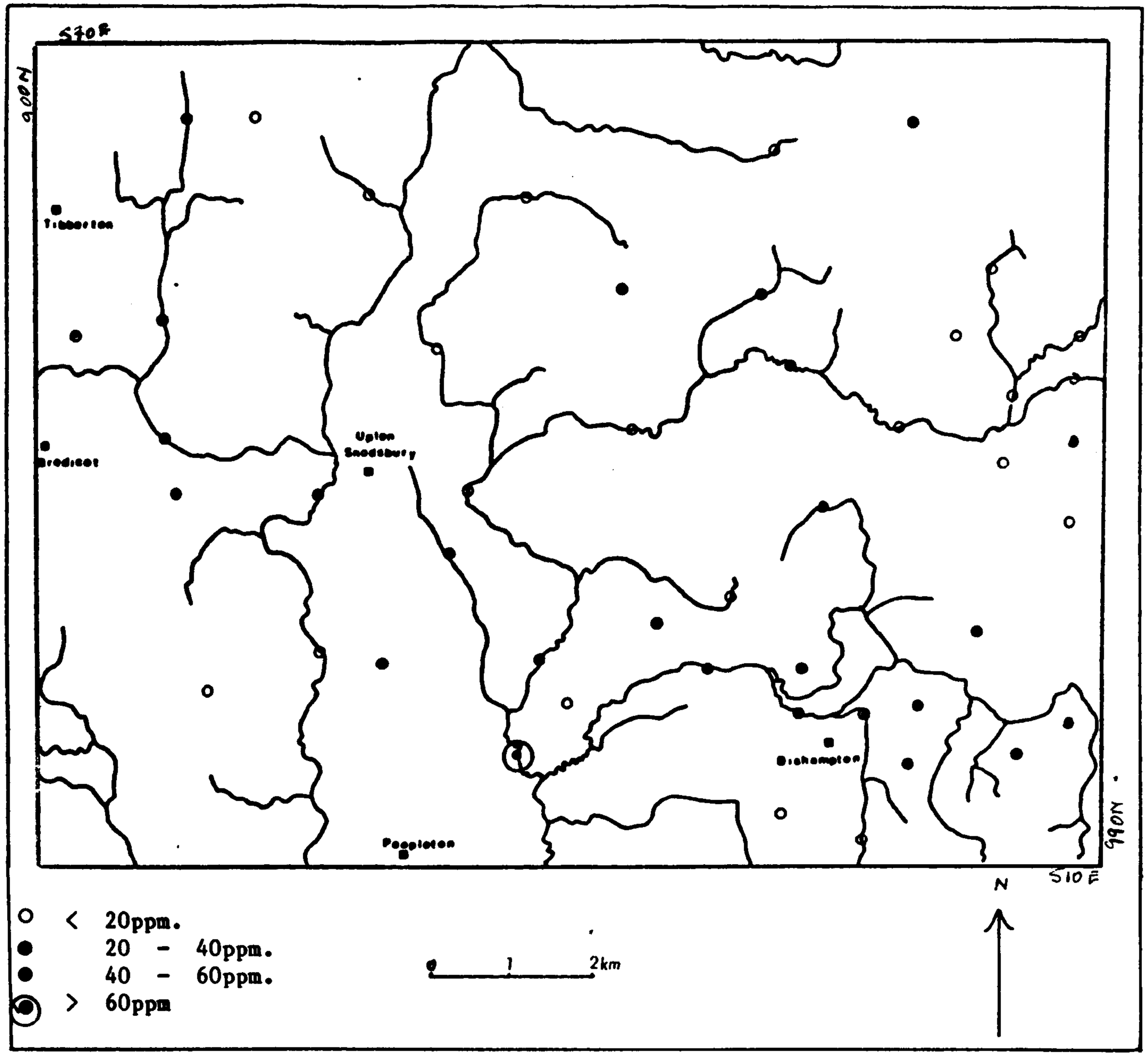


Fig 6-3

Lead concentrations in th topsoils and stream sediments in the Worce tershire study area.

Keuper Marl (2.5%). Magnesium concentrations on the other hand were higher in the Keuper Marl than in the Lower Lias. The concentrations of Fe varied. Occasional concentrations as high as 4% occurred in both the Lower Lias and the Keuper Marl, however majority of the rock samples had concentrations below 3% Fe.

Concentrations of Zn, Pb, Cu and Mn in the two units were similar. In the Lower Lias, the higher concentrations of these elements were recorded in the calcareous samples while over the Keuper Marl the lower concentrations were recorded in the sandstone facies of the Keuper Series. Cobalt lacked distinct pattern of distribution being generally low in both units.

(b) Geochemical patterns in the soils.

Element concentrations in the soils derived from both units reflected the lithological variations in the parent material. The distribution of Ca showed strong lithological control being higher in the soils derived from the Lower Lias than in those derived from the Keuper Marl (Tables 6-2, -3). Soil formation over both units resulted in decreased concentrations of Ca. The ranges and mean concentrations of Fe, Mn and Co in the topsoils and subsoils derived from the Keuper Marl were similar. In the Lower Lias where the soils tended to be gleyed and occasionally waterlogged concentrations of Fe and Mn were lower in the topsoils than in the subsoils. Topsoil concentrations of Cu were similar to the subsoil concentrations over both units.

(c) Geochemical patterns in the stream sediments.

Stream sediment concentrations of Ca and Mg over the Lower

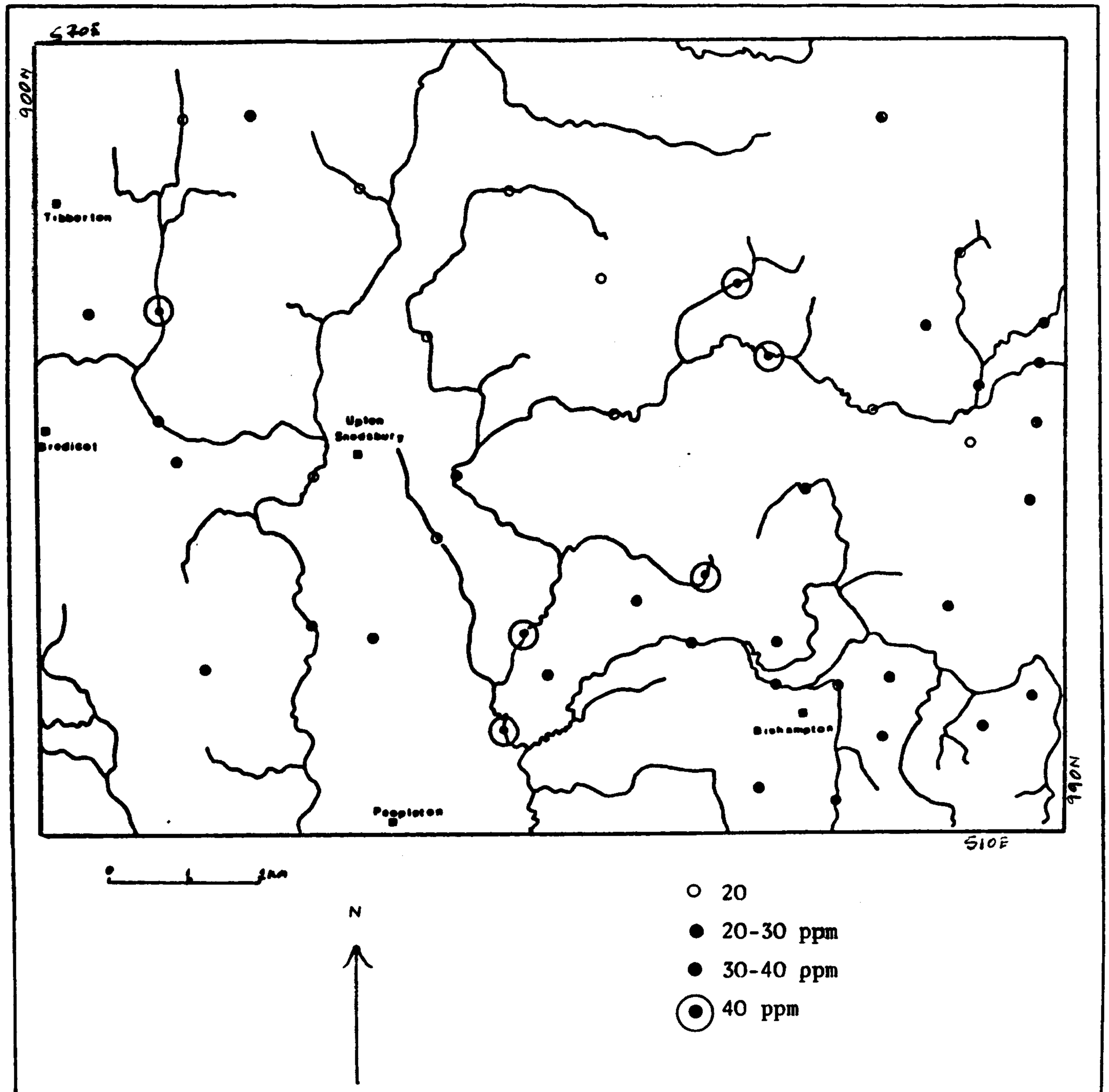


Fig. 6-4

Copper concentrations in the topsoils and stream sediments in the Worcestershire study area

Lias were similar to those in the soils. Over the Keuper Marl Ca, Zn, Pb and Cu concentrations in the stream sediments were higher than those in the soils. Iron concentrations in the stream sediments derived from the Keuper Marl were lower than those in the rocks and similar to those in the soils while over the Lower Lias iron concentrations in the stream sediments were similar to those in the rocks and topsoils. Copper concentrations were only slightly higher in the stream sediments derived from both units compared to their associated parent materials and soils. Manganese concentrations were higher in the stream sediments derived from the Lower Lias than those derived from the Keuper Marl.

6-7 Discussion of results.

The following factors were found to influence the distribution of elements in the soils and stream sediments

(a) influence of the parent material,

(b) pedological modification of element concentrations,

(c) influence of the secondary environment.

(a) Influence of the parent material.

The lithology of the parent material seemed to be dominant not only in determining the type of soils developed but also the element concentrations in the soils. Over the Lower Lias the distribution of Ca was strongly influenced by the concentrations in the rocks. The relationship between the element concentrations in the soils and those of the parent material are shown in Figs. 6-6, -7.

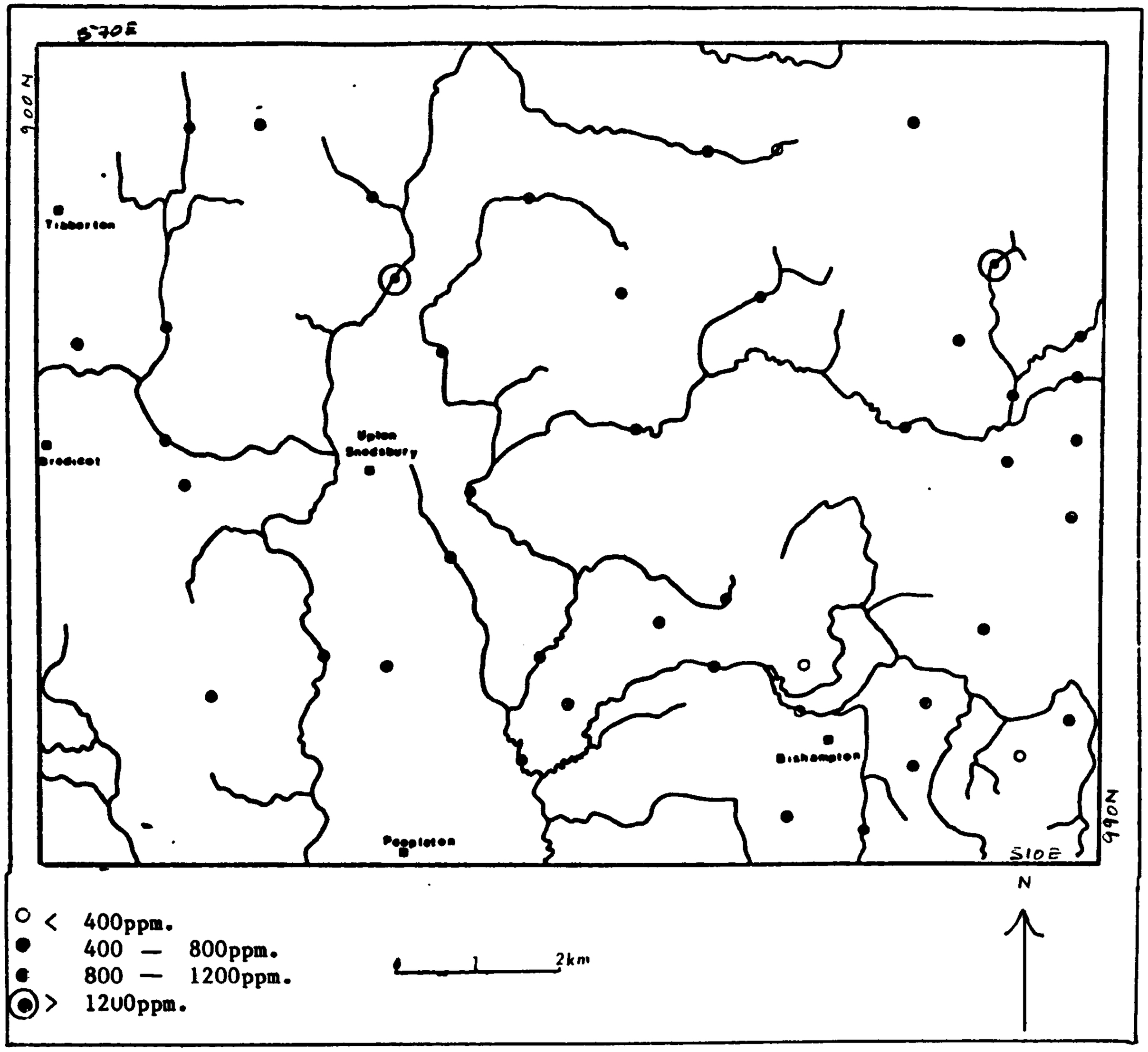
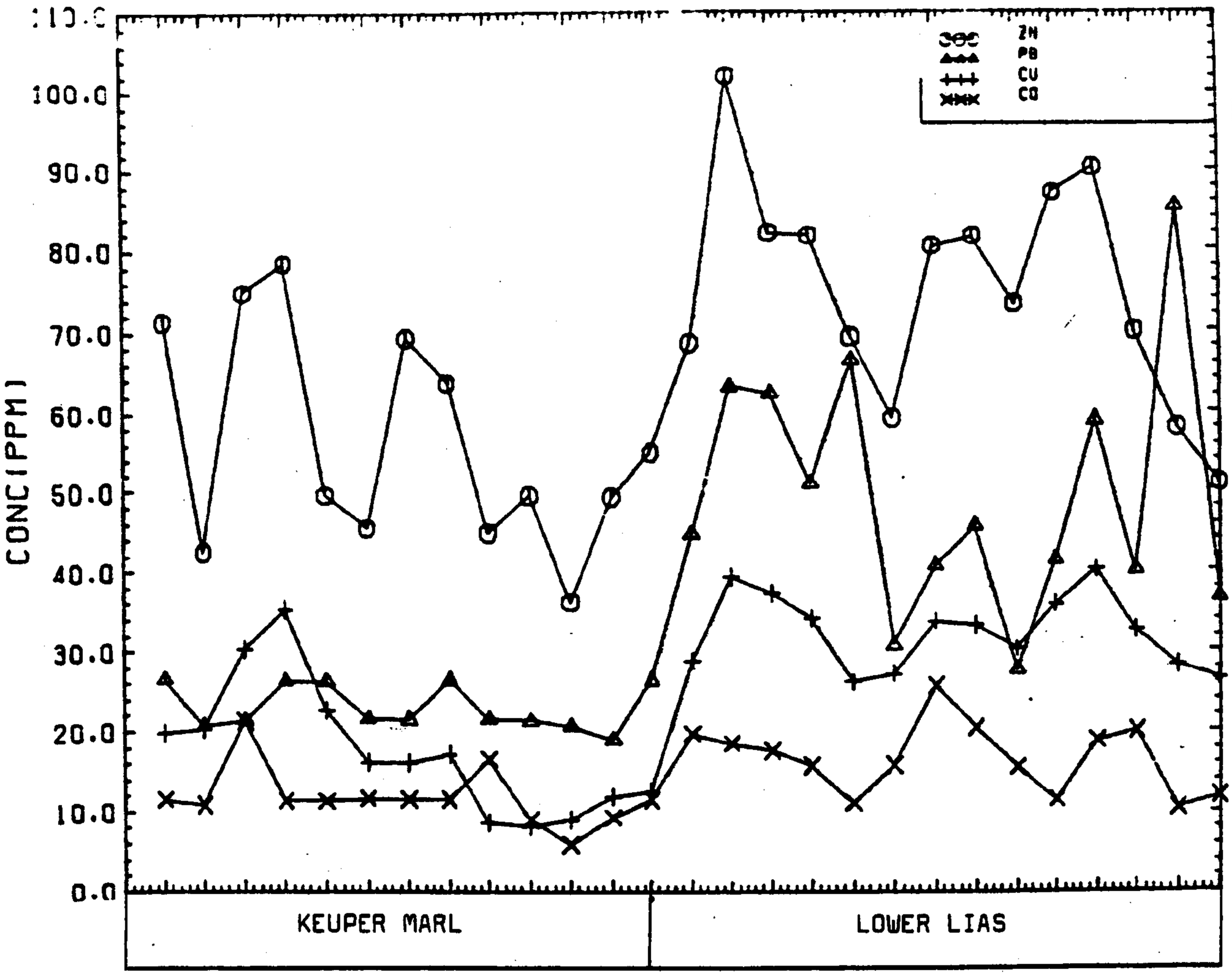


Fig. 6-5

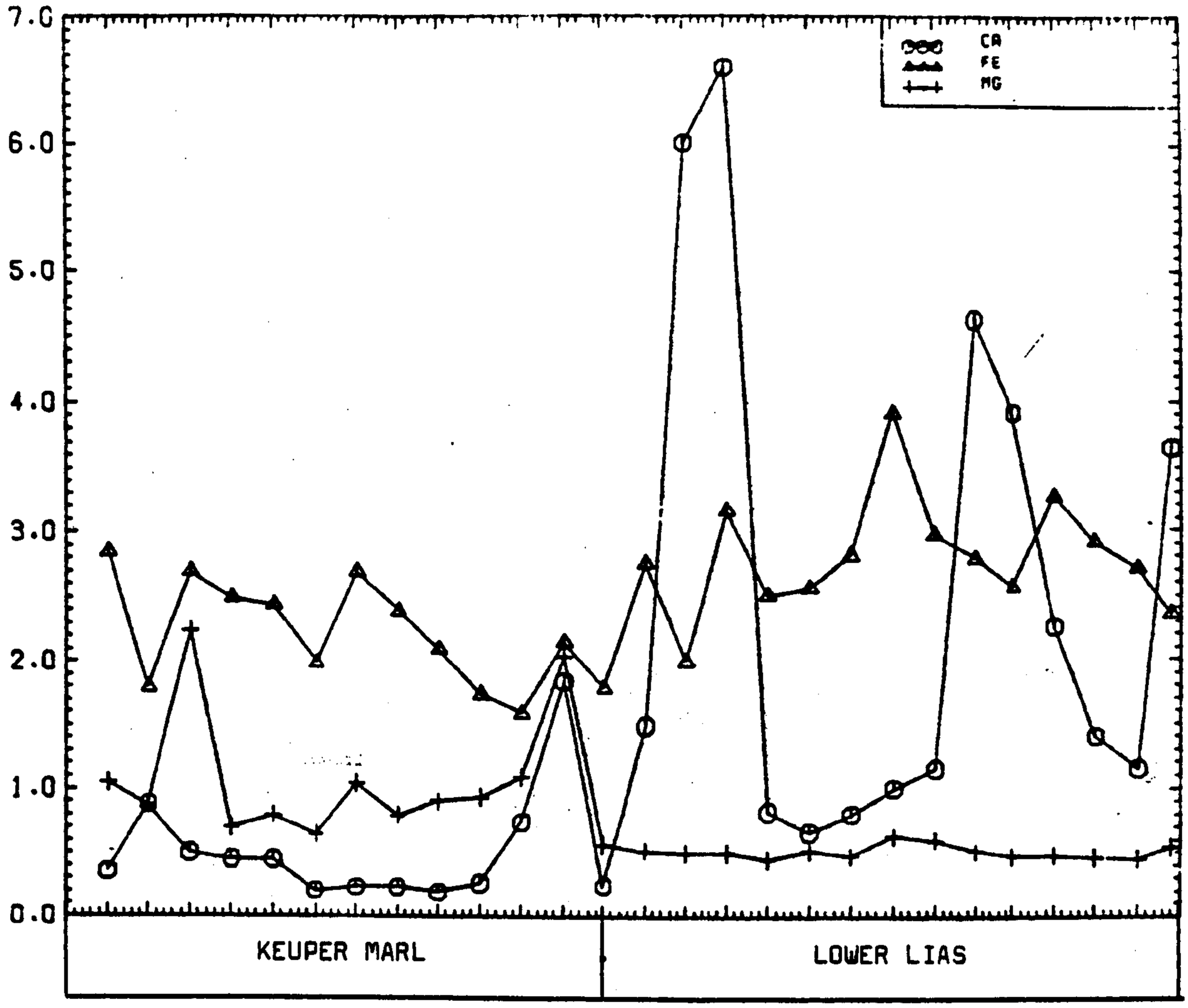
Manganese concentrations in the topsoils and stream sediments in the Worcestershire study area

FIG 6:6



Topsoil metal concentrations across the main geological units in the Worcestershire study area.

FIG 6:7



Topsoil metal concentrations across the main geological units in the Worcestershire study area.

Thus element concentrations along the transect across the Keuper Marl and Lower Lias showed that higher concentrations occurred in the topsoils derived from the Lower Lias while the lower concentrations occurred in the soils derived from the Keuper Marl.

(b) Pedological modification.

There was a general trend towards decreased concentrations of Ca in the soils compared to the rocks and slight increases in the concentrations of other elements. This may be due to the leaching of the calcium bearing minerals during soil formation. The enhanced concentrations of Pb, Zn and Cu in the topsoils derived from both units suggested an association with organic matter while the higher concentrations of Fe and Mn in the subsoils compared to the rocks over the Lower Lias suggested some degree of mobilisation in the soils. Thus manganese can be leached from the topsoils and redistributed in the subsoils. Over the Lower Lias mottling increased with depth in a number of soils and the increased concentrations of Fe and Mn in the subsoils suggested that the prevailing conditions in the soils may be encouraging the leaching of the hydrous oxides from the upper horizons of the soils. Over the Keuper Marl where Fe and Mn concentrations in the top and subsoils were similar, it was inferred that the hydrous oxides constituted a stable fraction in the soils.

(c) Influence of the secondary environment.

The higher concentrations of Ca, Zn, Pb and Mn in the stream sediments derived from the Keuper Marl compared with the associated

soils and rocks suggested a fixation process in the surface drainage. This was thought to be due to the formation of secondary carbonates in the stream beds. The decreased concentrations of Fe in the stream sediments derived from the Keuper Marl suggested a dilution process, probably involving the precipitation of secondary calcium carbonates.

6-8 Conclusions.

The following conclusions were drawn.

(a) Parent material was the dominant factor influencing the distribution of elements in the soils and stream sediments.

(b) Concentrations of elements were higher in the Lower Lias than in the Keuper Marl.

(c) Leaching of elements in the soils derived from the Keuper Marl was not found to contribute significantly in the distribution of elements in the soils, while over the Lower Lias leaching in the soil was responsible for the higher concentrations of Fe and Mn in the subsoils compared to the topsoils.

(d) Stream sediments generally reflected concentrations of elements in the soils and rocks from which they were derived.

CHAPTER 7

The Herefordshire Study Area.

A Discussion Of The Metal Concentrations In The Rocks, Soils And Stream Sediments Derived From The Old Red Sandstone.

7-1 Geology.

The geology of the study area has been reviewed by Richardson(1911) and Whitfield(1971) and this is shown in Fig. 7-1. The stratigraphic sequence is shown in (Table 7-1) . The dominant rock type in the study area is of Lower Devonian age. This is mainly medium grained thinly bedded sandstones with beds of marl. The oldest unit, the St. Maughans Group has been equated to the middle division of the Old Red Sandstone, the Ditton series in the Droitwich area (Pocock and Whitehead, 1948). It consists of interbedded marls and sandstones of approximately equal proportions with several thin concretionary limestones (cornstones). The individual cornstones are impersistent. The Brownstone group that overlies the St. Maughans group consists of reddish-brown, micaceous and argillaceous sandstones and green marls. The marls in the Brownstones are rarely calcareous (Earp et al. 1971). The Upper Devonian Quartzitic Sandstone group occurs less frequently in the study area. This consists of quartz conglomerate bands with widely scattered pebbles (Welch and Trotter,1961). The Tintern sandstone is confined to the south eastern sector of the area. It consists of soft olive grey medium grained sandstones with partings of marl. Discontinuous alluvial deposits of

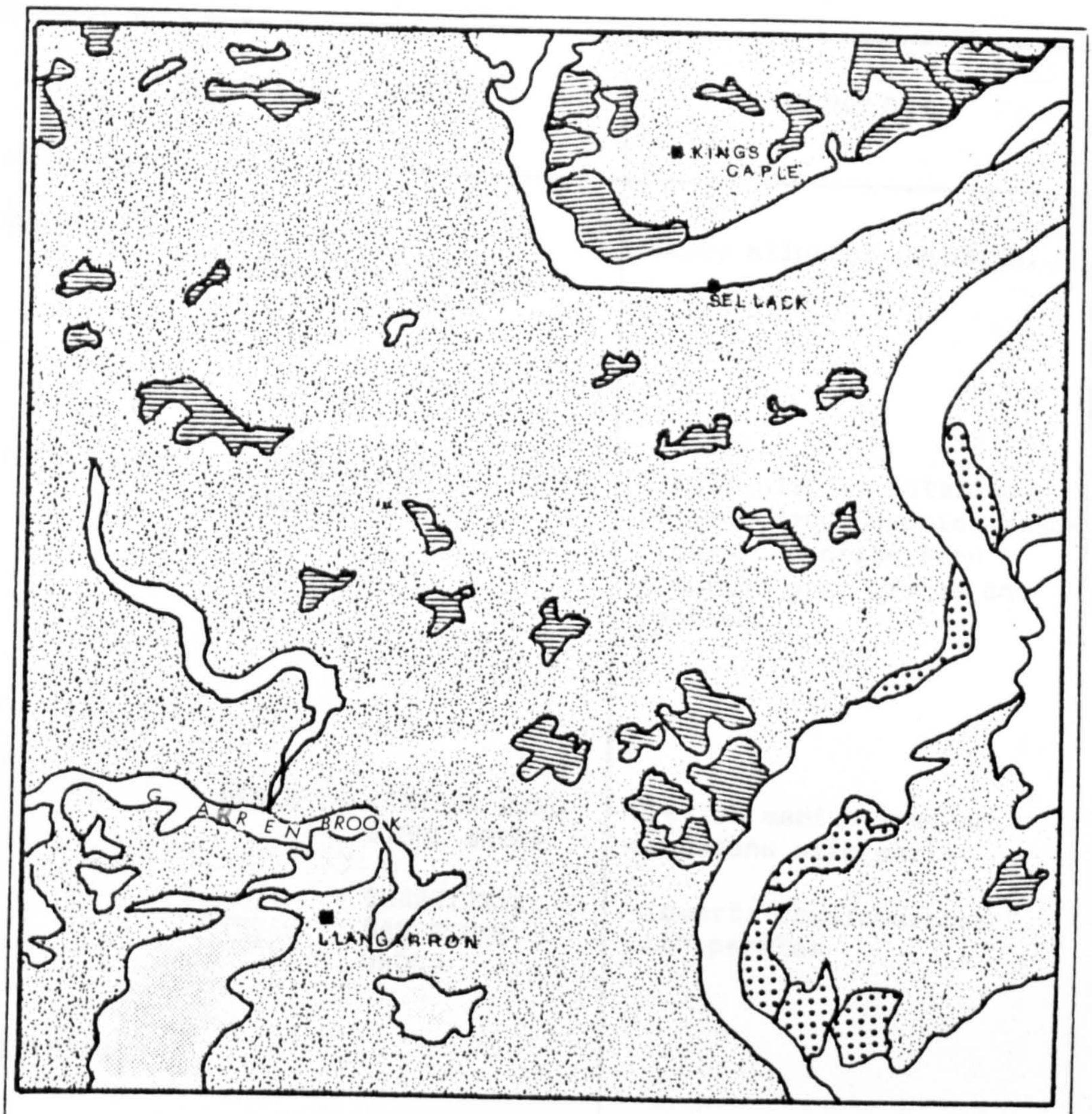


Fig. 7-1

Geological Map of The Herefordshire Study Area.

TABLE 7:1

GEOLOGICAL FORMATIONS			LITHOLOGY
RECENT	COLLUVIUM (Riverine Alluvium)		Silty alluvial deposits.
PLEISTOCENE	FLUVIO-GLACIAL TERRACE GRAVELS		Fluvio-glacial material derived from Devonian sandstones and grits from Silurian gray wackes and pebbles.
DEVONIAN	UPPER	- TINTERN SANDSTONE GROUP	Greyish medium grained sandstone with marls.
		- QUARTZITIC SANDSTONE GROUP	- quartz conglomerates with pebbles.
	LOWER	- BROWNSTONE GROUP	Dark reddish medium grained micaceous sandstones.
		- St MAUGHAN'S GROUP	Interbedded marls and sandstones.

Stratigraphy of the Herefordshire study area

(based on Whitfield 1971)

Pleistocene age are confined to the flood plain of the River Wye.

7-2 Drainage and Topography.

The southerly meandering River Wye is the dominant feature of the relief and drainage (Fig. 7-1) . Thus much of the area is drained by the tributaries of the River Wye. In general, the area is gently dissected with land rising slightly above 300ft O.D. In the eastern section where the River Wye is dominant, low land of about 100ft O.D. rises gently to over 300ft O.D. in the central portion of the area . The drainage in the western half is controlled by streams rising between 200ft and 300ft in the central and eastern halves of the study area. These join the Garren Brook which meets the River Wye above Whitchurch. West of the Garren Brook, the land rises again to a height of above 300ft O.D.

7-3 Climate.

Whitfield(1971) described the area as being "in the rain shadow of central Wales " with an average yearly rainfall of 27.8in. Maximum temperatures are recorded for the months of July and August with temperatures of over 20 C. Frost periods are generally short.

TABLE 7.2

Soil group	Texture and geology	Soil series
Brown earths (Sols bruns acides)	Coarse loamy (sandy loam) over medium grained Devonian sandstone Coarse loamy (fine and very fine sandy loam) over fine grained Devonian sandstone Coarse loamy over interbedded Devonian marl and medium grained sandstone Coarse loamy and stony reddish brown and brown terrace deposits derived mainly from Devonian and Silurian rocks	Ross Eardiston Sellack Newnham
Gleyed brown earths (sols bruns acides)	Coarse loamy (fine sandy loam) colluvium derived from Devonian sandstones	Biddlestone
Non-calcareous ground-water gley soils	Coarse loamy alluvium derived from Devonian rocks Silty alluvium derived from Silurian rocks	Elvastone Kingsland
Brown warp (alluvial) soils	Silty brown alluvium derived mainly from Silurian rocks Coarse loamy reddish brown alluvium derived from Devonain rocks Silty reddish brown alluvium derived mainly from Devonian rocks	Teme Walford Lugwardine

Soil groups, texture, geology and soil series of the Herefordshire study area.
(Whitfield 1971)

7-4 Soils.

The area has been mapped by the Soil Survey of England and Wales, (Whitfield, 1971). Table 7-2 shows the main soil series in the study area. Over 80% of the area is dominated by brown earths. Gleyed brown earths and gley soils occur to a limited extent in the area.The main soil sampled in the area was the Ross series.

7-5 Agriculture.

Over 65% of the area is cultivated. Arable cropping is generally confined to the brown-earths while permanent pasture is common over the alluvial soils. A variety of crops is cultivated. These include barley, oats, sugar beet and to a limited extent, potatoes.

7-6 Regional Geochemical patterns.

The metal concentrations found in the rock, soil and stream sediments are presented in (Table 7-3) . Rock samples were collected from all the facies of the Old Red Sandstone. Only the Ross soil series was sampled since it was the dominant soil type in the area. Stream sediment samples were taken from stream road intersections. Geochemical maps showing the distribution of elements in the topsoil and stream sediments are shown in Figs. 7-2 to 7-5. The patterns revealed by the present investigations are discussed below.

TABLE 7:3

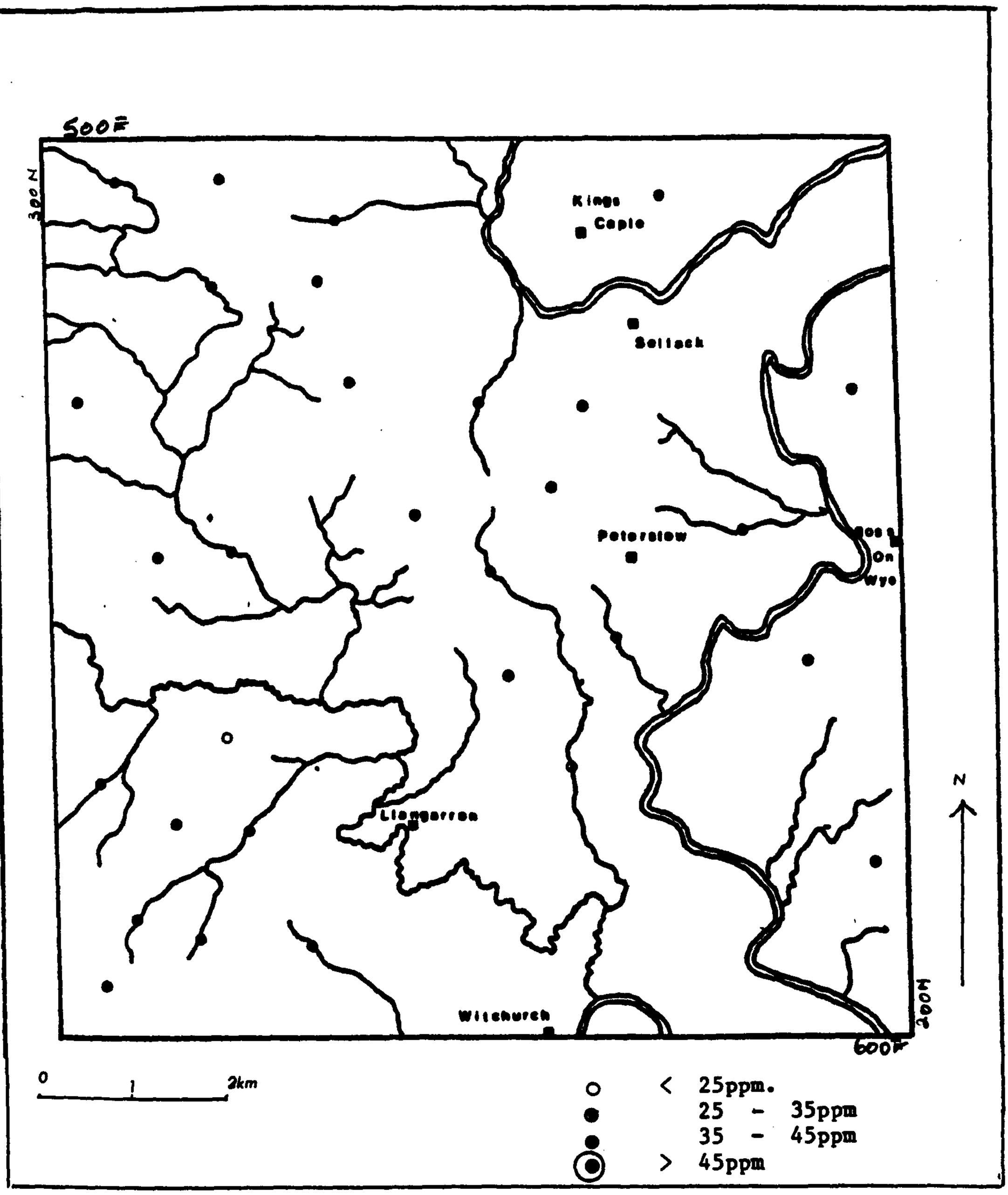
Medium	Number of Samples	Ca%	Zn(ppm)	Pb(ppm)	Fe%	Mg%	Cu(ppm)	Co(ppm)	Mn(ppm)
ROCK	15	5.5 (.1-13.6)	31.8 (15-75)	16.1 (10-37)	1.3 (.4-2.6)	1.04 (.19- 3)	15.0 (5-20)	7.9 (5-18)	938.1 (750-1360)
TOPSOIL 0 - 15cm*	48	0.66 (.16-.86)	37.2 (24-46)	20.9 (18-46)	1.5 (.75-2.3)	0.39 (.22-.78)	10.4 (5-15)	5.9 (8-14)	760.9 (450-800)
SUBSOIL 30 - 45cm*	40	0.62 (.4-.9)	40.1 (18-52)	15.5 (12-29)	1.4 (.5-2.9)	0.30 (.2-1.4)	12.5 (10-18)	7.0 (5-15)	770.0 (400-800)
STREAM SEDIMENT	16	1.80 (.22-2.4)	51.5 (45-66)	18.7 (11-43)	1.2 (.9-3.0)	0.42 (.19-1.6)	14.6 (9-26)	6.8 (5-19)	684.8 (505-960)

Range and mean element concentrations in the rocks, (ground to -80 mesh) soils and stream sediments (-80 mesh) derived from the Old Red Sandstones in the Herefordshire study area

( ) Range

* Depth of sample

Fig 7-2



Zinc concentrations in the topsoils and stream sediments in the Herefordshire study area.

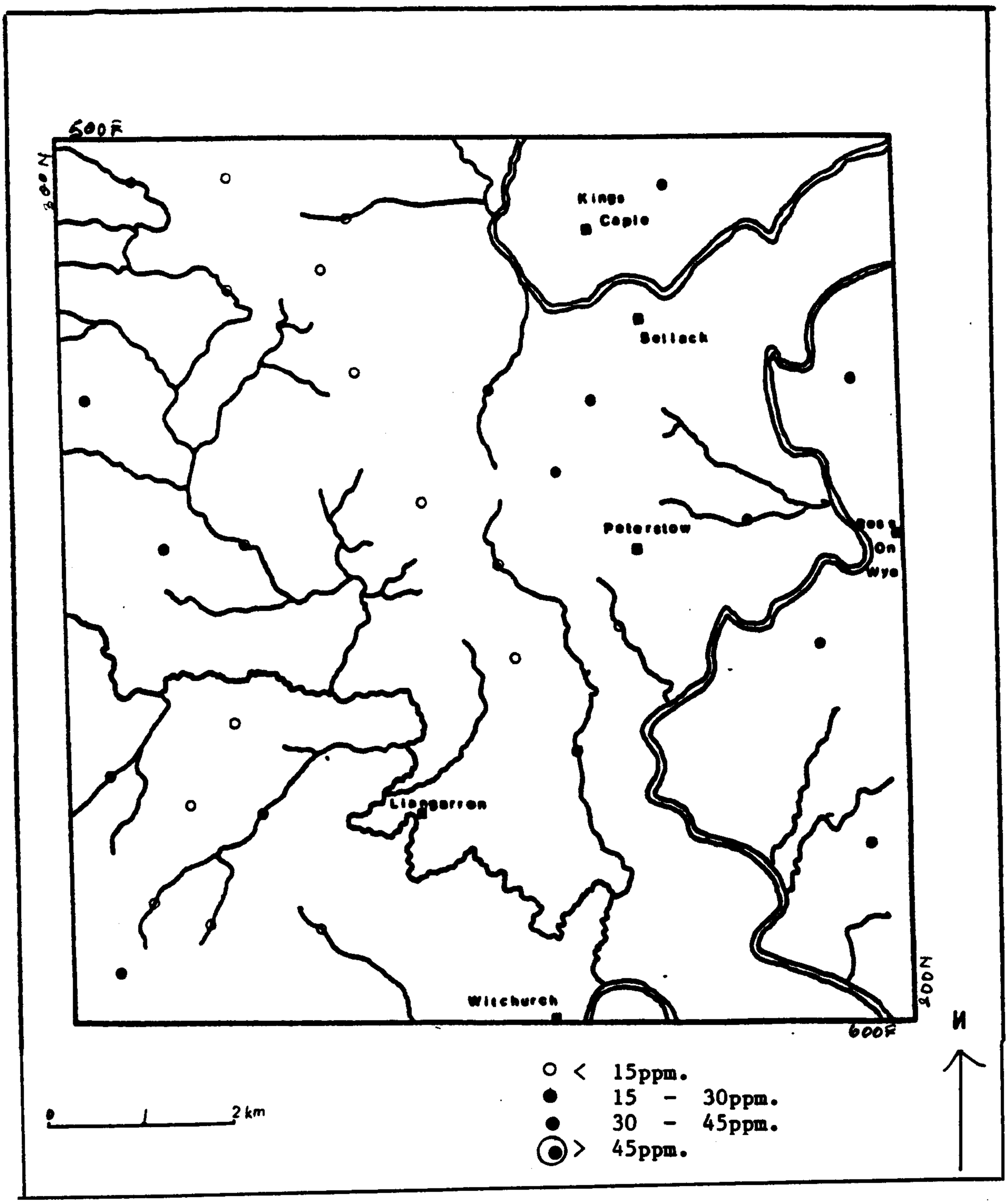
(a) Geochemical patterns in the rocks.

The wide range displayed by Ca reflected the main lithological variations found within the area (Table 7-3). Samples of the cornstones and a few unferruginised rocks had Ca concentrations in excess of 10%. This was usually accompanied by high concentrations of Mg (up to 3%). Iron concentrations were low despite the reddish colouration. Thus the maximum concentrations found in the rocks was below 3% Fe. This may be due to most of the iron present being locked up in the visible iron oxides that coats the sand grains in the ferruginous facies. Zinc, lead, copper and cobalt concentrations in the rocks also suggested a lithological control being in the main generally low in all the facies of the Old Red Sandstones in Herefordshire. Generally, concentrations of these elements were slightly higher in the marl facies than in the sandy facies. The coarse grained facies were particularly low in all the elements studied. Most marl and sandstone samples had concentrations of Cu and Co below 5ppm. In contrast manganese concentrations were high. The mean concentration (938ppm) was relatively higher than those of other elements studied. Concentrations as high as 1350ppm Mn were found in some calcareous samples. This suggested that manganese may be more related to the carbonates than the oxide phase in the rocks.

(b) Geochemical patterns in the soils.

There was a marked depletion of Ca concentrations in the soils compared to their parent materials. The mean concentrations of Ca and Mg in the top and subsoils were almost identical. This was

Fig. 7-3



Lead concentrations in the topsoils and stream sediments in the Herefordshire study area.

reflected in the similarity of their ranges. Iron concentrations in the soils were similar to those in the rocks. Topsoil and subsoil concentrations of Fe showed very little differences. Zinc concentrations were marginally higher in the soils than in the rocks while differences between the concentrations of Pb in the soils and rocks were small. Topsoil concentrations of Pb were marginally higher than those in the subsoil. The concentrations of Co and Cu in the soils were also similar to those in the rocks. As with Zn and Pb concentrations of these elements in the top and subsoils were similar. Although the mean concentration of Mn in the subsoil was slightly higher than that of the topsoil, the range of Mn showed that concentrations in the top and subsoils were similar.

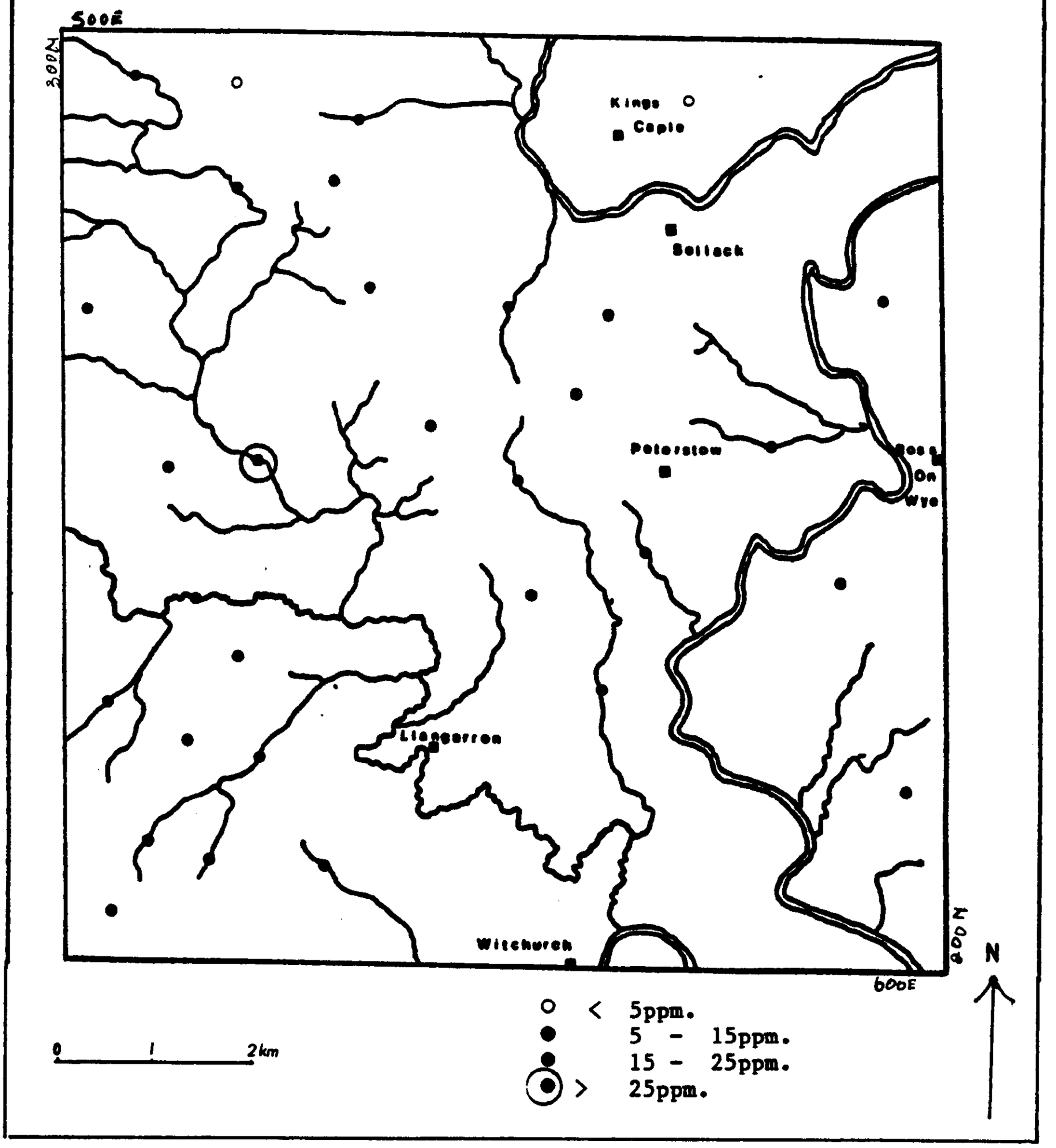
(c) Geochemical patterns in the stream sediments.

Calcium concentrations in the stream sediments were lower than those in the rocks and higher than in the soils. Concentrations of Zn were also higher in the stream sediments than in the soils and rocks while Pb, Fe, Mg, Cu and Co in the stream sediments showed very little differences with the concentrations in the rocks and soils (Table 7-3). As in the rocks the concentrations of Cu and Co were exceedingly low in the stream sediments with concentrations below 10ppm widespread. Manganese levels were slightly lower in the stream sediments than in the soils and rocks, although the range was wider.

7-7 Discussion of results.

Factors that influenced the distribution of elements in the soils and stream sediments were thought to be due to the following

Fig 7-4



Copper concentrations in the topsoils and stream sediments in the Herefordshire study area.

(a) Influence of the parent material.

(b) Pedological modification.

(b) Influence of the secondary environment.

(a) Influence of the parent material.

The elements found in low concentrations in the rocks were reflected in the small ammount found in the associated soils and stream sediments. Variation of Ca concentrations in the rocks were not however reflected in the soils and stream sediments. Thus soils and stream sediments derived from some calcareous beds of the Old Red Sandstone had similar Ca concentrations as those derived from the less calcareous beds.

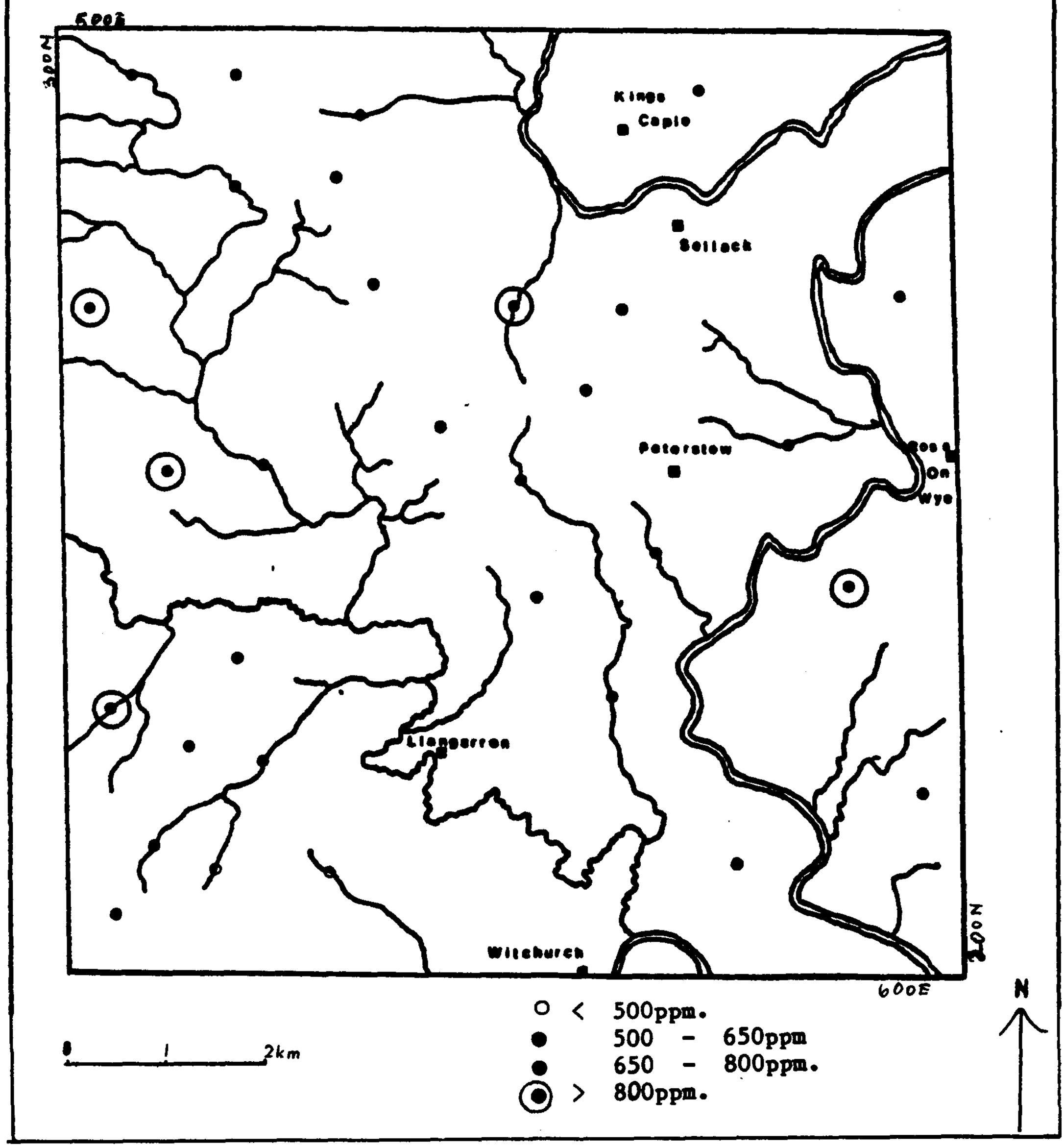
(b) Pedological modification.

Considerable leaching of Ca bearing minerals occurred in the transition from rocks to soils. The enhanced concentrations of Pb in the topsoils compared to the subsoils followed the trend observed in other study areas. This was thought to be due to an association with the organic matter. The similarities of the concentrations of Mn and Fe in the top and subsoils suggested that the hydrous oxides constituted a stable component of the soils.

(c) Influence of the secondary environment.

Processes operating in the secondary environment seemed to affect the distribution of Ca and Zn. The enhanced concentrations of Ca in the stream sediments compared to the soils suggested that some

Fig 7-5



Manganese concentrations in the topsoils and stream sediments in the Herefordshire study area.

of the Ca leached in the transition from rocks to soils may be redistributed in the stream sediments, possibly as secondary carbonates. Formation of secondary carbonates also seemed to account for the higher concentrations of Zn in the stream sediments. Dilution of the sediments by calcium carbonates alone could not account for the decreased concentrations of Mn in the stream sediments. The stream sediments were often very sandy with the sand grains reflecting the texture of the rocks upstream. It seemed likely that dilution with sand may contribute to the lower concentrations of Mn in the stream sediments.

7-8 Conclusions.

The following conclusions were made from the results

(a) The dominant control on the distribution of elements was the inherently low concentrations of most elements found in the rocks

(b) apart from Ca which displayed marked depletions in the transition from rock to soil and stream sediments, leaching of most elements in the soils was not a common feature

(c) differences between element concentrations in the top and subsoils were small except for Pb which tended to be higher in the topsoil.

CHAPTER 8

Somerset Study Area.

A Discussion Of The Metal Concentrations In The Rocks, Soils And Stream Sediments Derived From The Triassic And Jurassic Rocks.

8-1 Location.

The area lies in the centre of Somerset near the towns of Glastonbury and Street

8-2 Geology.

The stratigraphic succession in the study area has been reviewed by Avery (1955) and is shown in (Table 8-1) . The oldest unit is the Keuper Marl. This consists of red silty mudstones with thin beds of greenish grey calcareous sandstones (skerries) occurring locally. The top of the formation is made up of pale green marls and soft mudstones known as the Tea-Green Marl or Grey Marls. The Rheatic that overlies the Keuper Marl is more variable. It consists of black shales with thin bands of limestones and sandstones, marls and calcareous mudstone . The Jurassic period within the study area is represented by the Lower Lias which is divisible into the lower series, "the White and Blue Lias" and an upper series, "The Lower Lias clay". The White and Blue Lias consists of hard argillaceous limestone with interbedding of shales and marls. The upper series consists mainly of grey, calcareous clays. The Middle Lias occur around the town of Glastonbury . These are soft grey laminated

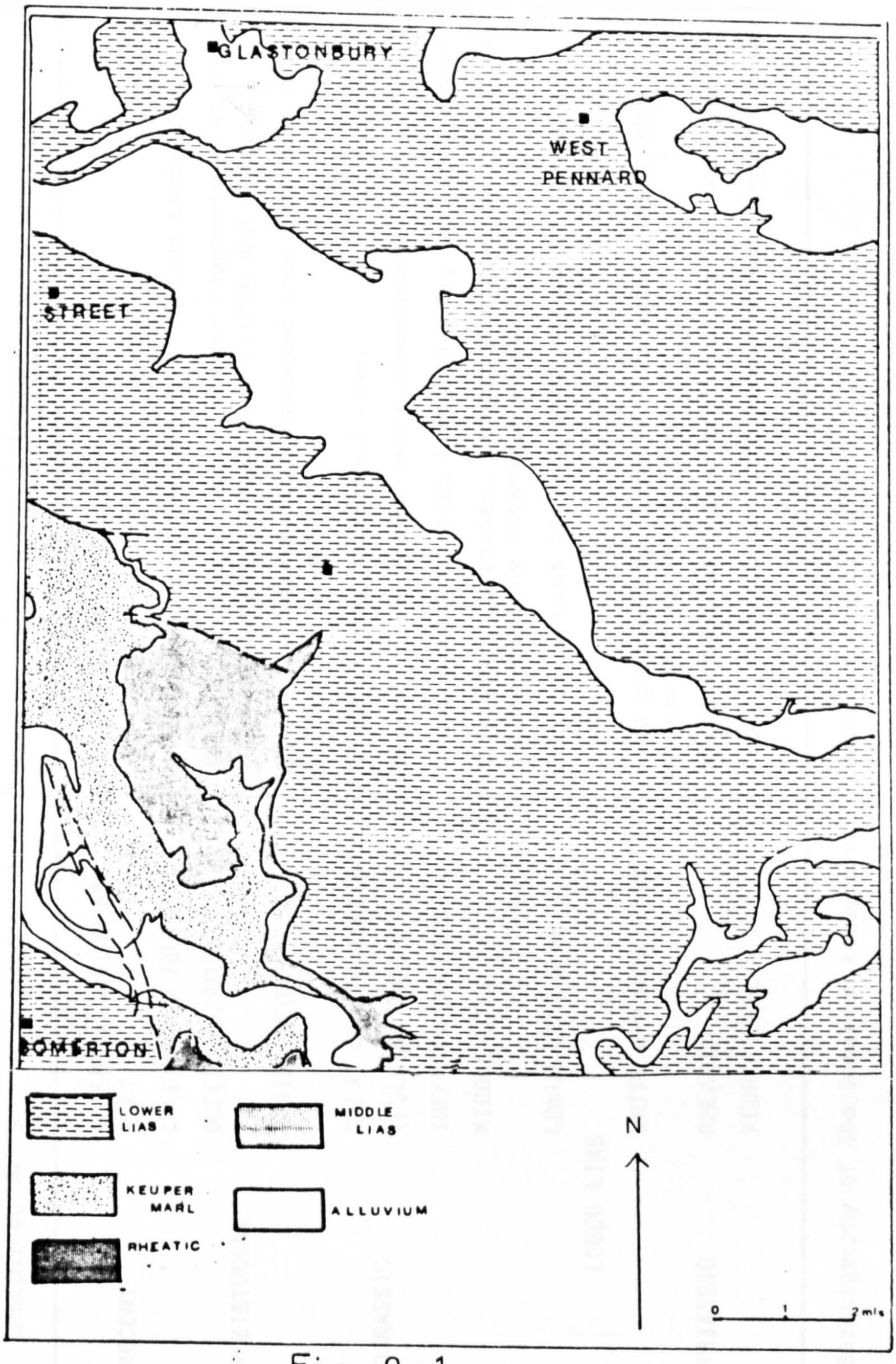


Fig 8–1
Geological Map Of Somerset Study Area

TABLE 8:1

GEOLOGICAL UNITS			LITHOLOGY
QUATERNARY	RECENT	RECENT ALLUVIUM AND PEAT	Clays, loams and peat.
		CALCAREOUS TUFFA	Unconsolidated accumulation of calcium carbonate.
	PLEISTOCENE	OLDER ALLUVIUM	Terrace gravels (roughly rounded fragments of oolitic and liassic limestones) with flints and cherts.
		BURTLE BEDS	Shells and quartz sands cemented into thin beds of calcareous sandstones.
MESOZOIC	JURASSIC	GREAT OOLITE SERIES	Cream or grey calcareous clay.
		(FULLERS EARTH)	Coarse ground fossilferous limestones.
		INFERIOR OOLITES	Cream, shelly oolitic limestones may be ferrugenous.
		MIDDLE LIAS	Soft,grey, laminated, micaceous siltstones with fine yellow and grey micaceous sands.
		LOWER LIAS CLAY	Grey calcareous clays with thin beds of limestones.
	LOWER LIAS		
		WHITE AND BLUE LIAS	Fine grained argillaceous limestones interbedded with shales and marls.
	TRIASSIC	RHEATIC	Black shales with beds of limestones and sandstones.
		KEUPER MARL	Red silty mudstones with bands and mottlings of green.

Stratigraphy of the Somerset study area (Based on Avery, 1955)

micaceous sands. Recent and Pleistocene deposits include alluvial deposits and shelly, marine sands and calcareous tufa.

8-3 Drainage and Topography.

The main topographic features are related to the geology. The clay and marls make up the low lands which flank the scarps of the more resistant beds of the Lower Lias and the Rhaetic. Between the towns of Glastonbury and Street, ground level is below 50ftO.D, having developed from alluvial deposits of the River Brue. North of the study area, ground level rises to over 200ft O.D near Glastonbury and is made up of the Middle and Upper Lias while in the south resistant beds of the Lower Lias and the Rhaetic make up the higher ground.

8-4 Climate.

The climate is mild with average temperatures of 20° C. Topography governs the local variations in temperature. Annual rainfall in the area is below 30" on average, although this increases towards Castle Cary and Shepton Mallet where over 35in of rainfall is recorded . Maximum evapo-transpiration takes place between the months of April and September.

8-5 Regional Geochemical Patterns.

Metal concentrations in the Lower Lias and the Keuper Marl are shown in (Tables 8-2, -3) . In general differences in the metal concentrations in the two formations are similar to those observed in the Worcestershire study area. The metal concentrations in the

TABLE 8:2

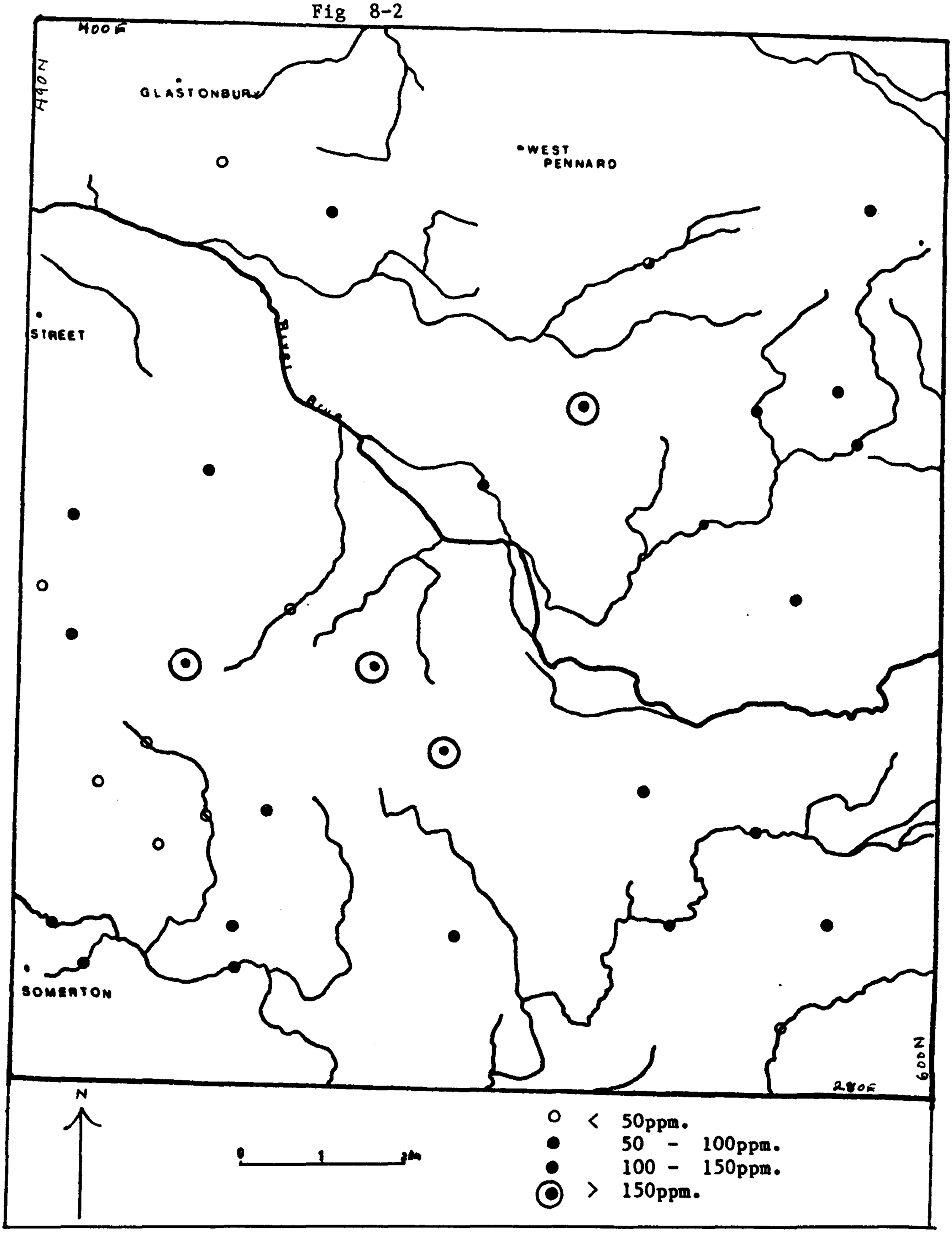
Medium	Number of Samples	Ca%	Zn(ppm)	Pb(ppm)	Fe%	Mg%	Cu(ppm)	Co(ppm)	Mn(ppm)
ROCK	6	6.8 (1.5-18)	73.4 (32-272)	32.0 (18-40)	3.5 (1.4-6.5)	1.6 (.1-2.7)	35.7 (23-45)	16.0 (9-36)	675.5 (400-100)
TOPSOIL 0 - 15cm*	12	3.7 (1.1-8.3)	73.9 (44-130)	35.8 (21-53)	2.2 (.9-3.2)	1.4 (.11-1.9)	28.2 (18-33)	11.1 (5-20)	687.9 (350-800)
SUBSOIL 30 - 45cm*	12	5.3 (2 - 12)	65.2 (39-84)	24.9 (19-42)	2.7 (1.2-4)	1.5 (.2-2.6)	23.9 (12-32)	12.8 (10-26)	714.0 (250-1000)
STREAM SEDIMENT	8	5.9 (.14-14.6)	55.6 (31-693)	35.9 (23-95)	1.9 (.24-3.5)	1.5 (.6-.30)	19.5 (10-30)	8.9 (5-17)	550.0 (360-850)

Range and mean element concentrations of elements in the rock (ground to -80 mesh) soils stream sediments (-80 mesh) derived from the Lower Lias in the Somerset study area.

( ) Range

* Depth of sample

Fig 8-2



Zinc concentrations in the topsoils and stream sediments in the Somerset study area.

different media are discussed and geochemical maps showing the concentrations of Zn, Pb, Cu and Mn in the topsoils and stream sediments are included.

(a) Geochemical patterns in the rocks.

Concentrations of most elements were higher in the Lower Lias than in the Keuper Marl (Tables 8-2, -3). As in the Worcestershire study area (see Chapter 6) the Keuper Marl was not calcareous while certain beds of the Lower Lias had concentrations of Ca in excess of 18%. In these samples Mg concentrations were also high. Thus the mean concentration of Ca in the Lower Lias (6.8%) was over three times as high as that of the Keuper Marl (1.9%). Apart from Cu the higher concentrations of other elements studied tended to occur in the calcareous beds of the Lower Lias. Zinc concentrations as high as 200ppm and Fe concentrations in excess of 6% were found in the calcareous beds of the Lower Lias while the lower concentrations of these elements occurred more frequently in the less calcareous beds of the Lower Lias. The reverse was true for Cu which tended to occur in larger amounts in the less calcareous beds of the Lias. Concentrations of Pb in the Lower Lias (mean concentration 32ppm) were similar to that in the Keuper Marl (mean concentration 30ppm). Cobalt and manganese were occasionally high in both units. Generally, Co concentrations were low in both units with concentrations of 15ppm widespread. The results showed that the calcareous beds of the Lower Lias contained greater amounts of most elements than the less calcareous beds of the Lower Lias and Keuper Marl.

TABLE 8:3

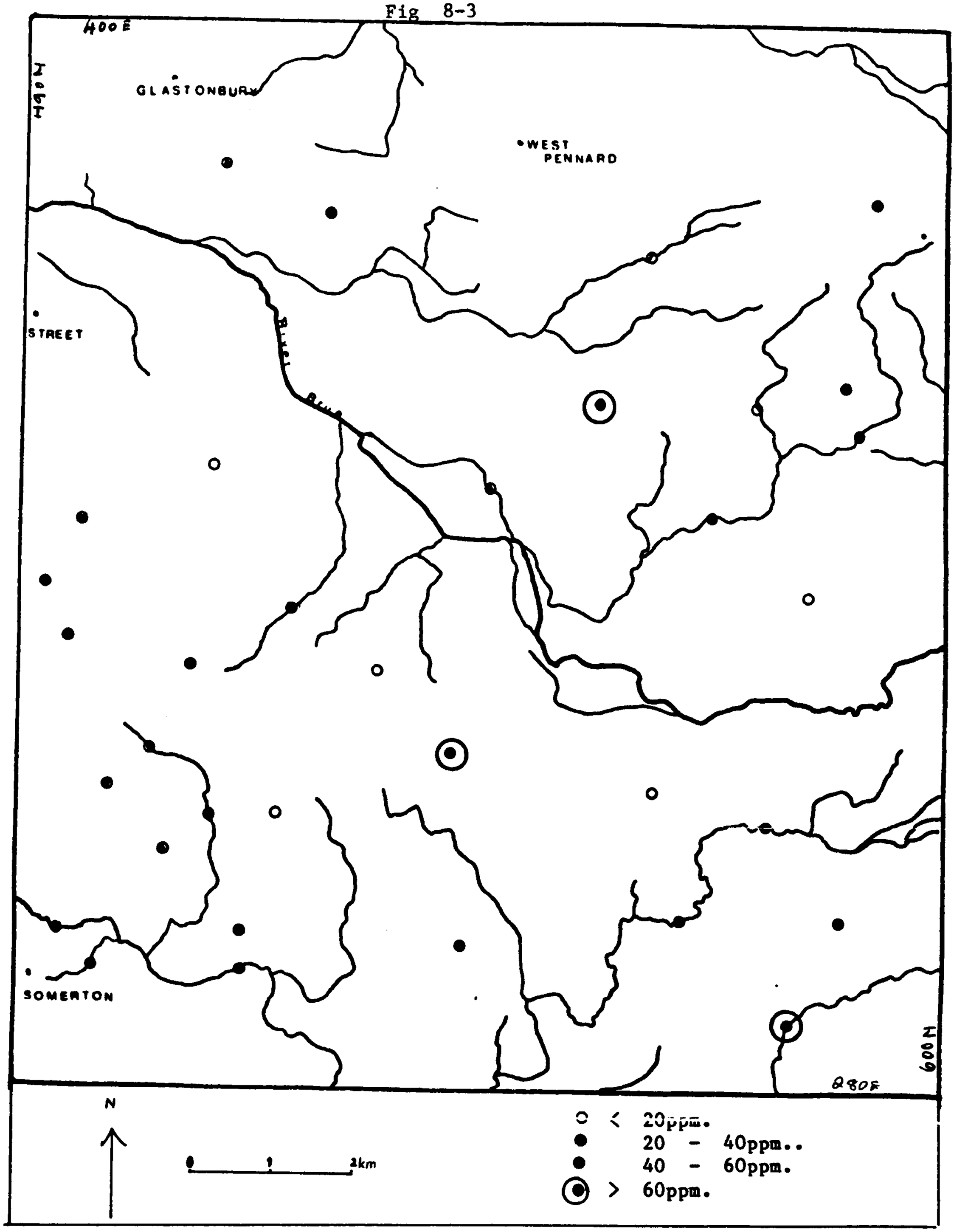
Medium	Number of Samples	Ca%	Zn(ppm)	Pb(ppm)	Fe%	Mg%	Cu(ppm)	Co(ppm)	Mn(ppm)
ROCK	9	1.9 (.2-2.4)	58.7 (32-89)	30.0 (15-43)	1.8 (.8-2.0)	1.2 (.1-1.7)	23.0 (15-30)	17.0 (8-25)	550 (350-850)
TOPSOIL 0 - 15cm*	8	1.1 (.45-1.9)	50.1 (41-79)	28.0 (19-40)	1.8 (.8-2.7)	0.95 (.8-1.8)	18.8 (14-27)	10.4 (5-17)	600 (300-750)
SUBSOIL 30 - 45cm*	8	1.45 (.39-2.1)	46.4 (28-59)	18.1 (16-28)	1.9 (.9-2.9)	0.94 (.7-2.1)	18.1 (10-30)	9.9 (5-20)	650 (450-1000)
STREAM SEDIMENT	7	2.5 (1.2-3.9)	75.1 (33-99)	32.1 (19-63)	1.6 (.4- .8)	2.6 (1.7-3.0)	19.0 (10-28)	8.8 (6-21)	774 (360-900)

Range and mean concentrations of elements in the rocks,(ground to -80 mesh) soil and stream sediments derived from the Keuper Marl in Somerset study area

( ) Range

* Depth of sample

Fig 8-3



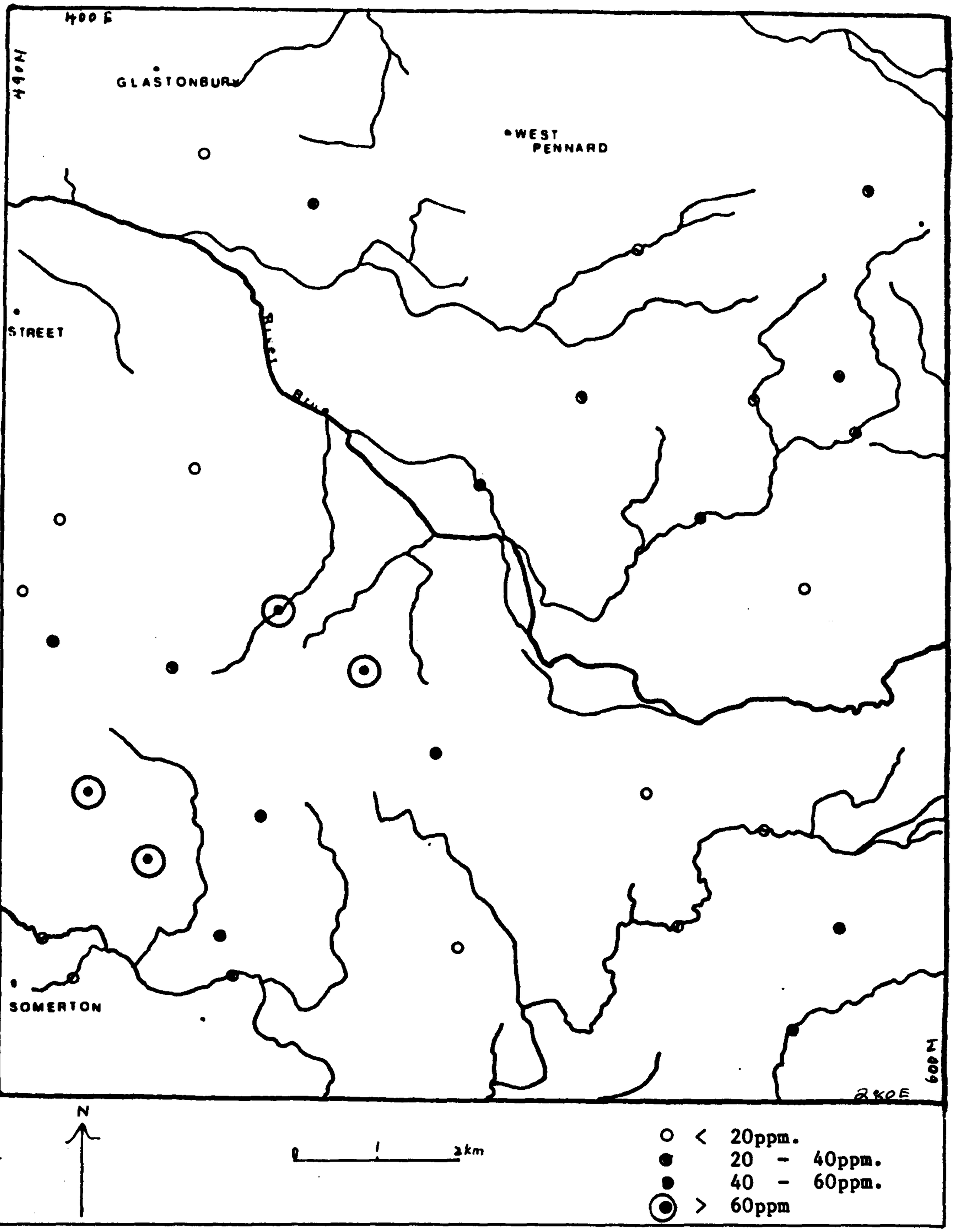
Lead concentrations in the topsoils and stream sediments in the Somerset study area.

(b) Geochemical patterns in the soils.

Soils developed over both units reflected the metal variations in the bedrocks. Calcium concentrations in the soils derived from the Lower Lias varied with the Ca concentrations in the bedrock, with the higher concentrations found in the subsoil. Thus concentrations of 7% and 2% Ca were found in soils derived from the White and Blue Lias respectively. The range and mean concentrations of Ca in the soils derived from the Keuper Marl were similar to that in the rocks. The mean concentration and range of Ca in the topsoils derived from the Keuper Marl were similar to those in the subsoils. Topsoil concentrations of Fe, Co, and Mn were lower than those in the subsoil in a few soil samples derived from the Lower Lias, although the mean concentrations of these elements in the top and subsoils were in the main similar (Tables 8-2).

Over the Keuper Marl the concentrations of Fe, and Mg in the soils were similar to those in the rocks, and for these elements the top and subsoil concentrations were also similar. Manganese concentrations tended to be higher in the soils than in the rocks while Co concentrations were lower in the soils than in the rocks. Soils derived from both units had higher concentrations of Zn and Pb in the topsoils than in the subsoils. Concentrations as high as 130ppm Zn were found in the topsoils derived from the calcareous beds while levels below 60ppm were common in the soils derived from the less calcareous beds of the Lower Lias.

Fig 8-4



Copper concentrations in the topsoils and stream sediments in the Somerset study area.

(c) Geochemical patterns in the stream sediments.

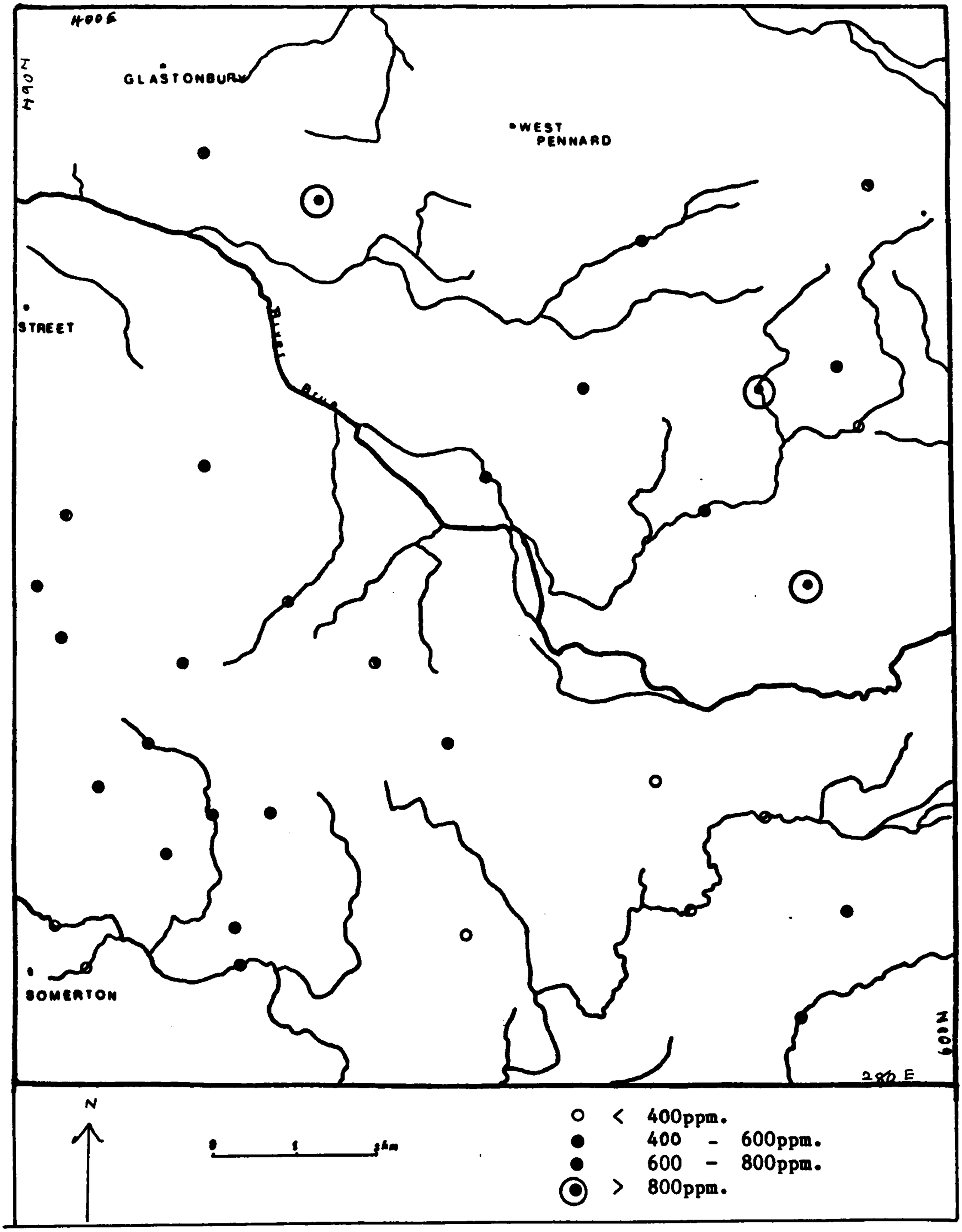
The mean concentration of Ca in the stream sediments derived from the Keuper Marl was higher than those in the rocks and soils (Table 8-2). Over the Lower Lias Ca concentrations in the stream sediments were similar to those in the subsoils, being only marginally lower than those in the rocks. Apart from Pb and Mg where concentrations in the stream sediments were similar to those in the rocks for most elements studied concentrations in the stream sediments were lower than in the rocks and soils over the Lower Lias. Manganese and cobalt concentrations were particularly low with concentrations below 5ppm Co and 400ppm Mn common. Over the Keuper Marl the increased concentrations of Ca was accompanied by increased concentrations of Zn, Pb, Mg and Mn in the stream sediments. Iron concentrations in the stream sediments showed very little difference with those in the soils and rocks, while Co and Cu concentrations were in the main similar to those in the soils.

8-6 Discussion of results.

The lithological variations within the Lower Lias resulted in the formation of more than one soil type. The present results indicated that higher concentrations of most elements occurred in the soils derived from the calcareous beds of the Lower Lias than those derived from the less calcareous beds. The Keuper Marl showed a rather uniform character with narrower ranges for most elements in the different media. Factors governing the distribution of elements in the different media were thought to be.

(a) Influence of the parent material.

Fig 8-5



Manganese concentrations in the topsoils and stream sediments in the Somerset study area.

(b) Modification In the soils.

(c) Influence of the secondary environment.

(a) influence of the parent material.

Variations in the metal concentrations in the Keuper Marl and Lower Lias were reflected by the soils and stream sediments. Thus the high Ca concentrations in the calcareous beds of the Lower Lias were reflected in the associated soils and stream sediments. This were also found in the case of Zn where the calcareous sediments reflected the higher concentrations in the calcareous rocks. In general, concentrations of elements in the soils and stream sediments derived from the Lower Lias were higher than those derived from the Keuper Marl. The lower concentrations of most elements in the Keuper Marl compared with the Lower Lias were reflected in the associated soils and stream sediments.

(b) Pedological modification.

Over the Keuper Marl the similarities in the mean concentrations of Ca, Fe, Co, Cu and Mn in the top and subsoils suggested that leaching of elements in the soils was not of widespread occurrence in the freely drained brown earths that develop from these parent materials. In the Lower Lias where elements tended to be marginally enhanced in the subsoils than in the topsoils it was inferred that the gleyed and waterlogging conditions that prevailed in the soils were encouraging the leaching of elements down the soil profile. The higher concentrations of Pb and Zn in the topsoils suggested an association with the organic matter.

(c) Influence of the secondary environment.

Redistribution of leached elements in the surface drainage was observed over both units. In the Keuper Marl the higher concentrations of Ca, Mg, Zn and Mn in the stream sediments compared with the rocks and soils suggested that these elements may be related to some fixation process in the stream sediments, possibly as secondary carbonates. Calcium was also observed over the Lower Lias to accumulate in the stream sediments. The lower concentrations of most elements in the stream sediments derived from the Lower Lias than the rocks and soils were thought to be due to the dilution of the sediments by the formation of calcium carbonates in the stream beds.

8-7 Conclusions.

It was concluded from the studies ofthe Keuper Marl and Lower Lias in Somerset that:-

(1) Higher concentrations of most elements tended to occur in the calcareous facies of the Lower Lias than the less calcareous beds and the Keuper Marl.

(2) Leaching of elements from the soils to the surface drainage was a common feature over the Lower Lias while over the Keuper Marl this affected only Ca.

(3) The lower concentrations of most elements in the stream sediments derived from the Lower Lias were thought to be due to the dilution of the sediments by the precipitation of secondary calcium carbonates.

CHAPTER 9

North Wales Study Area.

A Discussion Of The Metal Concentrations In The Rock, Soil And Stream Sediments Derived From The Silurian And Dinantian Rocks Of North Wales.

9-1 Geology.

The geology of the study area has been reviewed by Ball(1960) and shown schematically in Fig. 9-1 . The succession consists of Silurian and Carboniferous strata. Smith and George (1961) outlined the succession as:

Recent (alluvium and blown sands).

Pleistocene (boulder clay, glacial silts, sands and gravels).

Triassic (New Red Sandstone).

Carboniferous (Coal Measures, Millstone grits, limestone and Basement Beds).

Silurian (shales, mudstones and grits).

Ordovician (slates, acid volcanics with subordinate dolorites).

The western study area is mainly underlain by rocks of Silurian age. These consist of non calcareous silty mudstones and silty flags and sandstone of marine origin. The Carboniferous system

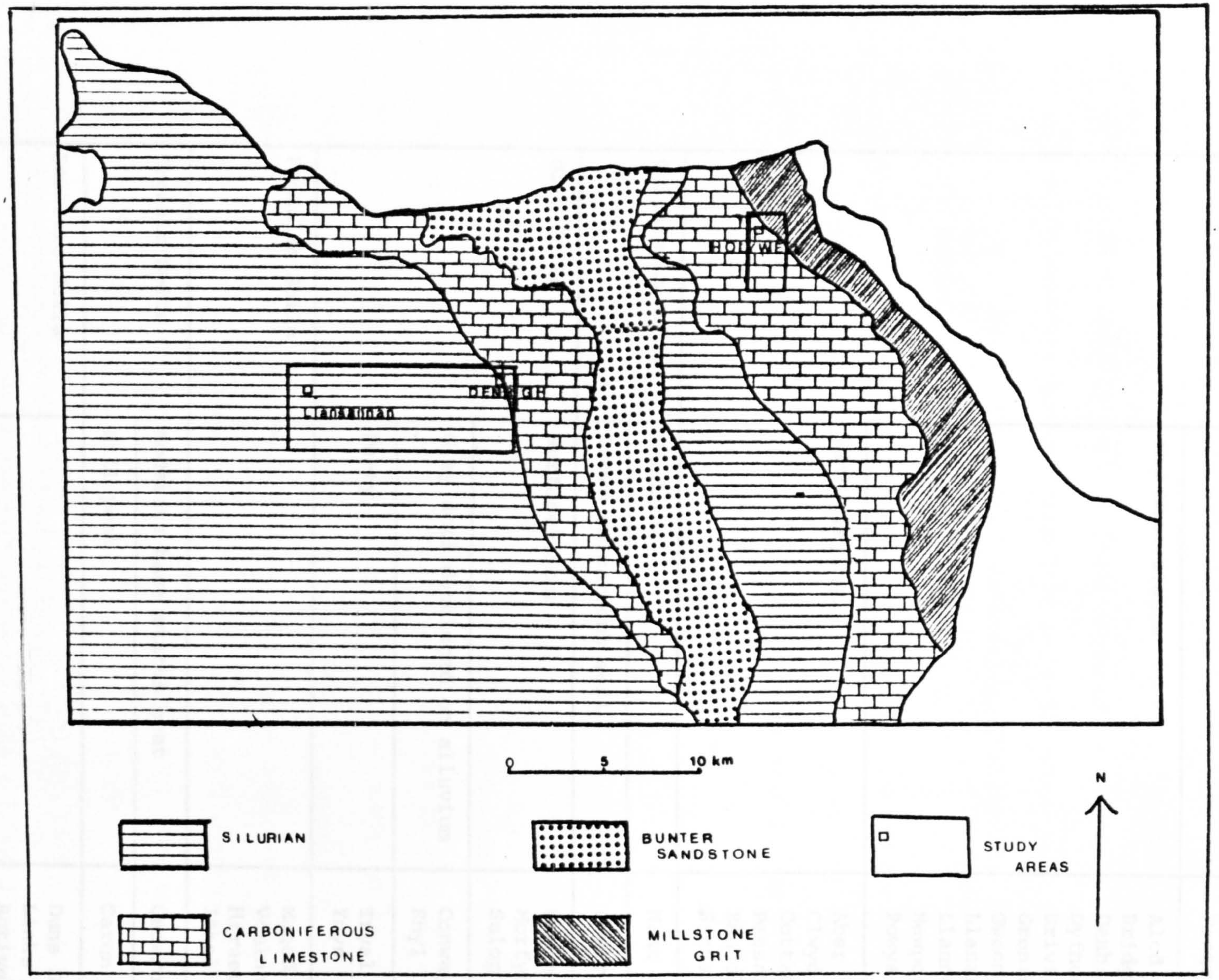


Fig. 9-1

Sketch Map Showing The Geology And Location Of North Wales Study Area.

TABLE 9.1

Major Soil Group	Sub-Group	Soil Series
Brown Earths	High base status	Abergele Dinorben Flint Ilysfaen Pentraeth
	Low base status	Alcd Bridgnorth Denbigh Dyfnog Eriviat Gronant Gwaenysgor Llanasa Llannerch Newport Powys
	With gleying	Aber Clwyd Cottam Pensarn Rhuddlan Sannan
Calcareous Soils	Rendzina	Nant
	Brown calcareous soil	Gower
Gley Soils	Surface-water	Cegin Morfydd Salop
	Gley soil developed on alluvium	Conway Rhyl
	Peaty	Tryal Ynys
Podzolic Soils		Manod Voelnant Hiraethog Ithel
Organic Soils	Moderate base status peat	Cadarn
	Hill peat	Caron
Immature Soils		Dune Sand Links Sand Active alluvium

Soil group and soil series in Rhyl and Denbigh. (Ball 1960)

occurs in the north eastern half of the area. This consists of limestones with subordinate shales and cherts. In the vale of Clwyd, fine grained Triassic rocks occur between boundary faults. Apart from the higher ground of the Clwydian hills, much of the area is covered by a mantle of locally derived drift deposits of Pleistocene age. Two main drift deposits can be identified in North Wales:

(a) the Northern Drift consisting of silty clay of Silurian origin, and

(b) Exotic Drift of Triassic origin in the low grounds of the vale of Clwyd and Flintshire. This is made up of silty clay.

The Northern Drift is widespread in the western half of the study area near Llansannan.

9-2 Topography.

Ball (1960) identified four well defined physical regions in the area which reflect the geology. The Denbigh Uplands lie mostly between 500ft and 1000ft O.D. while the Moors occur at a higher elevation 1,100-1,400ft O.D. The terrain is underlain by Silurian rocks and it is much dissected with "hill blocks separated by narrow steep-sided, flat floored valleys". Discontinuous limestone ridges in the north and eastern halves separate the Denbigh uplands and the vale of Clwyd. Triassic rocks and drift of the Northern Ice Sheets predominate the vale of Clwyd. The Clwydian hills that border the eastern flank of the area stretch from north to south and consist of Carboniferous limestone.

9-3 Drainage .

The Denbigh uplands and moors are drained by a network of streams and rivers that constitute the main tributaries of the River Clwyd. The rivers include the Rivers Elwy, Aled, Ystrad. The streams are usually moderately flowing and rich in sediments containing locally derived drift materials. The limestone ridges east of Denbigh are devoid of any significant surface drainage.

9-4 Climate.

The "maritime" climate is generally humid with warm winters and cool summers (Ball, 1960). In the inland area, where the ground level rises to over 1000ft O.D. the rainfall is higher (up to 50in per annum). In the coastal areas rainfall is lower, about 25in per annum.

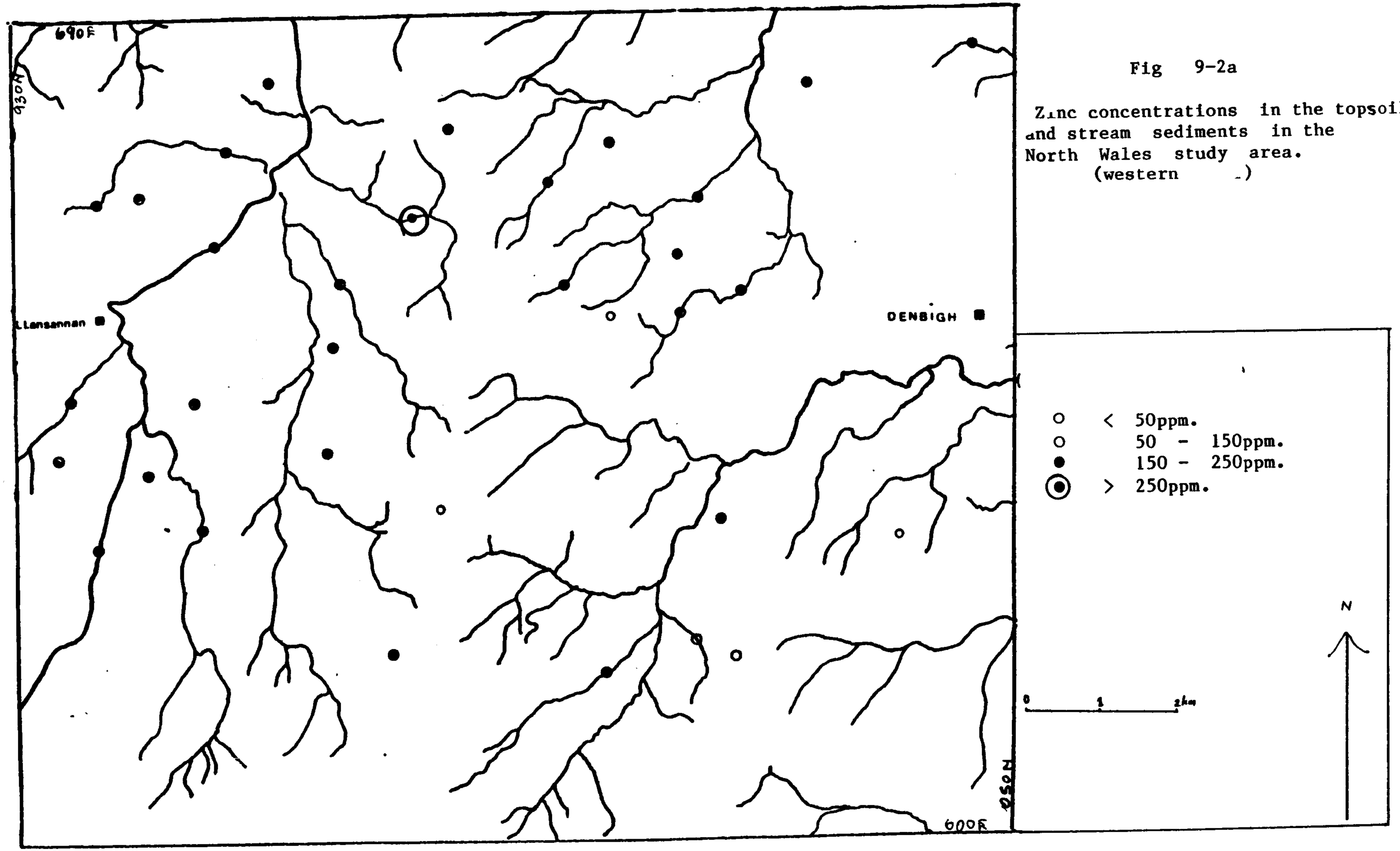
9-5 Soils.

The area has been mapped by the Soil Survey of England and Wales (Ball, 1960, 1964) . Soils in the study area consist mainly of brown earths, gleys and podzols (Table 9-1). Only soils of the brown earth group were sampled in the present study. These consisted predominantly of the Denbigh series which occupied a major part of the study area and the Dinorben series that occurred on the gentle slopes overlying the Carboniferous limestones.

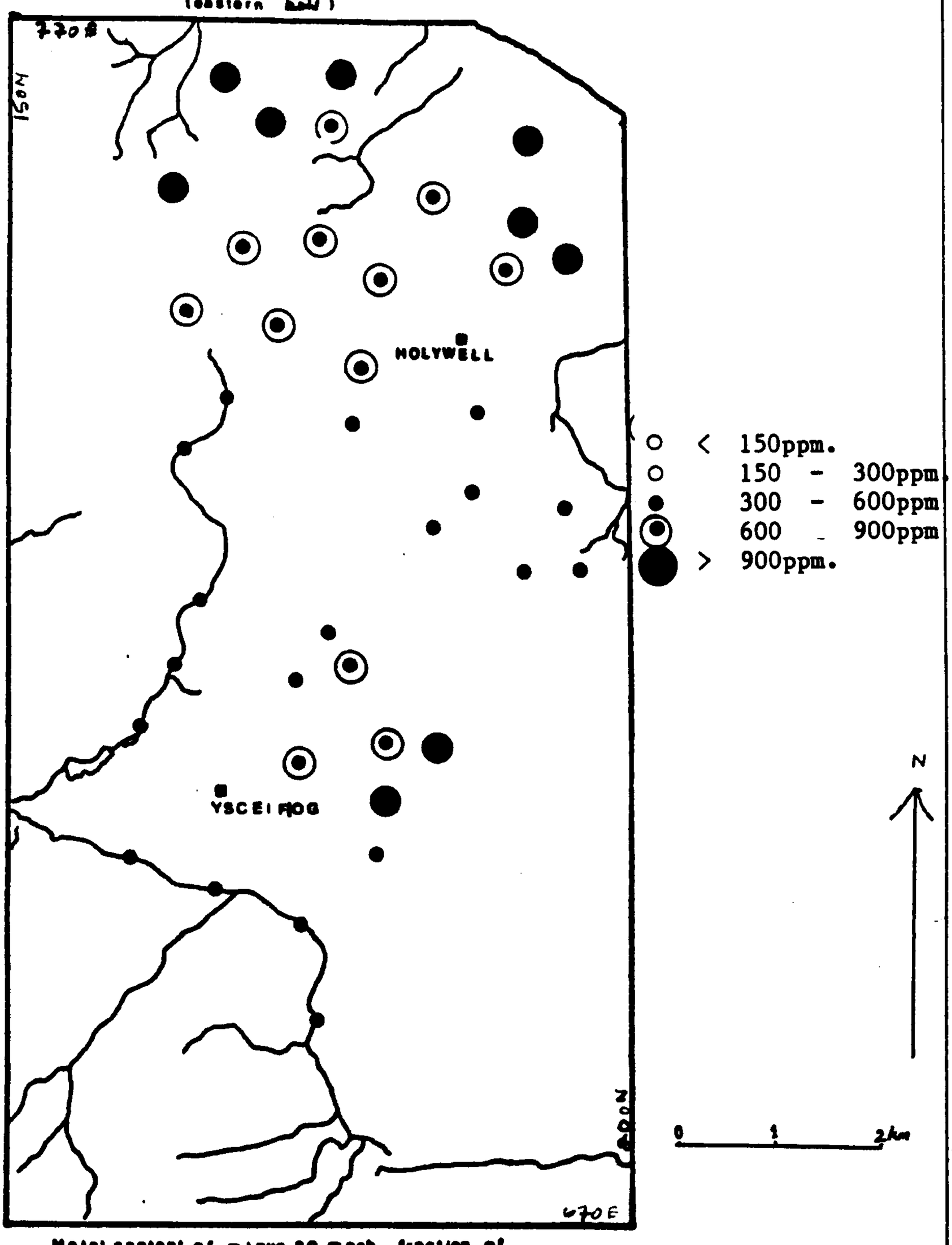
The Denbigh soil series consists of silty loams derived from

Fig 9-2a

Zinc concentrations in the topsoil and stream sediments in the North Wales study area. (western -)



NORTH WALES STUDY AREA
(eastern part)



Metal content of minus 80 mesh fraction of topsoil & stream sediment

Zn.

Fig 9 - 2b.

TABLE 9:2

Medium	Number of Samples	Ca%	Zn(ppm)	Pb(ppm)	Fe%	Mg%	Cu(ppm)	Co(ppm)	Mn(ppm)
ROCK	10	1.7 (.8-2.3)	91.8 (65-151)	29.6 (18-38)	4.1 (3.6-4.9)	.53 (.1-.61)	26.2 (13-39)	20.2 (19-31)	526 (340-1000)
TOPSOIL 0 - 15cm*	47	.47 (.12-1.1)	83.9 (24.3-115)	58.9 (18-118)	3.3 (2-4.9)	.42 (.22-.72)	13.2 (10-34)	23.7 (7 - 29)	638 (232-960)
SUBSOIL 30 - 45cm*	43	.87 (.08-5.5)	75.5 (24-107)	34.8 (22-112)	3.8 (2.5-4.6)	.49 (.12-.69)	14.7 (5-29)	25.0 (7 - 30)	727 (304-920)
STREAM SEDIMENT	18	.30 (.16-.48)	129.3 (100-307)	52.6 (38-110)	3.3 (3 - 4)	.50 (.07-.93)	18.5 (14-25)	29.3 (16-43)	960 (212-1800)

Range and mean element concentrations in the rock (ground to -80 mesh) soil and stream sediment (-80 mesh) derived from the Silurian Mudstone in the North Wales study area.

( ) Range

* Depth of soil

the Silurian drift. Its geographical extent in North Wales is considerable. Ball (1960) identified three phases of the Denbigh soil series in the study area:

(i) the normal phase on gently sloping ground (up to 750ft),

(ii) the upland phase occurring at heights of 750-1000ft, and

(iii) the shallow phase found on sharp crested ridges.

Other variants have been recognised elsewhere in Wales. Rudeforth (1970) recognised the mull and mor phases of the Denbigh series to approximate Ball's Denbigh series (brown earths) and Manod series (podzolic soils) respectively.

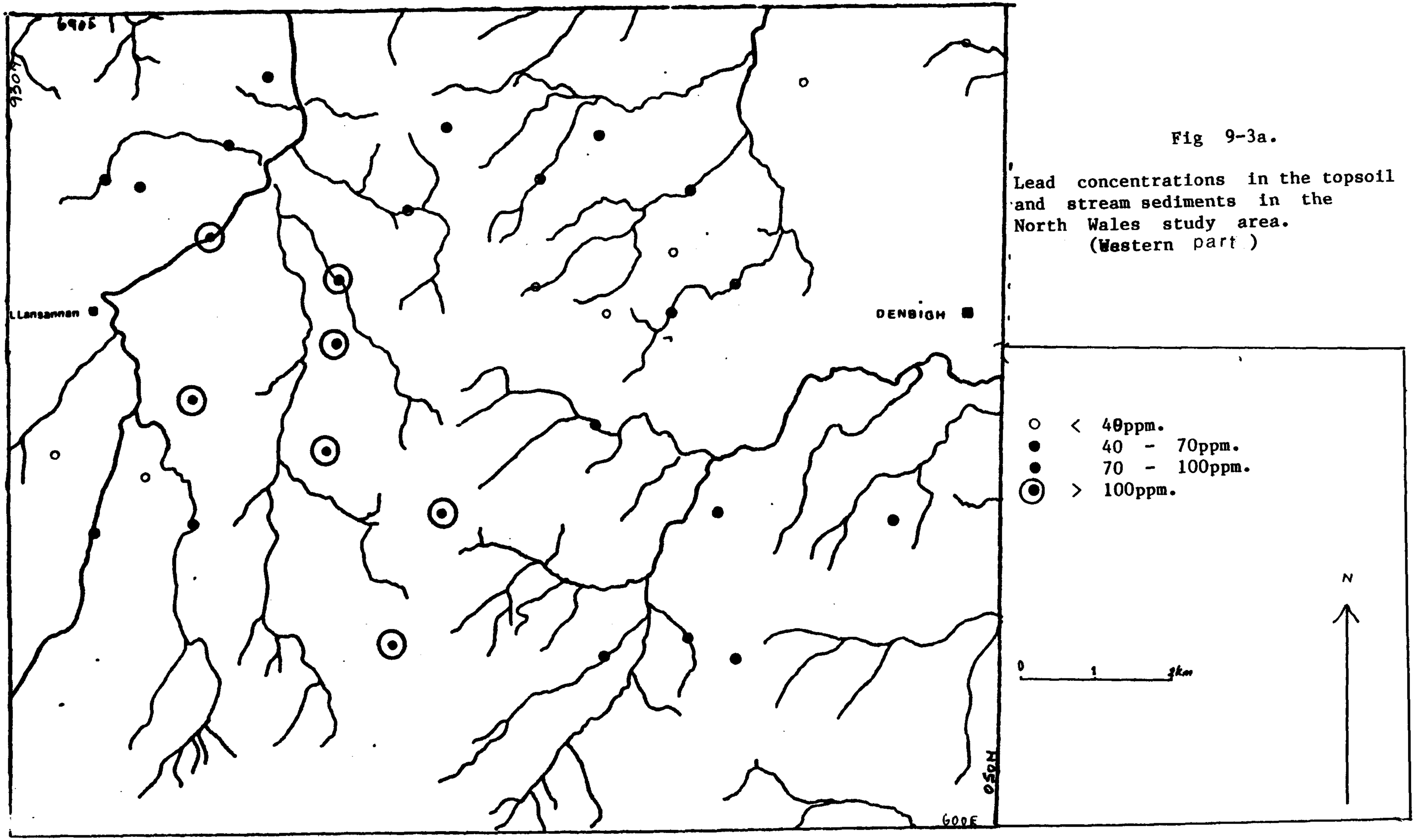
The Dinorben series is less common. It is generally associated with the limestone ridges of the east and west of the vale of Clwyd. Two phases have been recognised by Ball's (1960), the deeper phase developed from colluvial material and Silurian drift usually to be found on slopes, and a shallower phase developed on limestone bedrock. The drainage is generally free, tending to excessive in the shallower phases.

9-5 Agriculture.

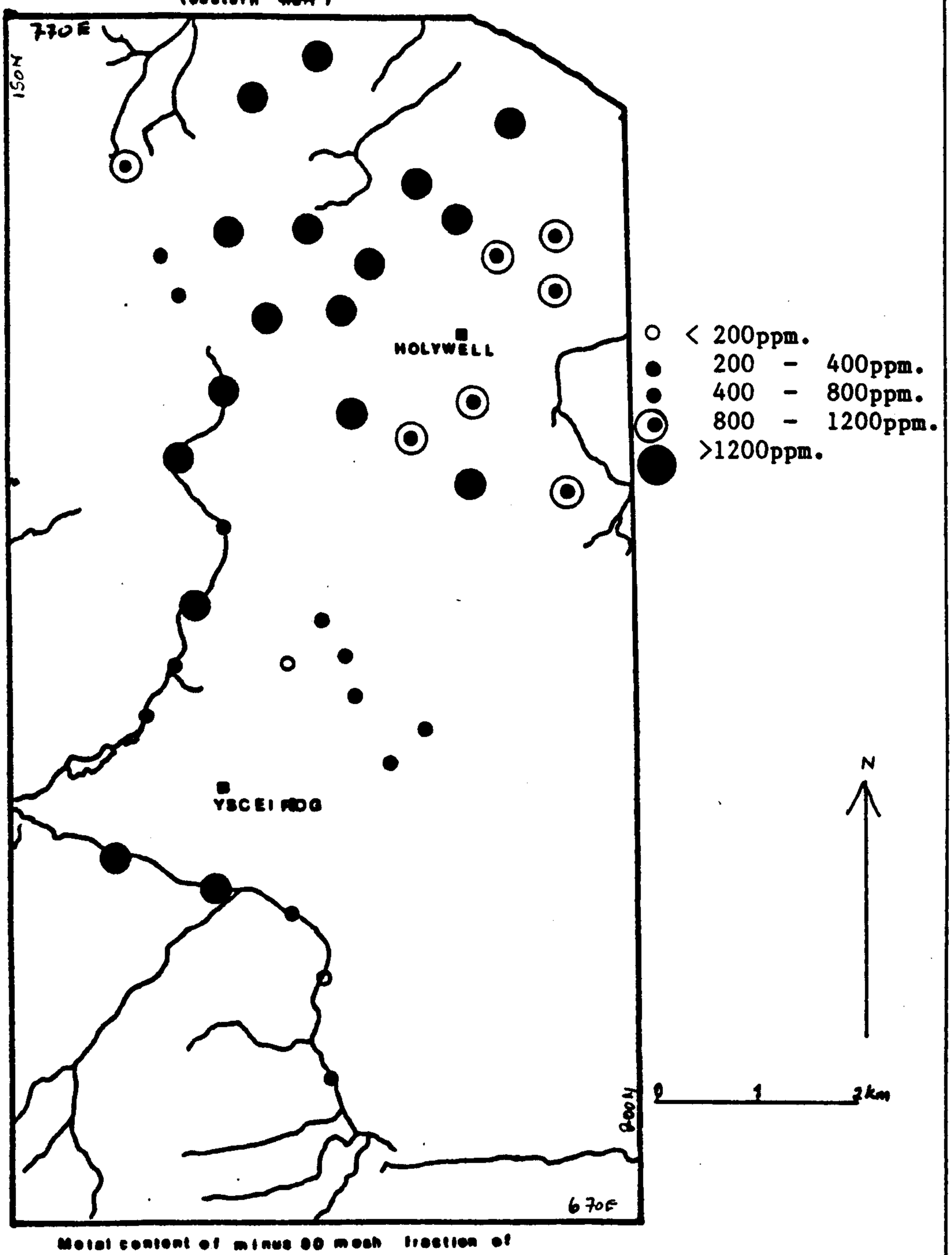
The Denbigh series is the most important agricultural soil in the area. They support mixed farms in the Llansannan area. Grains, mainly barley, are the dominant crops planted. Many farms commonly keep dairy cattle and sheep. On the fringes of the Denbigh moors most farms keep the Welsh mountain sheep.

Fig 9-3a.

Lead concentrations in the topsoil and stream sediments in the North Wales study area.
(Western part)



NORTH WALES STUDY AREA
(eastern part)



Metal content of minus 80 mesh fraction of topsoil & stream sediment

Pb.

Fig 9-3b.

TABLE 9:3

Sites*	Ca%	Mg%	Fe%	Zn	Pb	Cu	Co	Mn
A	6.0	0.32	2.4	15.6	40.6	5	20.4	210
B	5.8	0.25	2.3	12.5	37.0	5	26.6	360
C	4.3	0.09	1.7	10.4	41.1	5	25.3	400
D	6.8	0.28	1.9	9.9	39.6	5	19.6	295

Element concentrations in the four rock samples collected from the Dinantian Limestone (near Denbigh)

TABLE 9:4

Medium	Number of Samples	Ca	Zn	Pb	Fe	Mg	Cu	Co	Mn
TOPSOIL 0 - 15cm*	9	4.5 (1.5-5)	39.1 (31-81)	40.1 (19-48)	1.9 (.5-2)	0.25 (.01-.4)	9.0 (5-12)	15.0 (5-17)	500 (350-600)
SUBSOIL 30 - 45cm*	9	6.8 (3 - 7)	36.8 (29-50)	39.1 (21-42)	2.1 (.7-3)	0.20 (.01-.4)	10.2 (5-11)	22.0 (9-25)	550 (300-650)

Range and mean element concentrations in the Dinorben series from the western half (near Denbigh town) in the North Wales study area.

( ) Range
* Depth of soil

TABLE 9:5

Medium	Number of Samples	Ca%	Zn(ppm)	Pb(ppm)	Fe%	Mg%	Cu(ppm)	Co(ppm)	Mn(ppm)
TOPSOIL+ 0 - 15cm*	100	2.5 (1 - 6)	510.4 (150-1000)	695.0 (100-400)	3.0 (.9-4.5)	1.4 (.8 -2.3)	36 (10 - 45)	9.0 (<5 - 15)	650 (400-1500)
SUBSOIL 30 - 45cm*	10	2.9 (.9 - 4)	195 (150- 200)	205 (75-375)	1.9 (.7-2.5)	3.4 (1 - 5)	20 (12 - 27)	7.6 (<5 - 12)	700 (350-1200)
STREAM SEDIMENT	15	3.5 (1.9- 7)	475 (150- 700)	375 (100-600)	1.6 (.5- 3)	3.5 (.4 - 4)	12.2 (<5 - 19)	8.3 (<5 - 15)	600 (250- 700)

Range and mean element concentrations in the soil and stream sediments (-80 mesh) derived from the Dinantian Limestone in the eastern half (near Holywell) in the North Wales study area.

( ) Range

+ 89 contaminated topsoil samples supplied by Miss Thoresby of A.G.R.G.

* Depth of soil

9-7 Geochemical patterns.

Most of the samples collected were from the Silurian Mudstone and the associated soils and stream sediments (Table 9-2). Only four Dinantian limestone samples were collected near the town of Denbigh. The results are shown in (Table 9-3) . The Dinorben series that develop from the limestone and Silurian drift material were sampled on the western (Table 9-4) and eastern (Table 9-5) outcrops of the limestone. Topsoil samples (0-15cm) from the eastern half (mostly contaminated samples) were supplemented by samples collected by Thorseby * . Stream sediments from the eastern study area were collected near the town of Ysceifiog area to compare with the Silurian in the west. Geochemical maps showing the metal concentrations in the topsoil and stream sediments for the elements Zn, Pb, Mn, and Cu are included (see Figs. 9-2 to 9-9). The distribution of metals is discussed below.

(a) Geochemical patterns in the rocks.

The mean concentration of Ca in the Silurian rocks (1.7%) was low, with the higher concentrations (over 2%) found in the sandstone facies of the unit (Table 9-2). The paucity of samples hindered the full assessments of the concentrations of elements in the Dinantian Limestones. The few results (Table 9-3) suggested that apart from Ca the concentrations of other elements studied were either lower than, or similar to those in the Silurian rocks. Most of the Silurian rocks had Zn concentrations below 100ppm while over the Dinantian the maximum concentrations found in the four samples collected was below 16ppm. Lead concentrations in the Silurian rocks tended to be

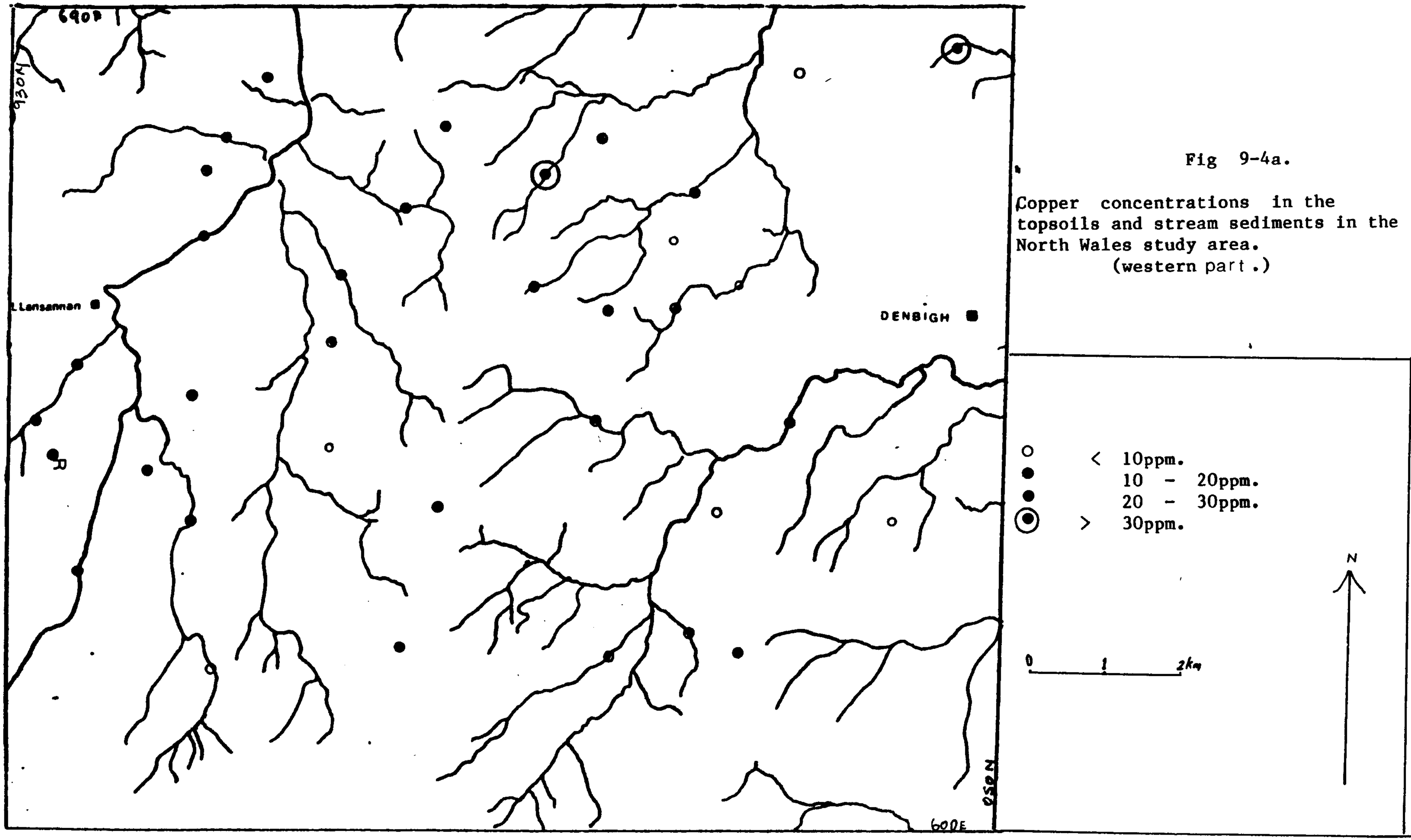
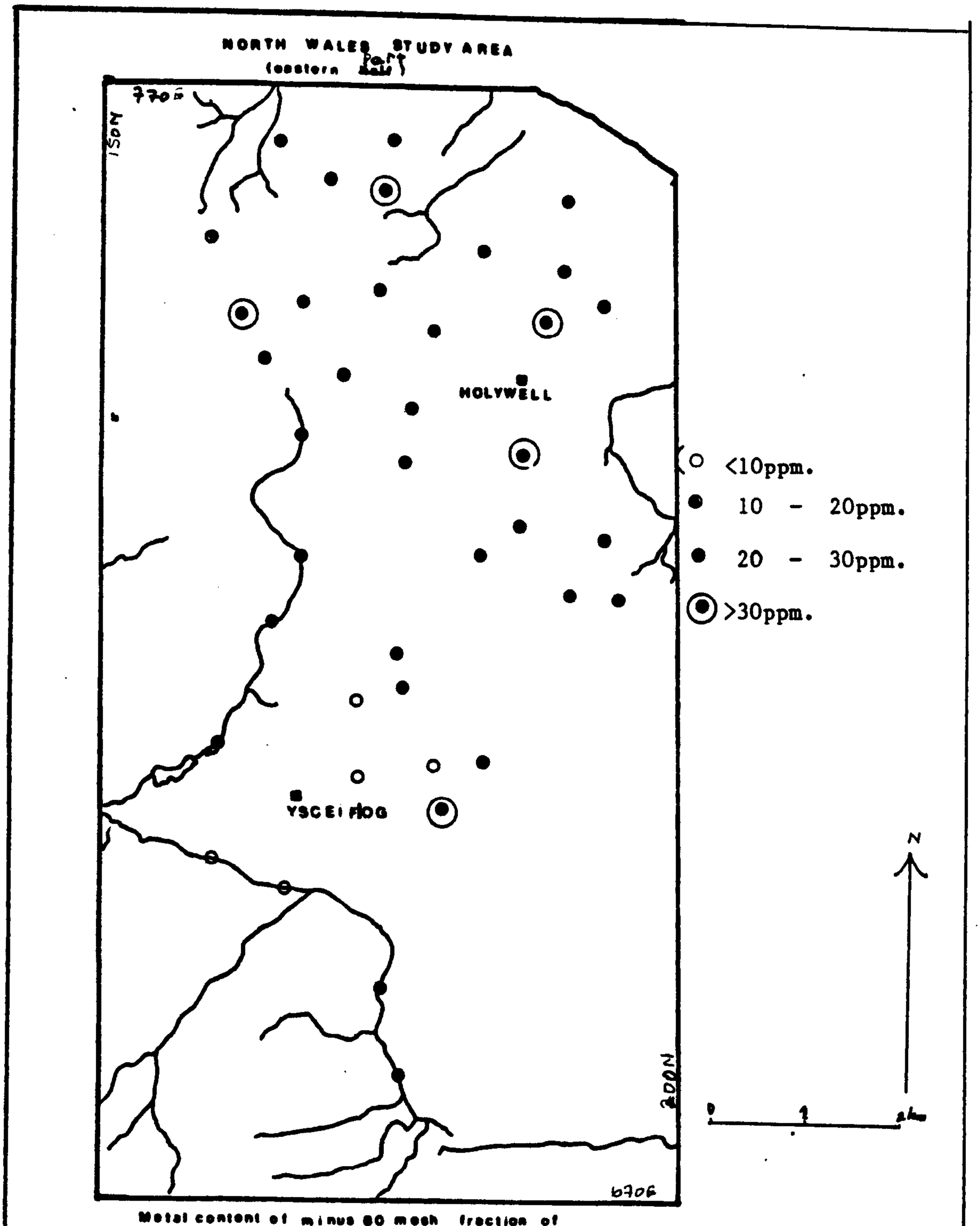


Fig 9-4a.

Copper concentrations in the topsoils and stream sediments in the North Wales study area.
(western part.)



Metal content of minus 80 mesh fraction of topsoil & stream sediment

Cu

Fig 9 - 4b.

slightly lower than those in the Dinantian rocks in the western half of the study area (near Denbigh). Copper concentrations in the Silurian were also higher than those in the Dinantian.

In the area east of Denbigh near Holywell, where there is a Pb-Zn mineralisation (no rock samples were collected) it seemed likely that concentrations of these elements may be many times higher in the Dinantian rocks than in the Silurian rocks. In the Silurian rocks higher concentrations of Cu and Co were found in the sandstone facies than in the mudstone facies.

(b) Geochemical patterns in the soils.

Apart from Ca and Co there were small differences between concentrations of elements in the top and subsoils of the Dinorben soil series (Table 9-4). In the Denbigh soil series concentrations of Fe, Mg, Cu and Co were similar in both the top and subsoils (Table 9-2). Calcium and Mn concentrations on the other hand were higher in the subsoils of the Denbigh series, with the mean concentration of Ca in the subsoil being nearly twice as high as that in the topsoil. Zinc and Pb concentrations, in contrast, tended to be higher in the topsoils than in the subsoil. Near Holywell where contamination from past metalliferous mining was high, concentrations of Zn in the Dinorben soil series in excess of 1000ppm, were common in the topsoils (Table 9-5). Although analytical results for most of the subsoils of the contaminated soils were not available (*), the uncontaminated subsoils (Table 9-5) collected near Holywell suggested that Zn contamination in the subsoils may not be as widespread as in the topsoils. A similar situation was seen in the case of Pb where

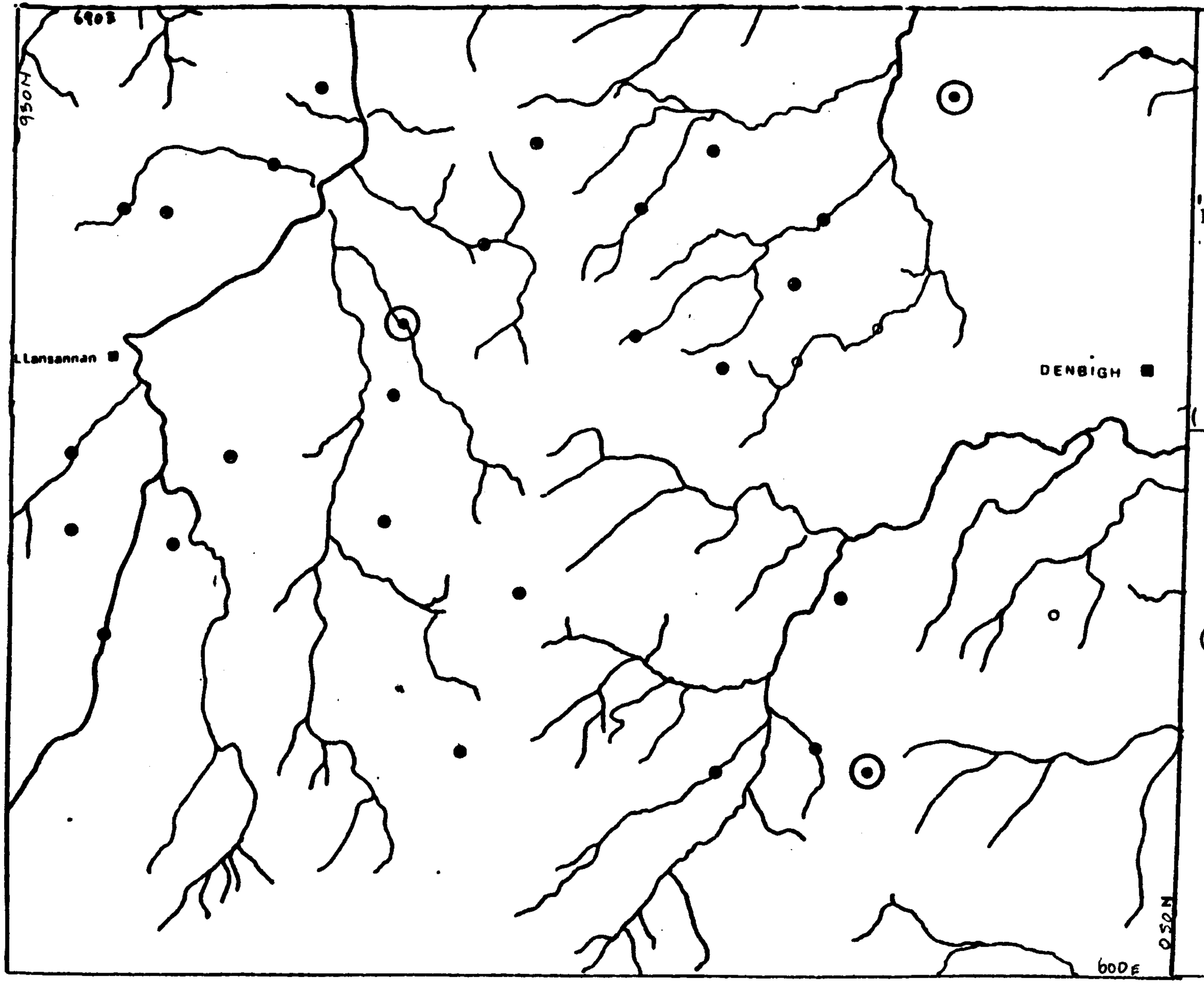
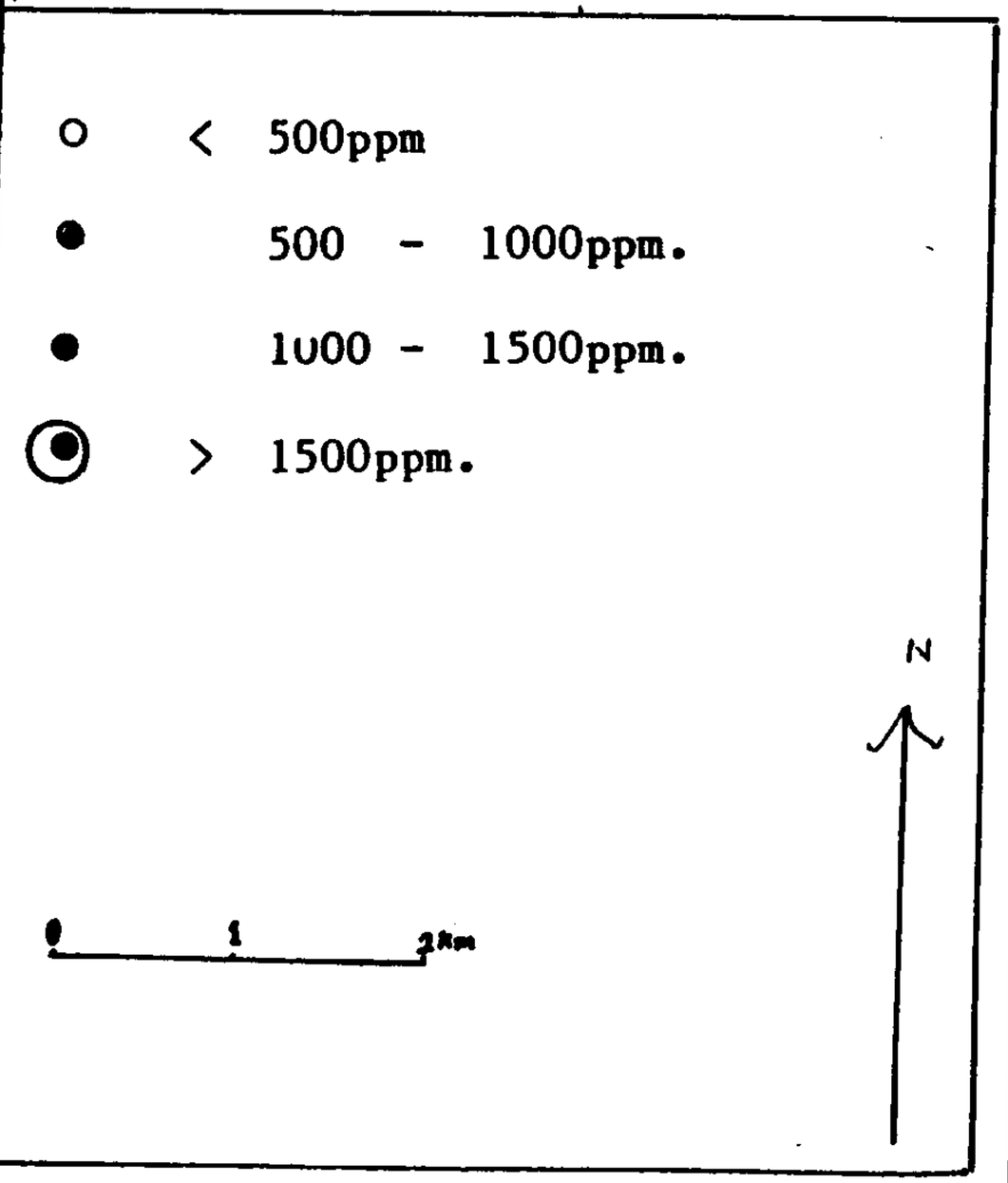
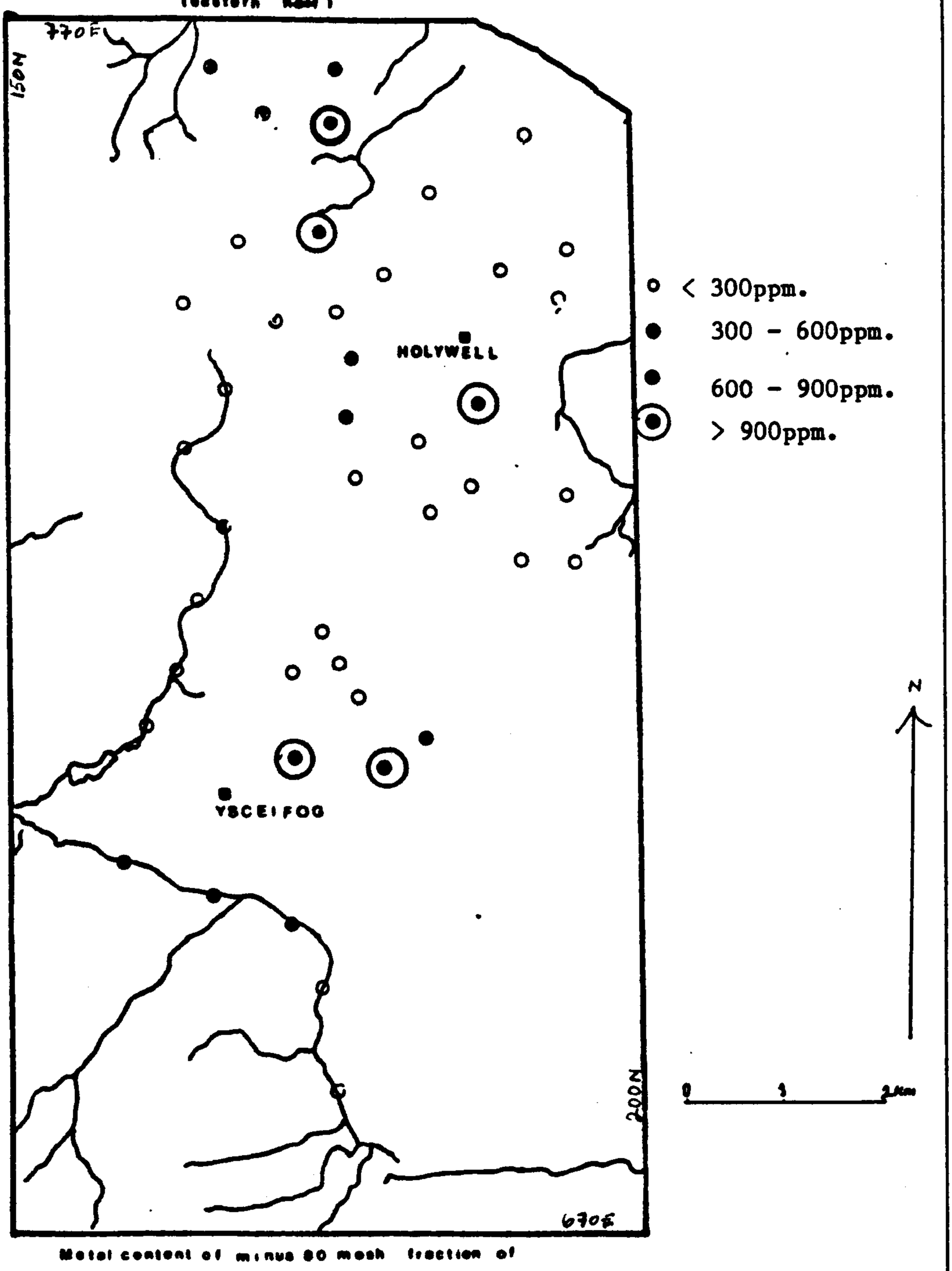


Fig 9-5a

Manganese concentrations in the topsoils and stream sediments in the North Wales study area.
(western part.)



NORTH WALES STUDY AREA
(eastern Part)



Metal content of minus 80 mesh fraction of
topsoil & stream sediment

Mn.

Fig 9- 5b

concentrations of Pb in the topsoils were as high as 4000ppm.

(c) Geochemical patterns in the stream sediments.

Over the Silurian stream sediment concentrations of Zn and Mn were higher than those in the soils and rocks(Table 9-2). Occasional anomalous concentrations of Zn (greater than 300ppm) were found near Llansannan. These anomalous concentrations seemed to be due to contamination by drift material rather than from mine wastes as was found in the eastern area near Holywell where concentrations of Pb and Zn in the sediments reflected the contaminations in the topsoil. The concentrations of Co were marginally higher in the stream sediments than in the soils over the Silurian. In the eastern study area Ca concentrations were higher in the stream sediments than in the soils while the concentrations of other elements were generally lower than in the soils. Very low concentrations of Co were widespread while Mn concentrations below 300ppm were common. This was thought to be due to dilution of the sediments by the precipitation of calcium carbonates.

9-8 Discussion and summary.

The preliminary investigations in the North Wales study area revealed four main factors governing the distribution of elements in the rocks, soils and stream sediments. These were:-

(a) influence of the parent material,

(b) contamination from mine waste,

(c) pedological modification,and,

(d) dilution with calcium carbonates.

TABLE 9:6

Profile, Drainage	Sample Depth (cm)	Ca%	Zn(ppm)	Pb(ppm)	Fe%	Mg%	Cu(ppm)	Co(ppm)	Mn(ppm)
UPLAND PHASE (Hill top) shallow with good drainage	0 - 15	0.15	29.4	25.4	2.6	0.2	8.0	10.6	250.0
	30 - 45	0.84	38.0	34.0	3.4	0.19	14.4	15.3	500.0
SHALLOW PHASE (At break of slope) Sandy and well drained. Parent material encountered at 12"	0 - 15	0.15	75.0	53.4	4.5	0.3	25.6	16.2	350.0
	25 - 30	0.73	77.9	55.4	4.4	0.2	27.2	18.4	500.0
NORMAL PHASE (At base of hill) deep and well drained	0 - 15	0.93	76.4	45.4	3.9	0.3	18.0	12.4	640.0
	30 - 45	3.4	73.0	34.6	4.3	0.4	23.4	15.0	800.0
DEEP PHASE	0 - 15	0.12	63.0	55.9	3.0	1.0	24.8	17.1	750.0
(near stream)	30 - 45	2.19	104.0	63.7	4.9	0.9	26.0	19.5	850.0

Element concentrations of selected soils of the Denbigh series.

(a) Parent material.

Over the Silurian rocks, the minor variations in the concentrations of most elements were reflected in the associated soils and stream sediments. Drift materials also influenced the concentrations of elements in the soils and stream sediments. Thus it seemed likely that the occasional high concentrations of Ca, Zn and Pb found in the soils of the Denbigh and Dinorben series reflected the degree of mixing with drift material. In the stream sediments near Llansannan, the occasional high concentrations of Pb and Zn in the stream sediments were thought to be due more to the influence of drift material rather than of contamination.

(b) Contamination from mine waste.

Concentrations of Zn and Pb in the topsoils (*) in the eastern study area near Holywell, showed evidence of considerable contamination and this was reflected in the stream sediments. It seemed from the results that the extent of contamination in the subsoils may not be as high as that in the topsoils. Contamination did not affect other elements although generally the contaminated soils had slightly raised concentrations of Mn and Cu.

(c) Pedological modification.

In general the different phases of the Denbigh soil series displayed varying metal contrasts. The variation in metal concentrations in selected top and subsoils from the different phases

of the Denbigh soil series are shown in Table 9-6. Lower concentrations of most elements were found in the shallower phases of the Denbigh series that tended to occur on the hill tops. Manganese concentrations increased down the slope with a consistent increase in the subsoil(30-45cm) concentrations. In the deeper phases element concentrations were generally higher than those of the shallower phases.

The lower concentrations of elements in the shallower phases were thought to be due to leaching of elements in the topsoils and the subsequent redistribution in the deeper phases down hill by circulating ground waters. The similarities in the top and subsoil concentrations of Cu, Co and Mn in the deeper phase of the Denbigh soil series suggested that leaching of elements may not be a common feature of the soils. In the Dinorben series where the differences in the concentrations of most elements in the top and subsoils were also similar it seemed that the preferential removal of calcium carbonates during soil formation may lead to the formation of insoluble residues with which most trace elements may be associated. In such forms they are not easily mobilised hence the reduced contrast.

(d) Dilution effects.

Dilution by calcium carbonates was thought to be the reason for the reduced concentrations of most elements except Pb and Zn in the stream sediments in the eastern study area.

9-9 Conclusions.

The following conclusions were made from the preceding discussion.

(a) Although leaching of Ca occurred during soil formation the process did not seem to affect the distribution of most elements in the soils.

(b) Contamination was a common feature of the topsoils developed over the Dinantian in the eastern study area.

(c) Dilution of the stream sediments by the precipitation of calcium carbonates in the eastern study area resulted in decreased concentrations of most elements.

(d) On a broad scale, the stream sediments were good indicators of metal concentrations in the soils and rocks. Extrapolation of stream sediment data to soils and rocks should take into account the dilution effects of the precipitation of calcium carbonates.

CHAPTER 10

Surrey Study Area.

A Discussion Of The Metal Concentrations In The Rocks, Soils And Stream Sediment Derived From The Lower Greensand.

10-1 Geology.

The geology. of the study area has been described by Thurrel et al. (1968). The oldest unit in the area is the Weald Clay which is predominantly argillaceous with subordinate silt, sand, limestone and ironstone. Thicknesses of 1500ft have been recorded in the study area. Marine transgression resulting from the subsidence of the Wealden basin in the Cretaceous led to the deposition of shallow water sands, silts, and, clays of the Lower Greensands and later the Gault.

The Lower Greensands in the study area consist of four Beds of which the Hythe Beds consisting of fine grained glauconitic sands and sandstones are the oldest. False bedding is common in the Hythe Beds and a maximum thickness of 300ft has been recorded in the study area (Thurrel et. al., 1968). This is suceeded by the Bargate Beds which consist of glauconitic and calcareous sands with characteristic current bedding. The Sandgate Beds which overlie the Bargate Beds consist of poorly graded fine sands which may contain glauconites and limonites locally. The Folkestone Beds consisting of poorly sorted coarse sands with pebbles are the youngest beds in the Lower Greensand.

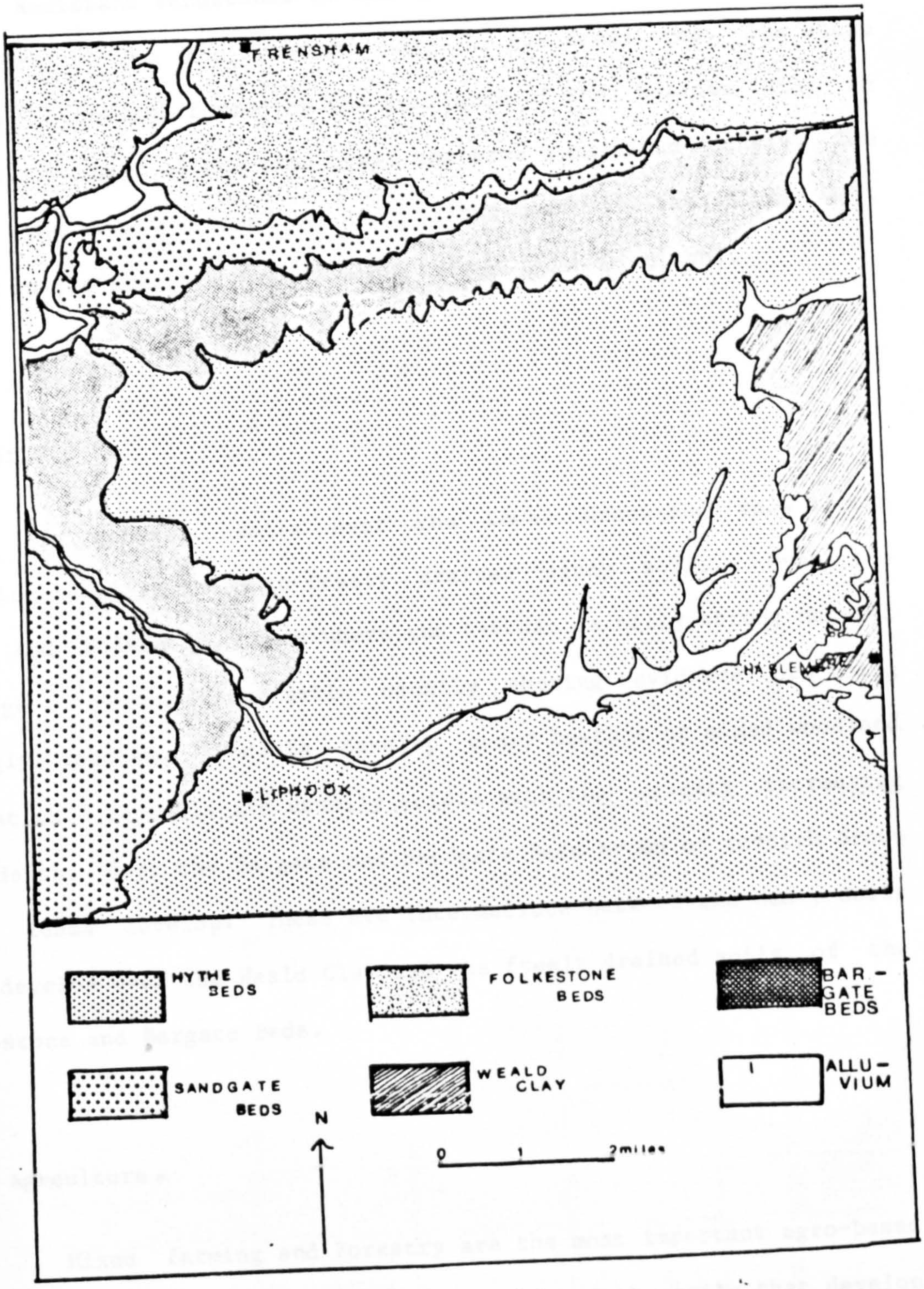


Fig. 10-1

Geological Map Of Surrey Study Area.

10-2 Drainage and Topography.

Resistant sandstones of the Hythe Beds make up the summits of over 800ft OD in the western half of the study area. The sharp topographic contrast formed by the low lands of the Wealden Clay in the eastern half of the area gives the area a majestic scenery. The area is extensively drained by the tributaries of the River Wey. Streams in the area are fast flowing, often laden with sand.

10-3 Soils.

In general, soils over the Lower Greensand show little variation being in the main freely drained sandy soils. Over the Hythe and Folkestone Beds where the terrain is hilly strong natural drainage is common in the soils usually showing evidence of being strongly leached. Podzols develop under heather or mixed woodland vegetation. Topsoils are usually acidic with the acidity increasing with depth. Over the Bargate and Sandgate Beds brown or reddish brown sandy loams develop. These are intermediate between the heavy soils that develop over the Weald Clay and the freely drained soils of the Folkestone and Bargate Beds.

10-4 Agrculture.

Mixed farming and Forestry are the most important agro-based industries in the area. On the Lower Greensand the soils that develop over the Bargate and Sandgate are the most important agriculturally.

TABLE 10:1

Medium	Number of Samples	Ca%	Zn(ppm)	Pb(ppm)	Fe%	Mg%	Cu(ppm)	Co(ppm)	Mn(ppm)
ROCK	12	0.21 (.01-3.5)	36.0 (10-80)	22.0 (15-37)	4.5 (.01-15)	0.08 (.02- .2)	8.2 (<5-30)	17.5 (<5-20)	170.0 (10-550)
TOPSOIL	20	0.74 (.03- 4)	36.8 (<10-69)	36.7 (12-71)	1.6 (.4-3.3)	0.17 (.01- .8)	8.6 (<5-14)	8.4 (<5-14)	185.5 (10-550)
SUBSOIL	20	0.80 (.01- 5)	28.6 (<10-80)	32.8 (15-56)	1.7 (.5- 4)	0.12 (.01- .3)	12.2 (<5-23)	11.2 (<5-17)	186.5 (10-475)
STREAM SEDIMENT	16	0.65 (.02-1.5)	42.2 (<10-75)	46.0 (20-71)	2.0 (.38-6)	0.08 (.01-.25)	13.5 (7-40)	15.6 (7-40)	294.5 (35-850)

Range and mean element concentrations in the beds (combined) of the Lower Greensand in the Surrey study area

( ) Range

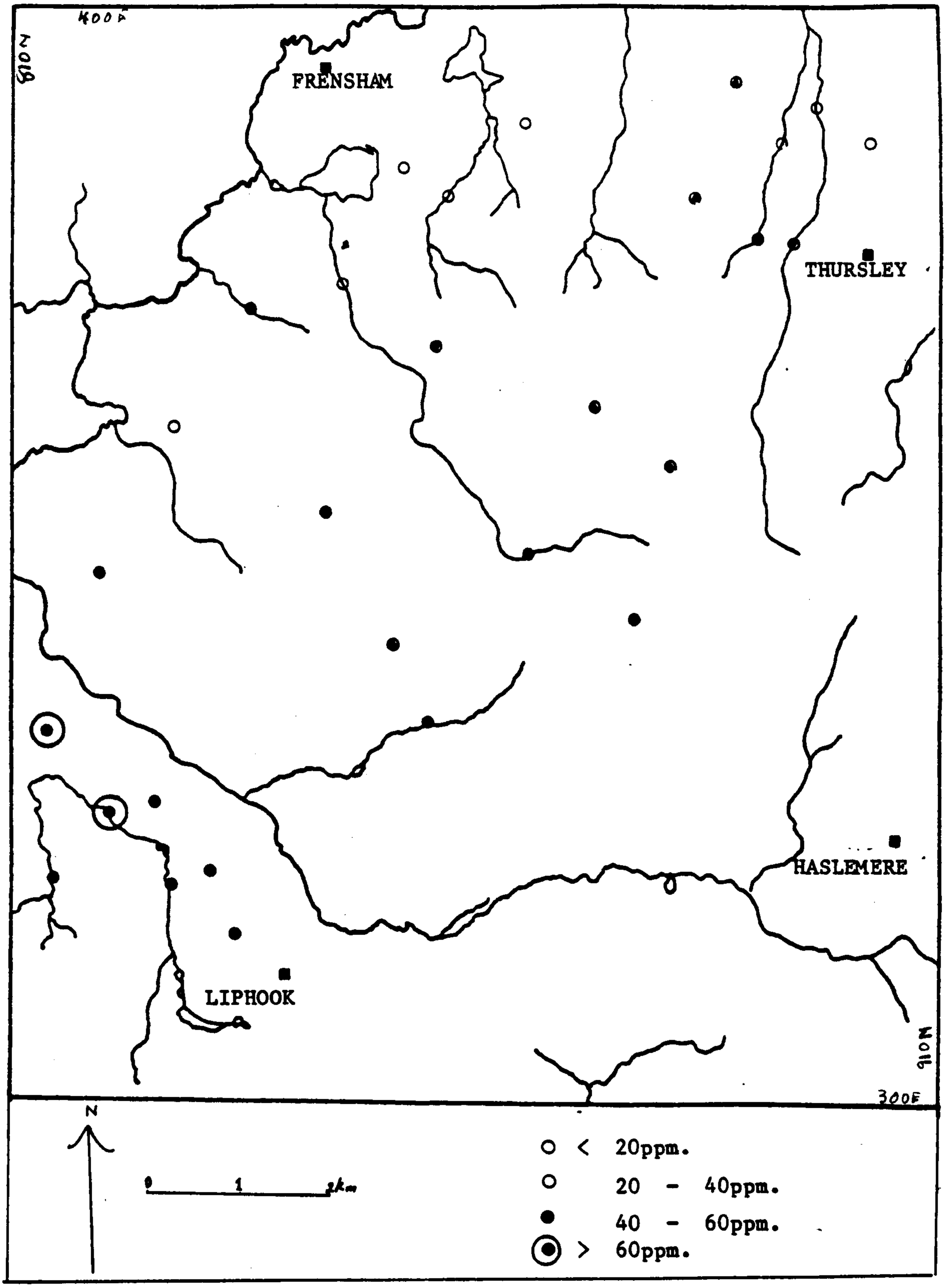
TABLE 10:2

Medium	Number of Samples	Ca%	Zn(ppm)	Pb(ppm)	Fe%	Mg%	Cu(ppm)	Co(ppm)	Mn(ppm)
ROCK	4	0.18 (.02-.7)	32.3 (19-42)	22.7 (19-26)	2.8 (1.5-3.4)	0.19 (.11-.34)	7.9 (5-11)	9.4 (11-20)	87.0 (50-100)
TOPSOIL	5	0.10 (.03-.15)	34.4 (29-41)	42.4 (24-56)	2.9 (1.5-3.3)	0.05 (.03-.07)	6.2 (6 - 8)	6.5 (5 - 9)	92.3 (55-195)
SUBSOIL	5	0.06 (.04-.09)	37.2 (29-46)	35.2 (21-45)	3.4 (1 - 4)	0.06 (.04-.08)	9.4 (5-12)	6.7 (5 - 8)	125.0 (50-390)
STREAM SEDIMENT	4	0.52 (.3-.7)	50.5 (29-72)	49.1 (27-61)	4.2 (.5- 6)	0.04 (.01-.07)	19.1 (4-21)	12.2 (10-26)	515 (225-600)

Range and mean element concentration in the rock, soil and stream sediments derived from the Hythe Beds of the Lower Greensand in the Surrey study area.

( ) Range

Fig 10-2



Zinc concentrations in the topsoils and stream sediments in the Surrey study area.

The sandy loams that develop over these soils support arable farming. Common crops include chestnut and corn.

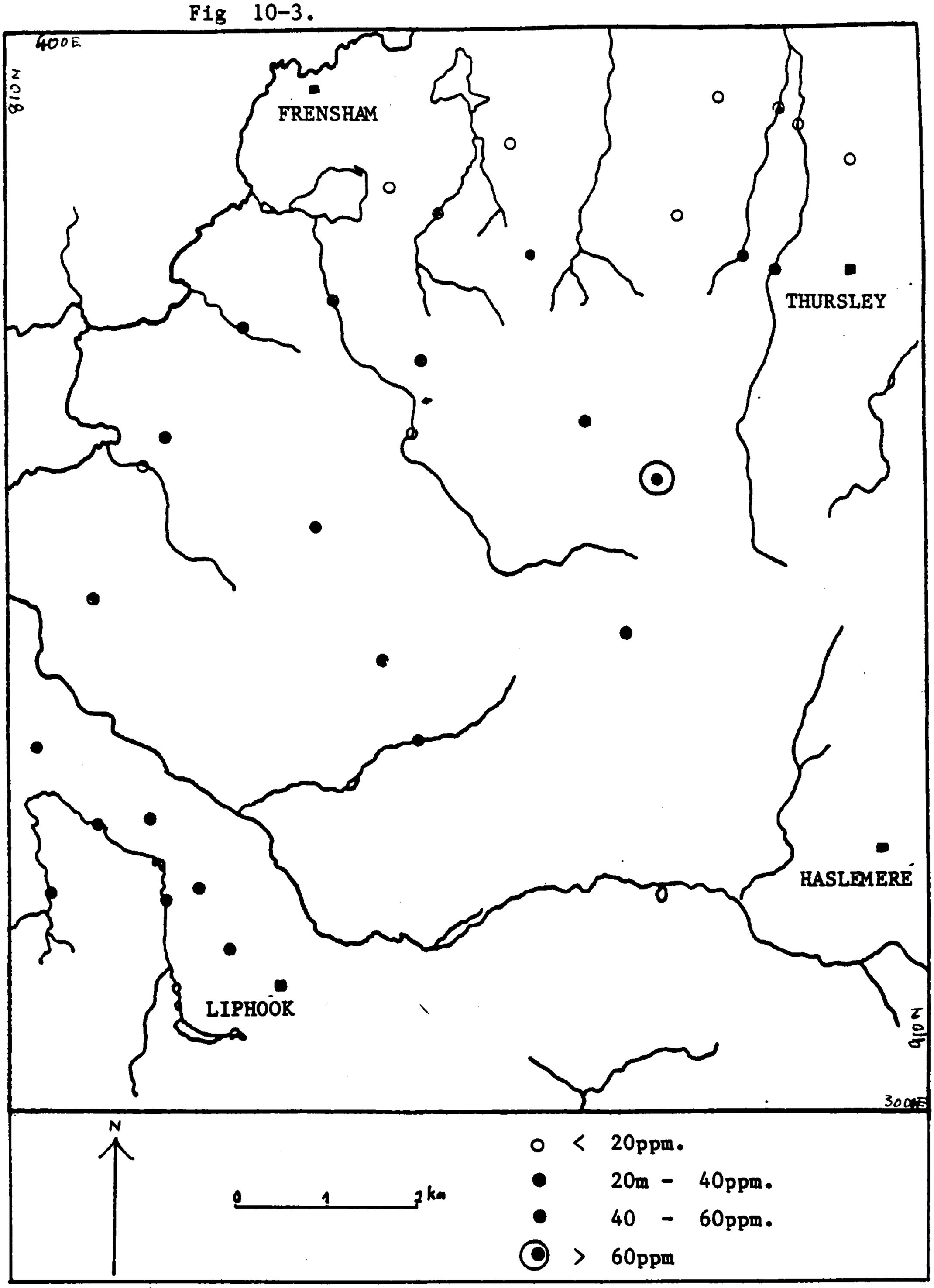
10-5 Geochemical Patterns.

The results presented in Table 10-1 represent a combination of the metal concentrations in the rocks, soils and stream sediments derived from all the beds of the Lower Greensand. This has been necessitated by the limited amount of samples collected from the individual beds of the formation. Tables 10-2, -3, -4, -5, show the metal concentrations in individual beds of the Lower Greensand. This was compiled to aid the interpretation of results of the combined data since the limited amount of samples collected for the individual beds cannot be taken to be representative of the beds. Furthermore stream sediments in the area are composite in character rarely reflecting the nature of the individual beds on which they were sampled. Geochemical maps of Pb, Zn, Cu, Co and Mn for the topsoils and stream sediments are included to aid interpretation. The patterns revealed in the present investigations are discussed below.

(a) Geochemical patterns in the rocks.

The concentrations of most elements were generally low in all the beds of the Lower Greensand in Surrey with the lowest concentrations tending to occur more frequently in the Folkestone Beds (Table 10-5) and comparatively higher concentrations tending to occur in the Sandgate Beds (Table 10-4). The combined results (Table 10-1) showed that the concentrations of Ca, Mg, Pb Cu and Co were low in all the beds. The results for individual beds showed that Ca

Fig 10-3.



Lead concentrations in the topsoils and stream sediments in the Surrey study area.

TABLE 10:3

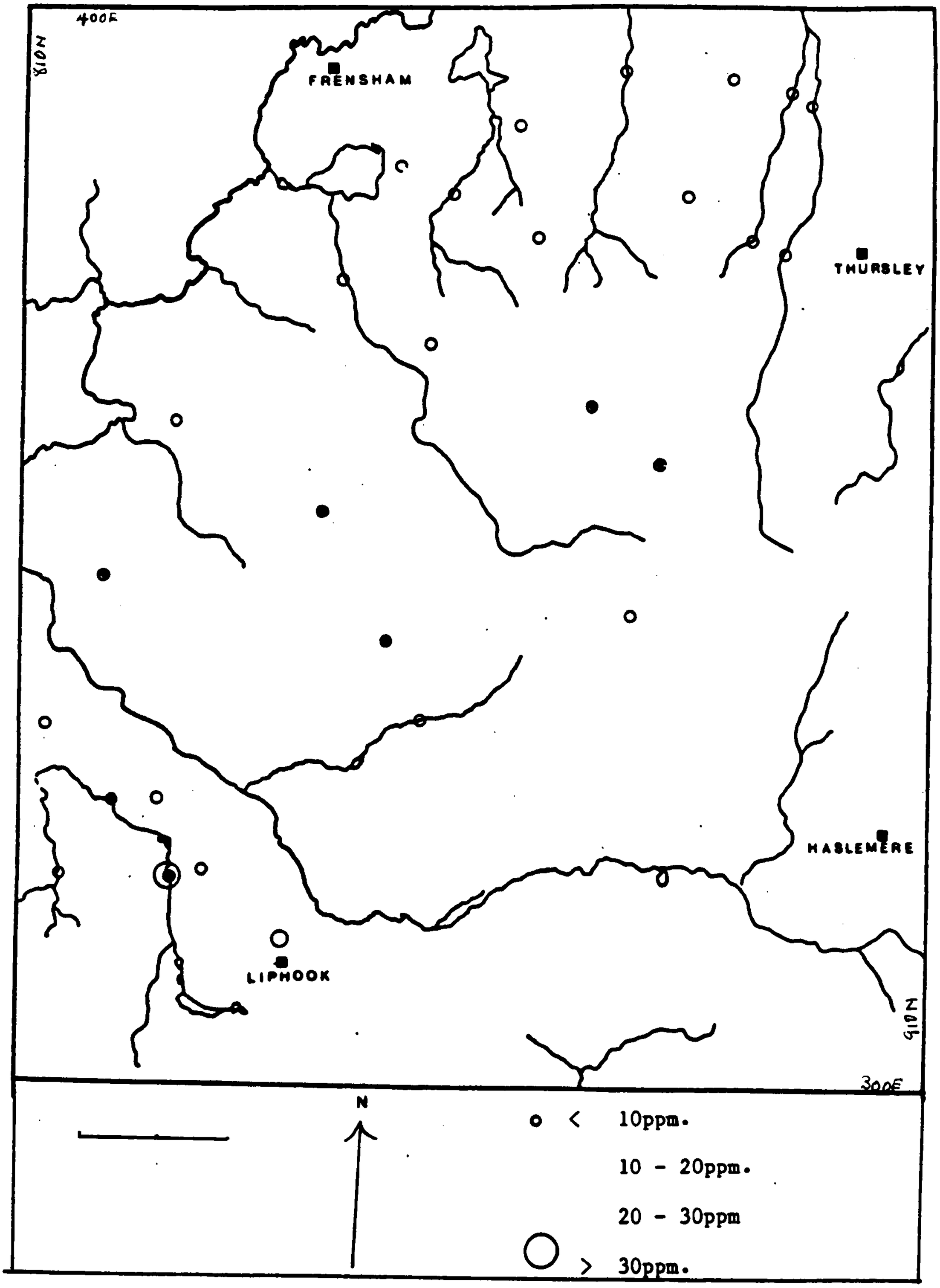
Medium	Number of Samples	Ca%	Zn(ppm)	Pb(ppm)	Fe%	Mg%	Cu(ppm)	Co(ppm)	Mn(ppm)
ROCK	3	2.0 (.9-3.5)	29.8 (26-31)	18.4 (15-22)	4.0 (3 - 5)	0.01 (.02-.07)	16.2 (6-20)	16.9 (8-12)	82.2 (50-125)
TOPSOIL 0 - 15cm*	4	0.36 (.25-.45)	25.8 (23-46)	30.5 (29-48)	1.2 (.95-1.6)	0.48 (.03- .8)	10.3 (7-14)	12.5 (11-17)	198.0 (150-300)
SUBSOIL 30 - 45cm*	4	0.26 (.14- .5)	26.6 (17-39)	19.7 (15-22)	2.6 (1 -3.6)	0.19 (.11- .3)	12.7 (6-17)	18.4 (16-30)	268 (170-360)
STREAM SEDIMENT	5	0.68 (.02-.19)	37.1 (22-51)	36.0 (20-45)	0.98 (.38-1.4)	0.02 (.01-.03)	17.4 (3-21)	28.8 (10-32)	352 (35-500)

Range and mean element concentrations in the rocks, soils and stream sediments derived from the Bargate Beds of the Lower Greensand in the Surrey study area

( ) Range

* Depth of sample

Fig. 10-4



Copper concentrations in the topsoils and stream sediments in the Surrey study area.

concentrations in the Bargate Beds (Table 10-3) were comparatively higher than in other beds of the formation with concentrations as high as 3.5% being recorded in some rocks. Rock samples of the Bargate Beds with high concentrations of Ca were usually friable and it seemed that Ca was part of the cementing medium.

High concentrations of Fe were recorded in the Sandgate Beds (Table 10-4). This was in contrast to concentrations of Fe below 1.5% which were common in other beds. It seemed likely that the higher concentrations of Fe recorded in the Sandgate Beds may not only be reflecting post depositional cementation within the unit but also the presence of glauconites in the rocks. As with other elements low concentrations of Zn, Pb, Cu and Mn were found in the Folkestone Beds while the higher concentrations were found in the Sandgate Beds. Zinc concentrations in the Bargate and Hythe Beds were comparable.

The concentrations of Cu and Co were particularly low in the Folkestone Beds (Table 10-5) where levels below 5ppm were common. The wide range of Mn in the combined results also reflected the variations within the formation. Thus concentrations as low as 10ppm were found in the Folkestone Beds while in the Sandgate Beds concentrations of Mn could rise as high as 500ppm.

(b) Geochemical patterns in the soils.

Soils developed over the various beds had Ca concentrations lower than those in the associated parent material(rock). Higher concentrations of Fe were found in the subsoils derived from the Bargate and Hythe Beds (up to 3%) than in the topsoils. These soils were podzolised with bleached topsoils(A_2). Over the Folkestone and Sandgate Beds top and subsoil concentrations of Fe were similar

TABLE 10:4

Medium	Number of Samples	Ca%	Zn(ppm)	Pb(ppm)	Fe%	Mg%	Cu(ppm)	Co(ppm)	Mn(ppm)
ROCK	4	0.24 (.15-.35)	72.4 (50-80)	21.0 (18-25)	9.8 (8 - 15)	0.09 (.06-.12)	10.4 (8-22)	26.1 (19-30)	343 (250-550)
TOPSOIL 0 - 15cm*	5	0.43 (.26-.65)	38.4 (24-69)	52.3 (36-71)	1.6 (.73-2.5)	0.10 (.07-.13)	12.3 (9-14)	6.2 (4-10)	374 (250-500)
SUBSOIL 30 - 45cm*	5	0.43 (.27-.67)	62.9 (45-80)	45.3 (21-56)	1.7 (.7 -2.3)	0.09 (.07-.11)	18.9 (15-23)	6.9 (4- 8)	397 (200-475)
STREAM SEDIMENT	3	1.2 (.6-1.5)	64.7 (50-75)	63.0 (20-71)	1.3 (1.4-2.4)	0.13 (.01-.19)	21.7 (7-29)	22.4 (17-40)	429 (250-850)

Range and mean element concentrations in the rock, soil and stream sediments derived from the Sandgate Beds of the Lower Greensand in the Surrey study area

( ) Range

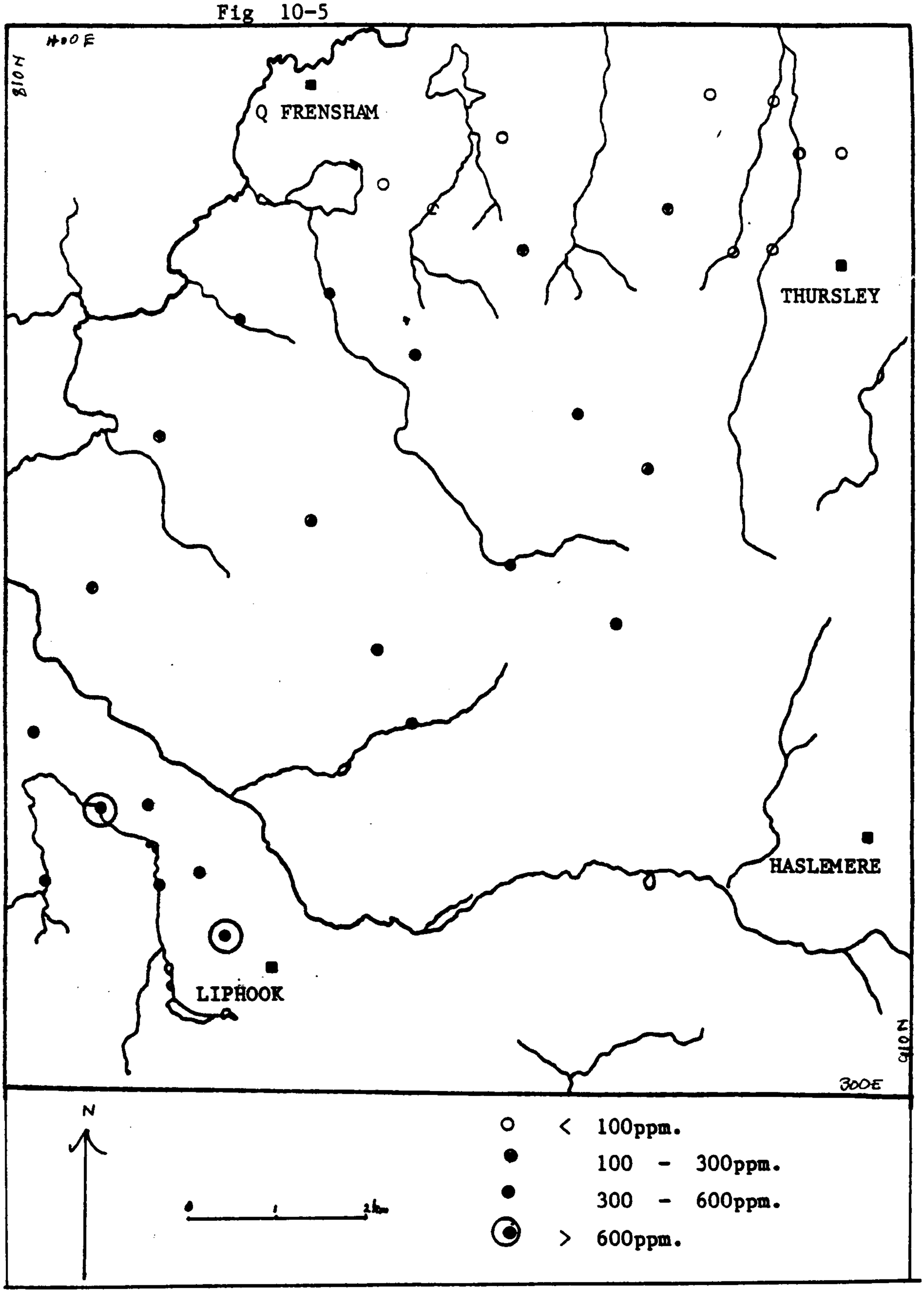
* Depth of sample

(Tables 10-4, -5). Zinc concentrations tended to be similar to those in the rocks over the various beds except on the Sandgate Beds where the mean concentrations of Zn were nearly twice as high as those in the topsoils. Topsoil concentrations of Zn were similar to those in the subsoils, again except over the Sandgate Beds. Lead concentrations were higher in the topsoil than in the subsoil. The concentrations of Mn tended to be higher in the soils than in the rocks with the subsoils showing higher concentrations than the topsoils. The susceptibility of Mn to leaching was thought to account for the decreased concentrations of Mn in the topsoils. Cobalt concentrations in the soils derived from the Folkestone Beds were below the detection limit(Table 3-1) in both the top and subsoils. Copper concentrations in the topsoils were also below the detection limit over the Folkestone Beds.

(c) Geochemical patterns in the stream sediments.

Apart from the Bargate Beds, Ca concentrations were higher in the stream sediments derived from other beds than in the associated rocks. Over the Hythe Beds Fe concentrations were higher in the stream sediments than in the rocks and soils while for other beds sampled Fe concentrations were lower in the stream sediments than in the rocks and soils. It seemed probable that the stream sediments draining the Hythe Beds in the eastern half of the study area may be reflecting Fe concentrations in the nearby Weald Clay which was not sampled. Stream sediments derived from all the beds of the Lower Greensand in the study area except the Sandgate Beds displayed varying degrees of enhancements of Zn compared to the associated rocks and soils. The concentrations of Pb and Cu were also higher in the stream

Fig 10-5



Manganese concentrations in the topsoils and stream sediments in the Surrey study area.

TABLE 10:5

Medium	Number of Samples	Ca%	Zn(ppm)	Pb(ppm)	Fe%	Mg%	Cu(ppm)	Co(ppm)	Mn(ppm)
ROCK	3	0.07 (.01-.13)	15.6 (10-18)	26.5 (20-37)	1.2 (.1-1.4)	0.02 (.01-.07)	6.4 (5- 9)	5.2 (5- 9)	17.0 (10-21)
TOPSOIL	6	0.06 (.03-.08)	15.9 (6-20)	21.7 (12-32)	0.74 (.5-1.1)	0.03 (.01-.05)	-	-	32.5 (10-50)
SUBSOIL	6	0.05 (.01-.07)	14.5 (7-21)	31.6 (17-41)	0.72 (.46-.80)	0.04 (.01-.04)	7.4 (5-12)	-	51.0 (10-70)
STREAM SEDIMENTS	4	0.2 (.15-.25)	16.4 (5-18)	36.4 (25-50)	0.6 (.75-2.6)	0.13 (.03-2.5)	16.7 (5-21)	10.9 (7-14)	18.1 (50-232)

Range and mean element concentration in the rock, soil and stream sediments derived from the Folkestone Beds of the Lower Greensand in the Surrey study area

( ) Range

sediments than in the rocks and soils. Staining of pebbles and gravels in the stream sediments were widespread in the study area. Thus, apart from the Folkestone Beds this was reflected in the higher concentrations of Mn in the stream sediments compared to the soils derived from other beds.

10-6 Discussion and summary.

The detailed assessment of the geochemistry of the individual beds was restricted by the few samples collected. On the basis of the available results the following generalised observations were made.

(a) Concentrations of elements were controlled by the inherently low concentrations in the rocks.

(b) Influence of the secondary environment controlled the modification of the initial concentrations of elements in the soils and stream sediments.

(a) Influence of the parent material.

In general, the low concentrations of most elements in the rocks were reflected in the associated soils and stream sediments. Thus soils and stream sediments derived from the Folkestone Beds reflected the relatively low concentrations found in the rocks while the reverse was true for the soils and stream sediments derived from the Sandgate Beds. Metal concentrations in the soils derived from the Bargate and Hythe Beds tended to be intermediate with the Hythe Beds tending towards the Folkestone Beds and the Bargate Beds towards the Sandgate Beds.

It was inferred from the results that the parent material was the dominant factor controlling the distribution of elements in the soils and stream sediments.

(b) Secondary environmental influence.

The nature and texture of the rocks was critical in determining the drainage status of the soils. In the soils derived from the Folkestone Beds drainage was excessive and the leaching of elements in the topsoils was a common feature. The higher concentrations of Zn, Cu, Co and Mn in the subsoils were thought to be due to leaching while the higher concentrations of Pb in the topsoils were thought to be due to the fixation by organic matter. In the podzolised soils higher concentrations of Fe were found in the subsoils than in the topsoils. This may reflect the translocation of materials, eg. organic matter and hydrous oxides from the top to subsoils during podzolisation (Bloomfield, 1955).

10-7 Conclusions.

The following conclusions were made from the present investigations.

(a) Metal concentrations in the soils and stream sediments were controlled primarily by the exceedingly low concentrations of elements in the rocks.

(b) Leaching in the soils led to enhanced concentrations of Zn, Cu, Co and Mn in the subsoils.

(c) The stream sediments reflected the variations of element concentrations in the different beds of the Lower Greensand in Surrey.

SECTION 3

General Introduction

Three main aspects of the relationship between the rock, soil and stream sediments were examined in detail:-

(1) Is there a significant relationship between the concentration of elements in the rock (parent material) and that of the soils and stream sediments derived from it?

(2) How accurately can the variation of elements in the rocks and soils be reflected by the variations in the stream sediments?

(3) Are the multi-element associations found in the rocks the same as those found in the associated soils and stream sediments ie, are there groups of elements within the rocks, soils and stream sediments that are associated by similar geochemical processes?

The above questions governed the lithological units selected and the sampling and analytical techniques employed. Three geological units were selected. These were,

(a) the Old Red Sandstone in Herefordshire,

(b) the Keuper Marl in Worcestershire,

(c) the Lower Lias in Somerset.

Preliminary investigations into these units have been discussed in Section 2. The soil series developed over these units

ranged from the brown earths (Ross series, Worcester series) developed over the Old Red Sandstone and the Keuper Marl, respectively, and surface water gleys and calcareous soils (Denchworth and Evesham series) over the Lower Lias.

Rock samples were taken by chip sampling at random over the Old Red Sandstone. Samples representing "rock samples" were taken from depths greater than 1.2m with a soil auger in areas overlain with the Keuper Marl and Lower Lias where rock exposures were sparse. Soil samples were taken from depths of 0-15cm (topsoil) and 30-45cm (subsoil). Stream sediment samples were mostly taken upstream at road stream junctions.

In each study area duplicate samples were collected from ten random sites for each medium. Each sample was analysed twice by atomic absorption spectroscopy (see Chapter 3) after a nitric/perchloric acid digestion. Ten elements were analysed. These were Ca, Mg, Al, Fe, Zn, Mn, Co, Pb, Ni, and Cu. Organic matter was measured by the loss on ignition method (Chapter 3) while the pH in water was measured on the rock, soil , sediment samples.

Statistical analysis of the data was used to answer the three questions raised above. The summary statistics (Appendix 1) including the means, standard deviations, coefficient of variation, and the range were used to answer the first question . This enabled the distribution of individual elements in the different media to be assessed. On the basis of the assumption that the mobility of elements in the transition from one medium to another could be assessed by measurements of the variation, the three level nested analysis of variance technique (Chapter 3) was used to compare the variability of elements in the different media. This technique

enabled the contributions of each level in the nested design to the total variation to be estimated and was used in examining the second question raised above.

The examination of the third question raised above was limited to a search for only those relationships that could satisfactorily be represented by a linear function given by:-

$$y = a + bx$$

where y and x are two variables and a, b are constants. The product moment correlation coefficient and factor analysis (Chapter 3) measures the closeness with which two or more variables approach such a linear relationship and these techniques were used to discern element groupings and associations in the different media. The element groupings were discerned indirectly. Thus by reference to characteristic elements it was generally possible to identify each element group with one of the major constituents of the geochemical environment eg. Al alone, or in combination with elements, such as Mg and Fe, if they showed strong inter-correlations, could be regarded as characteristic of the clay mineral fraction. The major geochemical constituents considered were:-

(i) clay minerals,

(ii) carbonates,

(iii) hydrous oxides,

(iv) organic matter.

The reference elements used were Al, Ca, and Mn together with the organic matter. These were used as indicators of associations with the clay minerals, carbonates, hydrous oxides and organic matter respectively. The fact that some of these reference elements are capable of being associated with two or more fractions , such as Ca

being adsorbed on exchange sites on the clay minerals or present in the carbonate phase, or trivalent Al forming stable complexes with organic matter, were considered in the geochemical interpretation of the statistical results.

CHAPTER 11

Detailed Investigations Into The Old Red Sandstone in Herefordshire.

11-1 Introduction:

The field area described in Chapter 7 is situated in the southern half of Herefordshire, enclosing the town of Ross-on-Wye. Preliminary investigations in the area involved comparison of the element concentrations in the rocks, soils, and stream sediments. The present investigation involved a more detailed assessment of the element distributions in the different media (rocks, soils, and stream sediments) , multi-element associations in the different media, and assessment of the variability of elements in the transition from one medium to another.

11-2 Geology.

The stratigraphic succession, lithology and distribution of the Lower Devonian Old Red Sandstone in the study area have been described in Chapter 7. Rock sampling was aimed at obtaining samples from the various facies of the Old Red Sandstone in the study area. The sample sites are shown in Fig. 11-1.

11-3 Soils

The dominant soil series is the Ross series (Whitfield, 1971). These are freely drained sandy loams developed from Lower Devonian sandstones . The soils are generally slightly acidic in

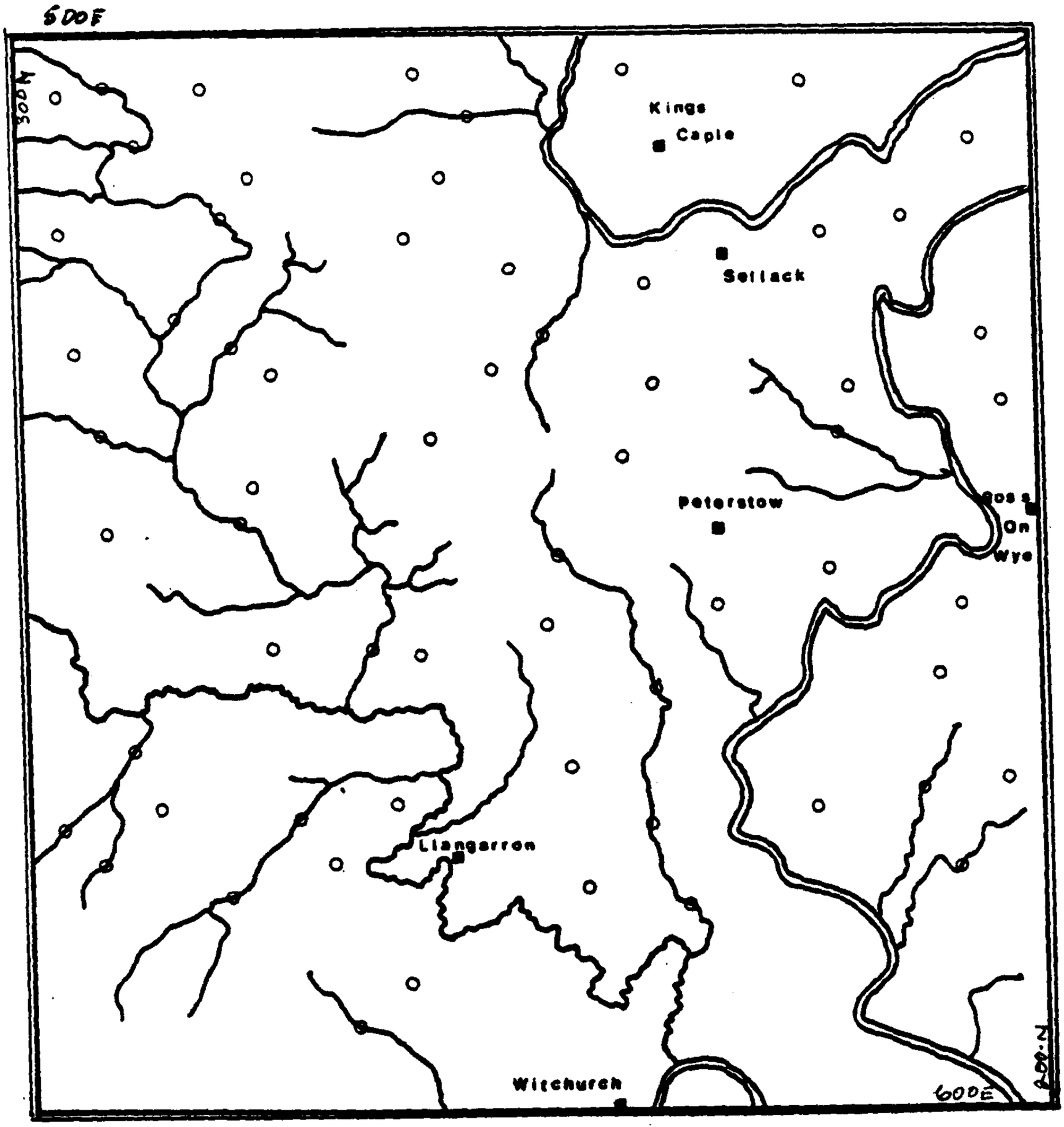


Fig 11-1

Sample Location In The Herefordshire Study Area

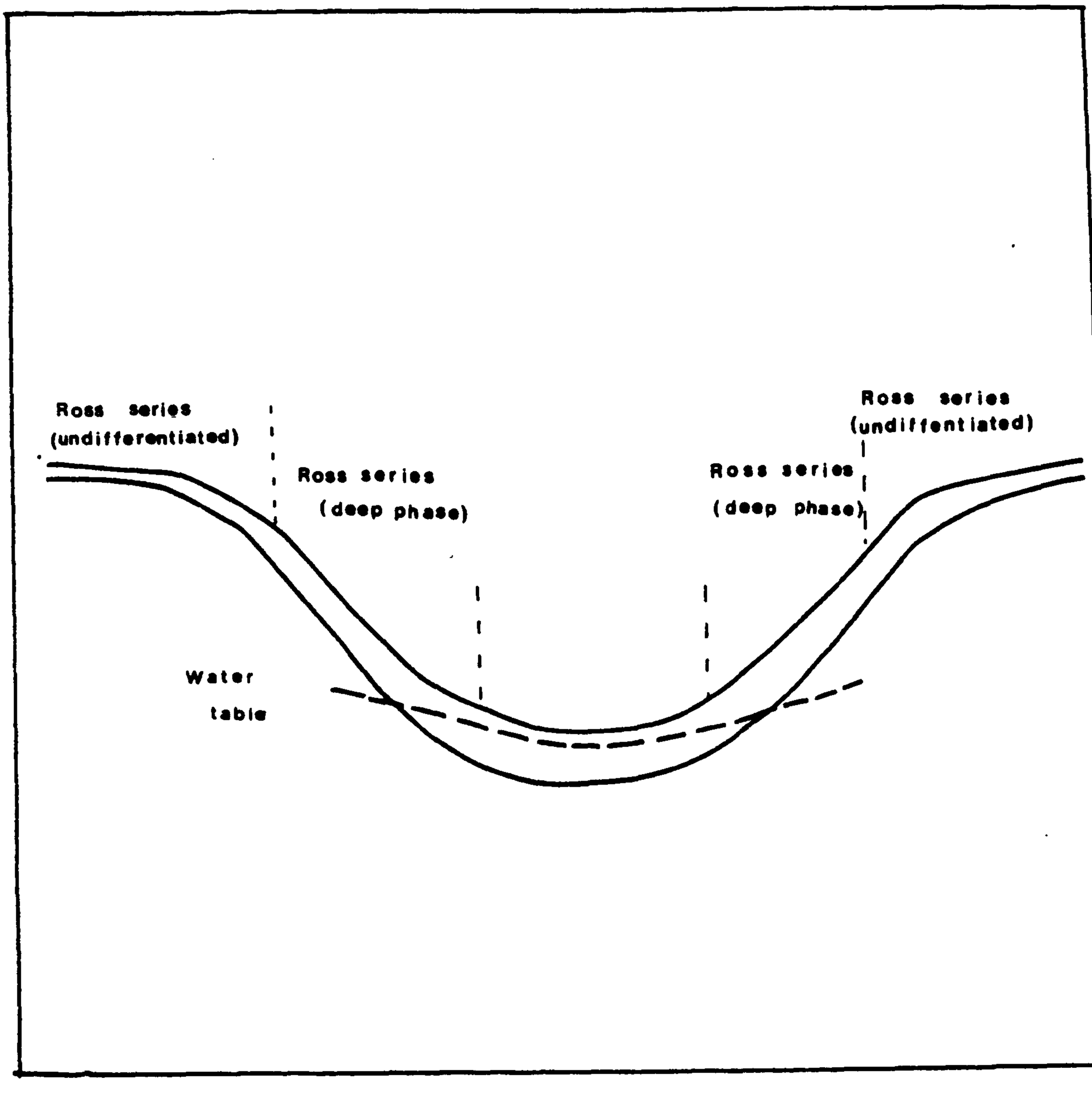


FIG II-2

Distribution of the Ross soil series in the Herefordshire study area

(Based on Whitfield 1971)

reaction with a weakly differentiated A, B and C horizons. Whitfield (1971) distinguished shallow, deep and steepland phases of the Ross series (Fig. 11-2). The normal phase of the Ross series has a weakly differentiated A and B horizon. Under permanent grass the profiles are very uniform with a thin A horizon. The cation exchange capacity is usually low to moderate (Whitfield, 1971). The shallow and deep phases have a similar sequence of horizons but in the shallow phase sandstones occur at depths of 45cm or less, while in the deep phase sandstones occur at depths in excess of 1m. The shallow phase is often restricted to the tops of small knolls and convex slope positions.

11-4 Regional Geochemical Patterns.

The following observations were made from the preliminary investigations (see Chapter 7):-

(1) the dominant control on the distribution of elements in the soils and stream sediments was the inherently low concentrations of most elements in the rock (parent material),

(2) apart from Ca which displayed marked depletions in the transition from rock to soil and stream sediments, leaching of most elements in the soils and subsequent redistribution in the surface drainage was uncommon,

(3) elements such as Zn and Pb tended to be enhanced in the topsoil compared to the subsoil, while for most other elements the differences between the the top and subsoil were negligible.

The results of the detailed assessment of individual elements are discussed below.

Table 11-1a Calcium Concentrations In The Rock Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	N	Mean (%)	S.D.	C.V.	Range Min (%)	Max (%)
Rock	40	6.7	2.8	42.2	1.0	12.5
T/Soil	49	0.3	0.2	56.8	0.1	0.9
S/Soil	45	0.4	0.2	64.2	0.1	0.9
S/Sedt	40	0.3	0.2	53.8	0.1	0.7

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 11-1b Significance of the Correlation Coefficients Between Ca And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock		-	-	-	**	-	-	***	**	-	ND	Nd
T/Soil		-	-	-	-	-	-	-	-	-	-	**
S/Soil		-	-	-	-	*	-	-	-	-	-	***
S/Sedt		-	-	-	*	*	-	**	**	-	-	-

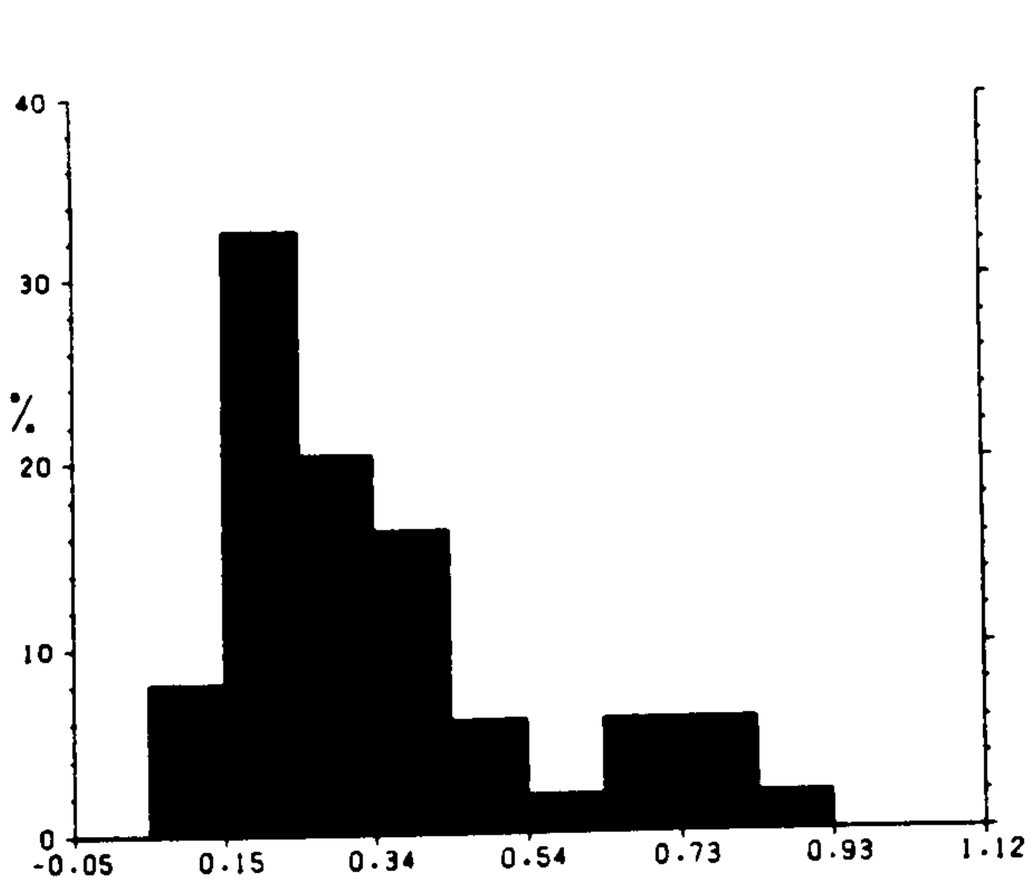
Level Of Significance - = Not Significant * = Significant at .10 level

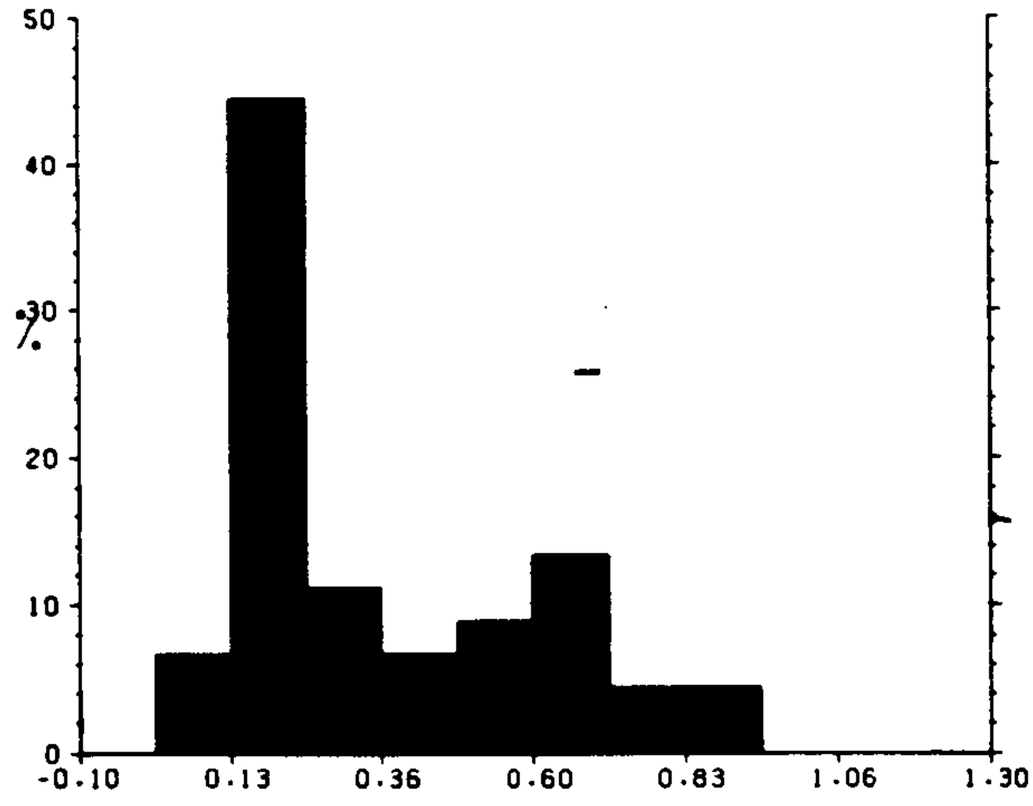
** = Significant at the .05 level

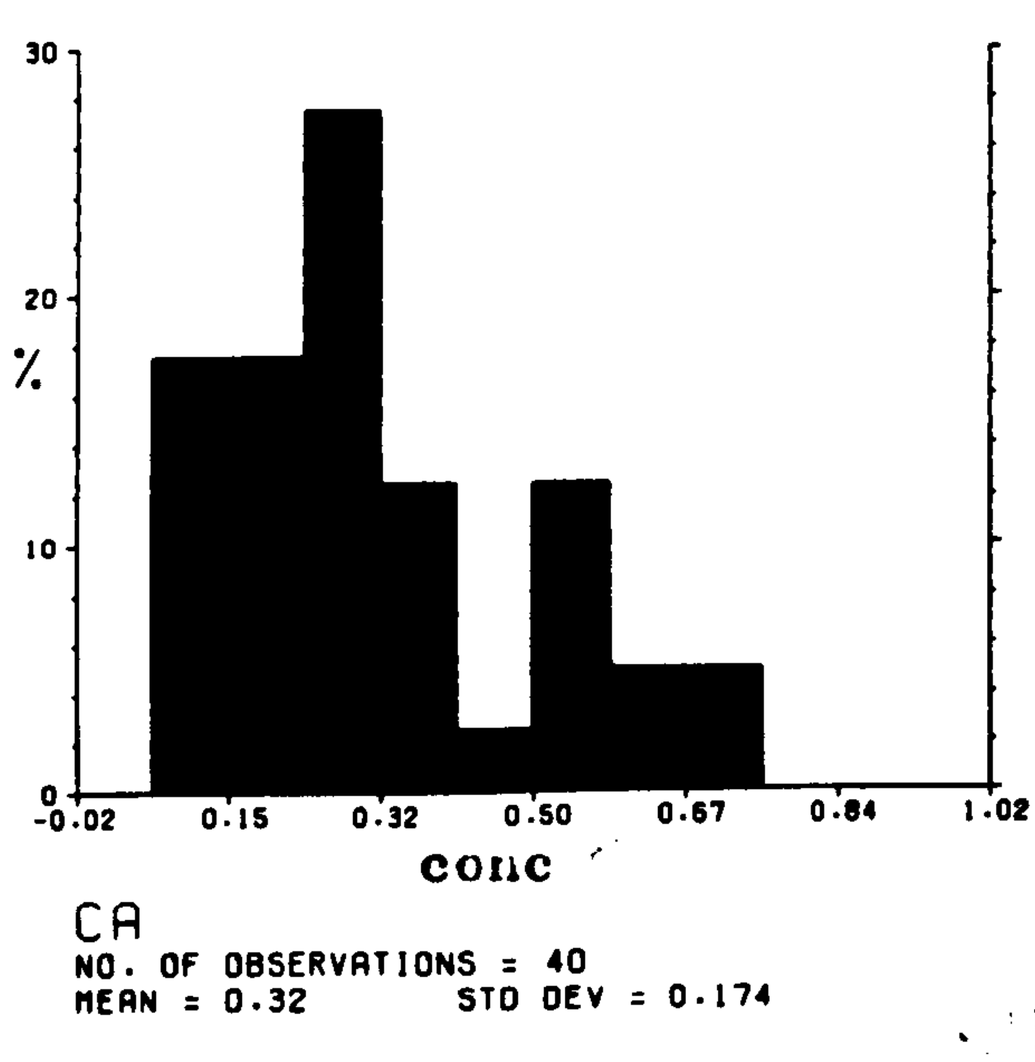
*** = Significant at .01 level

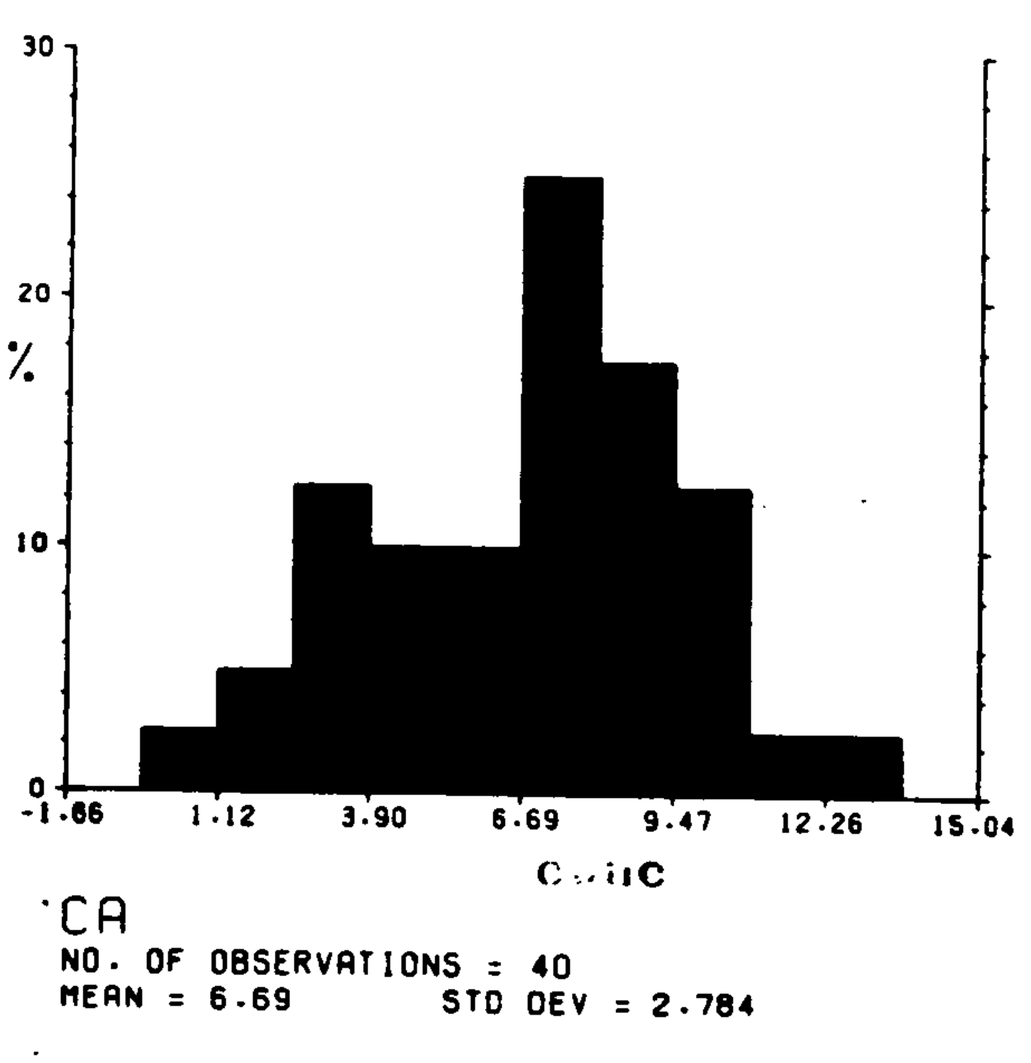
( ) = Negative Correlation. ND= Not Determined.

Fig. 11-3









Histograms of the distribution of Ca in rocks, soils and stream sediments derived from the Old Red Sandstones in the Herefordshire study area.

Interpretations of the results were based on:-

(a) the distribution of individual elements in the different media,

(b) the multi-element groupings identified by factor analysis, and,

(c) assessment of the mobility of elements between the parent material and associated soils and stream sediments using a three level nested analysis of variance (Chork, 1977).

(a) Calcium .

Calcium concentrations in the rocks were governed by the lithological variation in the Old Red Sandstone formation (Table 11-1a). Concentrations of Ca as high as 12% were recorded in some unferruginised samples near Ross On Wye. The histograms of the distribution (Fig. 11-3) showed that about 50% of the samples had Ca concentrations above 7% but that the number of samples with more than 10% Ca dropped sharply. Calcium concentrations below 3.9% were prevalent in the marl samples. Much of the Ca was lost in the transition from rock to soil and stream sediments. This was reflected by the narrower range and lower mean concentrations in the soils and stream sediments (Table 11-1a) compared to the rocks. In the top and subsoils the maximum concentration of Ca was below 1%. The mean concentrations in the topsoil and the subsoil were very similar and the histograms (Fig. 11-3) showed that concentrations below 0.5% were common. As with the soils, Ca concentrations were lower in the stream sediments than in the rocks. The coefficients of variation showed that maximum variation of Ca occurred in the subsoil.

Table 11-2a Magnesium Concentrations In The Rock Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	N	Mean (%)	S.D.	C.V.	Range Min (%)	Max (%)
Rock	40	0.5	0.2	37.0	0.1	0.9
T/Soil	49	0.6	0.2	40.9	0.3	0.8
S/Soil	45	0.6	0.2	28.9	0.4	0.9
S/Sedt	40	0.4	0.2	47.3	0.1	0.9

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 11-2b Significance of the Correlation Coefficients Between Mg And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-		**	**	**	-	-	-	-	-	ND	ND
T/Soil	-		***	***	-	-	-	-	***	-	-	-
S/Soil	-		***	***	-	*	-	-	***	-	-	-
S/Sedt	*		***	**	***	-	-	-	-	-	-	-

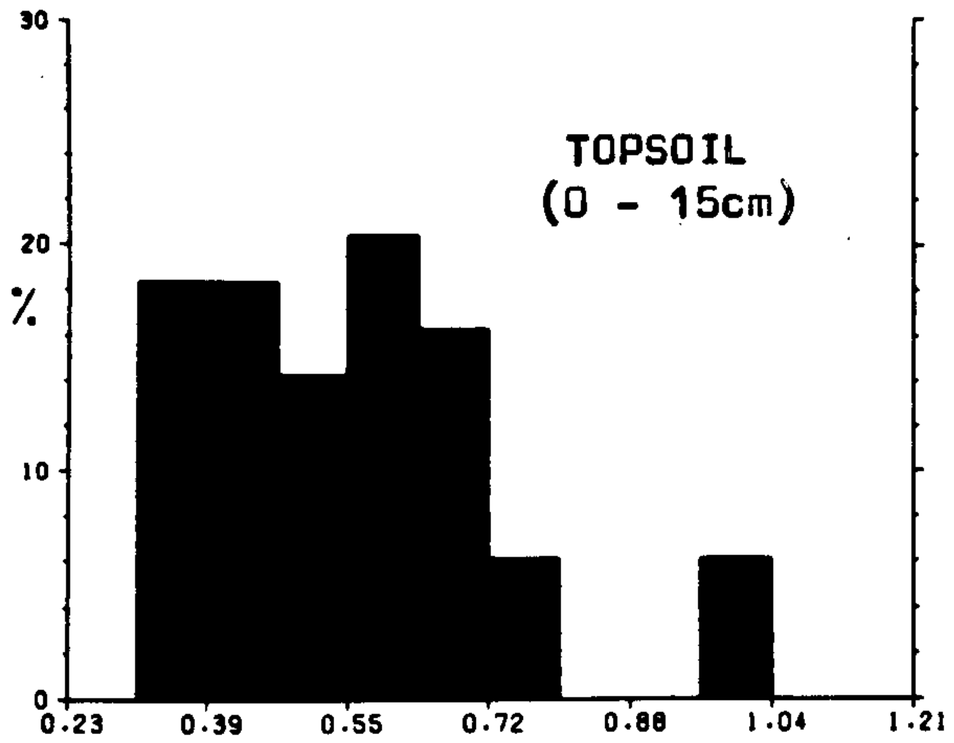
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

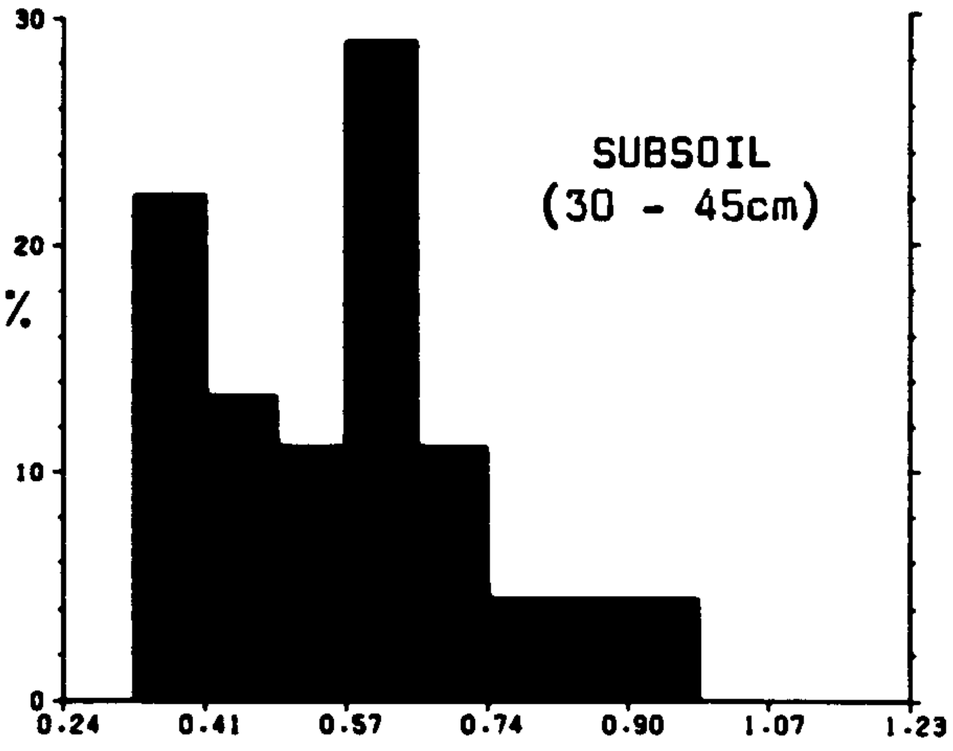
*** = Significant at .01 level

( ) = Negative Correlation. ND= Not Determined.

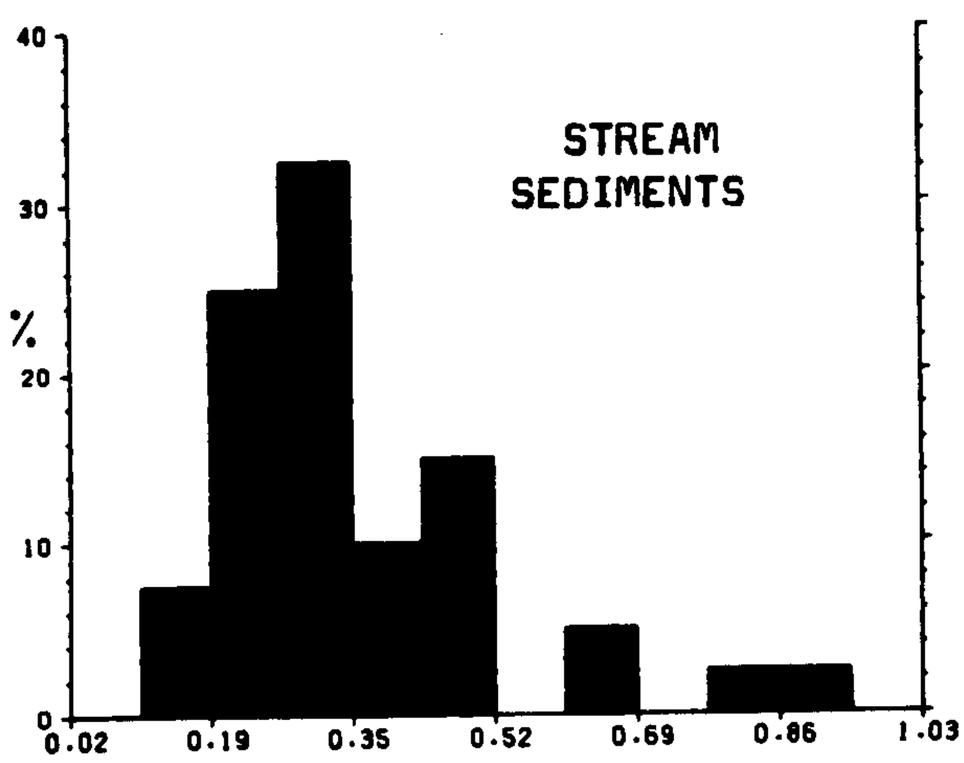
Fig. 11-4



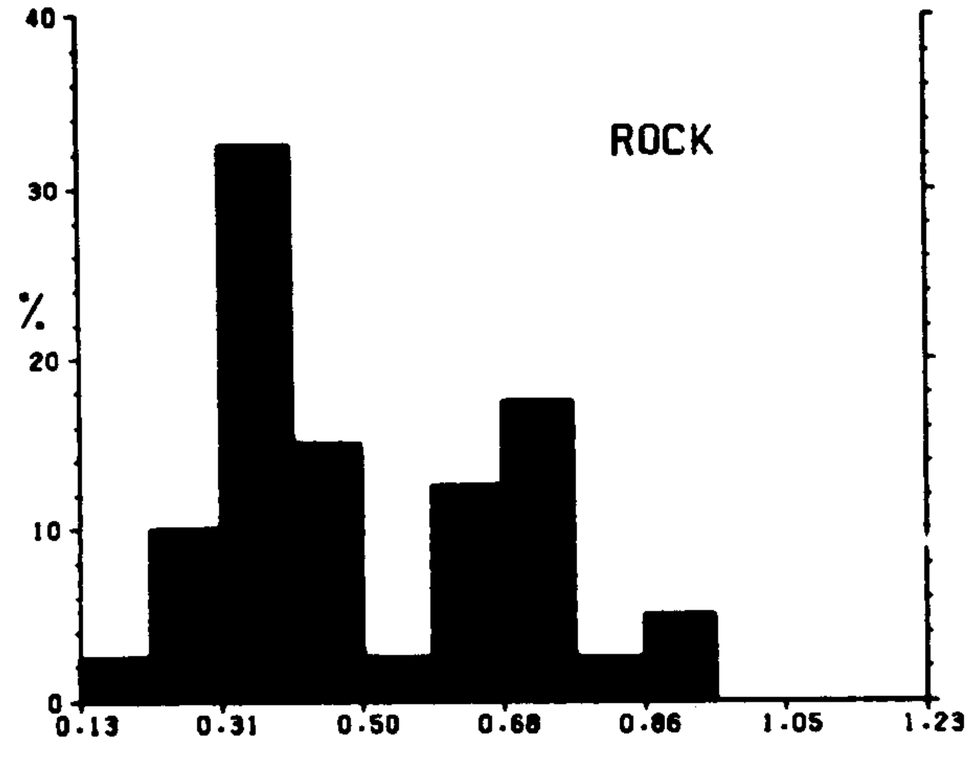
MG conc (%)
NO. OF OBSERVATIONS = 49
MEAN = 0.55 STD DEV = 0.163



MG conc (%)
NO. OF OBSERVATIONS = 45
MEAN = 0.57 STD DEV = 0.165



MG conc (%)
NO. OF OBSERVATIONS = 40
MEAN = 0.35 STD DEV = 0.168



MG conc (%)
NO. OF OBSERVATIONS = 40
MEAN = 0.50 STD DEV = 0.185

Histograms of the distribution of Mg in the rocks, soils and stream sediments derived from the Old Red Sandstones in the Herefordshire study area.

Inter-element correlation.

The pH of the rock water suspension was not measured and so it was not possible to include pH as one of the variables in the correlation coefficient calculations. In the rocks, the correlations with the elements Zn, Pb and Ni were significant (Table 11-1b). These elements may be associated with the carbonates present in the rocks, possibly as part of the cementing medium in the sandstones. In both the top and subsoils of the Ross series, the correlations with the pH were significant. Such strong correlation with pH may reflect the effect of soil acidity on the dissolution of the carbonates inherited from the soil parent material. In the stream sediments significant correlations existed between Ca with Ni and Pb, while relatively weak correlations were found with Zn and Mn in the sediments.

(b) Magnesium.

Apart from the slight depletion of Mg in the stream sediments there was very little difference between the concentrations in the soils and rocks (Table 11-2a). The coefficients of variation were similar except in the subsoil where it was relatively low. The histograms (Fig. 11-4) showed that a significant percentage of the samples in each medium had concentrations below 0.6%. In general, it can be inferred that Mg was associated with a stable component which remained unaffected by the processes operating in the soils and streams.

Table 11-3a Aluminium Concentrations In The Rock Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	N	Mean (%)	S.D.	C.V.	Range Min (%)	Max (%)
Rock	40	1.9	0.7	33.7	0.8	3.5
T/Soil	49	2.5	0.7	25.3	1.2	4.0
S/Soil	45	2.6	0.8	38.0	1.2	4.1
S/Sedt	40	1.3	0.7	48.2	0.5	3.2

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 11-3b Significance of the Correlation Coefficients Between Al And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	**		***	***	(**)	-	*	-	-	ND	ND
T/Soil	-	***		***	-	***	-	-	***	-	-	-
S/Soil	-	***		***	-	-	**	-	***	-	-	-
S/Sedt	-	***		***	***	-	-	-	-	**	-	-

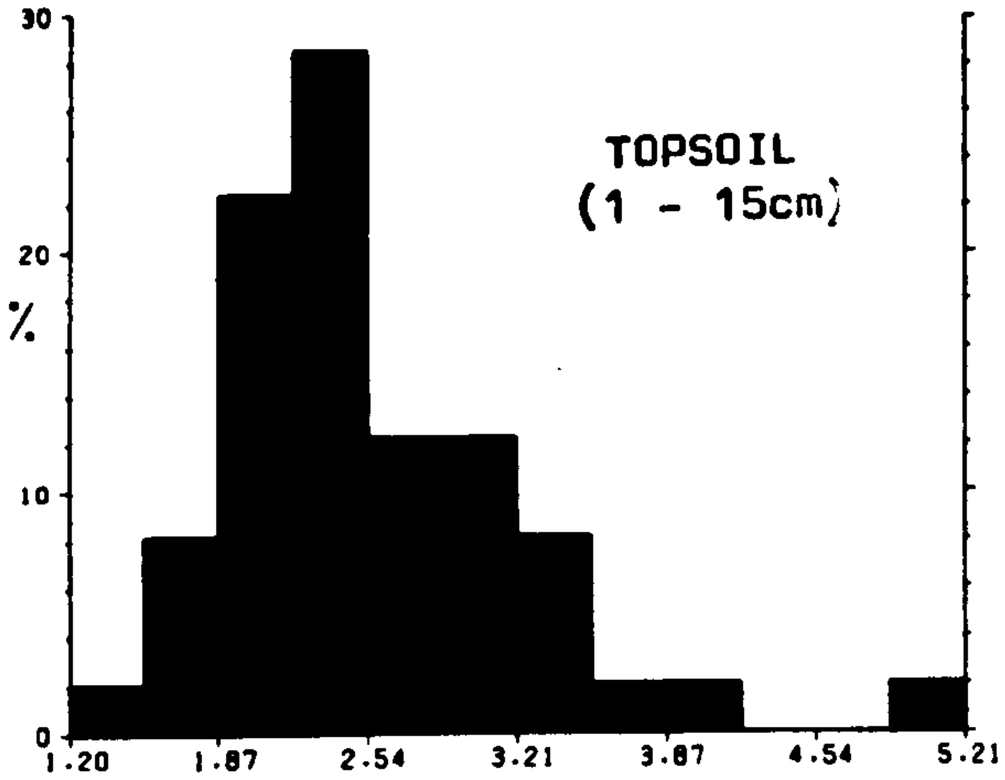
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

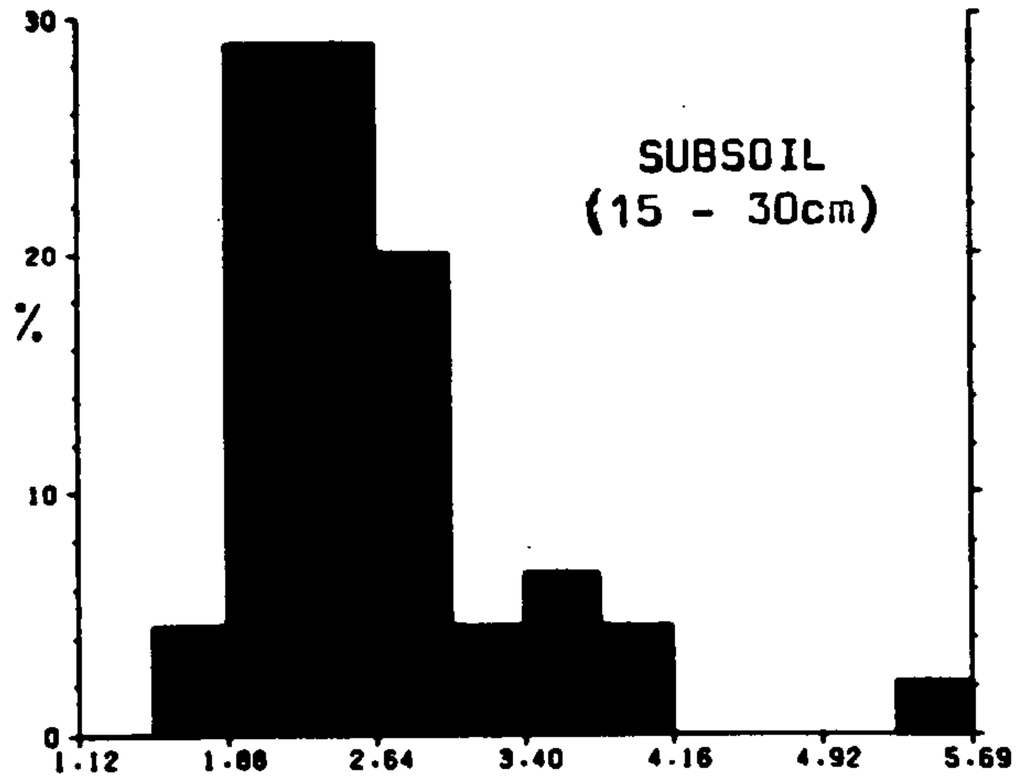
*** = Significant at .01 level

( ) = Negative Correlation. ND= Not Determined

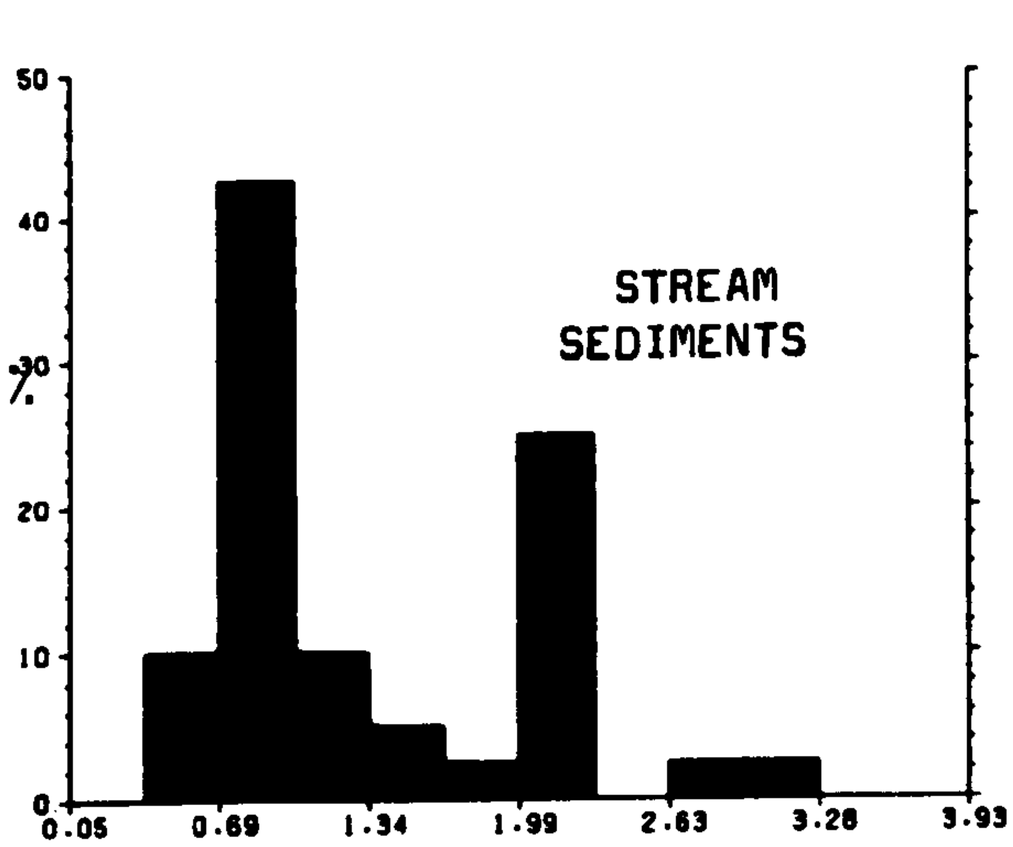
Fig. 11-5



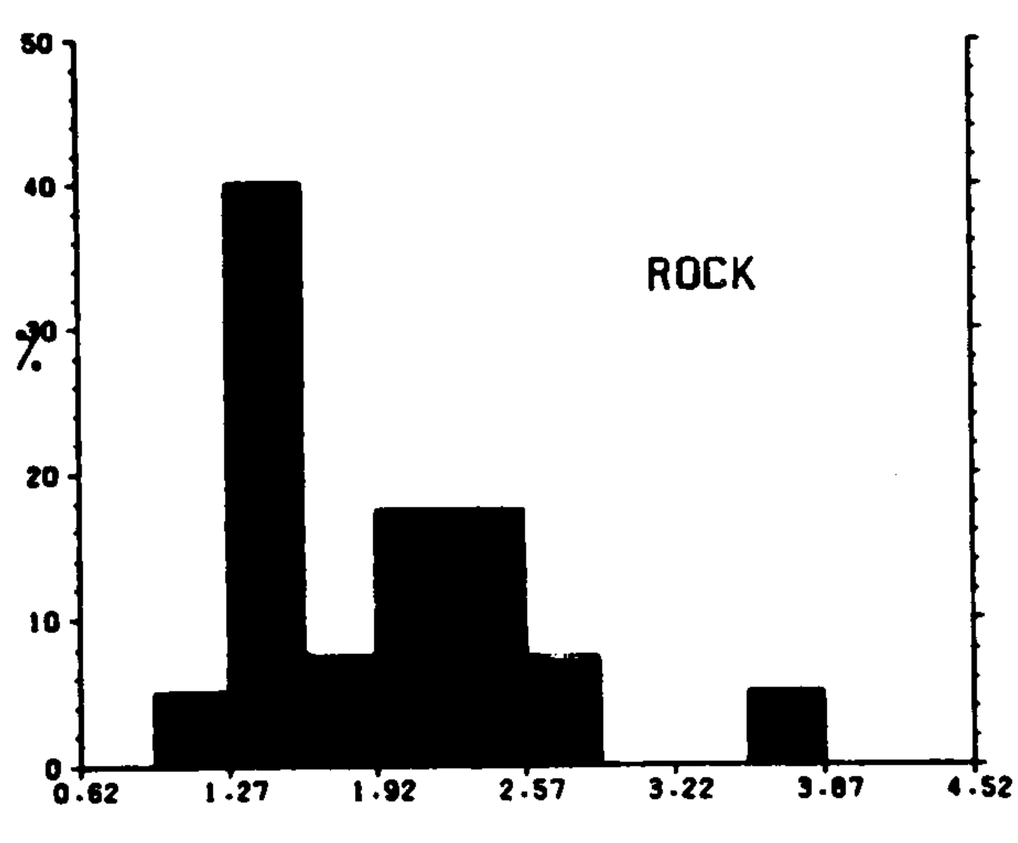
AL conc (%)
NO. OF OBSERVATIONS = 49
MEAN = 2.54 STD DEV = 0.667



AL conc (%)
NO. OF OBSERVATIONS = 45
MEAN = 2.64 STD DEV = 0.761



AL conc (%)
NO. OF OBSERVATIONS = 40
MEAN = 1.34 STD DEV = 0.646



AL conc (%)
NO. OF OBSERVATIONS = 40
MEAN = 1.92 STD DEV = 0.651

Histograms of the distribution of Al in the rocks, soils and stream sediments derived from the Old Red Sandstones in the Herefordshire study area.

Inter-element correlation.

In all the media investigated Mg was significantly correlated with Al and Fe (Table 11-2b). In the rocks and stream sediments the correlations with Zn were significant while in the top and subsoil the correlations with Ni were significant. Magnesium is more likely to be related to the clay minerals and it seemed from the persistent correlation with the clay related elements Al and Fe in the different media, that the clay minerals do not undergo significant alterations in the different media.

(c) Aluminium.

Aluminium concentrations in the rocks and soils were similar. The mean concentrations in the soils were marginally higher than the rock although the ranges were similar in the rock and soils (Table 11-3a) . The histograms (Fig. 11-5a) showed that a significant percentage of the rock and soil samples had Al concentrations below 3.0% with a gradual reduction in the frequency of occurrence of the higher concentrations. Concentrations in the stream sediments were only marginally lower than those in the soils and rocks. The coefficient of variation showed that the decreased concentrations in the stream sediments were accompanied by higher variation (Table 11-3a).

Aluminium is an important component of the clay minerals and like Mg may be associated with a stable fraction in the different media, possibly as constituents of the clay minerals.

Table 11-4a Iron Concentrations In The Rock Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	N	Mean (%)	S.D.	C.V.	Range Min (%)	Max (%)
Rock	49	1.4	0.6	38.7	0.8	4.5
T/Soil	45	2.1	0.5	21.0	1.0	3.8
S/Soil	45	2.2	0.4	20.1	1.0	3.0
S/Sedt	40	1.6	0.5	28.5	0.7	2.5

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 11-4b Significance of the Correlation Coefficients Between Fe And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	**	***		***	**	-	-	-	-	ND	ND
T/Soil	-	***	***		*	-	-	-	**	**	-	-
S/Soil	-	***	***		*	-	-	*	*	*	-	-
S/Sedt	-	**	***		***	**	-	-	-	-	*	-

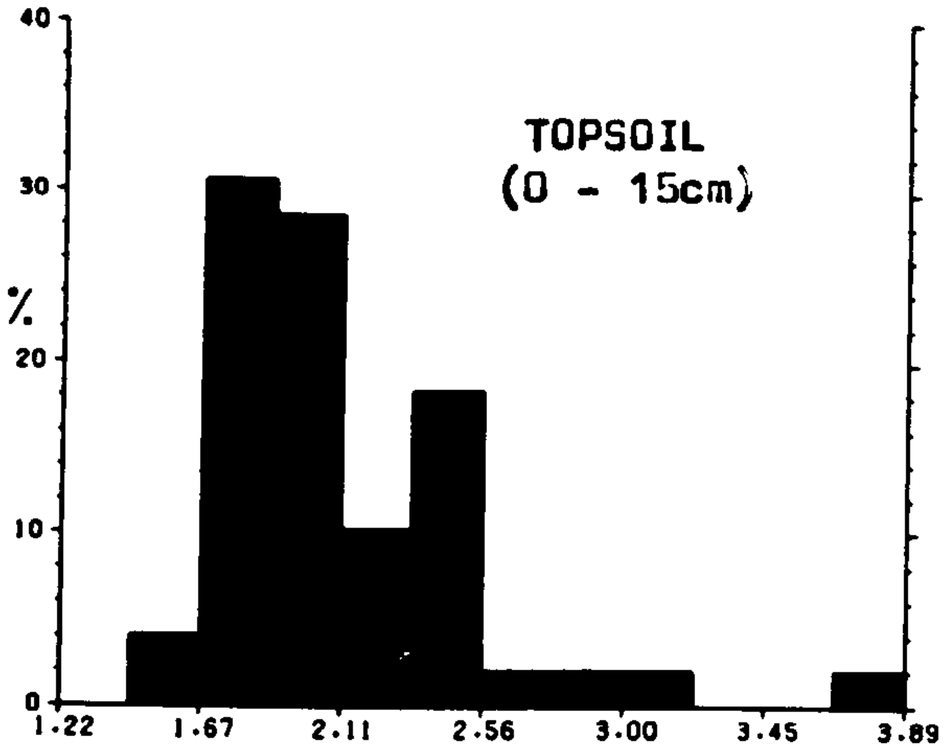
Level Of Significance - = Not Significant * = Significant at .10 level

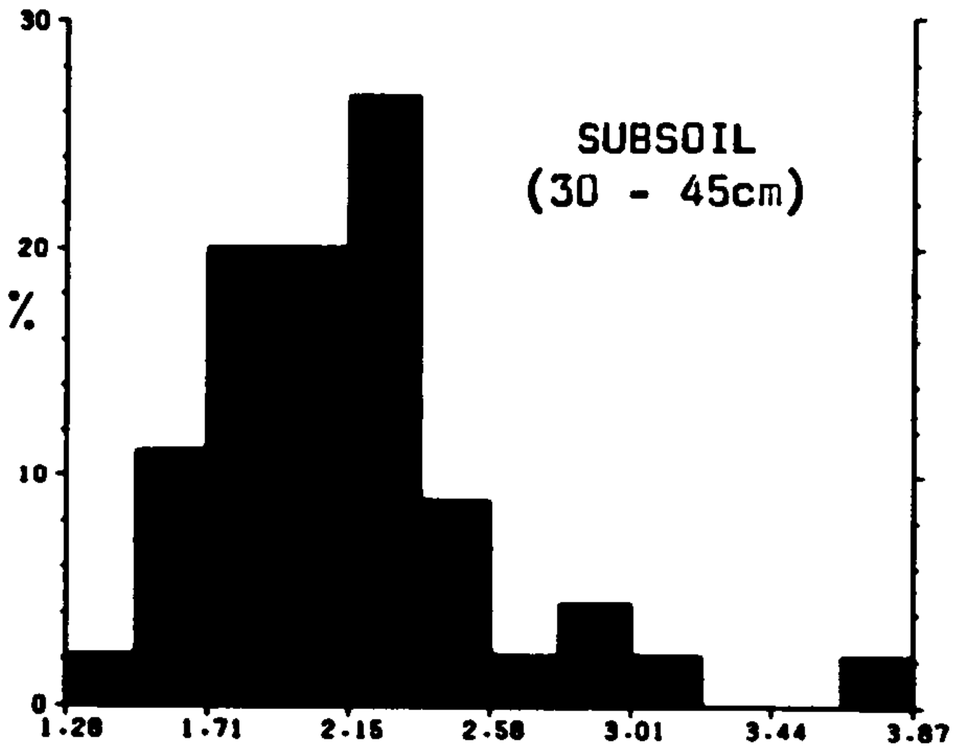
** = Significant at the .05 level

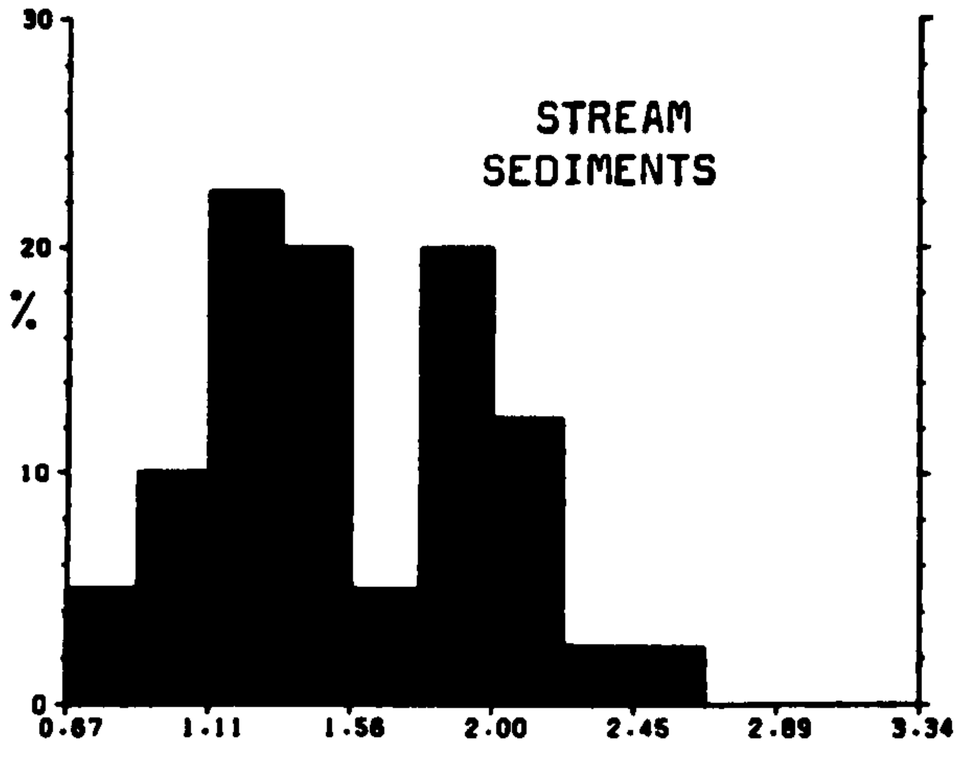
*** = Significant at .01 level

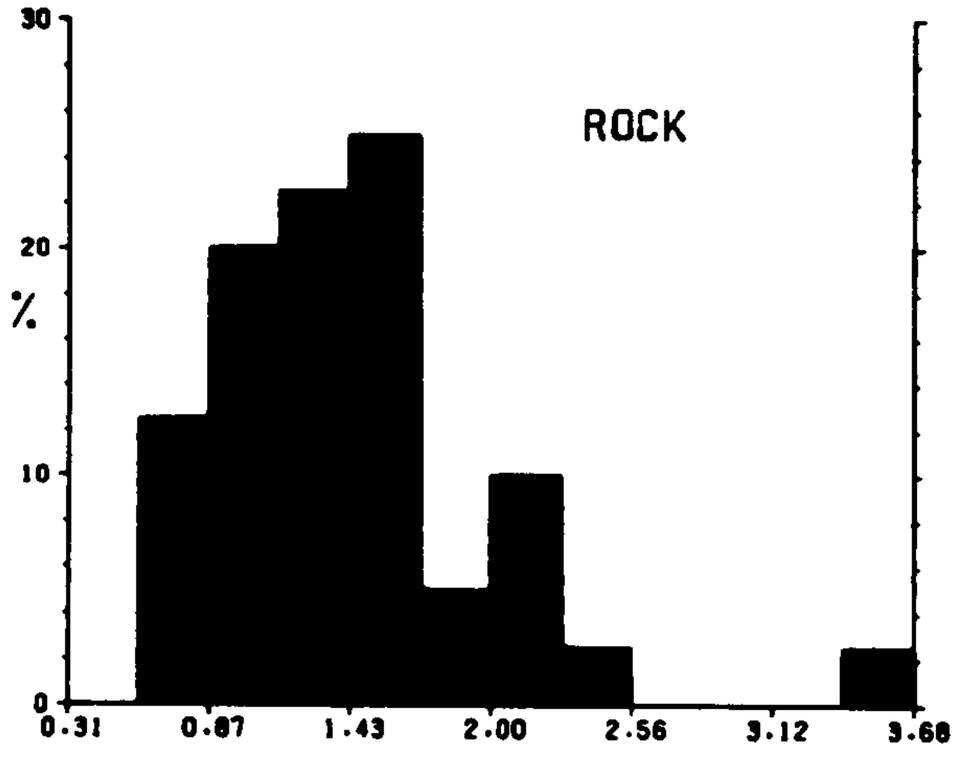
( ) = Negative Correlation. ND= Not Determined.

Fig. 11-6









Histograms of the distribution of .Fe in the rocks, soils and stream sediments derived from the Old Red Sandstones in the Herefordshire study area.

Inter-element correlations.

In all the media, Al was significantly correlated with Fe and Mg (Table 11-3b). The correlations with Zn were also significant in the rocks and stream sediments. The strong correlation with Fe and Mg indicated an association with the clay mineral group of elements while the correlation with Zn in the rocks and sediments, and with Ni in the soils may represent the adsorption of these cations by the clay minerals.

(d) Iron.

The mean concentrations of Fe in the rocks and stream sediments were similar (Table 11-4a). The histograms (Fig. 11-6) showed that concentrations below 2% were common. Top and subsoil mean concentrations were identical, being marginally higher than those in the rocks and stream sediments. The coefficients of variation showed that the increased concentrations of Fe in the soils resulted in decreased variation.

Inter-element correlations.

Iron was significantly correlated with Mg and Al in all the media (Table 11-4b). The correlations with Zn in the rocks and stream sediments were strong while in the top and subsoils the weak correlations probably indicates a weaker association with Zn. Weak correlations were recorded between Fe and Ni in the soils.

Iron may be associated with either the clay minerals or the hydrous oxide phase in the soils and stream sediments. The persistent correlation with Mg and Al suggested that Fe may be more related to

Table 11-5a Zinc Concentrations In The Rock Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	40	32.6	6.9	21.2	19.0	45.0
T/Soil	49	59.2	14.9	25.2	36.0	98.0
S/Soil	45	51.8	9.6	18.5	37.0	79.0
S/Sedt	40	42.6	13.6	31.9	19.0	75.0

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 11-5b Significance of the Correlation Coefficients Between Zn And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	**	***	***		-	-	-	-	-	ND	ND
T/Soil	-	-	-	*		-	-	**	-	*	**	-
S/Soil	-	-	-	*		-	-	*	*	**	*	-
S/Sedt	*	***	***	***		**	-	-	-	*	**	-

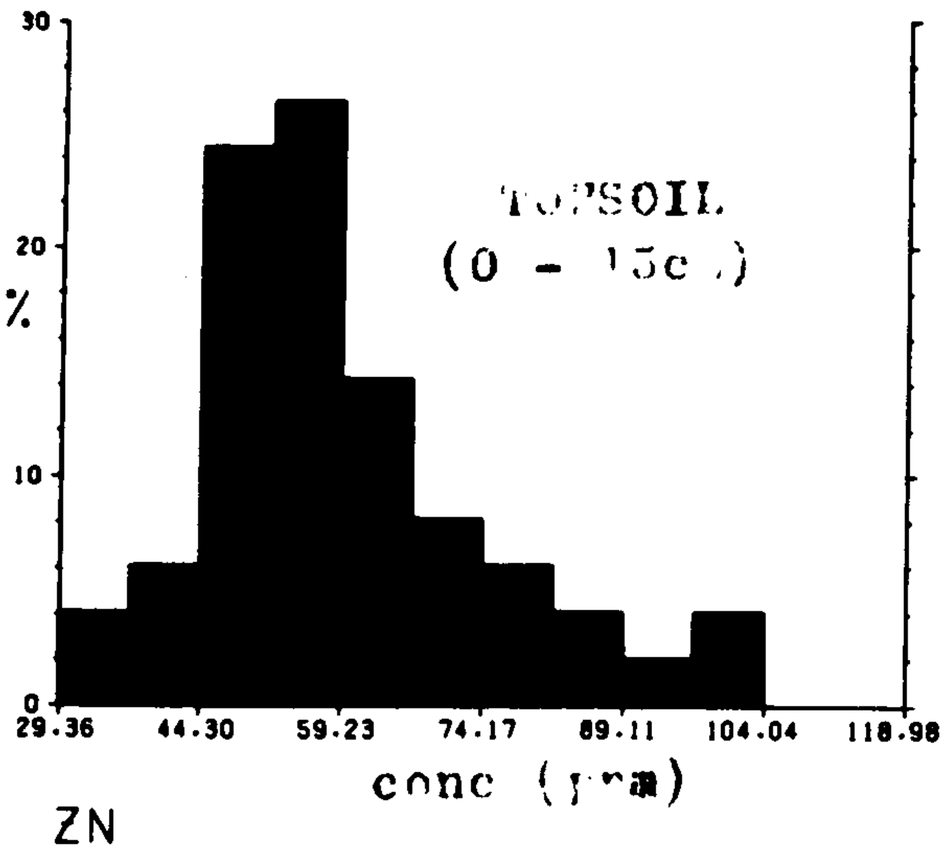
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

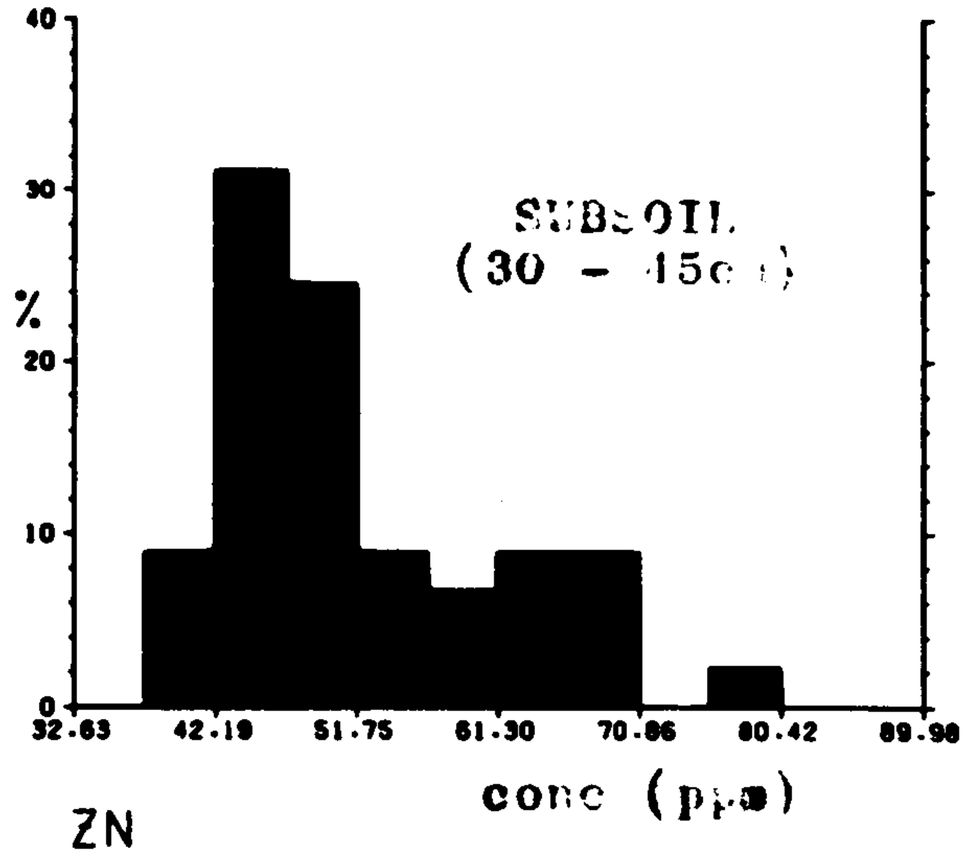
*** = Significant at .01 level

( ) = Negative Correlation. ND= Not Determined.

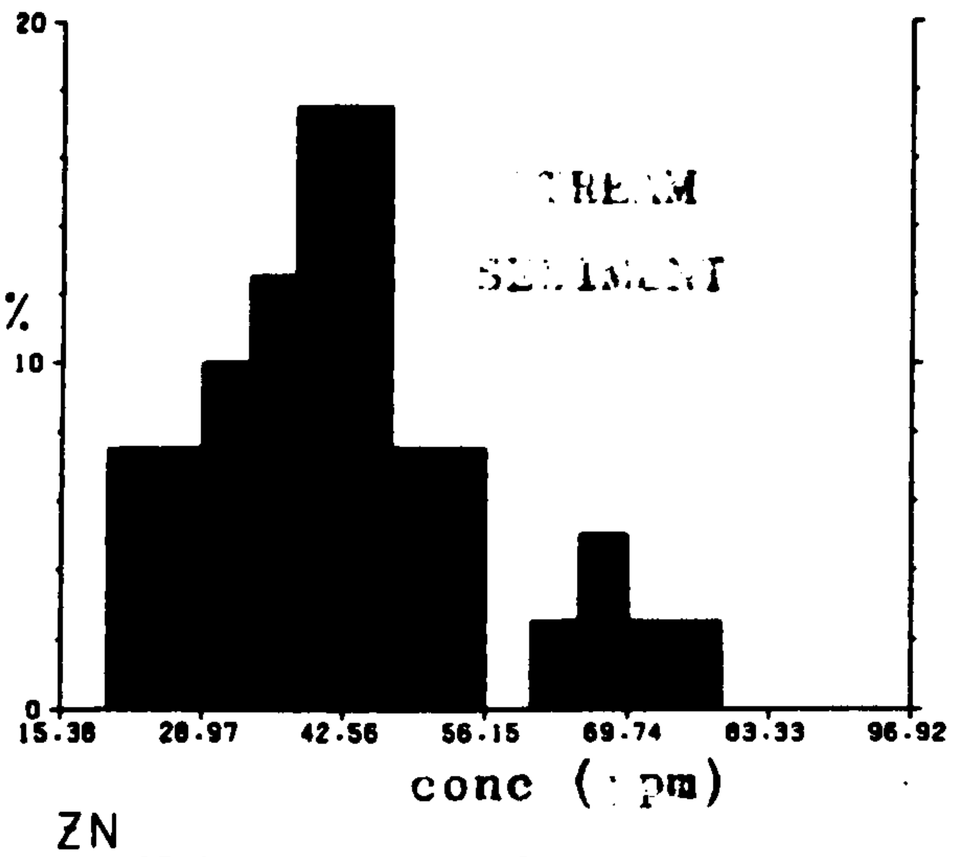
Fig. 11-7



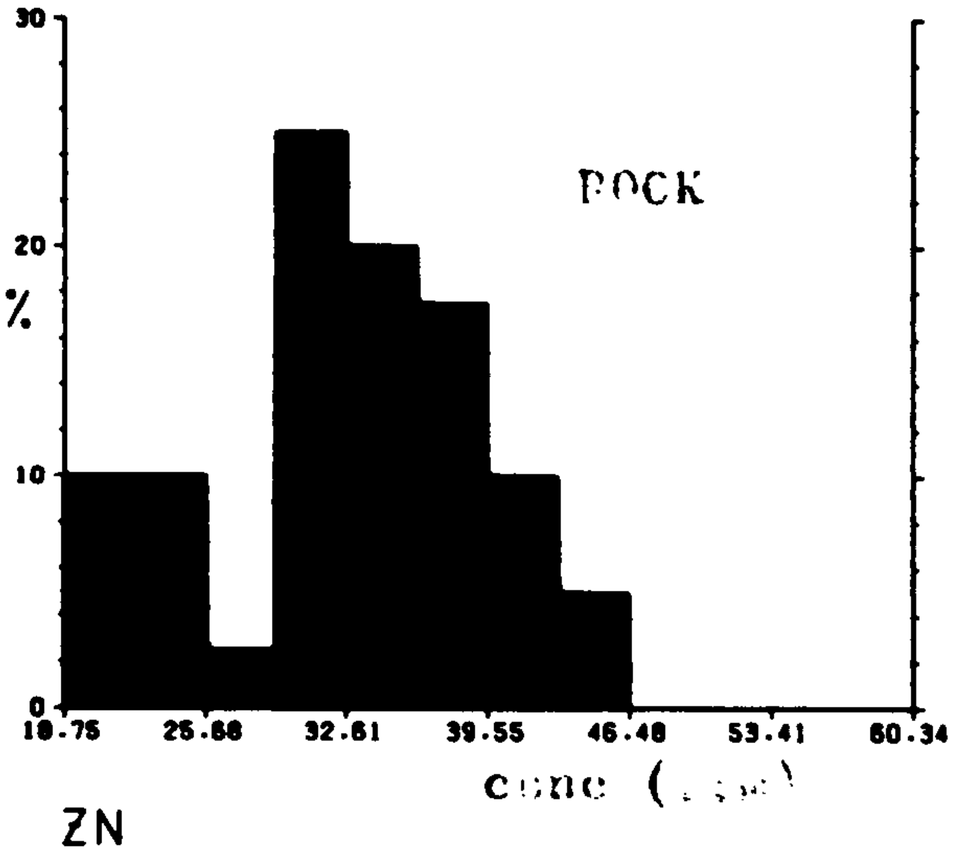
ZN
NO. OF OBSERVATIONS = 49
MEAN = 59.23 STD DEV = 14.937



ZN
NO. OF OBSERVATIONS = 45
MEAN = 51.75 STD DEV = 9.558



ZN
NO. OF OBSERVATIONS = 40
MEAN = 42.56 STD DEV = 13.591



ZN
NO. OF OBSERVATIONS = 40
MEAN = 32.61 STD DEV = 6.931

Histograms of the distribution of Zn in the rocks, soils and stream sediments derived from the Old Red Sandstones in the Herefordshire study area.

the clay minerals although the correlations with Mn in the stream sediments and rocks indicated that association with the oxide fraction was also important.

(e) Zinc.

Zinc concentrations were higher in the soils than in the rocks and stream sediments (Table 11-5a). The highest concentrations were recorded in the topsoils (greater than 90ppm) while maximum concentration in the rocks was below 50ppm. Stream sediment concentrations were also higher than those in the rocks and the coefficients of variation showed that maximum variation occurred in the sediments. The histograms (Fig. 11-7) showed that concentrations above 57ppm in the stream sediments formed a discontinuous distribution. It is likely that more than one process may control the distribution of Zn in the sediments.

Inter-element correlations.

In the rocks and stream sediments Zn was significantly correlated to Mg, Al and Fe (Table 11-5b). The correlations with Pb and organic matter(LOI) in the topsoils were positive and significant. This indicated that Zn was associated with the organic matter(LOI) in the topsoil. The correlation with the clay related elements in the rocks and stream sediments suggested an association with the clay minerals.

In the stream sediments the correlations with Mn and organic matter(LOI) indicated that the oxide fraction and organic matter(LOI) may also influence the distribution of Zn in the sediments.

Table 11-6a Manganese Concentrations In The Rock Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	40	801.9	216.2	27.2	450.0	1400.0
T/Soil	49	696.0	235.0	26.1	225.0	1150.0
S/Soil	45	755.9	173.1	22.9	400.0	1000.0
S/Sedt	40	555.9	236.1	42.5	200.0	1000.0

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 11-6b Significance of the Correlation Coefficients Between Mn And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	-	(**)	**	-		***	-	-	-	ND	ND
T/Soil	-	-	***	-	-		-	-	-	-	-	-
S/Soil	*	*	-	-	-		-	-	-	-	-	-
S/Sedt	*	-	-	**	**		**	-	-	-	**	-

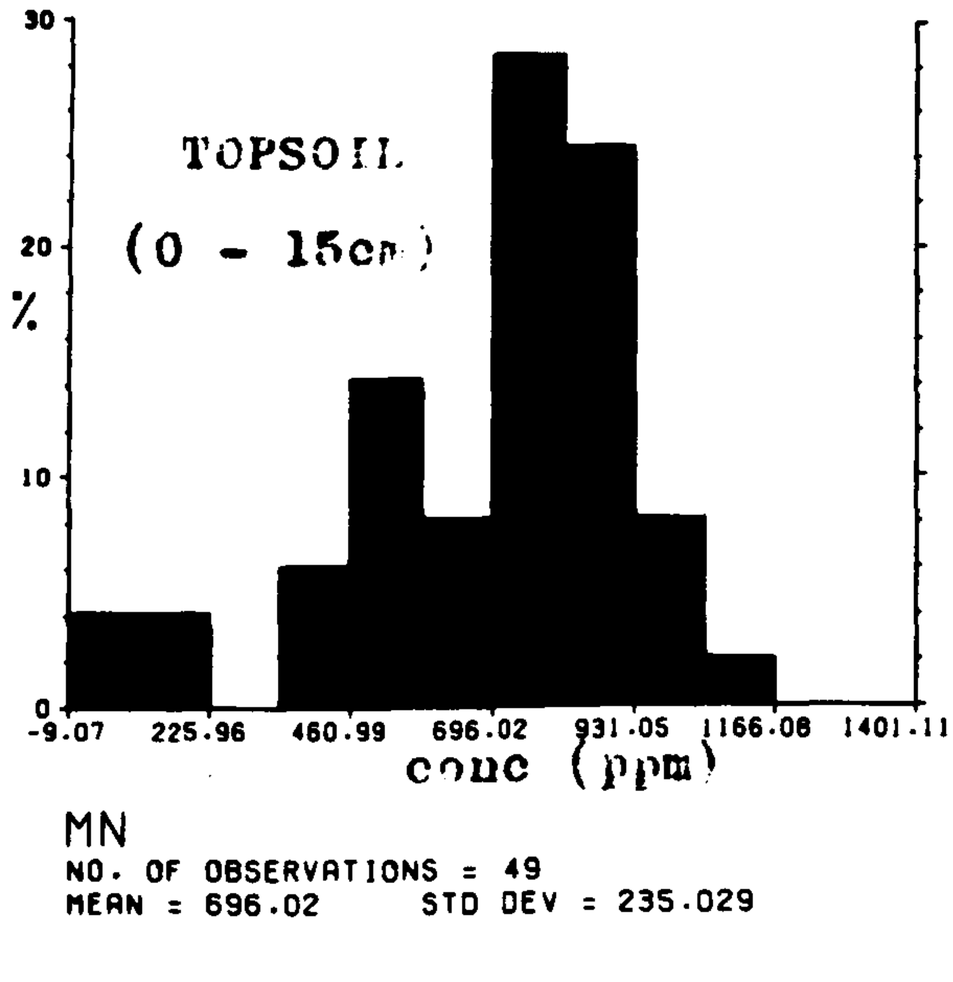
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

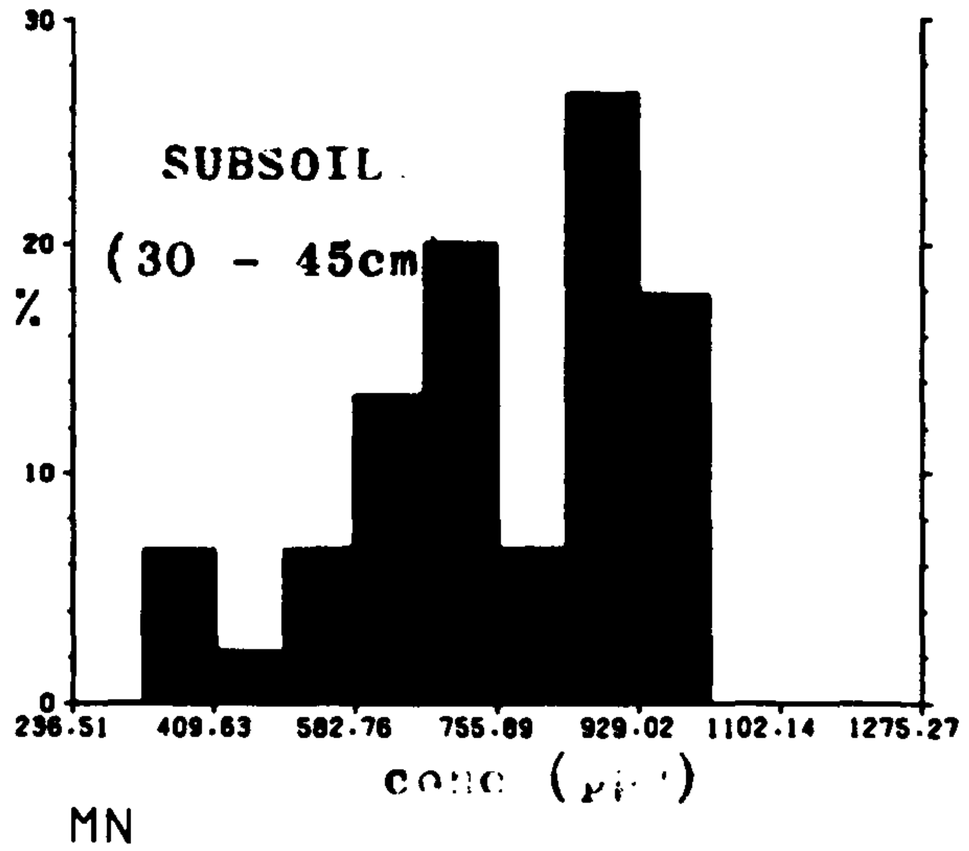
*** = Significant at .01 level

( ) = Negative Correlation. ND= Not Determined.

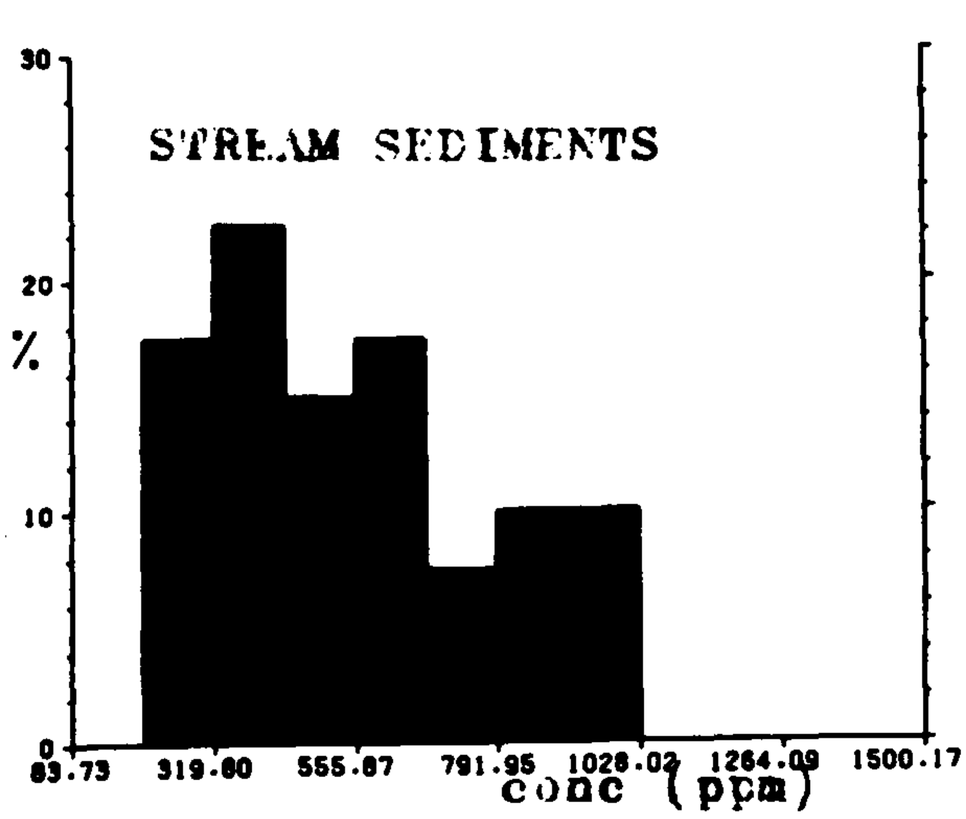
Fig. 11-8



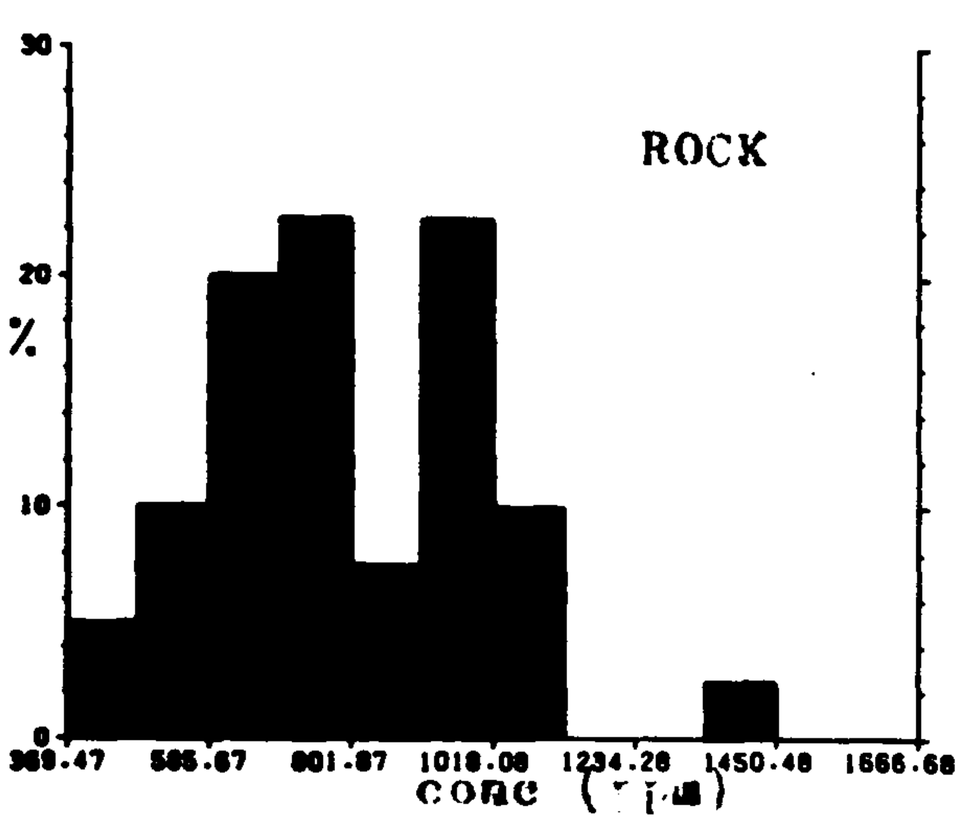
MN
NO. OF OBSERVATIONS = 49
MEAN = 696.02 STD DEV = 235.029



MN
NO. OF OBSERVATIONS = 45
MEAN = 755.89 STD DEV = 173.127



MN
NO. OF OBSERVATIONS = 40
MEAN = 555.87 STD DEV = 236.073



MN
NO. OF OBSERVATIONS = 40
MEAN = 801.87 STD DEV = 216.202

Histograms of the distribution of Mn in the rocks, soils and stream sediments derived from the Old Red Sandstones in the Herefordshire study area.

(f) Manganese:

Moderate concentrations were recorded in the rocks(Table 11-6a). In general, concentrations in excess of 1000ppm were common in both the sandstone and the marl facies. The lower levels (below 600ppm) tended to occur more frequently in the sandstone facies, particularly in the coarse sandy facies. The histograms (Fig. 11-8) showed a reduced frequency of occurrence of the higher and lower concentrations of the range in the rocks. The mean concentrations and the coefficients of variation showed that there was very little difference between the soils and rocks. In the soils concentrations above 600ppm were common. Lower concentrations were recorded in the stream sediments (below 250ppm). The histograms showed that over 40% of the stream sediment samples had Mn concentrations below 500ppm and this resulted in increased variation.

Inter-element correlations.

In the rocks and stream sediments Mn was significantly correlated with Fe and Co (Table 11-6b). Negative correlations occurred with Al in the rocks where the correlations with other elements were insignificant. In the topsoils only the correlations with Al was significant, while in the subsoil, apart from the weak correlation with Ca and Mg there were no significant correlations with other elements. In the stream sediments significant correlations were found with Ca, Fe, Zn, Co and the loss on ignition.

The significant correlations with Fe and Co suggested the formation of mixed oxides (Chao annd Sanzolone, 1973 ; Ponnamperuma

Table 11-7a Cobalt Concentrations In The Rock Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	49	22.9	7.8	32.9	10.0	40.0
T/Soil	45	11.7	3.6	30.6	<5.0	20.0
S/Soil	45	13.0	3.5	26.9	7.00	19.0
S/Sedt	40	9.0	3.1	34.1	<5.0	18.0

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 11-7b Significance of the Correlation Coefficients Between Co And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	-	-	-	-	**		-	-	-	ND	ND
T/Soil	-	-	-	-	-	-		-	**	-	-	-
S/Soil	-	-	**	-	-	-		-	**	-	-	-
S/Sedt	-	-	-	-	-	**		-	-	**	**	-

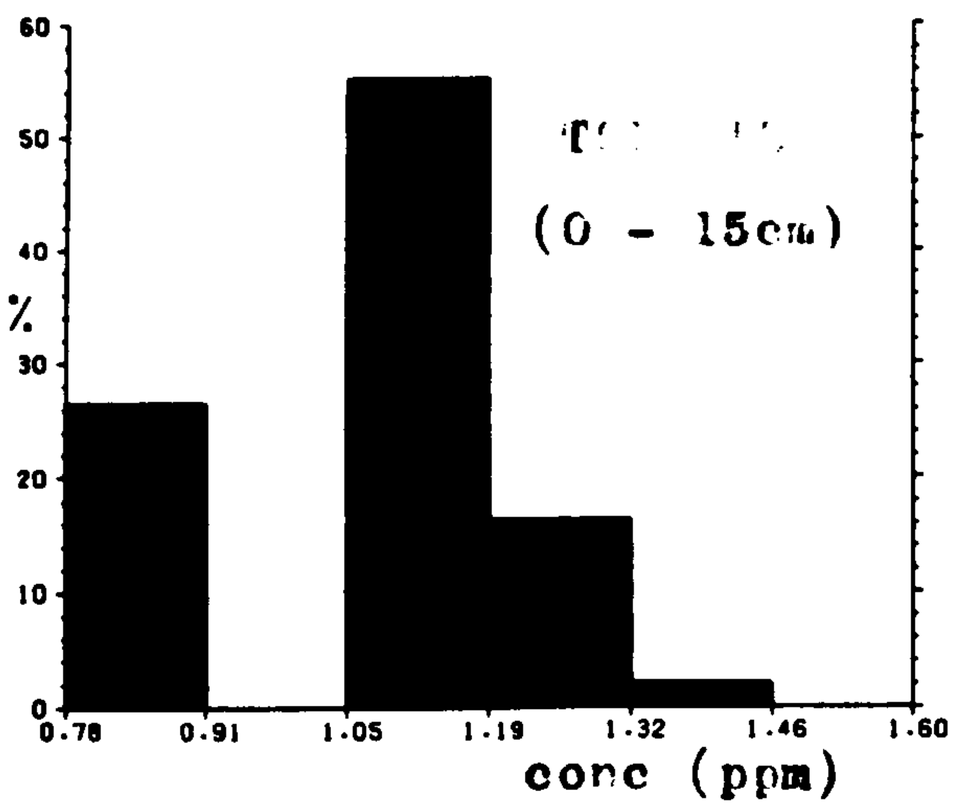
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

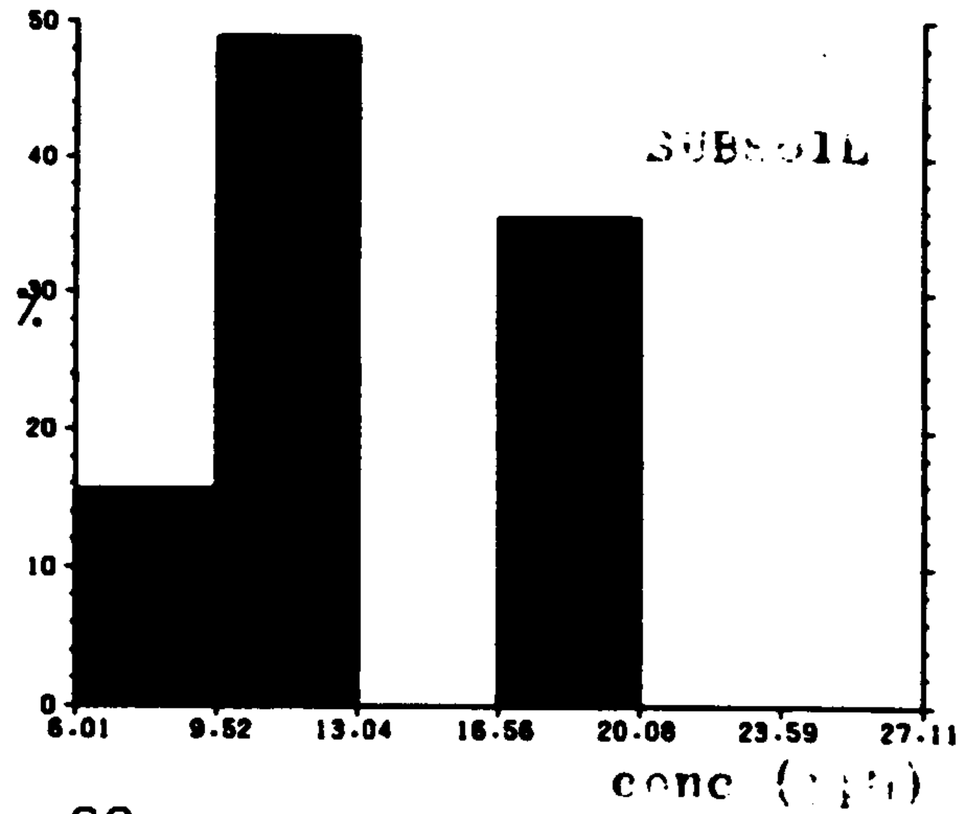
*** = Significant at .01 level

( ) = Negative Correlation. ND= Not Determined.

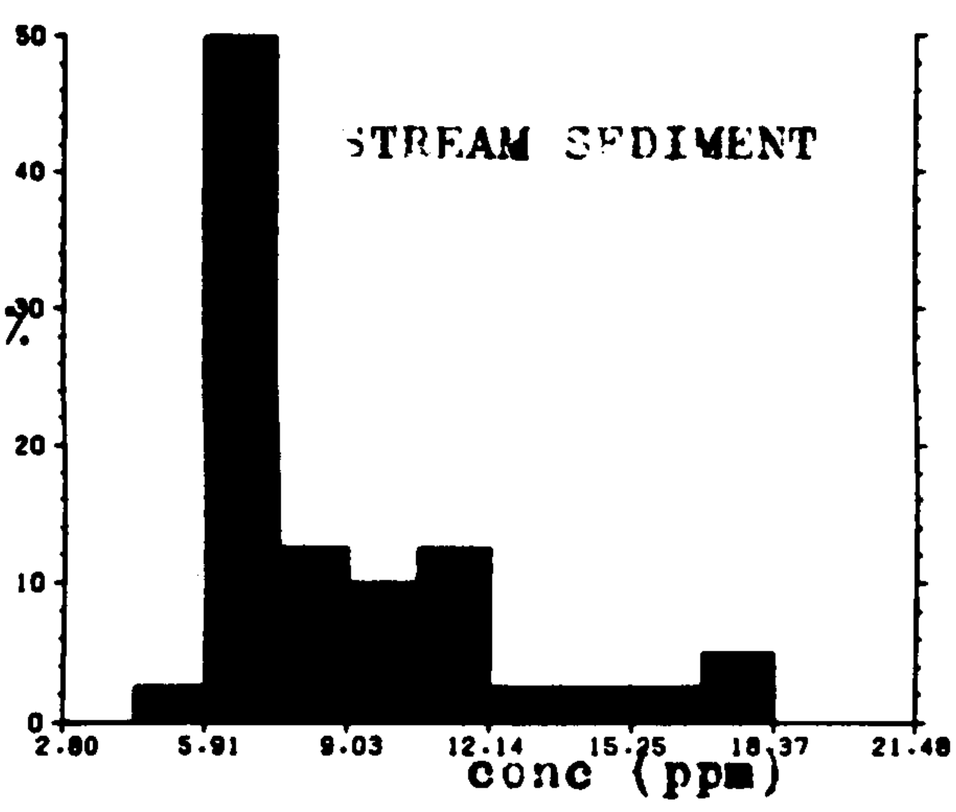
Fig. 11-9



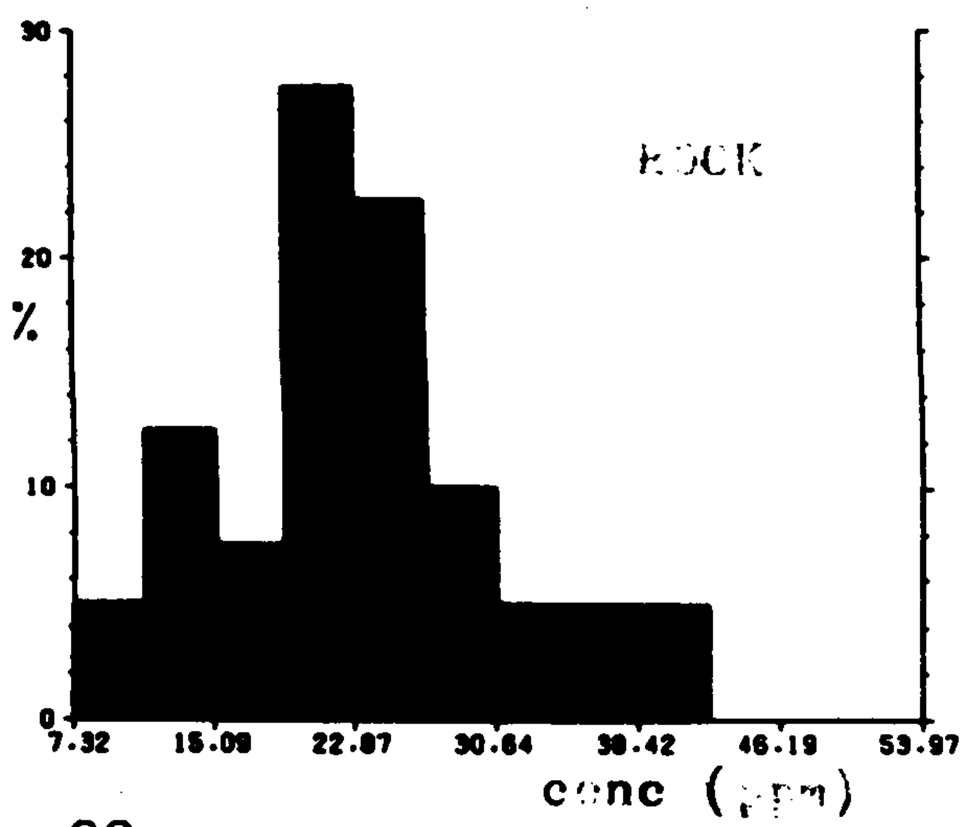
CO
NO. OF OBSERVATIONS = 49
MEAN = 1.05 STD DEV = 0.137
NO. OF LOG10 TRANSFORMS = 1



CO
NO. OF OBSERVATIONS = 45
MEAN = 13.04 STD DEV = 3.517



CO
NO. OF OBSERVATIONS = 40
MEAN = 9.03 STD DEV = 3.113



CO
NO. OF OBSERVATIONS = 40
MEAN = 22.87 STD DEV = 7.775

Histograms of the distribution of Co in the rocks, soils and stream sediments derived from the Old Red Sandstones in the Herefordshire study area.

et. al., 1969). Manganese in the divalent state can replace Ca in carbonates due to the similarity in their ionic radii and valency (Rankama and Sahama, 1950). The correlation with Ca and Mg in the subsoil suggested an association with the carbonates. In general it can be inferred that the activity of the hydrous oxides in adsorbing divalent cations in the soils were not as important as in the streams.

(g) Cobalt.

The pattern displayed by Co in the rocks tended to be similar to that of Mn (Table 11-7a). Thus samples high in Mn had correspondingly high concentrations of Co. For instance, the maximum concentration of Co in the rocks (40ppm) was recorded in the same sample that displayed maximum concentration of Mn (1400ppm). The mean concentration in the rocks was twice as high as that in the topsoil. Cobalt concentrations in the top and subsoils were similar. This was reflected by the similarities in their ranges and coefficients of variation. Stream sediment concentrations of Co were also low with the mean concentration being marginally lower than those in the soils.

It can be inferred from these results that mobilisation of Co from the soils to the stream sediments was not a common feature in the distribution of Co. In general, there was a trend towards a decrease of Co in the soils and stream sediments.

Inter-Element Correlations.

In the top and sub soils Co was significantly correlated to Ni (Table 11-7b). The geochemistry of Co is in many respects similar to that of Ni (Rankama and Sahama, 1950). The simiilarity of their ionic radii and valency means that they can easily replace each other in the geochemical environment. The results so far indicate that Ni

Table 11-8a Lead Concentrations In The Rock Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	40	16.9	7.5	44.8	5.0	36.0
T/Soil	49	28.7	13.3	46.2	15.0	80.0
S/Soil	45	26.2	10.0	38.0	11.0	65.0
S/Sedt	45	24.5	5.0	20.4	18.0	82.0

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 11-8b Significance of the Correlation Coefficients Between Pb And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	***	-	*	-	-	-	-		*	-	ND	ND
T/Soil	-	-	-	-	**	-	-		**	***	***	-
S/Soil	-	-	-	*	*	-	-		**	-	-	-
S/Sedt	**	-	-	-	-	-	-		-	-	*	-

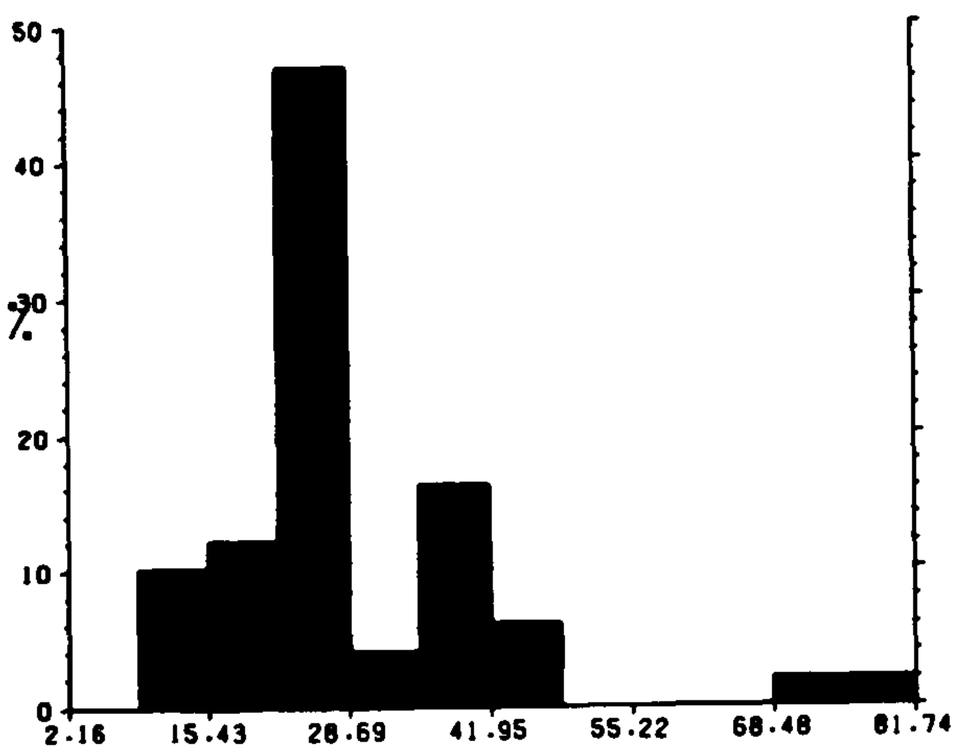
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

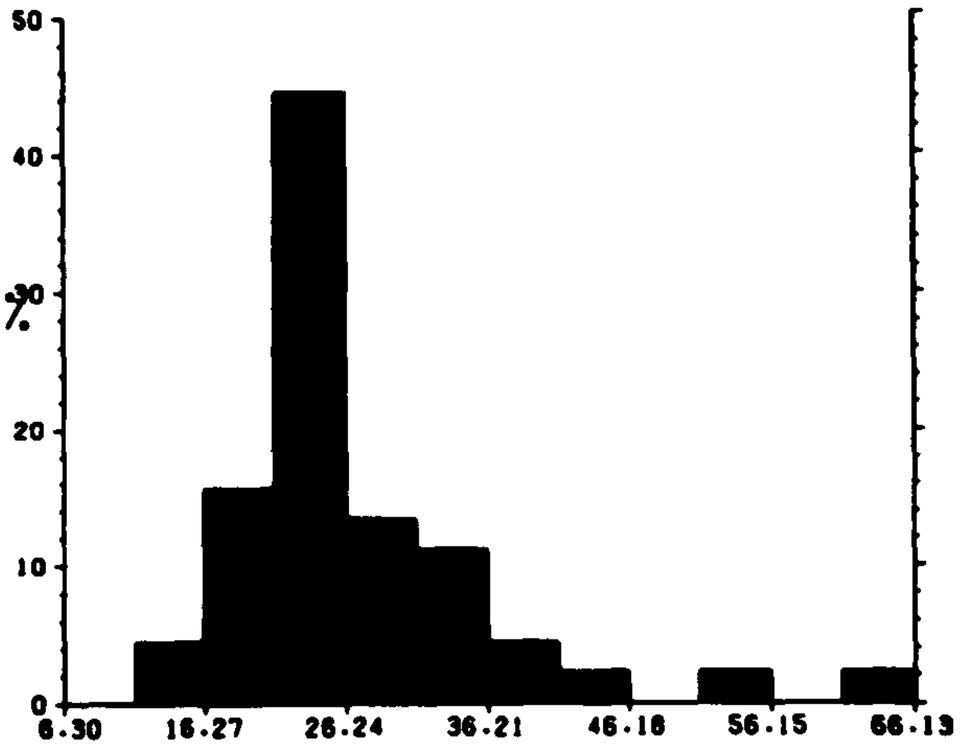
*** = Significant at .01 level

( ) = Negative Correlation. ND= Not Determined

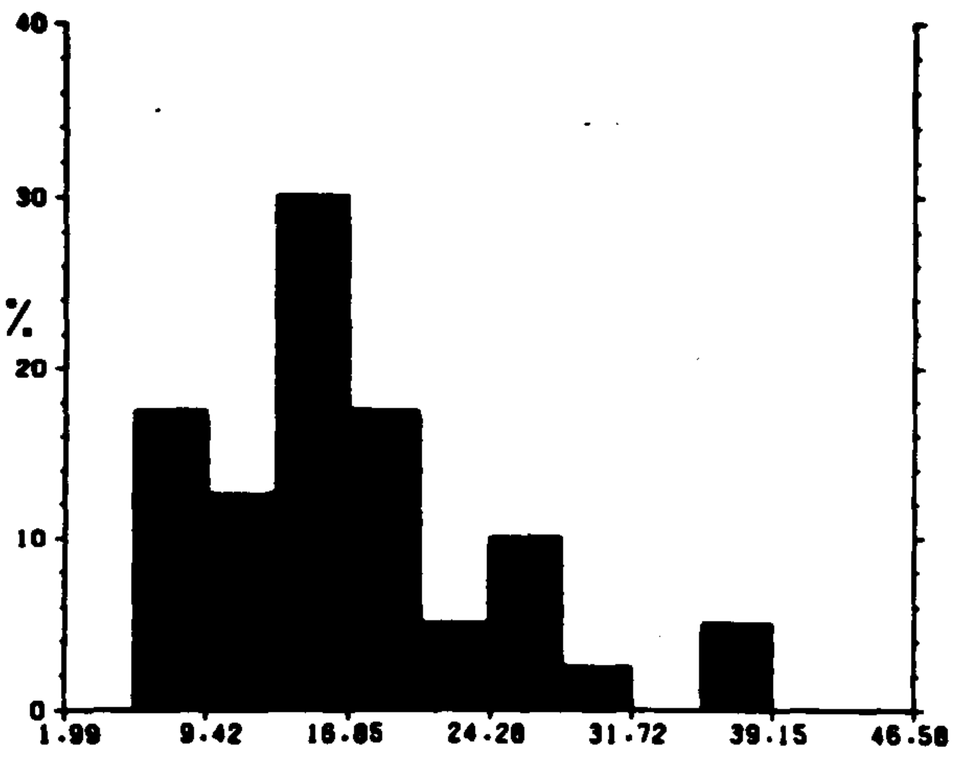
Fig. 11-10



PB
NO. OF OBSERVATIONS = 49
MEAN = 28.69 STD DEV = 13.263



PB
NO. OF OBSERVATIONS = 45
MEAN = 26.24 STD DEV = 9.972



PB
NO. OF OBSERVATIONS = 40
MEAN = 16.85 STD DEV = 7.432

Histograms of the distribution of Pb in the rocks and soils derived from the Old Red Sandstones in the Herefordshire study area.

may be related to the clay minerals in the soils. It seemed that part of the Ni associated with the clay minerals in the soils may be replaced by Co. This view was further supported by the weak correlations with Al in the subsoil. In the rocks and stream sediments Co was weakly correlated to Mn . There was a further correlation with Cu and the organic matter(LOI) in the stream sediments. Such an association may represent the "scavenging" activity of the Mn oxide fraction in the rocks and stream sediments.

(h) Lead.

Lead concentrations in the rocks were low (Table 11-8a). The marl samples had Pb concentrations marginally higher than the sandstone samples. The histograms (Fig. 11-10) showed that over 40% of the rock samples had Pb concentrations below 16ppm. The mean concentrations in the topsoil and subsoil were higher than in the rock. The results did not suggest an unusual concentration of Pb in the topsoil. Stream sediment mean concentration was similar to that of the soils although the coefficients of variation was lower than in the soils.

Inter-element correlation.

High positive correlations occurred between Pb and Ca in the rocks (Table 11-8b). Weaker correlations were found between Pb with Al and Ni. In the topsoil Pb was significantly correlated to Zn, Ni, Cu and the organic matter(LOI). subsoil. In the stream sediments the correlation with Ca was Vinogradov (1959) observed an association between the organic matter in the topsoil and Pb. Swaine and Mitchell (1960) also observed a strong association between Pb and organic matter in the soils. The strong correlation with organic matter(LOI)

Table 11-9a Nickel Concentrations In The Rock Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	40	21.1	5.9	24.9	9.9	37.0
T/Soil	49	27.7	6.9	24.9	14.0	50.0
S/Soil	45	27.1	6.1	22.6	16.0	43.0
S/Sedt	40	23.6	3.5	14.9	13.0	33.0

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 11-9b Significance Of The Correlation Coefficients Between Ni And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	**	-	-	-	-	-	*	*		-	ND	ND
T/Soil	-	***	***	**	-	-	-	**		-	-	-
S/Soil	-	***	***	***	*	-	-	**		**	-	-
S/Sedt	**	-	-	-	-	-	*	*		-	**	-

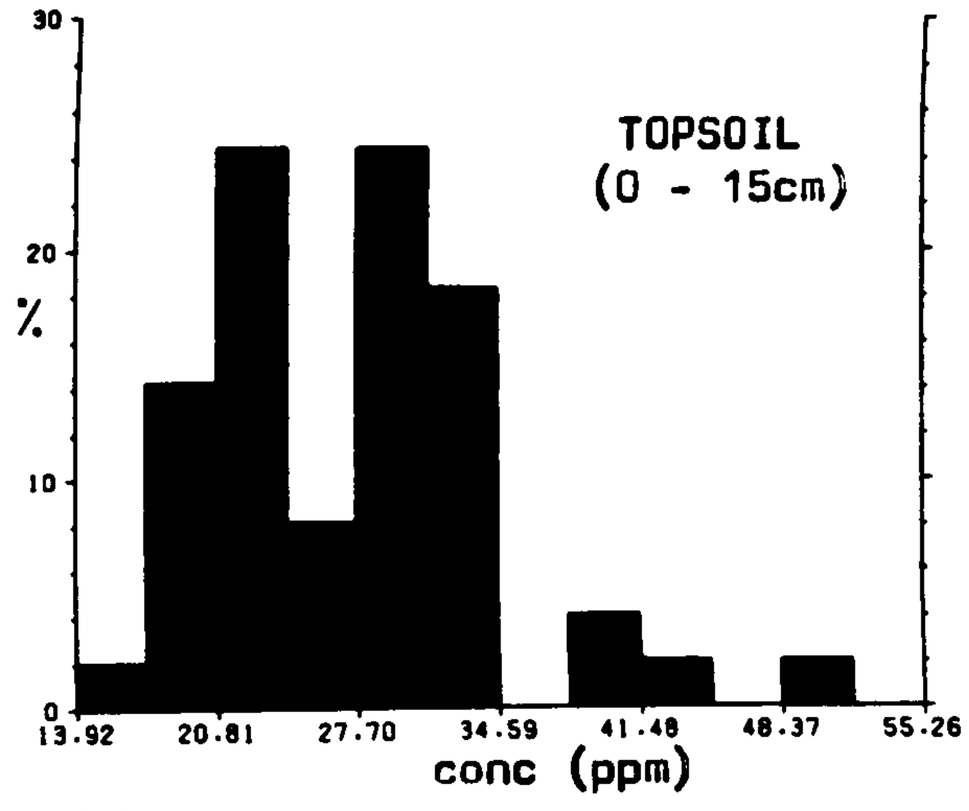
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

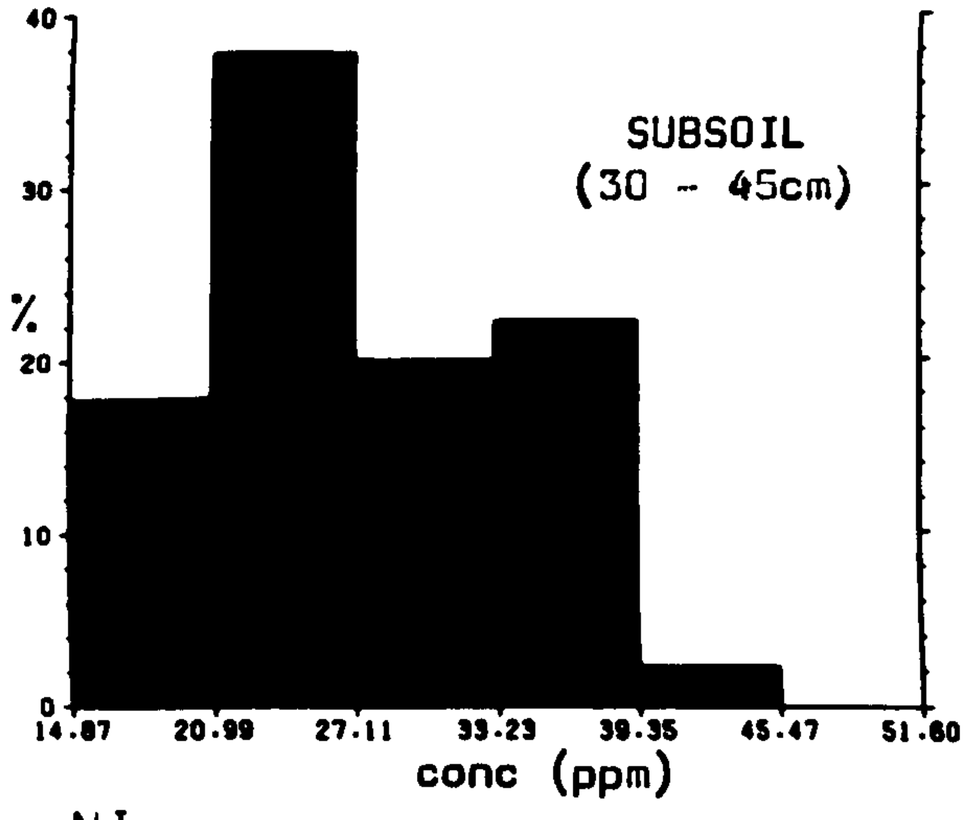
*** = Significant at .01 level

( ) = Negative Correlation. ND= Not Determined.

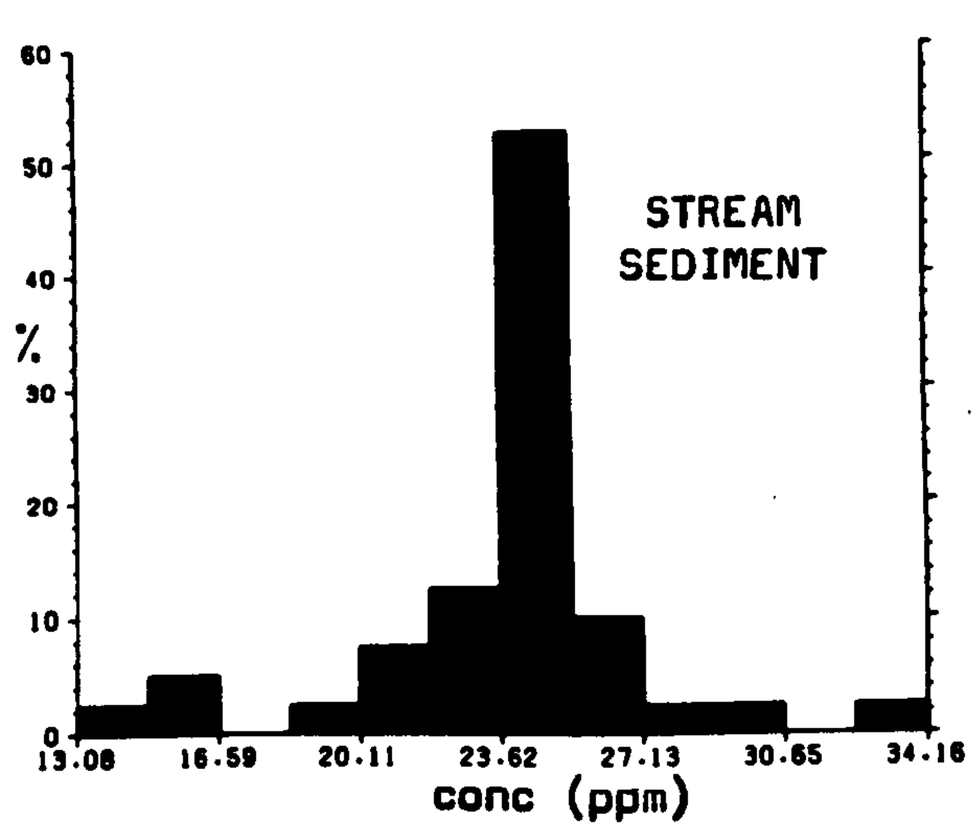
Fig. 11-11



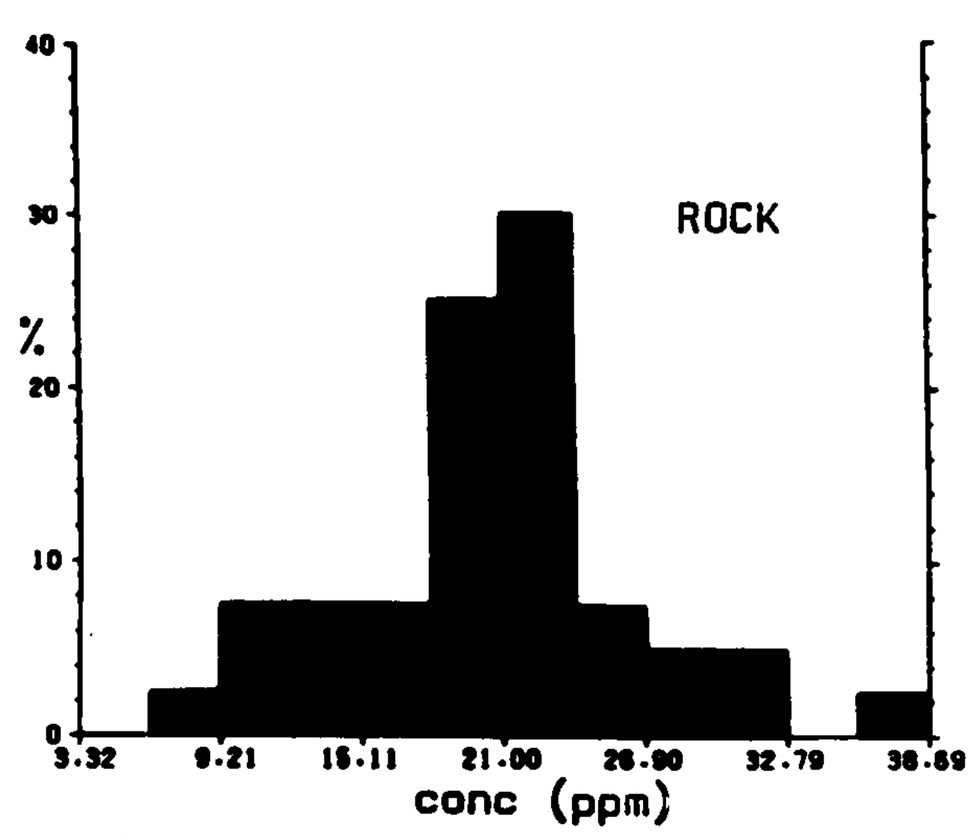
NI
NO. OF OBSERVATIONS = 49
MEAN = 27.70 STD DEV = 6.891



NI
NO. OF OBSERVATIONS = 45
MEAN = 27.11 STD DEV = 6.121



NI
NO. OF OBSERVATIONS = 40
MEAN = 23.62 STD DEV = 3.514



NI
NO. OF OBSERVATIONS = 40
MEAN = 21.00 STD DEV = 5.895

Histograms of the distribution of Ni in the rocks, soils and stream sediments derived from the Old Red Sandstones in the Herefordshire study area.

in the soils support these findings. The correlation with Ca in the rocks and stream sediments indicated that Pb was present in association with the carbonate phase.

(i) Nickel

The mean concentrations of Ni in all the media examined were similar (Table 11-9a). In general, the higher concentrations (greater than 50ppm) tended to occur in the soils while the lower concentrations occurred in the rocks. The coefficients of variation showed that the variation of Ni in the stream sediments was lower than in the rocks and soils . The histograms (Fig. 11-11) showed that in all the media there was a reduced frequency of occurrence of the higher and lower concentrations of the range. The results suggested that Ni was associated with a stable component of all the media.

Inter-element correlations.

Nickel was significantly correlated with Mg, Al and Fe in the soils (Table 11-9b). The correlation with Zn, Pb and Cu in the subsoil were weak. In the rocks and stream sediments Ni was correlated with Ca, Co and Pb. There was a further correlation with organic matter(LOI) in the stream sediments.

It can be inferred that Ni in the soils may be associated with the clay mineral group of elements while in the rocks and stream sediments the association with the carbonate fraction may be important.

Table 11-10a Copper Concentrations In The Rock Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	40	5.2	1.9	39.9	<5.0	9.9
T/Soil	49	12.1	3.8	31.3	<5.0	26.0
S/Soil	45	11.3	3.0	26.5	<5.0	17.0
S/Sedt	40	6.8	2.9	42.3	<5.0	15.0

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.)

Table 11-10b Significance Of The Correlation Coefficients Between Cu And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	-	-	-	-		-	-	-		ND	ND
T/Soil	-	-	-	**	*	-	-	***	-		*	-
S/Soil	-	-	-	*	**	-	-	-	**		-	-
S/Sedt	-	-	**	-	*	-	**	-	-		**	-

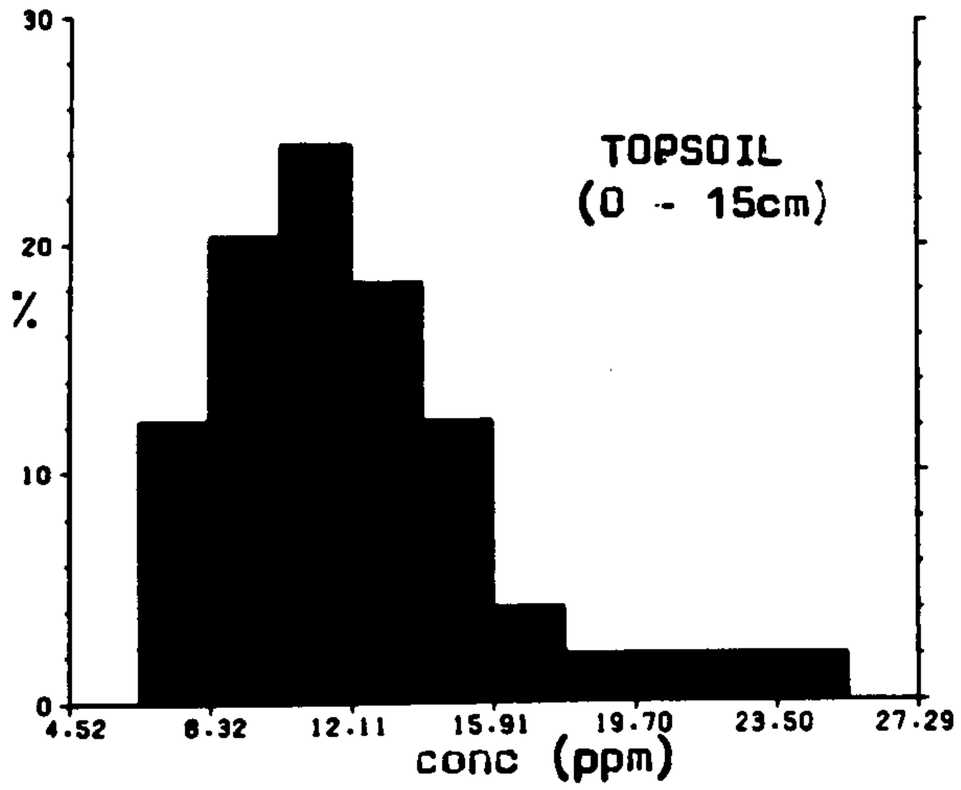
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

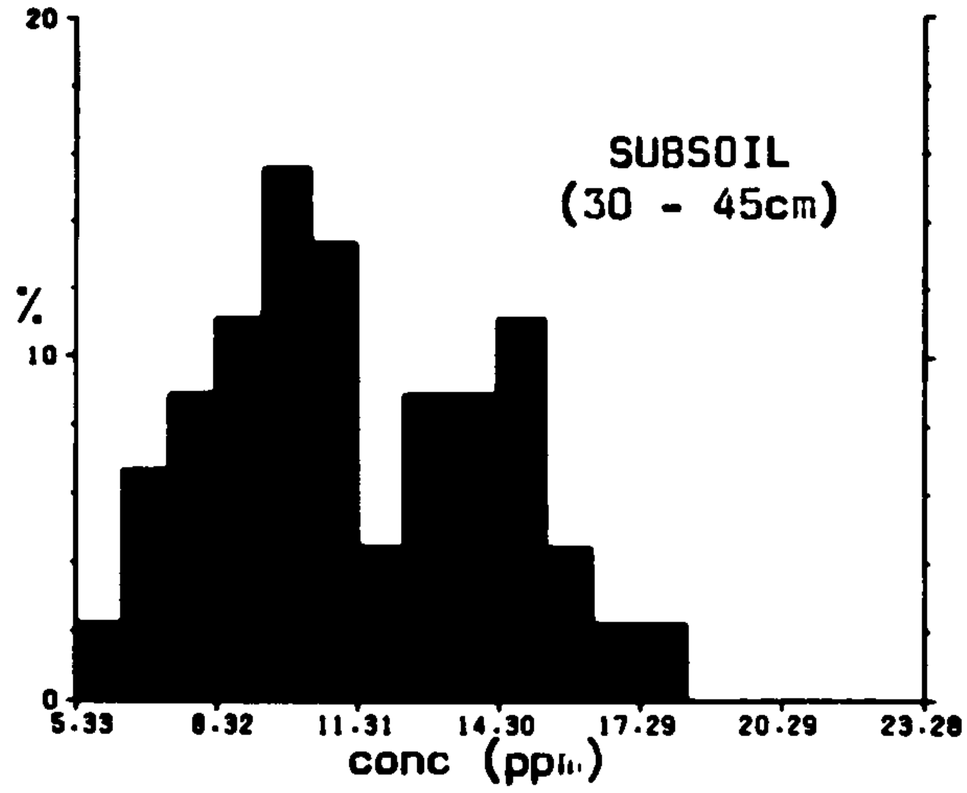
*** = Significant at .01 level

( ) = Negative Correlation. ND= Not Determined.

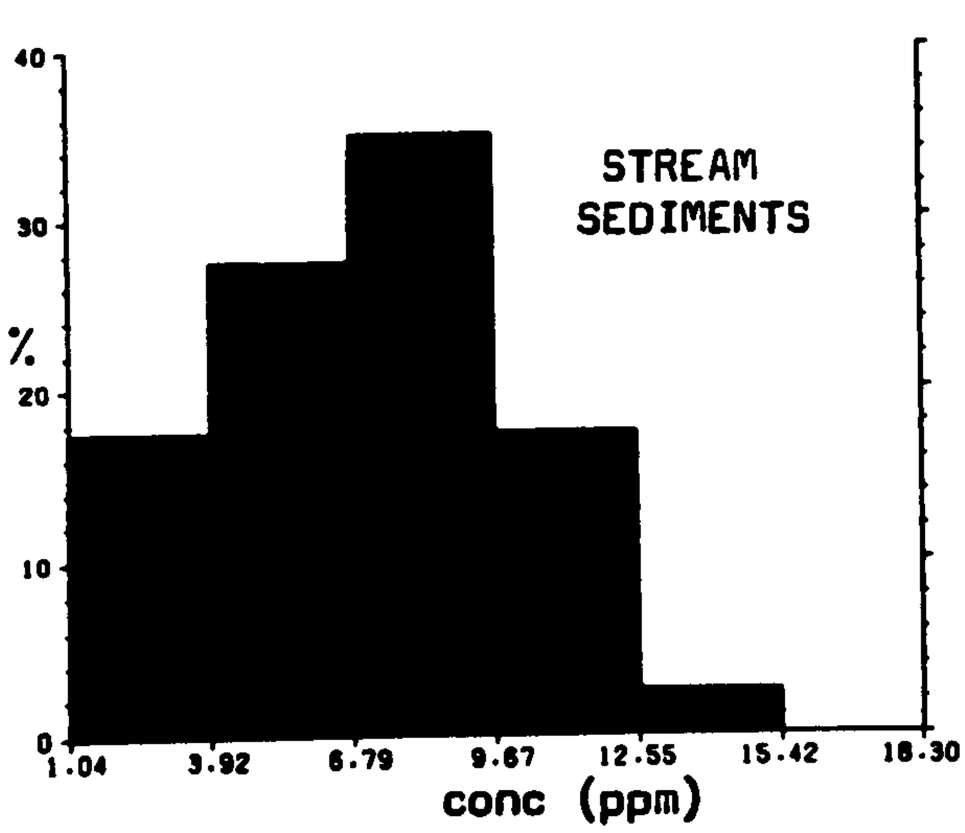
Fig. 11-12



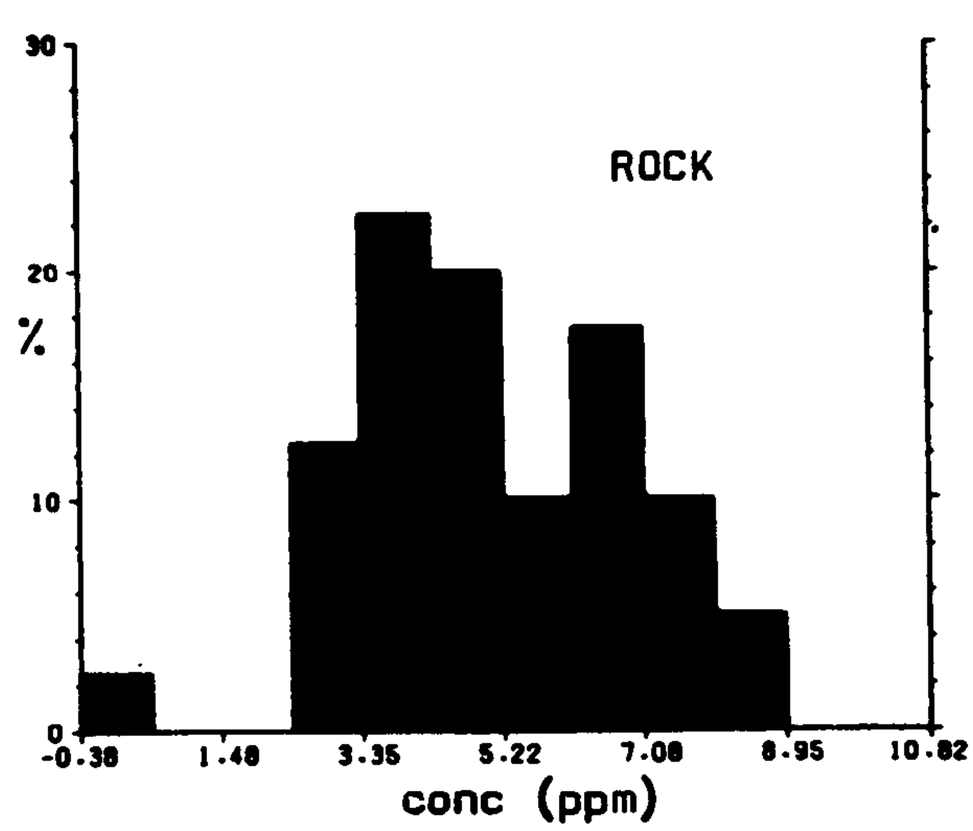
CU
NO. OF OBSERVATIONS = 49
MEAN = 12.11 STD DEV = 3.795



CU
NO. OF OBSERVATIONS = 45
MEAN = 11.31 STD DEV = 2.992



CU
NO. OF OBSERVATIONS = 40
MEAN = 6.79 STD DEV = 2.876



CU
NO. OF OBSERVATIONS = 40
MEAN = 5.22 STD DEV = 1.866

Histograms of the distribution of Cu in the rocks, soils and stream sediments derived from the Old Red Sandstones in the Herefordshire study area.

(j) Copper.

Concentrations of Cu in the rocks, soils and stream sediments were strikingly low (Table 11-10a). The histograms (Fig. 11-12) showed that concentrations below 15ppm were common in all the media. In general samples with high concentrations of Zn and Pb had relatively high concentration of Cu. It seemed likely that the distribution of Cu in the different media is controlled by the inherently low concentrations in the parent material.

Inter-element correlation.

In the rocks Cu was weakly correlated with Mn (Table 11-10b). Copper was significantly correlated with Al, Zn, Co, and organic matter(LOI) in the stream sediments. In the soils the correlations with Fe, Zn, Pb and organic matter(LOI) were significant in both the top and subsoils.

Copper in the soils have been shown to be associated with the organic matter phase (Fried and Broeshart, 1967), and the hydrous oxides of Mn and Fe (McKenzie, 1971). The results suggested that organically bound Cu was an important feature of the distribution of Cu in the soils and stream sediments, while in the rocks a weak association with the hydrous oxide may exist.

(k) Loss on ignition.

The loss on ignition values were higher in the topsoils than the subsoil and stream sediments (Table 11-11a). Thus the mean value was three times higher in the topsoil than the stream sediments. In general the coefficient of variation values were high with the maximum

Table 11-11a Percent Organic Matter In The Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium		Mean (%)	S.D.	C.V.	Range Min (%)	Max (%)
T/Soil	49	6.7	2.3	34.6	4.5	8.00
S/Soil	45	4.5	1.2	27.7	2.0	6.9
S/Sedt	40	2.0	0.8	39.9	0.5	4.00

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.)

Table 11-11b Significance Of The Correlation Coefficients Between Percent Organic Matter And Other Elements Analysed In The Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
T/Soil	-	-	-	-	**	-	-	***	-	*		-
S/Soil	-	-	-	-	**	-	-	***	-	-		-
S/Sedt	-	-	-	-	**	**	**	*	*	**		-

Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

*** = Significant at .01 level

( ) = Negative Correlation.

Table 11-12a pH Levels In The Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

T/Soil	49	5.9	0.6	10.1	5.2	6.5
S/Soil	45	6.1	0.6	10.2	5.3	6.8
S/Sedt	40	7.0	0.3	5.4	6.1	7.3

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.)

Table 11-12b Significance Of The Correlation Coefficients Between pH And Other Elements Analysed In The Soil And Stream Sediments Derived From The Old Red Sandstone In Herefordshire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
T/Soil	**	-	-	-	-	-	-	-	-	-	-	
S/Soil	***	-	-	-	-	-	-	-	-	-	-	
S/Sedt	-	-	**	-	-	-	-	-	-	-	-	

Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

*** = Significant at .01 level

( ) = Negative Correlation.

variation recorded in the stream sediments.

Correlation with elements.

In both the top and subsoils the organic matter(LOI) was significantly correlated with Zn and Pb and to a lesser degree to Cu. This indicated that the distribution of Pb and Zn in the soils were related to the organic matter(LOI). In the stream sediments the organic matter(LOI) was significantly correlated to a wider range of elements. Thus, the correlation with Zn, Co, Pb, Ni and Cu were all significant. It is probable that Mn oxides are deposited on organic fragments in the stream sediment; alternatively, these elements may be organically bound in the stream sediments.

(1) pH

pH was determined on oven dried samples by the method described in Chapter 3 on the soils and stream sediment samples (Table 11-12a). The pH values in the soils and stream sediments were basically similar. In both media pH values ranged from being slightly acidic to neutral. In the stream sediments more values were within the alkaline end of the range.

Correlations with other elements:

The pH of the medium is a very important factor controlling some of the major processes in the weathering, pedogenic and stream environments. In the top and subsoils pH was correlated to Ca (Table

11-12b). This may reflect a direct relationship between the carbonates and the acidity of the soils. In general, the correlations with most elements in the soils and stream sediments were not significant.

(m) Summary.

The high calcium concentrations found in the rocks suggested that Ca was present in the intergranular cement, possibly as calcium carbonate. The strong correlations between Ca, Pb and Zn were thought to reflect an association with the carbonates. Organic matter(LOI) was also found to be associated with Zn, Pb and Cu particularly in the soils. The elements Al, Mg, Fe and Ni showed very little differences in their concentrations in the rocks, soils and stream sediments. Furthermore, strong correlations were found between these elements in all the media studied. This was interpreted as an association with the clay minerals. Zinc was correlated with Mg, Al and Fe in the rocks and stream sediments. It is probable that Zn is adsorbed on exchange sites in the clay minerals present in these media.

The hydrous oxide phase was thought to be important in the distribution of only Co particularly in the stream sediments. In general, the hydrous oxides constituted a stable component of the rocks, soils and stream sediments. In the stream sediments where Mn concentrations were lower than those in soils and rocks this was thought to be due to the dilution of the sediments by colluvial material rather than calcium carbonates since the concentrations of calcium did not increase in the streams.

11-5 Multi-element associations:

Multi-element associations were investigated by factor analysis (Chapter 3). The results are presented as rotated factor loadings classified on the basis of the significance shown. The table of significance of the correlation coefficients(Appendix 3) have been used to determine the significance levels. The results from each medium are discussed below.

(a) Rocks:

The three factor model accounted for over 76% of the total variance and was found appropriate to describe the main multi-element associations in the rocks (Table 11-13).

Factor 1 was characterised by high positive loadings on Mg, Al, Fe, and Zn. Contributions from other elements were not significant. Factor 1 accounted for over 29% of total variance. This grouping of elements was interpreted as an association with the clay minerals present. Perrin (1971) has shown that about 90% of the clay minerals present in the Old Red Sandstone in Herefordshire are micaceous. Micaceous clays in the trioctahedral form are known to be associated with a range of cations (Russell, 1973). In the main such clays are potassium magnesium iron silicates and it seemed likely that factor 1 in the rocks may be defining such clay minerals.

Factor 2 associated Ca, Pb and Ni by significant positive loadings . In the sedimentary environment, Ca is commonly associated as a component of the carbonate minerals . In these environments the mobility of elements as Zn, Pb, Ni and Cu may be restricted by the formation of secondary carbonates. This group was interpreted as an

Table 11-13

Significance Of Factor Loadings Of Logarithmically Transformed Rock Data. Matrix Accounts for 76.5% Of Variance Of 40 Rock Samples From The Old Red Sandstone. ! Tables Of Levels Of Significance Of Correlation Coefficient (Appendix 3) Used To Determine Significance Levels Of Factor Loadings.

Metals	Factor		
	1	2	3
Variance (%)	29.5	22.0	25.0
Ca	-	**	-
Mg	***	-	-
Al	***	-	-
Fe	***	-	-
Zn	***	-	-
Mn	-	*	(***)
Co	-	-	(***)
Pb	-	***	-
Ni	-	***	-
Cu	-	-	(***)

- = Not significant
* = significant at 0.10 level
** = Significant at 0.05 Level
*** = Significant at 0.01 level
( ) = Negative Loading.

association with the carbonates in the rocks. The weaker loadings on Mn on this factor suggested that at least part of the Mn present was associated with the carbonates possibly replacing Ca.

The third factor displayed high negative loadings on Mn, Co, and Cu. Manganese oxide due to the negative charges on their surfaces when freshly precipitated are capable of adsorbing metal cations from solutions which may later be incorporated into its structure to form Mn oxide minerals such as birnessite and todorokite (Taylor et al. 1964). The third factor was therefore interpreted as representing an association with the Mn oxide fraction in the rock.

(b) Topsoil

Factor 1 showed high negative loadings on Mg, Al, Fe and Ni (Table 11-14). The highest loadings were on Al, Fe and Mg which are normal components of micaceous clays. This group was fairly similar to the clay mineral group defined in the rock except that Ni replaced Zn possibly at exchange sites on the clay mineral surfaces. Thus where the exchange sites on the clay mineral are relatively few, the introduction of ions whose complexing tendency or sorption potential are greater than those of the ions already present may cause the displacement of the original ions . Zinc, when associated with the clay minerals is more likely to occupy an octahedral position in the clays and it is very likely that Ni replaces Zn at such sites by such a displacement process.

Factor 2 was characterised by high positive loadings on Ca and the pH. Calcium may be present in the soil as either gypsum or more often as calcite. In slightly acidic environments as is the case

Table 11-14

Significance Of Factor Loadings Of Logarithmically Transformed Topsoil Data. Matrix Accounts for 79.0 Of Variance Of 40 Samples Of The Ross Series . ! Tables Of Levels Of Significance Of Correlation Coefficient (Appendix 3) Used To Determine Significance Levels Of Factor Loadings.

Metals	Factor		
	1	2	3
Variance (%)	30.2	27.6	21.2
Ca	-	***	-
Mg	(***)	-	-
Al	(***)	-	-
Fe	(***)	-	-
Zn	-	-	**
Mn	-	-	-
Co	-	-	-
Pb	-	-	**
Ni	(**)	-	-
Cu	-	-	**
LOI	-	-	***
pH	-	***	-

- = Not significant
* = significant at 0.10 level
** = Significant at 0.05 Level
*** = Significant at 0.01 level
( ) = Negative Loading.

in the topsoil (mean pH 5.9), the leaching of carbonates is an intense process. Owing to the fluctuations in the CO_2 content of soil air, the partial pressure of CO_2 varies considerably. As the CO2 pressure increases, the pH decreases and consequently carbonates are dissolved. The group defined by Factor 2 in the topsoil may be interpreted as representing the carbonates in the topsoil.

Factor 3 had high positive loadings on Zn, Pb, Cu and the organic matter(LOI) . These elements, together with the organic matter(LOI) were shown earlier to tend to be enhanced in the topsoil. The highest loading on this factor was on the organic matter(LOI). Considerable evidence indicated that soil organic matter formed stable complexes with di- and trivalent cations. Schnitzer and Skinner (1965) calculated the stability constants for complexes formed by Pb, Ni, Co, Mg and Cu at pH 5.0 and 3.5 with fulvic acid. They concluded that the stabilities of complexes formed between fulvic acid and these cations were pH dependent. At pH 5.0 the order of stabilities were Cu>Pb>Fe>Ni≈Co >Ca>Zn>Mg. Swaine and Mitchell (1960) observed the activity of soil organic matter in enriching elements such as Pb in the topsoil. The group of elements defined by this factor was interpreted as an association with the organic matter(LOI).

(c) Subsoil:

The three factor model described the main multi element associations in the subsoil (Table 11-15) As in the topsoil, factor 1 associated Mg, Al, Fe and Ni by high negative loadings. In addition, the loadings on Mn and Co were also significant. This group is probably the same as the clay mineral group discerned in the topsoil

and rock and it was similarly interpreted. The persistent association of the elements in this group in the rock and soil suggested that in this environment the clay minerals were unaffected by processes of weathering and pedogenesis.

Factor 2 associated Ca with the pH by high negative loadings. It is noted that in freely drained soils such as in the Ross series, Ca may tend to saturate the cation exchange complex, however the results do not suggest a significant association with the clay minerals. As suggested in the case of the topsoil such an association may represent the solution of the carbonates in the soils as a response to variation in the CO_2 concentrations in the soil atmosphere.

Factor 3 had positive loadings on Zn, Pb, Ni, Cu and organic matter(LOI). The weakest loading on this factor was on the organic matter(LOI) which indicated that organic matter(LOI) may not be as important in controlling the distribution of these elements in the subsoils as was found in the topsoil. Furthermore, correlations of these elements with organic matter(LOI) in the subsoils were not observed in the preceding section. It is probable that the group defined by factor 3 represents an association with other fractions in the subsoil such as the colloidal phase.

(d) Stream sediments.

The three factor model accounted for the main multi-element groupings in the stream sediments (Table 11-16). The first factor associated Mg, Al, Fe, and Zn by high positive loadings. This group is identical to the clay mineral group found the rocks, a further indication that the clay minerals undergo very little reconstitution in the transition from one medium to the other.

Table 11-15

Significance Of Factor Loadings Of Logarithmically Transformed Subsoil Data. Matrix Accounts for 82.5% Of Variance Of 45 Samples Of The Ross Series . ! Tables Of Levels Of Significance Of Correlation Coefficient (Appendix 3) Used To Determine Significance Levels Of Factor Loadings.

Metals	Factor		
	1	2	3
Variance (%)	39.6	18.6	24.3
Ca	-	(***)	-
Mg	(***)	-	-
Al	(***)	-	-
Fe	(***)	-	-
Zn	-	-	***
Mn	(**)	-	-
Co	(**)	-	-
Pb	-	-	**
Ni	(***)	-	**
Cu	-	-	**
LOI	-	-	*
pH	-	(***)	-

- = Not significant
* = significant at 0.10 level
** = Significant at 0.05 Level
*** = Significant at 0.01 level
( ) = Negative Loading.

The second factor displayed an inverse relationship between Ca on one hand and Pb, Ni and organic matter(LOI) on the other. Such an inverse relationship can only be explained by the known ability of organic acids to form stable complexes with cations such as Pb and Ni (Russell, 1973). Such acids may in turn be leaching the carbonates from the system hence the inverse relationship.

Factor 3 associated Mn with Co, Cu, and the organic matter(LOI). In general the soluble products of chemical weathering of rocks and soils are held in solution until there is a change in the geochemical environment. Such a change occurs when ground water encounters the relatively oxidising and generally less acidic conditions in the streams. Here metals are deposited on organic fragments, pebbles and gravels as hydroxides, oxides and salts (Hawkes and Webb, 1965). In this respect the oxides of Mn play an important role in the fixation of other cations through "scavenging " (Jenne, 1968). The association of this factor with the loss on ignition suggested an alternative interpretation. Thus certain colloidal forms of organic matter are good sorbents of metals. These, like the Mn oxides have negative charges on their surfaces and are capable of adsorbing cations. Whatever is the form of the association between this group and the organic matter, it seemed likely that the mechanism of incorporation of Mn in the stream sediments was partly related to the organic matter.

(e) Summary.

The results of factor analysis showed that multi-element associations were in most respects governed by similar processes

Table 11-16

Significance Of Factor Loadings Of Logarithmically Transformed Stream Sediment Data. Matrix Accounts for 70.0% Of Variance Of 30 Samples Derived From The Old Red Sandstones. ! Tables Of Levels Of Significance Of Correlation Coefficient (Appendix 3) Used To Determine Significance Levels Of Factor Loadings.

Metals	Factor		
	1	2	3
Variance (%)	29.6	24.3	16.1
Ca	-	(**)	-
Mg	***	-	-
Al	***	-	-
Fe	***	-	-
Zn	***	-	-
Mn	-	-	***
Co	-	-	***
Pb	-	***	-
Ni	-	***	-
Cu	-	-	**
LOI	-	**	**
pH	-	***	-

- = Not significant
* = significant at 0.10 level
** = Significant at 0.05 Level
*** = Significant at 0.01 level
( ) = Negative Loading.

operating in the different media. The clay mineral group of elements were similar in all the media, while the elements Pb, Cu and Zn seemed to be controlled by their association with organic matter in the soils and with the carbonates in the rocks. In the soils strong association was found between pH and Ca. This was thought to represent the pedochemical process of dissolution of the carbonates in the soils as a result of fluctuations of soil CO . The oxide phase was associated with Cu and Co in the stream sediments. A further association was found between the oxide phase and the organic matter(LOI) in the stream sediments. This was thought to represent the precipitation of Mn oxides on organic fragments in the sediments.

11-6 Comparison between media (analysis of variance results).

The analysis of variance(see Chapter 3) has been used to identify quantitatively the major source of variation found in the samples taken from the various media and sites. The three level nested analysis of variance technique involved a hierarchical scheme shown in Fig. 3-4 and the mathematical computations and degrees of freedom at each level are shown in Appendix 2. The table of F-ratios (Appendix 4) have been used to determine the significance levels of the F-ratios obtained. The results are presented as F-ratios and percent contributions from each level to the total variability. The F-ratios can be viewed as an indication of the significance of the contributions of a particular level in the hierarchical scheme. For instance, in Table 11-18, the F1-ratio for Co was not significant yet the contributions to the total variability was over 20%, while a similar contribution of the F1-ratio for Cu in Table 11-17 was

significant at the .05 level. Four comparisons have been made. These were between:-

(a) rock and soil(top and subsoil)

(b) top and subsoil

(c) the soil(top and subsoil) and stream sediments

(d) the rock and stream sediments

The results of each comparison are discussed below.

(a) Comparison between the rock and soil(top and subsoil)

The F1-ratios for the elements Mg, Al, Mn and Ni were not statistically significant at the .10 confidence level (Table 11-17). Contributions to the total variance were small in each case (less than 15%). This was in contrast to Ca, Fe, Zn, Co, Pb and Cu, where the variability between media were not only significantly different at the .01 and .05 levels but also their contributions to the total variance were high, ranging from 20% in the case of Cu to 69% in the case of Ca. Apart from Ca, for all the elements analysed the between site F2 - ratios were statistically significant with higher contributions to the total variability. Contributions from this source in the case of Ca was less than 20% of the total variability. Sampling (F3-ratio) and analytical errors did not contribute significantly to the total variability hence not a great source of random procedural errors.

(b) Comparison between topsoil and subsoil.

The results showed that for all the elements the F1-ratios were not statistically significant at the .10 level with very low

Table 11-17
F-ratios and Percent Variance Components For The Comparison Between The Rock And Soils Derived From The Old Red Sandstones As Estimated By The Three Level Nested Analysis Of Variance Model. Samples Collected From The Old Red Sandstones In Herefordshire Study Area.

Metal	Between Media		Between Sites		Between Samples		Bet. Anal
	F1	(%)	F2	(%)	F3	(%)	(%)
Ca	***	69.0	NS	18.0	NS	6.5	4.4
Mg	NS	10.5	***	75.6	NS	7.7	6.0
Al	NS	12.6	***	71.2	NS	8.2	8.0
Fe	*	25.8	***	63.5	NS	7.3	4.3
Zn	**	29.9	**	53.2	NS	9.0	7.9
Mn	NS	14.7	***	69.4	NS	7.0	8.9
Co	**	48.8	**	34.8	NS	9.4	7.0
Pb	**	31.3	**	49.3	NS	6.0	5.4
Ni	NS	14.9	***	75.3	NS	4.8	5.0
Cu	**	20.7	***	69.8	NS	5.5	4.0

NS = Not Significant, P> 0.10; * = 0.10 > P > 0.05; ** = 0.05 > P > 0.01; *** = P < 0.01.

contributions to the total variance (Table 11-18). In the case of Fe the contributions from this source was virtually nil. In contrast, the between site F2 - ratios were all significant at the .01 levels for all the elements. This source accounted for most of the variability for all the elements. In the case of Fe this source accounted for 90% of the total variability. Sampling error (F3 - ratio) and analytical error were not statistically significant and in general made only minor contributions to the total variability.

(c) Comparison between rock and sediment .

The between media F1-ratios for the elements Mg, Al, Fe, Zn, Ni and Cu were not statistically significant at the .10 confidence level (Table 11-19). The contribution to the total variation were low (generally below 25%). By contrast the F1 ratios for Ca, Mn, Co and Pb were significantly different at the .01 level with contributions to the total variance component ranging from 43% in the case of Mn to 79% in the case of Ca. The F2 ratios for the between site variability were significantly different at the .05 and .01 levels for all the elements but the percent total variance contributions were higher for the elements Fe, Zn, Ni, Mg and Al than the rest. Differences between samples, (sampling error) were significant at the .10 level for the elements Fe, Zn, and Pb but these accounted for less than 12% of the total variability hence was accepted to be within the bounds of experimental errors. In general, the percent total variance accounted for by analytical errors were very small for all elements.

Table 11-18
F-ratios and Percent Variance Components For The Comparison Between The Top And Sub Soils Derived From The Old Red Sandstones As Estimated By The Three Level Nested Analysis Of Variance Model. Samples Collected From The Old Red Sandstones In Herefordshire Study Area.

Metal	Between Media		Between Sites		Between Samples		Bet. Anal
	F1	(%)	F2	(%)	F3	(%)	(%)
Ca	NS	10.2	***	81.0	NS	4.7	3.9
Mg	NS	16.7	***	76.5	NS	3.8	3.0
Al	NS	12.6	***	72.3	NS	6.1	7.0
Fe	NS	5.0	***	90.0	NS	2.5	2.4
Zn	NS	14.0	***	77.9	NS	4.1	4.0
Mn	NS	12.7	***	75.4	NS	8.1	3.0
Co	NS	21.0	***	69.9	NS	5.1	4.0
Pb	NS	19.1	***	70.0	NS	6.0	4.9
Ni	NS	12.7	***	79.0	NS	5.1	3.0
Cu	NS	9.9	***	82.3	NS	3.8	4.0
LOI	NS	9.4	***	77.8	NS	5.0	5.8
pH	NS	12.3	***	76.4	NS	5.0	6.1

NS = Not Significant, P> 0.10; * = 0.10 > P > 0.05; ** = 0.05 > P > 0.01; *** = P < 0.01.

Table 11-19
F-ratios and Percent Variance Components For The Comparison Between The Rock And sediments Derived From The Old Red Sandstones As Estimated By The Three Level Nested Analysis Of Variance Model. Samples Collected From The Old Red Sandstones In Herefordshire Study Area.

Metal	Between Media		Between Sites		Between Samples		Bet. Anal
	F1	(%)	F2	(%)	F3	(%)	(%)
Ca	***	79.0	**	11.0	NS	5.0	4.0
Mg	NS	20.0	***	64.4	NS	10.6	5.0
Al	NS	19.0	***	65.0	NS	11.5	4.5
Fe	NS	15.0	***	70.3	*	8.0	6.6
Zn	NS	17.0	***	70.4	*	8.0	4.6
Mn	***	43.0	**	50.0	NS	3.4	3.6
Co	***	47.3	**	40.0	NS	6.7	5.9
Pb	***	43.0	**	39.4	*	7.0	11.5
Ni	NS	21.7	***	65.0	NS	6.9	5.9
Cu	NS	23.1	***	64.0	NS	6.9	5.9

NS = Not Significant, P> 0.10; * = 0.10 > P > 0.05; ** = 0.05 > P > 0.01; *** = P < 0.01.

(d) Comparison between soil (top and subsoil) and stream sediment.

Apart from Mn and Cu whose F1 ratios were significant at the .05 confidence level, for most other elements the F1 ratios were significant only at the .10 level with low contributions to the percent total variance component (Table 11-20). The main source of variability emanated from within the media. Thus, the F2 - ratios for all the elements analysed were significant at the .01 levels. Contributions from this source were generally high being over 70% for the elements Ca, Mg and Al. Sampling and analytical errors did not contribute significantly to the total variability showing that this source did not greatly affect the results.

(e) Summary of the analysis of variance results.

Inferences that can be drawn from the analysis of variance results agree with the observations made earlier. In the comparison between the top and subsoils, only negligible differences existed between the two media for all the elements analysed. The main source of variability arose from the spatial variability within individual media. Thus such pedogenic processes as leaching and translocation may be subdued in the soils. This was typified by Fe which showed no difference in the variability between the top and subsoil with exceptionally low contributions to the total variance. On the other hand it displayed a highly significant F2 ratio with a high contribution to the total variance from this source.

The elements Mg, Al, Fe, Ni, and Zn which have been shown by factor analysis to be related to the clay mineral group showed no significant difference in the transition from rock to soil and rock to

Table 11-20
F-ratios and Percent Variance Components For The Comparison Between The Soil And Sediments Derived From The Old Red Sandstones As Estimated By The Three Level Nested Analysis Of Variance Model. Samples Collected From The Old Red Sandstones In Herefordshire Study Area.

Metal	Between Media		Between Sites		Between Samples		Bet. Anal
	F1	(%)	F2	(%)	F3	(%)	(%)
Ca	*	12.1	***	76.0	NS	1.9	2.0
Mg	*	12.4	***	71.7	*	10.8	4.0
Al	*	17.3	***	74.6	NS	5.1	4.0
Fe	*	20.8	***	65.7	NS	7.3	6.0
Zn	*	9.9	***	70.8	NS	4.9	5.3
Mn	*	29.3	***	63.0	NS	4.7	3.0
Co	*	15.6	***	69.3	NS	8.1	7.0
Pb	*	12.0	***	73.6	NS	7.9	7.0
Ni	*	14.0	***	71.2	NS	7.1	8.0
Cu	**	27.2	***	57.7	NS	7.1	8.0
LOI	*	11.0	***	80.0	NS	5.4	3.5
pH	*	10.0	***	79.0	NS	6.5	9.6

NS = Not Significant, P> 0.10; * = 0.10 > P > 0.05; ** = 0.05 > P > 0.01; *** = P < 0.01.

sediment. This was a further evidence that the clay minerals undergo only minor alterations in the soils and stream sediments. It seemed probable that the clay minerals present in the streams may be detrital, in the sense that they may have been carried mechanically into the streams without undergoing significant chemical alteration. The comparison between the rocks and stream sediments showed that there were significant differences in the variability of Ca between the media. Earlier results indicated that there was considerable loss of Ca in the transition from rock to soil and stream sediment possibly through leaching.

11-7 Integrated Discussion and Summary.

Element concentrations in the rocks, soils and stream sediments derived from the Old Red Sandstone in the Herefordshire area have been discussed and groups of element associations identified by factor analysis. The mobility of elements in the transition from one medium to another were studied by analysis of variance variance and interpretation of the results was based on:-

(a) The chemical behaviour of individual elements in the geochemical, pedological and stream environments

(b) The multi element associations revealed by the present study.

The results revealed four main groups of element associations

(1) The clay mineral group.

(2) The carbonate mineral group.

(3) Organic matter(LOI) group.

(4) The hydrous oxide group.

(1) The clay mineral group (Mg, Al, Fe, Zn, Ni).

This group was characterised by the elements Mg, Al, Fe, Zn, and Ni. Concentrations of these elements in all the media investigated were similar although stream sediment concentrations of these elements may be lowered, probably due to the dilution with colluvial material. The analysis of variance results showed no significant variability in the transition to stream sediments for these elements. Inter-element correlations between pairs of these elements were strong and positive, and factor analysis further indicated that the association of these elements persisted in the rocks, soils and stream sediments. It seemed certain from the results that the clay minerals in the soil and stream sediments were inherited directly from the parent material, undergoing little or no alterations in the process. Any changes affecting the clay minerals occurred within individual media as was indicated by the analysis of variance results. Factor analysis also indicated that such processes may include the absorption and displacement of various cations such as Zn and Ni at exchange site.

(2) Carbonate group(Ca, Zn, Pb, Ni).

The elements in this group included Ca, Pb, Ni and Zn. The carbonate group undergo significant leaching in the transition from rocks to sediments and from rocks to soils. This was reflected by the differences in the concentrations of Ca in the rocks, soils and stream sediments. The analysis of variance results showed significant differences in the variability of Ca in the comparisons between the

rocks and soils and the rocks and sediments.

The correlation coefficients and factor analysis results indicated that elements such as Pb and Zn were related to the carbonate group in the rocks but in the soils it seemed that the elements Zn and Pb followed different geochemical pathways. Calcium concentrations in the soil and stream sediments showed, for instance, a tenfold decrease in mean levels when compared with the rocks while Zn and Pb showed a general tendency towards an increase in the soils. As might be expected, in both the top and subsoils, factor analysis associated Ca with pH. In the stream sediments it is probable that the antipathetic pattern displayed by Ca and the organic matter(LOI) may be due to the leaching of the carbonates by organic acids .

(3) Organic matter group(Zn, Pb, Mn, Ni, Cu).

Elements within this group included Pb, Mn, Cu, Zn and Ni. Fixation by organic matter seemed to be the main process responsible for the enhancement of Zn, Pb and Cu in the soil particularly in the topsoil. Factor analysis related these elements with the organic matter(LOI) in both the top and subsoils. This was further reflected by the analysis of variance results where significant differences occurred in the comparison between the rock and soil for the elements Zn, Pb and Cu. In the topsoil, the organic matter(LOI) was significantly correlated with Pb. This is thought to be due to vegetative recycling of Pb by plant debris that tends to accumulate in the surface horizons of the soils.

(4) Hydrous oxides (Mn, Fe, Co, Cu).

The results indicate that the oxides formed a very stable component in the rocks, soils and streams. Levels of Mn and Fe in the top and subsoils were strikingly similar. The analysis of variance results did not suggest any significant differences in the variability of these elements in the top and subsoils. In the rocks strong association was observed between Mn and Co. In the soils and stream sediments derived from the Old Red Sandstones, it seemed likely that processes such as the leaching and translocation of manganese may be subdued. Manganese oxides may be associated with the organic matter(LOI) in the streams.

11-8 Conclusions.

The following conclusions can be drawn from the above investigation

(1) The dominant influence on the distribution of trace elements was the parent material.

(2) There was very little difference between the concentrations of most elements in all the media investigated in the Old Red Sandstone environments. The only exception being Ca which tended to be lost in the transition from rock to soil and to sediment.

(3) Processes such as translocation and leaching of hydrous oxides and other components of the pedogenic environment were not common.

(4) Distribution of elements in the different media seemed to be controlled by similar processes. The following strong associations were found,

(a) Mg, Al, Fe, Zn and Ni

(b) Ca, Zn, Pb and Ni

(c) Zn, Pb, Mn, Ni and Cu

(d) Mn, Fe, Co and Cu.

CHAPTER 12

Detailed Investigations Into The Keuper Marl In The Worcestershire Study Area.

12-1 Introdution.

The location of the study area is shown in Fig. 6-1. The climate and drainage in the study area have been discussed in Chapter 6. The preliminary investigations involved a study of the element concentrations in the rocks, soils, and stream sediments derived from both the Lower Lias and the Keuper Marl. The present investigation was concentrated on the Keuper Marl and Worcester soil series.

12-2 Geology.

The lithology and environment of sedimentation of the Keuper Marl has been extensively discussed by Wills (1976). The series consists of slowly accumulated shallow water and evaporite deposits. Wills (1976) , proposed that sedimentation of the Keuper Marl occurred in cyclotherms and grouped the unit according to their dominant constituent as " argillaceous " or " arenaceous " sediments and evaporite bodies with the three groups interspersed. The argillaceous deposits, familiarly referred to as the Keuper Marl are the most dominant. They consist of pure mudstone or mudstone admixture of silts and sands, or mudstone impregnated with, or intermingled with evaporite minerals such as calcite, dolomites, anhydrite, gypsum and halite. The rocks are chocolate red in colour. The " arenaceous " deposits consist of bands of sandstones such as the " skerries ".

52° 14' 16" N

2° 00' 00" W

N

Inkberrow

Weethley

Rous Lench

Church Lench

Legend

Town

Stream

Sample point

Scale

½ Mile

Fig 12 - 1
Sample Location In The Worcestshire Study Area

These are coarse massive sandstone bands often calcareous and may be associated with dolomitic marls.

Wills (1976), attributed the formation of evaporite poor and evaporite rich marls to rythmic fluctuations in the amount of inflow of " river water and / or flooding by sea water ", temperature and rate of evaporation. Such fluctuations resulted in periods of maximum inflow during which evaporite poor marls were formed and periods of maximum aridity during which terrestial conditions prevailed with a consequent precipitation of evaporites and formation of seals or dusts or muds, over the evaporite rich marls . Such rythmic fluctuations resulted in the cyclotherms.

Rock samples were collected mainly from the marl facies. Few sandstone samples were collected near Inkberrow (Fig. 12-1).

Soils.

The dominant soil type over the Keuper Marl is the Worcester series. These are medium to heavy textured soils with moderate drainage and variable depths. A typical profile under grass, with weathered marl at depths of 60cm , consists of brown friable topsoil often granular in structure of varying depths 0 - 20cm, (generally 0 - 15cm). The subsoil is also variable in depth (30 - 45cm), usually reddish and firm of prismatic structure. Below 45cm the soil gets firmer often with greenish patches. A few soils showed evidence of periodic waterlogging. Deeper soils, sandy loams of dull greyish brown colour with a pale brown clayey subsoil, were found near the town of Inkberrow. These soils are of a limited occurrence mainly found in areas where the sandstone facies of the Keuper Marl dominates

TABLE 12.1

METAL	NUMBER OF SAMPLE	MEAN	S.D	RANGE MIN	RANGE MAX
Ca %	4	4.7	2.1	2.6	7.3
Mg %	4	4.3	1.1	2.8	5.6
Al %	4	0.7	0.4	0.4	1.3
Fe %	4	0.4	0.3	0.2	0.9
Zn ppm	4	25.4	6.6	19.0	34.5
Mn ppm	4	1120.0	275.0	900.0	2650.0
Co ppm	4	20.3	0.9	11.0	20.6
Pb ppm	4	16.3	6.1	10.0	33.3
Ni ppm	4	14.9	6.9	10.0	25.0
Cu ppm	4	8.9	2.7	5	13.5

Metal concentrations in the Sandstone facies of the Keuper Marl in Worcestershire (Near Inkberrow)

the terrain. In the present investigations these soils have been grouped with the Worcester series due largely to their limited occurrence, however it seemed possible that these soils may be equated to the Greinton series described by Avery (1955) in the Somerset district.

12-4 Regional Geochemical Patterns.

Preliminary investigations in the study area (Chapter 6) revealed that,

(1) the parent material played a dominant role in determining the concentrations of elements in the soils and rock,

(2) processes such as the translocation of clays and hydrous oxides in the soils were uncommon,

(3) the stream sediments reflected the element concentrations in the rocks and soils.

The present investigations assessed the distribution, mobility and associations of elements in the rocks, soils and stream sediments . The results are discussed below

(a) Calcium.

Contrary to expectation concentrations of Ca in the Keuper Marl were exceedingly low (Table 12-2a). Maximum concentration of Ca recorded in the rocks was below 1%. This was in contrast to the few sandstone samples where concentrations as high as 7% were recorded (Table 12-1). The mean concentration was higher than the marl facies. The histograms showed that in the marl facies over 80% of the total

Table 12-2a Calcium Concentrations In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	N	Mean (%)	S.D.	C.V.	Range Min (%)	Max (%)
Rock	40	0.5	0.3	60.0	0.1	0.7
T/Soil	40	0.4	0.1	37.1	0.1	0.7
S/Soil	40	0.4	0.2	55.8	0.2	1.0
S/Sedt	30	1.8	0.5	25.7	0.8	2.9

N = Number Of Samples.
S.D. = Standard Deviation.
C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 12-2b Significance Of Correlation Coefficients Between Ca And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock		***	-	-	-	**	***	-	*	-	-	**
T/Soil		*	-	-	-	-	-	-	-	*	**	*
S/Soil		**	-	**	***	-	-	-	-	**	-	***
S/Sedt		-	-	-	***	-	-	***	**	**	**	-

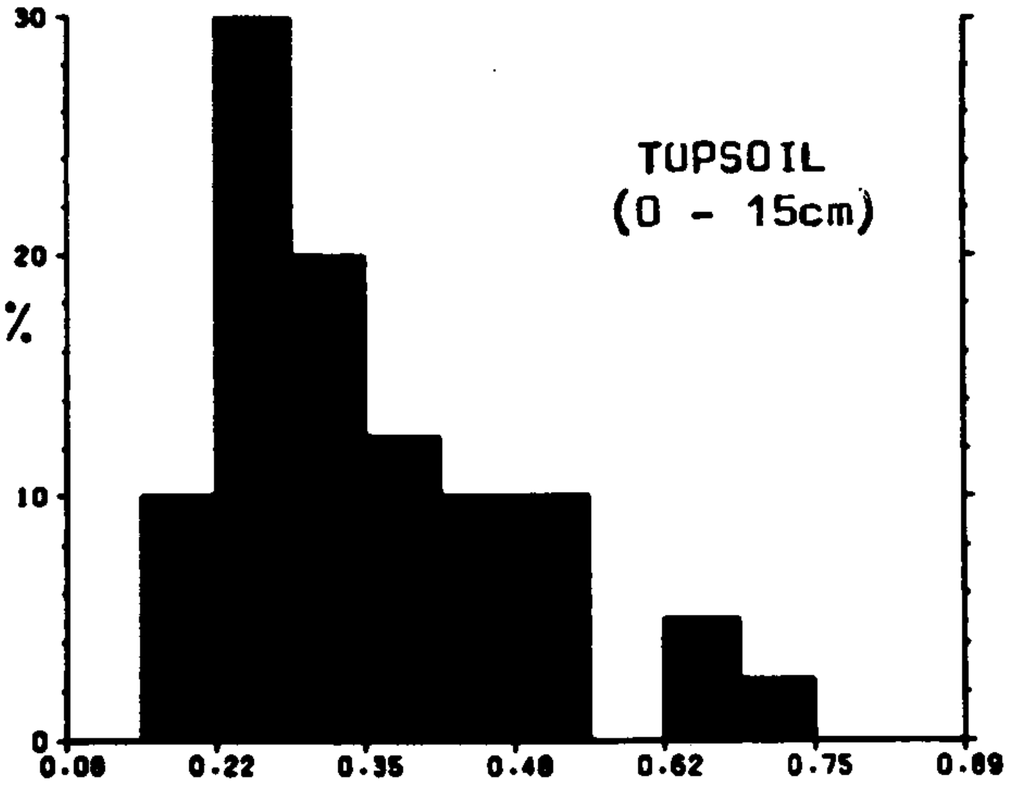
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

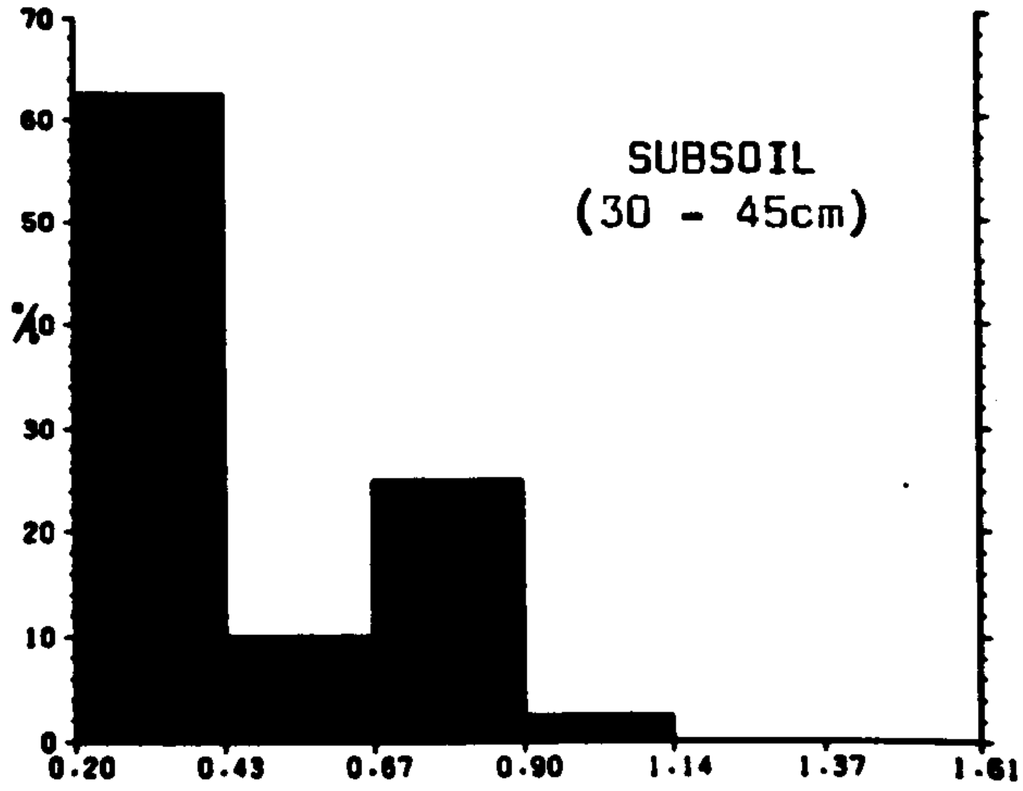
*** = Significant at .01 level

( ) = Negative Correlation.

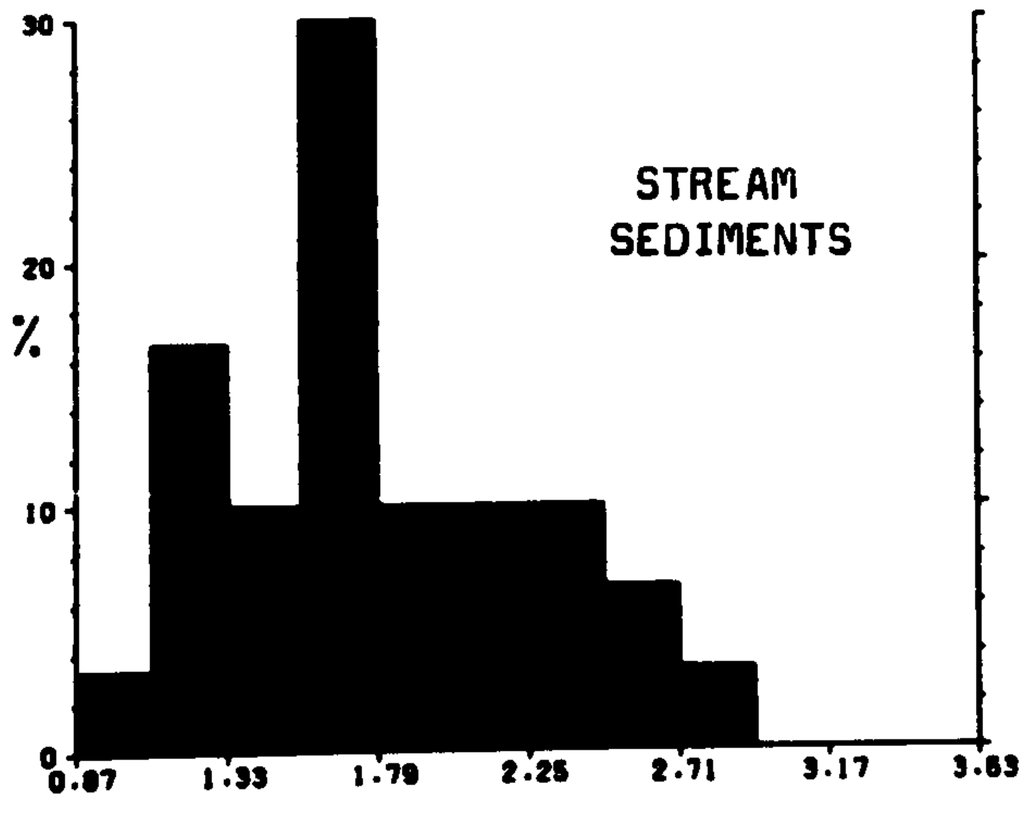
Fig. 12-2



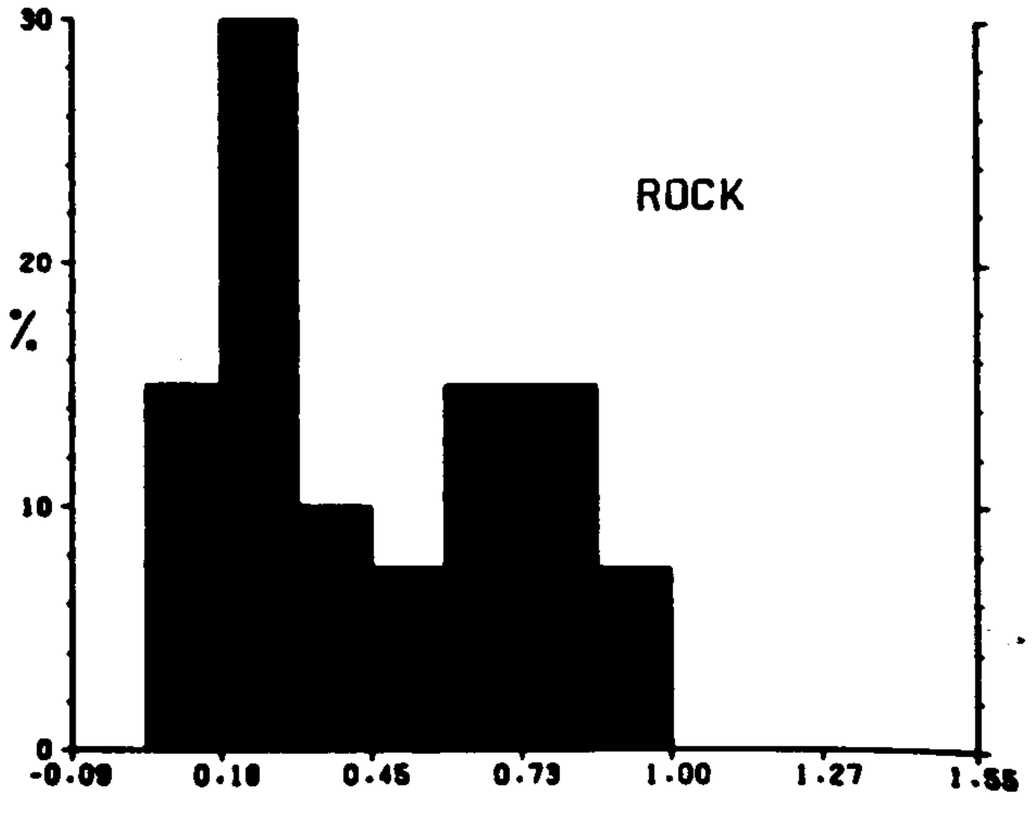
CA conc (%)
NO. OF OBSERVATIONS = 40
MEAN = 0.35 STD DEV = 0.134



CA conc (%)
NO. OF OBSERVATIONS = 40
MEAN = 0.43 STD DEV = 0.236



CA conc (%)
NO. OF OBSERVATIONS = 30
MEAN = 1.79 STD DEV = 0.459



CA conc (%)
NO. OF OBSERVATIONS = 40
MEAN = 0.45 STD DEV = 0.273

Histograms of the distribution of Ca in the rocks, soils and stream sediments derived from the Keuper Marl in the Worcestershire study area.

rock samples had Ca concentrations below 0.5%.

Differences in the Ca concentrations in the soils and marl facies (parent material of the Worcester series) were very small. Although there was a minor enhancement of the mean concentration of Ca in the subsoil, in general, the results did not suggest any major loss of Ca in the transition from rock to soil nor any significant leaching down the soil profile. The distribution of Ca in the top and subsoils were similar with over 60% of the samples having levels below 0.4%.

Concentrations of Ca were high in the stream sediments with concentrations of up to 2.9% being recorded. A significant percentage of the sediment samples had concentrations above 1.8% Ca , and the mean concentration was nearly four times as high as that in the rocks and soils. The higher concentrations were recorded in areas overlain by the sandy facies of the Keuper Series. Thus, a probable source of the higher concentrations of Ca in the stream sediments may be leaching of Ca bearing minerals from the sandy facies. The coefficient of variation values showed that maximum variation occurred in the rocks and subsoils (Table 12-2a) while the increased concentrations of Ca in the stream sediments were accompanied by a reduction of the coefficient of variation value.

Inter-element correlation.

There was a strong correlation between Ca with Mg, Mn and Co in the rocks (Table 12-2b). Calcium may be related to either the carbonates as calcites or to the clay minerals as part of the cation exchange complex. The correlation between Ca with Mn and Co indicated the presence of mixed carbonates in the rocks (Table 12-2b).

Table 12-3a Magnesium Concentrations In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	N	Mean (%)	S.D.	C.V.	Range Min (%)	Max (%)
Rock	40	1.5	0.5	35.3	0.7	2.6
T/Soil	40	1.1	0.4	32.7	0.4	1.7
S/Soil	40	1.2	0.4	33.3	0.4	1.9
S/Sedt	40	1.3	0.3	25.2	0.7	2.0

N = Number Of Samples.
S.D. = Standard Deviation.
C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 12-3b Significance Of Correlation Coefficients Between Mg And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	***		**	**	**	*	**	-	***	-	-	-
T/Soil	*		***	**	*	**	**	-	***	-	-	***
S/Soil	**		***	***	***	*	**	-	**	-	-	**
S/Sedt	-		**	**	-	-	-	-	-	-	-	-

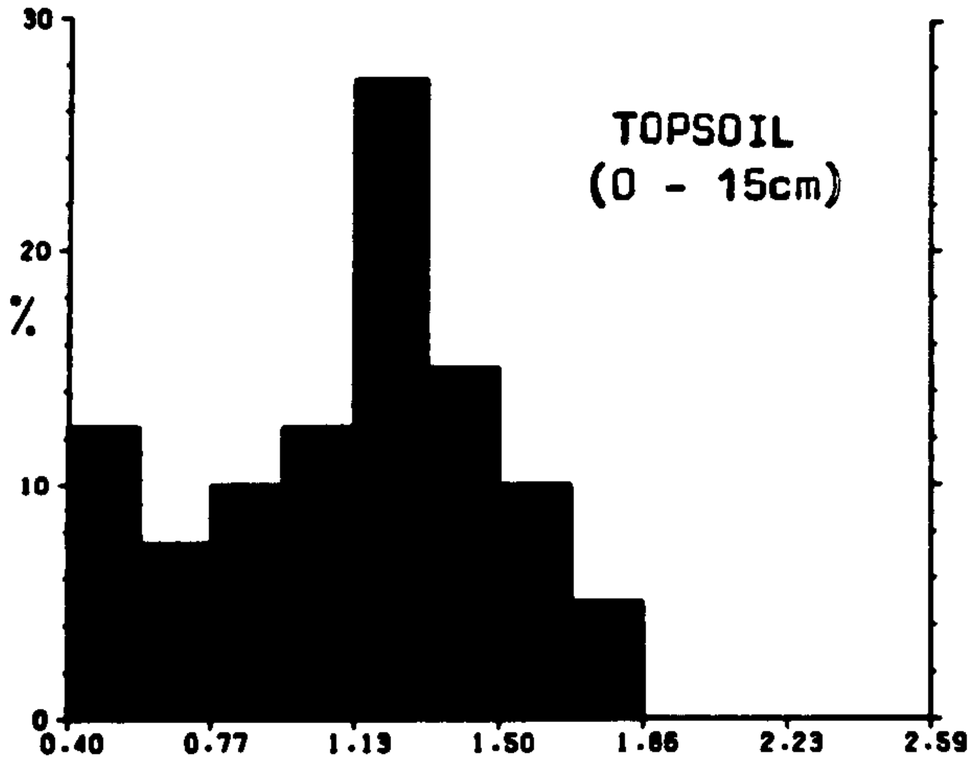
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

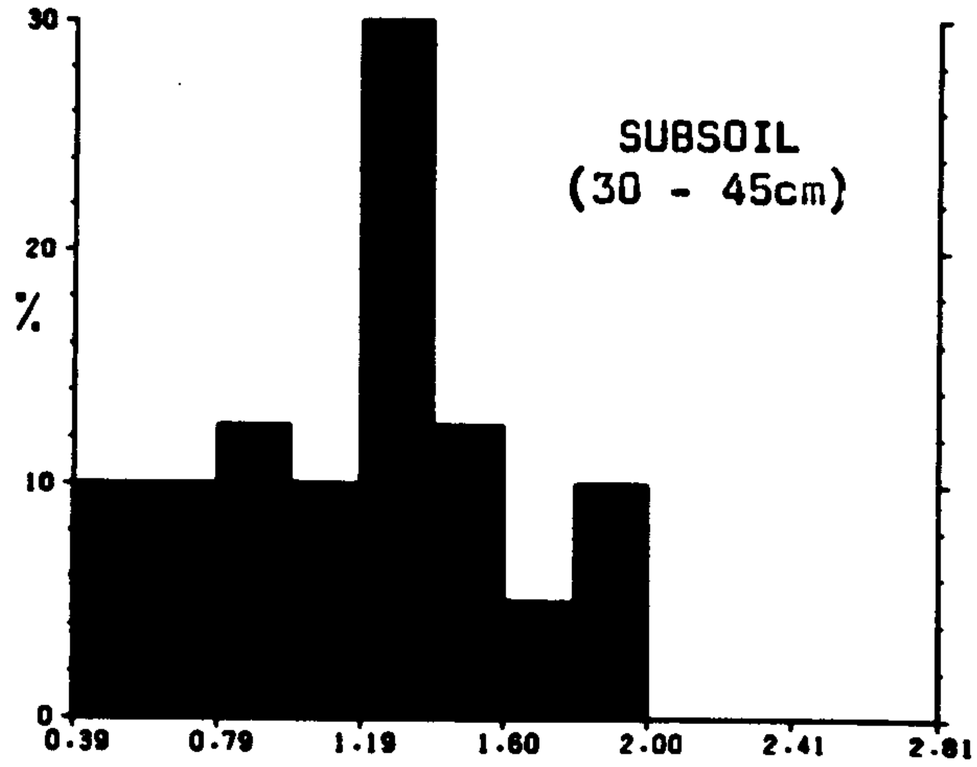
*** = Significant at .01 level

( ) = Negative Correlation.

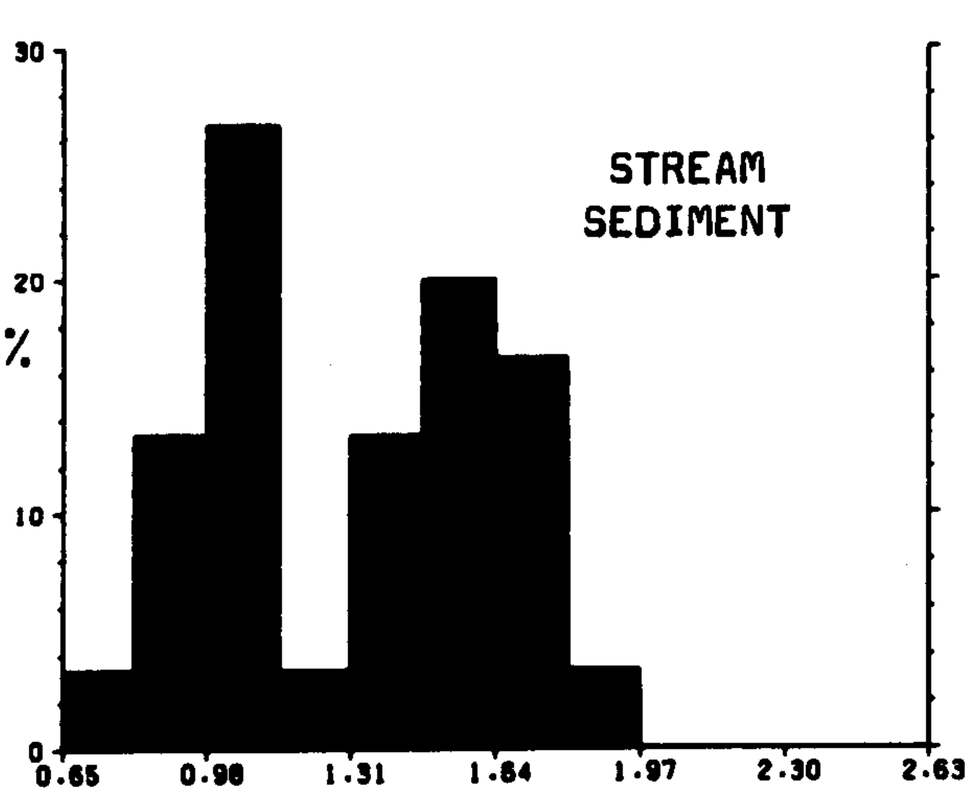
Fig. 12-3



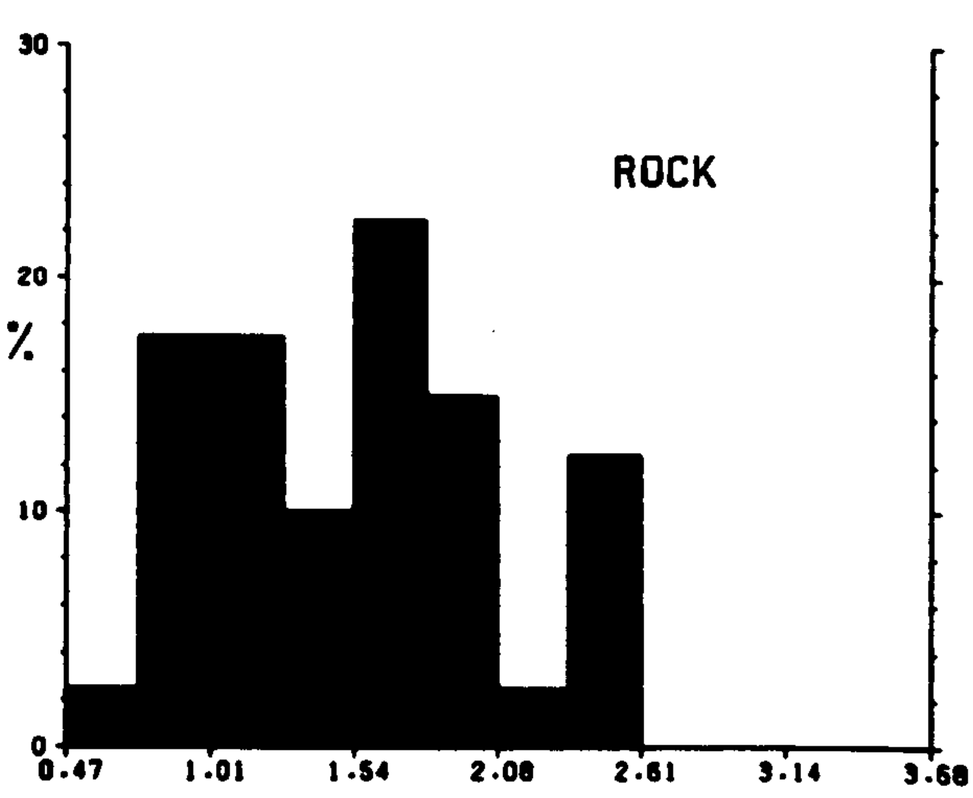
MG conc (%)
NO. OF OBSERVATIONS = 40
MEAN = 1.13 STD DEV = 0.365



MG conc (%)
NO. OF OBSERVATIONS = 40
MEAN = 1.19 STD DEV = 0.403



MG conc (%)
NO. OF OBSERVATIONS = 30
MEAN = 1.31 STD DEV = 0.331



MG conc (%)
NO. OF OBSERVATIONS = 40
MEAN = 1.54 STD DEV = 0.534

Histograms of the distribution of Mg in the rocks, soils and stream sediments derived from the Keuper Marl in the Worcestershire study area.

Manganese in the divalent state can replace Ca while Co can readily replace Mg in the dolomite structure which are known to occur in the Keuper Marl (Davis, 1967).

In the topsoil only weak correlations were found between Ca with Mg, Cu, pH and the organic matter(LOI). In the soils the correlation between Ca and the pH indicated the effect of the pH on the dissolution of carbonates.

In the stream sediments correlation between Ca with Zn, Pb, Ni, Cu and organic matter(LOI) were significant. This indicated that conditions in the streams may be encouraging the formation of secondary carbonates and such a process may contribute to the higher concentrations of Ca in the streams.

(b) Magnesium.

Magnesium concentrations in all the media investigated were similar although the range in the rocks was slightly wider than those in the soils and stream sediments (Table 12-3a). There was decreased occurrence of the lower and higher concentrations of the range (Fig.12-3). In the rocks and stream sediments Mg concentrations were higher in those samples with higher concentrations of Ca. This tendency was more typical of the sandstone facies where concentrations as high as 5% were recorded in some highly calcareous samples (Table 12-1) .

Inter-element correlations.

In the rocks the strongest correlations were with Ca and Ni.

Table 12-4a Aluminium Concentrations In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	N	Mean (%)	S.D.	C.V.	Range Min (%)	Max (%)
Rock	40	4.3	1.2	27.9	2.0	7.5
T/Soil	40	3.7	0.8	20.8	2.0	5.0
S/Soil	40	3.9	0.9	23.8	1.5	6.0
S/Sedt	30	3.2	0.6	19.7	2.0	4.5

N = Number Of Samples.
S.D. = Standard Deviation.
C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 12-4b Significance Of Correlation Coefficients Between Al And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	**		***	***	-	*	-	***	-	-	-
T/Soil	-	***		***	**	***	***	-	***	-	-	***
S/Soil	-	***		***	**	***	***	-	***	-	-	***
S/Sedt	-	**		***	***	-	-	-	***	-	*	**

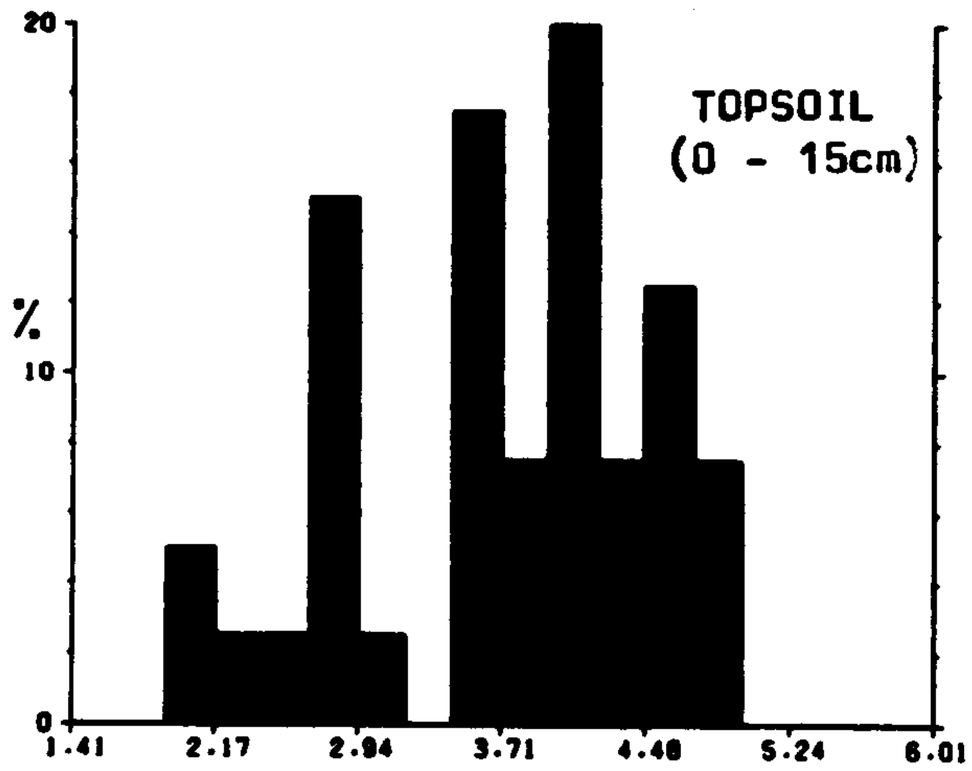
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

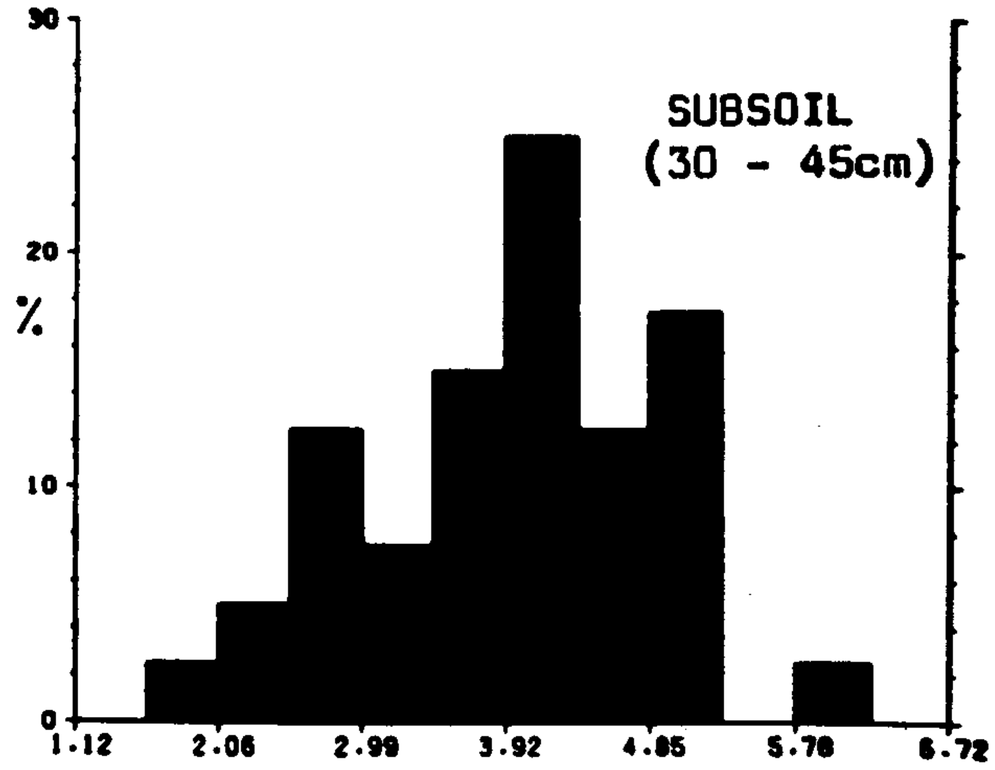
*** = Significant at .01 level

( ) = Negative Correlation.

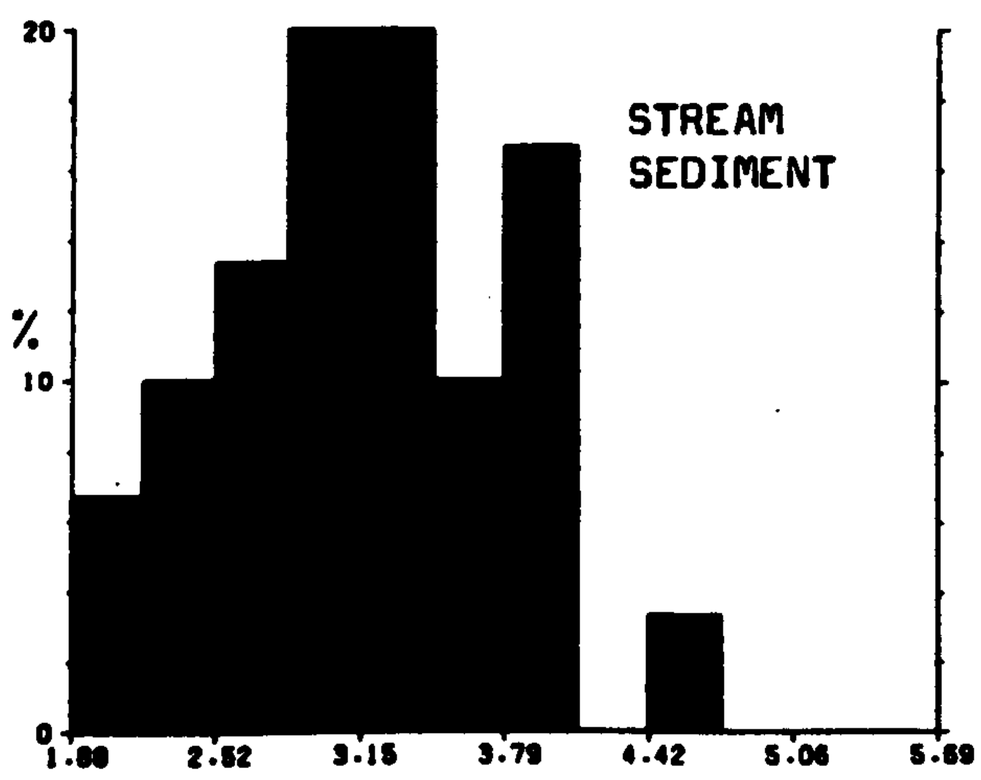
Fig. 12-4



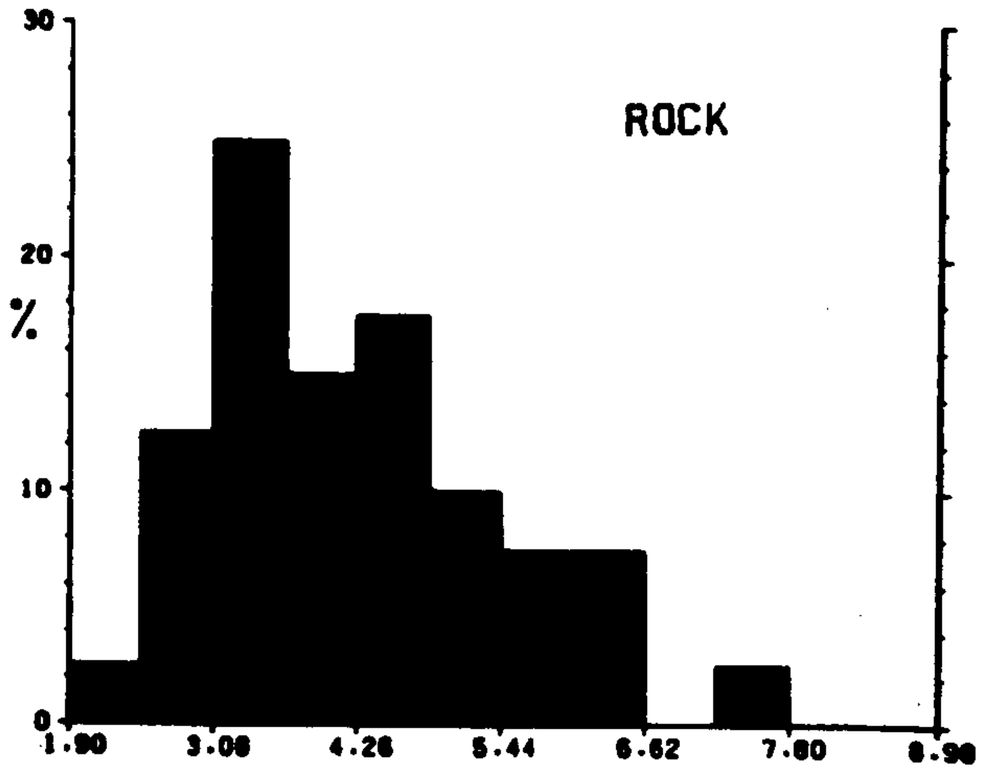
AL conc (%)
NO. OF OBSERVATIONS = 40
MEAN = 3.71 STD DEV = 0.768



AL conc (%)
NO. OF OBSERVATIONS = 40
MEAN = 3.92 STD DEV = 0.932



AL conc (%)
NO. OF OBSERVATIONS = 30
MEAN = 3.15 STD DEV = 0.634



AL conc (%)
NO. OF OBSERVATIONS = 40
MEAN = 4.26 STD DEV = 1.181

Histograms of the distribution of Al in the rocks, soils and stream sediments derived from the Keuper Marl in the Worcestershire study area.

This supported the view that part of the Mg present in the rocks may be associated with the carbonates. Weaker correlations existed with Al, Fe, Zn, Mn, and Co. This may be related to the clay minerals such as illites, chlorite and sepiolites present in the rocks (Davis, 1967).

In both the top and subsoils the correlations between Mg with Al, Fe and Ni were highly significant while the correlation with Ca was weak. The lack of significant correlation with Ca in the stream sediments indicated that Mg was not related to the carbonates in the stream sediments. Weak correlations existed between Mg with Al, and Fe in the stream sediments. It seemed likely that Mg in the streams was more related to the clay minerals than the secondary carbonates.

(c) Aluminium.

The mean concentration of Al in the rocks was slightly higher than those in the soils and stream sediments (Table 12-4a). The histograms showed that over 40% of the rock samples had concentrations above 5%. The sandstone facies had very low concentrations of Al (Table 12-1). Thus the mean concentration was over six times higher in the marl facies than in the sandstone. In the top and subsoils concentrations below 3% were common (Fig. 12-4).

The similarities of the mean concentrations, the coefficients of variation and the ranges of Al in in the soils and stream sediments suggested that Al was held as a stable component that was relatively unaffected by processes operating in the soils and stream sediments.

Table 12-5a Iron Concentrations In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium		Mean (%)	S.D.	C.V.	Range Min (%)	Max (%)
Rock	40	3.1	0.6	20.6	2.0	4.4
T/Soil	40	2.8	0.4	14.2	1.9	3.5
S/Soil	40	2.9	0.6	19.7	1.8	4.5
S/Sedt	30	2.8	0.5	18.9	2.0	3.9

N = Number Of Samples.
S.D. = Standard Deviation.
C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 5b Significance Of Correlation Coefficients Between Fe And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	**	***		**	*	**	-	***	-	**	-
T/Soil	-	**	***		*	**	**	-	***	-	-	**
S/Soil	***	***	**		**	**	**	-	***	-	-	**
S/Sedt	-	**	***		***	**	*	-	**	-	-	-

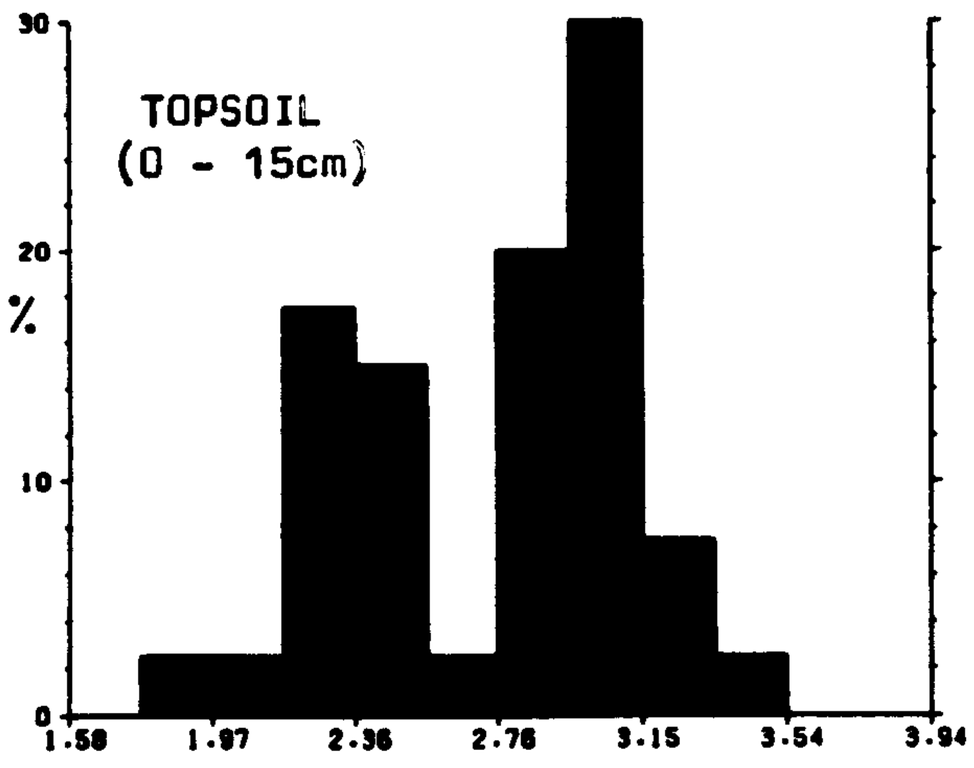
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

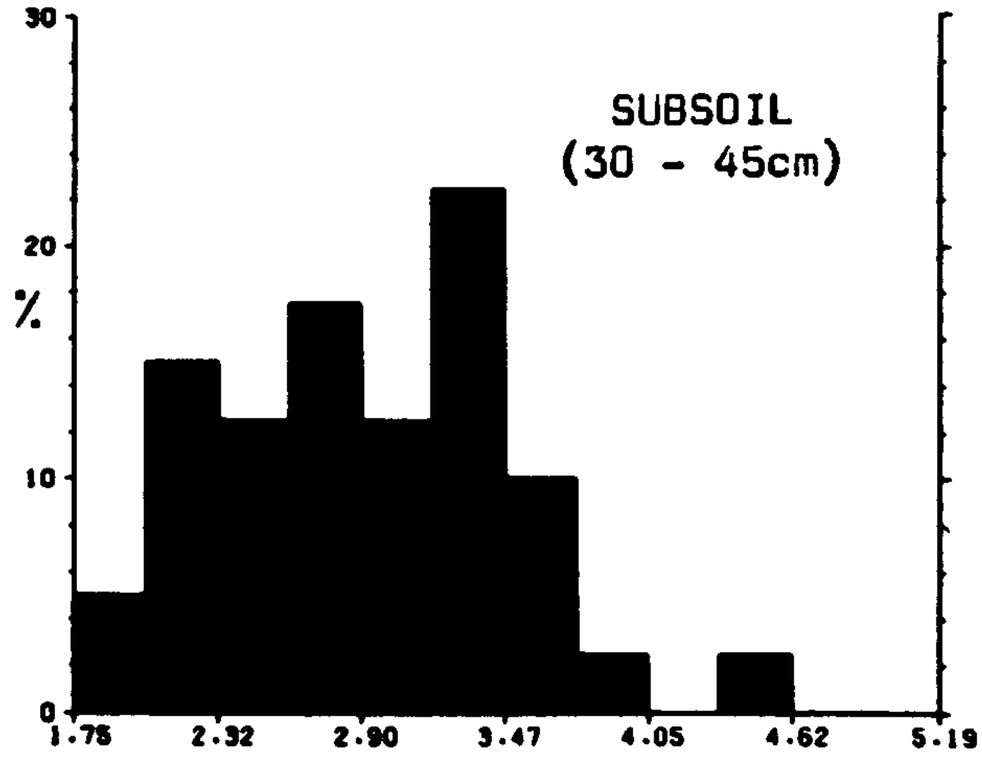
*** = Significant at .01 level

( ) = Negative Correlation.

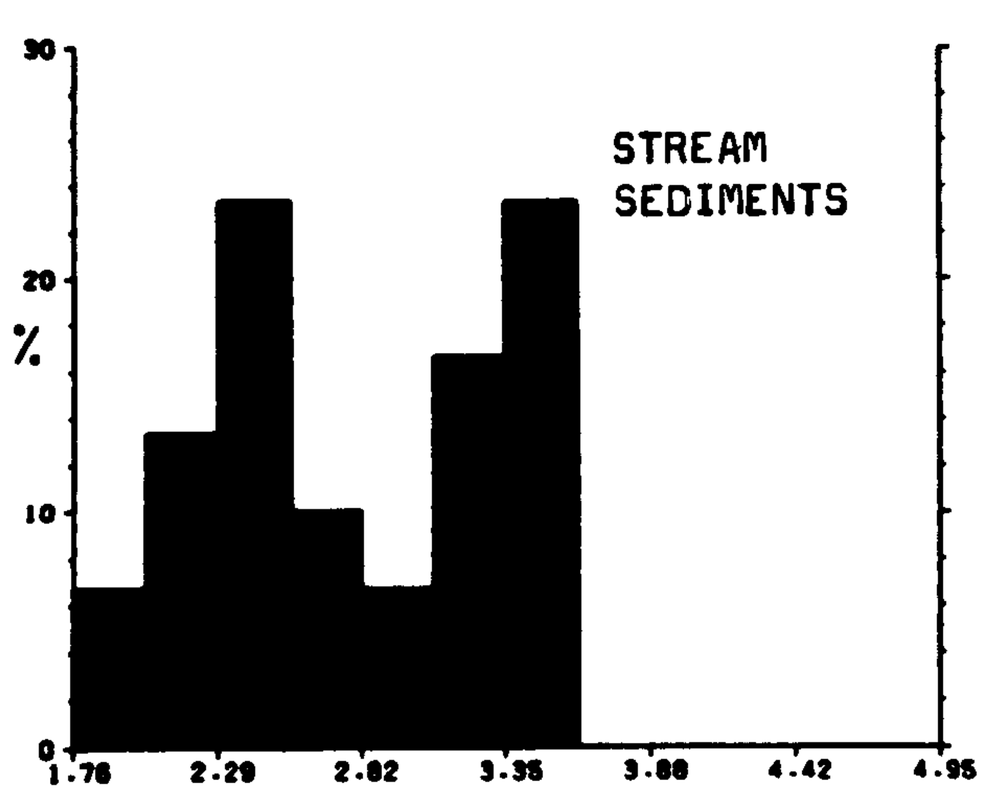
Fig. 12-5



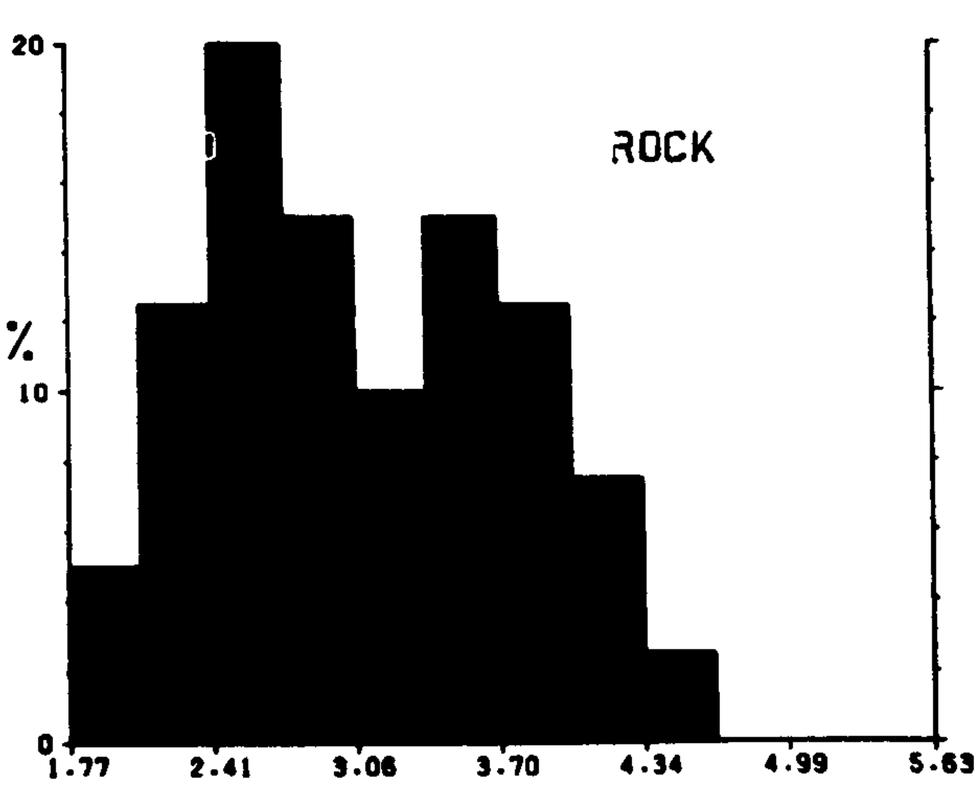
FE conc (%)
NO. OF OBSERVATIONS = 40
MEAN = 2.76 STD DEV = 0.393



FE conc (%)
NO. OF OBSERVATIONS = 40
MEAN = 2.90 STD DEV = 0.575



FE conc (%)
NO. OF OBSERVATIONS = 30
MEAN = 2.82 STD DEV = 0.532



FE conc (%)
NO. OF OBSERVATIONS = 40
MEAN = 3.06 STD DEV = 0.644

Histograms of the distribution of Fe in the rocks, soils and stream sediments derived from the Keuper Marl in the Worcestershire study area.

Inter-element correlation.

In all the media studied Al was significantly correlated with Mg, Fe, Zn and Ni (Table 12-4b). The correlations with Co in the rocks and soils were significant.

Aluminium is an important component of the clay minerals and the strong correlation with Fe and Ni suggested that Al was related with these elements in the clay minerals. In general, the clay minerals are capable of adsorbing cations onto exchangeable sites in its structure. The varying strengths of the correlations between Al with Mg, Zn, Mn and Co in the soils may indicate the degree of adsorption of these elements.

Weaker correlations were observed between Al with organic matter(LOI) and the pH in the stream sediments. Organic matter is capable of forming complexes with such trivalent cations as Al. Furthermore, clay minerals interact with organic matter in a number of ways such as through ligand exchange and polyvalent bonding (Russell,1973, p 117). Such reactions may be influenced by the pH of the environment, and the correlation with the pH may represent such an influence.

(d) Iron.

The concentations of Fe in the marl facies were very much higher than in the sandstone facies (Table 12-1). The mean concentrations of Fe in all the media were only marginally different (Table 12-5a). The histograms showed that concentrations below 3% Fe were common in each medium (Fig. 12-5). Waterlogged soil samples had lower Fe concentrations. This suggested some degree of mobilisation

in the soils. Stream sediment samples taken upstream had higher concentrations than those taken down stream. In the upstream samples the pH was higher than the downstream samples. It seemed likely that the pH and redox conditions in the streams and the downstream dispersion may be some of the factors affecting the distribution of Fe. It can be inferred from the results that Fe like Al and Mg may be locked up in the stable components of the rocks, soils and stream sediments.

Inter-element correlations.

In all the media Fe was significantly correlated with the elements Mg, Al, Zn, Mn, Co and Ni (Table 12-5b). The correlations with the pH were significant in the top and subsoil, while in the subsoil there was a further significant correlation with Ca. Two groups of associations can be discerned from these correlations. The strong correlations with Al and Ni suggested an association with the clay minerals while the relatively weaker correlations with Mn, Zn, and Co suggested an association with the hydrous oxides.

(e) Zinc.

The few samples of the sandstone facies of the Keuper Series indicated that concentrations of Zn were very low (Table 12-1). The mean concentration of Zn in the marl facies was nearly three times higher than that of the sandstone rocks (Table 12-6a). The histograms (Fig. 12-6) showed a tendency for the higher and lower concentrations to occur less frequently in the rocks. In general, concentrations

Table 12-6a Zinc Concentrations In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	40	75.3	17.9	23.8	35.0	108.0
T/Soil	40	77.4	13.3	17.2	38.0	101.0
S/Soil	40	75.5	12.3	16.3	46.0	101.0
S/Sedt	40	105.2	25.1	23.9	64.0	149.0

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.)

Table 12-6b Significance Of The Correlation Coefficients Between Zn And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	**	***	**		-	-	**	-	-	**	-
T/Soil	-	*	**	*		-	-	**	**	-	***	-
S/Soil	***	***	**	**		-	-	***	***	***	**	**
S/Sedt	***	-	***	***		-	-	***	***	***	**	**

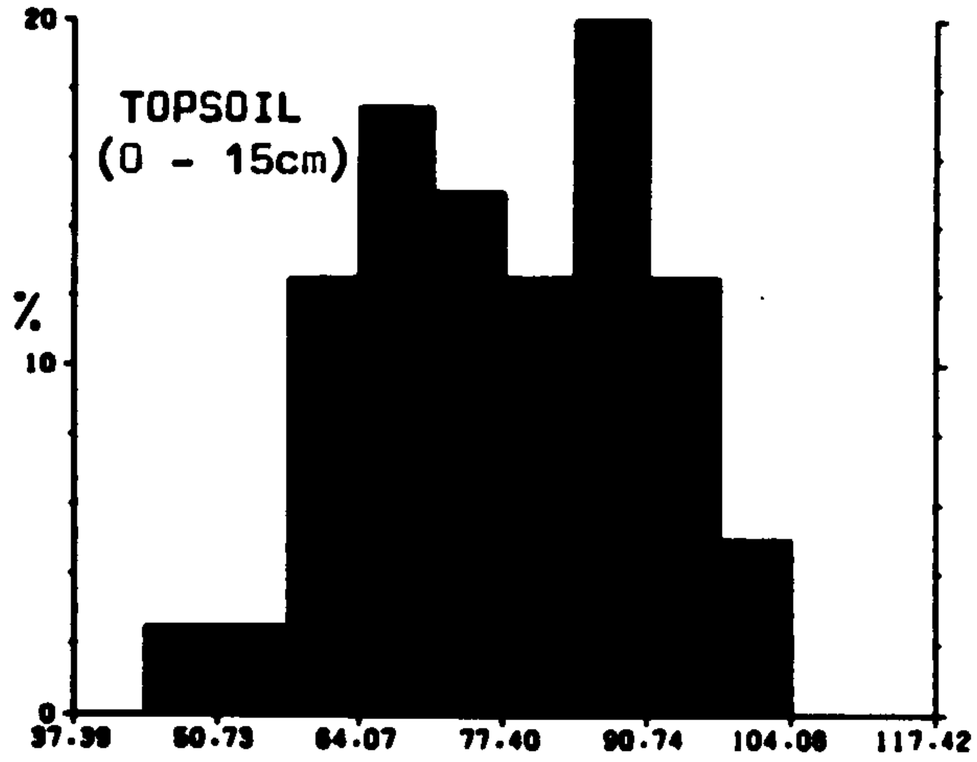
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

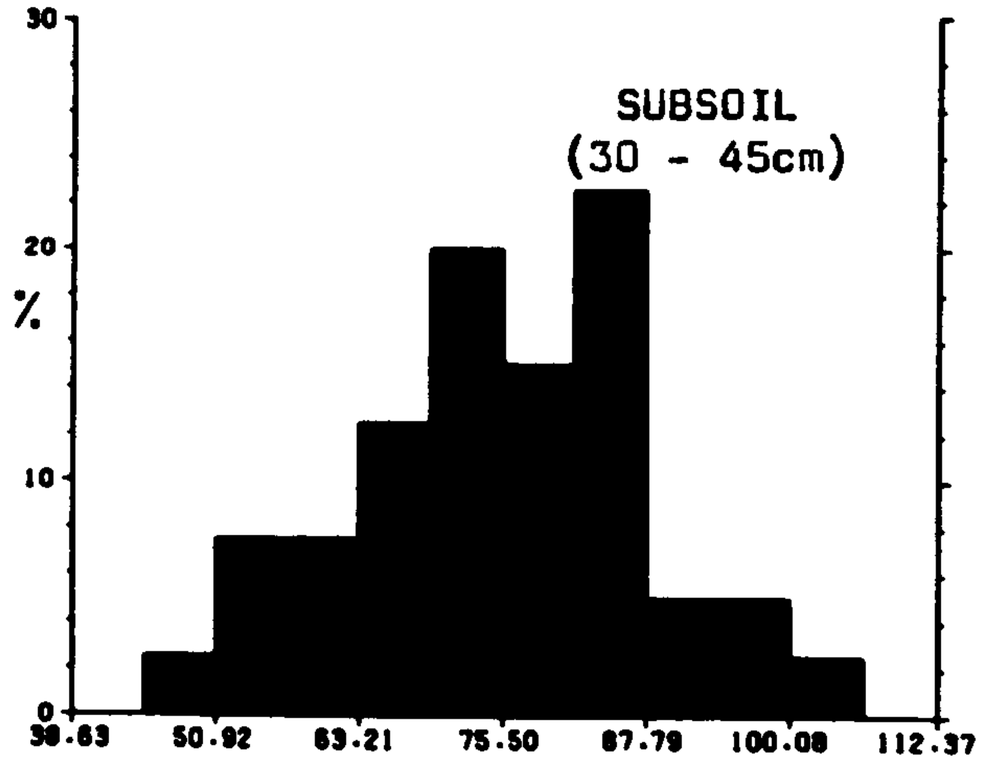
*** = Significant at .01 level

( ) = Negative Correlation.

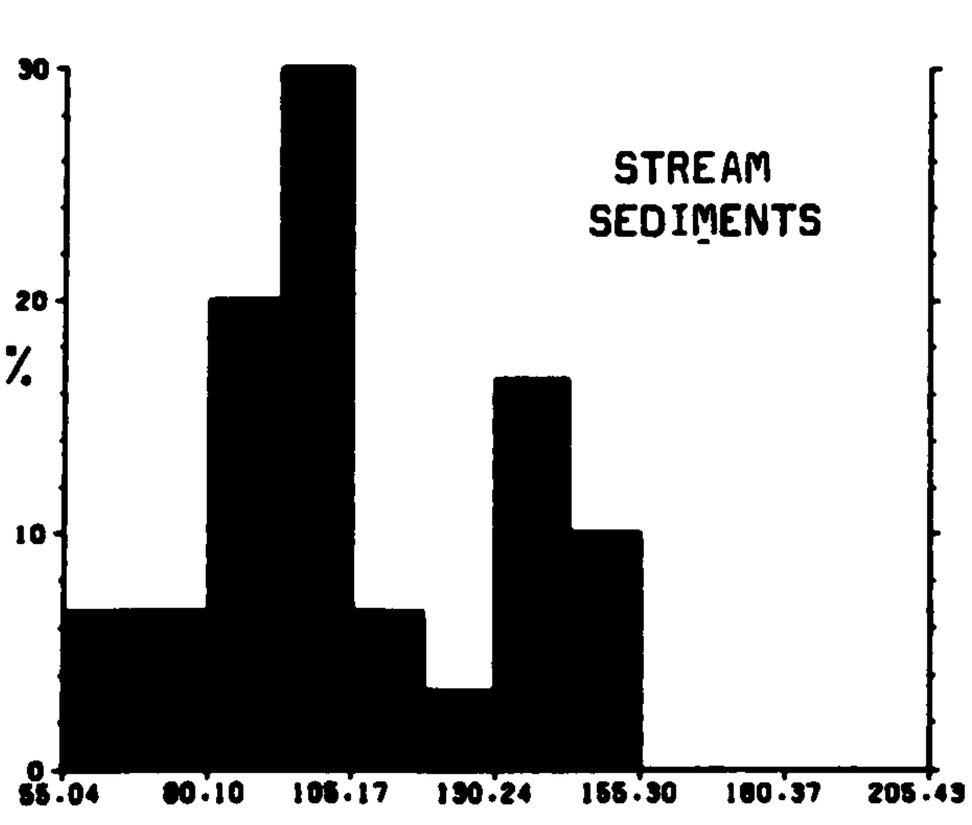
Fig. 12-6



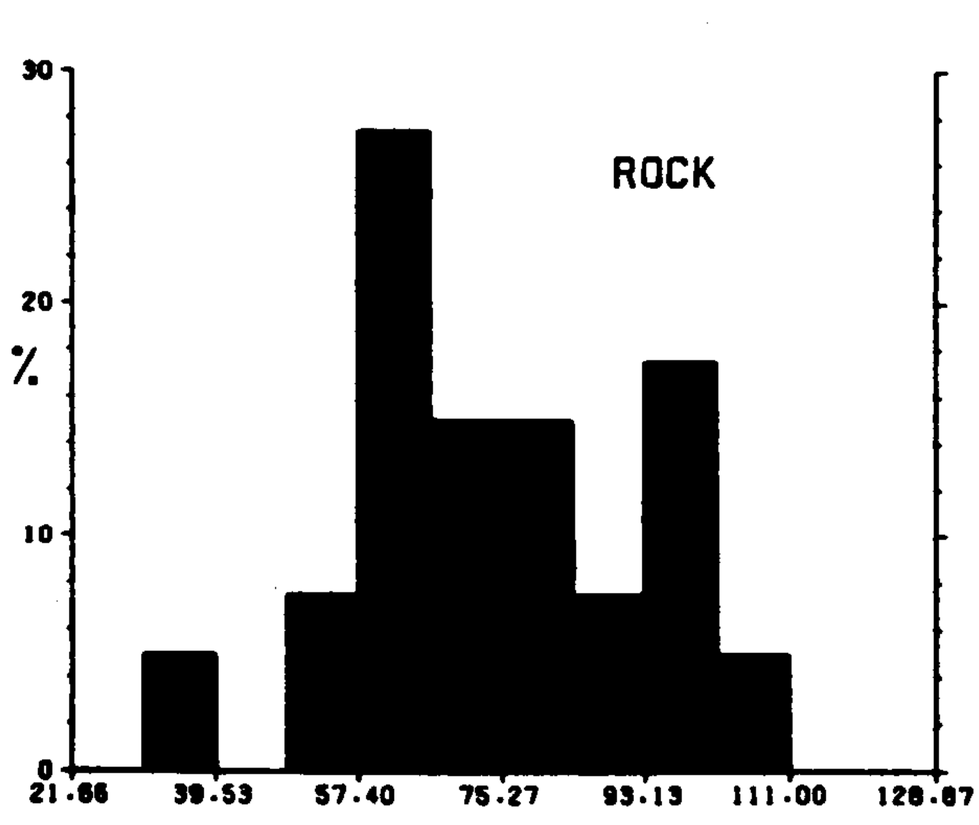
ZN conc (ppm)
NO. OF OBSERVATIONS = 40
MEAN = 77.40 STD DEV = 13.337



ZN conc (ppm)
NO. OF OBSERVATIONS = 40
MEAN = 75.50 STD DEV = 12.289



ZN conc (ppm)
NO. OF OBSERVATIONS = 30
MEAN = 105.17 STD DEV = 25.066



ZN conc (ppm)
NO. OF OBSERVATIONS = 40
MEAN = 75.27 STD DEV = 17.867

Histograms of the distribution of Zn in the rocks, soils and stream sediments derived from the Keuper Marl in the Worcestershire study area.

below 75ppm were common in the soils and rocks. The mean concentrations and ranges in the soils and rocks were very similar. Higher levels of Zn were found in the stream sediments where concentrations in excess of 80ppm were widespread (Fig. 12-6). Stream sediment samples with high concentrations of Zn had also high concentrations of Ca and Pb .

During weathering zinc enters into solution as soluble sulphates and chlorides (Turekian and Wedepohl, 1967). In this form it can be transported into the streams where it may be associated with the secondary carbonates, hydrous oxides and silicates. The results suggested that the higher concentrations in the sediments were due to the mobilisation from the soils and rocks to the surface drainage.

Inter-element correlations.

In the rocks Zn was significantly correlated with Mg, Al, Fe and organic matter(LOI) (Table 12-6b). Again, this suggested that Zn was associated with the clay minerals in the rocks. Zinc is capable of being adsorbed onto exchangeable sites in the clay mineral structure and it seemed likely that such a process may account for the relationship with the clay related elements in the rocks (Reddy et al. 1974).

In the topsoils the correlations with Mg, Al, Fe, Pb and Ni were weaker than that with organic matter(LOI) which was highly significant. In the subsoil apart from Mn and Co the correlations with other elements were highly significant.

In the stream sediments Zn was significantly correlated with most elements. Strong correlations occurred with Ca, Al, Fe, Pb, Ni

Table 12-7a Manganese Concentrations In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	40	741.7	163.1	22.0	500.0	1350.0
T/Soil	40	779.5	213.9	27.4	550.0	1200.0
S/Soil	40	738.2	187.7	25.4	450.0	1150.0
S/Sedt	30	948.3	346.2	36.5	500.0	1800.0

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.)

Table 12-7b Significance Of The Correlation Coefficients Between Mn And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	**	*	-	*	-		***	-	-	-	*	**
T/Soil	-	**	***	**	-		***	-	**	-	-	**
S/Soil	-	*	***	**	-		***	-	**	-	-	**
S/Sedt	-	-	-	**	-		***	-	-	-	-	-

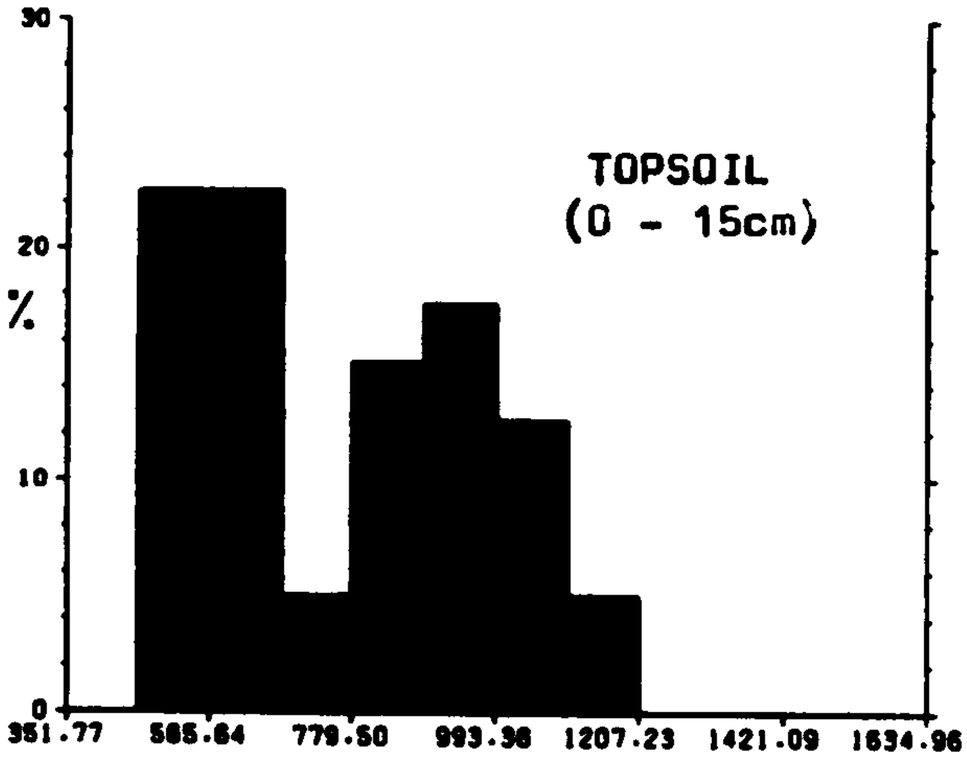
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

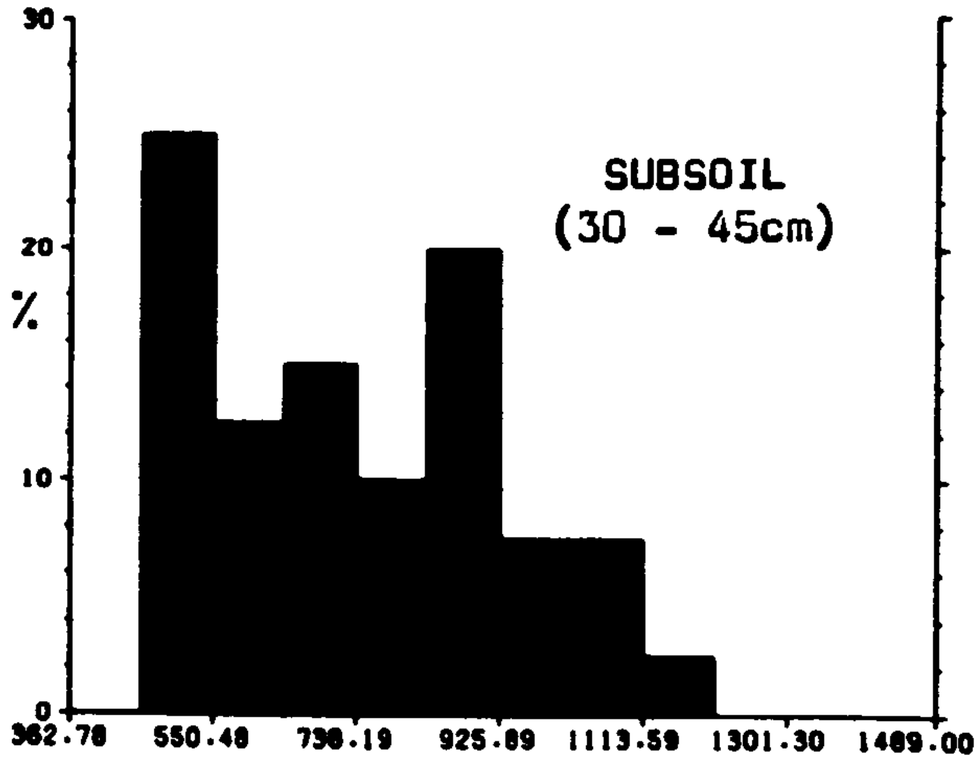
*** = Significant at .01 level

( ) = Negative Correlation.

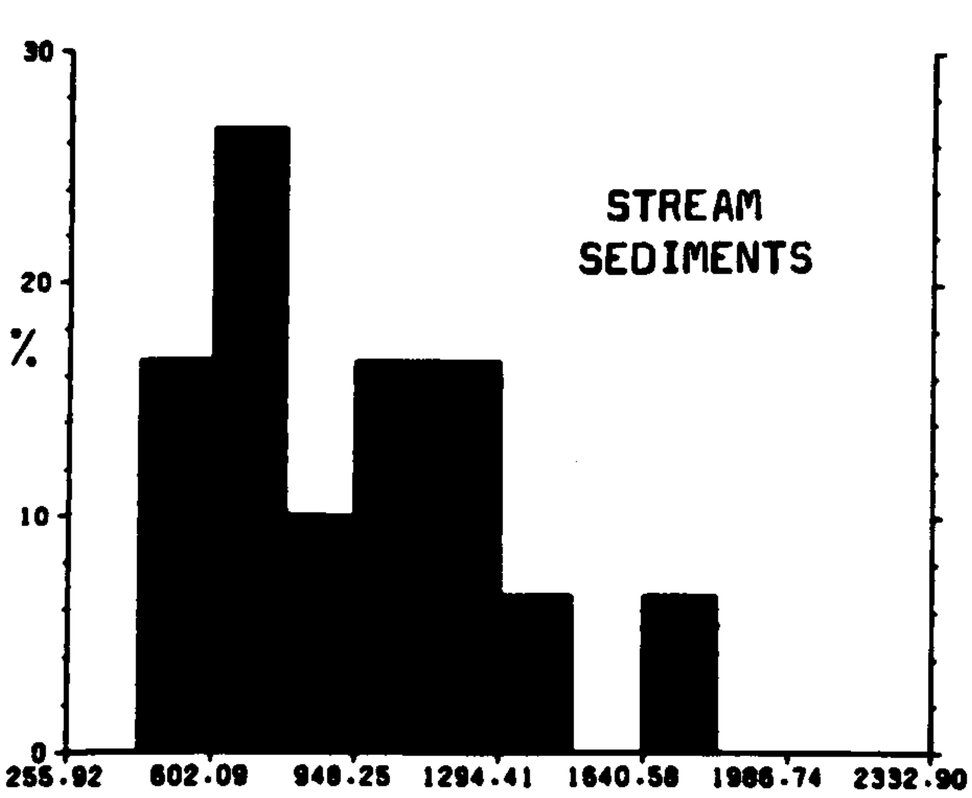
Fig. 12-7



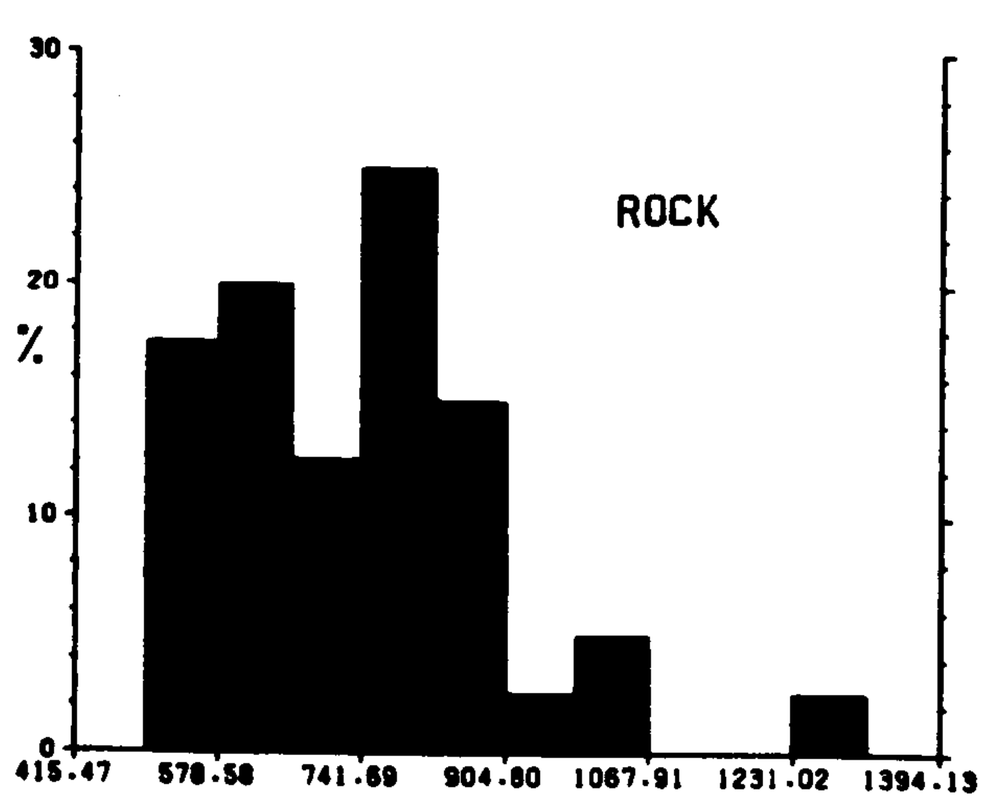
MN conc (ppm)
NO. OF OBSERVATIONS = 40
MEAN = 779.50 STD DEV = 213.865



MN conc (ppm)
NO. OF OBSERVATIONS = 40
MEAN = 738.19 STD DEV = 187.704



MN conc (ppm)
NO. OF OBSERVATIONS = 30
MEAN = 948.25 STD DEV = 346.163



MN conc (ppm)
NO. OF OBSERVATIONS = 40
MEAN = 741.69 STD DEV = 163.110

Histograms of the distribution of Mn in the rocks, soils and stream sediments derived from the Keuper Marl in the Worcestershire study area.

and Cu, while relatively weaker correlations were recorded between Zn with the organic matter(LOI) and pH. This indicated that Zn was associated not only with the clay minerals and secondary carbonates, but also the organic matter(LOI). The association with the clay minerals in the rocks and soils, the organic matter(LOI) in the soils and the secondary carbonates in the stream sediments seemed to be the dominant features of the distribution of Zn in the different media.

(f) Manganese.

Manganese concentrations in the calcareous sandstones of the Keuper Series were higher than those of the marl facies. Concentrations as high as 2600ppm were recorded in the more calcareous sandstone samples (Table 12-1). Manganese concentrations below 800ppm were common in the marl samples (Table 12-7a). The mean concentrations and ranges of Mn in the soils were similar to those of the rocks. In general, there was a tendency of Mn to be depleted in those samples that were waterlogged. Under the reducing conditions of the flooded environment the mobilisation of Fe and Mn is common. Leaching of Mn down the soil profile is not however a common feature of the Worcester series as the mean concentrations of Mn in the top and sub soils were only marginally different.

Concentrations of Mn in the stream sediments were higher than the rocks and soils. During weathering Mn like Fe enter into solution in the bicarbonate form (Rankama and Sahama, 1950). In such mobile form Mn can be redistributed in the soils and stream sediments. The oxidising conditions in the streams encourages the precipitation of Mn as hydrous oxides (Whitney, 1975). Such fixation processes may account for the higher concentrations found in the sediments.

Inter-element correlations.

In the rocks the strongest correlation was with Co (Table 12-7b). The oxides and hydroxides of Mn are weakly acidic and when freshly precipitated possess negative charges on their surfaces which can be neutralised by the adsorption of cations from solution, notably Co (Crawford, 1969). The correlations with Ca, Mg, Fe, organic matter(LOI) and pH in the rocks indicated that Mn may be associated with the carbonates possibly replacing Ca in such minerals. The relationship with the clay related elements in the soils was strong. In the stream sediments Mn was correlated significantly to only Fe and Co. It seemed likely that co-precipitation of Fe and Mn oxides occurred in the stream sediments (Chao and Sanzolone, 1973, Ponnamperuma et. al., 1969).

(g) Cobalt.

The mean concentration of Co in the sandstone facies (20.3ppm) was similar to that of the marl facies (19.7ppm). Unlike the marl facies where samples high in Mn had a correspondingly high Co concentration, the distribution of Co in the sandstones did not seem to follow that of Mn. Differences between the ranges of Mn in the soils and rock were small and the mean concentrations in the topsoil (18.1ppm) and subsoil(18.6ppm) were almost identical. The similarities in the ranges and coefficient of variation values in the soils and rocks suggested a stable form in the two media. The stream sediment mean concentration (23.2ppm) was only marginally higher than those of the soils and rocks. The histograms (Fig. 12-8) indicated that over 60% of the sediment samples had Co concentrations higher

Table 12-8a Cobalt Concentrations In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	40	19.7	4.1	20.8	12.0	26.0
T/Soil	40	18.6	4.9	26.3	9.0	27.0
S/Soil	40	18.1	4.0	22.1	10.0	29.0
S/Sedt	40	23.2	4.4	18.9	17.0	30.0

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.)

Table 12-8b Significance Of The Correlation Coefficients Between Co And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	***	**	*	**	-	***		-	*	-	-	*
T/Soil	-	**	***	**	-	***		-	**	-	-	**
S/Soil	-	**	***	**	-	***		-	**	-	-	**
S/Sedt	-	-	-	*	-	***		-	-	-	*	-

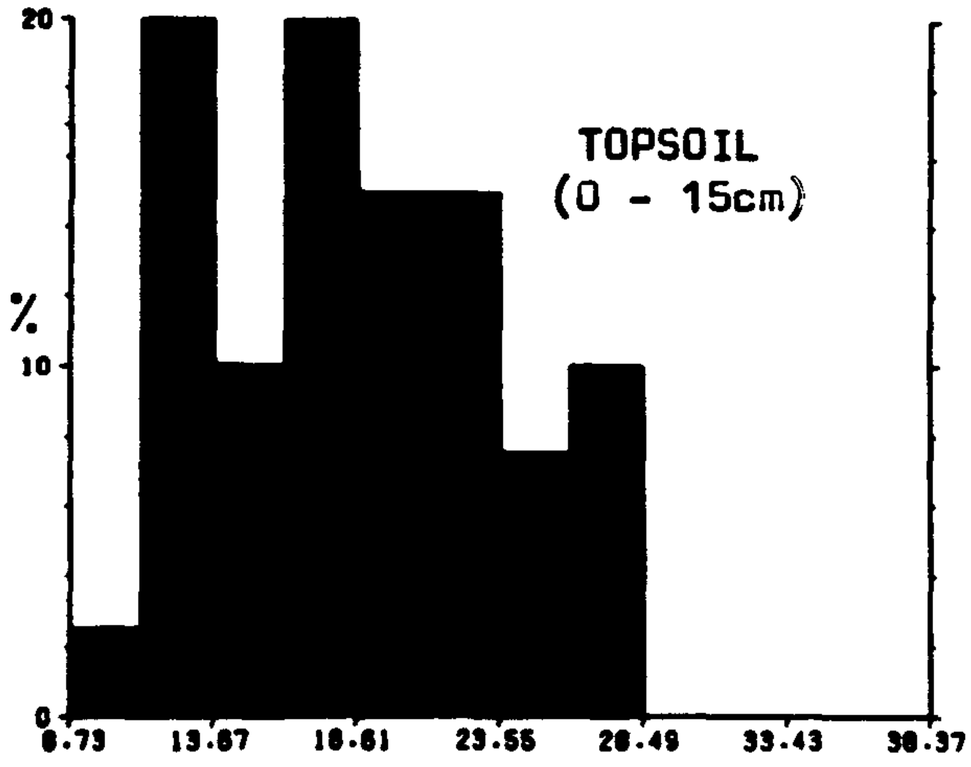
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

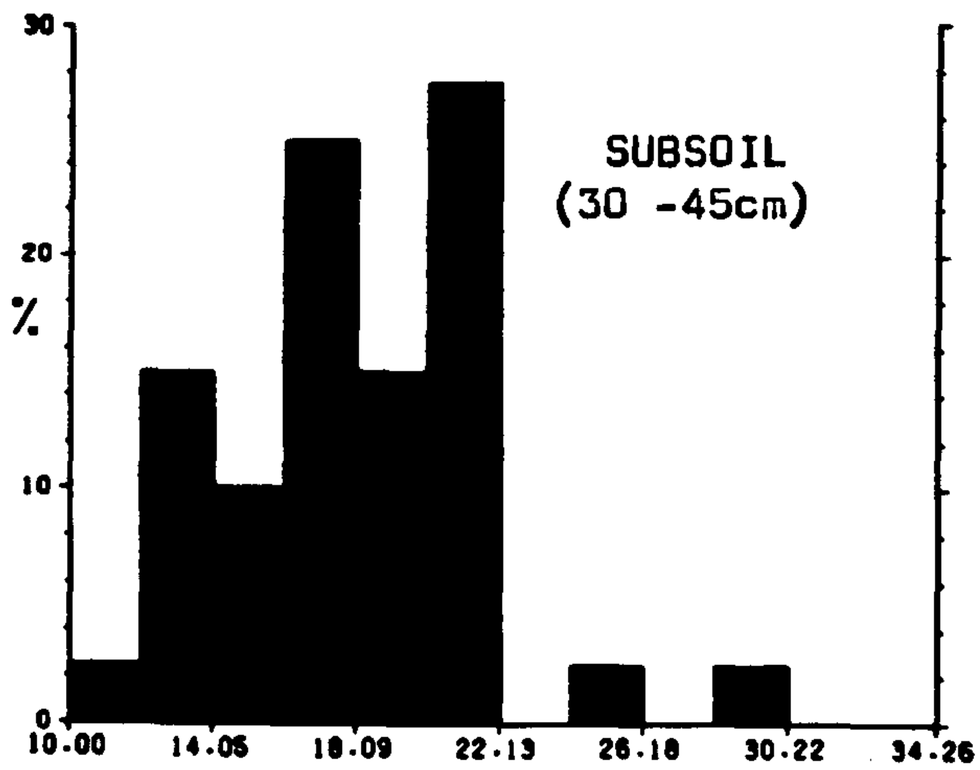
*** = Significant at .01 level

( ) = Negative Correlation.

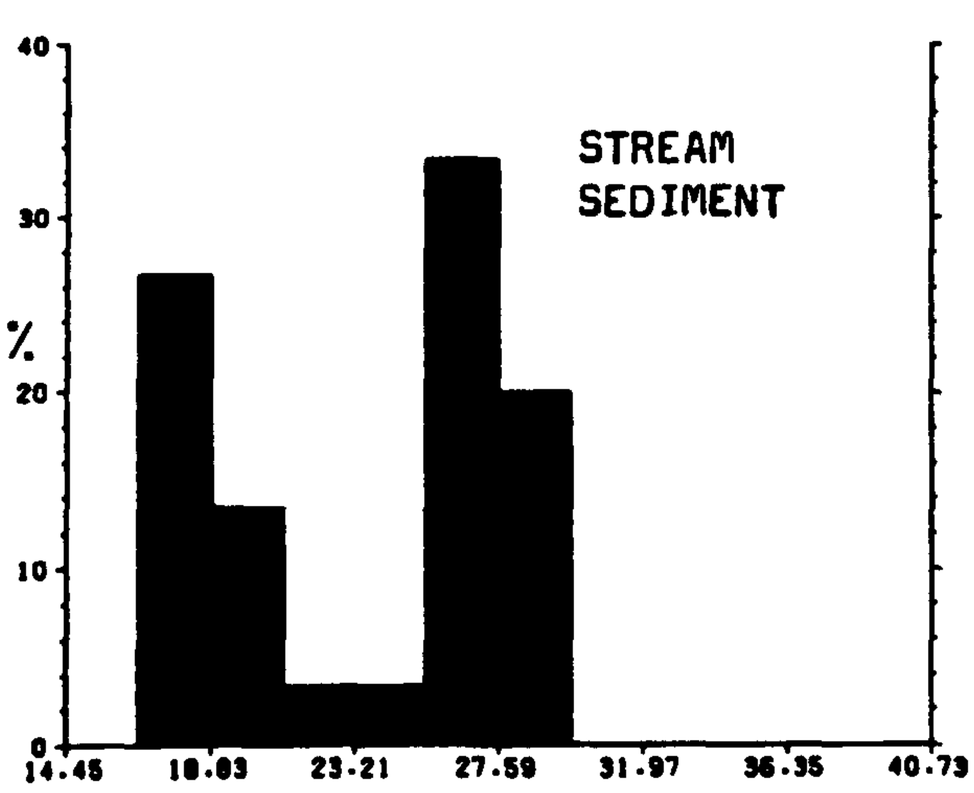
Fig. 12-8



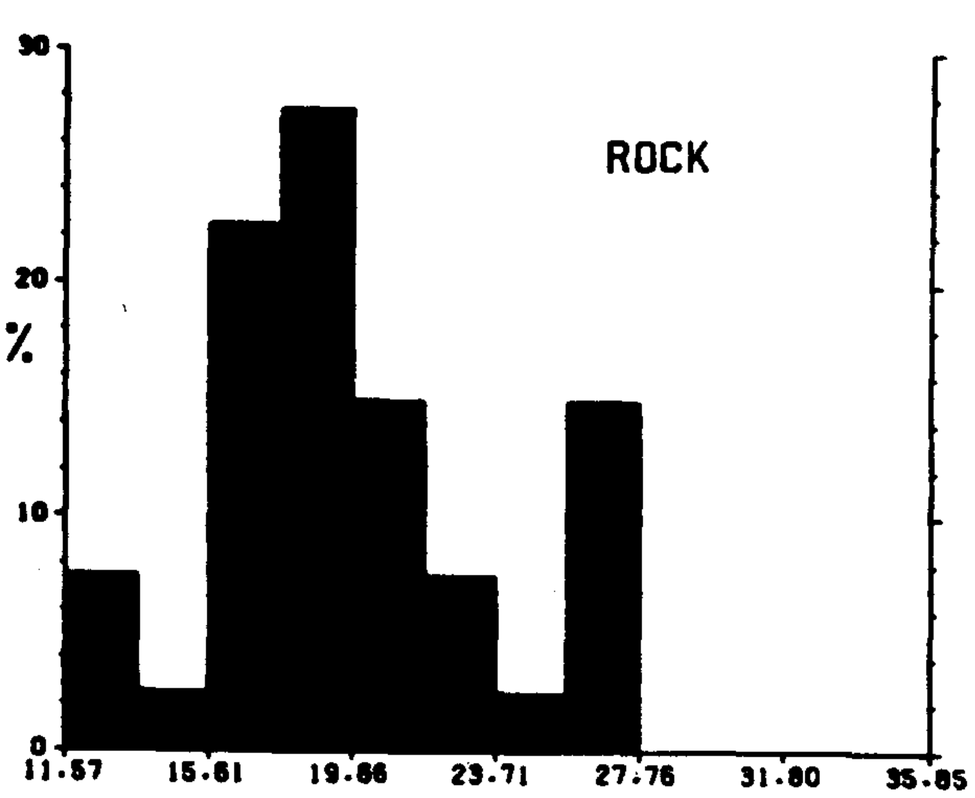
Co conc (ppm)
NO. OF OBSERVATIONS = 40
MEAN = 18.61 STD DEV = 4.940



Co conc (ppm)
NO. OF OBSERVATIONS = 40
MEAN = 18.09 STD DEV = 4.043



Co conc (ppm)
NO. OF OBSERVATIONS = 30
MEAN = 23.21 STD DEV = 4.380



Co conc (ppm)
NO. OF OBSERVATIONS = 40
MEAN = 19.66 STD DEV = 4.048

Histograms of the distribution of Co in the rocks, soils and stream sediments derived from the Keuper Marl in the Worcestershire study area.

than 25ppm.

During weathering Co remains in solution either as a bicarbonate or as colloidal hydroxide. In these forms it may be transported out of the system until conditions are met that encourage its fixation, usually by Mn oxides in the streams (Nichol et. al. 1967).

Inter-element correlations.

In all the media Co was significantly correlated to Mn and Fe (Table 12-8b). This was a further indication that the distribution of Co was controlled by the Mn oxides . The correlations between Ca, Mg, Al, Fe, Ni and the pH in the rocks suggested that part of the Co present may be related to the clay minerals.

Hodgson et al (1964) showed that Co is readily adsorbed in vacant sites in the clay minerals or it can displace Mg from the exchange sites in the clay mineral structure. The pH of the weathering environment, and the soils may also influence the relationship between Co and other fractions present in the respective media as the significant correlations with pH in the soils and rocks tended to suggest. The significant correlation with Mn in the soils suggested that in the soils the scavenging of Co by Mn-oxides was still playing an important role in the distribution of Co although in the soils the association with the clay related elements may also be important.

In the stream sediments Co was weakly correlated to Mn and the organic matter(LOI). This probably indicates a weak association with the organic matter.

Table 12-9a Lead Concentrations In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	40	32.4	6.9	21.3	19.0	50.0
T/Soil	40	34.7	5.7	16.5	18.0	46.0
S/Soil	40	33.5	6.5	19.4	21.0	49.0
S/Sedt	30	46.4	17.1	36.9	18.0	84.0

N = Number Of Samples.
S.D. = Standard Deviation.
C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 12-9b Significance Of Correlation Coefficients Between Pb And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	-	-	-	**	-	-		-	-	**	-
T/Soil	-	-	-	-	**	-	-		-	**	***	-
S/Soil	-	-	-	-	***	-	-		*	-	*	-
S/Sedt	***	-	-	-	***	-	-		**	**	**	-

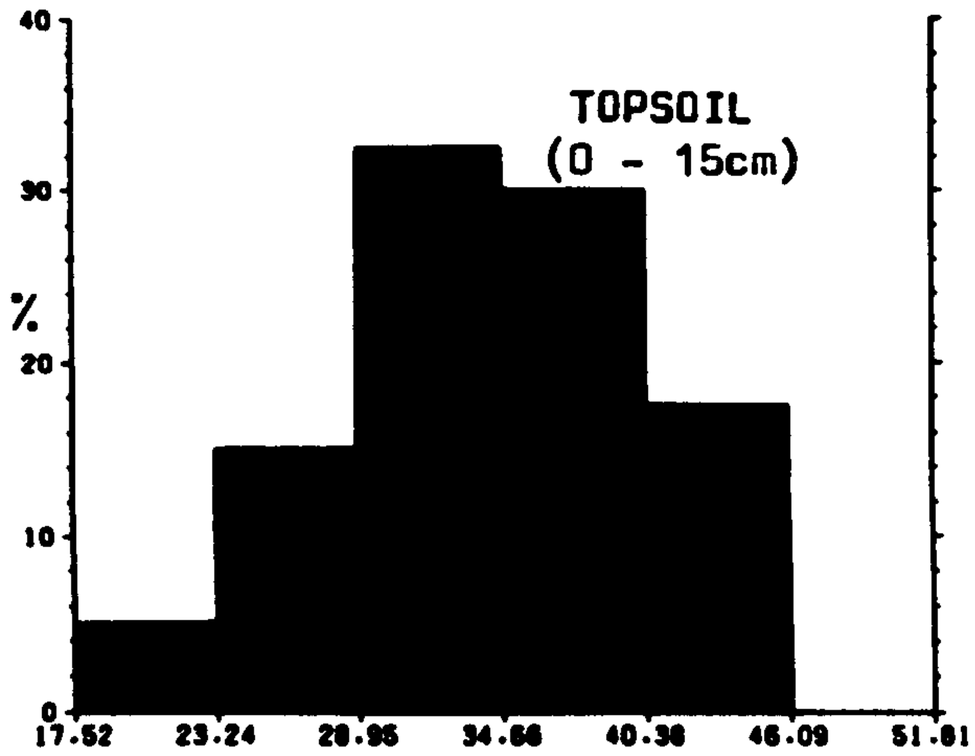
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

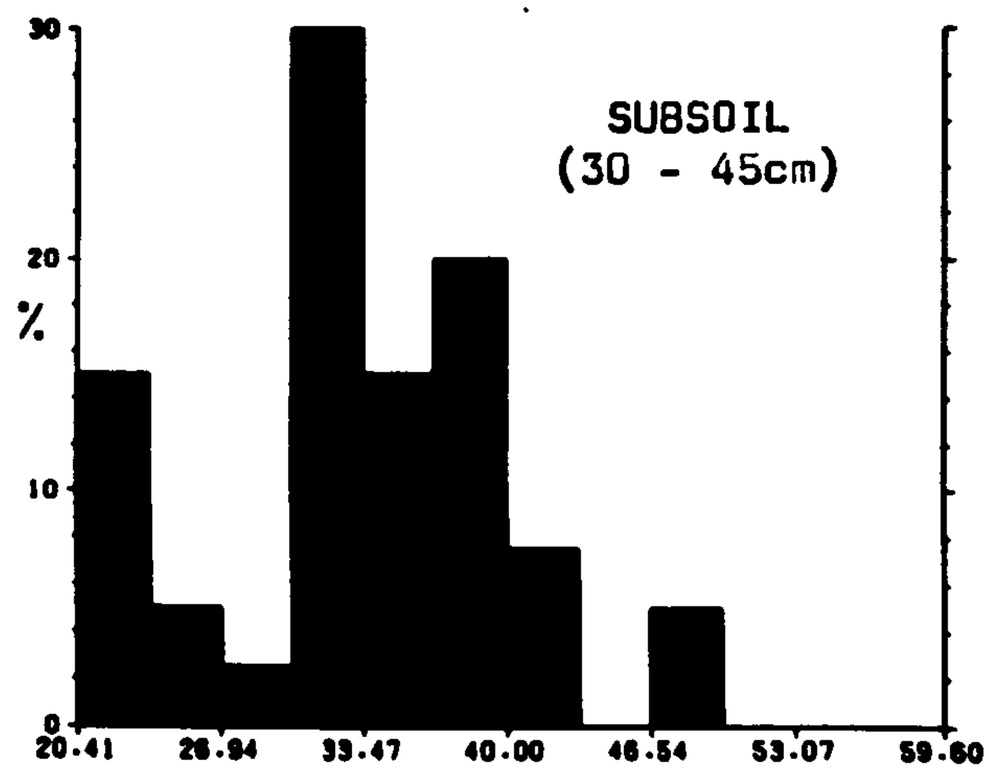
*** = Significant at .01 level

( ) = Negative Correlation.

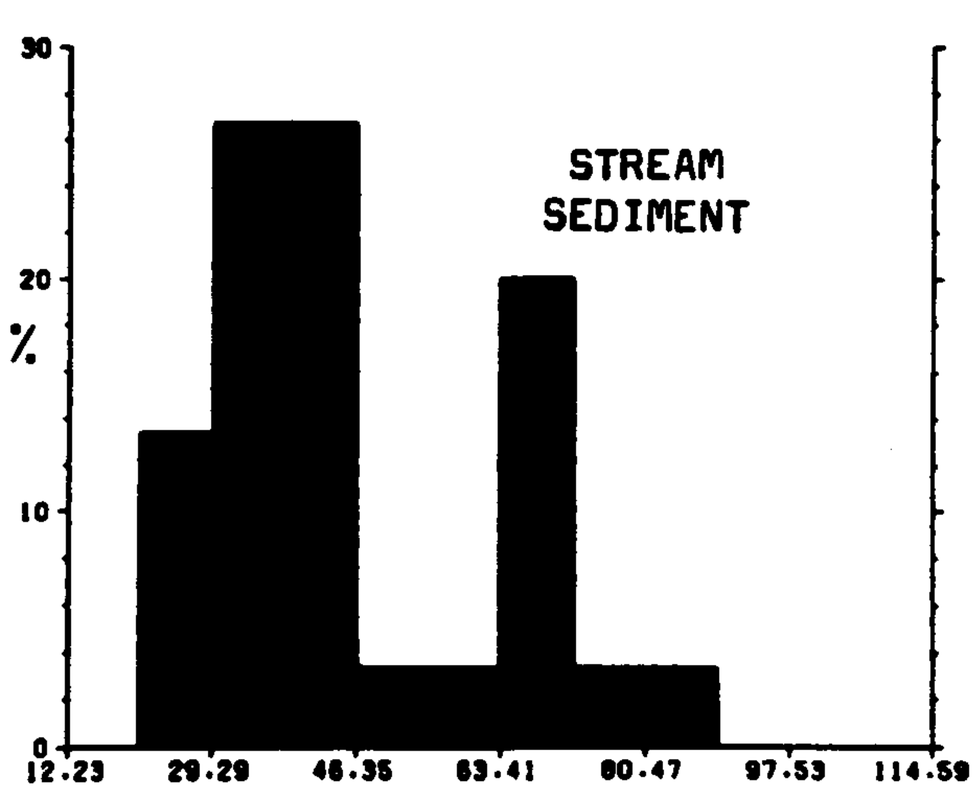
Fig. 12-9



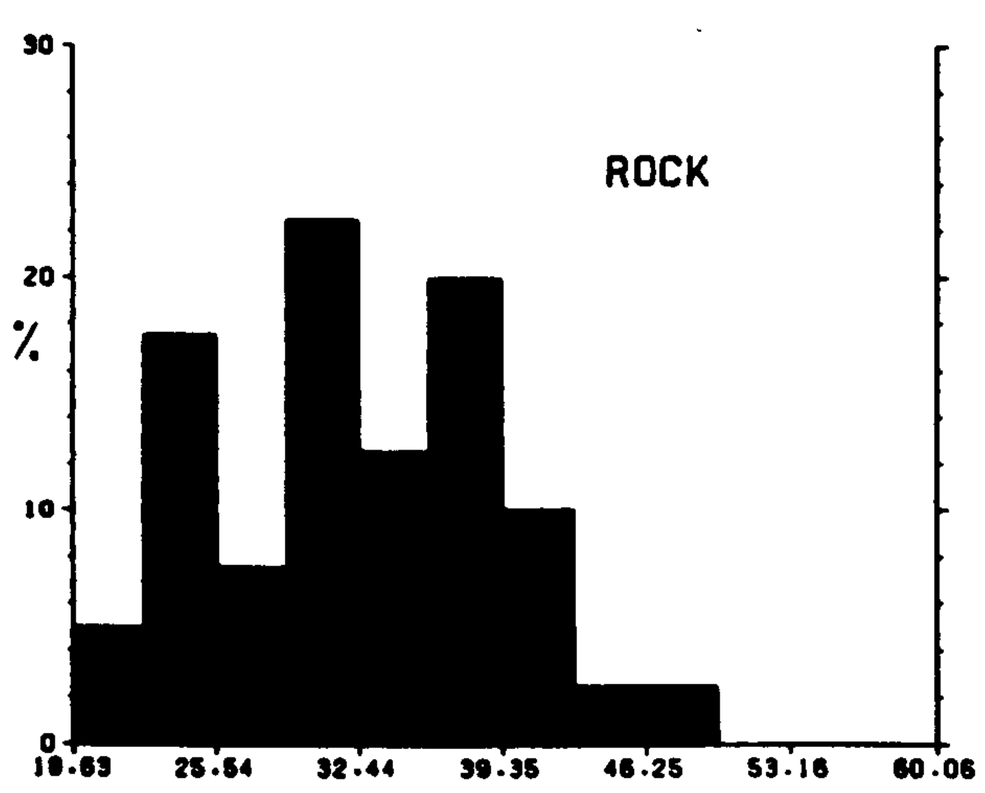
PB conc (ppm)
NO. OF OBSERVATIONS = 40
MEAN = 34.66 STD DEV = 5.715



PB conc (ppm)
NO. OF OBSERVATIONS = 40
MEAN = 33.47 STD DEV = 6.532



PB conc (ppm)
NO. OF OBSERVATIONS = 30
MEAN = 46.35 STD DEV = 17.060



PB conc (ppm)
NO. OF OBSERVATIONS = 40
MEAN = 32.44 STD DEV = 6.906

Histograms of the distribution of Pb in the rocks, soils and stream sediments derived from the Keuper Marl in the Worcestershire study area.

(h) Lead

The results of lead concentrations in the different media investigated are shown in (Table 12-9a) . The mean concentrations in the marl facies of the Keuper Series was twice as high as that of the sandstone facies (Table 12-1) . The mean concentration of Pb in the topsoil(34.7ppm) was only marginally higher than that of the subsoil(33.5ppm) and rock (32.4ppm). In general the histograms (Fig. 12-9) showed that there was a greater frequency of occurrence of the higher concentrations in the soil than in the rocks. There was an enhancement of Pb concentrations in the stream sediments with concentrations as high as 84ppm recorded in some samples. The coefficient of variation values indicated that variation was minimum in the topsoil(17%) and maximum in the stream sediments(37%).

Lead occurs in nature in the divalent and trivalent states with the former being dominant. During weathering it can be mobilised to form soluble and stable compounds. Its mobility in weathering is often restricted by the formation of secondary carbonates. Organic debris have been shown by a number of workers to be involved in the recycling of Pb (Swaine and Mitchell, 1960). Topsoil samples high in Pb had correspondingly high levels of organic matter(LOI). It seemed likely that the variety of the forms in which Pb can be fixed in the secondary environment may account for the enhanced levels of Pb in the stream sediments.

Inter-element correlation.

In all the media Pb was significantly correlated with Zn and

Table 12-10a Nickel Concentrations In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	40	37.9	8.8	23.2	22.0	55.0
T/Soil	40	33.1	6.8	20.5	16.0	45.0
S/Soil	40	35.5	8.1	22.8	20.0	50.0
S/Sedt	30	37.7	9.3	24.7	17.0	53.0

N = Number Of Samples.
S.D. = Standard Deviation.
C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 12-10b Significance Of Correlation Coefficients Between Ni And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	*	***	***	***	***	-	*	-		-	**	-
T/Soil	-	***	***	***	-	**	**	-		-	-	**
S/Soil	-	**	***	***	*	**	**	-		-	-	**
S/Sed	**	-	***	**	**	-	-	**		-	**	**

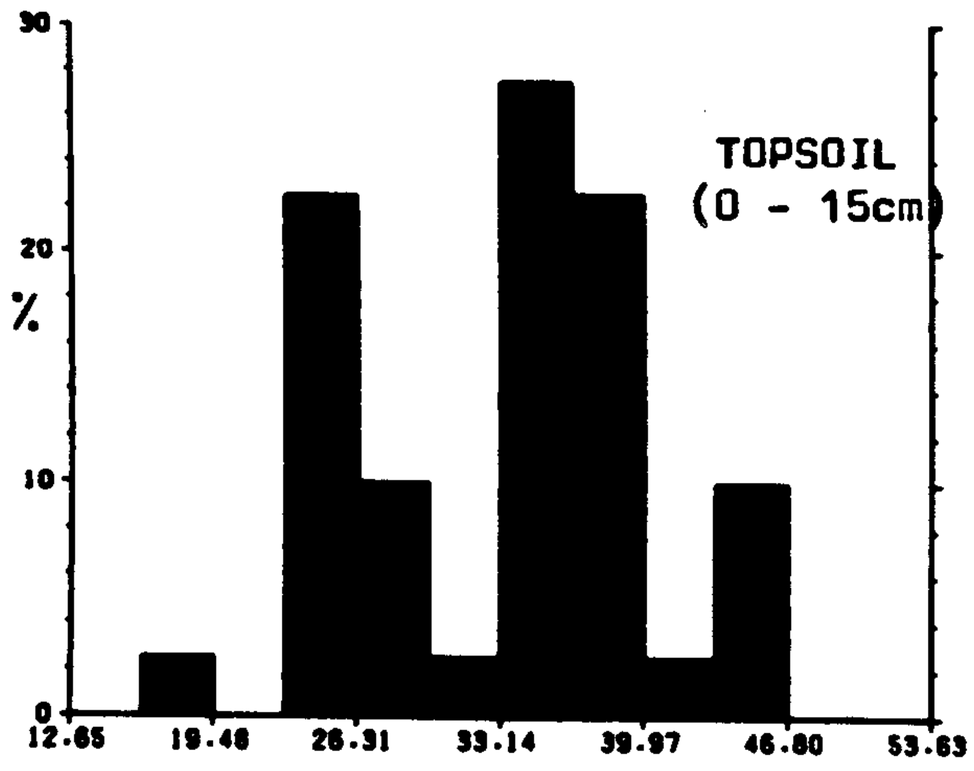
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

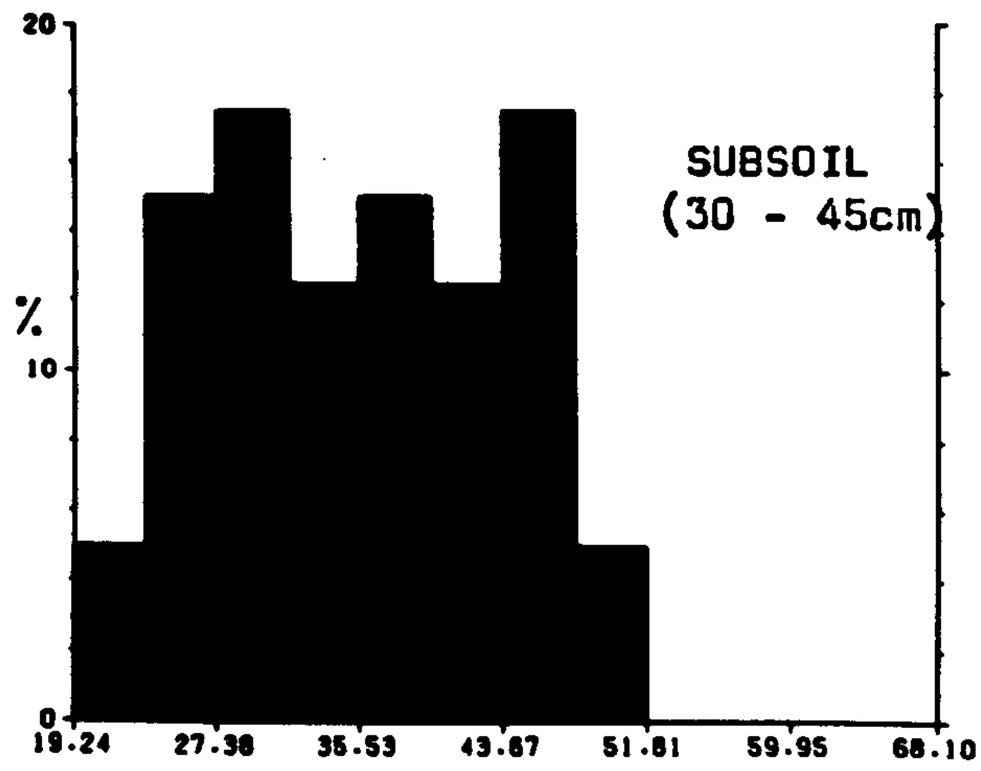
*** = Significant at .01 level

( ) = Negative Correlation.

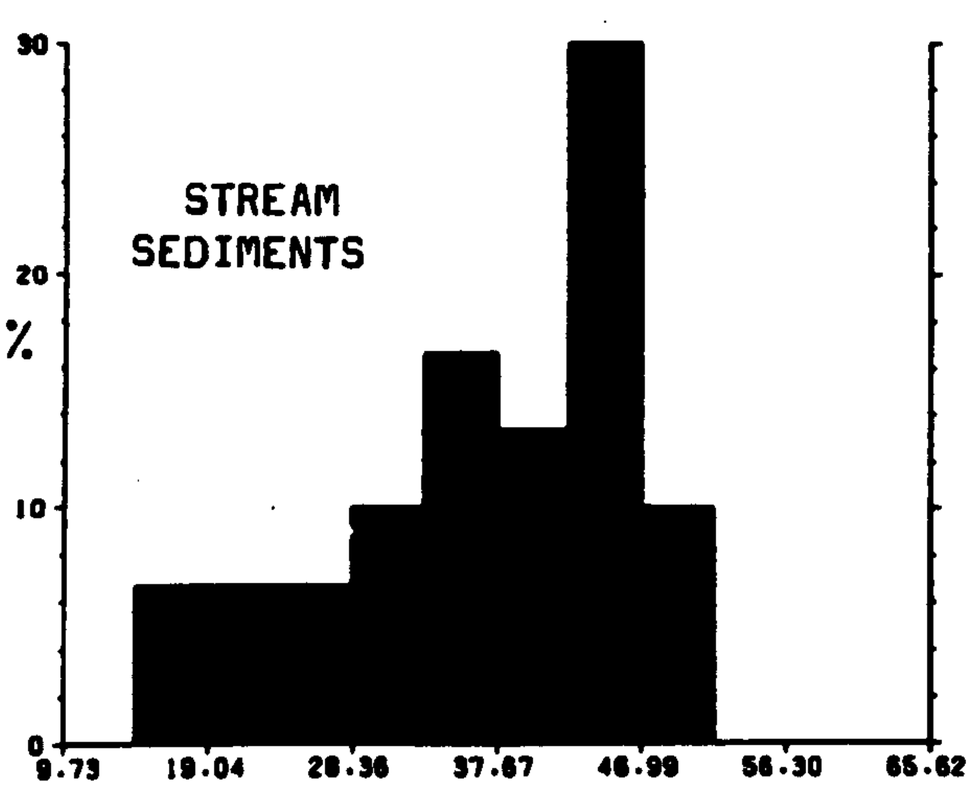
Fig. 12-10



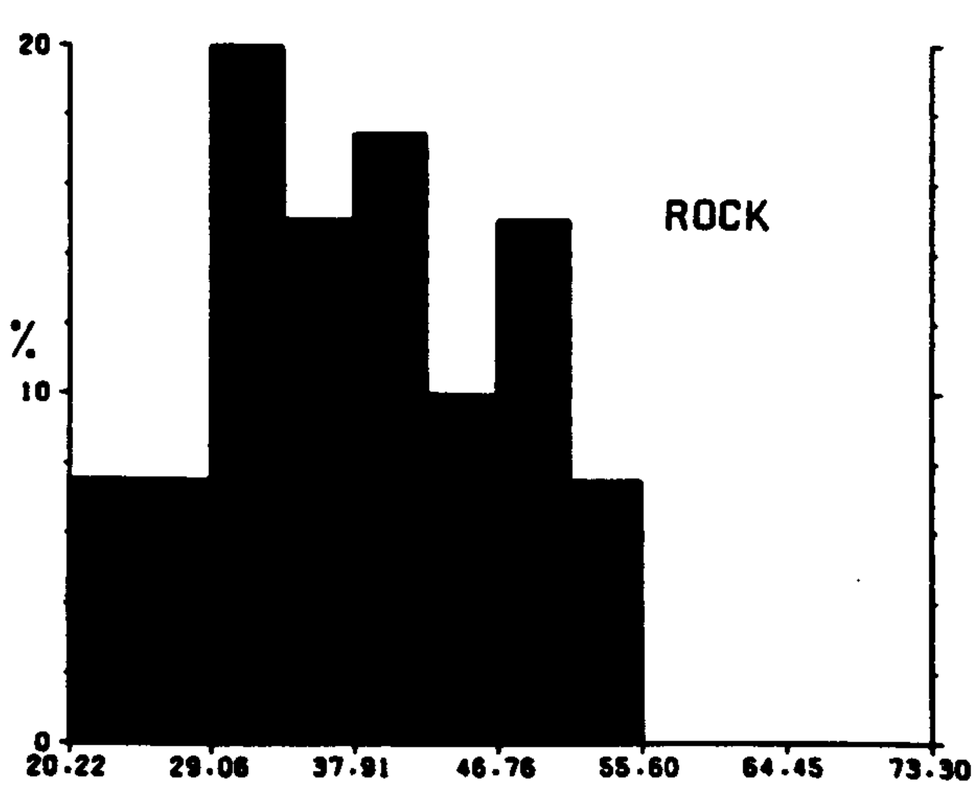
NI conc (ppm)
NO. OF OBSERVATIONS = 40
MEAN = 33.14 STD DEV = 6.830



NI conc (ppm)
NO. OF OBSERVATIONS = 40
MEAN = 35.53 STD DEV = 8.143



NI conc (ppm)
NO. OF OBSERVATIONS = 30
MEAN = 37.67 STD DEV = 9.315



NI conc (ppm)
NO. OF OBSERVATIONS = 40
MEAN = 37.91 STD DEV = 8.847

Histograms of the distribution of Ni in the rocks, soils and stream sediments derived from the Keuper Marl in the Worcestershire study area.

organic matter(LOI). The correlation with organic matter(LOI) was stronger in the topsoil and weaker in the subsoil (Table 12-8b). In the stream sediments there were weaker correlations with Ca, Ni and the organic matter(LOI).

The results suggested that organically bound Pb was the dominant feature of the distribution of Pb in the different media (Swanson et al. 1966). However, in the stream sediments where Pb was significantly correlated with Ca, there was the suggestion that Pb was also associated with the secondary carbonates.

(i) Nickel.

As with Pb the mean concentration of Ni in the marl facies was twice as high as that in the calcareous sandstones of the Keuper Series. A striking feature of the distribution of Ni in all the media investigated was the similarity of the means, ranges and coefficient of variation values (Table 12-10a). The histograms (Fig. 12-10) showed that there was an even distribution of Ni concentrations across the range in all the media although in the stream sediments there was a tendency of the higher concentrations to occur more frequently.

During weathering Ni is mobilised as soluble chlorides, nitrates and sulphates. Nickel in the divalent state is very stable in aqueous solutions hence can be transported great distances under proper geochemical conditions. In the soils, the mobility may be restricted by the formation of phosphates and carbonates or alternatively it can be adsorbed by clay minerals and organic matter. The results suggested that it was unlikely that the original form in which Ni was held in the rocks may have undergone any significant alteration in the soils and stream sediments.

Inter-element correlations.

In the rocks, Ni was strongly correlated to Mg, Al, Fe and Zn (Table 12-10b). This was interpreted as a relationship with the clay minerals. The weaker correlation with organic matter(LOI) indicated that some of the Ni present may be related to the organic matter . In both the top and subsoils the correlation with the clay related elements Mg, Al and Fe were highly significant. Nickel was also significantly correlated to the pH in the soils which indicated that the acidity was a contributory factor in determinig the geochemical pathway of Ni in the soils.

The geochemistry of Co and Ni are in most respects similar (Rankama and Sahama, 1950). The weak correlations with Mn and Co may indicate that Ni like Co may be incorporated by Mn oxides in the soils. In the stream sediments Ni was significantly correlated to Ca, Al, Fe, Zn, Pb and the organic matter(LOI). This suggested that in the stream sediments Ni may not only be related to the clay minerals but also the organic matter(LOI).

(j) Copper.

Copper concentrations displayed a distinct pattern of distribution with the low concentrations restricted to the sandstone facies of the Keuper Series. The range of Cu in the marl facies (Table 12-11a) was narrow with concentrations as low as 10 ppm found in some samples. The mean concentrations in the soils were slightly higher than those in the rocks while only minor differences occurred between Cu concentrations in the top and subsoils. This was reflected in the similarities of the coefficients of variation in the top and

Table 12-11a Copper Concentrations In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	40	16.9	3.9	23.0	10.0	28.0
T/Soil	40	18.0	5.0	27.9	11.0	38.0
S/Soil	40	17.8	4.4	24.7	9.0	30.0
S/Sedt	30	25.8	9.8	37.9	7.0	47.0

N = Number Of Samples.
S.D. = Standard Deviation.
C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 12-11b Significance Of Correlation Coefficients Between Cu And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	-	-	-	-	-	-	-	-		**	-
T/Soil	*	-	-	-	-	-	-	**	-		-	**
S/Soil	**	-	-	-	***	-	-	**	-		**	-
S/Sedt	**	-	-	-	***	-	-	**	-		**	-

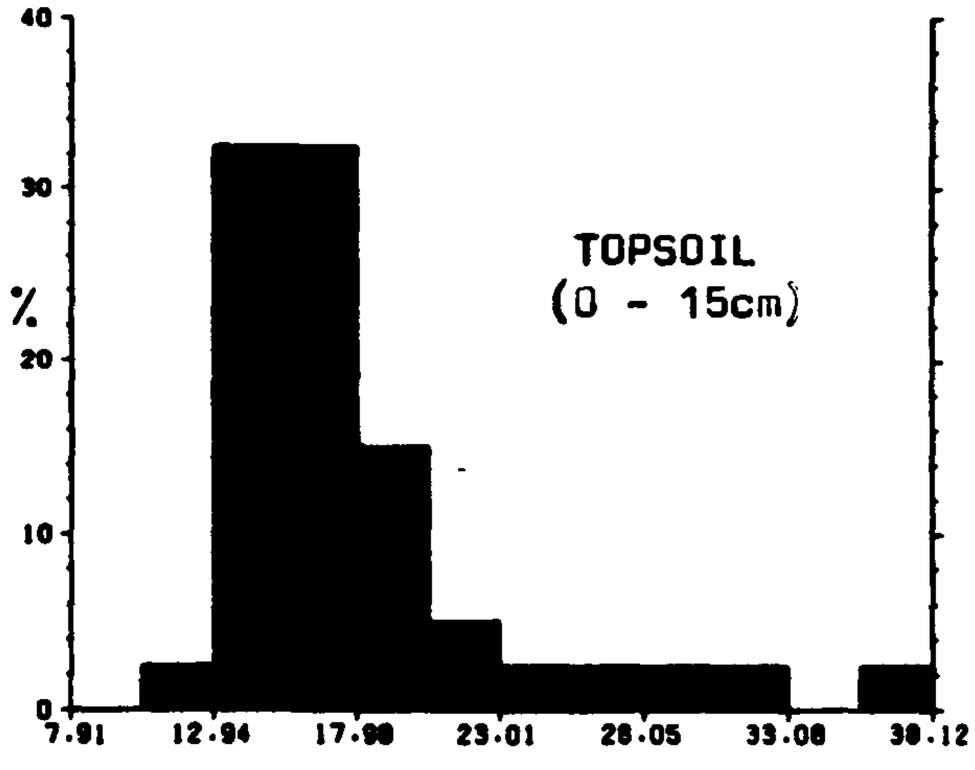
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

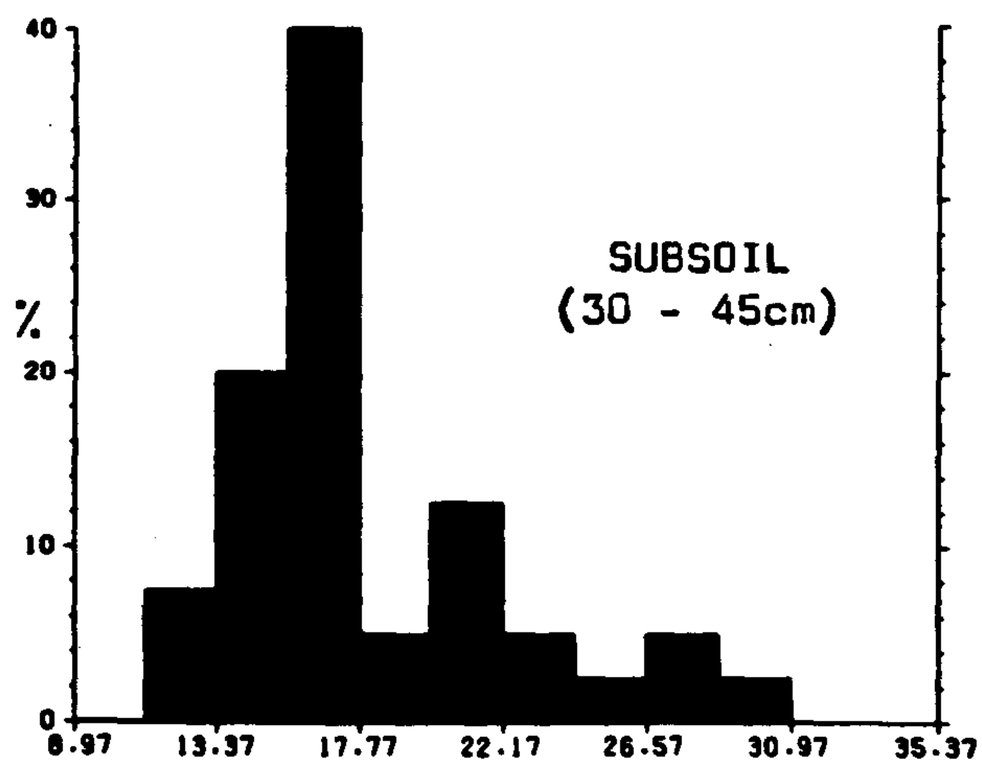
*** = Significant at .01 level

( ) = Negative Correlation.

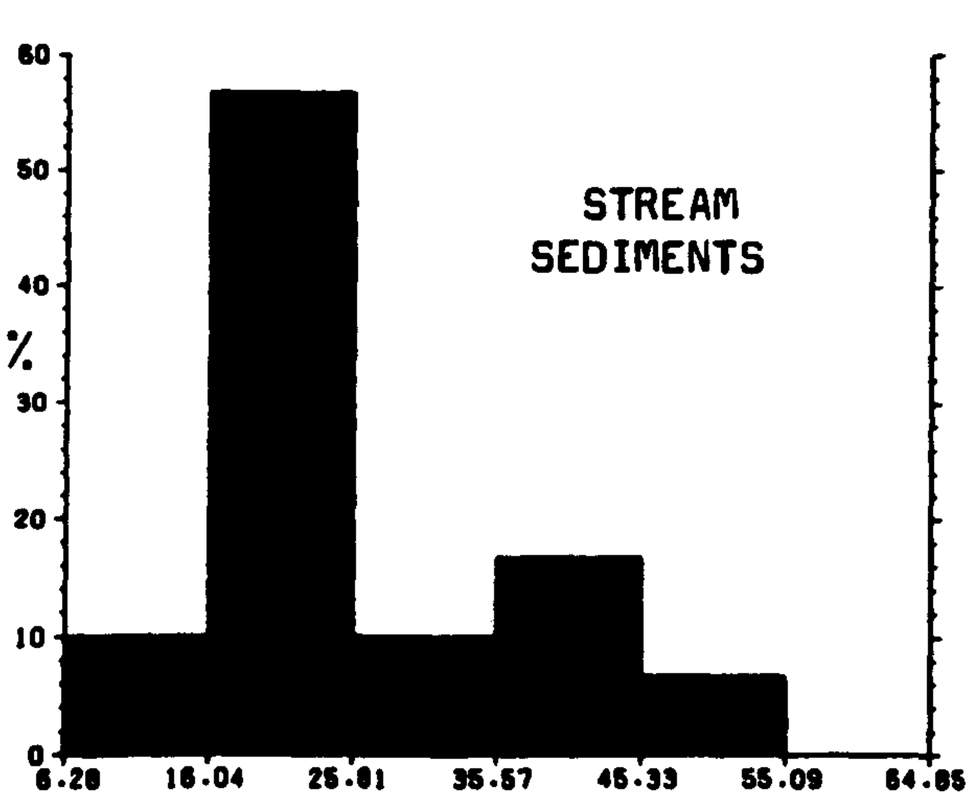
Fig. 12-11



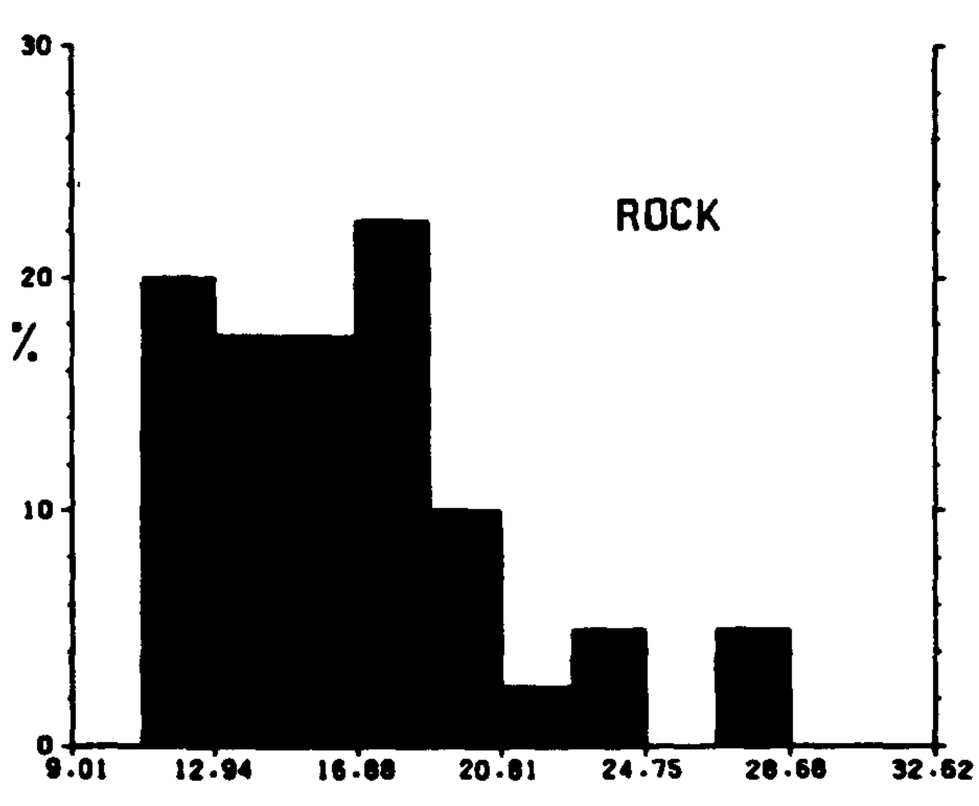
CU conc (ppm)
NO. OF OBSERVATIONS = 40
MEAN = 17.98 STD DEV = 5.034



CU conc (ppm)
NO. OF OBSERVATIONS = 40
MEAN = 17.77 STD DEV = 4.400



CU conc (ppm)
NO. OF OBSERVATIONS = 30
MEAN = 25.81 STD DEV = 9.762



CU conc (ppm)
NO. OF OBSERVATIONS = 40
MEAN = 16.88 STD DEV = 3.935

Histograms of the distribution of Cu in the rocks, soils and stream sediments derived from the Keuper Marl in the Worcestershire study area.

subsoils. Some topsoil samples displayed minor depletions of Cu compared to the subsoils, however the similarities in the mean concentrations and the ranges suggested that little mobilisation of Cu occurred in the soils. The histograms (Fig. 12-11) showed that lower concentrations occurred more frequently in the soils. The range in the stream sediments (7-47ppm) was wider than those of the rocks and soils with the coefficient of variation value indicating that there was greater variation in the stream sediments. This was reflected by the higher mean concentration.

During weathering, the mobility of Cu is generally controlled by the solubilities of its salts, such as sulphates, phosphates,hydroxides and carbonates. In the soils Cu can be adsorbed by organic matter to form chelates or co-ordinated compounds (Himes and Barber, 1957; Davies et. al. 1969). It can also be adsorbed by the hydrous oxides (Taylor et. al. 1964). The results did not suggest significant leaching and redistribution of Cu in the soils.

Inter-element correlations.

In the rocks Cu was significantly correlated to the organic matter(LOI) (Table 12-11b). This indicated that organically bound Cu was an important form of fixation of Cu in the rocks. In the stream sediments and soils Cu was significantly correlated to Ca and Pb.

It seemed from the results that the significant correlations with Ca and Pb may indicate an association with the secondary carbonates in the sediments and such a process may account for the increased concentrations and variation observed in the stream sediments. In the topsoils the significant correlation with organic matter(LOI) indicated that as in the rocks organically bound Cu was

Table 12-12a Percent Organic Matter Concentrations In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	N	Mean (%)	S.D.	C.V.	Range Min (%)	Max (%)
Rock		5.4	1.3	22.2	4.4	7.2
T/Soil	40	8.3	3.0	36.1	4.9	15.0
S/Soil	40	6.2	1.6	25.8	4.0	12.6
S/Sedt	40	6.7	1.9	28.4	2.0	11.0

N = Number Of Samples.
S.D. = Standard Deviation.
C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 12-12b Significance Of Correlation Coefficients Between Percent Organic Matter And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	-	*	**	**	*	-	**	**	*		-
T/Soil	*	-	-	-	**	-	-	***	-	***		-
S/Soil	-	-	*	-	-	-	-	-	-	-		*
S/Sedt	**	-	**	-	**	-	-	**	**	*		*

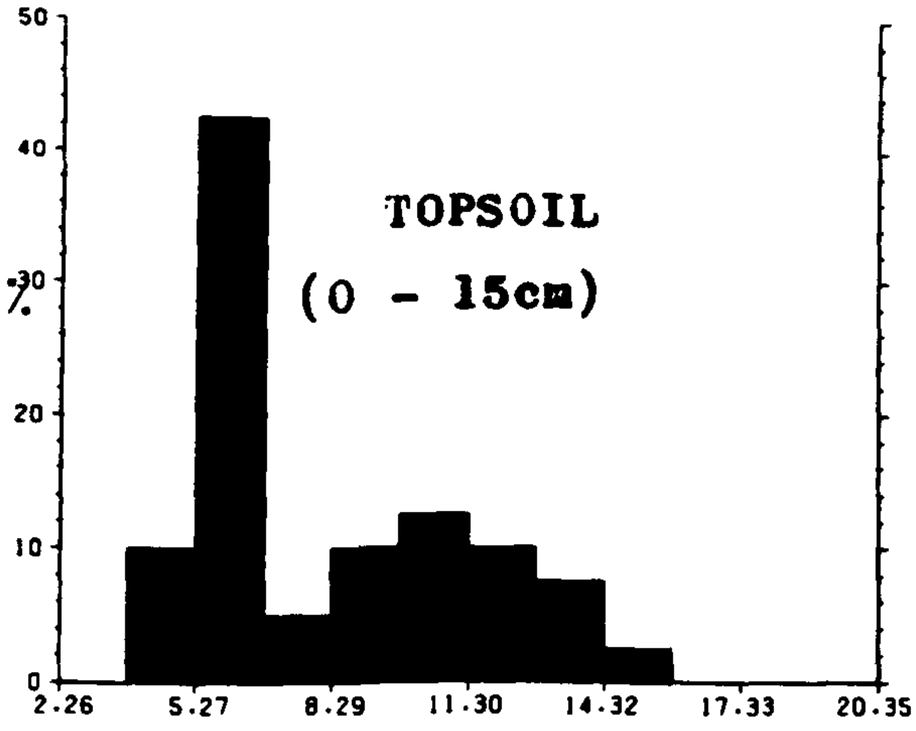
Level Of Significance - = Not Significant * = Significant at .10 level

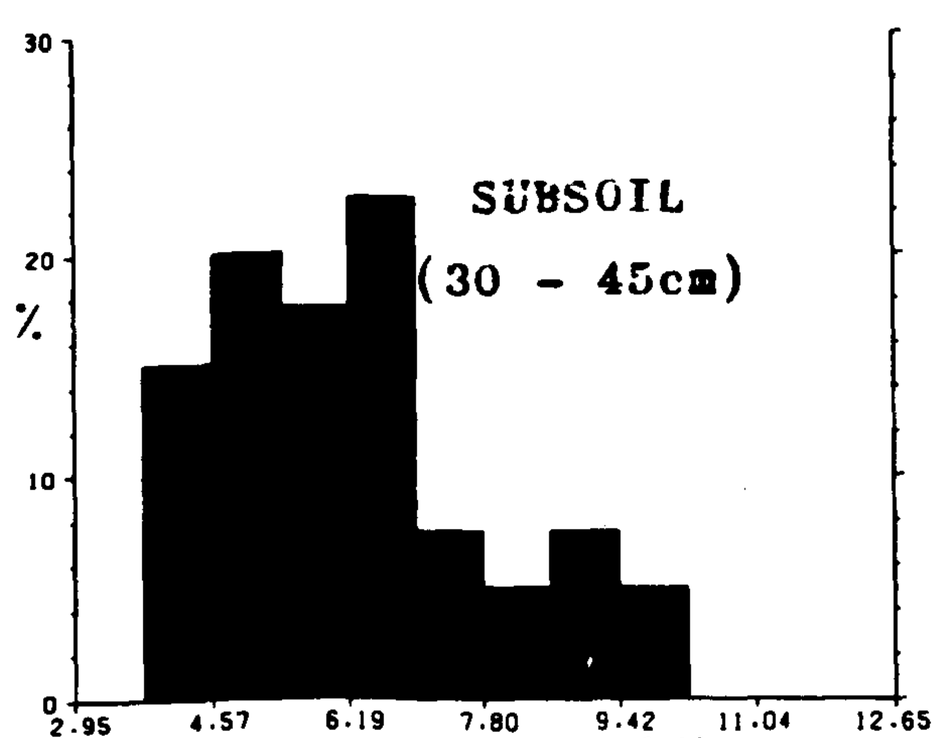
** = Significant at the .05 level

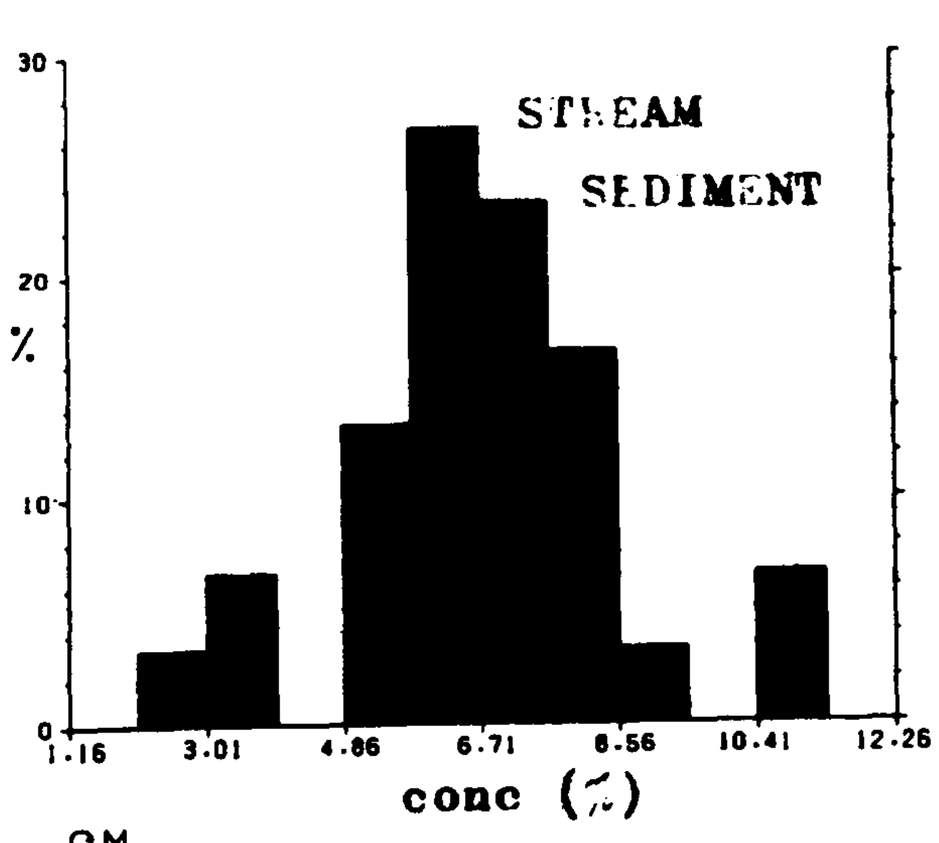
*** = Significant at .01 level

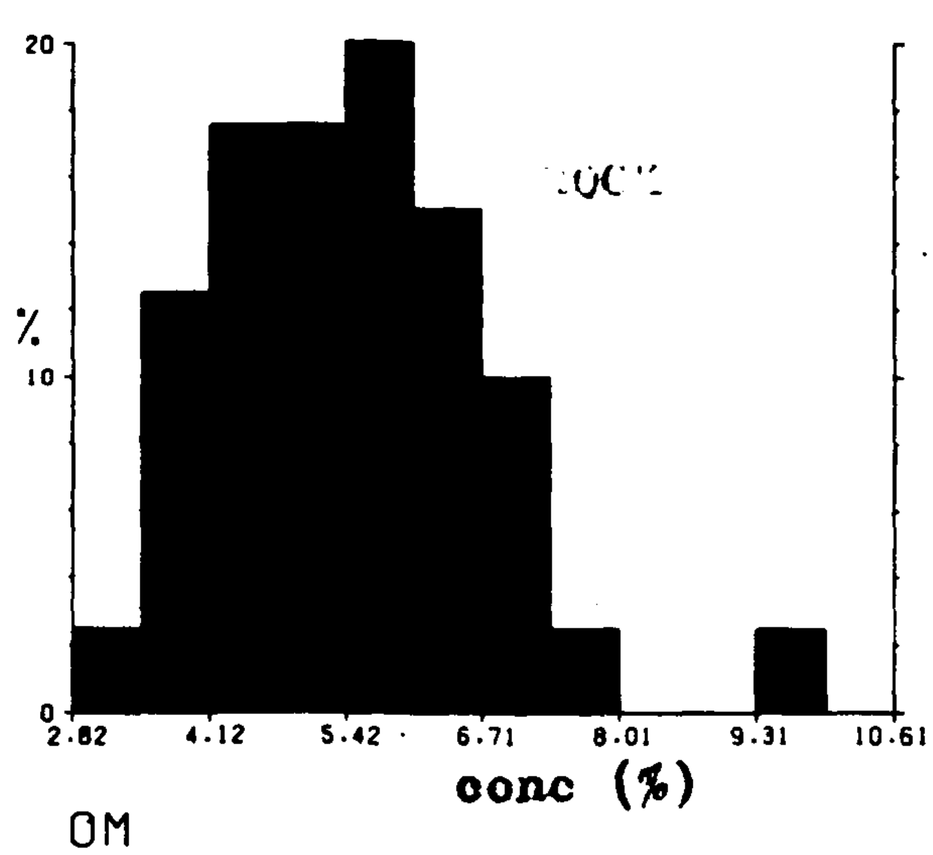
( ) = Negative Correlation.

Fig. 12-12









Histograms of the distribution of organic matter (LOI) in the rocks, soils and stream sediments derived from the Keuper Marl in the Worcestershire study area.

important.

(k) Loss on Ignition.

Measurements of the organic matter(LOI) were made by the loss on ignition method described in Chapter 3 . In the rocks organic matter(LOI) levels ranged from 3.4% to 9.2% with a mean level of 5.4%. There was enhancement of organic matter(LOI) levels in the topsoil compared to the subsoil. In general, the levels in the stream sediments were similar to those in the subsoils. The coefficients of variation showed that there was a general tendency towards an increase in the variation of organic matter(LOI) in the soils particularly in the topsoils.

Organic matter plays a major role in the fixation of a range of cations in the geochemical environment. In the colloidal state it may carry negative charges which may be neutralised by the adsorption of cations (Randhawa et al. 1965). They may form true chelates or may be bound to clay minerals to form organo-clay complexes. Organic acids in the weathering are powerful agents of weathering. The enhancement of organic matter(LOI) in the topsoils may indicate the accumulation of plant debris.

Correlations with elements.

In the rocks organic matter(LOI) was significantly correlated to Al, Fe, Zn, Mn, Pb, Ni and Cu. Only the significant correlations with Zn, Pb and Cu persisted in the topsoil and stream sediments. Further correlation with Ca was observed in the topsoil and stream sediments, while in the subsoil apart from the weak correlations with

Table 12-13a pH Levels In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	N	Mean	S.D.	C.V.	Range Min	Max
Rock	40	6.4	0.5	7.0	5.0	7.2
T/Soil	40	6.2	0.5	8.7	5.1	7.3
S/Soil	40	6.3	0.4	6.7	5.2	7.1
S/Sedt	30	7.2	0.3	3.6	6.4	7.3

N = Number Of Samples.
S.D. = Standard Deviation.
C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 12-13b Significance Of Correlation Coefficients Between pH And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Keuper Marl In Worcestershire

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	*	-	-	-	-	*	**	-	-	-	-	
T/Soil	*	***	***	**	-	**	**	-	**	-	-	
S/Soil	***	**	***	**	**	**	**	-	**	-	*	
S/Sedt	-	-	**	-	**	-	-	-	**	-	*	

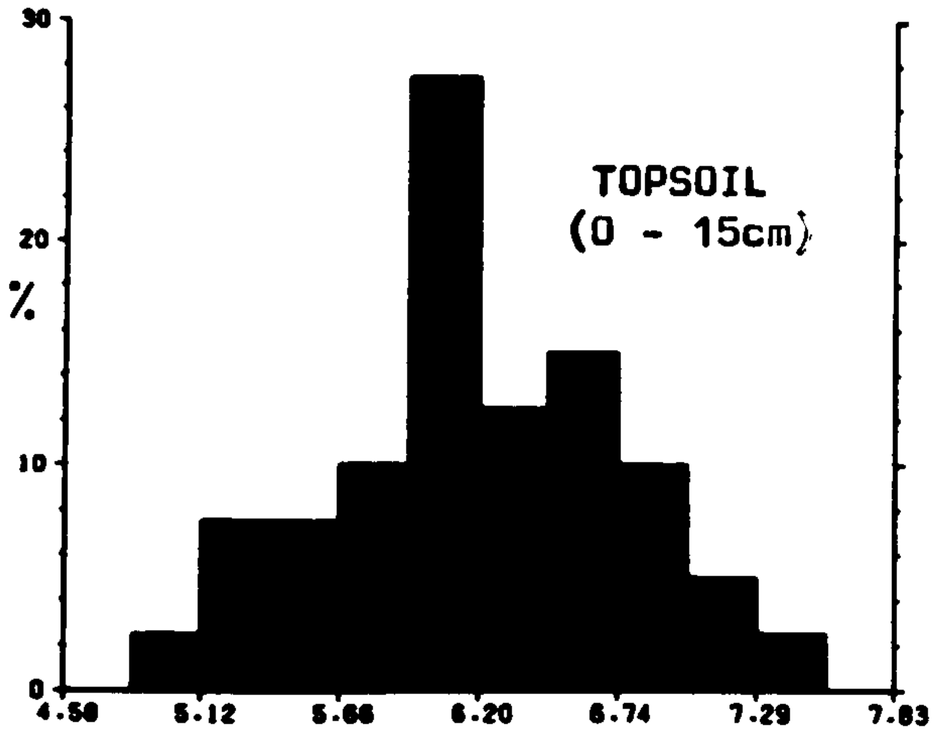
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

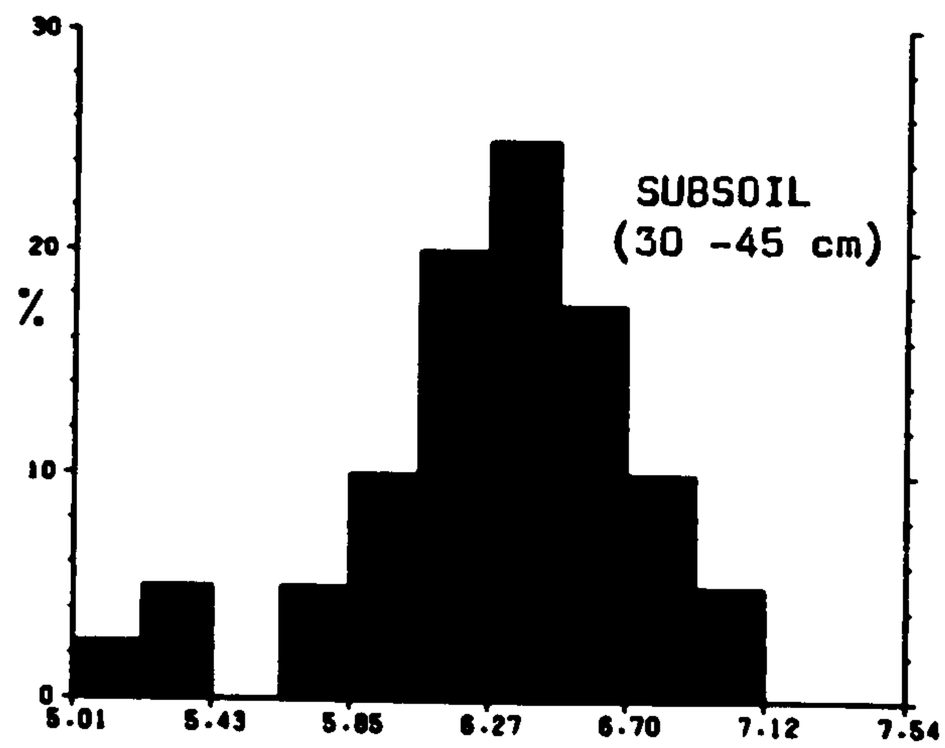
*** = Significant at .01 level

( ) = Negative Correlation.

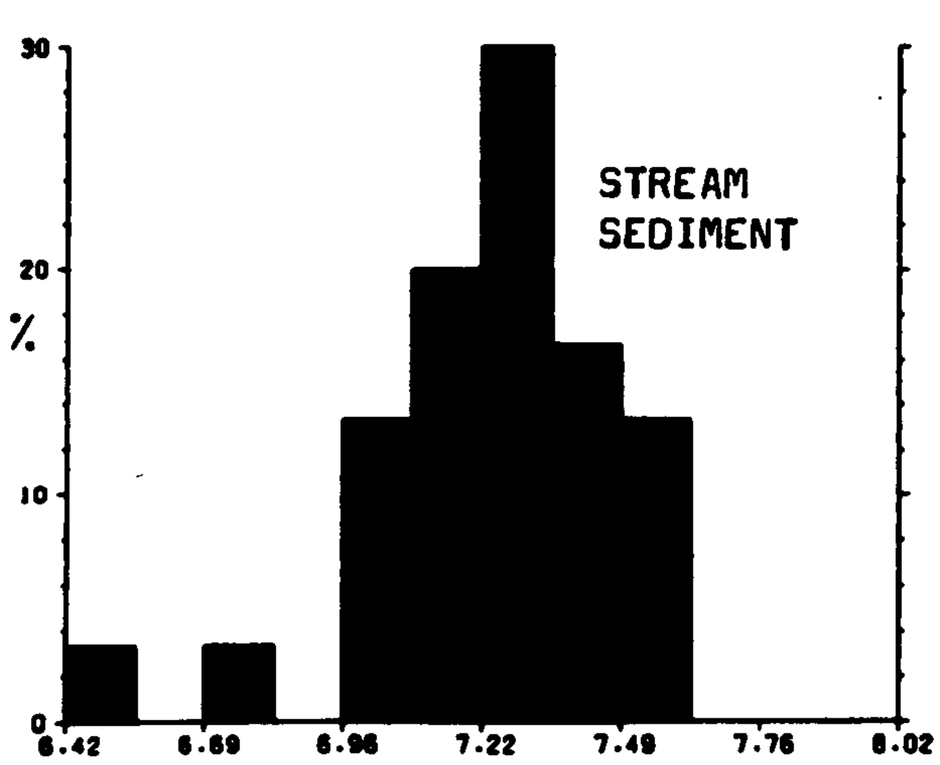
Fig. 12-13



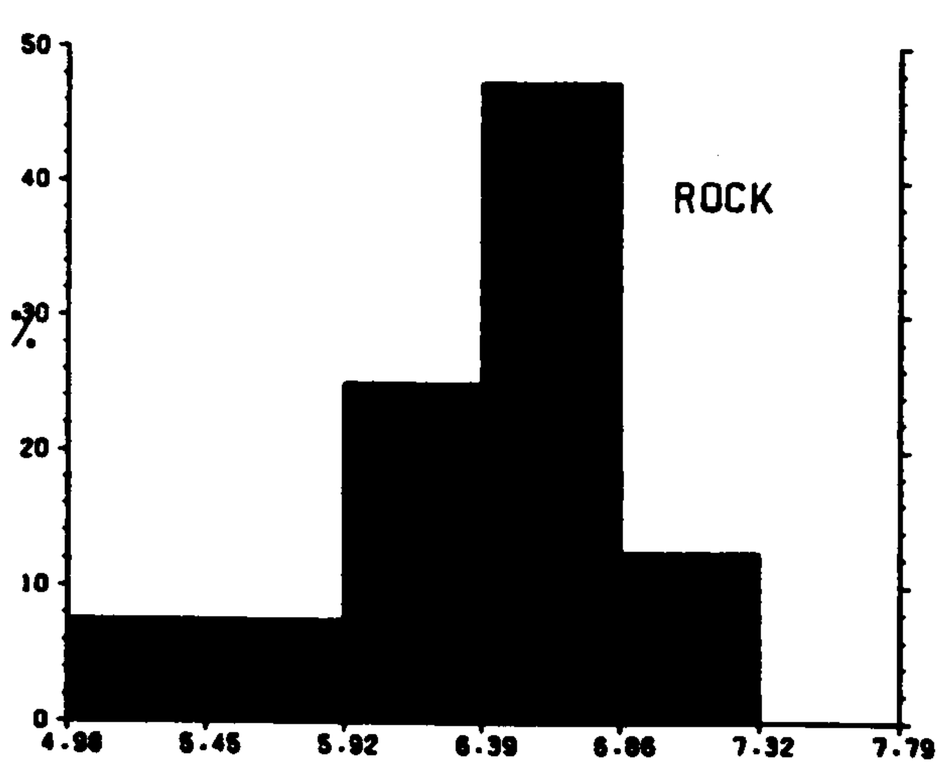
PH - pH
NO. OF OBSERVATIONS = 40
MEAN = 6.20 STD DEV = 0.542



PH - pH
NO. OF OBSERVATIONS = 40
MEAN = 6.28 STD DEV = 0.422



PH - pH
NO. OF OBSERVATIONS = 30
MEAN = 7.22 STD DEV = 0.266



PH - pH
NO. OF OBSERVATIONS = 40
MEAN = 6.39 STD DEV = 0.468

Histograms of the distribution of the pH in the rocks, soils and stream sediments derived from the Keuper Marl in the Worcestershire study area.

Al and pH there were no significant correlations with other elements.

Earlier results have shown that the organic matter(LOI) played an important role in the fixation of cations in the different media investigated. Thus organic matter forms compounds with divalent and trivalent cations by the formation of stable complexes, chelates and co-ordination compounds. In the topsoils organic matter have been noted by a number of workers to be related to the enhanced levels of Pb, (Vinogradov, 1959; Mitchell, 1966). Swanson et al (1966) showed that humates are capable of adsorbing about 10% its weight of Pb. The present investigations agrees with these findings.

(1) pH :

The pH of the rocks, soils, and stream sediments were determined by the method described in Chapter 3 . The results of the measurements are shown in (Table 12-13a) . In general the ranges in all the media were very narrow, ranging from being slightly acidic to slightly alkaline. The histograms showed that the alkaline pH was more predominant in the stream sediments.

The solubilities and the precipitation of most of the salts of the cations investigated depend, among others on the pH of the medium. The pH of the rocks was measured more to assess the conditions in the weathering environment rather than that of sedimentation. Samples with high Ca concentrations had high pH levels, usually this was accompanied by higher concentrations of other elements such as Zn and Pb. In the present investigations it was observed that concentrations of Al were higher in the more acidic soil samples. Waterlogged soil samples had acidic pH with decreased concentrations of such elements as Zn, Mn and Cu compared to the

better drained soils. In the stream sediments where the pH was neutral to alkaline levels of Ca and most elements were higher than in the soils and rocks.

Correlations with elements.

The significance of the correlations between the pH and other elements are shown in Table 12-13b. In the rocks the pH was significantly correlated with Ca, Mn and Co. Calcium and manganese may be present in the rocks in the carbonate phase and the correlation with the pH will thus indicate the control of the acidity on the solution of the carbonates. A similar situation was observed in the subsoils where there was significant correlation with Ca. In the top and subsoils the pH was significantly correlated to Al, Fe and Ni. It is probable that the various adsorption processes observed earlier in which the clay minerals were involved may be influenced by the pH of the medium. In the stream sediments the pH was significantly correlated to Al, Zn, Ni and the organic matter(LOI).

(m) Summary.

Calcium concentrations in the rocks were similar to those in the soils being generally low. The increased concentrations of Ca in the stream sediments suggested that leached Ca from the rocks and soils were being precipitated in the streams possibly as secondary carbonates and this was accompanied by increased concentrations of Zn and Pb. The strong inter correlations between Ca, Zn and Pb in the streams indicated that the enhanced concentrations of Zn and Pb in the

streams may be due to an association with the secondary carbonates.

Zinc and lead were also correlated to the organic matter(LOI) in the soils but these elements were not markedly enhanced in the soils compared to their parent material. The results did not show unusually high concentrations of Pb in the topsoils compared to the subsoils as was often observed in other study areas.

The elements Al, Mg, Fe and Ni showed very little differences in the rocks, soils and stream sediments. These elements correlated strongly with each other in the different media and combined with the similarities of their coefficients of variation values it was inferred that they constituted a stable component in all the media. The group was interpreted as an association with the clay minerals. Manganese and cobalt were found to be associated with this group in the soils possibly as adsorbed cations. The hydrous oxide group seemed to be important in the stream sediments where the correlations of Mn and Fe with Co and other divalent cations suggested an influence of the hydrous oxides on the distribution of elements.

12-5 Multi-Element Associations:

Multi-element associations were discerned by factor analysis of the data from individual media. The results are presented as factor loadings on individual elements. The table of significance of the correlation coefficients (Appendix 3) have been used to determine the significance of individual loadings. The results are discussed for each medium below.

(a) Rocks:

The results of factor analysis of the rock data are shown in Table 12-14 . The four factor model accounted for over 76% of the total variance and was found appropriate in describing the multi element associations in the rocks.

Factor 1 associated Al, Fe, Zn and Ni together by high negative loadings. Contributions from Mg and the organic matter(LOI), although significant, were relatively weak. This group was interpreted as an association defining the clay mineral assemblage in the rocks. The weaker loadings on Mg and organic matter(LOI) suggested a possible relationship between the clay minerals in the rocks and the organic matter(LOI). Organic matter is capable of being adsorbed onto clay minerals such as illites which is known to occur in the Keuper Series (Davis, 1967). Such adsorption processes may be either through van der Wall forces which develop at close contacts or through polyvalent bonding (Russell, 1973, p 100).

The second group of associations were defined by factor 2. which displayed high positive loadings on Ca and Mg. The loadings on Mn, Co and pH were relatively weak. The presence of carbonates such as calcite and dolomites have been remarked by a number of workers(Honeyborne, 1952; Davis, 1967). The elements defined by this group may be interpreted as describing the carbonate associations in the rocks. The weaker loadings on Mn and Co suggested an isomorphous replacement possibly of Ca by Mn and Mg by Co while the association of this factor with the pH agreed with the earlier observation in Section 12-4 on the effects of the acidity on the solution of the carbonates.

Factor 3 associated Pb, Cu, pH and the organic matter(LOI). This was interpreted as defining association with the organic

Table 12-14

Significance Of Factor Loadings Of Logarithmically Transformed Rock Data. Matrix Accounts for 76.4% Of Variance Of 40 Samples Of The Keuper Marl . ! Tables Of Levels Of Significance Of Correlation Coefficient (Appendix 3) Used To Determine Significance Levels Of Factor Loadings.

Metals	Factor			
Variance (%)	1	2	3	4
	25.1	18.6	17.3	15.4
Ca	-	***	-	-
Mg	(*)	***	-	-
Al	(***)	-	-	-
Fe	(***)	-	-	-
Zn	(***)	-	-	-
Mn	-	*	-	***
Co	-	*	-	***
Pb	-	-	*	-
Ni	(***)	-	-	-
Cu	-	-	***	-
LOI	(**)	-	*	-
pH	-	**	**	-

- = Not significant
* = significant at 0.10 level
** = Significant at 0.05 Level
*** = Significant at 0.01 level
( ) = Negative Loading.

matter(LOI) . Thus organic matter(LOI) readily fixes Cu and Pb in the geochemical environment and it is probable that the weaker loadings on the pH may indicate that Cu is associated with the acidic forms of organic matter.

Factor 4 associated Mn and Co by highly significant positive loadings. This may be interpreted as defining an association describing the hydrous oxides in the rocks. The association between Mn oxides and other divalent cations were observed in Section 12-4 and it seemed likely that the association with such divalent cations as Co represent the "scavenging" effects of Mn oxides in the rocks.

(b) Topsoil.

The four factor model described the main multi-element associations in the topsoil. The model accounted for 77% of the total variance.

Factor 1 associated the elements Mg, Al, Fe, Mn Co Ni and the pH together by significant positive loadings (Table 12-15). Two main groups of associations can be discerned from the structure of the loadings on this factor. The first group consisted of highly significant loadings on Mg, Al, Fe and Ni while the second group consisted of relatively weak loadings on Mn, Co and the pH. Both groups were interpreted as being associated with the clay mineral fraction in the topsoils. The weaker loadings may represent those divalent cations that are adsorbed onto vacant sites in the clay mineral structure while the higher loadings may be defining elements that constitute the lattice structure of the clay minerals. Changes in the pH of the medium may affect the type of charges on the clay

Table 12-15

Significance Of Factor Loadings Of Logarithmically Transformed Topsoil Data. Matrix Accounts for 77.0% Of Variance Of 40 Samples Of The Worcester Series. ! Tables Of Levels Of Significance Of Correlation Coefficient (Appendix 3) Used To Determine Significance Levels Of Factor Loadings.

Metals	Factor			
	1	2	3	4
Variance (%)	24.5	20.3	18.2	14.0
Ca	-	-	***	-
Mg	***	-	-	-
Al	***	-	-	-
Fe	***	-	-	-
Zn	-	***	-	-
Mn	*	-	-	***
Co	*	-	-	***
Pb	-	***	-	-
Ni	***	-	-	-
Cu	-	***	**	-
LOI	-	***	-	-
pH	**	-	**	-

- = Not significant
* = significant at 0.10 level
** = Significant at 0.05 Level
*** = Significant at 0.01 level
( ) = Negative Loading.

minerals, for instance, acid clays tend to carry negative charges which may be neutralised by the adsorption of cations such as Mn and Co (Russell, 1973). The association of this group with the pH suggested such an influence.

The group defined by factor 2 consisted of Zn, Pb, Cu and the loss on ignition associated by high positive loadings. In general, organic matter forms a number of stable compounds with a range of cations. The group of associations defined by this factor may be reflecting the well known vegetative recycling of elements such as Pb through the accumulation of plant debris in the topsoil.

Factor 3 defined an association between Ca, Cu and the pH by significant positive loadings. This group was interpreted as an association with the carbonates present in the topsoil. In general the mobility of elements such as Cu is often restricted in the soils by the formation of secondary carbonates. The relationship between the carbonate related elements and the pH has already been observed in the rocks and may likewise be interpreted as representing the effects of the pH on the solution or formation of carbonates.

Factor 4 defined the hydrous oxide group consisting of significant loadings by Mn and Co. This may represent the "scavenging" of divalent cations by Mn oxides

(c) Subsoil.

The three factor model described the main multi-element associations in the subsoil (Table 12-16). The model accounted for over 84% of the total variance.

Factor 1 associated Al, Mg, Fe, Mn, Co, Ni and the pH

Table 12-16

Significance Of Factor Loadings Of Logarithmically Transformed Subsoil Data. Matrix Accounts for 84.2% Of Variance Of 40 Subsoil Samples From The Worcester Series. ! Tables Of Levels Of Significance Of Correlation Coefficient (Appendix 3) Used To Determine Significance Levels Of Factor Loadings.

Metals	Factor		
Variance (%)	1	2	3
	33.9	26.3	24.0
Ca	-	-	-
Mg	*	*	-
Al	**	**	-
Fe	**	-	-
Zn	-	-	-
Mn	**	-	***
Co	**	-	***
Pb	-	-	***
Ni	**	-	-
Cu	-	-	-
LOI	-	***	-
pH	**	**	-

- = Not significant
* = significant at 0.10 level
** = Significant at 0.05 Level
*** = Significant at 0.01 level
( ) = Negative Loading.

together by significant positive loading. Compared to the topsoils the loadings were weaker on these elements and coupled with the fact that the strengths of the loading on each element in this group was about equal it was not possible to segregate the elements as was done in the case of the topsoil. This group is interpreted as representing the clay mineral assemblage in the subsoil and the similarity of the elements in this group to that observed in the topsoil agreed with the earlier observation that the clay minerals did not undergo significant alteration in the soils .

As in the topsoil the group defined by factor 2 may be interpreted as representing association with the organic matter in the subsoil. Unlike the topsoil, factor 2 in the subsoil grouped the organic matter(LOI) with Mg, Al and pH. Humic colloids in the soils generally contain appreciable amounts of Al and in the acidic form is further able to interact with trivalent cations of Al through ligand exchange (Russell, 1973, p 311). Ligand exchange requires the presence of both dissociated and undissociated acid, and since humic acids dissociate hydrogen ions over a wide pH range, this mechanism can also operate over the whole pH range found in soils, except the very acidic soils. Martin and Reeves (1958) have shown that Aluminium may be present in humus as a hydroxylated cation such as $Al(OH)^{2+}$ and $Al(OH)_2^{+}$. The associations between organic matter(LOI) and Al in the subsoil reflected at least one of these processes in the subsoil.

Factor 3 associated Mn, Co and Pb together by positive loadings. This group may be inferred as representing an association with the Mn oxides present in the sub soil.

Table 12-17

Significance Of Factor Loadings Of Logarithmically Transformed Stream Sediment Data. Matrix Accounts for 81.0 Of Variance Of 30 Sediment Samples From The Keuper Marl. ! Tables Of Levels Of Significance Of Correlation Coefficient (Appendix 3) Used To Determine Significance Levels Of Factor Loadings.

Metals	Factor		
	1	2	3
Variance (%)	30.1	27.6	23.3
Ca	(***)	-	-
Mg	(***)	-	***
Al	-	-	***
Fe	-	*	-
Zn	(***)	-	***
Mn	-	***	-
Co	-	***	-
Pb	(**)	-	-
Ni	-	-	***
Cu	-	-	-
Cu	(***)	-	-
LOI	***	-	-
pH	-	-	**

- = Not significant
* = significant at 0.10 level
** = Significant at 0.05 Level
*** = Significant at 0.01 level
( ) = Negative Loading.

(d) Stream sediment.

The results of the factor analysis of the stream sediment data are shown in Table 12-17. Factor 1 associated Ca, Mg, Zn, Pb and Cu by significant negative loadings on one hand and significant positive loading on organic matter(LOI). This group was interpreted as defining the carbonates in the stream sediments. In the streams, carbonates form as a secondary process and the inverse relationship between this group and organic matter(LOI) suggested that secondary carbonates were forming in areas depleted in organic matter. This is not difficult to imagine since organic matter present in the acidic form is a powerful agent for the solution for the carbonates.

The second factor associated Mn and Co by significant positive loadings. The additional loading on Fe was relatively weak. In the streams Mn occurs as nodules or stains on gravels and pebbles. Although Mn nodules were not observed in the streams in the study area, widespread staining was observed. This factor may represent the "scavenging" activity of Mn oxides in the streams.

Factor 3 associated Mg, Al, Zn, Ni and pH by significant positive loadings. This group was characteristic of the clay mineral group identified in the rock and soils and it was interpreted thus. The association of this group with the pH was also observed in the top and subsoils.

(e) Summary.

In all the media, the clay mineral group of elements included Mg, Al, Fe and Ni. In the subsoil, weak associations were found with Co and Mn while in the rocks this group was associated with the

organic matter(LOI). These were interpreted as representing adsorption processes involving the clay minerals. Calcium and magnesium were also found to be strongly associated with each other in all the media investigated. This was interpreted as representing a carbonate association. In the stream sediments this group was associated with other elements such as Pb and Cu. This was a further indication that the enhanced concentrations of these elements in the stream sediments were probably due to an association with the carbonates. Organic matter(LOI) was found to be associated with Al and Mg in the subsoils while in the topsoils the associations with Zn, Pb and Cu were strong. These associations were interpreted as the formation of stable complexes by organic matter(LOI) in the soils. In the stream sediments the association of the hydrous oxide related elements with organic matter(LOI) suggested that these oxides were probably being deposited on organic fragments in the streams.

12-6 Inter-media variation.

The three level nested analysis of variance have been used to compare the variability of elements in the different media investigated. The method was described in Chapter 3 and the results were assessed on the basis of the significance of the F-ratios and the contributions of each level in the nested design to the total variability. Four comparisons have been made. These were between:

(a) the soil(top and subsoils) and rock,

(b) the top and subsoils,

(c) the stream sediments and rock,

(d) the soil(top and subsoils) and sediment.

Table 12-18
F-ratios and Percent Variance Components For The Comparison Between The Rock And Soils Derived From The Keuper Marl As Estimated By The Three Level Nested Analysis Of Variance Model. Samples Collected From The Keuper Marl In Worcestershire Study Area.

Metal	Between Media		Between Sites		Between Samples		Bet. Anal
	F1	(%)	F2	(%)	F3	(%)	(%)
Ca	NS	15.2	***	74.4	*	5.0	5.4
Mg	NS	12.5	***	65.6	*	11.5	10.4
Al	*	10.1	***	81.0	NS	5.4	4.4
Fe	NS	16.9	***	70.2	NS	8.3	4.9
Zn	NS	9.9	***	72.1	*	10.7	9.3
Mn	NS	15.1	***	69.5	*	10.2	8.0
Co	NS	17.5	***	64.3	*	10.2	8.0
Pb	NS	16.5	***	66.0	*	12.8	4.7
Ni	NS	17.3	***	70.0	*	9.8	2.9
Cu	NS	13.7	***	76.2	*	8.1	2.0
LOI	NS	14.0	***	80.0	NS	3.2	2.8
pH	NS	9.0	***	79.6	*	8.4	3.0

NS = Not Significant, P> 0.10; * = 0.10 > P > 0.05; ** = 0.05 > P > 0.01; *** = P < 0.01.

The results are discussed below.

(a) Comparison between the Soil(top and subsoil) and Rock.

The results of the analysis of variance for the comparison between the variability of elements in the soil and rock are presented in Table 12-18. The F1-ratios showed that the between media variance components were not statistically significant for all the elements considered except Al. Contributions from this source to the total variation were generally small. The between sites (F2-ratios) variance components were statistically significant at the .01 confidence level for all elements with very high contributions to the total variance . The between sample components (F3-ratio) were significant at the .10 level for all the elements except Al and Fe together with organic matter(LOI). In general, the percent contributions to the total variability from such procedural errors as sampling and analysis were low with the sampling error making a greater contribution than the analytical error.

The results suggested that the main source of variability of elements in the transition from rock to soil was accounted for by processes operating within the respective media. In the case of Al where the F1-ratio was statistically significant this source made a negligible contribution to the total variability(10.1%) while the between sites variance component was as high as 81%. Processes operating within the media may include weathering and pedochemical processes. Earlier results have indicated that elements such as Al, Fe, and Ni that tended to be related to the clay minerals formed a stable group whose concentrations and distributions remained relatively unaffected in the transition from one medium to another.

Table 12-19
F-ratios and Percent Variance Components For The Comparison Between The Top And Sub Soils Derived From The Keuper Marl As Estimated By The Three Level Nested Analysis Of Variance Model. Samples Collected From The Keuper Marl In Worcestershire Study Area.

Metal	Between Media		Between Sites		Between Samples		Bet. Anal
	F1	(%)	F2	(%)	F3	(%)	(%)
Ca	NS	12.7	***	76.0	*	8.2	3.0
Mg	NS	15.6	***	69.7	*	11.7	2.9
Al	NS	9.3	***	81.9	NS	4.8	4.0
Fe	NS	14.2	***	75.6	NS	5.4	5.0
Zn	NS	10.8	***	75.0	*	10.1	3.0
Mn	NS	19.0	***	70.0	NS	5.0	6.0
Co	NS	10.4	***	70.0	*	11.6	8.0
Pb	NS	8.0	***	79.6	NS	5.4	5.0
Ni	NS	7.4	***	77.0	*	10.3	5.0
Cu	NS	9.7	***	79.0	*	8.3	3.9
LOI	**	30.6	***	61.0	NS	4.3	4.0
pH	NS	11.0	***	81.0	NS	5.0	2.9

NS = Not Significant, P> 0.10; * = 0.10 > P > 0.05; ** = 0.05 > P > 0.01; *** = P < 0.01.

The present results lead to similar conclusion.

(b) Comparison between the Topsoil and Subsoil.

Apart from the organic matter(LOI) the F1-ratios were not statistically significant for all the elements considered (Table 12-19). Contributions to the total variance component were generally small(less than 20%) except in the case of the organic matter(LOI) where this source accounted for over 30%.

By contrast the between sites variance component were statistically significant for all the elements with very high contributions to the total variability. In general contributions from the sampling error(F3-ratio) were significant at the .10 confidence levels for all elements considered except Al, Fe, Mn and Pb. Sampling contributed more to the procedural error component than analytical error.

The results accorded with the earlier observations that only negligible differences occurred between the concentrations of most elements in the top and subsoil. Thus the elements related to the carbonates, the clay minerals and the hydrous oxides were observed to be similar in both the top and subsoils. In the case of the organic matter(LOI) where the between media and between site variance components were significant, contribution from the between site source was twice as high as the between media source of variability. As in the comparison between rocks and soils a significant percentage of the total variation of all the elements studied was accounted for by the between site source. Processes such as the adsorption of divalent cations by the clay minerals, and by hydrous oxides together with the

Table 12-20
F-ratios and Percent Variance Components For The Comparison Between The Rock And Sediment Derived From The Keuper Marl As Estimated By The Three Level Nested Analysis Of Variance Model. Samples Collected From The Keuper Marl In Worcestershire Study Area.

Metal	Between Media		Between Sites		Between Samples		Bet. Anal
	F1	(%)	F2	(%)	F3	(%)	(%)
Ca	***	69.3	*	24.6	NS	3.1	3.0
Mg	***	63.1	*	12.1	NS	2.8	1.9
Al	NS	12.9	***	83.1	NS	2.0	2.0
Fe	NS	13.6	***	74.3	NS	5.7	5.4
Zn	***	76.0	NS	16.0	NS	4.0	3.6
Mn	***	65.5	NS	19.5	NS	7.9	6.1
Co	***	90.0	NS	5.0	NS	3.0	1.9
Pb	***	74.3	NS	15.4	NS	6.1	5.0
Ni	NS	15.2	***	73.2	NS	6.6	5.0
Cu	***	70.0	NS	20.3	NS	6.2	3.0
LOI	NS	9.0	***	78.9	NS	6.7	3.4
pH	NS	8.0	***	80.6	NS	6.9	4.4

NS = Not Significant, P> 0.10; * = 0.10 > P > 0.05; ** = 0.05 > P > 0.01; *** = P < 0.01.

formation of secondary carbonates were inferred to be the dominant processes operating within the respective media. Translocation of hydrous oxides, clay minerals and organic matter(LOI), or the reconstitution of the clay minerals into new forms were also thought not to be prominent features of the soils and it seemed probable that this may account for the lack of variability between the top and subsoil.

(c) Comparison between the rock and stream sediment.

The F1-ratios showed that apart from Al, Fe and Ni differences in the variability of other elements were statistically significant at the .01 level (Table 12-20). Contributions from this source to the total variability may be as high as 90% in the case of Co. Elements whose variability were not significantly different between media have in contrast very low contributions to the total variability. The F2 ratios showed that the variability for the elements Zn, Mn, Co and Pb were not statistically significant at the .01 level. For the rest of the elements there were significant differences in the variability between sites. Contributions from this source ranged from 12% in the case of Mg to over 83% in the case of Al. Sampling (F3-ratio) and analytical errors did not contribute significantly to the total variation.

(d) Comparison Between the Soils and Stream sediments.

The analysis of variance results for the comparison between the soils and stream sediments are presented in Table 12-21 . The

Table 12-21
F-ratios and Percent Variance Components For The Comparison Between The Soil And Sediments Derived From The Keuper Marl As Estimated By The Three Level Nested Analysis Of Variance Model. Samples Collected From The Keuper Marl In Worcestershire Study Area.

Metal	Between Media		Between Sites		Between Samples		Bet. Anal
	F1	(%)	F2	(%)	F3	(%)	(%)
Ca	***	70.0	NS	19.0	NS	6.5	4.4
Mg	NS	12.9	***	72.0	NS	6.9	7.0
Al	NS	17.0	***	69.0	NS	6.9	7.0
Fe	NS	12.0	***	70.0	*	12.2	5.7
Zn	**	75.0	NS	15.9	NS	5.0	4.9
Mn	***	69.0	NS	18.0	NS	5.1	4.9
Co	***	65.3	NS	20.0	*	9.8	4.9
Pb	**	41.0	***	50.0	NS	5.0	4.0
Ni	NS	10.2	***	77.5	NS	6.3	5.9
Cu	**	36.0	***	49.0	NS	5.1	4.9
LOI	NS	9.8	***	80.1	NS	5.1	4.9
pH	NS	8.6	***	86.0	NS	3.4	1.9

NS = Not Significant, P> 0.10; * = 0.10 > P > 0.05; ** = 0.05 > P > 0.01; *** = P < 0.01.

results showed that the F1-ratios for all the elements were statistically significant except Mg, Al, Fe and Ni. Contributions to the total variability from this source varied. In those cases where the F1 ratios were significant the contributions were as high as 75% as in the case of Zn while for those elements which were not statistically significant contributions were very low.

Apart from Ca, Zn, Mn and Co where the result showed no significant differences in the variability between sites, for the rest of the elements analysed the F2 ratios were significantly different at the .01 levels with very high contributions to the total variability. Although the F3-ratios were significant at the .10 level for the elements Fe and Co, contributions to the total variability was below 15% in each case. Contributions to the total variability from analytical errors were also small for most elements.

(e) Summary.

The analysis of variance results showed that in all the comparisons made spatial variability within individual media accounted for most of the variability of the elements Al, Fe and Ni. In the comparisons between the top and subsoils and between the soil and rock, the F2 ratios accounted for most of the variation of the clay related elements, the carbonate related elements and the hydrous oxide related elements. This showed that processes operating between the individual media were not as important as those operating within individual media to modify the initial concentrations of elements in the transition from rocks to soils. The clay related elements also showed very little differences in the transition to stream sediments

from soils and rocks.

Differences were however, found in the carbonate related elements where Ca showed significant F1 ratios in the comparison between the rocks and stream sediments, and between the soils and stream sediments. This confirmed that processes such as leaching of the carbonates from the rocks and soils and subsequent redeposition in the stream sediments had important influence on the distribution of the carbonate related elements.

Elements related to the hydrous oxide group showed significant differences only in the transition from rock and soil to stream sediments. In the comparisons between the soils and stream sediments, and the rocks and sediments the F1 and F2 ratios were both significant for Mn and Co. This suggested that processes operating between and within the media were equally important in modifying elements related to the oxide phase.

12-7 Integrated Discussion and Summary.

Levels of individual elements have been compared in the different media investigated. On the basis of the assumption that the mobility of elements can be assessed by their variability in the transition from one medium to another,comparisons have been made of the variability of individual elements between the different media investigated using the analysis of variance method. The three level analysis of variance technique used enabled the estimation of the sampling and analytical errors. These were found not to be a major source of variability. Correlation coefficients between element pairs and factor analysis have also been used to discern element groups and

associations.

Interpretations were based on the known associations of elements to components of the geochemical environment and the assessed pathway revealed by the present investigations. The following groups of elements have been discerned in the present investigations.

(a) Clay mineral group.

(b) Carbonate group.

(c) Organic matter(LOI) group.

(d) Hydrous oxide group.

(a) Clay Mineral Group (Al, Mg, Fe, Ni).

This group consists of Al, Mg, Fe and Ni. The concentrations of these elements in the respective media investigated were fairly similar. Strong positive correlations were observed between the elements within the group in all the media investigated and furthermore, factor analysis grouped these elements together in all the media. The strong association between the elements within this group was interpreted as representing an association with the clay mineral fraction in the various media. These observations agreed with the analysis of variance results which showed that in the main, there were no significant differences in the variability of these elements in the transition from the rock to the soil and stream sediments. The analysis of variance results further indicated that the main source of variation stemmed from the processes operating within the respective media. Davis (1967) identified the main clay minerals in the Keuper Marl to be illites, chlorites, corrensite and sepiolites. Sherwood (1967) showed that all the clay minerals present in the Keuper Marl

were Mg rich.

The results obtained from the present investigations suggested that the clay mineral group did not undergo significant alterations in the transition from one medium to another. Processes operating within the media may include the adsorption of various divalent cations or isomorphous replacements of suitable cations. This was shown by the persistent association of Mg,and Ni with this group. The organic matter(LOI) was found to be associated with the clay related elements in the rocks and stream sediments. This may also reflect an adsorption process. It was concluded that the clay minerals formed a stable component of the parent material that remained unaffected by processes of weathering and pedogenesis.

(b) Carbonates (Ca, Mg, Zn, Pb, Cu).

The presence of carbonates such as calcite, and dolomites in the Keuper Marl have been noted by a number of workers (Honeyborne, 1952; Davis 1967). In the present investigations Ca was taken as an indicator of the carbonates present. Contrast between Ca concentrations in the rocks and soils was negligible, while the enhanced concentrations of Ca in the stream sediments were accompanied by enhanced concentrations of such carbonate related elements as Cu, and Zn. These observations agreed with the analysis of variance results which showed significant differences in the variability of these elements between media in the transition from rock to sediment and from soil to sediment. Such differences were not observed in the transition from rock to soil.

In general, it can be inferred that the carbonates present in

the soils are primary, being largely inherited from the soil parent material. In the stream sediments it seemed likely that the enhanced concentrations of such elements as Cu, Ca, Zn, and Pb were due to the formation of secondary carbonates.

(c) Organic Matter Group(Pb Zn Ni Cu).

Organic matter(LOI) was singled out in all the media to be associated with Zn, Pb and in the case of the subsoil with Mg and Al. These associations were interpreted as representing the various interactions of organic matter(LOI) with cations in the soils. This may include adsorption, formation of chelates and complexes and co-ordination compounds. Organic matter(LOI) was also observed to be related to the clay minerals in the rocks.

(d) Hydrous oxide group (Mn, Fe, Co, Cu)

Davis (1967) showed that there was some uniformity of Fe O throughout the whole succession of the Keuper Marl. He used this as an evidence of the contemporaneous deposition of hematite in the Keuper Marl. Iron concentrations in all the media were low but enough to account for the red colouration of the rocks, soils and stream sediments. In the present investigations Mn oxides were thought to be the most important with respect to the distribution of elements in the different media studied. The analysis of variance results showed that significant differences in the variability of elements in this group occurred in the transition from rocks and soils to stream sediments. This was thought to reflect the mobilisation of these elements in the

rocks and soils and subsequent redistribution in the surface drainage.

12-8 Conclusions

The following conclusions can be drawn from the above results,

(1) There was a general trend for element concentrations to be enhanced in the stream sediment compared to the rock and soil. This was more pronounced in the case of Ca, and to a lesser degree, Zn, Pb, and Cu. In general concentrations of most elements in the soil and rock were similar.

(2) Top and subsoil concentrations of most elements were similar. Processes of leaching from the topsoil and redistribution in the subsoils were thought to be uncommon.

(3) Multi-element associations in the soils and stream sediments were similar to those in the parent material. The following strong associations were discerned in all the various media studied,

(a) Al, Mg, Fe and Ni.

(b) Ca, Mg, Zn, Pb and Cu.

(c) Mn, Fe, Co and Cu.

(d) Zn, Pb, Ni and organic matter(LOI).

(4) The main source of variability of elements arose from processes operating within individual media, although for the carbonate related elements, variability emanated from processes operating within and between media.

CHAPTER 13

Detailed Investigations Into The Lower Lias In The Somerset Study Area.

13-1 Introduction.

Rocks, soils and stream sediments derived from the calcareous and the less calcareous facies of the Lower Lias have been examined in detail in this Chapter. The aim of the present investigation was to examine and to compare the distribution , mobility and associations in the two facies of the Lower Lias and their associated residual soils and stream sediments in Somerset. The soils developed over the two facies were the Denchworth and Evesham series developed from the less calcareous and the more calcareous facies of the Lower Lias respectively.

13-2 Geology.

The basal beds of the Lower Lias , the White Lias are hard, fine grained argillaceous limestones, interbedded with clay shales and marls. They formed in an almost landlocked basin which slowly infilled with sediments (Arkell, 1933). Towards the Mendip Hills the formation becomes thinner and in central Somerset the White Lias attains a thickness of approximately 20ft, often fossiliferous towards the base (Kellaway and Welch 1948). The Blue Lias that overlies the White Lias consists of grey calcareous clays and clay shales with occasional bands of limestones. The thin shelly limestones that constitute the basal beds of the Blue Lias have been extensively

400E

490N

GLASTONBURY

WEST PENNARD

STREET

BRUE

SOMERTON

600N

280E

● Less Calcareous Sample Location

○ Calcareous Sample Location

■ Town

Stream

0 1 2km

N

Fig 13-1
Sample Location In The
Somerset Study Area

quarried at Street for building stones and paving slabs. North of the Mendip Hills the basal beds have yielded fossil skeletons of marine saurians, eg Icthiosaurus , (Arkell, 1933).

The Belemnite Marl, a tough pale grey marl with thin limestones, occur towards the top of the Blue Lias. This forms a distinct scarp near Glastonbury (Avery, 1955). The Belemnite Marl is succeeded by the Green Ammonite Beds, a series of non calcareous bluish grey, silty and micaceous clay-shales. Arkell (1933). attributed the dark grey colour of the Lias Clay to finely disseminated pyrites deposited within the mud.

13-3 Soils.

The two main soil series developed over the Lower Lias in the Somerset study area are the Evesham and the Denchworth sereis.

(a) Evesham series.

The soils are developed from the calcareous facies of the Lias. They are heavy grey-brown clays often found on gently undulating land. The soils are generally well fissured hence despite the impervious nature of the substratum drainage is satisfactory. The fissures develop as the soils dry up in the summer and persist probably in the winter months thus preventing waterlogging (Avery 1955). Most of the deeper soils are pipe drained. The pH is generally alkaline, with at least 40% clays in the surface horizon and 50% in the B horizon (Avery, 1955). The carbonate content is high in all the horizons, this may be up to 12%, but under old pasture may be lower (Findlay, 1965). Under permanent grass the organic matter content may be as high as 10% (Findlay, 1965).

(b) Denchworth Series.

The series consists of heavy textured silty clay or clay loams with poor drainage conditions developed from the less calcareous facies of the Lower Lias. In the study area it occurred extensively around West Pennard. The soils are surface water gleys often waterlogged in the winter months. The topsoil is 50 - 60% clay, often dark brown with a coarse crumb structure (Avery, 1955). The subsoil is a stiff greyish or olive brown clay with grey, yellow or brown mottling. The mottling increases with depth.

13-4 Regional Geochemical Patterns.

Preliminary investigation in the study area (see Chapter 8) involved the sampling of the Lower Lias and the Keuper Marl, with no distinction as to the effects of facies changes within the Lower lias and the associated soil types that develop on the different facies. Furthermore, the paucity of samples collected per unit, prevented the use of statistical techniques to characterise groups of elements that tend to follow similar geochemical pathways. Certain generalised observations were made. These were:-

1. elements such as Ca and Zn displayed exceptionally wide range over the Lias,

2. iron and magnesium concentrations remained fairly constant in the rocks and soils over the Lias,

3. concentrations of Ca were depleted in the transition from rock to soil over the Lias,

4. the elements Zn, Pb and Cu were enhanced in the topsoil compared to the subsoil,

Table 13-1a Calcium Concentrations In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias.

Medium	N	Mean (%)	S.D.	C.V.	Range Min (%)	Max (%)
Rock	30	10.2	2.0	19 4	6.5	16.5
T/soil	40	5.0	1.6	38 2	2.2	8.5
S/soil	40	6.4	1.9	29.0	3.0	9.5
S/Sedt	32	14.9	2.9	19.2	9.5	18.5

N =Total nuber of samples/medium collected

S.D = Standard Deviation.

C.V.= Coefficient Of Variation=S.D. / Mean x 100.

Table 13-1b Significance Of The Correlation Coefficients Between Ca And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock		-	(*)	(**)	-	-	-	*	-	(**)	(**)	**
T/Soil		-	(**)	(**)	(*)	-	-	*	-	(*)	(**)	-
S/Soil		-	(***)	(**)	-	-	-	*	-	(**)	(**)	***
S/Sedt	(*)	-	-	-	(*)	-	(*)	(*)	-	-	-	

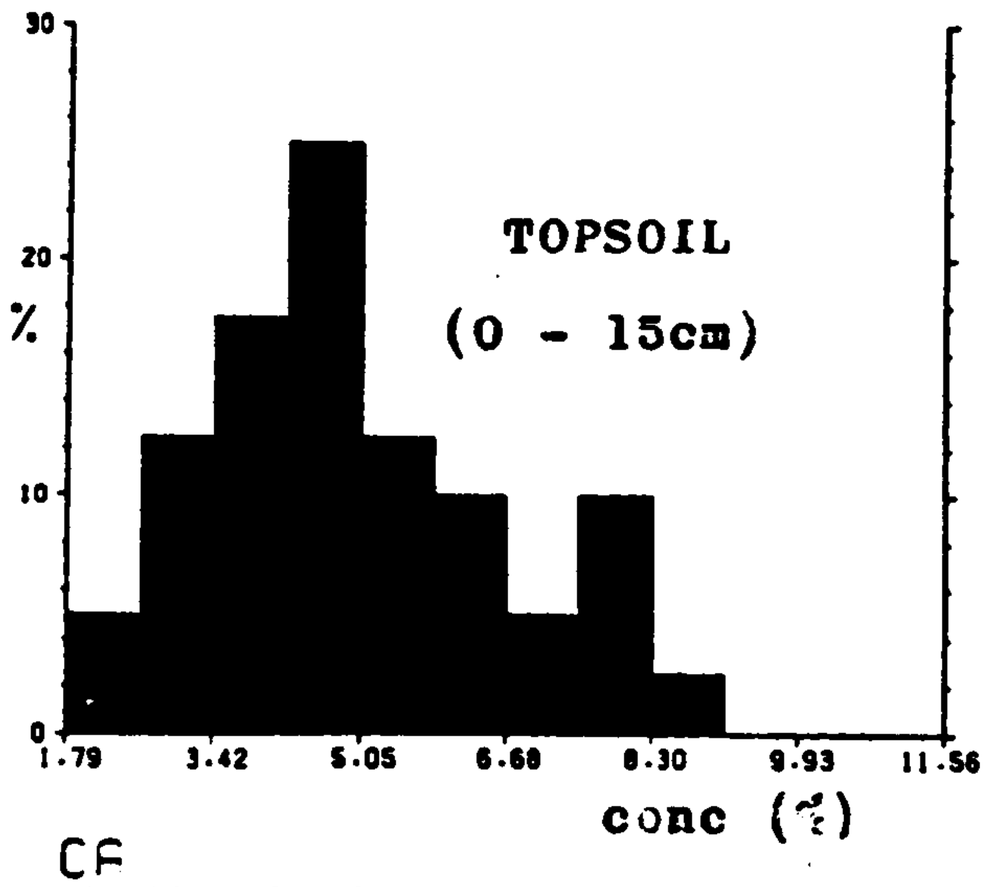
Level Of Significance - = Not Significant * = Significant at .10 level

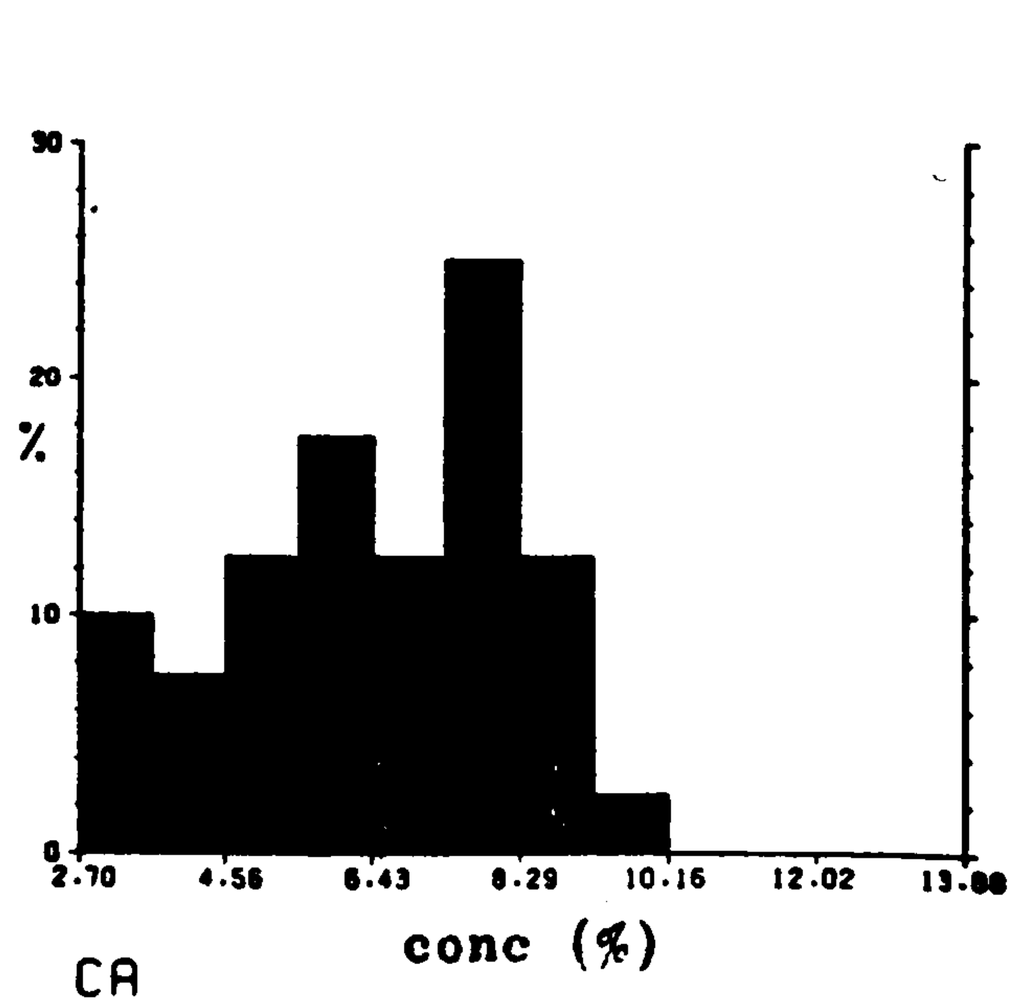
** = Significant at the .05 level

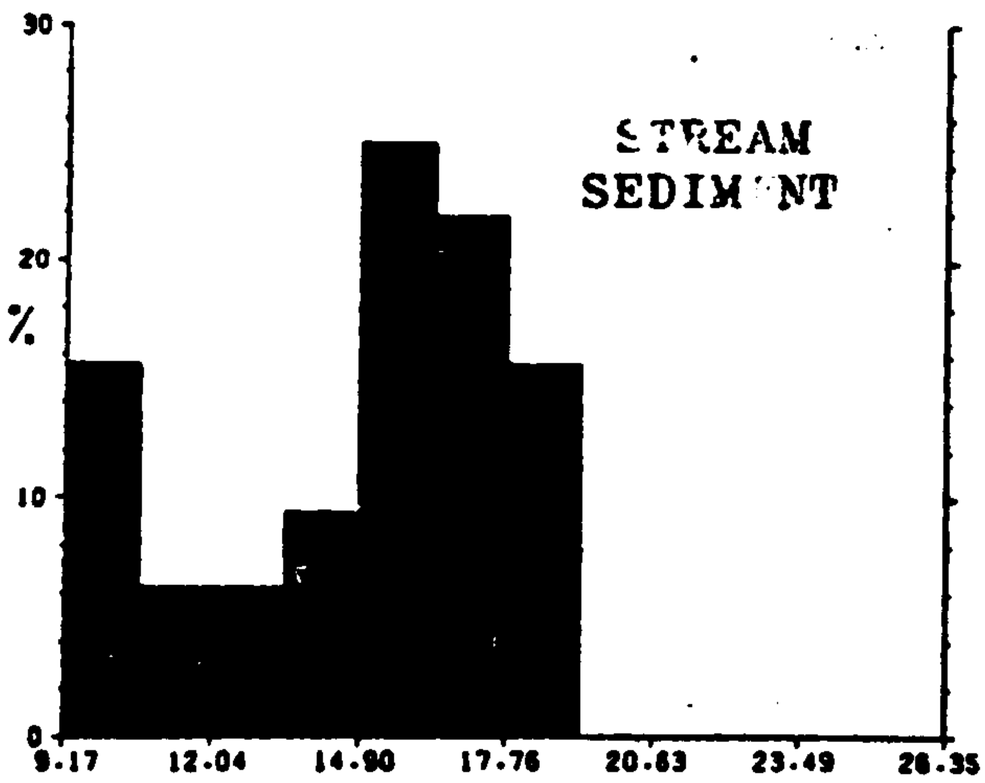
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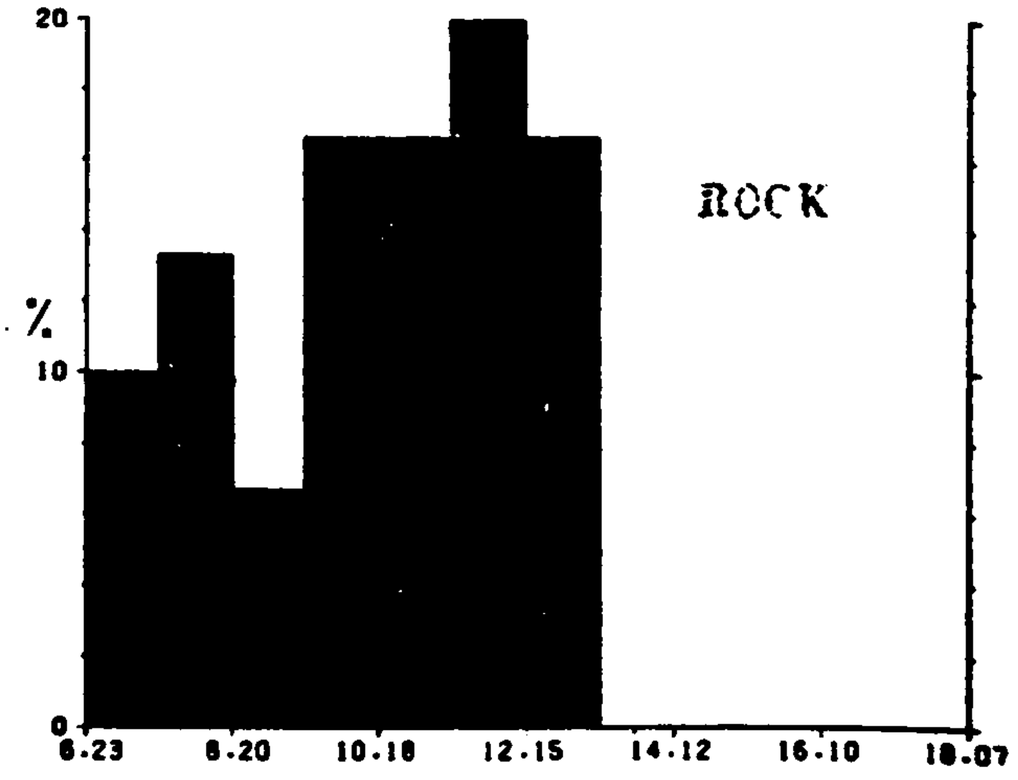
( ) = Negative Correlation.

Fig.13-2









Histograms of the distribution of Ca in the rocks, soils and stream sediments derived from calcareous facies of the Lower Lias in the Somerset study area.

5. concentrations of Mn and Co were enhanced in the soil compared to the rock and sediments.

The present investigation was carried out as a follow up to these. Figure 13-1 shows the sample locations in the study area. The Evesham and Denchworth soil series were sampled. Stream sediments derived from each bed were also sampled and analysed. A broader range of elements was analysed to elucidate element associations. Interpretations were based on:-

(1) the distributions of elements in the different media developed over the calcareous and the less calcareous facies of the Lias,

(2) element groupings as defined by both univariate and multivariate statistical techniques,

(3) assessments of the mobility of elements on the basis of comparisons between and within media by the use of analysis of variance technique.

The distribution of individual elements in the different media are described in this section. Histograms of the distribution of each element in the different media, and tables showing the summary statistics are included.

(a) Calcium.

Calcium displayed a distinct pattern in the rocks, being highly enriched in the calcareous beds which formed the parent material of the Evesham series. In the less calcareous beds of the Lias(parent material of Denchworth series), calcium concentrations in the rocks ranged from 1 to 4% with concentrations lower than 3% Ca

Table 13-2a Calcium Concentrations In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias

Medium	N	Mean (%)	S.D.	C.V.	Range Min (%)	Max (%)
Rock	30	2.8	0.9	31.3	1.0	4.0
T/Soil	40	1.1	0.4	39.1	0.4	1.9
S/Soil	40	1.1	0.6	54.5	0.3	2.8
S/Sedt	30	3.2	1.1	34.4	1.1	6.1

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 13-2b Significance Of Correlation Coefficients Between Ca And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock		-	-	-	-	-	-	-	-	-	-	**
T/Soil		**	-	-	-	-	-	-	-	**	-	**
S/Soil		-	-	-	-	-	-	-	-	-	-	**
S/Sedt		*	*	*	*	*	*	*	*	*	*	-

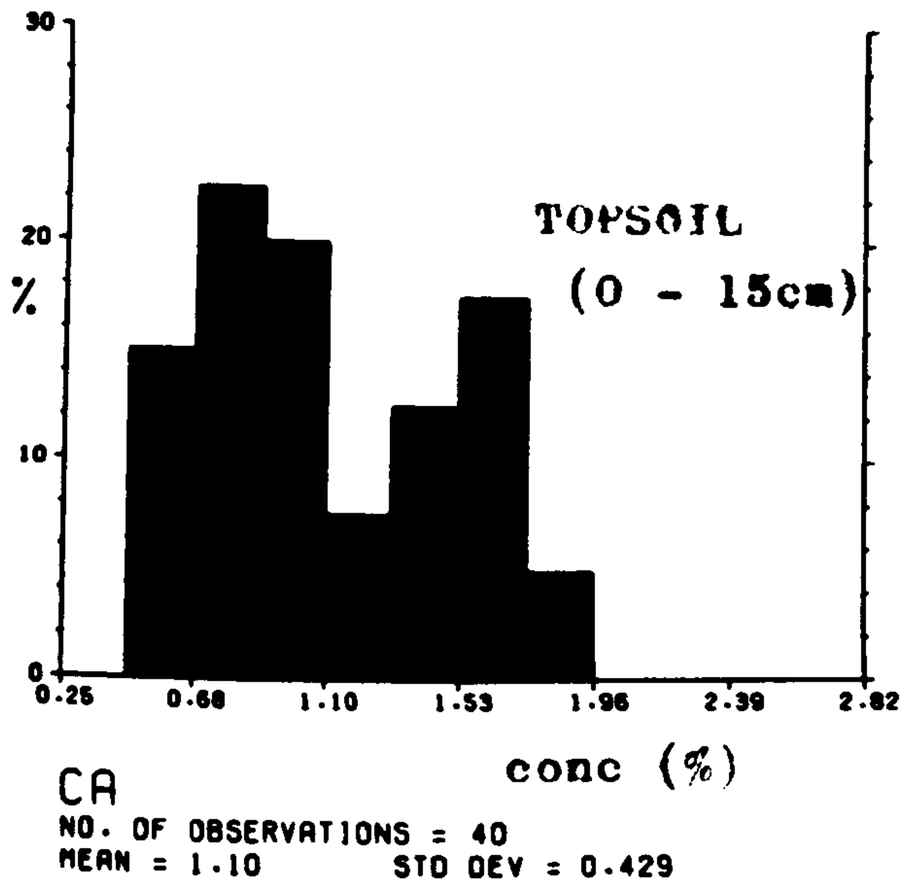
Level Of Significance - = Not Significant * = Significant at .10 level

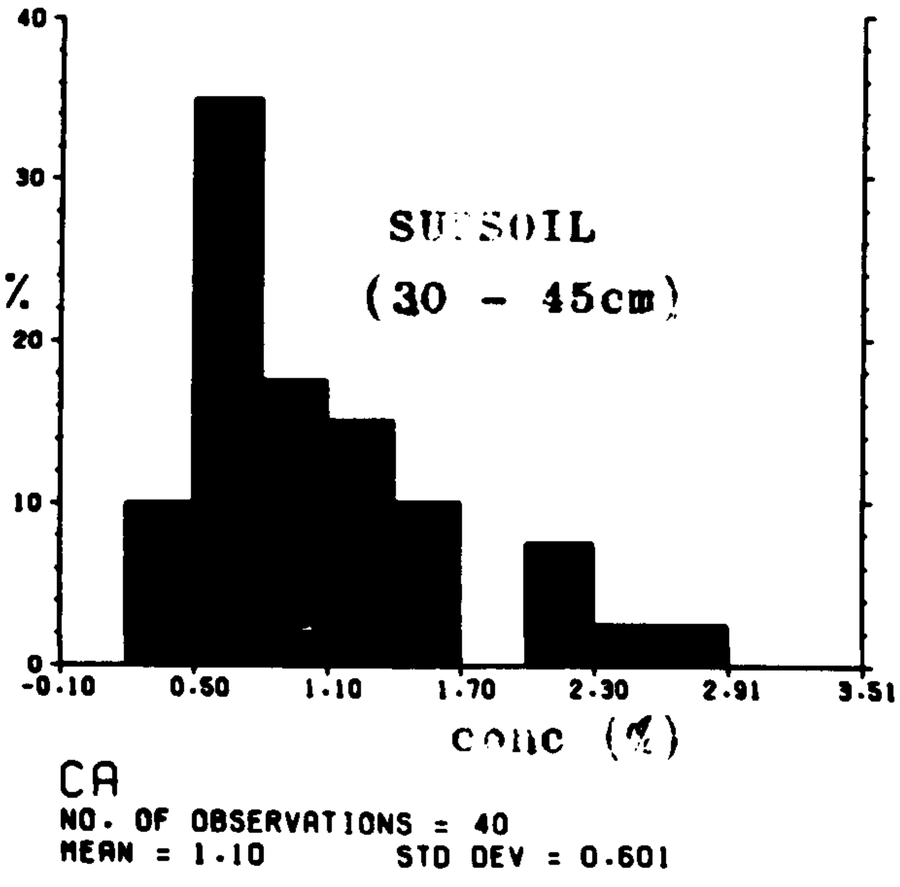
** = Significant at the .05 level

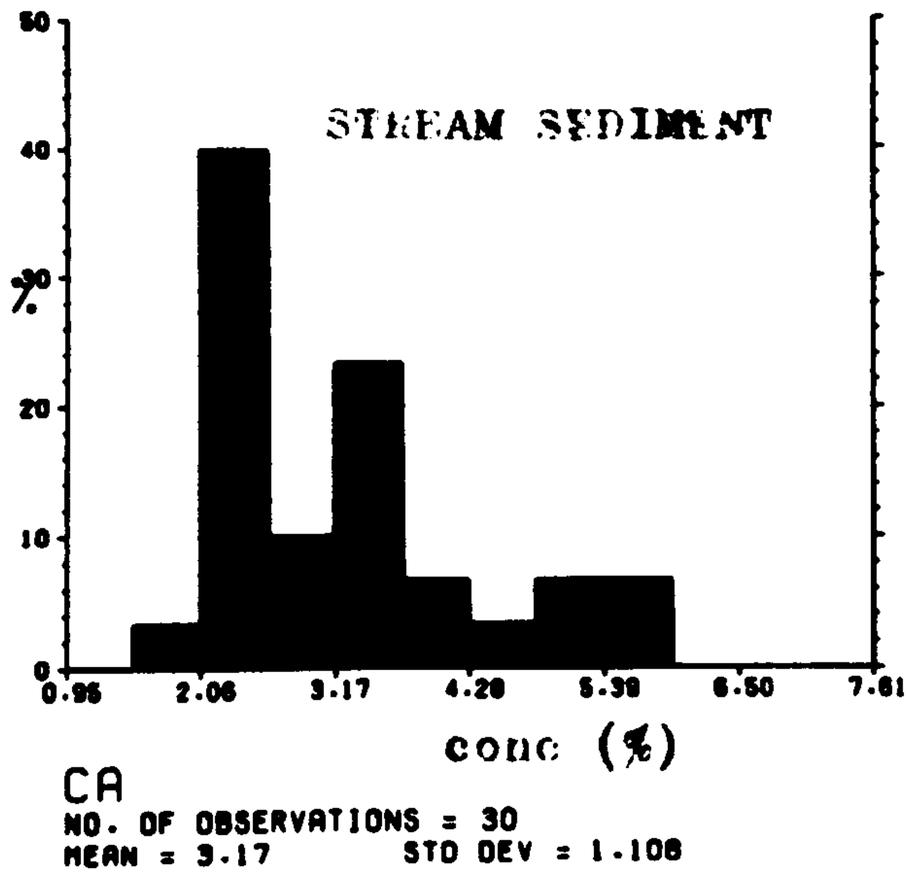
*** = Significant at .01 level

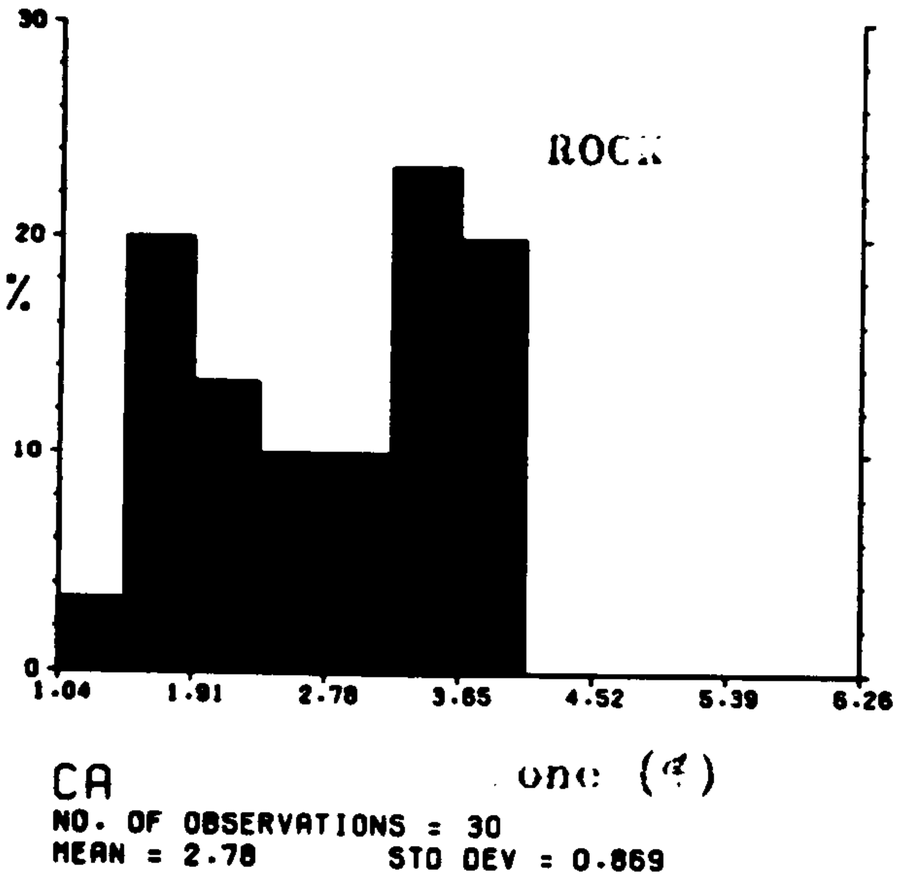
( ) = Negative Correlation.

Fig. 13-3









Histograms of the distribution of Ca in the rocks, soils and stream sediments derived from the less calcareous facies of the Lower Lias In the Somerset study area.

common (Table 13-2a). This was in contrast to the calcareous rocks where concentrations in excess of 10% were widespread (Table 13-1a). The coefficients of variation showed that there was a marked increase in the variation of Ca in the less calcareous beds compared to the calcareous beds.

Transition to soils resulted in lower concentrations of Ca in both the Denchworth and Evesham soil series compared to their respective parent materials. As expected, Ca concentrations in the Evesham soil series were higher than those in the Denchworth soil series. In the Evesham soil series the mean value of Ca in the topsoil (5%) was only marginally lower than that of the subsoil(6%). The histograms (Fig. 13-2) showed that a significant percentage of the samples collected had Ca concentrations below 8%.

In the Denchworth series mean concentrations in the topsoil (1.1%) and the subsoil(1.1%) were strikingly similar, although the range was wider in the subsoil. The coefficients of variation showed that in both soil series there was an increase in the variation of calcium in the soils compared to the parent materials.

There was a marked enrichment of Ca in the stream sediments derived from both facies of the Lias (Tables 13-1a,-2a) . In both cases the means were higher and the ranges wider than in the soils derived from each parent material. In the calcareous sediments the mean concentration of Ca was 14.9% with over 60% of the samples collected having concentrations in excess of 14%. A similar situation was observed in the less calcareous sediments where the mean concentration was nearly three times as high as in the soil.

Inter-element correlation.

In the less calcareous rocks (Table 13-2b) only the correlation with pH was significant. This persisted in the top and subsoils of the Denchworth soil series and in the topsoils further correlations were found with Mg and Cu . In the calcareous rocks (Table 13-1b) negative correlations were found with Al, Fe, Cu and organic matter(LOI). The strengths of the negative correlations increased in the Evesham soil series. Only the correlation with the pH was positive in the Evesham soil series. Weak negative correlations were found with Mg, Mn, Pb and Ni in the calcareous sediments. In contrast positive correlations were found with most elements in the less calcareous sediments.

Calcium in the sedimentary environment may either be associated with the carbonates or with the clay minerals. The negative correlations with the clay related elements and organic matter(LOI) suggested that the relationship may not be direct. Greenland (1971) proposed such an indirect relationship between cations, clay minerals and organic matter. Thus organic anions can be adsorbed by di- or tri- valent exchangeable cations under conditions in which the cation has one of its charges neutralising a negative charge on the clay surface and another a charge on the organic anion (Greenland, 1971). The cation is then the bridge between the clay and the organic anion, and Ca can bind humic colloids to clay by such a mechanism. In these conditions hydrogen bonding develops between the humic particle and the water molecules forming part of the hydration envelop around the cation (Russell, 1973, p 310). These bonds consequently lead to changes in the pH and the results showed that the relationship between Ca and pH was positive.

In the less calcareous facies it seemed that Ca was more associated with the carbonates. In the stream sediments the weak correlation between Ca and other trace elements over the less calcareous facies suggested the formation of secondary carbonates. A similar suggestion can be inferred from the positive correlation between Ca with Mn, Pb and Ni over the more calcareous facies.

(b) Magnesium.

There was essentially no difference between the mean concentrations and ranges of Mg in both the calcareous and non calcareous rocks of the Lias and their associated media (Tables 13-3a, -4a). Coefficients of variation and the standard deviations showed that despite the similarities in the mean concentrations there was greater variation of Mg in the less calcareous beds of the Lias.

The transition from rock to soil in both facies resulted in only minor depletions of Mg concentrations in the top and subsoils of both the Denchworth and Evesham soil series compared to their parent materials. The ranges and mean concentrations of Mg in both soil series were almost the same (Table 13-3a, 13-4a). Coefficients of variation showed a slight decrease in the variation of Mg in the soils. Stream sediment mean concentrations were also similar for both facies, (Tables 13-3a,-4a) being generally lower than those in the rocks and soils.

From the similarities of the distribution in the respective media derived from both facies of the Lias it can be inferred that the form in which Mg was held in the parent material was relatively unaffected in the transition from one medium to another. It seemed

Table 13-3a Magnesium Concentrations In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias.

Medium	N	Mean	S.D.	C.V.	Range Min (%)	Max (%)
Rock	30	0.8	0.1	11.7	0.6	1.0
T/Soil	40	0.7	0.1	10.8	0.5	0.9
S/Soil	40	0 8	0.1	12.0	0.6	0.9
S/Sedt	32	0.5	0.1	20.3	0.3	0.9

N = Number Of Samples.

S.D. = Standard Deviation .

C.v. = Coefficient Of Variation = S.D./Mean x 100.

Table 13-3b Significance Of The Correlation Coefficients Between Mg And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-		*	-	-	-	-	-	-	-	-	-
T/Soil	-		**	-	-	-	-	-	(*)	-	-	-
S /Soil	-		*	-	-	-	-	-	-	-	-	-
S/Sedt	(*)		**	-	-	-	-	-	-	-	-	-

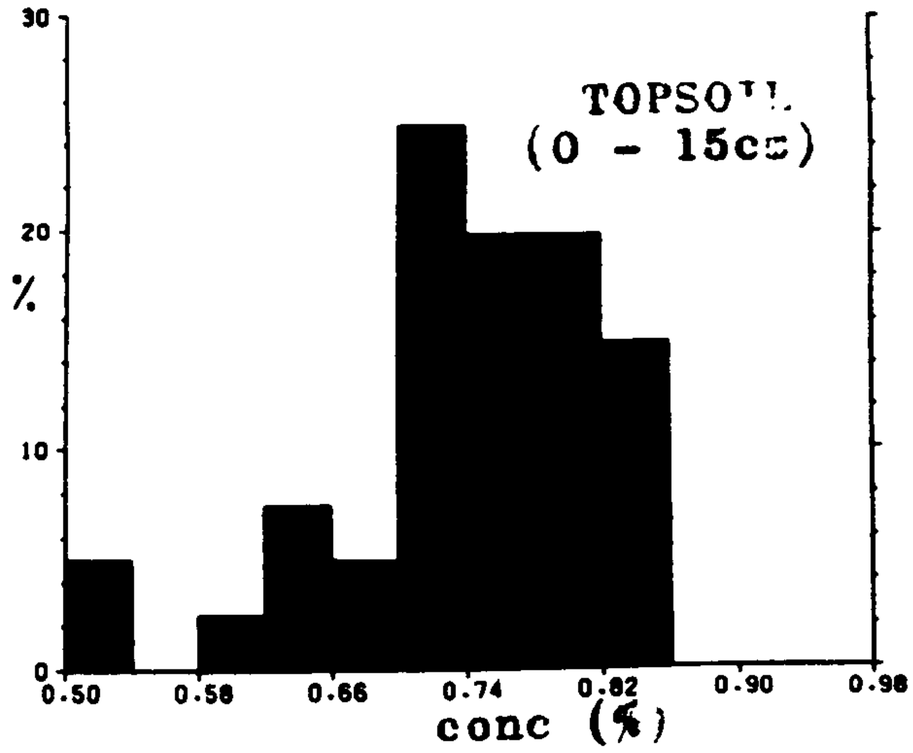
Level Of Significance - = Not Significant * = Significant at .10 level

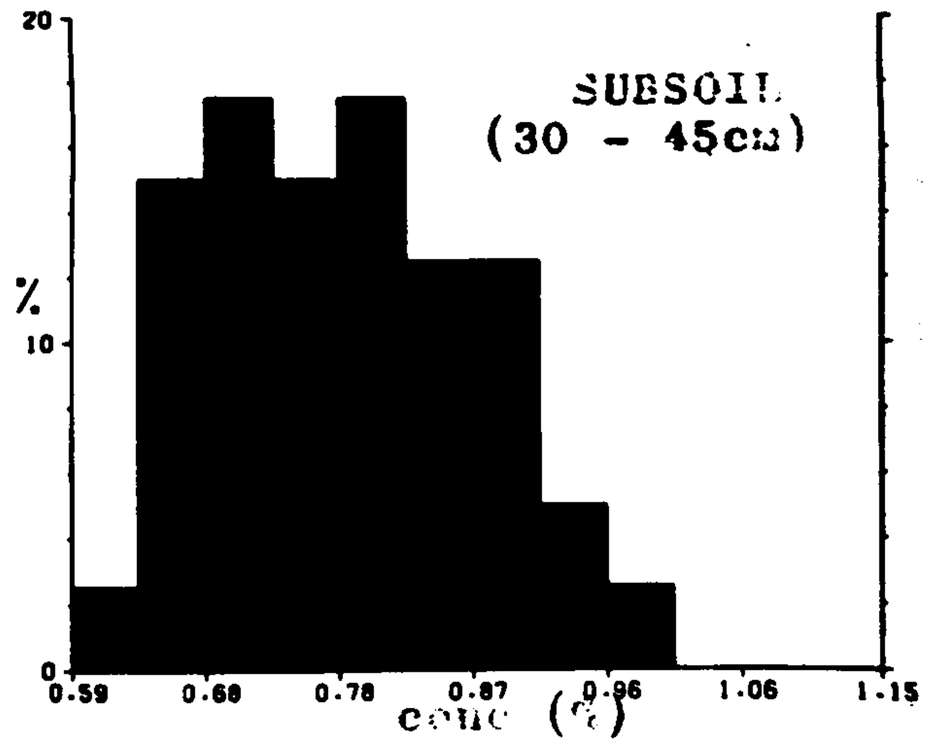
** = Significant at the .05 level

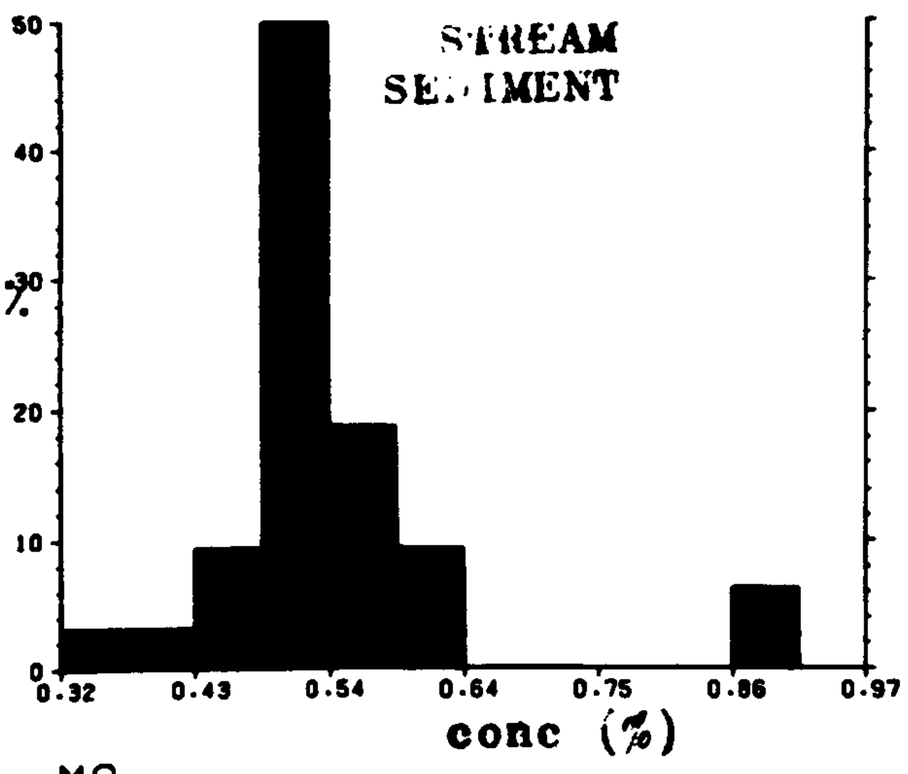
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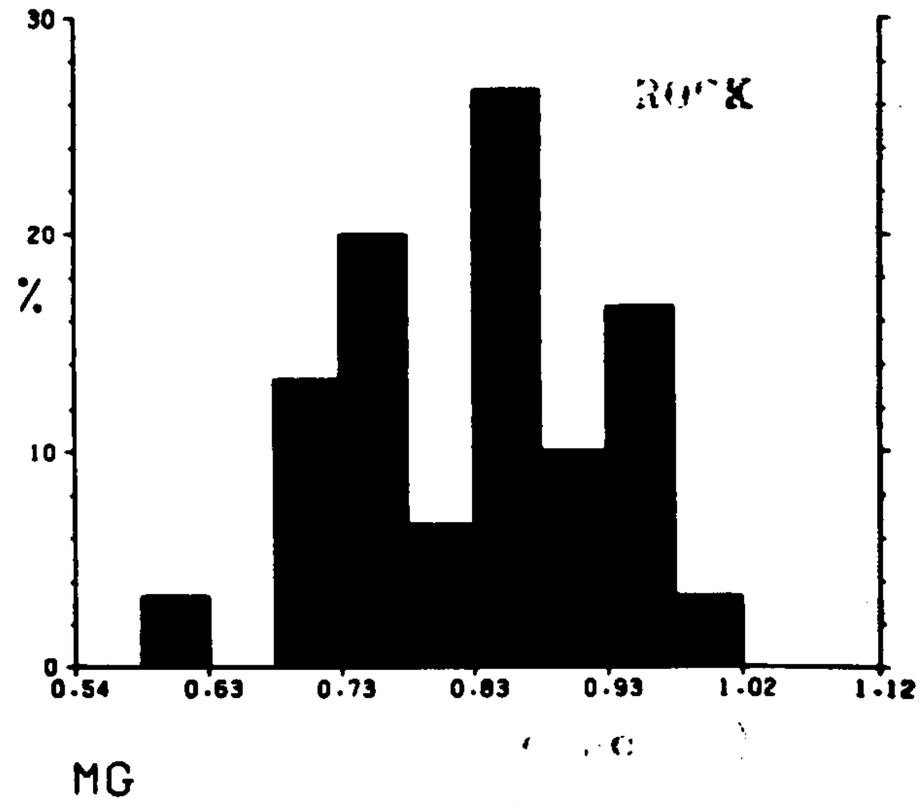
( ) = Negative Correlation.

Fig. 13-4









Histograms of the distribution of Mg in the rocks, soils and stream sediments derived from the calcareous facies of the Lower Lias in the Somerset study area.

Table 13-4a Magnesium Concentrations In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias

Medium	N	Mean (%)	S.D.	C.V.	Range Min (%)	Max (%)
Rock	30	0.8	0.2	21.7	0.4	1.2
T/Soil	40	0.7	0.1	18.8	0.3	1.0
S/Soil	40	0.7	0.1	15.3	0.4	0.9
S/Sedt	30	0.5	0.1	16.4	0.4	0.9

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 13-4b Significance Of Correlation Coefficients Between Mg And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-		*	*	-	-	-	-	*	-	-	*
T/Soil	**		**	**	-	-	-	-	(**)	*	-	*
S/Soil	-		*	-	-	-	-	-	-	-	-	*
S/Sedt	*		**	**	**	*	*	*	-	*	*	-

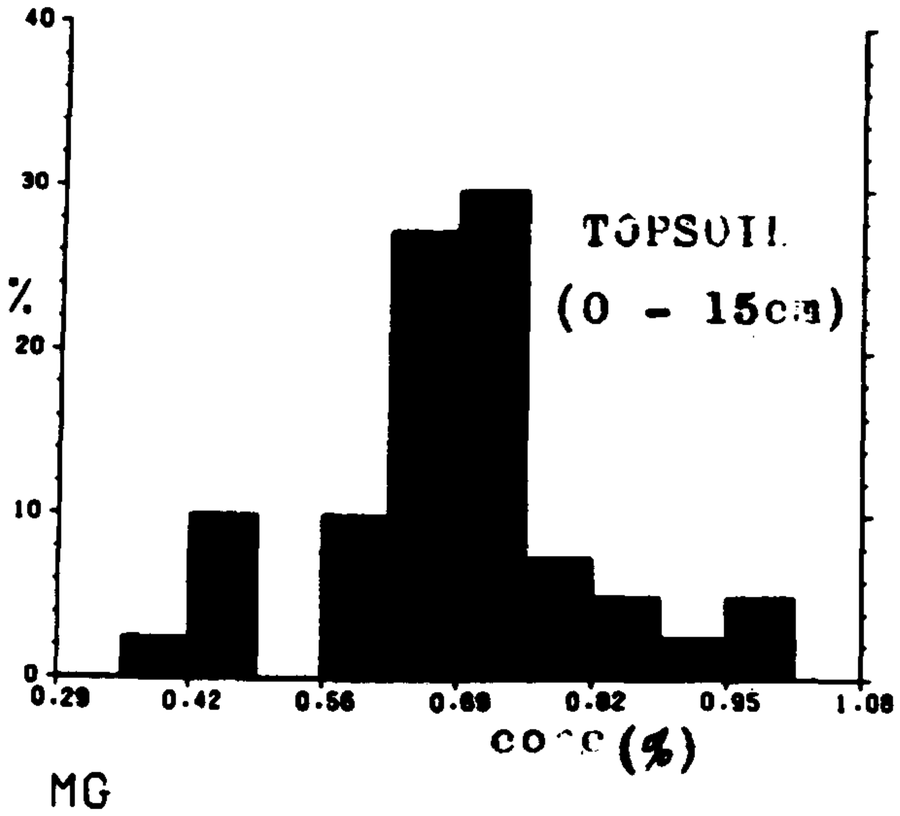
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

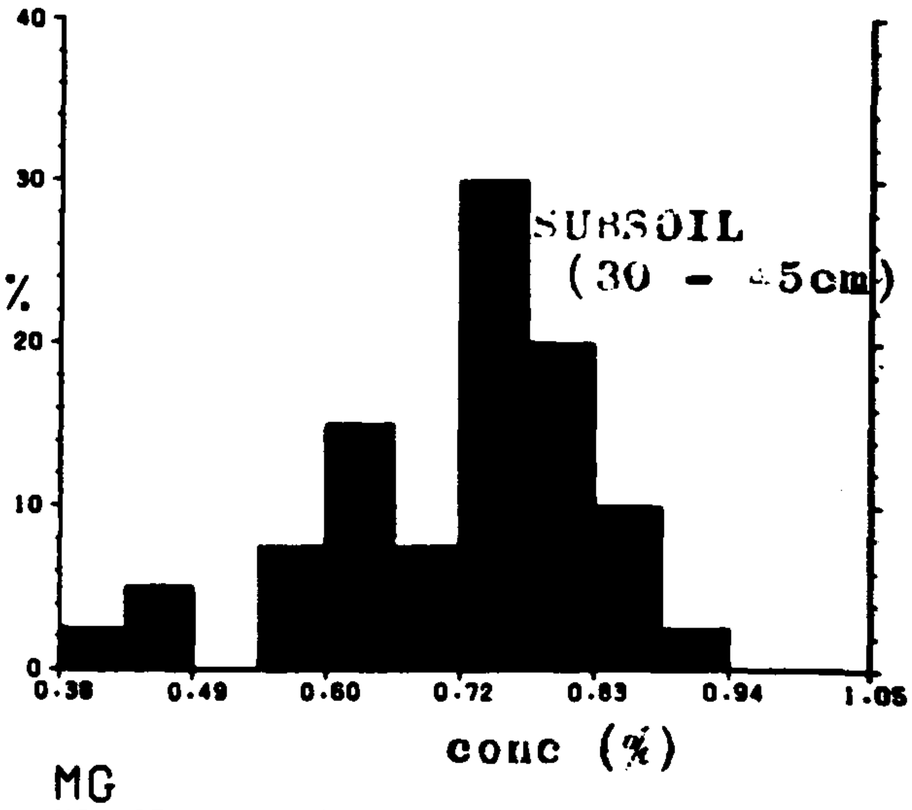
*** = Significant at .01 level

( ) = Negative Correlation.

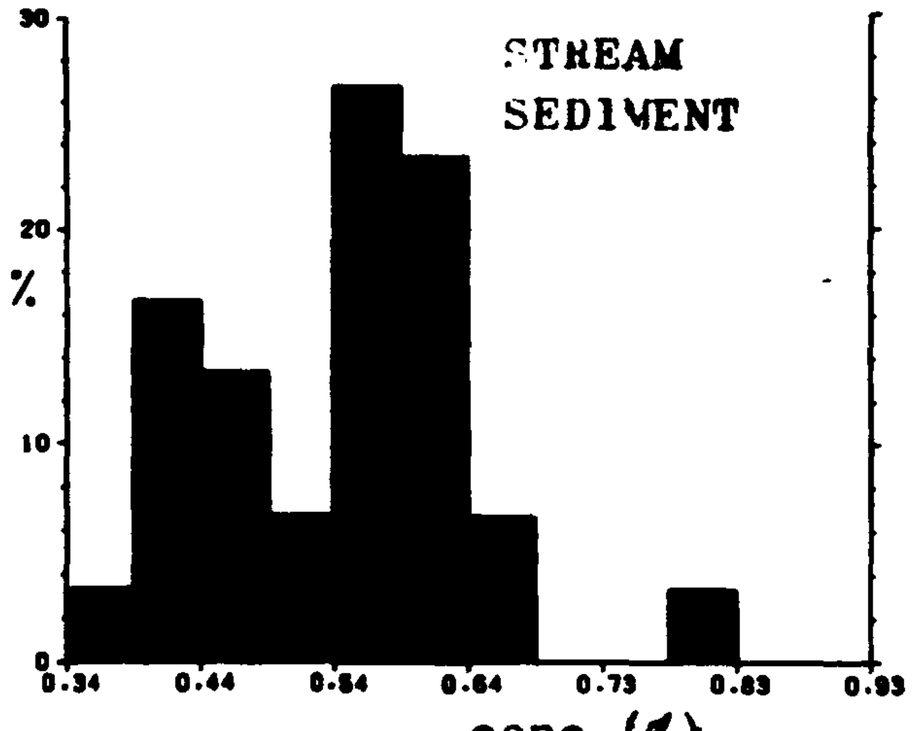
Fig. 13-5a



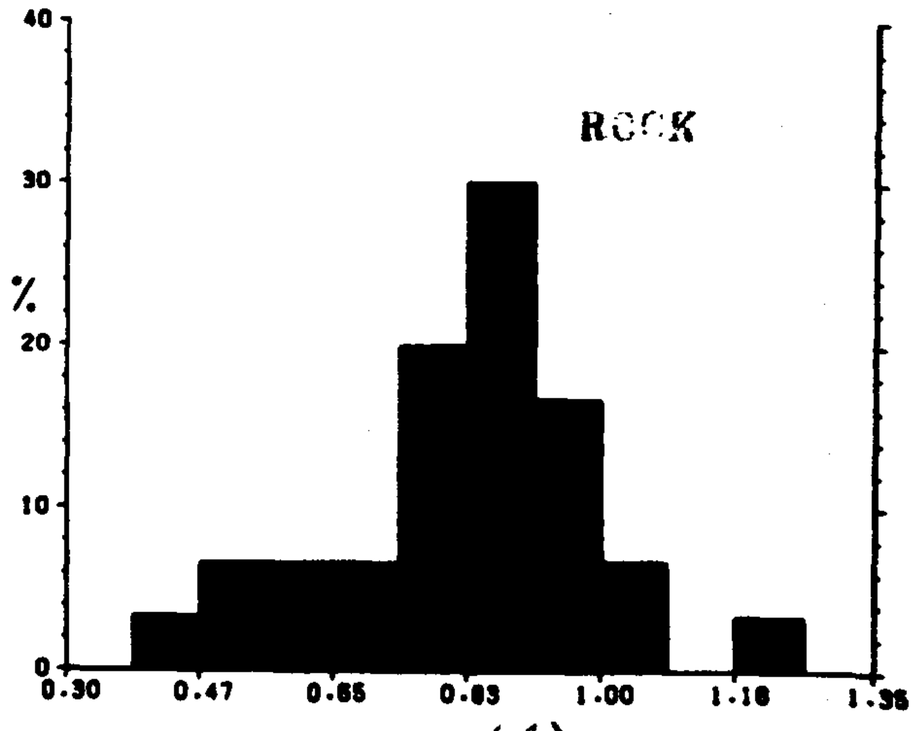
MG
NO. OF OBSERVATIONS = 40
MEAN = 0.69 STD DEV = 0.130



MG
NO. OF OBSERVATIONS = 40
MEAN = 0.72 STD DEV = 0.111



MG
NO. OF OBSERVATIONS = 30
MEAN = 0.54 STD DEV = 0.099



MG
NO. OF OBSERVATIONS = 30
MEAN = 0.83 STD DEV = 0.176

Histograms of the distribution of Mg in the rocks, soils and stream sediments derived from the less calcareous facies of the Lower Lias.

likely that if Mg was associated with the clay minerals then there would be little difference between the two facies, since the basis of the classification of the two facies is on its calcareous character.

Magnesium concentrations were however lower in the stream sediments derived from both beds than the associated rocks and soils. The formation of tufa in the streams was not observed in the study area, however it is probable that the lower concentrations of Mg in the streams may be due to dilution with precipitated carbonates.

Inter-element correlations.

In the more calcareous facies Mg was only correlated with Al in all the associated media (Table 13-3b). Correlations with other elements were either weak or insignificant in both the Evesham soil series and the calcareous sediments. In the less calcareous beds (Table 13-4b) the correlations with Al, Fe, Ni and the pH were weakly significant. The positive correlations with these elements were stronger in the topsoils of the Denchworth soil series where there was a further positive correlation with Cu. In the stream sediments Mg was significantly correlated with most elements except Ni. The strengths of the correlations with Al, Fe and Zn were greater than those with Mn, Co, Pb and Cu.

It seemed from the results that the persistent correlation with Al in all the media suggested that Mg was associated with the clay minerals.

(c) Aluminium.

Comparison between Al concentrations in the calcareous and

Table 13-5a Aluminium Concentrations In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias.

Medium	N	Mean (%)	S.D.	C.V.	Range Min (%)	Max (%)
Rock	30	6.2	1.0	16.9	4.5	8.0
T/Soil	40	5.9	0.9	15.9	3.9	7.9
S/soil	40	6.4	0.9	14.8	4.8	8.6
S/Sedt	32	3.3	0.5	16.2	2.0	3.9

N = Number Of Samples Collected

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 13-5b Significance Of The Correlation Coefficients Between Al And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	(*)	*		*	-	-	-	-	**	**	*	-
T/Soil	-	**		*	*	-	-	*	-	-	**	(*)
S/Soil	(***)	*		*	-	-	-	-	-	-	-	(***)
S/Sedt	-	**		**	-	-	-	-	*	*	-	-

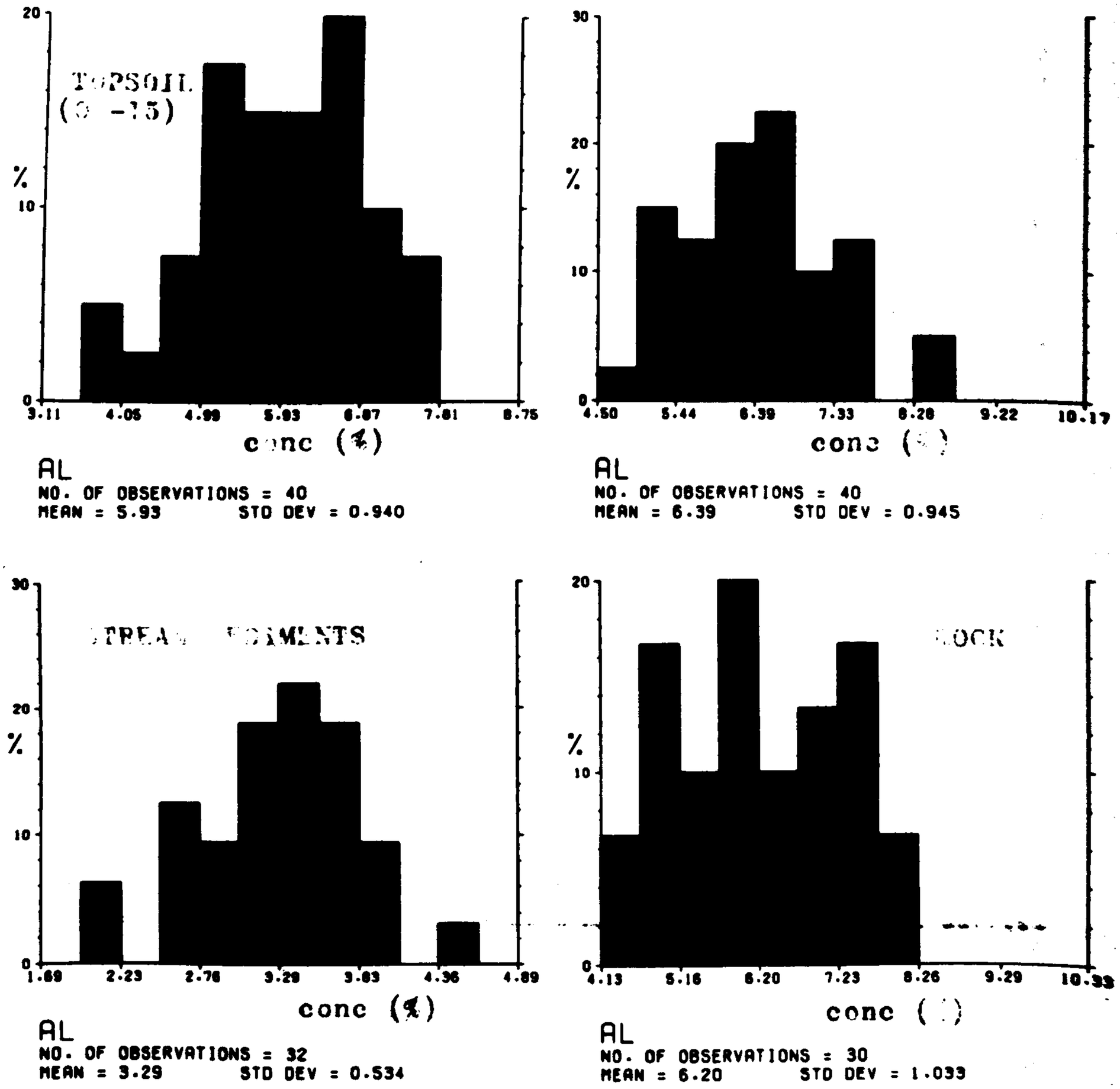
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

*** = Significant at .01 level

( ) = Negative Correlation.

Fig. 13-6



Histograms of the distribution of Al in the rocks, soils and stream sediments derived from the calcareous facies of the Lower Lias in the Somerset study area.

Table 13-6a Aluminium Concentrations In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias.

Medium	N	Mean (%)	S.D.	C.V.	Range Min (%)	Max (%)
Rock	30	6.4	1.8	28.1	3.0	8.6
T/Soil	40	6.9	1.3	18.1	3.5	8.8
S/Soil	40	7.3	1.2	15.9	3.5	9.4
S/Sedt	32	4.1	1.0	23.3	2.4	6.0

N = Total Number Of Samples

S.D. = Standard Deviation.

C.V.= Coefficient Variation = S.D./ Mean x 100.

Table 13-6b Significance Of The Correlation Coefficients Between Al And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	*		**	-	-	***	-	**	-	-	-
T/Soil	-	**		**	-	-	*	-	**	-	-	-
S/Soil	-	***		***	*	*	*	-	*	-	-	-
S/Sedt	*	**		**	*	-	-	*	-	-	-	-

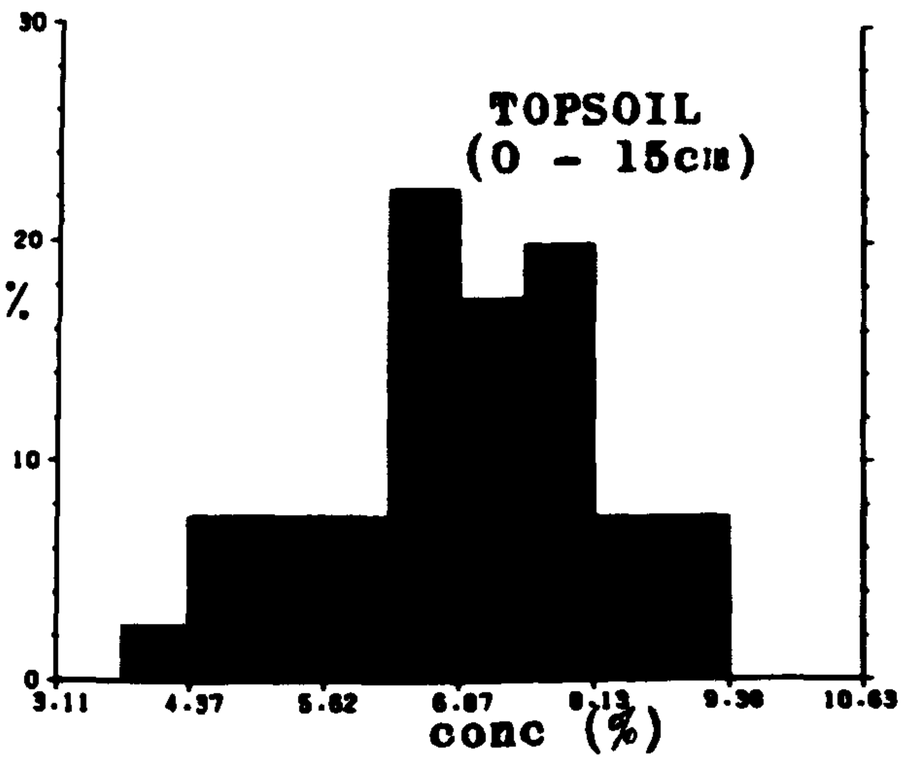
Level Of Significance - = Not Significant * = Significant at .10 level

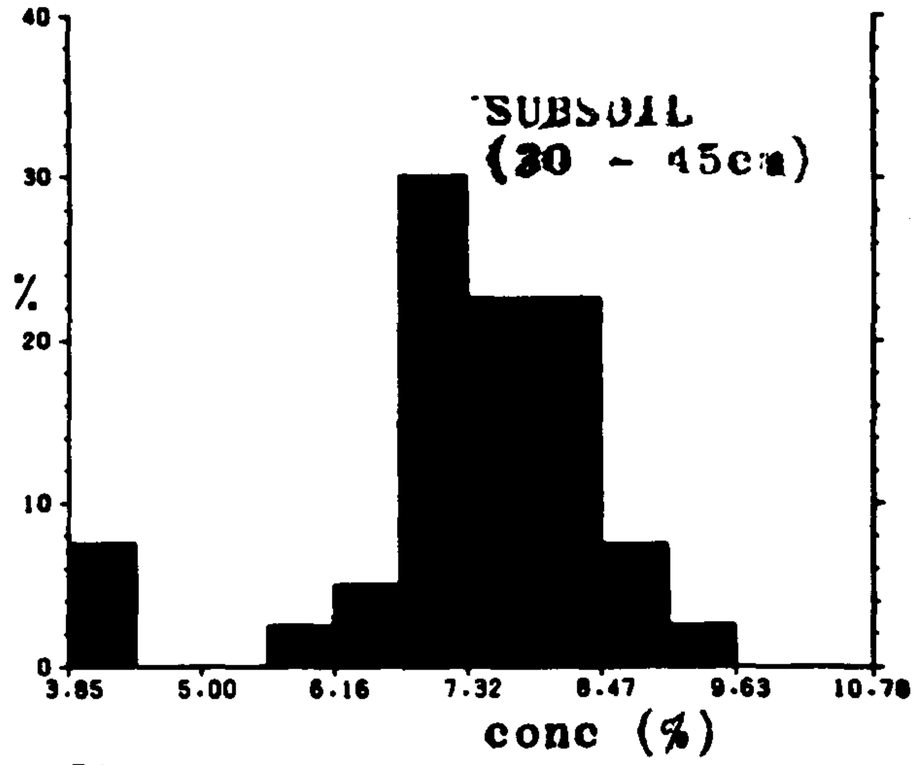
** = Significant at the .05 level

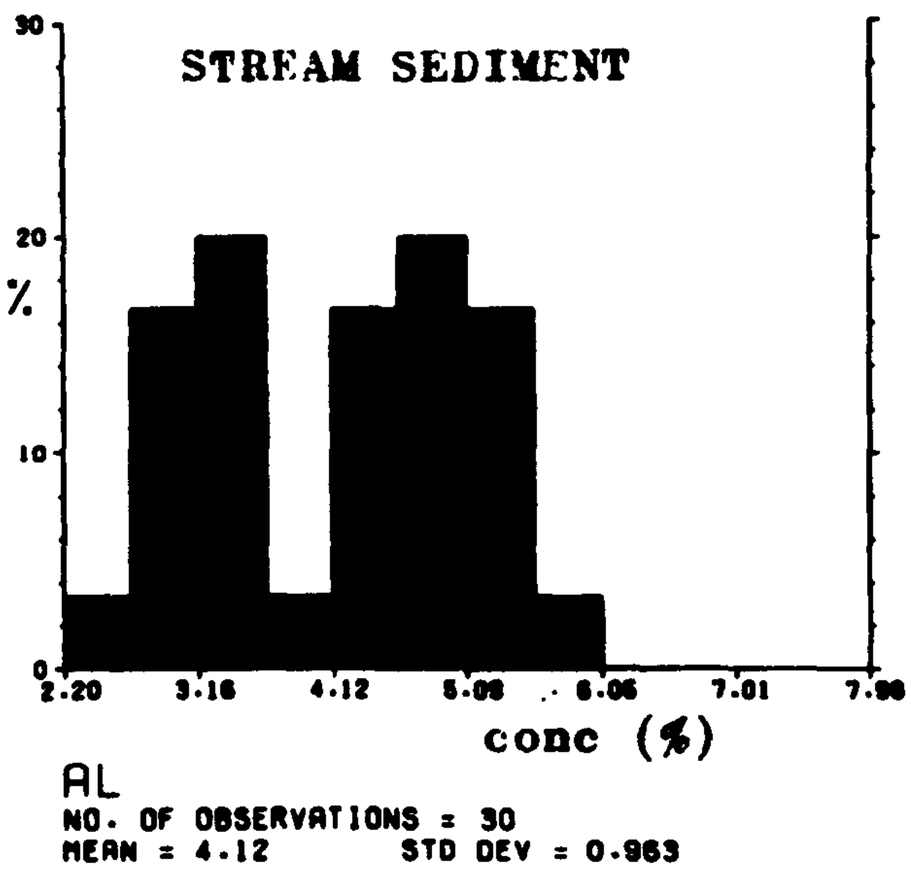
*** = Significant at .01 level

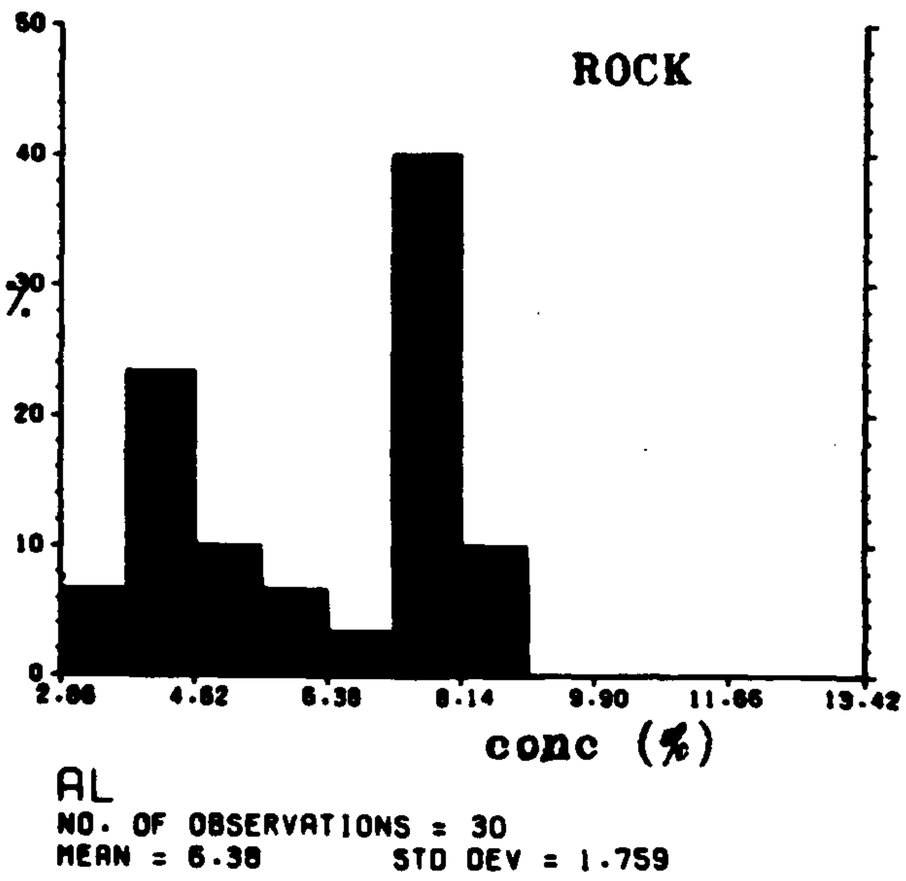
( ) = Negative Correlation.

Fig. 13-7









Histograms of the distribution of Al in the rocks, soils and stream sediments derived from the less calcareous facies of the Lower Lias in the Somerset study area.

less calcareous rocks of the Lias showed that the mean concentrations were similar (Tables 13-5a,-6a). The coefficients of variation indicated that there was greater variation of Al in the less calcareous beds (Table 13-6a). Apart from the minor depletions of Al in some topsoil samples of both the Denchworth and the Evesham soil series compared to the subsoil, in general, the mean concentrations of Al in both soil series were similar to those of the associated rocks (Tables 13-5a).

The results showed that the mean concentration of Al were lower in the stream sediments derived from both beds. The coefficients of variation values showed that variation of Al in the stream sediments were similar to those in the rocks. It was inferred that differences between the Al concentrations in the calcareous and the less calcareous phase of the Lias were only marginal.

Inter-element correlation.

In both facies of the Lower Lias Al was significantly correlated to Mg and Fe in all the associated media (Tables 13-5b, -6b). Further significant correlations were found with Ni and Cu in the calcareous rocks and sediments. In the Evesham soil series negative correlations occurred with the pH in both top and subsoil while in the topsoil a positive correlation was found with the organic matter(LOI).

In the geochemical environment Al tends to be related to the clay minerals and it seemed likely that the persistent correlation with such elements as Mg, Fe and Ni may represent an association with the clay minerals.

Table 13-7a Iron Concentrations In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias.

Medium	N	Mean (%)	S.D.	C.V.	Range Min (%)	Max (%)
Rock	30	4.4	0.8	18.3	3.0	6.0
T/Soil	40	4.4	0.7	15.9	3.2	5.8
S/Soil	40	4.3	0.7	15.1	3.3	5.8
S/Sedt	32	3.1	0.4	11.8	2.4	3.9

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 13-7b Significance Of The Correlation Coefficients Between Fe And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	(**)	-	*		-	-	-	-	**	**	*	-
T/Soil	(**)	-	*		*	-	-	-	*	**	-	-
S/Soil	(**)	-	**		**	-	-	-	*	**	*	(**)
S/Sedt	-	-	**		*	-	-	-	-	-	-	-

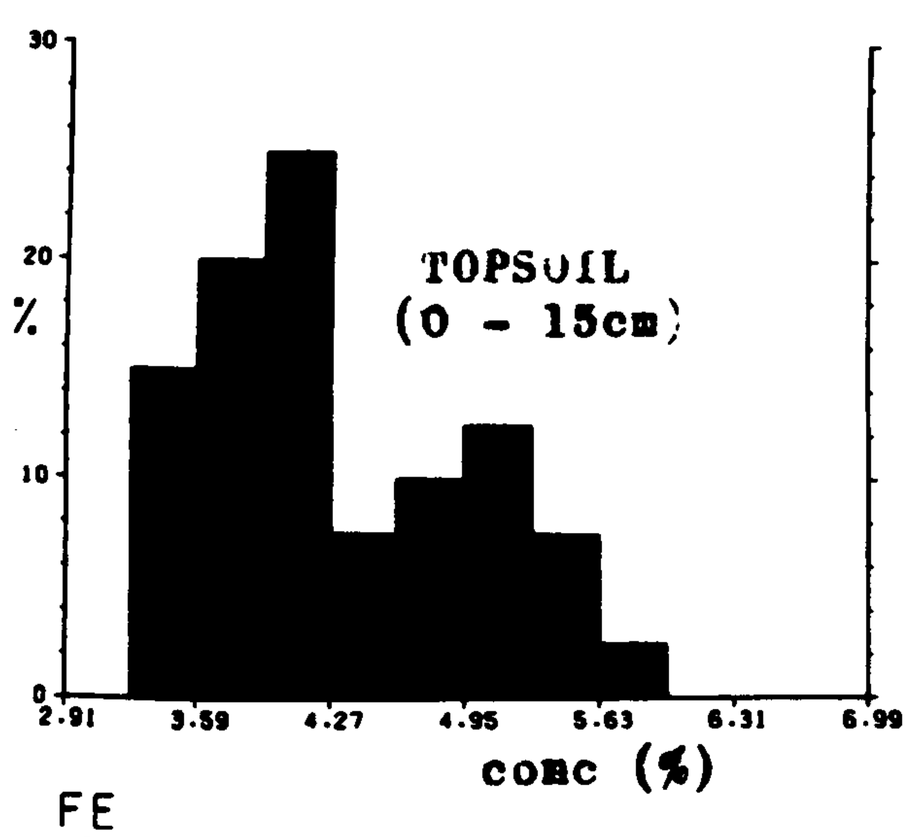
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

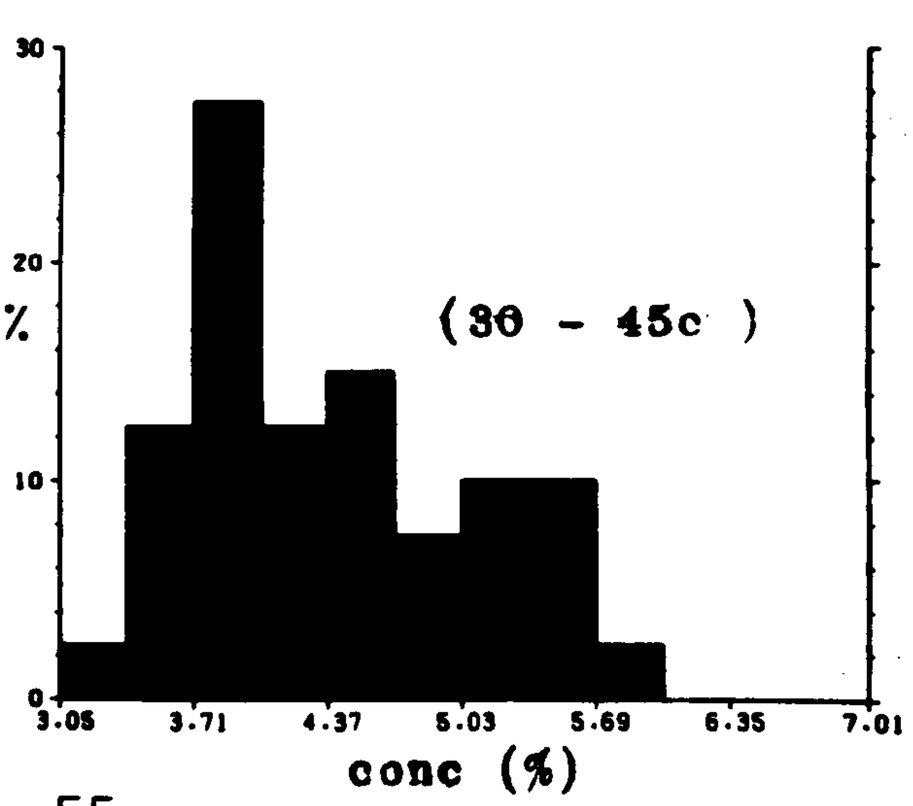
*** = Significant at .01 level

( ) = Negative Correlation.

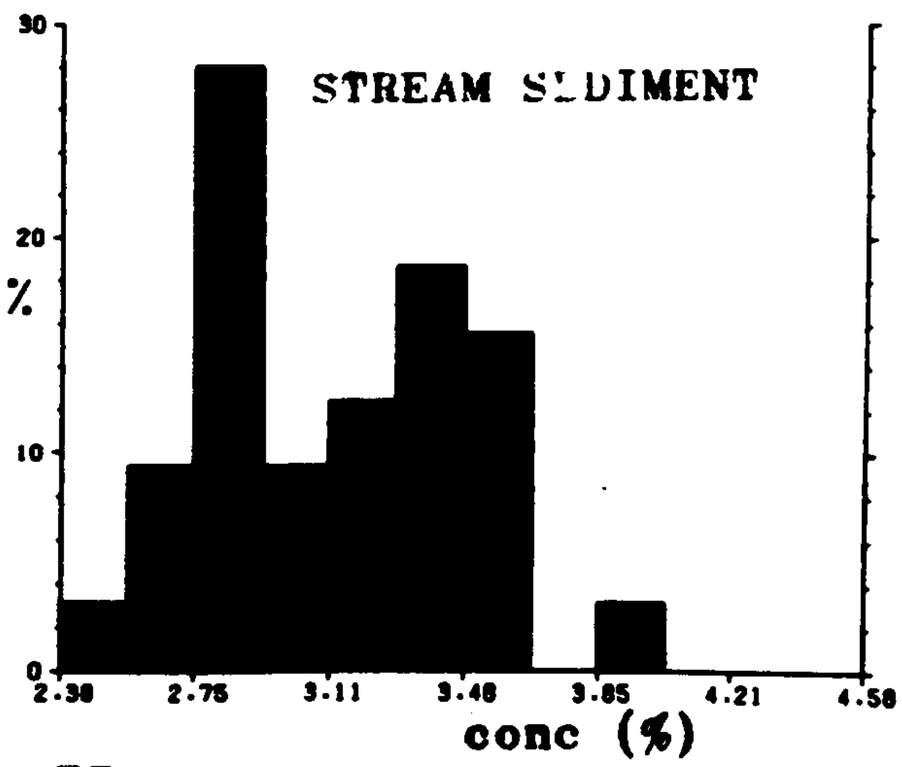
Fig. 13-8



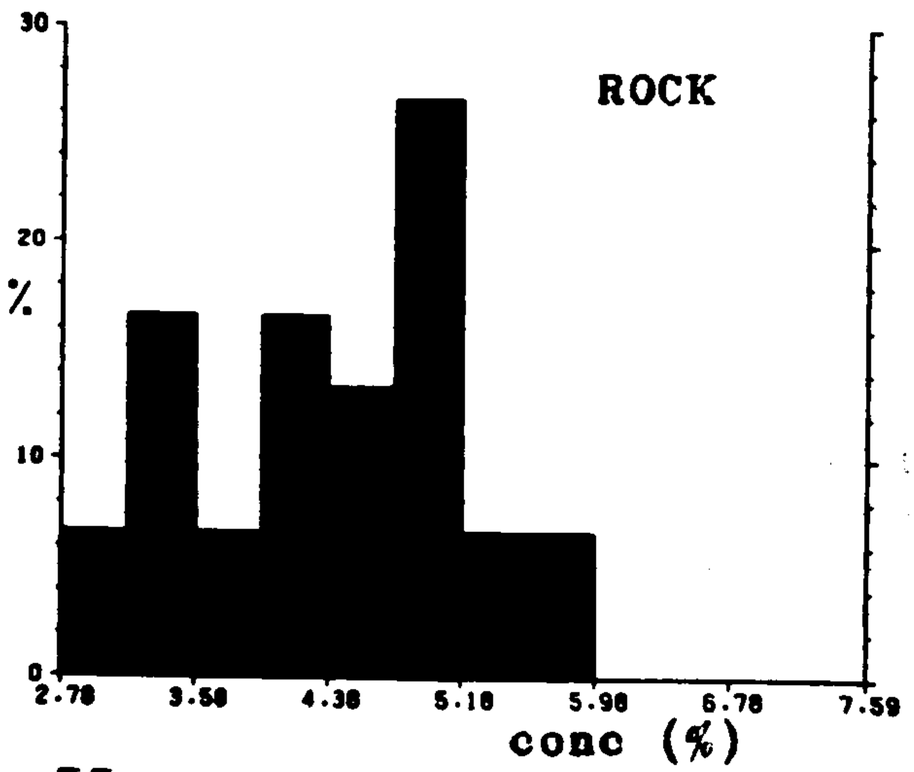
FE
NO. OF OBSERVATIONS = 40
MEAN = 4.27 STD DEV = 0.680



FE
NO. OF OBSERVATIONS = 40
MEAN = 4.37 STD DEV = 0.660



FE
NO. OF OBSERVATIONS = 32
MEAN = 3.11 STD DEV = 0.367



FE
NO. OF OBSERVATIONS = 30
MEAN = 4.38 STD DEV = 0.802

Histograms of the distribution of Fe in the rocks, soils and stream sediments derived from the calcareous facies of the Lower Lias in the Somerset study area.

(d) Iron.

As in the case of Mg and Al concentrations of Fe in the two facies of the Lias showed no obvious differences. The mean concentrations in the two beds were similar (Tables 13-7a, -8a). The histograms (Figs 13-8, -9) showed that over 40% of the calcareous samples had concentrations greater than 5% Fe. Coefficients of variation showed that the wider range in the less calcareous rock samples was accompanied by greater variation of Fe. In both the Denchworth and Evesham series the ranges and mean concentrations of Fe in the topsoil and subsoil were very similar.

Mean concentrations in the stream sediments derived from both beds were lower than those in the rocks and soils. The coefficients of variation showed that there was a decrease in the variation of Fe in the soils compared to the rocks and stream sediments. This was more marked in the Denchworth series where variation in the parent material was twice as high as that of the topsoil (Table 13-8a). In the Evesham series the variation in the top and subsoil were similar.

In general, it can be inferred that differences in the concentrations of Fe in the two parent materials were negligible. In the soils, variation was higher and the range wider in the subsoil than in the topsoil, while in the stream sediments the depressed concentrations are probably due to dilution with precipitated calcium carbonates.

Inter-element correlation.

The results showed that apart from the calcareous sediments (Table 13-7b) there were significant correlations with Al and Ni in

Table 13-8a Iron Concentrations In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias

Medium	N	Mean (%)	S.D.	C.V.	Range Min (%)	Max (%)
Rock	30	4.7	1.0	21.3	2.8	7.5
T/Soil	40	4.2	0.5	10.8	3.1	5.4
S/Soil	40	4.4	0.7	16.5	2.3	6.2
S/Sedt	30	3.5	0.8	23.3	2.5	5.5

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 13-8b Significance Of Correlation Coefficients Between Fe And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	*	**		-	-	-	-	**	*	-	-
T/Soil	-	**	**		**	-	**	-	**	-	-	-
S/Soil	-	*	***		-	-	-	-	**	-	-	-
S/Sedt	*	**	**		*	*	*	*	**	*	*	*

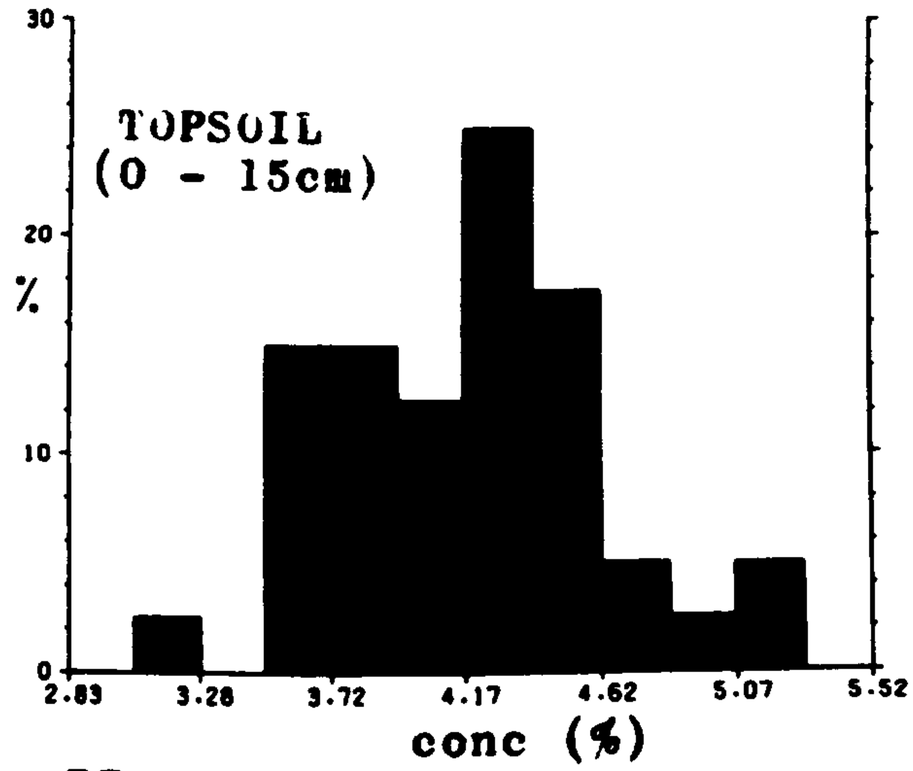
Level Of Significance - = Not Significant * = Significant at .10 level

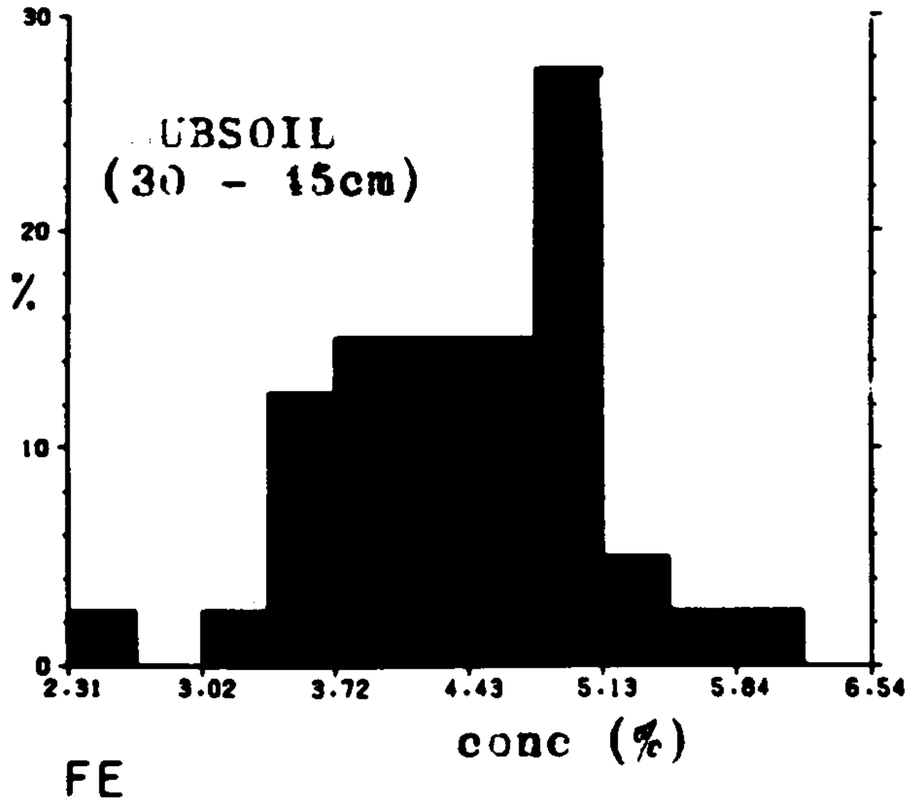
** = Significant at the .05 level

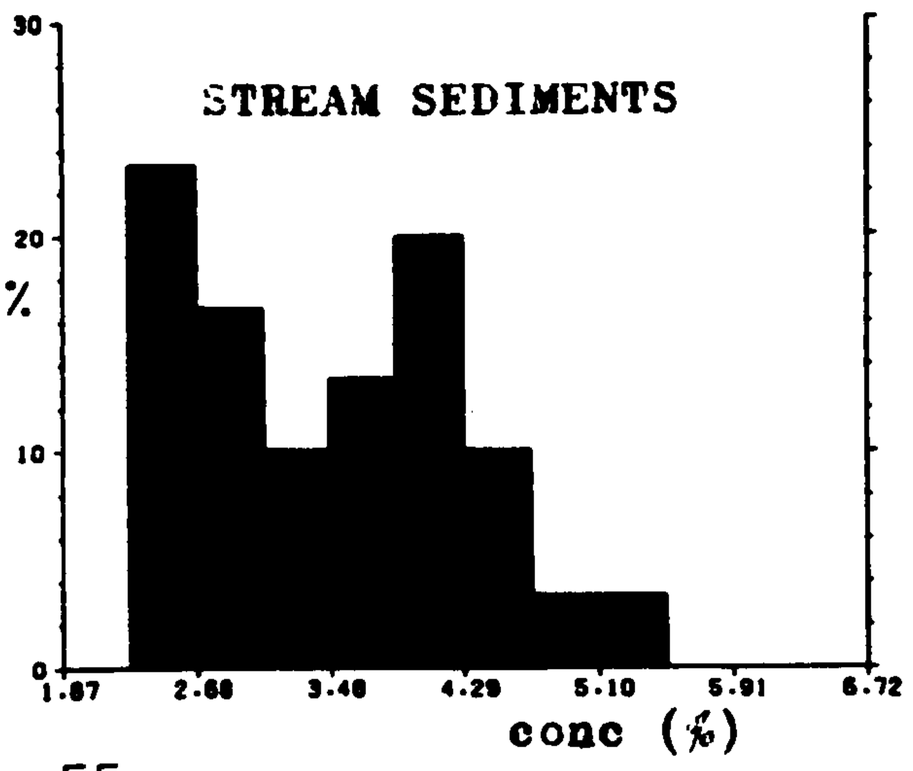
*** = Significant at .01 level

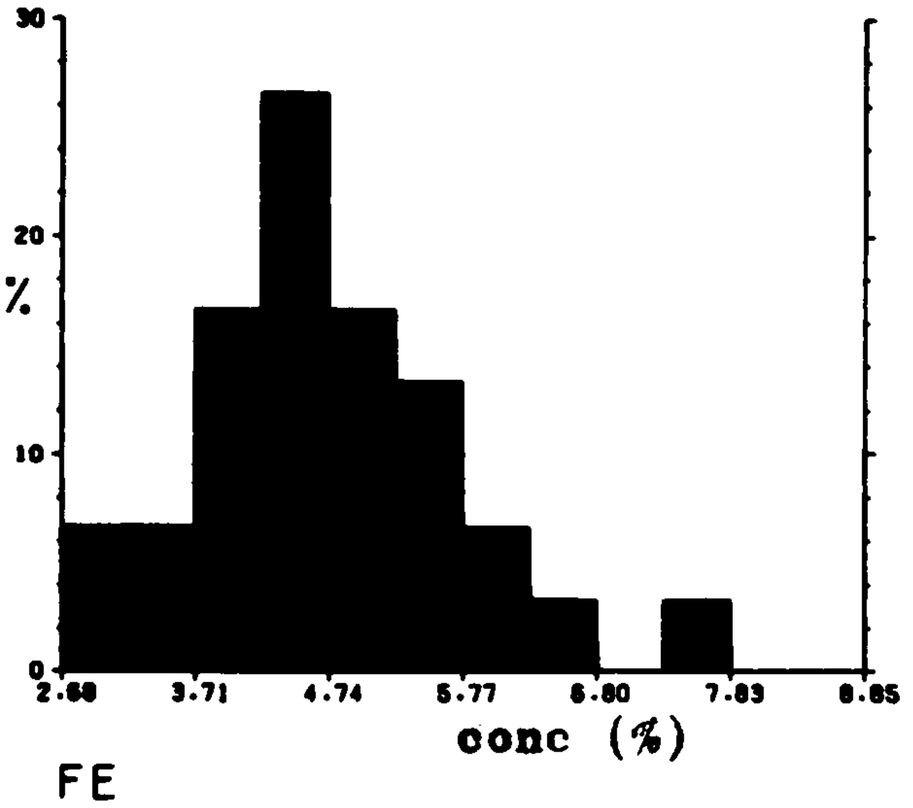
( ) = Negative Correlation.

Fig. 13-9









Histograms of the distribution of Fe in the rocks, soils and stream sediments derived from the less calcareous facies of the Lower Lias in the Somerset study area

all the media derived from both facies of the Lower Lias. In the calcareous rocks there were positive and significant correlations with Cu and organic matter(LOI) while the correlation with Ca was negative. In the top and subsoils of the Evesham series there were significant correlations with Zn (Table 13-7b). Apart from the correlations with Al and Ni, no significant correlations occurred with other elements in the calcareous sediments.

In the less calcareous facies Fe was significantly correlated to Mg, Al and Ni in all the media studied. Weaker correlations were found with Zn and Co in the topsoil. The correlations with most elements in the stream sediments were weak.

The results suggested that Fe was strongly associated with Al and Ni. The association persisted in the various media investigated and it seemed that pedogenic and stream processes did not greatly affect the relationship. This was interpreted as an association with the clay minerals in the various media.

(e) Zinc.

There was a marked difference in the zinc content of the calcareous and less calcareous beds of the Lower Lias (Table 13-9a, 10a). Higher concentrations were recorded in the less calcareous rocks (mean level =140ppm) than in the calcareous rocks (mean level=113ppm). The histograms showed that concentrations in excess of 113ppm were common in the calcareous rocks while in the less calcareous rocks concentrations below 140ppm were common. In the Denchworth series the mean concentrations in the top and subsoil were almost identical being in the main marginally lower than in the rocks.

Table 13-9a Zinc Concentrations In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	30	113.9	23.5	20.7	71.0	148.0
T/Soil	40	142.5	21.9	15.4	100.0	180.0
S/Soil	40	130.1	19.9	15.3	100.0	186.0
S/Sedt	32	163.2	21.7	13.3	122.0	192.0

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 13-9b Significance Of The Correlation Coefficients Between Zinc And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	-	-	-		-	-	-	-	**	**	*
T/soil	(*)	-	*	*		-	-	-	*	*	**	-
S/Soil	-	-	-	**		-	-	*	*	*	-	-
S/Sedt	-	-	-	*		-	-	-	**	-	-	-

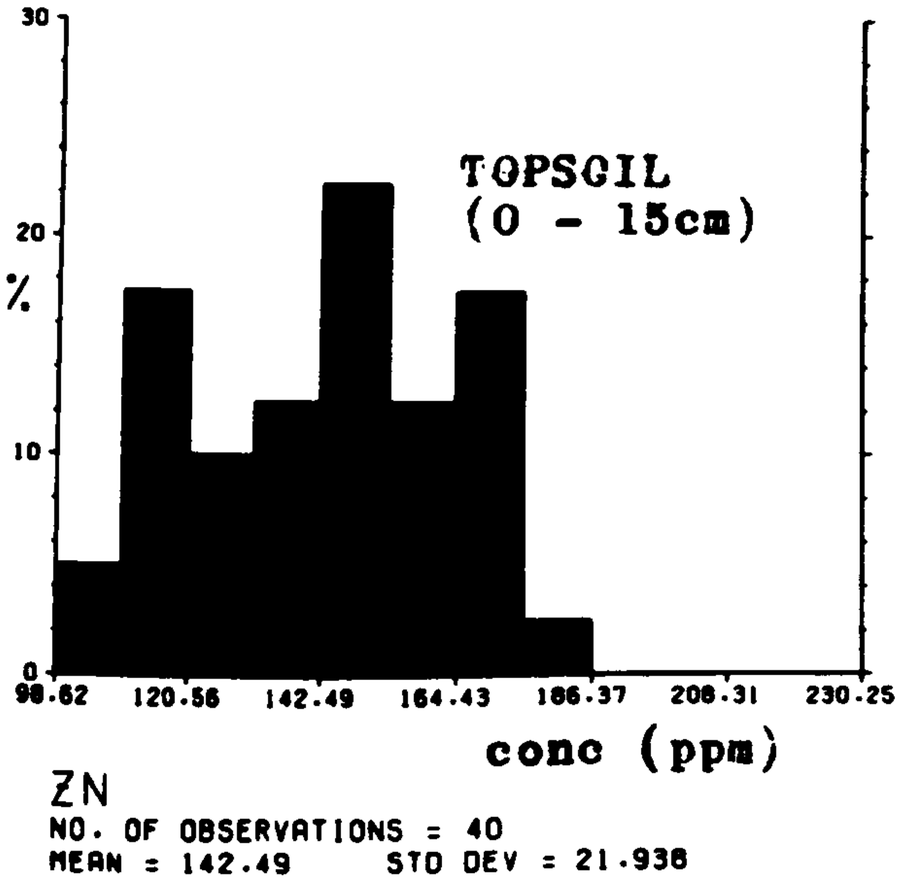
Level Of Significance - = Not Significant * = Significant at .10 level

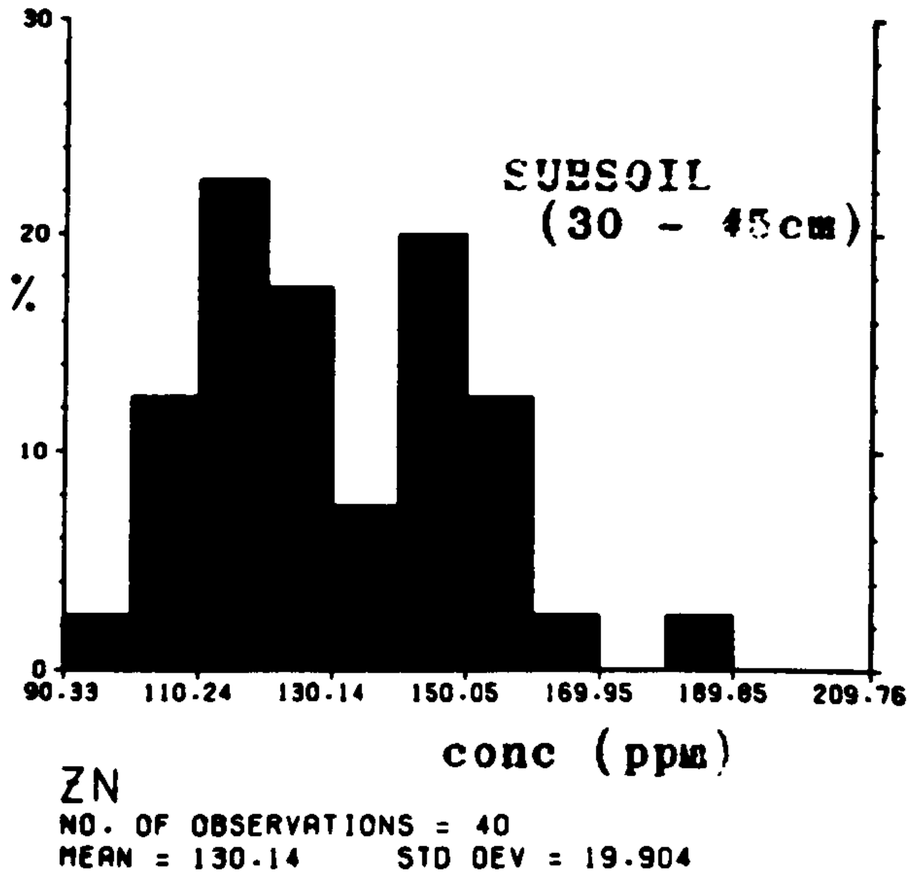
** = Significant at the .05 level

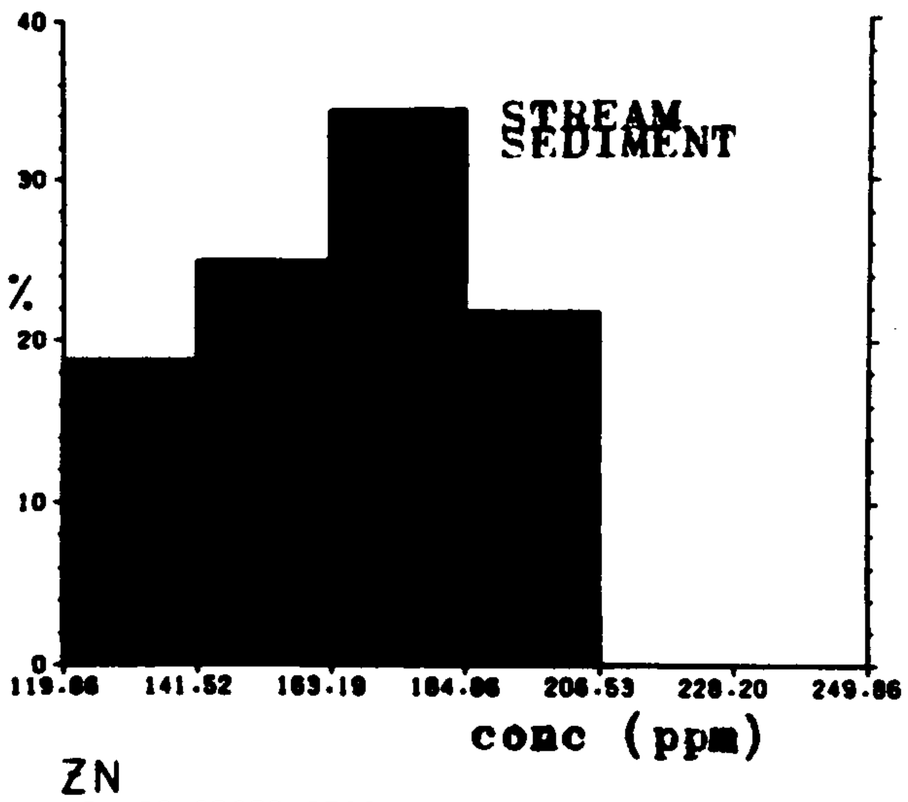
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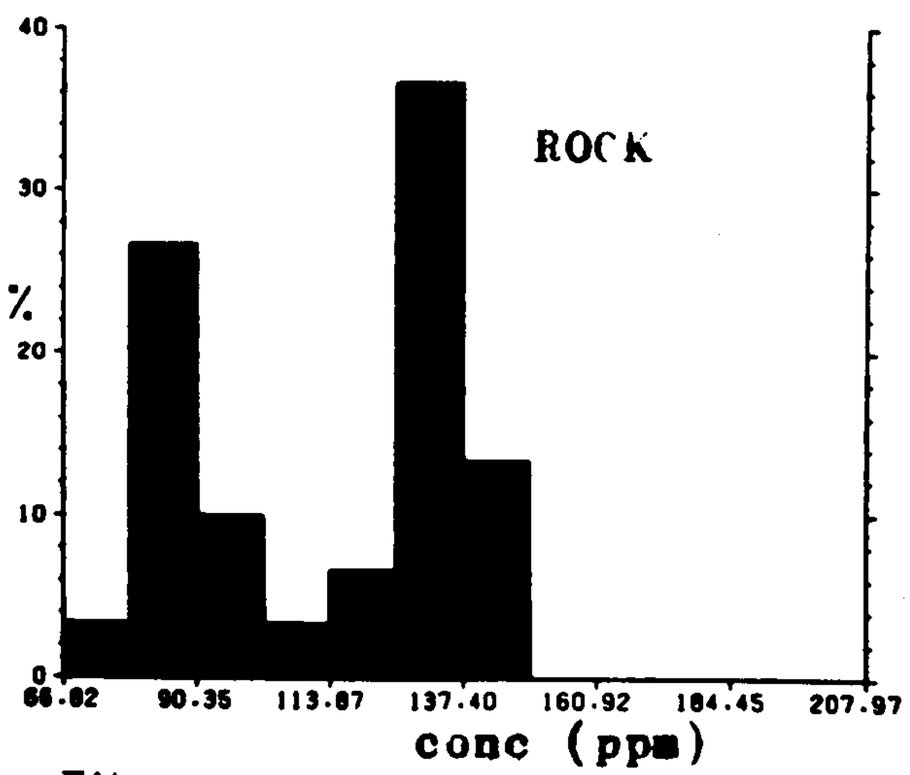
( ) = Negative Correlation.

Fig. 13-10









Histograms of the distribution of Zn in the rocks, soils and stream sediments derived from the calcareous facies of the Lower Lias in the Somerset study area.

Table 13-10a Zinc Concentrations In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	30	140.5	26.8	19.1	105.0	185.0
T/Soil	40	137.7	18.1	13.1	89.0	183.0
S/Soil	40	137.3	24.5	17.8	89.0	190.0
S/Sedt	40	150.0	25.0	16.7	80.0	194.0

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 13-10b Significance Of Correlation Coefficients Between Zn And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	-	-	-		*	*	*	-	-	-	-
T/Soil	-	-	-	**		*	*	*	*	**	-	-
S/Soil	-	-	*	-		-	-	-	*	-	-	-
S/Sedt	*	**	*	*		*	-	*	*	*	-	-

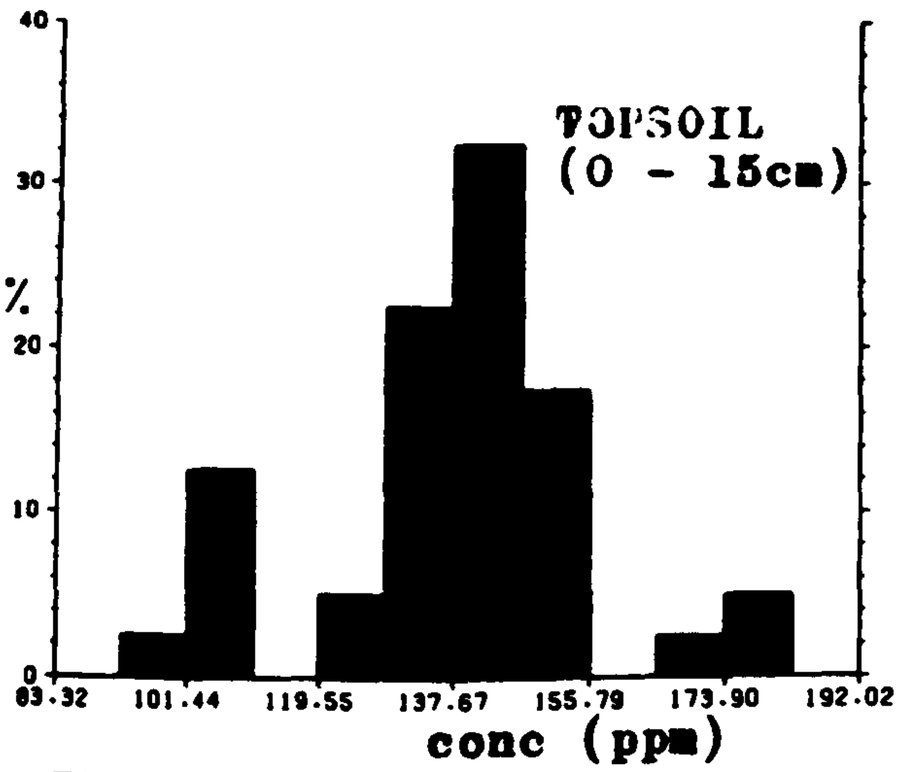
Level Of Significance - = Not Significant * = Significant at .10 level

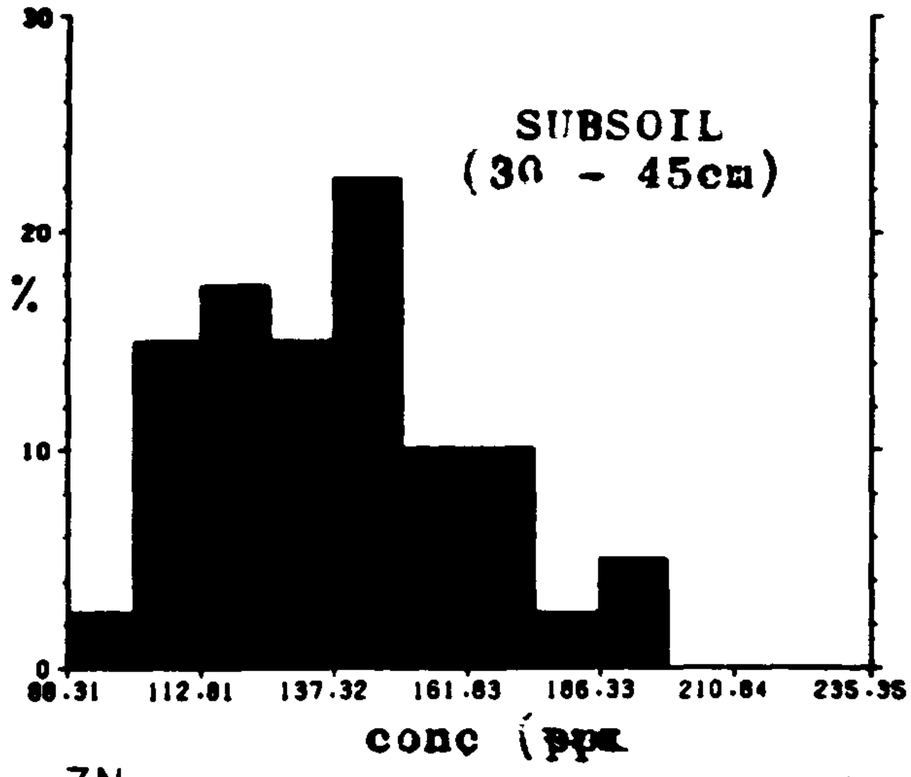
** = Significant at the .05 level

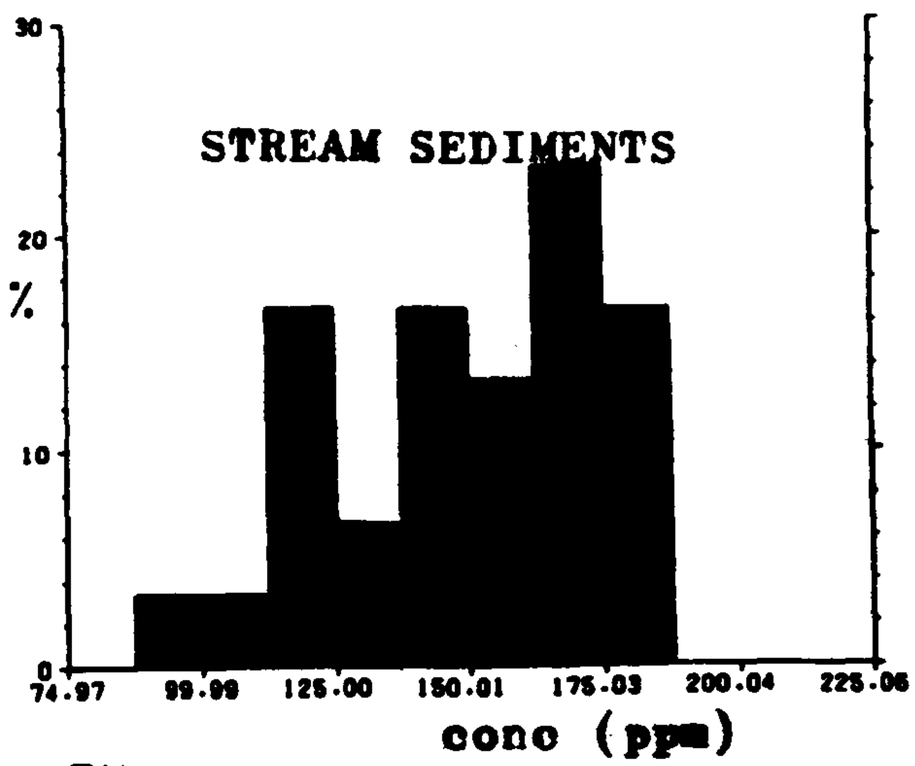
*** = Significant at .01 level

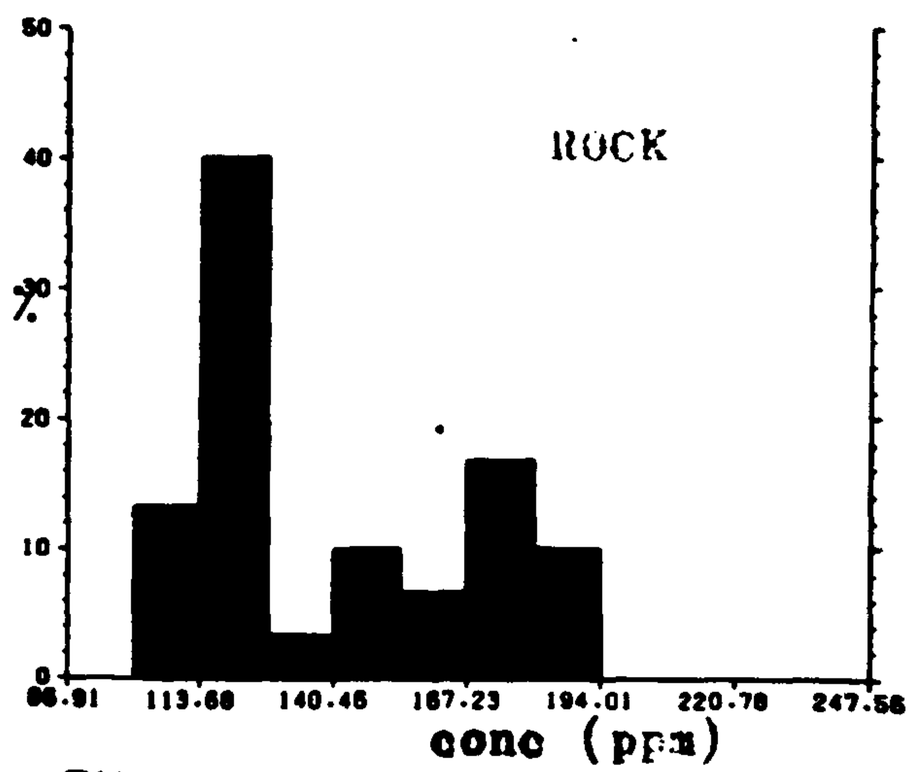
( ) = Negative Correlation.

Fig. 13-11









Histograms of the distribution of Zn in the rocks, soils and stream sediments derived from the less calcareous facies of the Lower Lias in the Somerset study area.

In contrast Zn concentrations were higher in the Evesham soil series than the calcareous beds from which it is derived.

Stream sediment concentrations of Zn in both facies were higher than those in the associated rocks. The histograms (Figs. 13-10, -11) showed that in both facies there was a tendency for the higher concentrations to occur more frequently. The coefficients of variation showed that maximum variation of Zn occurred in the rocks.

The build up of Zn in the stream sediments suggested an enrichment mechanism operating in the streams. This was thought to be due the formation of secondary carbonates in the streams. Thus samples high in Ca also had higher concentrations of Zn.

Inter element correlations.

In the calcareous rocks only the correlation with Cu, organic matter(LOI) and pH were significant (Table 13-9b). Weaker correlations were found with Al, Fe, Ni, Cu and organic matter(LOI) in the topsoils of the Evesham soil series. The correlations with Fe, Ni and Cu persisted in the subsoil where further significant correlation with Pb was found. In the calcareous sediments Zn was weakly correlated to only Fe and Ni.

In the less calcareous rocks weaker correlations occurred with Mn, Co and Pb (Table 13-10b). These persisted in the topsoils of the Denchworth series where a further significant correlations were found with Fe and Cu. In the subsoils, only the correlations with Al and Ni were significant. Apart from cobalt, zinc was significantly correlated to most elements in the less calcareous sediments.

The results show that in the calcareous rocks zinc tended to

be associated with the organic matter(LOI). This persisted in the topsoils of the Evesham series. In the less calcareous rocks the weaker correlations with Mn and Co suggested an association with the hydrous oxides. The weak correlations with most elements in the stream sediments suggested that Zn may be associated with most of the secondary processes in the streams. This may include associations with the secondary carbonates and the hydrous oxides. These processes may account for the higher concentrations of Zn in the stream sediments.

(f) Manganese.

The range of Mn concentrations in both beds of the Lower Lias were similar (Tables 13-11a, -12a). The histograms showed that concentrations below 1000ppm were common in the rock samples of both facies (Figs. 13-12, -13). Manganese concentrations were higher in the Evesham series than in the Denchworth series. In both soil series, concentrations of Mn in the subsoils were higher than those in the topsoils. In the Denchworth soil series this was accompanied by increased variation in the subsoil. The mean concentrations of Mn in the stream sediments derived from both beds of the Lias were lower than those of the rocks and soils, and samples with high concentrations of Ca had lower concentrations of Mn.

It can be inferred from the above account that while concentrations of Mn in both rocks were similar there was a tendency towards the enhancement of Mn in the soils with higher concentrations recorded in the subsoil of both soil series. The decreased concentrations of Mn in the stream sediments may be due to dilution of the sediments by the precipitation of calcium carbonates.

Table 13-11a Manganese Concentrations In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	30	941.7	205.1	21.8	600	1250
T/Soil	40	869.5	207.7	23.9	500	1350
S/Soil	40	998.9	245.7	24.6	500	1450
S/Sedt	32	812.2	197.2	24.3	500	1250

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 13-11b Significance Of The Correlation Coefficients Between Manganese And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	-	-	-	-		***	-	-	-	-	-
T/Soil	-	-	-	-	-		***	-	-	-	**	-
S/Soil	-	-	-	-	-		***	-	-	-	**	-
S/Sedt	(*)	-	-	-	-		***	-	*	**	-	*

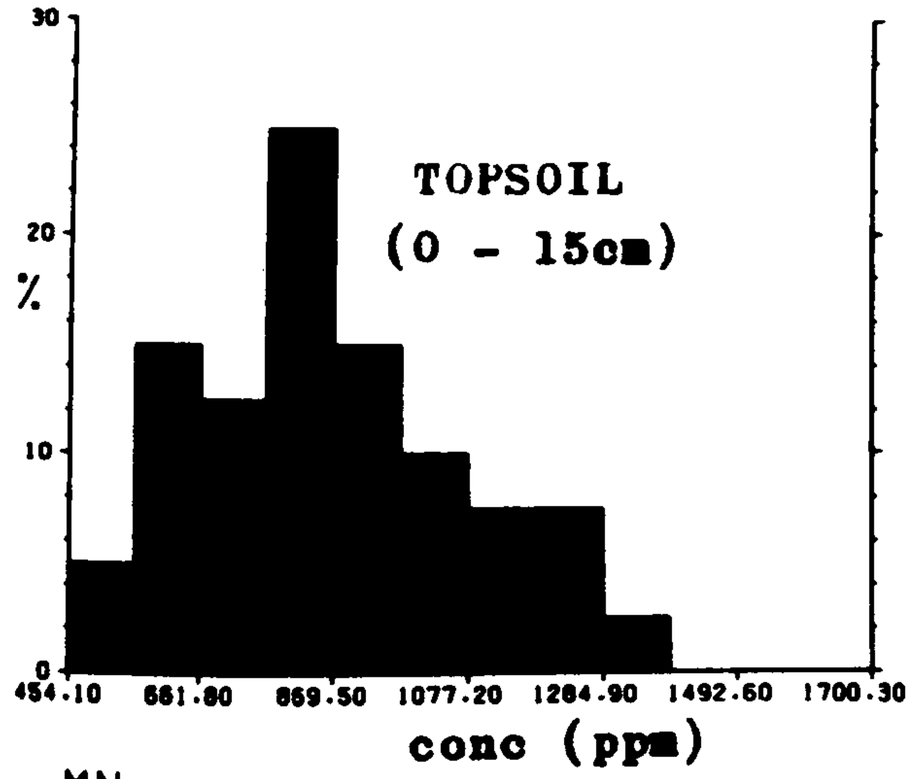
Level Of Significance - = Not Significant * = Significant at .10 level

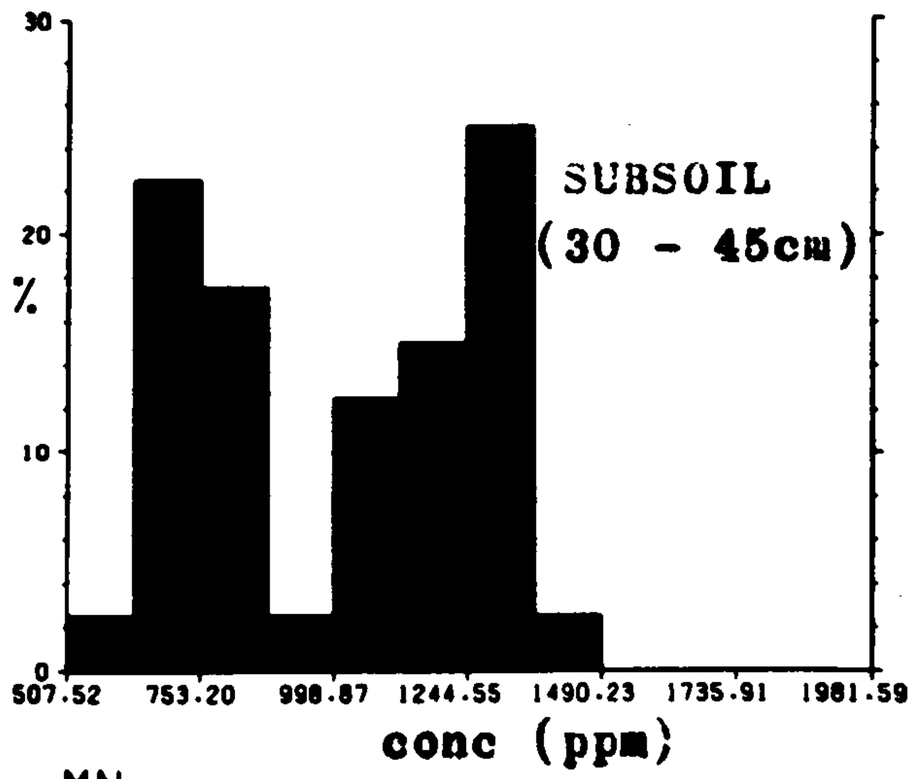
** = Significant at the .05 level

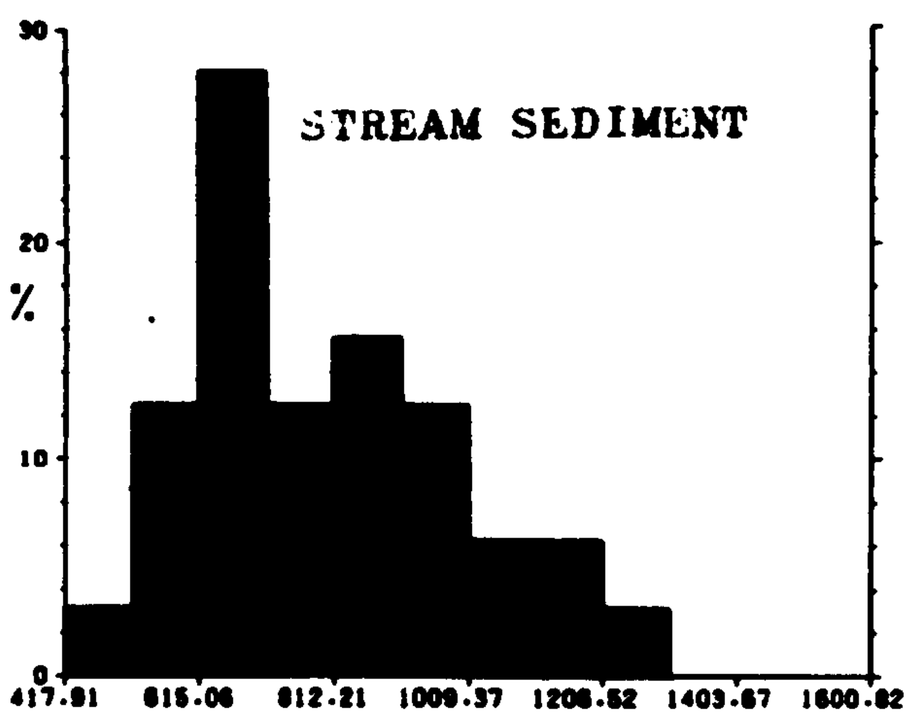
*** = Significant at .01 level

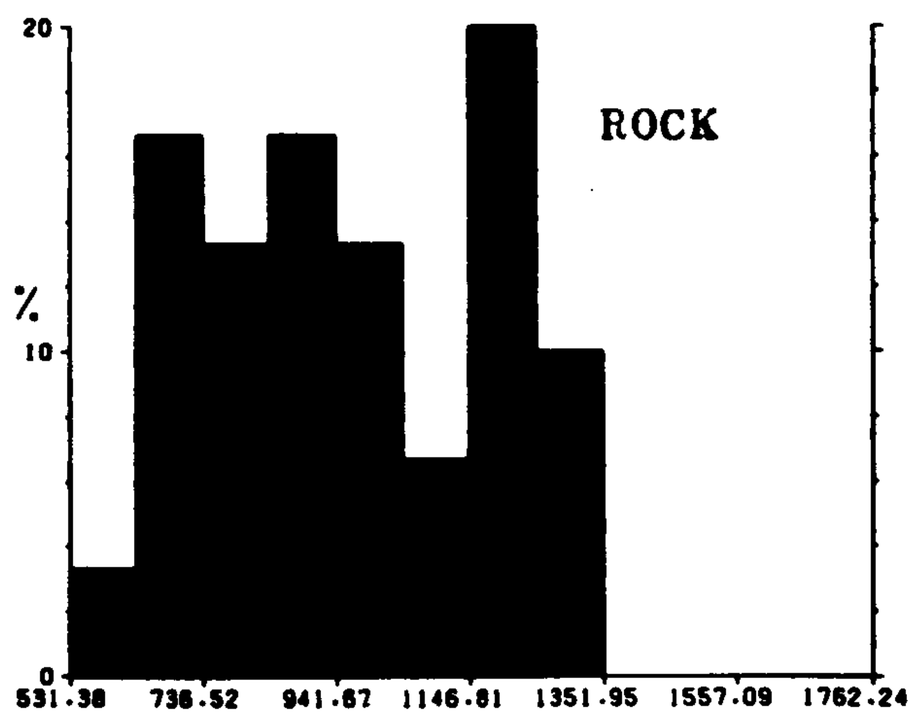
( ) = Negative Correlation.

Fig. 13-12









Histograms of the distribution of Mn in the rocks, soils and stream sediments derived from the calcareous facies of the Lower Lias in the Somerset study area.

Table 13-12a Manganese Concentrations In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	30	834.8	222.6	26.7	500.0	1350.0
T/Soil	40	692.6	166.1	23.9	400.0	1000.0
S/Soil	40	821.8	269.6	32.8	350.0	1550.0
S/Sedt	30	736.5	204.9	27.8	500.0	1350.0

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table13-12b Significance Of Correlation Coefficients Between Mn And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	-	-	-	*		**	-	-	-	-	-
T/Soil	-	-	-	-	*		***	-	-	-	-	-
S/Soil	-	-	-	-	-		***	-	-	-	-	-
S/Sedt	*	*	-	*	*		***	-	*	*	*	-

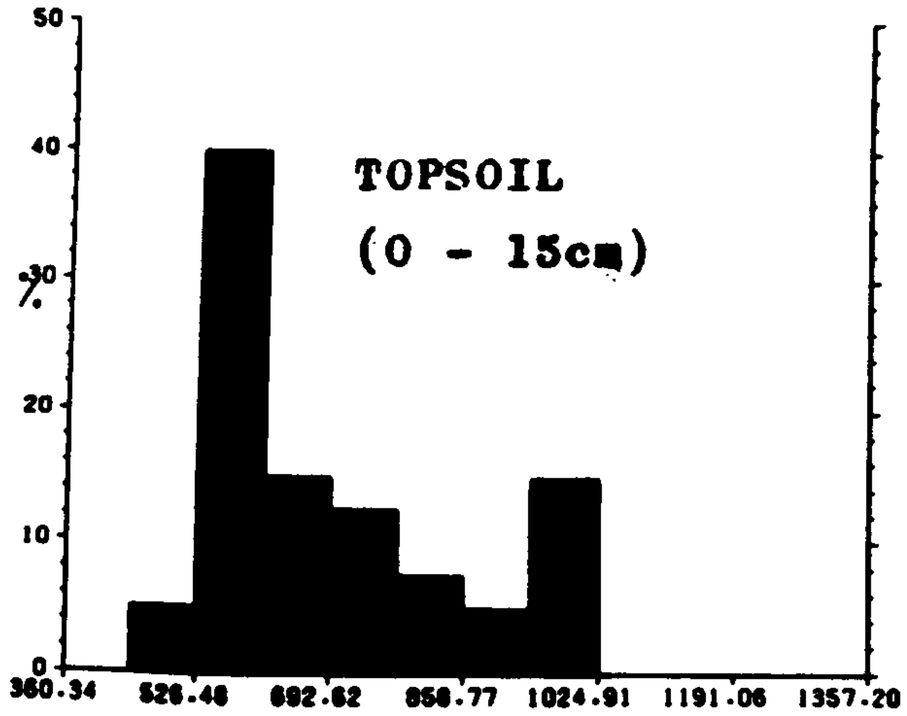
Level Of Significance - = Not Significant * = Significant at .10 level

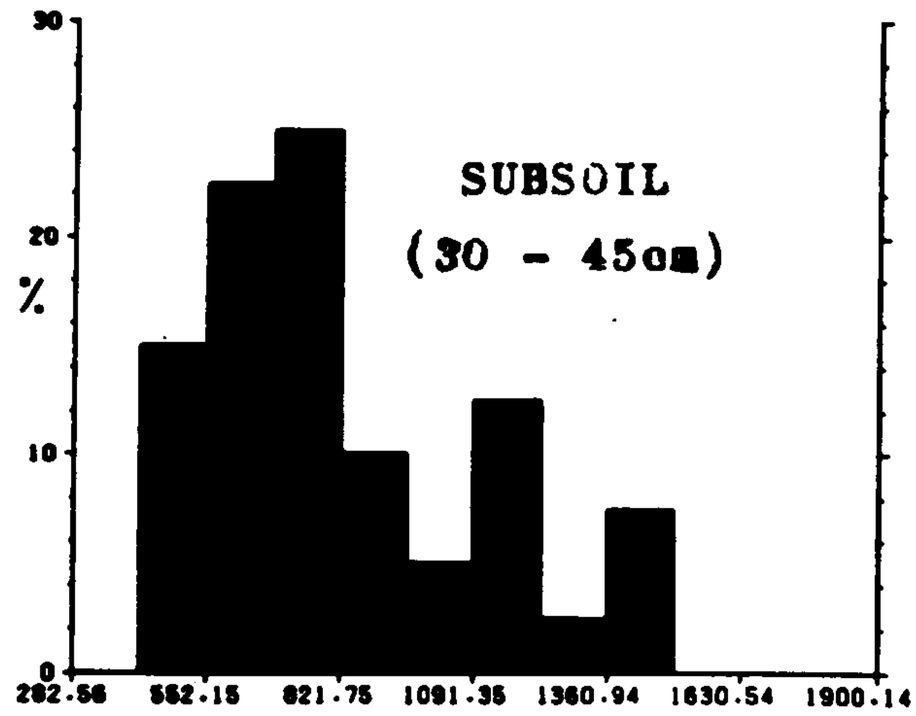
** = Significant at the .05 level

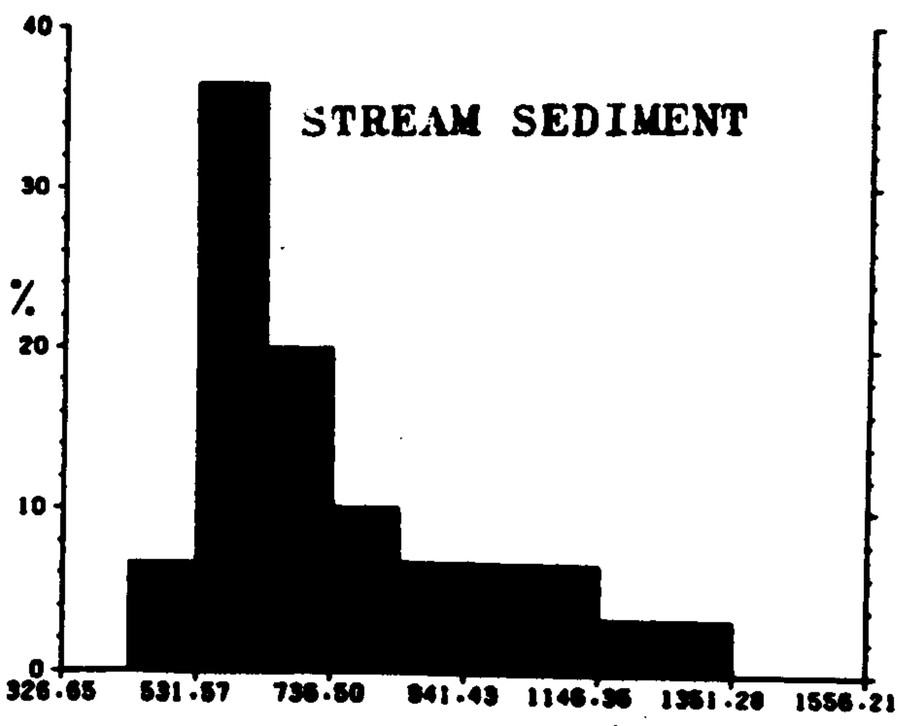
*** = Significant at .01 level

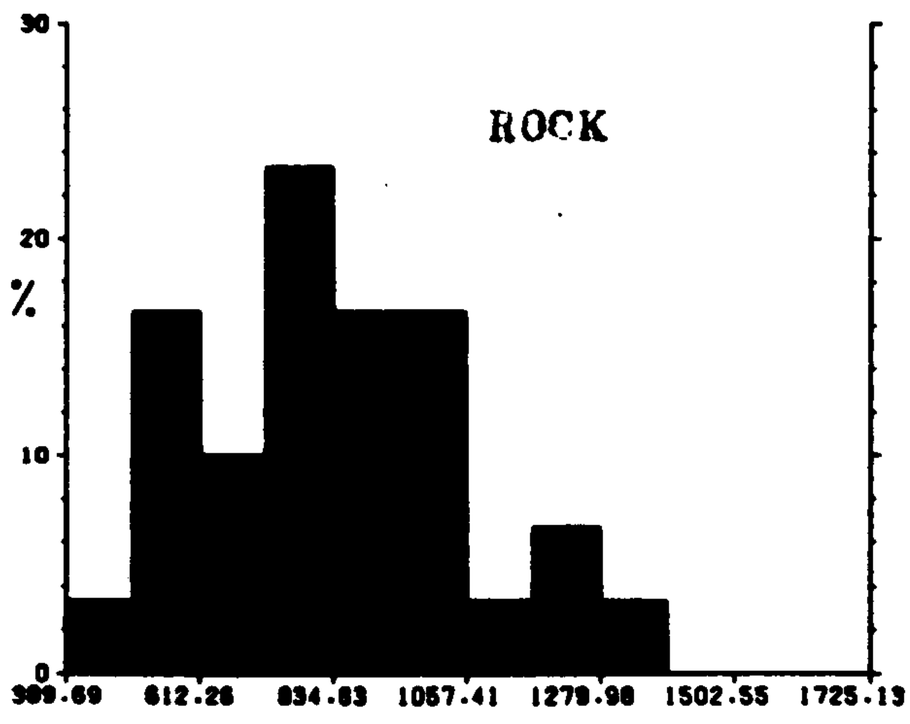
( ) = Negative Correlation.

Fig. 13-13









Histograms of the distribution of Mn in the rocks, soils and stream sediments derived from the less calcareous facies of the Lower Lias in the Somerset study area.

Inter element correlation.

In all the media Mn was highly correlated with Co (Table 13-11b, -12b). In the Denchworth soil series, Mn was weakly correlated with Zn in the topsoil while in the subsoils the correlation with Co was the only significant pair (Table 13-12b). In the less calcareous sediments, the strongest correlation was with Co while weaker correlations were found with all elements except Al and Pb.

Correlations with organic matter(LOI) in the top and subsoils of the Evesham soil series were significant while in the calcareous sediments, the correlations with Ni, Cu and pH were weak and positive (Table 13-11b). There was a negative correlation with Ca in the calcareous sediments.

The strong correlations with Co and other divalent cations were thought to reflect the "scavenging" activity of Mn oxides in all the media while the negative correlations with Ca were thought to reflect the dilution of the sediments by the precipitation of calcium carbonates.

(g) Cobalt.

As in the the case of Mn, the mean concentrations and ranges of Co in the two beds of the Lias were similar. The standard deviation and the coefficients of variation showed little differences in the variation of Co in the two facies (Tables 13-13a, -14a). In both the Evesham and Denchworth series concentrations of Co in the subsoil were slightly higher than in the topsoil, although the ranges

Table 13-13a Cobalt Concentrations In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	30	36.4	8.0	22.0	21.0	48.0
T/Soil	40	31.0	6.5	21.1	20.0	46.0
S/Soil	40	34.7	6.9	20.0	21.0	47.0
S/Sedt	32	36.4	8.4	23.1	23.0	49.0

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 13-13b Significance Of The Correlation Coefficients Between Cobalt And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	-	-	-	-	***		-	-	-	-	-
T/Soil	-	-	-	-	-	***		-	-	-	(*)	-
S/Soil	-	-	-	-	-	***		-	-	-	(*)	-
S/Sedt	-	-	-	-	-	***		-	-	-	-	-

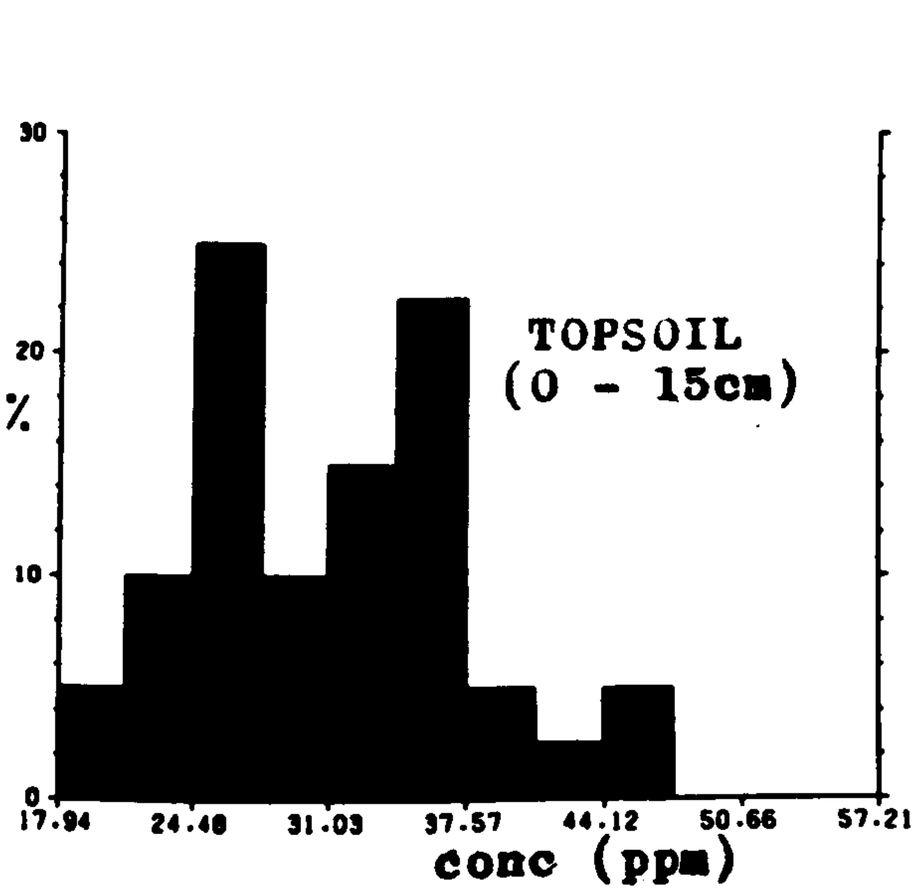
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

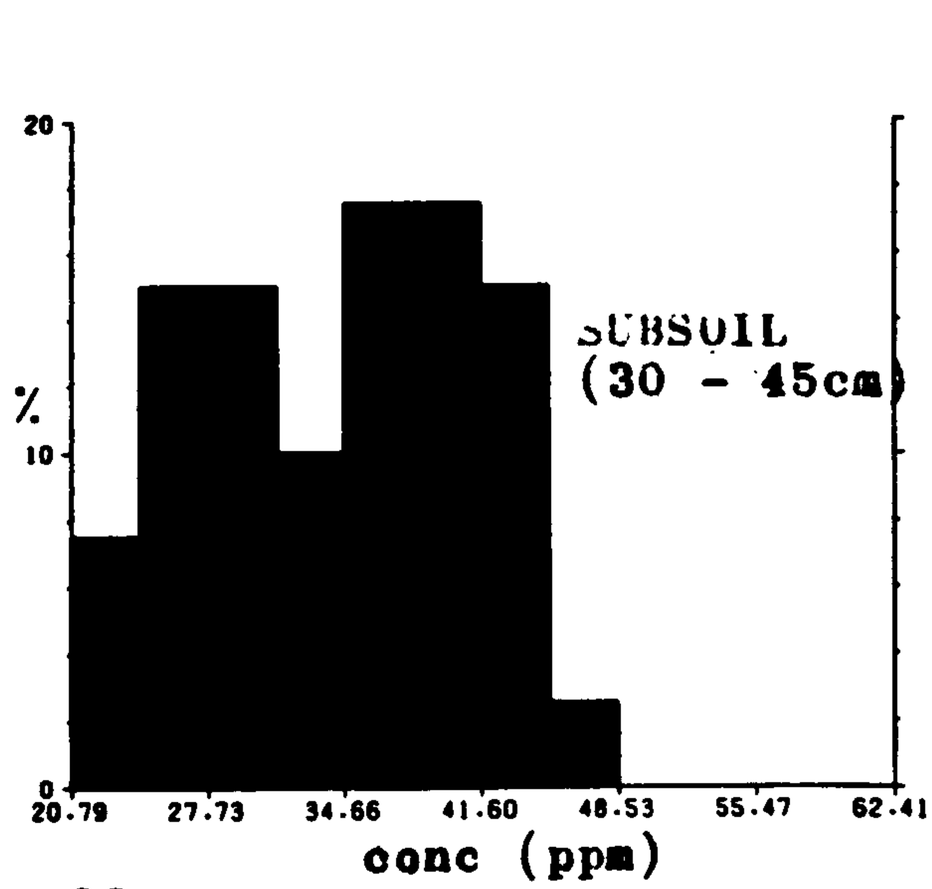
*** = Significant at .01 level

( ) = Negative Correlation.

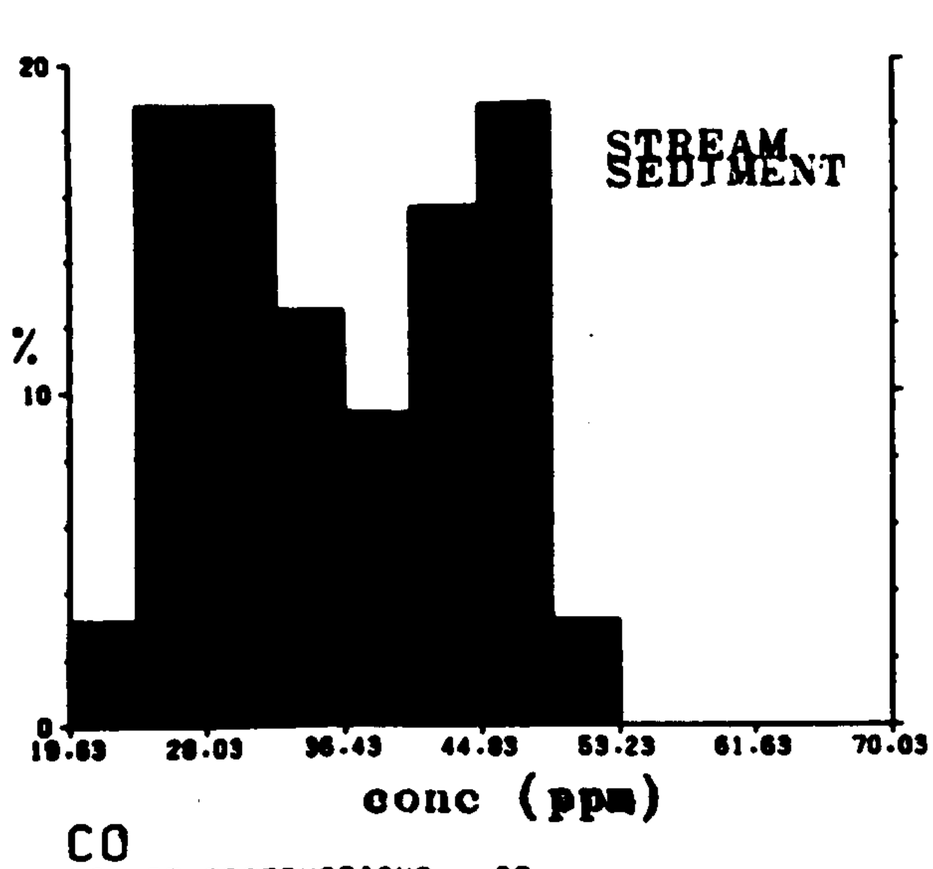
Fig. 13-14



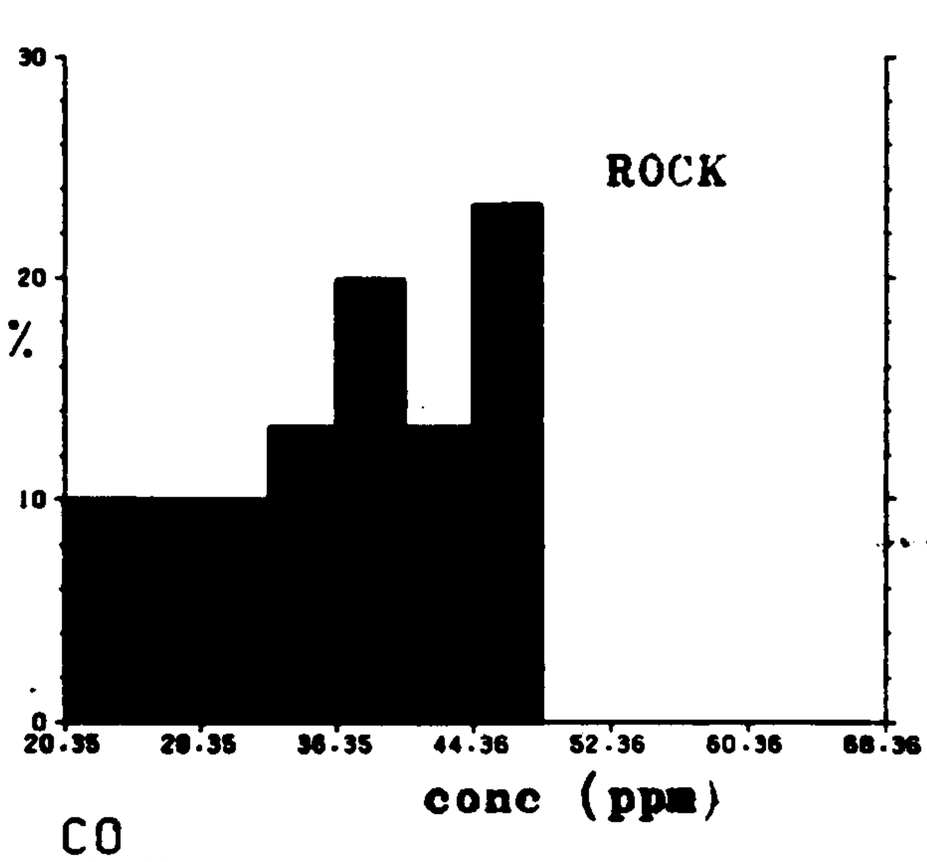
CO
NO. OF OBSERVATIONS = 40
MEAN = 31.03 STD DEV = 6.544



CO
NO. OF OBSERVATIONS = 40
MEAN = 34.66 STD DEV = 6.936



CO
NO. OF OBSERVATIONS = 32
MEAN = 36.43 STD DEV = 8.401



CO
NO. OF OBSERVATIONS = 30
MEAN = 36.35 STD DEV = 8.002

Histograms of the distribution of Co in the rocks, soils and stream sediments derived from the calcareous facies of the Lower Lias in the Somerset study area.

Table 13-14a Cobalt Concentrations In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	30	32.4	7.6	23.5	20.0	51.0
T/Soil	40	24.8	5.1	20.6	16.0	37.0
S/Soil	40	28.2	7.1	25.2	14.0	34.0
S/Sedt	30	26.6	6.7	25.2	17.0	45.0

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 13-4b Significance Of Correlation Coefficients Between Co And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	-	***	-	*	**		-	-	-	-	-
T/Soil	-	-	*	**	*	***		-	**	*	-	-
S/Soil	-	-	*	-	-	***		-	-	-	-	-
S/Sedt	*	*	-	*	-	***		*	-	*	*	-

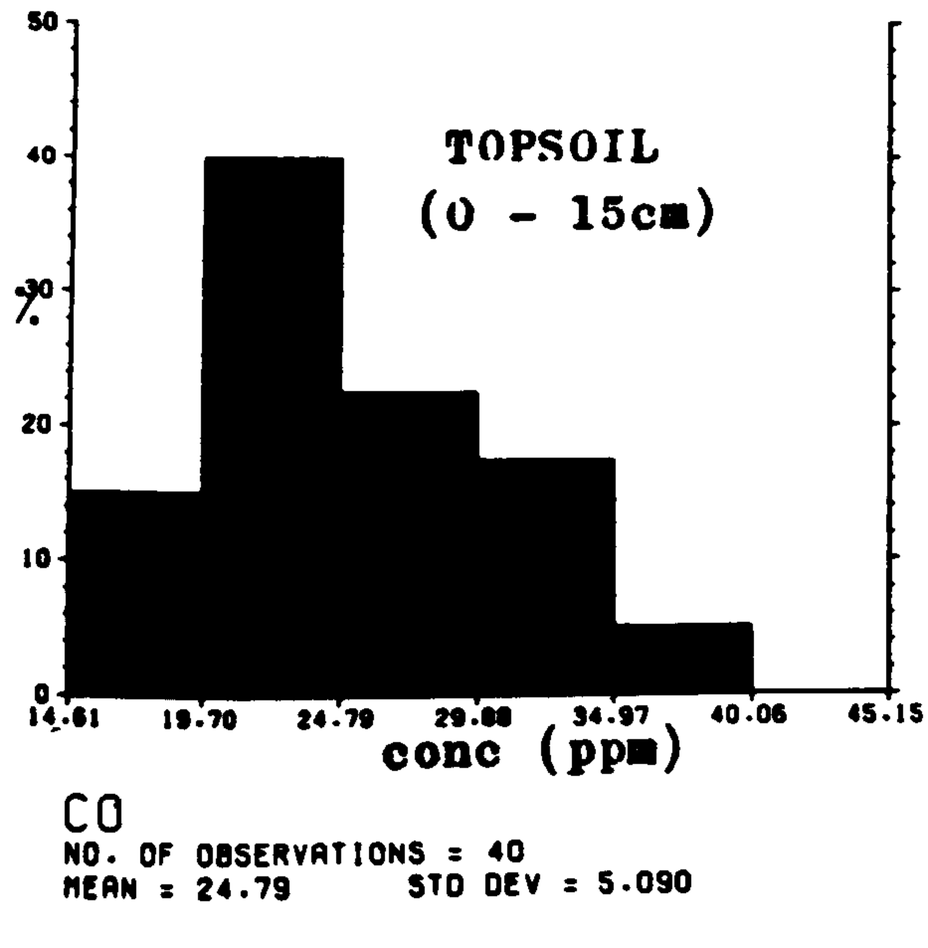
Level Of Significance - = Not Significant * = Significant at .10 level

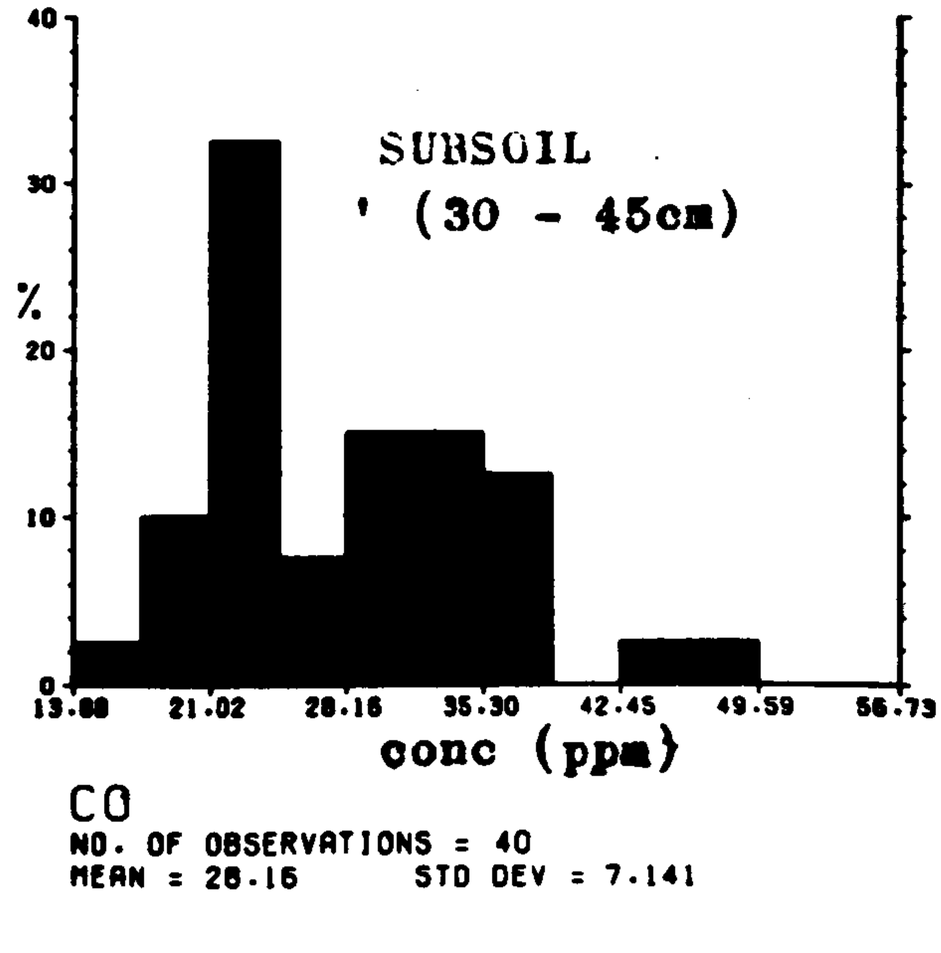
** = Significant at the .05 level

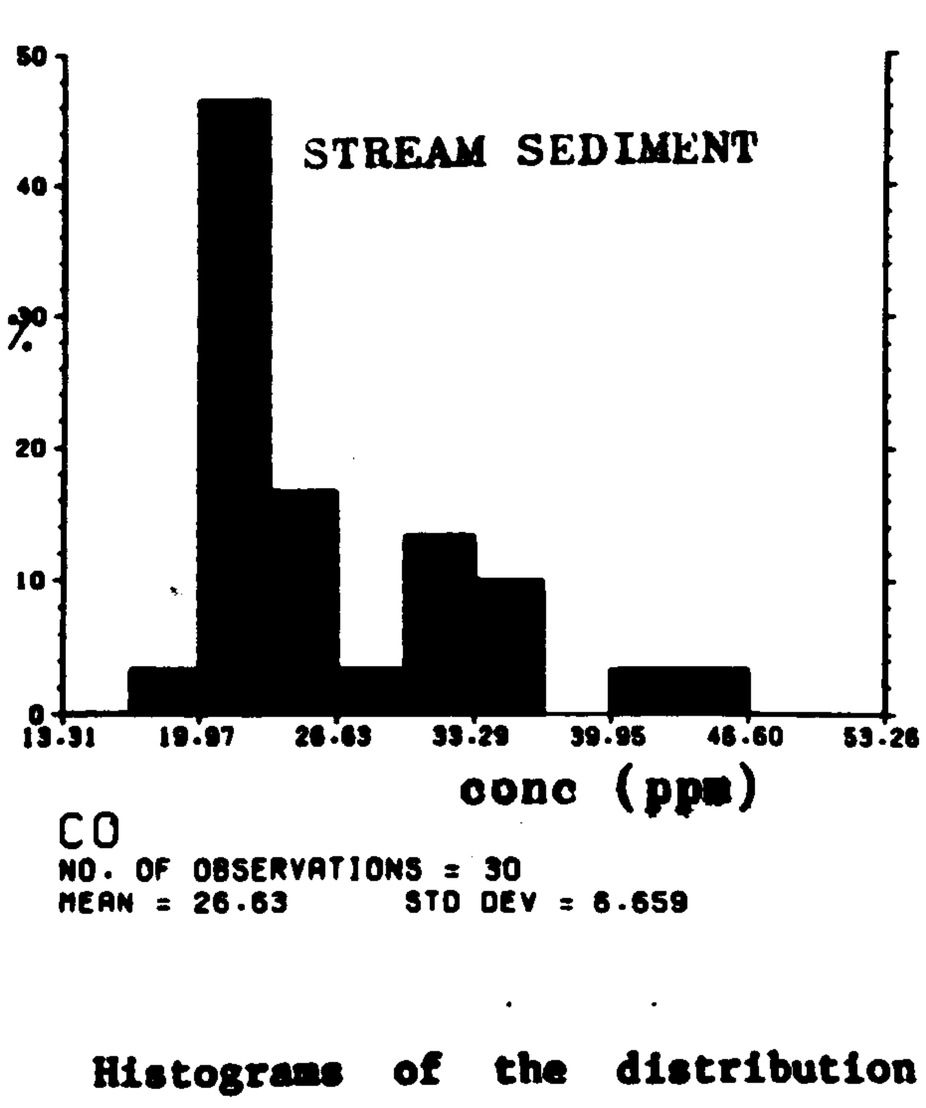
*** = Significant at .01 level

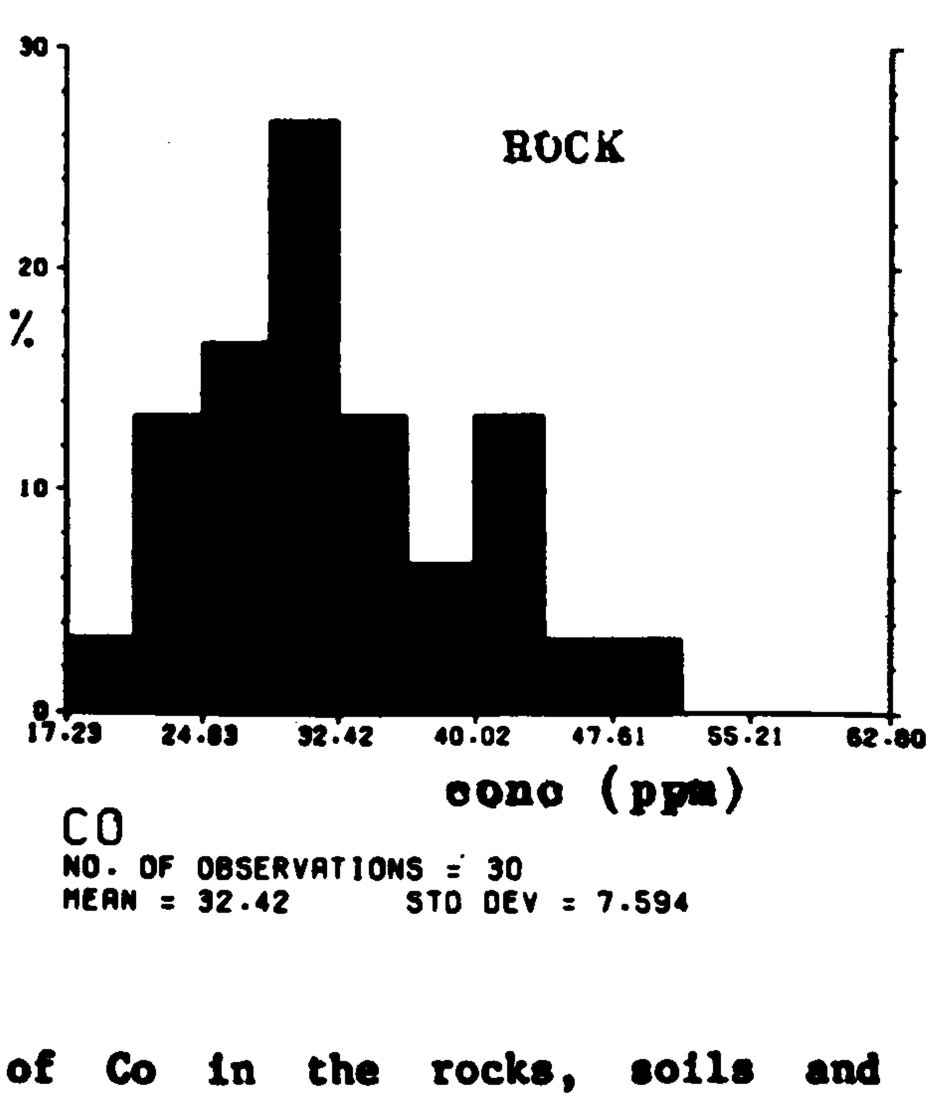
( ) = Negative Correlation.

Fig. 13-15









Histograms of the distribution of Co in the rocks, soils and stream sediments derived from the less calcareous facies of the Lower Lias in the Somerset study area.

were fairly similar . In the less calcareous sediments Co concentrations tended to be similar to those of the soils, being marginally lower than in the rocks. In the calcareous beds, contrasts between the mean concentrations in the rocks, soils and stream sediments were negligible and the coefficient of variation values were fairly similar.

The slight enhancement of Co in the subsoils follow a pattern similar to Mn and it seemed likely that the distribution of Co may be controlled by that of Mn, possibly incorporated into Mn oxide minerals.

Inter-element correlations.

The results showed that in both facies Co was significantly correlated with Mn in all the media studied (Table 13-13b, -14b). In the more calcareous rocks correlations with other elements were not significant, while in the less calcareous rocks the correlation with Zn and Al were significant. In the Evesham soil series Co was negatively correlated with organic matter(LOI) in both the top and subsoils, (Table 13-13b).

There were weak correlations with Al, Fe, Zn and Ni in the topsoils of the Denchworth series while in the subsoils only the correlation with Mn and Al were significant. In the less calcareous sediments the correlation with Ca, Mg, Pb, Cu and organic matter(LOI) were significant, although these were relatively weak .

The inferences that can be drawn from the above results are similar to those described in the preceding section on Mn. The main factor governing the distribution of Co seemed to be its relationship

with the hydrous oxide phase, although association with organic matter(LOI) in the less calcareous sediments and the clay minerals in the Denchworth series may also play a role in the distribution of Co.

(h) Lead.

The results showed that the range was wider in the less calcareous rocks and the mean concentration higher than in the calcareous rocks (Tables 13-15a, -16a). In both the Evesham and Denchworth soil series mean concentrations of Pb were higher than in the associated parent materials. In the Evesham series the topsoil mean concentration (52.7ppm) was higher than that of the subsoil(42.6ppm), while in the Denchworth series subsoil mean concentration was only slightly lower than that of the topsoil.

There was a marked enhancement of Pb in the stream sediments derived from the calcareous beds. The mean concentration (88.2ppm) showed a two fold increment over those of the rock and soil. The range was wide (55-128ppm) and the histograms (Fig. 13-16) showed that over 60% of the samples collected had Pb concentrations greater than 80ppm. In the stream sediments derived from the less calcareous facies concentrations of Pb were in many cases similar to that of the rocks.

Inter-element correlation.

Tables 13-15b, -16b shows the significance of the correlation coefficients between Pb and other elements analysed in the two facies of the Lias. The results showed that Pb was weakly correlated only

Table 13-15a Lead Concentrations In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	30	36.6	7.7	21.0	22.0	49.9
T/Soil	40	52.7	8.2	15.6	36.0	67.0
S/Soil	40	42.6	7.1	16.7	26.0	56.0
S/Sedt	32	88.2	20.3	22.9	55.0	128.0

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 13-15b Significance Of Correlation Coefficients Between Lead And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	*	-	*	-	-	-	-	-	*	-	-	
T/Soil	*	-	-	-	*	-	-	-	**	*	-	
S/Soil	-	-	-	*	*	-	-	-	**	-	-	
S/Sedt	(*)	-	-	-	-	*	-	-	**	*	-	

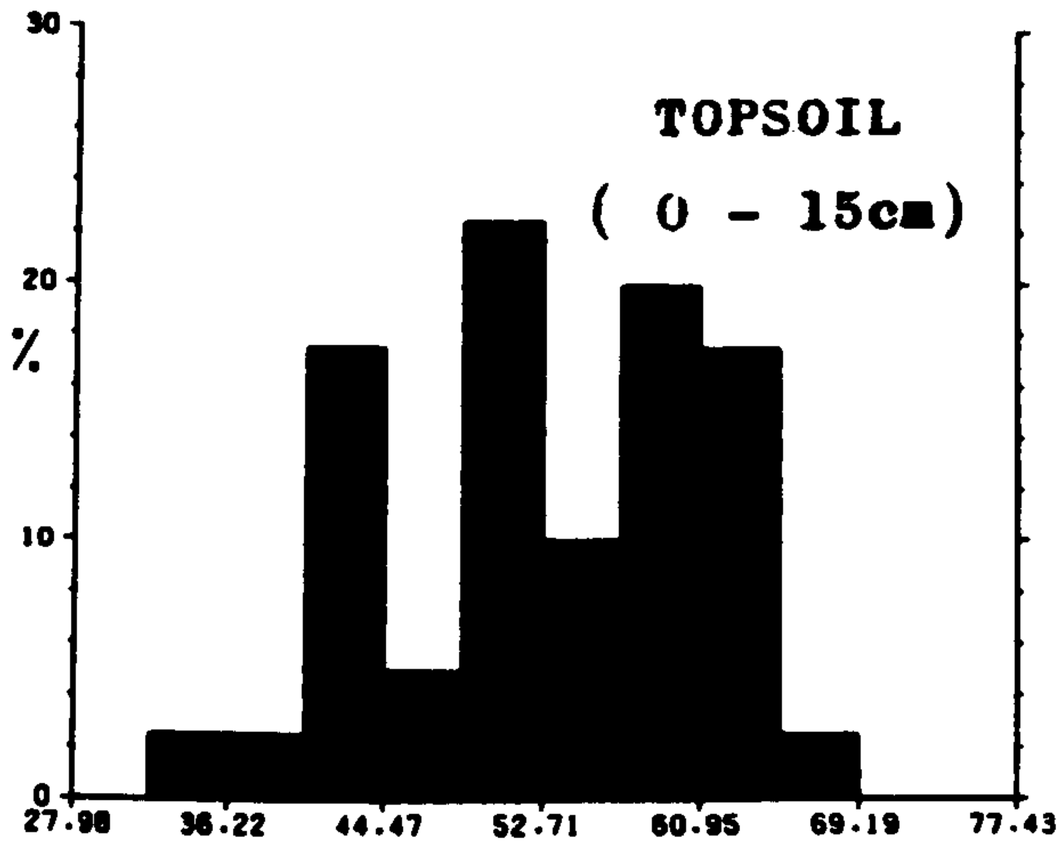
Level Of Significance - = Not Significant * = Significant at .10 level

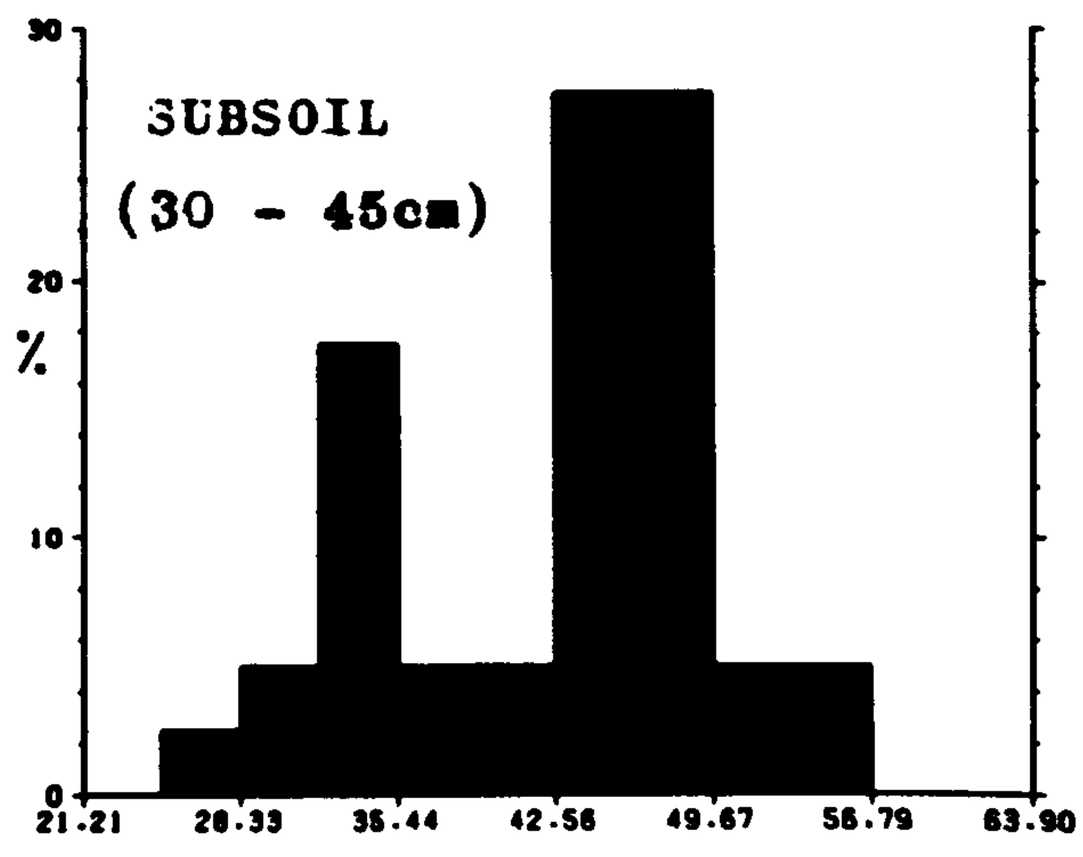
** = Significant at the .05 level

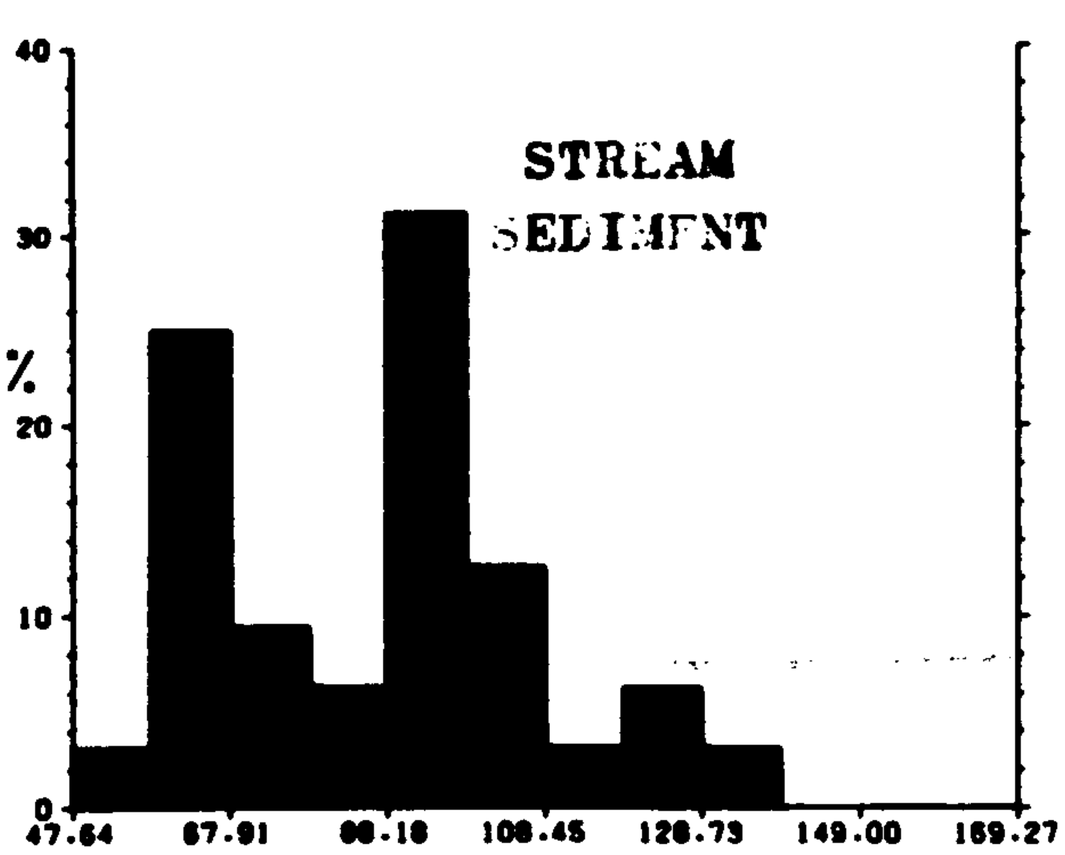
*** = Significant at .01 level

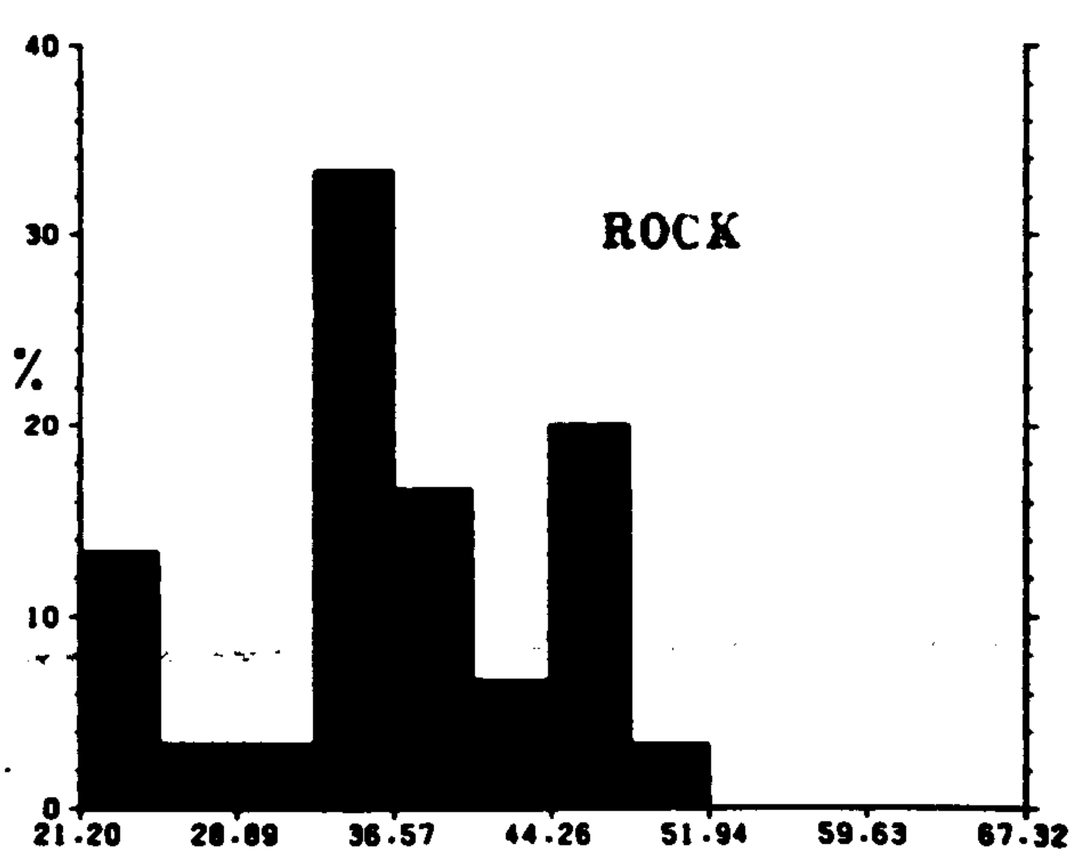
( ) = Negative Correlation.

Fig. 13-16









Histograms of the distribution of Pb in the rocks, soils and stream sediments derived from the calcareous facies of the Lower Lias in the Somerset study area.

Table 13-16a Lead Concentrations In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	30	42.5	11.0	25.9	28.0	80.0
T/Soil	40	52.7	13.9	26.4	26.0	79.0
S/Soil	40	51.4	9.9	19.3	32.0	69.0
S/Sedt	30	44.2	12.3	27.3	20.0	60.0

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 13-16b Significance of the Correlation Coefficients Between Pb And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	-	-	-	*	-	-		-	-	-	-
T/Soil	-	-	-	-	*	-	-		*	*	**	-
S/Soil	-	-	*	-	-	-	-		-	-	-	-
S/Sedt	*	*	-	*	*	-	*		**	**	*	-

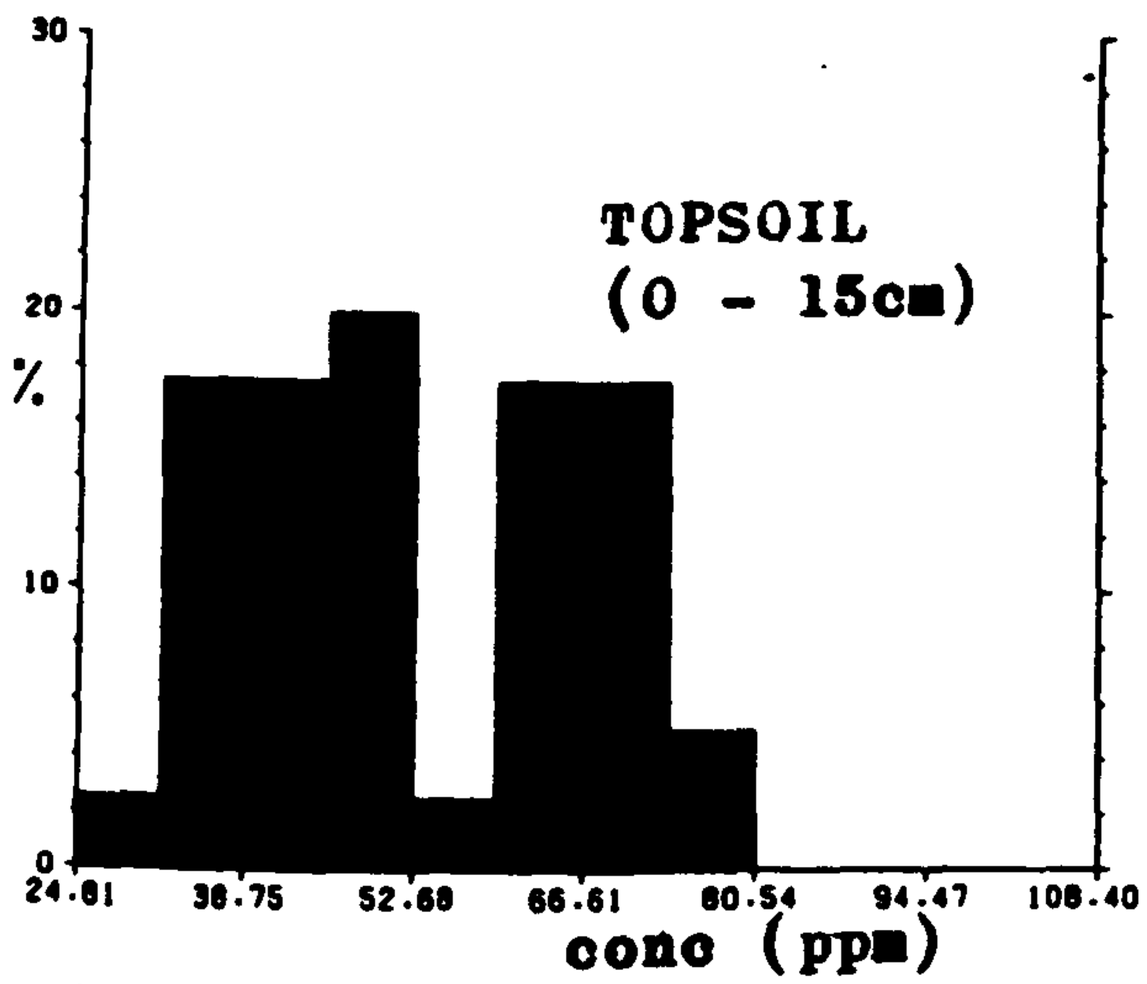
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

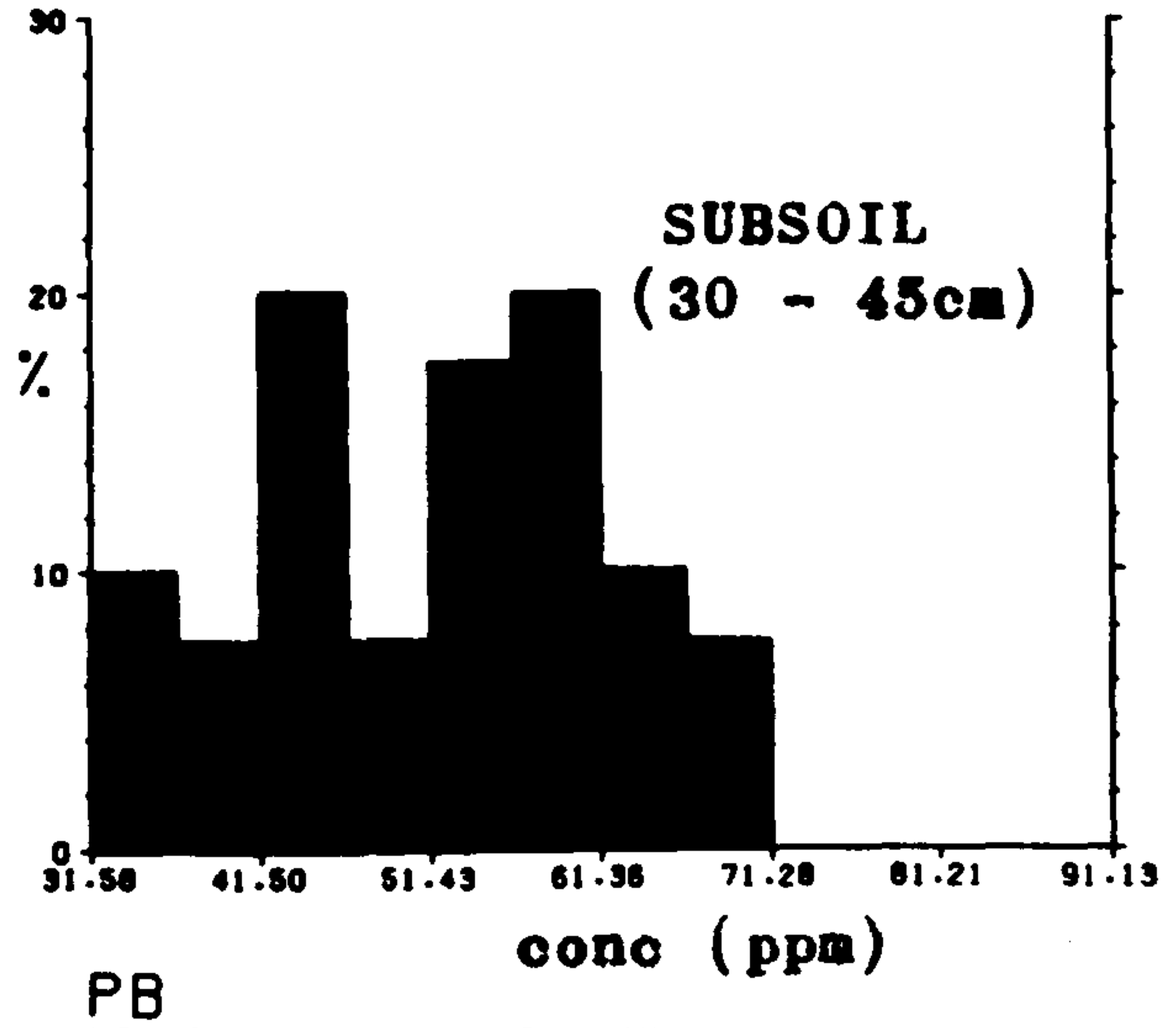
*** = Significant at .01 level

( ) = Negative Correlation.

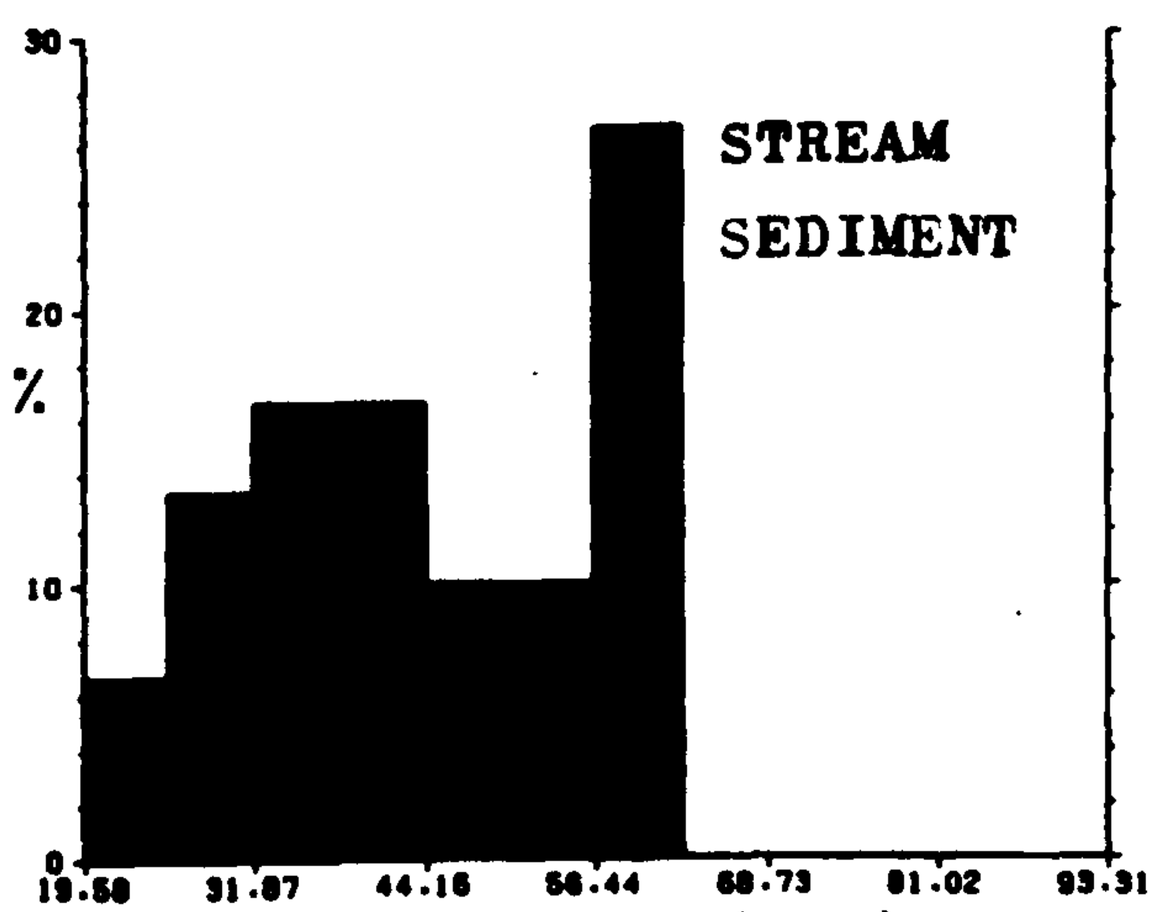
Fig. 13-17



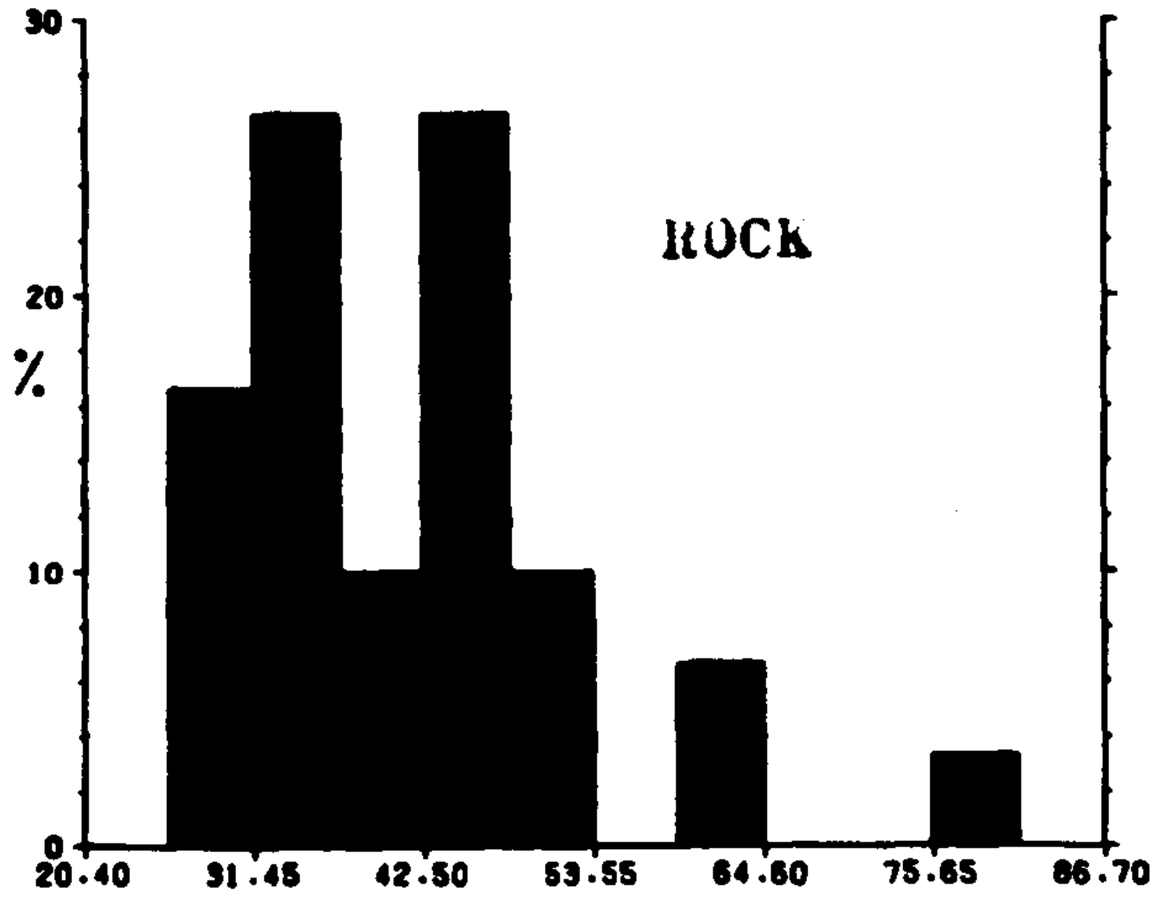
PB
NO. OF OBSERVATIONS = 40
MEAN = 52.68 STD DEV = 13.931



PB
NO. OF OBSERVATIONS = 40
MEAN = 51.43 STD DEV = 9.926



PB
NO. OF OBSERVATIONS = 30
MEAN = 44.16 STD DEV = 12.287



PB
NO. OF OBSERVATIONS = 30
MEAN = 42.50 STD DEV = 11.049

Histograms of the distribution of Pb in the rocks, soils and stream sediments derived from the less calcareous facies of the Lower Lias in the Somerset study area.

with Ca, Al and Cu in the calcareous rocks. The correlations with other elements analysed were not significant. In the Evesham series Pb was significantly correlated with Fe, Zn and Cu in the subsoil, while in the topsoil the correlation with Ca and the organic matter(LOI) were in addition significant. In the calcareous sediments Pb was significantly correlated with Mn, Cu and organic matter(LOI) while the correlation with Ca was negative.

Most of the correlations between Pb and other elements were either weak or insignificant in the Denchworth soil series (Table 13-16b). The correlation with Al was the only significant pair in the subsoil, while in the topsoil the correlation with Zn, Cu, Ni and organic matter(LOI) were weak. In the less calcareous sediments Pb was weakly correlated with most elements.

The results indicated that in the calcareous facies at least Pb may be related to the carbonates in the rocks. The significant correlations with organic matter(LOI) in the topsoil suggested that the distribution of Pb in the topsoil was related to the organic phase. In the stream sediments the results suggested that Pb was associated with both the carbonates and the organic matter(LOI) .

(i) Nickel.

The concentrations of Ni in the rocks and the associated soils derived from both facies of the Lower Lias were essentially similar. In general, the mean concentrations of Ni in the calcareous rocks and the Evesham soil series were higher than those in the less calcareous rocks and the Denchworth soil series. The histograms showed that concentrations below 75ppm were common in both soil

Table 13-17a Nickel Concentrations In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	30	70.9	12.5	17.6	42.0	72.3
T/Soil	40	67.8	10.0	14.7	43.0	83.0
S/Soil	40	68.9	10.6	15.4	35.0	84.0
S/Sedt	32	49.0	13.3	27.1	28.0	75.0

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 13-17b Significance Of Correlation Coefficients Between Nickel And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	*	**	**	-	-	-	-		**	**	-
T/Soil	-	*	*	*	*	-	-	-		**	-	-
S/Soil	-	-	-	*	*	-	-	-		-	-	-
S/Sedt	(*)	-	-	*	**	-	-	-		-	-	-

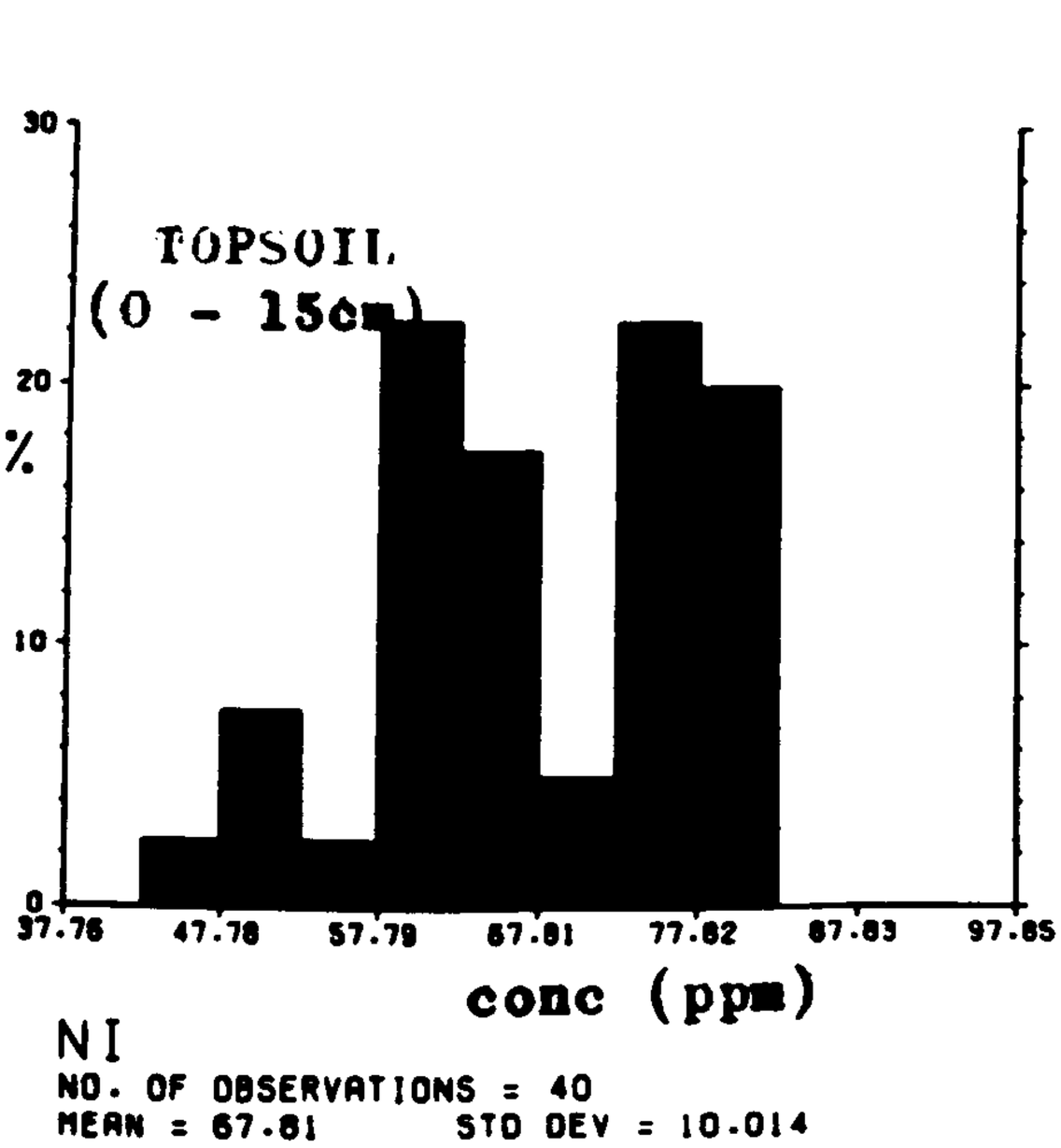
Level Of Significance - = Not Significant * = Significant at .10 level

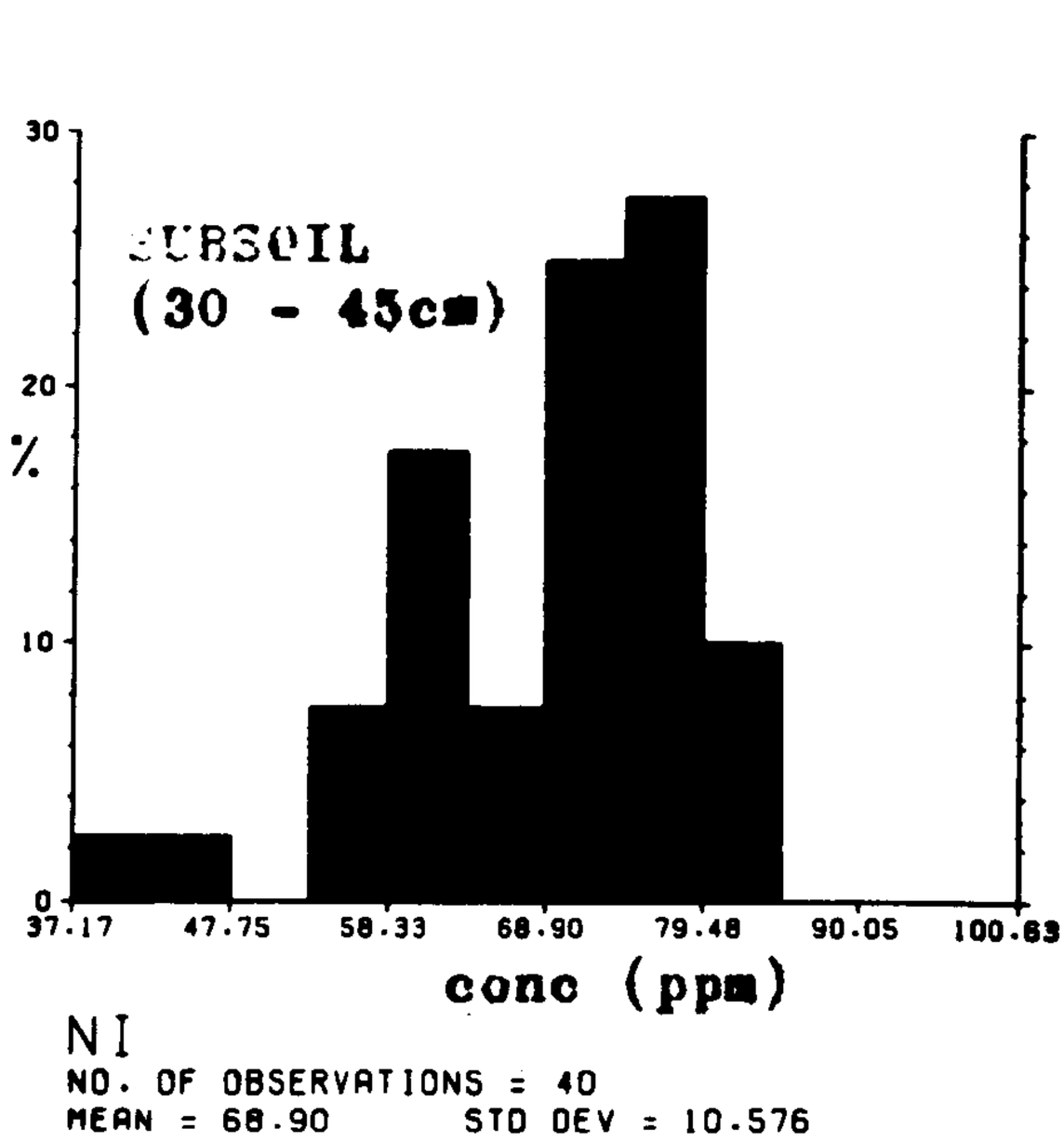
** = Significant at the .05 level

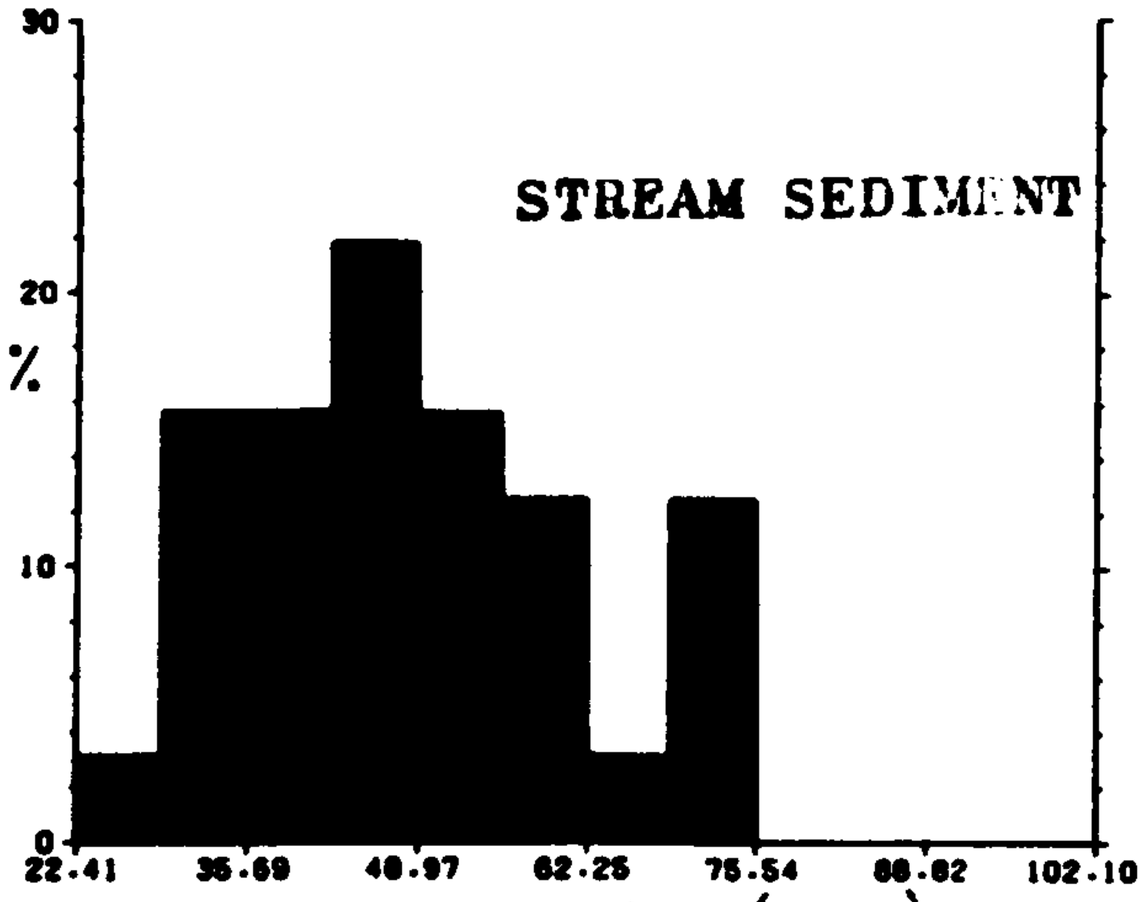
*** = Significant at .01 level

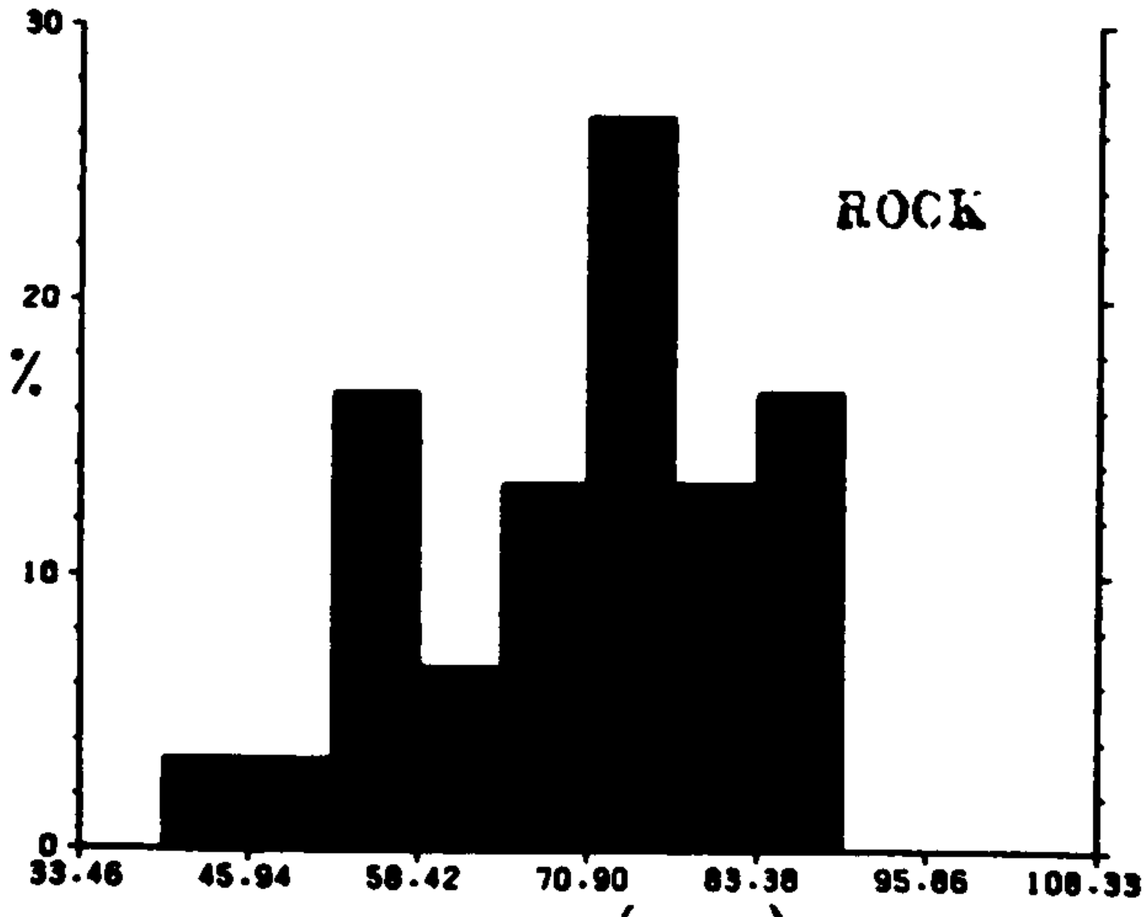
( ) = Negative Correlation.

Fig. 13-18









Histograms of the distribution of Ni in the rocks, soils and stream sediments derived from the calcareous facies of the Lower Lias in the Somerset study area.

Table 13-18a Nickel Concentrations In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Range Max (ppm)
Rock	30	61.1	17.9	29.3	24.0	86.0
T/Soil	40	57.9	13.7	23.7	24.0	93.0
S/Soil	40	60.8	13.8	22.7	35.0	99.0
S/Sedt	30	52.1	11.0	20.9	33.0	71.0

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 13-18b Significance of the Correlation Coefficients Between Ni And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	*	**	**	-	-	-	-		*	-	-
T/Soil	-	*	**	**	*	-	**	*		*	-	-
S/Soil	-	**	*	**	*	-	-	-		*	-	-
S/Sedt	*	-	*	**	*	*	-	**		*	-	-

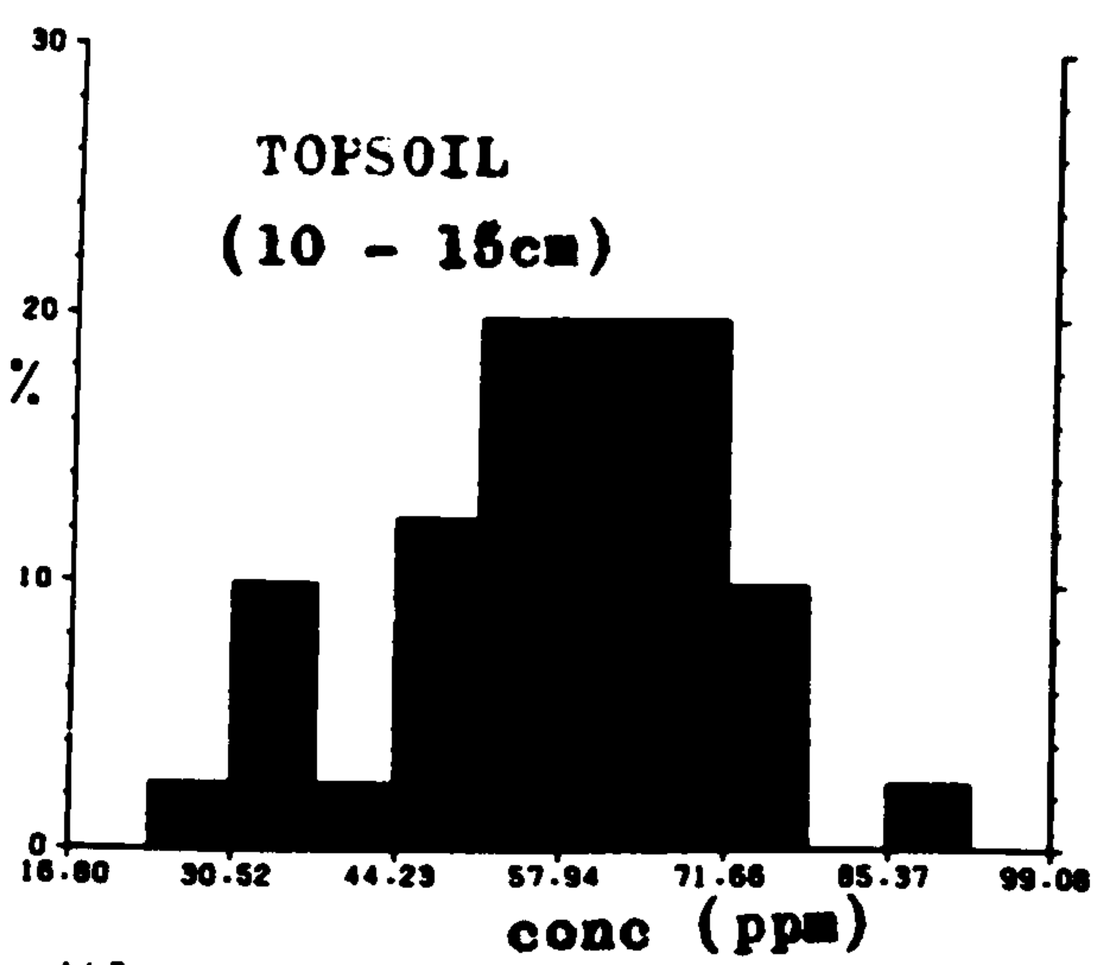
Level Of Significance - = Not Significant * = Significant at .10 level

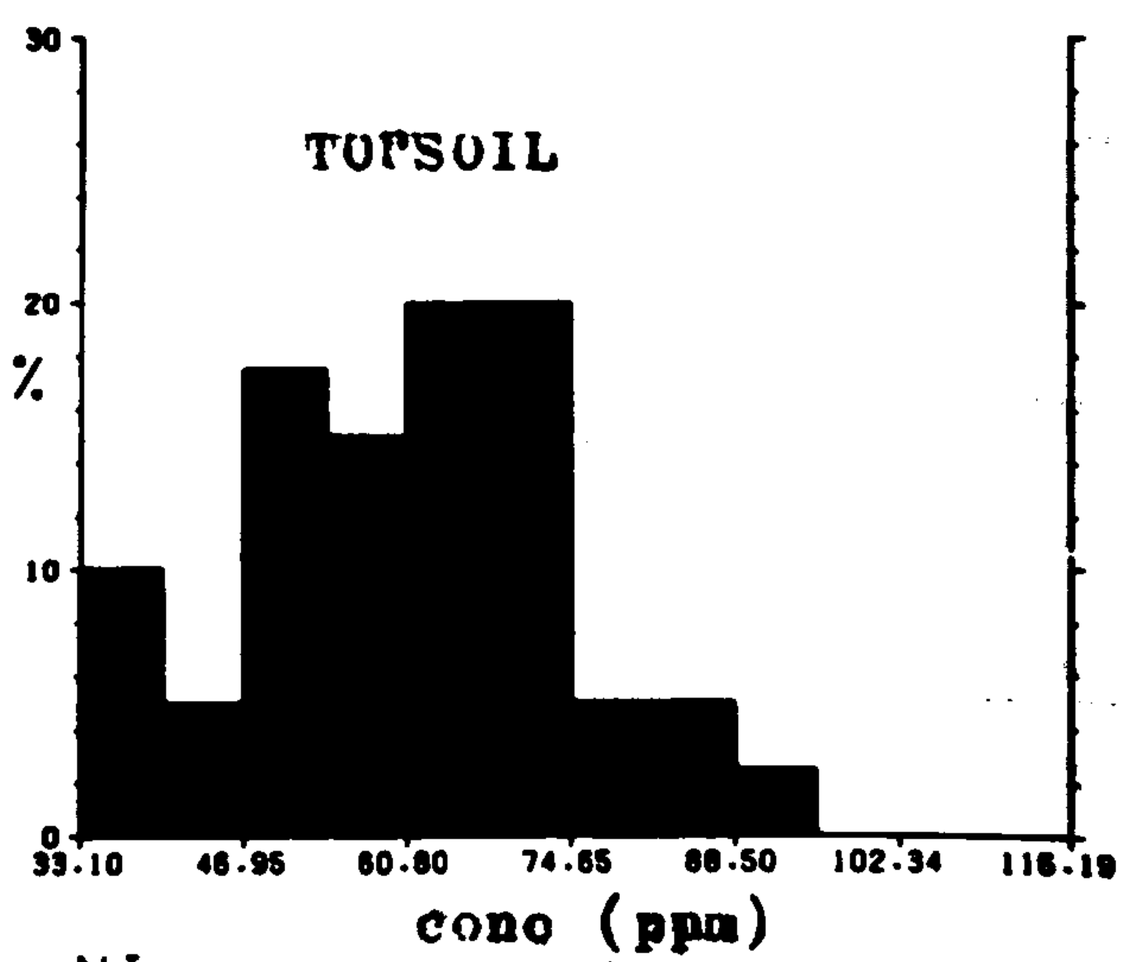
** = Significant at the .05level

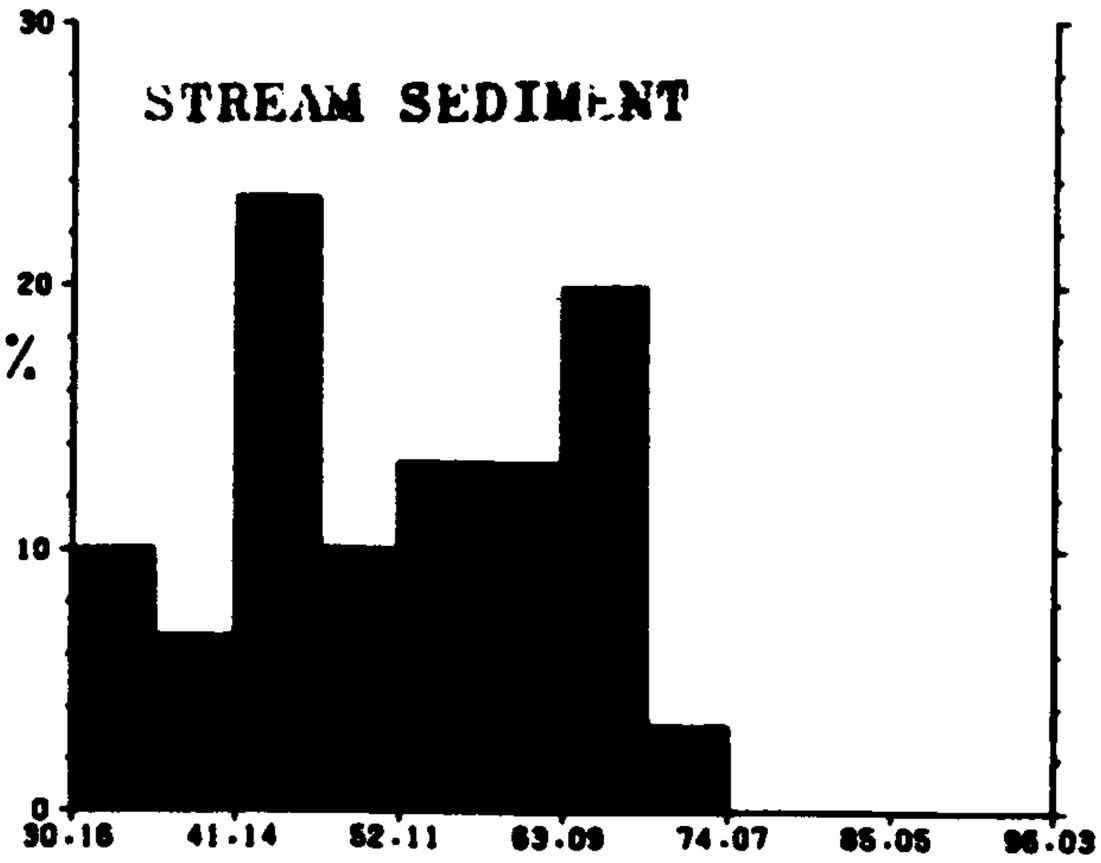
*** = Significant at .01 level

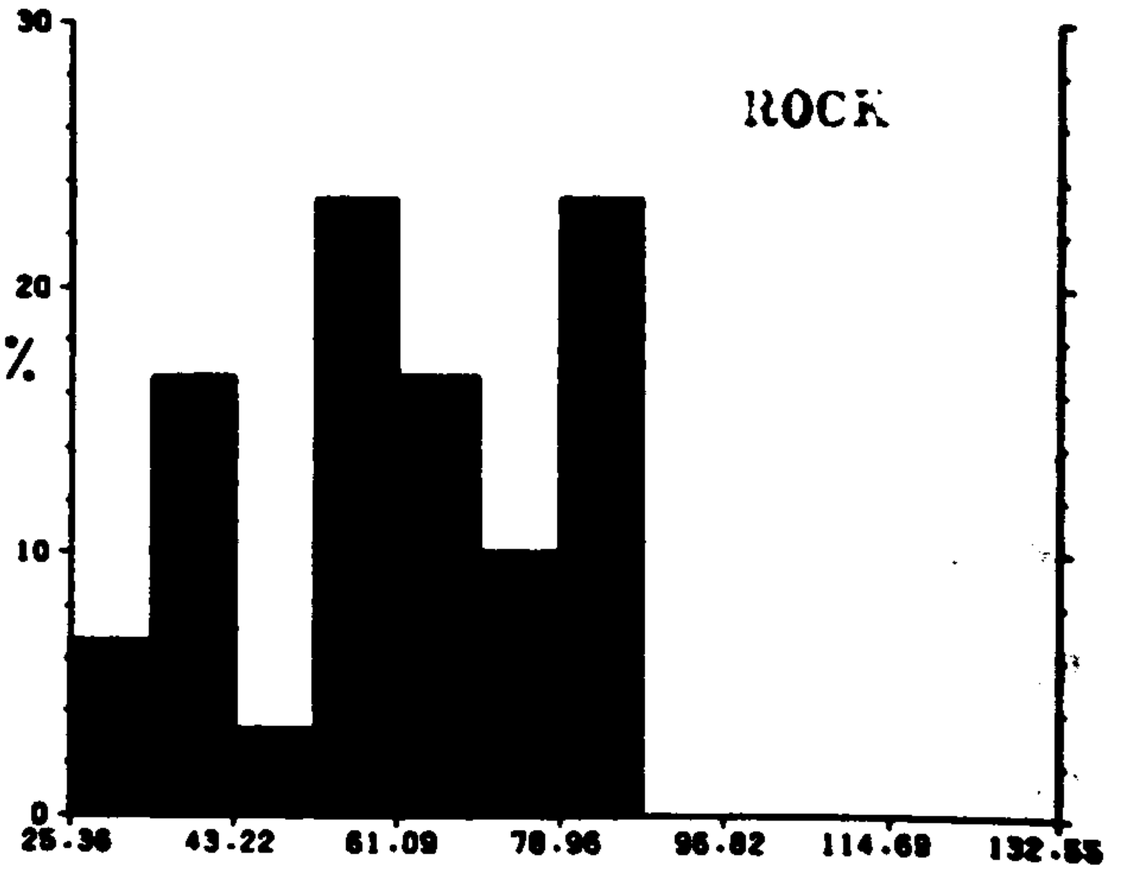
( ) = Negative Correlation.

Fig. 13-19









Histograms of the distribution of Ni in the rocks, soils and stream sediments derived from the less calcareous facies of the Lower Lias in the Somerset study area.

series. The mean concentrations in the top and subsoils of both soil series were also similar, while stream sediments derived from both beds tended to have lower concentrations than the rocks and soils from which they were derived. In the calcareous facies the coefficients of variation showed that maximun variation occurred in the stream sediments while the reverse was true for the less calcareous facies.

It can be inferred from the results that the form in which Ni is held in the parent materials may be unaltered in the soils and stream sediments. The lower concentrations found in the stream sediments, again, may be due to the dilution of the stream sediments by secondary carbonates.

•

Inter element correlations.

The significance of the correlation between Ni and other elements analysed are shown in Tables 13-17b, -18b. In the less calcareous facies Ni was significantly correlated with Al, Fe and Cu in all the associated media (Table 13-18b). In the calcareous facies correlations with Al, Mg and Cu persisted only in the rocks and topsoils. There was a further negative correlation with Ca in the calcareous sediments while in the less calcareous sediments positive correlations were found with Ca and Mn. Nickel was significantly correlated with Zn in the soils and stream sediments derived from both beds.

The persistent correlations with Al, Fe and Mg suggested an association with the clay minerals. Thus Ni like most divalent cations can be adsorbed by the clay minerals onto exchange sites, and it is probable that the association with the clay minerals is the main

Table 13-19a Copper Concentrations In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	30	39.1	12.4	31.7	14.0	64.0
T/Soil	40	49.3	9.1	18.4	30.9	70.0
S/Soil	40	46.5	6.7	14.5	34.0	62.0
S/Sedt	32	36.4	7.7	21.1	20.0	50.0

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 13-19a Significance Of Correlation Coefficients Between Copper And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	(**)	-	**	**	**	-	-	*	**		-	-
T/Soil	(**)	-	-	**	*	-	-	**	**		-	-
S/Soil	(**)	-	-	**	*	-	-	**	-		-	-
S/Sedt	-	-	*	-	-	**	-	**	-		-	-

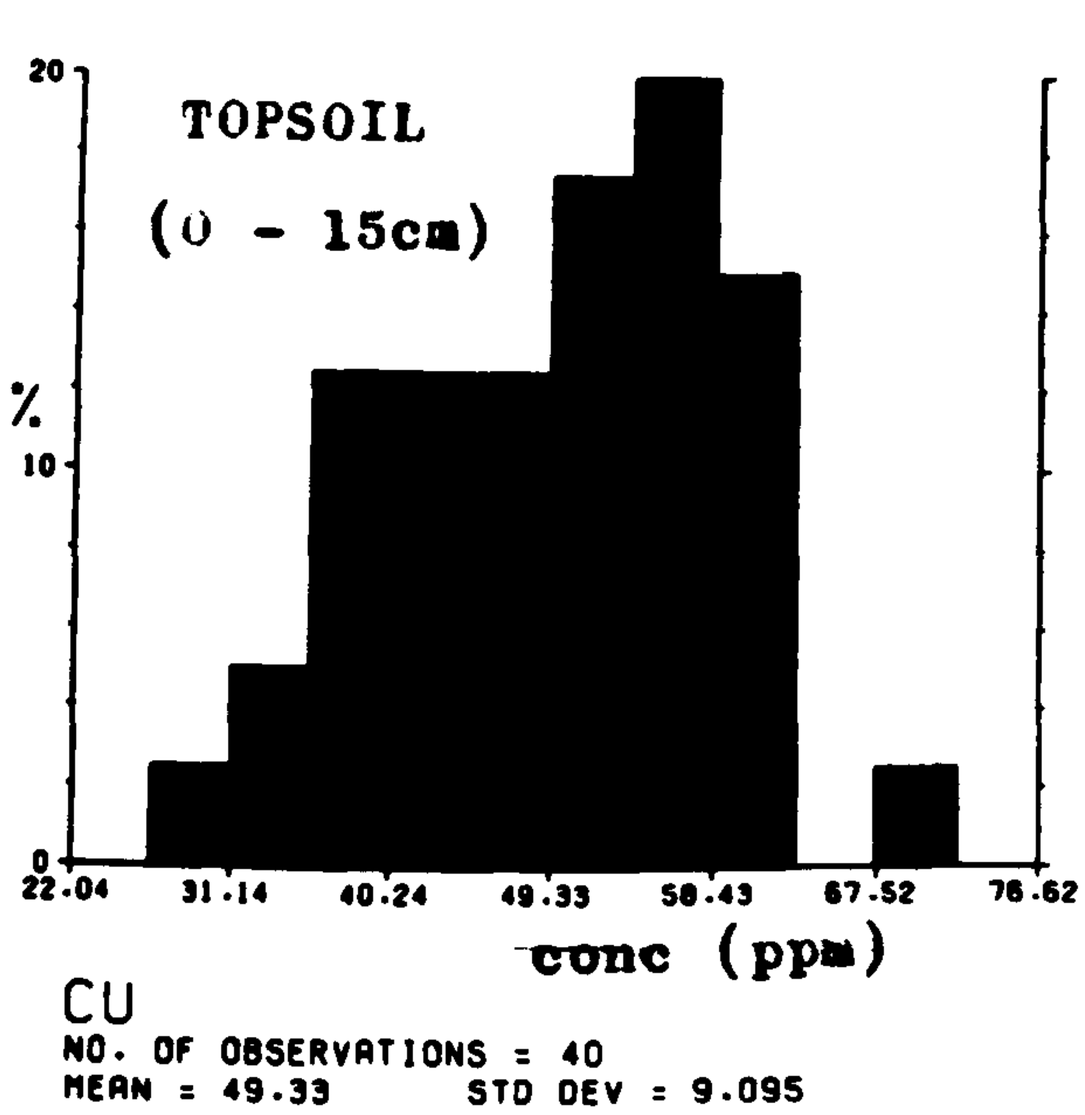
Level Of Significance - = Not Significant * = Significant at .10 level

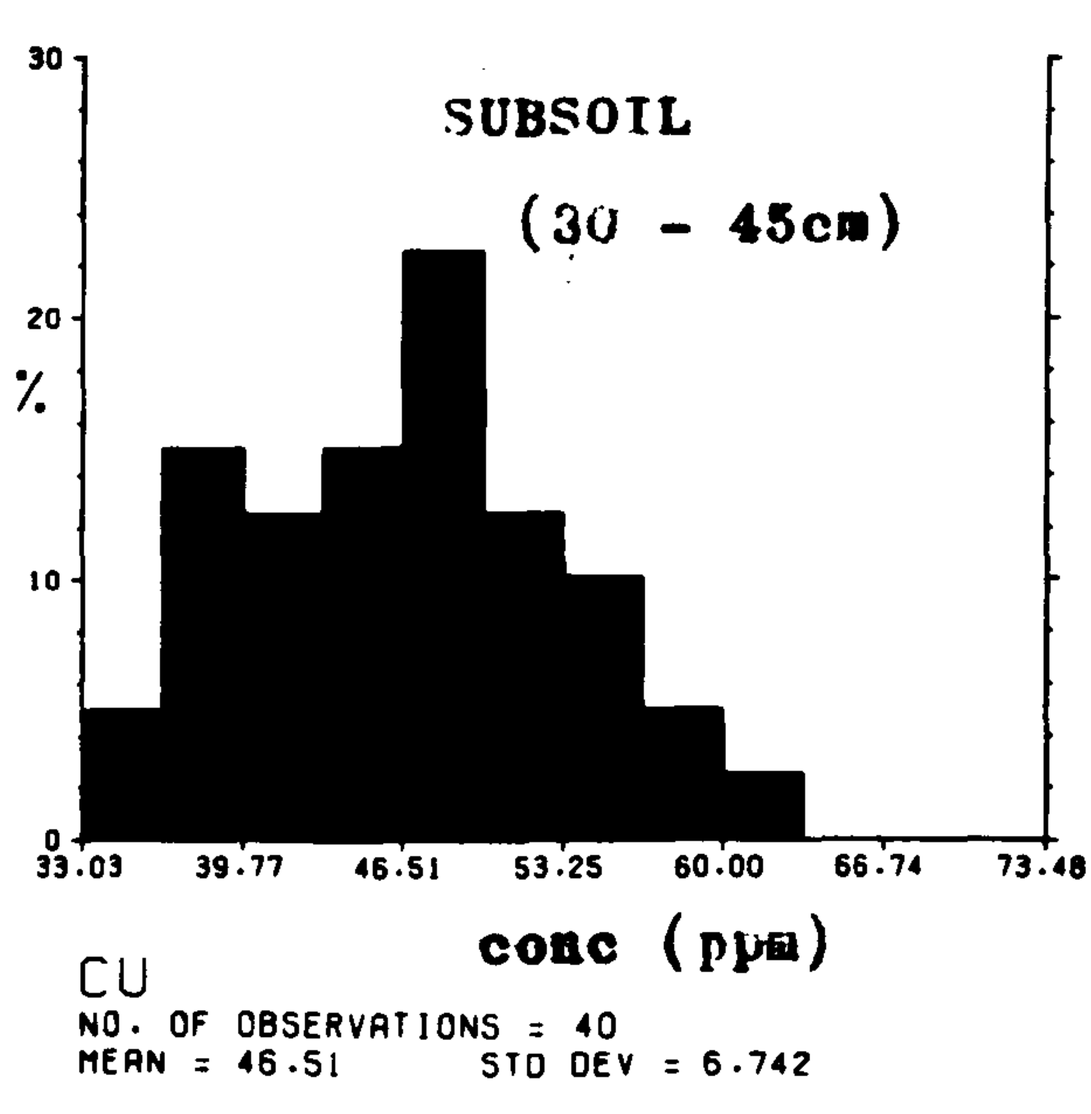
** = Significant at the .05 level

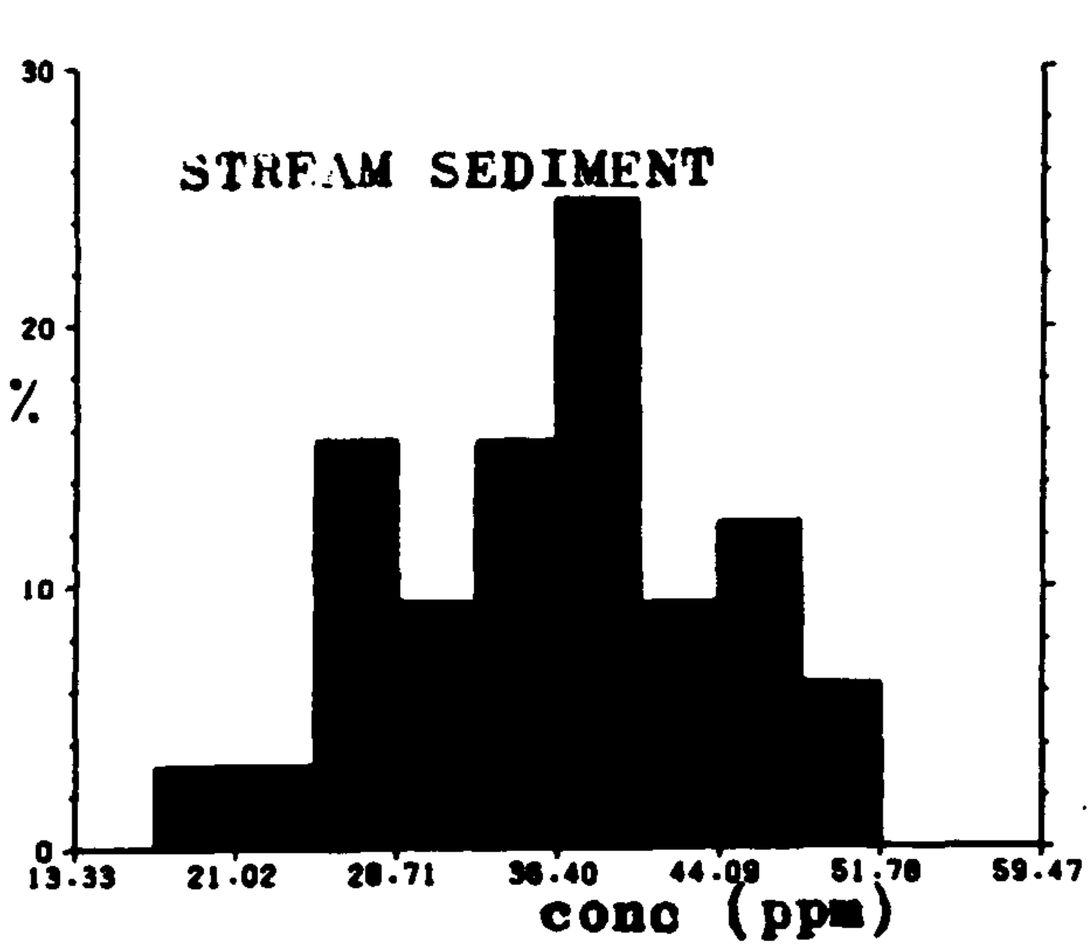
*** = Significant at .01 level

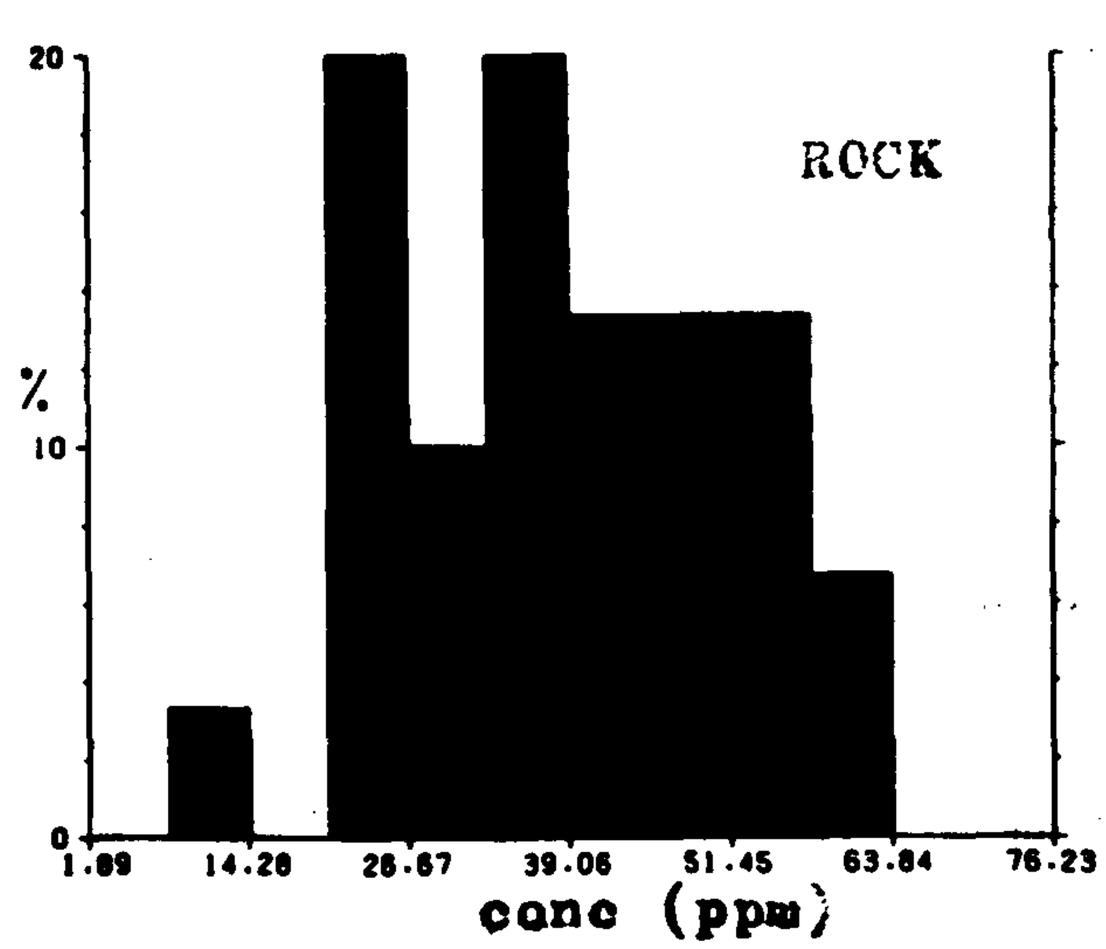
( ) = Negative Correlation.

Fig. 13-20









Histograms of the distribution of Cu in the rocks, soils and stream sediments derived from the calcareous facies of the Lower Lias in the Somerset study area.

Table 13-20a Copper Concentrations In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias

Medium	N	Mean (ppm)	S.D.	C.V.	Range Min (ppm)	Max (ppm)
Rock	30	33.8	9.4	27.8	21.0	64.0
T/Soil	40	36.0	10.8	30.0	23.0	64.0
S/Soil	40	34.0	9.9	28.9	15.0	60.0
S/Sedt	30	24.6	8.8	35.9	10.0	41.0

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 13-20b Significance of the Correlation Coefficients Between Cu And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	-	-	*	-	-	-	-	*		-	-
T/Soil	-	*	-	-	**	-	*	*	*		-	-
S/Soil	-	-	-	-	-	-	-	-	*		-	-
S/Sedt	*	*	-	*	*	*	*	**	*		*	-

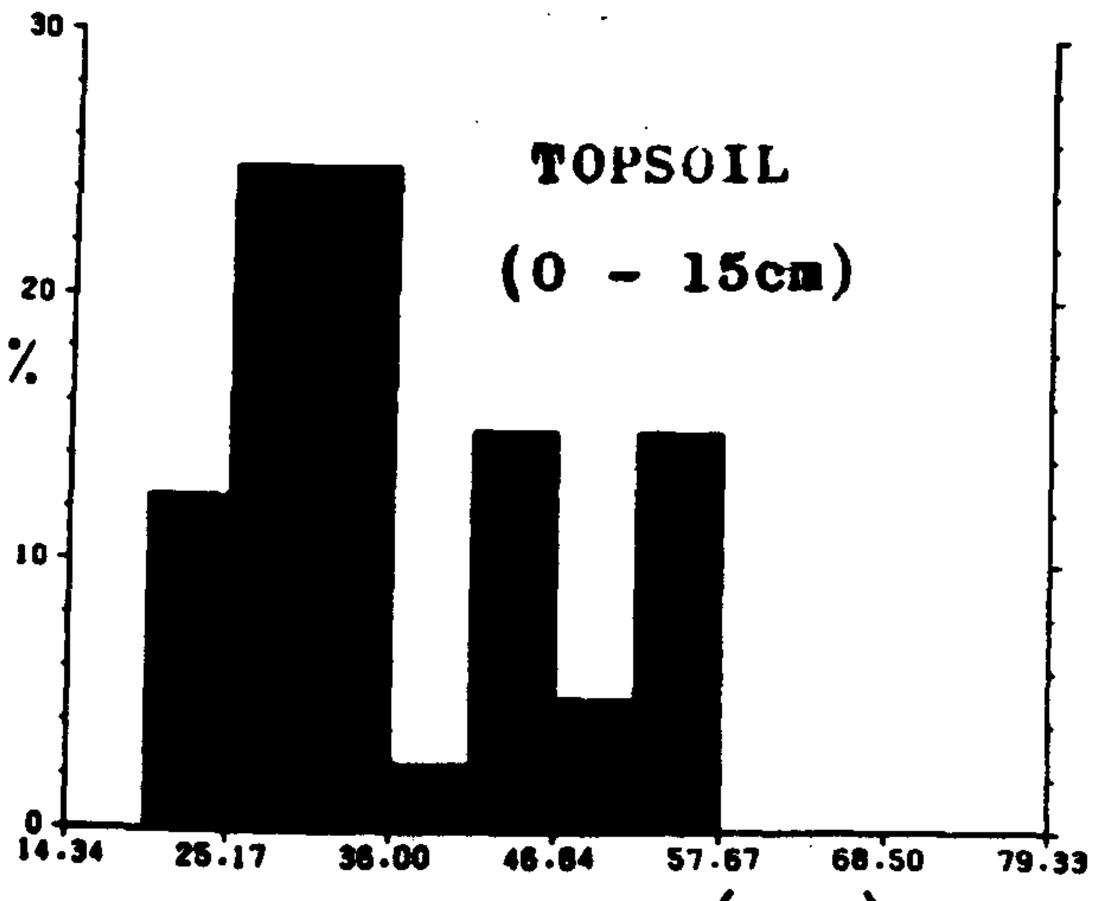
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

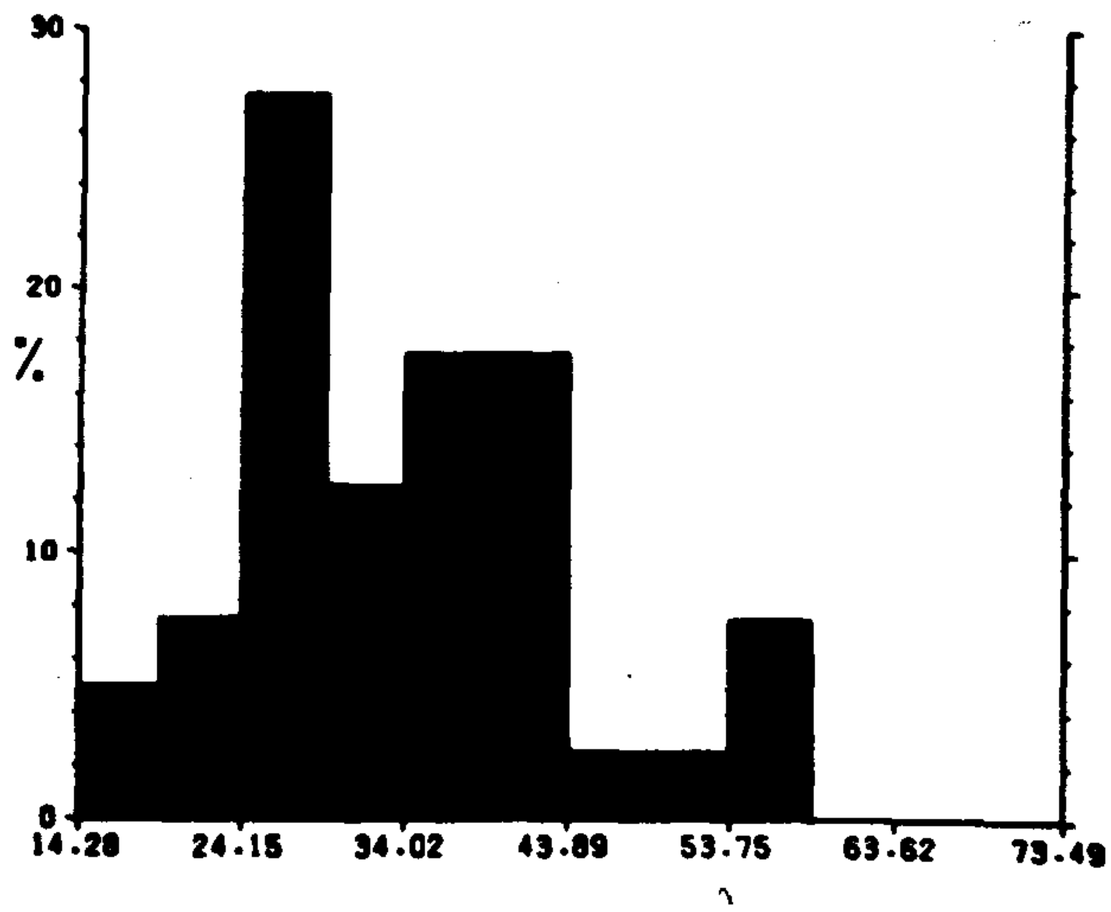
*** = Significant at .01 level

( ) = Negative Correlation.

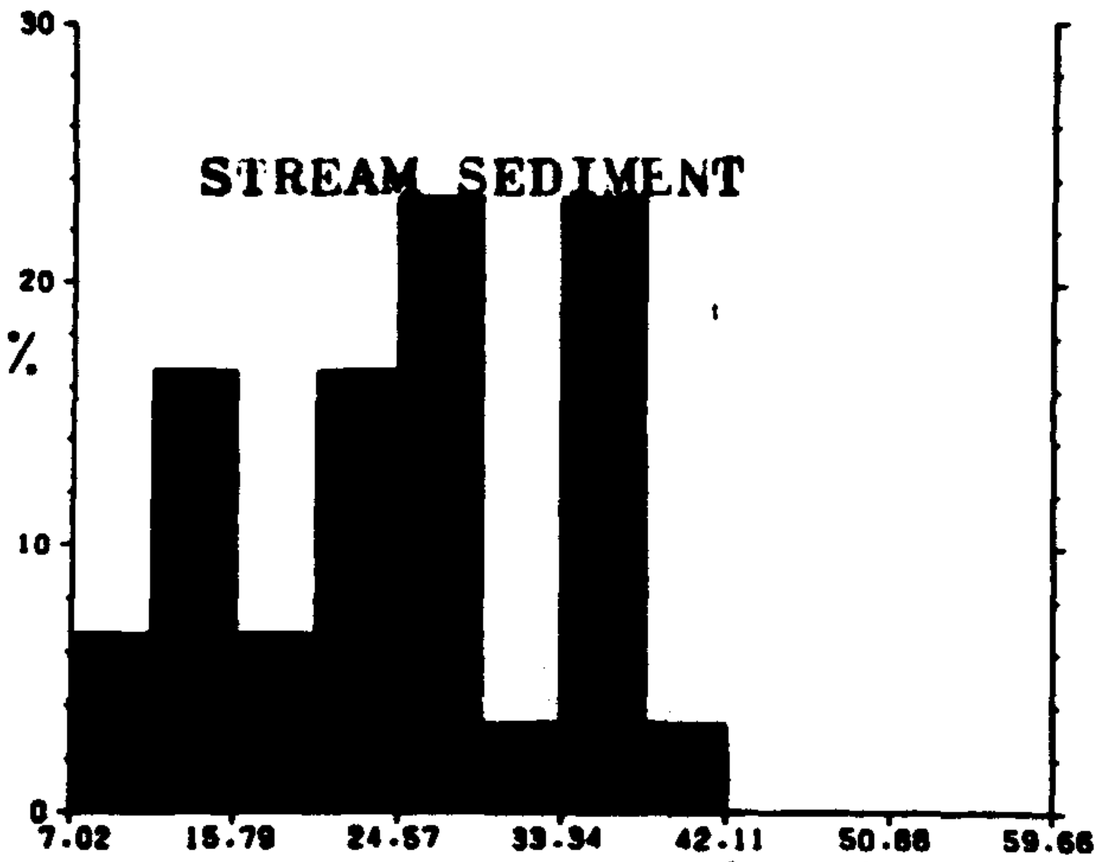
Fig. 13-21



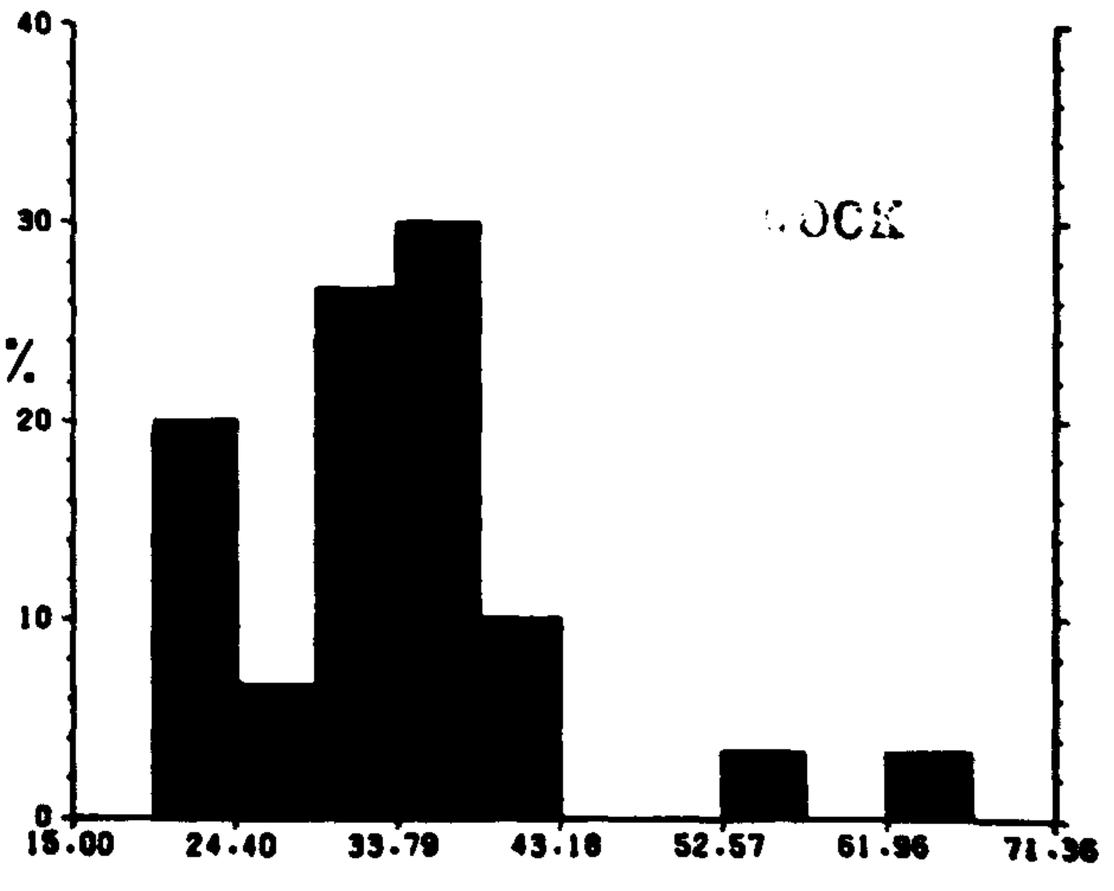
CU
NO. OF OBSERVATIONS = 40
MEAN = 36.00 STD DEV = 10.832



CU
NO. OF OBSERVATIONS = 40
MEAN = 34.02 STD DEV = 9.867



CU
NO. OF OBSERVATIONS = 30
MEAN = 24.57 STD DEV = 8.773



CU
NO. OF OBSERVATIONS = 30
MEAN = 33.79 STD DEV = 9.392

Histograms of the distribution of Cu in the rocks, soils and stream sediments derived from the less calcareous facies of the Lower Lias in the Somerset study area.

factor controlling the distribution of Ni in all the media studied.

(j) Copper.

Copper concentrations in both the calcareous and the less calcareous rocks of the Lias were similar. Generally, a large percentage of the samples collected from both beds had Cu concentrations below 40ppm (Figs. 13-20, -21).

In the Evesham series the mean concentration of Cu in the soils were higher than in the rocks (Table 13-19a) . The coefficients of variation indicated that such enhanced concentrations of Cu were accompanied by decreased variation in the soils. Copper concentrations in the Denchworth series were similar to those in the rocks (Table 13-20a).

Stream sediments derived from both facies had Cu concentrations lower than in the rocks and soils. In the less calcareous facies this was accompanied with increased variation.

Inter-element correlations.

In the calcareous rocks and the Evesham soil series, Cu was negatively correlated with Ca (Table 13-19a). This may be due to an association with the insoluble residues left after the leaching of the carbonates during pedogenesis (Curtis et. al. 1976, p 100). The significant positive correlations with Al, Fe, Zn and Ni in the calcareous rocks indicated that Cu was also associated with the clay minerals, possibly as part of the cation exchange complex.

In the less calcareous rocks Cu was significantly correlated

with only Fe and Ni (Table 13-20b). In the topsoils of the Denchworth soil series Cu was significantly correlated with Mg, Zn, Co, Pb and Ni. These significant correlations were lost in the subsoil where only weak correlation with Ni was found.

Only the correlations with Al, Mn and Pb were significant in the calcareous sediments. In the less calcareous sediments Cu was weakly correlated with most of the elements determined except Al. This suggested that Cu may be related to most of the secondary processes in the streams such as the formation of secondary carbonates, adsorption by organic matter and Mn oxide minerals.

(k) Loss On Ignition.

Organic matter in the rocks, soils and stream sediments were measured by the loss on ignition method described in Chapter 3 . The results (Tables 13-21a -22a) indicated very high levels of organic matter(LOI) in the soils. It was unlikely that these high values were due to the method used (Chapter 3) since at the ignition temperature (450$^{\bullet}$C) very little of the water locked up in the the clays and other minerals were affected. Furthermore, calcium carbonates break down at higher temperatures than was employed, hence they were assumed to be unaffected by the ignition process. In the Denchworth and Evesham series the loss on ignition values were higher in topsoil than in the subsoil (Table 13-22a). In general, topsoil samples high in Pb and Cu had correspondingly high concentrations of organic matter(LOI). The stream sediments generally yielded concentrations similar to the rocks.

The organic matter plays an important role in the geochemical environment and soils by its ability to form different compounds with metallic cations. This may include chelates and co-ordination

Table 13-21a Loss On Ignition Concentrations In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias

Medium	N	Mean (%)	S.D.	C.V.	Range Min (%)	Max (%)
Rock	30	10.1	1.6	16.0	6.1	13.2
T/soil	40	16.4	3.8	23.5	10.0	25.0
S/Soil	40	12.6	2.2	17.2	7.9	17.4
S/Sedt	32	10.3	2.0	19.6	5.0	14.5

N = Number Of Samples.

S.D. = Standard Deviation.

C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 13-21b Significance Of Correlation Coefficients Between Loss On Ignition And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	(**)	-	*	-	**	-	-	-	**	-		-
T/Soil	-	-	*	-	-	**	**	-	-	-		-
S/Soil	(**)	-	-	*	-	**	*	*	-	-		*
S/Sedt	-	-	-	-	-	-	-	*	-	-		-

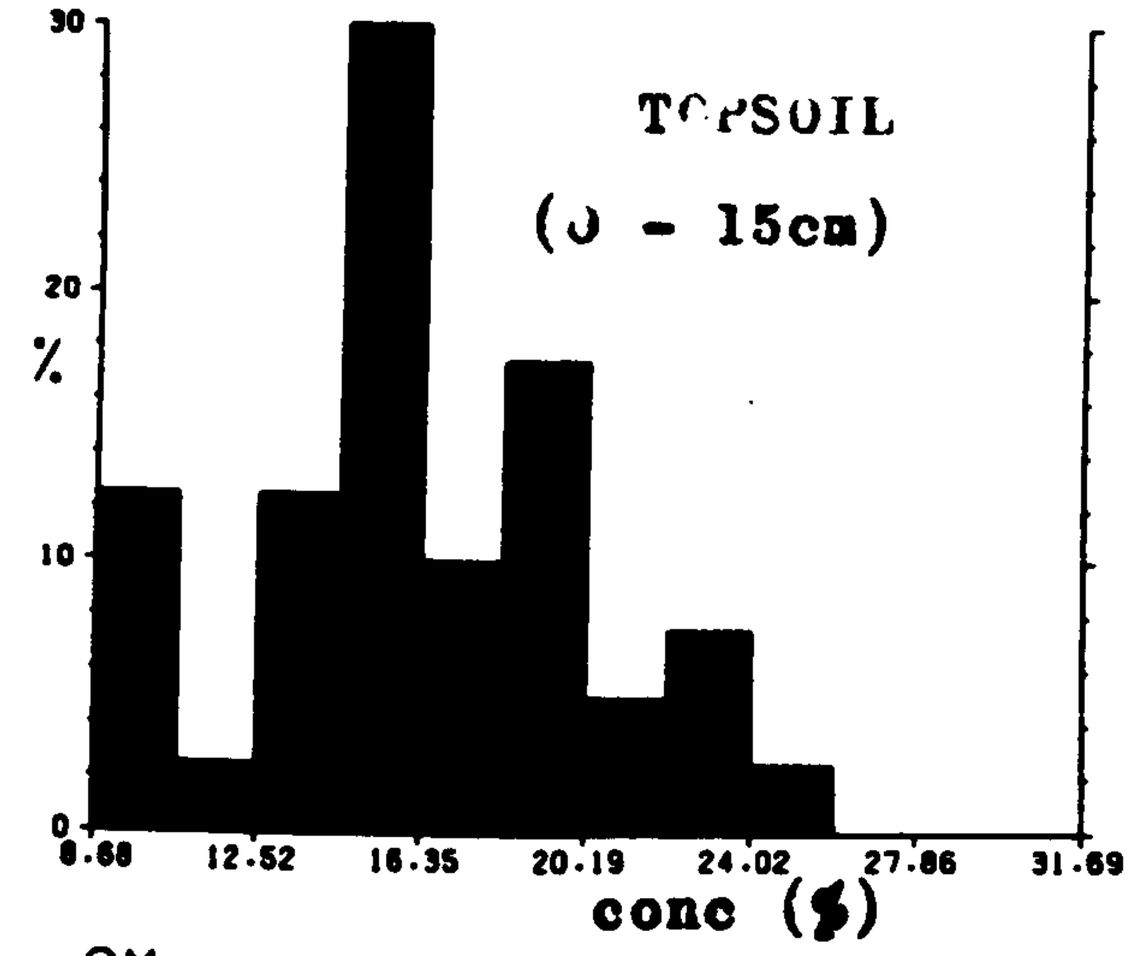
Level Of Significance - = Not Significant * = Significant at .10 level

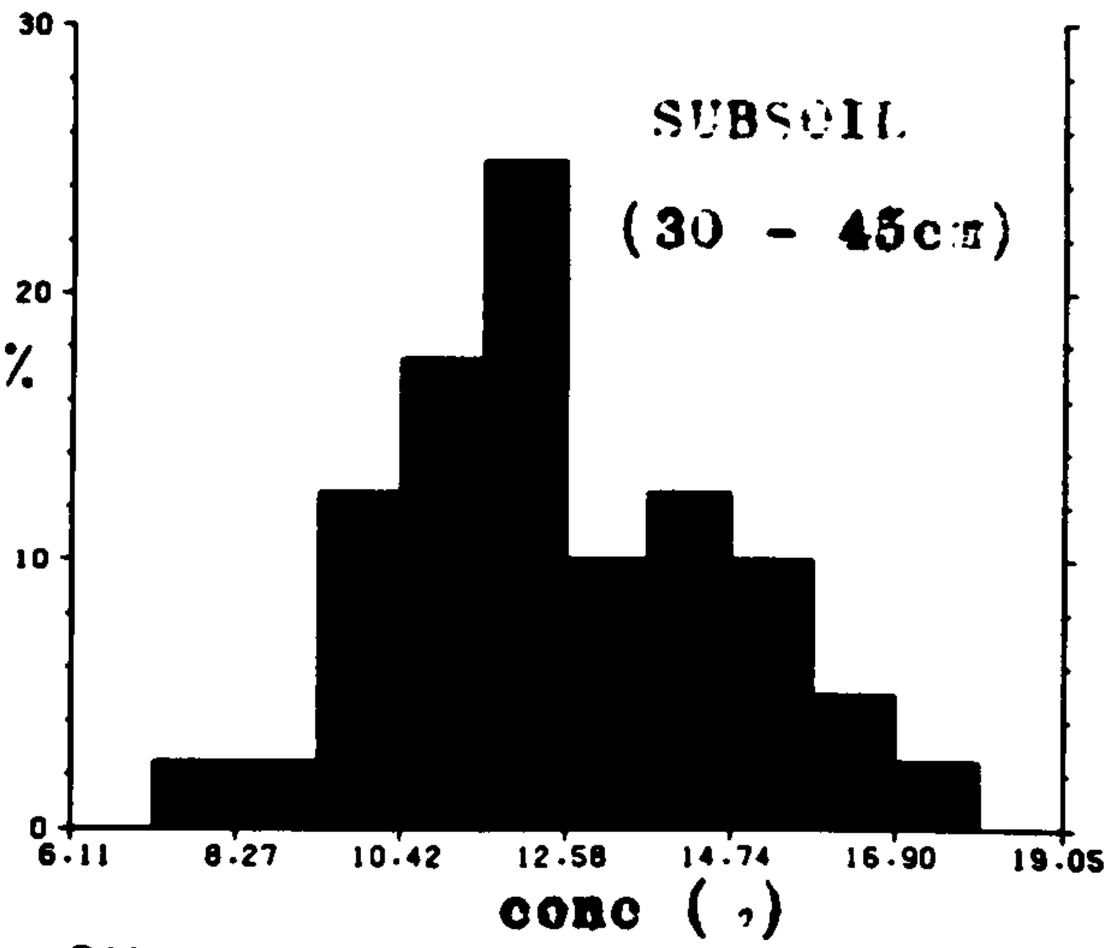
** = Significant at the .05 level

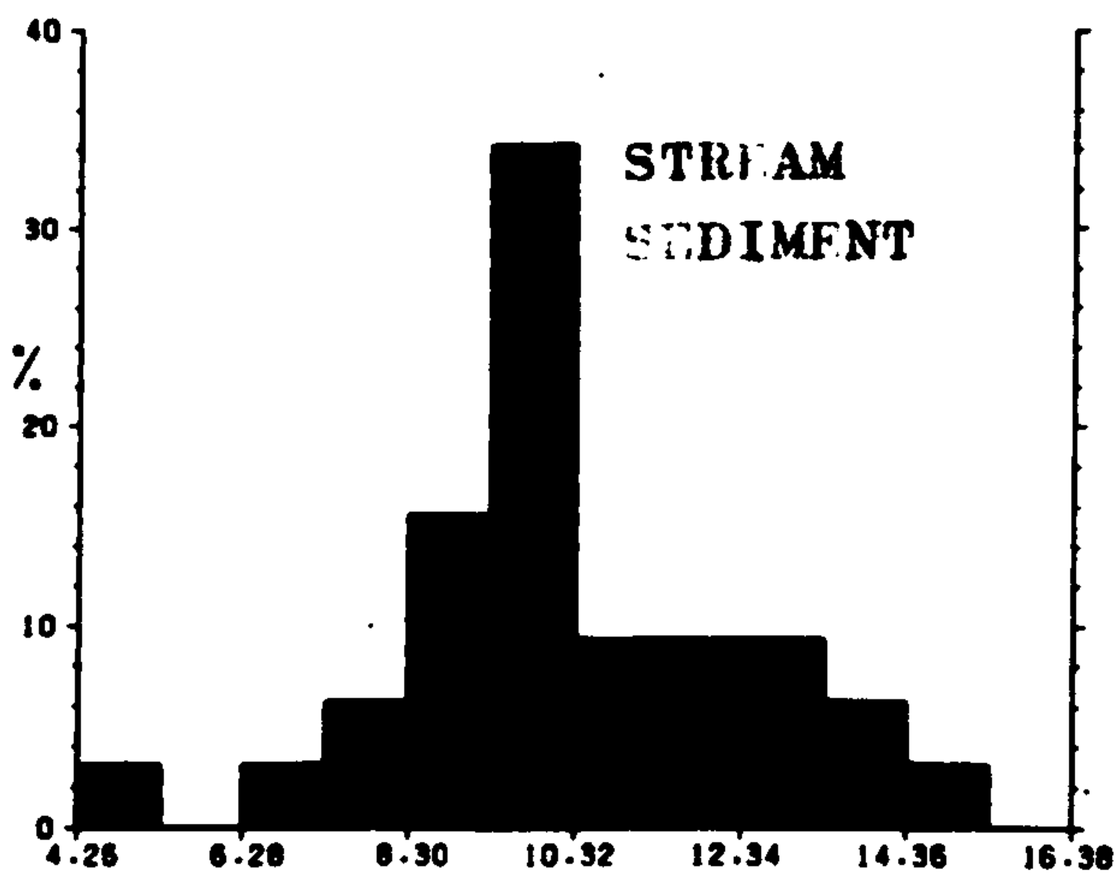
*** = Significant at .01 level

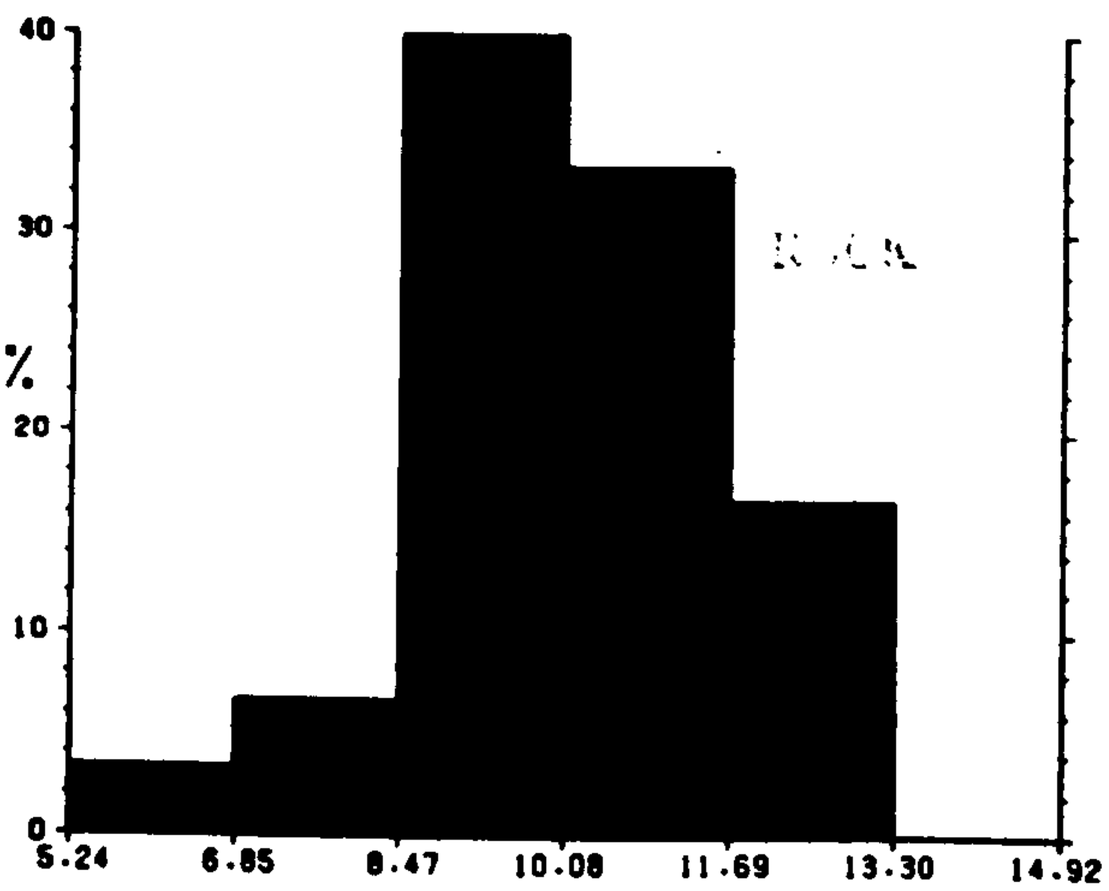
( ) = Negative Correlation.

Fig. 13-22









Histograms of the distribution of organic matter (LOI) in the rocks, soils and stream sediments derived from the calcareous facies of the Lower Lias in the Somerset study area.

Table 13-22a Loss On Ignition Levels In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias.

Medium		Mean (%)	S.D.	C.V.	Range Min (%)	Max (%)
Rock	30	11.7	2.2	18.8	7.5	17.0
T/Soil	40	16.6	2.6	15.7	10.0	20.0
S/Soil	40	14.1	2.9	20.6	8.7	21.0
S/Sedt	30	11.4	2.9	24.6	6.0	15.0

N = Number Of Samples.
S.D. = Standard Deviation.
C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 13-22b Significance Of Correlation Coefficients Between Percent Organic Matter And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	-	-	-	-	-	-	-	-	-	-		-
T/Soil	-	-	-	-	-	-	-	-	-	-		**
S/Soil	*	-	-	-	-	(**)	(**)	-	-	-		(**)
S/Sedt	*	*	-	*	-	*	*	*	-	*		-

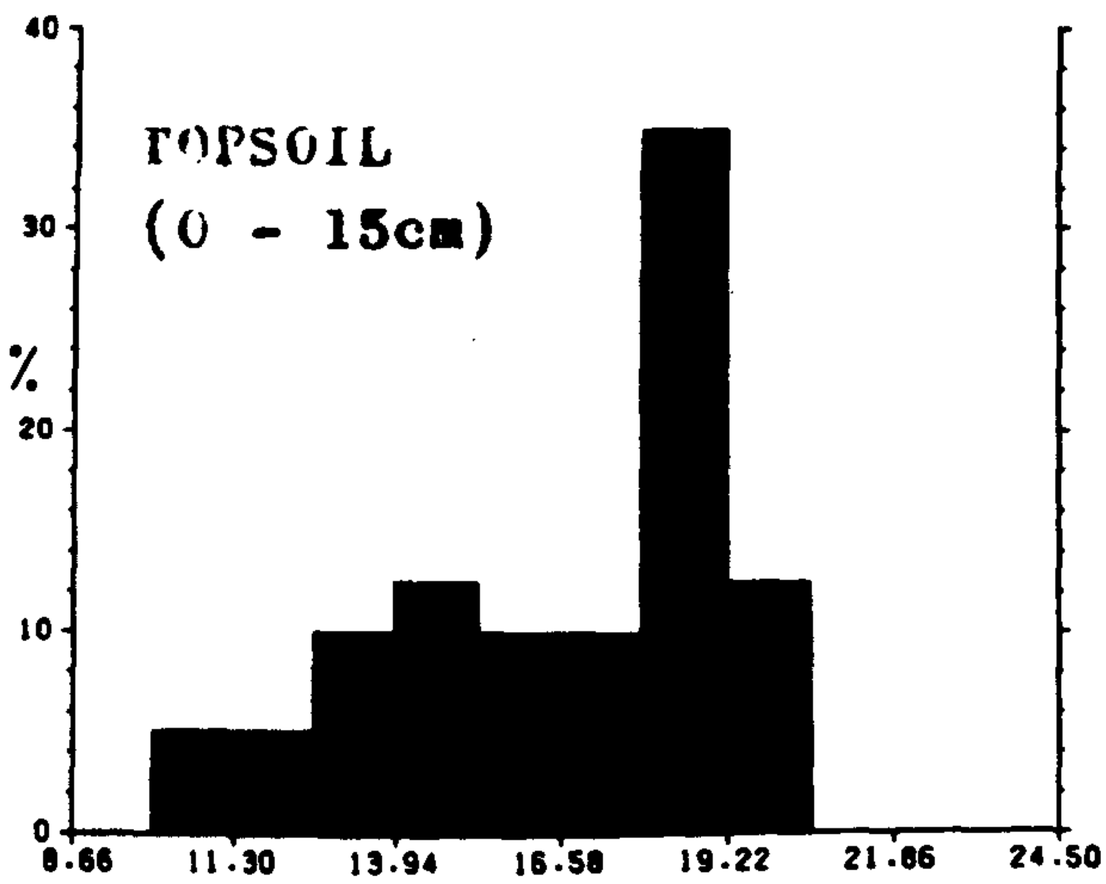
Level of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

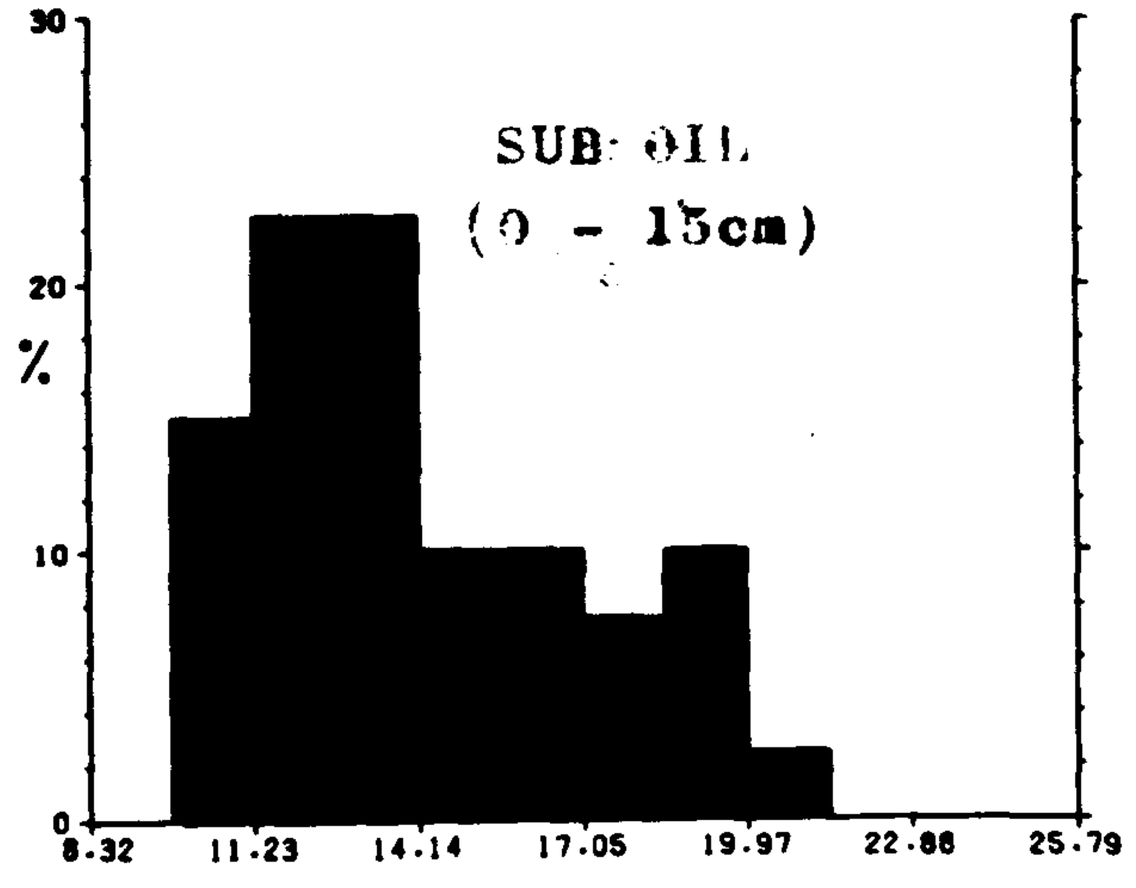
*** = Significant at .01 level

( ) = Negative Correlation.

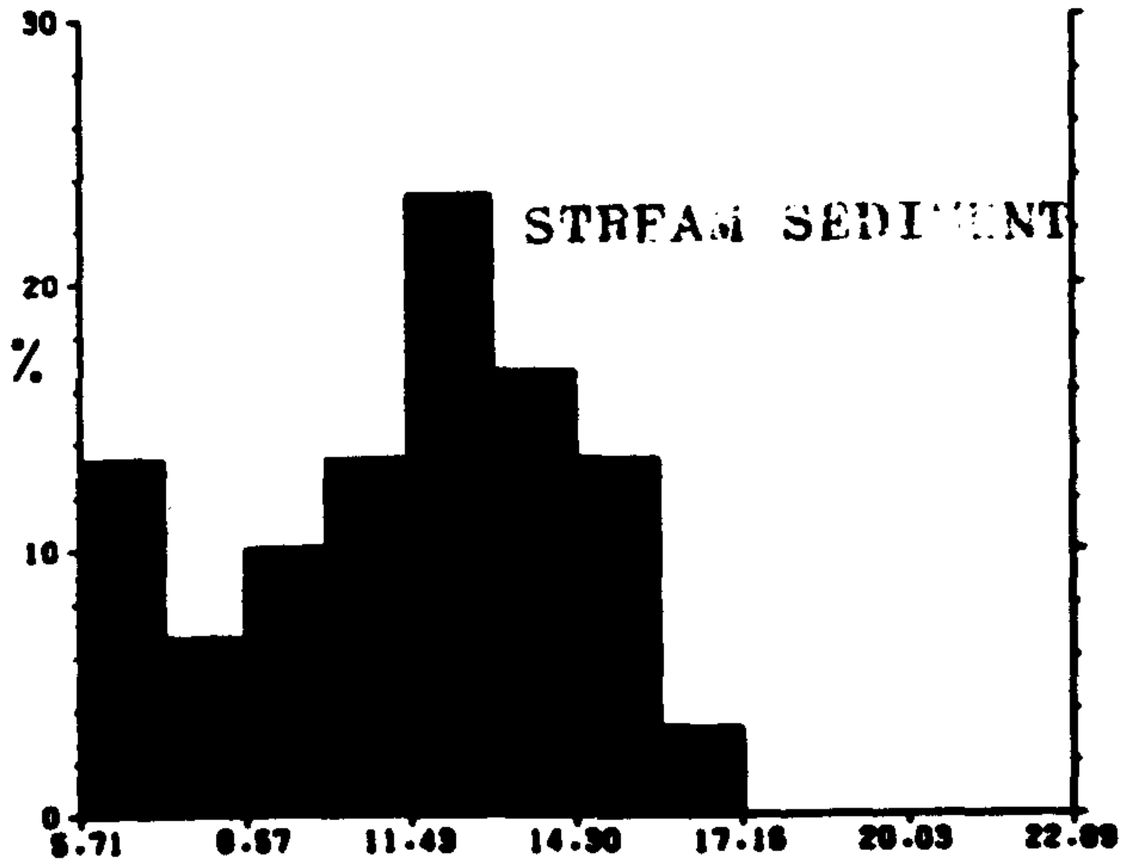
Fig. 13-23



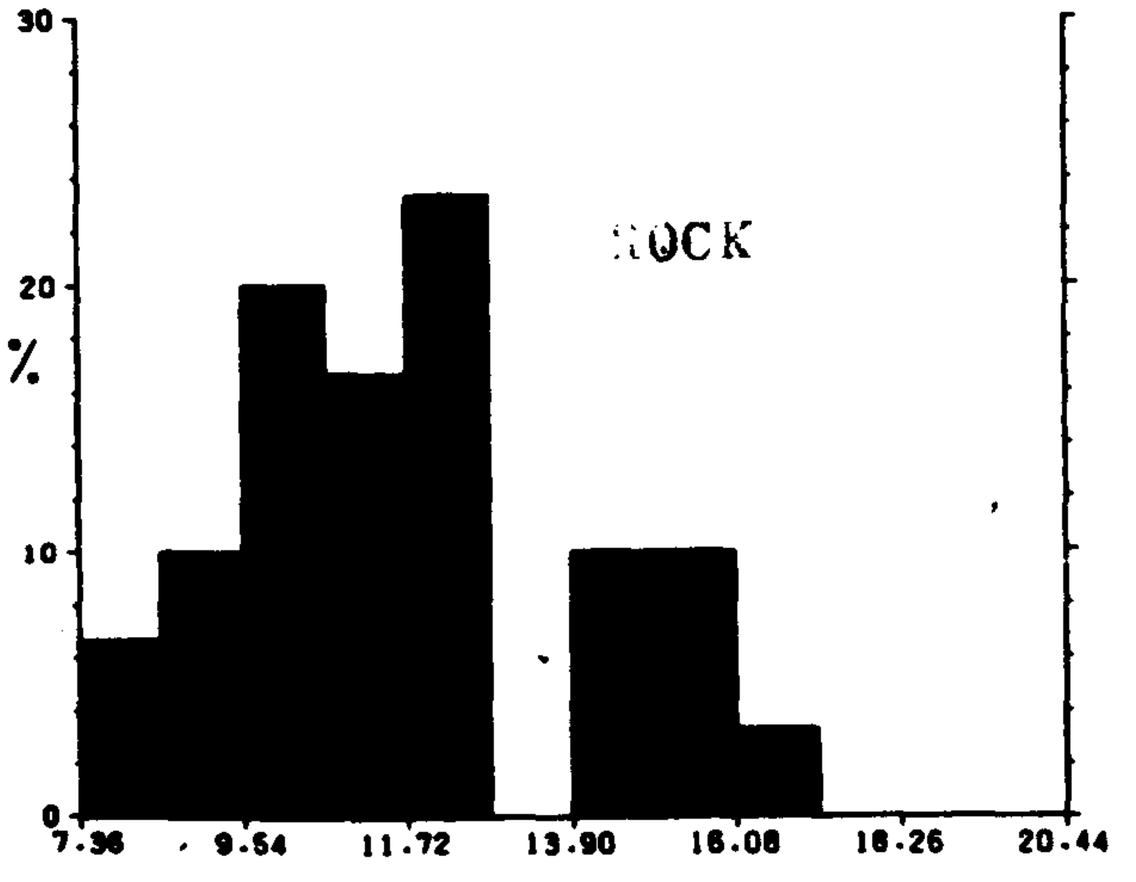
OM
NO. OF OBSERVATIONS = 40
MEAN = 16.58 STD DEV = 2.640



OM
NO. OF OBSERVATIONS = 40
MEAN = 14.14 STD DEV = 2.913



OM
NO. OF OBSERVATIONS = 30
MEAN = 11.43 STD DEV = 2.864



OM
NO. OF OBSERVATIONS = 30
MEAN = 11.72 STD DEV = 2.181

Histograms of the distribution of organic matter (LOI) in the rocks, soils and stream sediments derived from the less calcareous facies of the Lower Lias in the Somerset study area.

compounds It is further capable of adsorbing or being adsorbed by the clay minerals.

Correlations with elements.

In the calcareous rocks and the Evesham series the organic matter(LOI) was negatively correlated with Ca (Table 13-21b) while the correlations with Al, Zn and Ni were positive and significant. In the Evesham soil series organic matter(LOI) was significantly correlated with Mn, Co and Pb in both the top and subsoils.

In the less calcareous rocks no significant correlations were observed between the organic matter(LOI) and all the elements determined. In the Denchworth soil series only the correlation with pH were significant in the top and subsoils while a further significant correlation occurred with Pb in the topsoil. In contrast, organic matter(LOI) was significantly correlated with all the elements determined in the less calcareous sediments except Mg, Zn and Ni.

(1) pH.

The pH in the rocks, soils and stream sediments are shown in (Tables 13-23a; -24). In the calcareous rocks and Evesham series the pH ranged from being slightly acidic to alkaline. A similar condition was observed in the less calcareous rocks and the Denchworth soil series. Stream sediments derived from both beds were dominantly alkaline, (Figs. 13-24; -25).

Table 13-23a pH Concentrations In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias.

Medium		Mean	S.D.	C.V.	Range Min	Max
Rock	30	7.0	0.2	3.4	6.4	7.5
T/Soil	40	6.9	0.3	4.8	5.6	7.3
S/Soil	40	7.0	0.3	3.8	6.3	7.3
S/Sedt	32	7.4	0.2	2.8	6.5	7.6

N = Number Of Samples.
S.D. = Standard Deviation.
C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 13-23b Significance Of Correlation Coefficients Between pH And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	**	*	-	-	-	-	-	-	-	-	-	
T/Soil	**	*	-	-	-	-	-	-	-	-	**	
S/Soil	*	*	(***)	(**)	-	-	-	-	-	-	**	
S/Sedt	-	-	-	*	-	-	-	-	-	-	(*)	

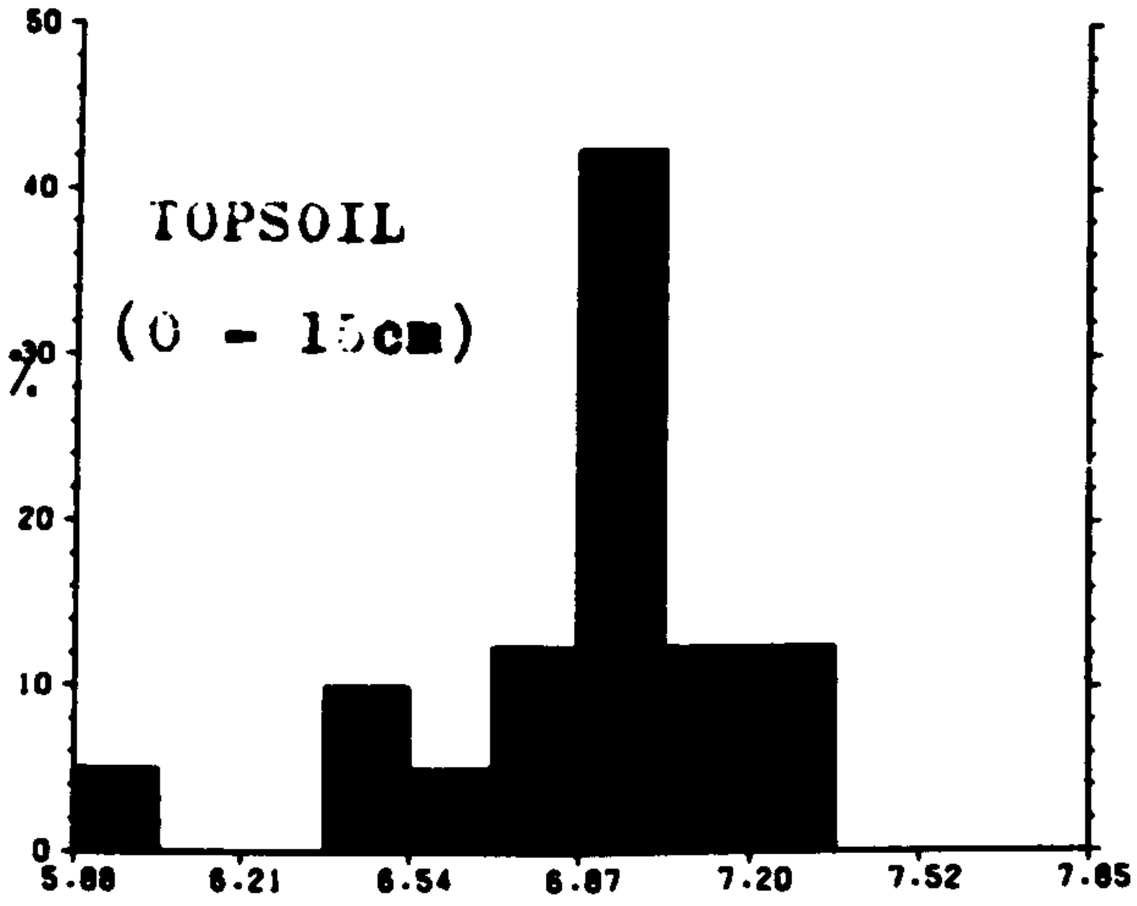
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

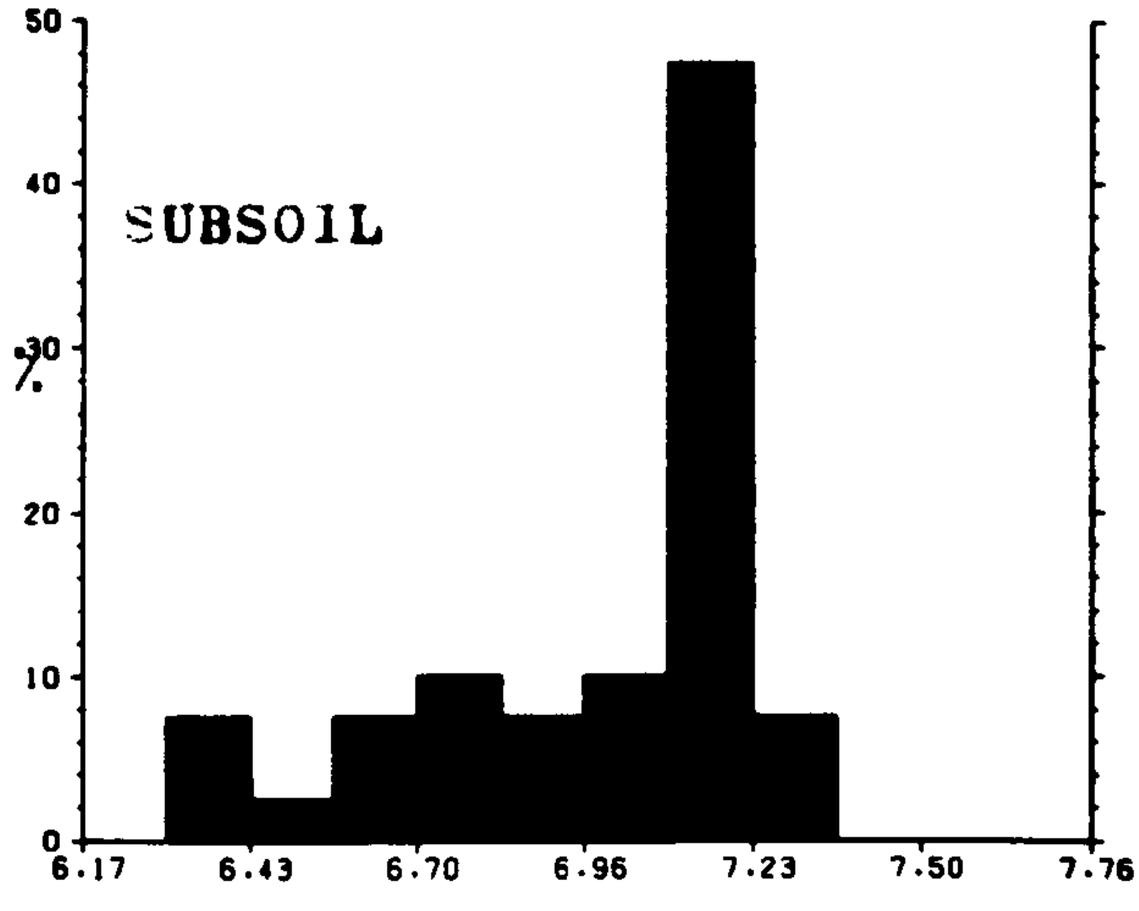
*** = Significant at .01 level

( ) = Negative Correlation.

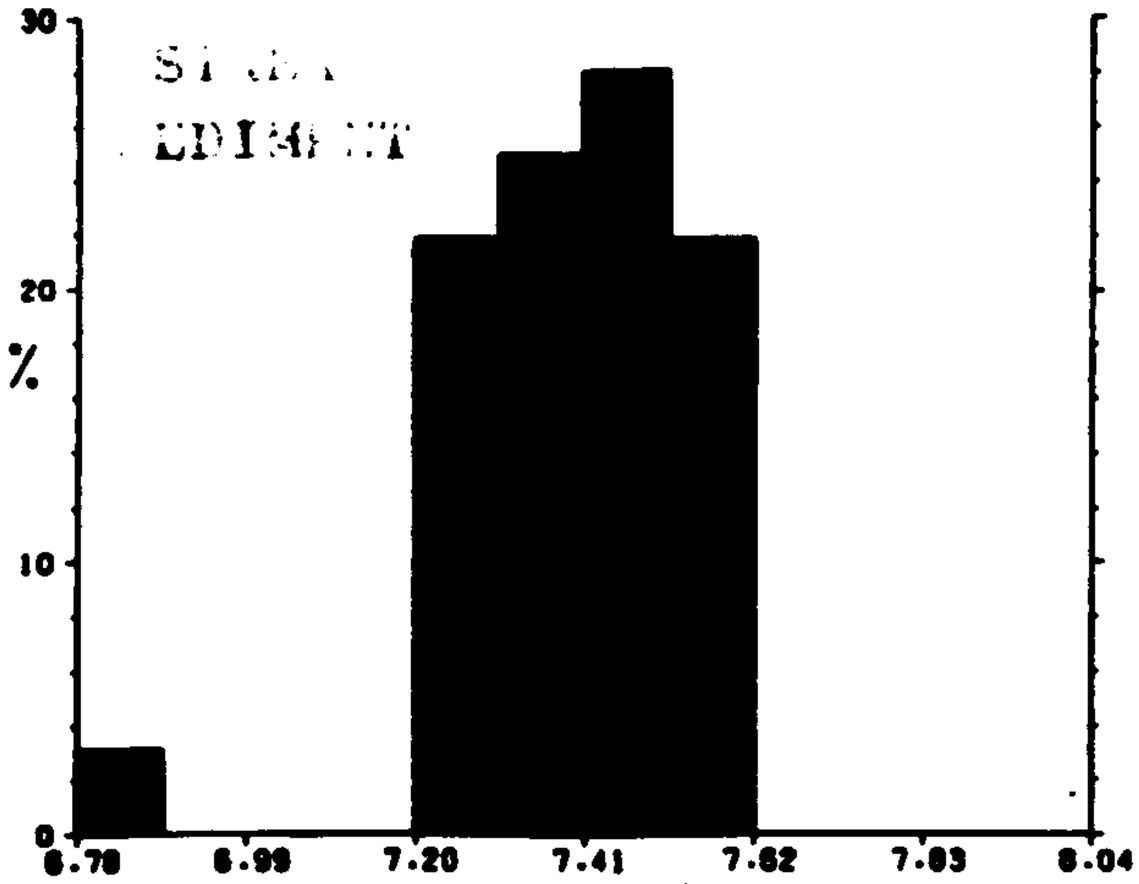
Fig. 13-24



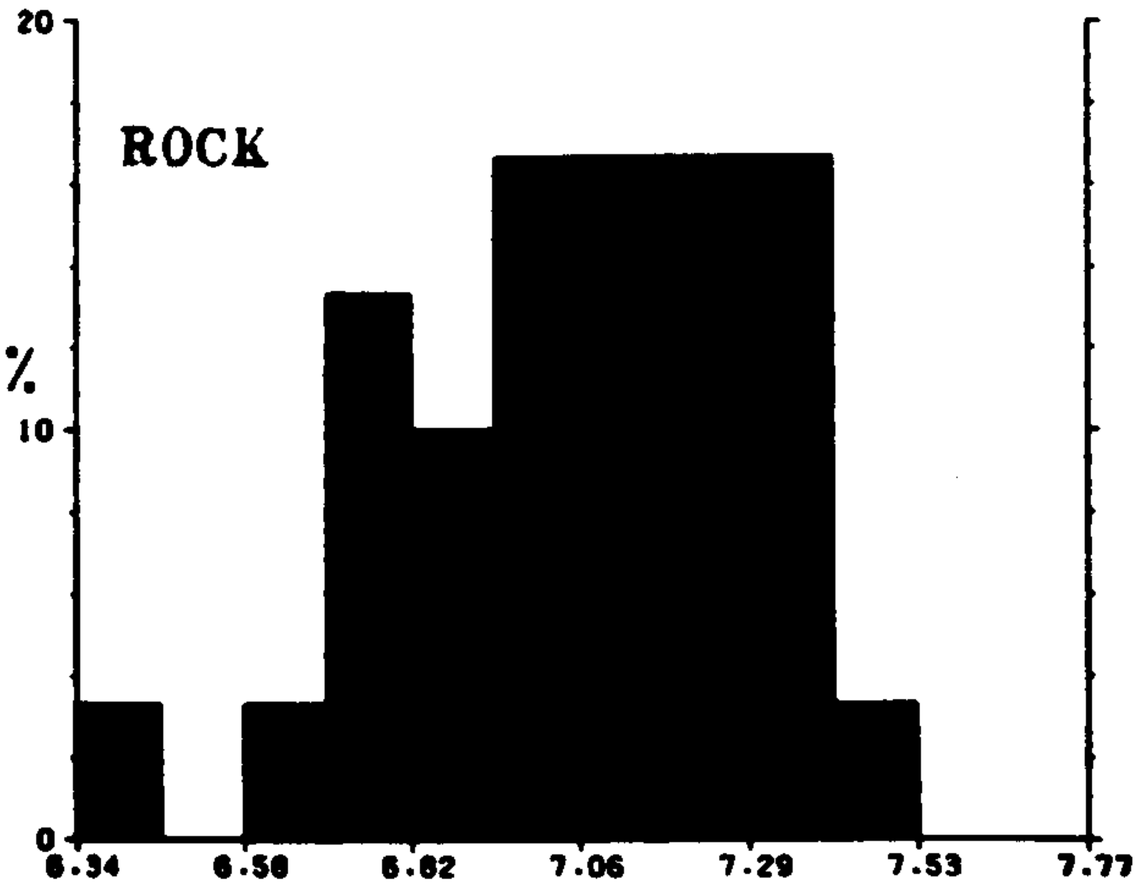
PH
NO. OF OBSERVATIONS = 40
MEAN = 6.87 STD DEV = 0.328



PH
NO. OF OBSERVATIONS = 40
MEAN = 6.97 STD DEV = 0.267



¬PH
NO. OF OBSERVATIONS = 32
MEAN = 7.41 STD DEV = 0.210



PH
NO. OF OBSERVATIONS = 30
MEAN = 7.06 STD DEV = 0.237

Histograms of the distribution of the pH in the rocks, soils and stream sediments derived from the calcareous facies of the Lower Lias in the Somerset study area.

Table 13-24a pH Concentrations In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias.

Medium	N	Mean	S.D.	C.V.	Range Min	Max
Roclk	30	7.0	0.4	6.3	5.6	7.5
T/Soil	40	6.6	0.5	9.3	5.2	7.3
S/Soil	40	6.6	0.4	6.7	5.4	7.2
S/Sedt	32	7.1	0.4	6.2	6.0	7.5

N = Number Of Samples.
S.D. = Standard Deviation.
C.V. = Coefficient Of Variation = S.D./Mean x 100.

Table 13-24b Significance Of Correlation Coefficients Between pH And Other Elements Analysed In The Rock Soil And Stream Sediments Derived From The Less Calcareous Facies Of The Lower Lias In The Somerset Study Area.

Medium	Ca	Mg	Al	Fe	Zn	Mn	Co	Pb	Ni	Cu	LOI	pH
Rock	**	-	-	-	-	-	-	-	-	-	-	
T/Soil	**	-	-	-	-	-	-	-	-	-	*	
S/Soil	**	-	-	-	-	-	-	-	-	-	-	
S/Sedt	-	-	*	*	-	-	-	-	-	-	-	

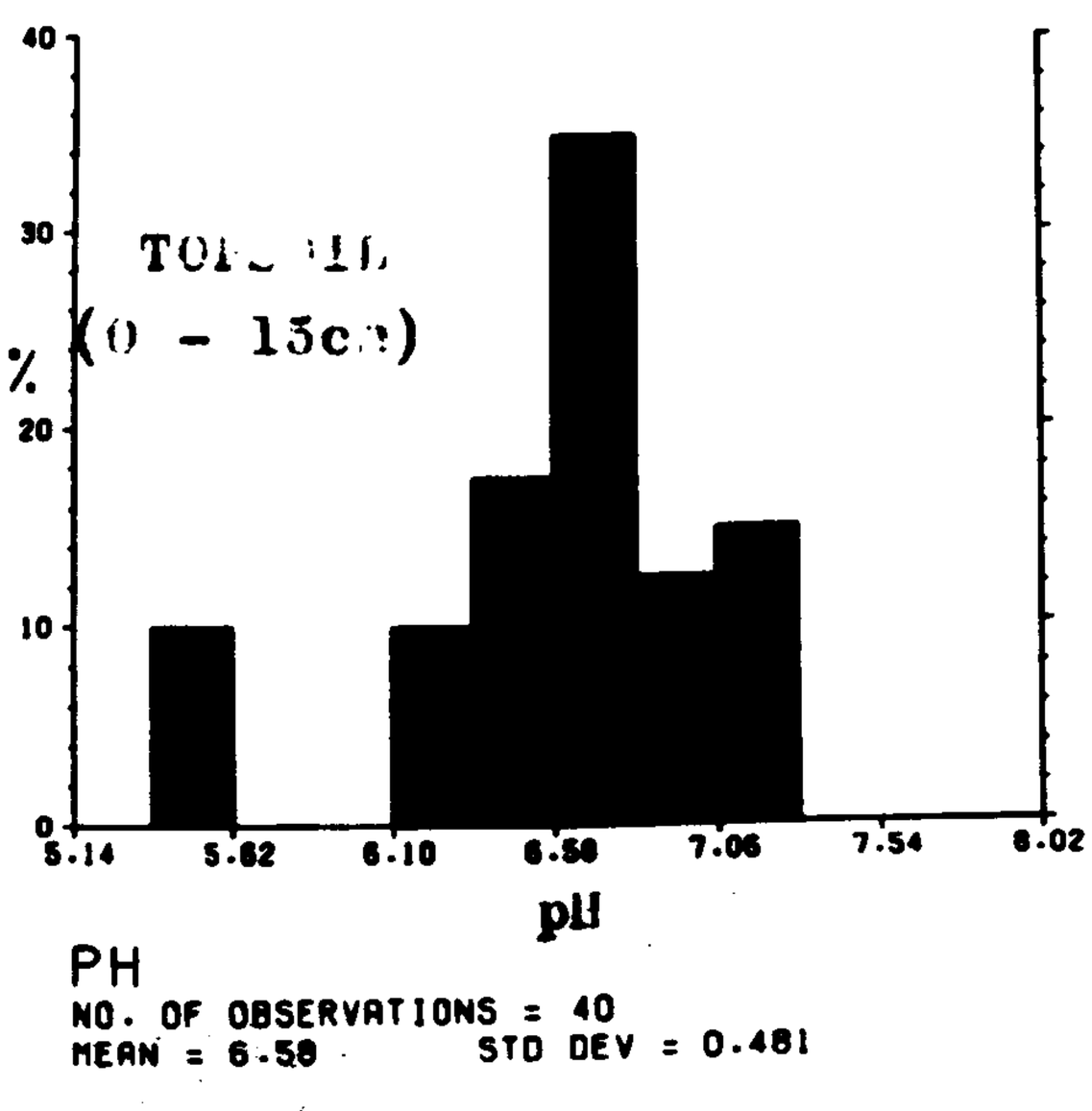
Level Of Significance - = Not Significant * = Significant at .10 level

** = Significant at the .05 level

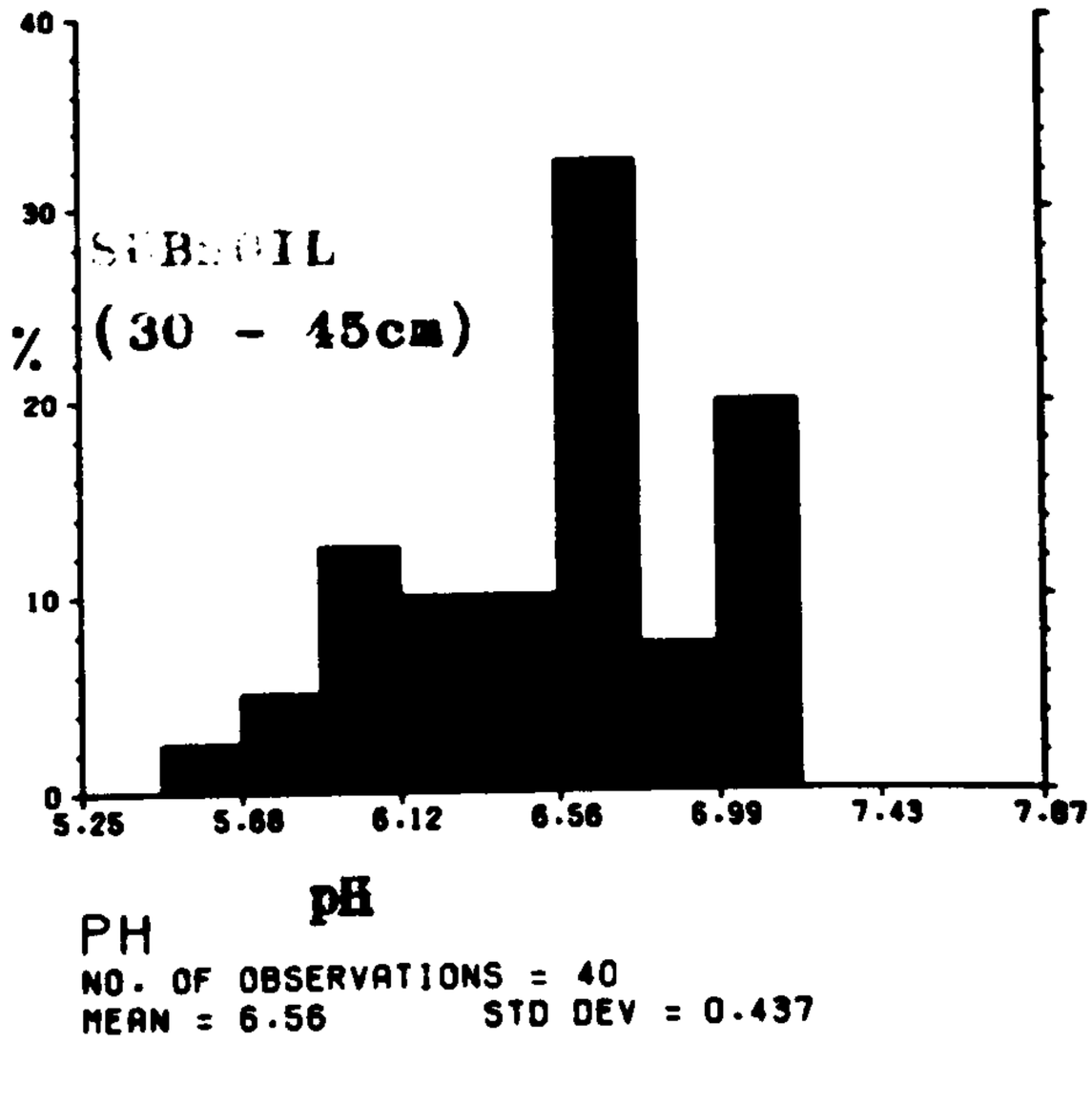
*** = Significant at .01 level

( ) = Negative Correlation.

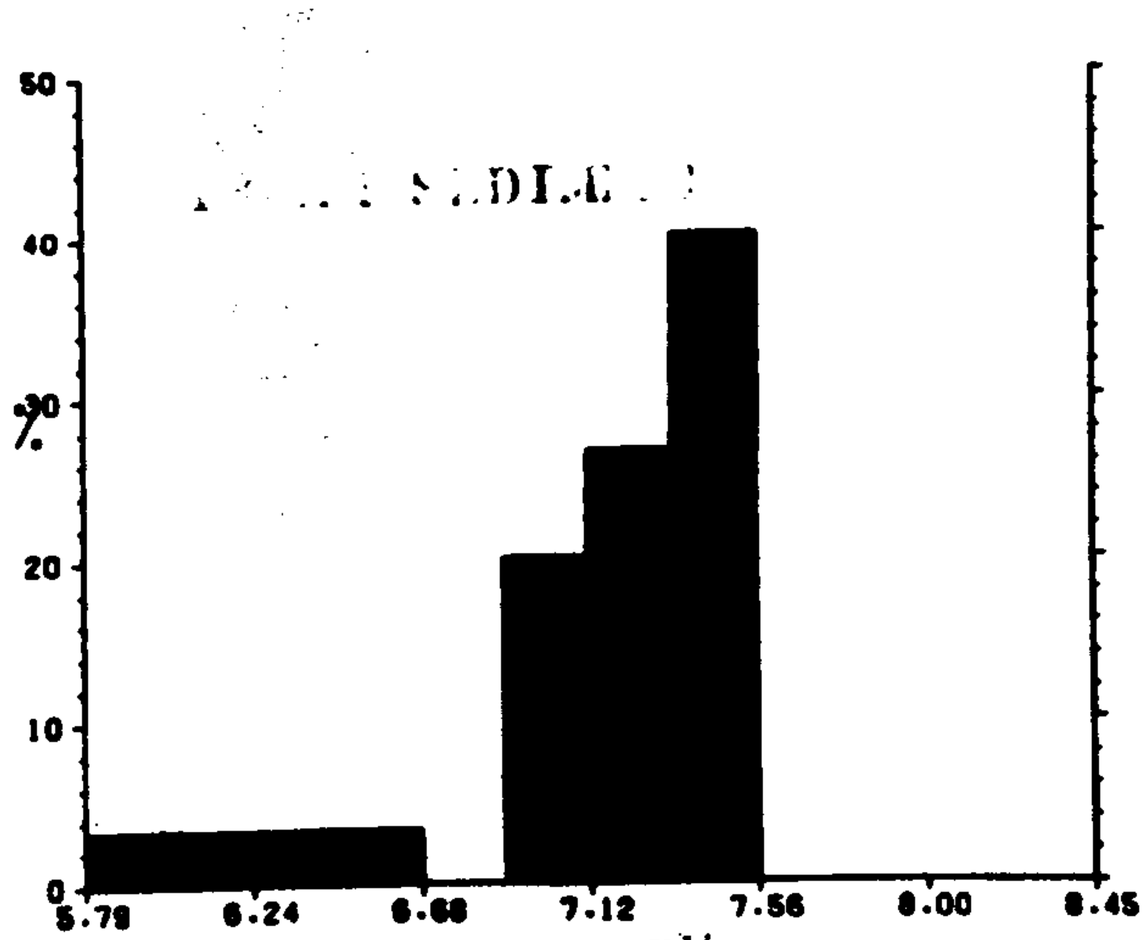
Fig. 13-25



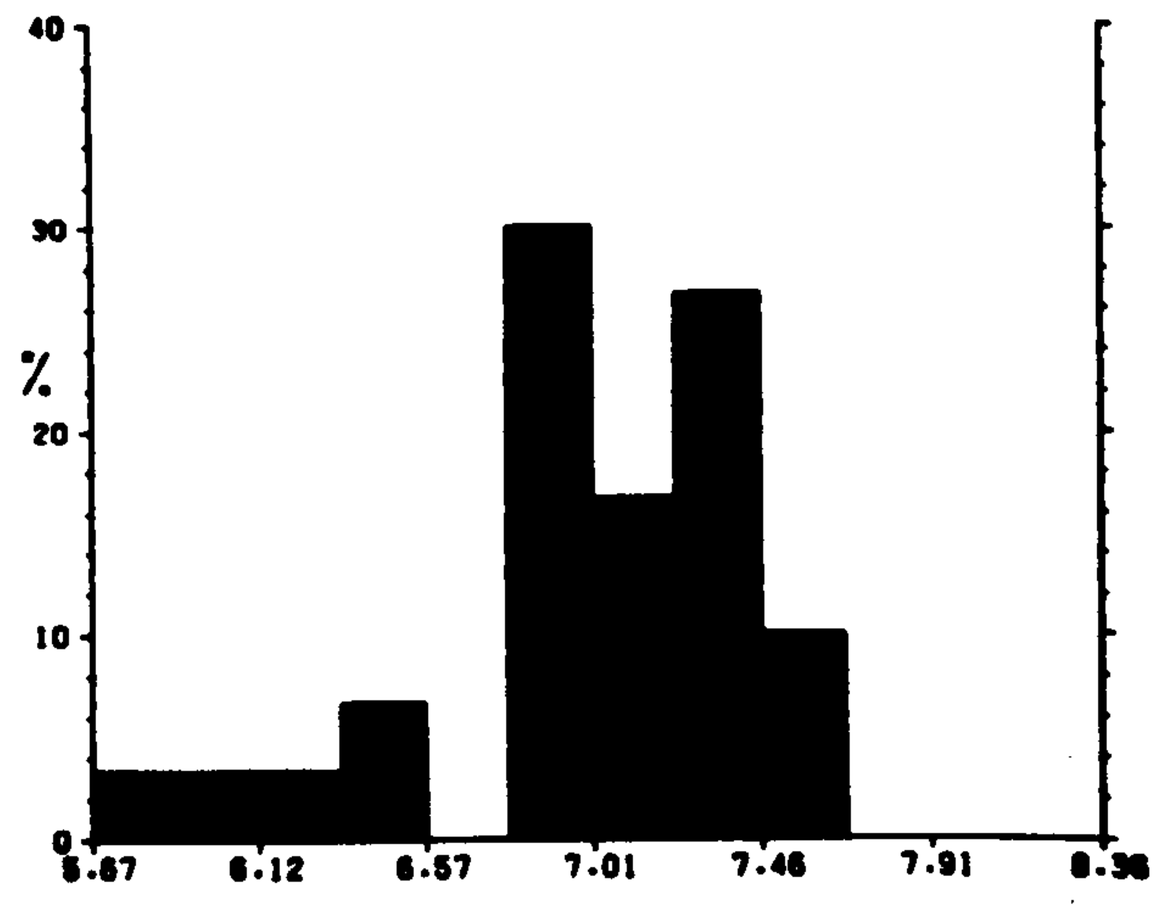
PH
NO. OF OBSERVATIONS = 40
MEAN = 6.58 STD DEV = 0.481



PH
NO. OF OBSERVATIONS = 40
MEAN = 6.56 STD DEV = 0.437



PH
NO. OF OBSERVATIONS = 30
MEAN = 7.12 STD DEV = 0.442



PH
NO. OF OBSERVATIONS = 30
MEAN = 7.01 STD DEV = 0.448

Histograms of the distribution of the pH in the rocks, soils and stream sediments derived from the less calcareous facies of the Lower Lias in the Somerset study area.

Correlations with elements:

Tables 13-23b, -24b show the correlation between the pH and the elements determined. Generally, correlations with most elements in the various media derived from the calcareous beds were either weak or insignificant. In the rocks the correlation with the Ca was significant in both facies of the Lower Lias. The correlation with the loss on ignition in the topsoils of the Evesham soil series was significant while in the Denchworth series the correlation with Mg and Ca were significant in both the top and subsoils. In the calcareous sediments the correlations with Al and Fe were weak. The weak correlation with Fe persisted in the less calcareous sediments.

(m) Summary.

The presence of limestone bands in the Lower Lias accounted for the exceptionally high concentrations of Ca recorded in the calcareous facies of the Lias. There was obviously a leaching process in the transition from rock to soil. The lack of contrast between the top and subsoil of the Denchworth series may reflect more the lack of redistribution of leached material by underground waters rather than lack of mobilisation of Ca, which in the moderately drained Evesham series showed evidence of being leached in the topsoil and redeposited in the subsoil. Elements such as Mn, Co, Zn, and Cu were present in larger amounts in the Evesham series than in the Denchworth series. This may be due to their being formed from parent materials with different concentrations of these elements and to pedological modification. Furthermore, the poor drainage in the Denchworth soil series in addition to conditions that encouraged waterlogging in the

soils may impede ground water from circulating and redistributing these elements in the soils and stream sediments. In the Evesham series Zn, Pb and Cu were higher in the topsoils compared to the subsoils. In the Denchworth soil series differences in the concentrations of these elements were small in both media. In the soils these divalent cations may be associated with either the clay minerals, hydrous oxides or organic matter.

The minor enhancements of such clay forming elements as Al, Fe, Ni and Mg in the subsoil indicated that some measure of translocation of the clays occurred in the soils, however the persistent correlation between these elements in all the media investigated showed that reconstitution of the clay minerals was not a common feature of at least the soils. In the stream sediments higher concentrations of Ca were accompanied by raised concentrations of Zn and Pb. This indicated the formation of secondary carbonates. Such a process was further indicated by significant correlations between Ca with Zn and Pb in the stream sediments. Dilution effects of the carbonates in the stream sediments may be the cause of the reduced concentrations of Mn, Co and Cu in the stream sediments derived from both facies.

13-5 Multi-element associations:

Multi-element associations within the different media investigated were derived by factor analysis. The number of factors retained were based on the subjective scheme outlined in Chapter 3. The results are presented as factor loadings on the elements determined and the interpretations are based on the significance of

the loadings in each element. The calcareous and the less calcareous facies are discussed as separate units.

(a) Rocks.

Factors 1 and 2 in the calcareous and less calcareous facies of the Lias respectively defined by significant positive loadings a group consisting of Al, Mg, Fe and Ni (Tables 13-25, -26). This group was interpreted as an association with the clay minerals in the rocks. In the more calcareous beds (Table 13-25) the group was associated with the loss on ignition while in the less calcareous rocks (Table 13-26) the group was associated with Cu . Thèse associations illustrate adsorption processes affecting the clay minerals in the two facies. Thus clay minerals can adsorb organic matter on to its structure while the adsoption of divalent cations such as Cu is a common feature of the geochemical environment. It can be inferred that the clay minerals in the two beds were similar.

Factors 2 and 3 in the calcareous and the less calcareous facies respectively, defined by significant loadings, a group consisting of Fe, Mn, Zn, Co and Cu. The two factors were interpreted as an association with the hydrous oxides present in the rocks. The geochemistry of Fe and Mn are similar (Mason, 1952), being mobile in the divalent states and less mobile in the higher oxidation states. Due to the greater affinity of iron to oxygen than of manganese, ferric hydroxide tends to precipitate more readily than manganic hydroxide in the geochemical environment. Brewer et al. (1973) showed that in Mn nodules Fe and Mn occurred as separate phases, and when freshly precipitated Fe(OH)3 hydrosols are positively charged

Table 13-25

Significance Of Factor Loadings Of Logarithmically Transformed Rock Data. Matrix Accounts for 83.5% Of Variance Of 30 Samples Of The Calcareous Facies Of The Lias. ! Tables Of Levels Of Significance Of Correlation Coefficient (Appendix 3) Used To Determine Significance Levels Of Factor Loadings.

Metals	Factor			
	1	2	3	4
Variance (%)	25.4	22.5	18.6	17.0
Ca	-	-	-	***
Mg	***	-	-	-
Al	***	-	-	-
Fe	**	(*)	-	(**)
Zn	-	**	***	-
Mn	-	***	-	-
Co	-	***	-	-
Pb	-	-	-	(**)
Ni	***	-	-	-
Cu	-	-	**	(***)
LOI	***	-	**	-
pH	-	-	*	-

- = Not significant
* = significant at 0.10 level
** = Significant at 0.05 Level
*** = Significant at 0.01 level
( ) = Negative Loading.

Table 13-26

Significance Of Factor Loadings Of Logarithmically Transformed Rock Data. Matrix Accounts for 76.9% Of Variance Of 30 Samples Of The Less Calcareous Facies Of The Lias. ! Tables Of Levels Of Significance Of Correlation Coefficient (Appendix 3) Used To Determine Significance Levels Of Factor Loadings.

Metals	Factor			
(%) Variance	1 24.2	2 21.0	3 16.4	4 15.3
Ca	***	-	-	-
Mg	-	**	-	-
Al	-	***	-	-
Fe	-	***	***	-
Zn	-	-	**	**
Mn	-	-	***	*
Co	-	-	***	-
Pb	-	-	-	-
Ni	-	**	-	-
Cu	-	*	*	*
LOI	-	-	-	***
pH	***	-	-	-

- = Not significant
* = significant at 0.10 level
** = Significant at 0.05 Level
*** = Significant at 0.01 level
( ) = Negative Loading.

(Rankama and Sahama, 1950), and Mn(OH)4 are negatively charged hence Mn oxides are more likely to adsorb other divalent cations such as Co, Zn and Cu. Factor 2 in the calcareous facies was bipolar with significant positive loadings on Mn and Co, and significant negative loadings on Fe. This may reflect the less mobile nature of the trivalent ferric ion to the quadrivalent manganic ion. The association between Mn, Co and Zn in the less calcareous rocks may also reflect the "scavenging" effect of Mn oxides (Jenne, 1968).

Factors 1 and 4 in the less calcareous and the calcareous rocks, respectively, defined a group which was interpreted as an association with the carbonates in the rocks. In the less calcareous rocks, factor 1 (Table 13-26) grouped Ca and the pH by significant positive loadings . This represents a direct relationship between the carbonates and the acidity in the geochemical environment. In the more calcareous rocks (Table 13-25) factor 4 showed an inverse relationship, with positive loading on Ca on one hand and negative loadings on Fe, Pb, Cu, and organic matter(LOI) on the other. Such a relationship betweeen the carbonates, trace elements, and the organic matter may not be as direct as in the case of the less calcareous rocks. Le Riche (1959a) suggested that such an indirect relationship was a result of the association between the carbonates and organic matter with which the trace elements are associated. Twenhofel(1926, p240) had postulated a mechanism of such a relationship. He suggested that under anaerobic conditions decaying organic matter will liberate ammonia which forms soluble ammonium carbonates with dissolved CO hence precipitating calcium salts from solution as carbonates.

Factors 3 and 4 in the calcareous and less calcareous rocks grouped the elements Zn, Mn, Cu and organic matter(LOI). Organic

matter is capable of forming stable compounds in the geochemical environment and this group is interpreted as an association with the organic matter fraction.

It can be inferred from the results that processes operating within both beds of the Lias were essentially similar. Thus elements within the rocks were associated with either clay minerals, hydrous oxides, carbonates or organic matter(LOI).

(b) Topsoil.

The four factor model accounted for over 80% of the total variance in the topsoils of both the Denchworth and Evesham soil series (Tables 13-27, -28). Factors 1 and 2 in the Denchworth and Evesham series respectively defined groups which were interpreted as an association with the clay minerals . In the Denchworth series (Table 13-28) factor 1 associated Al, Mg, Fe, and Ni by significant positive loadings. In the Evesham soil series (Table 13-27) this was less straight forward. Factor 2 grouped Mg, Al, Fe, Ni and organic matter(LOI) by significant positive loadings on one hand and the pH by significant negative loading on the other. In general, organic colloids carry negative charge as do pure clays hence the clay minerals would not be expected to adsorb these organic colloids. Greenland (1971), has shown that there are at least three major mechanisms by which clays bind organic matter such as humus to their surface:-

(a) through polyvalent exchange cations,

(b) through ligand exchange,

(c) though van der Wall or London forces.

Table 13-27

Significance Of Factor Loadings Of Logarithmically Transformed Topsoil Data. Matrix Accounts for 80.6% Of Variance Of 40 Samples Of The Calcareous Soils Of The Lias. ! Tables Of Levels Of Significance Of Correlation Coefficient (Appendix 3) Used To Determine Significance Levels Of Factor Loadings.

Metals	Factor			
	1	2	3	4
Variance (%)	24.7	21.0	18.5	16.4
Ca	***	-	-	-
Mg	-	***	-	-
Al	-	***	-	-
Fe	(***)	***	-	-
Zn	(***)	-	-	-
Mn	-	-	(***)	-
Co	-	-	(***)	-
Pb	-	-	-	(***)
Ni	(***)	***	-	-
Cu	(***)	-	-	-
LOI	-	***	**	(**)
pH	-	(**)	**	(**)

- = Not significant
* = significant at 0.10 level
** = Significant at 0.05 Level
*** = Significant at 0.01 level
( ) = Negative Loading.

Table 13-28

Significance Of Factor Loadings Of Logarithmically Transformed Topsoil Data. Matrix Accounts for 81.4% Of Variance Of 40 Samples Of The Less Calcareous Soils Of The Lias. ! Tables Of Levels Of Significance Of Correlation Coefficient (Appendix 3) Used To Determine Significance Levels Of Factor Loadings.

Metals	Factor			
	1	2	3	4
Variance (%)	23.4	20.5	21.3	16.2
Ca	-	***	-	-
Mg	**	**	-	-
Al	***	-	-	-
Fe	**	-	**	-
Zn	-	-	***	-
Mn	-	*	***	-
Co	-	*	***	-
Pb	-	-	-	**
Ni	**	-	-	-
Cu	-	-	**	-
LOI	-	-	-	***
pH	-	**	-	-

- = Not significant
* = significant at 0.10 level
** = Significant at 0.05 Level
*** = Significant at 0.01 level
( ) = Negative Loading.

The organic matter present may be related to the clay minerals by one or more of the above processes. The inverse relationship between the clay related elements and the pH suggested that this association was influenced by the pH of the medium. Thus, in the soils uncharged organic compounds such as amines can accept protons to become charged cations which can then take part in exchange reactions with the clay minerals (Russell, 1973). The reductions of the protons in the system may consequently increase the pH.

Factors 1 and 2 in the Evesham and Denchworth series respectively defined a group which was interpreted as being associated with the carbonates.

Factor 1 in the Evesham series (Table 13-27) was bipolar with a significant positive loading on Ca on one hand and significant negative loadings on Fe, Zn, Ni and Cu on the other. During the weathering of carbonates, insoluble residues are formed with which most trace elements are associated. The bipolar effect of the carbonates in the topsoils of the Evesham series can be explained by the formation of such insoluble residues which are left after the weathering of the carbonates (Curtis et al. 1976).

In the Denchworth series factor 2 grouped Ca, Mg, Co, Mn and the pH by significant positive loadings. In general the precipitation of magnesium carbonates in the soils is uncommon and it is more likely that Mg is associated with the carbonates as mixed carbonates. Diadochic replacements of Ca by Mg and Mn in calcite takes place very readily in the soils. A similar process may be responsible for the association of Co with this group since Co readily replaces Ni and Mg due to the similarities of their ionic radii (.78k, .82k).

Factor 3 in both soil series defined a group consisting of Fe, Mn, Co, Zn and Cu. This group was interpreted as an association with the hydrous oxides present . As previously discussed, Mn oxides in general, are capable of incorporating other divalent cations in the soils into its structure (Taylor et al. 1964). In the Evesham series this group was associated with the organic matter(LOI) . Grass et. al. (1973) showed that reactions that decompose complex organic matter in the soils to simpler soluble forms also resulted in the dissolution of Fe and Mn oxides in the soil. In the Denchworth series Factor 3 associated Mn, Fe, Co, Zn and Cu by significant positive loadings. In general soils contain greater amounts of Fe-oxides than Mn-oxides, but the Mn-oxides exhibit greater chemical reactivity and more complex mineralogical compositions than do Fe-oxides (Taylor et al 1964).

Chao and Sanzolone (1973) attributed this to the following specific features of Mn:

(a) the ability to exist in several oxidation states,

(b) the ability to form non-stoichiometric oxides,

(c) the crystalline or pseudo- crystalline nature of the higher valent oxides.

The Denchworth soil series is a poorly drained soil which showed evidence of periodic waterlogging. Under these conditions Ponnaramperuma et al. (1969) have postulated that co-precipitation of iron and manganese oxides is likely to form. These act as a sink for such divalent cations as Zn, Co and Cu (Jenne, 1968, Taylor et al. 1964).

Factor 4 in each of the soil series associated by significant positve loadings Pb and the organic matter(LOI) . The association

between Pb and the organic matter(LOI) was weak in the Denchworth series (Table 13-28) than in the Evesham series (Table 13-27). This association between Pb and organic matter has been observed by a number of workers (Davies et al. 1969). This group was interpreted as reflecting the vegetative recycling of Pb and accumulation of organic debris.

(c) Subsoil:

Factors 1 in both soil series were interpreted as an association with the carbonates in the subsoil (Tables 13-29, -30). In the Denchworth series significant positive loadings grouped Ca, Cu and the pH together (Table 13-30). In general, the leaching of calcium in the bi-carbonate form in the soil is a very active process particularly in the slightly acidic environment that prevails in the poorly drained Denchworth series. The association with such divalent cations as Cu indicated that secondary carbonates were forming in the subsoil. In the Evesham series factor 1 (Table 13-29) had weak positive loadings on Ca and Mg while the loadings on Fe, Zn, Ni, Cu and Pb were negative. Such an inverse relationship was observed in the topsoil and it was interpreted as an association of the trace elements with the insoluble residues left after the leaching of the carbonates which may later be incorporated with the soil.

Factors 3 and 2 in the Evesham and Denchworth soil series were interpreted as defining the clay mineral group in the subsoil. In the Evesham series factor 3 was bipolar with positive and significant loading on the pH on one hand and significant negative loadings on Ca, Al, Mg, Fe and Zn on the other. In the soils, Ca and

Table 13-29

Significance Of Factor Loadings Of Logarithmically Transformed Subsoil Data. Matrix Accounts for 75.7% Of Variance Of 40 Samples Of The Calcareous Soils Of The Lias. ! Tables Of Levels Of Significance Of Correlation Coefficient (Appendix 3) Used To Determine Significance Levels Of Factor Loadings.

Metals	Factor		
	1	2	3
Variance (%)	28.5	22.4	24.8
Ca	*	-	(**)
Mg	*	-	(*)
Al	-	-	(***)
Fe	(**)	-	(*)
Zn	(***)	-	(**)
Mn	-	***	-
Co	-	***	-
Pb	(*)	-	-
Ni	(**)	-	-
Cu	(***)	-	-
LOI	-	(**)	-
pH	*	-	***

- = Not significant
* = significant at 0.10 level
** = Significant at 0.05 Level
*** = Significant at 0.01 level
( ) = Negative Loading.

Table 13-30

Significance Of Factor Loadings Of Logarithmically Transformed Subsoil Data. Matrix Accounts for 76.0% Of Variance Of 40 Samples Of The Less Calcareous Soils Of The Lias. ! Tables Of Levels Of Significance Of Correlation Coefficient (Appendix 3) Used To Determine Significance Levels Of Factor Loadings.

Metals	Factor		
Variance (%)	1 29.1	2 27.6	3 19.3
Ca	***	-	-
Mg	-	**	-
Al	-	***	-
Fe	-	**	-
Zn	-	*	-
Mn	-	-	***
Co	-	*	***
Pb	-	-	-
Ni	-	***	-
Cu	**	-	-
LOI	-	-	-
pH	**	-	-

- = Not significant
* = significant at 0.10 level
** = Significant at 0.05 Level
*** = Significant at 0.01 level
( ) = Negative Loading.

other divalent cations such as Mg can be adsorbed onto exchange sites on the clay minerals to neutralise the negative charges on the clays. An inverse relationship between the soil clay and the pH can be conceived. Thus as the base saturation is reduced so the hydrogen ion concentration is increased and consequently a lower pH results. The converse is also true and the bipolar nature of factor 3 in the Evesham subsoil may depict such an inverse relationship between the bases in the subsoil and the clay minerals. In the Denchworth series factor 2 defined a rather straight foward association of the clay mineral group. Thus Mg Al, Fe, Ni, Zn and Co were grouped together by significant positive loadings. The association of this group with Zn and Co reflected the adsorption of cations by the clay minerals explained earlier.

Factors 3 and 2 in the Denchworth and the Evesham series respectively defined a group consisting of Mn, Co and organic matter(LOI) . Such an association was observed in the topsoil. Manganese and cobalt may be related to organic matter in the soils through a number of processes, for instance,

(a) both elements may be organically bound in the soils. Manganese fixed in this way is in the lower valence state,

(b) organic matter may be related to the hydrous oxides in the soils in the sense that both are affected by similar conditions in the soils eg. the pH and the oxidation reduction levels attained. These conditions may have the effect of encouraging the breakdown of organic matter as well as influencing the precipitation or solution of Mn oxide minerals (Grass et. al. 1973).

Table 13-31

Significance Of Factor Loadings Of Logarithmically Transformed Stream Sediment Data. Matrix Accounts for 80.0% Of Variance Of 40 Samples Of The Calcareous Facies Of The Lias. ! Tables Of Levels Of Significance Of Correlation Coefficient (Appendix 3) Used To Determine Significance Levels Of Factor Loadings.

Metals	Factor		
	1	2	3
Variance (%)	30.3	27.6	22.9
Ca	-	-	***
Mg	(***)	-	-
Al	(**)	-	-
Fe	-	**	-
Zn	(*)	-	-
Mn	(**)	***	-
Co	(*)	***	-
Pb	-	***	-
Ni	(***)	-	-
Cu	-	***	-
LOI	-	***	(***)
pH	-	-	***

- = Not significant
* = significant at 0.10 level
** = Significant at 0.05 Level
*** = Significant at 0.01 level
( ) = Negative Loading.

Table 13-32

Significance Of Factor Loadings Of Logarithmically Transformed Stream Sediment Data. Matrix Accounts for 78.0% Of Variance Of 30 Samples Of The Less Calcareous Facies Of The Lias. ! Tables Of Levels Of Significance Of Correlation Coefficient (Appendix 3) Used To Determine Significance Levels Of Factor Loadings.

Metals	Factor		
	1	2	3
Variance (%)	27.4	25.7	24.4
Ca	***	*	-
Mg	-	**	-
Al	-	**	-
Fe	-	***	-
Zn	-	-	-
Mn	-	-	***
Co	-	**	***
Pb	*	-	-
Ni	-	*	*
Cu	-	-	***
LOI	-	-	-
pH	**	-	-

- = Not significant
* = significant at 0.10 level
** = Significant at 0.05 Level
*** = Significant at 0.01 level
( ) = Negative Loading.

(d) Stream sediments.

Factors 1 and 2 in the calcareous and less calcareous sediments respectively defined a group consisting of Al, Mg, Fe and Ni (Tables 13-31, -32). These elements have been shown in other media to be ralated to the clay minerals. In addition weaker loadings occurred on Mn and Zn in the calcareous sediments and on Ca, Co and Ni in the less calcareous sediments. These divalent cations may be associated with the clay minerals by adsorption processes.

Factors 2 and 3 in the calcareous and less calcareous sediments respectively defined a group which was interpreted as defining an oxide related group. This consisted of highly significant loadings on Mn, Co and Cu. In the calcareous sediments (Table 13-31) the group was related to Fe, Pb and organic matter(LOI) while in the less calcareous sediments the group was related to Ni by weak positive loadings (Table 13-32). As discussed earlier, the association was defining the "scavenging" activity of Mn oxides in the streams.

Factors 3 and 1 in the calcareous and the less calcareous facies respectively defined by significant loadings the carbonate related elements, which consisted of Ca and pH. In the calcareous facies factor 3 was bipolar with a significant negative loading on the organic matter(LOI). Such an inverse relationship is conceivable. Thus organic acids are powerful agents of the solution of carbonates and increase of such acids is bound to increase the solution of the carbonates.

(e) Summary.

The results indicated that the elements Al, Fe and Ni were strongly associated with each other in the various media studied. Earlier results showed that these elements were strongly correlated to each other and the group was interpreted as being associated with the clay minerals. There was a persistent association between Ca and pH in all the media. An inverse relationship between Ca and Fe, Mg, Ni and Cu was found in the rocks and soils derived from the calcareous beds. This was thought to represent an association with the insoluble residues formed after the leaching of the carbonates during pedogenesis. Other associations found included Mn, Fe, Zn, Co and organic matter(LOI). These were thought to represent associations with the hydrous oxides and the organic matter.

It was inferred that despite the differences observed earlier in the metal concentrations in the two facies of the Lower Lias, multi element associations were similar in both beds.

13-6 Comparison Between Media (Analysis Of Variance Results).

The analysis of variance have been used to compare the variability between element concentrations in the transition from one medium to another. The theory of the method was described in Chapter 3. The results are presented as F-ratios and the percent contributions of the F-component to the total variability. The significance and the degrees of freedom are shown in Appendix 4. As with other units studied four comparisons have been made . The comparisons made were between the:

(a) the top and subsoils.

(b) the soil (top and subsoils) and rock.

(c) the soils(top and subsoils) and stream sediments

(d) the rock and stream sediments.

Two sets of results are presented for the calcareous and less calcareous facies of the Lower Lias.

(a) Comparison between topsoil and subsoil

The analysis of variance results for the comparison between the topsoil and subsoil results are presented in Tables 13-33, -34. The results showed that for the elements Ca, Zn, Mn and Pb variability between media (F1 ratio) were statistically significant at the .05 confidence level in the Evesham series. Contributions to the total variabilty ranged from 20% in Ca to 30% in Mn. Variability between media for the elements Fe and Cu together with the the loss on ignition were significantly different only at the .10 level with comparatively lower contributions to the total variability. For other elements such as Mg, Al and Ni differences in the variability were not statistically significant between the two media. The main source of the variability arose from within individual media. Thus the F2 ratios for all the elements analysed were statistically significant at the .01 level with high contributions to the total variability (Table 13-33) .

In the Denchworth series (Table 13-34) apart fron Mn, Co and Pb where the F1 ratios were statistically significant at the .05 and .10 levels respectively, for the rest of the elements the variability between the media were insignificant at the .10 level. As in the Evesham series the between site source accounted for most of the

Table 13-33
F-ratios and Percent Variance Components For The Comparison Between The Top And Sub Soils Derived From The Calcareous Facies Of The Lias As Estimated By The Three Level Nested Analysis Of Variance Model. Samples Collected From The Lower Lias In Somerset Study Area.

Metal	Between Media		Between Sites		Between Samples		Bet. Anal
	F1	(%)	F2	(%)	F3	(%)	(%)
Ca	**	20.6	***	67.4	NS	6.5	5.5
Mg	NS	10.7	***	72.3	NS	10.7	6.3
Al	NS	15.5	***	70.8	NS	5.3	6.4
Fe	*	19.3	***	64.6	NS	8.7	7.4
Zn	**	22.2	***	68.1	NS	5.4	4.4
Mn	**	30.0	***	60.3	NS	6.4	3.3
Co	NS	12.9	***	76.1	NS	6.5	4.4
Pb	**	26.6	***	64.7	NS	5.4	3.2
Ni	NS	9.4	***	77.9	NS	7.7	5.0
Cu	*	19.1	***	67.0	NS	10.0	3.9
LOI	*	24.4	**	58.0	NS	7.3	10.4
pH	NS	23.9	***	72.1	NS	2.0	2.1

NS = Not Significant, P> 0.10; * = 0.10 > P > 0.05; ** = 0.05 > P > 0.01; *** = P < 0.01.

Table 13-34
F-ratios and Percent Variance Components For The Comparison Between The Top And Sub Soils Derived From The Less Calcareous Facies Of The Lias As Estimated By The Three Level Nested Analysis Of Variance Model. Samples Collected From The Lower Lias In Somerset Study Area.

Metal	Between Media		Between Sites		Between Samples		Bet. Anal
	F1	(%)	F2	(%)	F3	(%)	(%)
Ca	NS	18.8	***	68.2	NS	7.5	5.4
Mg	NS	12.2	***	70.9	NS	8.3	8.6
Al	NS	14.4	***	70.8	NS	8.6	6.2
Fe	NS	9.3	***	74.8	NS	7.7	8.2
Zn	NS	11.9	***	69.8	NS	9.8	7.6
Mn	**	23.4	**	62.3	NS	8.0	6.0
Co	**	30.1	**	63.5	NS	3.3	3.9
Pb	*	19.9	***	63.8	NS	8.9	7.5
Ni	NS	8.7	**	77.6	NS	6.6	7.1
Cu	NS	10.4	**	72.8	NS	7.4	9.3
LOI	NS	6.7	***	80.1	NS	8.1	5.0
pH	NS	7.9	***	88.1	NS	2.0	1.0

NS = Not Significant, P> 0.10; * = 0.10 > P > 0.05; ** = 0.05 > P > 0.01; *** = P < 0.01.

variabilty. Thus the F2 ratios were significant for all elements with very high contributions to the total variability. Sources of errors such as sampling and analysis were found in both comparisons not to be a main source of great errors.

The results indicated that processes operating between media were not the main source of variability in both soil series. Spatial variability within individual media accounted for most of the variability of elements. The elements Al, Mg, Fe and Ni that showed no significant variability between the top and subsoil have been shown earlier to be associated with the clay minerals. This confirmed the view that the clay minerals undergo only minor, if any, alterations in the soils. Thus most of the changes affecting the clay minerals may involve such processes operating within the soils as adsorption of divalent cations.

(b) Comparison between the Soil and Steam-sediment.

The results of the comparison between the two soil series and stream-sediments derived from similar parent materials are presented in Tables 13-35, -36 . The results showed that the Fl ratios for most elements were statistically significant at the .01 and .05 levels. Contributions from this source however varied ranging from over 70% in the case of Al to 9% in the case of Co in the calcareous facies (Table 13-35). The F2 ratios were also significant at the .01 and .05 levels with high contributions to the total variability for such elements as Mg, Mn and Co and lower contributions for such elements as Ca, Al and Pb.

Over the less calcareous facies (Table 13-36) the between

Table 13-35
F-ratios and Percent Variance Components For The Comparison Between The Sediment And Soils Derived From The Calcareous Facies Of The Lias As Estimated By The Three Level Nested Analysis Of Variance Model. Samples Collected From The Lower Lias In Somerset Study Area.

Metal	Between Media		Between Sites		Between Samples		Bet. Anal
	F1	(%)	F2	(%)	F3	(%)	(%)
Ca	***	67.7	**	23.7	NS	5.4	3.2
Mg	**	21.1	***	72.8	NS	3.6	2.2
Al	***	70.0	**	18.1	NS	6.5	5.4
Fe	**	29.7	**	65.5	NS	2.5	2.4
Zn	**	34.0	**	54.6	NS	7.3	5.0
Mn	*	12.9	***	75.0	NS	7.9	4.2
Co	*	9.0	***	74.2	NS	9.6	7.3
Pb	***	57.1	**	31.3	NS	6.5	5.1
Ni	**	42.5	**	47.9	NS	4.1	6.0
Cu	***	58.9	**	30.0	NS	7.1	4.0
LOI	***	64.0	**	30.4	NS	3.6	3.0
pH	NS	8.9	***	78.8	NS	7.3	5.0

NS = Not Significant, P> 0.10; * = 0.10 > P > 0.05; ** = 0.05 > P > 0.01; *** = P < 0.01.

Table 13-36
F-ratios and Percent Variance Components For The Comparison Between The Sediment And Soils Derived From The Less Calcareous Facies Of The Lias As Estimated By The Three Level Nested Analysis Of Variance Model. Samples Collected From The Lower Lias In Somerset Study Area.

Metal	Between Media		Between Sites		Between Samples		Bet. Anal
	F1	(%)	F2	(%)	F3	(%)	(%)
Ca	***	42.7	***	40.9	NS	9.4	7.1
Mg	***	50.7	**	40.7	NS	4.9	3.7
Al	***	62.2	**	29.8	NS	5.5	2.5
Fe	**	39.7	**	42.9	NS	11.3	6.1
Zn	***	39.1	***	41.3	*	12.8	6.8
Mn	**	28.8	**	54.0	NS	10.0	7.0
Co	**	39.0	**	43.4	NS	9.6	8.0
Pb	***	65.5	*	21.6	NS	8.7	4.1
Ni	**	30.7	***	65.0	NS	2.3	2.0
Cu	***	62.5	**	30.0	NS	4.8	2.7
LOI	NS	10.0	**	70.1	NS	5.6	4.3
pH	NS	11.6	***	83.6	NS	2.8	2.0

NS = Not Significant, P> 0.10; * = 0.10 > P > 0.05; ** = 0.05 > P > 0.01; *** = P < 0.01.

media variability were significantly different for all the elements investigated at the .01 level except Fe, Mn, Co and Ni where the variability were significantly different at the .05 level. The F2 ratios were also significantly different at the .05 and .01 levels. The F1 and F2 sources contributed about equally to the total variability in the case of Ca and Zn while for the rest of the elements analysed the F2 source contributed more to the total variability. Sampling and analytical errors were not a major source of variability as the results show (Table 13-36).

It can be inferred from the results that in both facies the between and within media sources contributed significantly to the total variability of elements. Processes operating between and within the media seemed to affect the variability of elements differently, for instance, the between media source contributed more to the total variability of the elements Al, Pb and Cu than the within media source, while for the elements Fe, Zn, Mn, Co and Ni the within media source accounted more than the between media source of variability.

(c) Comparison between the soil and rock.

In the calcareous facies the F1 ratios for the elements Ca, Zn, Pb and Cu were statistically significant at .05 and .01 levels (Table 13-37) while those of the rest of the elements were not significant. This source accounted for over 60% the total variability of Zn while relatively lower contributions were made by this source for the rest of the elements considered. In contrast the F1-ratios for Mg, Al, Fe, organic matter(LOI) and pH were not statistically significant with contributions of less than 20% recorded in each case.

Table 13-37
F-ratios and Percent Variance Components For The Comparison Between The Rock And Soils Derived From The Calcareous Facies Of The Lias As Estimated By The Three Level Nested Analysis Of Variance Model. Samples Collected From The Lower Lias In Somerset Study Area.

Metal	Between Media		Between Sites		Between Samples		Bet. Anal
	F1	(%)	F2	(%)	F3	(%)	(%)
Ca	**	18.7	***	67.9	NS	9.4	4.0
Mg	NS	20.0	***	73.3	NS	4.4	2.2
Al	NS	11.1	***	74.5	NS	8.3	6.0
Fe	NS	12.9	***	75.0	NS	7.1	5.1
Zn	***	62.5	**	20.1	*	10.3	7.2
Mn	NS	15.4	***	73.6	NS	6.0	5.0
Co	NS	10.6	***	78.8	NS	6.3	4.2
Pb	**	18.8	***	67.1	NS	5.9	8.2
Ni	NS	12.0	***	76.7	NS	5.1	6.2
Cu	**	19.0	***	70.6	NS	7.4	4.0
LOI	NS	11.3	***	70.4	*	10.2	8.0
pH	NS	8.9	***	80.7	NS	5.8	4.6

NS = Not Significant, P> 0.10; * = 0.10 > P > 0.05; ** = 0.05 > P > 0.01; *** = P < 0.01.

Table 13- 38
F-ratios and Percent Variance Components For The Comparison Between The Rock And Soils Derived From The Calcareous Facies Of The Lias As Estimated By The Three Level Nested Analysis Of Variance Model. Samples Collected From The Lower Lias In Somerset Study Area.

Metal	Between Media		Between Sites		Between Samples		Bet. Anal
	F1	(%)	F2	(%)	F3	(%)	(%)
Ca	***	70.0	**	18.3	NS	5.7	6.0
Mg	*	20.9	***	67.2	NS	7.6	4.4
Al	*	25.5	***	64.3	NS	6.1	4.1
Fe	NS	19.6	***	71.7	NS	5.8	3.0
Zn	NS	12.5	**	70.0	*	15.0	2.5
Mn	**	40.4	**	47.2	NS	9.3	2.0
Co	**	44.0	***	50.0	NS	2.5	3.4
Pb	**	37.6	***	50.8	NS	6.5	5.0
Ni	NS	10.4	***	85.0	NS	2.3	2.2
Cu	**	19.7	***	72.2	NS	10.0	8.1
LOI	***	50.7	***	40.9	NS	5.1	3.4
pH	*	14.0	***	80.6	NS	3.0	2.3

NS = Not Significant, P> 0.10; * = 0.10 > P > 0.05; ** = 0.05 > P > 0.01; *** = P < 0.01.

The F2 ratios for all elements were significant at the .01 and .05 levels. This source accounted for most of the variability of the elements as is shown by the high contributions to the total variability .

Over the less calcareous facies Ca and the loss on ignition displayed significant Fl ratios at the .01 level (Table 13-38). At the .10 and .05 levels the Fl ratios for the elements Mg, Al, Mn, Co, Pb and Cu were statistically significant. As in the more calcareous facies a significant percentage of the variability of the elements analysed was accounted for by the between site source. Thus the F2 ratios were significant at the .05 and .01 levels for all the elements analysed with contributions from this source as high as 85% in the case of Ni. Sampling and analytical procedure did not account for much of the total variability, although in the case of Zn sampling procedure accounted for over 15% the total variability over the less calcareous facies and about 10% in the calcareous facies.

(d) Comparison between the rock and stream sediments.

In the calcareous facies the Fl-ratios for Mn, Co, Cu, organic matter(LOI) and the pH were not statistically significant at the .10 level (Table 13-39). Contributions from this source were generally low (below 20%) . The Fl ratios for the remaining elements were significant at the .01 level with contributions from this source ranging from 31% in the case of Mg to 60% in Ca .

The F2-ratios of all the elements studied were statistically significant. In case of Mg, Mn, Co and Cu the between site source contributed more to the total variability than the between media

Table 13-39
F-ratios and Percent Variance Components For The Comparison Between The Rock And Sediment Derived From The Calcareous Facies Of The Lias As Estimated By The Three Level Nested Analysis Of Variance Model. Samples Collected From The Lower Lias In Somerset Study Area.

Metal	Between Media		Between Sites		Between Samples		Bet. Anal
	F1	(%)	F2	(%)	F3	(%)	(%)
Ca	***	60.7	**	22.8	NS	9.5	7.5
Mg	***	31.0	***	54.7	NS	8.2	7.1
Al	***	52.6	***	33.5	NS	6.6	7.3
Fe	***	50.4	**	40.0	NS	5.5	4.1
Zn	***	46.5	**	40.9	NS	7.3	5.3
Mn	NS	17.1	***	70.0	NS	6.6	6.3
Co	NS	15.7	**	72.8	NS	7.5	4.0
Pb	***	44.0	**	39.5	NS	7.9	8.6
Ni	***	48.9	***	41.7	NS	5.2	4.2
Cu	NS	16.0	***	66.4	**	9.5	8.0
LOI	NS	17.9	**	67.1	NS	9.0	5.0
pH	NS	10.7	***	73.0	NS	5.5	10.8

NS = Not Significant, P> 0.10; * = 0.10 > P > 0.05; ** = 0.05 > P > 0.01; *** = P < 0.01.

Table 13-40
F-ratios and Percent Variance Components For The Comparison Between The Rock And Sediment Derived From The Less Calcareous Facies Of The Lias As Estimated By The Three Level Nested Analysis Of Variance Model. Samples Collected From The Lower Lias In Somerset Study Area.

Metal	Between Media		Between Sites		Between Samples		Bet. Anal
	F1	(%)	F2	(%)	F3	(%)	(%)
Ca	**	34.1	**	58.2	NS	5.4	4.2
Mg	**	19.4	***	63.0	NS	8.5	9.1
Al	**	15.6	**	71.7	NS	7.2	5.8
Fe	**	23.7	**	63.1	NS	8.0	5.2
Zn	**	30.3	**	47.9	*	11.4	10.2
Mn	*	23.7	**	63.8	NS	7.3	5.2
Co	**	19.3	**	62.4	*	10.2	8.1
Pb	NS	10.5	***	74.0	NS	8.3	7.1
Ni	**	17.4	***	68.3	NS	2.5	2.1
Cu	**	18.7	***	76.7	NS	2.5	2.1
LOI	NS	9.9	***	81.2	NS	5.8	3.0
pH	NS	11.8	***	80.6	NS	4.9	2.5

NS = Not Significant, P> 0.10; * = 0.10 > P > 0.05; ** = 0.05 > P > 0.01; *** = P < 0.01.

source. The between site and the between media sources contributed about equal amounts to the total variability of the elements Ni, Pb and Zn. Apart from Cu where sampling error (F3-ratio) contributed up to 9.5% of the total variability, in general these were not major sources of variation.

Over the less calcareous facies (Table 13-40) apart from Pb, organic matter(LOI) and the pH whose F1 ratios were not significant, the F1 and F2 ratios were statistically significant for all the observations. The within media source accounted more to the total variability than the between site source. Earlier results have shown that the formation of secondary carbonates in the streams was one of the principal processes affecting the variability of elements in the stream sediments. Other factorrs were thought to include the associations with the organic matter phase and the clay minerals.

(e) Summary Of The Analysis Of Variance Results.

The analysis of variance was used to assess quantitatively the differences in the mobility of elements in the transition from one medium to another and where possible characterise the source of the mobilisation. The following general observations were made from the results.

(a) Spatial variability was an important component of the total variability of elements in the comparison between the rocks and soils. It seemed, however, from the results that in the transition from rocks and soils to stream sediments, the between media source of variability was equally an important component of the total variability. In the calcareous facies apart from Mn, Co and Cu there

were significant differences in the variability of elements in the rocks and stream sediments. It was inferred that stream sediments, particularly in the calcareous facies may not be good indicators of the variability of elements in the soils and rocks.

(b) The results showed that the variability of Mn and Co in the topsoils and subsoils of the Evesham and Denchworth soil series were significantly different. This was thought to be due to the leaching of hydrous oxides to the lower horizons in the soil. Calcium also displayed significant differences in the variability between the top and sub soils in the Evesham soil series. The elements Zn, Cu, Pb and organic matter(LOI) also showed significant differences between the topsoil and subsoil. This was shown earlier to be due to the tendency of these elements to be associated with the organic matter(LOI) in the topsoil.

(c) The elements Mg, Al, Fe and Ni showed only very minor differences in their variability between media in the transition from rock to soil, however in the transition from rock and soil to stream sediments significant differences in the variability occurred.

13-7 Integrated Discussion and Summary.

Concentrations of metals in the rocks, soils and stream sediment have been compared and differences in the mobility of elements in the transition from one medium to another also compared by the analysis of variance method. Processes governing the associations of elements have been investigated by factor analysis. From the results four main groups of elements were discerned. These were

(a) the clay mineral group,

(b) the carbonate group,

(c) the hydrous oxide group,

(d) the organic matter group.

(a)The clay mineral group(Al Mg Fe and Ni).

Elements within this group showed a persistent association within each other in all the media investigated. Contrast between the concentrations of these elements in the rocks and soil were very small. Differences between media occurred in the transition to stream sediments where these elements showed lower concentrations compared to the rocks and soils. The analysis of variance results confirmed that significant differences occurred in the variability of these elements in the transition from rock and soil to stream sediments. This may be due to the dilution of the sediments by the precipitation of secondary carbonates in the streams. The association of the elements in the group were unaffected by the dilution process since factor analysis associated these elements together in all the media studied. The main processes affecting the clay minerals were thought to include adsorption of cations, organic matter and isomorphous replacements of cations in the lattice structure. It was concluded that the clay minerals formed a stable group in the different media studied.

(b) Carbonate group (Ca, Mg, Zn, Pb, Cu).

Calcium was used as an indicator of the geochemical pathway of the carbonates in the transition from one medium to another. In general the relationship between Ca and other elements within the

group was not very direct. A persistent inverse relationship was observed between Ca and such elements as Zn, Pb, and Cu over the different media derived from the calcareous beds of the Lias. In the rocks it seemed that solution processes may involve possibly organic acids and other organic compounds. The inverse relationships was interpreted as reflecting the association of these elements with the insoluble residues left after the solution of the carbonates in the weathering environment. In the soil the association between Ca and pH was persistent in both soil series. Factor analysis indicated that in the stream sediments the formation of secondary carbonates was at least part of the enrichment processes affecting Zn and Pb.

(c) Hydrous oxide group (Mn, Co, Ni, Cu).

The results showed that Mn oxides were the dominant form of hydrous oxides present in all the media studied. The enhanced concentrations of Mn and Co in the subsoil indicated that there was some form of mobilisation of the hydrous oxides in the soils. The persistent association between Mn and other divalent cations such as Co reflected the "scavenging" effects of Mn oxides. The hydrous oxides may also be related to the organic matter present in the stream sediments and soils.

(d) Organic matter (Pb, Co, Ni, Cu).

The results indicated that organic matter(LOI) exerted varying effects on the distribution of elements in the different media investigated. In the rocks organic matter(LOI) was related to the

hydrous oxides in the calcareous facies. The distribution of such divalent cations as Zn and Pb in the topsoil were thought to be due to the strong association with organic matter(LOI) observed in the topsoils. In the stream sediments it seemed probable that the organic matter(LOI) present was involved in the fixation of elements such as Zn and Pb.

13-8 Conclusions.

The following conclusions can be drawn from the above discussion:-

(1) The calcareous beds of the Lower Lias in Somerset had greater concentrations of most elements than the less calcareous beds.

(2) Calcium tended to be leached in the transition from rocks to soils over both units.

(3) Zinc, lead and copper were higher in the topsoils than in the subsoils. These elements were found to be strongly associated with the organic matter(LOI).

(4) Higher concentrations of Ca, Zn and Pb were found in the stream sediments derived from the calcareous beds compared with the associated soils and rocks. This was accompanied by reduced concentrations of other elements in the sediments compared with the soils and rocks. It was concluded that the lowering in the concentrations of elements in the stream sediments was due to the dilution of the sediments by the precipitation of calcium carbonates.

(5) Variability of most elements in the stream sediments were significantly different from those in the soils and rocks. In general, the stream sediments were not good indicators of element

concentrations in the soils and rocks over the calcareous facies. The following strong element groupings were discerned in the different media studied,

(a) Al, Mg, Fe and Ni,

(b) Ca, Mg, Zn and Pb,

(c) Mn, Co, Ni and Cu ,

(d) Pb, Co, Ni, Cu and organic matter(LOI).

CHAPTER 14

Summary and Conclusions.

14-1 Initial statements:

(1) Previous studies related element concentrations in stream sediments to bedrock geology (parent materials), soils and incidence of trace element disorders in crops and livestock.

(2) Examination of the literature showed considerable amount of work had been done on the use of stream sediment maps to delineate areas of potential agricultural and epidemiological problems in England and Wales.

(3) The present investigations set out to explore multi element patterns and associations in rocks, soils and stream sediments under conditions of contrasting geology and secondary environments.

(4) Three main lithological types (sandstones, clays, mudstones) were chosen from the following study areas.

Lincolnshire- Chalk, Kimmeridge Clay, Lower Greensand.

Wiltshire- Corallian Limestone, Kimmeridge Clay, and Upper Greensand.

Worcestershire- Keuper Marl, Lower Lias.

Herefordshire- Old Red Sandstones.

Somerset- Keuper Marl, Lower Lias.

North Wales- Silurian Mudstones, Dinantian Limestones.

Surrey- Lower Greensand.

14-2 Regional geochemical trends.

The following general trends were found:

(a) The concentrations of Mg, Al, Fe and Ni were of similar magnitude in the stream sediments and the associated soils and rocks from which they were derived. These elements showed strong correlations between each other in all the media over the various units studied. A significant percentage of the variability of these elements in the transition from rocks to soils was accounted for by the spatial variability within individual media. The variability of these elements in the stream sediments derived from the calcareous facies were significantly different from those in the rocks and soils, although factor analysis grouped these elements together in the different media studied. This group was interpreted as an association with the clay minerals.

(b) Calcium concentrations in the stream sediments varied with the lithology of the parent material. In general there were varying degrees of depletion of Ca in the course of weathering and soil formation. Over the sandstone units where soils were predominantly freely drained brown earths, Ca concentrations decreased markedly in the transition from rocks to soils while stream sediment concentrations of Ca were similar to those in the soils. In the clay and mudstone units, Ca tended to be higher in the stream sediments than in the soils and rocks.

(c) Lead concentrations in the stream sediments tended in most units to be similar to those of the associated rocks. Generally, Pb concentrations were higher in the soils than in the rocks. Lead in the soils was found to be strongly associated with the organic matter(LOI), particularly in the topsoils, while in the calcareous

units Pb was strongly associated with Ca. It was concluded that the distribution of Pb in the soils was controlled by its association with organic matter(LOI) while the formation of secondary carbonates in the stream sediments may lead to higher concentrations of Pb in the sediments derived from the calcareous units.

(d) Copper and zinc concentrations were generally higher in the soils than in the rocks and stream sediments. These elements were found in the soils to be strongly associated with organic matter(LOI) and the hydrous oxides. In the stream sediments these elements tended to be associated with the secondary carbonates, organic matter(LOI) and the hydrous oxides.

(e) Manganese and cobalt were strongly associated with each other in all the media developed from most of the units studied. This was interpreted as an association with the hydrous oxides.

(f) Stream sediments derived from the calcareous units showed decreased concentrations of most elements. Often these were accompanied with increased concentrations of Ca. Dilution of the stream sediments by the precipitation of calcium carbonates was thought to account for the decreased concentrations of elements.

14-3 Comparison between units.

The distribution and associations of elements in the rocks, soils and stream sediments derived from three main lithological types in England and Wales have been studied.

These are:

(a) Sandstones - The Old Red Sandstones in Herefordshire.

The Lower Greensand in Lincolnshire and Surrey.

(b) Clays- The Lower Lias in Worcestershire and Somerset.

-The Kimmeridge Clay in Lincolnshire and Wiltshire.

(c) Mudstone- The Keuper Marl in Worcestershire and Somerset.

- The Silurian Mudstone in North Wales.

These units have been investigated on a generalised basis, discussed in Section 2, and type areas have been investigated in detail described in Section 3. In this Section the general trends observed in each lithological type is discussed.

(a) Sandstones:

Over the sandstones metal concentrations were generally low. Elements such as Ca, Fe and Zn displayed wide variations within the individual formations. In the Old Red Sandstone in Herefordshire concentrations in excess of 10% Ca were found in sandstones with calcareous cement while in general low concentrations were widespread for most elements. A similar situation was observed in the Lower Greensand in Surrey where despite the widespread low concentrations of most elements in all the beds, higher Ca levels were recorded in the calcareous Bargate Beds than in other beds of the unit (see Chapter 10). Variations in the cementing material also had a marked effect on the distribution of some elements including Fe. Thus certain ferruginous facies of the Lower Greensand in Lincolnshire and Surrey had higher concentrations of Fe and most other elements than the unferruginised forms. A similar situation was observed in the Old Red Sandstone in Herefordshire.

Lithological variation within the individual units also played an important role in the distribution of elements. In Herefordshire, where the Old Red Sandstones ranged from marls through fine to coarse sands differences in the metal concentrations were observed. The marls and the finer sands, contained more of the elements Zn, Pb, and Cu than the coarser facies.

In general Cu and Co were exceedingly low in all the sandstone units studied with concentrations less than 5ppm widespread. In the Old Red Sandstone Mn concentrations were relatively high (over 1000ppm) while in the Lower Greensand in Surrey Mn concentrations were exceedingly low in some beds (below 50ppm).

Soils developed over the sandstones were in the main freely drained brown earths. Calcium concentrations were generally lower in the soils than in the rocks. Elements including Al, Mg, Fe, and Ni were inferred by statistical methods to be strongly associated with each other in all the media and this was interpreted as being related to the clay minerals. In addition elements related to the hydrous oxides (including Mn and Fe) were found to be unaffected by processes of translocation and leaching. Over the Old Red Sandstones Pb was positively correlated with organic matter(LOI) in the topsoils.

In the stream sediments the concentrations of most elements were found to be similar to those in the rocks and soils, although over the Lower Greensand in Lincolnshire lower concentrations were recorded for Zn, Fe and Cu in the stream sediments. This was interpreted as being due to the dilution of the sediments by the precipitation of calcium carbonates.

The following general conclusions were drawn from the results:

(a) Concentrations of elements in the soils and stream

sediments were controlled by the inherently low patterns in the rocks. In the rocks, lithological variations and post depositional changes such as cementation by calcareous and ferruginous material affected the distribution of elements.

(b) Multi-element associations in the stream sediments can be broadly correlated to the associations in the rocks and soils from which they are derived.

(c) Top and subsoils displayed a uniform character with respect to the distribution of elements. This was marked in the case of Al and Fe which were inferred to be part of the clay mineral group of elements.

(d) Leaching of Ca during soil formation was one of the principal processes observed, although reprecipitation of Ca in the stream beds was not observed.

(b) Clays.

The main clay units studied were the Lower Lias and the Kimmeridge Clay. In general the clays displayed higher concentrations of most elements than the sandstones. Lithological control was an important factor in determining the distribution of elements in the rocks. This was reflected on the wide variation of such elements as Ca, Zn, and Pb over the Lower Lias. Thus these elements were more enhanced in the calcareous facies than in the less calcareous facies. In the Lincolnshire area, the Wragby Till displayed marked enhancement of Ca compared to the fresh rock.

Soils developed over the clays ranged from moderately drained to poorly drained. Gleying was a common feature of the soils over the clays and this exerted profound influence on the element

concentrations in the soils. Generally, concentrations of Ca decreased in the transition from rock to soils. This was inferred to be due to leaching. The concentrations of the elements Mn, Cu and Co were generally lower in the soils than in the rocks, with the topsoils displaying varying degrees of depletions compared with the subsoil. This was observed to be related to the nature of the soils. Thus soils which showed evidence of gleying and waterlogging had greater depletion of Mn in the topsoils than those soils which had good drainage. By contrast, Zn and Pb tended to be higher in the soils than in the rocks. This was marked in the case of the topsoils where the higher concentrations of these elements were thought to be due to an association with organic matter(LOI). Thus strong correlations were observed between Zn and Pb in the soils. In the topsoils the results suggested that the enhancement of Pb was related to an association with the organic matter(LOI).

The elements Al, Fe, Mg and Ni were found to be strongly associated with each other in the rock, soil and stream sediment. This was interpreted as defining the clay minerals present and it was inferred that the clay minerals formed a stable component of the geochemical environment.

In the stream sediments, while the elements, Ca, Zn and Pb tended to be higher than in the associated rocks and soils, most elements studied including Mn, Co, Cu had concentrations lower than in the rock and soils. This was thought to be due to the dilution of the stream sediments by the precipitation of secondary carbonates.

In general multi- element associations in the stream sediments were similar to those discerned in the rocks and soils. The following general conclusions were drawn from the results:

(a) The elements associated with the carbonate materials tended to be leached during soil formation and redistributed as secondary carbonates in the surface drainage.

(b) Element associated with the clay minerals remained relatively unaffected by pedogenic and stream processes.

(c) The organic matter(LOI) in the soils was an important factor in controlling the distribution of Pb particularly in the topsoil.

(d) Mobilisation of the hydrous oxides in the soils and redistribution in the surface drainage was common particularly in the gleyed soils.

(c) Mudstones:

As indicated in Chapter 12, mudstones constituted the main lithology of the Keuper Marl. The present investigations showed that the unit was not calcareous in Worcestershire and Somerset where it was studied. In North Wales the Silurian Mudstone was not generally calcareous.

The brown earths that developed on both units showed no evidence of mobilisation of the hydrous oxides nor of the clay minerals. Lead was markedly enhanced in the topsoils of the Denbigh soil series than in the subsoils. In the Worcester soil series a similar trend was observed, although the contrast between the top and subsoils was less. Detailed investigations on the Keuper Marl confirmed that Pb was strongly associated withthe organic matter(LOI) as was the case of the sandstones and clays.

Calcium tended to be higher in the stream sediments derived from the Keuper Marl than in the soils and rocks. The elements Zn, Mn, Co, Pb and Cu were also present in larger amounts in the stream

sediments than in the rocks and soils.

As with the sandstones and clays strong associations were observed between the clay related elements in all the media derived from the mudstones. In general, the following conclusions were drawn from the results.

(a) The clay minerals and the hydrous oxides formed stable groups which were not altered chemically in the transition from rock to soils and stream sediments.

(b) Organic matter(LOI), Zn and Pb tended to be enhanced in the topsoils when compared to other media.

(c) Multi element associations discerned in the stream sediments were similar to those in the rock and soils.

14-4 Comparison between the distribution of elements in the media derived from different units:

Table 14-1 shows the average concentrations of the elements analysed in the different media derived from the main lithological units studied. Several differences were indicated by the geochemistry of the soils and stream sediments derived from the different units. In most cases, it appeared that soils and stream sediments derived from the clays had more of most of the elements determined than those derived from the mudstones and sandstones. Differences between element concentrations in the rocks and soils over the sandstones were few. Only Ca was noticeably higher in the rocks than in the soils. This was thought to be due to lithological variability and post depositional introduction of Ca bearing minerals as inter granular cement within the sandstone units. Differences in the concentrations

TABLE 14-1

Average Concentrations* of Elements in the Different Lithologies

LITHOLOGY	MEDIUM	Ca(%)	Mg(%)	Al(%)	Fe(%)	Zn(ppm)	Mn(ppm)	Co(ppm)	Pb(ppm)	Ni(ppm)	Cu(ppm)
SANDSTONE	ROCK	3.40	0.6	1.9	2.0	40.0	850.0	15.0	19.0	20.7	10.0
	T/SOIL	0.34	0.6	2.5	2.1	45.0	860.0	12.0	35.0	27.7	16.5
	S/SOIL	0.30	0.5	2.6	2.3	36.0	850.0	11.0	23.0	27.1	17.0
	S/SEDT.	0.33	0.4	1.3	2.4	41.0	600.0	10.0	24.0	23.6	9.0
MUDSTONE	ROCK	0.50	1.0	4.3	3.5	69.0	700.0	20.0	43.4	37.9	20.1
	T/SOIL	0.43	0.9	3.7	3.0	84.3	750.0	19.1	33.5	33.1	18.3
	S/SOIL	0.60	1.2	3.9	3.1	77.0	760.0	18.9	30.6	35.5	17.0
	S/SEDT.	2.5	1.5	3.2	2.0	125.0	1000.0	23.0	50.1	37.7	26.5
CLAYS	ROCK	6.5	0.4	6.2	3.3	120.0	1000.0	35.0	35.0	64.1	37.0
	T/SOIL	2.6	0.3	6.0	3.4	127.0	650.0	26.0	50.5	59.5	44.5
	S/SOIL	4.3	0.3	6.8	5.0	109.0	850.0	30.0	41.3	60.5	38.0
	S/SEDT.	8.0	0.2	3.6	3.0	154.0	700.0	29.0	64.5	55.0	30.0

* Combination of both preliminary and detailed investigation samples

of elements in the soils (mainly freely drained brown earths) and rocks over the mudstones were also few. Over the clays Ca, Mn and Co tended to be depleted in the soils compared to their respective parent materials (rocks).

Stream sediments derived from the sandstone units generally had similar concentrations of elements with those of the associated soils and rocks while over the mudstones and clays, apart from Ca, Zn and Pb, most elements had lower concentrations than in the soils and rocks.

The element concentrations and associations in the different media drew attention to some possible mechanisms involved in the accumulations and depletions of elements in the different media. The lower concentrations of most elements in the stream sediments derived from the clays and mudstones were thought to be due to dilution of the sediments by the precipitation of calcium carbonates in the streams. In these units inter correlations between Ca, Zn and Pb were strong in the stream sediments and this was generally accompanied by increased concentrations and variations of these elements. Over the sandstones where precipitation of calcium carbonate in the streams was not common, element concentrations in the stream sediments were similar to those in the rocks and soils. The elements Pb, Zn and Cu were found to be strongly associated with the organic matter(LOI) in the soils derived from the various units. In general, these elements were higher in the topsoils than in the subsoils. The elements generally assumed to be associated with the clay minerals Al, Fe, Mg and Ni were found to be strongly associated with each other in all the media derived from the various units studied. Concentrations of these elements were similar in the different media, although over the clays

they tended to be lower in the stream sediments than in the soils and rocks, probably due to the dilution of the sediments by the precipitation of calcium carbonates.

14-5 General conclusions.

The following general conclusions were made from the present investigations:-

(1) The parent material had an overriding influence on the distributions of elements in the soils and stream sediments. The higher concentrations of most elements in the clays and lower concentrations in the sandstones were reflected in the associated soils and stream sediments. Lithological variations within the parent materials also played an important role in the distribution of elements in the soils and stream sediments. Examples of these were observed in all the units studied eg.,

(a) Variations in the Ca, Zn and Pb contents of the calcareous and less calcareous beds of the Lower Lias in Somerset were reflected in the concentrations of these elements in the associated soils and stream sediments.

(b) The higher concentrations of Ca, Zn and Mn in the calcareous sandstones of the Keuper Series in Wocestershire were reflected in the associated soils and stream sediments compared with those derived from the marl facies.

(c) In North Wales frequent facies changes in the Silurian Mudstones were reflected in the element concentrations in the soils and stream sediments.

(2) In all the soils and stream sediments derived from the various units the pH was found to be strongly correlated with the

carbonate related elements. In the poorly drained and gleyed soils where the pH was acidic the topsoils had lower concentrations of Fe and Mn than the subsoil. Most often Co and Cu were affected similarly. This was thought to be due to the influence of the pH on the mobilisation of the hydrous oxides in the soils. This phenomenon was not observed in the freely drained brown earths developed over the sandstones.

(3) Strong associations were observed between Mn and Co and Cu in most of the media derived from the various units. This was thought to be due the adsorption of divalent cations by Mn oxide minerals.

(4) The clay mineral group of elements in the soils and stream sediments were found to be similar to those of the associated rocks, irrespective the lithology and soil type. Spatial variability of these elements was an important component of the total variability. In most cases this source accounted more to the total variability than the between media source and the stream sediments were good indicators of element variability in the soils and rocks. In the calcareous facies, however, this was not the case, the variability of these elements were significantly different, and the stream sediments did not reflect element variability in the soils and rocks.

(5) Strong associations were found between Zn, Pb, Cu and organic matter(LOI). The enhanced concentrations of these elements in the topsoils were thought to be due to such an association with organic matter(LOI). Organic matter(LOI) was also found to be associated with the clay minerals and the hydrous oxide group of elements. These were interpreted as the formation of organo-clay complexes and the deposition of Mn oxide minerals on organic fragments

in the stream sediments.

(6) The formation of secondary carbonates in the stream sediments often led to increased concentrations of Zn and Pb and the lowering of the concentrations of other elements as a result of dilution.

14-6 Recommendations for future work.

It is recommended that future work be aimed at the following areas:-

(1) Studies on the factors governing multi- element patterns in rocks, soils and stream sediments. This may involve the use of partial extraction techniques and detailed mineralogical studies to characterise associations of elements.

(2) Studies on the relationship between multi- element patterns in the rocks, soils and stream sediments and those in plants and livestock. This may increase the value of the use of regional geochemical reconnaissance survey as a cheap means of evaluating the mineral and agricultural potential in areas of the world where resources are lacking as in the developing world.

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APPENDIX 1

CALCULATIONS OF SUMMARY STATISTICS

(1) Means, Standard Deviations and Coefficients of Variation

(a) **Mean:-** In a series of measurements X_1, X_2, ... X_n, the mean was calcuated by

$$\bar{X} \qquad \frac{\sum_{i\ 1}^{n} X_1}{N}$$

(b) Standard Deviation was calculated using the formula

$$\sqrt{\frac{\sum\left(x - \bar{x}\right)^2}{N - 1}}$$

(c) The Coefficient of Variations was calculated by using the formula:

$$C\ V = \frac{S.D.}{\bar{X}} \times 100$$

(2) Correlation Coefficients

Step 1 List in parallel columns the paired X and Y scores, making sure that corresponding scores are together.

Step 2 Determine the two means $\bar{X}$, $\bar{Y}$.

Step 3 Determine for every pair of series the two deviations X and Y i.e.

$$x - \bar{X} \ ; \ y - \bar{Y}$$

Step 4 Square all the deviations and list in two columns.

Step 5 Sum the squares of the deviations to obtain

$$\sum x^2 \quad \sum y^2$$

Step 6 Apply the formula

$$r_{xy} = \frac{\sum xy}{\sqrt{\left(\sum x^2\right)\left(\sum y^2\right)}}$$

All the calculations were computed by standard routines in the Geolib Library of the Department of Geology, Imperial College, and the MINITAB Package provided by the Imperial College Computer Center.

Appendix 2

Terms in the Analysis Variance (Adapted from Webster 1977)

Source	Degree of Freedom	Sums of Squares	Components of Variance estimated by mean square
Stage 1 Between Media	$n_1 - 1$	$\sum_{i=1}^{n_1} n n_2 n_3 \left[\bar{x}_i - \bar{x}\right]^2$	$\sigma_4^2 + n_4\sigma_3^2 + n_3 n_4 \sigma_2^2 \quad n n_3 n_4 \sigma_1^2$
Stage 2 Between sites within media	$n_1(n_2 - 1)$	$\sum_{i=1}^{n_1}\sum_{j=1}^{n_2} n n_3 \left[\bar{x}_{ij} - \bar{x}_i\right]^2$	$\sigma_4^2 + n_4\sigma_3^2 \quad n_3 n_4 \sigma_2^2$
Stage 3 Between samples within site	$n_1 n_2(n_3 - 1)$	$\sum_{i=1}^{n_1}\sum_{j=1}^{n_2}\sum_{k=1}^{n_3} n \left[x_{ijk} - \bar{x}_{ij}\right]^2$	$\sigma_4^2 \quad n_4\sigma_3^2$
Stage 4 Between Analysis within areas	$n_1 n_2 n_3(n_4 - 1)$	$\sum_{i=1}^{n_1}\sum_{j=1}^{n}\sum_{k=1}^{n_3}\sum_{l=1}^{n_4} \left[x_{ijkl} - \bar{x}_{ijk}\right]^2$	σ_4^2
Total	$n_1 n_2 n_3 - 1$	$\sum_{i=1}^{n_1}\sum_{j=1}^{n_2}\sum_{k=1}^{n_3} \left[x_{ijkl} - \bar{x}\right]^2$	

For each stage is the number of subdivisions within each class of stage -1 and is the component of variance.
Group means at each stage are indicated by appropriate subscripts, and the general mean by *

n_1 = number of media = 4
n_2 = number of sites/medium = 10
n_3 = number of samples/site = 2
n_4 = number of analysis per sample = 2

APPENDIX 3

C O R R E L A T I O N

Lowest levels of the linear correlation coefficient (sign ignored) that are significantly different from zero

No. of Pairs	Probability		
n	0.10	0.05	0.01
3	.99	1.00	1.00
4	.90	.95	.99
5	.81	.88	.96
6	.73	.81	.92
7	.67	.75	.87
8	.62	.71	.83
9	.58	.67	.80
10	.55	.63	.76
11	.52	.60	.73
12	.50	.58	.71
13	.48	.55	.68
14	.46	.53	.66
15	.44	.51	.64
16	.43	.50	.62
17	.41	.48	.61
18	.40	.47	.59
19	.39	.46	.58
20	.38	.44	.56
21	.37	.43	.55
22	.36	.42	.54
27	.32	.38	.49
32	.30	.35	.45
37	.27	.32	.42
42	.26	.30	.39
47	.24	.29	.37
52	.23	.27	.35
62	.21	.25	.32
72	.20	.23	.30
82	.18	.22	.28
92	.17	.21	.27
102	.16	.19	.25

APPENDIX 4

CRITICAL VALUES OF F-ratios FOR ν AND ν DEGREES OF FREEDOM

10% (α = .10) LEVEL OF SIGNIFICANCE .

ν_2 \ ν_1	1	2	3	4	5	6	7	8	9	10	15	20	40	60	120	∞
1	39.86	49.50	53.59	55.83	57.24	58.20	58.91	59.44	59.86	60.19	61.22	61.74	62.53	62.79	63.06	63.33
2	8.53	9.00	9.16	9.24	9.29	9.33	9.35	9.37	9.38	9.39	9.42	9.44	9.47	9.47	9.48	9.49
3	5.54	5.46	5.39	5.34	5.31	5.28	5.27	5.25	5.24	5.23	5.20	5.18	5.16	5.15	5.14	5.13
4	4.54	4.32	4.19	4.11	4.05	4.01	3.98	3.95	3.94	3.92	3.87	3.84	3.80	3.79	3.78	3.76
5	4.06	3.78	3.62	3.52	3.45	3.40	3.37	3.34	3.32	3.30	3.24	3.21	3.16	3.14	3.12	3.10
6	3.78	3.46	3.29	3.18	3.11	3.05	3.01	2.98	2.96	2.94	2.87	2.84	2.78	2.76	2.74	2.72
7	3.59	3.26	3.07	2.96	2.88	2.83	2.78	2.75	2.72	2.70	2.63	2.59	2.54	2.51	2.49	2.47
8	3.46	3.11	2.92	2.81	2.73	2.67	2.62	2.59	2.56	2.54	2.46	2.42	2.36	2.34	2.32	2.29
9	3.36	3.01	2.81	2.69	2.61	2.55	2.51	2.47	2.44	2.42	2.34	2.30	2.23	2.21	2.18	2.16
10	3.29	2.92	2.73	2.61	2.52	2.46	2.41	2.38	2.35	2.32	2.24	2.20	2.13	2.11	2.08	2.06
11	3.23	2.86	2.66	2.54	2.45	2.39	2.34	2.30	2.27	2.25	2.17	2.12	2.05	2.03	2.00	1.97
12	3.18	2.81	2.61	2.48	2.39	2.33	2.28	2.24	2.21	2.19	2.10	2.06	1.99	1.96	1.93	1.90
13	3.14	2.76	2.56	2.43	2.35	2.28	2.23	2.20	2.16	2.14	2.05	2.01	1.93	1.90	1.88	1.85
14	3.10	2.73	2.52	2.39	2.31	2.24	2.19	2.15	2.12	2.10	2.01	1.96	1.89	1.86	1.83	1.80
15	3.07	2.70	2.49	2.36	2.27	2.21	2.16	2.12	2.09	2.06	1.97	1.92	1.85	1.82	1.79	1.76
16	3.05	2.67	2.46	2.33	2.24	2.18	2.13	2.09	2.06	2.03	1.94	1.89	1.81	1.78	1.75	1.72
17	3.03	2.64	2.44	2.31	2.22	2.15	2.10	2.06	2.03	2.00	1.91	1.86	1.78	1.75	1.72	1.69
18	3.01	2.62	2.42	2.29	2.20	2.13	2.08	2.04	2.00	1.98	1.89	1.84	1.76	1.72	1.69	1.66
19	2.99	2.61	2.40	2.27	2.18	2.11	2.06	2.02	1.98	1.96	1.86	1.81	1.73	1.70	1.67	1.63
20	2.97	2.59	2.38	2.25	2.16	2.09	2.04	2.00	1.96	1.94	1.84	1.79	1.71	1.68	1.64	1.61
21	2.96	2.57	2.36	2.23	2.14	2.08	2.02	1.98	1.95	1.92	1.83	1.78	1.69	1.66	1.62	1.59
22	2.95	2.56	2.35	2.22	2.13	2.06	2.01	1.97	1.93	1.90	1.81	1.76	1.67	1.64	1.60	1.57
23	2.94	2.55	2.34	2.21	2.11	2.05	1.99	1.95	1.92	1.89	1.80	1.74	1.66	1.62	1.59	1.56
24	2.93	2.54	2.33	2.19	2.10	2.04	1.98	1.94	1.91	1.88	1.78	1.73	1.64	1.61	1.57	1.53
25	2.92	2.53	2.32	2.18	2.09	2.02	1.97	1.93	1.89	1.87	1.77	1.72	1.63	1.59	1.56	1.52
26	2.91	2.52	2.31	2.17	2.08	2.01	1.96	1.92	1.88	1.86	1.76	1.71	1.61	1.58	1.54	1.50
27	2.90	2.51	2.30	2.17	2.07	2.00	1.95	1.91	1.87	1.85	1.75	1.70	1.60	1.57	1.53	1.49
28	2.89	2.50	2.29	2.16	2.06	2.00	1.94	1.90	1.87	1.84	1.74	1.69	1.59	1.56	1.52	1.48
29	2.89	2.50	2.28	2.15	2.06	1.99	1.93	1.89	1.86	1.83	1.73	1.68	1.58	1.55	1.51	1.47
30	2.88	2.49	2.28	2.14	2.05	1.98	1.93	1.88	1.85	1.82	1.72	1.67	1.57	1.54	1.50	1.46
40	2.84	2.44	2.23	2.09	2.00	1.93	1.87	1.83	1.79	1.76	1.66	1.61	1.51	1.47	1.42	1.38
60	2.79	2.39	2.18	2.04	1.95	1.87	1.82	1.77	1.74	1.71	1.60	1.54	1.44	1.40	1.35	1.29
120	2.75	2.35	2.13	1.99	1.90	1.82	1.77	1.72	1.68	1.65	1.55	1.48	1.37	1.32	1.26	1.19
∞	2.71	2.30	2.08	1.94	1.85	1.77	1.72	1.67	1.63	1.60	1.49	1.42	1.30	1.24	1.17	1.00

5% (α = .05) LEVEL OF SIGNIFICANCE.

ν_2 \ ν_1	1	2	3	4	5	6	7	8	9	10	15	20	40	60	120	∞
1	161.4	199.5	215.7	224.6	230.2	234.0	236.8	238.9	240.5	241.9	245.9	248.0	251.1	252.2	253.3	254.3
2	18.51	19.00	19.16	19.25	19.30	19.33	19.35	19.37	19.38	19.40	19.43	19.45	19.47	19.48	19.49	19.50
3	10.13	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79	8.70	8.66	8.59	8.57	8.55	8.53
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.86	5.80	5.72	5.69	5.66	5.63
5	6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.62	4.56	4.46	4.43	4.40	4.36
6	5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	3.94	3.87	3.77	3.74	3.70	3.67
7	5.59	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.51	3.44	3.34	3.30	3.27	3.23
8	5.32	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.22	3.15	3.04	3.01	2.97	2.93
9	5.12	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.01	2.94	2.83	2.79	2.75	2.71
10	4.96	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.85	2.77	2.66	2.62	2.58	2.54
11	4.84	3.98	3.59	3.36	3.20	3.09	3.01	2.95	2.90	2.85	2.72	2.65	2.53	2.49	2.45	2.40
12	4.75	3.89	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.62	2.54	2.43	2.38	2.34	2.30
13	4.67	3.81	3.41	3.18	3.03	2.92	2.83	2.77	2.71	2.67	2.53	2.46	2.34	2.30	2.25	2.21
14	4.60	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60	2.46	2.39	2.27	2.22	2.18	2.13
15	4.54	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.40	2.33	2.20	2.16	2.11	2.07
16	4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.35	2.28	2.15	2.11	2.06	2.01
17	4.45	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49	2.45	2.31	2.23	2.10	2.06	2.01	1.96
18	4.41	3.55	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41	2.27	2.19	2.06	2.02	1.97	1.92
19	4.38	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42	2.38	2.23	2.16	2.03	1.98	1.93	1.88
20	4.35	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.20	2.12	1.99	1.95	1.90	1.84
21	4.32	3.47	3.07	2.84	2.68	2.57	2.49	2.42	2.37	2.32	2.18	2.10	1.96	1.92	1.87	1.81
22	4.30	3.44	3.05	2.82	2.66	2.55	2.46	2.40	2.34	2.30	2.15	2.07	1.94	1.89	1.84	1.78
23	4.28	3.42	3.03	2.80	2.64	2.53	2.44	2.37	2.32	2.27	2.13	2.05	1.91	1.86	1.81	1.76
24	4.26	3.40	3.01	2.78	2.62	2.51	2.42	2.36	2.30	2.25	2.11	2.03	1.89	1.84	1.79	1.73
25	4.24	3.39	2.99	2.76	2.60	2.49	2.40	2.34	2.28	2.24	2.09	2.01	1.87	1.82	1.77	1.71
26	4.23	3.37	2.98	2.74	2.59	2.47	2.39	2.32	2.27	2.22	2.07	1.99	1.85	1.80	1.75	1.69
27	4.21	3.35	2.96	2.73	2.57	2.46	2.37	2.31	2.25	2.20	2.06	1.97	1.84	1.79	1.73	1.67
28	4.20	3.34	2.95	2.71	2.56	2.45	2.36	2.29	2.24	2.19	2.04	1.96	1.82	1.77	1.71	1.65
29	4.18	3.33	2.93	2.70	2.55	2.43	2.35	2.28	2.22	2.18	2.03	1.94	1.81	1.75	1.70	1.64
30	4.17	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.01	1.93	1.79	1.74	1.68	1.62
40	4.08	3.23	2.84	2.61	2.45	2.34	2.25	2.18	2.12	2.08	1.92	1.84	1.69	1.64	1.58	1.51
60	4.00	3.15	2.76	2.53	2.37	2.25	2.17	2.10	2.04	1.99	1.84	1.75	1.59	1.53	1.47	1.39
120	3.92	3.07	2.68	2.45	2.29	2.17	2.09	2.02	1.96	1.91	1.75	1.66	1.50	1.43	1.35	1.25
∞	3.84	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88	1.83	1.67	1.57	1.39	1.32	1.22	1.00

1% (α = .01) LEVEL OF SIGNIFICANCE.

ν_2 \ ν_1	1	2	3	4	5	6	7	8	9	10	15	20	40	60	120	∞
1	4052	4999.5	5403	5625	5764	5859	5928	5981	6022	6056	6157	6209	6287	6313	6339	6366
2	98.50	99.00	99.17	99.25	99.30	99.33	99.36	99.37	99.39	99.40	99.43	99.45	99.47	99.48	99.49	99.50
3	34.12	30.82	29.46	28.71	28.24	27.91	27.67	27.49	27.35	27.23	26.87	26.69	26.41	26.32	26.22	26.13
4	21.20	18.00	16.69	15.98	15.52	15.21	14.98	14.80	14.66	14.55	14.20	14.02	13.75	13.65	13.56	13.46
5	16.26	13.27	12.06	11.39	10.97	10.67	10.46	10.29	10.16	10.05	9.72	9.55	9.29	9.20	9.11	9.02
6	13.75	10.92	9.78	9.15	8.75	8.47	8.26	8.10	7.98	7.87	7.56	7.40	7.14	7.06	6.97	6.88
7	12.25	9.55	8.45	7.85	7.46	7.19	6.99	6.84	6.72	6.62	6.31	6.16	5.91	5.82	5.74	5.65
8	11.26	8.65	7.59	7.01	6.63	6.37	6.18	6.03	5.91	5.81	5.52	5.36	5.12	5.03	4.95	4.86
9	10.56	8.02	6.99	6.42	6.06	5.80	5.61	5.47	5.35	5.26	4.96	4.81	4.57	4.48	4.40	4.31
10	10.04	7.56	6.55	5.99	5.64	5.39	5.20	5.06	4.94	4.85	4.56	4.41	4.17	4.08	4.00	3.91
11	9.65	7.21	6.22	5.67	5.32	5.07	4.89	4.74	4.63	4.54	4.25	4.10	3.86	3.78	3.69	3.60
12	9.33	6.93	5.95	5.41	5.06	4.82	4.64	4.50	4.39	4.30	4.01	3.86	3.62	3.54	3.45	3.36
13	9.07	6.70	5.74	5.21	4.86	4.62	4.44	4.30	4.19	4.10	3.82	3.66	3.43	3.34	3.25	3.17
14	8.86	6.51	5.56	5.04	4.69	4.46	4.28	4.14	4.03	3.94	3.66	3.51	3.27	3.18	3.09	3.00
15	8.68	6.36	5.42	4.89	4.56	4.32	4.14	4.00	3.89	3.80	3.52	3.37	3.13	3.05	2.96	2.87
16	8.53	6.23	5.29	4.77	4.44	4.20	4.03	3.89	3.78	3.69	3.41	3.26	3.02	2.93	2.84	2.75
17	8.40	6.11	5.18	4.67	4.34	4.10	3.93	3.79	3.68	3.59	3.31	3.16	2.92	2.83	2.75	2.65
18	8.29	6.01	5.09	4.58	4.25	4.01	3.84	3.71	3.60	3.51	3.23	3.08	2.84	2.75	2.66	2.57
19	8.18	5.93	5.01	4.50	4.17	3.94	3.77	3.63	3.52	3.43	3.15	3.00	2.76	2.67	2.58	2.49
20	8.10	5.85	4.94	4.43	4.10	3.87	3.70	3.56	3.46	3.37	3.09	2.94	2.69	2.61	2.52	2.42
21	8.02	5.78	4.87	4.37	4.04	3.81	3.64	3.51	3.40	3.31	3.03	2.88	2.64	2.55	2.46	2.36
22	7.95	5.72	4.82	4.31	3.99	3.76	3.59	3.45	3.35	3.26	2.98	2.83	2.58	2.50	2.40	2.31
23	7.88	5.66	4.76	4.26	3.94	3.71	3.54	3.41	3.30	3.21	2.93	2.78	2.54	2.45	2.35	2.26
24	7.82	5.61	4.72	4.22	3.90	3.67	3.50	3.36	3.26	3.17	2.89	2.74	2.49	2.40	2.31	2.21
25	7.77	5.57	4.68	4.18	3.85	3.63	3.46	3.32	3.22	3.13	2.85	2.70	2.45	2.36	2.27	2.17
26	7.72	5.53	4.64	4.14	3.82	3.59	3.42	3.29	3.18	3.09	2.81	2.66	2.42	2.33	2.23	2.13
27	7.68	5.49	4.60	4.11	3.78	3.56	3.39	3.26	3.15	3.06	2.78	2.63	2.38	2.29	2.20	2.10
28	7.64	5.45	4.57	4.07	3.75	3.53	3.36	3.23	3.12	3.03	2.75	2.60	2.35	2.26	2.17	2.06
29	7.60	5.42	4.54	4.04	3.73	3.50	3.33	3.20	3.09	3.00	2.73	2.57	2.33	2.23	2.14	2.03
30	7.56	5.39	4.51	4.02	3.70	3.47	3.30	3.17	3.07	2.98	2.70	2.55	2.30	2.21	2.11	2.01
40	7.31	5.18	4.31	3.83	3.51	3.29	3.12	2.99	2.89	2.80	2.52	2.37	2.11	2.02	1.92	1.80
60	7.08	4.98	4.13	3.65	3.34	3.12	2.95	2.82	2.72	2.63	2.35	2.20	1.94	1.84	1.73	1.60
120	6.85	4.79	3.95	3.48	3.17	2.96	2.79	2.66	2.56	2.47	2.19	2.03	1.76	1.66	1.53	1.38
∞	6.63	4.61	3.78	3.32	3.02	2.80	2.64	2.51	2.41	2.32	2.04	1.88	1.59	1.47	1.32	1.00