A

THESIS

entitled

THE INFLUENCE OF ENVIRONMENT ON REGIONAL GEOCHEMICAL PATTERNS IN NORTHERN IRELAND.

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ABSTRACT

The results are described of a multi-element stream sediment reconnaissance survey in a glaciated area in the west of Northern Ireland. Regional geochemical patterns have been related to variations in metal abundance and to the varying influence of the local environment on metal dispersion. The patterns are considered in terms of their possible significance in geology, mineral exploration, agriculture and soil science. The mechanisms of metal translocation in the soil-sediment system are discussed.

There is mostly a good correlation between the metal contents of sediments and soils, particularly in lowland areas and where streams do not have heavy ferromanganese precipitation. However, the correlation can be distorted by fractionation occurring during physical or chemical dispersion.

As a result of sorting in streams, the copper contents of active sediments tend to be lower than those of most soils. Consequently, widespread patterns of 5 - 12 ppm Cu do not necessarily delineate areas of possibly copper deficient soils.

Strong coincident patterns shown by cobalt, iron, manganese and zinc are related to variations in the physico-chemical environment, defined by Eh and pH, and to differences in soil fabric and the secondary occurrence of free iron oxides. The metals are mobilized in acid or gleyed soils and reprecipitated under less acid, more oxidizing conditions in the stream channel, hence sediments become greatly enriched where such soils are widespread. Hydromorphic processes of this type have influenced the dispersion of copper, lead and zinc from mineralisation near Keady, Armagh, and Newtownstewart, Tyrone. Elsewhere they have produced false anomalies unrelated to mineralisation.

The reconnaissance technique is considered valuable for detecting regional variations in metal abundance, despite the limitations imposed by the fractionation processes. The effects of sorting are minor, whilst severe leaching and strong sediment enrichment are serious only in wet, upland areas.

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CHAPTER ONE APPLICATIONS OF REGIONAL GEOCHEMICAL RECONNAISSANCE SURVEYS

1.1 INTRODUCTION

The techniques of regional geochemical reconnaissance have made it possible to compile atlases showing the distribution of the minor and trace elements on a provincial scale. This knowledge is already useful in a number of fields and will become so in others. Present applications are those involving the primary location of potentially mineralised areas within large regions, and the delineation of areas where an abnormal trace element content may have an agricultural significance. In geology, trace elements can be used to detect geochemical facies variations within individual formations. Further uses are envisaged in the fields of medical geography, public health and pollution studies (Webb, Nichol and Thornton, 1968).

Initial surveys in parts of England and Wales have demonstrated the feasibility of compiling a geochemical atlas of the United Kingdom (Nichol et al, 1970). The first stage of this programme has been a survey of Northern Ireland. In this introductory chapter, the validity and applicability of such a survey is discussed. Particular reference is made to previous work in the various fields of interest in areas having conditions comparable to those in Northern Ireland.

1.2 SAMPLE REPRESENTIVITY

Regional geochemical maps are intended to show the real variation of the mean bedrock content of a number of elements. For rapidity and low cost, the survey data must be obtained from samples as widely spaced and as generally representative of the bedrock as possible. The optimum sampling media and densities vary according to the locality and usage. They are chosen on the basis of a preliminary small scale orientation survey with the aim of maximising information and minimising time and cost.

The sample medium preferred for regional surveys is normally the active stream sediment. This can be considered to be a natural composite of the bulk erosion products of the catchment upstream. Nevertheless, since it is at the end of the weathering, erosion and deposition sequence, the link between sediment and bedrock composition can become tenuous. Rocks (where exposed) and overburden are only representative of very small areas and, unless sampled on a very strict grid, are liable to bias on collection. For example, hard rocks are more likely to be exposed and sampled than soft rocks.

In the British Isles, a sample density of one per square mile has proved suitable for regional surveys. For convenience of access, the sample sites are chosen as the intersection of the tributary drainage and the road network.

1.3 METAL DISPERSION

1.31 The Secondary Environment

The interpretation of geochemical data based on soil or stream sediment analysis must be based on a knowledge of the dispersion mechanisms of weathering and erosion involved in their derivation. These are the processes of the 'secondary environment' which has been defined by Hawkes and Webb (1962) as:

> "the environment of weathering, erosion and deposition at the surface of the earth. It is characterised by low temperatures, nearly constant low pressures, and abundant free oxygen, water and carbon dioxide."

It is contrasted with the 'primary environment' of:

> "high pressure and temperature, restricted fluid circulation and low free oxygen content."

Minerals formed in the primary environment or in the deposition phase of a pre-existing secondary environment become unstable on exposure to changed conditions. The response to these changes can cause physical (mechanical) and chemical fractionation during weathering and erosion, and produce characteristic dispersion patterns.

1.32 Physical Fractionation

Certain physical processes, especially during transport and sedimentation, result in a differentiation of clastic material on the basis of size and density. The degree of sorting is greatest in the stream environment, with the separation of fine and coarse fractions increasing with the strength of the current. The effect is largely overcome by the choice of a particular size fraction for analysis. For most purposes, the minus 80-mesh fraction (204 microns) of the disaggregated sample is suitable without further preparation. This fraction is composed of the finer primary minerals, organic matter and most of the secondary minerals, such as clays and sesquioxides. The latter usually predominate, hence the processes of chemical weathering involved in their formation are more important in determining sample composition than physical processes.

1.33 Chemical Fractionation

The chemical response to the change from the primary to the secondary environment is represented by a change in the mineralogy. Thus, chemical weathering of rocks entails the ultimate breakdown of most mineral lattices. The mobilised products are carried in solution or suspension in the groundwater until the system becomes unstable and secondary minerals can form. In the prevailing conditions of nearly constant temperature and pressure, the stability of such systems is controlled by the oxidation potential (Eh) and the hydrogen ion activity (pH). The various dissolved and suspended chemical species become unstable under different conditions, at different rates and at different distances from the same source, leading to a degree of chemical fractionation. This fractionation is essentially vertical if completed during profile differentiation in pedogenesis, but becomes increasingly lateral when appreciable amounts of the mobilised species enter the circulating groundwater.

Where these processes are carried virtually to completion in the overburden and soil, the overall change is a negligible loss of metal due to leaching. Thus, the rock - stream sediment correlation may be expected to be fairly close, assuming moderate bedrock homogeneity. The soil - stream sediment correlation may be poorer, however, particularly where there has been strong differentiation within the soil profiles and between soil types in the catchment. For, although the sediment is composed of eroded soil and thus may represent a full bank profile, a single soil sample is not representative of the profile, nor is a single profile normally representative of the whole soil sequence.

In an environment where certain chemical species remain stable in groundwater solution through much of the soil sequence, the lateral fractionation processes may reach completion in the stream itself. In this case, precipitation or deposition occurs on the banks and bed of the stream, altering the composition of the sediment considerably. The most common precipitates are iron and manganese oxides and calcium carbonate. The former may also coprecipitate other elements, causing an enrichment in the sediment whilst the latter tends to dilute.

Whenever either physical or chemical fractionation processes reach extremes, the sediment no longer represents that of the soil or bedrock but tends to reflect weathering and erosion conditions. For example, where strong chemical fractionation has given patterns of stream enrichment, the high metal content suggests that certain environmental conditions exist in the catchments. This will be discussed more fully in Section 1.7.

1.34 Dispersion Patterns

The dispersion patterns revealed by soil and sediment sampling are the results of the interaction of physical and chemical weathering processes. They can be classified according to time and mode of origin (Hawkes and Webb, 1962).

Syngenetic patterns are formed at the same time as the host matrix and result (generally) from the mechanical movement of solid particles.

Epigenetic patterns are introduced after the emplacement of the matrix, and thus must be hydromorphic or biogenic.

This classification cannot be applied rigorously where normal chemical fractionation is extreme. Epigenetic dispersion patterns, for example, are often the result of metals being coprecipitated with iron or manganese oxides in the matrix of soils or sediments. However, when bog ores are produced by an identical mechanism, the oxides themselves become the matrix. Thus, the included metals are coprecipitated contemporaneously, resulting in a pattern syngenetic by definition but essentially epigenetic in origin.

1.4 APPLICATION OF REGIONAL GEOCHEMICAL RECONNAISSANCE IN MINERAL EXPLORATION

1.41 Introduction

Geochemical methods as applied to mineral exploration are well documented and have proved practicable in a wide variety of situations and conditions. In areas of residual soils, weathering of mineralized bedrock normally gives rise to anomalies in soil and sediment that can be detected by appropriate techniques. In areas of transported overburden, additional factors such as the age, origin and direction of movement of overburden must also be considered in data interpretation. Such factors are of great importance in Northern Ireland since glacial drift of various types and origins overlies much of the country. It is pertinent, therefore, to discuss the application of regional reconnaissance in the light of previous work in such terrain.

1.42 Exploration in Glaciated Terrain

Exploration in glaciated terrain has been undertaken in Russia, Canada, Scandinavia and, latterly, in Ireland. In Scandinavia, techniques of sampling soils and boulder clay to detect anomalies arising from clastic dispersion during glacial erosion have been developed from methods of tracing the origin of exotic mineralised boulders back to their source, i.e. 'prospecting for infinitesimal boulders'(Kauranne, 1958).

Boulder clays tend to be locally derived, so that resultant syngenetic clastic patterns are similar to those of residual soils, although probably more diluted and diffuse, fanned in the direction of ice movement. Such tills may, in fact, reflect any chemically significant changes in bedrock lithology and anomalies, like those in residual soils, must be interpreted with reference to the known geology. Glaciofluvial and glaciolacustrine deposits, on the other hand, are less local in origin so that syngenetic patterns become indetectable by virtue of dilution by exotic materials. In a truly exotic overburden, any geochemical anomaly related to the underlying bedrock must be epigenetic, introduced by chemical dispersion after the glacial event. When the origin of the glacial overburden is unknown, the initial problem is to classify any anomaly as syngenetic, epigenetic or a mixture of both - perhaps even to determine whether the syngenetic metal has the same source as the epigenetic metal.

1.43 Syngenetic Soil Anomalies

The thorough investigations by Donovan and James (1967) and Donovan (1965) of the base metal deposit at Tynagh, Eire, serves as an orientation survey for work elsewhere in Ireland. The orebody associated with an Armorican fault between Old Red Sandstone and Lower Carboniferous Limestone has a unique secondary 'mud' ore overlying primary sulphides. It is obscured by between 10 - 50 feet of glacial till which, apart from an upper oxidized layer 8 - 10 feet thick, is apparently homogeneous. There have been at least two glaciations, but nevertheless about 80 - 90 per cent of the material is local in origin. A lack of systematic variation in metal concentration with depth in the till indicated random mechanical dispersion and hence a syngenetic anomaly.

The dispersion fan in the finer matter, as disclosed by soil and till sampling, showed a marked difference from that of the mineralised boulders observed in the field. The boulders appear to show the effects of both glaciations, with a wide fan stretching up to 5 miles from source. The soil/till fan was much narrower, elongated only in the direction of the final glaciation, parallel to the strike of the mineralized fault, for at least 1½ miles. The difference is probably accounted for as follows:

i. the peculiar nature of the Tynagh deposit. Boulders and till could have separate, though nearby, sources, with that of the latter largely shielded from erosion during the earlier glaciation by a ridge or scarp. Any dispersion pattern would have been weak and subsequently diluted to become indetectable.

ii. different mechanisms for the transport of coarse and fine fractions, such that the latter tend to migrate shorter distances.

Despite glacial smearing, the Pb and Cu patterns in the overburden showed the relative displacement of the two metals in the underlying bedrock. The Zn pattern, however, was more widespread. Since Zn is more mobile than Pb and Cu under the secondary environmental conditions prevailing in Ireland, this suggests a hydromorphic expansion of the anomaly after deposition.

It was found that sampling soils on a regular grid adequately displayed the dispersion patterns and provided a suitable exploration method for largely syngenetic anomalies of this type. Indeed, the soils were found to be enriched in comparison with the parent till, increasing the anomaly contrast by up to two-fold, The enrichment has occurred as the till apparently loses bulk during pedogenesis. Physical and chemical processes of translocation have led to the accumulation of metal-rich clays and sesquioxides in the podzol B horizon in particular. The metals, particularly Zn, also tend to occur in peat bogs; Pb concentrated in the top 3 inches. In this situation, metals may be derived from lateral migration in groundwater solution or from underlying mineralisation.

1.44 Epigenetic Soil Anomalies

Soil sampling may well be less useful in detecting purely epigenetic anomalies than syngenetic anomalies. A soil can have matured long before the upward migration of ions has penetrated the underlying thickness of till into the solum. Consequently, the soil may not reflect bedrock enrichment in many cases and, in fact, may be depleted in the metal concerned. Migration is dependent upon the composition and depth of the overburden and the physio-chemical environment. An illustration of the effects of pH on the mobility of base metals was described by Dreimanis (1960) in eastern Canada. He found that in a calcareous till, Cu migrated 2 - 3 cm. above ore, Zn up to 7 cm. above ore. In a non-calcareous till, Cu, Pb and Zn enrichment persisted for 25 cm., decreasing upwards; above this, Zn only was found to increase upwards in the surface 40 cm. of the 70 cm. till. Where the till cover was thicker, about 11 metres, no surface anomaly was detected.

Since the metal distribution was not homogeneous and anomalous values were low, it was considered that the dispersion was entirely epigenetic and had taken place by two mechanisms:

i. basal hydromorphic enrichment, with greater mobility occurring in the more acid, non-calcareous environment;
ii. downwards leaching of a biogenic surface accumulation of Zn, present where roots could reach the basal hydromorphic zone.

Topographic depressions at some distance from the ore have raised metal contents, probably resulting from seepage enrichment.

In the Yukon, Boyle (1963) found that glacial materials only gave good, strong contrast anomalies in Ag, Ph and Zn when sampled close to bedrock. It was concluded that the anomaly was hydromorphic in origin and that in this situation, near-surface sampling was ineffective.

According to Dreimanis, the vertical extent of hydromorphic dispersion is often limited by considerable downward leaching. Although this can be partially offset by biogenic surface enrichment, as shown by his own example, the usefulness of soil sampling in areas of thick exotic drift may be limited. Lateral hydromorphic dispersion in such areas can give a widespread anomaly only reaching surface in depressions, seepages and drainage channels; consequently follow-up can be limited by the lack of near-surface expression of the anomaly.

Metals in the hydromorphic zone are probably highly available to plants and this can ultimately produce an enriched surface layer, but the sampling of vegetation itself has met with limited success. It appears better to sample litter and humus, or the near-surface mineral soil, thereby obtaining a more homogeneous sample with possibly greater metal concentration, and avoiding the disadvantages of sampling single plants with their individual characteristics. Makarova (1960), for example, using the Pb content of the humus of forest litter, detected an anomaly which subsequently provided a drilling target.

1.45 Stream Sediment Reconnaisance Surveys

Orebodies obscured by transported overburden can be located by sampling a suitable horizon of soil or till for anomalies of either syngenetic or epigenetic origin. Stream sediment reconnaissance surveys are satisfactory for the initial detection of the anomalies themselves. Syngenetic anomalies are represented in the metal content of the clastic sediment. Purely epigenetic anomalies, or epigenetic processes associated with syngenetic anomalies, will yield some clastic metal from erosion of the secondarily enriched horizon. However, since metal dispersion depends on aqueous migration, the metals will concentrate in depressions, seepages and sediments - particularly where hydrous oxides are present.

The density of sediment sampling employed in a detailed exploration programme must be sufficient to detect significant anomalies of all origins, preferably with at least two samples defining each individual deposit. For a regional reconnaissance, such a density is impractical, but the interval should be close enough to locate mineralized districts if not specific major anomalies.

Donovan (1965) found that the drainage anomaly for Cu, Hg and Pb in the vicinity of Tynagh persisted up to ¾ mile farther than the soil anomaly, which was itself fanned about 1½ miles down-ice of the mineralisation. Zn dispersion, partially hydromorphic, was greater than for these metals in both soils and sediments. He concluded that "any exploration programme in streams in this type of terrain using Cu, Pb or Hg as analytical elements should ... entail sampling at not more than 2000 ft. The use of Zn allows the interval to be at least doubled".

In glaciated regions of Eastern Canada, with deep, locally derived till, stream sediment reconnaissance has often been used successfully. Hawkes et al (1956), in New Brunswick, used a sampling density of approximately one per 5 square miles to delimit 43 local anomalies, of which 9 were selected and proved significant. Similarly, Holman (1962,) using a density of rather less than one sample per two square miles, found that Cu, Pb and Zn plotted into zones worthy of further investigation and that the technique responded to quite small bedrock variations.

In Norway, Mehrtens (1966) considered that in a moraine area of hydromorphic dispersion, sampling at intervals as close as 500 - 1,000 ft. might be necessary to discover Zn - Cu mineralisation. Elsewhere, Band (1969) showed that a density of only one per 4 square miles adequately detected areas of Mo and Ni mineralisation. Dispersion of Ni was at least partially hydromorphic, with the metal concentrated in iron oxides.

Thus, the efficiency of a given sampling interval depends upon the area. In general, a density of about one sample per square mile is seen to be adequate for a reconnaissance survey. On a regional scale at least, local areas of raised metal content should be discovered, to provide targets for subsequent detailed work. In areas of exotic drift, where anomalies are dependent on the access of groundwater to oxidizing ore, success is less certain and rather higher sampling densities might be more efficient.

1.5 APPLICATIONS OF REGIONAL GEOCHEMICAL RECONNAISSANCE IN AGRICULTURE

The continuing need for increased food supplies demands greater productivity from available agricultural land. This intensification results in greater requirements for soil nutrients, upon which all productivity ultimately depends. Initial demands are for lime, phosphates, potash and nitrates, but secondly they are for certain trace elements which are equally limiting to growth. Conversely, the overabundance of the same elements, whether due to the underlying bedrock or to contamination, can cause toxicity disorders; in some cases, these in turn induce secondary deficiencies of other elements.

About twenty trace elements figure prominently in plant and animal nutrition and imbalances in one or more of the elements can have associated diseases (Schutte, 1964). The problems may be clinical, sub-clinical or latent. Where sub-clinical, they may be expressed merely as poor productivity or fertility of indeterminate cause or as a drop in the nutritive value of a foodstuff without a drop in its yield. Problems are described as latent when metals are at marginal levels and there are no present manifestations of imbalance even at a sub-clinical level. However, at a later date, a change in farming practice may cause them to appear.

Therefore, for healthy plant and animal growth, the soil content of these elements must be between well-defined limits and perhaps in some set ratio. The 'availability' of an element to the plant is more important than the absolute amount in the soil. This depends upon its chemical state and location, in turn conditioned by the environment. Nevertheless, there is frequently a correlation between total and available metal content.

Geochemical reconnaissance techniques have been applied to the location of areas with potential trace element disorders. To date, the methods have been used to show toxicities of molybdenum and selenium, and deficiencies of manganese, cobalt and copper. However, to some extent progress is limited by the absence of suitable rapid analytical techniques for a number of nutritionally significant elements, particularly at the very low concentrations at which deficiencies are to be expected.

In Co. Limerick, Eire, geochemical reconnaissance delineated approximately coincident Mo and Se anomalies over a 30 square mile area (Webb, 1964; Atkinson, 1965; Webb and Atkinson 1965). These were shown to relate to toxic levels in soils and herbage, and to have originated in the Namurian Clare shales and the drift derived from them. Both metals tend to accumulate in boggy and poorly drained organic soils (pH >5.5) in areas of metal rich glacial drift and alluvium, precipitated from groundwater in the reducing environment. Whereas selenium only becomes available to plants when conditions are changed by drainage and liming, molybdenum appears to be available under most conditions.

Clinical selenium and molybdenum toxicity were already known, but the survey suggested that the Mo problem was more extensive and important than previously suspected. Mo-induced hypocuprosis (Cu-deficiency) was expected to be widespread, at least at a sub-clinical level, over much of the anomalous area. This was confirmed by comparing blood copper levels of cattle from farms within and well outside the molybdeniferous area. Cattle grazing molybdeniferous herbage were found to have significantly lower levels of blood copper than those grazing outside the area, although showing no clinical symptoms of hypocuprosis (Thornton et al, 1966).

Reconnaissance surveys in parts of England and Wales have located further bedrock sources of selenium and molybdenum. The principal sources are Lower Carboniferous marine shales in Staffordshire and Devon, Ordovician Volcanics in North

Wales (Webb et al 1966, 1968), parts of the Lower Lias (Thornton et al 1969), parts of the Oxford Clay (Thornton 1968) and several other black shale groups throughout the country (Thomson,pers comm)

In Staffordshire, the Mo patterns (4-40 ppm) were shown in sediments over a 60 square mile area, corresponding to outcrops of Namurian shales. The anomalies indicated molybdeniferous soils and herbage. Where shale outcrops were obscured by barren drift, neither sediments nor soils gave a Mo-anomaly. Clinical molybdenum induced hypocuprosis was already known, but analysis of blood sampled from cattle throughout the anomalous area showed a widespread incidence of the subclinical problem. Subsequently, Cu-supplementation trials have given an encouraging response in liveweight gain (Thornton, 1968).

The existence of molybdeniferous soils over parts of Lias are well known; molybdenosis and hypocuprosis have been reported from the 'teart' pastures of Somerset for many years. Elsewhere, some molybdenum patterns are not apparently associated with known hypocuprosis in cattle, but the existence of the sub-clinical problem may be predicted (Thornton et al, 1969).

In one area, stream sediments have delineated hypocuprosis that has not been molybdenum induced (Thornton, 1968). Very low levels of copper (<10 ppm) in sediments from streams draining the Bagshot beds in Dorset relate to copper-poor soils and cattle with deficiency symptoms. Seedling Sitka Spruce grown in the area also have confirmed copper deficiency. Low levels of Cu in streams draining Devonian and Triassic rocks, however, have no associated deficiencies in plants or livestock.

In Ireland, cobalt deficiencies have been reported as closely related to granites and their derived drift. The overall area of deficiency was successfully defined by stream sediment reconnaissance. Concentrations of <15 ppm Co were found in sediments from areas of sporadic incidence of 'pining' in sheep, <7 ppm in areas of severe incidence (Webb, 1964). Similarly, low Co patterns (<10 ppm) define Co-deficient soil and cobalt pine on Dartmoor, and a possibly suspect area of sub-clinical or latent pine is indicated by moderate levels (10 - 15 ppm) on the adjacent Culm measures. A sporadic incidence of pining is known in the latter area (Thornton, 1968). Further patterns of low cobalt have been found over Triassic drift in the Vale of Clwyd and the Bagshot Beds.

In all cases the sediments also had low contents of manganese and there is some correlation with bovine infertility in Devon and unthriftiness in the Vale of Clwyd. Obvious Mn deficiencies in cereals have been noted in these areas, but this may have been due to overliming limiting availability, rather than asolute deficiency.

The application of regional reconnaissance to problems of deficiencies of Mn, Co and Zn is limited, however, since the secondary environment conditions over much of the country are such that these trace elements tend to be enriched in the sediment to values far exceeding the soil value (Horsnail, 1968). Indeed, in certain areas gross enrichment may indicate deficient levels in associated soils. Consequently, extensive patterns of intermediate levels may be produced by moderate enrichments, thereby obscuring potential deficiency situations.

Nevertheless, surveys of this type have been proved to be a useful tool in detecting areas of trace element imbalance. In particular, they can delineate regions of previously unknown incidence and regions where a change of farming practice may aggravate a latent condition.

1.6 APPLICATIONS IN FUNDAMENTAL GEOLOGY.

Multi-element geochemical surveys generally show that a number of elements have similar distributions. Consequently, much of the data can be described in terms of a number of associations which express the agencies controlling the trace element provenance. These can be selected either 'by inspection' (Webb et al, 1964) or statistically by principal component analysis which also enables the effect of each agency to be quantified (Nichol et al, 1966). Khaleelee (1969) investigating data from regional surveys in England and Wales could identify the source of several associations - for example:

Pb - Zn - Ag - Cu	Base metal mineralisation or mining contamination
Mo - Fe ± Cu, As,Se,V,Ni	Black shales or pyritic volcanics
Cu - Ga - Fe - Ti - V	Previously unrecognised, assigned to argillaceous minerals in sedimentary rocks

Ultimately, it may be possible to establish the principal associations which characterise major lithologies. Hence, in regions of residual or local transported overburden, reconnaissance surveys may be applied to geological mapping. Already, such data can be shown to delineate geochemical provinces and suggest lateral or vertical facies variations in individual formations.

A survey was carried out over the 1500 square miles of the Basement Complex in Sierra Leone, with a mean sample density of approximately one per 70 square miles (Garret and Nichol, 1967). This showed a belt of low metal content trending NE - SW across the region, bordered by higher contents, particularly of chromium, in the NE and SE. The high levels in the SE reflected the area of known chromite occurrences, and suggested that the area was a distinct geochemical province.

In the British Isles, work on Namurian black shales in Limerick and Staffordshire has shown an interesting variation in geochemistry. The shales in both areas shown enrichment in a number of elements, particularly Mo, Se, Cu and V, but only in the Staffordshire area does there appear to be associated enrichment in As and Ni. Such lateral facies variations within an essentially similar formation may indicate a differentiation of geochemical province, or of palaeoenvironment at the time of deposition.

In Devon, stream sediments demonstrate vertical facies variations within a formation. The Lower and Middle Culm measures have enhanced levels of Cu, Mo, V and Zn and can be differentiated on this basis from the more arenceous Upper Culm.

As more data becomes available, further such variations will probably become apparent and indicate promising areas for research into palaeogeography, palaeoecology and other fields.

1.7 INFLUENCE OF THE SECONDARY ENVIRONMENT

In the United Kingdom surveys, the main element association is As-Co-Fe-Mn-Zn$\pm$Ni, which was shown by Horsnail (1968) to be the result of chemical fractionation effects in the secondary environment. Mn and Fe, dissolved in groundwater under conditions of low Eh and/or pH, are precipitated in the higher Eh - pH environment of the stream, simultaneously co-precipitating the other elements. Under certain extreme conditions, such precipitation can result in major distribution patterns of raised levels of Mn and Fe, with associated patterns of other elements. The latter, particularly in Zn, are false anomalies, arising by coprecipitation and unlikely to be confused with patterns derived from mineralisation. Nevertheless, the possibility exists that the enrichment is an enhancement of a weak hydromorphic anomaly.

The phenomenon also complicates the interpretation of analysis for cold extractable heavy metals (cx HM), useful for the rapid field delineation of base metal anomalies. The coprecipitated metals (mainly Zn) tend to give a positive reaction regardless of the presence of mineralisation. Canney (1966) suggested there was an exponential relationship, of the form:

$$\text{ppm cx HM} = a\,(\text{ppm Mn})^{b} \qquad a \text{ and } b \text{ are constants}$$

Thus, a conventional areal threshold would give rise to a number of false anomalies. In mineralised terrain, however, the heavy metal content is much greater than this equation predicts, hence he advocates its use to establish thresholds in areas where precipitation occurs. Nichol et al (1967), however, preferred to consider the chemical state and derivation of the manganese. Supposing that quinol-reducible Mn represents fresh stream precipitate, they suggest that high levels of total Mn with a high (quinol-reducible Mn/total Mn) ratio characterise sediments where high precipitation would lead to false anomalies.

This 'environmental' association is of particular importance in agricultural interpretation, since the enhancement of Co, Mn and Zn may well occur in areas where these metals are in fact deficient in the soil. Since such enrichment must represent strong leaching, however, soil conditions may be inferred in certain instances. Thus, **by soil sampling,** Horsnail (1968) related patterns of this association not to bedrock or overburden geochemistry, but to the development of poorly drained peaty gleys and podzols from which metals were being leached under conditions of low Eh and pH. He predicted that the association would be particularly important in areas with greater than 200 raindays per annum. In such areas, continually overcast skies limit evaporation and thus maximise the amount of water available for leaching. Hence, a knowledge of climatic conditions and soil types is as important for correct interpretation of data as a knowledge of the parent material.

1.8 CONCLUSIONS

The techniques of regional geochemical reconnaissance by stream sediment sampling can be shown to have applications and potential in several fields, even in glaciated terrain. The standard mean sample density of one per square mile is adequate for the rapid and inexpensive delineation of major geochemical features.

In relatively advanced countries, such surveys most probably have a greater potential in agriculture than mineral exploration. Continuing intensification in agriculture brings problems associated with trace element imbalances into greater prominence, hence their detection is increasingly important. Nevertheless, in Eire essentially similar techniques have contributed to recent base metal discoveries.

The effects of domestic, agricultural and industrial contamination can be minimised by careful sampling, although they may be a problem near old mines and centres of population. The factors controlling secondary dispersion, however, can mask significant patterns or result in spurious patterns that are not reflected in bedrock or overburden. A full knowledge of the environmental conditions and their effects on dispersion is, therefore, an essential prerequisite for the accurate interpretation of regional stream sediment data.

1.9 OBJECT AND PRESENTATION OF THE CURRENT RESEARCH

The research programme of the Applied Geochemistry Research Group in regional geochemistry, initiated in 1957 and under the direction of Professor J. S. Webb, has the object of determining the scope and application of regional geochemical reconnaissance by stream sediment sampling. The survey of Northern Ireland is one of a series undertaken in different parts of the world, in a wide range of environments. Its purpose has been to determine the feasibility of compiling regional geochemical atlases of the British Isles and the possible applications of the data.

The current research, described in this thesis, is based on part of the Northern Ireland survey. Its aim has been to identify problems in interpretation under local conditions with particular reference to:

i. the location of areas of mineralisation;
ii. the delineation of areas where trace element imbalances may be of significance to agriculture;
iii. the furthering of knowledge of the fundamental geology of the area.

The description of the study area and the results of the survey and initial follow-up programmes are presented in Chapters 2 to 5 inclusive.

It was found that the major distribution patterns of the elements selected for study (Co, Cu, Fe, Mn, Mo, Pb and Zn) were those of the secondary environment association (Section 1.7). Consequently, detailed studies have been made into the mode and conditions of origin of such patterns, using chemical, micromorphological and allied techniques. The results of these investigations are given in Chapters 6 to 8.

A summary and the main conclusions of the research are given in Chapter 9.

CHAPTER TWO THE TYRONE AREA AND ITS REGIONAL SETTING

2.1 LOCATION OF THE TYRONE AREA

The Tyrone area is a 70 kilometre square in the west of Northern Ireland, including most of County Tyrone and parts of Counties Armagh, Fermanagh and Londonderry. Those parts of Counties Donegal and Monaghan lying within this area are not considered (Fig: 2-1). In this chapter the area is described in its regional setting in terms of those features important in the interpretation of the geochemical reconnaissance. Much of the factual information has been derived from Charlesworth (1963), Symons (1963) and The Ulster Yearbook (HMSO, 1969).The locations of places mentioned in the text are shown on Fig: 2-4.

2.2 PRE-QUATERNARY GEOLOGY

2.21 General

Study of the geology of Northern Ireland progressed slowly between the completion of the One Inch series in 1890-1 and the establishment of the Northern Ireland Geological Survey in 1947. Subsequently, re-surveying has been initiated in many parts of the country.

2.22 North of Ireland

The North of Ireland exhibits a most complete geological section and, throughout, both structure and lithology

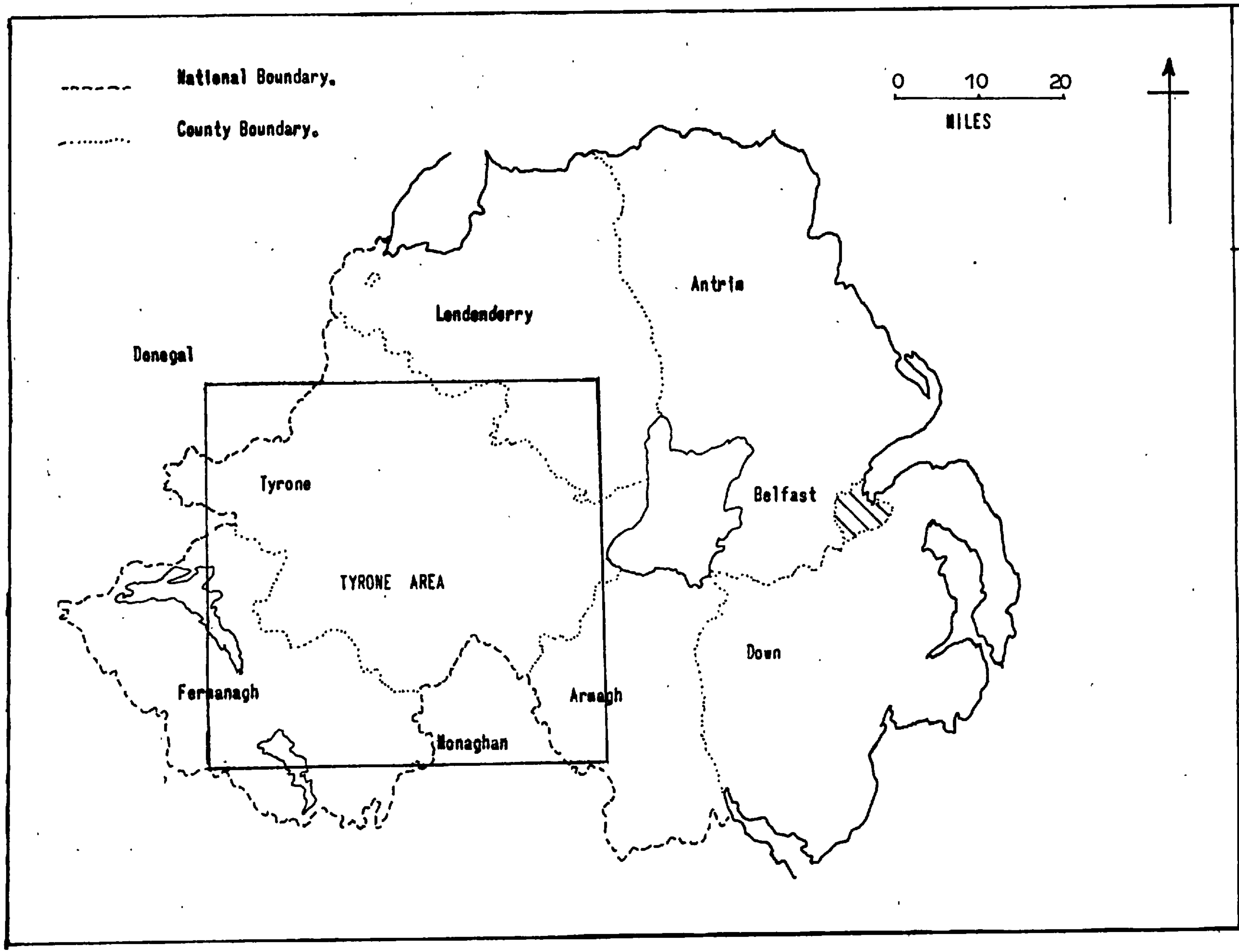


Figure 2 - 1

LOCATION OF THE TYRONE AREA.

Irish Grid References :

2160 4000	2860 4000
2160 3300	2860 3300

demonstrate a south-westerly continuation of Scottish trends. Dalradian and Siluro-Ordovician are structural extensions of their Scottish counterparts. The Highland Boundary fault and probably the Southern Uplands fault continue into Ireland from the north east, together with the tectonic trough of Scotland. Finally, Tertiary Igneous activity, as the plateau basalts and plutonic ring complexes of the Brito-Arctic province, show a common north-south trend. To the south, the similarities become less obvious with the development of the Carboniferous limestones of the Central Plain.

2.23 Tyrone Area

The Tyrone area (Fig: 2-2) is situated across the Midland Valley, with the Highland Boundary Fault forming a NE-SW diagonal. Most of the principal pre-Rhaetic rocks of the Province are represented, the omissions being the Moinian granulites of Belleek, Fermanagh, and the Newry granodiorite. The important Tertiary igneous rocks, namely the Mourne granites and Antrim basalts, lie totally outside this area.

The Dalradian, tentatively divided into Upper and Lower divisions (Cobbing, 1964), underlie the moors to the south towards Pomeroy and extend west along the Derg valley into Donegal; an inlier occurs south-west of Omagh. The Lower Dalradian schists and meta-basic rocks lie wholly south-east of the Highland Boundary fault as the 'Central Inlier' within the Tyrone Igneous Complex. Locally, these rocks are of sillimanite grade and considered possibly to be associated

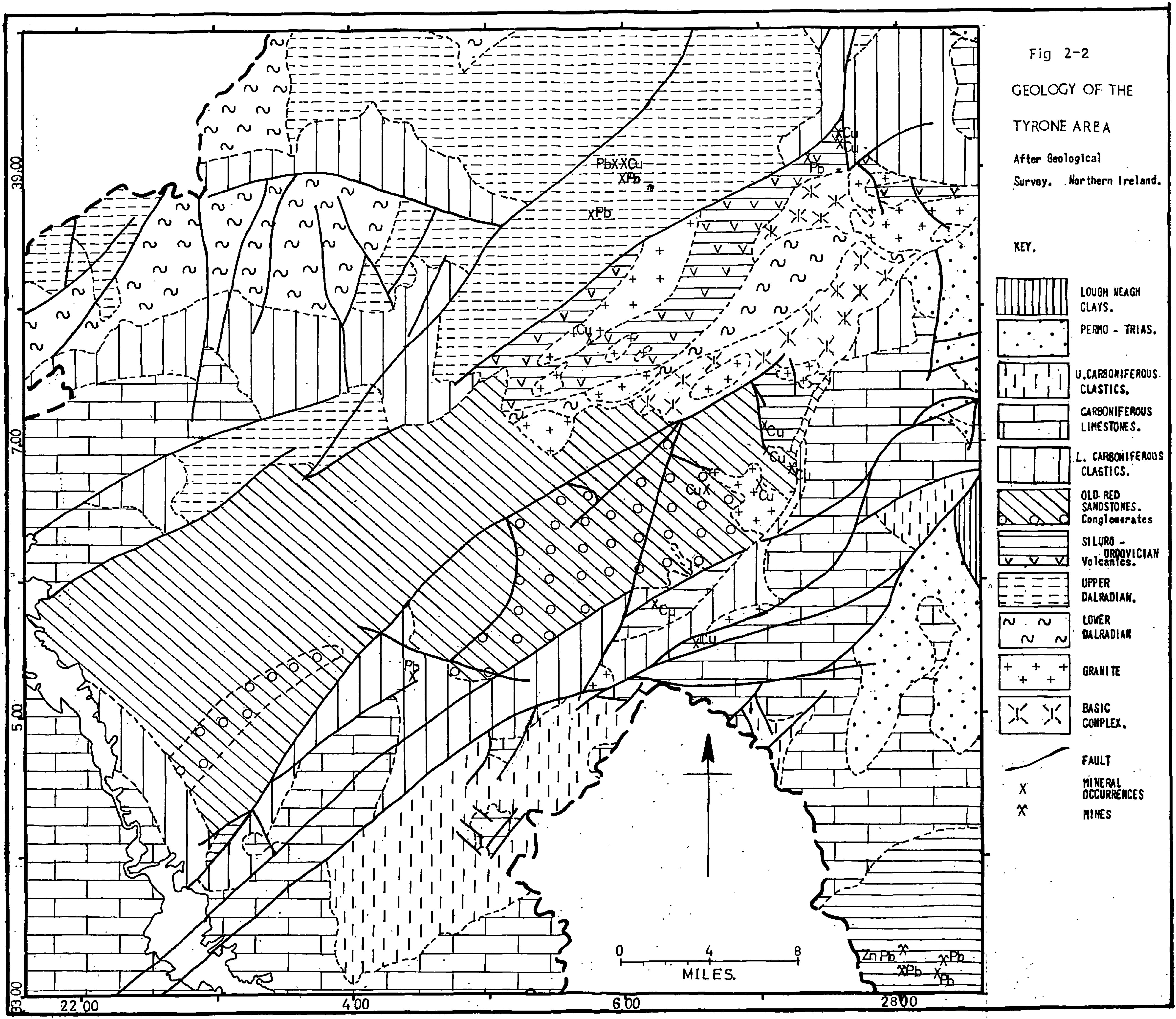


Fig 2-2

GEOLOGY OF THE TYRONE AREA

After Geological Survey. Northern Ireland.

with a regional metamorphism or migmatisation of deeper levels. This contrasts with the more widespread schists of the Upper Dalradian. Originally pelites and semi-pelites, these are metamorphosed rarely higher than biotite grade, reaching garnet grade only locally.

Ordovician and Silurian geosynclinal sediments occur in two areas:

i. the Southern Uplands continuation (Longford-Down massif): a non-volcanic series of greywackes and flags, with conglomerates, grits and occasional mudstones and shales in the south-east around Keady;

ii. the Midland Valley: as the volcanic series of the Tyrone Igneous Complex and as flags and mudstone (both) near Pomeroy; as mudstones and conglomerates in the Lisbellaw inlier.

Devonian rocks outcrop in the wide belt between Lough Erne and Pomeroy, deposited unconformably in the fault-controlled Midland Valley depression. They consist of shales, flags, sandstones and conglomerates, red, brown, purple and green in colour, with local volcanics at Ballygawley and Sixmilecross - the usual post-Caledonian freshwater and semi-arid accumulations of the Lower Old Red Sandstone of the British Isles. The sub-aerial denudation during and after this period left a near peneplained surface for sedimentation during the Carboniferous transgression. Basal (Tournasian) conglomerates and sandstones fill the hollows in the old land surface - for example, 4,000 ft. of highly siliceous sandstones in the Omagh Syncline - passing upwards to calcareous shales and into the hard crystalline blue and grey Lower Limestones.

The sandstones predominate in the north, near Newtownstewart, the limestones further south. The overlying Calp 'limestones', of mid-Visean age, consist mostly of impure earthy limestones and calcareous shales near Lough Erne, but farther east, around Aughnacloy, the equivalent rocks are massive yellow sandstones. This formation is succeeded by the massive, crinoidal Upper Limestone, again Visean, which is in turn overlain by the 'Yoredale Beds', outcropping on Slieve Beagh and near Drumquin. The Lower Yoredale sandstones are coarse and gritty, with occasional flaggy and calcareous partings, locally much folded. The upper Shales are brown, black and fissile; probably they are not the true equivalents of the molybdeniferous Namurian Clare shales of the Limerick district, and lie in a relatively unimportant area agriculturally. On Slieve Beagh, the shales are succeeded by the almost horizontal 'Millstone Grit', forming a nearly flat cap to the hill.

Near Coalisland, the limestones are overlain by 600 feet of Namurian mudstones and siltstones, covered by the Millstone Grit and fining upwards to mudstones and dolomitic limestones into the Coal Measures.

There is a considerable lateral and vertical variation in the Carboniferous, particularly in the Calp and lower transgressive beds which mark the fluctuating change from fluvial to estuarine and marine conditions. Thick drift cover make stratigraphic correlation nearly impossible. In the Tyrone area, the sediments are dominantly arenaceous facies, stratigraphic equivalents of the limestones of the Central Plain to the south.

The subsequent Armorican folding was generally fairly gentle but the movements reactivated past lines of weakness, such as the Highland Boundary fault, and produced major northeast-southwest fractures, for example along the Clogher Valley, and some approximately north-south cross faults, especially north and west of Omagh. The post-orogenic red-bed continental period is represented by the tract of Bunter sandstones with local pebble beds, and minor Permian outcrops along the eastern margin of the area from Slieve Gallion to Armagh.

Later Mesozoic and Tertiary rocks have been eroded from the area except for a small Cretaceous outlier on Slieve Gallion. The Tertiary igneous activity is represented merely by a few dykes.

Post-basaltic Tertiary movements activated old and new fault lines and caused depressions around Loughs Neagh and Foyle, with minor uplifts in central Donegal. During this period came the ultimate land severance of Ireland from Britain. Relics of the erosion are planation surfaces, monadnocks and drainage patterns. Sediments are rare, but east from Coalisland the Oligocene-Pliocene Lough Neagh clays represent deposits of the lough at an earlier stage of its development. Severe faulting of the clays is evidence of still later movements.

2.24 Mineralisation and Mining History

2.241 Introduction Known non-ferrous mineralisation in Northern Ireland is restricted to galena - sphalerite - chalcopyrite veins in the Silurian of Counties Down and Armagh, and minor occurrences of these minerals elsewhere, chiefly in the Dalradian and Devonian outcrops. Baryte, as the main gangue mineral, can also appear barren in faults. Most of the known mineral occurrences were listed by Cole (1922). This information has recently been updated and depicted in map form (G.S.N.I., 1970). The most important localities are shown on Fig: 2-2.

2.242 Down - Armagh Vertical lodes striking NNW-SSE occur in east Down and in the Keady area of south Armagh. They contain galena, sphalerite, chalcopyrite and occasional stibnite and manganese ore, in a gangue of baryte, calcite and quartz. The Silurian sediments, however, appear to be poor host rocks and not susceptible to metasomatic replacement. Consequently, the minerals are confined to veins in fault breccias and unwidened fractures, etc.

A frequent association with Tertiary dykes suggests the mineralisation of this age, with emplacement in the more favourable host rock of the dyke (Fowler, 1958). However, lead isotope dates from Conlig and Castleward in east Down give Caledonian and Hercynian ages respectively, corresponding to results from the Southern Uplands and Eire (Moorbath, 1962). Thus, the dykes appear to have been intruded into already mineralised fractures, or alternatively to have re-mobilised deposits 'at depth'.

Certain of the lodes have had a long but intermittent mining history, which had ceased by the end of the nineteenth century. Near vertical dip with rapid lateral and vertical variation in thickness and grade made extraction difficult, but in all cases it appears that work was limited more by the low price of lead than by exhaustion of the deposits. At present it is unlikely that such a lode would be economic unless much larger than the mile-long Conlig-Newtownards lode of north east Down, the largest of this type yet known.

2.243 Minor occurrences of the Midland Valley Many minor showings of Ph-Zn-Cu-Fe minerals have been recorded from the Tyrone area (Cole, 1922, G.S.N.I. 1970,). There are several types; for example, massive pink baryte with flecks of green copper minerals (Aughnacloy), two-inch Pb-Zn-Fe quartz veins in schist (Glenlark) and four-foot thick haematite-quartz veins on Slieve Gallion (G.S.N.I., 1962). Some of these occurrences show an association with faults. Interest has been expressed by the Northern Ireland Geological Survey in haematized quartzites with black shales in the Tyrone inlier.

However, the main interest in this area lies in the possibility of major base metal mineralisation of the type found in Eire, for example at Tynagh, Gortdrum and Aherlow. These deposits occur along major Armorican faults which bring Carboniferous limestone into contact with the Old Red Sandstone. In Northern Ireland, such faults systems are important, forming the Midland Valley and other features, and produce this contact in several localities. Consequently, if purely structural features control Irish mineralisation, the area can be considered promising. However, if lithological factors are important - such as the presence of limestone as host to Mississippi valley type deposits - the Tyrone area is less promising, since the Carboniferous is essentially more clastic here.

This mineral exploration potential was a major consideration in the choice of this area for the initial study.

2.3 QUATERNARY GEOLOGY

2.31 North of Ireland

Superficial drift, completely obscuring bedrock, is common throughout Ireland, especially on lower ground. Evidence from large-scale structures, erratics, striae and till fabrics has indicated a complex series of ice movements, with changes in dispersion centres and topographic control of ice flow. Three main phases are recognised, all belonging to the last glaciation:

i. A period of Scottish ice flowing from the east across Down, Antrim and Londonderry. The material is preserved as a calcareous lower till (rare in Londonderry), often with erratics from Scotland and Ailsa Craig.

ii. An Irish ice period, probably dominated by centres in Donegal from which ice flowed eastwards and minor centres around high ground elsewhere. An upper till with Irish erratics has been left. The majority of the drumlins were formed during this period.

iii. Halt and retreat period as the ice sheet decayed and melted back. Extensive glaciofluvial 'dead ice' deposits are found in the low ground and valleys, particularly in the west.

Dwerryhouse (1923) and Charlesworth, 1924, 1963) suggest a continuing strong influence of Scottish ice during the second period, producing a confluent ice flow about Lough Neagh. This has been disputed by Hill and Prior (1968) who suggest that the limit of the Scottish ice is shown by the Armoy moraine of northeast Antrim, and that there is thus no evidence for the re-advance during the retreat period previously suggested to explain this moraine.

2.32 Tyrone Area

Glacial deposits of the Tyrone area mainly show the influence of the second and third periods (Fig: 2-3), for the limit of the Scottish ice passed north of the Sperrins, east of Draperstown and south-west to Slieve Beagh. The westerly ice flow from Donegal produced an overall cover of boulder clay, moulded into drumlins in lowland (below 500 ft.). South-east of a line Cookstown-Aughnacloy lies part of the great belt of drumlins which stretches from Down to Mayo. More occur around Lough Erne and, where drowned, result in the intricate shore of the Upper Lough.

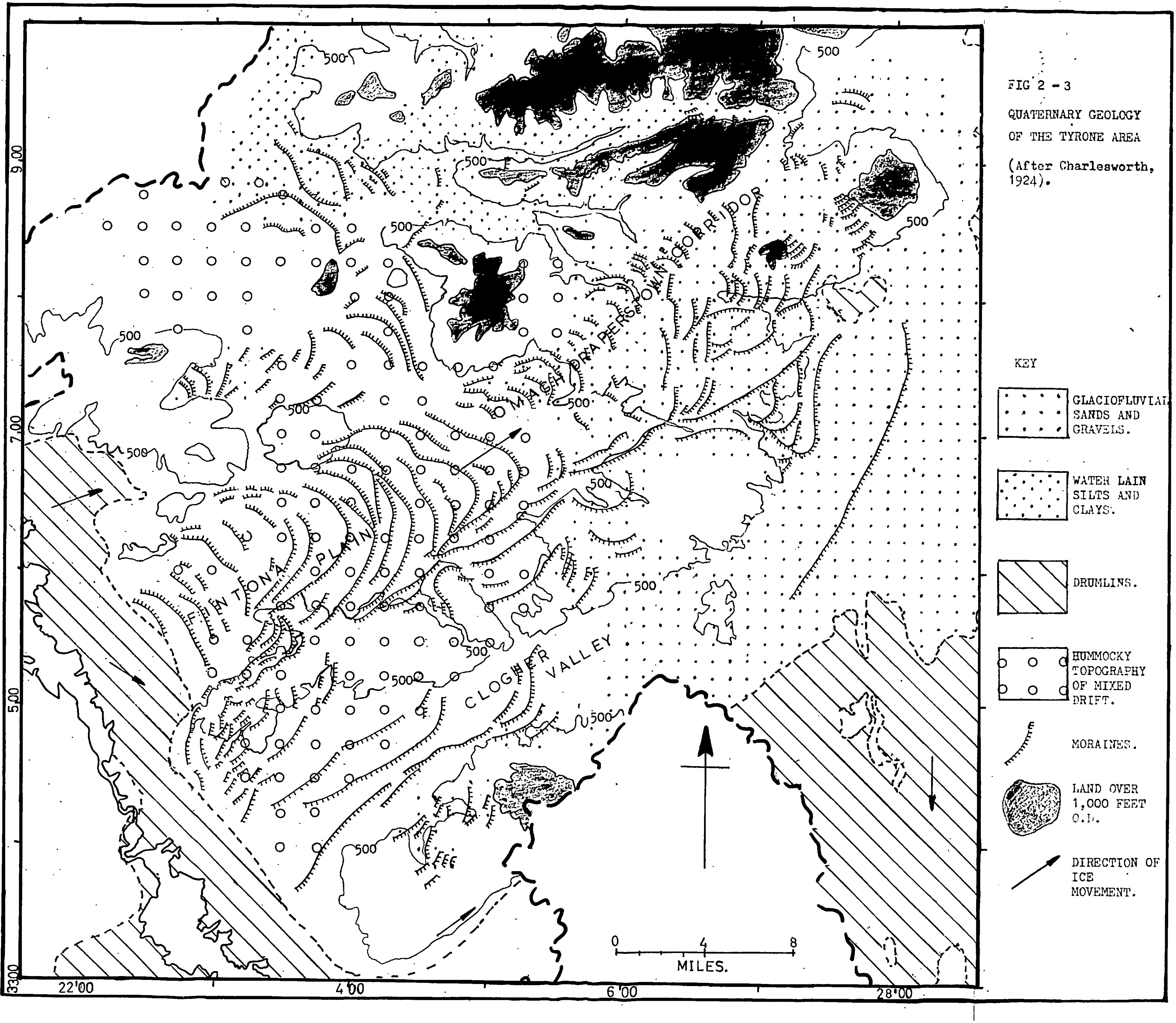


FIG 2 - 3

QUATERNARY GEOLOGY OF THE TYRONE AREA

(After Charlesworth, 1924).

Elsewhere, the predominant features are those of the retreat stages. Ice dammed lakes formed in the Sperrins, Slieve Beagh and other high ground, dumping sand and gravel in overflow channels. Melting from the summits left tongues of ice extending through lower ground. Progressive recession of these resulted in the series of arcuate moraine ridges and mounds of glaciofluvial sands and gravels along the Clogher Valley, the Draperstown-Omagh-Fintona 'corridor' and valleys in the northwest. Further moraines and outwash fans are found south and east of Cookstown. In many places, the sands and gravels are deposited over boulder clay; around Cookstown they partially obscure drumlins.

In general, the composition of the tills seems to reflect that of the underlying bedrock despite the complex glacial history. However, for the more exotic, waterworn glaciofluvial deposits, the link is more tenuous, although the coarse fractions at least seem to reflect the local geology to some extent.

2.4 PHYSIOGRAPHY AND DRAINAGE

The physiography of the Tyrone area (Fig: 2-4) largely reflects late Tertiary plantation and rejuvenation, modified by glaciation. The highest elevations and strongest relief are found in the rounded mountain ridges of the High Sperrins (Sawel Mtn. 2,240 ft.), whose Caledonian trending valleys show a depth of dissection of 1,000 - 1,500 ft. They are delimited by the Highland Boundary Fault line, giving way southwards

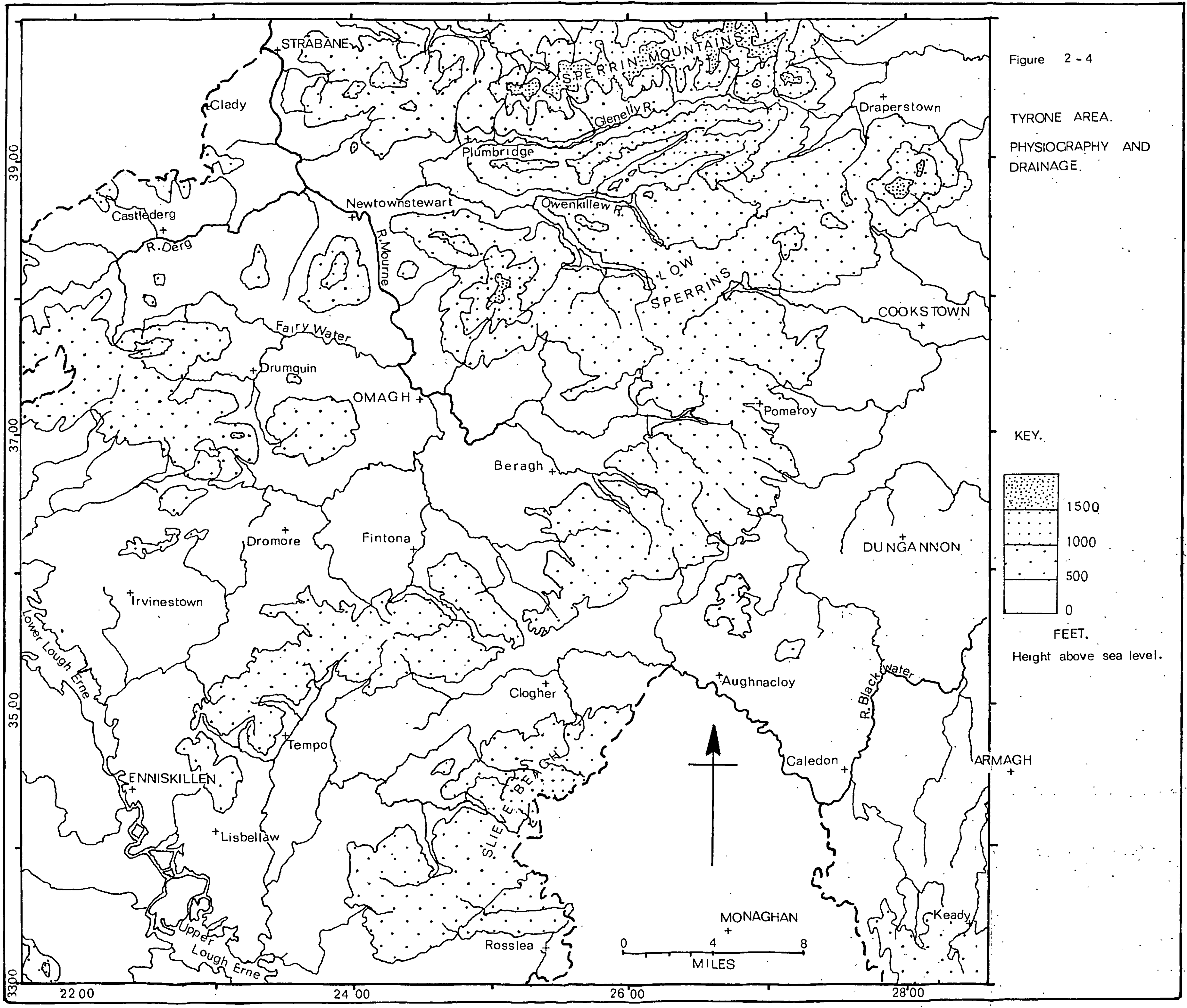


Figure 2 - 4

TYRONE AREA.

PHYSIOGRAPHY AND DRAINAGE.

to the moraine-covered moors of the Low Sperrins. Three lines of uplands over 500 ft. trend northeast-southwest across the area, defining the Draperstown-Omagh-Fintona 'corridor' and the Clogher Valley, both important in the retreat stages of the glaciation. These die out in the southwest, with poorly drained lowlands around Lough Erne, but mountain limestone scarps rise on the borders of the area. In the northwest, the lower ground and enlarged valleys of the rivers Finn, Derg, Fairy Water and Mourne form an important topographical break between the rugged Donegal mountains and the smoothed Sperrins.

Regionally, glaciation has mostly softened the relief, but on a local scale, the form of the drift gives characteristic topography. The drumlin areas found in the southeast and around Lough Erne have a typical 'basket of eggs' topography. Sand and gravel moraines and kames of the ice retreat stages give steep-sided hills and/or hummocky terrain. They form huge mounds in the boggy alluvial flats of the Fairy Water valley. More featureless boulder clays produce undulating country, for example in the Clogher Valley, around Fintona and in some low hill areas.

The main river system is the Strule, with its tributaries the Derg, Glenelly, Owenkillew and Mourne, draining northwest through Strabane. The other major drainages are the Erne in the southwest and the Blackwater in the southeast. The lowlands of the eastern margin of the area are drained by smaller systems entering Lough Neagh, whose headwaters have been captured by the Strule.

Glacial modification and interruption of pre-existing drainage lines have caused numerous stream diversions. In upland areas the rejuvenated streams have cut steep-sided valleys through the drift. In the lowlands, they follow particularly winding courses. Drumlin, till and hummocky moraine country are typically very poorly drained, with peat bogs between hillocks. Drainage schemes, initiated in 1947 and 1964, are successfully raising the agricultural status of much of this land which was previously waterlogged throughout the year.

2.5 CLIMATE

The Atlantic situation of the country results in a mild temperate climate. There are mild winters, late springs and cool summers - the annual mean temperature variation is only 10°C. Winds blow almost continually, mainly from the southwest (Stephens, in Symons, 1963).

Rainfall varies widely, decreasing from west to east, but is high over all major elevations (Fig: 2-5). Most of the Tyrone area receives 40 - 45 inches per annum, but in the extreme west and over the Sperrins the average exceeds 65 inches per annum. Along the east and southeast margins, the average is below 35 inches per annum. Precipitation is typically as showers rather than as extended periods of rain. With a calculated evaporation rate of 14 inches per annum for the whole of Northern Ireland, there is a considerable water surplus, although in exceptionally dry years (such as 1959 and 1968) even this has proved insufficient to meet the needs of plants and livestock in some areas.

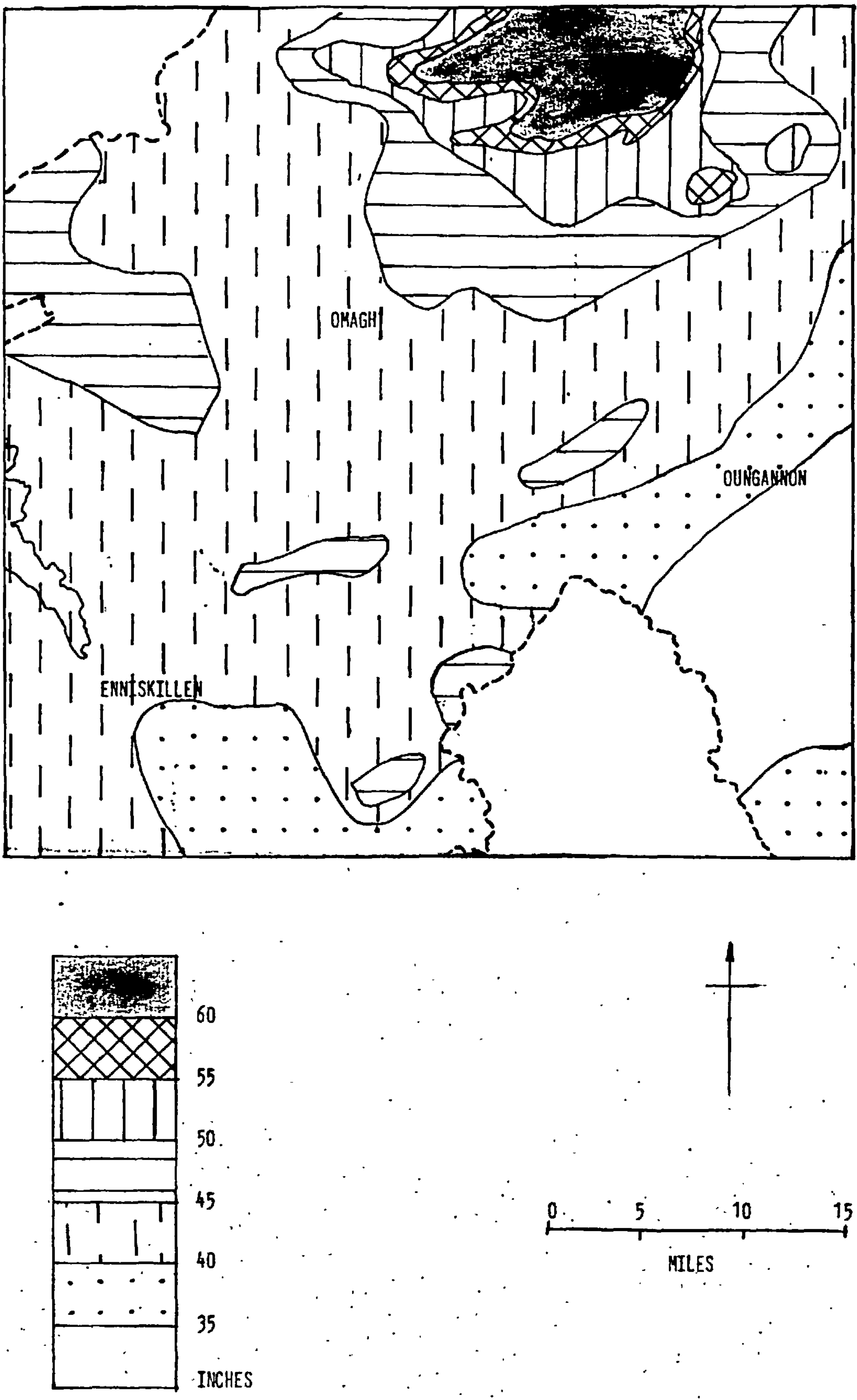


FIG. 2 - 5. ANNUAL AVERAGE RAINFALL, 1916 - 1950, TYRONE AREA.
(After Stephens, in Symons, 1963)

The average number of raindays ($\geqslant$ 0.01 inch per day) and wet days ($\geqslant$ 0.04 inch per day) exceed 215 and 160 per annum respectively throughout the Tyrone area. Horsnail (1968) suggested that where there were more than 200 raindays per annum, secondary oxide precipitation in streams might become important in the interpretation of geochemical data.

2.6 SOILS

The soils developed in the area are determined by the nature of the glacial drift and underlying bedrock, with modifications induced by climate and topography. The soils in the Tyrone area have not been studied in great detail, but a classification, based on drainage and weathering characteristics, has been drawn up by McConaghy and McAllister (in Symons, 1963). They have categorised the soils as follows:

A. Freely drained soils Formed on glaciofluvial sands and gravels, and sandy tills.

1. Podzols. Thin, infertile and often peaty, found particularly in the Sperrins and on high ground over all bedrocks and drift types.
2. Brown earths - low base status. These include arable loams of the Siluro-Ordovician (Co. Armagh), and lighter textured soils on the schists (Strabane), Devonian (Beragh) and Trias (Cookstown). Under natural conditions most would be podzolised and hence can be termed 'agricultural brown earths'.

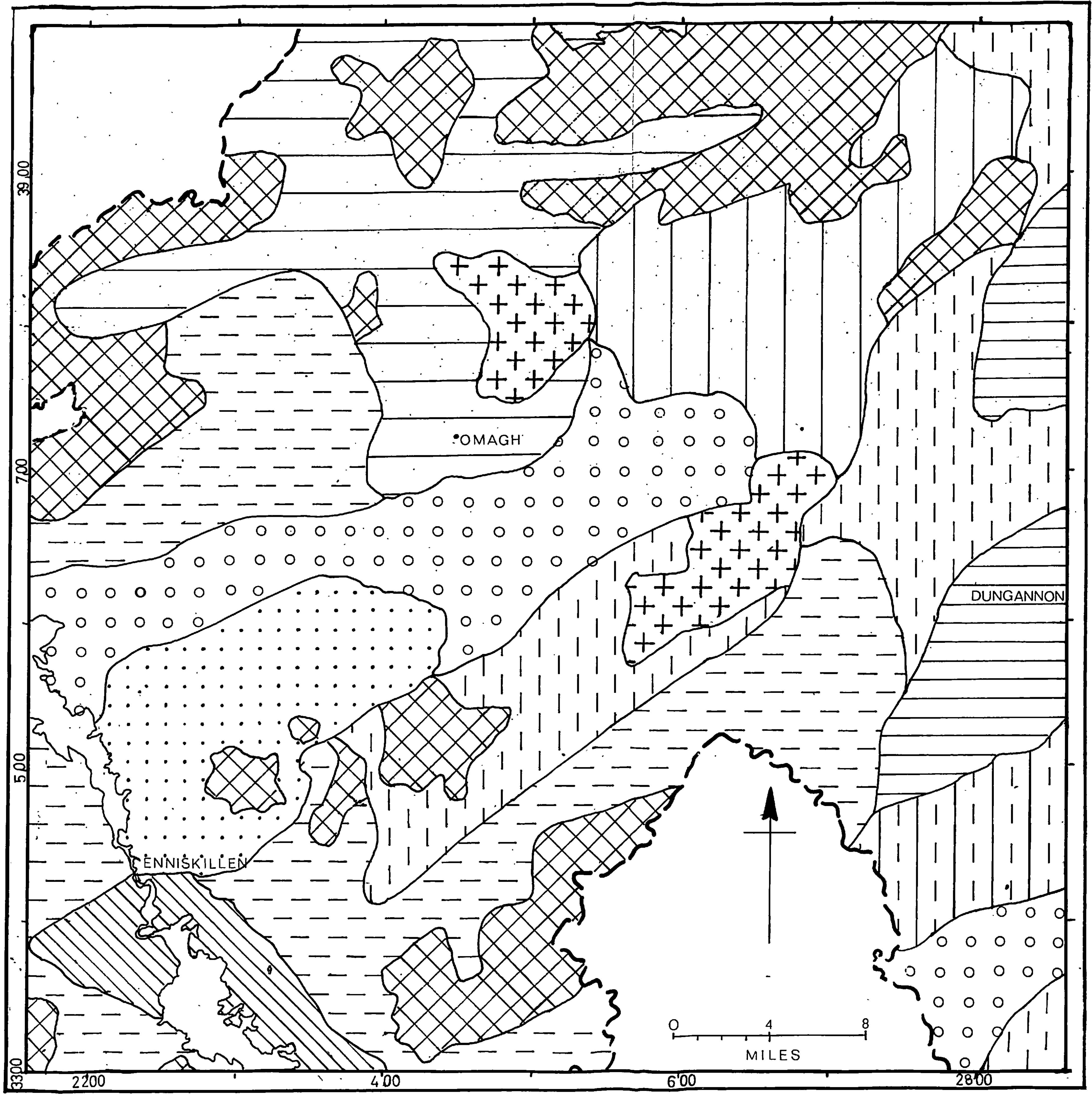


FIG. 2 - 6. SOILS OF THE TYRONE AREA

(After McAllister and McConaghy, 1968).

	Soil Association				Principal Parent Material. Drift type in parenthesis.
	Principal Soils	Per Cent of area	Associated Soils	Per cent of area	
✚	Peaty Podzols.	75	Climatic peats.	25	Schist; Old Red Sandstone; Granite (sandy till)
▩	Peaty Gleys.	60	Climatic peats; Organo-mineral Soils.	40	Schist; Old Red Sandstone; U. Carboniferous Clastics (sandy till).
‖	Reclaimed Podzols.	75	Gleys.	25	Central Tyrone Inlier (glaciofluvial sands)
☰	Acid Brown Earths (light textured).	60	Sandy Brown Podzolics.	40	Permo-Triassic Sandstones (glaciofluvial sands)
▤	Acid Brown Earths.	60	Brown Podzolics.	40	Schist; Old Red Sandstones; Carboniferous Clastics (sandy till).
⁘	Gleys.	75	Peaty Gleys.	25	Old Red Sandstone. (till).
▧	Gleys.	90	Acid Brown Earths; Peat.	10	Carboniferous Shales (till).
○	Gleys.	60	Acid Brown Earths.	40	Siluro-Ordovician; Old Red Sandstones (till).
╌	Gleys, Peaty Gleys Interdrumlin Peat.	90	Acid Brown Earths.	10	Carboniferous Shales and sandstones (till).
▥	Grey Brown Podzolics.	60	Gleys, Peaty Gleys, Peat.	40	Carboniferous Limestones; Old Red Sandstones (till).
¦	Acid Brown Earths	60	Gleys; Peaty Gleys.	40	Siluro-Ordovician; Old Red Sandstone (till).

3. Brown earths - high base status. These occur over limestones; slightly acid at the surface, becoming alkaline with depth.

B. Imperfectly drained soils Somewhat gleyed brown earths, mottled at depth, developing on stony till, particularly on drumlins in the southeast.

C. Poorly drained soils Heavy and gleyed, with a high clay and silt content and high water-table. Typical of lowland drumlin areas and plateau lands, they support a rush and sedge flora. The heavy, sticky gleys of the south and west of the Devonian, and the tenacious 'cheesy' soils over some calcareous drift derived from the Calp. are of this type.

D. Peat soils

1. Basin peats over gleys between drumlins, mounds, etc., mostly highly acid. Heather, cotton grasses and *Sphagnum* are dominant vegetation.

2. Shallow hill and mountain (blanket) peats on moors and uplands.

Areas of uniform soil type are rare. Normally sequences are found, such as that from crest to base of drumlins: leached brown earth - slightly gleyed brown earth - ground or surface water gleys with peat.

Usually one or two soil types predominate and such associations have been mapped by McAllister and McConaghy (1968) to show a broad correlation with physiography and parent material (Fig: 2-6). This presentation is quite successful in showing the inter-relationships of the controlling factors, especially when compared with geological, drift, physical and rainfall maps.

2.7 AGRICULTURE

2.71 Farming Practice

The patterns of increasing intensification and mechanisation in agriculture in Northern Ireland are similar to elsewhere in Great Britain. Mixed farming is declining steadily, with a growing emphasis on specialisation, suited to local conditions. As a result of this rationalisation, total farm stock by 1963 was 64% higher over pre-war levels (then only up 10% since 1850) and exports are rising steadily. Nevertheless, the standard of farming is generally poorer than in Britain.

The Tyrone area contains about one third of all the agricultural land in Northern Ireland. However, about one third of this is rough hill grazing, including much high, poor land covered in blanket peat. The large proportion of small farms and the infertility of the land induce farming of a marginal character and hence the productivity of the land is well below the average for the Province.

In Fermanagh and parts of Tyrone, the majority of soils are poorly drained so that most of the improved lands have to be given over to permanent grassland. Thus, dairying predominates in the lower lands and the rearing of store and beef cattle in the uplands.

Arable farming is mostly concentrated on the better drained brown earths of the east and northwest, though in fact nearly all farms have some arable land. Grasses, oats and barley are the principal rotation crops; roots, fruit and horticulture are locally important in the east. Dairy herds are larger than the regional average.

Sheep are becoming increasingly rare away from the hill and mountain areas of the north and west. Pigs and poultry are only locally important.

Hill peats and marginal uplands are being acquired for afforestation under a scheme initiated in 1947. Under present conditions this is considered the most economical utilisation of the land, since the climate is ideal for the rapid growth of conifers. Natural forests are virtually unknown.

2.72 Known Nutritional Disorders

Most soils are phosphate, potash and/or lime deficient and have to be treated accordingly. At least 90 per cent of soils not derived from limestone require liming. Deficiencies of Mg, Mo and B have been encountered on well drained soils, especially over Permo-Trias (McAllister and McConaghy, 1968).

The major known trace element problem is one of cobalt deficiency, acknowledged to be widespread but not considered serious in normal years. When soil contents of less than 5 ppm total Co and 0.25 ppm acetic acid extractable Co are found, pasture may be expected to be deficient. McConaghy (1950) states that no soils contain less than 10 ppm total Co, but quotes mean values for acetic acid extractable Co over most bedrocks as low as 0.30 - 0.50 ppm (Table 2-1).

GEOLOGY	Schist	Silurian	Devonian	Carboniferous	Granite	Basalt
Available Co range ppm.		% Samples	Within	Range		
0 - 0.25	30	6	6	13	33	0
0.25 - 0.50	60	29	50	37	60	9
0.50 - 1.00	10	59	44	50	7	41
> 1.00	0	6	0	0	0	50
Mean	0.34	0.57	0.42	0.43	0.30	1.20
No.of samples	10	17	16	16	33	23

TABLE 2-1 AVAILABLE COBALT (ACETIC ACID EXTRACTABLE) IN SOME SOILS FROM NORTHERN IRELAND (after McConaghy, 1950)

Surprisingly, the first case of clinical Co-pine occurred over basalt-derived soils containing 38 ppm total Co and 1 ppm extractable Co, but such cases are rare. Treatment with $CoSO_4$ has had little apparent effect in deficient areas, but the sub-clinical effects of the treatment may be considerable in young stock.

No problems of molybdenum toxicity have been reported, but isolated soils near Kesh and in the Sperrins are known to contain 6 - 7 ppm Mo. (McConaghy, pers comm.).

Manganese deficiencies (in oats) can occur on limestone or over-limed soils. Copper (and phosphorus) deficiencies in peats are known and may affect new forests. Cattle with low blood copper were detected by chance near Enniskillen (Todd et al, 1967).

The incidence of grass tetany (hypomagnesaemia) in Northern Ireland is apparently geologically controlled. High incidences are known in the schist areas of Counties Tyrone, Londonderry and Antrim, but the disease is relatively rare elsewhere. Pasture Mg is not abnormal and the evidence suggests an unknown conditioning factor.

CHAPTER THREE REGIONAL GEOCHEMICAL RECONNAISSANCE OF THE TYRONE AREA

3.1 SAMPLE COLLECTION AND PREPARATION

The stream sediment samples for the whole Northern Ireland Reconnaissance survey were collected during the period July-September 1967. The writer and three assistants, working in two-man teams under the direction of Dr. I. Nichol, collected 4,832 samples at a mean density of approximately one per square mile. (The area of Northern Ireland is 5,242 square miles, including about 250 square miles of water and urban districts.)

Sample sites were preselected as the points at which streams, with catchments usually between one and ten square miles, intersected the road network. In Northern Ireland, the tributary drainage is very poorly represented on the most recent Ordnance Survey One Inch maps (Third Series). Consequently, the sites chosen were from the older Popular series, now out of print, on which a more complete drainage is depicted.

Duplicate samples were taken of the active stream sediment, each from at least two sites 20 feet apart, 50 feet upstream of the road bridge or any other obvious source of contamination. Silty samples of unsorted sediment were preferred, but the types varied from coarse sands to peats. Material from bank collapse or the clay beds of recently cleared streams was avoided. At the time of collection, note was taken of:

1. Irish Grid reference of the sample site.
2. Dimensions and flow rate of the stream.
3. Mechanical and mineral composition of sediment.
4. Type of stream precipitation, where present.
5. Bank type - alluvial or colluvial.
6. Sources of possible contamination.
7. Vegetation and land use.

The wet samples were dried for one or two days in portable ovens. One sample per pair was stored unsieved, the other disaggregated in a porcelain pestle and mortar, and sieved through 80-mesh nylon bolting cloth. The fine fraction was retained for analysis, the coarse discarded.

Despite poor weather, the sampling was completed in 2½ months, averaging about 240 samples per team per 6 - 7 day week. Obviously, in country with fewer and/or poorer roads, a comparable sample density would take longer to achieve. Nevertheless, this demonstrates the rate and hence the cost at which such a sampling operation can be completed by inexperienced labour.

3.2 ANALYSIS OF SAMPLES FROM THE TYRONE AREA

The samples, approximately 1600, from the Tyrone area were ashed and submitted for routine spectrographic analysis by the method of Nichol and Henderson-Hamilton (1965). The results for Ag, Co, Mo, Pb, and Fe_2O_3 from this analysis were used, but those for Cu and Zn were considered too unreliable and imprecise in this instance. The non-ashed samples were therefore reanalysed for these two metals by atomic absorption spectrophotometry using a standard perchloric acid/nitric acid mixture digestion (Appendix A).

Control samples of different metal contents were included regularly as a check on both methods of analysis. Analytical precisions at the 95 per cent confidence level have been calculated from the replicate analyses of these controls by the method shown in Appendix A. Results through the useful ranges are shown on Table 3-1 and compared to the overall mean concentrations of the metals in the samples from the Tyrone area.

Precision is always poor at the lower end of the range, near the analytical detection limit. For Pb and Co, this affects most samples, since the mean values for the reconnaissance data are at these low levels. Precisions for Fe_2O_3 and for Co at levels above the reconnaissance mean are acceptable, but those for Mn and Pb at levels above this mean were not tested by the controls, although they show improvement with increasing concentration. Precisions for spectrographic Cu and Zn were very poor throughout the range.

The atomic absorption analyses for Cu and Zn have a much better precision than the spectrographic analyses for the other metals. However, the mean concentration of Cu is near the detection limit for the rapid method employed, hence precision is poorer than might be expected.

	Spectrographic analysis						Atomic absorption analysis	
	Co ppm	Cu ppm	Fe_2O_3 %	Mn ppm	Pb ppm	Zn ppm	Cu ppm	Zn ppm
R*	12- 25	4- 20	1.3-2.6	85-400	2-40	<50-200	14-20	15- 30
M*	17(9)	8(11)	1.8(9)	150(9)	18(9)	120(11)	18(9)	18(12)
%*	80	110	45	155	130	110	26	65
R	35- 60	85-200	2.6-3.8	160-400	10-50	50-200	20-30	40- 75
M	48(9)	103(9)	3.2(9)	195(10)	30(10)	150(11)	25(10)	60(12)
%	50	100	35	75	80	90	23	30
R	25- 95	200-600	2.0-9.2	130-300			35-42	110-165
M	64(11)	480(9)	6.5(11)	270(10)			40(9)	145(13)
%	70	60	69	50			11	20
R	70-150		7.4-11.5				48-63	195-270
M	100(9)		9.5(9)				55(9)	235(13)
%	45		40				17	20
Mean metal content of reconnaissance data								
	30	-	5.5	1200	30	-	14	85

* M = Arithmetic mean; R = Range; % = Precision percent at the 95% confidence level

Number of samples in parenthesis.

TABLE 3-1 ANALYTICAL PRECISIONS OF STREAM SEDIMENT RECONNAISSANCE DATA FOR THE TYRONE AREA

(Calculated from replicate analyses of control samples of different metal content.)

3.3 RESULTS OF THE RECONNAISSANCE SURVEY OF THE TYRONE AREA

3.31 Introduction

Distribution maps of the metals Co, Cu, Fe (as Fe_2O_3), Mn, Mo, Pb and Zn, and of the major types of stream precipitate for the Tyrone area have been plotted on Figures 3 - 1 to 3 - 8 over a simplified geology. Ag, detection limit 0.2 ppm, was found in less than ten samples and the results have not been plotted.

Horsnail (1968) demonstrated that manganese precipitation in particular can have a marked influence on the distributions of several elements as shown by stream sediment reconnaissance surveys. Consequently, the nature of the stream precipitates, as observed during sampling in 1967, are described first.

3.32 Distribution of stream precipitates

The types of precipitates and stains in the stream courses at the point of sampling are plotted on Figure 3 - 8.

Manganese oxides. These are present in about 75% of all streams in the Tyrone area as dark grey or black precipitates on pebbles and fine sediments, varying in thickness from a thin film to a crust of 3 to 4 mm. They are most commonly found in free-running streams away from limestone areas, especially in the north and west.

Iron oxides. These are found as rusty stains, soft precipitates or ochreous gelatinous suspensions and seepage slimes. Their occurrence is less widespread than that of manganese oxides, being particularly concentrated in upland moors, although they are sometimes associated with poorly drained or boggy lowlands.

The thick gelatinous suspensions of iron oxide can obscure the manganese oxides, hence on the map the presence of both is assumed where only iron was seen. Nevertheless, in some streams where suspensions of this type are found, the underlying sediment is free from either ferruginous or manganiferous staining.

Calcium carbonate. Found in less than 2% of the streams in the Tyrone area. It occurs as a thick greenish grey, or rarely pinkish, encrustation on the stream bed, cementing the sediment. It is found over some limestone areas, principally west of Enniskillen, occasionally with an accompanying precipitate of manganese and/or iron oxides.

Peat staining This was noted in most streams in upland peat areas, as a brown humic stain on boulders.

3.33 Distribution of metals

3.331 Manganese (Fig: 3-4) Manganese shows the strongest patterns, with fairly extensive areas having levels of 5000 ppm or more, suggesting the influence of environmental enrichment effects (see Section 3-4). The data indicate background values generally ranging 500 - 2000 ppm, though rather higher levels (1000 - 2000 ppm) occur over Dalradian, Silurian and Upper Carboniferous bedrocks. Prominent patterns of high values (> 4000 ppm), mostly with accompanying Fe or Mn oxide precipitation in streams, are found:

i) widespread on the moors and rough grasslands over the Central Inlier and Dalradian schists of the Sperrins, north of Pomeroy. They extend east to Slieve Gallion and north beyond the Glenelly valley and the margin of the area. The highest concentrations occur mostly on the poorly drained hummocky country of the Low Sperrins, with rather lower levels elsewhere.

ii) over a small area of moorland north and west of Dromore, on schist and Old Red Sandstone bedrocks.

iii) over the schist moorlands on the Donegal border, near Castlederg.

iv) over the Upper Carboniferous clastics on Slieve Beagh, between Clogher and Rosslea.

There are also large areas where Mn levels are below 1000 ppm, and frequently below 500 ppm. These are found over Lower Carboniferous bedrock and in lowlands. Particular areas are:-

a) along the eastern border of the Tyrone area, extending westwards near Draperstown, and south west along the Clogher valley.
b) within a six mile radius of Enniskillen.
c) over Carboniferous bedrock from Kesh to Omagh.
d) less distinctly, on the Carboniferous outlier and schists, between Newtownsteward and Strabane.

There are very few streams with greater than 2000 ppm Mn in which no precipitation was observed in the stream bed. All the patterns of high manganese, including those apparently related to bedrock, lie within the precipitate zones. Conversely, most of the lowest levels (below 1000 ppm) are from streams with no observable precipitate. Streams draining the Old Red Sandstone near Enniskillen and Beragh, and the Lower Carboniferous near Caledon and Kesh, however, have precipitate and low manganese levels. Here, precipitation is usually slighter and confined to the coarser fractions.

3.332 Iron (Fig: 3-3) The iron distribution, expressed as Fe_2O_3, is similar to that of manganese, but there are a greater number of sporadic high values. Overall background ranges 1.5% to 7%, mean 5.3%. As with manganese, background over Dalradian, Silurian, Upper Carboniferous and Trias is rather higher (5% to 9%). Patterns of high background and anomalous concentrations are found:

i) in a belt from Draperstown in the northeast to Irvinestown in the southwest, particularly in the moorland areas of the Low Sperrins and near Dromore.

ii) on the moors near Castlederg.

iii) on Slieve Beagh, between Clogher and Rosslea.

iv) in the low-lying area by Upper Lough Erne, near Lisbellaw.

v) around Dungannon, from streams draining poorly drained or boggy inter-drumlin areas.

In part, the apparent sediment enrichment in the last two areas may be due to the ashing of fairly organic samples. They are accompanied by only marginal enrichments of manganese.

Areas where Fe_2O_3 contents of 4% or below coincide with those where manganese is also low:

a) over Lower Carboniferous rocks in the east, particularly near Draperstown, south of Dungannon and along the Clogher Valley.

b) over Old Red Sandstone between Enniskillen and Tempo and between Ballygawley and Sixmilecross.

c) over the Lower Carboniferous, between Kesh and Omagh.

d) less distinctly, on Dalradian and Carboniferous between Strabane and Newtownstewart.

Unlike manganese, however, the iron levels west of Lough Erne are not particularly low.

In most cases where the sediment Fe_2O_3 content exceeds 10%, iron oxide precipitation had been observed in the streams. However, not all samples from the oxide precipitate zones depicted on Figure 3-8 have this high Fe content, even where precipitation was observed. Iron oxide suspensions often have little effect on the sediment Fe content. Conversely, some sediments without observable precipitate have Fe contents above 10%.

3.333 <u>Cobalt</u> (Fig: 3-1) The cobalt distribution patterns are similar to those of manganese, but regional differences in level are less pronounced. Most samples lie in the range 20-40 ppm, with an overall mean of 30 ppm, with the higher levels particularly over Dalradian, Siluro-Ordovician and Upper Carboniferous rocks. The higher cobalt values (85 - 300 ppm) are almost exclusively coincident with raised manganese (> 5000 ppm), both for multi-sample patterns and isolated samples. For example, such patterns on the moors north of Pomeroy, near Dromore and near Castlederg coincide with those of manganese, but are smaller in extent.

Areas of low cobalt - 16 ppm and below - similarly follow low levels of manganese and iron, particularly around Draperstown, south of Dungannon and along the Clogher Valley. Elsewhere, the patterns of low Co are more diffuse and ill-defined.

3.334 Zinc (Fig: 3-7) The zinc distribution is again similar to that of manganese in outline. The overall background range is 60 - 120 ppm, mean 90 ppm, being lower over the Lower Carboniferous and parts of the Old Red Sandstone, and rather higher over Dalradian, Siluro-Ordovician and Upper Carboniferous bedrocks.

The samples with low manganese generally contain below 60 ppm Zn, whilst those greatly enriched in manganese, for example from the moorlands, tend to show a Zn enhancement to above the regional threshold of 230 ppm Zn (section 3.61), reaching probably anomalous levels (maximum 530 ppm Zn). This enhancement, in common with that of cobalt, is probably due to co-precipitation with manganese oxides in the streams.

Samples with anomalous Zn (up to 2200 ppm) but without markedly raised Mn occur in the mineralised district around Keady. Similarly, there is a region of high background Zn with moderate Mn extending east along the Derg Valley to the hill Bessy Bell.

3.335 Lead (Fig: 3-6) The lead distribution shows little areal contrast, with most samples in the range 20-50 ppm (mean 30 ppm). In this range, the analytical precision is very poor and it was found also that many of the background variations were merely analytical batch effects. The most important feature that has since been confirmed is the increase in level in the Keady area, reaching a peak value of 4000 ppm. There are few other samples with lead above threshold (145 ppm); they include those north east of Omagh on Mullaghcarn which lie in an area of high background (50 - 100 ppm Pb).

Low values, < 25 ppm Pb, are found along much of the eastern margin, especially near Draperstown and south of Dungannon.

3.336 Copper (Fig: 3-2) The copper distribution is rather different from those of the previous elements, showing less distinct patterns. The low abundance of the metal is the most important feature. Overall background range is 10-20 ppm, mean 14 ppm, with over 50% of samples containing 12 ppm or less. Samples with low Cu values are widespread, but are grouped particularly east of Aughnacloy, east of Enniskillen, between Kesh and Omagh, and over a wide area around Pomeroy, including much of the moorland region where manganese and iron are enriched.

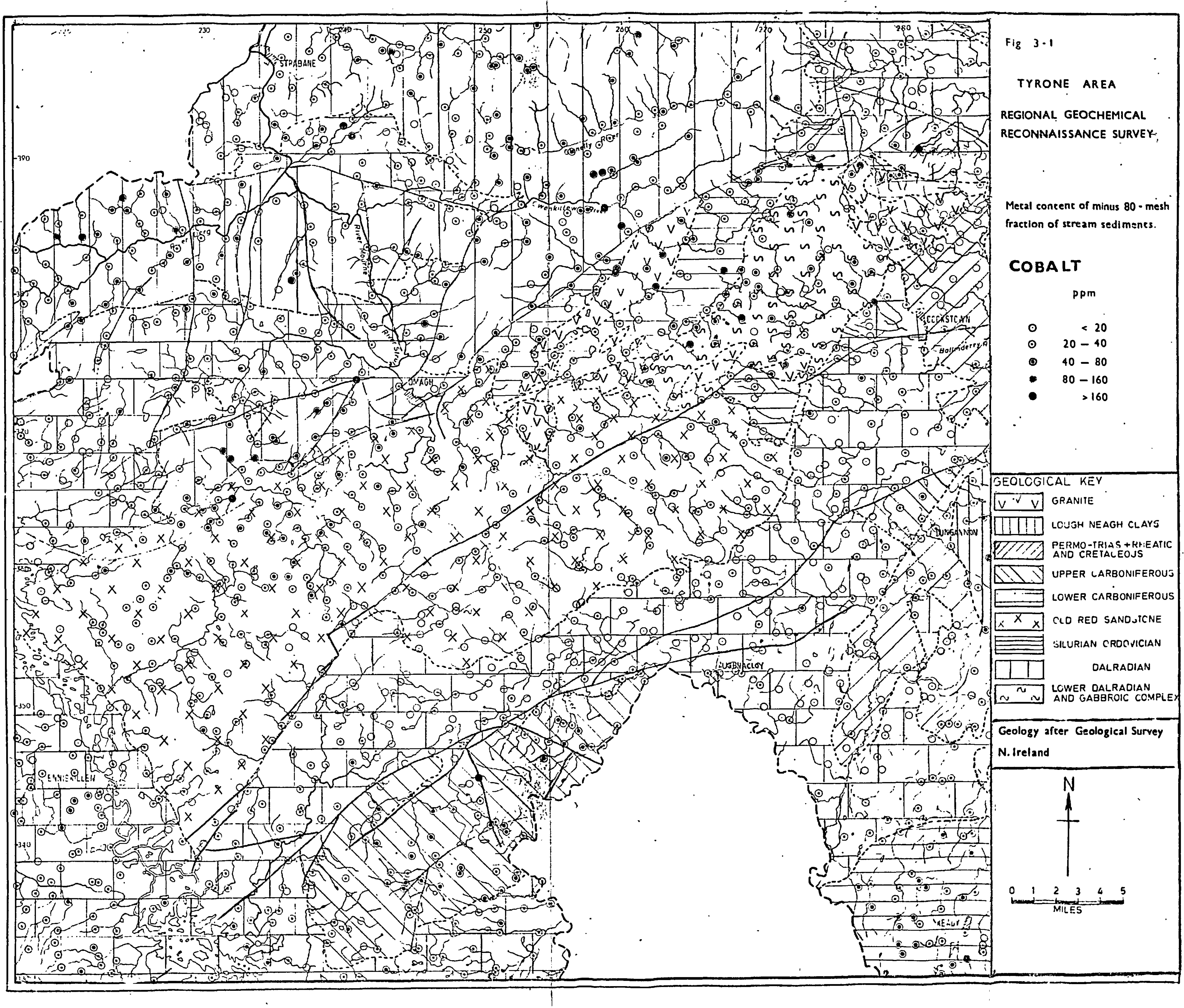


Fig 3-1

TYRONE AREA

REGIONAL GEOCHEMICAL RECONNAISSANCE SURVEY

Metal content of minus 80 - mesh fraction of stream sediments.

COBALT

Geology after Geological Survey N. Ireland

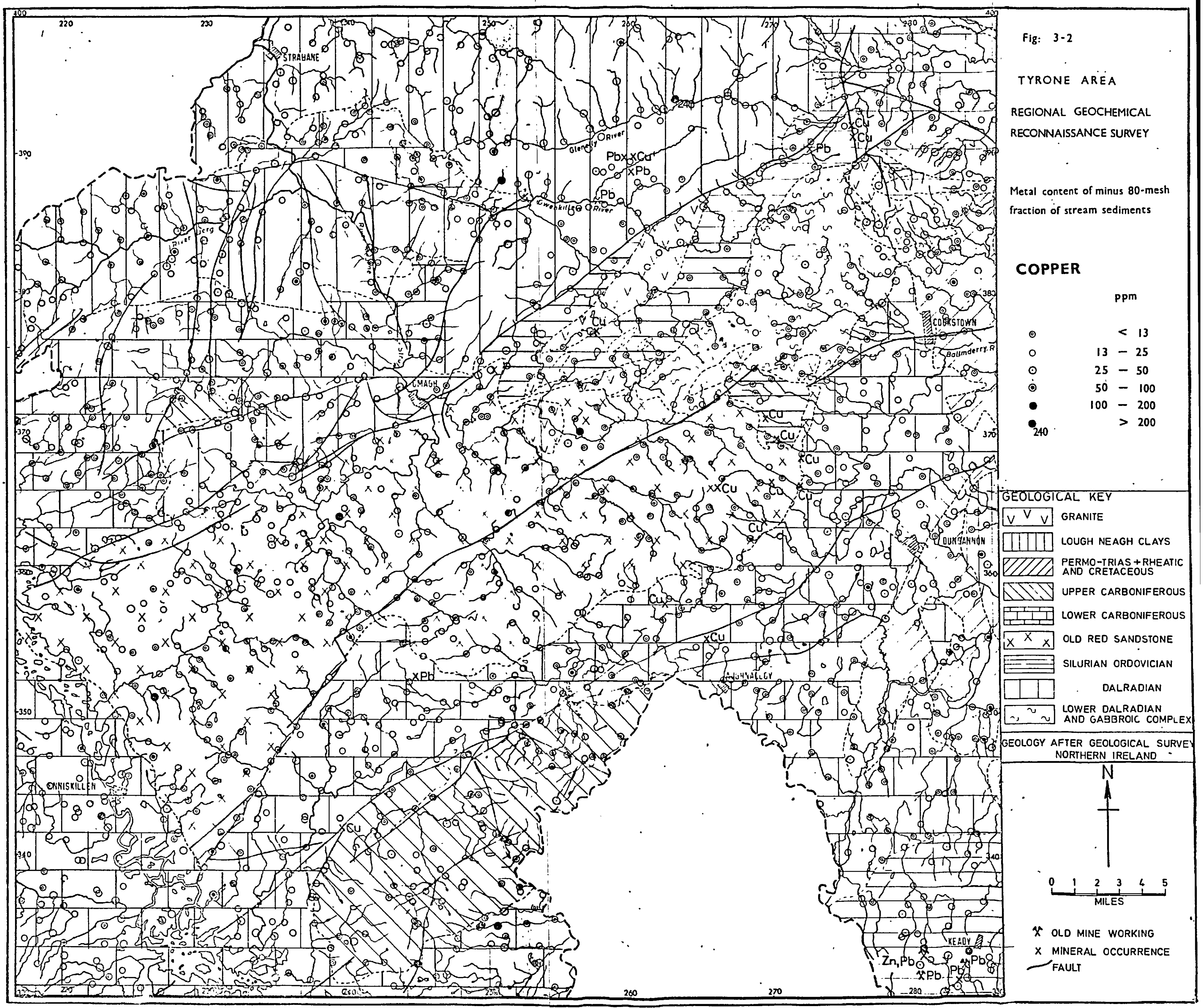


Fig: 3-2

TYRONE AREA

REGIONAL GEOCHEMICAL RECONNAISSANCE SURVEY

Metal content of minus 80-mesh fraction of stream sediments

COPPER

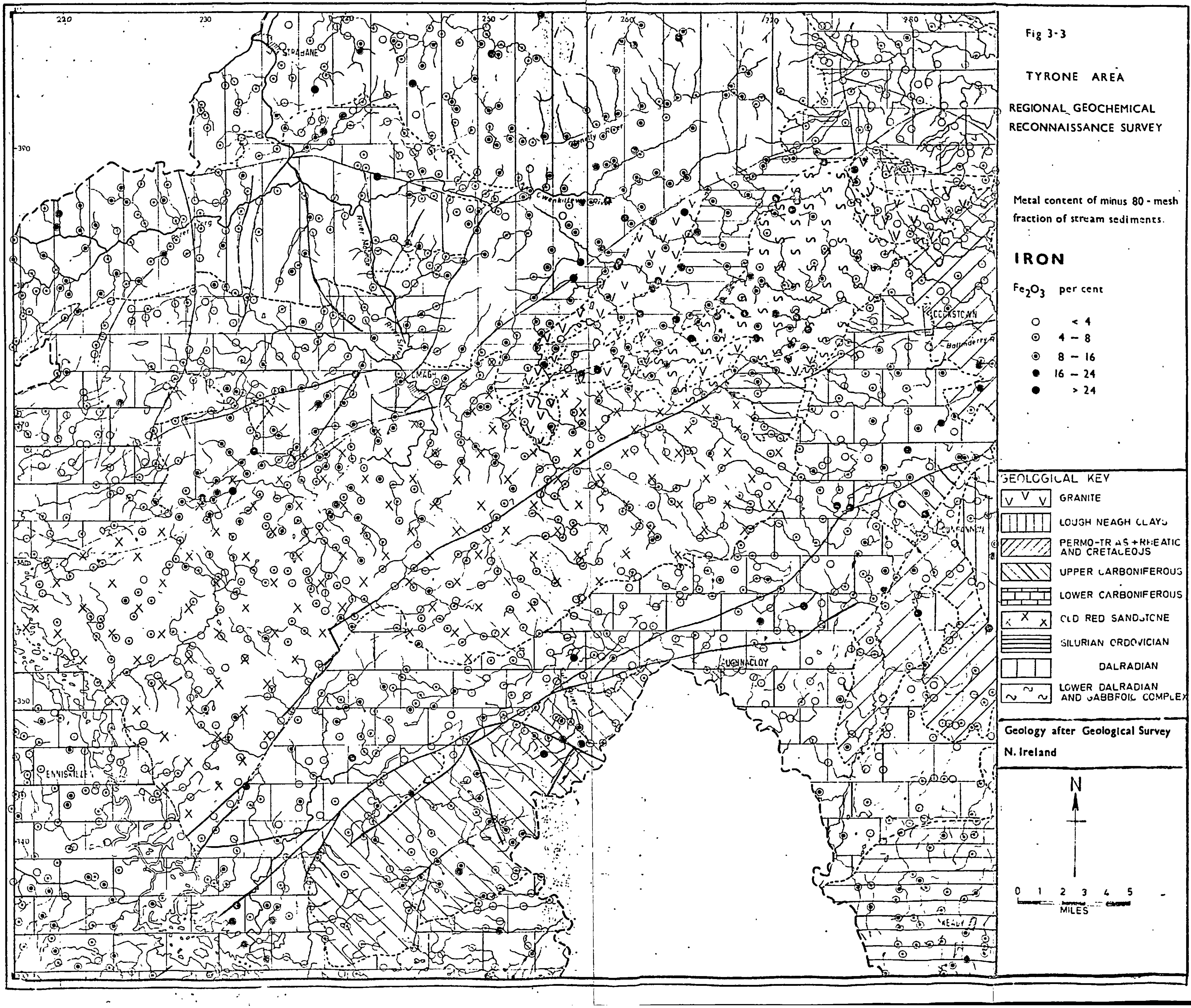


Fig 3-3

TYRONE AREA

REGIONAL GEOCHEMICAL RECONNAISSANCE SURVEY

Metal content of minus 80 - mesh fraction of stream sediments.

IRON

Geology after Geological Survey N. Ireland

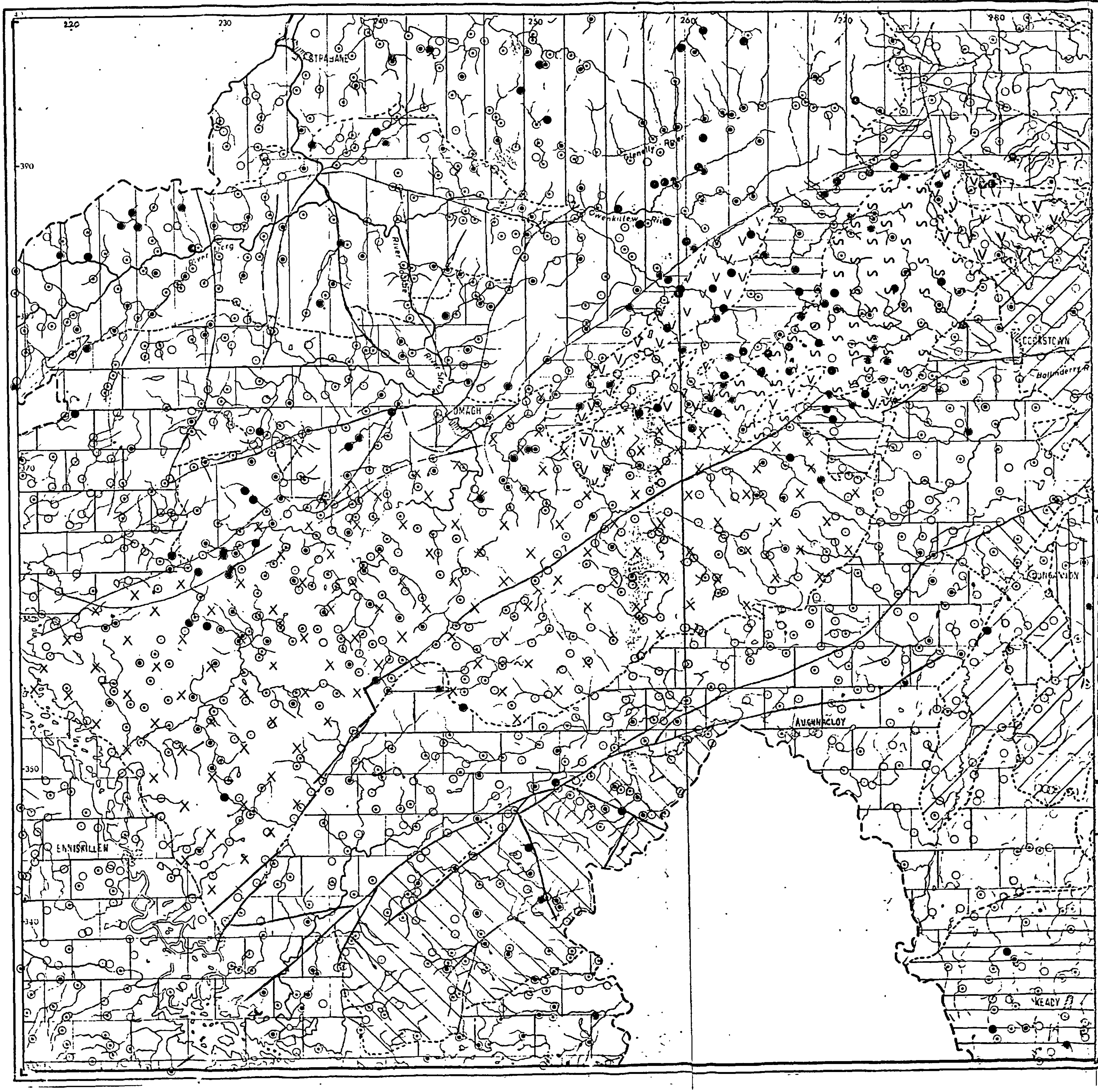


Fig 3-4

TYRONE AREA

REGIONAL GEOCHEMICAL RECONNAISSANCE SURVEY

Metal content of minus 80 - mesh fraction of stream sediments.

MANGANESE

per cent

○ < 0·11
⊙ 0·11 – 0·25
◉ 0·26 – 0·45
● 0·46 – 0·80
● > 0·80

GEOLOGICAL KEY

V V V GRANITE
▥ LOUGH NEAGH CLAYS
▨ PERMO-TRIAS + RHEATIC AND CRETACEOUS
▧ UPPER CARBONIFEROUS
▦ LOWER CARBONIFEROUS
X X X OLD RED SANDSTONE
▤ SILURIAN ORDOVICIAN
□ DALRADIAN
~ ~ ~ LOWER DALRADIAN AND GABBROIC COMPLEX

Geology after Geological Survey N. Ireland

N

0 1 2 3 4 5
MILES

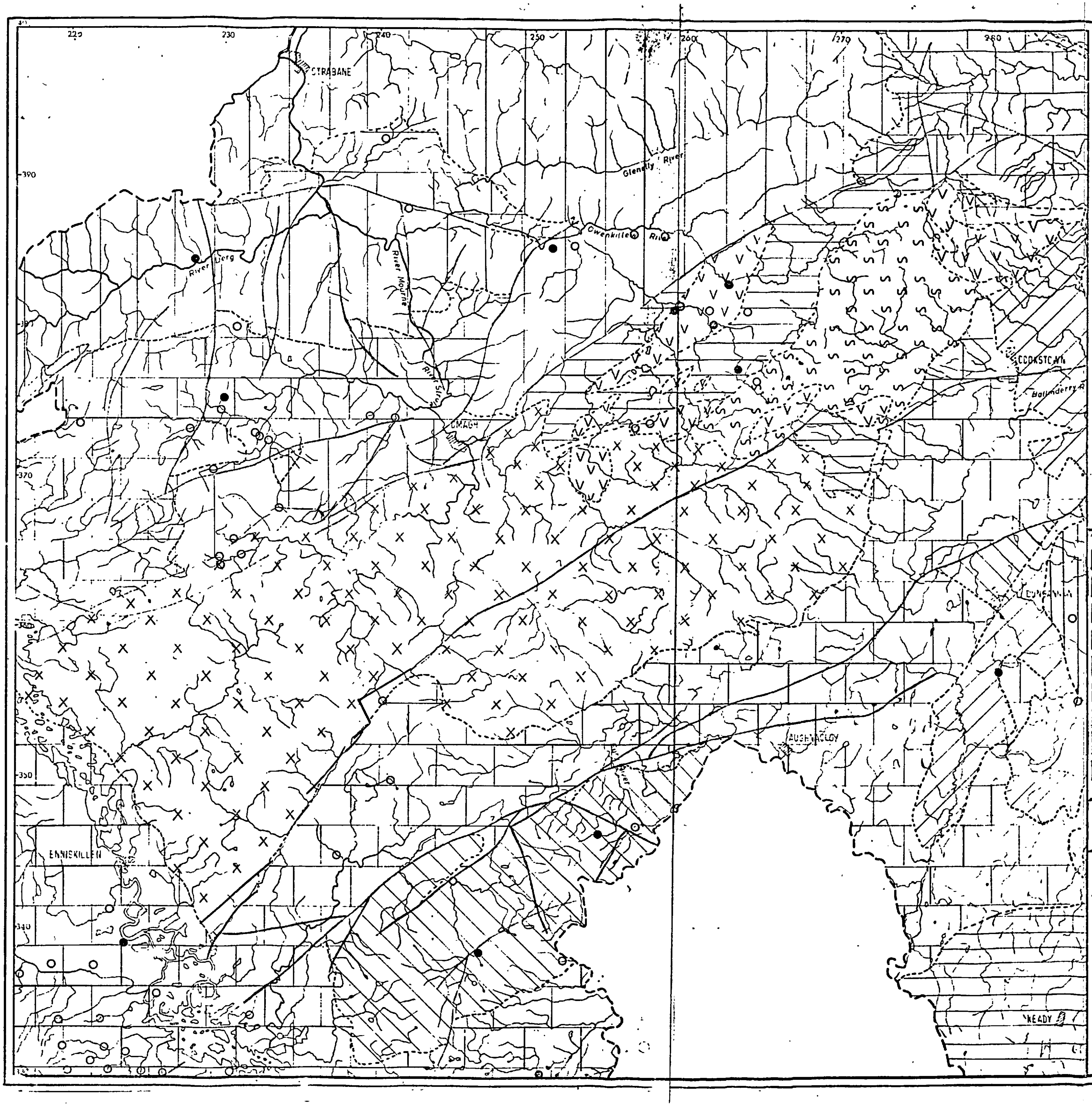


Fig 3-5

TYRONE AREA

REGIONAL GEOCHEMICAL RECONNAISSANCE SURVEY

Metal content of minus 80-mesh fraction of stream sediments

MOLYBDENUM

ppm

○ 2 - 5

● > 5

GEOLOGICAL KEY

GRANITE

LOUGH NEAGH CLAYS

PERMO-TRIAS + RHEATIC AND CRETACEOUS

UPPER CARBONIFEROUS

LOWER CARBONIFEROUS

OLD RED SANDSTONE

SILURIAN ORDOVICIAN

DALRADIAN

LOWER DALRADIAN AND GABBROIC COMPLEX

Geology after Geological Survey N. Ireland

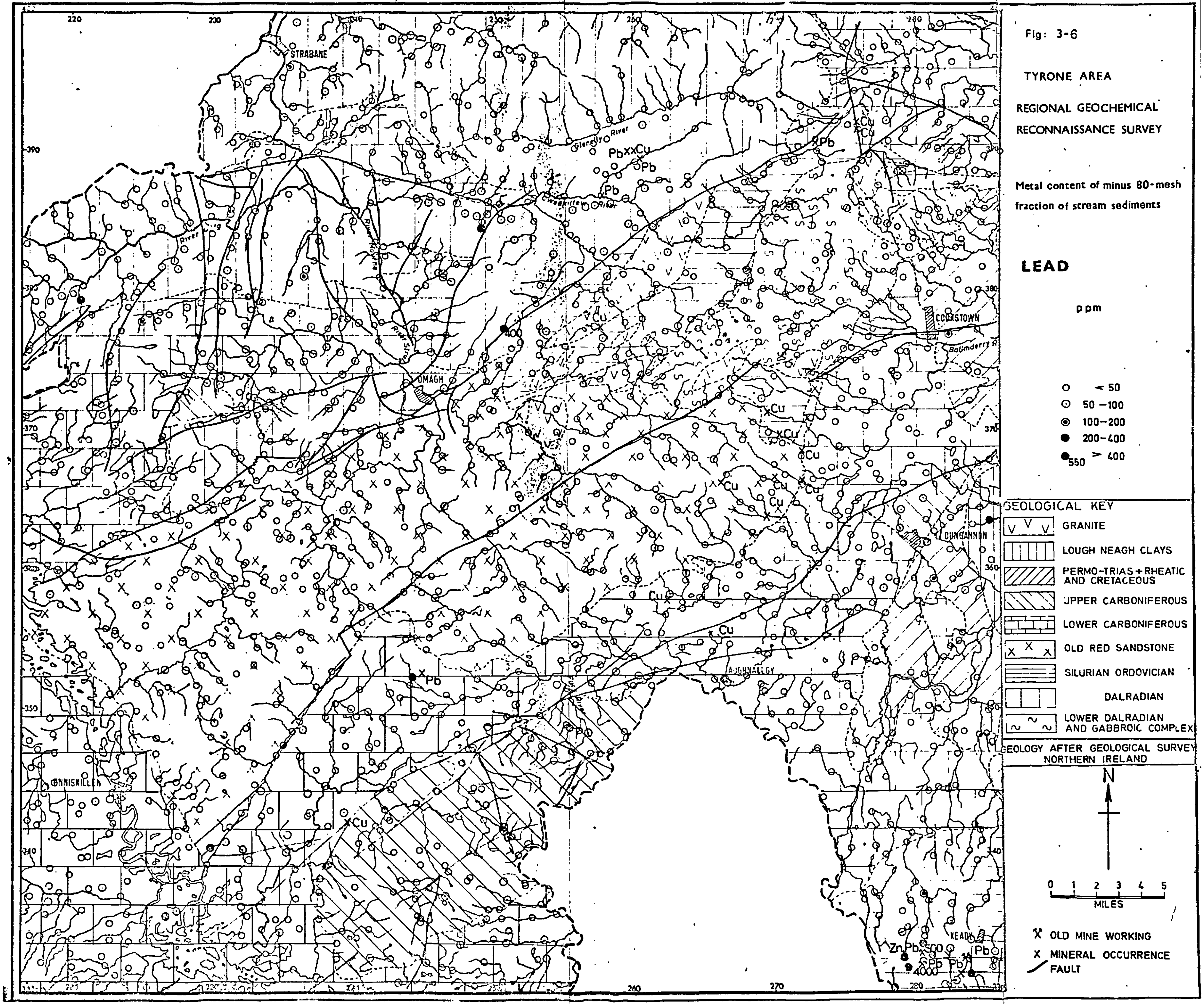


Fig: 3-6

TYRONE AREA

REGIONAL GEOCHEMICAL RECONNAISSANCE SURVEY

Metal content of minus 80-mesh fraction of stream sediments

LEAD

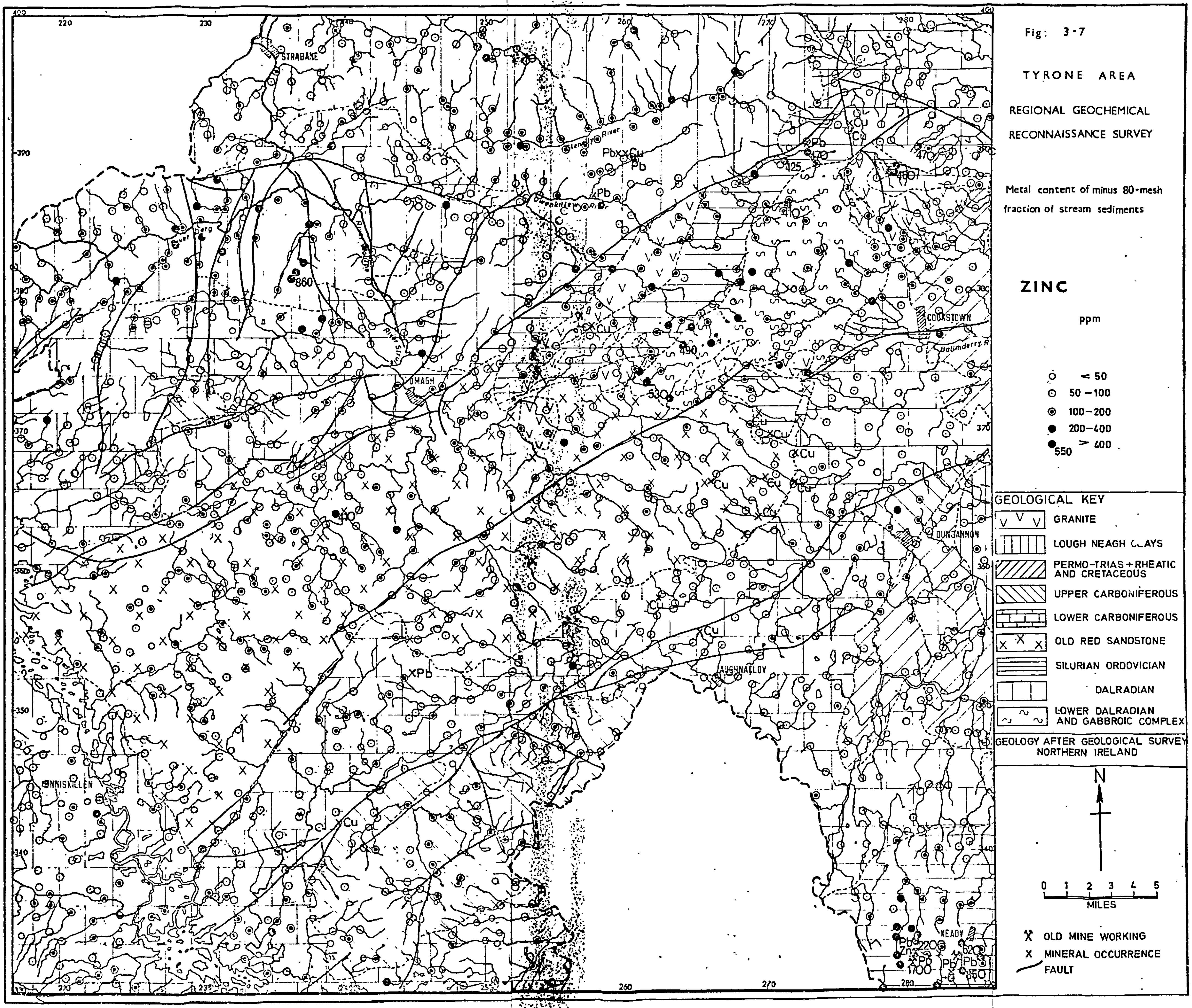


Fig: 3-7

TYRONE AREA

REGIONAL GEOCHEMICAL RECONNAISSANCE SURVEY

Metal content of minus 80-mesh fraction of stream sediments

ZINC

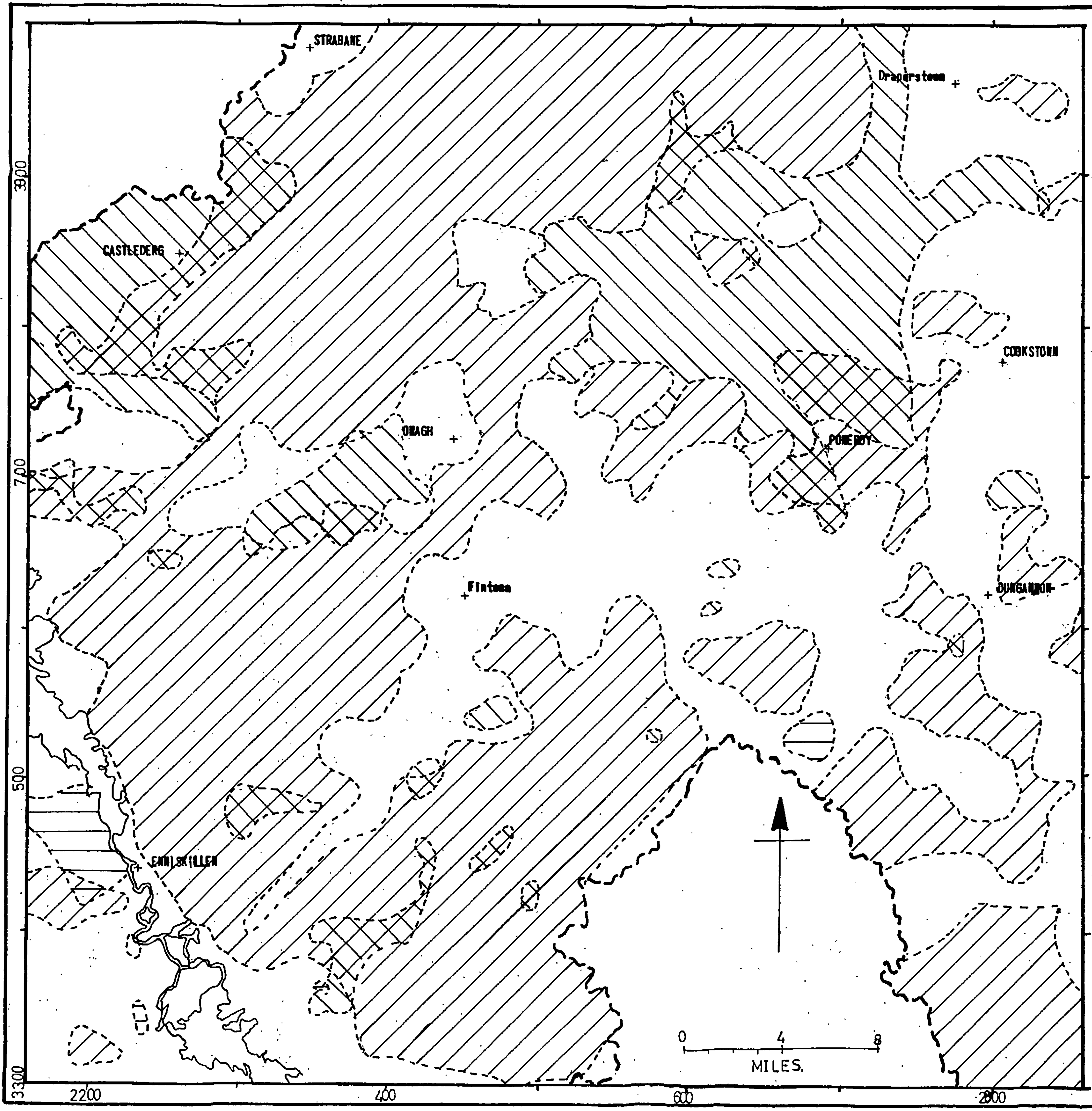


FIG : 3 - 8

TYRONE AREA.

DISTRIBUTION OF STREAM PRECIPITATES.

KEY.

▨ MANGANESE OXIDE.

▧ IRON OXIDE Probably with Manganese oxide.

▩ MANGANESE AND IRON OXIDES.

▤ CALCIUM CARBONATE.

Compiled from observations made during stream sediment sampling. 1967.

Higher values of copper (> 50 ppm) occur in the Keady area and sporadically in the Derg Valley, the High Sperrins and south east of Dungannon.

3.337 Molybdenum (Fig: 3-5) Over much of the area, the molybdenum level is below detection limit (2 ppm). Small areas with samples containing 2 - 10 ppm occur over the Calp limestones to the south of Enniskillen and near Drumquin, with sporadic samples in the moors north of Pomeroy and on Slieve Beagh.

3.4 PATTERNS RELATED TO THE SECONDARY ENVIRONMENT

As already indicated, strong, coincident patterns of raised values of Mn, Fe, Co and Zn, with accompanying stream precipitation of manganese and iron oxides, are widespread in the area. The association is similar to that recognised by Horsnail (1968) as being a function of certain physico-chemical conditions in the secondary environment. The patterns imply that these areas are characterised by mainly acidic soils of low Eh, subject to strong leaching. Under these conditions, chemical fractionation occurs, with metals leached from the soils and concentrated in the streams.

This interpretation is confirmed by the fact that the patterns are confined largely to uplands where the wetter, cooler climate favours such soil conditions.

To some extent, however, there appears to be some bedrock control over the distribution of the secondary environment patterns, for they are found almost exclusively over the siliceous Dalradian, Silurian and Upper Carboniferous rocks. On weathering, these rocks and the drift derived from them have given rise to coarse soils of low base status which have had little resistance to acid leaching. Thus, these areas are characterised by podzolic soils, either peaty or 'reclaimed' for agricultural use, with gleys and peaty gleys where poorly drained.

The strong manganese-iron patterns north of Pomeroy, for example, are almost coincident with the distribution of reclaimed podzolics and gleys - as defined by McAllister and McConaghy (1968) - developed over the hummocky moraines of the Low Sperrins (Fig: 2-6). The land in this region is very infertile, supporting poor grass and peat moor. Further north, the slightly weaker Mn-Fe patterns over the High Sperrins occur where peaty gleys and climatic peats are widespread. Indeed, all patterns of this type occur where these two soil associations are found.

Perhaps surprisingly, precipitation and enrichment patterns are much weaker over the Old Red Sandstone uplands which extend south west from Pomeroy almost to Enniskillen. Between Pomeroy and Ballygawley, for example, where climatic conditions are similar to those of the Low Sperrins, peaty podzols and climatic peats are extensively developed - but with gleys apparently less common than in the Sperrins. Relatively few streams in this area show very strong precipitation, although most sediments have high background Mn contents (1300 - 4000 ppm). It is possible that Mn is less abundant in soils derived from this bedrock or that its mobility through the soil sequence is restricted so that less metal is available for precipitation in the streams. A less probable alternative is that stream Eh-pH conditions are unfavourable for heavy oxide precipitation.

Iron oxide is enriched up to sixfold in stream sediments in areas by Lough Erne and near Dungannon. Often, but not always, there are associated iron seepage slimes. The sediments, mostly organic muds, are from sluggish streams and ditches draining lowland and interdrumlin bogs. Mn, Co and Zn are partially enriched in some of the sediments only, but not to the same extent as the iron.

This iron concentration appears to be an environmental effect. Many soils in these areas are gleyed, but since they are derived from calcareous till, pH remains near neutral. The sediment enrichment suggests that Fe is more mobile under these conditions and hence may migrate independently. The preferential concentration may be being increased by the presence of iron bacteria such as Leptothrix in seeps (Chapter 8.35), which are capable of precipitating iron oxides without a co-enrichment of Mn and other elements.

The enhancement of Fe relative to Mn in sediments over much of the Carboniferous limestone outcrop, particularly around Lough Erne, may be an expression of the differing mobilities of these elements. **More probably, it may be due to a real difference of abundance in the bedrock.**

3.5 PATTERNS RELATED TO BEDROCK GEOLOGY

3.51 General

For a number of metals, namely Fe, Mn, Co and Zn, differences in bedrock content are unlikely to be shown clearly by the sediment reconnaissance survey since they are strongly affected by the secondary environment. The patterns having the strongest contrast are, in fact, related to the weathering conditions, as described in the previous section. However, certain regional variations, discussed below, can be ascribed to apparent differences in the bedrock geochemistry.

The data have been grouped on Table 3-2 on the basis of the major bedrock units as differentiated on Fig: 2-2, with the exception of those for the Central Inlier region, where both bedrock and quaternary geology are very complex and streams have heavy oxide precipitation. Because of glacial smearing, no sediment is likely to be entirely derived from a specific bedrock source. However, where boulder clays are the main drift type, smearing is unlikely to be great.

3.52 Lower and Upper Dalradian

Sediments over much of the Upper Dalradian have raised levels of all elements, except Pb and Mo, in comparison with the other bedrock units. The enrichment is probably the result of environmental effects, with Mn and Fe oxides coprecipitating Co and Zn in the streams. In contrast, the sediments from the Lower Dalradian, away from the Inlier, are enriched in Zn only. This is clearly not the result of coprecipitation, since both Mn and Fe_2O_3 are not greatly enriched and the Zn levels are higher than such an effect could produce. Thus, the Lower Dalradian, particularly the Calcareous Group of the Derg Valley district, may be comparatively zinc rich. The previously unrecorded base metal mineralisation discovered at Barons Court during the later phase of this work (Chapter 4.4) may be related to this enrichment.

In the Central Tyrone Inlier region, where heavy oxide precipitation is found in streams, many of the highest Zn levels occur in Lower Dalradian areas. These may reflect a greater abundance of Zn available for leaching in bedrock and soil, but are more probably due to secondary environment enrichment alone.

3.53 Upper Dalradian

High Cu contents (40 - 100 ppm) over the Upper Dalradian of the Glenelly Valley may arise from the Green Beds or the many basic intrusives. Some - but not all - comparable rocks from the Dalradian of north east Antrim have shown fairly high Cu contents (G.S.N.I., 1966):

Epidiorite	150 ppm Cu
Hornblendic Green Bed	100 ppm Cu

Rocks containing similar levels of Cu may give rise to the raised sediment contents in the Sperrins.

Bedrock Unit	No. of Samples		Co ppm	Cu ppm	Fe_2O_3 %	Mn ppm	Pb ppm	Zn ppm
Permo-Trias	60	R*	3- 50	4-50	1.5-18.2	100-2200	6- 80	20-155
		M*	25	20	5.7	820	35	75
Upper Carboniferous Clastics	102	R	13- 80	5-30	1.9-22.0	100-7700	4- 60	35-185
		M	40	15	7.6	2100	40	90
Lower Carboniferous Limestone	340	R	3- 60	4-55	1.1-18.0	100-4000	2-100	20-145
		M	30	18	6.1	1195	40	80
Lower Carboniferous Clastics	220	R	3- 90	4-40	1.7-14.2	85-1%	2-100	25-195
		M	35	15	5.4	2030	40	85
Devonian(O.R.S.)sandstones	242	R	8- 65	4-65	1.3-17.0	100-6600	4-120	35-245
		M	35	17	6.7	1970	40	100
Devonian(O.R.S.) conglomerates	70	R	13- 50	4-27	1.5- 8.3	85-3750	2- 60	25-120
		M	30	13	4.4	1090	30	80
Siluro-Ordovician (Keady)	42	R	20-120	5-40	4.1-12.0	500-5000	10-150	70-250
		M	50	20	7.1	1600	60	135
Upper Dalradian	221	R	10-100	5-60	2.6-22.0	85->1%	2-115	30-205
		M	45	20	9.9	3240	40	100
Lower Dalradian	86	R	10- 70	5-50	1.3-11.0	300-6500	2- 95	50-335
		M	40	20	5.9	2020	40	140

*R = Range (Upper limit = mean + 2 standard deviations)
M = Geometric Mean

TABLE 3-2 METAL CONTENTS OF STREAM SEDIMENTS OVER MAIN BEDROCK UNITS, TYRONE AREA

3.54 Siluro-Ordovician

The sediments over the Siluro-Ordovician outcrop in the south east appear slightly enriched in most elements in comparison with those from other bedrocks. The boundary of this pattern is particularly sharp to the north, and lies very close to the contact with the Carboniferous. This coincidence could be taken as evidence for there being little glacial smearing in drumlin areas but equally, it may be the result of a largely southward glacial flow counteracted by north draining streams.

Certain of the streams draining this south east area have anomalous levels of Cu, Pb and Zn, arising from mineralisation or contamination from old mine workings. These are discussed in Section 3.62.

3.55 Old Red Sandstone

Sediments from small areas to the north east and south west of the Old Red Sandstone outcrop are appreciably lower in all elements, particularly Cu, than the remainder of the formation. These areas correspond approximately to the outcrop of conglomerate facies.

3.56 Lower Carboniferous

Lower Carboniferous clastic rocks, whether of the basal transgressive phase or occurring as facies variations within the Calp, appear low in several elements, particularly Cu. Especially low values (4-12 ppm Cu) occur south east of a line Dungannon to Clogher, near Draperstown and near Newtownstewart. The limestones and calcareous facies, however, generally give rise to rather higher sediment metal contents (for example, 10-25 ppm Cu). Manganese tends to behave differently, being relatively raised over the clastics, partly as a result of oxide precipitation in streams. Where source rocks are calcareous, Mn mobility is reduced and stream precipitation unusual. For both clastics and limestones, however, sediment metal contents in the Lough Erne area appear slightly enriched relative to sediments from similar bedrocks elsewhere.

3.57 Calp Limestone

Part of the Calp (middle) limestone, south west of Enniskillen, may be molybdeniferous.

3.58 Permo-Trias

Oxide precipitation in streams is mostly very slight in areas underlain by Triassic rocks and sediments are low in Mn, Co and Zn. Soils derived from these rocks are already known to be deficient in several trace elements, notably boron and molybdenum (McConaghy and McAllister, in Symons, 1963).

3.6 PATTERNS OF SIGNIFICANCE TO MINERAL EXPLORATION

3.61 Introduction

Base metal mineralisation may be indicated where sediments contain anomalous levels of one or more of Cu, Pb or Zn. By definition the upper limit of background variation, or threshold, and the 'probably anomalous' level are taken as equal to two and three standard deviations above the geometric mean respectively. Values for these can thus be calculated for all the data (excluding obviously anomalous samples) and used as a guide to establish the major exploration targets within the survey area. Where there are contrasting bedrock and/or environmental conditions, however, the threshold and anomaly levels can vary from place to place. For example, in the Tyrone area probably anomalous levels for Zn, calculated for major bedrock units away from the Central Inlier, vary from 136 ppm over Devonian conglomerates to 430 ppm over the Lower Dalradian, in comparison with the areal level of 300 ppm (Table 3-3).

It is important to consider the effects of the secondary environment on Zn, since it is possible that there are a number of false anomalies due to coprecipitation of the metal with manganese. By comparing the analytical data with the distribution of obvious precipitation on the stream bed, it can be estimated that the major environmental effects are liable to be strongest when Mn exceeds 2000 ppm. Threshold and probably anomalous levels have been calculated for samples with this level of Mn (Table 3-3) which suggests that in areas of heavy precipitation threshold is raised to 330 Zn and probable anomaly to 425 ppm Zn. Pb and Cu levels are little affected; hence in such areas an association of anomalous Zn with raised Pb and/or Cu in stream sediments is more likely to indicate mineralisation than anomalous Zn alone.

It is emphasised that these are necessarily only statistical estimates, to be used as a guide to selecting targets for

	No. of Samples	Cu ppm			Pb ppm			Zn ppm		
		*M.	*T.	*A.	M.	T.	A.	M.	T.	A.
Permo-Trias	60	20	55	75	35	80	105	75	145	180
Upper Carboniferous Clastics	102	15	30	40	40	65	75	90	185	235
Upper Carboniferous Limestones	340	20	55	70	40	100	130	80	145	180
Lower Carboniferous Clastics	220	15	35	70	40	100	130	85	195	230
Devonian(O.R.S.)sandstones	242	15	35	50	40	120	160	100	245	320
Devonian(O.R.S.)conglomerates	70	15	65	90	30	60	75	80	115	135
Siluro-Ordovician (Keady)	42	20	35	45	60	140	180	135	260	320
Upper Dalradian	221	20	60	85	40	115	155	100	205	260
Lower Dalradian	86	20	50	70	40	95	120	140	335	430
Samples with over 2000 ppm Mn	327	15	55	75	40	110	145	145	330	425
Regional	1383	15	55	75	35	105	140	90	230	300

* M = Geometric Mean; T = Threshold; A = Probably Anomalous

TABLE 3-3 THRESHOLD AND ANOMALY LEVELS FOR RECONNAISSANCE DATA, TYRONE AREA further investigations. Those described below are the more important anomalous samples.

3.62 Keady area

The raised levels of Zn, Pb and Cu in stream sediments in a 25 square mile area near Keady, County Armagh, are clearly due to the known mineralisation. Many of the single anomalies probably result from contamination from past mining, with the streams draining the old spoil heaps. For example, sample 0016 drains Derrynoose mine and sample 6501 drains College mine:

Sample No.	Grid reference	Cu ppm	Pb ppm	Zn ppm
0016	2841 3318	40	4000	1700
6501	2806 3336	170	500	2200

Streams near Clay Lake, south of Keady, are of interest, with two sediments being anomalous in Zn and Pb:

Sample No.	Grid reference	Cu ppm	Pb ppm	Zn ppm	Mn ppm
0041	2840 3312	25	300	850	5000
6504	2841 3335	100	500	620	1000

The concentrations are noticeably much lower than in the contaminated samples, presumably because much of the sediment of the latter is derived directly from the spoil heaps. Sample 6504 is from the stream draining Clay Lake and may be contaminated by the nearby railway. Sample 0041 is from a stream feeding the lake. There are no obvious contaminants and no mineralisation has previously been recorded from its catchment.

3.63 Midland Valley

3.631 Fintona Only one of the trace occurrences of Pb or Cu as defined by the Geological Survey of Northern Ireland (G.S.N.I., 1970) appears to have been detected by the current survey. This is the Pb occurrence south of Fintona, apparently on the line of an Armorican fault in the Lower Carboniferous:

Sample No.	Grid reference	Cu ppm	Pb ppm	Zn ppm
2053	2443 3524	30	300	135

Lead is above local threshold (100 ppm) in this sample alone. The stream has not been resampled to confirm the anomaly.

3.632 Lisbellaw The threshold and anomaly levels for the conglomerate facies of the Old Red Sandstone are much lower than for most other bedrocks. Thus, some samples, which may be considered only high background on neighbouring formations, may be anomalous locally. Near Lisbellaw, a sample in an Armorican fault area is marginally anomalous:

Sample No.	Grid reference	Cu ppm	Pb ppm	Zn ppm
1925	2300 3403	55	130	145
Local threshold		25	60	115
Local anomaly		35	75	135

(The stream has not been resampled to confirm the anomaly.)

Weak anomalies of this type may be significant in these areas where metal abundance is low, especially when thick drift is diluting clastically dispersed metal and local conditions restrict hydromorphic dispersion. Consequently, they must be considered carefully in any detailed exploration programme.

3.633 Low Sperrins This area is characterised by heavy iron and manganese precipitation in the streams. Most sediments contain over 2000 ppm Mn and have raised Zn contents. Threshold and probable anomaly limits were calculated for all samples containing over 2000 ppm Mn and the levels for Zn were found to be higher than those calculated for the individual bedrock units (Table 3-3). Several sediments from the Low Sperrins have probably anomalous Zn contents when calculated on this basis (Table 3-4). However, in no sample does the Zn content greatly exceed this somewhat arbitrary anomaly level. Hence, in view of the very high Mn concentration in these sediments, it is probable that the raised Zn levels result from leaching and coprecipitation and do not relate to mineralisation.

3.634 Derg Valley and Barons Court A pattern of raised Zn without correspondingly raised Mn or Fe_2O_3 in sediments over the Lower Dalradian of the Derg Valley has been mentioned previously (section 3.52). There is no particular focus for this local increase, except in the east. Streams draining the hill Bessy Bell in the Barons Court estate contain above threshold and anomalous Zn, with threshold Pb and Cu in one sample (Table 3-5). Although some enhancement of Zn may be due to coprecipitation with Mn, the amount is rather greater than would be expected from secondary enrichment alone, even when the locally increased abundance of the metal is considered. The threshold levels of Pb and Cu in sample 630 are significant since these metals are not normally affected by secondary enrichment in streams.

Sample No.	Grid reference	Cu ppm	Pb ppm	Zn ppm	Mn %	Fe_2O_3%
940	2617 3737	5	5	555	1	14.0
2374	2788 3892	10	60	490	> 1	9.0
2379	2732 3904	30	85	475	1	8.5
2464	2809 3912	8	40	475	>1	6.4
887	2641 3765	7	85	445	>1	>30.0
Threshold*		50	90	330		
Probably anomalous*		70	120	430		

*Levels calculated for all samples containing over 2000 ppm Mn.

TABLE 3-4 STREAM SEDIMENT SAMPLES CONTAINING PROBABLY ANOMALOUS ZINC FROM THE LOW SPERRINS, COUNTY TYRONE
(Data on minus 80-mesh fraction).

Sample No.	Grid reference	Cu ppm	Pb ppm	Zn ppm	Mn ppm	Fe_2O_3%
628	2369 3824	20	85	350	3000	11.4
629	2365 3819	35	50	340	1300	4.7
630	2362 3814	50	100	860	4500	10.7
717	2384 3785	14	40	270	2000	6.0
719	2369 3778	25	60	225	1300	9.8
Threshold*		50	90	330		
Probably anomalous*		70	120	430		

*Levels calculated for all samples containing over 2000 ppm Mn.

TABLE 3-5 STREAM SEDIMENT SAMPLES FROM BARONS COURT, COUNTY TYRONE (Data on minus 80-mesh fraction)

3.635 Glenelly Valley Sediments derived from the Upper Dalradian schists of the Glenelly Valley in the Sperrins appear enriched in copper (40 - 240 ppm). Copper is normally unaffected by secondary enrichment processes; thus the Cu source could be mineralisation, although the absence of accompanying base metals makes this unlikely. A more probable source of Cu may be the Green Beds or the many basic intrusives of the valley, as suggested previously (section 3.53).

3.636 Dromore One sample near Dromore, Co. Tyrone (Grid reference 2391 3644) is probably anomalous in Zn (405 ppm), Cu (100 ppm) and Pb (130 ppm). The ashed sample contained 20% Fe_2O_3. The sediment, an organic mud taken from a narrow ditch may have been contaminated by a nearby roadway. Samples from adjacent streams show no similar concentration of these metals.

3.637 Conclusion The most promising of the above patterns are those near Keady and at Barons Court. None lie in the geologically favourable areas, the Armorican faulted Carboniferous - Old Red Sandstone contacts, although Barons Court is near a cross fault of this age, cutting the Lower Dalradian. On the basis of the survey results and the known geology, there does not appear to be any evidence for major base metal mineralisation in the Tyrone area similar to the recent discoveries in Eire. This does not, of course, preclude the existence of such mineralisation.

3.7 PATTERNS OF SIGNIFICANCE TO AGRICULTURE

3.71 Introduction

The assessment of the agricultural significance of the trace element distribution is one of the most important aspects of the interpretation of regional geochemical data. In the British Isles, reconnaissance surveys have successfully delineated areas where toxicity or deficiency conditions, associated with several metals, affect plants and animals. It has been found that variations in stream sediment metal contents can reflect similar variations in soil metal contents except where obvious secondary enrichment is occurring in streams. Therefore, areas in which abnormally high or low soil metal contents may give rise to trace element imbalances can be indicated by the metal distributions shown by the stream sediments.

3.72 Deficiency conditions

3.721 Copper Thornton (1968) showed that simple copper deficiencies in cattle and seedling Sitka spruce occurred in Dorset, within an area delineated by a pattern of low Cu levels (10 ppm) in stream sediments.

In the Tyrone area, there are very extensive regions where the Cu content of sediments is less than 10 ppm. They are found over most bedrocks, but especially over the Lower Carboniferous, the Devonian conglomerates and much of the Central Inlier, north of Pomeroy. To some extent, the low values appear to occur in the regions of better drained, often arable, land. If the soil content is approximately that of the sediments, latent deficiency conditions at least may be widespread.

3.722 Cobalt, manganese and zinc

Cobalt Many soils of the Tyrone area are known to be cobalt deficient (McConaghy, 1950) and this is partially borne out by a fairly low level in stream sediments over much of the area. Sediments with below 16 ppm Co were shown by Webb (1964) to delineate areas over granite in Eire where a moderately sporadic incidence of cobalt pine is found in sheep. Sediment patterns of this level of Co are found about Cookstown, east of Aughnacloy, along the Clogher valley and over parts of the Old Red Sandstone outcrop, suggesting that deficient soils may occur in these areas.

Manganese and zinc Patterns of low levels of Mn and Zn in stream sediments have been related to the occurrence of deficiency diseases in cereals and livestock in parts of England and Wales (Thornton, 1968). Mn deficiencies, for example, are linked with 'grey speck' in oats and, tentatively, with bovine infertility. The disorders can occur where soil metal contents are low and also where soils are calcareous or limed, since the mobility and availability of Mn in particular is restricted in a neutral to alkaline environment.

Low levels of Mn ($<$ 700 ppm) and Zn ($<$ 40 ppm) occur in sediments in several parts of the Tyrone area, mainly in the east. They indicate areas where soil metal contents are low and may be deficient, particularly if overlimed.

The patterns of low Co, Mn and Zn occur mainly where streams are free of Mn oxide precipitation. In other areas, where such precipitation is common in streams, the sediment metal contents may be enriched relative to the mean soil contents, thus camouflaging areas of potential deficiency. Indeed, the lowest soil metal contents are probably associated with patterns of strongly enriched sediments, since these can reflect the widespread occurrence of acid leaching conditions. Combatting soil acidity by heavy liming in such areas may well aggrevate the situation further by reducing metal availability.

3.723 Multi-element deficiencies Low levels of most of the elements studied tend to occur together, either inherited from the parent material or as a result of leaching. Consequently, the occurrence of multi-element disorders must be considered, as well as those of single metals, since effective remedial treatment requires the recognition of all deficiencies. Thus, in the east of the area, where soils over the Perm-Trias are already known to be deficient in Mo and B (McConaghy and McAllister in Symons, 1963), the sediment results indicate that there are also low abundances of Mn, Co, Zn and, in part, Cu, which may have an agricultural significance.

3.73 Toxicity conditions

3.731 Molybdenum Toxic levels of molybdenum in soils are readily detected by regional reconnaissance surveys. Thus, the general absence of detectable Mo (2 ppm), apart from a small area in Fermanagh and some sporadic samples elsewhere, suggests that no real problem exists in the Tyrone area.

The two known occurrences of molybdeniferous soils, near Kesh and in the Sperrins, were not located by the drainage survey. Hence, the affected areas probably represent only a small proportion of any individual catchments and cannot contribute much sedimentary material.

Samples from a small area south west of Enniskillen have Mo ranging from 2 to 8 ppm. If these levels reflect those in the soils and pasture, a minor Mo-toxicity problem may be present in the immediate vicinity.

3.732 Lead and zinc Toxic quantities of these metals may be present in soils in mineralised areas, particularly in the vicinity of old mines. These conditions may exist in the Keady area, where sediments show high levels of both Pb and Zn. Since the ore minerals seem to be confined to the lodes and not replacing country rock, only the land adjacent to the old workings or immediately downdrift of a lode outcrop is liable to be affected.

3.74 Hypomagnesaemia

Hypomagnesaemia is particularly prevalent over the Dalradian schist areas, especially in a belt stretching north east from Castlederg to Limavady (north of the Tyrone area). In comparison with the relatively disease-free Carboniferous to the south, the schists are richer in most metals - except Ca, Mg and associated elements (McAllister, 1969, pers comm.). No conclusions can be drawn from these data, but with analyses for more elements over a wider area becoming available, a more detailed study into the problem will be possible.

3.8 STREAM CONTAMINATION

During the reconnaissance sampling programme, it was noted that very many streams contained domestic, agricultural or industrial refuse or effluent. It was found that water-courses were commonly used for the disposal of all types of waste, including: bricks and cement; fertilizer; metallic and non-metallic domestic rubbish; oil, petroleum and industrial chemical effluent; quarry waste and spoil from earthworks; road drainage; untreated domestic and agricultural sewage, including seepages from silage; machinery. The pollution was greatest near urban areas but could be serious even in remote rural areas. The extent of the problem in a dominantly agricultural economy is startling. Its ultimate impact on public health, via the destruction of amenities, the disturbance to freshwater life and contamination of water supplies may become quite considerable. Yet this form of pollution is only minor in comparison with that in industrial environments elsewhere in the British Isles.

During sediment sampling, every effort was made to avoid obvious contaminants. Consequently, only very few samples in the Tyrone area appear to be affected. Excluding those near old mine workings near Keady, the most strongly contaminated sample came from a stream at Aughnacloy, which contained 1350 ppm Zn, 1300 ppm Pb, 215 ppm Cu, and 2.0 ppm Ag. It was found that the sample had been collected in error from an old stream channel, then full after rain, which normally acted as a collecting area for a small seepage from a disused railway and new factory development. The metals appeared to be concentrated locally in an organic, slightly ferruginous, sediment. The sediment from the main stream, at the channel outflow, contained less than 20 ppm of all three metals. A similar sample near Cookstown was also enriched by contamination, but not to the same extent.

Few samples, therefore, were contaminated. The two mentioned, however, demonstrate the scavenging power of organic matter and iron oxides and their ability to retain potentially toxic quantities of metals and perhaps other chemical species.

3.9 PROBLEMS SELECTED FOR FURTHER INVESTIGATION

3.91 Mineral exploration

The anomalies of importance appear to be those in the area of known mineralisation near Keady and those on the Barons Court estate, near Newtownstewart. In both instances, sediments have high metal contents suggesting previously unknown mineralisation within the catchments. These anomalies were followed up and the results are presented in Chapter 4.

3.92 Agriculture

Where oxide precipitation is occurring in streams, the sediment-soil correlation for several elements, such as Zn, is poor and may be inverse. Copper, however, is thought to be unaffected by this process, so that the correlation is expected to be direct and close. In the Tyrone area, the sediments indicate that if this is so, soils over much of the region may be deficient in Cu, with consequent effects on plant and animal health. Joint investigations have been made into this soil - sediment correlation for Cu and Zn in the same catchments and the results are given in Chapter 5. Similarly, the Mo status of soils near Enniskillen, Drumquin and in the Sperrins have been studied, since even minor patterns of this element may have a local importance.

3.93 Soil chemistry

The most prominent aspect of the regional geochemistry of the Tyrone area is the influence of the secondary environment on the elements studied. Over much of the area, the precipitation of Mn and Fe oxides in the streams has distorted the element distribution patterns shown by the stream sediments to represent, in part, the weathering conditions in the catchments rather than the bedrock geochemistry. It is of importance, therefore, to understand the processes of soil chemistry and formation involved so as to interpret such patterns more accurately. Detailed investigations have been made in Central Tyrone where precipitation is strongest and such processes most active. These studies and their results are considered in Chapters 6 to 8 inclusive.

CHAPTER FOUR GEOCHEMICAL ANOMALIES RELATED TO MINERALISATION

4.1 INTRODUCTION

The regional reconnaissance survey showed several anomalies possibly indicating base metal mineralisation. These fall into three groups:

i strong anomalies, in one or more metals, on both local and regional scales, near Keady and at Barons Court (near Newtownstewart).

ii weak anomalies, such as those near Dromore and Lisbellaw.

iii apparently false anomalies, with samples enriched in Zn as the result of coprecipitation with Mn and Fe oxides.

Two of the major anomalies of the first group were followed up, that at Barons Court in more detail, and the results are presented in this chapter. The weak anomalies were not studied, but the origins of the false anomalies have been considered in depth in Chapters 6 to 8.

4.2 SAMPLING AND ANALYSIS

4.21 Sampling

The strong anomalies were followed up by more detailed stream sampling in the vicinity of the reconnaissance discovery samples. Subsequently, all anomalous streams, their tributaries and associated seepages were sampled to delimit the source areas as accurately as possible. The soils at Barons Court were collected using a hand auger. Soil and water pH were measured by the method detailed in Appendix A.

4.22 Field Analysis

Sediment sampling was guided by rapid field analysis for cold extractable heavy metals (cxHM). The method is given in Appendix A. However, where there is heavy Mn-Fe oxide precipitation in the streams, the use of such procedures is limited. Coprecipitated metals, principally Zn, are readily extractable by the reagents and give high readings even in background areas. Quantitative field estimation of the heavy metal content is time-consuming and, since it depends more upon the secondary oxide concentration than the proximity of mineralisation, of little use. Precipitates in the streams near Pomeroy, for example, contain up to 1000 ppm Zn, mostly 'cold extractable', yet no related mineralisation is known.

It was noted, however, that coprecipitated heavy metals react relatively slowly, whereas those derived from mineralisation react immediately. Therefore, it was possible to make a semi-quantitative estimate of the significant cxHM content from the colour of the solvent phase (varying green-purplish red) after shaking for one second only, rather than for 15 seconds. Such an estimation, expressed as low, medium, high, etc., was used merely as a guide to sampling, prior to total metal analysis in the laboratory.

The optimum procedure was found to be as follows:

1. Choose suitable samples, preferably from the area of operation, of known total heavy metal content as controls, for testing that each batch of reagents is correct.

2. Check the reaction of the original unsieved discovery sample to cxHM analysis.
3. Test that a fresh sample from the discovery site reacts similarly, bearing in mind that the cxHM content of the original may have decreased on drying. Any major differences in behaviour may affect interpretation of subsequent cxHM analyses.
4. Use cxHM analysis only as a guide to sampling, continuing collection well beyond indicated cut-offs.

It was found that the limits of the anomalies so determined by field cxHM analysis were little different from those later given by total metal analysis. The main discrepancies occur when cxHM:

i overestimates, where there is heavy oxide precipitation, particularly on coarse particles in more rapidly flowing streams;

ii underestimates metal in precipitate-free organic sediments.

4.23 Laboratory Analysis

All samples, sediments and soils, were dried and sieved, and the minus 80-mesh fraction analysed in the laboratory for total Cu, Pb, Zn, Mn and Fe by atomic absorption. The leaching procedure, after a standard nitric/perchloric acid digestion, was modified to ensure complete solution of manganese and iron (Appendix A).

4.3 KEADY AREA

4.31 Location and Topographic Setting

This district lies in the uplands of South Armagh close to the Monaghan border, in the south east of the Tyrone area (Fig: 4-1). The town itself is near a boundary between the hills to the south and the rolling drumlin country to the north. The superimposed land forms - the valleys, loughs, drumlins and ridge-like hills - all have an approximately north-south trend, contrasting with the major (Caledonian) trend of the Longford-Down massif of which they are part.

4.32 Geology and Mineralisation

The uplands are composed of Lower Palaeozoic rocks, here strongly folded Silurian grits, greywackes and shales, intruded by NNW-SSE Tertiary doleritic dykes.

The area includes the northerly continuations of the Castleblayney (Monaghan) system of small, discontinuous, near vertical veins carrying base metals (Fig: 4-1). Some were worked until the last century, but none were as productive as the similar but much larger Conlig-Newtownards lode of north east Down. Pb and Zn are the principal metals, but Cu and Mn are also known at the Clay Mine (Cole 1922).

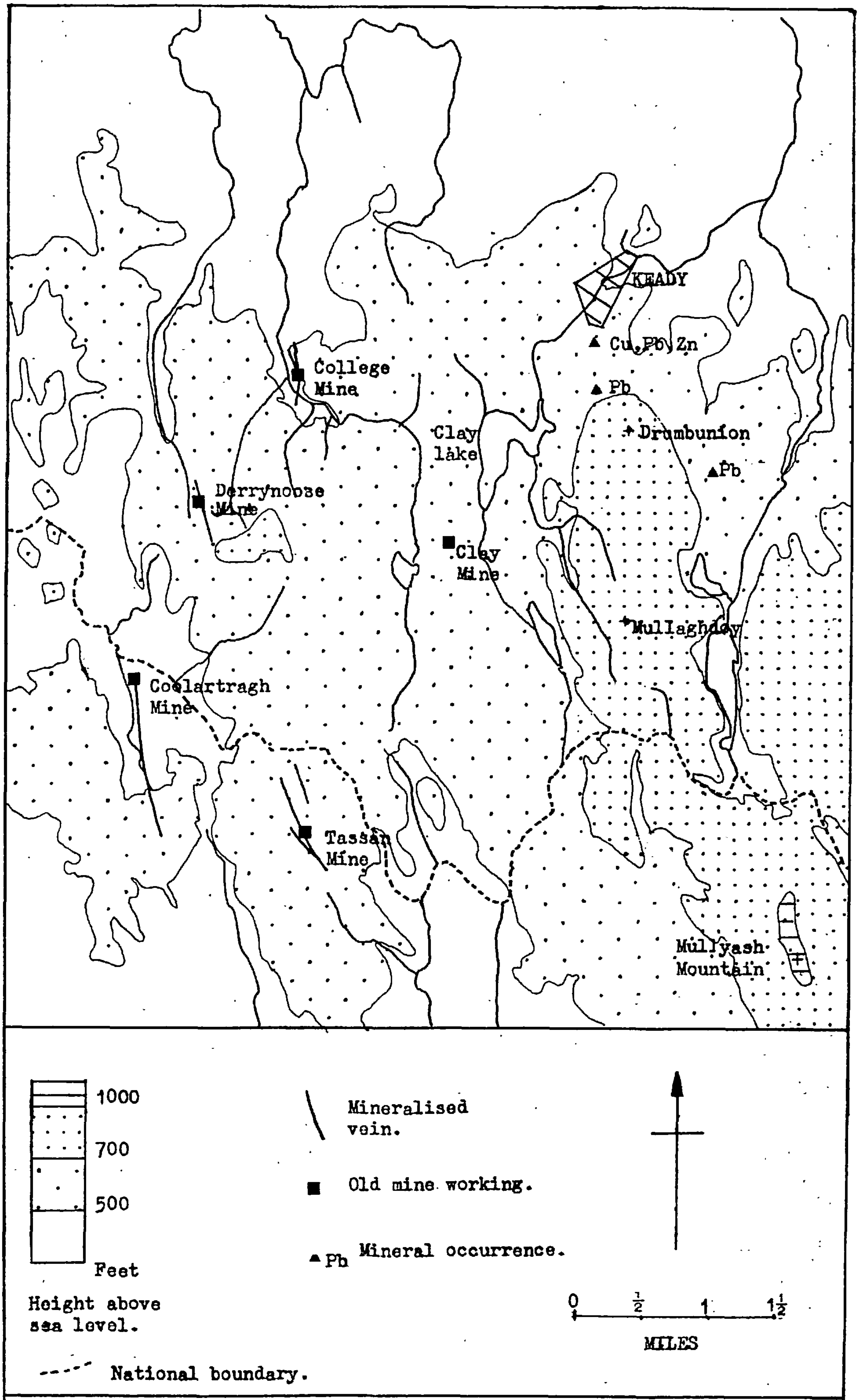


FIG. 4 - 1. TOPOGRAPHY AND DRAINAGE, KEADY AREA.
Indicating location of past mining activity.

Mine	Minerals	Notes
College	Galena, sphalerite in calcite and quartz. Argentiferous.	Lode up to 9 ft. wide, branched to trend N-S and N by W. Worked 1857 - 1864. Yield 1858: 69 tons ore.
Clay	Galena and manganese ore.	Two shafts worked 1826.
Derrynoose	Galena, sphalerite, pyrite in quartz.	Worked late seventeenth century until 1842.

College and Derrynoose are on the same vein system as Tassan, Annagogh and Coolartragh mines in Monaghan. The veins, probably of Hercynian age, are often associated with Tertiary dykes, which are now thought to have been intruded along the same planes of weakness.

4.33 Local Drainage Survey

The results of detailed stream sediment sampling in the Keady area (Fig: 4-2) confirm the Pb-Zn anomalies near the old mine workings and around Mullaghdoy located by the reconnaissance survey. One other anomalous sediment, containing 520 ppm Zn, 9000 ppm Mn and 1000 ppm Pb was found in the area, 1½ miles south of Clay Mine. Although the Zn-Mn enrichment may be a false anomaly, due to local environmental conditions, it possibly reflects mineralisation, for the stream is near the projected strike of the manganiferous lode at Clay Mine.

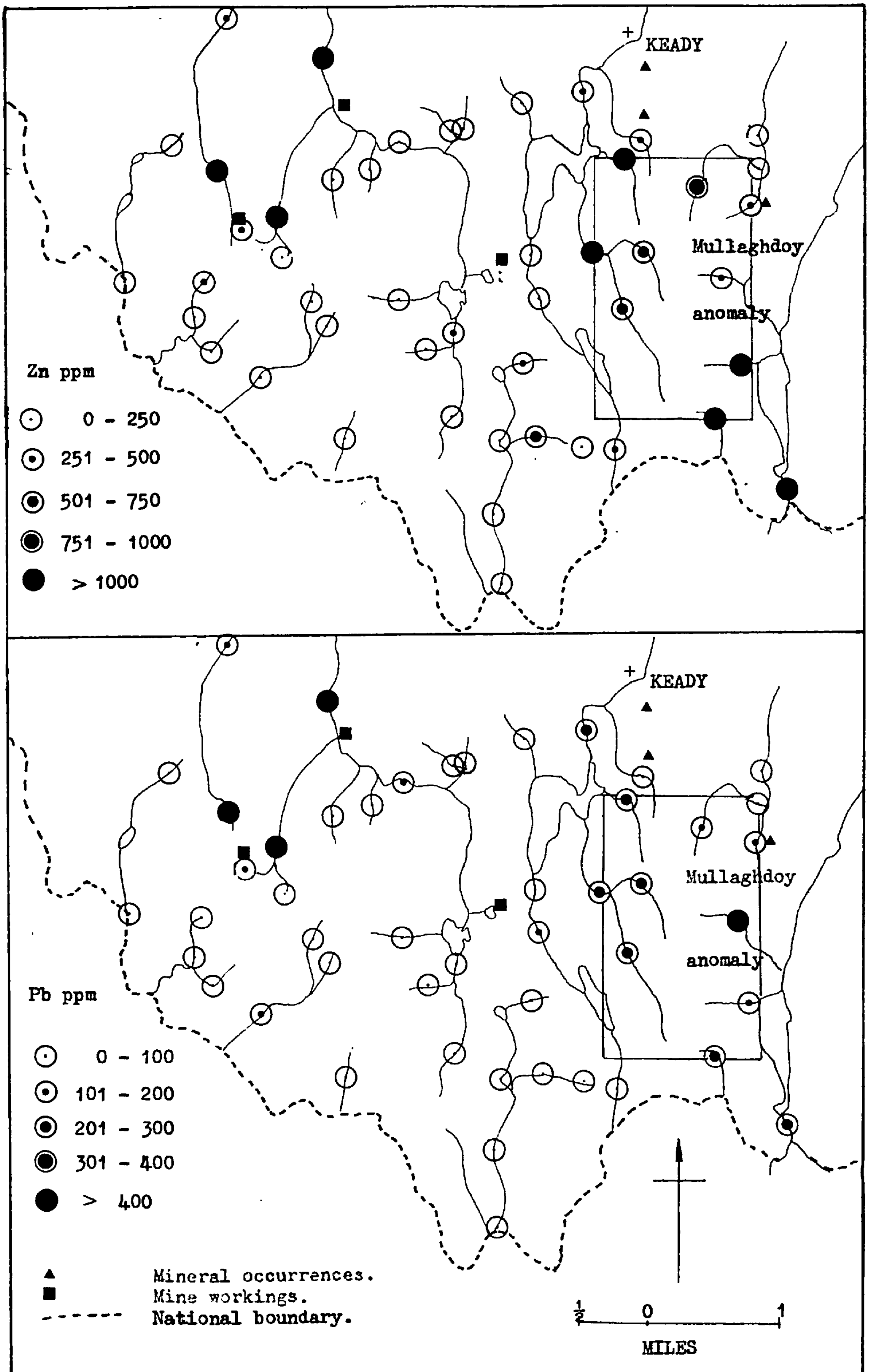


FIG. 4 - 2. LEAD AND ZINC CONTENTS OF STREAM SEDIMENTS, KEADY AREA. (Data on minus 80-mesh fraction).

4.34 Mullaghdoy Drainage Anomaly

The anomalous reconnaissance samples were taken from a stream draining the west flank of Mullaghdoy, a ridge-shaped hill one mile south of Keady.

Sample No.	Grid refs.	Zn ppm	Pb ppm	Cu ppm	Mn ppm	Fe_2O_3%
0041	2840 3312	850	300	26	5000	17.0
6504	2841 3335	620	650	100	1000	8.3

Known mineralisation is restricted to two small occurrences (Fig: 4-1):

i a vein of chalcopyrite with minor galena, sphalerite and siderite in a gangue of calcite and quartz, found in a quarry near Keady.

ii a vein of galena, about ¾ mile south of the town.

These veins, probably of the same system, lie just to the north of the main drainage anomaly.

Streams and seepages around the hill were sampled, using the cxHM test as a guide. This delineated an anomaly lying between the hills Drumbunion and Mullaghdoy, with a firm southward cut-off. Total metal analysis, however, showed that there was no such cut-off - the field test having underestimated the metal contents of non-peaty, organic sediments. In an extreme example, an organic sample showing only moderate levels of cxHM even after 15 seconds reaction contained over 6000 ppm total Zn+Pb+Cu.

Zinc anomalous sediments (Fig: 4-3) occur particularly in an area 1¾ x ¾ miles. The Pb anomaly is slightly smaller but that of Cu is very restricted, reflecting the known low abundance of the metal in the area. The overall anomaly extends southwards, probably to the border. Work by Larsson (1969, pers comm.) suggests that it continues SSE to Mullyash, Co. Monaghan, following the regional trend of the Castleblayney mineralisation.

The Zn anomaly is approximately co-extensive with that of Pb and shows only a poor correlation with Mn. This suggests a largely clastic dispersion process, since an hydromorphic mechanism would produce a weaker lead anomaly and a stronger Mn-Zn correlation. However, hydromorphic components do affect the Zn anomaly in two situations:

1. Where streams are free-running and have heavy Mn precipitates. This occurs on the flanks of the hills and Zn levels appear enhanced in comparison with those of Pb, probably by coprecipitation, thus extending the drainage anomaly laterally.

2. Where sediments are very organic. All Zn contents over 1500 ppm occur in such sediments, the metal apparently being preferentially enriched in the organic matter. This is shown particularly near Mullaghdoy itself and in the extreme south.

In this region, the role of glacial dispersion must be considered, for the sediments are derived from soil and till.

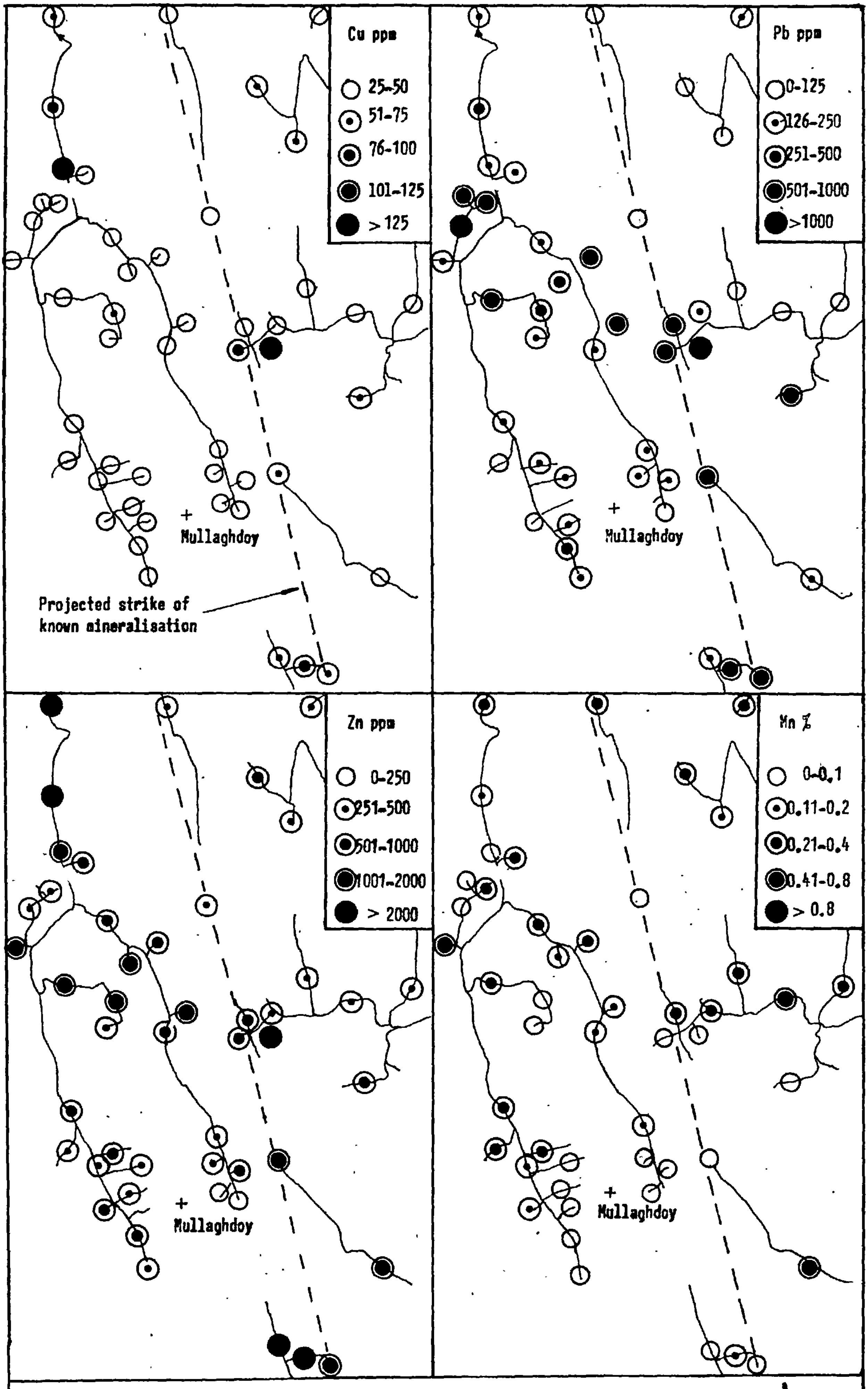


FIG 4 - 3. MULLAGHDOY DRAINAGE ANOMALY
(Data on minus 80-mesh fraction of stream sediments)

There is ample field evidence of glacial erosion, with drumlins subsequently formed in the lowlands and till, often thin, deposited extensively in the hills. In places, however, some upland soils may be residual. Since the direction of ice movement was approximately parallel to the lode strike, glaciation will have tended to lengthen anomalies without much lateral dispersion. In the hills, glacial smearing of the anomalies may have been slight, so that sediments probably relate closely to bedrock.

Metal Source The two mineral occurrences are aligned such that they could be part of the same vein, assuming the normal near vertical NNW-SSE strike. The projection is shown in Fig: 4-3 and any outcrop, possibly intermittent, along this line can explain a number of anomalous source areas. The data from this preliminary follow-up alone suggest there could be a number of similar sub-parallel veins with this trend. Together with the southerly extension to Mullyash Mountain, such veins could form a system similar to that formerly mined at Tassan and Derrynoose.

4.4 BARONS COURT, NEWTOWNSTEWART

4.41 Location and Topographic Setting

The anomalous reconnaissance samples were taken from streams draining from the forests of the Barons Court Valley, 3 miles south west of Newtownstewart (Fig: 4-4). This glacially enlarged valley lies between the rounded hills of Mullaghcroy (803 ft.) and Bessy Bell (1387 ft.) which, with Manus Hill

(848 ft.) can be considered the westernmost extensions of the Sperrin Mountains. They are separated from the main range by the wide Mourne Valley. To the west they give way to the low hills which form the watershed between the River Derg and the Fairy Water.

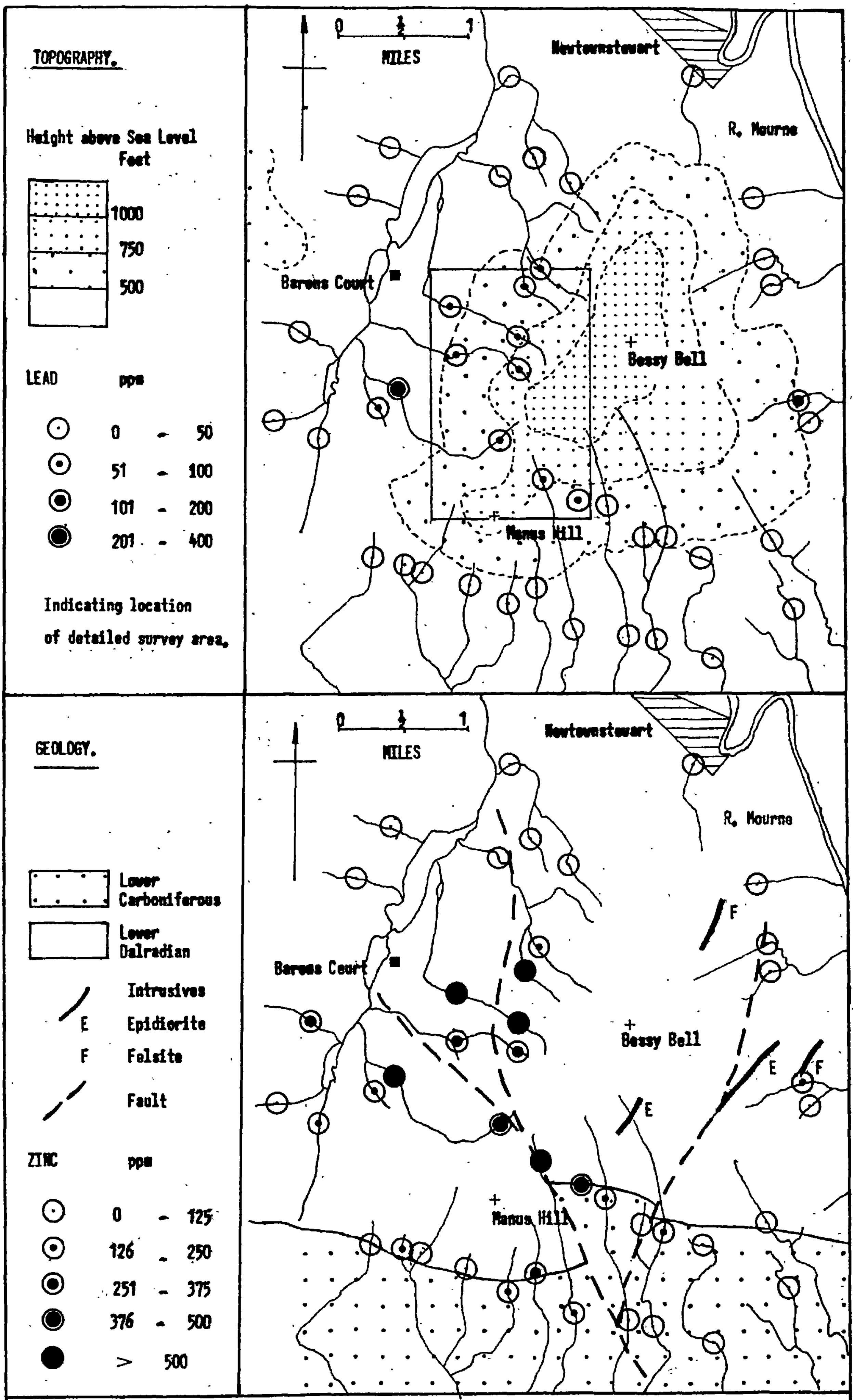
4.42 Geology and Mineralisation

4.421 Geology (Fig: 4-4) The Calcareous Group of the Lower Dalradian, comprised of limestones, calcareous schists and mica schists, outcrops in the Derg Valley. To the east, it is overlain by the more resistant and siliceous Newtownstewart Quartzite Group which forms the Barons Court hills. These are quartzites and gneisses, with associated quartz-, sericite-, and phyllitic schists. In turn, these are overlain by the white Dungiven limestone of the Upper Dalradian, outcropping on the hill Mary Gray (828 ft.) across the River Mourne. To the south, the schists are unconformably overlain by Lower Carboniferous (Tournaisian) clastics, mainly conglomerates and pink sandstones derived from the schists.

The schists are intruded by basic and felsic sills. The whole area is affected by post-Tournaisian, probably Hercynian, cross faults, trending approximately NNW-SSE.

4.422 Mineralisation Baryte has been recorded by Hallissey (1923) from three sites on Bessy Bell (Fig: 4-5):

i Grid reference: 2376 3806. Massive white opaque baryte, with minor quartz, is found in a stream by



FIG; 4 - 4 TOPOGRAPHY, GEOLOGY AND LEAD + ZINC DRAINAGE SURVEY AROUND BESSY-BELL, NEWTOWNSTEWART. (data refer to minus 80-mesh fraction of stream sediments).

the road between Bessy Bell and Manus Hill. The main outcrop is about 25 ft. long, pinching to narrow veins to the south west, under the road bridge.

ii Grid reference: 2379 3804. Baryte in gneiss, and baryte blocks were once found in till and on the surface.

iii A minor showing about a mile north. Location uncertain.

During the course of follow-up work in 1968-69, further veins were discovered, in one case associated with galena and sphalerite. Base metal mineralisation was unknown in this area, prior to the geochemical survey.

4.423 Glaciation The retreating ice tongues of the last glaciation left hummocky deposits of glaciofluvial sands in the Derg and Fairy Water valleys, with some fine moraine development, particularly on the northern slopes of Bessy Bell. The hills are mostly drift covered, but this is thin or absent on spurs and summits, where shallow, peaty, probably residual soils have developed on ice-smoothed bedrock. The drift, micaceous and sometimes sandy, is thought to be locally derived, but there is little clear evidence of its origin.

4.43 Soils and Vegetation

Soils on the drift covered slopes are acid brown earths.

They tend to be fairly poorly drained, reverting from grassland to a rush and sedge flora when neglected. Much of the land has been afforested, leading to increased podzolization. In the Barons Court valley, farm and wooded park land is found in the lower ground, giving way to a belt of largely coniferous forest on middle and upper slopes, with blanket peats developed on the hill tops.

4.44 Drainage and Soil Anomalies

4.441 Local drainage survey As described in Chapter 3, the reconnaissance survey indicated a local enrichment of Zn over the Lower Dalradian of the Derg valley. This is apparently unrelated to Mn oxide precipitation, except possibly in the east, at Barons Court. Nevertheless, here the Zn contents of three samples (350-860 ppm) is greater than would normally be expected for such levels of Mn (1,000 - 5,000 ppm) by secondary enrichment alone and, in one case, is also accompanied by high background Pb and Cu.

Further stream sediment sampling, guided by cxHM field analysis, confirmed that the Pb-Zn anomaly is restricted to the Barons Court area (Fig: 4-4). Field analysis for cxHM in this partially forested district (Fig: 4-5) shows that the anomalous streams drain two areas, on Bessy Bell and in Manus Wood, separated by a hill spur. The results of detailed sediment and soil sampling in these areas are described below.

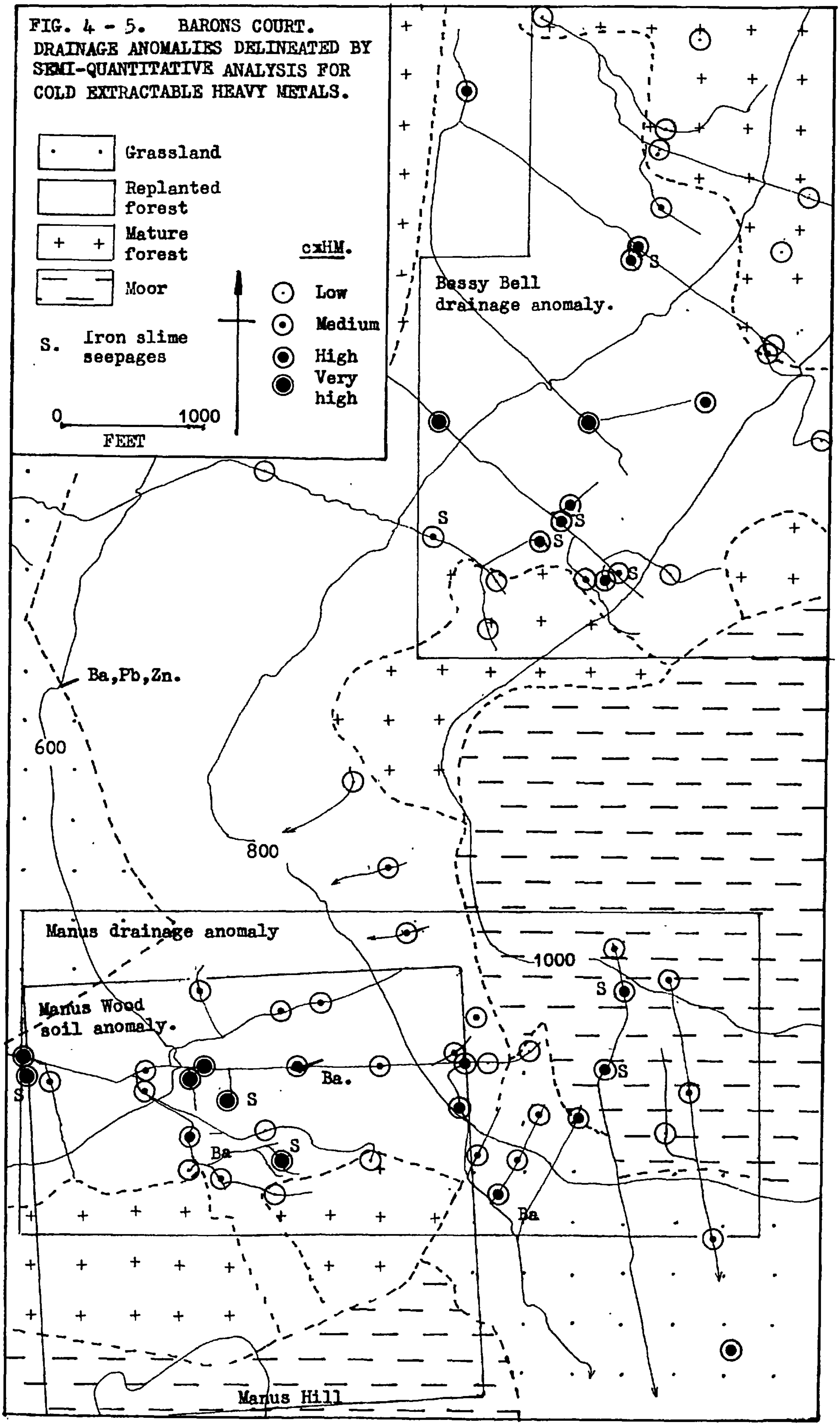


FIG. 4 - 5. BARONS COURT. DRAINAGE ANOMALIES DELINEATED BY SEMI-QUANTITATIVE ANALYSIS FOR COLD EXTRACTABLE HEAVY METALS.

4.442 Bessy Bell drainage anomaly This is principally a Zn anomaly which is traceable to seepage sources spread over a half mile (Fig: 4-6). Maximum concentrations are reached in the south, where ferruginous seepages contain up to 2,900 ppm Zn. Cu and Pb are at high background levels only (range 10-40 ppm Cu, 30-100 ppm Pb). Sampling took place in the abnormally dry summer of 1968 and cut - off mostly corresponds to the then persisting springs. Continuations of the ditches above the seepage line were dry and have very low metal contents. Laterally, the anomaly cut-off is very sharp and appears to correspond to a vegetation change, from replanted to mature forest.

There is a correlation between sediment metal content (cxHM total Zn, total Mn), stream water pH and soil pH (Fig:4-7). Stream water pH is always greater than that of adjacent soils but shows similar variations. The pH of both is lowest in mature forest, highest in replanted forest. Sediment metal content rises when stream water pH rises and hence the anomaly occurs in the area of replanted forest. This suggests hydromorphic dispersion, with dissolved Fe and Mn precipitating in the less acid streams and co-precipitating the Zn, which can subsequently react as cold extractable heavy metal. The probable source of the metal and the dispersion mechanism are discussed below (Section 4.45).

4.443 Manus drainage anomaly The Manus drainage anomaly has several seepage sources extending over half a mile

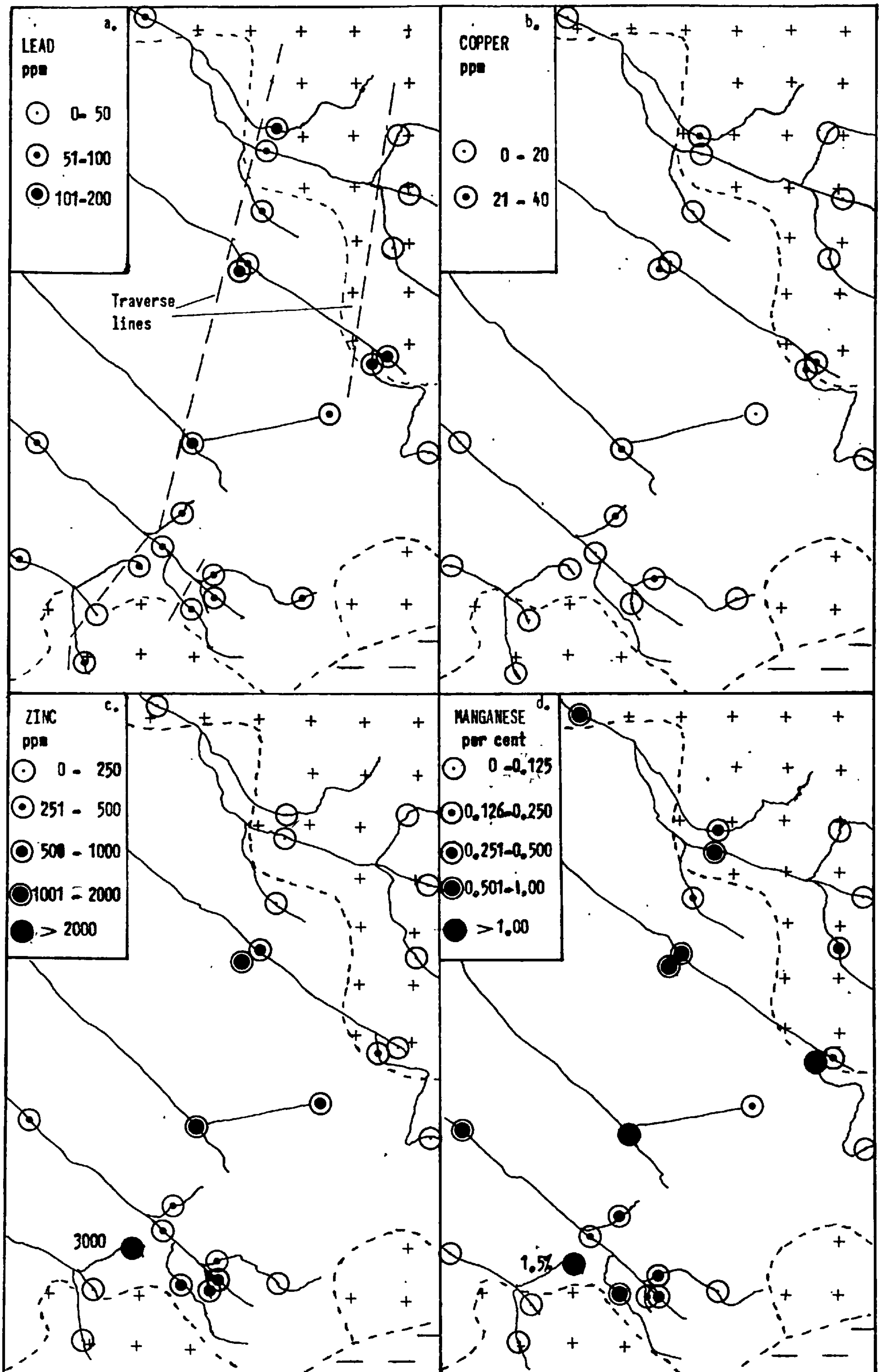


FIG. 4 - 6 BESSY BELL DRAINAGE ANOMALY.
Vegetation as Fig 4 - 5
(Data on minus 80-mesh fraction of stream sediments).

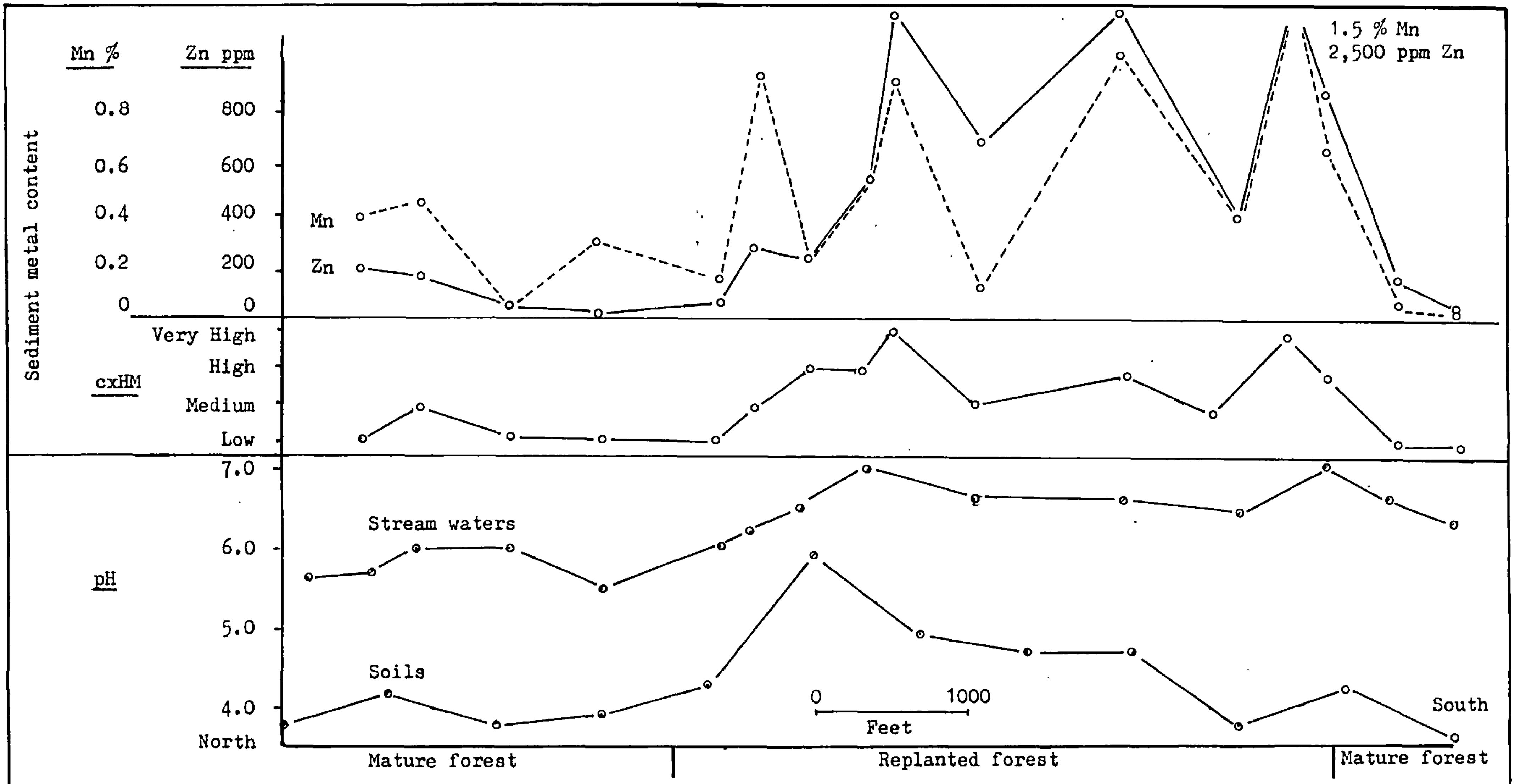


FIG. 4 - 7 RELATIONSHIP BETWEEN THE pH OF SOILS AND THE pH AND METAL CONTENTS OF SEDIMENTS FROM ADJACENT STREAMS. BESSY BELL ANOMALY, BARONS COURT. (Traverse lines shown on Fig. 4 - 6a.)

across the major north-south watershed (Fig: 4-8). Again mainly in Zn, there is also an accompanying, very local, Pb anomaly, with values > 200 ppm occurring only in iron seepages. Copper is generally lower than on Bessy Bell, with many samples containing less than 10 ppm. The apparent extent of the anomaly is again partially determined by the vegetation or land use, with for example the cut-off coincident with sands of tall conifers.

All anomalous drainage trains could be traced back to large iron slime seepages, most of which occur in areas of reafforestation. The seeps are found in drainage ditches as gelatinous ochre masses which can extend for several yards, impeding water flow. They have subsequently been shown to be colonies of filamentous iron bacteria, probably Lepothrix ochraceae (Chapter 7-32). The locations and metal contents of the major iron seepages occurring in Manus Wood are shown on Fig: 4-9. Iron content is mostly in the range 25-35% and manganese 0.05 - 0.5%. It can be seen that not all the seeps are rich in Pb and Zn and that seeps only a few yards apart can have widely different base metal contents. Two seeps are particularly metal rich:

Sample No.	Cu ppm	Pb%	Zn%	Mn%	Fe%
1667	25	0.12	1.30	3.00*	30.0
B/S/16	35	3.80	8.50	0.03	25.0

* The Mn content of this sample is unusually high.

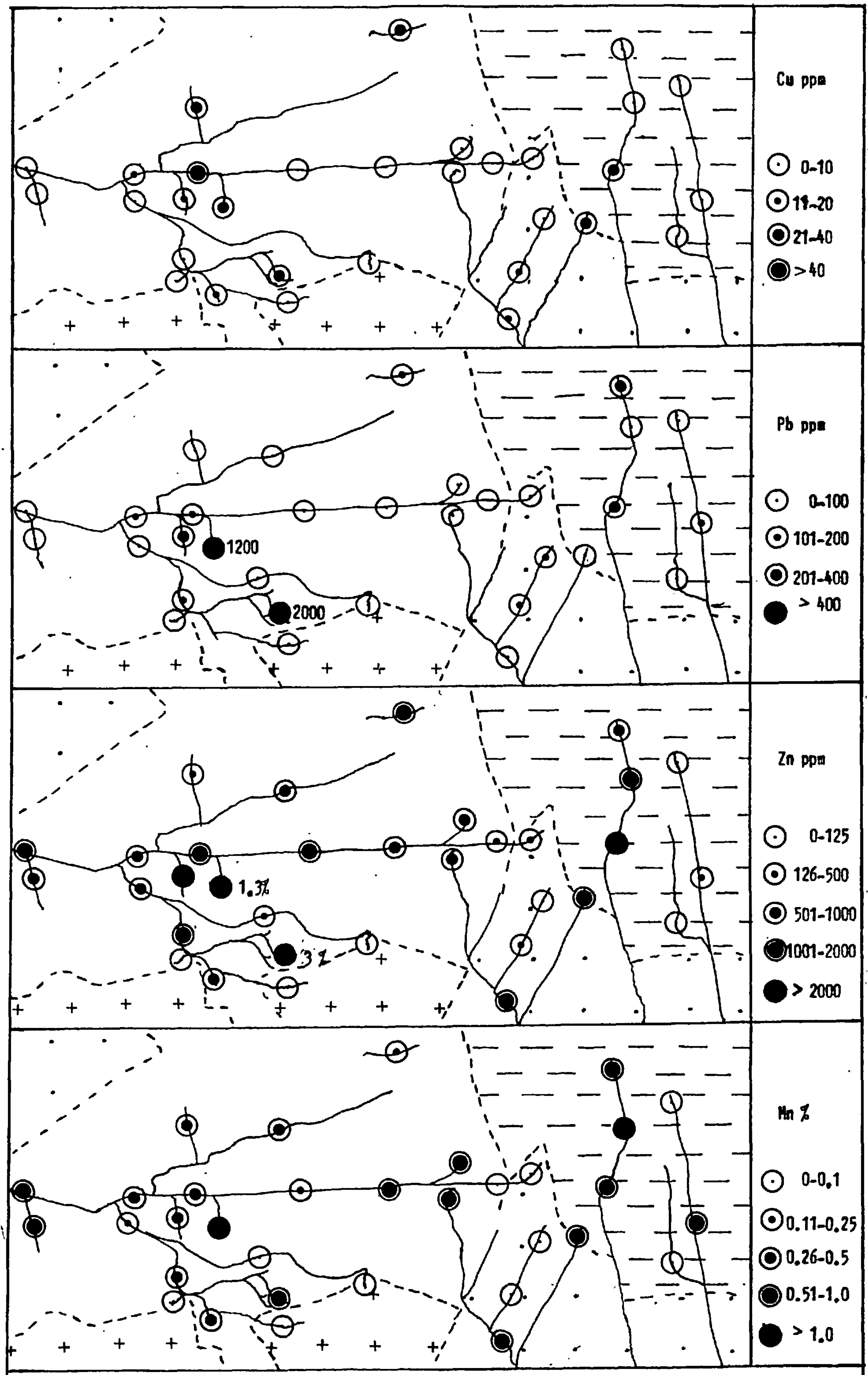


FIG 4 - 8. MANUS DRAINAGE ANOMALY
(Data on minus 80-mesh fraction of
stream sediments)

Vegetation as Fig. 4 - 5

0 1000
FEET

Seep B/S/16 (above) is the source for a major drainage train (Fig: 4-9). It is an ochreous mass, up to 2 feet deep, with an irridescent oily sheen arising from a platy oxide film on the surface. Below, the material is gelatinous, becoming increasingly peaty with depth. The base metal content varies from about 0.65% Pb+Zn in the surface gel to over 10% Pb+Zn in the peaty sludge at the bottom. This seep, and the smaller adjacent one, enter a small ditched stream which arises in the nearby mature forests. The ditch and seeps are here in deep peat, so that there is no direct source of mineral sediment.

Immediately upstream from the seeps, the ditch has a peaty non-ferruginous sediment with a background metal content (330 ppm Pb+Zn). A mineral sediment from a nearby stream in the forest contains only 90 ppm Pb+Zn. The drainage anomaly can thus be seen to have a local, specific source and a sharp, high contrast cut-off.

Downstream from the seeps, the bottom of the ditch has a layered crust of iron oxide, ½-inch thick. This crust persists for over 100 yards until the stream cuts into till. Here the precipitate encrusts the mineral sediment to a depth of ½ inch, but becomes rapidly broken up downstream. The base metal content of the crust and the 'sediment' it encloses remains nearly constant (3,200 ppm Zn, 520 ppm Pb). Where it becomes broken, however, the sediment content falls sharply to about 700 ppm Zn, 150 ppm Pb, but these levels are maintained, with additional metal from other seepages

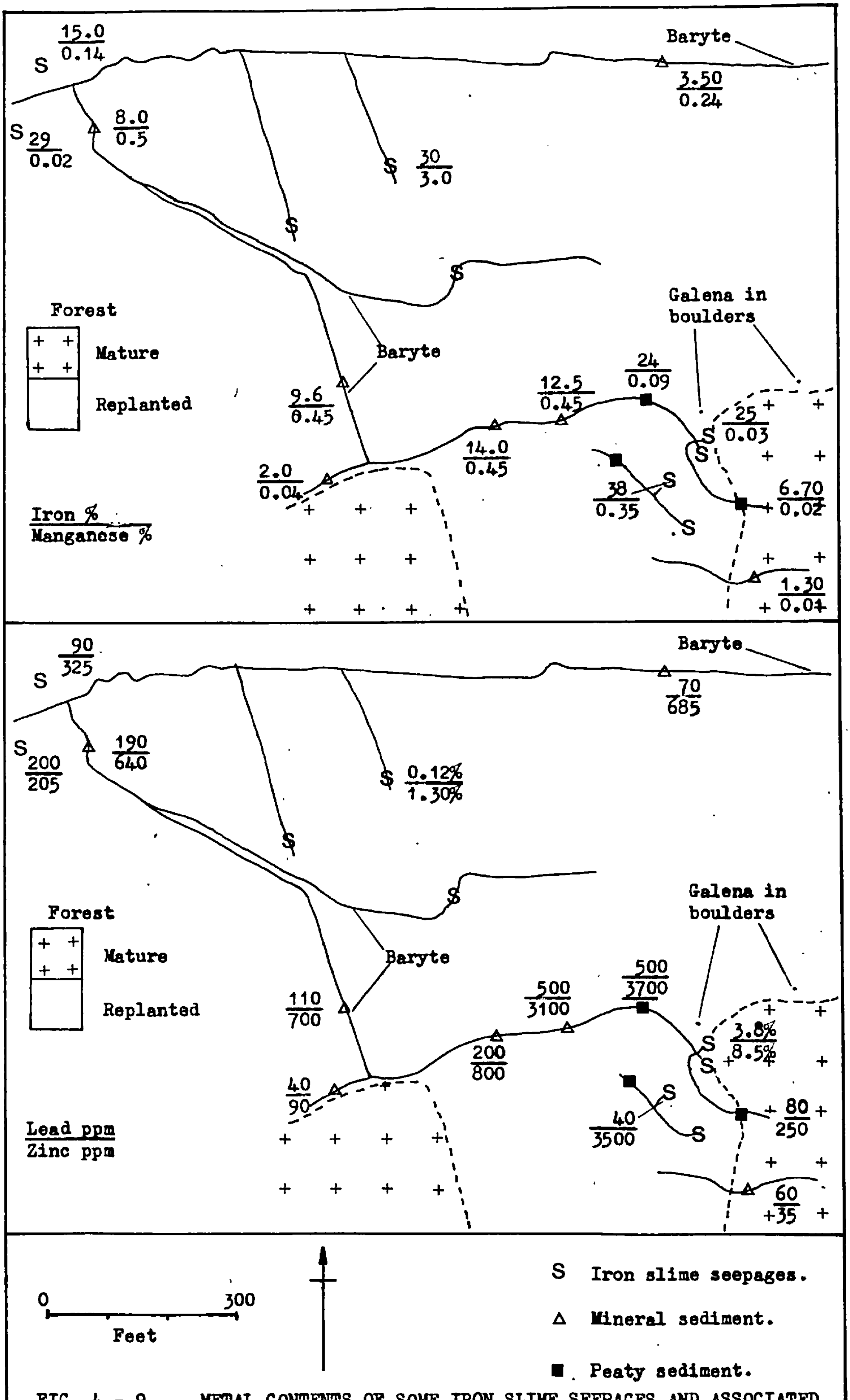


FIG. 4 - 9. METAL CONTENTS OF SOME IRON SLIME SEEPAGES AND ASSOCIATED STREAM SEDIMENTS, MANUS WOOD. (Data on minus 80-mesh fraction).

in the catchment, to the reconnaissance discovery site one mile downstream. It is noticeable that the Fe content decreases steadily downstream from 30% in the precipitate crust to 8% in the mineral sediments. The Mn content, however, rises sharply from 600 ppm in the crust on peat to 4,500 ppm where the sediment is mineral and the stream becomes aerated. Most of the additional manganese is presumably derived by direct precipitation from stream water, since precipitate-free mineral sediments from streams in the nearby forests contain less than 200 ppm Mn.

4.444 Manus Wood soil anomaly In view of the abnormally high metal contents of the sediments, soils were collected over part of the anomalous area. As far as possible, a constant horizon was chosen for analysis. Since it was frequently impossible to sample the B horizon, the grey-brown humic stained silty clay beneath the peat or litter was selected. This corresponds approximately to a podzolic A_{1-2} horizon. In the south, near the top of Manus Hill, soils are peaty and very shallow, resting directly on ice-smoothed rock; elsewhere they are deeper and developed on till. Soil pH was measured at the time of collection.

The contoured distributions of the four metals and pH are shown in relation to the vegetation and land use on Fig: 4-10. The metal contents of the soils are mostly lower than those of the sediments, in which secondary concentration has been considerable. There are broad correlations between the five variables, the general increase northwards suggesting an

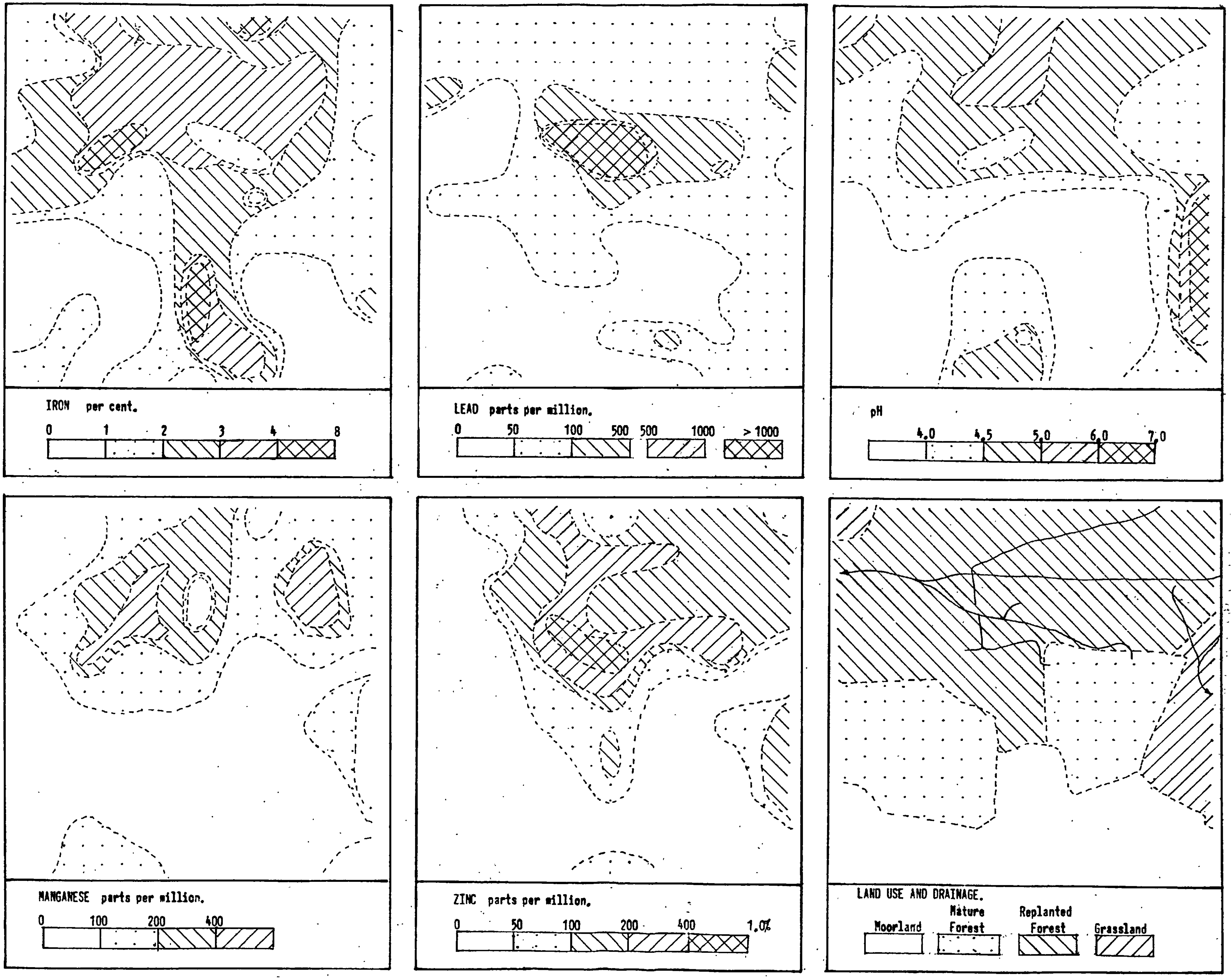


FIG. 4 - 10. MANUS WOOD SOIL ANOMALY. Iron, manganese, lead and zinc distribution in relation to pH and land use. (Data on minus 80-mesh fraction of soils).

extensive soil anomaly, corresponding to that of the drainage. As in the sediment anomaly, there is a sharp cut-off at the edge of the mature forest. The metals have accumulated particularly in the less freely drained soils of the valley to some extent downslope of the metal rich iron seepages. The Pb anomaly is restricted to these soils, but that of Zn is rather more widespread. Iron and pH differ in being raised in the shallow peaty soils on Manus Hill.

4.45 Metal Source

At Barons Court, the exceedingly high levels of both Pb and Zn, with low to moderate Mn, in iron seepages and sediments, suggest base metal mineralisation. This was confirmed by the discovery of:

i disseminated galena in schist boulders near seeps at Manus Wood (Fig: 4-9);

ii baryte veins with sphalerite, galena and manganiferous iron oxide in the quarry between the two anomalies (Fig: 4-5). The strike of this vein is approximately parallel to that of the baryte veining elsewhere, although the latter has a low metal content, as shown below:

	Zn	Pb	Fe	Mn
Iron oxide from sulphide veins	2%	5.8%	35%	4.8%
Baryte from known vein (ppm)	25	25	2800	25

Continued to the northeast, the mineralized vein would outcrop in the area of the iron seeps of the Bessy Bell anomaly. There are presumably similar mineralised veins near the Manus Hill seeps. The present soil and sediment data, however, are insufficient for accurate location of the outcrops, for which further sampling of deep soil and till horizons would be necessary.

4.46 Dispersion Mechanism

The Manus Wood drainage anomaly, arising in some places in iron seepages almost free of mineral sediment, is clearly the result of hydromorphic dispersion. The Bessy Bell anomaly arises similarly, being dependent upon the occurrence of seepages and the distribution of manganese and iron oxide precipitates. In soils, the metal accumulations are associated with the less acid soils of the shallow valley, near several iron seeps, where the water table is near the surface.

Hydromorphic dispersion of this type is well known, although details of the chemical reactions involved are not clearly understood. The reactions are, however, essentially similar to the normal processes of pedogenesis discussed in Chapter 8, but involve the mobilisation of unusually high quantities of the metals.

Iron, manganese and certain trace elements, particularly Co, Mo, Ni and Zn, are removed from soil by acid leaching. They remain in ground-water solution, probably as organic complexes, whilst acid or reducing conditions prevail. Fe and Mn precipitate as hydrous oxides on entering a less acid, oxidizing environment, whether in soil or stream. The other trace element complexes become unstable also and the metals can coprecipitate with the hydrous oxides.

At Barons Court, the observed **distribution patterns, related to those of Fe and Mn, suggest such a mechanism, although most of** the leached metals will have been derived from the mineralisation rather than normal leaching of soil and till. The distribution patterns have two unusual characteristics:

i. <u>The occurrence of 'hydromorphic lead'</u> Pb, unlike Zn, is not normally considered mobile under these conditions, yet its concentrated occurrence here is of undoubted hydromorphic origin. The only common soluble Pb compound is the chloride, which is unlikely to occur naturally. Hence, the metal is probably carried in groundwater solution as an organic complex, possibly sparingly soluble and travelling only a short distance from source.

The restriction of Pb **to** iron seepages indicates a coprecipitation mechanism, where ferric iron hydrolysis appears to be a necessary condition. It is well known that water-soluble lead salts do not precipitate when pH is raised, for example, by the addition of dilute sodium hydroxide to the solution. However, in the presence of ferric salts, the addition of NaOH causes immediate hydrolysis of the ferric iron with precipitation of the hydrous oxides and coprecipitation is liable to be complete at seepages, where pH and Eh rise and most oxidation and hydrolysis of iron takes place. This would explain the rapid downstream decline of the Pb anomalies in comparison with Zn, the latter apparently more stable in solution and thus coprecipitating more slowly in the stream itself.

ii. The influence of vegetation The occurrence of soil and sediment anomalies, Mn oxide precipitation and iron slime formation is restricted to areas of recent afforestation and moor only. Their distribution is thus partially controlled by the vegetation and land use, which appear to influence hydromorphic dispersion by two interacting mechanisms:

a) Soil and water pH Waters and soils are usually more acid (pH < 5.0) in the areas of established forest than elsewhere (pH > 5.5). A general relationship between soil pH and land use in Manus Wood is shown on Fig: 4-10 where it can be seen that moors and established forests are acidic (pH 4.0) and the younger forests and cultivated fields increasingly less so (pH 5.0-6.5). Metals are leached from acid soils and do not precipitate until the pH of ground- or stream water is raised. In part, the differences in pH and the extent of leaching may reflect differences in the organic complexing agents derived from the vegetation cover.

b) Level of water table Seepages, ditches and streams are more common in the heathy areas planted with young trees where soils are damper than in the established forest. This suggests that the water table is nearer the surface in these cleared and reafforested areas. A similar situation was reported by Wilde et al (1953) who showed that the removal of trees on podzolised land caused a rise in the level of the water table (that is, the saturated zone of phreatic groundwater) within a few months. They found that a flat lying but reasonably drained podzolic soil was converted to semi-swamp by tree-felling.

At Barons Court, in the established forest, soils are moderately drained and the water table not near surface. Groundwater flow is predominantly downward and, being very acid, leached metals strongly. Ditches in these established forests derive most moisture from surface run-off rather than phreatic groundwater. In contrast, the higher water table in cleared areas brings a supply of metal-rich groundwater to the surface and supports springs even in very dry conditions. Since soils and streams are less acid than in the mature forest, the metals can accumulate to give anomalies in these areas.

In part, therefore, the existence of the anomaly appears to have depended upon the cutting and replanting of trees and the consequent effect on groundwater and drainage. If the area were wholly afforested with mature trees, it is possible that the anomaly would have been restricted to the main streams only, since topsoils and ditches would remain too acidic for precipitation.

There is no evidence for clastic dispersion, although metals accumulated hydromorphically in some soils may subsequently be eroded to give an anomalous clastic sediment.

It is not possible to assess the effect of glaciation on metal dispersion. The main Manus Wood seep must be within 200 yards of a sulphide vein - the distance to the watershed - and possibly immediately adjacent to it. However, mineral sediments and soils upslope are low in the metals, indicating that any clastically dispersed material has been leached or strongly diluted, either by totally exotic drift or because the mineralisation is only minor.

The extent of the mineralisation, therefore, is probably greater than suggested by the drainage anomaly. In particular, the Bessy Bell anomaly ceases abruptly northward, at the edge of established forest. It is possible that any such extension would not be delineated by sampling the A_{1-2} horizon, but enrichment may be shown biogenically in the litter or by illuviation or diffusion in the B horizon. Alternatively, less acid deep soil or till horizons below the zones of leaching may prove useful in detecting any hydromorphic or weak clastic anomalies.

4.5 CONCLUSIONS

The anomalies at Keady and Barons Court are examples of widely different dispersion mechanisms operative under slightly different environmental conditions. At Keady, predominantly clastic dispersion has occurred in a cultivated area with basin peat in hollows. Hydromorphic processes have served only to extend the drainage anomaly. At Barons Court, the dispersion is almost entirely hydromorphic, in a forested and moor peat area.

The overall extent of the Zn drainage anomalies are similar ($1\frac{1}{2}$ x $\frac{1}{2}$ miles) and both were detected by the reconnaissance survey at the normal sample density. Though relatively small, both mineralisations are probably larger than many of the 'trace mineral occurrences' reported by the Geological Survey of Northern Ireland (1970), most of which gave no stream sediment anomalies.

However, both anomalies occur in uplands where the drift is either local or sufficiently thin or porous to allow diffusion by metal rich groundwater. It cannot be stated with certainty that either would have been located had they been in lower ground, obscured by drumlins, double tills or other thick glacial deposits. The very thickness of drift tends to dilute clastic anomalies, whilst lower rainfall, different land use and thick clayey till may restrict hydromorphic dispersion.

In the Keady area, anomalies were found in the uplands but not in the drumlin lowlands. This apparent restriction of mineralisation to the uplands may be due either:

i. to a possible genetic relationship between high ground and mineralisation. That is, rocks uplifted or given greater resistance to erosion as a result of processes accompanying mineralisation.

or ii. to the technique being unsuitable for exploration in such terrain. Although Larsson (1969, pers. comm.) detected a clastic anomaly in partial drumlin country at Tassan, Co. Monaghan, the area had predominantly upland characteristics with fairly thin drift.

Previous work in Ireland has suggested that the reconnaissance techniques are adequate to detect soil/till anomalies of over two square miles in area. A survey with the density of one sample per square mile, for example, would have located the Tynagh till anomaly (Donovan, 1965). However, glacial erosion played an important part in the formation of the unique secondary mud ore, hence the extent of the clastic dispersion here may have been greater than normal. Elsewhere, where such mud ore has not formed, detection may be less certain, with lower anomaly contrast.

Where drift is exotic, the formation of goechemical anomalies must depend on hydromorphic dispersion. In lower ground, the prevailing environmental conditions may be less likely to promote such processes, hence anomalies will again tend to be of low contrast.

Regional drainage reconnaissance, however, does not aim to detect individual deposits. Its main use is to detect areas for more detailed sediment surveys. Since contrasts are liable to be low for such areas or individual anomalies, particularly in lower ground, it is important that all samples with metal content above local threshold should be investigated.

CHAPTER FIVE GEOCHEMICAL PATTERNS OF POSSIBLE AGRICULTURAL SIGNIFICANCE

5.1 INTRODUCTION

The techniques of regional geochemical reconnaissance have been shown to be successful in the delineation of areas of trace element imbalance in crops and livestock in the British Isles (Webb and Atkinson, 1965; Fletcher, 1968; Thornton, 1968). Interest has been focussed particularly on cobalt, copper, manganese, molybdenum, selenium and zinc. The distributions of these elements, with the exception of selenium, have been studied in the reconnaissance survey of the Tyrone Area, as described in Chapter 3.

Previous work has shown there to be a complex relationship between the metal contents of stream sediments, soils, plants and animals. Consequently, the current studies have been limited to determining the degree of correlation between sediment and soil metal contents, as a first step in the interpretation of the reconnaissance data in terms of its possible significance to agriculture. Detailed follow-up investigations have been concentrated as follows:

i. where raised molybdenum levels (2-8 ppm) occur in stream sediments;

ii. in the several areas where sediments contain less than 10 ppm copper; and

iii. where there are low to moderate (30 - 70 ppm) contents of zinc in stream sediments.

5.2 SAMPLING AND ANALYSIS

5.21 Sampling

Sediments and topsoil samples were collected in a number of individual catchments, usually less than 5 square miles in area, selected from the results of the reconnaissance survey.

Sediments were resampled at one or more points in the catchments to confirm the original results. Topsoils (0-6 inches) were collected with a hand auger from sites representative of the main topographic and environmental situations within each catchment. Six sub-samples, taken at 15 - 25 foot intervals, were bulked to give a composite sample from each site. Note was taken of site characteristics, including drainage, slope, vegetation, soil texture and soil colour. Subsoils (6-12 inches) were collected from selected sites.

Soil and water pH were measured using a portable pH meter, as described in Appendix A.

This site selection method, as used by Thornton (1968), is subjective in approach, but has the advantage that the important features of each catchment can be investigated rapidly. Traverse sampling of whole patterns or individual catchments is objective and more thorough, but tends to be slower and to require a larger number of samples.

5.22 Sample preparation and analysis

The soil samples were dried and gently disaggregated in a pestle and mortar, coned and quartered and part of each passed through a 10-mesh (2mm) sieve. After further coning and quartering, part of this minus 10-mesh fraction was ground to minus 80-mesh.

Sediments were disaggregated and **sieved to minus** 80-mesh.

The minus 80-mesh material was analysed colorimetrically for total molybdenum and by atomic absorption for total copper and zinc, by the methods given in Appendix A. All results are expressed on a dry matter (D.M.) basis.

5.3 INVESTIGATIONS INTO AREAS OF RAISED SEDIMENT MOLYBDENUM

5.31 South Enniskillen

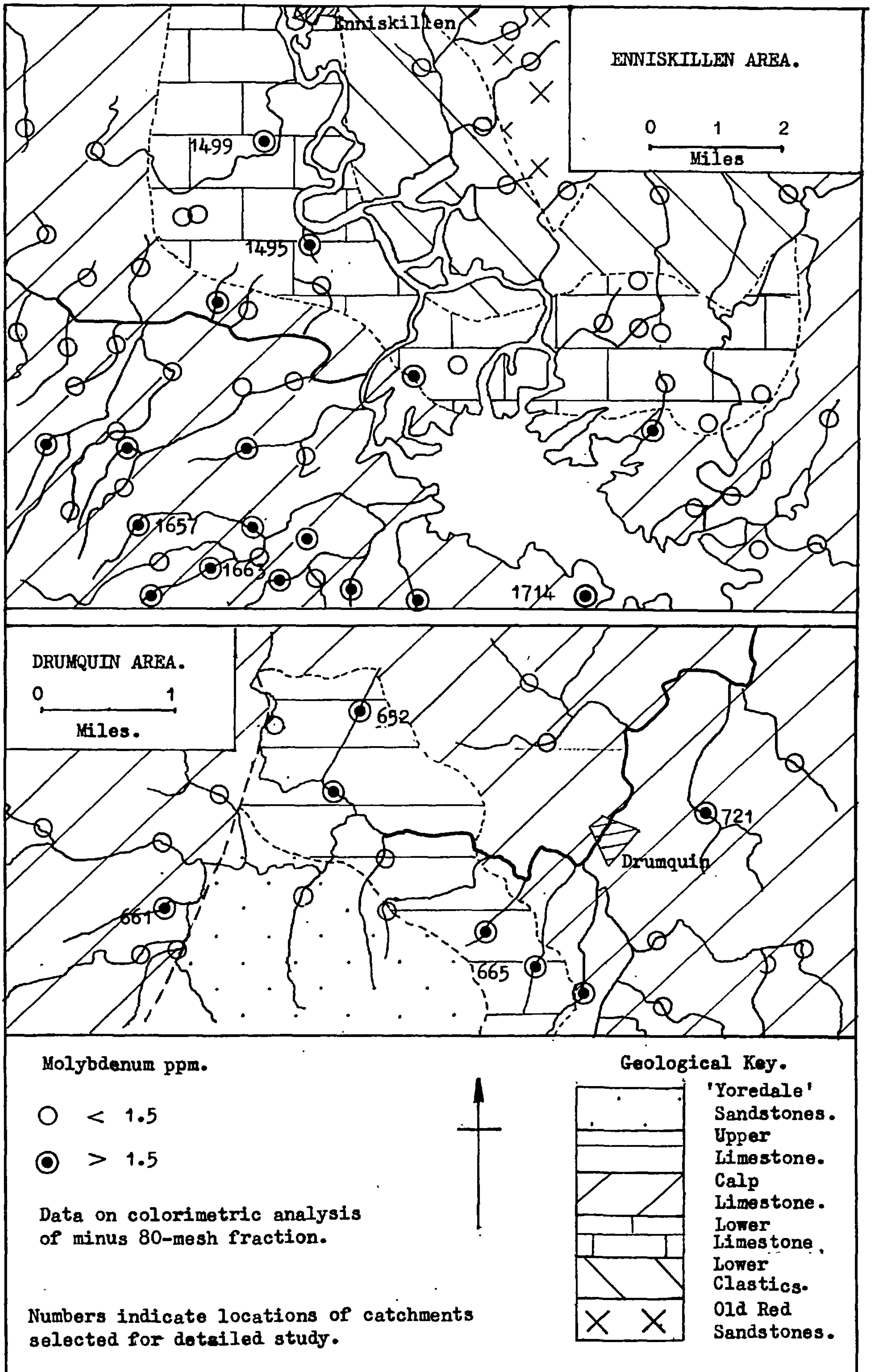
5.311 Description of area The main pattern of molybdeniferous sediments in the Tyrone area lies over about 20 square miles south of Enniskillen, Fermanagh, where stream sediments contained 2 - 8 ppm Mo. It is situated in the lowlands about Upper Lough Erne, where a typical drumlin topography obscures the Lower and Calp limestones of the Lower Carboniferous. Soils are mostly sticky and often poorly drained, even on fairly steep slopes, supporting only poor to medium quality permanent pasture. Interdrumlin peats are worked for fuel or reclaimed for agriculture. Soil pH ranges from over 6.5 on better drained slopes to 5.5 in boggy areas; peats have pH levels as low as 4.0. Stream water pH is 7.0 - 7.5.

5.312 <u>Results</u> Six catchments yielding molybdeniferous sediments were studied in this general area. Their locations are shown on Fig: 5-1, and results for Mo and Cu analysis are given on Table 5-1.

The resampled sediments tend to confirm the reconnaissance results where based on comparable colorimetric analysis of non-ashed sediments.

In all catchments, maximum soil Mo contents are similar to those of the sediments, being in the range 2 - 4 ppm. There is, however, a variation over individual catchments, related to soil type, with the metal tending to concentrate in the organic soils of the seepage areas. The copper contents of the topsoils (5 - 65 ppm) are generally similar to, or rather greater than, the sediment values (12 - 40 ppm) with the highest values again in the organic soils. In control catchments, the molybdenum content of all sediments and soils were below the detection limit (0.8 ppm).

5.313 <u>Discussion</u> The weak pattern of raised Mo in this area, shown by the reconnaissance survey, appears to reflect a similar slight increase in the soil content, compared to nearby control areas. The agricultural significance is hard to assess, since even peak levels in the soils are below those normally considered toxic in Ireland. However, in Oregon, Kubota and co-workers (1967) found that legumes could accumulate toxic levels of Mo (10 - 100 ppm) when growing in soils of similar type and Mo content (0.8 - 6.0 ppm) to those at Enniskillen.



Data on colorimetric analysis of minus 80-mesh fraction.

Numbers indicate locations of catchments selected for detailed study.

FIG. 5 - 1. MOLYBDENUM CONTENT OF STREAM SEDIMENTS NEAR ENNISKILLEN AND DRUMQUIN, TYRONE AREA.

ENNISKILLEN AREA

Catchment No.	Grid Reference	Molybdenum ppm		Copper ppm	
		Sediments	Soils*	Sediments	Soils*
1495	2235 3390	1,2.5	0.8-3.0(6) 2.0	20,25	5-45(6) 25
1499	2222 3414	1,2	0-3.0(9) 1.0	20,40	25-65(9) 40
1657	2195 3319	1,3	1.0-3.0(9) 1.5	10,20	5-35(9) 12
1663	2214 3308	2,3	1.0-4.0(9) 2.5	17,30	7-20(9) 13
1714	2301 3303	2	0.8-2.0(5) 1.2	25	9-40(5) 25
3074	2503 3302	2	0.5-3.5(7) 1.0	25	20-55(7) 30

DRUMQUIN AREA

Catchment No.	Grid Reference	Molybdenum ppm		Copper ppm	
		Sediments	Soils*	Sediments	Soils*
652	2300 3758	6,3	2.0-3.0(5) 2.6	15,30	8-28(5) 14
661	2276 3734	0,3	0-2.0(8) 1.0	3,8	4-20(8) 9
665	2322 3727	2,5	0-2.0(6) 1.2	5,8	5-25(6) 13
721	2341 3747	1,5	0-2.0(8) 0.8	8	7-22(8) 14

* Range and arithmetic mean; number of samples in parenthesis

Soil data on minus 10-mesh fraction; sediment data on minus 80-mesh fraction

TABLE 5-1 RANGE AND MEAN CONTENT OF MOLYBDENUM AND COPPER IN SOILS AND SEDIMENTS FROM NEAR ENNISKILLEN AND DRUMQUIN

Hypocuprosis without clinical symptoms has been reported in calves from an estate 6 miles north west of Enniskillen (Todd et al, 1967). The farm is outside the area of raised molybdenum delineated by the reconnaissance survey, but its geology, soils and environment are generally similar. Liver and blood copper were at deficient levels in the calves, particularly during the growing season when there was also a rise in the mean intake of Mo (1.1 to 2.3 ppm D.M.) and SO_4^{--} (0.28 - 0.36% D.M.). Although there could be several reasons for this coincidence, the herbage Mo content approaches that of suspected toxicity, (approximately 3 ppm D.M.; Thornton pers comm) and may be a significant factor.

The causes for the hypocuprosis at Enniskillen were not established, but it was suggested that in this high pH limestone area, reduced Cu absorption may have resulted from an increased $CaCO_3$ uptake. If this is so, the tolerance for Mo in herbage may have been reduced, antagonising the situation further. It is possible that where, under similar conditions, the Mo contents of soils and herbage are higher, there is more likelihood of such problems arising.

5.32 Drumquin

5.321 Description of the area A limited sediment Mo pattern (2 - 5 ppm) occurs over part of the Carboniferous limestone outcrop near Drumquin, Co. Tyrone (Fig: 5-1). This is more upland than near Enniskillen, with thinner drift cover. Soils are mostly light textured, but heavy gleyed soils occur in the valleys and on some slopes. Soil pH varies from 5.0 to 6.7.

5.322 Results Four catchments were investigated and the resampled sediments from three confirm the reconnaissance results. These reflect the Mo contents, maximum 3 ppm, of some of the soils in each catchment (Table 5-1). The copper levels (5 - 30 ppm), particularly in the lighter less organic soils, are often lower than in the Enniskillen area (5 - 56 ppm).

5.323 Discussion No cases of hypocuprosis have been recorded in this area and, in view of the low levels and localised occurrence of molybdeniferous soils, there is unlikely to be any hazard to livestock.

5.33 Isolated molybdeniferous sediments

5.331 Description of areas Sediments containing over 2 ppm Mo occur sporadically throughout the Tyrone area, particularly in the Low Sperrins region and on Slieve Beagh (Fig: 3-5). These are mainly over acid bedrocks, often obscured by exotic glaciofluvial drift. Most soils are more acid and lighter than near Enniskillen and Drumquin and peat is widespread. Cultivated soils are limed to pH 5.0 - 7.0.

5.332 Results The molybdeniferous sediments mostly occur in streams with high manganese and/or iron oxide precipitation. Six catchments were investigated and in each it was found that only a few soils contain over 0.8 ppm Mo. It is possible that in the very acid conditions (pH 3.5 - 5.0) of peaty and neglected soils, the metal has been mobilised and subsequently reconcentrated in the stream precipitate. It is unlikely, therefore, that there is any agricultural significance in such sporadic values.

5.34 Conclusion

The weak molybdenum patterns in the Tyrone area appear to reflect local enrichments in some of the soils of the catchments. It is possible that in all areas any bedrock effect is being diluted by overlying drift. Only in the district south of Enniskillen is the pattern sufficiently widespread to be of possible significance to agriculture.

Further work, including herbage sampling and blood copper analysis would be necessary in the suspect areas to test whether the patterns have any real agricultural significance. The Mo levels in sediments and soils, although above normal, are still lower than has been generally associated with molybdenum induced hypocuprosis elsewhere in the British Isles (Webb and Atkinson, 1965; Thornton, 1968).

5.4 INVESTIGATIONS INTO AREAS OF LOW COPPER AND ZINC

5.41 Introduction

Previous work has shown that stream sediment patterns of 10 ppm or less Cu may indicate regions in which soils poor in copper may be found, and hence delimit areas of potential deficiency of the metal in plants and animals (Thornton, 1968). In the Tyrone area, over half the sediments contain less than

12 ppm Cu, indicating the widespread occurrence of potentially suspect areas. There are also extensive patterns of sediments with zinc levels below 50 ppm. Since this metal can be secondarily enriched in sediments in comparison to mean soil and rock contents (Chapter 1-7) such patterns may indicate the occurrence of even lower levels of zinc in many of the soils.

Although the patterns of low Cu and Zn are not wholly co-extensive, the metals have been studied together, as it is possible that complex Cu-Zn deficiencies of the type described in Norway by Dynna and Havre (1963) may be found where both metals are low in the soil.

5.42 Preliminary Investigations

5.421 Sampling Soils and sediments were collected from 29 catchments with stream sediment contents of less than 10 ppm Cu, and 12 control catchments with sediment contents in the range 14 - 40 ppm Cu. The low Cu catchments were selected from the major geological and physiographical environments within the Tyrone area, at the locations shown on Fig: 5-2. The analytical results for Cu and Zn are shown on Tables 5-2 and 5-3.

5.422 Results of sediment sampling

Copper Resampling of sediments has confirmed most reconnaissance results. Major differences are usually due to variations in the mechanical composition of the samples, but nevertheless in only one low-Cu catchment were all samples above 10 ppm on resampling. Sediments from the control catch-

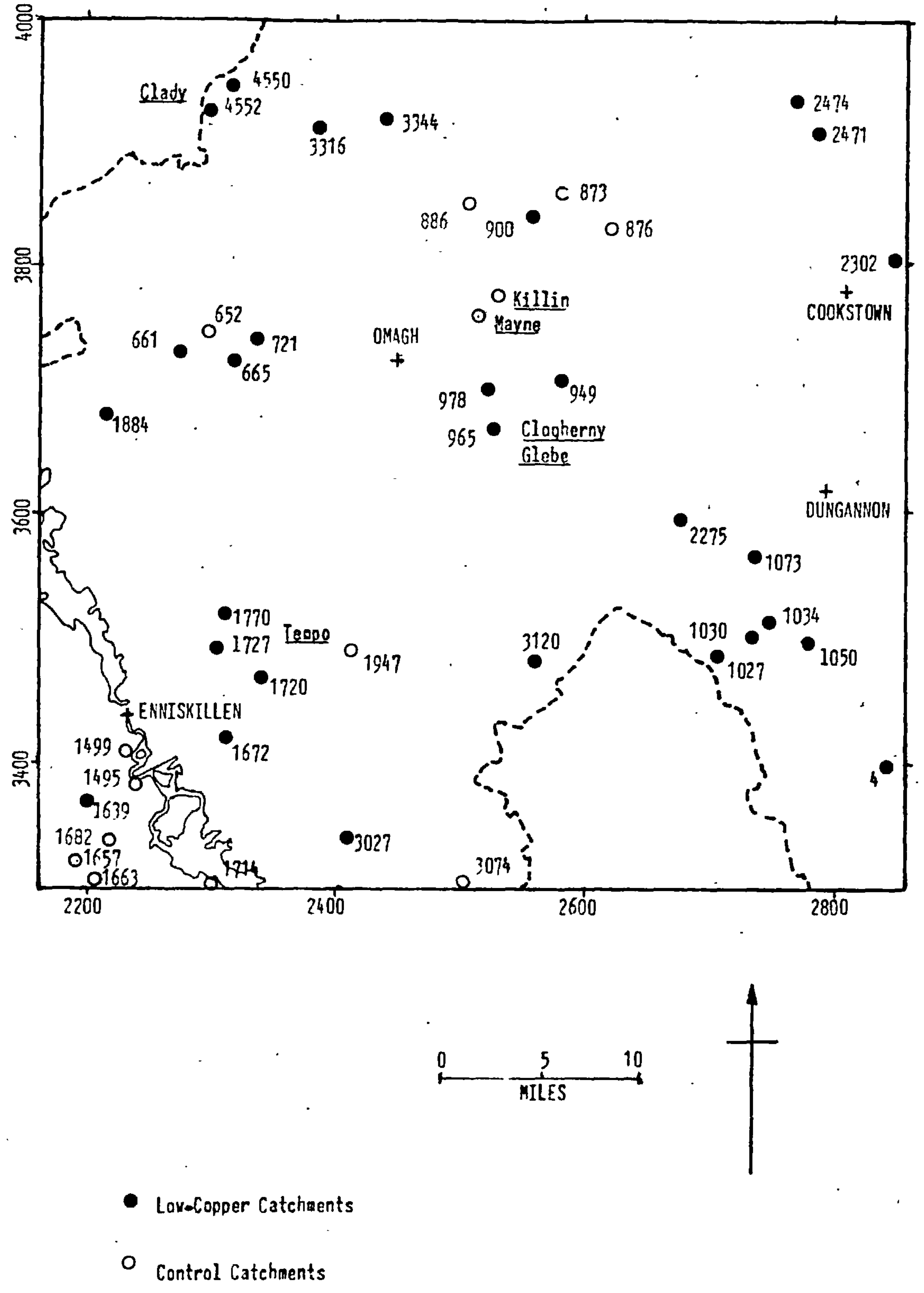


FIG. 5 - 2 LOCATION OF CATCHMENTS SELECTED FOR DETAILED STUDIES INTO COPPER AND ZINC DISTRIBUTION, TYRONE AREA.

ments were again in the range 14 - 40 ppm.

Zinc In more than half the catchments, the resampled sediments were over 10% lower in zinc than the original reconnaissance samples. The greatest difference occurred in those taken from streams in which heavy Fe-Mn precipitation observed during the reconnaissance in 1967 was absent on resampling in 1968.

5.423 Results of soil sampling

Copper There is only a poor correlation between sediment and topsoil Cu contents in the low-Cu catchments (Table 5-2). In nearly all cases there are some soils with less than 10 ppm Cu, but mostly the levels are higher with maxima varying from 4 - 10 times the sediment value.

In the control catchments the correlation is generally closer, with the maximum soil content rarely more than twice that of the sediment.

Ranges and mean levels of soil Cu do not differ significantly between the contrasted areas. Thus, although the sediments delineate regions of apparent difference in copper abundance, there is no such difference in the soils.

Zinc The soil zinc contents in each catchment show less variation that those of copper, with a closer correlation to the sediment levels - particularly to those of the resampled sediments (Table 5-3). It is possible that in the very dry summer of 1968, the secondary enrichment processes were less active than in the previous, much wetter year,

LOW COPPER CATCHMENTS.

GEOLOGY	LOCATION	CATCHMENT NUMBERS.	COPPER CONTENT ppm		
			SEDIMENTS.		SOILS.
			Reconnaissance	Follow - up.	
Dalradian	Strabane	4550, 4552	3 - 5 (3) 4 *	6 - 7 (3) 7 *	10 - 40 (14) 23 *
Central Inlier	Low Sperrins	900	4 (1)	5, 8 (2)	4 - 24 (7) 12
Silurian	Caledon	4	5 (1)	12, 17 (2)	20 - 45 (9) 33
Old Red Sandstone	Beragh	949, 965 978	3 - 6 (3) 4	5 - 9 (3) 7	3 - 50 (25) 17
	Tempo	1672, 1720 1727, 1770	3 - 8 (4) 6	4 - 9 (4) 7	3 - 90 (30) 25
L. Carboniferous Clastics	Aughnacloy	2275	9 (1)	7 (1)	6 - 55 (8) 25
	Draperstown	2471, 2474	5, 8 (2)	8, 10 (2)	3 - 30 (13) 17
	Newtownstewart	3316, 3344	5, 8 (2)	3, 5 (2)	3 - 27 (15) 7
L. Carboniferous Limestones	Aughnacloy	1030, 1034	3, 3 (2)	4, 8 (2)	6 - 35 (17) 16
Carboniferous Calp and Upper Limestones	Aughnacloy	1027, 1073	3, 3, (2)	6, 10 (2)	7 - 44 (17) 21
	Drumquin	661, 665 721, 1884	5 - 8 (4) 7	3 - 8 (5) 6	4 - 25 (36) 10
	Enniskillen	1639	5 (1)	7 (1)	7 - 42 (7) 23
U. Carboniferous Clastics	Rosslea	3027, 3120	3, 4 (2)	5 - 13 (3) 9	3 - 37 (16) 11
Trias	Aughnacloy, Cookstown	1053, 2302	4, 7 (2)	4, 5 (2)	15 - 32 (13) 23

CONTROL CATCHMENTS

GEOLOGY	LOCATION	CATCHMENT NUMBERS.	Reconnaissance	Follow - up.	SOILS.
Central Inlier	Low Sperrins	873, 876 886	14 - 30 (3) 20	14 - 30 (3) 20	6 - 85 (20) 23
L. Carboniferous Limestones.	Enniskillen	1495, 1499 1947, 3074	15 - 35 (4) 24	15 - 40 (5) 23	5 - 66 (28) 26
Carboniferous Calp and Upper Limestone.	Drumquin	652	32 (1)	14 (1)	8 - 30 (5) 14
	Enniskillen	1657, 1663 1682, 1714	15 - 50 (4) 18	10 - 30 (9) 19	5 - 60 (32) 17

* Arithmetic Mean. Number of samples in parenthesis

Soil data on minus 10 - mesh fraction; sediment data on minus 80 - mesh fraction.

TABLE 5 - 2. RANGE AND MEAN COPPER CONTENT OF SOILS AND SEDIMENTS FROM 41 CATCHMENTS TYRONE AREA.

GEOLOGY	LOCATION	CATCHMENT NO.	ZINC CONTENT ppm.		
			SEDIMENTS.		SOILS.
			Reconnaissance	Follow - up.	
Dalradian	Strabane	4550, 4552	55 - 65 (3) 58 *	36 - 65 (3) 55 *	30 - 70 (14) 45 *
Central Inlier	Low Sperrins	873, 876 886, 900	65 - 350 (4) 155	40 - 120 (5) 65	12 - 75 (26) 35
Silurian	Caledon	4	75 (1)	65, 80 (2)	55 - 100 (9) 70
Old Red Sandstone	Beragh	949, 965 978	40 - 180 (3) 90	30 - 70 (4) 50	12 - 50 (23) 30
	Tempo	1672, 1720 1727, 1770	55 - 75 (4) 65	35 - 70 (4) 50	9 - 85 (30) 45
L. Carboniferous Clastics	Aughnacloy	2275	70 (1)	90 (1)	22 - 60 (8) 45
	Draperstown	2471, 2474	50, 90(2)	60, 140 (2)	16 - 70 (12) 40
	Newtownstewart	3316, 3344	30, 30 (2)	10, 16 (2)	6 - 27 (15) 11
L. Carboniferous Limestones	Aughnacloy	1030, 1034	65, 45 (2)	70, 30 (2)	5 - 85 (17) 45
	Enniskillen	1495, 1499 1947, 3074	70 - 165 (4) 105	55 - 130 (5) 90	20 - 150 (28) 40
Carboniferous Calp and Upper Limestones	Aughnacloy	1027, 1073	50, 55 (2)	60, 30 (2)	30 - 140 (17) 60
	Drumquin	652,661,665 721,1884	40 - 120 (5) 65	40 - 85 (6) 60	7 - 100 (34) 40
	Enniskillen	1634, 1657 1663,1682,1714	55 - 230 (5) 120	70 - 90 (9) 75	20 - 105 (39) 65
U. Carboniferous Clastics.	Rosslea	3027, 3120	40, 65 (2)	50, 60 (2)	8 - 70 (16) 30
Trias	Aughnacloy	1050	65 (1)	40 (1)	35 - 85 (8) 45

* Arithmetic Mean. Number of samples in parenthesis.

Soil data on minus 10 - mesh fraction; sediment data on minus 80 - mesh fraction.

TABLE 5 - 3. RANGE AND MEAN ZINC CONTENT OF SOILS AND SEDIMENTS FROM 40 CATCHMENTS, TYRONE AREA.

thereby giving lower sediment contents and improving the correlation. Such a close climatic dependence would be surprising, however, and requires confirmation.

5.424 Discussion The results of the preliminary investigation suggest that the patterns of low sediment copper are not reflected by similar levels in the topsoils. Patterns in the range 5 - 40 ppm Cu may relate to geology in that low levels tend to occur where bedrock or drift is siliceous and higher levels where they are argillaceous or calcareous. In soils, however, there is a wide range of Cu contents (5 - 90 ppm) from both low copper and control catchments. In part, the sediment metal contents may reflect the relative proportions of soils with 'high' ($>$ 20 ppm) and 'low' ($<$ 10 ppm) copper contents within a catchment, but this does not appear to account wholly for the poor soil-sediment correlation.

A closer analysis of the data suggests that the variations of soil and sediment metal contents depend on additional factors related to the physico-chemical environment and to topography.

i) Physico-chemical environment The physico-chemical environment has been investigated in terms of pH, in the absence of a suitable technique for the rapid measurement of Eh.

The relationship of soil pH to soil Cu and Zn contents is shown on Fig: 5-3. Only in very acid soils is there a

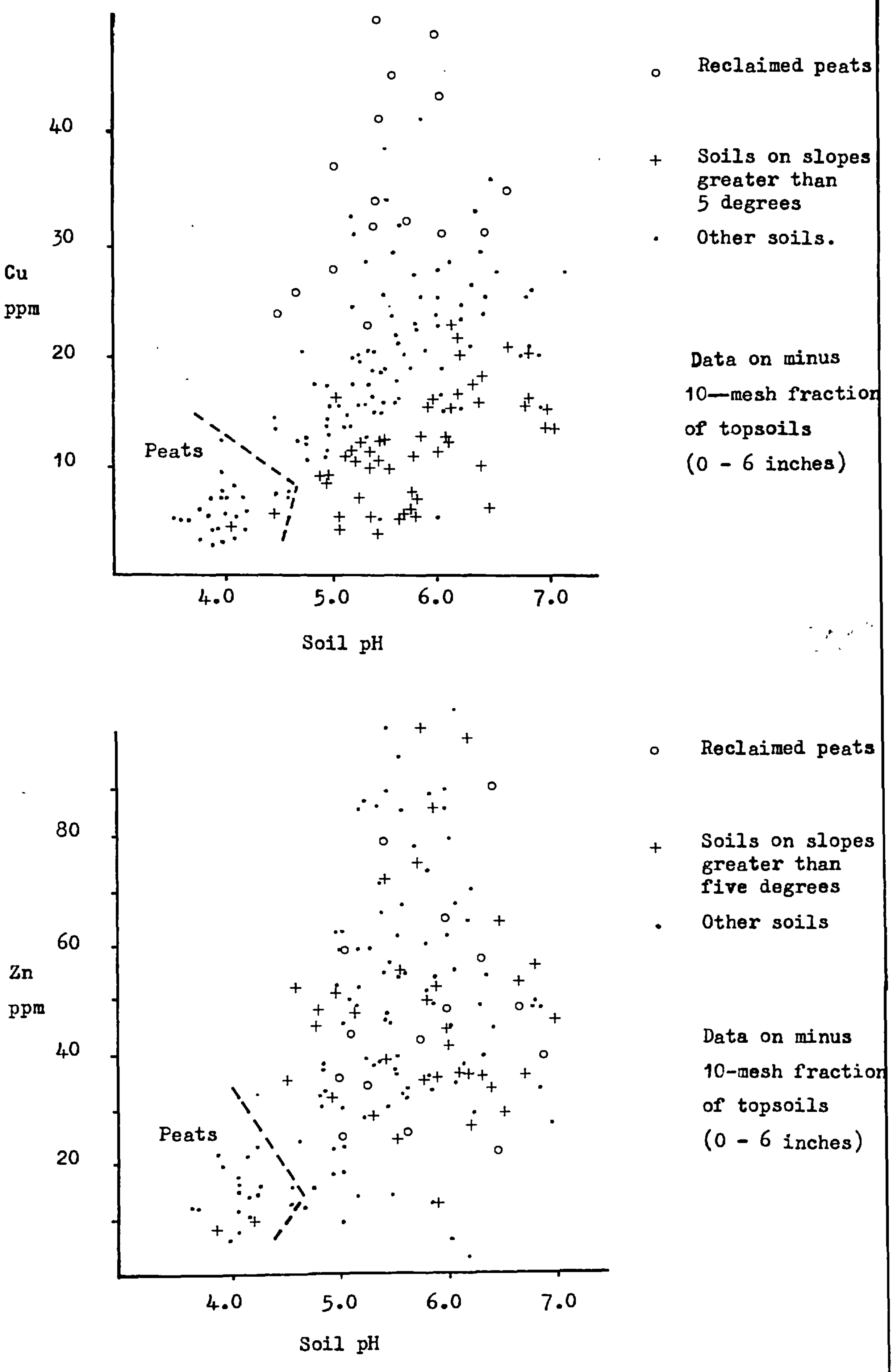


FIG. 5.- 3. RELATIONSHIP BETWEEN COPPER AND ZINC CONTENTS AND pH IN SOILS, TYRONE AREA.

correlation between pH and metal content, in that all soils, mostly peats, with pH below 4.5, contain less than 10 ppm Cu and 25 ppm Zn, D.M. In less acid soils metal content varies over a wide range.

Field observations showed two important features of the Cu distribution in the soils. At any pH:

a) the low soil Cu contents are found on steeper slopes;
b) the higher soil contents are associated with soils on reclaimed peat lands.

These two groups are discussed below, but in the remaining soils, namely the mineral soils on the flatter land, there is an apparent relationship between Cu and pH, suggesting that pH is always important in determining soil Cu content. The relationship between soil pH and Zn content is much weaker but nevertheless both metals are leached when soil pH is below 5.0.

Stream water pH is in the range 5.5-7.5, reflecting geology only in that streams draining limestones are usually neutral to weakly alkaline. Differences in pH do not correspond to variations in sediment content. Water pH can fluctuate periodically, but in some instances shows a general relationship to the pH of adjacent soils. Thus, the catchments of the more acid streams (pH below 6.0-6.5) seem to have a high proportion of acid soils. Most streams in the Tyrone area, however, have pH > 6.0 but it is shown in Chapter 6 that if sediments in such streams are enriched by the co-precipitation of Zn with Fe - Mn oxides, this also indicates that many soils in the catchment are acid and depleted in metals. Although Cu is leached also, it does not re-precipitate to enrich the sediment.

It is suggested that the occurrence of acid, potentially deficient soils may be inferred from data obtainable from a reconnaissance survey, if pH is measured at the time of sampling. Catchments yielding sediments with low Cu contents may be divided into three groups (Table 5-4):

1. Acid streams pH < 6.0. Sediments contain <13 ppm Cu; <30 ppm Zn. Many soils acid and leached; metal contents similar to sediments.
2. Enriched streams pH > 6.0. Sediments contain <12 ppm Cu; >125 ppm Zn; $>2,000$ ppm Mn. Soils similar to previous group.
3. Normal streams pH > 6.0. Sediments contain <12 ppm Cu; 40-100 ppm Zn, $<2,000$ ppm Mn. Soil Cu mostly > 20 ppm; Zn close to sediment value.

Metal values are only approximate; those for Zn in groups 2 and 3 are somewhat arbitrary, but are based on the regional mean content of 90 ppm Zn (Table 3-4).

ii) Topographic environment This is best described in terms of relief and slope of the land. It affects the metal contents of sediments and soils by causing physical fractionation.

		STREAMS				SOILS			
Catchment No.	Geology	Water pH	Cu ppm	Zn ppm	Mn ppm	pH Range Mean*	Cu ppm Range Mean*	Zn ppm Range Mean*	Number Samples
ACID STREAMS									
3316	L.Carboniferous Clastics	5.5	5	17	1300	3.7-6.4 4.4	3-23 7	6-19 10	7
3344		5.8	3	11	600	3.5-5.0 4.5	4-27 8	6-27 10	7
ENRICHED STREAMS									
873	Dalradian	7.0	14	350	>10000	4.0-6.5 5.0	6-19 10	12-53 25	8
2471	L.Carboniferous Clastic	6.8	5	140	4000	3.5-6.0 4.8	2-27 12	16-32 24	6
NORMAL STREAMS									
965	Old Red Sandstone	6.7	9	60	1000	4.2-7.0 6.2	6-34 20	23-50 40	7
1727		6.8	4	35	300	3.9-6.8 5.5	3-36 18	9-50 35	8
2471	L.Carboniferous Clastic	7.0	8	60	500	4.5-6.5 5.8	9-30 18	35-70 50	5

* Arithmetic mean

Soil data on minus 10-mesh fraction;
sediment data on minus 80-mesh fraction.

TABLE 5-4 RELATIONSHIP BETWEEN SOIL METAL CONTENT AND THE pH AND SEDIMENT METAL CONTENT OF ASSOCIATED STREAMS TYRONE AREA

Sediments The sediments from all 29 low-copper catchments and 2 of the control catchments (14 ppm Cu) were coarse and sandy but those from the remaining 10 control catchments were fine and organic. Thus, the patterns shown by the Cu contents of these sediments appear to reflect their mechanical composition and degree of sorting, rather than real variations in metal abundance. It is suggested, therefore, that the Cu distribution patterns are being influenced by regional differences in relief and topography, since these control stream velocity and hence determine the degree of sorting and physical fractionation of the sediments.

Geology has a partial influence in that argillaceous rocks are less resistant to erosion than siliceous rocks, so that relief will be lower and stream sorting poorer where they outcrop.

Mechanical composition has little influence on sediment Zn contents, with sands containing 10-140 ppm Zn and organic muds 60-130 ppm Zn. Although coarse sediments can have very low Zn contents, they can also be secondarily enriched by Zn coprecipitating with Mn oxides.

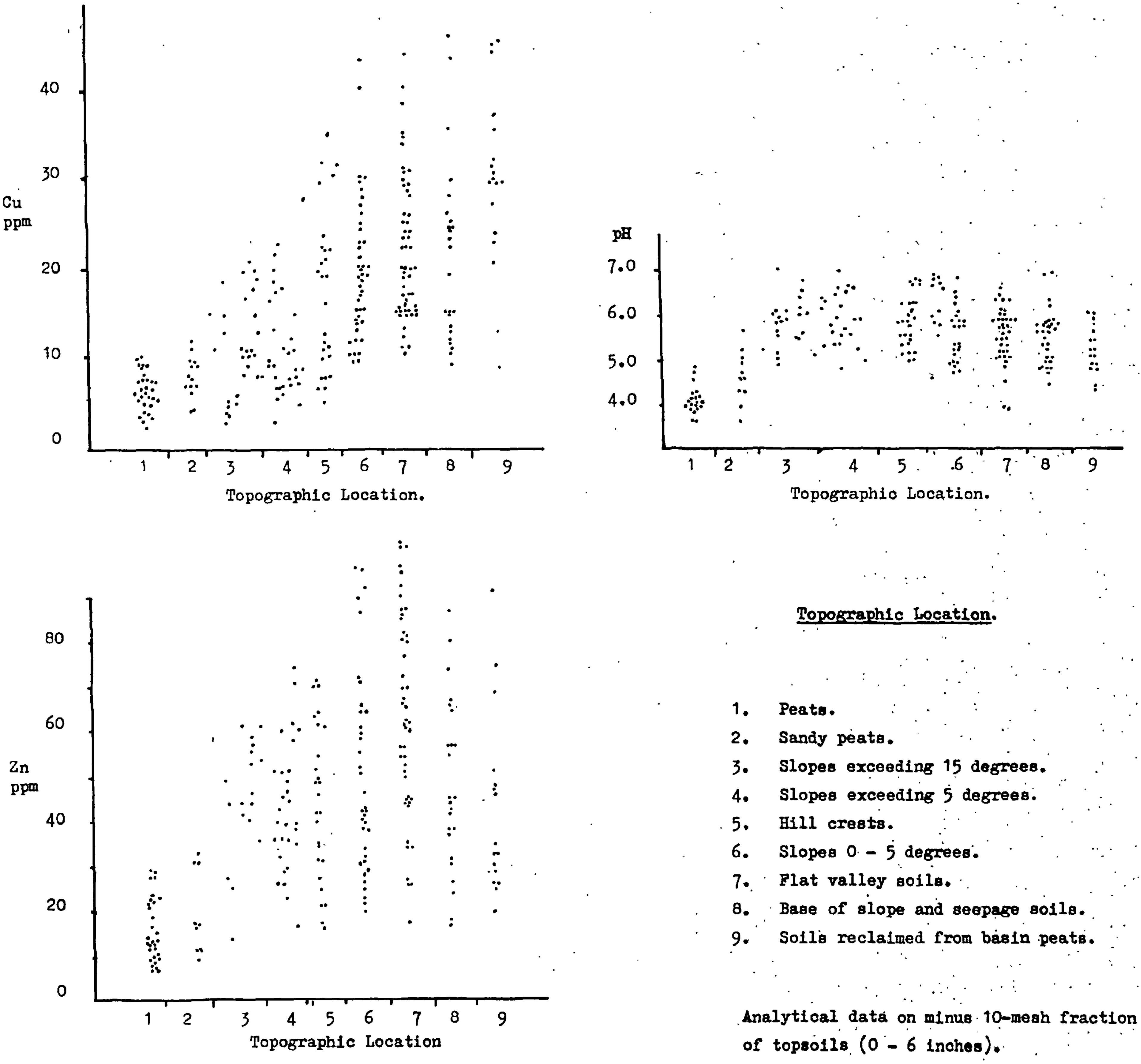
Soils The dependence of soil Cu content on relief can be shown by plotting metal content against topographic location (Fig: 5-4). All peats and sandy peats contain less than 12 ppm Cu, often less than 10 ppm, whereas most other low Cu contents in topsoils are associated with steep slopes - in all catchments, irrespective of geology. Of the 104 mineral soils sampled containing 15 ppm Cu or less, 48% occurred on slopes greater than 5 degrees, and of the 45 samples containing less than 10 ppm Cu, 65% occurred on such slopes. Some 60 samples were collected from slopes greater than 5 degrees and of these 70% had below 15 ppm Cu, 45% below 10 ppm Cu.

The coarser sediments of the low-Cu catchments have Cu contents of approximately the same levels as steep slope and acid soils, whereas the finer sediments from the control catchments have contents similar to the soils from the flatter land.

Neither the Zn content nor the pH of soils show any regular variation with topography, although steep slope soils tend to contain below 60 ppm Zn and peats below 30 ppm Zn (Fig: 5-4), presumably because of increased leaching at these sites.

The origin of the high Cu content of soil reclaimed from basin peats is uncertain. The metal is possibly derived from heavy liming or other treatment, or from increased copper retention by the very organic soils.

The influence of physico-chemical and topographic environments are shown by the investigation by Thornton (1968). Comparative studies were made in catchments over the Bagshot Beds, Wealden Beds and London Clay in Dorset. The results, summarised on Table 5.5, show that stream sediment patterns of 10 ppm Cu occur in areas where most topsoils also have



Topographic Location.

1. Peats.
2. Sandy peats.
3. Slopes exceeding 15 degrees.
4. Slopes exceeding 5 degrees.
5. Hill crests.
6. Slopes 0 - 5 degrees.
7. Flat valley soils.
8. Base of slope and seepage soils.
9. Soils reclaimed from basin peats.

Analytical data on minus 10-mesh fraction of topsoils (0 - 6 inches).

FIG. 5 - 4. VARIATION OF SOIL COPPER AND ZINC CONTENTS AND pH WITH TOPOGRAPHIC LOCATION.
(Data from 41 selected catchments, Tyrone area).

		BAGSHOT BEDS	WEALDEN BEDS	LONDON CLAY
STREAM SEDIMENTS				
Reconnaissance survey Cu content (ppm)	Range	2 - 60	3 - 40	4 - 40
	Mean(No.samples)	10 (33)	11 (17)	12 (13)
		Sediments mostly sandy. Higher copper contents in finer, organic sediments.	Sediments mostly sandy. Higher copper contents in finer, organic sediments.	
		Water pH:below 5.5.	Water pH: approximately 7.0.	
SOILS				
Copper content	Range	4 - 37	10 - 50	10 - 40
	Mean(No.samples)	13 (22)	20 (23)	27 (14)
		Podzolic,very acid. Higher copper contents may reflect pipe-clay outcrops in valleys.	Brown earths. pH maintained near 6.0. Lower copper contents (<15 ppm) on steep slopes, ridges.	
		Mainly coniferous forest. Some poor pasture.	Mainly arable.	

TABLE 5-5 COMPARATIVE STUDIES OF SOILS AND SEDIMENTS FROM THE BAGSHOT BEDS, WEALDEN BEDS AND LONDON CLAY, DORSET

(After Thornton, 1968)

low metal contents and give rise to simple copper deficiencies in cattle and seedling Sitka spruce. However, similar patterns over adjacent areas show no such correlation. There is a variability in topsoil copper content comparable to that found in the Tyrone area with low levels (15 ppm) Cu only in soils on steep slopes.

The copper deficiencies were confined to the outcrop of the Bagshot Beds - and the only difference shown by the reconnaissance appears to be that the stream waters are more acid than over adjoining formations. As in the Tyrone area, therefore, acid stream waters are reflecting the acidity of the majority of soils in the catchments.

The deficiency situation, however, probably arises from leaching intensifying the effects of a low Cu abundance in the bedrock, rather than being a function of soil acidity alone. Elsewhere, in catchments with nearly neutral stream waters and relatively unleached soils, the Cu content is influenced by the relief, with lowest values occurring on steep slopes.

5.425 Preliminary conclusions These preliminary investigations show that in the Tyrone area, sediment patterns within the range 5-40 ppm Cu do not reflect corresponding patterns in topsoils. In general, coarser sediments have low levels of Cu, approaching those of acid or steep slope soils, and finer, organic sediments have higher levels of Cu, closer to soils on flatter or more poorly drained land.

Sorting into mechanical fractions during erosion and stream transport thus appears important in determining the Cu distribution patterns. Sorting is greatest in regions of high relief and such areas tend to have patterns of sandy sediments with low Cu content. Where relief is low, sorting is poorer and sediments are finer with higher metal contents. The patterns examined reflect geology mainly in that the erosion of argillaceous rocks gives low relief and fine sediments.

The variation in Zn content of soils within a catchment is generally less than that for Cu. The Zn contents of sediments free of heavy Fe-Mn precipitation, regardless of mechanical composition are a close approximation to those of the soils.

Acid stream waters, or sediments enriched in Zn and Mn, may indicate that many soils in the catchments are leached and hence depleted in both Cu and Zn.

5.43 Detailed Investigations

5.431 Introduction Clastic sediments are derived from the erosion of a soil profile, hence sediment metal contents may reflect the contents of the subsoils and parent material more closely than those of topsoils. Further studies were therefore initiated to confirm the preliminary results and to:

i) determine the relationship between sediment and subsoil metal contents;

ii) investigate the form and distribution of soil copper;

iii) devise an improvement in sampling technique to aid interpretation of low contrast sediment patterns.

The six catchments named on Fig: 5-2 were studied. The two controls were chosen because sandy sediments contain over 15 ppm Cu.

Soils and sediments were collected from each catchment. Soils were sampled at 6-inch intervals to a depth of 24 inches, along traverses across the important features of the catchment. Full profiles were examined in two catchments. A variety of sediment types, based on textural differences, was collected from several sites in each stream.

Composite samples of mixed grasses and clover were collected from near several soil sample sites in each catchment. The results, summarised in Table 5-6 below, are discussed for each catchment in turn.

Catchment	Environment	No. Samples	Cu ppm	Zn ppm
Clogherny	Moraine crest	2	13,14	30,32
Glebe	Steep slope	2	12,13	30,30
	Poorly drained valley	2	6,9	24,32
Tempo	Moorland	2	8,9	53,55
	Steep slope	2	6,7	31,38
	Gentle slope	4	11-16 14	28-45 36
Clady	Gentle slope	5	12-18 14	24-30 27
Mayne	Gentle slope	4	9 12 10	21-41 31

TABLE 5-6 COPPER AND ZINC CONTENT OF MIXED HERBAGE FROM SELECTED CATCHMENTS, TYRONE AREA

(Data on analysis of dry matter)

5.432 Low-Copper Catchments

5.4321 Clogherny Glebe, near Beragh, Co. Tyrone Catchment 965.
Grid reference 2325 3675.

Geology Old Red Sandstone, obscured by large sand and gravel moraines.

Topography The moraines form steep-sided hills, with flat, rounded or ridged tops, enclosing valleys containing extensive basin peat.

Soils and Land Use Soils are mainly friable sandy loams, freely drained and suitable for arable farming. Soils reclaimed from basin peat are wetter and often organic. The soils are 'agricultural brown earths', supposed to have lost most podzolic characteristics after blanket peats were cleared from the hills (McConaghy and McAllister, In Symons, 1963). The reddish sands of the parent moraine become visible at about 18 inches.

Preliminary Results

The results of the preliminary topsoil (0-6 inches) study were:

Metal	SOILS No.Samples	Range	Mean	Sediments
Cu ppm	9	6-34	20	3, 9
Zn ppm	7	26-52	40	60

The low levels occur in peats and, for Cu, on steep slopes.

Detailed studies The results of the detailed sampling are shown in part on Fig: 6-5 (Section 5.434) and on Table 5-7 where the soil data have been grouped according to topographic location.

Metal contents of soils In each group of mineral soils, the topsoils are enriched in Cu and organic carbon relative to the subsoils. The Cu content of the topsoils varies with environment, being lowest on steep slopes and highest on reclaimed peat land, but that of the reddish subsoils, representing the C horizon, is nearly constant at about 13 ppm. The Cu content does not exceed this level in deep horizons of a freely drained moraine soil (profile CGP/3, Fig: 6-12), but silty clays in an imperfectly drained valley soil (profile CGP/2) contain 20-25 ppm Cu. The topsoils from the steep slopes have similar organic carbon contents to those from other environments, but the organic horizons are shallower. The red sands occur at a depth of about 8 inches on steep slopes, at 15-24 inches elsewhere.

Zinc contents of moraine soils vary little either within the profiles or according to topography, being only marginally lower on steep slopes (50 ppm Zn) than flat crests (60 ppm).

Base of slope and seepage soils, and soils reclaimed from peat, have deep topsoils enriched in Cu and organic carbon, even when very acid (pH 4.0). Zinc contents are mostly similar to those of freely drained soils. The mineral subsoils, however, particularly below reclaimed peats, are usually bleached and depleted in Cu and Zn.

There is an apparent correlation between copper and organic contents within individual profiles - excluding those in

SOILS. Related to topography	Depth (ins.)	No. Samples	Cu ppm	Zn ppm	Organic Carbon %	pH
Hill Crests						
Topsoils	0-6	3	20-25 23	50-70 60	2.5-2.8 2.7	-
Subsoils	12-18	3	10-17 14	55-75 70	1.0-1.2 1.1	5.8-7.6 6.7
Steep Slopes						
Topsoils	0-5	4	10-18 14	43-60 50	2.3-2.4 2.3	-
Grey subsoils	5-10	3	9-16 11	52-55 54	1.0-1.3 1.1	6.8-8.0 7.3
Red subsoils	12-18	3	11-17 13	45-55 47	0.2-1.0 0.5	6.8-7.0 6.9
Poorly drained soils						
Topsoils	0-6	3	23-34 27	45-60 55	2.3-4.0 3.3	6.0-6.7 6.3
Grey subsoil	12-18	2	19,21	40	3.1,3.3	-
Red subsoil	18-24	3	7-10 9	40-50 45	0.6-1.2 1.0	-
Bank soils						
Topsoils	0-6	6	11-32 22	45-60 55	2.3-5.8 3.7	-
Subsoils	12-24	4	9-20 13	40-70 50	0.3-3.2 1.7	5.2-6.8 6.0
Stream level	40	6	7-20 12	40-50 45	0.4-2.25 1.1	-
Basin peat	0-10	3	4-15 8	18-45 32	>20	3.7-4.2 3.9
Reclaimed peat						
Topsoils	0-6	3	26-30 28	48-50 49	>15	4.5-6.0 5.0
Grey subsoil	12-18	2	12	30-35 32	>10	4.0
SEDIMENTS						
Sands	-	4	4-8 7	37-55 47	0.4-1.5 0.8	-
Silty sands	-	4	9-14 11	50-65 60	-	-
Muddy silt	-	6	9-19 13	60-95 70	2.3-4.0 3.1	-
Organic mud	-	3	18-29 22	80-135 105	3.0-4.6 3.6	-

Soil data on minus 10-mesh fraction; sediment data on minus 80-mesh fraction.

TABLE 5-7 RANGE AND MEAN CONTENT OF COPPER, ZINC AND ORGANIC CARBON IN SOILS AND SEDIMENTS, CATCHMENT 965, CLOGHERNY GLEBE peats and on steep slopes. The relationship is weak when profiles are compared, however, so that points on a correlation diagram (Fig: 5-5) are well scattered. There is no correlation between the mechanical composition and metal content of soils (Table 5-8), although in the valley (profile CGP/2) the raised copper level below 40 inches is associated with an increase in silt and clay.

Metal content of stream sediments The Cu, Zn and organic contents of stream sediments all decline steadily with increasing particle size, with a threefold difference in Cu content between sands and organic muds (Tables 5-7, 5-8). The silts and sands, which comprise the active sediment normally chosen for reconnaissance sampling, have similar Cu contents (6-15 ppm Cu), to most subsoils but to less than 20% of topsoils. The majority of topsoils have Cu contents in the same range as those of organic muds (18-30 ppm Cu), sediments which occur in gently flowing streams and back eddies.

Metal content of herbage The copper and zinc contents of herbage (Table 5-6) show no significant variation with change of slope on the moraine (mean 13 ppm Cu, 30 ppm Zn). The Cu content falls to 8 ppm in alluvial and reclaimed areas, however, although the topsoil Cu content is greater than elsewhere. This may reflect a change in grass species or, more probably, a change in Cu availability, with the metal held strongly in the organic topsoils.

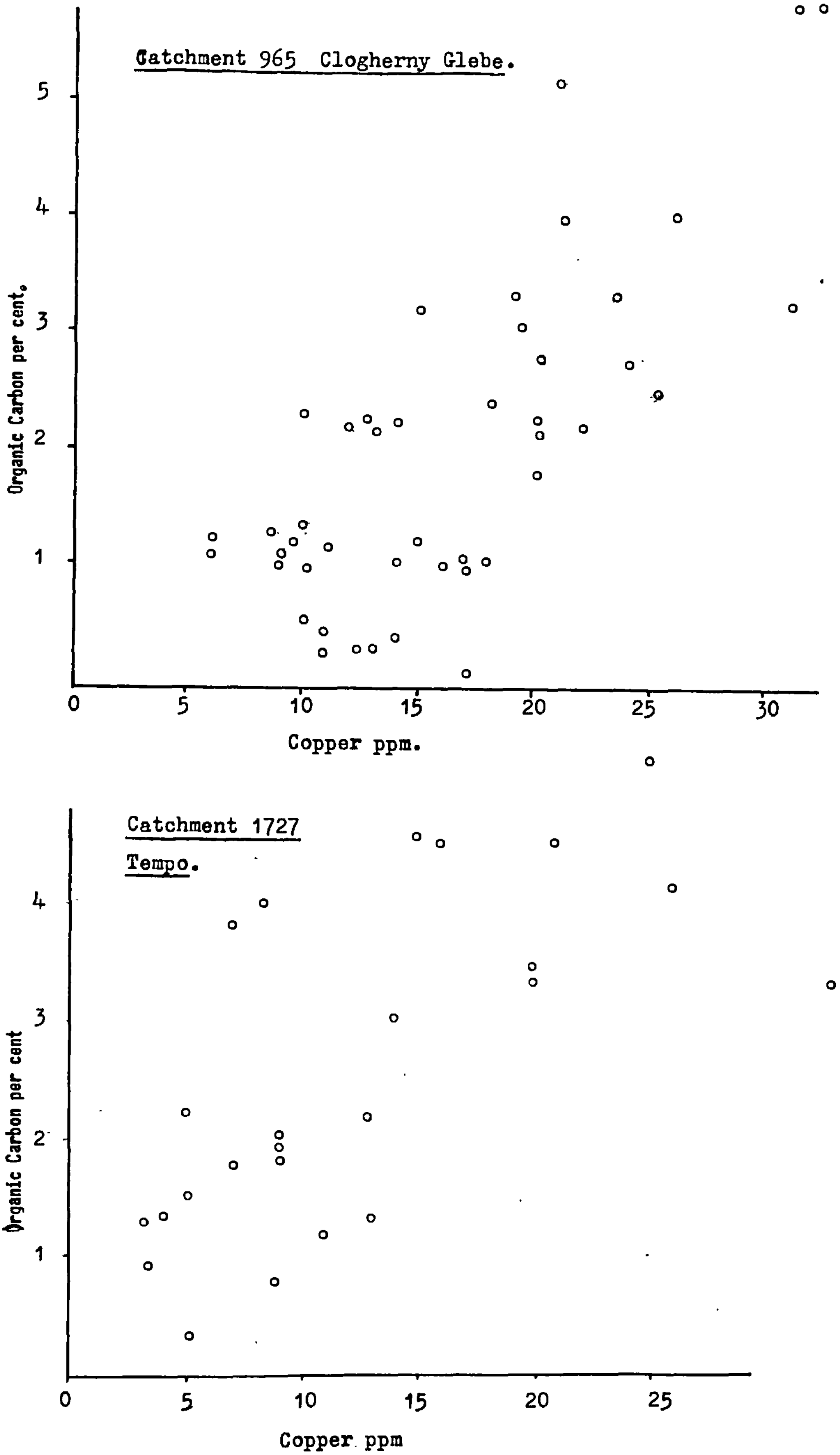


FIG. 5 - 5. RELATIONSHIP BETWEEN THE COPPER AND ORGANIC CARBON CONTENTS OF SOILS AT CLOGHERNY GLEBE AND TEMPO.
(Data on minus 10-mesh fraction).

		Depth (ins)	% Sand	% Silt	% Clay	Cu ppm	Zn ppm	% Organic Carbon
Catchment 965 Clogherny Glebe								
Moraine Crest (Profile CGP/1)	Topsoil	0-6	75	21	4	20	45	3.1
	Subsoil	12-18	70	23	7	13	40	1.5
	Sand	24-30	83	15	2	11	70	0.9
	Silty sand	45	75	20	5	8	35	0.2
Steep Slope	Topsoil	0-5	70	26	4	13	45	2.3
	Subsoil	10-16	68	26	6	13	45	0.4
Valley (Profile CGP/2)	Topsoil	0-6	84	15	1	25	35	5.5
	Subsoil	12-18	85	13	2	4	18	2.5
	Silty clay	40	60	28	12	20	55	0.2
Stream Sediments	Sand	-	94	5	1	8	50	1.2
	Silty sand	-	86	10	4	12	55	1.5
	Organic silt	-	80	17	3	30	100	3.5
Catchment 791516 Mayne								
Hill Crest (Profile MP/2)	Topsoil	0-6	70	26	4	45	60	3.6
	Subsoil	12-18	68	25	7	35	65	2.5
	Pink clay	30	50	34	16	30	75	0.2
	Grey clay	40	50	30	20	50	75	0.2
Stream Sediments	Coarse sand	-	93	5	2	25	70	1.5
	Fine sand	-	82	16	2	35	90	1.8
	Black mud	-	73	25	2	40	80	7.1

Mechanical composition determined by Bouyoucous method. Analytical data: soils on minus 10-mesh fraction; sediments on minus 80-mesh fraction.

TABLE 5-8 MECHANICAL COMPOSITION AND METAL CONTENTS OF SOILS AND SEDIMENTS FROM CLOGHERNY GLEBE AND MAYNE, Co. TYRONE

5.4322 Ballyreagh, Tempo, Co. Fermanagh Catchment 1727. Grid reference 2306 3483.

Geology Old Red Sandstone, obscured by sandy, probably local, till.

Drainage and topography The stream drains a basin bog between small peat-covered drumlins. It flows rapidly through cultivated land for its remaining course, finally dropping down a small escarpment to the reconnaissance site.

Soils and land use Soils are mostly freely drained acid brown earths, with peaty podzols and gleys near the stream source. The topsoils, mostly grey-brown sandy clay loams, overlie purplish pink sandy clays. The better drained land is suited for arable farming, except where too steep.

Preliminary results

The results of the preliminary topsoil study were:

	SOILS			
Metal	No.Samples	Range	Mean	Sediments
Copper ppm	8	3-35	18	6,4
Zinc ppm	8	10-60	35	35,65

Detailed studies Analytical results for copper and organic carbon in soils and sediments are shown on Table 5-9.

Soils The copper content of topsoils varies widely, 7-70 ppm Cu, with the highest levels on reclaimed peats and some arable land. In the latter the enrichment may be artificial resulting from treatment with Bordeaux mixture or copper sulphate. The lowest levels ($<$ 10 ppm Cu) occur in peaty areas and on steep slopes.

Soils in relation to topography		Depth (ins)	No. Samples	Cu ppm*	Organic Carbon %*	pH*
Well drained crests & slopes	Topsoil	0-6	4	15-20 18	3.4-4.6 4.0	5.7-6.6 6.1
	Subsoil	12-18	3	5-9 7	1.6-2.2 1.9	
Steep slopes	Topsoil	0-6	3	7-9 8	2.0-3.9 3.3	5.3-5.6 5.5
	Subsoil	6-12	2	4,7	1.4,1.8	
Flat Valley	Topsoil	0-6	3	20-33 26	3.4-4.2 3.8	4.9-6.8 5.7
	Subsoil	12-18	3	9-13 11	1.2-2.0 1.5	
Seepages	Topsoil	0-6	2	65,74	8,11	5,6
	Subsoil	12-18	2	16,25	5.4,7.4	
Moors	Peats	0-6	5	3-6 4	nd.	3.7-4.1 3.9
	Sandy Subsoils	10-16	4	2-4 3	nd.	3.9
Sediments						
	Gravelly Sands		2	5,5	2.8,2.8	4.6,5.5
	Silty Sands		3	3-7 5	0.7-1.7 1.4	6.0-6.6 6.3
	Organic Muds		2	18,20	3.3	6.7

*Range /Arithmetic mean.

Soil data on minus 10-mesh fraction; sediment data on minus 80-mesh fraction.

TABLE 5-9 COPPER AND ORGANIC CARBON CONTENT OF SOILS AND SEDIMENTS. CATCHMENT 1727. TEMPO, Co. TYRONE

Soil Cu content declines down profile, with most subsoils containing less than 10 ppm Cu. This corresponds to a decrease in organic carbon, suggesting that the latter controls the Cu distribution. This relationship is partially shown by a correlation diagram (Fig: 5-5) but, as at Clogherny, although there is a general relationship in the individual profiles, it is not quantitative from profile to profile. In some soils, the Cu content can rise again in deep clayey horizons. For example, in two profiles, the Cu content falls from 25-30 ppm in topsoils to 8 ppm at 12-18 inches, as organic carbon falls from about 4.5% to 1.5%. However, sandy clays at 24 inches contain 25 ppm Cu, although organic carbon is below 1%. In bank soils, the minimum Cu contents occur in the zone of water table fluctuation.

Sediments The stream runs swiftly from the peat bog to the base of the scarp and has only coarse sediments with a mean content of 5 ppm Cu. Downstream from the scarp, however, the water is sluggish and has allowed the deposition of finer sediment fractions in back eddies and on banks. The organic muds have a significantly higher Cu content (18 ppm) than the fine sands (6 ppm) from an adjacent site. As at Clogherny, the Cu contents of the majority of topsoils are more accurately represented by those of the organic sediments. The more abundant coarse sediments represent most subsoils but less than 20% of topsoils.

Metal contents of herbage Eight composite samples of mixed grasses were collected. Two were comprised of species of moor grass.

Analytical results (Table 5-6) show that grasses from peat areas and steep slopes have lower Cu contents (7-9 ppm D.M.) than those from elsewhere (11-16 ppm D.M.). The Zn content of moor grasses (54 ppm D.M.), however, is higher than that of other herbage (mean 35 ppm D.M.).

5.4323 Sion Mills, Co. Londonderry Catchment 4550. Grid reference 2315 3915.

Clady, Co. Londonderry Catchment 4552. Grid reference 2298 3930.

Geology Lower Dalradian mica schists, overlain in both catchments by thick sandy till.

Topography Rolling lowland.

Soils and land use Soils are acid brown earths giving grey brown micaceous clay loams which become more sandy with depth. They are mostly freely drained, particularly in catchment 4550, and suited for arable farming.

Preliminary results

The results of the preliminary study were:

	Range and Mean Cu Content (ppm)	
	Catchment 4550	Catchment 4552
Topsoils (0-6 inches)	12-23 (6) 17	15-40 (7) 27
Subsoils (6-12 inches)	9-20 (6) 15	10-50 (7) 22
Sediments	3,6 (2)	4-7 (4) 5

(number of samples in parenthesis)

Detailed studies Stream sediments and bank soils were sampled to determine the relationship between sediments and eroded soil.

Copper content of bank soils The results (Table 5-10) show that the Cu contents are lowest (12 ppm) in the zone of water table fluctuation below the organic topsoil. The topsoils themselves mostly contain over 25 ppm Cu, with the highest levels (> 30 ppm Cu) in samples with over 3% organic carbon. The Cu content is also raised relative to the subsoils in the finer horizons below stream level, with the metal possibly associated with clay or silt fractions.

CATCHMENT 4550		Depth (ins)	Copper ppm Range/Mean	Organic Carbon % Range/Mean
Soils				
	Topsoils	0-10	25-45(7)* 30	1.6-4.2(5)* 2.2
	Subsoils	12-30	9-16(10) 12	0.3-1.5(10) 0.9
	Stream level	36	11-25(6) 18	0.2-1.5(3) 0.7
Sediments				
	Silty sands	-	10,10(2)	0.4,0.5(2)
	Silty muds	-	19,21(2)	1.6,1.9(2)
CATCHMENT 4552				
Soils	Topsoils	0-10	17,21(2)	1.3,2.2(2)
	Stream level	36-40	8-13(6) 10	0.4-0.9(6) 0.6
	Boulder clay	72	23,25(2)	0.2,0.2(2)
Sediment				
	Silty sands	-	7-9(3) 8	0.4(1)

* No. of samples in parenthesis.
Soil data on minus 10-mesh fraction; sediment data on minus 80-mesh fraction.

TABLE 5-10 RANGE AND MEAN CONTENT OF COPPER AND ORGANIC CARBON IN BANK SOILS AND STREAM SEDIMENTS. CATCHMENTS 4550 and 4552. CLADY, Co. LONDONDERRY

Copper content of sediments The fine sediments, muddy silts, have higher contents of Cu (20 ppm) and organic carbon (1.8%) than the active silty sands ($<$ 10 ppm Cu, 0.5% carbon). Thus it appears that, on erosion, the bank subsoils contribute Cu-poor material for the coarser sediments and the topsoils and deep horizons contribute Cu-rich materials for the finer, organic sediment. In both catchments, the stream flow is rapid and fine organic samples are uncommon, although the Cu-rich horizons form over 50% of the bank profile.

Metal contents of herbage Five composite samples of mixed grasses and clover were collected (Table 5-6). The Cu content varies little (12-18 ppm D.M.), with the highest level in vigorously growing grasses. The Zn content is generally very low (mean 27 ppm).

5.433 Control catchments

Catchments with sandy stream sediments containing over 15 ppm Cu.

5.4331 Killin, Mountfield, Co. Tyrone

Catchment 919. Grid reference 2533 3778.

Geology Upper Dalradian garnet mica schist obscured by boulder clay of apparently local origin.

Drainage and topography The small stream rises in a semi-moorland area on the lower slopes of Mullaghcarn. It flows rapidly down the scarp at the foot of the hill, cutting through over 30 feet of drift to bedrock in narrow gullies.

Soil and land use Soils are acid brown earths, which give imperfectly drained clay loams. On steep slopes, the soils are sandy and more freely drained. The land is mostly down to pasture.

Analytical results

The results for Cu, Zn and organic carbon in soils, rocks and sediments are shown on Table 5-11 below.

SOILS. In relation to topography		Depth (ins)	No. Samples	Cu ppm	Zn ppm	Organic Carbon %	pH
Hill crests & gentle slopes	Topsoils	0-6	4	33-42* 36	60-95* 82	3.8-4.0* 3.9	6.2-6.9 6.5
	Subsoils	12-18	4	18-30 23	70-160 100	1.5-3.1 2.35	
Steep slopes	Topsoils	0-6	4	15-21 19	60-90 78	2.1-4.5 3.5	5.4-5.9 5.6
	Subsoils	6-12	4	15-25 20	60-99 77	0.5-2.3 1.7	
Base of slope and seepage	Topsoils	0-6	3	45-55 50	70-80 75	1.6-5.5 3.5	6.0-6.5 6.3
	Subsoils	12-18	3	36-52 40	75-85 80	1.1-6.0 3.0	
SEDIMENTS							
	Silty sand		2	15,17	73,80	0.8,0.9	6.5
	Silty mud		1	22	73	1.5	5.9
ROCKS							
	Mica schist		2	23,50	30,310	-	-

* Range and arithmetic mean.
Data on minus 80-mesh fraction.

TABLE 5-11 RANGE AND MEAN CONTENTS OF COPPER, ZINC, AND ORGANIC CARBON IN ROCKS, SOILS AND SEDIMENTS. CATCHMENT 919. KILLIN, Co. TYRONE

Metal contents of soils The Cu content of the topsoils varies from 18-50 ppm, with higher levels generally occurring in the flatter land and the lower levels on the steep slopes. The Cu contents of subsoils (18-30 ppm) are generally lower than

than those of topsoils, with the decrease corresponding to a fall in organic carbon content. On steep slopes, however, the Cu contents of topsoils and subsoils are similar (20 ppm).

The soil Zn content, like those of Mn and Fe (Table 6-14), is particularly high in this catchment and varies little with topography or soil horizon.

Metal content of bedrock The rocks have widely varying metal contents (25, 50 ppm Cu; 30, 210 ppm Zn) and soil parent material is probably best represented by the boulder clays (50 ppm Cu; 70 ppm Zn). These metal contents are similar to those of many of the soils in the catchment but are higher than those of similar silty clays in the low copper catchments.

Metal content of sediments The raised metal content of sediments from this catchment, relative to those of the low Cu catchments, reflects the raised metal content of soils and boulder clay. There were no fine, organic sediments but, as in the low Cu-catchments, the Cu contents of the sandy sediments (15-22 ppm) are again closest to those of topsoils, on steep slopes and most subsoils.

5.4332 Mayne, Mountfield, Co. Tyrone Catchment 791516.
Grid reference 2515 3758.

Geology Upper Dalradian garnet schist, and Silurian volcanics are overlain by 6-10 feet of locally derived grey till. In part of the catchment at least there is an upper till, probably derived from the Old Red Sandstone.

Topography Gently rolling lowlands at the base of Mullaghcarn. The stream flows rapidly and can be incised deeply to bedrock.

Soils and land use The soils are imperfectly to poorly drained acid brown earths which give micaceous, dark grey clay loams. The land is suitable for arable farming.

Analytical results

The results of Cu, Zn and organic carbon analysis of rocks, soils and sediments are shown on Table 5-12 below.

SOILS. Related to topography		Depth (ins)	No. Samples	Cu* ppm	Zn * ppm	Organic * Carbon %	* pH
Crests (Imperfectly drained)	Topsoils	0-6	4	26-65 45	70-90 80	3.2,3.3	6.2-6.8 6.5
	Subsoils	12-18	4	33-50 40	75-100 85	1.0,1.3	
Gentle slopes (Freely drained)	Topsoils	0-6	3	30-50 40	65-85 75	2.4-3.0	4.8-5.2 5.0
	Subsoils	12-18	3	30-45 40	65-95 80	1.5,1.8	
Gentle slopes (Imperfectly drained)	Topsoils	0-6	7	28-40 35	60-80 75	3.0-4.5 3.6(3)	5.1-6.7 6.1
	Subsoils	12-18	8	26-36 30	53-90 75	1.2-1.9 1.4(3)	
Flat areas, seepages (Poorly drained)	Topsoils	0-6	3	28-45 35	56-80 65	3.5,4.0	5.5-6.1 5.8
	Subsoils	12-18	3	28-52 35	60-80 75	1.3,1.8	
SEDIMENTS							
	Coarse sand		2	20,30	60,80	0.9,1.5	7.3
	Fine sand		3	31-33 32	80-90 85	1.6-2.0 1.8	-
	Mud		1	40	80	7.1	6.8
ROCKS							
	Greenstones		2	45,50	70,80	-	-

* Range and arithmetic mean
Data on minus 80-mesh fraction.

TABLE 5-12 RANGE AND MEAN CONTENTS OF COPPER, ZINC AND ORGANIC CARBON IN ROCKS, SOILS AND SEDIMENTS. CATCHMENT 791516. MAYNE, Co. TYRONE.

Metal contents of soils There are few differences in topographic environment in the catchment and there is, consequently, little variation in topsoil Cu content. Most subsoils have a lower Cu content than topsoils, but the differences are much less marked than in the other catchments studied. The Zn content also shows little variation, but tends to be lower in imperfectly drained soils (55-85 ppm Zn; pH 5.0-6.0) than in less acid, freely drained soils (70-100 ppm Zn; pH 6.0-7.0).

Two profiles were examined in the catchment (Fig: 6-14). In free draining alluvial sands near the stream (profile MP/1), the Cu content falls steadily from 40 ppm in the organic topsoils to 15 ppm in the sands at 5 feet. The Cu content in an imperfectly drained soil over boulder clay (profile MP/2) also declines with depth, from 50 ppm Cu in topsoils to 30 ppm at 3 feet. The underlying till, however, contains 50 ppm Cu, the high level reflecting a similar abundance in the parent material. There is no obvious relationship between variations in the Cu content and mechanical composition in the soils of the latter profile (Table 5-8, p. 127). The Cu content tends to follow that of organic carbon in the upper horizons. The correlation is poor, however, possibly because the impeded drainage has given rise to deeper organic topsoils than in the free-draining soils of other catchments, with less metal depletion from subsoils.

Metal contents of bedrock The metal content of the Silurian 'greenstones' (40-50 ppm Cu; 70-80 ppm Zn) is similar to those of most soils and sediments. In view of the occurrence of exotic tills and alluvial sands, both of which have lower Cu contents, it is uncertain to what extent these rocks represent the true parent material.

Metal contents of sediments As at Killin, the raised Cu contents of the sediments of the catchment relative to those of the low-Cu catchments, reflect raised levels in most soils. The sediments are mostly fine to coarse silty sands with 20-35 ppm Cu levels, lower than most soils except some freely drained subsoils. Organic muds are less common than sands, but the Cu content (40 ppm) is similar to many topsoils. The Zn content varies little with sediment type.

Metal content of herbage Four samples of mixed grasses were collected (Table 5-6). The Cu content does not vary regularly and the mean (10 ppm) is lower than for other catchments. The Zn content is more variable, though with a similar range (20-40 ppm) as herbage elsewhere.

5.434 Discussion The detailed studies of these six catchments have shown that certain features of Cu and Zn distribution are common to all areas.

1. The stream sediment Cu content will vary according to the mechanical composition and organic carbon content of the sample. In general, the active sediment normally sampled is sandy and non-organic and has the lowest Cu content, whereas the muds from sluggish parts of the stream are organic and have raised Cu contents.

2. Soils are normally surface enriched in both Cu and organic carbon. Topsoil Cu content varies according to environment and topography, being lowest in peats and on steep slopes, highest in organic soils reclaimed from peat (even where very acid) and in certain seepage areas. There is no direct correlation between total Cu and total organic carbon in the soil. The organic carbon content of steep slope topsoils is similar to that of topsoils elsewhere, but the organic horizon is much shallower in this environment.

3. Most subsoils (12-18 inches) have lower Cu and organic carbon contents than topsoils. The Cu contents vary little throughout a given catchment, although they are lowest in mineral soils beneath peats.

4. There is no relationship between the Cu content and mechanical composition of soils, although raised Cu levels in sandy clays in some profiles correspond to an increase in silt and clay content compared with adjacent horizons. The imperfect drainage of heavy soils, however, can encourage the development of a deeper organic topsoil than on freely drained soils and possibly restrict the copper depletion of non-organic subsoils.

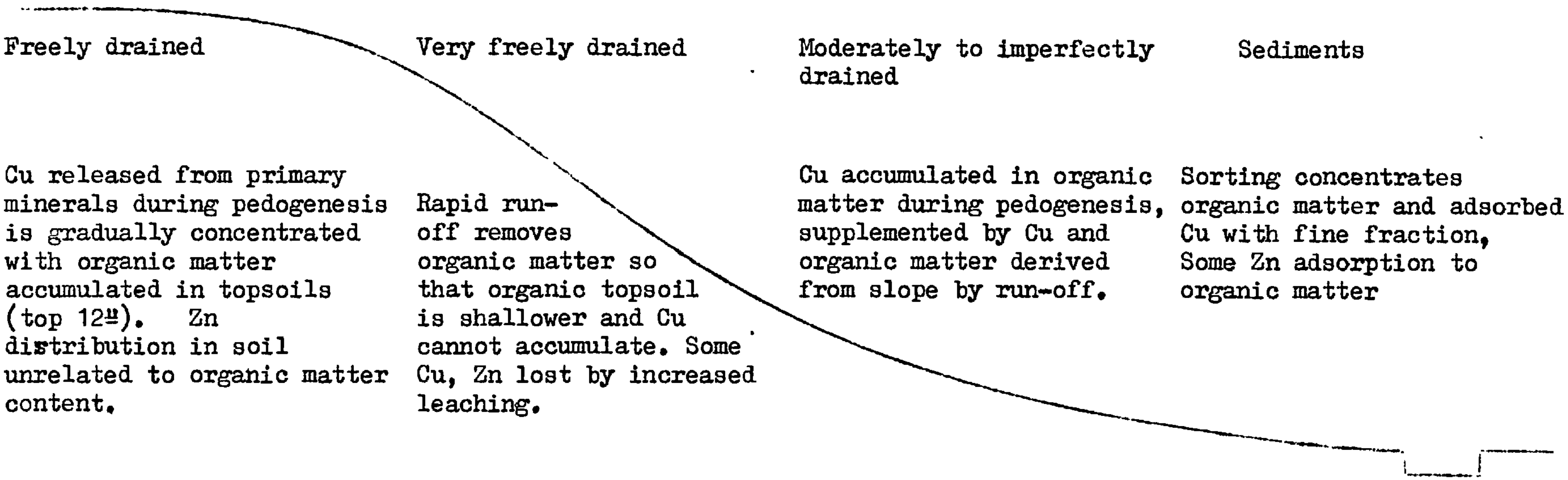
5. There is a relationship between sediment type, chosen according to mechanical composition, and soil Cu content. The Cu contents of silty sands most closely represent peats, subsoils and topsoils on steep slopes; the contents of organic muds represent those of most other topsoils.

Significant regional differences in the Cu content of similar sediment types, therefore, can represent differences in soil Cu contents. Sediment patterns which correspond to variations in sediment type, however, may not reflect differences in soil content, but reflect changes in the sorting capacity of the streams.

5. Stream sediment Zn shows little variation according to sediment type or to organic carbon content. There is little variation in soil Zn content in a catchment according to topography or depth, but the metal can be leached where soils are acid or waterlogged. The Zn content of most soils tends to reflect that of bedrock or parent material. Consequently, the bedrock-soil-stream sediment correlation is generally close, the major exceptions being where Mn oxide precipitation and Zn coprecipitation are active in streams, seepages and soils.

The data suggests that the following processes control Cu dispersion (Fig: 5-6). The metal, released during pedogenesis by the chemical weathering of parent material, is partially refixed with organic matter, either by adsorption from groundwater to the organo-mineral complex of the soil or via uptake and ultimate decay of plants. Unless soil pH falls below 4.5 to 5.0, there will be little leaching and most Cu will be retained in the solum and be potentially available for recycling via the plant. Weathering continues to supply Cu from primary sources, so that there is a slow accumulation of the metal in the organic matter of topsoils.

LOCATION	FLAT CRESTS. GENTLE SLOPES	STEEP SLOPES	GENTLE SLOPES FLAT VALLEY FLOORS	STREAMS
SOILS	Freely drained	Very freely drained	Moderately to imperfectly drained	Sediments
	Cu released from primary minerals during pedogenesis is gradually concentrated with organic matter accumulated in topsoils (top 12"). Zn distribution in soil unrelated to organic matter content.	Rapid run-off removes organic matter so that organic topsoil is shallower and Cu cannot accumulate. Some Cu, Zn lost by increased leaching.	Cu accumulated in organic matter during pedogenesis, supplemented by Cu and organic matter derived from slope by run-off.	Sorting concentrates organic matter and adsorbed Cu with fine fraction, Some Zn adsorption to organic matter



Depth (inches)	Organic Carbon%	Cu ppm	Zn ppm	Organic Carbon%	Cu ppm	Zn ppm	Organic Carbon%	Cu ppm	Zn ppm	Organic Carbon%	Cu ppm	Zn ppm
0-6	2.70	23	60	2.30	14	50	3.30	27	55	Fine organic sediment		
6-12	2.30	20	55	1.40	12	50	3.10	19	45	3.60	22	105
12-18	1.10	14	70	1.10	11	55	3.20	20	40	Silty sands		
36	0.70	10	60	0.50	13	45	1.0	9	45	0.8	7	550

Data from catchment 956, Clogherny Glebe, Co. Tyrone.

FIG. 5 - 6. DISPERSION OF COPPER, ZINC AND ORGANIC MATTER DURING PHYSICAL EROSION

On steep slopes, however, rapid run-off increases leaching and, more importantly, the physical erosion of the fine soil particles. Organic matter, clays and secondary minerals with adsorbed Cu are steadily removed to the slope base and, ultimately, to the stream. Thus, the depth of organic topsoils and the amount of accumulated Cu are partly controlled by the topography. The free drainage and rapid erosion on steep slopes prevent the formation of a deep organic topsoil and the accumulation of Cu. In poorly drained soils and at the base of slopes, however, a deep organic horizon can develop and Cu is gradually accumulated.

The physical processes also control the composition of the stream sediment. The bulk sediment comprises all insoluble physically or chemically derived weathering products of the catchment. In most streams, the sediment is mostly derived from erosion of bank materials, rather than adsorption or chemical precipitation from groundwater solution. Although Zn is accumulated by the latter process, Cu appears to be unaffected. Subsequent sorting in the stream on the basis of particle size and density is a physical fractionation process which results in a preferential concentration of copper in the fine, low density organic muds - by a factor of 3-5 in the streams studied - compared with the more sandy material. Consequently, the mechanical composition of the sediment must be considered in the interpretation of some low contrast patterns shown by regional drainage surveys.

5.5 CONCLUSIONS

5.51 Interpretation of low copper stream sediment patterns

In the Tyrone area, stream sediments mostly contain 4-35 ppm Cu, a range which can readily be found in most streams if sampled according to the mechanical composition of the sediment. Since the degree of sorting is related to stream velocity and hence relief, variations within this range may reflect differences in topography rather than regional geochemistry.

In general, such variations are only expected to influence single samples but in some instances may result in regional patterns. Around Upper Lough Erne, for example, streams between the drumlins are generally slow-flowing so that most sediments are poorly sorted, organic muds containing 20-35 ppm Cu. Drumlins derived from similar bedrock occur between Aughnacloy and Caledon, but in this area streams are mostly rejuvenated and free-flowing. Sampling of active sandy sediments gives patterns of less than 10 ppm Cu, although organic muds contain over 20 ppm Cu. The Cu contents of the majority of the topsoils are similar in both areas and do not differ in the manner shown by the sediments.

Such sediment patterns reflect differences in geology and geochemistry in that:

i. sandy sediments ($<$13 ppm Cu) can characterise areas of high relief in which a marginally higher proportion of soils are acid or steeply sloping and hence depleted in copper relative to areas of low relief.

ii. organic sediments (20-35 ppm Cu) tend to occur where non-resistant rocks have weathered to give areas of low relief and poorly drained soils.

In general, regional variations in geochemistry are best considered on the basis of a common sediment type, to eliminate spurious patterns resulting from differences in topographic environment.

In the Tyrone area, it has been shown that an investigation into potential Cu, Zn and other trace element deficiencies may require a more detailed stream sediment investigation than a normal reconnaissance. At each site, samples of both silty sands and organic muds should be collected and stream water pH measured. With multi-element analysis, various characteristics of the soil geochemistry within the catchments can be inferred.

1. Acid stream water ($pH < 6.0$), accompanied by low sediment metal contents, may indicate acid, leached soils, potentially deficient in several elements.
2. In streams with near neutral waters (pH 6.0-7.5) silty sediments secondarily enriched in Mn, Fe, Co and Zn may indicate acid, leached soils, potentially deficient in these metals and copper.
3. In streams with near neutral water (pH 6.0-7.5) without appreciable sediment enrichment, analysis of silty sands and organic muds will give the approximate range of soil Cu contents. The lowest Cu levels, similar to those of sandy sediments, will occur in free draining topsoils on steep slopes, in subsoils and in peats. Higher levels, similar to those of the muds, will occur in topsoils from other environments.

5.52 Agricultural significance of the copper and zinc distribution patterns

The agricultural significance of the low contrast patterns studied cannot be fully assessed from the available data. The herbage was collected in the spring of 1969 and the results (Table 5-6) show that at this period at least the Cu content of plants is mostly adequate for the dietary requirements of grazing animals - thresholds of 5 ppm D.M. Cu for sheep and 10 ppm D.M. Cu for cattle are recommended by the Agricultural Research Council (1965). Only in Catchment 1727, at Tempo, does there appear to be any relation between low topsoil Cu and low herbage Cu. Grasses growing on steep slopes (6-7 ppm Cu) and moors (9 ppm Cu) contrast with 11-16 ppm Cu in grasses elsewhere. Such levels are deficient for cattle by A.R.C. standards and Cu deficiencies in cattle grazing moorland areas are well known in Eire.

Fleming and Murphy (1968) showed that, under Irish conditions, the Cu content of plants decreases during the growing season. Consequently, herbage in most of the catchments may become marginally Cu-deficient for cattle later in the year. It is possible that the decreases are greater where reserves of total metal are low, but this could not be tested in the present study.

Mean herbage levels of Zn are mostly in the range 27-36 ppm D.M. Except for moor grasses (mean 54 ppm Zn), all the samples are significantly below the minimum threshold of 50 ppm (A.R.C. 1965). The experiments of Fleming and Murphy

(1968) indicate that whole plant Zn contents do not vary regularly throughout the growing season, although there is a significant concentration in seed heads. Hence, total Zn contents found in herbage from Tyrone are also probably constant throughout the year, at a level deficient by A.R.C. standards.

Judged by the thresholds given, therefore, most herbage sampled probably has adequate Cu but is deficient in Zn. Simple deficiencies in Cu also may be expected, however, if uptake decreases later in the growing season or if liming increases the dietary requirements of Cu. MacPherson and Hemingway (1968) found that herbage contents of 8-9 ppm were insufficient for sheep grazing limed pasture, in comparison with the 5 ppm recommended by A.R.C. There is also the possibility that complex deficiencies of Cu and Zn may occur, since levels are similar to the thresholds established by Dynna and Havre (1963). These authors found such deficiencies in cattle in Norway where herbage contained less than 5 ppm Cu and 40-50 ppm Zn.

In conclusion, therefore, the stream sediment reconnaissance patterns of 5-12 ppm Cu do not themselves delineate regions where topsoils are deficient in copper, although deficient areas may occur within these regions. The patterns do indicate, however, that the soil parent material over much of the Tyrone area has a low Cu content. In contrast, the close sediment-soil correlation for zinc suggests that low Zn patterns may delineate potentially deficient areas.

Simple Cu deficiencies are probably likely only in moorland areas, but simple Zn deficiencies or complex Cu-Zn deficiencies may be more widespread, at least at latent or subclinical levels. These conditions may become important with any change to more intensive methods of farming and it is possible that such changes may have their greatest effect in the areas where the reconnaissance survey has indicated a low metal content in the soil parent material.

CHAPTER SIX GEOCHEMICAL PATTERNS RELATED TO THE SECONDARY ENVIRONMENT

6.1 INTRODUCTION

6.11 Statement of the problem

The major features of the stream sediment reconnaissance survey of the Tyrone area are the associated patterns of iron, manganese, zinc and cobalt. Raised levels of these metals occur where iron and manganese oxide precipitates are observed in streams. The highest concentrations of over 1% Mn and 30% Fe_2O_3 represent contrasts of six to tenfold over sediments from surrounding areas. Many of these sediments contain Zn above the regional anomaly level of 300 ppm (Table 3-7) with peak values of over 450 ppm. Similarly, Co can exceed 150 ppm, a fivefold contrast to mean background.

Oxide precipitation and raised sediment metal contents occur principally in hill areas of rough grassland and peat moor, where the predominant soil association is peaty podzols with peaty gleys, as described in Chapter 3. The metal association, with its apparent relationship to regional relief and soil type, suggests that the distribution patterns are a reflection of the secondary weathering environment, rather than bedrock geology.

Detailed studies have been made to establish:

a) whether the raised Fe, Mn, Co and Zn levels in stream sediments are 'false anomalies' with no geological significance, caused by depletion and enrichment processes in the soils and sediments respectively.

b) the critical differences in the secondary environment that such patterns represent.

c) the significance of the patterns and the effect of the secondary environment on their interpretation in agriculture and soil science.

These problems have been considered by a comparison of the chemistry and micromorphology of soils and sediments from geochemically contrasting areas. The results are presented in the following two chapters; field observations and results of chemical analyses are discussed in this chapter, the micromorphology and some detailed studies on ferromanganese accumulations in Chapter 7.

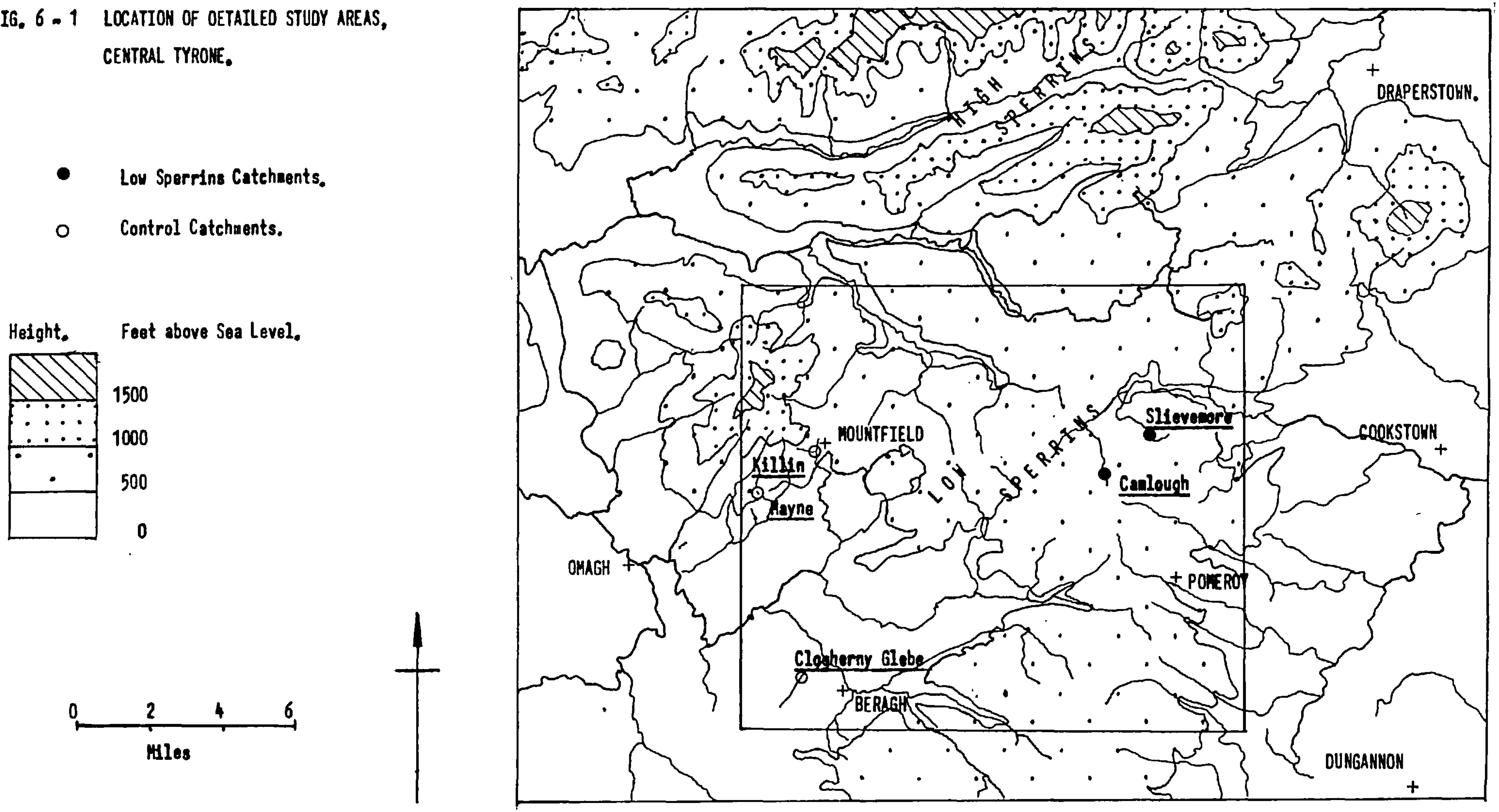
6.12 Choice of field areas

The most important Fe-Mn-Co-Zn pattern lies in Central Tyrone, between Omagh, Draperstown and Cookstown (Chapter 3-4). Comparative studies were made of contrasting catchments in this area at locations shown on Fig: 6-1.

Sediments from streams in the Low Sperrins, north of Pomeroy, show strong Fe-Mn precipitation and metal enrichment. Detailed investigations were made in two catchments, Camlough and Slievemore.

Sediments from streams to the south and west of Pomeroy have some Fe-Mn oxide precipitation but no apparent metal enrichment.

FIG. 6 - 1 LOCATION OF DETAILED STUDY AREAS, CENTRAL TYRONE.



Detailed control investigations were made in three catchments, Clogherny Glebe, Killin and Mayne.

The catchments were selected on the basis that:

i. sediment metal contents were similar when sampled both in 1967 and 1968;

ii. they were small and could be studied with a minimum number of soil and sediment samples;

iii. land forms, vegetation and land use are typical of their areas.

6.2 THE CENTRAL TYRONE AREA

6.21 Geology

The geology of the area, shown on Fig: 6-2 and described in Chapter 2, is complex and, owing to glacial deposits and extensive bog development, poorly exposed. The area lies centrally in the Draperstown-Omagh-Fintona corridor of the retreat stages of the last glaciation. Most of the area is covered by arcuate, ridged moraines and mounds of water-washed sands and gravels. Towards the western margins, however, the deposits become more hummocky; near Mountfield they are drumlinoid and composed of apparently locally-derived boulder clay.

6.22 Soils

The soils developing naturally in the area are hill and basin peats, peaty podzols and peaty gleys. Some have been reclaimed by peat removal and deep ploughing; in the higher land of the Low Sperrins such soils retain podzolic characteristics but elsewhere they can be maintained as 'agricultural' brown earths (McAllister and McConaghy . 1968).

The soils have been mapped and described in Hill (1960). He has classified the agricultural soils in association on the basis of parent material, with subdivisions into series according to drainage characteristics.

i. <u>Sixmilecross Association</u> Parent material: basic igneous complex.

a) Mountfield series. Reclaimed podzolic soils on moderately drained slopes, characterised by an organic A_1 horizon, with humus intermediate between mull and mor, a thin, bleached A_2 horizon and an ochreous B_2 horizon.

ii. <u>Sperrin Association</u> Parent material: Dalradian mica schist.

a) Sperrin, Lenelly and Plumbridge series. Free draining podzolics on the slopes of glaciofluvial deposits in high rainfall areas.

b) Strabane series. micaceous acid brown earths on gently undulating land. Most are heavier, more argillaceous and less freely drained than the other soils.

iii. Mid-Tyrone Association Parent material: Old Red Sandstones.

a) Shantaveny series: peats and peaty podzols.

b) Beragh and Garvaghy series: freely drained acid brown earths, mostly with the purplish-pink colours of the bedrock.

c) Dromore series: poorly drained brown earths.

6.23 Reconnaissance results

The reconnaissance samples from this area, and some further sediments collected to confirm the original findings, were analysed by atomic absorption for Fe, Mn. Co and Zn. Data for Mn are shown in conjunction with the geology and soil maps, Fig: 6-2 and 6-3. Those for the other metals show similar patterns and hence are not reproduced.

The Mn patterns transgress all the geological boundaries following, in the main, the line of the major glacio-fluvial deposits. There is, however, a fairly sharp cut-off to the south where drift is of granitic and Old Red Sandstone origin, and a gradual cut-off to the west, near Mountfield, towards the margin of the glacial retreat corridor, where the drift becomes more clayey.

The patterns show some correlation with the soil associations and series. High sediment contents ($>$ 4,000 ppm Mn) occur where hill peats are found in association with the reclaimed podzols of the Mountfield and Sperrin series, and lower

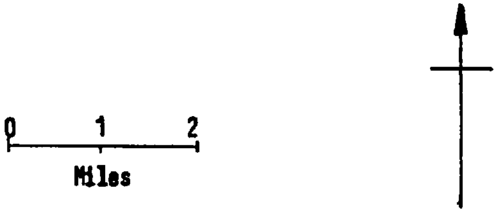
FIG. 6 - 2. MANGANESE CONTENTS OF STREAM SEDIMENTS IN RELATION TO BEDROCK GEOLOGY, CENTRAL TYRONE.

GEOLOGICAL KEY.

⁙	Old Red Sandstone.
▤	Silurian volcanics
▤	Silurian sediments
▨	Upper Dalradian
▧	Lower Dalradian
▥	Basic Igneous Complex
+ +	Granites, Felsites

Manganese per cent

○	0 - 0.1
⊙	0.1 - 0.2
⊙	0.2 - 0.4
◉	0.4 - 0.8
◉	0.8 - 1.6
●	> 1.6



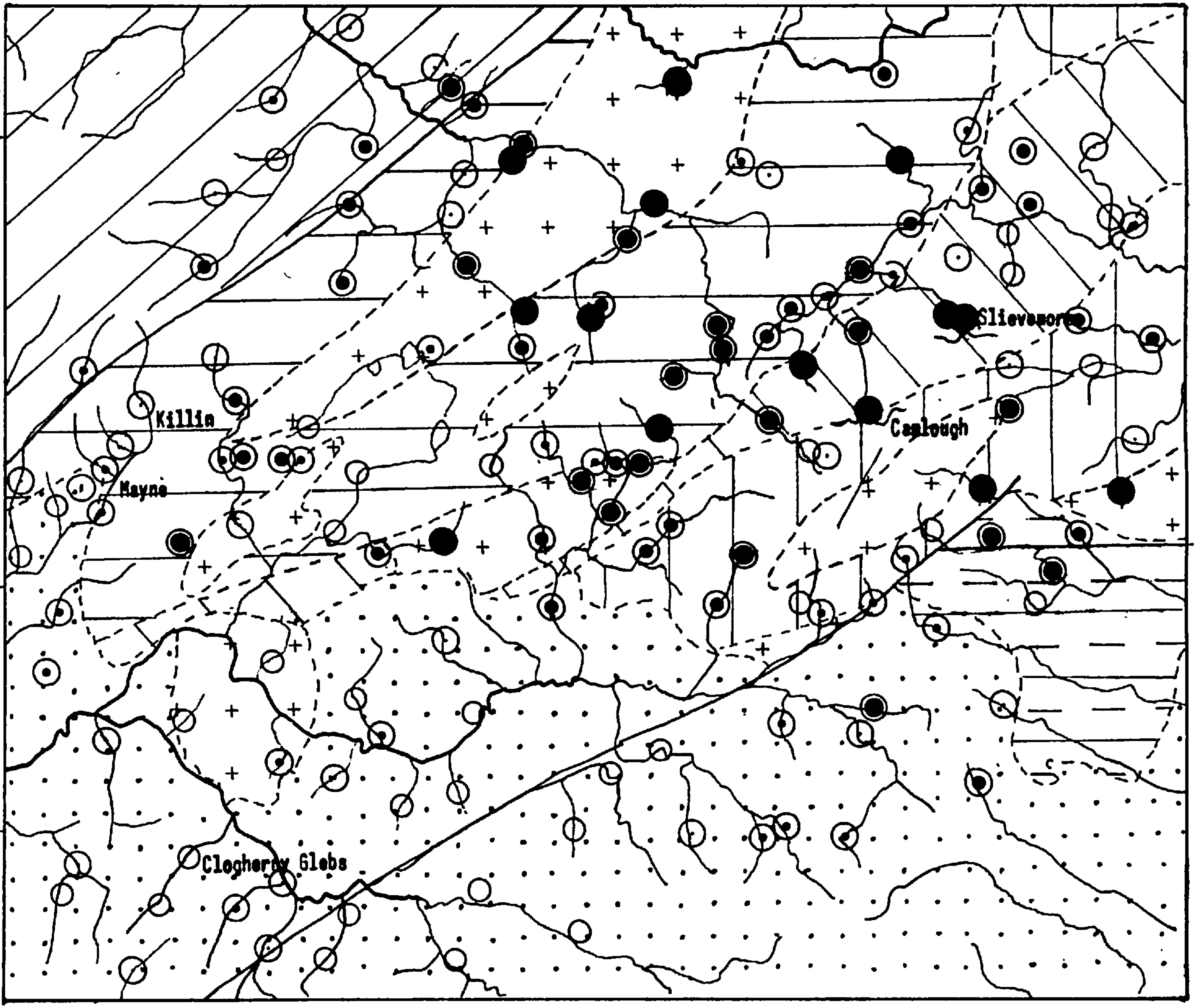
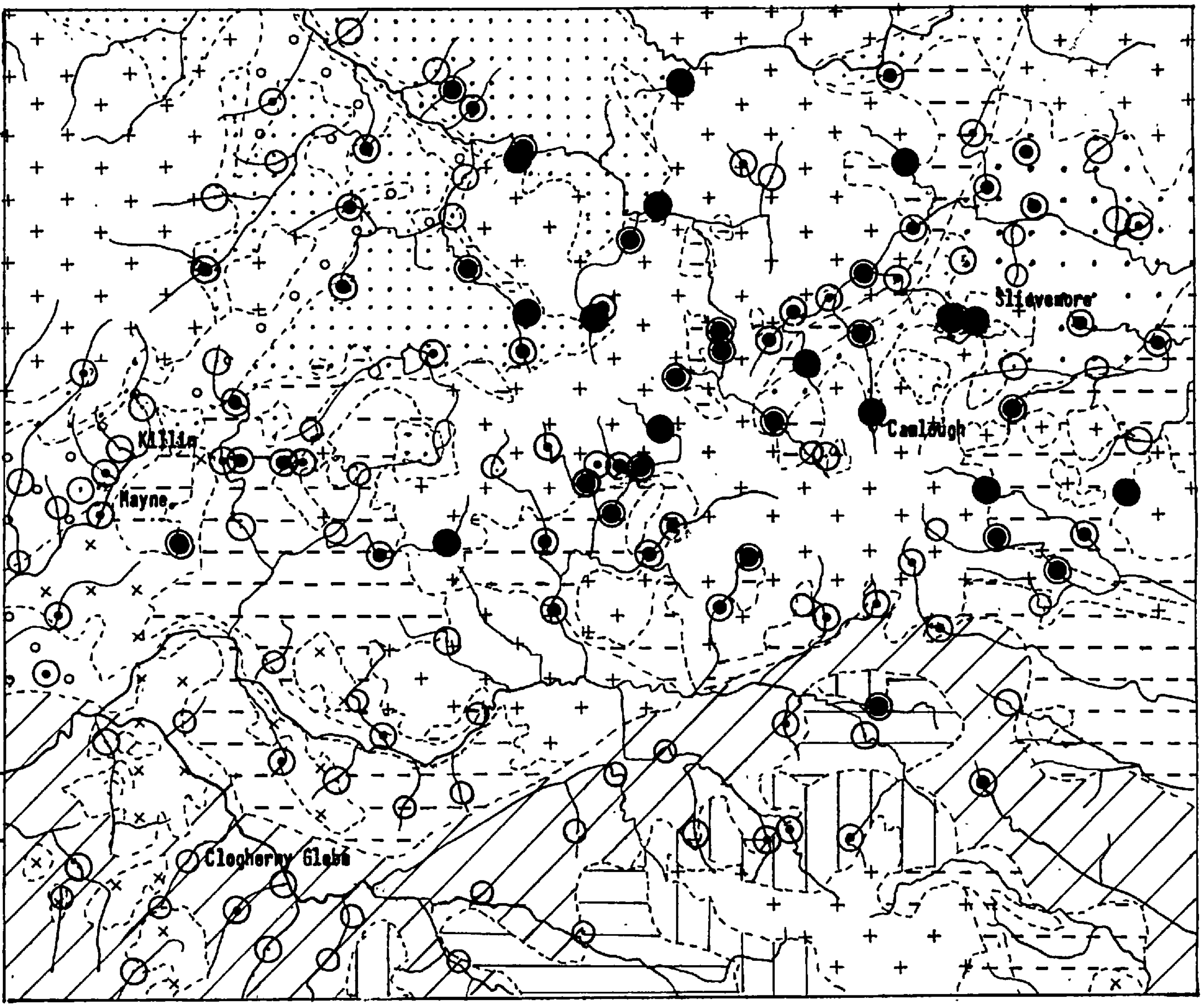


FIG. 6 - 3. MANGANESE CONTENT OF STREAM SEDIMENTS IN RELATION TO SOILS, CENTRAL TYRONE. (Soils after Hill, 1960).

SOIL :	ASSOCIATION	SERIES	TYPE
- - -	Sixmilecross	Mountfield	Reclaimed podzols.
⋯	Sperrin.	Sperrin/ Lenelly.	Podzolics.
• •	Sperrin	Plumbridge	Podzolics.
○ ○	Sperrin	Strabane	Acid brown earths.
▥	Mid-Tyrone	Shantaveny	Peaty podzols.
▨	Mid-Tyrone	Beragh / Garvaghy	Acid brown earths.
▤	Mid-Tyrone	Dromore	Gleys and brown earths.
+ +	Hill peats.		
× ×	Basin peats.		

Manganese contents as for Fig. 6 - 2.



levels ($< 1,600$ ppm Mn) where there are no hill peats or the soils are predominantly the brown earths of the Strabane series.

Particularly low levels occur where soils are of the Mid-Tyrone association. Hill peats and peaty podzols of the Shantaveny series on high ground give sediments containing 1,000 - 3,000 ppm Mn, while brown earths of the Beragh series are associated with sediments contents of 200 - 1,000 ppm Mn. These low levels may result from a combination of a lower abundance of the metal in the bedrock, a better climate and less severe leaching than occurring further north.

6.3 SAMPLING AND ANALYSIS

Sediments and precipitates were sampled at several sites in the course of each stream. Soils were collected on traverses across the selected catchments, sampling either each horizon or at 15 cm intervals to a depth of about 60 cm. Rocks were sampled wherever exposed.

Representative soil profiles were examined in each catchment to trace the vertical and lateral dispersion of metals through the soil sequence. Soils were sampled for chemical analysis and micromorphological examination at each recognisable horizon.

The Eh and pH of selected soils, sediments and stream waters were measured using a portable meter, as described in Appendix A.

Samples were analysed for Co, Cu, Fe, Mn and Zn by nitric/perchloric acid digestion and atomic absorption. Profile samples and selected sediments were analysed in addition for organic carbon and exchangeable and easily reducible manganese. The analytical techniques are given in Appendix A.

6.4 LOW SPERRINS CATCHMENTS

6.41 Field Areas

6.411 Camlough Catchment 934. Grid reference 2663 3767.

i. Location 3 miles north west of Pomeroy, Co. Tyrone. The stream drains northwards from Cregganconroe (993 ft.) through basin peats and moraines (Fig: 6-4).

ii. Geology Gabbro, with felsite veining, is exposed on Cregganconroe. The catchment is encompassed by sharp moraine ridges 30-40 ft. high, with a 30 degree slope. Moraine mounds occur banked up against the mountain and as rounded islands in the extensive basin peat. They are composed of poorly stratified sands, gravels and boulders. The rock fragments are mostly gabbro and granite, with occasional schist and reddish (Devonian) sandstone.

iii. Soils Although steeper slopes are still peat covered, most of the moraines have been reclaimed to give moderately free draining podzolic soils (Plumbridge and Mountfield series). Much of the valley is covered by basin peat, but where reclaimed, soils are mostly gleyed and organic.

6.412 Slievemore Catchment 927. Grid reference 2682 3784.

i. Location $3\frac{1}{2}$ miles north of Pomeroy, the stream draining Slievemore (842 ft.) and Evishanoran Mountain (886 ft.) (Fig: 6-4).

ii. Geology Lower Dalradian schists and gneisses are exposed on Slievemore and some moraines have been dumped between Slievemore and Evishanoran as hummocky mounds and ridges. Quarries on the south of Evishanoran expose 100 ft. of well-stratified sands and gravels.

iii. Soils Hill tops are covered by a blanket peat, with cultivated land on middle and lower slopes and extensive basin peat bogs in the valleys. There is, therefore, a sequence of peaty podzols, reclaimed podzols, gleys or peaty gleys, and deep peats down the hillsides.

6.42 Structure and metal contents of stream sediments

6.421 The occurrence of ferromanganese stream precipitates

Little Fe-Mn oxide precipitation was observed near the sources of the streams and sediment metal contents are low. On Slievemore, for example, sediments contain 2.1 % Fe, 170 ppm Mn and 60 ppm Zn, and on Cregganconroe 2.7% Fe and 800 ppm Mn. The raised Zn level on Cregganconroe (180-200 ppm) is high background on the regional scale and may be attributed to a local bedrock source.

At Camlough, below Cregganconroe, the stream enters the area of basin bog and, after about 350 metres, where there is little mineral sediment in the stream, ferromanganese

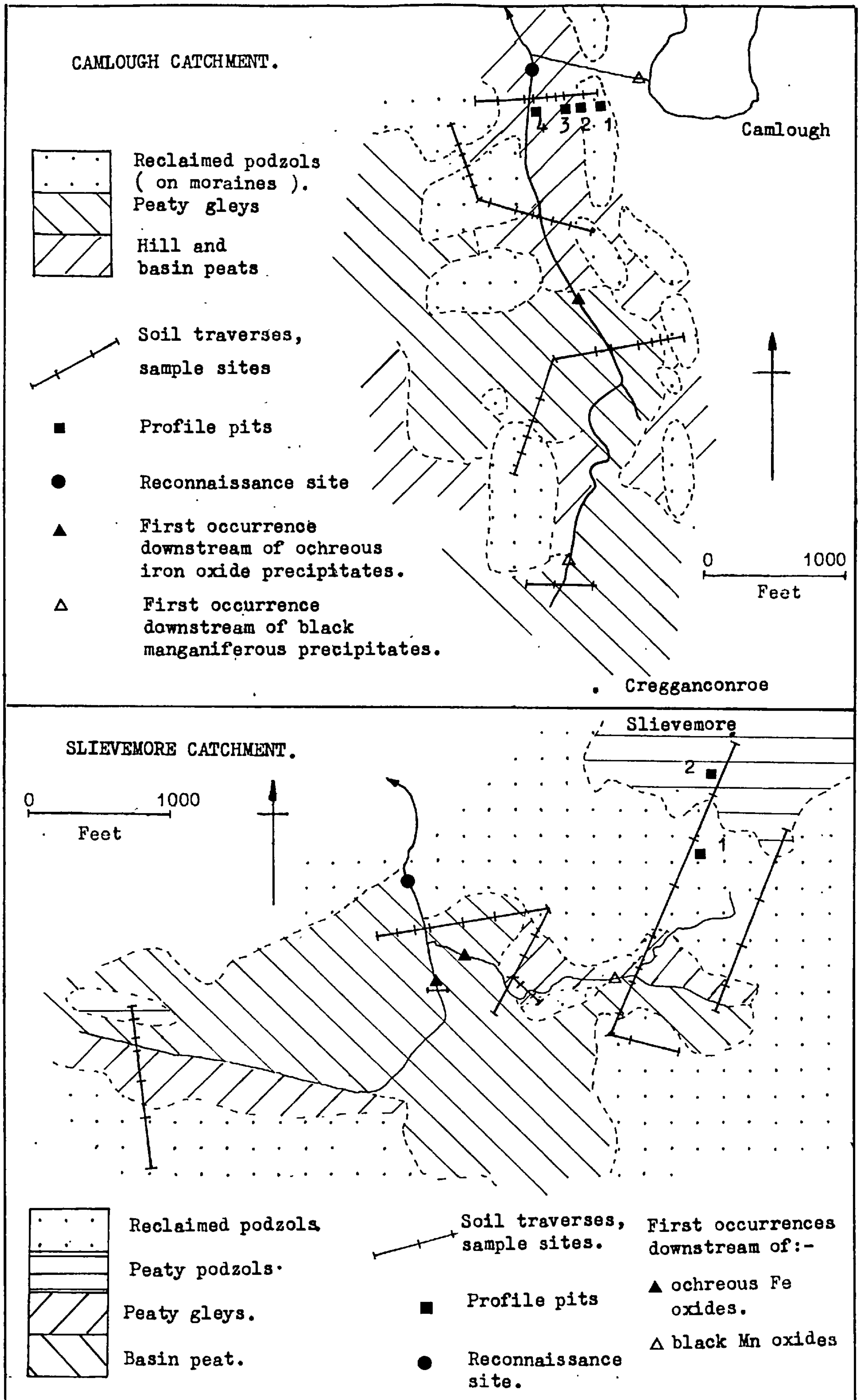


FIG. 6 - 4. PREDOMINANT SOIL TYPES AND SAMPLE SITES IN THE LOW SPERRINS CATCHMENTS, CAMLOUGH AND SLIEVEMORE.

precipitation is observed. The peat forming the stream bed has a hardened surface layer, 1.5 cm. thick, which, relative to the underlying peat, is enriched in Mn, Fe, Zn and Co (Table 6-1). Downstream, the peats become increasingly enriched in iron, until ochre staining becomes visible in the channel. The ochreous layer, about 0.7 cm. thick, is fibrous and peaty, merging into underlying brown peats. These peats (1.5 cm. thick) are richer in iron (21% Fe) than the ochre (16% Fe) but both are enriched about tenfold relative to peat below 3.0 cm. (1.8% Fe). Mn, Co and Zn levels, however, are raised only in the ochreous surface layer, by factors of ten, six and two respectively.

It is significant that this precipitation is occurring where:

i. sediment and bank pH rises sharply downstream from 5.2 to 5.9-6.3; and

ii. stream bed Eh rises downstream, from 0.3 to 0.5 volts.

Thus, the precipitation is taking place where the conditions are becoming more oxidizing, and this occurs where the peat thins rapidly and sandy drift comes to the surface.

Three metres downstream from the first appearance of the ochre, the peat becomes sandy and gives way to a mineral stream bed. The metal content of the ochre layer appears to drop from 38% Fe, 2,000 ppm Mn on peat, to 10% Fe and 1,200 ppm Mn on sand. This may be due to high adsorption by the organic matter, but more probably to dilution by mineral material in the latter. Thick precipitates on

Stream Bed	Depth cm.	Distance* metres	Fe%	Mn ppm	Zn ppm	Co ppm	Cu ppm	pH	Eh volt
Silty sands	-	-350	2.60	850	220	15	15	nd	nd
Peat									
Hardened	0-15	-13	1.15	1925	85	12	7	5.2	0.30
'Normal'	2-3		0.15	115	35	<3	8		
Peat									
Hardened	0-15		3.25	1825	65	6	17		
Brown peat	15-30	-2	5.50	285	40	<3	13	5.3	nd
Brown peat	30-40		2.65	260	40	<3	17		
Peat									
Ochre	0.7		16.75	2575	80	20	20		
Peat	07-20	0	21.25	230	55	3	20	5.9	0.4
Brown peat	20-30		1.80	235	50	3	25		
Peat									
Ochre	0-10	+3	38.0	2000	60	30	5	6.3	nd
Peat	10-20		1.75	285	10	10	5		
Sand									
Ochre	0-07		10.50	1200	45	12	4		
Grey sand	07-20	+4	1.20	135	30	10	4	6.3	0.5
Grey sand	20-40		1.10	120	25	8	8		
Grey sand	40-70		1.10	100	25	4	10		
Sand									
Layered crust	0-05	+7	4.0	5800	150	25	5	6.3	nd

Stream waters: Eh 0.4 volt; pH 6.3

* Distance from point of first precipitation in metres:
- = upstream; + = downstream

nd : not determined

Data on minus 80-mesh fraction.

TABLE 6-1 METAL CONTENTS OF STREAM BED AND SEDIMENTS ASSOCIATED WITH THE OCCURRENCE OF OXIDE PRECIPITATION AT CAMLOUGH pebbles have a dark manganiferous encrustation (6,000 ppm Mn) below the ochreous layer. The crust also has a higher Zn content (150 ppm) than precipitates upstream.

The Cu content is unaffected by oxide precipitation. Oxide stained peats show a threefold enrichment (from 6-8 ppm to 17-24 ppm) over both unstained peats and stained sands. The metal is, therefore, possibly associated with the organic matter but not with manganese.

Similar ochreous precipitation occurs in the western tributary at Slievemore, which has peat banks for its whole course. From the source, stream sediments are acid (pH 5.0) organic and low in metals (sample S/14, Table 6-2). After half a mile, ochreous precipitates occur, initially in rapids, subsequently over the whole bed. Sediments here are less acid (pH 6.2) and are enriched in metals (sample S/9). Gelatinous iron slimes form near the banks where the peat bog becomes waterlogged (Sample S/12).

The eastern tributary at Slievemore rises in the zone of reclaimed podzols where the sediments, gneissic silty sands, have similar metal contents to associated topsoils, approximately 2.20% Fe, 150 ppm Mn (Table 6-3). Oxide precipitation is not seen until peaty gleys form the stream banks, on the edge of the basin bog, where peaty sediment is enriched in Mn (4,750 ppm), Fe (5.75%) and Zn (100 ppm). For a ¼ mile downstream, the sediment is mostly sandy, with visible precipitate confined to the coarser, active particles, which

Sediment	Fe%	Mn ppm	Zn ppm	Co ppm	Cu ppm	pH
Organic mud (S/14)	1.15	265	55	8	15	5.2
Ochreous peat(S/9)	11.70	10,000	205	25	15	6.2
Iron slime seepage (S/12)	29.60	3,325	70	10	10	6.2

TABLE 6-2 METAL CONTENTS OF STREAM SEDIMENTS AND SEEPAGES, WESTERN TRIBUTARY, SLIEVEMORE

(Datq on minus 80-mesh fraction)

		Fe%	Mn ppm	Zn ppm	Co ppm	Cu ppm	pH	Eh volts
Silty sands near source	R*	1.0-3.0	115-220	40-80	5(1)	10-40	4.8-5.2	nd
	M*	2.12(4)	170(4)	60(4)		23(4)	5.0	
Silt;at margin of bog		5.75	4,750	100	nd	24	5.2	nd
Coarse sands	R*	2.7-3.4	1675-2025	60-80	10(1)	15-50	5.4-5.8	0.35(1)
	M*	3.2(3)	2000(3)	70(3)		30(3)	5.6(3)	
Silty sands	R*	2.2-3.2	280-650	50-70	5-15	8-65	5.1-5.4	0.30(1)
	M*	2.75(5)	515(5)	65(5)	9(5)	30(5)	5.2(5)	
Iron slime seepages	R*	26.5-31.0	1100-9750	30-80	10(1)	5-20	5.5-5.7	0.30(2)
	M*	28.7(4)	3,900(4)	55(4)		13(4)	5.5(4)	
Black muds		8.6	1,225	30	5	14	5.5	0.15

*R = range; *M = arithmetic mean; number of samples in parentheses.

nd = not determined

Data on minus 80-mesh fraction

TABLE 6-3 METAL CONTENTS OF STREAM SEDIMENTS AND SEEPAGES, EASTERN TRIBUTARY, SLIEVEMORE are consequently richer in metals than adjacent finer sediments. Water pH increases downstream from 5.0 to 5.8, with oxide precipitation occurring where pH exceeds about 5.5.

6.422 Stream sediments at the reconnaissance site At the reconnaissance sites in both catchments, the stream bed and sediments have a distinct structure. All the active sediment is covered by an organic, gelatinous layer of ochreous iron oxide, up to 0.5 cm. thick. This has a thin yellow-green surface film, probably bacterial in origin (Chapter 7-32). The sediment is coarse at the surface, with pebbles coated with a black manganese oxide precipitate, 0.1 to 0.5 cm. thick. These overlie black stained gravels, which become finer and less stained with depth.

Analyses of each of these layers (Table 6-4) shows that when Mn is enriched, levels of Co and Zn are also raised, reaching peak levels of 105 ppm Co and 1,000 ppm Zn in the Mn-rich (6.7%) precipitate crust. In contrast, the Cu contents (6-12 ppm) show little variation.

Variations in the metal contents of sediment collected from these sites at different times (Table 6-5) can probably be ascribed to errors arising from sampling different layers. It is possible, however, that seasonal changes in climate may influence rates of leaching and precipitation and cause further variations. For example, it was observed that Fe-Mn precipitation in streams appeared to be less widespread in a wet year (1967) than in a dry year (1968). This may have resulted in the low sediment zinc contents noted in many streams in 1968 (Chapter 5.432) but the present data is insufficient for an adequate comparison.

Layer	Thickness cm.	Organic Carbon %	Fe%	Mn%	Co ppm	Cu ppm	Zn ppm
Green-yellow bacterial film	0.1	9.7	24.0	0.56	13	12	145
Gelatinous iron oxide	0.5	10.6	24.0	1.96	28	10	340
Black manganiferous precipitate	0.2-0.5	6.7	28.8	6.7	105	6	1000
Strongly stained gravels*	1.5	4.2	22.0	4.7	70	12	770
Lightly stained gravels*	2.0	3.8	7.2	0.65	20	12	160

* Data on minus 80-mesh fraction

TABLE 6-4 METAL AND ORGANIC CARBON CONTENTS OF PRECIPITATE AND SEDIMENT LAYERS AT RECONNAISSANCE SITE, CAMLOUGH

	Date of Sampling		Water pH	Fe%	Mn%	Co ppm	Cu ppm	Zn ppm
CAMLOUGH	1967,	August	nd	12.2	2.80	60	18	320
	1968,	July	6.3	15.0	2.65	nd	16	260
	1968,	December	6.2	17.0	3.00	nd	nd	300
	1969,	May	6.3	26.8	2.70	35	10	310
SLIEVE-MORE	1967,	August	nd	27.4	3.00	35	27	310
	1968,	July	6.5	17.0	1.95	nd	20	285
	1968,	December	6.2	24.5	3.1	nd	30	235
	1969,	May	6.5	15.0	1.45	50	15	185

nd = not determined

Data on minus 80-mesh fraction

TABLE 6-5 VARIATIONS IN METAL CONTENTS OF ACTIVE STREAM SEDIMENTS WITH TIME AT SINGLE LOCATIONS, LOW SPERRINS

6.423 Iron slime seepages These occur as gelatinous ochres in the waterlogged basin peats and peaty gleys. The iron content of the ochres is fairly constant (28% Fe) but Mn and Zn are more variable (Table 6-3). Underlying black muds have a similar pH (5.5) but lower Eh (0.15 v) and metal contents than the ochres, the metals apparently concentrated in the more oxidized environment.

6.424 Metal associations in stream sediments There is a strong relationship between total Zn and total Mn in most sediments (Fig: 6-5), particularly where Mn exceeds 2,000 ppm. The Zn content is approximately ten times that of Co in the Camlough sediments, and the Mn-Co relationship is similar to that for Mn and Zn. There is insufficient data for a similar comparison at Slievemore.

Two groups of sediments deviate from this relationship in having high Zn/Mn ratios:

i. Black organic muds. These have a high proportion (45%) of the total Mn in the exchangeable form (Table 6-16). Low or negative Eh readings indicate a reducing environment.

ii. Silty sands, at the source of the Camlough stream. These may reflect a locally increased contribution from a bedrock source on Cregganconroe, but soils nearby are not similarly enriched.

Iron shows a poor correlation with Mn, Co and Zn (Fig: 6-5). Although manganiferous sediments are always iron-rich, the ratio is not constant. Ferruginous materials, however, are not always manganese-rich. For example, ochreous iron precipitates in

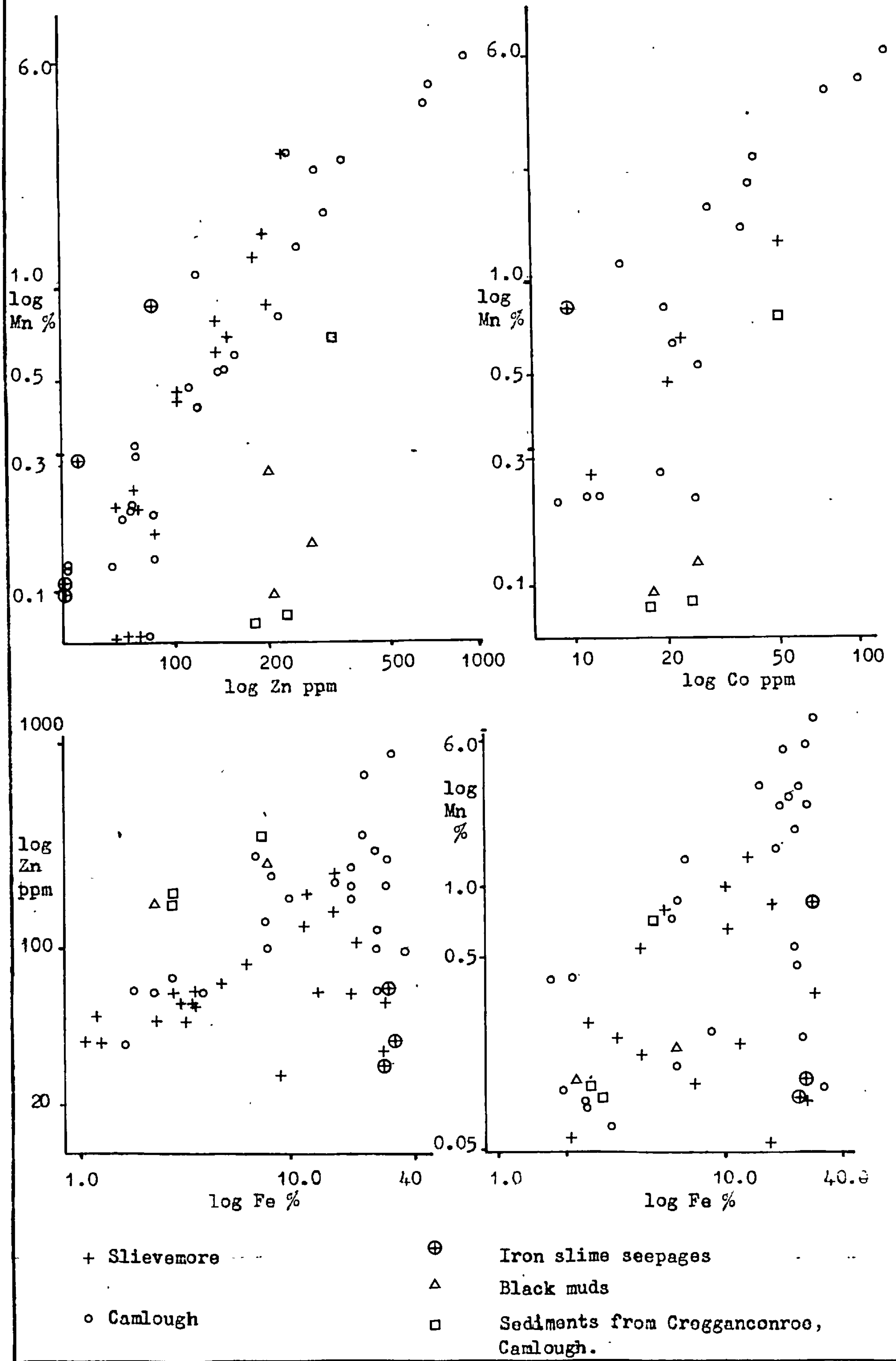


FIG. 6 - 5. CORRELATIONS BETWEEN THE COBALT, IRON, MANGANESE AND ZINC CONTENTS OF STREAM SEDIMENTS FROM CAMLOUGH AND SLIEVEMORE, LOW SPERRINS. (Data on minus 80-mesh fraction.).

streams and some seepages can contain over 20% Fe but less than 2,000 ppm Mn. Zn and Co are only enriched in such precipitates if Mn exceeds 5,000 ppm, indicating the greater scavenging power of Mn oxides over Fe oxides under these conditions.

6.43 Metal contents of soils

The results of analyses of soils collected on traverses across the catchments are shown on Tables 6-6 and 6-7. Metal distributions in the soil profiles are shown on Figs: 6-6 and 6-7.

6.431 Peaty podzols These are developed on Slievemore, Cregganconroe and some of the moraines. Acid, sandy peats (pH < 4.0) overlie humose silty sands of the A_2 horizon, with a transition to ochreous sands of the B horizon (pH > 4.5) at about 30-40 cm. The peat and A_2 horizons are thinner at Camlough, where iron pans (3mm thick) can be developed at the top of the B horizon. The B horizons, about 40 cm thick, become paler with depth but in deep horizons, below 80 cm., sands and boulders are stained heavily with organic matter and Fe-Mn oxides. At Slievemore, the staining mostly occurs below a 4 cm. horizon of translocated organic matter found at 85 cm.

All metals are depleted in the surface horizons and tend to concentrate in the less acid, lower mineral horizons. Thus, the B horizon is enriched by a factor of 1.5 to 2.0, relative to the A horizon. For example, at Slievemore, the A horizon contains 1.75% Fe, 85 ppm Mn, and the B horizon 4.5% Fe, 120 ppm Mn. In the two profiles examined, however, the strongest enrichment

	Mean Depth cm.	No. Samples	Fe%	Mn ppm	Zn ppm	pH
RECLAIMED PODZOLS						
Humose A horizon	0 -20	8	1.25-3.90 2.75	75-525 290	15-75 52	4.6-6.2 4.9
Ochreous B horizon	25-40	9	3.30-5.10 4.00	225-625 455	20-105 70	4.7-5.2 5.0
Sandy C horizon	45-60	2	3.35,3.55	350,600	21,74	nd
PEATY PODZOLS						
Bleached A_2 horizon	30-40	3	0.85-1.60 1.32	75-100 90	30-34 32	4.5-4.8 4.7
Ochreous B horizon	40-55	4	1.30-3.30 2.50	100-300 205	35-60 45	4.7-4.8 4.8
Paler B horizon	55	2	2.50,3.05	175,250	54,73	nd
PEATY PODZOLS (CREGGONCONROE)						
Sandy peat	30-45	1	2.60	100	40	4.1
Bleached A_2 horizon	45-55	2	3.75-5.0 4.37	125-225 175	40-70 55	4.3-4.7 4.5
PEATY GLEYS						
Clayey peat	0 -15	5	1.10-1.50 1.30	100-225 125	15-50 34	4.2-5.2 4.7
Peat	15-30	3	0.50-1.43 0.83	50-200 115	25-30 27	4.2-4.9 4.5
Sub-peat sands	45-60	4	1.00-4.00 2.2	100-175 125	10-60 35	4.3-5.1 4.7
BASIN PEAT						
Marshy stream bank	0 -15	2	1.00,1.45	100,350	32,32	4.6,4.7
Peat	0 -15	4	0.80-2.95 1.52	10-25 15	20-35 30	3.3-3.9 3.6
MINERAL SOILS ON MOUNDS IN BASIN BOG						
Bleached A_2 horizon	35-45	2	0.65,0.95	25,100	20,23	3.8,4.9
Ochreous B horizon	45-60	1	3.90	100	36	3.9
Grey C horizon	65-70	1	2.75	275	115	4.4
Stream sediment(Dec. 1968)		1	17.00	27,000	300	6.2
Stream sediment, Creggan-conroe		1	2.70	800	180	nd

Data on minus 80-mesh fraction.

TABLE 6-6 RANGE AND MEAN METAL CONTENT OF SOILS, CAMLOUGH

	Mean Depth cm.	No. Samples	Fe%	Mn ppm	Zn ppm	Cu ppm	pH
PEATY PODZOLS							
Sandy peat	0 -30	4	R* 0.20-1.70 M* 0.75	25-45 30	30-55 45	7-30 15	4.0-4.8 4.3
Bleached A_2horizon	30-40	8	0.70-3.0 1.75	50-120 85	20-45 30	8-35 15	3.8-5.3 4.4
Ochreous B horizon	40-50	2	3.75-4.80 4.28	115-125 120	40-60 50	18-19 19	3.8-4.0 3.9
RECLAIMED PODZOLS							
Topsoil	0 -20	8	1.10-3.70 2.71	65-250 145	35-65 50	20-40 35	4.6-6.4 5.5
Bleached A_2horizon	20-30	3	1.80-3.35 2.52	85-180 120	30-70 50	20-35 25	nd
Top Ochreous B Horizon	30-40	9	2.30-4.6 3.52	105-280 175	30-70 50	10-40 30	4.9-6.1 5.5
Base Ochreous B horizon	40-50	5	2.80-3.75 3.37	125-350 220	55-95 75	20-55 35	nd
RECLAIMED PEATY GLEYS							
Topsoils	0 -15	2	2.20-4.75 3.48	80-110 95	30-45 40	17-22 20	4.6-5.2 4.9
Subsoils	15-30	4	0.50-2.60 1.25	50-185 95	20-40 30	5-22 15	4.1-5.2 4.6
BASIN PEATS							
	0 -15	6	0.10-1.65 0.59	40-120 55	20-45 30	5-25 12	3.6-4.8 4.6
	30-45	4	0.20-0.90 0.5	10-60 35	15-40 30	5-20 10	3.6-4.3 4.0

*R = Range; *M = Arithmetic mean; nd = not determined

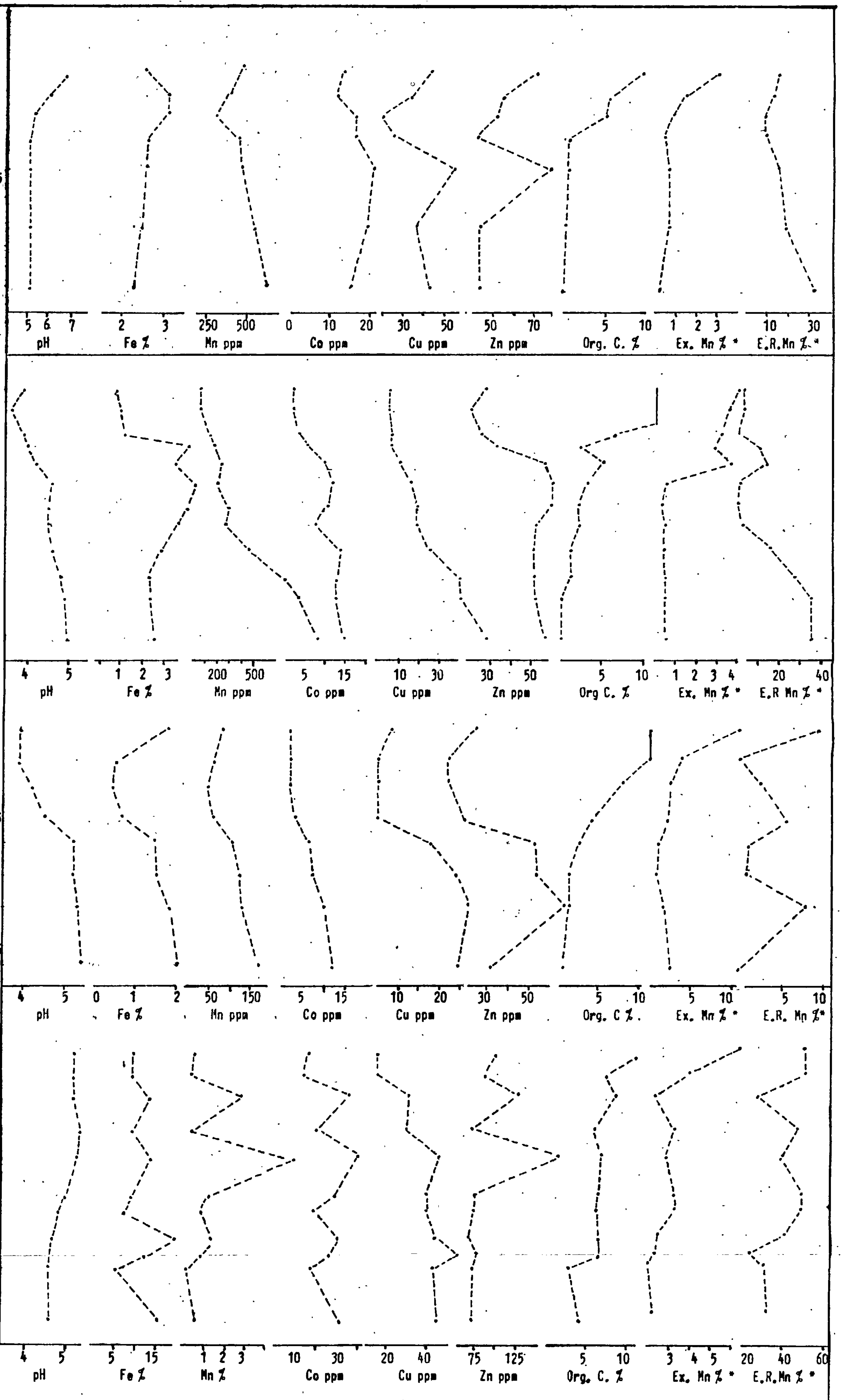
Data on minus 80-mesh fraction.

TABLE 6-7 RANGE AND MEAN METAL CONTENTS OF SOILS, SLIEVEMORE occurs in the deep Fe-Mn stained horizons. Thus, in profile AP/2 at Camlough (Fig: 6-6), although Fe (4.40%) and Zn (60 ppm) are concentrated in the B horizon, Mn (1,000 ppm), Co and Cu are highest below 80 cm. At Slievemore (profile SP/2, Fig: 6-7) there is little enrichment in the B horizon but all metals, especially Fe, are concentrated in the stained horizon below 85 cm (10% Fe, 350 ppm Mn, 120 ppm Zn). In both profiles, the metal in this stained horizon may be partly derived from soils upslope.

Easily reducible and exchangeable Mn reach maximum levels of 40 ppm (12% of total Mn) in the B horizon and 350 ppm (35%) in the B/C horizon of the profile at Camlough. This suggests that there is active precipitation in both and that the lower does not represent fossil horizon development (Leeper, 1947). At Slievemore, however, both Mn fractions are very low (3-5 ppm). This profile is more acid than that at Camlough, and it is possible that, as a result, Mn is more mobile, and less is precipitated and retained within the profile.

6.432 Reclaimed podzols These have dark, fairly organic topsoils, becoming paler with depth, with a sharp transition to an ochreous B horizon at about 30 cm. This merges to C horizon of mottled sands and gravels below 60 cm. No Fe-Mn oxide precipitation was observed below the B horizon in either profile examined, although an horizon of translocated organic matter, probably formed before peat was cleared from the land, was found at 60 cm at Slievemore. An iron pan (3 mm thick) had developed below the surface loam at Slievemore within 3-4 years of ploughing, but at Camlough, pans were only seen immediately below boulders (Chapter 7-314).

	Munsell colour	Depth cm.	Eh v.
RECLAIMED PODZOL. Profile AP/1			
Organic, reddish brown sandy loam; A_1 horizon. Merges to A_2, friable gravelly sands.	5YR 2/3 5YR 4/4	30	
Narrow transition to B horizon. Coarse, yellowish brown sands. Gravelly, with boulders over 20 cm. diameter Merges to	2.5 YR 3/6 to 5YR 4/8	60	0.35
very friable yellow-brown and grey sands. Merges to	10YR 5/7		
C horizon: grey sandy gravel	10YR 5/1	90	
PEATY PODZOL. Profile AP/2			
A_0 Fibrous sandy peat merges to fine peat with silty clay. Sharp transition to thin (3mm) iron pan over ochreous sandy clays of B horizon; soft, friable.	5YR 2/1 5YR 6/7	25	0.25
Merging to C horizon of coarse sands and sandy gravels with boulders. All stained by organic Fe - Mn oxides.	5YR 5/8 5YR 4/4 10YR 4/4	60	0.30
PEATY GLEY. Profile AP/3			
Fibrous peat; with sand and gravel. Finer with depth, merging to humose sandy clay with many roots.	10YR 2/1 10YR 5/3	30	
Merges to greyish brown sandy clay; blocky to columnar.	10YR 4/3		0.25
Greyish brown silty clay. Pebbles show iron staining.	10YR 5/2	60	
Sand and gravels with iron oxide staining			0.25
ALLUVIAL BANK SOIL. Profile AP/4			
Coarse, organic sandy loam merges to gravelly sandy loam; blocky. Dark reddish brown becoming black. Merges to coarse sandy gravels stained by black encrustations of organic Fe - Mn oxides. Merges to sands with some pebbles. Little encrustation particularly below 60 cm.	5YR 3/2 5YR 2/1	15 30 60	0.35

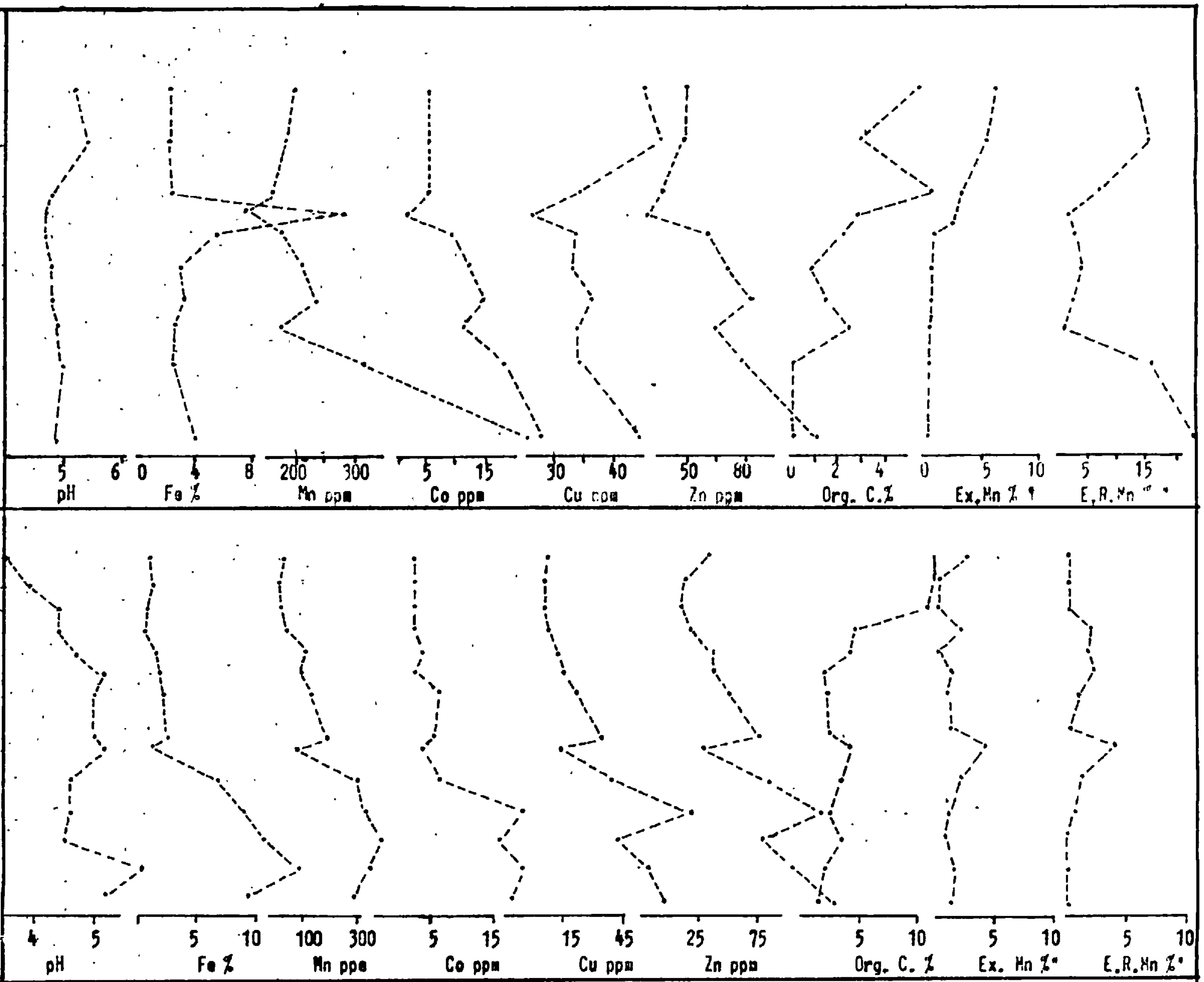


* Ex.Mn = $\frac{\text{exchangeable Mn}}{\text{total Mn}}$ %. E.R.Mn = $\frac{\text{easily reducible Mn}}{\text{total Mn}}$ %. Analytical data on minus 80-mesh fraction.

FIG. 6 - 6. VARIATIONS IN pH, ORGANIC CARBON AND METAL CONTENT IN SOIL PROFILES ON MORAINE SANDS, CAMLOUGH CATCHMENT, Co. TYRONE.

RECLAIMED PODZOL. Profile SP/1	Munsell colour	Depth cm	Eh v.
A_{1-2}. Organic greyish brown sandy clay loam; micaceous. Paler with depth. Slightly blocky. Sharp transition to B. Thin (2mm) intermittent iron pan above ochreous sandy silty clay. Merges to yellow brown silty clay. Sharp transition to 5 cm dark brown organic horizon. Sharp transition to pebbly, micaceous silty sand; yellow brown; coarser with depth.	10YR 3/2 7.5YR 5/6 10YR 5/5 10YR 3/4 10YR 5/4	30 60 90	nd

PEATY PODZOL. Profile SP/2.	Munsell colour	Depth cm	Eh v
A_0 Dark brown peat; fibrous, sandy. Merges to fine peat and sandy clay. A_2 horizon. Humose, dark brown sandy clay. Pebbly, many roots. Merges to brown and yellow sands of B horizon. Sharp transition to 4 cm dark brown organic horizon. Narrow transition to boulder horizon. Strong staining by organic Fe (-Mn) oxides. Merges to sandy clay with stained pebbles.	5YR 2/2 5YR 2/1 10YR 4/3 10YR 3/4 10YR 2/2 10YR 5/2	30 60 90 120	0.26 0.23 0.30



* Ex.Mn = $\frac{\text{exchangeable Mn}}{\text{total Mn}}$ %. E.R.Mn = $\frac{\text{easily reducible Mn}}{\text{total Mn}}$ %. Analytical data on minus 80-mesh fraction.

FIG. 6 - 7 VARIATIONS IN pH, ORGANIC CARBON AND METAL CONTENT IN SOIL PROFILES, SLIEVEMORE CATCHMENT, Co. TYRONE.

The soils are generally less acid ($pH < 5.0$) and have higher metal contents than the peaty podzols, suggesting that less leaching is taking place. They again show an increase in metal content down the profile. For example, A horizons at Camlough contain 2.75% Fe, 290 ppm Mn and B horizons 4.00% Fe, 455 ppm Mn.

In general, the soils at Slievemore are less freely drained than those at Camlough. This may account for the low metal contents in A horizons (2.6% Fe, 130 ppm Mn) and the stronger horizon development. Iron is highly enriched in the iron pan (12% Fe) and at the top of the B horizon. Co, Cu, Mn and Zn are lowest in the iron pan, increasing steadily down the profile, particularly below the horizon of translocated organic matter. This differentiation, which is less pronounced at Camlough, illustrates the lower mobility of Fe in comparison with the other metals.

Both organic carbon and the proportion of exchangeable to total Mn decrease steadily down profile, although exchangeable Mn does not increase in the horizon of translocated organic matter. The proportion of easily reducible to total Mn is greater at Camlough than at Slievemore, but in both profiles, levels exceed 12% in A horizons, 25% in C horizons. High levels of easily reducible Mn in most horizons of these soils, particularly at Camlough, suggest that the metal is less mobile than in peaty soils, with more precipitation and retention in the profile.

6.433 Peats and peaty gleys The gleys develop at the margins of the basin bog where varying thicknesses of peat overlie humose and bleached sandy soils. Iron staining occurs below 70 cm. in profile AP/3 at Camlough, Surface peats are very acid (pH 4.0) but in the profile mineral soils become steadily less acid (to pH 5.4) with depth; Eh is constant at 0.25 v. throughout the profile. Metal contents, particularly of Mn, are mostly very low, but increase down profile to reach maxima of 2.2% Fe, 120 ppm Mn, 12 ppm Co, 25 ppm Cu and 50 ppm Zn, in iron-stained sands at 90 cm. (Fig: 6-6). Higher contents of Fe and Cu (3.5% Fe, 35 ppm Cu) occur in less acid (pH 5.0) topsoils of reclaimed gleys.

6.434 Bank soils Some bank soils are metal enriched, occasionally to the same extent as the stream sediments. Soils near the reconnaissance site at Camlough, for example, are strongly stained by Mn oxides in the top 60 cm, where gravelly sands (pH 5.4) contain up to 14% Fe, 4.5% Mn, 40 ppm Co and 175 ppm Zn (profile AP/4, Fig: 6-6). Waterlogged gravels below 60 cm, however, are more acid (pH 4.6), have less precipitation and are less enriched (8% Fe, 0.8% Mn, 70 ppm Zn) than the upper horizons. Thus, the precipitation occurs mostly in the periodically oxidized soils of the zone of water table fluctuation.

The contents of organic and exchangeable Mn are high throughout the profile, although decreasing with depth. The proportion of easily reducible Mn (24-50% of total Mn) is always higher than in other profiles, suggesting that active precipitation is taking place in all horizons.

The precipitates enclose rootlets and are associated with soil fabric elements such as ped faces. Thus, although the gravels are mostly alluvial, the oxide precipitation occurred mostly after their deposition. The metals are derived either from the stream or from groundwater solution, precipitating as the water table falls and oxidising conditions are restored. A groundwater source is more probable, for at the time of examination, water filled the profile pit to stream level from the face away from the stream.

At the reconnaissance site at Camlough, the metal content of topsoils decreases steadily away from the stream - from 9.0% Fe and 2,200 ppm Mn at the bank to 1.0% Fe and 100 ppm Mn after 90 metres (Table 6-8). Similarly, at Slievemore peats and reclaimed peats in seepage areas by streams and iron oxide slimes can be metal enriched (for example, 2.55% Fe, 675 ppm Mn), although not to the same extent as most sediments (Table 6-9).

The Cu content of enriched bank soils (maximum 40 ppm) is little greater than in other soils of the catchment and is unaffected by oxide precipitation.

6.435 <u>Metal associations in soils</u> There are correlations between Mn and Zn in both A and B horizons of the soils collected by traverse sampling, the major deviations here being soils by iron seeps and stream banks where Mn enrichment has no equivalent enhancement of Zn (Fig: 6-8). There appears to be a weak correlation between Fe and Zn in A horizons only. Results from individual profiles suggest that whereas Fe concentrates at the top of the B horizon, any Zn and Mn accumulation is at the base.

Distance from stream bank (metres)	Fe%	Mn ppm	Zn ppm	pH
2	9.00	2,200	120	5.2
35	2.65	700	120	4.8
70	1.90	210	60	nd
90	0.95	100	20	4.9
Stream sediment(Dec.1968)	17.00	30,000	300	6.2

Data on minus 80-mesh fraction.

TABLE 6-8 METAL ENRICHMENT OF SOILS NEAR STREAM BANKS, CAMLOUGH CATCHMENT.

	Fe%	Mn ppm	Zn ppm	Cu ppm	pH
Normal reclaimed peat	2.20	80	30	20	5.2
Normal bank peat	0.50	50	20	8	4.3
Enriched reclaimed peat	2.80	330	45	17	4.5
Enriched bank peat	2.55	675	65	23	4.9
Enriched peat by iron slime	2.95	2025	45	22	5.9
Stream sediment(Dec. 1968)	24.50	31,000	235	30	5.9

Data on minus 80-mesh fraction.

TABLE 6-9 METAL ENRICHMENT OF PEATS NEAR STREAM BANKS AND IRON SLIME SEEPAGES, SLIEVEMORE CATCHMENT

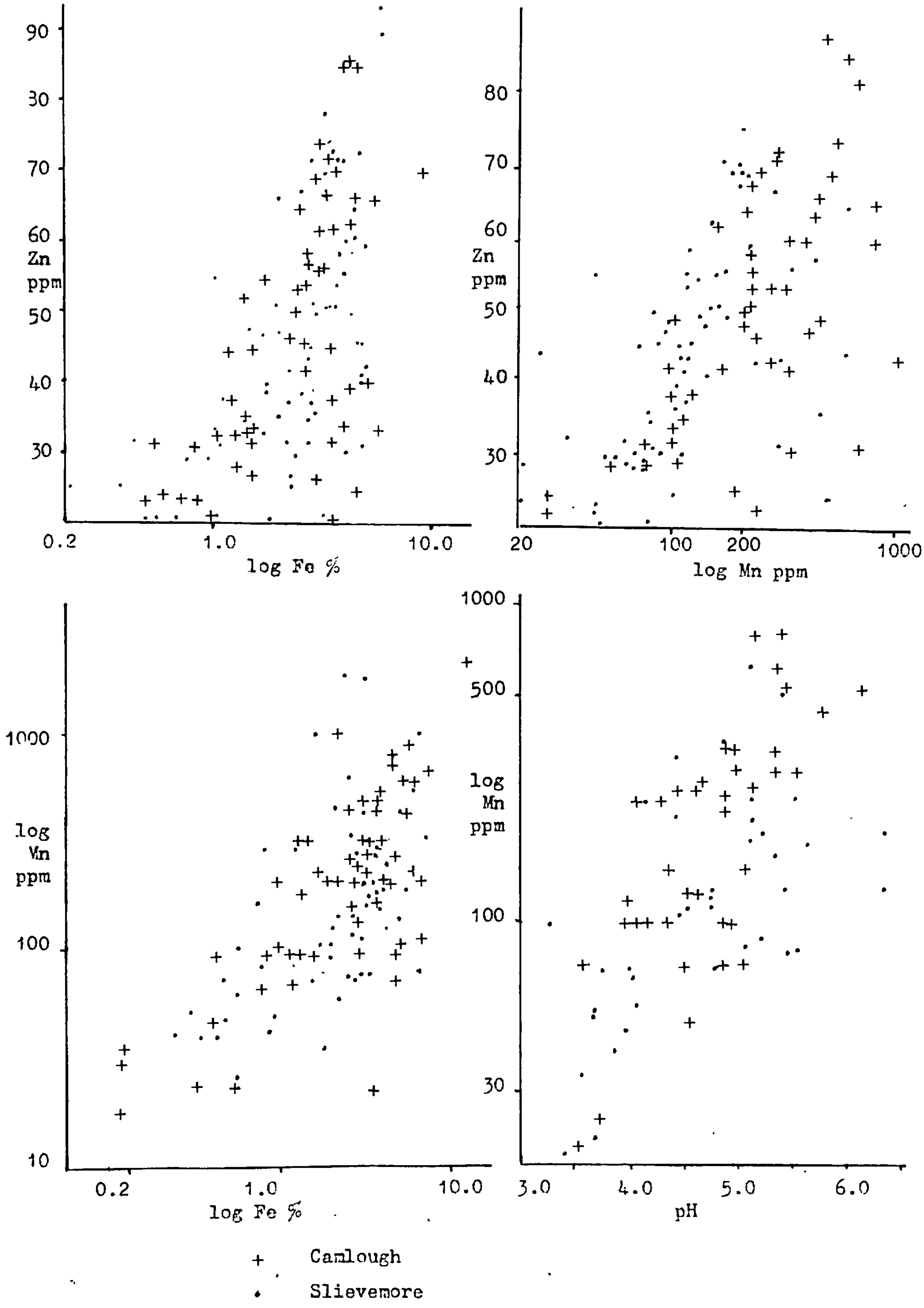


FIG. 6 - 8. CORRELATIONS BETWEEN THE IRON, MANGANESE AND ZINC CONTENTS AND pH AND MANGANESE CONTENT OF SOILS FROM CAMLOUGH AND SLIEVEMORE, CENTRAL TYRONE. (Data on minus 80 - mesh fraction).

Soil metal content is apparently related to pH only in acid soils. Where pH is below 4.5, most soils in the Low Sperrins contain less than 2% Fe, 100 ppm Mn, 10 ppm Co, 10 ppm Cu and 40 ppm Zn.

Correlation coefficients have been calculated for soil profile samples from the two catchments (Table 6-10). Strong correlations ($r = 0.62 - 0.68$) are shown by Zn with Cu, Co and Fe, Co with Cu and Fe. There are weaker correlations ($r = 0.53 - 0.58$) between several variables, such as pH/Cu, Mn/Fe and Mn/Zn. The Mn/Zn correlation applies to either total exchangeable or easily reducible Mn. Co, however, shows a stronger correlation with the proportions of easily reducible Mn ($r = 0.55$) than with total Mn ($r = 0.35$) or the proportion of residual Mn ($r = 0.5$), indicating an apparent concentration in the recently precipitated oxide.

The results show that Mn, Fe, Co and Zn tend to occur together. Co, Zn and especially Cu are more strongly influenced by pH than Mn or Fe, and show similar variations in the profiles. The fact that Cu does not concentrate in secondary oxides is reflected in the poor correlation of Cu with Fe ($r = 0.45$) and, particularly, easily reducible and total Mn ($r = 0.2$).

6.44 Metal migration in the soil sequence

The locations of the major soil types in the soil sequences and associated processes of metal dispersion in the Low Sperrins catchments are summarised on Fig: 6-9. Strong leaching of Fe, Mn, Co and Zn occurs in acid, peaty and gleyed soils and the

Significant correlations (P = 0.001)

	r
○	+0.40 - +0.49
⊙	+0.50 - +0.59
◉	+0.60 - +0.69
●	> +0.90
□	-0.40 - -0.55
■	> -0.75

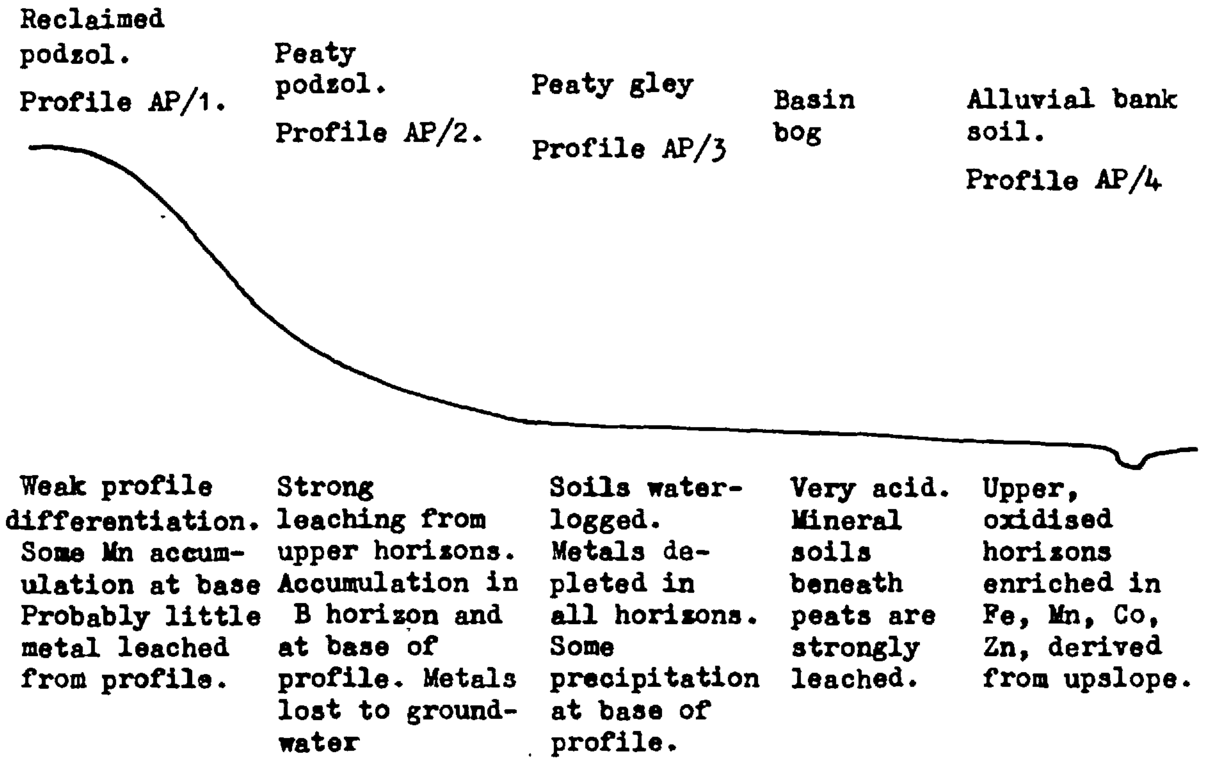
Non-significant correlations.

	r
•	-0.39 - +0.39

(Number of samples = 64)

	Residual Mn	Reducible Mn	Exchangeable Mn	Residual/Total Mn	Reducible/Total Mn	Exchangeable/Total Mn	Copper	Cobalt	Zinc	Manganese	Iron	Organic Carbon
Easily reducible Mn	●											
Exchangeable Mn	●	●										
Residual/Total Mn	•	□	□									
Reducible/Total Mn	○	⊙	⊙	■								
Exchangeable/Total Mn	•	•	•	□	•							
Copper	•	•	•	•	•	•						
Cobalt	○	○	⊙	□	⊙	•	◉					
Zinc	⊙	⊙	⊙	•	•	•	◉	◉				
Manganese	●	●	●	•	○	•	•	•	⊙			
Iron	⊙	⊙	⊙	□	○	•	○	◉	◉	⊙		
Organic carbon	•	•	•	•	•	⊙	□	•	•	•	•	•
pH	•	•	•	•	•	•	⊙	•	○	•	•	□

TABLE 6 - 10 CORRELATION MATRIX FOR METAL AND ORGANIC CARBON CONTENTS AND pH IN SOIL PROFILES, CAMLOUGH AND SLIEVEMORE, CENTRAL TYRONE.



Weak profile differentiation. Some Mn accumulation at base Probably little metal leached from profile.

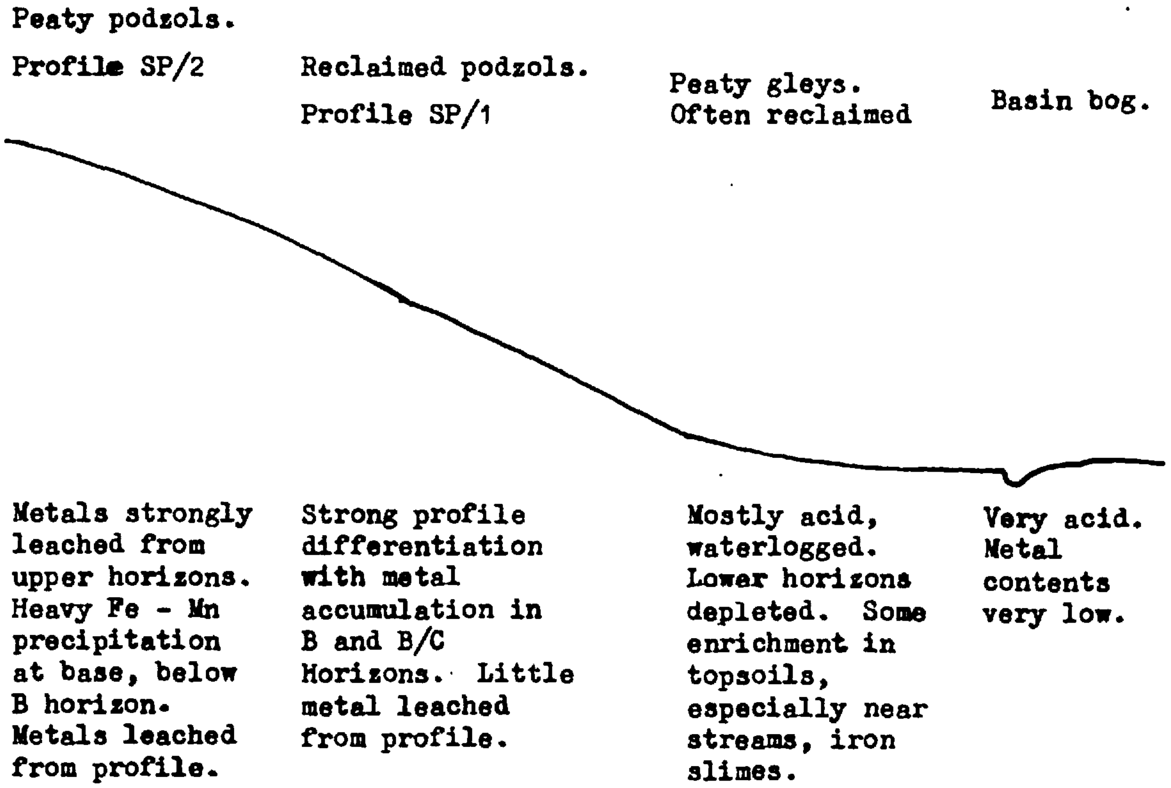
Strong leaching from upper horizons. Accumulation in B horizon and at base of profile. Metals lost to groundwater

Soils waterlogged. Metals depleted in all horizons. Some precipitation at base of profile.

Very acid. Mineral soils beneath peats are strongly leached.

Upper, oxidised horizons enriched in Fe, Mn, Co, Zn, derived from upslope.

MORAINE SEQUENCE, CAMLOUGH CATCHMENT.



Metals strongly leached from upper horizons. Heavy Fe - Mn precipitation at base, below B horizon. Metals leached from profile.

Strong profile differentiation with metal accumulation in B and B/C Horizons. Little metal leached from profile.

Mostly acid, waterlogged. Lower horizons depleted. Some enrichment in topsoils, especially near streams, iron slimes.

Very acid. Metal contents very low.

UPLAND SEQUENCE, SLIEVEMORE CATCHMENT.

FIG. 6 - 9. MIGRATION OF IRON AND ASSOCIATED METALS IN SOIL PROFILES AND SEQUENCES, LOW SPERRINS CATCHMENTS, CENTRAL TYRONE.

mobilised metals are carried in groundwater to precipitate in more oxidizing conditions in lower horizons or downslope. Relatively little leaching, however, occurs in the less acid, cultivated soils.

At Camlough, there is a sequence of acid or gleyed soils from the moraine slopes to the stream. Upper horizons are leached and, although some precipitation occurs deep in the profiles, the remaining metal is left in solution or suspension to precipitate in stream bank or sediment.

At Slievemore there is no complete sequence of leached soils from hill top to valley, since a belt of reclaimed podzols occurs on the middle slopes. Thus, it is possible that metals leached from the peaty podzols on the upper slopes are reprecipitated in the reclaimed area before reaching the streams. Consequently, much of the metal precipitated in the streams may be derived from the peaty soils of the valleys rather than those of the upper slopes.

The behaviour of copper differs from that of the other metals in that although mobilized under the same conditions, it remains in solution and does not reprecipitate.

6.5 CONTROL CATCHMENTS

6.51 Field Areas

6.511 Clogherny Glebe

Catchment 965. Grid reference 2525 3677.

i. Location 1½ miles west of Beragh, Co. Tyrone (Fig. 6-10).

ii. Geology Old Red Sandstone, overlain by large rounded moraines composed of reddish micaceous sandstones and shales, indicative of the underlying bedrock.

iii. Soils Acid brown earths, Beragh series. Mainly freely drained, friable sandy loams are found in the crests and slopes of the moraines. Gleyed soils occur in the valleys, often overlying peats of varying thickness. There are extensive areas of basin bog,

6.512 Mayne Catchment 791516. Grid reference 2525 3758.

i. Location A small lowland catchment near Mountfield, at the base of Mullaghcarn (Fig: 6-10).

ii. Geology Silurian volcanics. These are overlain by boulder clays, over three metres thick, derived from Dalradian schists, Silurian volcanics and the Old Red Sandstones.

iii. Soils Acid brown earths, Strabane series. Imperfectly drained grey clay loams which become browner and more sandy with depth. pH is mostly in the range 5.2 - 6.2.

6.513 Killin Catchment 919. Grid reference 2533 3778.

i. Location Mountfield, Co. Tyrone. The stream rises in semi-moorland on the lower slopes of Mullaghearn and is incised through drift 10 metres thick in narrow gullies.

ii. Geology Upper Dalradian garnet mica schist.

iii. Soils Acid brown earths, Strabane series. Topsoils are slightly mottled, imperfectly drained, micaceous clay loams.

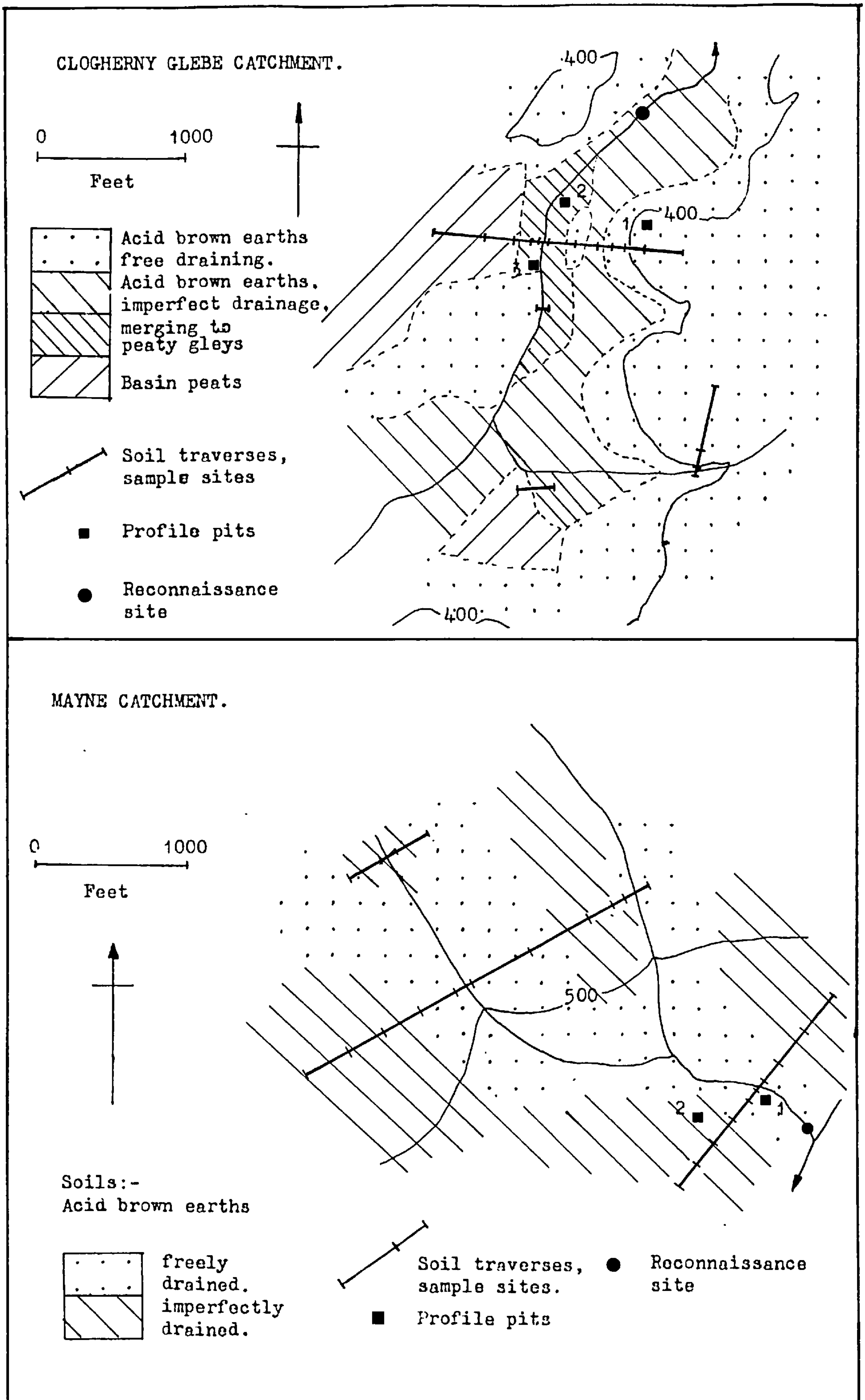


FIG 6 - 10 PREDOMINANT SOIL TYPES AND SAMPLE SITES IN THE CONTROL CATCHMENTS, CLOGHERNY GLEBE AND MAYNE.

6.52 Metal contents of stream sediments

Manganese oxide precipitation occurs in all three catchments on the exposed surface of pebbles, particularly in rapids, but not on sands, silts and muds. Thick encrustations (2-3 mm) are found on pebbles in stretches of the streams where peaty gleys formed the banks, for example near the source at Killin and between moraines at Clogherny. Elsewhere in these streams and at Mayne, precipitation is mostly only very slight.

Sediment samples were selected from each site on the basis of their mechanical composition. The results (Table 6-11) indicate that they have lower metal contents than most sediments from the Low Sperrins. The contents of sandy, active sediments at Mayne are nearly constant throughout the catchment (3.30% Fe, 440 ppm Mn). At Clogherny the coarser sediments are progressively enriched in Mn and Fe, from 2.15% Fe, 265 ppm Mn in silty sands, 2.35% Fe, 640 ppm Mn in sands, to 3.35% Fe, 1,800 ppm Mn in coarse sands. This is presumably the result of an increased contribution of precipitated Fe-Mn oxides in the coarse fractions, since the oxides are very rich in Mn (19.7%) and Fe(17.5%). Co and Zn, however, are not enriched, although the precipitates contain 270 ppm Co and 1050 ppm Zn. The oxides themselves may be precipitated directly or derived by attrition from pebble crusts. Similar enrichments occur in some coarse sands from Killin.

Sluggish sections of the streams have two sediment types:

i. Brownish, fairly organic silty muds, as exposed mud banks and a surface layer (1 cm.) of 'active' sediment (Eh 0.17 v; pH 6.6).

ii. Black organic muds (Eh 0.05 v; pH 6.4).

Sediment Type	No. Samples	Fe%	Mn ppm	Zn ppm	Cu ppm	Co ppm	Eh volt
Precipitate	1	17.50	197,000	1,050	nd	270	nd
Very coarse sand	1	3.35	1,800	53	8	9	nd
Coarse sand	3	R*2.10-2.65 M* 2.35	460-950 640	50-70 60	7-9 8	6-8 7	nd
Silty sand	4	1.60-2.65 2.15	250-390 265	35-65 50	5-14 11	11	nd
Silty brown mud	7	2.50-3.55 2.75	240-990 670	60-95 70	9-18 12	8-11 10	0.20
Black organic mud	3	3.50-4.70 3.90	175-490 295	60-135 100	13-30 20	7	0.05
Iron oxide slime	1	13.50	1125	140	18	5	nd

Stream water: pH 6.4-6.8; Eh 0.40 v.

TABLE 6-11a METAL CONTENT OF STREAM SEDIMENTS, CLOGHERNY GLEBE

Coarse sand	3	3.00-3.70 3.30	295-495 410	60-95 75	19-32 27	14-18 16	nd
Silty sand	7	2.80-4.10 3.30	310-535 465	80-105 90	30-33 32	18-21 19	nd
Black muds	3	3.40-5.70 4.30	825-850 835	75-90 80	30-40 35	nd	0.01
Iron oxide slime	2	16.5-23.0 19.8	5700-8000 6900	65-75 70	25-32 27	55	pH 6.2

Stream water: pH 6.7-7.3; Eh 0.40 v.

TABLE 6-11b METAL CONTENT OF STREAM SEDIMENTS, MAYNE

Sands, with precipitate	3	2.9-3.4 3.30	2725-3625 3130	60-80 70	25	30
Sands, no precipitate	1	2.90	975	80	20	25
Iron oxide slime	1	5.80	850	125	nd	nd

TABLE 6-11c METAL CONTENT OF STREAM SEDIMENTS, KILLIN

*R - Range; *M = Arithmetic mean; nd = not determined.
Data on minus 80-mesh fraction.

TABLE 6-11 METAL CONTENTS OF SORTING FRACTIONS OF STREAM SEDIMENTS, CONTROL CATCHMENTS, CENTRAL TYRONE

The black muds tend to be richer in iron and, at Mayne, in manganese, than other sediments. At Cloghorny, the Mn enrichment (900 ppm) was confined to a surface layer of brown silt. Cu and Zn can be enriched in organic samples (Chapter 5.43).

Ochreous iron oxide slimes can be associated with waterlogged soils in all catchments, with enrichments in Fe (20%) and Mn (6,900 ppm) but not in other metals.

Metal associations

There is an apparent relationship between Fe and Zn in sediments from Clogherny and Killin (Fig. 6-11), possibly reflecting a similar association in the soils (Section 6.536). The Mn levels in sediments are mostly below 2,000 ppm and there is no correlation with either Fe or Zn.

6.53 Metal contents of soils

6.531 Introduction

The differences in parent materials in these catchments (Section 6.52) have given rise to differences in texture and metal content in soils. Thus, soils at Clogherny tend to be more sandy and poorer in metals than those at Killin and Mayne. The soil sequences (Fig: 6-16) differ also, in that at Clogherny, poorly drained soils occur only in valleys, but at Killin and Mayne, they can occur on hill crests and slopes. Nevertheless, variations in metal contents between soil types and within profiles of similar soils tend to be the same.

The metal contents of soils collected on traverses across the catchments are given on Tables 6-12 to 6-14. Metal distributions in the soil profiles are shown on Figs: 6-12 to 6-14.

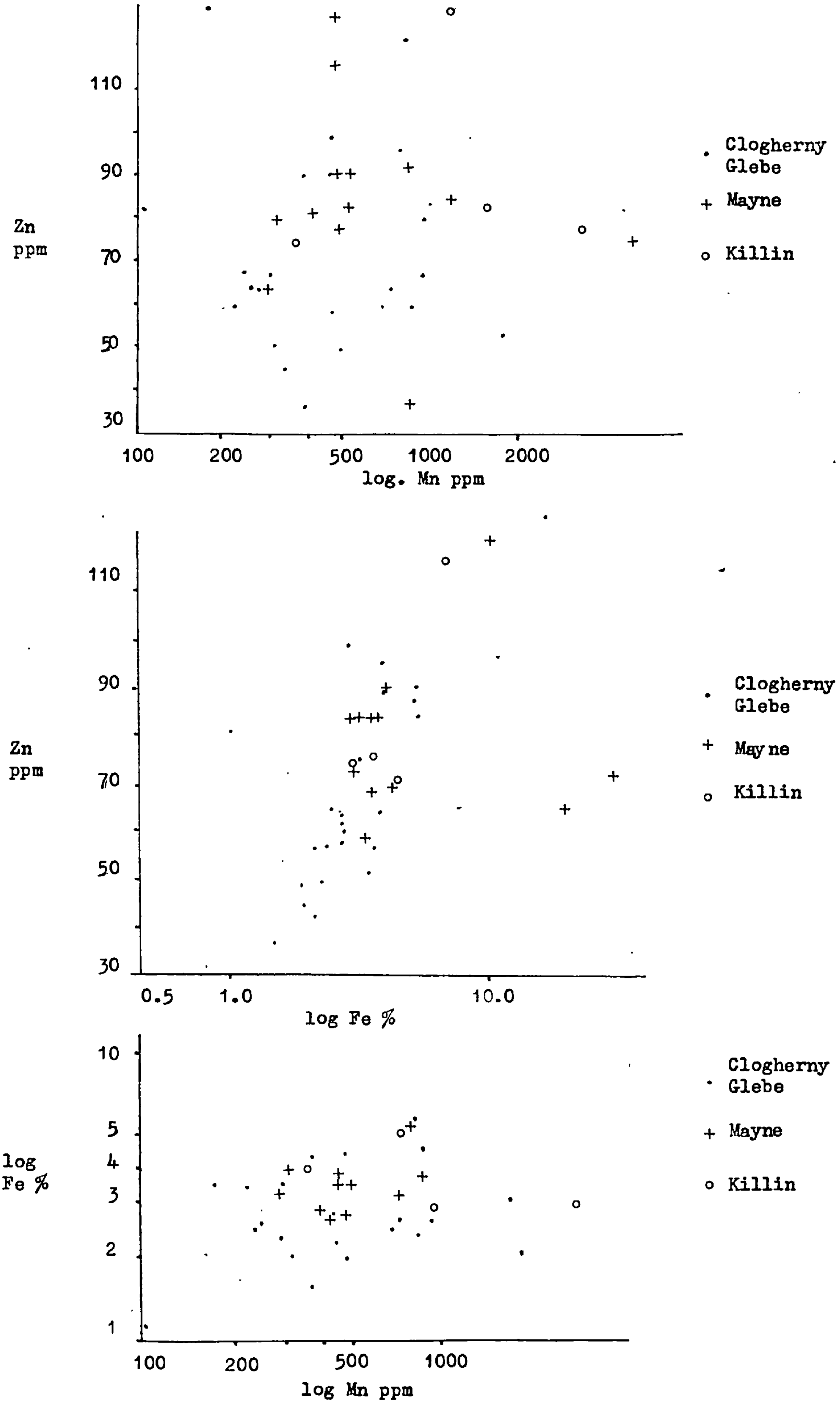


FIG. 6 -11 . CORRELATIONS BETWEEN THE IRON, MANGANESE AND ZINC CONTENTS OF STREAM SEDIMENTS FROM CLOGHERNY, KILLIN AND MAYNE, CENTRAL TYRONE.

	Depth cm.	No. Samples	Fe%	Mn ppm	Zn ppm	Cu ppm	pH
MORAINE CREST							
Freely drained							
Topsoils	0 -15	3	R*2.00-2.70 M* 2.45	325-580 450	50-70 60	20-35 25	5.8-7.6 6.7
Reddish subsoil	30-45	3	2.50-3.25 2.80	185-445 300	55-75 70	10-17 14	
MORAINE SLOPE							
Freely drained							
Topsoils	0 -12	4	2.40-2.70 2.55	290-520 390	45-60 50	10-18 14	6.8-8.0 7.3
Grey subsoils	12-25	3	2.50-3.25 2.80	140-330 260	52-55 54	9-16 11	6.8-7.0 6.9
Reddish subsoils	30-45	3	2.50-2.80 2.60	275-445 365	45-55 50	11-17 13	
VALLEY & BANK SOILS							
Imperfectly drained							
Topsoils	0 -15	4	2.25-3.10 2.55	175-500 365	45-60 50	19-21 20	6.3-7.3 6.8
Grey subsoils	30-45	4	1.85-3.35 2.45	240-690 360	30-55 40	8-30 17	5.2-6.7 6.0
Reddish subsoil	Below 60	4	1.45-2.60 2.05	120-275 175	35-75 50	11-17 14	
Poorly drained							
Topsoils	0 -15	6	1.70-3.30 2.35	150-465 295	35-60 50	12-30 25	4.5-6.7 6.0
Bleached subsoils	30-45	6	0.85-2.10 1.55	60-290 135	20-65 40	6-22 12	4.0-6.5 5.6
Reddish subsoils	Below 60	4	1.70-2.45 2.16	145-270 195	45-65 55	10-21 15	
BASIN PEAT	0 -25	4	0.09-0.30 0.17	18-30 23	18-45 30	4-15 8	3.7-4.2 3.9

*R = Range; *M = Arithmetic mean.
Data on minus 80-mesh fraction.

TABLE 6-12 RANGE AND MEAN METAL CONTENTS OF SOILS, CLOGHERNY GLEBE

	Depth cm.	No. Samples	Fe%	Mn ppm	Zn ppm	Cu ppm	pH
SOILS							
CREST Imperfectly drained							
Topsoil	0 -15	4	R*3.7-5.15 M* 4.16	200-800 460	70-90 80	25 65 45	6.2-6.8
Subsoil	30-45	4	4.35-5.4 4.80	215-725 435	75-100 85	35-50 40	6.5
SLOPES Freely drained							
Topsoil	0 -15	3	4.2-4.5 4.30	365-710 550	65-85 75	30-50 40	4.8-5.2
Subsoil	30-45	3	4.7-5.4 5.00	375-700 580	65-95 80	30-45 40	5.0
SLOPES Imperfectly drained							
Topsoil	0 -15	7	2.65-4.15 3.60	125-337 235	60-80 75	30-40 35	5.1-6.7
Subsoil	30-45	8	3.2-6.3 4.55	160-290 215	55-95 75	25-35 30	6.1
SLOPES Poorly drained							
Topsoils	0 -15	3	2.55-4.2 3.3	140-360 220	55-80 65	30-45 35	5.5-6.1
Subsoils	30-45	3	3.33-5.0 4.33	115-615 300	60-80 75	30-50 35	5.8
SEDIMENTS							
Silty sands		7	2.8-4.1 3.31	310-535 465	80-105 90	30-35 30	6.7,7.3

*R = Range; *M = Arithmetic mean.
Data on minus 80-mesh fraction.

TABLE 6-13 RANGE AND MEAN METAL CONTENTS OF SOILS, MAYNE

	Depth cm.	No. Samples	Fe%	Mn ppm	Zn ppm	Cu ppm	pH
SOILS							
SLOPES Freely drained							
Topsoils	0 -15	5	R*4.3-5.5 M* 4.92	1000-1425 1165	85-95 90	33-42 35	5.4-7.0 6.2
Subsoils	30-45	7	5.55-8.8 6.4	900-1650 1270	65-160 95	15-30 22	5.4-7.0 6.1
SLOPES Imperfectly drained							
Topsoils	0 -15	5	2.93-4.4 3.6	525-900 720	55-72 60	25-40 35	4.8-6.3 5.8
Subsoils	30-45	5	3.05-4.45 3.8	225-750 450	53-72 64	18-35 25	
SLOPES Poorly drained							
Topsoils	0 -15	3	3.6-5.35 4.43	175-375 265	75-120 95	45-55 50	5.5-6.5 6.1
Subsoils	30-45	4	3.1-4.4 3.9	175-300 260	60-85 70	35-50 40	
PEAT		1	1.45	225	30	8	4.5
SEDIMENTS		1	2.90	975	80	20	nd.

*R = Range; *M = Arithmetic mean; nd = not determined.
Data on minus 80-mesh fraction.

TABLE 6-14 RANGE AND MEAN METAL CONTENTS OF SOILS, KILLIN

6.532 Freely drained brown earths In all catchments, the metal contents of these soils are similar to those of the stream sediments, containing approximately 300-400 ppm Mn at Clogherny, 450 ppm Mn at Mayne, and 1,000 ppm Mn at Killin.

On the moraine slope at Clogherny (profile CGP/1, Fig: 6-12), grey-brown sandy loams form the topsoil, with a narrow transition to a friable yellow-brown (B) horizon at 35 cm. This merges to the pink and grey sands of the(B)/C horizon below 60 cm and to firm purplish silty sands at 120 cm. Pebbles in the (B) horizon are strongly weathered; below, in the (B)/C horizon, they have Mn oxide stains on fractures. The pH of all horizons is over 6.0.

Mn and Cu are concentrated in the topsoils (450 ppm Mn, 15-25 ppm Cu), possibly with organic carbon, and tend to decline in lower horizons (350 ppm Mn, 5-10 ppm Cu). Fe shows little variation, with minima of 2% in topsoils and the (B)/C horizons and maxima of about 3.3% in the (B) horizons. Similarly, Co and Zn are mostly higher in the (B) horizons but in lower horizons, their variations are similar to Mn. All metal contents are lowest in the(B)/C horizons, but most are raised in silty sands below 120 cm.

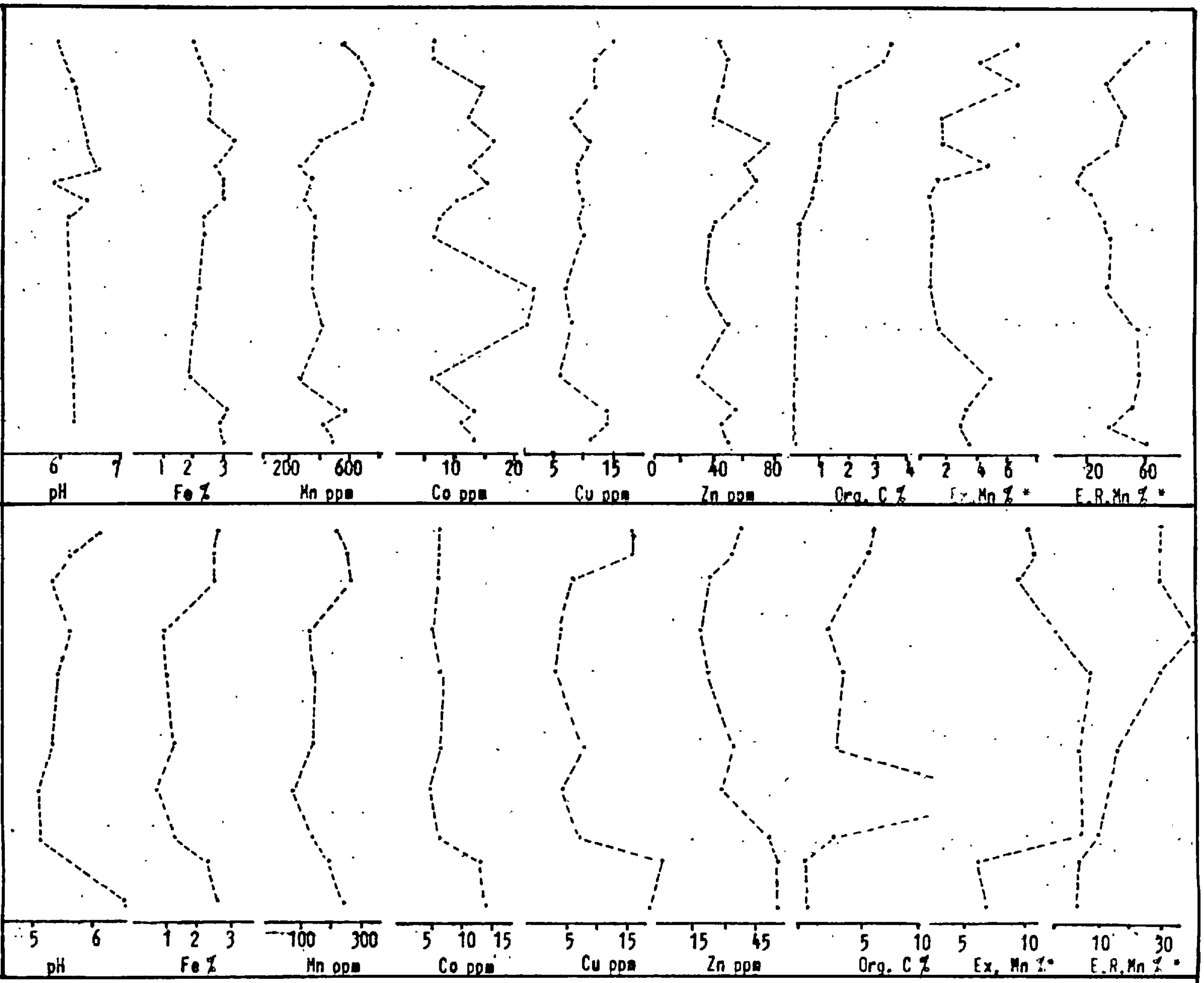
At Mayne, freely drained soils tend to occur in areas of alluvial sands and where slopes are incised by the stream. Profile MP/1 (Fig: 6-14) shows that about 40 cm of grey-brown silty clay loam overlie a series of silty, sandy or gravelly alluvial horizons. The soils tend to be strongly mottled throughout, often developing indurated pedotubules up to 2 cm. in diameter around root channels. The pH (5.0) is lower than in other soils in the catchment or in similar soils at Clogherny.

Copper and organic carbon tend to decline with depth in the top 60 cm., but Mn and Fe reach maxima (about 5.00% Fe, 600 ppm Mn) at the mottled transition to the bedded sands at 40 cm. Co and Zn, however, show no regular variation and even where pedotubules concentrate Fe (17%) and Mn (2,600 ppm), the Co and Zn contents are similar to those of the surrounding soils (40 ppm Co, 65 ppm Zn). In the bedded sands, however, the metals all show similar trends, responding to the layering, reaching maxima where there is iron staining.

In both profiles examined, the variations in exchangeable and reducible Mn tend to follow those of total Mn. The proportion of exchangeable Mn declines down profile from 7% to 2% of total Mn, following organic carbon. The proportion of easily reducible Mn is mostly in the range 20-50% of total Mn, with maxima in topsoils, iron stained alluvium and, at Clogherny, the silty sands at 120 cm.

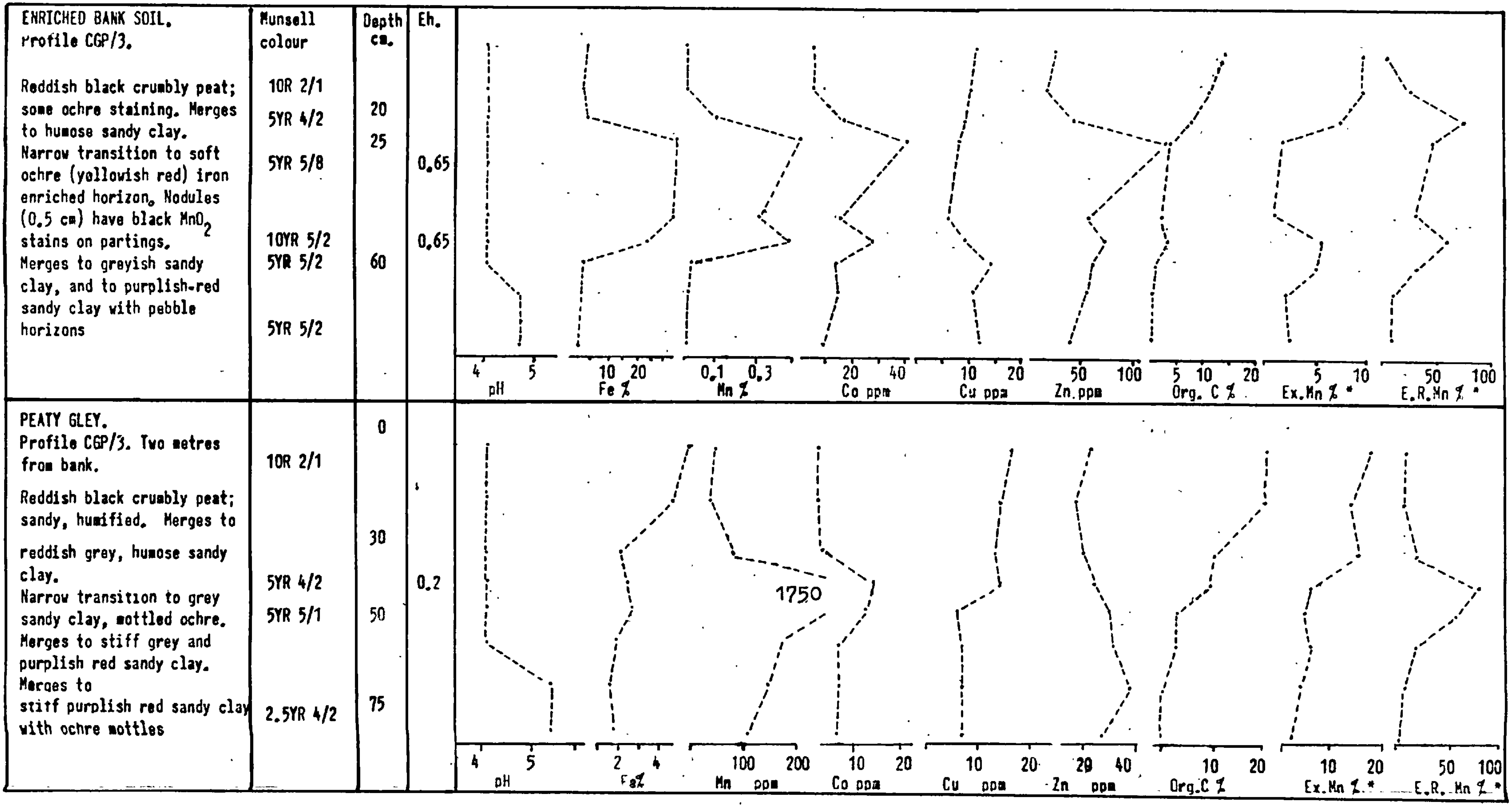
6.533 <u>Imperfectly drained and gleyed soils</u> In all three catchments the Fe, Mn, Co and Zn contents of partially gleyed soils are lower than in freely drained soils. At Mayne, for example, poorly drained soils contain 220 ppm Mn, freely drained soils 450-500 ppm Mn. Cu contents, however, can be raised, with the metal accumulating in organic topsoils.

	Munsell colour	Depth cm	Eh v.
ACID BROWN EARTH. Freely drained. Profile CGP/1 Dark brown sandy silty loam merging to dark yellow-brown sandy loam. Good crumb structure. Narrow transition (at 30 cm) to yellow brown sands of (B) horizon. Merges to friable grey brown and and reddish sands. Becoming coarses with depth; pebbles and boulders in coarse, friable grey brown sands. Narrow transition to firm purplish pink sandy clay Some grey and ochre mettling.	10YR 4/3 10YR 4/4 10YR 5/5 10YR 4/2 10YR 6/2	30 60 90 120	0.55 0.55
ACID BROWN EARTH. Imperfect drainage. Profile CGP/2 Organic, slightly sandy clay loam; dark greyish brown. Merges to brownish grey silty sandy clay mottled ochre along root channels. Merges to fibrous peat with bands of organic, grey silty sand. Water saturated. Fibrous peat with wood. Sharp transition to firm purplish pink sandy clay. An upper pebbly horizen is a prolific seepage source.	10YR 3/2 10YR 6/2 mottled 3YR 3/4 10YR 4/2 2.5YR 4/2 2.5YR 5/2	20 40 75	0.15 0.25 0.20



* Ex. Mn = $\frac{\text{exchangeable Mn}}{\text{total Mn}}$ % E.R. Mn = $\frac{\text{easily reducible Mn}}{\text{total Mn}}$ %. Analytical data on minus 80-mesh fraction.

FIG. 6 - 12 . VARIATIONS IN pH, ORGANIC CARBON AND METAL CONTENT IN SOIL PROFILES, CLOGHERNY GLEBE CATCHMENT, Co. TYRONE.



ENRICHED BANK SOIL. Profile CGP/3.	Munsell colour	Depth cm.	Eh.
Reddish black crumbly peat;	10R 2/1		
some ochre staining. Merges	5YR 4/2	20	
to humose sandy clay.		25	
Narrow transition to soft ochre (yellowish red) iron enriched horizon. Nodules (0.5 cm) have black MnO_2	5YR 5/8		0.65
stains on partings.	10YR 5/2		0.65
Merges to greyish sandy clay, and to purplish-red	5YR 5/2	60	
sandy clay with pebble horizons	5YR 5/2		

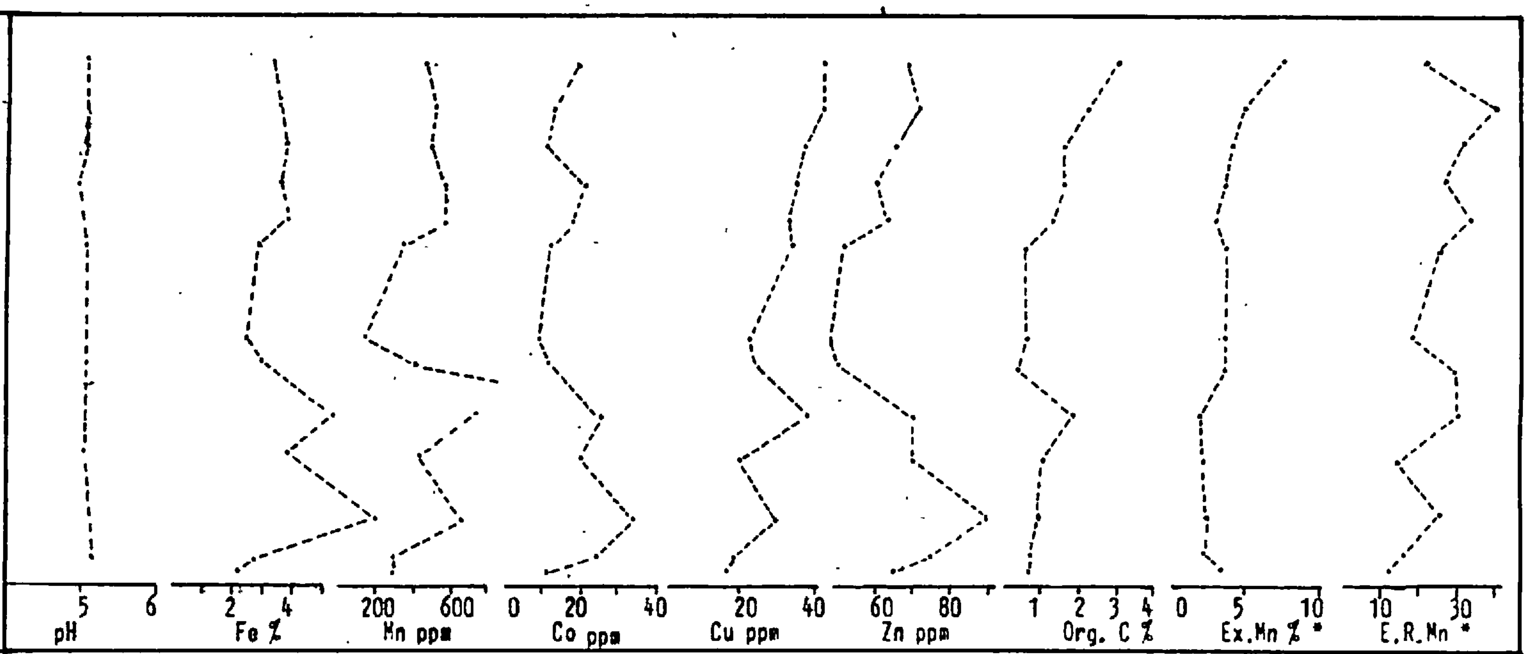
PEATY GLEY. Profile CGP/3. Two metres from bank.	Munsell colour	Depth cm.	Eh.
		0	
	10R 2/1		
Reddish black crumbly peat; sandy, humified. Merges to		30	
reddish grey, humose sandy clay.	5YR 4/2		0.2
Narrow transition to grey sandy clay, mottled ochre.	5YR 5/1	50	
Merges to stiff grey and purplish red sandy clay. Merges to			
stiff purplish red sandy clay with ochre mottles	2.5YR 4/2	75	

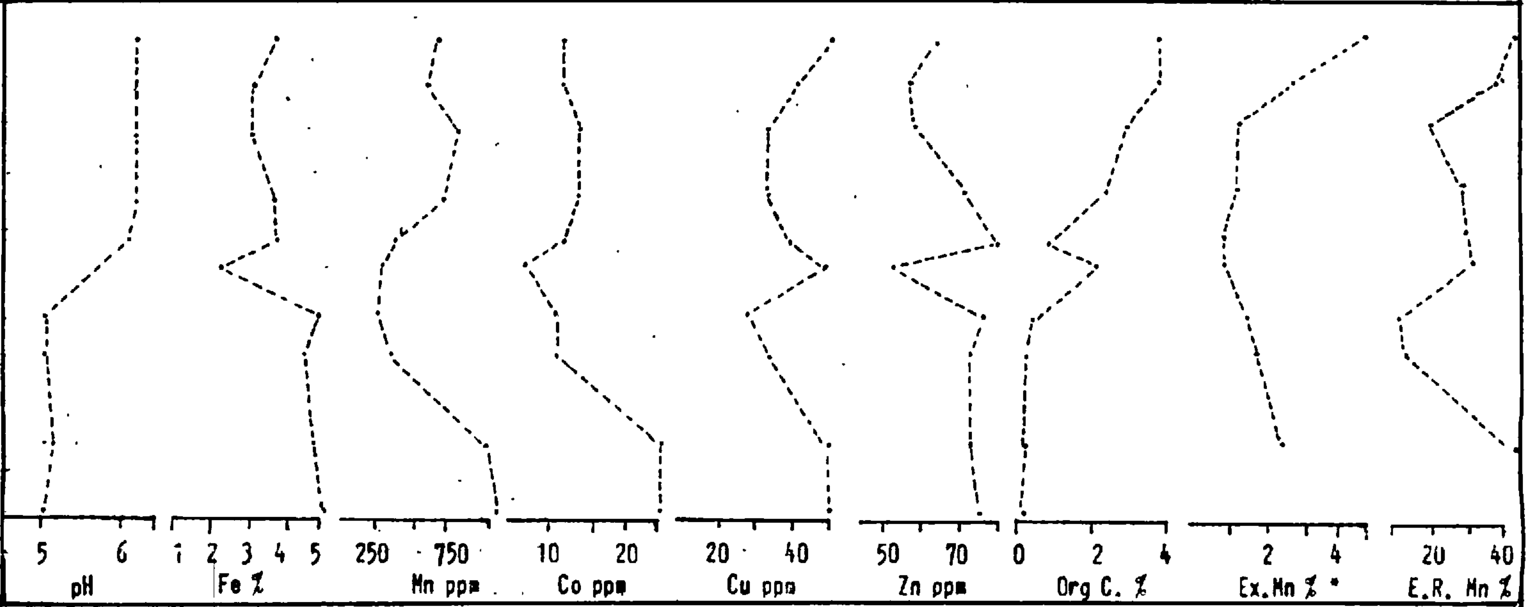
* Ex.Mn = $\frac{\text{exchangeable Mn}}{\text{total Mn}}$ %. E.R.Mn = $\frac{\text{easily reducible Mn}}{\text{total Mn}}$ %

Analytical data on minus 80-mesh fraction.

FIG. 6 - 13. VARIATIONS IN pH, ORGANIC CARBON AND METAL CONTENTS IN BANK SOILS, CLOGHERNY GLEBE CATCHMENT, Co. TYRONE.

	Munsell colour.	Depth cm	Eh v.
ACID BROWN EARTH. Freely drained. Profile MP/1. Grey, micaceous, sandy clay loam, becoming coarser, and pebbly. Charcoal fragments common. Mottled along root channels, some forming indurated pedotubules. Merges to bedded silty sands with lenses of clay and coarse sand. Pebbly sands and gravels Silty grey clays, mottled ochre. Some lenses of iron stained gravel. Merges to firm, silty grey clay.	5YR 5/2 10YR 5/2 10YR 6/1	30 60 90 120	0.25 0.45 0.45
ACID BROWN EARTH. Impeded drainage. Profile MP/2. Dark grey-brown micaceous clay loam; coarser and lighter in colour with depth. Charcoal fragments common. Narrow transition to sticky grey and reddish silty clay Strongly mottled in top 5 cm. Horizon water saturated. Sharp transition to very stony sandy clay. Strongly stained by black Mn-Fe oxides.	7.5YR 5/2 7.5YR 4/2 5YR 5/3 5YR 5/2 10YR 6/2	30 60 90	0.20 0.20 0.30





* Ex Mn = $\frac{\text{exchangeable Mn}}{\text{total Mn}}$ %. E.R. Mn = $\frac{\text{easily reducible Mn}}{\text{total Mn}}$ %. Analytical data on minus 80-mesh fraction.

FIG. 6 - 14 . VARIATIONS IN pH, ORGANIC CARBON AND METAL CONTENTS IN SOIL PROFILES, MAYNE CATCHMENT, Co. TYRONE.

A groundwater gley was examined at Clogherny (Profile CGP/2, Fig: 6-12). The topsoil, 40 cm of mottled organic silty sands, is probably derived from moraine outwash and alluvium. It merges to sands and coarse peat, 35 cm. thick, overlying purplish sandy clays. The profile pit was filled rapidly with water issuing from beneath the peat. The metal contents are low in all horizons, being highest in topsoils and sandy clays (2.50% Fe, 250 ppm Mn) and lowest in the sandy peats (1.00 % Fe, 130 ppm Mn). The proportions of exchangeable and easily reducible Mn are high ($<$ 20% of total Mn) in most horizons except the sandy clay. Easily reducible Mn reaches 30-50% of total Mn in mottled topsoils, exchangeable Mn 20-25% of total Mn in the peats, suggesting that much of the metal is freshly precipitated or adsorbed to organic matter, rather than as aged oxides or in mineral lattices.

Imperfectly drained soils at Clogherny are mostly groundwater gleys, but at Mayne and Killin drainage can be impeded by impervious subsoils. Profile MP/2 (Fig: 6-14), on a hill crest at Mayne, has a micaceous grey-brown clay loam as topsoil, with a sharp transition to waterlogged pink and grey silty clays at 35 cm. This horizon is underlain by better drained, very stony clays in which each pebble is heavily stained with Fe-Mn oxides. All horizons are strongly mottled.

The organic carbon and Cu contents decrease down profile, but have a joint enrichment in the pink clays. In general, however, these clays are depleted in metals (2.1% Fe, 250 ppm Mn) relative to overlying horizons (3.5% Fe, 650 ppm Mn) and the underlying clays (4.7% Fe, 1,000 ppm Mn). Thus, whereas at Clogherny, metals leached from waterlogged horizons are lost from the profile, at Mayne they are apparently reprecipitated in adjacent horizons as mottles and stains. This is reflected by the high proportion of easily reducible Mn, which exceeds 30% of total Mn in topsoils, the transition to the pink clays and the grey clays.

The additional mobility observed in the imperfectly drained soils is probably due to a lower Eh (< 0.25 v) than in free draining sites (> 0.35 v), since pH shows very little variation.

6.534 Peats The peats at Clogherny and Killin have very low metal contents but the upper horizons of reclaimed areas have levels similar to poorly drained mineral soils (1.27% Fe, 225 ppm Mn) despite being very acid (pH 4.5).

6.535 Bank soils Most bank soils have similar metal contents to equivalent soils elsewhere, but in some circumstances topsoils can be enriched in Fe and Mn. If soils away from the banks are acid or gleyed, these metals are mobilised and can reprecipitate in more oxidising environments - such as in the zone of water table fluctuation near the stream. For example, peaty gleys 15 metres from the bank at Clogherny are acid (pH 4.0) with low levels of Fe (1.6%) and Mn (110 ppm). Essentially similar soils about 2 metres from the stream are less acid (pH 5.8) and are relatively enriched in Fe (3.7%) and Mn (350 ppm).

Downslope from the raised bog at Clogherny, an extreme bank enrichment was examined in profile CGP/3 (Fig: 6-13). On the exposed bank surface, the profile is podzolic, with 15 cm. of sandy peat, a bleached A_2 horizon and a soft, ochreous B horizon, 35 cm. thick. This is underlain by strongly mottled grey-ochre sands, merging to pink-ochre sands at 70 cm. The ochre is highly oxidizing (Eh = + 0.65 volt) and has concentrated Fe (35%), Mn (0.54%), Co (40 ppm) and Zn (130 ppm). The iron content of the peat is enriched (3.25%) relative to peat elsewhere (0.17%) but the content of other metals in the peat and parent material is similar to other soils of the catchment.

Away from the bank face, the ochreous horizon thins out laterally in about 130 cm., giving way to humose sandy clays and mottled grey-ochre sands. These are enriched in Mn (1,750 ppm) and Co (25 ppm), with Fe and Zn at near normal levels (2.7% Fe; 30 ppm Zn). Exchangeable Mn is enriched (70-240 ppm) in the B horizon but the proportion only rises above 3% of total Mn in peats and the base of the ochre. The amount and proportion of easily reducible Mn is high at the base of the peat and enriched horizons, reaching maxima of 1,500-3,000 ppm (50-80% of total Mn), reflecting the importance of recent secondary precipitation in these horizons.

6.536 <u>Metal associations in soils</u> In upper soil horizons (0 - 40 cm.) correlations are shown by iron with manganese and zinc (Fig: 6-15). The Fe/Mn relationship is weak at Mayne, however, especially where the Fe content exceeds 4%.

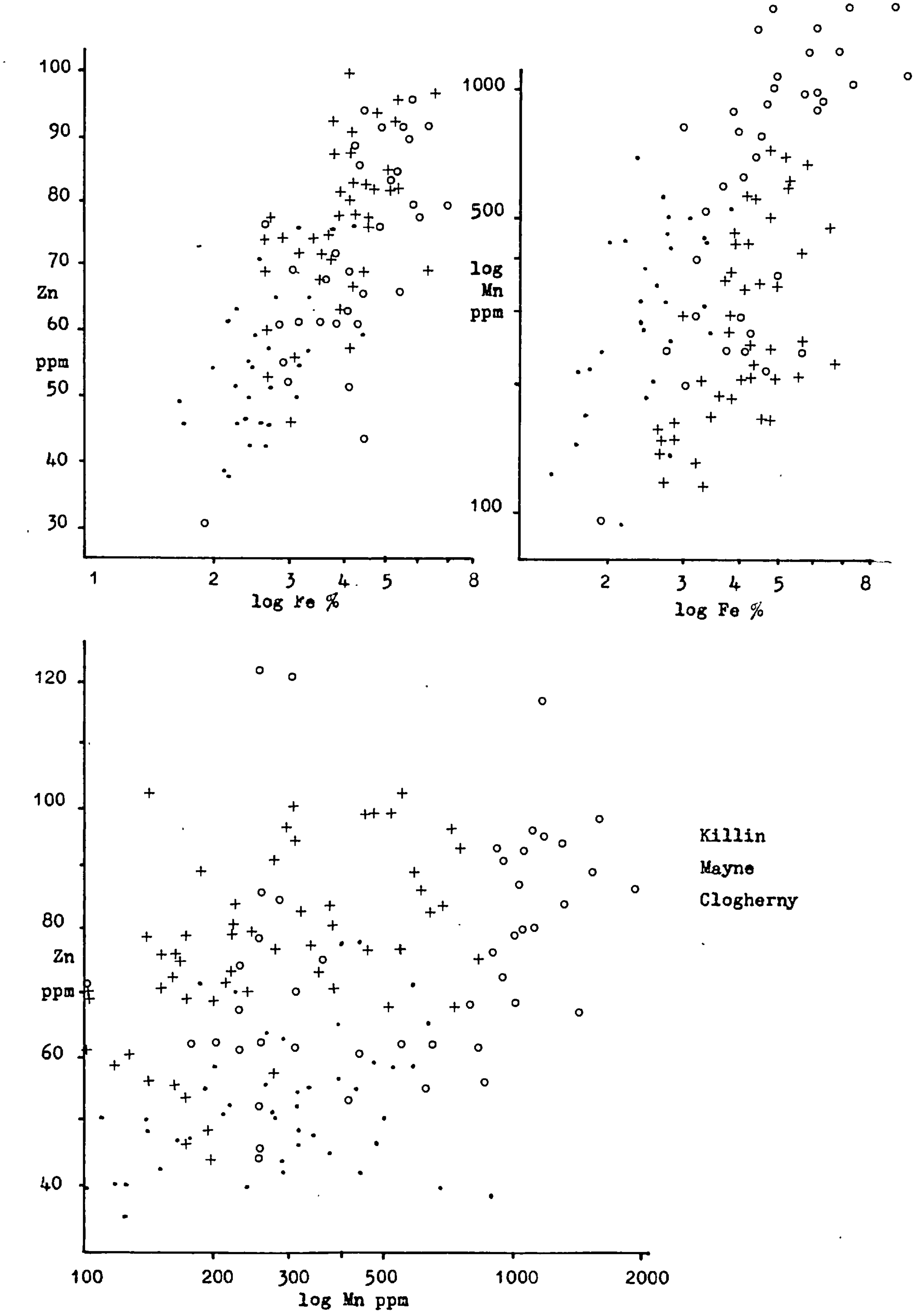


FIG. 6 - 15. CORRELATIONS BETWEEN THE IRON, MANGANESE AND ZINC CONTENTS OF SOILS FROM CLOGHERNY, MAYNE AND KILLIN, CENTRAL TYRONE. (Data on minus 80-mesh fraction).

Significant correlations (P = 0.001).

	r
○	+0.40 - +0.49
⊙	+0.50 - +0.59
⦿	+0.60 - +0.69
◉	+0.70 - +0.79
◍	+0.80 - +0.89
●	> +0.90
□	-0.40 - -0.55
■	> -0.90

Non-significant correlations.

	r
•	-0.39 - +0.39

(Number of samples = 63).

	Residual Mn	Reducible Mn	Exchangeable Mn	Residual / Total Mn	Reducible / Total Mn	Exchangeable / Total Mn	Copper	Cobalt	Zinc	Manganese	Iron	Organic Carbon
Easily reducible Mn	◉											
Exchangeable Mn	○	◉										
Residual / Total Mn	•	□	□									
Reducible / Total Mn	•	⊙	⊙	■								
Exchangeable / Total Mn	•	•	•	•	•							
Copper	•	•	•	•	•	•						
Cobalt	⊙	⊙	•	•	•	□	•					
Zinc	⦿	•	•	•	•	□	○	◉				
Manganese	●	◍	◉	•	○	•	•	⊙	⊙			
Iron	●	◉	○	•	•	•	•	○	○	◍		
Organic carbon	•	•	•	•	•	○	•	•	□	•	•	
pH	•	•	•	•	•	•	•	•	•	•	•	□

TABLE 6 - 15. CORRELATION MATRIX FOR METAL AND ORGANIC CARBON CONTENTS AND pH IN SOIL PROFILES, CLOGHERNY GLEBE AND MAYNE, CENTRAL TYRONE.

Correlation coefficients were calculated for the soil profile samples (Table 6-15). Significant correlations are shown by: Fe/total Mn (r = 0.90), Co/Zn (0.75), Co/Mn (0.60), Zn/Fe, Zn/Mn (0.50). Negative correlations (r =-0.50) are shown by organic carbon with both pH and Zn. Zn also shows a negative correlation with the proportion of exchangeable Mn. These results suggest much closer Mn/Fe and Mn/Zn relationships for whole profiles than in upper horizons alone and that the metals are closely associated in both soils and parent materials.

Cu shows little correlation with the other variables. This differs from the Low Sperrins profiles, in which it showed a positive correlation with Co and Zn and a negative correlation with organic carbon. Although Cu is mobilised under similar conditions as the other metals, it does not precipitate with them. Consequently, it can show positive correlations where leaching predominates, as in the Low Sperrins, but not where reprecipitation is occurring.

6.54 Metal migration in the soil sequence

The soil sequences and associated processes of metal dispersion at Clogherny Glebe and Mayne are summarised on Fig: 6-16. Most soils in both catchments are near neutral so that metal mobility probably depends largely on variations in Eh. In free draining soils, reducing and possibly acidic conditions may occur only locally, for example, near decaying organic matter, particularly when soils are wet. On migration from such micro-environments or as the soil dries, Fe, Mn, Co and Zn reprecipitate rapidly

Acid brown earths,
(surface water gley)
Profile MP/2.

Acid brown earths,
(free draining).
Profile MP/1

Upper horizons may be organic, strongly mottled. Drainage impeded by impervious till below 40 cm. Metals mobilised in these water-logged clays but reprecipitated in more oxidising conditions in underlying stony till.

Soils developed on alluvium, often deeply incised by stream. Topsoils strongly mottled, especially 10 - 35 cm., developing indurated pedotubules. Probably little leaching or metal loss to stream.

LOWLAND SEQUENCE, MAYNE CATCHMENT.

Acid brown earths,
(free draining).
Profile CGP/1

Acid brown earths,
(ground-water gleys).
Profile CGP/2

Peaty gleys.
Profile CGP/3.

Limed to pH 6.5 - 7.5 May show a well defined (B) horizon - weakly podzolic in some profiles Slight mottling to 100 cm., but probably little metal leached from profile.

Developed on alluvium and/or peat. Mottled in top 40 cm., water-logged below. Metals depleted from gleyed horizons, with reprecipitation in the stream.

Very acid, strongly leached. Reprecipitation either in stream bank or on the sediment.

MORAINE SEQUENCE, CLOGHERNY GLEBE CATCHMENT.

FIG. 6 - 16. MIGRATION OF IRON AND ASSOCIATED METALS IN SOIL PROFILES AND SEQUENCES, CONTROL CATCHMENTS, CENTRAL TYRONE.

whereas Cu tends to concentrate in the organo-mineral complex. Consequently, redistribution within the profile is slight and little metal loss takes place. Stronger mobilisation, however, occurs under reducing conditions in imperfectly drained soils, with metals migrating from the gleyed horizons.

At Clogherny, soils on the moraine are freely drained and little metal is lost by leaching. Some mobilisation occurs in the imperfectly drained valley soils and in the vicinity of the basin peats. Groundwater can enter the stream directly from many such soils and mobilised Fe, Mn, Co and Zn are precipitated as encrustations on pebbles. In some cases, however, metals are precipitated in soils downslope, enriching bank soils, for example, in upper, oxidized horizons. At Mayne there is a different sequence, with the imperfectly drained soils on hill crests and slopes, and free draining soils near the stream. Metals mobilised in gleyed horizons are mostly re-precipitated within the profile or in the free draining soils downslope, so that little metal reaches the stream and pebble encrustation is only very slight.

6.6 METAL DISTRIBUTION AND MIGRATION IN THE CONTRASTING ENVIRONMENTS

The detailed investigations have shown several differences in metal dispersion between the Low Sperrins and control areas:

1. Soils In the Low Sperrins, the prevailing climate and vegetation have encouraged acid soil conditions and a high degree of metal mobility. This has resulted in podzolisation,

with the development of very distinct horizons and a proportionately greater depletion of all metals relative to that occurring under the less severe conditions of the control catchments. The podzolic and gleyed profiles all show evidence of Fe-Mn accumulation below the B horizon, even in soils waterlogged at the time of sampling. Organic matter, apparently derived from the overlying peat horizons, is associated with such accumulations and may be involved in metal translocation (Chapter 8-3).

In the control catchments, cultivation and a marginally better climate have resulted in the development of acid brown earths. There is little peat and both soil pH and metal contents are higher than in the Low Sperrins, indicating that metal mobility is restricted. In all control catchments, however, Fe, Mn, Co and Zn are mobilised in imperfectly drained soils, resulting in a redistribution in the soil profiles and sequences, with some loss of metals to the stream.

2. Easily reducible manganese in soils The amount and proportion of easily reducible Mn has previously been shown to indicate the active precipitation of hydrous Mn oxides in soils (Leeper, 1947) and sediments (Horsnail, 1968). In the Low Sperrins, the proportions of this fraction and hence the occurrence of active precipitation are appreciable (> 5% of total Mn) in most horizons of the reclaimed podzols (profiles AP/1, SP/1), the B and basal horizon of the peaty podzol (AP/2), the base of the peaty gley (AP/3) and at very high levels (> 24% of total Mn) in the enriched bank soil (AP/4). In the

most acid profile, peaty podzol SP/2, there is a gradual accumulation of total Mn down profile, but the reducible fraction is always negligible.

The amount and proportion of easily reducible Mn are at much higher levels in all profiles in the control catchments than the Low Sperrins. The proportion falls below 20% of the total Mn only in gleyed or acid horizons, for example the pink clays of profile MP/2 and the waterlogged peaty sands in profile CGP/2. This suggests that there is continued Mn mobilisation throughout the profiles but, whereas the metal is lost from acid or gleyed horizons, it is rapidly reprecipitated within less acid or free draining soils with only a minor loss. The high levels in such soils may also be associated with a particular form of Fe/Mn accumulation (glaebules) found mainly in the control catchments (Chapter 7-53).

The proportion of this fraction of total Mn in soils thus in part reflects the mobilisation of Mn and associated metals (Fe, Co, Zn) under acid - reducing conditions, and their concentration or reprecipitation under less acid, more oxidising conditions. A low proportion of easily reducible Mn indicates that little precipitation is occurring and that mobilisation and removal from the profile are the dominant processes.

3. <u>Stream precipitates</u> Despite retention or precipitation in some soil horizons, there is a general loss of Fe, Mn, Co and Zn by way of groundwater solution. They remain dissolved until increasing Eh or pH conditions favour oxidation and precipitation, frequently in or near the streams.

Stream precipitates take two common forms, suggesting different mechanisms of formation:

i. Manganiferous precipitates. These are the black or dark grey precipitates which encrust stream pebbles in all five catchments, although only weakly developed at Mayne and Killin. Analyses of such crusts show the Fe/Mn ratio varies from 5 (Low Sperrins, Camlough) to 1 (control, Clogherny). Their location on the upper surfaces of the sediments indicates precipitation from stream waters. In the Low Sperrins, these precipitates occur in the eastern tributary at Slievemore, near the source at Camlough and on peat in much of the Camlough bog. In the lower reaches of these streams, they are obscured by the second form of precipitate, the ochreous iron oxides.

The distribution of manganiferous crusts suggests that they occur alone:

a) where soil leaching is mostly slight, as in the control catchments; and

b) where much of the stream water is derived from groundwater that has penetrated leached, upper horizons of soils only, as in the upper reaches of the Low Sperrins streams.

ii. Ochreous iron oxide precipitates. These appear abruptly on the peaty stream banks and bed in the Low Sperrins catchments. They form gelatinous precipitates with Fe/Mn ratios ranging from 10-50. Neither Eh or pH of stream waters change rapidly at these sites, hence waters from upstream are unlikely to be the metal source, assuming that these parameters control precipitation. In both catchments, it is probable that phreatic groundwater, that is water from the saturated zone, is entering the streams at these points and continually or intermittently downstream. For example, at Slievemore iron seepages and ochreous precipitates first occur where the water table is near the surface and the streamside peat bog becomes waterlogged. At Gamlough, the precipitate is found where the sandy moraine base to the bog first outcrops in the stream, providing a source of groundwater that will have leached a considerable volume of moraine sands. The stream bed pH rises sharply from 5.2 to 6.3 where the ochre precipitates occur. Upstream, the pH is influenced by acid seepage from the peat, but the rise downstream is probably the result of an influx of less acid, phreatic groundwater from the moraine.

The metal contents of the precipitates suggest this groundwater source to be iron-rich, relative to that forming Mn crusts upstream. Since ferric oxides are more stable than the equivalent manganese oxides, a high groundwater Fe content indicates strong leaching (- or an iron-rich source). Hence, it is significant that the ochreous precipitation occurs in basin peat areas where such conditions prevail. Although the pH of saturated moraine sands, as measured in soil profiles and the stream bed, can be high (6.0), the Eh of such environments (less than 0.2 volt) is sufficiently low for the complete solution of iron. The possible role of humic compounds derived from peat in metal migration is discussed in Chapter 8.

There is no evidence of ochreous precipitation of this type in the control catchments. However, the strong local enrichments of some bank soils, such as profile CGP/3, are probably evidence of lateral migration by a similar mechanism. The metals are leached from the moraine sands beneath the raised bog and remain in solution until reaching the stream bank. Here, however, the stream is incised below the horizon channelling the metal-rich groundwater and precipitation occurs in the bank above stream level.

In all five catchments investigated, oxide precipitation and metal enrichment of sediments are highest where bank soils are gleyed and/or acid. The strongest precipitation, in the Low Sperrins, is associated with a long sequence of leached or waterlogged soils from hill slopes to the stream. The least precipitation occurs at Mayne and Killin where most soils in the catchment, including stream banks, are free draining. To some extent, the Clogherny catchment represents an intermediate situation between those in the Low Sperrins and the other control catchments. There is a larger area of imperfectly drained and peaty soils adjacent to the stream than at Mayne or Killin, resulting in a greater amount of visible oxide precipitation. However, the area is less than in the Low Sperrins and the precipitation is insufficient to enrich the sediment.

6.7 CONCLUSIONS

Iron, manganese, cobalt and zinc enrichment in sediments from the Low Sperrins area is the result of secondary environment processes, with the difference between the control and Low Sperrins catchments being in the extent and severity of acidic and reducing conditions in the soils. This conclusion has several implications in the interpretation of the reconnaissance patterns.

1. Mineral Exploration The patterns of raised Zn in sediments in the Low Sperrins is a false anomaly, not reflecting base metal mineralisation. Horsnail (1968) suggested that false anomalies could be detected by a determination of the proportions of exchangeable and easily reducible Mn. He showed that in streams containing freshly precipitated Mn and secondarily enhanced Zn levels, the ratio of reducible to total Mn was 5 times that of the precipitate-free streams. Conversely, the ratio of exchangeable to total Mn was 4 times greater in the precipitate-free streams.

Similar trends are shown by several sediments from each of the catchments investigated in Central Tyrone (Table 6-16) but the differences are very much less, factors of less than two for the easily reducible fraction and three for the exchangeable. Hence, although the difference is apparent, the usefulness of the distinction is doubtful; The presence of heavy precipitation is normally observable at the time of sampling and much greater contrasts are shown by the total Mn analyses themselves.

The close Zn/Mn correlation in stream sediments from an area of mixed bedrock in Central Tyrone is shown on Fig: 6-17. The Zn content appears to be influenced where Mn exceeds about 2,000 ppm, with high Zn values due to coprecipitation with Mn oxides and not to mineralisation. Elsewhere, this threshold may vary, depending upon bedrock metal content. Deviations from the correlation refer to major differences in either sediment type or parent materials (Section 6.424) and may therefore be a useful indication of mineralisation in areas of this type.

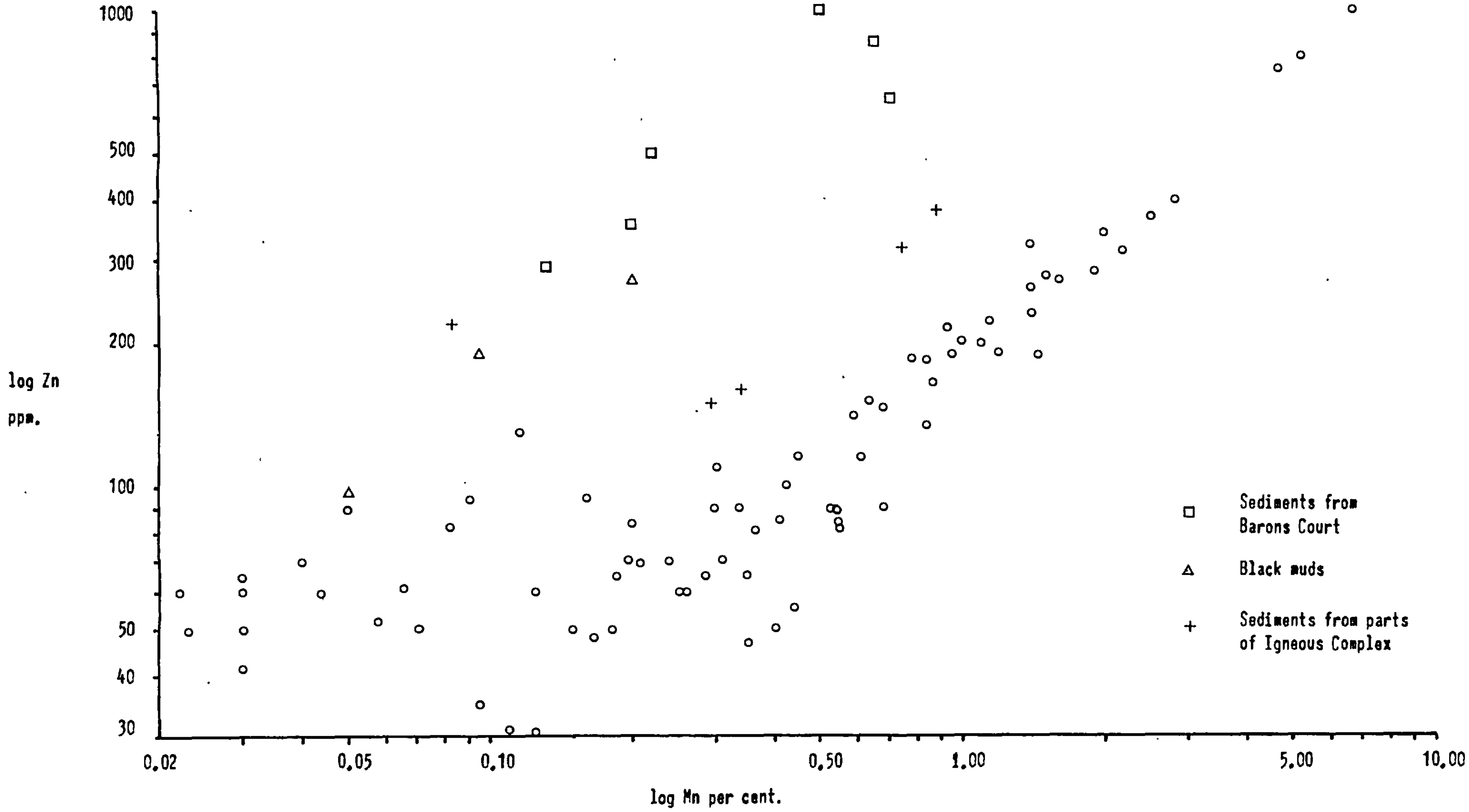


FIG. 6 - 17 CORRELATION BETWEEN THE ZINC AND MANGANESE CONTENTS OF STREAM SEDIMENTS, CENTRAL TYRONE.

(Data on minus 80-mesh fraction).

LOW SPERRINS CATCHMENTS	No. Samples	Total Mn ppm	Exchangeable Mn / Total Mn %	Easily Reducible Mn / Total Mn %	Total Zn ppm
SLIEVEMORE					
Metal rich silty sand	3	0.68-1.44 0.99%	3.0-10 6.5	30-65 50	130-185 155
Metal poor silty sand	4	150-2325 795	3.0-25 14	2-50 30	40-70 60
Black mud	1	1225	28	50	30
CAMLOUGH					
Metal rich silty sand	3	0.65-4.7 1.9%	0.5-10 5.5	30-75 50	115-770 320
Metal poor silty sand	4	650-850 765	9.5-18 14	40-55 47	75-220 147
Black mud	2	940-1460 1200	35-57 45	8-22 15	195-270 230
CONTROL CATCHMENTS					
MAYNE					
Silty sands	5	295-525 425	12-25 18	25-60 40	60-90 80
Black muds	1	830	45	20	80
CLOGHERNY GLEBE					
Sands	6	295-1800 730	14-28 21	10-60 40	50-95 65
Black muds	3	220-490 320	20-30 27	6-18 12	60-100 80

TABLE 6-16 RANGE AND MEAN CONTENTS OF TOTAL ZINC AND EXCHANGEABLE, EASILY REDUCIBLE AND TOTAL MANGANESE IN STREAM SEDIMENTS FROM CENTRAL TYRONE (Data on minus 80-mesh fraction).

The sediments from Barons Court, for example, have very high Zn/Mn ratios (1,000 ppm Zn / 5,000 ppm Mn) and reflect hydromorphic dispersion from base metal mineralisation (Chapter 4.4).

The above conclusions refer to areas in which hydromorphic dispersion predominates. The situation presented by clastic dispersion from oxidising manganiferous sulphides has not been encountered in this area. Zinc enriched oxides from such a source will be well aged. At Camlough, it was found that ageing of precipitates did result in a change in the proportions of extractable Mn, as shown below:

	Silty Sand	Fresh gelatinous ochre	Aged Crust
Total Mn %	1.90	1.96	6.70
$\frac{\text{Easily reducible Mn}}{\text{Total Mn}}$ %	50	34	20
$\frac{\text{Exchangeable Mn}}{\text{Total Mn}}$ %	6	10	2

Consequently, determination of these fractions may aid identification of aged Mn oxides of clastic origin. However, great care is necessary in the interpretation of individual results, since there is a wide variation, depending on sample type (Table 6-16) and samples may contain material from fresh stream precipitates.

2. Geology Rock samples were collected from four of the catchments, but, since the drift is mostly exotic, it is uncertain if they represent the soil parent material.

The results (Table 6-17) demonstrate variation in each catchment and show no constant differences between bedrock from Low Sperrins or

Locality Rock Type	Fe%	Mn ppm	Zn ppm	Co ppm	Cu ppm
CAMLOUGH					
Gabbro	5.40	600	45	30	14
Gabbro	2.70	460	50	35	9
Felsite vein	1.80	270	60	9	35
SLIEVEMORE					
Biotite gneiss	3.45	345	75	15	40
Gneiss	2.45	195	55	9	10
Gneiss	2.20	335	65	7	30
MAYNE					
Weathered greenstone	4.90	210	80	25	45
Weathered greenstone	4.30	1050	65	35	50
KILLIN					
Garnet mica schist	3.45	350	50	17	50
Garnet mica schist	1.15	270	25	5	25

TABLE 6-17 METAL CONTENT OF ROCKS FROM CENTRAL TYRONE CATCHMENTS

control catchments. This confirms that the major sediment reconnaissance patterns of Fe, Mn, Co and Zn do not reflect differences in bedrock abundance. The patterns in Cu, however, may be similar, with sediments and basic rocks at Camlough containing 10-15 ppm Cu and those at Mayne 40-50 ppm Cu.

The rock-soil-sediment correlation is closest at Mayne, where metal precipitation is slightest with, for example, 210-1,050 ppm Mn in rock, 370-700 ppm Mn in free-draining soil and 300-540 ppm Mn in active sediment. In the Low Sperrins, however, rocks and free-draining soils contain 300-600 ppm Mn, but the content of active sediments is often 1.0-3.0% Mn.

No rocks were exposed at Clogherny. However, a comparison of soils from the control catchments suggests that the abundance of all metals studied are lowest in the Clogherny catchment, over Old Red Sandstone bedrock, a result anticipated from the reconnaissance survey.

3. Agriculture The precipitation of Mn and Fe oxides in streams indicates that leaching conditions exist in the catchment, even where the fine fractions of the sediment are not enriched.

In order to obtain a preliminary assessment of the agricultural influence of the metal depletion and to compare leached with control soils, samples of mixed herbage were collected from each catchment. The results are shown, with equivalent topsoil content, on Table 6-18. They suggest that herbage Mn and possibly Zn levels are higher in the Low Sperrins catchments as a whole,

LOW SPERRINS CATCHMENTS	No; Samples	Mn ppm		Zn ppm		Cu ppm		Soil pH
		Soil	Herbage	Soil	Herbage	Soil	Herbage	
CAMLOUGH								
Reclaimed podzol	1	360	290	60	46	43	10	5.0
Peaty slope	2	65	295	27	47	7	10	4.9
Enriched soil	1	4000	305	85	42	16	9	5.0
SLIEVEMORE								
Blanket peat	1	40	235	37	54	4	11	4.5
Reclaimed podzol	2	155	150	42	32	42	11	5.3
Peaty gleys	1	345	220	50	38	14	12	4.2
Enriched soil	2	600	210	70	32	26	10	4.5
Basin peat	1	20	520	45	38	6	10	3.9
CONTROL CATCHMENTS								
MAYNE								
Freely drained soil	2	350	80	73	25	31	9	5.8
Poorly drained soil	2	250	385	65	36	34	11	6.2
CLOGHERNY								
Freely drained soil	4	480	108	51	30	18	13	7.1
Poorly drained soil	2	320	150	45	28	19	8	6.2

TABLE 6-18 MEAN METAL CONTENT OF SOIL (0-15 cm) AND HERBAGE (D.M.) FROM THE CENTRAL TYRONE CATCHMENTS

and in locally acid or gleyed soils of the control catchments, than in free-draining soils. The factors that cause an increase in metal mobility probably increase availability to herbage. Thus, although the total metal content may be lower in free-draining less acid soils, metal uptake by herbage is greater. This implies that when land is improved by draining and liming, mobility and availability may both decrease. Hence, although such environmental patterns do not themselves necessarily delineate areas where herbage deficiencies occur, they indicate the presence of a significant area of leached soils which are potentially deficient when 'improved'.

CHAPTER SEVEN MICROMORPHOLOGICAL INVESTIGATIONS OF SOILS AND SEDIMENTS

7.1 INTRODUCTION

7.11 Object of investigations

Micromorphological studies of rocks, as polished blocks or thin sections, are normally considered a necessary complement to any geochemical investigation. Structure, mineralogy and chemistry contribute jointly to the solution of geological problems which frequently involve systems that are virtually inert under present conditions. In pedology, however, the tendency has been to conduct detailed chemical and mineralogical analyses with little reference to the gross characteristics observable in the field. Weathering, soil formation and erosion are active systems in which the exposed rocks are reacting to the altered conditions. The various physical and chemical transformations taking place - for example, faunal activity, diffusion, illuviation, precipitation - give rise to different structures and minerals which must by definition indicate different modes and conditions of origin. The relative importance of such processes can be deduced from the arrangement of the constituent particles. Consequently, complementary chemical and micromorphological investigations can lead to a fuller understanding of the processes involved and hence their influence on soil fertility.

In this chapter the results are presented of some micromorphological investigations of soils and sediments from the areas of contrasting secondary environment discussed in Chapter 6. The object has been to determine the inter-relationship of structure and chemistry in these contrasted soils and sediments, with particular reference to the occurrence of iron and manganese oxides. These investigations have served also to make an assessment of the applicability of micromorphological techniques to geochemical problems of this type.

7.12 Techniques of investigations

1. Optical microscopy The micromorphology of soils and sediments has been studied mainly by optical microscopy, using thin sections of undisturbed samples. Soil structure and fabric are described using classification of Brewer (1964) in which fabric is defined as the element of structure dealing with the "physical construction of the soil material as expressed by the spatial arrangement of the solid particles and associated voids". Many new terms have been coined to describe features peculiar to soils and to avoid the difficulties implied by using terms borrowed from other sources. Brewer's classification and terminology have been generally accepted, with certain modifications or extensions (for example, Bisdom 1967) and are used in the pedographic descriptions in this chapter. A glossary of terms is given in Appendix B.

2. Scanning electron microscopy Scanning electron microscopy (S.E.M.) has been used to continue micromorphological studies beyond the range of the optical microscope.

The instrument (Cambridge Stereoscan) is designed to produce a magnified image of a surface, equivalent to that of a reflected light microscope. The advantages over optical systems are:

i) the high resolving power - theoretical limit 100-200 Angstroms;
ii) a wide range of useful magnifications - 14 to 50,000 times;
iii) a large depth of focus at all magnifications, greater by a factor of 300 over optical microscopes at similar power.

Specimens up to 5 x 12 mm can be accommodated on the standard stage with no restriction of movement.

3. Electron probe micro-analysis Normal chemical analyses yield average values for bulked samples with no reference to structure. Electron probe micro-analysis, however, provides a technique by which the composition of relatively undisturbed samples can be studied at a scale comparable to that of the smallest recognisable units. Consequently, the technique is potentially useful in the assessment of the distribution of minor elements within the soil fabric.

4. Diffraction X-ray and electron diffraction techniques have been used in an attempt to estimate the mineralogy of certain ferromanganese accumulations. With specimens that appear amorphous under X-ray diffraction, the shorter wavelength and single particle observation of electron diffraction may yield a positive result.

7.2 SAMPLE COLLECTION AND PREPARATION

7.21 Sample collection

The collection and preparation techniques have been designed such that a given feature can, if necessary, be examined in successive stages from field inspection to optical or electron microscopy, from whole sample bulk analysis to individual particle electron probe micro-analysis.

Soil profiles were examined at selected sites in the catchments in Central Tyrone, as described in the previous chapter. One face of each pit was cleaned, described and photographed. Ideally, a whole soil monolith would have been collected for laboratory examination but transportation over long distances, particularly of sandy soils, is liable to cause disturbance and probable fabric distortion which, in this context, is obviously undesirable. Consequently, soils were sampled in 5 cm x 2 cm blocks, using a clean knife cut or natural surfaces as bounds, but including natural surfaces within the sample. The blocks were inserted into glass specimen tubes, labelled to note location and orientation. Particular attention was paid to sampling important features such as horizon transitions, pedotubules, etc. Stream sediments were also sampled, but, for these, structure is very difficult to retain. The tubes were capped and samples kept slightly damp to reduce disturbance during transport.

Duplicate bulked samples for chemical analysis were collected at the same time. All samples were air dried.

7.22 <u>Sample preparation</u>

7.221 <u>Optical microscopy</u> Most of the soils were impregnated with the 'Penler' styrene resin system* recommended by Jenkins

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* manufactured by Margros Ltd., Woking, Surrey

(1969 pers comm.). Certain sandy soils and stream pebbles, however, were successfully embedded using an Araldite epoxy resin system, AY 105/HY 951*. Samples were vacuum impregnated by a method similar to that described by Brewer (1964) and longitudinal thin sections cut from strain-free samples.

Neither Penler nor Araldite systems gave adequate penetration of clays. Penler resin was much better and could be improved slightly by placing the samples in a pressure vessel (3 atmospheres) at room temperature for the first 24 hours of curing.

7.222 Scanning electron microscopy The instrument functions under conditions of high vacuum, so that samples must be dried before examination. Ideally, water should be removed by a technique such as freeze drying which eliminates surface tension forces. In the present study, however, samples had to be air dried, hence artificial features caused by shrinkage under these forces were commonly observed.

Selected features were normally examined on fracture surfaces, with specimens mounted on aluminium stubs. They were vacuum coated with a thin conducting layer of gold-palladium to prevent any build up of electric charge, which would cause loss of resolution. Charging was lessened also by mounting specimens with aluminium paint as adhesive.

7.223 Electron probe micro-analysis Thin sections and blocks of resin-impregnated soils and sediments were prepared for microprobe

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* manufactured by C.I.B.A. Ltd., Duxford, Cambridge

analysis by modified petrological techniques. False concentration measurements are attributable to relief differences, hence flat polished surfaces are necessary for precise analysis. All sections prepared for optical microscopy were purposely cut slightly thicker than the normal 30 microns and mounted without a cover-slip. Features for analysis were selected by optical microscopy and the slides in question polished further in stages, with diamond paste in paraffin on nylon cloth laps (final grade 0.25 microns). Since samples were mostly required for rapid qualitative analysis only, and the instrument used (Cambridge Geoscan) has a high X-ray emergence (take off) angle which lessens relief effects, it was considered that the final polishing could be omitted, particularly for poorly impregnated samples. Specimens were vacuum coated with a conducting layer of carbon prior to analysis. Operating conditions are given in Table 7-1, below.

Instrument :	Cambridge Geoscan
X-ray emergence angle:	75°
Operating current :	20 KV
Specimen current :	0.05 - 0.10 μA
Operating modes :	
1. Rast scan	Electron beam scanned over small areas of the specimen surface to determine the distribution of selected elements. Results displayed on an oscilloscope and recorded photographically.
2. Line scan	Electron beam set to traverse distances up to 1 mm over specimen surface, variations displayed by oscilloscope and chart recorder.

TABLE 7-1 OPERATING CONDITIONS FOR ELECTRON PROBE MICRO-ANALYSIS

7.224 **Diffraction techniques** Samples were crushed, ground to below 2 microns e.s.u. and packed into cavity mounts for X-ray diffraction. Minerals were identified with a Phillips Proportional Counter X-ray Diffractometer, with wide-angle goniometer, using Co-Kα radiation.

For electron diffraction crushed samples were dispersed ultrasonically and mounted on an electron microscope grid. They were examined using a Jeol (JEM - 7) transmission electron microscope, and diffraction patterns obtained where possible from single particles.

7.3 LOW SPERRINS CATCHMENTS

Micromorphology of the soils and associated metal enriched sediments of the podzolic sequence.

7.31 Soils

7.311 **Introduction** Six profiles were examined at Slievemore and Camlough, representing the main soil types occurring in the catchments. These are peaty podzols, reclaimed podzols, peaty gleys and metal enriched bank soils. The locations of the profiles are shown on Fig: 6-4, with metal distributions illustrated on Figs: 6-6 and 6-7. The micromorphology is summarized on Tables 7-2 to 7-5.

7.312 **Parent materials** The soils at Camlough are developed on quartzose glaciofluvial sands, gravels and boulders. The sands are mostly granular, with any plasma as grain argillans (Table 7-2).

STRATIFIED MORAINE SANDS

Soil parent material at 8 metres

Slide nos. : Q/2, Q/5

Distribution : Granular, locally porphyroskelic

Skeletal grains : Quartz, with fragments of granite, Devonian sandstones and dolerite. 0.1-7.0 mm.

Plasma : Silasepic, locally insepic to skelsepic

Cutans : Free grain argillans

Iron oxide glaebules : Rare, discrete rounded bodies, 0.05 mm diameter. Probably inherited.

The sands are crossed by several semi-indurated, contorted iron pans, with Fe and Mn oxides as thick grain cutans. Oxides are X-ray amorphous, although central grey band is cleaved and apparently crystalline under S.E.M. (Fig: 7-1).

TABLE 7-2 MICROMORPHOLOGY OF SOIL PARENT MATERIAL, CAMLOUGH CO. TYRONE.

Free iron oxides occur as small, discrete glaebules (0.05 mm) and in several contorted iron pans. Some pans have a narrow (0.65 mm) central band of a steely grey mineral. Under S.E.M. this shows a platy cleavage on fracture surfaces and appears crystalline in comparison with associated encrustations of ochreous iron oxides (Fig: 7-1). The mineral resembles haematite or lepidocrocite but X-ray diffraction showed no iron oxide minerals, probably because of insufficient concentration in available samples. The iron pans, and possibly the glaebules, are postdepositional structures, but it is uncertain if they are forming under present conditions.

Unaltered parent materials were not sampled at Slievemore, but soils are developed on moraine sands and sandy tills derived from schists and gneiss. In general, the soils tend to be heavier than those at Camlough, reflecting the finer, micaceous nature of their parent materials.

7.313 Peaty podzols Camlough profile AP/2 (Table 7-3); Slievemore profile SP/2 (Table 7-5).

The soils are formed below 30-40 cm. of peat. Humified organic matter occurs in the plasma and coats skeletal grains in all horizons, although becoming less important with depth. Clays in the plasma form separations in the lower horizons, so that the soils vary from porphyroskelic at the surface to intertextic and granular in the B/C horizon. In the B horizon, the s-matrix is fragmented into rounded aggregates (0.3 mm) with a central silt granule surrounded by plasma. Thin grain and void argillans indicate that some clay illuviation has taken place.

Free iron oxides are absent from the A horizons but occur in lower horizons in oxidising minerals, ferrans and rare discrete glaebules.* Ferrans and ferri-argillans occur in the B horizon,

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* Iron oxide structures, particularly ferrans, can be difficult to identify in thin section, especially in the presence of organic matter. Any estimates of composition are made with reference to data from bulk or microprobe analysis.

being more strongly developed at Camlough than Slievemore, reflecting the stronger Fe enrichment of the former. Several iron pans up to 4 mm thick occur immediately below the peat in profile AP/2. Skeletal grains near the pan often have thick, weakly layered ferrans which coalesce in the pan itself. Ferrans around some basic fragments in the pan appear to be continuous with iron oxides derived from direct weathering of ferro-magnesian minerals. The texture suggests partial replacement of rock minerals by precipitated oxides.

The ferrans become more diffuse towards the base of the horizon, occurring mainly within 4 mm of channels and cracks. Thick, discrete grain ferrans, however, occur in the B/C horizon of both profiles (Fig: 7-2). These appear organic and accompany the Fe-Mn enrichment (Chapter 6.431). Some are darker on the outer (void) surface, but Mn was not detected by microprobe analysis.

7.314 Reclaimed podzols Camlough profile AP/2 (Table 7-3); Slievemore profile SP/2 (Table 7-5).

The soils have similar texture and fabric to the peaty podzols, but are less acid and less strongly leached. At Camlough, in particular, they are much less organic, although humic matter stains the plasma yellow-brown in the top 10-15 cm and forms thin films on grain surfaces, cracks and cleavages in most horizons. Lenticular aggregates, bonded by organic matter, occur in the topsoils at Camlough. Some are smoothed and may be faecal pellets but the remainder are probably formed by the pressure and tension effects of wetting and drying (Allison, 1968).

Free iron oxides occur within weathering rock fragments in all horizons of both profiles but form plasma separations mainly in B and B/C horizons. Thin grain ferrans and small discrete glaebules occur in the argillaceous, organic A horizon at Slievemore but are not seen in the lighter Camlough soil. In both profiles, however, the transition to the B horizon is marked by the occurrence of free grain ferrans. These tend to be dark and organic at the top of the horizon, becoming paler and diffuse with depth. At Slievemore, the iron pan has apparently formed by grain ferrans occupying packing voids and permeating and engulfing plasma. Below the pan, the oxides are weakly dispersed throughout much of the plasma, locally concentrating as neo-ferrans near interpedal voids, and giving an iron enrichment to the whole horizon.

At Camlough iron pans (1.5 mm thick) occur only beneath large boulders. Clays and silts, present in amounts similar to the parent material, are probably protected from eluviation by the boulders and provide nuclei for oxide accumulation. Elsewhere, the B horizon is granular with iron oxides only as thin, diffuse ferrans (Fig: 7-3) so that, despite the ochreous colour, there is no iron enrichment.

7.315 Peaty gleys Camlough profile AP/3 (Table 7-4).

The fabric of the waterlogged, sub-peat, mineral soils is generally similar to that of the peaty podzols. The distribution varies from porphyroskelic in the peaty upper horizons to agglomeroplasmic and granular as the plasma becomes less organic.

Free iron oxides become visible only as the pH rises from below 4.0 in the surface horizons to 5.4 below 50 cm. Their appearance corresponds to an increase in the content iron and other metals. However, the enrichment is only slight, reaching maxima of 2.15% Fe and 170 ppm Mn in iron stained sands and gravels at 80-100 cm. The oxides occur mainly as discrete ferrans, possibly organic and weakly layered, on grains and voids. Accompanying neo-ferrans can form diffuse plasma enrichments for up to 1 mm away from the walls of cracks, root channels and interpedal voids (Fig: 7-4).

7.316 <u>Metal enriched bank soils</u> Camlough profile AP/4 (Table 7-4).

The soil is a peaty gley, developed on alluvial sands, with fabric mostly obscured by the Fe-Mn oxides dispersed throughout the plasma. The oxides are also accumulated in:

i. ochreous glaebules, with a weak concentric structure shown by dark cores and/or rims.

ii. ochre and black mangani-ferrans (0.8 mm) cementing roots and grains. They tend to be ochreous against the grains, darker towards the outer surfaces. Microprobe analysis confirmed that the ferrans are iron rich throughout, becoming manganiferous where dark.

The oxide structures tend to be concentrated in the upper soil horizons, in the zone of water-table fluctuation, and are clearly formed after deposition of the alluvial sands.

PROFILE AP/1 RECLAIMED PODZOL

Very freely drained soil on moraine apex.

HORIZON	A_{1-2}	B	B/C
Depth cm	0- 30	30 - 60	60 - 100
Slide no.	1,3	5,7	8
Distribution	Agglomeroplasmic.	Granular.	Granular to intertextic.
Skeletal grains	Quartz, gabbro, granite. Fragments strongly oxidized. Sub-angular to sub-rounded. 0.2 - 7.0 mm.	Idem.	Idem 0.1 - 0.5 mm
Plasma	Silasepic.	-	Silasepic,
Organic matter	Plant fragments at surface. Humified matter bonds matrix into aggregates. These are Lenticular at surface, 3x2 cm, smaller and less organic with depth.	Thin coatings on most grains, particularly below boulders.	Thin coatings on some grains.
Cutans	Thin free grain organo-argillans at base (0.01 mm thick).	Organo-ferrans on all surfaces. Below boulder, they coalesce to give 1.5 mm iron pan. Ferrans less organic, more diffuse with depth. (Fig 7-3).	Thin, diffuse free grain ferrans.

PROFILE AP/2 PEATY PODZOLS.

Developed on steep moraine slope.

HORIZON	A_{1-2}	B	B/C
Depth cm.	20 - 25	25 - 45	45 - 70
Slides	4,5	4,5,7	9,10
Distribution	Porphyroskelic to agglomeroplasmic.	Agglomeroplasmic, but porphyroskelic in iron pans.	Agglomeroplasmic to granular.
Skeletal grains	Quartz, granite, dolerite. Sub-angular to sub-rounded.	Idem. 0.5 - 7.0 mm. Dolerite oxidizing in rims.	Idem. Less oxidized.
Plasma	Silasepic to insepic; very organic.	Iron oxide in pans, below, silasepic to insepic. Plasma in aggregates (0.25 mm) around grains.	Idem.
Organic matter	Fibrous, peaty. Humified matter coats grains.	Some roots. Humified matter as coatings on grains.	Thin coatings to grains.
Cutans	- -	- Organo-ferrans. These are weakly concentric about grains, coalescing to form 2-4 iron pans. Ferrans less organic with depth, diffuse.	Weak grain argillans. Organo-ferrans around all skeletal grains; some diffuse. Darker below 60 cm, possibly manganiferous, cementing grains. Fig 7-2.

TABLE 7 - 3 MICROMORPHOLOGY OF PEATY AND RECLAIMED PODZOLS, CAMLOUGH, CO. TYRONE.

PROFILE AP/3. PEATY GLEY.

On margin of basin bog at moraine base. Lower horizons waterlogged.

HORIZON	A_{1-2}	B/G	C
Depth cm	20 - 30	30 - 60	60 - 90
Slide no.	3,	6,7	8,10
Distribution.	Porphyroskelic to agglomeroplasmic.	Agglomeroplasmic to granular.	Idem. Locally porphyroskelic.
Skeletal grains	Quartz, granite, dolerite. Sub-rounded to sub-angular. 0.3 - 5.0	Idem.	Idem; some oxidizing.
Plasma	Silasepic; very organic	Silasepic locally insepic to skelsepic. In aggregates (0.3 mm) about grains.	Silasepic; locally insepic, mosepic and skelsepic.
Organic matter	Fibrous peat, with dark humified matter in plasma.	Some roots; many grains coated by humified matter.	Thin coatings to some grains.
Cutans	-	-	Weak grain argillans.
	-	-	Free grain ferrans; probably organic; possibly weakly layered.
		Complex ferrans and neo-ferrans to grain and void surfaces in aggregates; also along interpedal voids, cracks. Discrete against void surface, merging to diffuse plasma enrichments for up to 1 mm. Free iron oxides become more common below 70 cm.	
Iron oxide glaebules	-	Rare.	Rare, discrete; weakly concentric (0.01 mm).

PROFILE AP/4 METAL ENRICHED BANK SOIL

Developed on alluvial sands two metres from stream bank.

HORIZON	A_1	G
Depth cm	0 - 15	30 - 50
Slide no.	1	5,7
Distribution.	Porphyroskelic to agglomeroplasmic.	Granular.
Skeletal grains	Quartz; granite; dolerite. Sub-rounded 0.2 - 10.0 mm; strongly oxidizing	Idem.
Plasma	Silasepic. In rounded, weakly layered aggregates (3 - 5 mm) of organic matter and sesquioxides.	-
Cutans	Thin, grain argillans. Organo-ferrans.	Mangani-ferrans (up to 0.8 mm) on all grains and roots. Probably organic. Many darker to void surface.
Iron oxide glaebules.	Discrete ochreous bodies, in aggregates. Some have dark, probably manganiferous, rims and/or cores.	-

TABLE 7 - 4 MICROMORPHOLOGY OF A PEATY GLEY AND METAL ENRICHED BANK SOIL, CAMLOUGH, CO. TYRONE.

PROFILE SP/1 RECLAIMED PODZOL.

Developed on sandy till on the lower slopes of Slievemore.

Horizon	A_{1-2}	B	B/C
Depth cm.	10 - 30	30 - 60	60 - 80
Slide no.	3, 12.	12, 6	9
Distribution.	Porphyroskelic to egglomeroplasmic	Porphyroskelic in iron pan. Below, agglomeroplasmic to intertextic.	Agglomeroplasmic to intertextic.
Skeletal grains.	Quartz, muscovite, gneiss. 0.1 - 1.0 mm.	Idem; gneiss oxidizing.	Idem; gneiss oxidizing.
Plasma.	Insepic, omnisepic; locally skelsepic.	Asepic in pan; below, insepic, silasepic, skelsepic.	Asepic, skelsepic.
Organic matter.	Plant fragments. Plasma stained yellow by humified matter.	Humified matter as coatings to some grains. Possibly bonding matrix in aggregates.	Thin coatings to some grains.
Cutans.	Weak organo-argillans on voids.	Free grain argillans.	Argillans to interpedal voids and skeletal grains.
	Organo-ferrans on embedded grains, voids. Occasional neo-ferrans.	Ferrans, possibly organic, on voids and grains. Iron pans apparently formed by ferrans coalescing across voids. Ferrans become diffuse with depth. Neo-ferrans (0.5 mm.) enrich plasma near interpedal voids.	Diffuse grain ferrans. Neo-ferrans, with discrete boundaries, enrich plasma around voids.

PROFILE SP/2 PEATY PODZOL.

Developed on coarse sandy till on the upper slopes of Slievemore.

Horizon.	A_{1-2}	B	B/C
Depth cm.	20 - 45	45 - 80	90 - 120
Slide no.	3, 4.	6, 8.	12.
Distribution.	Porphyroskelic, locally granular.	Porphyroskelic to agglomeroplasmic or intertextic.	Granular.
Skeletal grains.	Quartz, muscovite, gneiss, granite. 0.1 - 5.0 mm.	Idem; fragments oxidizing.	Idem; 0.5 - 7.0 mm. fragments oxidizing.
Plasma	Insepic to asepic. Very organic	Silasepic to asepic. Locally skelsepic.	Idem.
Organic matter.	Fibrous peat. Humified matter as coatings to grains.	Roots. Dark coatings on some grains.	-
Cutans	-	Thin, embedded grain argillans. Embedded grain ferrans, Ferri-argillans, mostly organic, on channels and grains. Some diffuse neo-ferrans.	Thick, dark ferrans bonding skeletal grains. Probably organic, possibly manganiferous.
Iron oxide glaebules.	-	Rare, discrete bodies (0.2 mm) in matrix. Occasionally 1.0 mm enclosing grains.	

TABLE 7 - 5 MICROMORPHOLOGY OF PEATY AND RECLAIMED PODZOLS, SLIEVEMORE, CO. TYRONE

7.32 Stream sediments

Stream sediments from both catchments are mostly enriched by Fe and Mn oxide precipitation, which takes three forms.

i. Ochreous oxides These appear abruptly in stream beds, apparently where phreatic groundwater enters the stream. Sections of peat and, at Camlough, moraine sand stream bed show that there is little true sediment and that iron oxides occur in the upper layer of the substrate. They permeate 1 cm. into the bed, bonding the component particles but not altering the basic structure.

ii. Gelatinous ochreous oxides overlying black manganiferous crusts. These occur downstream and are particularly well developed on pebbles. A thin yellowish-green film covers a layer of gelatinous iron oxide ochre, 0.5 cm. thick, which blankets all active sediments. At Camlough, the sediment is coarse at the surface, with pebbles coated with a black, manganiferous precipitate 0.1-0.4 cm. thick.

Both precipitates are amorphous to electron and X-ray diffraction.

The morphology is shown clearly by S.E.M., despite damage caused by drying. The surface ochre is composed of smoothed cylindrical filaments embedded in a mucilaginous mass (Fig: 7p5). The filaments have an outer diameter of about 5 microns, with an outer wall about 1 micron thick. Drying is probably responsible for many appearing split longitudinally and fragmented such that the largest is only 75 microns in length. They show no other regular structure. The mucilaginous matrix can appear weakly platy, but this again may be caused by drying. The filaments are tentatively identified as the iron bacterium <u>Clonothrix fusca</u> (Zajic, 1969).

The underlying manganiferous crust has a distinct platy layering parallel to the pebble surface. No algal or microbial remains could be identified in this layer.

Microprobe analyses of the black crusts showed them to have a narrow Fe-rich layer adjacent to the pebble, and an outer Mn-rich layer (Fig: 7-7). Spot analysis by microprobe showed Zn to be preferentially concentrated in the manganiferous crust, but it was not possible to make a quantitive estimate of composition, even though the bulk Zn content of the crust exceeds 1,000 ppm.

Pebbles from nearby streams have black crusts, but with no outer ochreous layer. They have a variety of organisms on their surfaces but no filamentous forms. The crusts are perforated by a number of well-smoothed holes (0.7-1.25 microns diameter) of indeterminate origin.

The precipitates occasionally form small nodules (Fig: 7-6) with a black manganiferous crust around a coarser ochreous core. The structure is perforated by smoothed holes, 0.4-0.6 microns in diameter.

iii. <u>Iron oxide slimes</u> These occur in seepages at Slievemore. Under S.E.M., they are seen to be comprised of a mass of cylindrical filaments (Fig: 7-8) which have an outer diameter of 1.7-2.5 microns, an inner channel approximately 1 micron in diameter and a length exceeding 60 microns. They have two or three layers, of which the outermost is rough with the oxides sometimes showing a weak hexagonal symmetry. The filaments are associated with masses of formless iron oxide. They are very rarely branched. They differ from Clonothrix in having a smaller cross-section and a rough, rather than mucilaginous, oxide sheath.

Similar filaments occur in the seeps at Barons Court (Chapter 4-4). Metal enrichments of the sheaths was shown by analyses for Fe, Pb and Zn, using an X-ray spectrometer attached to the scanning electron microscope.

The filaments are probably the sheaths of iron bacterium Leptothrix ochraceaa,an environmental variety of Sphaerotilus natans (Pringsheim, 1949). The variety develops in media with a high ferrous ion content, continually depositing ferric oxides on the outer surface. It is considered to be the final phase in the development of the organism, almost devoid of living cells. Branching is normally prevented by the oxide sheath. Pringsheim states a diameter of 1 micron without the sheath, which is in agreement with the measured internal diameter of filaments from both Slievemore and Barons Court.

7.4 CONTROL CATCHMENTS (Micromorphology of the soils and associated sediments of the brown earth soil sequence.)

7.41 Soils

7.411 Introduction Soil profiles were examined in two control datchments, Clogherny Glebe and Mayne.

FIG. 7 -1. CONTORTED IRON PAN, CAMLOUGH MORAINE. (S.E.M.; x 30).

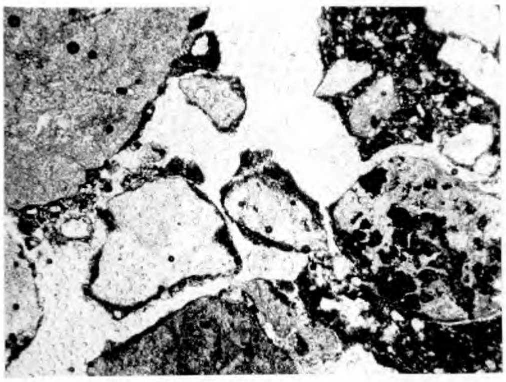


FIG. 7 - 2. DISCRETE GRAIN FERRANS, PEATY PODZOL, CAMLOUGH. Organic, possibly manganiferous, at 50 cm.; granular fabric (x 5).

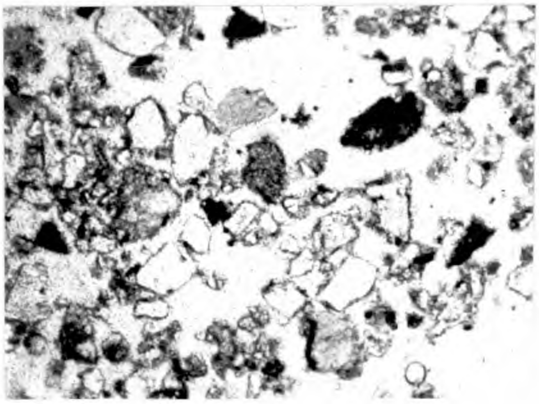


FIG.7 - 3. DIFFUSE GRAIN FERRANS, RECLAIMED PODZOL, CAMLOUGH.
B horizon; granular fabric (x 5).

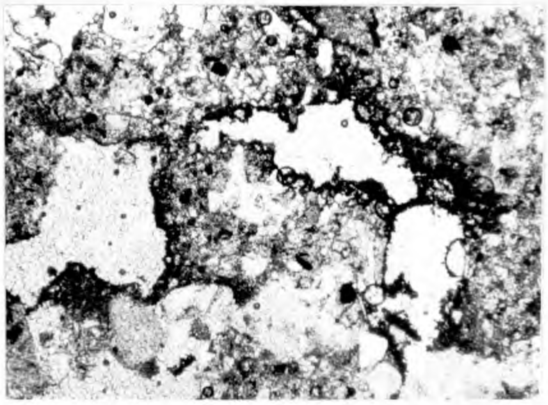


FIG..7 - 4. THIN VOID FERRANS, PEATY GLEY, CAMLOUGH.
Porphyroskelic fabric, at 80 cm. (x 5).

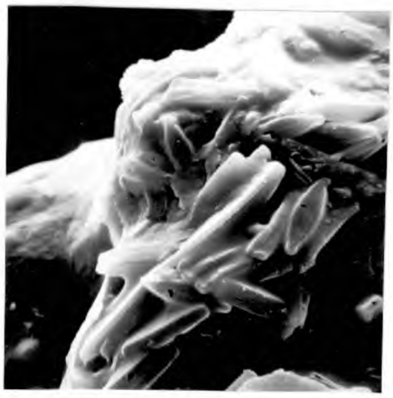


FIG.7 - 5. BACTERIAL FILAMENTS ON GELATINOUS STREAM PRECIPITATE, CAMLOUGH.
Possibly a <u>Clonothrix</u> species. (S.E.M. x 500).

FIG. 7 - 6. FERROMANGANE NODULE, SLIEVEMORE STREAM.
Fine, manganiferous rim; coarser, ochreous core. (S.E.M.x 10).

Pebble precipitate
Iron; Fe Kα

pebble precipitate
Manganese; Mn Kα

FIG. 7 - 7. DISTRIBUTION OF IRON AND MANGANESE IN STREAM PRECIPITATES CAMLOUGH.

a) Filaments probably *Leptothrix ochraceae*, encrusted by iron oxides. (S.E.M.; x 1000).

b) Single *Leptothrix* filament. (S.E.M. x 11000).

FIG. 7 - 8. BACTERIAL FILAMENTS FROM IRON SLIME SEEPAGES, SLIEVEMORE.

FIG. 7 - 9. RADIAL STRUCTURES IN AGED IRON OXIDE PEDOTUBULE, MAYNE.
Profile MP/1. (S.E.M.; x 1100).

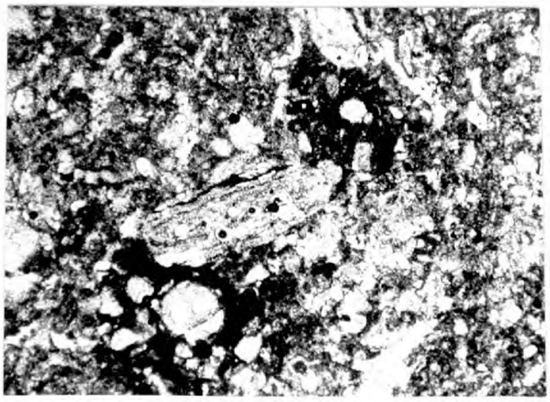


FIG. 7 - 10. ROOT MOTTLES, BROWN EARTH, MAYNE.
Ramifying boundaries, agglomeroplasmic fabric. (x 10).

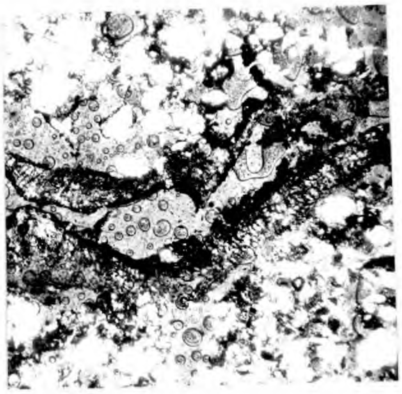


FIG. 7 - 11. ROOT CHANNEL FERRI-ARGILLAN, GLEYED BANK SOIL, CLOGHERNY.
Intertextic fabric (x Nicols; x 10).

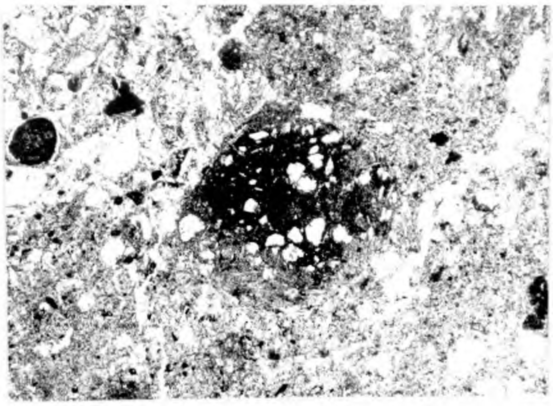
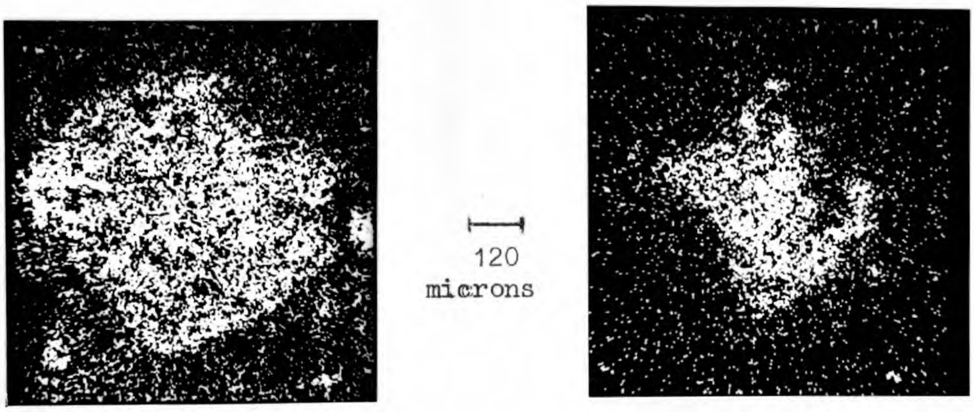


FIG. 7 - 12. WEAKLY ZONED GLAEBULE, BROWN EARTH, MAYNE.
Dark core, with engulfed skeletal grains; porphyroskelic fabric. (x 15).



Iron; Fe $K\alpha$ Manganese; Mn $K\alpha$

FIG. 7 - 13. DISTRIBUTION OF IRON AND MANGANESE IN ZONED GLAEBULE, MAYNE.

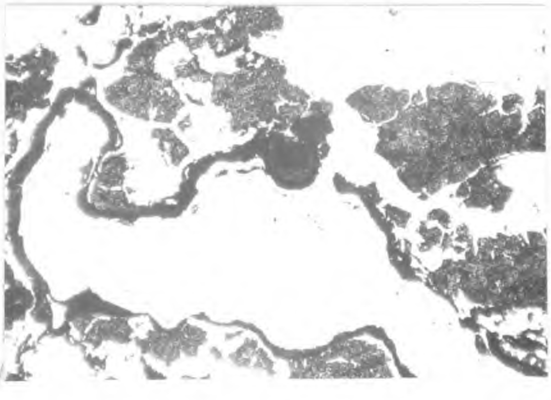


FIG. 7 - 14. VOID FERRAN, IN ENRICHED BANK SOIL, CLOGHERNY.
S-matrix stained and partially replaced by iron oxides (x 15).

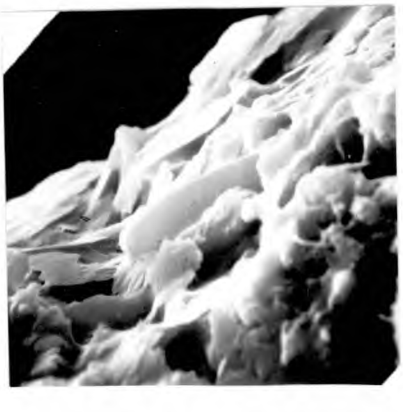


FIG. 7 - 15. PLATY SURFACE TO STREAM PRECIPITATE, CLOGHERNY. (x 1000).

i. freely drained brown earths - profiles CGP/1, MP/1.
ii. imperfectly drained brown earths - profiles CGP/2, MP/2.
iii. Fe-Mn enriched bank soil - profile CGP/3.

The locations of the profiles are shown on Fig: 6-10, with metal distributions illustrated on Figs: 6-12 to 6-14. The soil micromorphology is summarised on Tables 7-6 to 7-9.

7.412 Parent materials The soils at Clogherny are developed on moraine sands derived from Old Red Sandstones and shales. The sands are porphyroskelic with sub-angular quartz grains and rock fragments separated by narrow bands of plasma (Table 7-6). Some secondary alteration is shown by the occurrence of free iron oxides as weak, ramifying plasma enrichments and indistinct glaebules. The plasma of these sands and the soils developed from them mostly appears diffuse, amorphous and isotropic. Detail is obscured by the reddish colour of the very fine grained turgite ($Fe_2O_3 . nH_2O$) inherited from the bedrock.

Soils at Mayne are developed on boulder clays of mixed derivation and, locally, on alluvial sands. As a result they tend to be heavier and less freely drained than equivalent soils at Clogherny. There appear to be two tills in profile MP/2 (Table 7-9). In both, illuviation argillans and Fe-Mn oxide precipitates, with accompanying metal enrichment, are evidence of alteration subsequent to deposition.

7.413 Free draining acid brown earths Clogherny profile CGP/1 (Table 7-6); Mayne profile MP/1 (Table 7-8).

The soils of the two profiles are mostly light textured. The structure alters from prophyroskelic and agglomeroplasmic in the A horizons to intertextic to granular in the (B)/C horizons. The changes occur as the organic content declines and the remaining plasma forms aggregates and separations associated with the skeletal grains. Clays form argillans around the central grains and outer void surfaces of aggregates. These tend to merge with the skelsepic fabric of the plasma and in granular horizons appear as simple free grain argillans.

Voids, vughs and channels in (B) and (B)/C horizons are smoothed by argillans, indicating that some clay illuviation is taking place.

Free iron oxides are visible in weathering rock fragments and as plasma separations in all horizons. They are most prominantly developed in the mottled transition from A to (B) horizons and become less frequent down the profile as the degree of secondary alteration decreases.

Ferrans are uncommon in the A horizons; at Clogherny, for example, they occur mainly on grains in faecal pellets. In the transition to the (B) horizons, however, ferrans and neo-ferrans are common on grains, voids and root channels. At Mayne, the latter can develop into indurated pedotubules, enriched in iron (35%) and manganese (0.26%).

Root tubules of this type were examined by S.E.M. Much of the oxide has a 'honeycomb' structure, but against the inner void a distinct columnar arrangement is developed (Fig: 7-9). Fibres approximately 3 x 25 microns radiate outwards, possibly in concentric bands. This arrangement was observed in large, old tubules but not in actively growing accumulations and is probably the result of ageing and incipient crystallisation. The oxides are X-ray amorphous.

Iron oxide glaebules, varying from diffuse enrichments to discrete bodies, are common in both profiles, particularly in fine grained horizons. The more discrete bodies frequently have a weakly concentric structure, with the ochreous oxides becoming darker towards the core (cf Fig: 7-12). Microprobe analysis has shown them to be iron rich throughout, becoming manganiferous in the core (cf Fig: 7-13).

7.414 <u>Imperfectly drained soils</u> Clogherny profile CGP/2 (Table 7-7); Mayne profile MP/2 (Table 7-9).

The Clogherny soil is a groundwater gley, developed on peats and peaty sands by the stream. The Mayne soil is a surface-water gley on a hill crest, with drainage impeded by the sticky, reddish clays of the upper till.

The difference in location, parent material and drainage characteristics of the two profiles lead to differences in texture and fabric. Nevertheless, in upper horizons the forms taken by clays and iron oxides are similar. Clays, for example, occur as illuviation argillans on voids, vughs and channels in both profiles, and iron oxides are concentrated into ferrans and glaebules. At Mayne, ferrans and ferri-argillans are particularly common in the mottled transition at the top of the pink till, where iron is slightly concentrated (3.75%) relative to adjacent horizons (2.3-3.0%). At Clogherny, ferrans (0.1-0.25 mm thick) coat the walls of cracks and root channels. The outer (void) margins tend to be dark, smooth and cuspate, the inner margins light, with the oxide ramifying through the adjacent matrix. Well orientated argillans occur between the ferrans and void walls in horizontal channels (Fig: 7-11). Under S.E.M., the ferrans have a porous, honeycomb structure without apparent layering or crystallinity; the clays appear as platy crystals aligned parallel to the ferran. Microprobe analysis demonstrated the known iron and clay (aluminimum) distribution, but manganese was below detection limit.

Iron oxide glaebules are common in the fine grained soil at Mayne, but tend to be rare in the coarse peaty subsoil at Clogherny. Larger discrete forms appear to engulf or displace plasma so that only skeletal grains are visible, often concentrated in the dark, manganiferous core.

The micromorphology of these soils differs strongly in lower horizons below 40 cm. In both profiles, metals such as Co, Fe, Mn and Zn are depleted in the gleyed horizons, namely the reddish till at Mayne and peaty sands at Clogherny. At Mayne, most of the mobilised metal is probably reprecipitated with iron oxides within the profile. These form, for example, plasma enrichments, glaebules and ferrans in the oxidising environment of the underlying grey till. At Clogherny, however, all horizons below about 50 cm. are waterlogged, with few oxide accumulations. Most of the mobilised metal is lost to the groundwater and little is retained in the profile.

7.415 Metal enriched bank soils Strong enrichments of iron (35%) and manganese (0.3-0.5%) occur locally at Clogherny, where the B horizons of peaty soils are exposed on stream banks. The equivalent horizon 3 metres from the bank contains 0.17% Mn, but only 2.7% Fe. The enrichment is accompanied by a marked lateral change in the micromorphology. Skeletal grains become uncommon and are mostly small and corroded. Ochreous iron oxides permeate and replace or displace the normal soil plasma. They form concretions and layered ferrans, the latter giving a vesicular appearance to voids and channels (Fig: 7-13).

Micro-probe analysis has confirmed that black partings on glaebules and ferrans are manganiferous. S.E.M. shows that all surfaces are coated by fine oxide particles which have an angular honeycomb structure on fracture. In nodules, the oxides have a weakly platy concentric arrangement which becomes more prominant on the dark manganiferous surfaces. However, they are amorphous to X-ray diffraction.

The chemistry and micromorphology of this enriched horizon are the products of the extreme, localised concentration of secondary oxides. The fabric indicates that the skeletal grains and plasma minerals are being corroded during pedogenesis either by the Fe-Mn oxides themselves or by organic ligands released during their precipitation. Dobrovolsky (1964) has suggested that freshly precipitated Fe-Mn oxides are particularly active in such replacement reactions, which he considered to be metasomatic processes occurring at the stage of diagenesis.

7.42 Stream sediments.

Streams from the control catchments contain secondary oxide precipitates of two types. These are most strongly developed at Clogherny, indicating a greater degree of metal mobility than in the other control catchments.

i. Manganese oxides. These appear to occur exclusively on coarse sediments. At Clogherny, they coat the upper surface of each pebble as a crust up to 2 or 3 mm thick. The precipitate is mostly dark brown, grey or black, but there is always a thin ochreous layer immediately adjacent to the pebble surface. Where pebbles are shallowly embedded in fine sediments, the ochreous layer occurs without an overlying black crust.

Under S.E.M., much of the precipitate has a porous honeycomb structure - pore size 0.1 - 0.4 microns. Larger, smoothed holes up to 0.7 microns are occasionally visible. Near the upper surface, precipitates have a platy structure, orientated parallel to the pebble, which may represent either depositional layering or incipient crystallisation (Fig 7 -15).

The precipitate was amorphous to X-ray diffraction, but gave an electron diffraction pattern similar to that of goethite.

ii. Iron slime seepages. Small seeps contain numerous bacterial filaments of the type observed in similar deposits at Slievemore and Barons Court.

PROFILE CGP/1 ACID BROWN EARTH

Free draining, developed on moraine slope.

HORIZON	A_{1-2}	(B)	(B)/C
Depth cm.	0 - 30	30 - 75	75 - 120
Slide No.	1,3,4	5,9	13
Distribution.	Agglomeroplasmic to intertextic locally porphyroskelic.	Agglomeroplasmic to intertextic, granular,	Granular, locally intertextic.
Skeletal grains	Quartz; O.R.S. fragments. 0.1 - 0.7 mm. Oxidized.	Idem; oxidized	Idem; 0.2 - 7.0 mm. oxidized.
Plasma	Insepic to skelsepic. Organic matter and clays aggregated about grains.	Insepic, to skelsepic in aggregates. Detail obscured by reddish amorphous turgite.	Idem.
Organic matter.	Plant remains in surface; humified matter in plasma obscures clays, especially near ped margins. Shows weak flow structure.	-	-
Cutans	Argillans weak on void walls, strong on embedded grains.	Argillans on central grains and outer surface of aggregates. These merge to single free grain argillan where soil granular.	Grain argillans.
	Thin grain ferrans in some aggregates. Neo-ferrans and plasma enrichments along channels.	Neo-ferrans enrich plasma of some aggregates.	Neo-ferrans around grains can merge to give ramifying plasma enrichments.
Iron oxide glaebules.	Diffuse, rounded enrichment (2mm), some discrete (0.3 mm)	Rare, discrete (0.05 - 0.2 mm).	Discrete glaebules (0.1 mm) Larger diffuse forms merge with neo-ferrans.

Miscellaneous. Faecal pellets occur as smoothed globular or elongate bodies (2-4 mm) in upper 30 cms. Single or in groups. Iron rich, humic plasma encloses skeletal grains with thin ferrans. Grey and grey brown glaebules of uncertain composition are found enclosing grains in most horizons.

MORAINE SANDS.

Soil parent material derived from Old Red Sandstones.

Slides	CGP/1/16; CGP/2/11; CGP/3/26.
Distribution	Porphyroskelic.
Skeletal grains	Quartz; O.R.S. shales; Dalradian schist. Sub-angular to sub-rounded.
Plasma	Amorphous, reddened by turgite ($Fe_2O_3 . nH_2O$) of bedrock. Mostly isotropic under crossed nicols; locally weakly skelsepic.
Cutans	Thin grain argillans, merging with skelsepic fabric.
Iron oxide glaebules.	Ramifying diffuse plasma enrichments and indistinct bodies (0.1 mm) darker about central foci.

TABLE 7 - 6 MICROMORPHOLOGY OF AN ACID BROWN EARTH AND MORAINE SANDS, CLOGHERNY GLEBE, CO. TYRONE.

PROFILE CGP/2. IMPERFECTLY DRAINED BROWN EARTH.

Groundwater gley near stream bank; developed on alluvial sands and thin peats.

Horizon	A	A/G Alluvial sands.	G Mineral horizon in peat
Depth cm.	0 - 25	25 - 40	40 - 75
Slide no.	2,4	13	6,8
Distribution.	Porphyroskelic to agglomeroplasmic.	Agglomeroplasmic intertextic, locally granular.	Granular, locally intertextic.
Skeletal grains.	Quartz, shale. Sub-rounded, 0.1 - 0.5 mm. Oxidized.	Idem. Some oxidized.	Idem. 0.3 - 0.6 mm. Unoxidized.
Plasma	Insepic to weakly skelsepic. Often obscured by amorphous organic matter and turgite.	Insepic; skelsepic in aggregates; vosepic near channels.	Organic, locally silasepic.
Organic matter.	Humified; stains plasma dark brown.	In plasma and as coatings to some grains.	Peaty; some fibrous humified matter as dark coatings to grains.
Cutans.	Thin grain and void argillans associated with aggregates.	Rare argillans.	-
	Ferrans strongly developed along root channels; 0.1 - 0.25 mm thick. Void walls smooth, cuspate; inner walls ramify through matrix; diffuse against plasma.		Ferrans along vertical and horizontal cracks and channels. Illuviation argillans occur between ferrans and walls of horizontal cracks.
Iron oxide glaebules.	Discrete glaebules (0.1 mm) in fabric; more numerous and merging within 0.5 mm of root channels. Some larger, 2.5 - 4.0 mm. Diffuse plasma enrichments near roots.		

PROFILE CGP/3. BANK SOIL. Downslope from raised bog.

Micromorphology of metal enriched B horizon.

Distance from exposed bank surface cm.	200 Unenriched soil	20 Transition zone	20 Enriched soil
Slide no.	15	7	5, 7
Distribution.	Porphyroskelic	Agglomeroplasmic	Porphyroskelic
Skeletal grains.	Quartz; oxidized shale 0.1 - 1.0.	Quartz; grains are rounded and appear corroded.	Quartz; rare; appear corroded.
Plasma	Weakly masepic, locally skelsepic; often amorphous, grey	Weakly skelsepic; amorphous, containing diffuse iron oxides.	Mosaic of fine ochreous iron oxides.
Iron oxide glaebules.	Diffuse enrichments around grains, channels abd in textural banding; locally more discrete, with ramifying outer boundaries.		Spherical concretions; up to 4.0 mm. Thin black Mn-rich coatings on partings. Some glaebules have a core of fine unaltered matrix.
Cutans	Grain and channel void argillans.	Ferri-argillans on skeletal grains.	-
	Ferrans on packing voids and vughs, Neo-ferrans enrich adjacent plasma.	Neo-ferrans merge with oxide enrichment throughout plasma.	Dark ferrans give vesicular appearance to voids, channels. Some layered with pale oxides 0.1 mm thick, with radiate structure. Fig 7-14

TABLE 7 - 7 MICROMORPHOLOGY OF AN IMPERFECTLY DRAINED BROWN EARTH AND METAL ENRICHED BANK SOIL. CLOGHERNY GLEBE, CO. TYRONE.

PROFILE MP/1. ACID BROWN EARTH.

Developed on free draining alluvial sands.

Horizon	A	(B)	C
Depth cm.	0 - 30	30 - 50	50 - 75
Slide no.	2	5,16	6,9
Distribution.	Porphyroskelic to agglomeroplasmic.	Idem.	Porphyroskelic to granular.
Skeletal grains.	Quartz, muscovite, schist. To 1.0 cm diameter. Oxidized. Some charcoal.	Idem.	Idem.
Plasma	Skelsepic, omnisepic, vosepic. Plasma forms aggregates about skeletal grains.	Lattisepic, vosepic, skelsepic. Some aggregates formation.	Omnisepic, lattisepic.
Organic matter.	Plant fragments; humified matter bonds matrix aggregates.	Some humified matter in plasma of aggregates	-
Cutans	Argillans around grains, aggregates, glaebules; weak along voids.	Idem.	Argillans smooth voids, vughs.
	Rare grain and void ferrans.	Neo-ferrans and ferrans commonly along voids, root channels (Fig. 7-10). Some develop into pedotubules up to 1.5 cm diameter (Fig 7-11). Mostly with sharp, ramifying boundaries.	Weak ferrans and neo-ferrans associated with cracks and vughs.
Iron oxide glaebules.	Discrete 0.1 - 1.5 mm. Enclosing skeletal grains. Weak concentricity, with dark Mn rich core. (cf. Figs 7-12,13).	Idem. Some with outer diffuse haloes.	Idem. 0.1 - 0.6 mm some with diffuse haloes. Often associated with diffuse plasma enrichments.

TABLE 7 - 8 MICROMORPHOLOGY OF A FREE DRAINING ACID BROWN EARTH, MAYNE, CO. TYRONE.

PROFILE MB/2 ACID BROWN EARTH

Surface water gley, drainage impeded by reddish-pink clays below 65 cm.

HORIZON	A	(B) Reddish-pink clays.*	C. Stony, grey clays.
Depth cm.	0 - 35	35 - 65	65 - 90
Slide no.	2,3,5	7,9	12
Distribution.	Porphyroskelic	Porphyroskelic, locally intertextic.	Porphyroskelic.
Skeletal grains.	Quartz, muscovite; schist oxidizing. Charcoal. 0.1 - 8.0 mm.	Quartz, muscovite; oxidizing. 0.1 - 1.0 mm	Quartz; volcanics; oxidizing. 0.1 - 5.0 mm.
Plasma	Insepic at surface. Omnisepic at base. Plasma often dark, amorphous.	Insepic to omnisepic; locally vosepic; silasepic. Plasma amorphous, reddened by turgite.	Omnisepic, locally vosepic, skelsepic.
Organic matter.	Some plant remains; dark, humified matter intimately mixed in plasma especially near surface.	Some humified matter in plasma at top of horizon.	-
Cutans	Thin argillans on ortho-vughs, channels and grains.	Argillans and ferri-argillans on vughs and cracks, especially at base of horizon.	Strong void and grain argillans. Latter can merge with skelsepic fabric.
	Rare grain and void ferrans.	Neo-ferrans around some voids.	Many dark void ferrans, with neo-ferrans enriching plasma of walls. Possibly manganiferous.
Iron oxide glaebules.	Round, discrete bodies 1.15 - 1.0 mm. Enclosed grains are concentrated in centre. Core often dark, manganiferous, (Fig 7-12,13) Boundaries discrete, ramifying or diffuse. Plasma enrichments to 1mm, strongly developed at base of horizon.	Discrete and diffuse bodies, weakly concentric, engulfing plasma and skeletal grains. Diffuse plasma enrichments throughout horizon. Iron oxides concentrated at top, in mottled (B) horizons,	Irregular, discrete, bodies up to 2 mm, with dark core. Large (5 mm) diffuse enrichments

* It was not possible to obtain satisfactory impregnations of dense, gleyed clays below 40 cm. Consequently, the horizon description is incomplete.

TABLE 7 - 9. MICROMORPHOLOGY OF AN IMPERFECTLY DRAINED BROWN EARTH, MAYNE, CO. TYRONE.

7.5 COMPARISON AND INTERPRETATION OF THE MICROMORPHOLOGY OF SOILS AND SEDIMENTS FROM THE CONTRASTING ENVIRONMENTS

7.51 Soil organic matter

The podzolic soils of the Low Sperrins, even where reclaimed, are more organic than the brown earths of the control catchments. In the Low Sperrins, organic matter is broken down slowly, with the accumulation of more humus and development of peats which maintain acid, leaching soil conditions. Mobile constituents of the organic matter are deposited as illuviation cutans throughout the profile, occasionally forming distinct horizons and are possibly carried into the streams. They penetrate cracks and fractures in minerals, producing potentially acidic, leaching micro-environments and possibly providing a substrate for micro-organisms capable of degrading minerals. In the control catchments, there is greater biological activity and organic matter is broken down more rapidly than in the Low Sperrins soils. Consequently, humus and peat accumulation is less common in these soils, in which less metal depletion takes place. Nevertheless, where peats do occur they are associated with the same mobilisation phenomena as in the Low Sperrins. It is uncertain, however, if the acid conditions which lead to metal depletion are the result of low biological activity and peat development. Peat formation and high metal mobility, for instance, may be independent responses to soil acidity, both retarded when pH is raised by liming. The possible role of humic compounds in metal mobilisation is discussed in Chapter 8-3.

7.52 Soil texture and fabric

The soils from the contrasted environments show some general differences in texture and fabric, mostly related to differences in the parent materials. Thus, soils in the Low Sperrins, derived mainly from coarse moraine sands, are light textured, tending to be intertextic or granular, with a silasepic fabric. Soils in the control catchments, derived from fine moraine sands and boulder clays, are heavier, often porphoroskelic or agglomeroplasmic, with a variety of sepic fabrics.

These differences, however, are not pronounced. With the exception of those on boulder clays at Mayne, soils from both environments vary from agglomeroplasmic at the surface to intertextic or granular in lower horizons. Changes often correspond to the decline of organic matter down profile and to a tendency for any plasma - organic matter, clays, sesquioxides - to separate into aggregates about skeletal grains or to leave the solum entirely. In A horizons, the aggregates are large (1-3 mm) and similar to welded faecal pellets, so that some may be of biological origin. In B and B/C horizons, however, they are smaller (< 1.0 mm) and probably result from reorientation within the horizon induced by the pressure and tension effects of wetting and drying (Allison, 1968). The translocation and loss of clays from the soils, however, does not appear to have been strong, although some illuviation argillans occur in the lower horizons of most profiles.

Stresses from compaction and wetting and drying also lead to the development of sepic plasma fabrics, with striations forming perpendicular to the major stress directions. The orientations of the striations can vary locally, where there are surfaces against which pressure can be exerted. Thus, fabrics can become skelsepic or vosepic near skeletal grains or voids respectively. In some cases, the striations can merge into argillans against such a surface, as a reaction to continuing stress.

Soil texture and fabric appear to have some significance in controlling metal translocation in the four catchments studied. Acid leaching and Fe-Mn oxide precipitation in streams are greatest in the Low Sperrins, least at Mayne and intermediate at Clogherny. The decrease in metal mobility corresponds to a change from coarse, mostly granular soils at Camlough and Slievemore, to rather finer and more densely packed soils at Clogherny and, particularly, Mayne. Although mobilisation occurs in dense, gleyed horizons of heavy soils, it is strongest in light textured soils. These have a lower exchange capacity and, with a high porosity increasing groundwater flow, a lower resistance to acid leaching than heavy soils. Furthermore, iron oxides appear to require a fine s-matrix for nucleation and accumulation, so that their retention is restricted in coarse soils, even where physico-chemical conditions favour precipitation.

7.53 Soil iron oxides

Iron oxides are visible in soils as ochreous precipitates in weathering minerals and as ferrans and glaebules. Their appearance corresponds to variations in the content of iron and other metals in soil profiles. They are most prominant in less acid, oxidized horizons in which metal enrichment is taking place.

i. Oxides in weathering minerals These occur in all horizons of reclaimed podzols and freely drained brown earths, but are most common in the B horizons. They are absent or rare in acidic or waterlogged horizons of peaty soils and imperfectly drained brown earths. Their appearance, therefore, is restricted to horizons in which mineral degradation is taking place, but in which ferric oxides are stable in the vicinity of the mineral. Where oxides are not stable, however, the released metal remains mobile and will precipitate elsewhere.

ii. Ferrans In all soils investigated, iron and the associated metals have precipitated on or near surfaces in a number of apparently distinct types of ferran, which probably have different compositions and modes of origin. They are the most important form of iron oxide separation in the soils of the Low Sperrins.

a) Ochre ferrans and darker organo-ferrans These are found on embedded grains in A horizons of reclaimed podzols. In brown earths, they also form against voids and channels, mainly in organic, imperfectly drained horizons. Associated neo-ferrans can form diffuse enrichments in surrounding plasma. Ferrans of this type can occur in apparently depleted horizons, where some of the mobilised metal has reprecipitated near channels. The leached metals are either deposited as illuviation ferrans in lower horizons or lost from the profile entirely.

b) Yellow, diffuse ferrans These are found in the B horizons of peaty and reclaimed podzols. They are possibly associated with other plasma constituents in thin aggregates or illuviation cutans around grains, particularly at Slievemore. Ferrans of this type were not recognised in the control soils but some neo-ferrans may have the oxide in a similar form, concentrated in the plasma, yet associated with a void or grain surface.

c) Dark ochre, organic mangani-ferrans These are formed around grains and voids in some bank soils and in lower horizons of peaty podzols and gleys in the Low Sperrins, accompanying Fe-Mn enrichment. The organic matter in the precipitates is presumably derived from the peats and may be involved in the translocation of the metals. Similar precipitates, however, are seen in the lower horizons of an imperfectly drained brown earth (profile MP/2, Table 7-9). These do not appear organic, suggesting either that humic matter is not essential in the formation of ferrans of this type or that a different dispersion mechanism is involved.

Ferrans of type (a) resemble the diffusion ferrans and those of types (b) and (c), the illuviation ferrans defined by Brewer (1964).

The location of diffusion ferrans suggests a local origin. The metals have been mobilised in restricted reducing or acidic environments - for example, in moisture-retaining, organic plasma - and partially redeposited in more oxidizing conditions near and against voids and skeletal grains. They are probably initiated as diffuse plasma enrichments, such as neo-ferrans, which grow into discrete forms as the oxides.

coalesce and engulf plasma. In extreme cases, they can develop into root mottles and indurated cylindrical bodies composed of a dense central area about a void and a widening halo of oxides dispersed in the plasma (Fig: 7-10).

Some root mottles, however, can enclose well-orientated illuviation argillans (Fig: 7-11). The clays are derived from overlying horizons and the iron oxides may have a similar origin. The metal in these and other illuviation ferrans are mobilised under more acid or reducing conditions than associated with diffusion ferrans, and are possibly in more stable chemical states. They are precipitated on channel walls in less acid horizons or during periods of aeration, possibly penetrating the s-matrix as ramifying or diffuse concentrations.

iii. Iron oxide glaebules One of the most important micromorphological differences between the contrasted soils is shown by the distribution of iron oxide glaebules. They are rare in the Low Sperrins, occurring only as small (0.01 mm), probably inherited, discrete forms and as occasional diffuse enrichments at Slievemore. Dark, organic, manganiferous concretions are also found in enriched bank soils.

In the brown earths of the control catchments, however, glaebules are common as:

a) discrete, rounded bodies (0.01-5.00 mm). Larger forms are weakly concentric, with a manganiferous core.

b) discrete bodies, with a diffuse plasma enrichment forming an outer halo.

c) diffuse plasma enrichments, up to 5 mm across.

Their formation and growth is probably dependent upon the presence of a fine, argillaceous substrate. There is an initial nucleation as a plasma enrichment, with further accretion forming a dense, discrete body. The possible mechanisms by which manganese is concentrated in the core of many glaebules are discussed in Chapter 8.34

7.54 Stream precipitates

Although the study areas were selected on the basis of their contrasting metal contents (Chapter 6-1), streams in both areas have layered Fe-Mn oxide crusts on pebbles. However, the crusts from the enriched Low Sperrins streams are thicker, more abundant, more organic and have more Fe (35%) and less Mn (7%) than those from the control streams (17% Fe, 20% Mn Chapter 6.6). A major difference is the occurrence of a ferruginous gel over crusts in the Low Sperrins streams.

The Fe-Mn layering of the crusts indicates chemical partition, more probably via selective precipitation than selective solution. The ferrous ion is more readily oxidized than the manganous ion and precipitates first when the metals occur together (Krauskopf, 1957). The ferruginous gel may represent the initial stages of a second precipitation cycle, but this seems unlikely as it appears to be present throughout the year in the Low Sperrins streams but was never seen in the controls. It is possibly associated with increased mobilisation given to the metals, mainly Fe, by humic compounds derived from the peats, with oxidation . and precipitation catalysed by iron bacteria.

Iron bacteria, of a different type to those in the streams, occur in iron slime seepages in both areas.

7.55 Metal migration in the soil sequences

The processes of metal depletion and enrichment in the soil profiles and sequences are shown by corresponding changes in the micromorphology. In the Low Sperrins, depleted horizons are mostly peaty or stained by organic matter, with free iron oxides rare or absent. The thin ferrans in the podzolic B horizons demonstrate the deposition of iron and other metals in an oxidising environment. In reclaimed podzols, precipitation is probably complete in this horizon. However, the occurrence of organic, probably manganiferous ferrans in deep horizons of peaty podzols suggests that greater metal mobilisation is taking place in these soils, possibly associated with humic compounds derived from the peats. Some metal is probably lost from the profile and deposited either elsewhere in the sequence, for example as ferrans in deep horizons of peaty gleys, and mangani-ferrans and glaebules in bank soils, or as precipitates in the stream channel.

The occurrence of free iron oxides in most horizons of the freely drained brown earths of the control catchments indicates that they are much less strongly leached than the podzolic soils of the Low Sperrins. There is little depletion or profile differentiation and any metal mobilisation has resulted in a redistribution within the s-matrix, with the iron oxides and associated metals in ferrans, glaebules and plasma enrichments. The presence of these secondary oxide accumulations probably accounts for the high proportion of easily reducible to total Mn in these soils. This fraction is considered to represent active precipitation (Chapter 6.6) and it is suggested that the high values refer to a continuing process of solution and reprecipitation of free oxides.

Strong mobilisation is associated with gleying. Some metal is precipitated in cutans along periodically oxidised channels, but most is either deposited in adjacent horizons or lost from the profile entirely, possibly to enter the stream channel. Strong mobilisation also occurs locally in these catchments, near peats. At Clogherny, most of the metal precipitates in the bank, replacing the other soil constituents.

The observed differences in the morphology of the soils and sediments from the contrasted areas are the result of the varied reactions of soil parent materials to differing natural and modified secondary environments during pedogenesis. The nature of the physical and chemical reactions involved, reflected in the patterns shown by the sediment reconnaissance survey, are discussed in the following chapter.

7.6 ASSESSMENT OF MICROMORPHOLOGICAL TECHNIQUES

The present studies have shown that micromorphological and related techniques can demonstrate the physical and chemical rearrangements taking place during pedogenesis. The local concentration of elements within particular pedological features, for example, could be of importance in understanding their mode of dispersion and influence on soil fertility and lead to a fuller understanding of data obtained from the estimation of bulk properties.

Optical microscopy was found suitable for the study of basic structure and fabric and could show the distribution of free iron oxides, clays and some mobile constituents of organic matter. Contrasts in the secondary environment, initially located by stream sediment reconnaissance, have been related to differences in the occurrence of iron oxides in soils and sediments. The morphology of these accumulations suggests differences in modes of origin and chemical structure. In some instances, chemical partition has been shown by microprobe analysis.

Optical studies were limited, however, by the poor depth of field, poor resolution of plasma minerals, and difficulties of identification in the presence of highly coloured substances. This was partly overcome using S.E.M., which could, for example, show the relief and structure of various features, indicate incipient crystallisation in 'amorphous' oxides and be used to locate and identify bacteria associated with chemical transformations.

The studies show that the root environment, which is important in determining nutrient availability, is often dominated by the occurrence of channel cutans and local enrichment phenomena. The physical and chemical properties of the components of such features are minor in comparison with the properties of the s-matrix as a whole, but of more immediate importance to plant nutrition. The relationship of many bulk properties - mineralogy, chemical availability, etc. - to those of the root environment is not generally known, but the combination of optical and scanning electron microscopy with electron probe micro-analysis is a powerful technique for solving problems of this type. The potential is being recognised by many pedologists (for example, Brewer, 1964; Qureshi et al, 1968; Cescas et al, 1968).

In general, the sample preparation techniques employed have been satisfactory. It is obvious, however, that the changes caused by shrinkage during drying can be severe and that results could be improved by freeze-drying prior to impregnation or to observation by S.E.M. The latter shows that drying can cause cracking, fabric distortion and even curling of clay minerals.

The use of normal thin sections for microprobe analysis is more versatile than removal of a feature from the soil prior to impregnation (Cescas et al, 1968), since this is impractical for the examination of most pedological features and requires the destruction of the soil fabric to which the analysis is being related. Similarly, the method is more satisfactory than the preparation of near duplicate surfaces on slides and polished blocks (Rutherford, 1969). Whilst it is possible to obtain qualitative results from poorly polished surfaces, polishing is necessary for quantitative work or for the detection of elements present in low concentrations. Microprobe analysis is unsuitable for the detection of elements in trace amounts, unless they are highly concentrated at the micron level of observation. In Central Tyrone, even Mn was rarely sufficiently concentrated to be detected.

Samples for the combined S.E.M. and microprobe systems require no further preparation than for normal S.E.M. techniques (Sutfin and

Ogilvie, 1970), so that morphological studies can be complemented with immediate qualitative analysis. Sample polishing is unnecessary but the preparation of a suitable fracture surface can present problems. Fractures will occur along, rather than across, natural planes of weakness such as fabric orientations and cutans, tending to provide faces of nearly constant composition rather than the more useful transverse sections.

CHAPTER EIGHT MECHANISMS OF METAL TRANSLOCATION IN THE SOIL-SEDIMENT SYSTEM

8.1 INTRODUCTION

The preceding chapters have been concerned with various aspects of the regional geochemical survey of the Tyrone area. It has been shown that in certain instances the stream sediment composition is not representative of the mean composition of soil and bedrock upstream. Where this occurs, the discrepancy is due to the influence of local environmental conditions.

The dominant environmental influence has been on the rate of chemical weathering. The coincident patterns of raised levels of Mn, Fe, Co and Zn in stream sediments have been shown to be the result of extensive soil leaching, with reconcentration in the stream bed. The areas in which such enrichment is common are characterised by the development of peaty podzols and gleys. In surrounding areas, where precipitation is lighter and no enrichment occurs, the soils are predominantly acid brown earths.

The topographic environment has influenced copper patterns by controlling stream velocity and the sorting of sediments. Copper is preferentially concentrated in fine, organic muds, the only sediment available in many slow flowing streams in low relief areas. In these areas, therefore, spurious patterns of raised Cu content can result from the collection of organic muds instead of the normal, active sediment.

In this chapter, the mechanisms of physical and chemical dispersion of Fe, Mn, Co, Cu and Zn are discussed to determine the probable processes operating under varying environments in the Tyrone area. The metals have similar structural properties and, in general, exhibit similar behaviour during geochemical dispersion. Since the formation of enriched sediments is closely linked to the processes of podzolisation and gleization, particular reference is paid to the theories concerning metal migration and precipitation during pedogenesis.

8.2 NATURE OF IRON, MANGANESE AND ASSOCIATED METALS IN SOILS AND SEDIMENTS

Fe, Mn, Co, Cu and Zn occur in soils:

i) as primary minerals whose nature depends upon the soil parent material;

ii) as secondary minerals, formed during the current cycle of weathering and pedogenesis.

iii) adsorbed to soil minerals, especially hydrous oxides; and

iv) adsorbed to or complexed with organic matter.

Because of their chemical similarity, these metals tend to occur together. Their common primary and secondary minerals are shown on Table 8-1. Many of the minerals listed as secondary may be primary in some soils, having been inherited from the parent material or fossil soils.

In the Tyrone area, no specific secondary oxide minerals were identified in soils, although goethite was tentatively identified

	IRON	MANGANESE	COBALT, COPPER, ZINC
PRIMARY	Sulphides: chalcopyrite, pyrite, pyrrhotite. Ferromagnesian minerals (amphiboles, pyroxenes, olivine). Biotite. Oxides: haematite, ilmenite, magnetite. Turgite: (Fe_2O_3. H_2O) in soils over Old Red Sandstone.	Essential only in less common igneous minerals. Mn^{2+} replaces Fe^{2+} in ferromagnesian silicates. Common in metamorphic rocks in almandine garnet, biotite, muscovite. (Goldschmidt, 1954).	Common in all sulphides, particularly cobaltite, chalcopyrite, sphalerite, pyrite. Minor in common minerals, replacing Fe^{2+} and Mg^{2+} in ferromagnesian silicates, especially in absence of sulphide phase. (Goldschmidt, 1954). Associated with inherited Fe, Mn oxides.
SECONDARY	Essential in hydromicas: chlorite, nontronite. Adsorbed as oxide to clays and often substituting in illite, montmorillonite etc. Common as oxides, often amorphous as hydrous ferric oxides $Fe(OH)_3H_2O$ and Fe_2O_3. nH_2O Crystalline as haematite, $-Fe_2O_3$ goethite, -FeO.OH; lepidocrocite, -FeO.OH Limonite: fine goethite plus water. (Oades 1963). Oxides are adsorbed to organic matter; disseminated in s-matrix; or forming glaebules, ferrans etc.	Occurring mainly as non-stoichiometric oxides, varying $MnO_{1.2}$ to $MnO_{2.0}$ including:- Lithiophorite $Li_2Al_8(Mn^{2+},Co,Ni)_2Mn^{4+}_{10}O_{35}.14H_2O$ Birnessite $(Ca,Mn,Na_2K_2)_x Mn^{4+}M^{2+}(O,OH)_2$ Hollandite Ba $(Mn^{4+}, Fe^{3+})_8 O_{16}$ Todokorite $(Mn^{2+},Mg,Ca).Mn_6O_{13}.3\text{-}4H_2O$ Pyrolusite MnO_2. (Taylor et al, 1964). Important feature is high content of adsorbed metals. Also precipitates as mixed oxides with Fe, such as bixbyite $(Mn, Fe)_2O_3$; Fe (III) manganites.	Adsorbed to clays and incorporated in clay lattices. More importantly adsorbed to Mn oxides:- <u>Cobalt</u>. Co^{2+} oxidizes and replaces Mn^{3+} in Mn oxide lattices (McKenzie, 1970). <u>Zinc</u>. In lithiophorite or sorbed to hydrous Fe and Al oxides via adsorbed polyvalent phosphate ions; sorbed directly to goethite and lepidocrocite in absence of phosphate (Stanton and Burger 1967). <u>Copper</u>. Sorbed by Fe and Mn oxides in near neutral to alkaline environment. Most strongly bound to organic matter; metal forms strong complexes with organic ligands.

TABLE 8 - 1 PRINCIPAL PRIMARY AND SECONDARY MINERALS OF IRON, MANGANESE, COBALT, COPPER AND ZINC FOUND IN SOILS.

in stream precipitates at Clogherny. In general, the oxides appeared amorphous, forming distinct structures in both soils and sediments, as described in Chapter 7.

8.3 CHEMICAL TRANSLOCATION

8.31 Weathering

Most primary minerals in soils, formed under igneous, metamorphic or sedimentary conditions, are thermodynamically unstable in the surface environment. On exposure to the atmosphere they are attacked and dissolved by water, oxygen or carbon dioxide entering through pores, cleavages and microcracks. The surface of minerals have ions and atoms with unsaturated valencies which can attract and polarize water dipoles. The cations attract hydroxyl ions and the anions, hydrogen ions. Owing to their small size and high charge/density ratio, hydrogen ions can penetrate and disrupt the crystal lattice, ultimately replacing cations. Different cations tend to react at different rates to such replacement, but in general, those with similar chemical affinities, such as Fe, Mn and associated elements, will behave similarly. The rate at which minerals are broken down is accelerated by the presence of carbonic acid and a supply of organic acids derived from decaying organic matter or liberated as metabolic products of micro-organisms.

Once released from the primary lattice, the subsequent migration of a given cation will depend upon its immediate physico-chemical environment and other chemical species present.

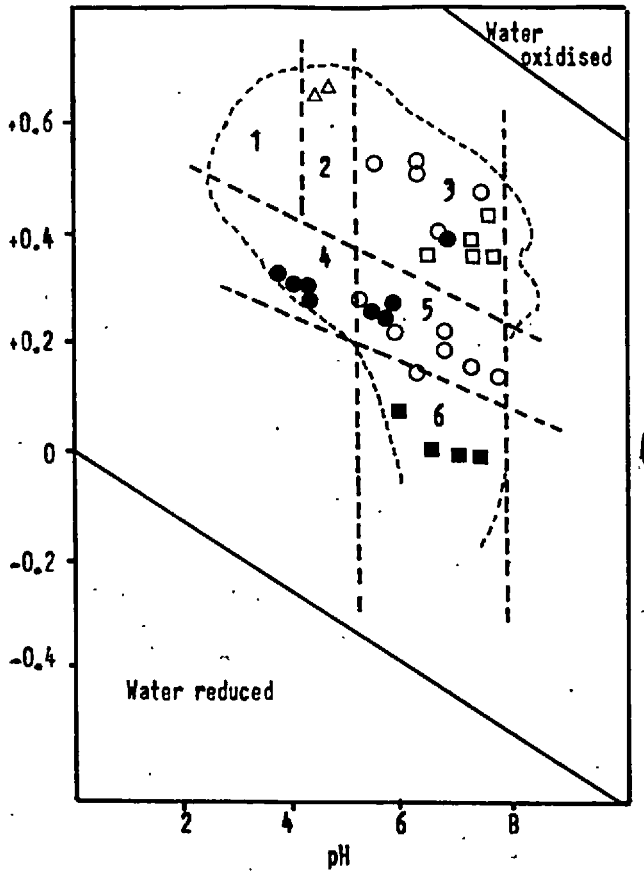
8.32 The physico-chemical environment

8.321 Definition The physico-chemical environment determines the oxidisation state and chemical association of a cation in a system of given chemical composition. In surface waters, it is defined by temperature, pressure, hydrogen ion concentration (pH) and redox potential (Eh). In the aqueous weathering system, pressure and temperature variations are of minor importance, so that the chemical dispersion of a cation during pedogenesis is largely controlled by the prevailing Eh and pH.

Eh and pH measurements, however, may obscure strong contrasts between adjacent micro-environments, particularly in water unsaturated soils. For example, a grain surface against a void may be in an oxidizing environment, but a similar surface in the same soil may be against a root, in an acid or reducing environment. The measured Eh and pH, even if constant and reproducible, are at best only averages of such contrasts and in consequence cannot be used as full descriptions of the physico-chemical environment.

8.322 Eh and pH of natural environments All available Eh and pH values for natural environments have been accumulated by Baas Becking and co-workers (1960) and Garrels and Christ (1965). These indicate that for soils and sediments in the Tyrone area the approximate maximum ranges would be: Eh -0.10 to +0.60 volts, pH 3.5 to 8.0. The accumulated results are reproduced in Fig: 8-1a, upon which the few results from Central Tyrone have been superimposed. They are grouped as follows:

i. The values for stream waters (Eh 0.35 to 0.45; pH 5.5 to 7.5) are very close to the values given by Baas Becking and co-workers



a. Eh and pH of natural aqueous environments.

1. Leached soils.
2. Iron rich soils.
3. Normal soils; stream waters.
4. Acid soils.
5. Wet soils.
6. Waterlogged soils.

(After Baas Becking et al 1960).

△ Iron enriched soil.

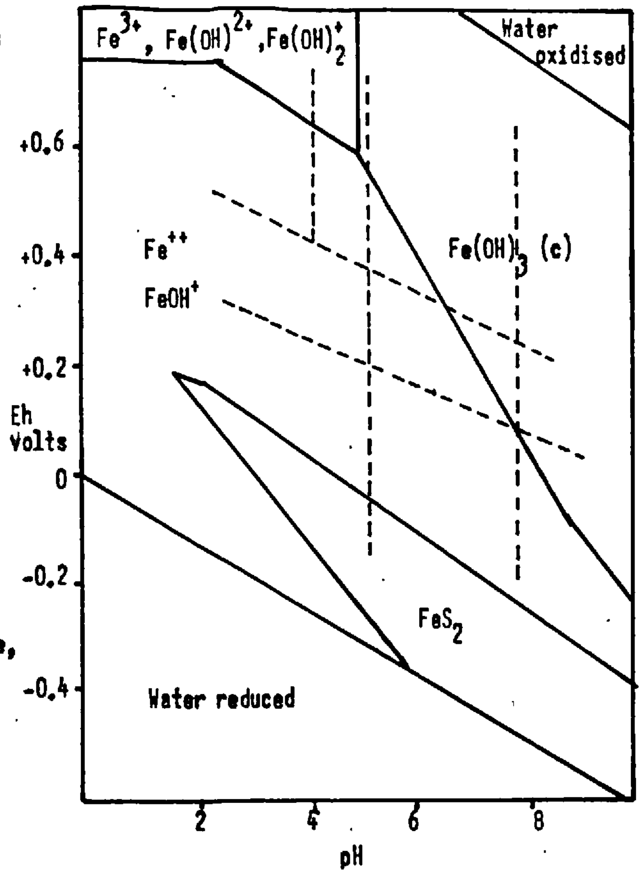
○ Soils of the brown earth sequence, control areas.

● Soils of the podzol sequence, Low Sperrins.

■ Black mud sediments.

□ Stream waters.

(Results from Central Tyrone).

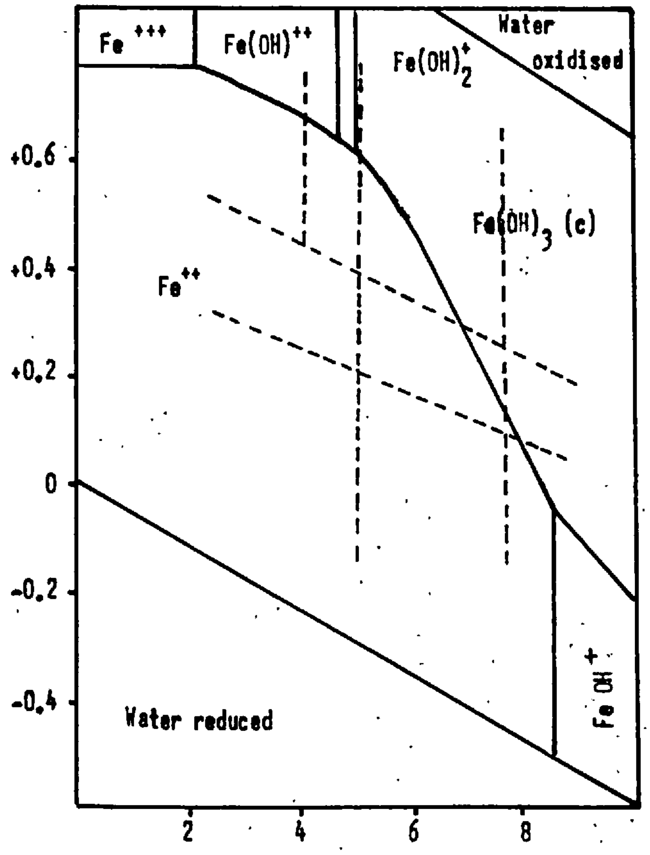


c. Stability field diagram for aqueous ferrous - ferric systems in the presence of dissolved sulphate.

Fe^{++} activity = 0.01 ppm

Total sulphur activity = 10^{-5} molal.

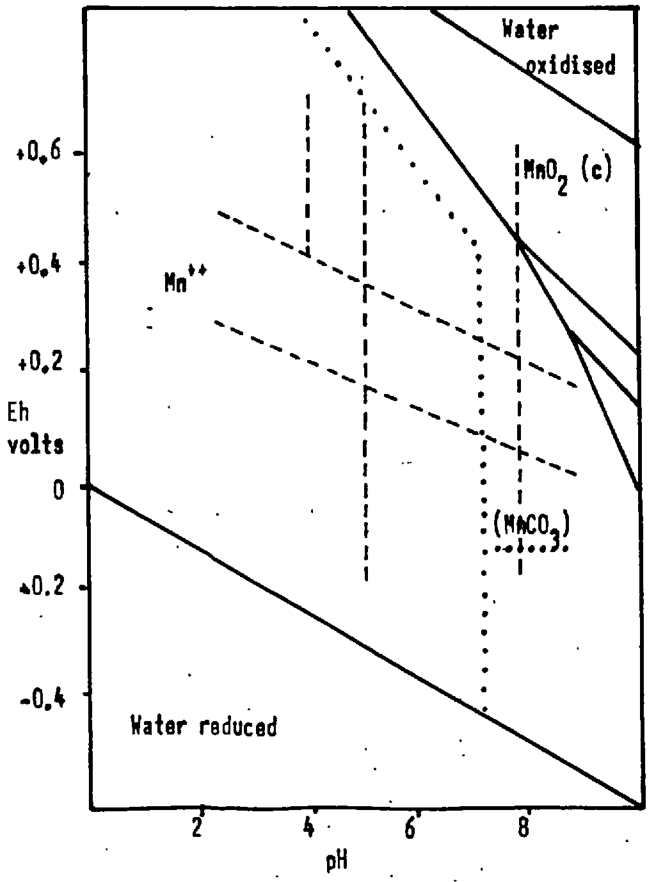
(After Hem, 1960).



b. Stability field diagram for aqueous ferrous - ferric systems.

Fe^{++} activity = 0.01 ppm.

(After Hem and Cropper, 1959).



d. Stability field diagram for aqueous manganese systems.

——— defining fields for systems free of dissolved sulphate and bicarbonate.

Mn^{++} activity = 0.01 ppm.

· · · · · defining fields for systems in the presence of precipitated $MnCO_3$.

Mn^{++} activity = 1.0 ppm.

HCO_3^- activity = 100 ppm.

(After Hem, 1964).

FIG. 8 - 1. THE Eh AND pH OF NATURAL AQUEOUS ENVIRONMENTS IN RELATION TO THE STABILITY FIELDS OF AQUEOUS IRON AND MANGANESE SYSTEMS.

Garrels and Christ (1965), Hem (1960) and Hem and Cropper (1959).

In the Eh-pH ranges of most interest, the chemistry of iron is dominated by the oxidation of ferrous iron:

$$4Fe^{2+} + O_2 + 4H^+ \rightleftharpoons 4Fe^{3+} + 2H_2O$$

The location of the ferrous/ferric boundary is governed by the active concentration of the dissolved species. The higher the concentration, the greater the fields of the solid phases in equilibrium with them. An Eh-pH diagram for the aqueous iron oxide system is shown on Fig: 8-1b (Hem and Cropper, 1959), calculated on the basis of a total Fe activity of 2×10^{-7} moles (0.01 ppm Fe in solution).

Ferric ions are only soluble in very acid, oxidizing environments so that the solubility of iron in natural conditions is due almost entirely to the ferrous ion. Ferrous iron is soluble in most acid, waterlogged and wet soils, but most normal soils and stream waters lie in the field of insoluble hydrous oxides. The sum of the possible soluble ferric species, namely Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)^+$ and $Fe(OH)_4^-$ cannot exceed 10^{-8} molar in the pH range 6-9 (Stumm, 1967). Natural waters frequently have contents above this, hence the iron must be in soluble complexes, as colloidal particles or in a metastable state.

The most important inorganic species in natural waters are dissolved CO_2 and sulphate. The effects of atmospheric CO_2 are negligible but in limestone areas, the concentrations of dissolved carbonate are raised so that siderite may form in alkaline, reducing conditions.

Sulphur species can be important in waterlogged soils and organic sediments (for example, Bloomfield 1969), but have not been studied in the Tyrone area. In such environments, FeS_2 can be precipitated in the presence of approximately 0.3 ppm sulphide, the minimum level at which H_2S is detectable by odour (Hem, 1960). On oxidation the reverse process releases Fe into solution (Fig: 8-1c). However, the transformations are slow and sulphur species may remain metastable unless the reactions are catalysed.

ii. Stability diagrams for manganese The stability of manganese in aqueous environments has been studied by Ponnamperuma and co-workers (1968), Morgan (1967), Hem (1964) and Krauskopf (1957). The major reaction is the oxidation of divalent manganese:

$$Mn^{2+} + 2H_2O \rightleftharpoons MnO_2 + 4H^+ + 2e$$

The most important feature is the large stability field of divalent manganese (Fig: 8-1d) with the oxidation to the hydrous oxides requiring higher Eh and/or pH conditions than for the ferrous-ferric oxidation. This implies that the manganous ion is more soluble than the ferrous ion. The greater stability is attributable in part to the fact that the Mn^{2+} ion has a half-filled electron shell (Orgel, 1966).

The presence of sulphate and bicarbonate anions has little effect on the Mn equilibria in the Eh-pH ranges of interest (Hem, 1964).

In limestone terrain, however, where dissolved bicarbonate may exceed 100 ppm, the solubility of Mn may increase with the formation of the $MnHCO_3^-$ complex, although $MnCO_3$ can precipitate under reducing conditions (Fig: 8-1d).

iii. Stabilities of cobalt, copper and zinc The stability fields of these metals tend to be similar to those of Mn and Fe. Their behaviour is controlled by the solubility of Fe and Mn oxides and sorption to these oxides and organic matter. Cobalt is the most firmly bound of the trace metals sorbed by Mn oxides and its migration is controlled by Mn solubility (McKenzie and Taylor, 1968). Cu and Zn are more readily desorbed by diluted acids than Co and may be soluble when Mn and Co are insoluble, or alternatively, become fixed more firmly to iron oxides or organic matter.

8.324 Discussion The stability diagrams illustrate that under the conditions existing in many acid or waterlogged soils, the metals are mobile as the divalent ions. An important feature is the greater solubility of Mn^{2+} relative to Fe^{2+}. Consequently, in accordance with the conclusions of Krauskopf (1957), it can be stated that at any given pH, Fe (III) oxides are precipitated at a lower Eh than the equivalent Mn (IV) oxides. Thus, the thermodynamic relationships shown by the diagrams account satisfactorily for the separation of Mn and Fe during oxidation as commonly observed in secondary accumulations.

Natural systems deviate in composition from these theoretical models, hence the diagrams do not account for the alterations in stability fields caused by the presence of other cations, the formation of stable complexes in solution nor for the precipitation of non-stoichiometric, amorphous or mixed oxides showing solid solution. Work by Garrels and Christ (1965) suggests that the fields of amorphous iron oxides, and probably those of hydrous manganese oxides, are larger than those of the more ordered crystalline forms upon which much of the thermodynamic data is based. Consequently, the oxides may be stable under lower Eh/pH conditions than the diagrams suggest.

The rate and reversibility of the predicted reactions is uncertain. It is probable that precipitation is more rapid than solution. The hydrous oxides (either of Mn or Fe) can catalyse the oxidation of both Mn^{2+} and Fe^{2+} even under unfavourable conditions (Hem, 1963). The rates of solution, by oxide reduction, have been studied in less detail but they appear to be slow relative to precipitation reactions and to the rates of wetting and drying in soils. In freely drained soils, reducing conditions may prevail for short periods only, hence slow solubilisation rates will prevent much loss of metal. During subsequent drying, oxidation will be most rapid near voids, with precipitation occurring preferentially with pre-existing oxides to give very localised concentrations, as in ferrans and neoferrans.

8.33 <u>Mechanisms of metal migration</u>

8.331 Introduction Several theories have been put forward to account for the mobilisation of Fe and associated metals in soils. These are summarised on Table 8-2. Most postulate migration within the general framework of the Eh-pH diagrams, with metals stabilised as organometallic complexes and colloids. The main differences are the organic compounds involved and the oxidation states, particularly of Fe, in solution.

8.332 Chemical state of metals in groundwater No data concerning the state of the metals in groundwater during migration were obtained from the Tyrone area. The mobilised metals may be expected to be in true solution or in suspension, stabilised in complexed or dispersed forms with other species in solution. These species are liable to be bicarbonate, sulphate and organic ligands, although both inorganic forms, particularly bicarbonate, are unlikely to be significant in areas of siliceous bedrock developing peaty podzols.

i. Soluble complexes In aqueous solution, metals readily form complexes with various ligands (Orgel, 1966). The ligands may be arranged in a series, the spectrochemical series, according to their capacity to cause d-orbital splittings in cations and thereby impart crystal field stabilisation energy (C.F.S.E.) to the complex. The complexes are formed by the displacement of water molecules by the ligands. Most organic ligands are farther along the series than water or inorganic ligands, hence organo-metallic complexes are expected to form since they give greater stability by virtue of greater C.F.S.E.

Different ions can experience different amounts of C.F.S.E. for a given ligand. Consequently, they also can be arranged in a series, the Irving-Williams stability series. For divalent ions, this is normally:

$$\mathrm{Mn} < \mathrm{Fe} < \mathrm{Co} < \mathrm{Ni} < \mathrm{Cu} > \mathrm{Zn}$$

Divalent Mn has no C.F.S.E., so that although complexes may form, there is no additional stabilisation.

ii. Organometallic colloids Metals, especially iron, may migrate in suspension in two forms of organometallic colloid:

a) as metal ions adsorbed to negatively charged, hydrophilic colloids; and

b) as ferric 'hydroxide' micelles dispersed and stabilised by the adsorption of organic ions.

8.333 Role of humic compounds

In the Tyrone area, the strongest leaching and stream precipitation is associated with areas of peaty podzols. Hence, it is possible that organic compounds derived from peat are responsible for the increased mobilisation in the area. Evidence of this apparent association between peats and increased mobilisation comes from four detailed studies:

i. Mineral soils immediately beneath peats are strongly leached of all metals. Heavy iron-manganese precipitation occurs deep in such profiles, however, associated with translocated humic matter.

ii. At Camlough, iron-rich gelatinous precipitates occur downstream from the point where waters from the saturated moraine sands beneath the basin peats enter the channel.

iii. At Slievemore, gelatinous precipitates in streams, and iron seeps in peats, occur at the lowest point in the basin peat area. Upstream, manganese precipitates are common on coarse fractions of the stream sediment.

iv. At Clogherny Glebe, a very strong enrichment occurs in bank soils above stream level, directly downslope from a raised bog. There is evidence for strong lateral mobilisation of all elements in the vicinity of the peat.

Source of Organic Compounds	Organic Compounds Involved	Form of Metal in Groundwater	Cause of Precipitation	References
Podzol B_h horizon	Low molecular weight Fulvic acids, These have a high proportion of oxygen in comparison with medium-high molecular weight humic acids and a greater acidity, derived from - COOH and - OH groups.	a. Complex with divalent ions, in stability series pH 3.5. Cu > Fe > Ni > Pb > Co > Ca > Zn > Mn > Mg pH 5.0. Cu > Pb > Fe > Ni > Mn > Co > Ca > Zn > Mg b. As metal/acid complexes. Ferric iron as $Fe(OH)^{2+}$ in 1:1 and 3:1 complexes. $Fe(OH)_2^+$ in 6:1 complexes.	a. Precipitates as metal/acid ratio rises with increasing Eh or pH. The more stable complexes precipitate later to give zonation. Ionic compounds are important e.g. Ca^{2+} induces high pH and rapidly saturates complexes. b. Precipitated when metal/acid ratio approaches 6.	1
Humic matter (peat)	High molecular weight humic acids which act as negative hydrophilic colloids	Adsorbed to colloids	Ultimately discharged and coagulated by continued adsorption of metal ions. Coagulation power of ions:- trivalent > divalent > monovalent	2
Anaerobic fermentation Canopy drip Sterile aqueous extracts of plants	Polyphenols, including D- and Epi-catechin, reducing sugars, organic acids. Polyphenols, polysaccharides nitrogenous compounds.	1. Organic compounds reduce oxides, including turgite, desorb trace elements to form soluble aqueous complexes. Metals as ions or partially hydroxylated species e.g. $Cu(OH)^+$, $Zn(OH)^+$ etc. Ferric iron reduction via:- a. electron donation from phenolic - OH to Fe^{3+} b. free radicals $R^\bullet$ in organic matter: $R^\bullet + Fe^{3+} = R(stab) + Fe^{2+}$ 2. Stabilize Fe^{3+} as complexes.	Aeration gives rapid precipitation Order of coprecipitation with ferric oxides Mo, V > Zn > Cu > Co > Ni. Precipitation at high metal/acid ratio	3 4
Aqueous extracts of pine needles	α-carboxylic acids, including citric, malic, quinic acids. Phosphoric acid; amino acids.	1. Dissolve Fe^{3+} oxides by complexing via hydroxyl group. Complexes with divalent ions. 2. $Fe(OH)_3$ sols and at low pH, $Fe(OH)_2^+$, and $Fe(OH)^{2+}$, stabilized by adsorption of citrate anions.	Precipitation at high metal/acid ratio At any pH, size of micelles increases as Fe/acid ratio increases. Precipitation when ratio near 20.	5 6
A_0 horizon of loams	2 aliphatic acids 1 amino acid.	1:1 complexes with Zn^{2+}, Cu^{2+} (pH < 5.0). Probably chelates via monobasic phosphoric acids and carboxyl groups.	Increase in pH	7

References:
1. Schnitzer 1968, 1969 ; Schnitzer and Skinner, 1964, 1967 ; McKeague et al 1967.
2. Ling Ong and Bisque 1968.
3. Ng and Bloomfield, 1961.
4. Bloomfield, 1963 ; Coulson et al, 1960 ; Malcolm and McCracken 1968.
5. Delong and Schnitzer, 1955 ; Schnitzer and Delong, 1955.
6. Muir et al 1964.
7. Geering and Hodgson, 1968.

TABLE 8 - 2. SUMMARY OF SOME THEORIES DESCRIBING THE ROLE OF ORGANIC COMPOUNDS INVOLVED IN METAL TRANSLOCATION IN SOILS.

The acids derived from peats are frequently considered important agents in metal translocation and podzolisation. Their chemical structures are complex, with molecular weights ranging from 2,000 - 300,000 (Possible structures for humic components have been discussed by Mendez, 1967; Felbeck, 1965; Kononova, 1960.) Schnitzer and co-workers (reference 1. Table 8-2) have used a low molecular weight extract, fulvic acid, derived from translocated organic matter in the podzol Bh horizon, to demonstrate the mobilisation of metals in podzols. The acid can form complexes with various divalent ions, with stabilities generally increasing with a rise in pH. The stability series (Table 8-2) differ from the Irving-Williams series, although Cu complexes are again the strongest.

Fulvic acids also complex trivalent Fe and Al ions, demonstrating that mobilisation does not need an initial reduction step. The complexes become increasingly insoluble as the metal/acid ratio rises to 6. Oxides in iron pans in Newfoundland, for example, were found to contain complexes with this ratio (Schnitzer, 1968).

Higher molecular weight humic acids may cause mobilisation by migrating in colloidal suspension with adsorbed metal ions. Coagulation and precipitation occur when the colloids are discharged by continued adsorption of metal ions.

In general, ionic concentration is considered as important as Eh and pH in the precipitation of humic complexes and colloids. The presence of other ions, such as Ca^{2+}, can cause a rapid increase in metal/acid ratios, so that migration is restricted and precipitation rapid in their presence.

8.334 Role of non-humic compounds Many authors consider that the accumulation of acid mor humus and peat over podzols is largely coincidental (Bloomfield, 1963; Coulson et al, 1960). They suggest that simple non-humic compounds are the agents of mobilisation and that these are most active in areas of siliceous bedrock and wet, base-poor soils, the same conditions that favour mor humus and peat accumulation.

Mechanisms based on humic acids derived from podzol Bh horizons are criticised since the acids may be products of the extraction process. Furthermore, oxidation and polymerisation during precipitation are liable to have altered the original compounds very considerably. Thus, the translocated organic matter may have little resemblance to any possible causative agents. To some extent, this criticism is invalidated, since ferric iron can be mobilised without reduction, and hence the reactions are little more than neutralisation or coagulation.

Relatively simple organic compounds, such as polyphenols, carboxylic acids and reducing sugars derived from aqueous extracts of plant materials and canopy drip, have been shown to be effective in producing metal mobilisation of the type that may occur during podzolisation (references 3-6, Table 8-2). These compounds can reduce ferric oxides and form stable complexes with ferrous iron and trace elements in true solution, or stabilise sols of hydrous ferric oxides and, at low pH, the partially hydroxylated dissociation products $Fe(OH)_2^+$ and $Fe(OH)^{2+}$.

In the Tyrone area, some metal depletion was observed to have occurred in soils without peat or mor humus. Depletion was greatest in poorly drained, gleyed soils, with metals concentrated into distinct ferromanganese accumulations or lost to the groundwater. Heavy Mn-Fe precipitation, for example, occurred in profile MP/2 at Mayne, in stony till beneath an horizon with impeded drainage. The metals are presumed to have been mobilised under the reducing conditions of this waterlogged horizon and re-precipitated in the more oxidising stony till. This demonstrates, therefore, that humic compounds are not essential for metal mobilisation.

During gleying, the reactions occurring are probably reduction and complextion. Organic compounds, formed in waterlogged soils by processes akin to the sterile anaerobic fermentation reactions conducted by Ng and Bloomfield (1961), can reduce ferric iron and form stable complexes in true aqueous solution. Schnitzer and Delong (1955) and Delong and Schnitzer (1955), however, considered that all the iron dissolved by various leaf leachates is in the ferric form. Thus, although recognising that ferrous iron may be present in gleyed soils, they doubted that reduction was necessary before mobilisation could occur in podzols.

8.335 Discussion It is very probable that all mechanisms operate to some extent, with non-humic compounds important in all areas but humic compounds imparting greater mobility where they occur in abundance. Thus, in most free-draining soils, relatively mild leaching occurs, with metals mobilised as inorganic or simple organic complexes. Where soils are more acid or waterlogged, leaching may be stronger, possibly with metals leaving the profile entirely, to be precipitated in more oxidising soils or in the stream. Strong leaching also occurs in high rainfall areas, where humic compounds are generated in the organic matter accumulating in surface horizons.

As the compounds migrate down the profile, they complex or adsorb polyvalent cations and, after reaching a certain point of saturation, precipitate. The point of precipitation is normally governed by the physico-chemical conditions, but in base-poor soils, the saturation point occurs later and the humic matter can migrate further. With time, the accumulation horizon can itself migrate, since unsaturated acids can presumably redissolve precipitated oxides. In the very acid and/or water saturated soils beneath peats, precipitation may be incomplete, hence a large proportion of the mobilised metal can be lost to the groundwater and, ultimately, the stream.

Thus, the presence of two apparently active accumulation horizons in peaty podzols from the Low Sperrins, namely the upper podzolic B horizon and the lower 'organic' horizon suggests that two mechanisms may be operating. For example, the upper horizon may be formed by the rapid oxidation of metals migrating as ions or in non-humic complexes and the lower horizon by the slow precipitation of metals associated with humic compounds. Such lower horizons were not present in nearby reclaimed podzols where peats have been removed. They are not considered to be fossil horizons (McAllister, 1969, pers comm.).

8.34 Nucleation and precipitation

8.341 Conditions of precipitation The precipitation of Mn and Fe occurs when the mobilised species become unstable. This is brought about by:

i. raised Eh and/or pH;
ii. concentration of dissolved species by drying; and
iii. saturation of complexes and colloidal sols by metal ions.

The pH and Eh environment of the dissolved species will change when the groundwater migrates into less acid and less saturated soil horizons, or when the soil dries. Oxidising conditions may only be very local, for example in the vicinity of channel voids, or more general, throughout the soil as a whole.

Where acid and/or gleyed soils extend to the stream bank, the mobilised metals can enter the stream water. Precipitation is then very rapid since any dilution effects will be offset in most streams by a marked rise in Eh and pH.

8.342 Mechanisms of precipitation of iron and manganese.

The morphology of many Fe-Mn accumulations, such as ferrans and streams precipitates, with a lower, iron-rich layer, indicates an initial precipitation by iron. This is in agreement with the thermodynamic data, which predicts that under any natural Eh-pH conditions, Fe will precipitate before Mn, unless the concentration of Mn in solution exceeds that of Fe (Krauskopf, 1957).

1. Chemical state of precipitated iron oxides.

It is not clear whether, at the moment of precipitation, the iron is in the form of colloidal ferric oxide or as hydrated Fe^{2+} or Fe^{3+} ions in organometallic colloids or complexes. Experimental work has shown that, if iron is present in solution as the ferric ion, it will hydrolyse and precipitate as a gelatinous form of the α-hydrated oxides, $Fe_2O_3.nH_2O$. This gel will be organic if the iron precipitates as a saturated complex or organometallic colloid. On ageing and dehydration, goethite and haematite form, with any organic matter liberated, possibly with the aid of micro-organisms. However, if the iron is present as the ferrous ion, it may oxidise to the ferric ion and react as before, or precipitate initially as the ferrous hydroxide, $Fe(OH)_2$, which on oxidation can age to lepidocrocite (Oades, 1963).

Lepidocrocite has been identified in root mottles in poorly drained soils in Scotland (Brown, 1953) and, with goothite, in mottles in Japanese soils (Kojima and Kowaguehi, 1968). Although radiate structures are seen in pedotubules in the Mayne catchment (Fig: 7-9), the oxides are amorphous. However, if formed in the same way as root mottles elsewhere, this would indicate ferrous iron in solution and precipitation as $Fe(OH)_2$ around a root, with oxidation occurring in periodic dry conditions. In stream precipitates, the probable occurrence of goethite suggests nucleation by ferric iron.

ii. Nucleation of iron oxides.

If the iron oxides are formed below their iso-electric point (pH 5.5 to 6.0, Hem 1964) both ionic and colloidal forms will be positively charged and be attracted to the net negative charge of mineral surfaces. The low pH required for colloidal adhesion need merely be a temporary fluctuation and can readily occur in soils and poorly buffered streams in acidic terrain. Elsewhere, such fluctuations may be rare and nucleation may be more commonly via the adsorption of ionic species, with more complete oxidation on ageing or temporary exposure to the atmosphere. Subsequent precipitation will be about the nuclei so formed, which can catalyse further oxidation of iron and co-precipitate manganese by replacement reactions.

iii. Nucleation in soils.

The nucleation of plasma enrichments, diffusion ferrans and glaebules may be the result of microbial action or simply periodic wetting and drying concentrating the soil solution or oxidising metal adsorbed to clays. The mechanisms may be via that outlined above for ferric oxides, or involve the intermediate precipitation of

$Fe(OH)_2$, at least in the case of root mottles. However, after nucleation has occurred, a concentration gradient is set up and the structure grows accordingly.

iv. Nucleation in streams.

The iron-manganese stream precipitates are mainly observed on the coarser particles. There are several possible causes:

a) The adhesion of colloidal particles to a surface requires the penetration of the hydrated layer on the surface. Davis (1968) has shown that the rate of penetration and adhesion depends upon the particle having sufficient energy. This energy can be derived from the motion of the solution, so that up to a certain maximum velocity, an increasing rate of flow increases precipitation. Above this maximum, the viscous drag overcomes the adhesive forces and dislodges the particles. In a stream, the fine sediment will tend to move also, so that the relative velocities will be lower and penetration less frequent.

b) Where precipitation does occur on the finer sediments, unless it is heavy and binding, it will be rapidly removed by attrition as the sediment is washed downstream.

c) Nucleation may involve the intermediate steps of adsorption followed by oxidation during ageing or drying before catalytic precipitation can take place. Ions adsorbed to clays in fine sediments may be too firmly bound for much oxidation to occur and hence precipitation is only slight.

v. Precipitation of manganese oxides.

Manganese precipitation is considered to occur when most of the iron has precipitated, particularly if Eh and pH rise. Hem (1964) showed that precipitation could occur, even under very unfavourable conditions, by the reaction of Mn^{2+} with hydrous ferric oxides:

$$Fe_2O_3 \cdot nH_2O(c) + 2H^+ + Mn^{2+} \rightleftharpoons MnO_2(c) + 2Fe^{2+} + (n+1)\ H_2O$$

(c = solid)

The equilibrium constant, K =

$$\frac{[Fe^{2+}]^2}{[Mn^{2+}][H^+]^2} = 10^{-5.67}$$

Normally, the equilibrium is displaced to the left. However, as the concentration of Fe^{2+} ions in solution decreases, the reaction may proceed to the right. The MnO_2 so formed can then catalyse the oxidation of further Mn^{2+} in solution. Since the MnO_2 is above iso-electric point (pH 3.0; Morgan and Stumm, 1964), it can also adsorb Fe^{2+} and other metal ions to form mixed, non-stoichiometric oxides.

If the pH rises to above the iso-electric point of the iron oxides, their charge will reverse and Mn^{2+} and other ions can be adsorbed. If Eh rises, iron oxidation will become more rapid and Mn may oxidise directly. Thus, with time the precipitate can become more manganiferous and produce a layered or zoned accumulation.

8.343 Zonation in glaebules.

Glaebules from the brown earths at Mayne showed a concentric structure, with Mn concentrated in the core. This is opposite to that normally observed and predicted by the thermodynamic data. Cescas and co-workers (1968), for example, found glaebules with a ferruginous core and manganiferous rim, and considered them to be formed under conditions of increasing Eh and pH.

At Mayne, the zonation may result from either:

i. continuing replacement of Fe by Mn; or

ii. a change from highly oxidising conditions, with both metals precipitating together, to less oxidising conditions, with Fe precipitating alone. Such a change, however, would tend to give a different zonation in glaebules of different sizes and ages, but these were not observed; or

iii. initially, MnO_2 precipitating after iron oxides, in the normal way, or adsorbed to these oxides as Mn^{2+}, with oxidation to Mn^{4+} during ageing and drying. Subsequently, Mn precipitation takes place mainly on this preformed MnO_2, thus concentrating the core, whilst Fe precipitation continues outward growth.

The latter is the most probable mechanism and would result in a zoned but unlayered glaebule, even if precipitation is only spasmodic. It differs from the mechanisms of formation of layered glaebules in which each layer is taken to represent a wetting and drying cycle (for example, Brewer and Sleeman, 1969). In Tyrone, such forms, probably with each layer Mn-rich towards the outer rim, are only found in enriched bank soils.

8.344 Zonation in ferrans and stream precipitates.

The Fe-Mn layering observed in some ferrans and in stream precipitates is ascribed to the precipitation of iron before manganese under conditions of increasing oxidation. Each double layer may, therefore, represent:

i. a short precipitation phase, responding, for example, to the oxidation taking place after heavy rainfall and stream flooding. The process is, however, most unlikely to be this rapid.

or ii. an annual precipitation phase, in response to the gradual alteration of metal mobility with season. Such alterations have commonly been observed in connection with seasonal variations in the availability of nutrients to plants (for example, Fleming and Murphy, 1968) and hence are possibly responsible for the availability of metal for translocation and precipitation. Mobilisation would be expected to be greatest during the wet winter months and hence precipitation in streams may be greatest at this time.

or iii. a continuing precipitation phase in which, once MnO_2 nucleation has occurred, both metals precipitate together on the performed oxides.

Hypothesis (iii) is favoured since both (i) and (ii) imply the formation growth rings - such as those reported in glaebules by Brewer and Sleeman (1969) and in freshwater manganese nodules by Harris and Troup (1969). In the nodules, for example, each double band was taken to represent an annual growth ring. In the Tyrone area, however, cyclic layering is only observed in ochre precipitates downstream from iron slimes at Barons Court and in some Fe-Mn enriched bank soils. The upper, gelatinous layer of stream precipitates in the Low Sperrins is unlikely to represent a second precipitation cycle (Chapter 7.54). Nevertheless, it is possible that the absence of cyclic layering may be because either:

a) insufficient samples were examined. Most stream precipitates studied in thin section or by electron microprobe were on small pebbles subject to attrition and precipitate removal. Nevertheless, there was no suggestion of more than one double layer on larger pebbles or boulders in streams.

or b) accumulations are periodically redissolved. It was noted that in certain streams, the amount of observable precipitate tended to vary from year to year. Particularly noticeable was the difference between a wet year, 1967, when precipitates were common, and a very dry year, 1968, when precipitates were less abundant, suggesting that resolution has occurred. Similar resolution may well occur in soils.

Continuous observations on the development of precipitates is necessary for a full understanding of the processes involved.

8.345 The precipitation of trace metals Cobalt, copper and zinc can remain in soil solution under a much wider Eh-pH range than Mn and Fe, largely because of their low initial concentration. Their presence in the soil is due to adsorption to or coprecipitation with, organic matter, clays and hydrous oxides. The hydrous oxides in particular have high adsorption powers because of their very high surface area. The soil data from Tyrone (Chapter 6) indicate that Co is most closely correlated to hydrous oxides, Cu the least. In sediments, the Co/Mn and Zn/Mn correlations are very strong, particularly where the Mn content exceeds 2,000 ppm. The poorer correlations shown by Co and Zn at the lower Mn and Fe levels in some sediments and most soils is probably because:

a. at these low levels of Mn and Fe, the proportions of the trace metals adsorbed to the oxides is similar to or smaller than that associated with the more abundant organic matter, clays and primary minerals, so that any preferential concentration is not significant.

b. the soils in particular are more acid and precipitated trace metals will be resorbed.

Coprecipitation is generally considered to be the adsorption or occlusion of an ion to a colloidal particle, before, during, or just after precipitation. The adsorption occurs when ion and colloid are oppositely charged. Hence, for cations it must occur above the iso-electric pH for the colloid. The iso-electric pH for ferric oxides varies from pH 8.5 for amorphous hydrous oxides to pH 2.1 for crystalline haematite (Marshall, 1964). Ng and Bloomfield (1961) found that Zn and Cu in particular could coprecipitate from fermentation solutions with the hydrous oxides at pH 6.0 and above. Similarly, Hem and Skougstad (1960) found that Cu coprecipitation from ionic solution occurred above pH 5.5. These values seem most applicable to the situation in soils and streams. The iso-electric point of hydrous manganese oxides is at pH 3.0 (Morgan and Stumm, 1964), so that they are increasingly negative throughout the natural pH range.

In both soils and sediments, organic matter, clays and manganese oxides compete with iron oxides for the sorption of cations. The preferential concentration of As, Co, Ni, Zn and other metals in the Mn fraction of sediments, for example, has been described by many authors, including Ljunggren (1955), Canney (1960), Theobald and co-workers (1963) and Nichol and co-workers (1967). Copper, however, tends to concentrate slightly in organic matter. It can be adsorbed very strongly by manganese oxides, as demonstrated by MacKenzie and Taylor (1968) but is not strongly fixed and can be desorbed readily. Cobalt undergoes a secondary reaction so that over 85% of sorbed metal is retained. The ability of the Mn oxides to adsorb large amounts of trace metals is ascribed to their large surface area and their non-stoichiometry, which gives the structure a strong negative charge. The charge is balanced by adsorbed H^+, K^+, Na^+ and Mn^{2+} which are readily exchanged for divalent cations such as Co^{2+}, Ni^{2+} and Zn^{2+}.

The reasons for preferential retention are not fully understood, but stem from the ability of one of the competing hosts to incorporate the metal into specific sites, by virtue of similar ionic radii or additional stabilisation from crystal field effects. For example,McKenzie (1970) has proposed that Co^{2+} ions replace exchangeable Mn^{2+} ions on adsorption and then diffuse into the surface layers of the lattice of the manganese oxides to be oxidised by and replace lattice Mn^{3+} ions.

The precipitation of zinc may involve phosphate. Phosphoric acid may be active in metal migration in soils (Muir et al, 1964) and phosphate links to iron oxides were postulated for Zn in soils by Stanton and Burger (1967). MacKenzie and Taylor (1968) showed that Zn tends to be concentrated in lithiophorite but by a smaller factor than for Co. In stream sediments, the Zn distribution, like that of Co, is linked closely to Mn (Chapter 6.7). It is not certain whether Zn undergoes an exchange reaction with lattice Mn^{2+} in the same way as Co. The divalent ion has a similar radius to that of Co^{2+} and has a similar electronic configuration to that of Mn^{2+}, in that Mn^{2+} is stabilised by having a half-filled d electron shell and Zn^{2+} is stabilised by having a complete d electron shell. It is possible that the Zn ion can diffuse into the oxide lattice to replace Mn^{2+} but it will have no additional stabilisation energy, other than a higher charge/density ratio than Mn^{2+}.

Copper would be expected to behave similarly to Zn. However, in the Tyrone area, although it is mobilised with the other metals when the pH falls below about 5.0, there is little evidence of any subsequent reconcentration in hydrous oxides in soils or sediments. This is probably because Cu forms the most stable organometallic complexes, both in the conventional Irving-Williams series, or in that for fulvic acid established by Schnitzer (Table 8-2) and is not readily precipitated under the conditions prevailing in soils or streams. Experiments by Ng and Bloomfield (1961) and Hem and Skougstad (1960) showed that hydrous iron oxides could co-precipitate copper above pH 5.5, but the experimental concentrations were greater than those in natural waters.

8.35 The influence of micro-organisms on metal dispersion

8.351 Introduction The processes of solution, migration and precipitation of metals considered in the preceding sections can all occur in sterile conditions. However, micro-organisms are ubiquitous in the weathering environment and are undoubtedly involved in the chemical reactions taking place. Silverman and Ehrlich (1964) have shown that most elements can be involved in microbial metabolism but, although these transformations can occur, their significance may be slight. In their metabolism the microbes may:

i. utilise the metal, or radical or ligand to which it is bound;

ii. dissolve or precipitate the metal;
iii. adsorb the metal in the cell surface.

The reactions involved are frequently just one step of a multi-stage redox reaction, but this step may often be rate determining, catalysed by the microbial action.

8.352 Mineral degradation and formation by organisms Mineral degradation by organisms has been reported by several authors, but has not been studied in the Tyrone area. Webley and co-workers (1963), for example, found that certain bacteria and fungi could release strong acids capable of dissolving or corroding many minerals, including some silicates and metal oxides. Bacteria are associated with the sulphate cycle and are probably involved in the reduction of iron in podzols and gleys, via the production of hydroxy-carboxylic acids as metabolic by-products (Oades 1963; Zarjic, 1969).

Organisms are most commonly associated with reactions involving mineral formation, particularly the precipitation of iron and manganese oxides. Iron bacteria are probably present in the accumulation horizons of soils, but are more frequently observed in precipitates in natural waters. Their role appears to be to catalyse oxidations that would normally occur under prevailing conditions.

In the Tyrone area, bacteria were identified in iron slime seepages and ferruginous stream precipitates.

i. Iron slime seepages These are common in areas of acid or gleyed soils where iron mobility is high. They can be a problem in blocking drainage ditches with dense ochreous deposits (Parr, 1969; Spencer et al, 1963). About six species or varieties of filamentous bacteria have been recognised in such slimes, depending upon the locality. Bacteria of this type, probably Leptothrix ochraceae, were observed in ochre slimes in the Tyrone area. The slimes normally contain over 30% Fe, with variable amounts of other metals. In general, other metals are not concentrated relative to the mean soil content, but near mineralisation at Barons Court the Pb-Zn concentration exceeds 10% without apparent inhibition to growth. The Mn concentration in slimes rarely exceeds 2,000 ppm; Pringsheim (1949) showed that the development of Leptothrix was retarded by Mn in solution, but only at concentrations rare in the natural environment.

The role of the bacteria in precipitation is uncertain. Presumably they catalyse the oxidation of ferrous iron, or the release of ferric iron, whilst utilising associated organic compounds for the formation of the cell walls and polysaccharide sheath. Pringsheim (1949) and Dondero (1961) showed Leptothrix to be an environmental variant of Sphaerotilus natans. Pure cultures of Leptothrix yield growth of S. natans and conversely, cultures of S. natans which normally inhabit slow moving, polluted streams, can yield Leptothrix in an iron rich medium. Thus, iron is not essential to their metabolism, though when the metal is present the oxides are precipitated concentrically around the sheath (Fig: 7-7) by an unknown mechanism.

ii. Iron-manganese stream precipitates Yellowish-green filamentous forms occur on the surfaces of gelatinous precipitates in certain streams in the Low Sperrins. They are tentatively identified as the bacterium Clonothrix fusca (Zajic, 1969) which has an inner polysaccharide sheath and outer coating of apparently mucilaginous iron oxides. The filaments are larger than the bacteria found in iron seeps, but are considered by some authors to be another variant of Sphaerotilus natans.

Russian authors (in Kuznetzov et al, 1963) have similarly observed filamentous bacteria on the surfaces of Fe-Mn precipitates and concretions, in both fresh and salt-waters. The bacteria involved were generally filamentous and permeated by the metal oxides. The species observed are named as Sphaerothrix latens, Metallogenium personatum Perf, Bacterium precipitatum Kalin and Leptothrix ochraceae.

It is thought that these bacteria grow on the precipitate surfaces, catalysing the oxidation and precipitation of both Mn and Fe oxides and that the colonies migrate outwards as the oxidation proceeds. The bacteria in the Tyrone streams are of this type, but it is surprising, nevertheless, that although the filaments are clearly observable on the surfaces, they are not visible in the underlying ochreous oxide.

Micro-organisms are not visible in the black manganiferous precipitates, although smoothed holes in most precipitates suggest that they may have been present. Since the form and role of organism to be expected was not known, and drying, ageing and partial crystallisation may have obliterated most traces, microbial action during precipitation cannot be ruled out. Diatoms visible on precipitate surfaces are probably unrelated to their mode of formation, but it is possible that they may accelerate precipitation by liberating oxygen during photosynthesis and creating a local, highly oxidising environment.

8.4 PHYSICAL TRANSLOCATION

Metal translocation in most soil-sediment systems is a combination of physical and chemical processes. Physical processes, involving the transport of soil particles, are most important for elements that are chemically immobile in a given environment.

Physical processes usually have little influence on the dispersion of iron and associated metals within the soil profile. The pressure and tension effects of wetting and drying are of obvious textural importance, causing the reorientation of clays and the formation of soil aggregates. However, the physical effects are minor in comparison with the simultaneous alterations in the physico-chemical environment that such changes produce. In sols lessivés, physical processes cause an apparent podzolic profile differentiation when iron oxides and other metals are eluviated as coatings to clays. The micromorphological studies showed that such movement is occurring in the Tyrone area, with the formation of argillans in illuvial horizons. However, this again is of minor importance in comparison with the processes of chemical differentiation.

In most environments, chemical differentiation is largely completed within the profile or sequence, although there is inevitably some metal loss from the soil in groundwater solution. Subsequent metal dispersion is largely controlled by physical processes, as soil particles are transported from hills to valleys and enter the streams in suspension or via bank collapse. Relief is of major importance during erosion. The rate at which soil particles are transported increases on steeper slopes whilst rapid run-off at these sites probably hastens the removal of metals associated with smaller and less dense components, such as clays and organic matter. Similarly, scouring is more rapid in streams in high relief or rejuvenated areas.

Sediments are sorted by the stream current into various size and density fractions. On a regional scale, sorting is stronger in upland or high relief areas than in lowland or low relief areas. This is relevant in the interpretation of low-contrast patterns, such as that of copper in the Tyrone area (Chapter 5), and in the follow-up of individual drainage anomalies, when the metal is in a single mineral phase (such as tin in cassiterite) which concentrates in a particular fraction. The well sorted, active sediment is the fraction normally selected for routine reconnaissance surveys. In areas of low relief, however, such sediments are uncommon and another fraction, such as the fine, organic muds, has to be sampled instead. Consequently, in such areas the contents of metals that concentrate in organic muds may increase. Thus, sorting can give rise to distribution patterns related more closely to differences in sediment type than to variations in metal abundance.

In general, many effects of sorting are offset by analysing only the fine, minus 80-mesh sediment. . Physical fractionation processes, therefore, are unlikely to produce the major spurious patterns than can occur as the result of extreme chemical fractionation. Consequently, in areas where physical translocation predominates, there is a moderately good correlation between the metal contents of soils and stream sediments.

8.5 DISCUSSION AND CONCLUSIONS

8.51 The processes of metal translocation in soils

The discussion in this chapter has been concerned with the major physical and chemical processes influencing metal translocation during pedogenesis and erosion. A number of terms have been employed in the literature to summarise the most important processes taking place:

Lessivage : the process of migration and deposition of unaltered clay sized particles. 'Illimerization' refers to clay migration alone.

Gleization : the process of reduction of soil compounds, particularly Fe and sulphate, caused by permanent or seasonal waterlogging of all or part of the soil profile.

Soluviation: solution and eluviation of mineral components during leaching.

Cheluviation: solution of metals, particularly Fe and Al, in chelated complexes.

Lessivage (or illimerization) and cheluviation are considered as the two ends of a sequence of eluvial processes. Profile differentiation increases as purely physical eluviation is superceded by additional chemical translocation in solution. Podzolisation occurs when soluviation and particularly chelation are dominant (van den Broek and van der Marel, 1969).

This is, however, an over-simplification, since the eluviation of organo-metallic colloids is ignored. Furthermore, since it is still a matter of some speculation as to which organic compounds are the most significant in metal translocation, regardless of their mode of bonding, the separate usage of soluviation and chelation is not fully justified. Soluviation should, perhaps, refer only to the solution of simple ions, with other terms used for the formation of the organo-metallic complexes and colloids, depending upon the origin of the organic compounds.

Thus, translocation may be considered to increase as ionic, non-humic and then humic species become involved. Where gleization occurs in conjunction with the other processes, mobilisation can be intensified still further. It is possible that this is taking place in gleyed soils beneath basin peats, for example, in profile AP/3 at Camlough.

Stream sediments, however, are only influenced when these chemical processes make a significant contribution to metal translocation, such that metals are leached from the profile and reprecipitation is not completed within the sequence.

8.52 Metal oxide stream precipitates

Secondary oxides occur in several forms in the Tyrone streams. These are flocculant dispersions of iron oxides, iron oxide seepage slimes, black manganese oxide precipitates, and combined precipitates of gelatinous iron oxide over black manganese oxides. Only Mn and combined Fe-Mn precipitates are regularly enriched in trace metals. The iron slimes are enriched only in the vicinity of mineralisation. The flocculand dispersions and some slimes have a pH of 5.5 to 6.0. **and since this value is near the iso-electric** pH of iron oxides, **sorption,** coprecipitation and enrichment of other metals is unlikely.

The distribution of the stream precipitates (Fig: 3-8) indicates the areas in which strong chemical mobilisation is occurring. However, although the Mn oxide precipitates are widespread and can contain high levels of Fe, Mn, Co and Zn, they tend to have little influence on the sediment metal content. The oxides precipitate preferentially on the surface of coarse particles and do not enrich the fine fractions used for analysis. For example, precipitates on pebbles from the Clogherny stream contain 20% Fe, 20% Mn, 270 ppm Co and 1050 ppm Zn, yet the sediment content is 2.5% Fe, 500 ppm Mn, 10 ppm Co and 60 ppm Zn. Sediments from streams with heavy combined Fe-Mn precipitates, however, contain raised levels of these metals, with Co and Zn concentrated with the manganese. The difference lies in the degree of leaching taking place within the catchment. Heavy precipitates covering the stream bed and enriching all sediment fractions are found only where leaching is severe **and widespread.**

8.53 Causes of soil leaching and oxide precipitation in streams

The ultimate causes of the leaching conditions which result in the secondary concentration of metal oxides in streams are climate and geology.

i. Climate Strong leaching is promoted by a combination of high rainfall, low temperature and low evaporation rate, since this results in a net water surplus and a continuous downflow of water through the soil.

In the Tyrone area, oxide precipitation in streams occurs mainly where rainfall exceeds 40 inches per annum, but is heaviest and enriches stream sediments where rainfall exceeds 45 inches per annum. In general, this may be considered to be at an elevation of about 350 - 400 feet. Horsnail (1968) considered that precipitation would be important in areas where the number of raindays (> 0.01 inch) exceeds about 200 per annum. The average throughout Northern Ireland is greater than this figure, and the critical level is probably closer to 240 raindays. Precipitation is probably seasonal also, in that it will increase when rainfall is high and leaching strongest. In a normal year, the highest rainfall occurs during the period July to January and the least, March to May. There is normally a water surplus from October to mid-March, so that leaching and precipitation would be expected to be greatest during this period. However, from year to year, this pattern may alter markedly, giving rise to differences in the degree and extent of precipitation in streams.

Climate also influences the type of vegetation and its rate of decomposition. In a cool, wet climate such as that over most of the Tyrone area, there is a natural moorland vegetation. Decay is slow, leading to the development of peat and sustained acidic conditions which increase leaching, podzolisation and, consequently, oxide precipitation in streams. Peat removal and cultivation modify the conditions by removing the immediate source of soil acids and allow the complete humification of organic matter. Liming provides cations for the saturation of organic compounds and reduces the mobility of most metals by raising pH. Drainage and ploughing aerate the soil and reduce metal mobility by raising Eh. Thus, although the climate still favours strong leaching, the rate is greatly diminished.

Metal mobilisation and stream precipitation can remain high in agricultural areas where soils are predominantly acid or gleyed in valleys and on hill tops, and where podzols occur on slopes. This situation was encountered in North Devon by Horsnail (1968) but does not appear to be common in the Tyrone area.

ii. Geology Under a given climate, soils developed from certain rock types are particularly prone to podzolisation and metal depletion. In general, the rate of chemical translocation leading to podzolisation is enhanced where rocks are acid and siliceous, and soils light textured and porous. The low base status of such soils results in acid conditions and only slow saturation of organic compounds, whilst their coarse texture is unsuitable for the retention of iron oxides, particularly as diffuse plasma enrichments or glaebules. Consequently, the soils are strongly leached and give rise to heavy oxide precipitation in streams.

Chemical translocation can also occur where argillaceous rocks have weathered to give heavy soils. Gleization takes place and gives rise to precipitation in streams.

Conversely, soils derived from calcareous rocks are of high base status so that soil pH is high and metal mobilisation relatively low. Podzols can develop under a particularly severe climate but **organo-metallic complexes** become saturated by excess calcium in the C horizon and precipitate rapidly.

The geology also influences the amount of precipitated and co-precipitated metals by controlling their initial abundance. Precipitation will be heaviest where thereis more Fe and Mn available for leaching. Similarly, the amount of adsorbed or coprecipitated metals will be dependent upon the concentration present in the stream water and this is ultimately controlled by the bedrock contents.

CHAPTER NINE SUMMARY, CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

9.1 SUMMARY AND CONCLUSIONS

9.11 Regional Geochemical Reconnaissance

1. A regional geochemical reconnaissance survey, based on stream sediment sampling at a density of approximately one per square mile, has been made of the Tyrone area, in the west of Northern Ireland. Approximately 1,600 samples were analysed by emission spectrography for Ag, Co, Cu, Fe, Mn, Mo, Pb and Zn, and by nitric/perchloric acid digestion and atomic adsorption spectrophotometry for Cu and Zn.

2. The strongest distribution patterns shown by the metal contents of the stream sediments are those of Mn, Fe, Co and Zn. Coincident patterns of raised levels of these metals - that is, over 4,000 ppm Mn, 7% Fe, 85 ppm Co and 150 ppm Zn - are found:

    i. over the igneous and metamorphic rocks of the Sperrin Mountains; highest concentrations are mostly from moraine-covered moorlands in the Low Sperrins, between Omagh and Draperstown;

    ii. over the moors north and west of Dromore, on schist and Old Red Sandstone bedrock;

    iii. on moors near Castlederg, over schist bedrock;

and iv. over Upper Carboniferous bedrock on Slieve Beagh, between Clogher and Rosslea.

Low levels of the same metals (below 1,000 ppm Mn, 4% Fe, 20 ppm Co and 60 ppm Zn) also tend to occur together. The patterns are found mainly in lowlands:

i. over Triassic and Lower Carboniferous bedrock, in the east of the Tyrone area, particularly near Draperstown, around Dungannon and along the Clogher Valley;

ii. over the Old Red Sandstone, east of Enniskillen and between Ballygawley and Sixmilecross;

iii. over the Lower Carboniferous, between Kesh and Omagh;

and iv. over the Dalradian and Lower Carboniferous between Strabane and Newtownstewart.

The highest concentrations of these metals occur in streams in which sediments are coated by precipitates of Mn and Fe oxides. They are found mainly in upland areas characterised by acid leached soils such as climatic peats, podzols and gleys. The patterns are therefore considered to be related more closely to the secondary processes of soil leaching and sediment enrichment than to regional variations in metal abundance.

3. Lead contents are mostly in the range 30-80 ppm and show little areal contrast. Analytical precision was mostly poor (± 80% at the 95% confidence level) and many variations appeared to be analytical batch effects. A pattern of raised Pb (> 100 ppm), Zn and Cu in sediments over Silurian bedrock in the Keady district is related to known base-metal mineralisation.

4. High background to possibly anomalous levels of Zn (130 ppm) occur in sediments from the Derg Valley and around Bessy Bell Hill. This pattern does not appear to be the result of secondary enrichment associated with the precipitation of Mn oxides in streams. Streams on Bessy Bell have been shown to be draining an area of base metal mineralisation. The remainder may reflect a local increase in Zn in the Lower Dalradian.

5. The abundance of copper is very low over most of the Tyrone area with more than half of the samples containing less than 13 ppm Cu. Patterns of low values are found especially east of Aughnacloy, east of Enniskillen, near Newtownstewart, between Kesh and Omagh and around Pomeroy. They occur in sediments over all bedrock units, including parts of the Low Sperrins where Co, Fe, Mn, and Zn are enriched. Values exceeding 50 ppm Cu are rare, even in the mineralised area around Keady.

6. Molybdenum is below the detection limit (2 ppm) over most of the Tyrone area. Sediments containing 2-10 ppm Mo occur south of Enniskillen and near Drumquin, over the Carboniferous Calp limestone, and sporadically over the Low Sperrins and Slieve Beagh

7. Obvious sources of contamination were avoided during sampling and as a result very few samples appear to have been affected. Several sediments rich in Cu, Pb and Zn near Keady are probably contaminated by mine waste and some others, for example near Aughnacloy and Cookstown, were found to be contaminated by urban waste.

9.12 Geochemical Patterns of Significance to Mineral Exploration

8. Patterns of stream sediments containing anomalous levels of Cu, Pb and Zn were followed up in two areas. Detailed sediment sampling was guided by rapid field analysis for cold-extractable heavy metals, with subsequent confirmation by total metal analysis in the laboratory.

9. A pattern of anomalous levels of Pb (> 300 ppm) and Zn (> 500 ppm) near Keady is unrelated to known mine workings. The main anomaly occurs in an area 1¾ x ¾ miles around Mullaghdoy Hill. Work by Larsson (1969, pers. comm.) suggests that the overall anomaly extends a further 5 miles south, to Mullyash Mountain, Co. Monaghan.

The anomaly lies approximately along the strike of a mineralised vein found near Keady. The coextensive Pb and Zn patterns suggest that the anomaly is syngenetic, with the metals derived by clastic dispersion from this or a similar vein. Some hydromorphic mobilisation of Zn has occurred, however, since all sediments containing over 1,500 ppm Zn were organic and the Zn anomaly also appeared to have been extended laterally by coprecipitation with Mn oxides in free-running streams on the hill sides.

10. Threshold to probably anomalous contents of Pb and Zn occur in sediment from streams draining Bessy Bell Hill, near Newtownstewart. The anomaly, with Zn levels exceeding 800 ppm, lies in an area 1½ x ½ miles in the Barons Court Forest. The highest concentrations of Zn (> 1,500 ppm) and Pb (> 200 ppm) are found in iron slime seepages, reaching a maximum of over 10% combined Pb and Zn.

Soil sampling over part of the area has established a relationship between soil metal content and pH. Raised levels of the metals occur where pH is over 4.5, reaching maxima of 5% Fe, 450 ppm Mn and 7,500 ppm combined Pb and Zn in some valley soils.

The close association of Pb and Zn with Fe and Mn, particularly in secondary accumulations, suggests that the anomalies are epigenetic, with the metals dispersed by a hydromorphic mechanism. The metals are being mobilised in acid and/or reducing environments and transported in groundwater solution. Precipitation occurs where the groundwater enters a less acid, more oxidising environment in soils and sediments. Strong precipitation, developing hydromorphic anomalies occurs in areas of cleared and replanted forests, where the soils and streams are less acid and the zone of water-table fluctuation shallower than in adjacent areas of mature forest.

Lead is not normally very mobile in the secondary environment, and is precipitated in seepages without giving long drainage trains. The metal is coprecipitated in the presence of hydrolysing ferric iron, with the reaction possibly catalysed by the iron bacterium Leptothrix ochraceae.

Boulders containing disseminated galena, and baryte veins with sphalerite and galena, were discovered within the area of the drainage anomaly. Base-metal mineralisation is previously unrecorded from this area.

11. It is concluded that, in glaciated terrain with conditions similar to those in Northern Ireland, the reconnaissance survey technique is most applicable:

i. in areas of thin, siliceous drift. Thick drift may dilute clastically dispersed metals whilst its depth, particularly if calcareous or impervious, may inhibit hydromorphic dispersion so that no samples have anomalous metal concentrations.

ii. in uplands. Although false anomalies may be expected under the environmental conditions prevailing in such areas, the absence of these conditions in lowlands can restrict hydromorphic dispersion so that where drift is exotic, any epigenetic anomalies may be weak and indetectable.

iii. where mineralisation is associated with a regional increase in metal abundance. The reconnaissance technique only aims to detect such increases, for individual anomalies may be missed because of the wide sampling interval.

Thus, the absence of individual anomalies and patterns of raised metal abundance in drift-covered lowlands in the Tyrone area, such as in the Midland Valley, does not preclude the existance of mineralisation.

9.13 Patterns of Significance to Agriculture

12. The restricted patterns of sediments containing 2-8 ppm Mo over the Calp limestones near Enniskillen and Drumquin reflect

similar or lower contents in some soils, but the areal extent of such soils is mostly very small. Molybdeniferous soils are most common in the area south of Eniskillen , but the contents ($\nless$ 5 ppm Mo) are lower than previously considered to be potentially hazardous to livestock, hence their agricultural significance is uncertain. However, the results indicate that the technique may be used to locate areas of molybdeniferous soils in strongly glaciated terrain.

13. Patterns of sediments containing 5-12 ppm Cu are widespread in the Tyrone area, occurring over several bedrocks and in varying environmental conditions. The correlation between the Cu contents of soils and sediments has been studied as a step towards determining the agricultural significance of the patterns. Comparative studies have been made concurrently into the soil-sediment correlation for zinc.

14. The Cu content of sediments varies according to their mechanical composition and organic carbon content. The sediments with low Cu contents (5-12 ppm) are well sorted sands and silty sands containing $< 0.5\%$ organic carbon, whereas many sediments with higher Cu contents (20-35 ppm) are poorly sorted silts and muds containing $> 1.5\%$ organic carbon. This range of sediment type and Cu content, similar to that of the main reconnaissance patterns, has been demonstrated in adjacent sites in the same stream. The sands and silty sands form the active sediment normally sampled in a reconnaissance survey, so that the fine, organic material, accumulating under slow flowing waters, is collected only rarely.

Variations in the range 5-35 ppm Cu can, therefore, reflect changes in stream sorting capacity, which depend in turn upon stream velocity and local relief. Mostly, such changes lead to differences between single samples but, in some instances, may result in regional patterns. Thus, the raised contents (20-35 ppm Cu) around Upper Lough Erne reflect the low relief, sluggish streams and poorly sorted, organic sediments of the area. They reflect geology indirectly, in that relief can be a function of lithology.

15. Soils have been sampled in regions delineated by patterns of 5-12 ppm Cu in sandy sediments and 20-35 ppm Cu in organic sediments. The Cu contents of most subsoils (12-18 inches) are similar to those of the sandy sediments, whereas the contents of most topsoils (0-6 inches) are similar to those of fine organic sediments.

In all catchments, low, possibly deficient, levels of Cu ($<$ 13 ppm) in topsoils are found only in acid, peaty areas and on steep slopes. However, the stream sediment patterns are not related to significant variations in the areal abundance of such soils.

16. The copper contents of subsoils are reflected by those of sandy sediments, whether they contain low levels ($<$ 13 ppm Cu) or raised levels ($>$ 20 ppm Cu). Comparisons of sediments of similar mechanical composition therefore indicate regional differences in the Cu abundance related to the underlying geology. They cannot, however, necessarily indicate the total Cu content of topsoils since this is influenced in addition by pH, organic matter status and slope.

17. The copper content of most acid soils (pH $<$ 5.0) is low, but in less acid soils the metal is gradually accumulated in the organo-mineral complex of the topsoil. On steep slopes, however, the organic topsoils are shallower (5 inches) than in flatter areas (12 inches) and have a lower Cu content. This is partly due to the rapid run-off at such sites which tends to remove the organic surface horizons and restrict copper accumulation. As in streams, therefore, the distribution of copper can be controlled by the influence of relief on the physical dispersion of the organic fraction.

18. Although copper deficient soils may be found in parts of each area delineated by the low-Cu ($<$ 13 ppm) patterns, not all topsoils have low copper contents. Acid stream waters, or sediments enriched in Mn, Fe, Co and Zn, however, can indicate the occurrence of strongly leached soils. Consequently, it is suggested that the patterns may indicate areas of acid, potentially deficient soils when these are either:

i. acid stream waters (pH $<$ 6.0), with sediments containing low background Mn ($<$ 1,000 ppm) and Zn ($<$ 50 ppm);

or ii. near neutral stream waters, with sediments secondarily enriched by oxide precipitation to over 2,000 ppm Mn and 125 ppm Zn.

19. Variations in zinc content between mechanical fractions of sediments are less pronounced than for Cu. Zinc does not appear to accumulate with organic matter in the soil, and shows no regular

variations between either soil horizons or soils in different topographic locations. As with copper, however, it is lowest in acid soils.

20. Stream sediments containing background levels of Zn tend to reflect similar levels in non-acid soils (pH $>$ 5.0) and soil parent material. High background to above threshold levels of Zn in sediments, accompanying similarly raised Mn contents, however, may result from leaching and reprecipitation processes of the secondary environment. In these cases, there is little correlation between the metal contents of sediments and the majority of soils.

21. The Cu contents of mixed herbage from several catchments is mostly marginal with regard to the dietary requirements of cattle (10 ppm D.M.; A.R.C., 1965). Herbage zinc contents, however, are mostly below 35 ppm D.M., well under the recommended level of 50 ppm D.M.

9.14 Patterns related to the Secondary Environment

22. The major features of the stream sediment reconnaissance are the coincident Fe-Mn-Co-Zn patterns. Detailed studies have been made of the chemistry and micromorphology of sediments and soils from contrasting areas in Central Tyrone to determine the origin of the patterns and their significance in soil science and agriculture.

23. High concentrations of the metals in stream sediments (30% Fe_2O_3; 0.8-3.0% Mn; 50-150 ppm Co; 200-450 ppm Zn) are associated

with ferromanganese precipitates, of which four main types were observed in the Tyrone area:

i. Iron slime seepages occur in ditches as gels composed of amorphous iron oxides and sheaths of filamentous bacteria, probably Leptothrix ochraceae. They tend not to concentrate metals other than iron and possibly manganese, except near mineralisation.

ii. Flocculant iron oxides form ochreous dispersions in some acidic streams (pH < 6.0) but rarely stain the sediment or influence its metal content.

iii. Manganese oxides form dark brown to black precipitates, with an ochreous lower layer, which encrust pebbles in many rapidly flowing streams. They can concentrate Co ($>$ 200 ppm) and Zn ($>$ 1,000 ppm) in the outer manganiferous layer. Goethite was tentatively identified in one such precipitate.

iv. Gelatinous iron oxide precipitates are found in some upland streams as coatings 0.5 cm. thick over black manganiferous precipitates and on all sediment types. They are organic (10% organic carbon) and have a greenish surface film composed of bacterial filaments - possibly a Clonothrix species - over an amorphous gel of ochreous iron oxides.

Metal enrichment of the minus 80-mesh fraction of the sediment only occurs where the manganiferous precipitates are accompanied by the gelatinous iron oxides. The former are more widespread and richer in Mn, Co and Zn than the Fe oxides but are only sufficiently abundant to influence sediment metal contents in streams in which both forms are found.

24. Stream sediments in the Low Sperrins area of Central Tyrone are strongly enriched in Fe, Mn, Co and Zn. Soils in this area are predominantly acid or waterlogged, with peaty and reclaimed podzols on hill slopes and peaty gleys and basin peats in valleys.

The upper horizons of the peaty podzols and most horizons of the peaty gleys are very acid ($pH < 4.5$) and strongly depleted in Co, Cu, Fe, Mn and Zn. In peaty podzols, some reprecipitation of iron occurs in the B horizon, but the highest metal contents (2.5-12.0% Fe; 350-1,000 ppm Mn) are associated with dark, organic Fe-Mn precipitates in the B/C horizons. Some iron staining, with only slight enrichment, can occur in deep, less acid (pH 5.4) horizons of peaty gleys. In general, the metals are leached from these peaty soils and, although there is some reprecipitation elsewhere in the sequence, for example in stream banks and adjacent to iron slime seepages, the remainder enters the stream to enrich the sediments.

The reclaimed podzols are less acid and less leached than the peaty soils. Metal mobilisation, leading to strong horizon development, is taking place, but reprecipitation is probably completed within the profile, with Fe concentrated at the top of the B horizon and Co, Mn and Zn in the B/C horizon.

25. In areas of Central Tyrone where sediment enrichment is slight or does not occur, soils are predominantly acid brown earths (pH 5.5 to 7.5). There is often little differentiation of metals between either soil horizons or other profiles in the sequence, suggesting that the metals are less mobile than in the Low Sperrins and that little leaching is taking place. Co, Fe, Mn and Zn are mobilised in areas of acid or gleyed soils, however, with precipitation either elsewhere in the soil sequence or in the stream. Locally, these depletion and enrichment phenomena can be as strong as in the Low Sperrins, but the extent of the soils affected is too small to influence the sediment metal content.

26. Precipitated manganese in soils has been estimated by analysis for the easily reducible fraction. In all profiles, the proportion of easily reducible to total Mn is below 5% in acid or gleyed horizons, but becomes higher in horizons in which active precipitation is taking place. The proportion can be over 10% in B and B/C horizons of peaty podzols and exceeds 50% in enriched bank soils. Proportions of over 15% also occur in many horizons of relatively unleached soils, such as the reclaimed podzols of the Low Sperrins and brown earths of the controls. This suggests that although metals are being mobilised in such soils, they are being actively reprecipitated.

27. A study of micromorphology has shown differences in soil fabric and the occurrence of ferromanganese accumulations related to the differing chemical environments of the contrasted areas. Optical microscopy, scanning electron microscopy and electron probe micro-analysis have been used in the investigation.

28. Soils in the Low Sperrins, developed on sands and gravels, are coarse with a silasepic fabric, whereas those in the control catchments, developed from sands and boulder clays, tend to be fine with a variety of sepic fabrics. These differences in texture and fabric, largely inherited from the parent materials, influence the degree of leaching and metal depletion from the soils. Although the depletion of iron and associated metals can occur in heavy, gleyed horizons, it can be stronger in coarse porous soils since these have a lower exchange capacity and hence a lower resistance to acid leaching. The absence of fine soil plasma in such soils, as in the Low Sperrins, also reduces the surface area on which the nucleation and accumulation of iron oxides can take place, so that less metal is retained within the profile.

29. The visible appearance of free iron oxides corresponds to variations in the profile distribution of both total metal (Fe, Mn, Co and Zn) and precipitated Mn, shown by the proportion of easily reducible to total Mn. The oxides are rare or absent in acid or gleyed horizons, suggesting that metals released during pedogenesis do not reprecipitate under such conditions. They become more common in less acid or better drained horizons in weathering primary minerals, ferrans and glaebules. In general, the most mobile metal precipitates either as illuviation ferrans, enriching soil horizons lower in the profile or sequence, or in the stream sediment. Where mobility within the soil is restricted by high Eh-pH conditions, the metals form either diffusion ferrans or glaebular accretions.

30. In the podzolic soil sequence of the Low Sperrins, ferrans are the most important iron oxide separations. Glaebules are rare, except in Fe-Mn enriched bank soils.

Diffusion ferrans in the organic A_{1-2} horizons of reclaimed podzols suggests that metals mobilised within the horizon are partially reprecipitated in the vicinity of voids and skeletal grains. In lower horizons, illuviated iron oxides occur as:

i. yellow, diffuse ferrans in podzolic B horizons;

and ii. dark ochre, organic and manganiferous ferrans in B/C horizons of peaty podzols and gleys, and in enriched bank soils.

These ferrans cause marked enrichment only where the s-matrix is fine and the oxides form thick precipitates and permeate the adjacent plasma.

31. In the brown earths of the control catchments, free iron oxides separate as both ferrans and glaebules. Diffusion ferrans are common in imperfectly drained horizons and can develop into root mottles and pedotubules. It appears from the present study that most metal mobilised in such horizons in a groundwater gley are lost from the profile but in a surface-water gley enrich underlying horizons as manganiferous illuviation ferrans.

Iron oxide glaebules occur in three forms:

i. discrete rounded bodies (0.01-5.0 mm), occasionally weakly zoned, with a manganiferous core;

ii. discrete bodies with a diffuse halo of oxide enriched plasma;

and iii. diffuse plasma enrichments, up to 5 mm across.

Glaebules are only formed in soils in which there is a fine s-matrix for nucleation and growth. Their development suggests that, although active weathering is occurring, metal mobility and depletion are restricted by high pH and/or Eh.

32. Secondary oxide accumulations in the soils examined were found to be amorphous, although radial structures in pedotubules may indicate incipient crystallisation.

33. The studies of the contrasting areas in Central Tyrone have shown that the migration of Fe and Mn in the soil-sediment system is controlled by the physico-chemical environment defined by pH and Eh. The metals are mobilised in the low pH and Eh conditions of acid and waterlogged soils and precipitate either on entering less acid and/or more oxidising conditions in soils or streams, or as pH and Eh rise. The differentiation between the metals in some soil profiles, and the layering observed in stream precipitates and some glaebules and ferrans, are due to partition during precipitation. The iron species are least stable and precipitate first, followed by manganese as pH and Eh continue to rise and the iron concentration falls.

The high mobilities observed in many soils suggest that the metals are being stabilised in solution by the formation of organo-metallic complexes and colloids. The strongest mobilisation phenomena in the area are associated with peats and may be due to:

i. humic compounds derived from peat;

or ii. non-humic compounds forming strong complexes under very acid conditions, implying that high mobility and peat development are independant reactions to the siliceous soil and prevailing climatic environment.

34. Cobalt and zinc migrate under similar conditions to Fe and Mn. During precipitation, they are preferentially sorbed to Mn oxides, resulting in the close correlations between these metals observed in soils and, in particular, stream sediments.

Although copper is mobilised under similar conditions to Co, Fe, Mn and Zn, it does not coprecipitate with them. Copper can form stronger organo-metallic complexes than other transition metals and probably remains in solution, or becomes fixed to organic matter, under the conditions prevailing in the Tyrone area. Consequently, the metal is not concentrated in ferromanganese accumulations and does not become enriched in stream sediments.

35. In most areas where the regional geochemical reconnaissance shows background levels of Co, Fe, Mn and Zn in precipitate-free streams, there is a close correlation between the metal contents of stream sediments and soils. The metal in the sediments is mostly derived from erosion of bank soils which, in the absence of strong chemical differentiation in the soil sequence, will represent the majority of soils in the catchment.

Moderate oxide precipitation, resulting in black manganiferous crusts on pebbles, occurs in over 50 per cent of the streams in the Tyrone area. They do not enrich the active stream sediments relative to most soils. The metal in these sediments is again derived by physical erosion, although the occurrence of precipitates indicates that leaching and differentiation are taking place in the soil sequence. In most of the Tyrone area, therefore, clastic processes are the most important mechanism of metal translocation in the soil-sediment system.

Sediments are enriched relative to soils when the chemical mobilisation processes of the secondary environment become extreme. In the Tyrone area, this occurs only in streams in which black Mn-Fe oxides are accompanied by gelatinous Fe oxides. Strong chemical fractionation is occurring in the soil sequence and chemical processes are the most important mechanisms of metal translocation. Such processes are strongly influenced by the interaction of climate, vegetation, soil type and geology. In the Tyrone area, enrichment occurs where rainfall exceeds 45 inches per annum, falling in about 240 raindays (i.e. above about 800 ft. O.D.). The fractionation processes are promoted by peat accumulation, podzolisation and/or gleization, and a siliceous bedrock, and retarded by cultivation, free drainage and a basic or calcareous bedrock.

36. In areas where stream sediments are enriched in Co, Fe, Mn and Zn to levels exceeding the regional mean content by two or three standard deviations, many soils may be depleted and hence potentially deficient in these metals. Such deficiencies may only become apparent, however, when the land is cultivated and metal mobility and availability decline.

Enrichments of this magnitude also represent threshold and probably anomalous levels of Zn unrelated to mineralisation. In the Tyrone area, such false anomalies have not been satisfactorily distinguished by the determination of exchangeable or easily reducible Mn in the sediment.

True Zn anomalies may be recognised by raised contents of other metals such as Cu and Pb, which are not secondarily enriched. In areas of exotic drift, however, any true superjacent anomalies must be hydromorphic so that Cu and Pb will remain at background levels. Such anomalies may show as deviations from the linear relationship between total Zn and total Mn found in areas of false secondary enrichment, but the distinction is unreliable, particularly in regions of contrasting geology.

9.15 The Scope of Regional Geochemical Reconnaissance

37. It is concluded from the current studies and previous work in glaciated terrain in the British Isles (Chapter 1) that multi-element regional geochemical reconnaissance has immediate applications in detecting:

i. regions of increased metal abundance associated with mineralisation;

ii. geochemical facies variations within geological formations;

iii. areas where molybdeniferous and seleniferous soils may lead to toxicity disorders in livestock;

and iv. areas in which low levels of Co, Mn and possibly Zn in soils may lead to deficiency conditions in plants and livestock.

In these cases, there is a fairly direct relationship between the metal contents of sediments, soils and overburden and/or bedrock. As has been shown, however, this relationship can be modified by the influence of local environment on metal dispersion. Thus, as a result of sorting, the Cu content of active sediments tends to be lower than that of the majority of soils. Conversely, as a result of soil leaching, sediments in wet, upland areas can be enriched in Co, Fe, Mn, and Zn to give false anomalies and spurious distribution patterns unrelated to regional variations in metal abundance.

Despite these limitations, however, multi-element geochemical reconnaissance has potential in many fields. Continuing research in the Applied Geochemistry Research Group includes the further delineation of geochemical provinces and areas of latent or subclinical trace element disorders in plants and animals, and investigating possible applications in medical geography and pollution surveys. As an integral part of these programmes, techniques are being developed for the handling, presentation and statistical analysis of the large volumes of data involved.

9.2 RECOMMENDATIONS FOR FUTURE RESEARCH

The following topics, arising out of the work described in this thesis, warrant further investigation:

1. Mineral exploration

Stream sediments, soils and rocks should be sampled in the Derg Valley to confirm the increased abundance of Zn in the Lower Dalradian shown by the reconnaissance survey. The programme should investigate the possible relationship between this increased abunddance and the further occurrence of base metal mineralisation of the type at Barons Court.

2. Agriculture

i. Further sediments, soils and herbage should be sampled south of Enniskillen to assess the agricultural significance of the molybdenum pattern in the area.

ii. The possible changes in the availability of Cu and Zn with season should be studied in areas where subsoils and some topsoils have low metal contents. It is also important to assess the Zn requirements of livestock since most herbage sampled was deficient according to the A.R.C. minimum of 50 ppm D.M.

3. Soil-stream sediment chemistry

i. A study made of the mode of precipitation of Fe-Mn oxides in streams to determine the conditions, rate and periodicity of deposition, the role of bacteria in catalysing the reactions and the distribution of coprecipitated elements and compounds within the accumulations. A study of regional variations may indicate periods during which sediment sampling will be least affected by secondary enrichment.

The scavenging power of micro-organisms and oxides may have uses in reducing water pollutants, such as agricultural fertilizers leached from soils.

ii. Ferromanganese accumulations in soils should be studied to determine:

i) the conditions and rate of formation and degradation;

ii) the relationship between their morphology and the chemical extractability of Fe and Mn;

iii) the distribution and availability of other elements (Ba, Ca, Mg, P, S, Zn, etc.) in relation to morphology; and

iv) their ability to corrode and replace quartz and other minerals.

Investigations of this type, aided by micromorphological techniques of the type described in Chapter 7, can give detailed information on the locations of metals in soils and lead to a fuller understanding of dispersion mechanisms and the bulk properties used in their estimation.

APPENDIX A ANALYTICAL TECHNIQUES.

The analytical techniques employed during the current studies are mostly procedures adopted as standard by the Applied Geochemistry Research Group.

1. **Analytical precision.** Precision has been calculated from replicate analyses of control samples.

From the standard deviation $s = \sqrt{\frac{\Sigma (x_i - \bar{x})^2}{n - 1}}$

precision at the 95% confidence level is given by

$$\frac{200\ s}{\bar{x}}\ \%$$

where
x_i = individual determination.
$\bar{x}$ = arithmetic mean of all determinations.
n = no. of determinations.

2. **Cobalt, copper, iron, manganese, lead and zinc.**

Rock, soil and sediment samples are digested in a 4 : 1 mixture of nitric/perchloric acids and evaporated to dryness. The residue is leached in 1M. HCl and metal contents are estimated using a Perkin-Elmer 303 atomic absorption spectrophotometer. It is found, however, that when samples contain more than 0.2% Mn, a black, insoluble residue of MnO_2 may be left after the acid digestion. Full solution is obtained by reduction with 30 mg of potassium metabisulphite and leaching with 2M. HCl. This solution is diluted to 1M. HCl and metal contents estimated as before, against standards spiked with potassium metabisulphite. Interference and contamination are negligible and the modified leaching procedure has been used for all determinations. Precision : ± 5 - 20% through range.

Herbage has been treated similarly; 5.0 gm of milled herbage are decolourised with nitric acid prior to digestion with the acid mixture and slow evaporation. The residue is leached with 1M. HCl and filtered before analysis for Cu, Mn, and Zn. Potassium metabisulphite is not added.

3. Molybdenum. Molybdenum is determined colorimetrically by the method of Stanton and Hardwick (1967). Samples are fused with potassium bisulphate and the residue leached with hydrochloric acid. Suitable aliquots are reacted with zinc dithiol to form the green Mo-dithiol complex which is extracted with petroleum spirit and compared with standards. Precision : better than ± 25%.

4. Cold-extractable heavy metals (cxHM).

Heavy metals are estimated rapidly in the field by a colorimetric method (after Bloom, 1955). Approximately 0.1 gm of fresh sample are reacted with 1M. ammonium citrate and extracted by shaking with dithizone for 15 seconds. Additions of dithizone are contained until the colour of the solvent phase is the same as that of a standard. In the present study, the method was modified further, as described in Chapter 4.

5. Organic carbon.

The method is modified after Schollenberger (1927), as described in A.G.R.G. Tech. Comm. 32 (1967). Samples are oxidized with potassium dichromate and sulphuric acid, and organic carbon estimated by titration with ferrous ammonium sulphate. Precision : better than ± 20%

6. Exchangeable and easily reducible manganese.

The method is adapted from Sherman and co-workers (1942) as described by Horsnail (1968). Exchangeable Mn is determined by shaking the sample overnight with ammonium acetate (pH 7.0); exchangeable plus easily reducible Mn are determined by shaking overnight with ammonium acetate with 0.2% hydroquinone (quinol). The solutions are filtered and Mn contents determined by atomic absorption spectrophotometry using suitably spiked standards. The content of the easily reducible fraction is obtained by difference. Precision : ± 8 - 25 % through range.

7. Eh and pH measurements.

pH. Soil pH is determined in duplicate within hours of sample collection by inserting the glass calomel electrode of a portable pH meter into a 1 : 1 slurry of soil in de-ionized water. Water pH is measured either directly in the stream or on two samples collected in test tubes.

The meter is calibrated at pH 4.1 and 9.2 using buffer tablets dissolved in de-ionized water.

Eh. Soil Eh is measured by inserting the platinum electrode of a portable meter directly into the soil, allowing 15 minutes for equilibration. Water pH was measured after 5 minutes equilibration. The meter was standardised at 0.43 volts using the ZoBell solution (ZoBell 1946). The limitations of the method, particularly in water unsaturated soils, are realised, but meaningful results can be obtained (Chapter 8.3).

APPENDIX B. GLOSSARY OF MICROMORPHOLOGICAL TERMS.

The following terms (after Brewer, 1964) have been used to describe the micromorphology of the soils.

1. S-MATRIX: the soil matrix, which includes skeletal grains, plasma and voids.

2. PLASMA: the plasma is that part of a soil which is capable of being or has been moved, reorganised and/or concentrated during pedogenesis. It includes all the material of colloidal size which is not bound up in skeletal grains.

3. PLASMA FABRICS.

   i. Asepic fabrics: domains in the plasma are mainly unorientated with regard to each other. (Domains are clusters of anisotropic plasma grains in which some degree of orientation exists).

      a. Argillasepic: plasma dominantly of clay minerals.

      b. Silasepic: plasma dominantly of clays and silt particles.

   ii. Sepic fabrics: domains in the plasma are mainly orientated with regard to each other.

      a. Insepic: isolated patches have a striated orientation.

      b. Mosepic: numerous patches are striated and may adjoin.

      c. Vosepic: orientation is parallel to void walls.

      d. Skelsepic: orientation parallel to surfaces of skeletal grains.

      e. Lattisepic: two sets of short, discontinuous domains, usually orientated approximately at right angles.

      f. Omnisepic: the plasma exhibits a complex, striated, orientation pattern.

4. RELATED DISRIBUTION OF PLASMA AND SKELETAL GRAINS.

   i. Porphyroskelic: plasma occurs as a dense groundmass in which skeletal grains are set after the manner of phenocrysts in a porphyritic rock.

ii. Agglomeroplasmic: plasma occurs as a loose or incomplete fillings in the spaces between skeletal grains.

iii. Intertextic: skeletal grains are linked by intergranular braces or are embedded in a porous groundmass.

iv. Granular: there is no plasma or all plasma occurs as pedological features.

5. VOIDS.

i. Packing voids: voids due to the random packing of single grains or compound individuals.

ii. Vughs: relatively large, irregular voids.

iii. Vesicles: vughs with smooth, regular walls.

6. CUTANS: modificatioms of the texture, structure or fabric at natural surfaces in soils due to concentration of particular soil constituents or in situ modifications of the plasma.

i. Surfaces affected: Cutans can form on the surfaces of peds, grains and voids. Neo-cutans form near, but not on, such surfaces

ii. Composition of cutans: cutans can consist of any of the component substances of the soil material.

a. Argillans: consist mainly of clay minerals.

b. Ferrans: consist of iron oxides.

c. Mangans: consist of manganese oxides.

7. GLAEBULES: three dimensional units within the s-matrix, usually approximately prolate to equant in shape. They are recognised because of the concentration of some constituent and/or a difference in fabric compared with enclosing soil material and/or because they have distinct boundaries. Nodules and concretions are types of glaebule.

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