GEOLOGICAL INTERPRETATION OF THE GEOCHEMISTRY OF STREAM SEDIMENTS, WATERS AND SOILS IN THE BRISTOL DISTRICT, WITH PARTICULAR REFERENCE TO THE MENDIP HILLS, SOMERSET

by

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ABSTRACT

A regional stream sediment geochemical survey of England and Wales has revealed striking enrichment of a number of elements in the area around Bristol and the Mendip Hills. This enrichment is related to the normal geochemical variations in the bedrock of the area, and to the presence of mineral deposits and industrial activity. However, comparison with other geologically similar areas, where regional geochemical enrichment is not as great, suggests that some previously unexplained factors have contributed to the enrichment in the Bristol area.

Detailed studies based on geochemistry of stream sediments, ground waters, surface waters and soils from within the study area have shown that most of the regional geochemical enrichment can be related to an episode of weathering and mineralisation, which took place under hot and dry conditions during Permian and Triassic times, and affected a major part of the study area. Geochemical variations on both local and regional scales provide evidence that all of the important mineral deposits within the study area, including those of lead and zinc, iron and manganese, and strontium, were formed during this episode.

It has been shown that ground waters and soils can be used successfully for regional mineral exploration programmes in karstic regions, and in fact a zone of previously unknown lead and zinc mineralisation on the Mendip Hills has been detected by both of these methods. It has also been shown that geostatistical methods are useful for determining optimum sample spacing parameters for geochemical surveys.

Several computer programs have been written as part of the research. These include a method for realistic interpolation of stream sediment data onto a regular grid, and an interactive-graphics routine for interpretation of probability graphs.

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"As to the finding out the Calamine, which I think the first thing to inform you of, the Groovers tell me that there is no certainty at all, but that it is a meer Lottery..."

Giles Pooley, 1693, on the Mendip zinc mines

"...there are no certain signes above ground, that afford any probability of a Mine, to my knowledge."

Joseph Glanvil, 1667, on the Mendip lead mines

CHAPTER 1 INTRODUCTION

1-1 Objectives of the Research

A regional stream sediment survey of England and Wales, carried out by the Applied Geochemistry Research Group at Imperial College (Webb et al, 1978), has revealed a number of areas of striking geochemical enrichment. One of the most extensive of these areas is centred around Bristol and the Mendip Hills, in the counties of Avon and Somerset. Here, many of the samples from an area of several hundred square kilometres, fall within the top 5% of all the data from England and Wales. Elements which are specifically enriched include barium, cadmium, calcium, copper, lead, molybdenum, strontium and zinc. For most of these elements the enhanced concentrations have not been adequately explained on the basis of what is known about the geology and industry of the area. One of the primary objectives of the research described in this thesis is to elucidate the features which control stream sediment geochemistry in the area, and to advance some explanation for the high concentrations observed over such a broad region.

One of the most important of the features which affect the geochemistry of surficial materials, is the presence of economic minerals and associated alteration. Part of the research involves study of the distribution and types of mineral occurrences within the area, and an attempt to gain some understanding of their genesis.

The lead and zinc ores of the study area are essentially confined to the Carboniferous Limestone anticlinal areas and the surrounding Dolomitic Conglomerate. In these karstic uplands, drainage is primarily below surface, and regional stream sediment geochemistry cannot be used as a mineral exploration tool. Part of the research involves an investigation into alternative methods of regional geochemical exploration in a karstic area. Techniques studied include geochemistry of widely spaced soil samples, and geochemistry of ground waters.

1-2 Nature of the Research

The research program has involved study of a variety of geochemical data from samples collected by the author and by others. The data have been

interpreted in relation to lithological variations, the effects of mineralisation, the effects of urbanisation and industry, and the effects of geochemical fractionation within the sample media.

The Main topics of investigation are as follows:

1) geochemistry of stream sediments,
2) geochemistry of ground waters from the Mendip Hills with specific reference to hydrological characteristics, the effect of base metal mineralisation and the effect of flow rate variations,
3) geochemistry of soil samples from mineralised and unmineralised areas of the Mendip Hills, with emphasis placed on studying spatial variations in the geochemistry of the mineralisation,
4) geochemistry of soil samples from the areas of celestite mineralisation northeast of Bristol,
5) a review of available information on the geology and depositional history of the important mineral deposits within the study area, and presentation of an original and comprehensive model to explain their genesis,
6) development of computer programs for geochemical data processing and interpretation,
7) assessment of the applicability of geostatistical analysis to geochemical sampling.

1-3 Presentation

An overview of the geology, geomorphology, climate and industry of the study area is presented in Chapter 2; the results of the various geochemical studies are presented in Chapters 3 to 6; the depositional history of the ore deposits is discussed in Chapter 7; and the summary and conclusions are presented in Chapter 8.

Sample preparation and analytical procedures, along with estimates of sampling and analytical precision are given in Appendix A. Listings of computer programs written for data processing and for statistical analysis, along with comprehensive description and discussion of their use, are included in Appendices B, C, and D. A summary of the results of the geostatistical analysis is given in Appendix E. Alternative mineral exploration methods, and suggestions for further research are presented in Appendix F.

CHAPTER 2 THE STUDY AREA

2-1 Location

The area of study comprises some 2 400 km^2 centred around the city of Bristol in southwest England (Figure 2-1). Parts of the counties of Gloucestershire, Avon, Wiltshire, Somerset and Gwent are included. In terms of the National Grid, the area lies within the 100 km square ST, and is bounded by lines 340 and 380 km east, and 140 and 200 km north. National Grid co-ordinates are given to the nearest 100 m. Localities referred to are shown on Figure 2-2.

2-2 Geology

The east-west trending boundary between the Caledonian and Variscan tectonic provinces lies just north of Bristol (Figure 2-3), and the study area exhibits tectonic and lithological features of both provinces. The Caledonian rocks, to the north, are characterised by folding with north-south and northeast-southwest trends. The Variscan rocks, to the south, are characterised by east-west trending folding and thrust faulting. Post Variscan strata, deposited on a high-relief post-Carboniferous unconformity, are only slightly deformed.

The geology, as shown in Figure 2-4, has been taken from 1:63 360 scale maps published by the Institute of Geological Sciences (Sheets 250, 251, 264, 265, 280 and 281). A list of formations is given in Table 2-1.

The oldest rocks are the Micklewood Beds and Breadstone Shales of Lower Tremadoc age, outcropping near Charfield (725 925) and Berkeley (685 995). The strata include micaceous shale with subordinate sandstone pockets and layers (Smith and Stubblefield, 1933).

In the north, near Berkeley, Silurian limestone, sandstone and shale unconformably overly the Breadstone shales (Kellaway and Welch, 1948). In the eastern Mendip Hills, Silurian fossiliferous tuff and lava are succeeded by augite and oligioclase-andesine bearing andesite, and mudstone (Green and Welch, 1965). The base of the Silurian is not seen here.

Much of the northwest corner of the study area is underlain by Old Red Sandstone (ORS) of Devonian age. The lower ORS, which is up to 1 200 m thick, includes red sandstone with minor mudstone and limestone - the St. Maughans

Figure 2-1 Location of the study area

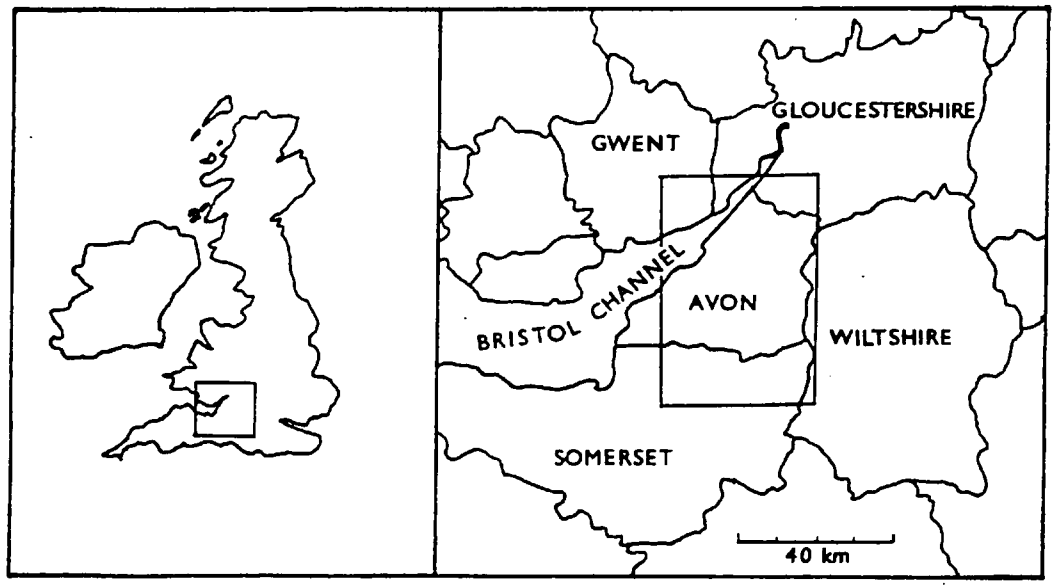


Figure 2-2 Localities referred to in the text

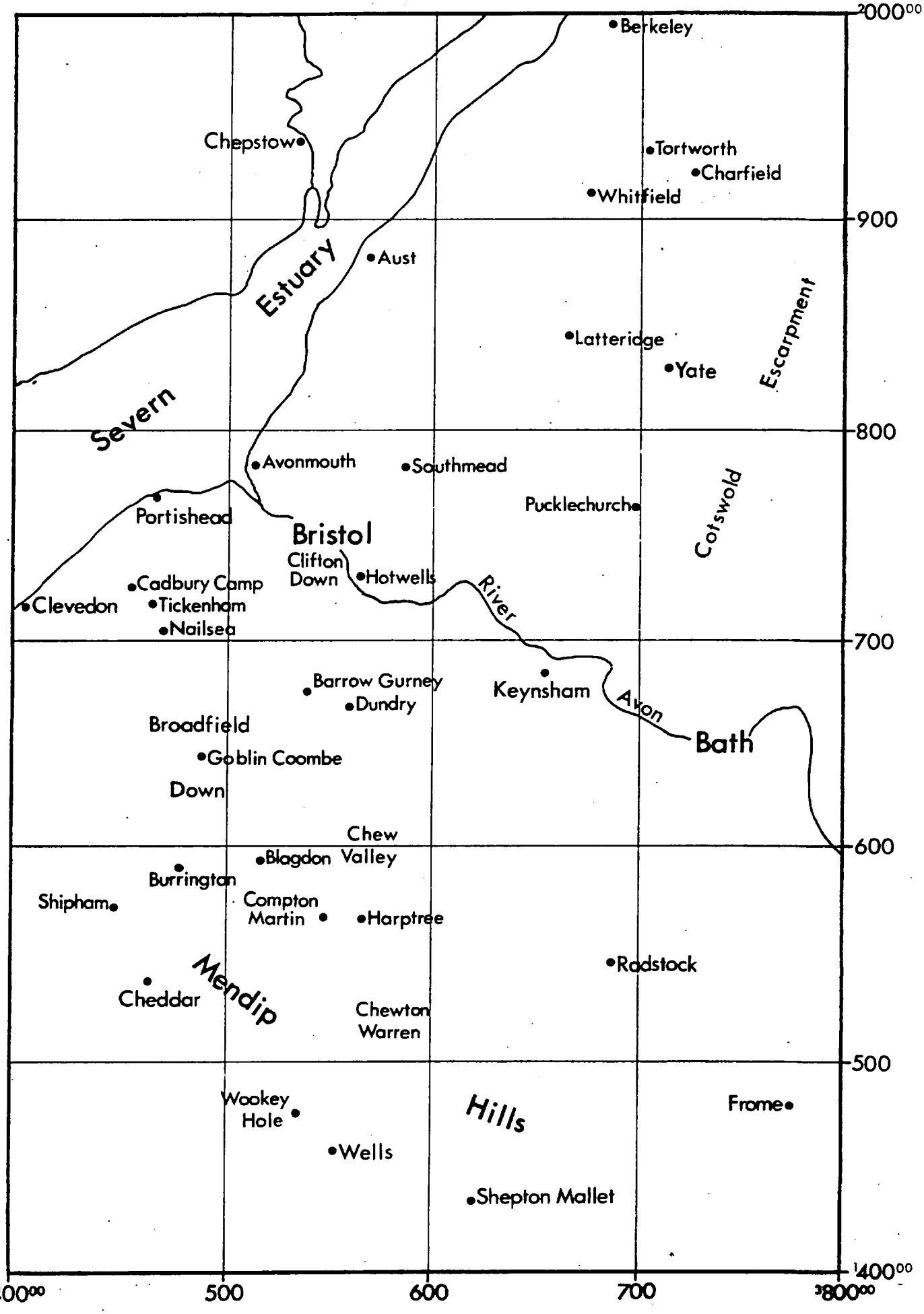
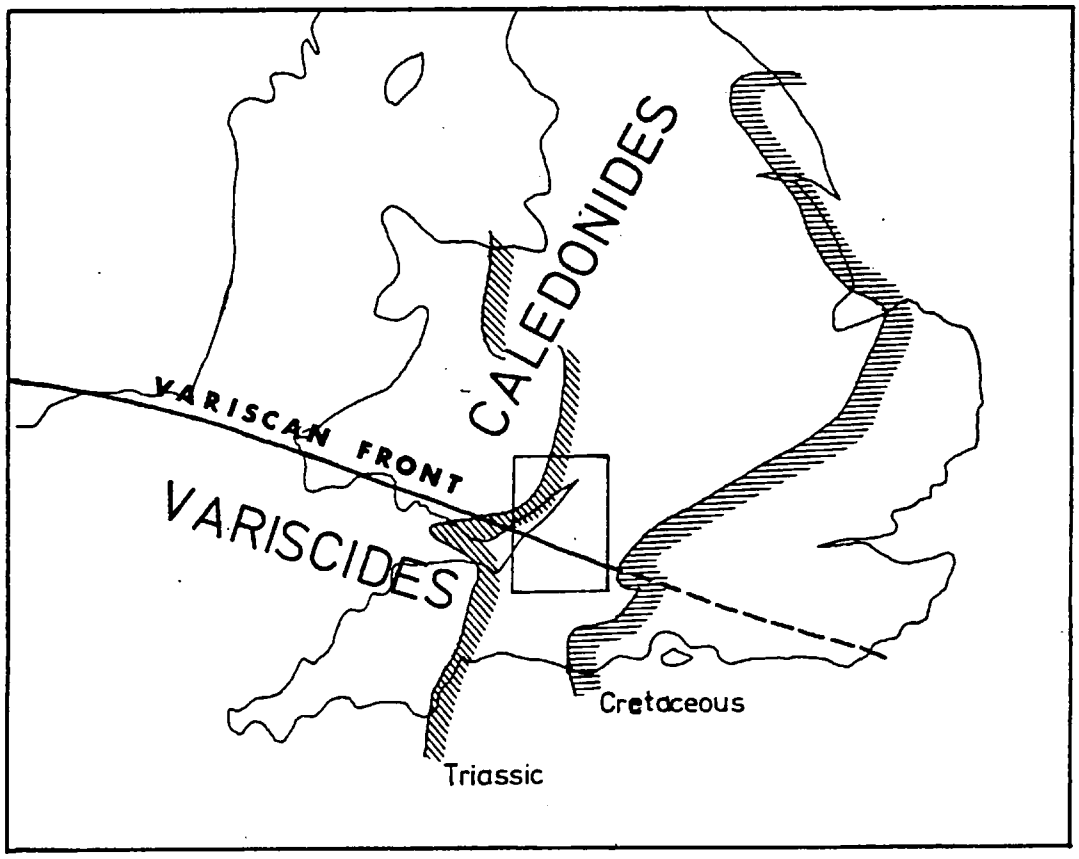


Figure 2-3 Major tectonic features of England and Wales



GEOLOGICAL KEY

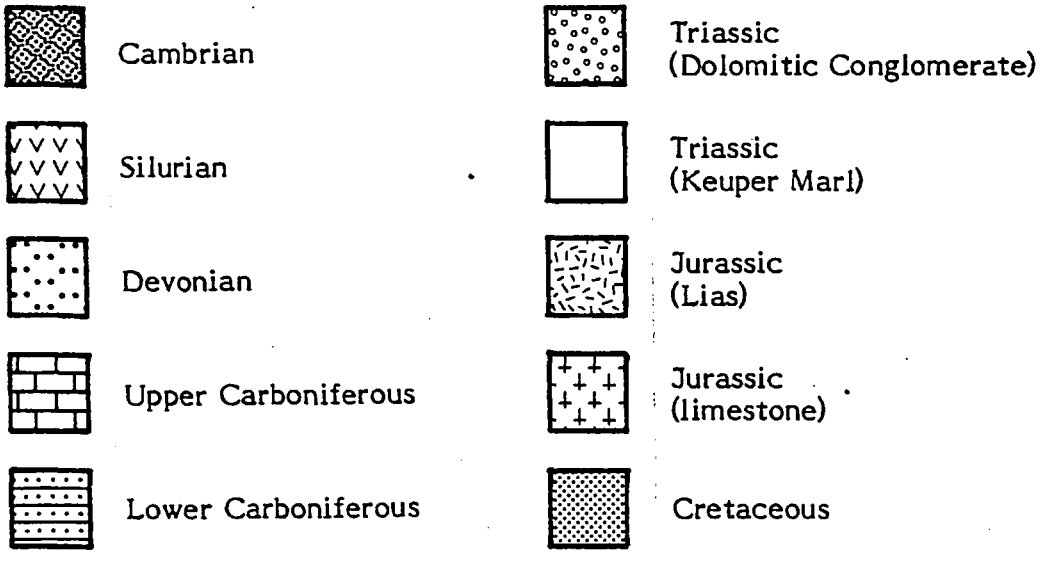


Figure 2-4 Geological map of the study area

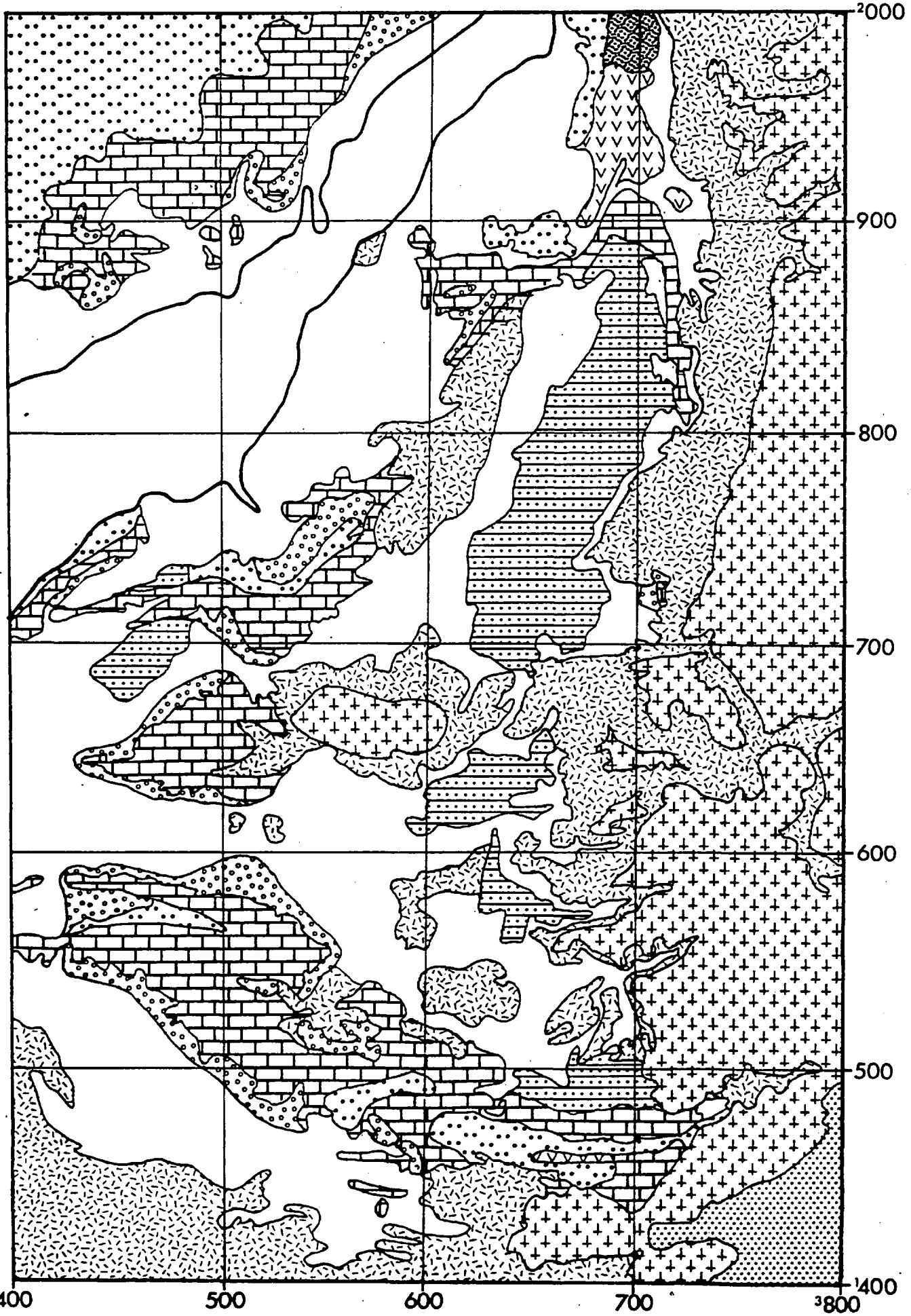


Table 2-1 Table of formations for the Bristol and Mendip Hills area

SYSTEM	GROUP/SERIES		LITHOLOGY	THICKNESS (m)	OROGENIC EVENTS
JURASSIC	U. Jurassic		clay, limestone	100	ALPINE
	U. Liassic		clay, sandstone, limestone	60-200	
	L. Liassic		mudstone, limestone, (conglomerate)		
TRIASSIC	Rhaetic		shale, mudstone, limestone	10	
	Tea Green Marl		mudstone		
	Keuper Marl		red mudstone	600	
	Dolomitic Cglm.		red conglomerate.		
	major unconformity				
CARBONIFEROUS	U. Coal Series		sandstone, shale, (coal)	1100	HERCYNIAN
	Pennant		sandstone, shale, mudstone, (coal)	1200	
	local unconformity				
	L. Coal Series		shale, mudstone, sandstone, (coal)	450	
	Millstone Grit		chert, quartzite, sandstone, mudstone	200	
	Hotwells		limestone, sandstone	100-300	
	Clifton Down		sandstone, limestone, mudstone, (basalt, ash)	100-450	
	Black Rock		dolomite, crinoidal limestone, chert	100-500	
	Lower Lmsn. Shale		shale, limestone, sandstone	80-140	
DEVONIAN	EAST	Portishead	sandstone, conglomerate	440	
		Black Nore	sandstone, shale	?	
		Thornbury Beds	mudstone, sandstone	?	
	WEST	Tintern S'stone	sandstone, mudstone	120	
		Quartz Cglm.	conglomerate		
		Brownstones	sandstone, (shale)	1200	
		St. Maughans	sandstone, (mudstone, limestone)		
	unconformity				
SILURIAN	MENDIP	Wenlock	mudstone, pyroxene andesite	170	CALEDONIAN
		Llandovery	tuff, lava	35	
	NORTH	Ludlow-Wenlock	sandstone, limestone, shale	30	
		Llandovery	sandstone, lava, shale, limestone	270	
	unconformity				
CAMBRIAN	Breadstone		shale	?	
	Mickelwood		sandstone	?	

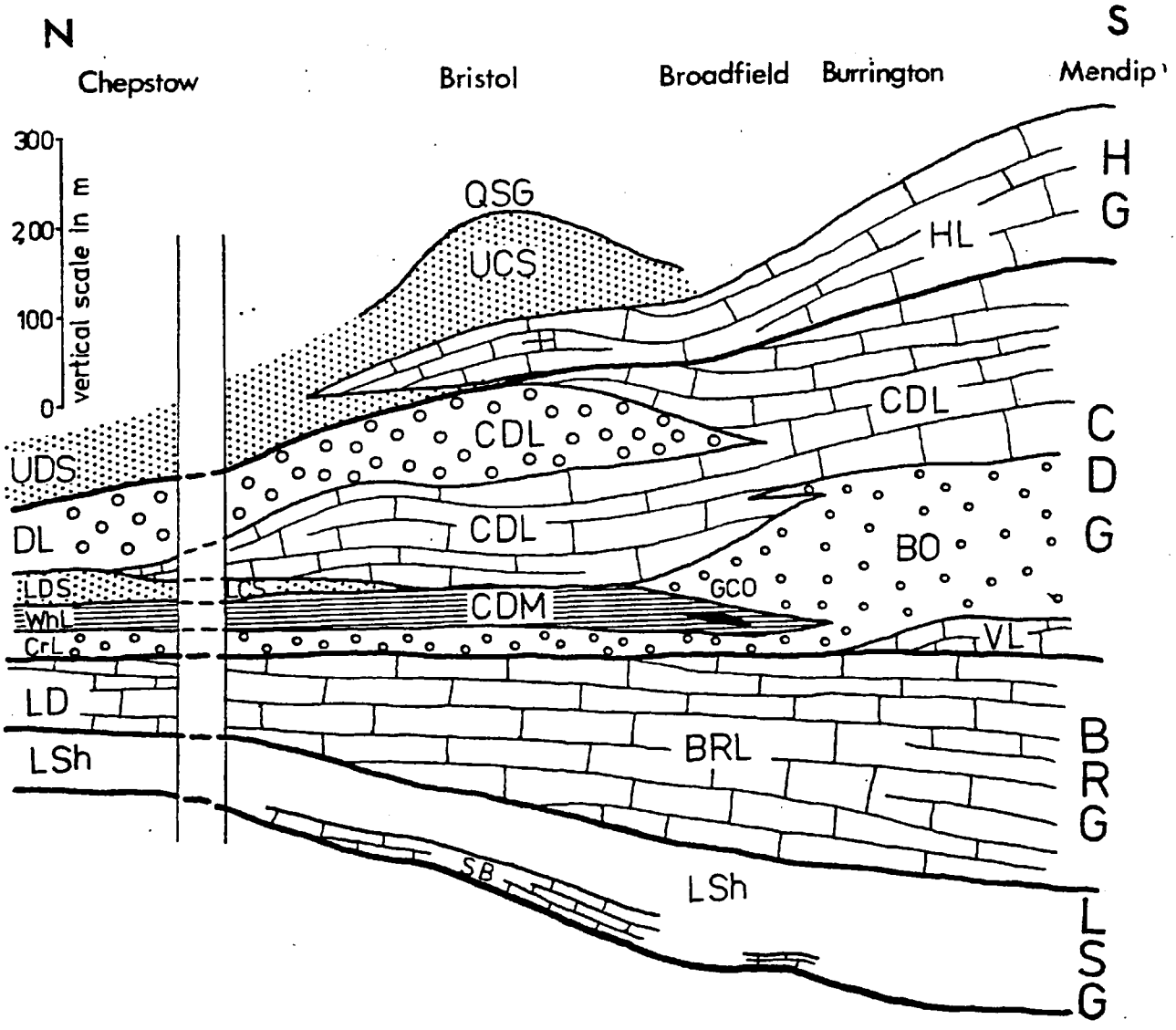
Group, and current-bedded sandstone with shale partings - the Brownstones Group. East of Severn Estuary, Devonian rocks are mainly exposed in eroded anticlines, although early Devonian red mudstone with minor sandstone is present on the upthrown side of a fault near Whitfield (673 913). Early Devonian strata are also exposed near Bristol, and in the Portishead-Clevedon area. The lower members thin to the east, so that at Tortworth (704 933), and in the eastern Mendip Hills, the upper ORS lies directly and unconformably on Silurian rocks.

The upper ORS consists of the basal Quartz Conglomerate, overlain by up to 120 m of yellow-brown sandstone with red mudstone - the Tintern Sandstone Group (Kellaway and Welch, 1948, 1955). Near Bristol, and in the Mendip Hills, the conglomerate and sandstone are collectively termed the Portishead Beds. These thicken to the east and are characterised by feldspathic and quartzitic sandstone, and - in lower parts - by beds and channels of quartz conglomerate.

Sedimentation continued, apparently without interruption, into the Carboniferous, and it is only west of the River Severn and in the Mendip Hills, that the division between Devonian and Carboniferous is easily discernible (Kellaway and Welch, 1955). The Carboniferous Avonian strata are predominantly calcareous. The succession thickens and becomes increasingly calcareous towards the south. A comprehensive study of variations in thickness and lithology of the Avonian beds was made by Kellaway and Welch (1955), and is summarised in Figure 2-5.

The Shirehampton beds mark the gradation from ORS to Carboniferous Limestone, and consist of sandy limestone, shale, calcareous sandstone and crinoidal limestone interbedded with sandstone and mudstone which are similar to the sandstone and mudstone of the ORS. The first truly Carboniferous horizon is the Lower Limestone Shale, comprising shale with limestone layers, the latter increasing in relative abundance towards the top. The dominantly calcareous Black Rock Group is characterised by dark and massive crinoidal limestone. In the Mendip Hills, chert sheets and nodules and more pervasive silicification are common features of the Black Rock Group (Green and Welch, 1955). Dolomite and dolomitised limestone characterise the Black Rock Group in the Bristol area, and become increasingly important to the northwest.

Figure 2-5 Schematic cross-section showing the various facies within the Carboniferous Limestone of the Bristol and Mendip Hills area (after Kellaway and Welch, 1955)



UDS-Upper Drybrook Sandstone, DL-Drybrook Limestone, LDS-Lower Drybrook Sandstone, WhL-Whitehead Limestone, CrL-Crease Limestone, LD-Lower Dolomite, LSh-Limestone Shale, QSG-Quartzitic Sandstone Group, UCS-Upper Cromhall Sandstone, CDL-Clifton Down Limestone, CDM-Clifton Down Mudstone, GCO-Goblin Coombe Oolite, BRL-Black Rock Limestone, SB-Shirehampton Beds, HL-Hotwells Limestone, BO-Burrington Oolite, VL-Vallis Limestone

HG-HOTWELLS GROUP, CDG-CLIFTON DOWN GROUP, BRG-BLACK ROCK GROUP, LSG-LIMESTONE SHALE GROUP

The Clifton Down Group includes two separate beds of oolitic limestone which merge in the Mendip area to form the Burrington Oolite. The lower part of the Burrington Oolite grades into a coarse grained grey crinoidal limestone (Vallis Limestone) in the eastern Mendip Hills. The Whitehead Limestone and the calcareous Clifton Down Mudstone overlie the oolitic rocks. In Goblin Coombe (487 645) on Broadfield Down, beds of olivene basalt and calcareous ash are present within the Clifton Down Mudstone. Similar volcanic rocks have been observed at Tickenham (456 716) and Cadbury Camp (454 725). To the north the Clifton Down Mudstone is overlain by sandstone, whereas to the south it is overlain by the Clifton Down Limestone. In its lower sections the latter is a uniform splintery calcitic and dolomitic mudstone with chert bands and silicified fossils. In the western Mendip Hills the belt of silicification is up to 50 m thick, and near Cheddar (468 549), an oolitic horizon is present. Oolitic limestone, developed in the upper part of the Clifton Down Limestone at Clifton Down (560 735), grades upward into fine-grained concretionary limestone showing evidence of algal origin.

The Hotwells group can be divided into a northerly arenaceous facies and a southerly calcareous facies. The lithology of the southerly Hotwells Limestone contrasts with the underlying muddy and fossil-poor Clifton Down Limestone. The arenaceous facies, which is best developed near Bristol and west of the Severn Estuary, includes sandstone, calcareous sandstone and shale, with local development of carbonaceous and pyritic beds.

The Quartzitic Sandstone Group, comprising chert, quartzitic sandstone and mudstone, belongs to the Millstone Grit Series, although the upper unsilicified strata are similar to the succeeding sandstones of the Coal Measures.

Upper Carboniferous coal bearing shales and sandstones have been completely eroded from the anticlinal areas, and in the low-lying synclinal areas they are largely covered by Mesozoic strata. The lower boundary of the Upper Carboniferous is defined as the Ashton Vale Marine Band.

The Lower Coal Series is dominated by shale and mudstone, with sandstone near the base and local developments of nodular siderite. Several workable coal seams vary in thickness from 15 to 200 cm (Green and Welch, 1965).

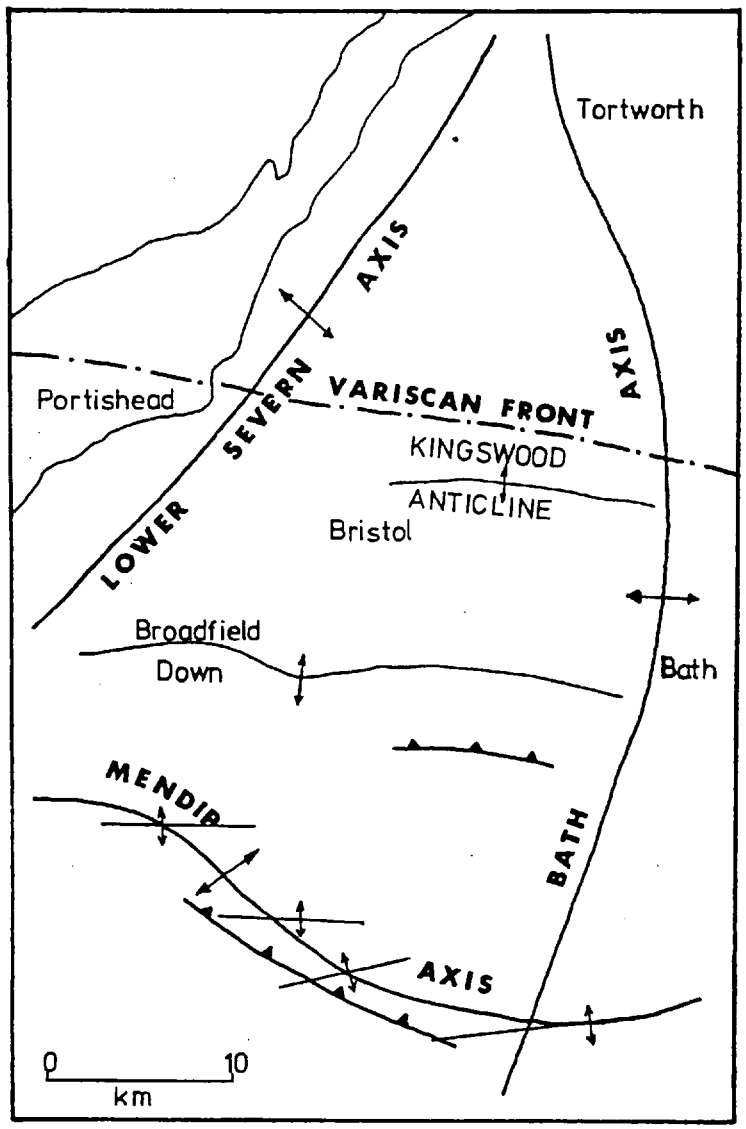
Uplift along the Lower Severn Axis (Figure 2-6) during the middle Carboniferous precluded deposition of the Lower Coal Series to the northwest of Broadfield Down (Kellaway and Welch, 1948). South of Portishead, for example, the younger strata of the Pennant Series lie directly on Lower Carboniferous and Devonian rocks.

The Pennant Series is predominately composed of coarse sandstone, with argillaceous beds near the top and bottom. Worked coal seams, all within the lower 100 m, vary from 30 to over 100 cm in thickness (Green and Welch, 1965). The Upper Coal Series exhibits considerable regional variation. Northeast of Bristol, within the arms of the Lower Severn and Bath Axes, reddened sandstones are characteristic. A shale bed near the base contains coal seams up to 200 cm thick. Elsewhere, the Upper Coal Series comprises mudstone and shale with minor sandstone. Several coal seams are present, but most are too thin to be worked.

Various unconformable relationships noted above suggest localized middle and early-Paleozoic tectonic activity. Much more intensive and widespread Hercynian activity resulted in east-west trending folds and thrust faults (Figure 2-6). The most prominent are the four major anticlines of the Mendip Hills, which are asymmetric, with thrust faulting along the shallower southern limbs. Towards the north, from the vicinity of Radstock (689 548) to the Kingswood anticline, the incompetent Coal Measures are intensively and disharmonically folded and faulted. The Variscan Front defines the northern extent of rocks affected by the Hercynian activity. Coincident with the Hercynian deformation, folding continued along the previously established Bath and Severn trends.

Much of Britain was characterised by rugged terrain during the Permian and Triassic (e.g. Audley-Charles, 1970) and this area is no exception. Permo-Triassic erosion resulted in pronounced dissection of the limestone into deep gorges, which, under arid conditions, became filled with thick colluvial deposits. These comprise pebble- to boulder-sized angular fragments of Carboniferous Limestone and ORS, cemented by fine-grained sandstone or limestone debris (Green and Welch, 1965). Evidence of thick (120 cm) horizontal bedding has been recognised by Weaver (1819). The term Dolomitic Conglomerate has been applied to these rocks which have been extensively silicified, hematised and dolomitised.

Figure 2-6 Tectonic features of the study area



Similar rocks in south Wales have been described by Bluck (1965), Thomas (1968) and Tucker (1978) as alluvial outwash fans.

The area north of the Mendip Hills, enclosed by the Bath and Severn anticlinal axes was exposed until the Carnian (late Triassic) when transgression resulted in a deposition of sandstone and saliferous silty mudstone (Keuper Marl), (Audley-Charles, 1970). Up to 600 m of Keuper Marl are present, with the greatest thickness south of the Mendip Hills within the Central Somerset Basin. The strata are strongly reddened, and essentially free from fossils. It has been suggested that they were deposited from shallow and briney inland waters (Dumbleton and West, 1960; Klein, 1962; Audley-Charles, 1970; Warrington, 1970; Wills, 1970; Tucker, 1978). The Keuper Marl is succeeded by greenish mudstone, the Tea Green Marl, and by strata indicating a return to marine conditions during the Rhaetic. The Rhaetic beds comprise dark shale, light mudstone and limestone.

Lower Liassic strata include light-coloured calcareous mudstone and limestone, with a littoral facies developed in the Mendip area. The non-sequential Upper Lias includes clay, sand and limestone. These rocks form the Cotswold Scarp, and are exposed as foundered strata on steep slopes in the vicinity Bath and Dundry (558 669). Upper Jurassic rocks are confined to the southeastern corner, and comprise limestone, montmorillonite-rich clay and oolitic limestone.

The presence of the Mendip littoral facies indicates that shallow water conditions existed during part of the lower Jurassic. The Mendip area probably remained exposed almost continuously from Rhaetic times through to the end of the Jurassic (Bennison and Wright, 1969 - pp. 283, 289; Anderson and Owen, 1968). This concept is supported by the identification of terrestrial fossils ranging in age from Triassic to lower Jurassic within fissures in the Carboniferous limestone of the Mendip Hills (Robinson, 1957).

On the northern side of the Mendip Hills, near Harptree (562 568) silicification has affected the Jurassic strata. Idiomorphic and microcrystalline quartz crystals are present through thicknesses of up to 10 m, and over an area of several square kilometres. Barite is also a common

constituent, and some sphalerite has been observed (Green and Welch, 1965). Similar alteration is characteristic of some of the Triassic rocks in the vicinity.

Ford and Stanton (1968) have suggested that the main topographic features of the western part of the Mendip Hills were shaped by Tertiary weathering. At the end of the Triassic the Mendip area was still a rugged upland area, although most of the area remained submerged from Rhaetian to early Tertiary times. By the end of the Pliocene, the Paleozoic rocks had been eroded to a gently rolling but essentially flat plateau. The major Pliocene drainage system was to the south through what is now Cheddar Gorge.

Hawkins and Kellaway (1970) and Kellaway (1971) have established evidence for Anglian glaciation (c. 350 000 y BP, Figure 2-7), and more recently, Gilbertson and Hawkins (1978) have indicated evidence of Wolstonian ice (c. 50 000 y). Gilbertson and Hawkins (1978) suggest that although much of the Somerset lowlands were ice-covered, upland areas such as the Mendip Hills, Broadfield Down and the Cotswold Hills were not affected. Weichselian glaciation (c. 10 000 y) did not directly affect the area, but the peri-glacial climate resulted in raised beaches at 15, 25 and 30 m above present sea level (O.D.). Under the same conditions, stony debris, comprising chert, limestone and sandstone (Head), formed by frost action and solifluction (Kellaway and Welch, 1965; Gilbertson and Hawkins, 1978). The Head is generally 1 to 2 m thick, and is best developed on slopes extending away from the Paleozoic uplands (Figure 2-8).

Holocene estuarine alluvium covers low-lying areas inland from the Severn Estuary (Figure 2-8). Beds of sand, clay and peat up to 30 m thick date from about 7 000 y (Kellaway and Welch, 1965).

Mineral deposits of economic importance include lead and zinc sulphides and carbonates within the Carboniferous limestone and Dolomitic Conglomerate (Figure 2-9). Spatially associated with these are occurrences of iron and manganese oxides. Strontium sulphate is present within evaporite horizons in the upper part of the Keuper Marl, and has been worked over a wide area.

Figure 2-7 Flow directions of Anglian glaciation (after Kellaway, 1971)

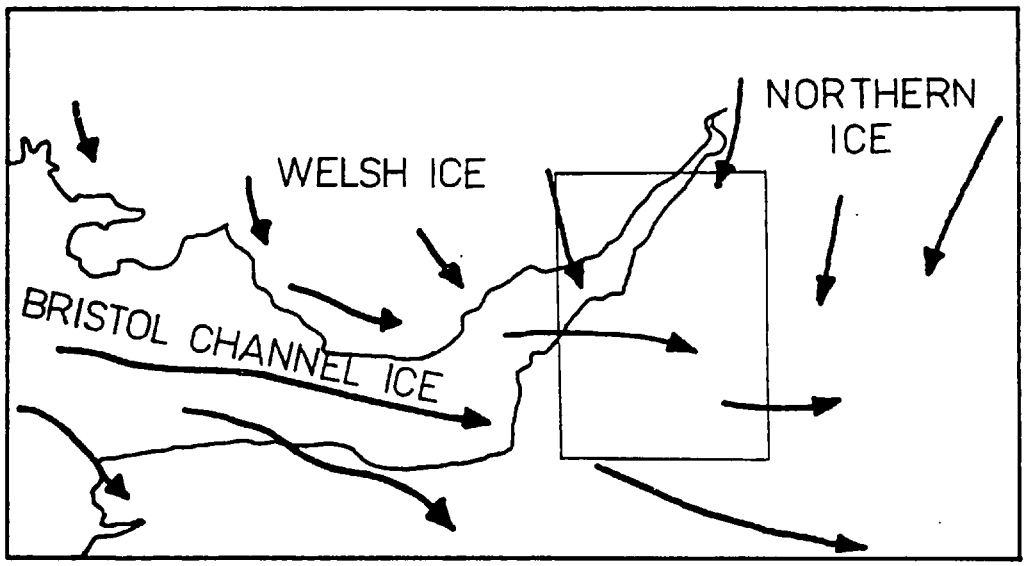


Figure 2-8 Distribution of drift deposits in the study area

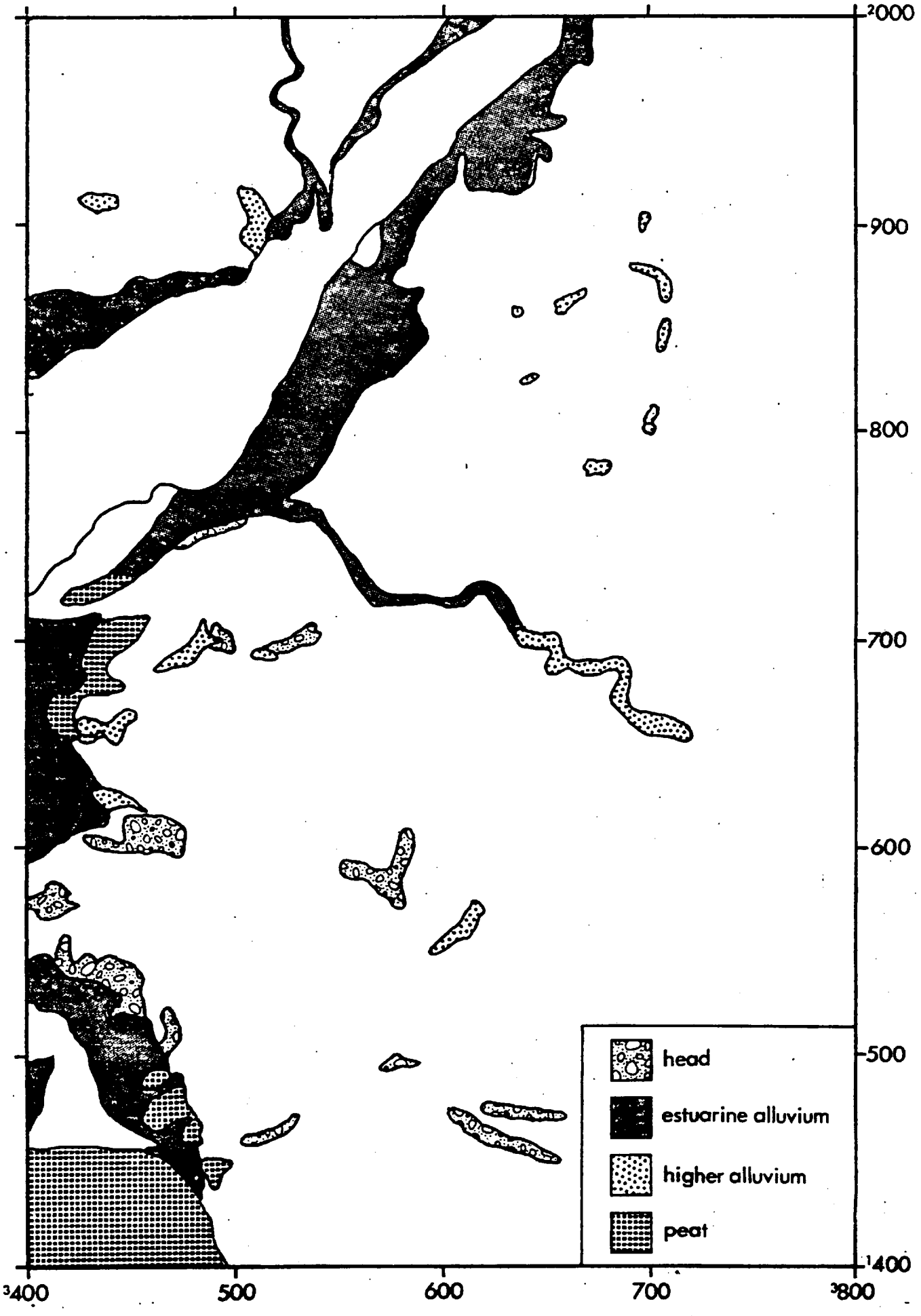
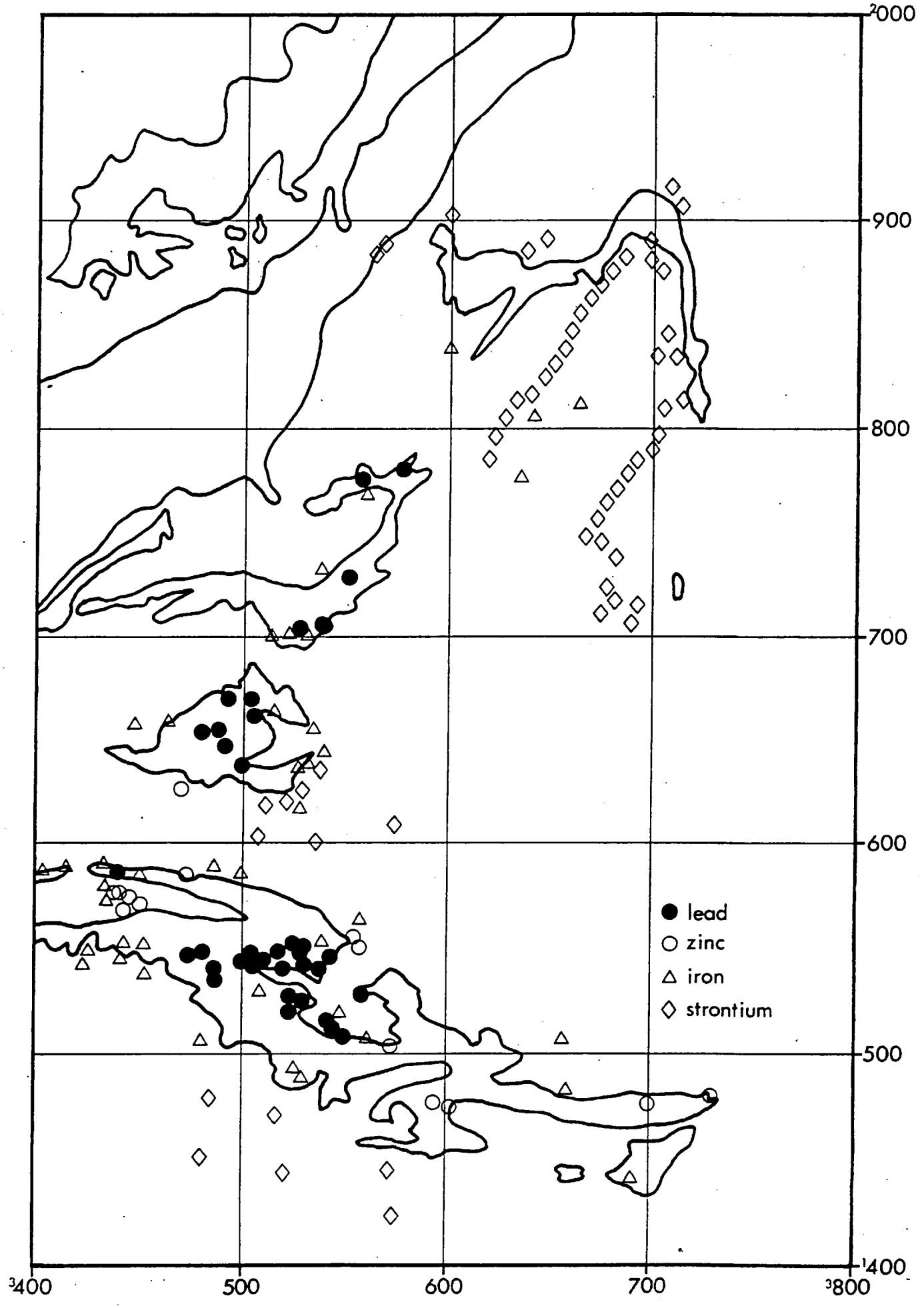


Figure 2-9 Locations of mineral occurrences within the study area
(The outcrop area of the Carboniferous Limestone is outlined)



2-3 Physiography and Drainage.

Prominent uplands are underlain by both Paleozoic and Upper Jurassic rocks. Examples include the Mendip Hills, Broadfield Down, and the ridge from Clevedon (402 716) north through Bristol to Southmead (587 783), as well as the area of Paleozoic rocks in Gwent (Figure 2-10). The Cotswold Scarp and the uplands near Bath and Dundry are comprised of Upper Liassic strata.

Areas underlain by Keuper Marl and the Coal Measures are generally less than 60 m above O.D., and where estuarine alluvium is present the elevation is consistently less than 7 m.

The Paleozoic uplands are characterised by deeply incised gorges such as those at Cheddar (463 537) and Burrington (479 593). Karstification is well developed, particularly in the Mendip Hills (Smith and Drew, 1975). In these areas surface drainage is minimal, and runoff emerges as springs, near the contacts with the surrounding Mesozoic rocks. Mineral and thermal waters discharging at Bath and Hotwells (564 731), have temperatures of 49^{o} and 24^{o} C respectively. Edmunds et al (1968) suggest that the waters at Bath springs circulate to a depth of about 2 000 m. Elevated concentrations of sodium, strontium, sulphate and chloride have been noted by Riley (1961).

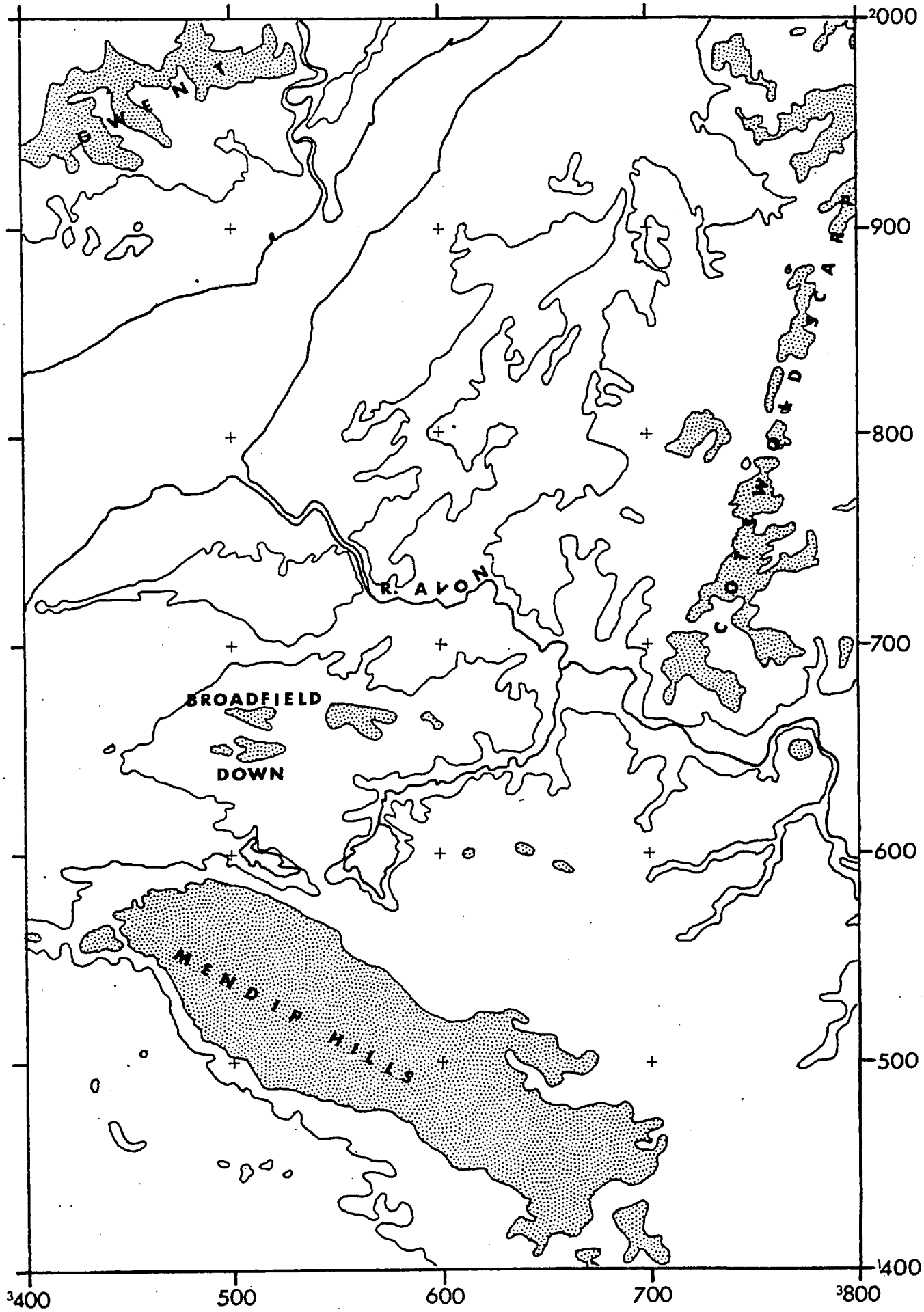
Surface drainage is generally well developed, although large artificial reservoirs have been created at Barrow Gurney (539 674), Blagdon (515 596), Chew Valley (570 600) and Cheddar (442 537). On the alluvial flats drainage is poor and has been enhanced by ditching.

2-4 Soils, Vegetation and Climate

Calcareous brown earths predominate on the Paleozoic uplands, whereas rendzinas characterise the Upper Jurrasic uplands. Alluvial gleysols are developed on the poorly drained estuarine lowlands, and argillic brown earths are formed elsewhere on the Keuper Marl. Highly argillic horizons of the Coal Measures and Lower Lias are overlain by stagnogleys (Avery et al, 1975).

Approximately 90% of the study area, excluding built up regions, is given over to agriculture, most of which is used for grazing cattle. About 25% of the remainder is natural grassland, and the rest is natural broadleaf woodland or forestry plantation.

Figure 2-10 Major physiographic features of the study area



Monthly mean temperatures vary from less than 5^{o} C in January to almost 17^{o} C in July. On the basis of the temperature of ground waters from the Mendip Hills, the mean annual temperature is approximately 11^{o} C. Annual precipitation is over 1 100 mm west of the River Severn, and about 800 mm elsewhere, except on higher ground such as the Mendip Hills where it varies from 950 to 1 000 mm. Roughly 60% of the precipitation occurs during the six months from August to December (Bickmore and Shaw, 1963). Prevailing winds are from the west to southwest.

2-5 Urbanisation and Industry

Principal conurbations include Bristol (pop. 443 000 in 1951) and Bath (pop. greater than 50 000) plus about 20 centres with populations between 10 000 and 50 000.

Apart from agriculture, most industry involves light manufacturing, and is centred around Bristol. An industrial complex at Avonmouth (516 781) includes chemical and petro-chemical works and a large zinc smelter. The Newport steel works (375 865) are within 1 km of the western edge of the study area. Quarrying is a very important industry, especially where Carboniferous Limestone is exposed. Extraction of celestite from the Keuper Marl near Yate (714 828) is being carried out on a small scale.

Although there is no coal mining at present, deposits at Radstock (689 548) were worked until the early 1960's. Operations had also existed within the Kingswood anticline and near Nailsea (700 470).

In the past the mining industry has been dominated by lead and zinc, extraction of which dates back roughly 2 000 years (Gough, 1967). Activity was centred on the Mendip Hills, but some mining was carried out on Broadfield Down and in the Bristol area. Because smelting procedures became increasingly efficient, much of the slag has been reworked several times, the most recent being in the late 19th century (Gough, 1967). Iron and manganese oxides have been recovered from several of the locations shown in Figure 2-9. Most of the iron and manganese ores were used as pigments or glazes.

CHAPTER 3 STREAM SEDIMENT GEOCHEMISTRY

3-1 Introduction

The following section includes a description of the geochemistry of stream sediments collected as part of a regional geochemical survey of England and Wales (Webb et al, 1978). In order to establish a regional picture, data are first presented for a 150 by 200 km rectangular area extending from Exeter in the southwest to Leicester in the northeast. Data for the study area itself are presented using an interpolative technique which allows for weighting in the upstream direction for each sample. Both univariate and multivariate statistical procedures have been used to interpret the data.

3-2 Description of Surficial Drainage

Surficial drainage is poorly developed in areas underlain by the Carboniferous Limestone and Dolomitic Conglomerate, but well developed where non-calcareous rocks such as the Old Red Sandstone, Coal Measures and Keuper Marl are present. Exceptions include the low-lying flat areas covered with estuarine alluvium. Here natural drainage is poor and a network of ditches and canals has been established to improve drainage. Enlargement of stream channels has been carried out elsewhere as well, particularly on agricultural land, to improve field drainage. In areas of argillaceous strata, and over the Mesozoic limestones, stream sediments are dominantly composed of clay and silt-sized material, with calcareous fragments. Because the relief is consistently low, downstream mechanical transportation is slow and physical composition of the sediments are probably most closely related to the composition of the adjacent bank material. This is especially true where ditching has been carried out.

3-3 Sample Collection, Preparation and Analysis

Sampling was carried out by the Applied Geochemistry Research Group over a period of ten weeks during 1969, as part of a stream sediment survey of all of England and Wales (Webb et al, 1978). Samples were collected above road/stream intersections with the aim of attaining a sample density of 1 per 2.5 km^2. The distribution of the approximately 850 samples collected from

within the study area is given in Figure 3-1. Excluding large unsampled areas (i.e., Bristol, Bath and the Severn Estuary), the sample density is 1 per 2.8 km^2.

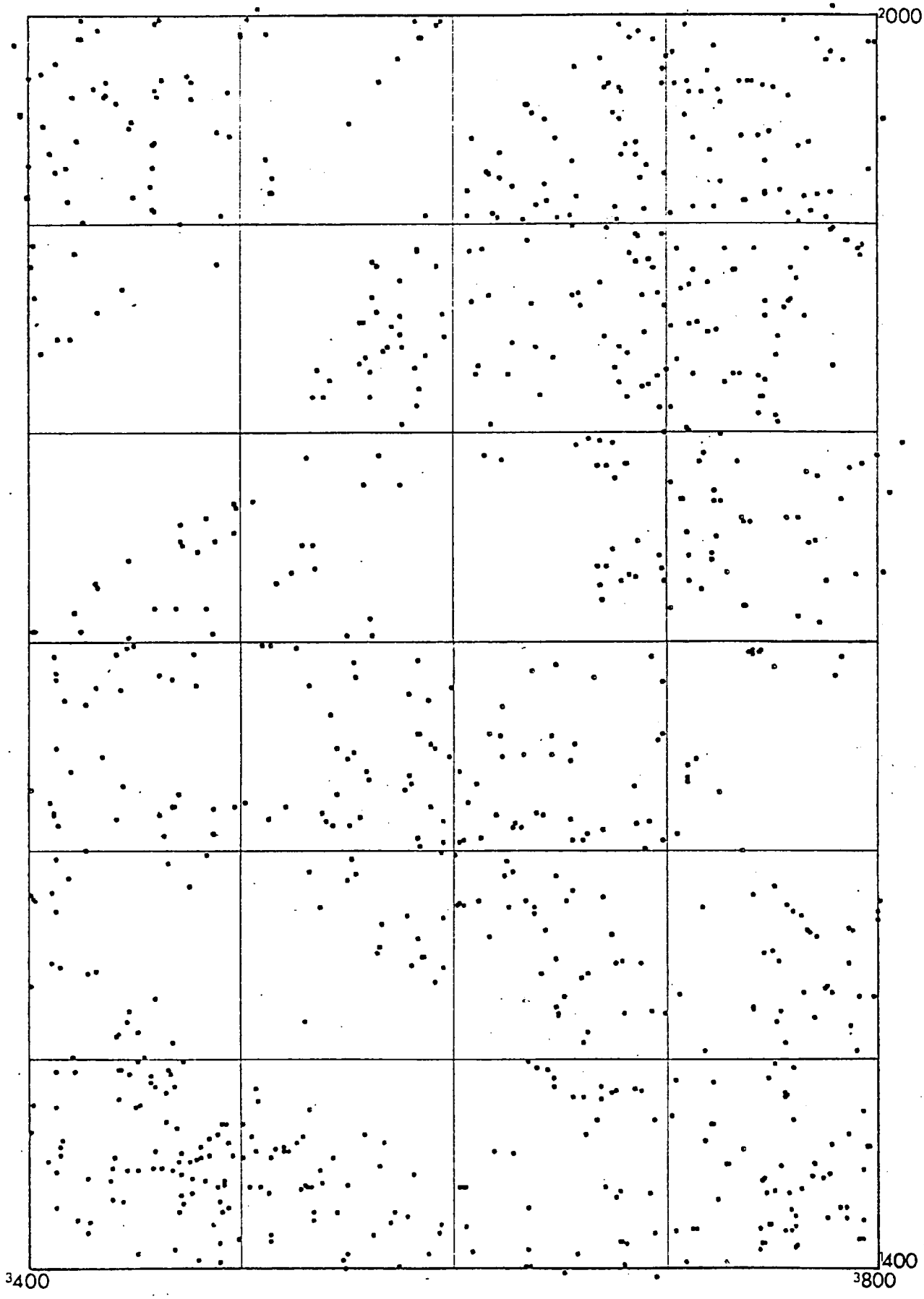
At each sample location composite samples were collected from two sites at least 10 metres apart. Samples were dried for several hours at 60 to 80°C and then disaggregated and sieved to retain the fraction smaller than 200 um (minus-80 mesh). Calcium, magnesium, manganese, strontium, barium, copper, lead and zinc were determined by direct reading DC-arc emission spectrophotometry. Nitric-acid-extractable cadmium and zinc were determined by atomic absorption spectophotometry. After fusion with potassium-hydrogen-sulphate, molybdenum was determined by spectrophotometry as its dithiol complex, and arsenic was determined by colorimetry. A comprehensive description of analytical procedures, and estimates of analytical error are given in Webb et al (1978). For most elements between batch precision is about 50% at background levels.

3-4 Regional Distribution of Metals in Stream Sediments

Data for barium, cadmium, calcium, copper, lead, molybdenum, strontium and zinc for roughly 9 500 samples from within the area extending from Exeter to Leicester are presented in Figures 3-2 to 3-9. The area shown is bounded by the National Grid lines 100 000 m N to 300 000 m N and 300 000 m E to 450 000 m E. The data have been extracted from computer files for the Geochemical Atlas of England and Wales. Map distributions were calculated by averaging all samples lying within each 2.56 km square map cell, and then smoothed using a 9-cell moving average technique (Howarth and Lowenstein, 1974). Such spatial averaging significantly improves the effective precision of the data. For example, when the value for any map cell is based on the average concentrations of several samples (n), its precision is improved by a factor of $1/\sqrt{n}$ (Webb et al, 1978).

Webb et al (1978) have pointed out the strong relationship between regional stream sediment geochemistry and lithology. Some examples are: enrichment of molybdenum over black marine shales, enrichment of calcium and strontium over limestone, enrichment of barium, cadmium, copper, lead and zinc in former base-metal mining districts, and elevated levels of cadmium, copper, lead and zinc associated with industrial areas and large urban centres.

Figure 3-1 Distribution of stream sediment samples within the study area





b–Silurian c–Devonian d–Carboniferous d'–C. Limestone
e–Permian f–Triassic g–Jurassic g'–Lias h–Cretaceous i–Tertiary

Geological overlay for
Figures 3-2 to 3-9

Figure 3-2 Map of barium concentrations in stream sediments in west-central England and eastern Wales. Concentrations from light to dark are as follows: <162, 162-214, 215-321, 322-413, 414-1026, >1026 ppm.

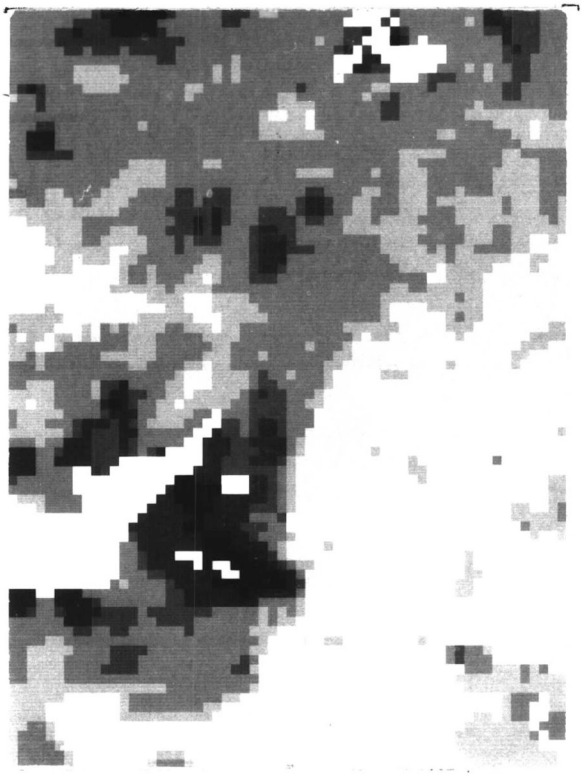


Figure 3-3 Map of cadmium concentrations in stream sediments in west-central England and eastern Wales. (<.37, .37-1.24, 1.25-1.70, 1.71-3.43, >3.43 ppm)

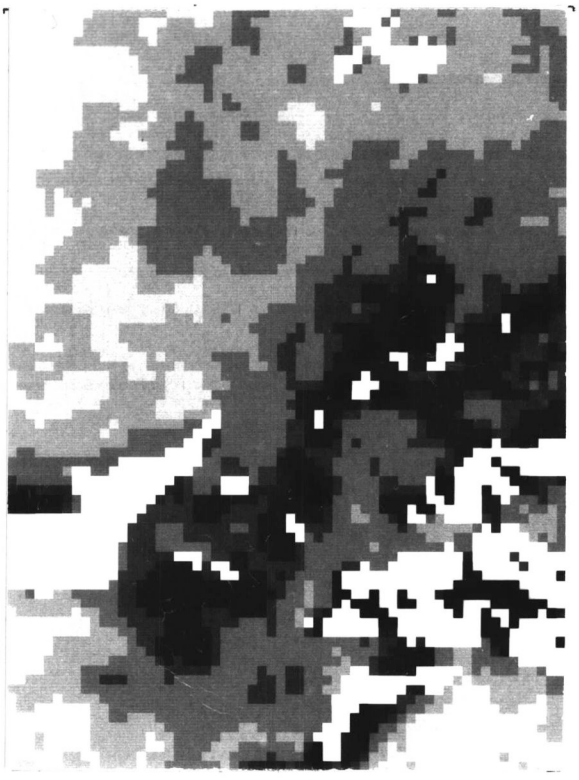


Figure 3-4 Map of calcium concentrations in stream sediments in west-central England and eastern Wales. (<.7, .7-1.7, 1.8-7.2, 7.3-10.6, 10.7-21.4, >21.4%)



Figure 3-5 Map of copper concentrations in stream sediments in west-central England and eastern Wales. (<12, 12-19, 20-32, 33-41, 42-73, >73 ppm)

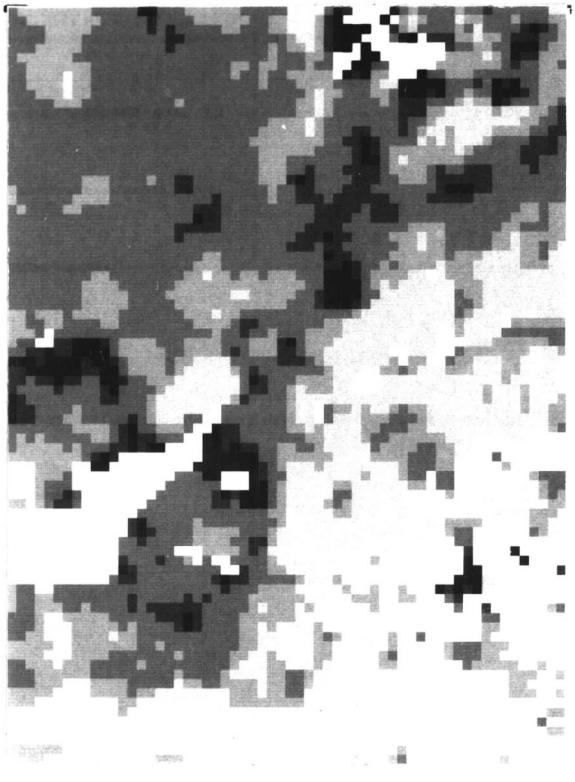


Figure 3-6 Map of lead concentrations in stream sediments from west-central England and eastern Wales.
Concentrations from light to dark are as follows:
<20.8, 20.8-32.3, 32.4-70.6, 70.7-104, 105-272, >272 ppm



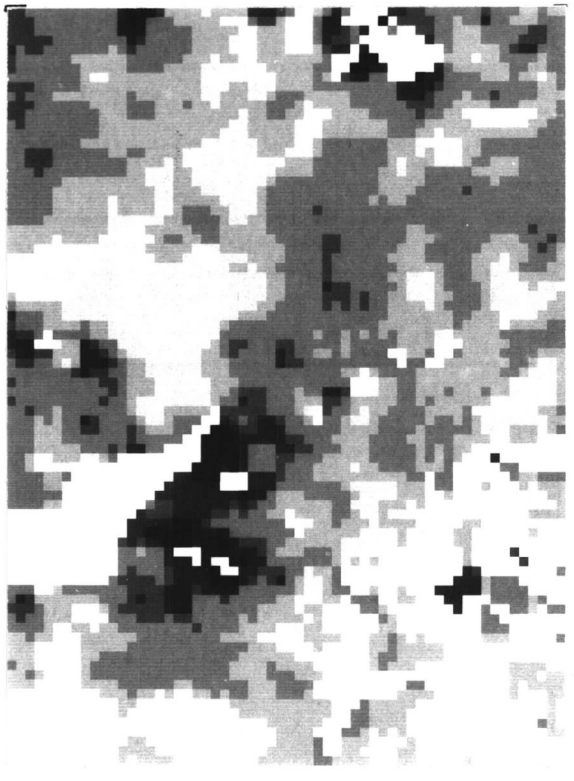
Figure 3-7 Map of molybdenum concentrations in stream sediments from west-central England and eastern Wales.
(<.76, .76-1.08, 1.09-1.77, 1.78-2.21, 2.23-3.61, >3.61 ppm)



Figure 3-8 Map of strontium concentrations in stream sediments from west-central England and eastern Wales.
(<34, 34-51, 52-106, 107-144, 145-286, >286 ppm)



Figure 3-9 Map of zinc concentrations in stream sediments from west-central England and eastern Wales.
(<75, 75-111, 112-196, 197-244, 245-451, >451 ppm)



For the data shown here, the calcium-strontium association is evident in areas underlain by the Chalk and Inferior Oolite. There is a broad band of calcium and strontium enrichment extending from Gloucester to the Central Somerset Basin. The Inferior Oolite is present in the eastern part of this area, where calcium values are greatest, but towards the west, where strontium values are greatest, the major lithologies are the clay, silt and sandstone of the Keuper and Lias. Here, strontium concentrations fall within the top 5 percentile of all the data for England and Wales (140 ppm). In other parts of England and Wales underlain by the Keuper and Lias, strontium concentrations rarely exceed 70 ppm.

Also within the belt of strontium enrichment, but more closely confined to the vicinity of the Carboniferous Limestone uplands, is an area which is enriched in barium and lead (top 10 percent), and cadmium, zinc and copper (top 20 percent). Similar patterns are characteristic of other base-metal mining districts of England and Wales, although, compared with the other districts, the area and magnitude of barium enrichment here is disproportionately large.

A zone of high molybdenum concentrations extends from near Northhampton to eastern Devon. Areas of particular enrichment include the Central Somerset Basin and the immediate vicinity of Bristol, both of which are underlain by the Lower Lias black shales.

3-5 Distribution of Metals in Stream Sediments within the Study Area

The results of most stream sediment surveys are presented as maps with symbols or numbers corresponding to concentrations at sample site locations. Although this method is suited to identifying individual anomalies, regional geochemical patterns are more clearly shown by maps which portray a continuous surface of data for the area sampled. Since it is impossible to obtain continuous geochemical data, all contour or grey-level maps must rely on interpolation between data points.

Interpolation is a valid technique for grid surveys of isotropic sampling media such as soils, but it is generally inapplicable to drainage data because of irregular sampling patterns, and because the material sampled at a particular site may be no more representative of that site than of part of the area upstream. The only case in which isotropic interpolation of drainage data is

viable, is on a regional scale where several samples over a wide area are used to calculate the value for each grid point. This method was used by Webb et al (1978) for the England and Wales data, and although it is suitable for showing regional variations in geochemistry, it does so at the expense of local detail. Resolution on the England and Wales maps and on the maps shown in Figures 3-2 to 3-9 is about 7.5 km.

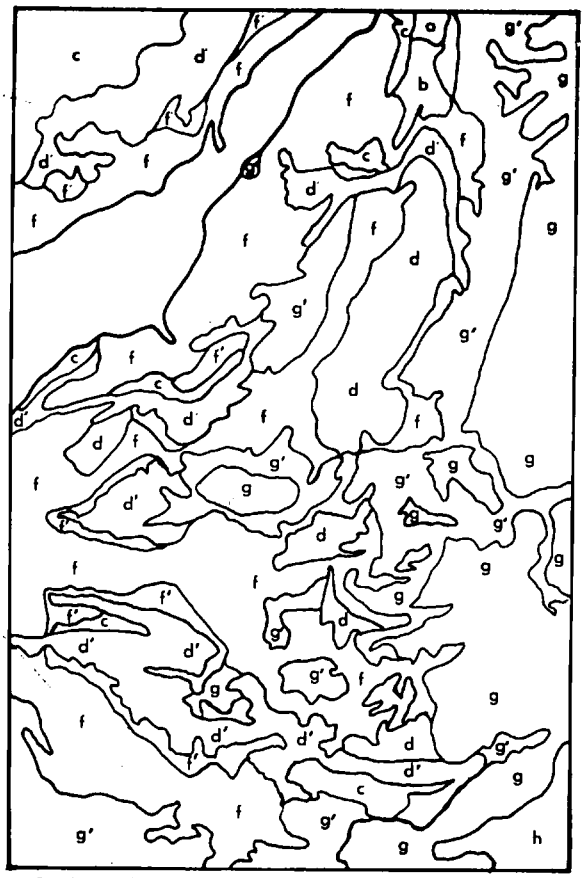
For presentation of the stream sediment data from within the study area a resolution of 1 km was desired. In such a case isotropic interpolation would have resulted in serious distortion. To solve this problem, a method was devised which involves interpolation with upstream weighting from each sample site, that is towards the source of the sediment comprising the sample. A description of the method used is given in Appendix B, and in Earle (1978).

3.5.01 Calcium

The histogram and probability plot for calcium (Figure 3-10 a and b) indicates a positively skewed unimodal distribution (see Appendix C for a description of the histogram and probability plot program, and a discussion of its use). The spatial distribution of calcium is shown in Figure 3-10 c, with class intervals chosen as the 20, 40, 60, 80, 90, 95 and 99th percentiles. Calcium is consistently low over the Old Red Sandstone, and high in areas around the Carboniferous uplands. The Jurassic limestone areas have the highest concentrations of calcium, however, and the change in lithology along the Cotswold Scarp is easily discernible.

3-5.02 Magnesium

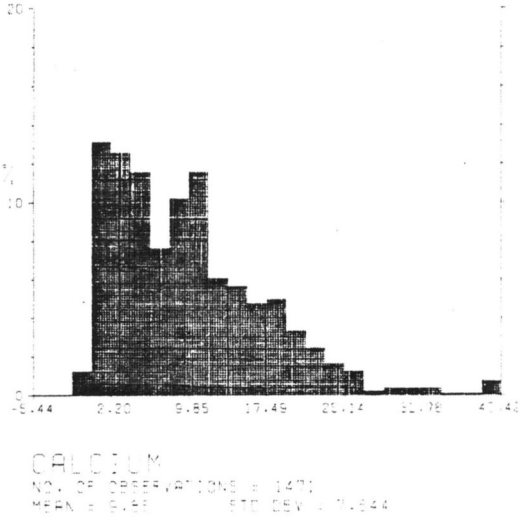
The magnesium histogram also shows positive skewness, and the data can be divided into three sub-populations, all of which are slightly positively skewed (Figure 3-11 a and b). The sub-populations have been transformed to near normality, by using the general power transform method of Box and Cox (1964), so as to give reliable estimates of their upper limits. (A discussion of the method is given in Appendix C, and in Howarth and Earle, 1979). Probability plots have been used to determine natural groupings within the data by selecting partitioning values as the 99th percentile of the next lowest sub-population (cf. Sinclair, 1976). Maps based on percentile classes and on the probability



a-Cambrian b-Silurian c-Devonian d-Carboniferous (Coal M.)
d'-Carb. Limestone f-Keuper Marl f'-Dolomitic Conglomerate
g-Jurassic (limestone) g'-Lower Lias h-Cretaceous

Geological overlay for
Figures 3-11 to 3-21

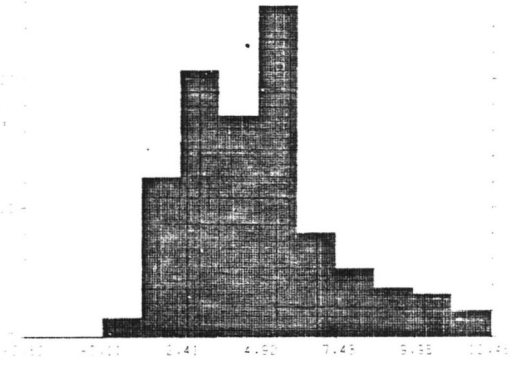
Figure 3-10
(a) Histogram for % calcium in stream sediments from the Bristol-Mendip area. Data are from 1 square km map cells calculated by the STRMPLT routine.



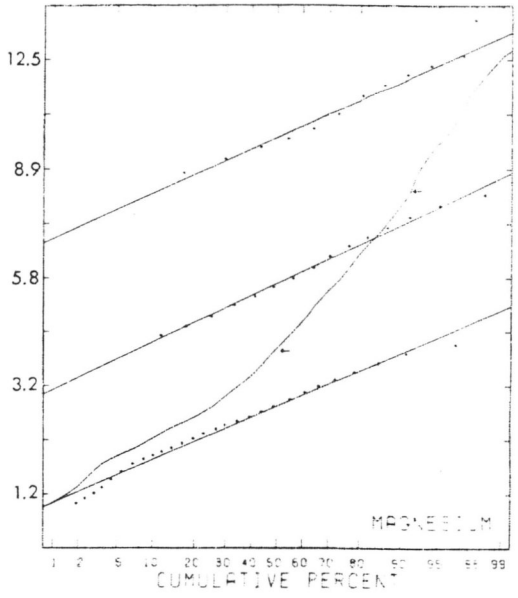
(b) STRMPLT map of calcium concentrations of stream sediments - 20, 40, 60, 80, 90, 95, 98 and 99th percentiles. Concentration levels from light to dark are as follows: < 3.2, 3.2-6.4, 6.5-10.4, 10.5-15.7, 15.8-19.8, 19.9-23.8, 23.9-35.4, >35.4%)



Figure 3-11
(a) Histogram for % magnesium (as for 3-10a)



(b) Probability plot for % magnesium. The original data are represented by the curved line, with inflection points shown by arrows. Points for derived sub-populations are portrayed as '+', and the sub-populations are represented as straight lines through these points.



(c) STRMPLT map for magnesium with subjectively chosen class intervals. (< 2.5, 2.5-3.5, 3.6-4.5, 5.6-7.5, 7.6-8.5, 8.6-10.5, >10.5%)



(d) STRMPLT map of sub-populations from probability plot. (light < 5, medium 5-8, dark >8%)



plot subdivisions (Figure 3-11 c and d) indicate that stream sediments over the Old Red Sandstone, Carboniferous Limestone and Upper Jurassic limestone are generally low in magnesium. Samples from streams over the Coal Measures, Keuper Marl and Lower Lias have moderate to high magnesium concentrations, the Keuper Marl being the highest.

3-5.03 Manganese

The manganese population itself is highly skewed, but it can be divided into three essentially normal sub-populations (Figure 3-12 a and b). Apart from general low levels over the Old Red Sandstone and Jurassic strata, sporadic high concentrations are distributed throughout the study area (Figure 3-12 c and d). Some of the anomalies are spatially related to areas of manganese mineralisation in the Carboniferous Limestone and Dolomitic Conglomerate. There is an extensive area of high manganese concentrations in the poorly drained lowlands south of Mendip, and some more localized highs in similar terrain along the banks of the Severn Estuary.

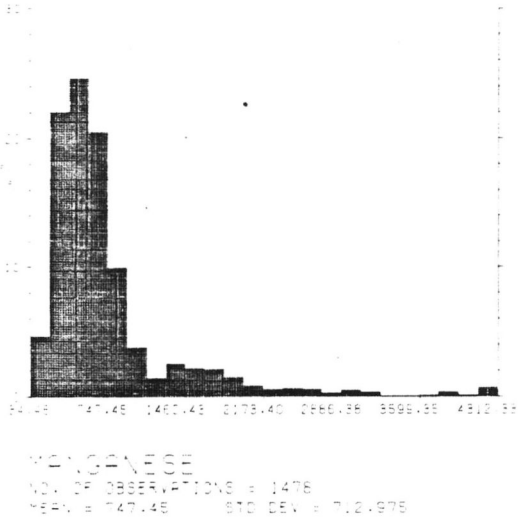
3-5.04 Strontium

Strontium also shows strong positive skewness and the data can be divided into two positively skewed sub-populations (Figure 3-13 a). The Old Red Sandstone and Upper Jurassic Oxford Clay are consistently low in strontium, whereas most of the other strata, especially the limestone, are moderately but irregularly enriched (Figure 3-13 b). The upper 7% of the data is restricted to the Keuper Marl (Figure 3-13 c), and correlates closely with the evaporitic celestite occurrences (Figure 2-12).

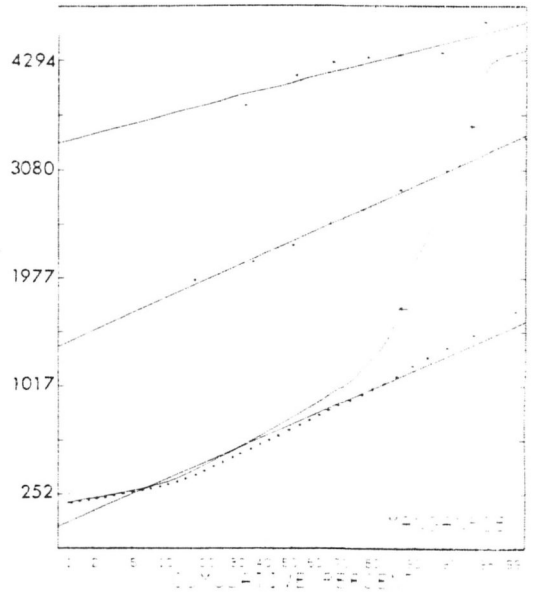
3-5.05 Barium

The barium data are comprised of two positively skewed sub-populations (Figure 3-14 a). Data between the 80th and 90th percentiles are generally confined to areas underlain by Keuper Marl. The upper 10% of the data, and the upper subset (Figure 13-14 b and c) are spatially related in part to the zone of strontium enrichment, and in part to the areas of sulphide mineralisation (see Figure 2-12).

Figure 3-12
(a) Histogram for ppm manganese (as for 3-10a)



(b) Probability plot for ppm manganese (as for 3-11b)



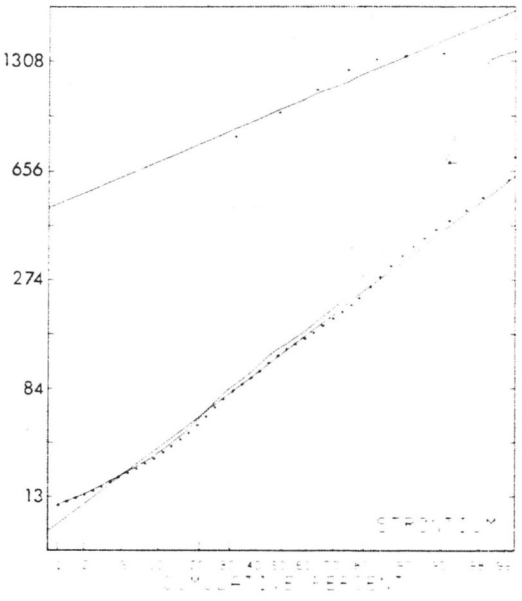
(c) STRMPLT map of manganese percentiles (as for 3-10b)
(< 343, 343-491, 492-643, 644-880, 881-1515, 1516-1958, 1959-3528, >3528 ppm)



(d) STRMPLT map for manganese sub-populations.
(light <1000, medium 1000-2200, dark >2200 ppm)



Figure 3-13
(a) Probability plot for ppm strontium (as for 3-11b)



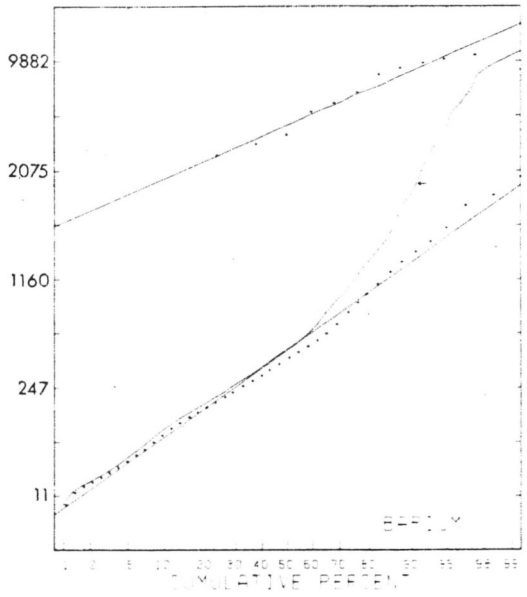
(b) STRMPLT map of strontium percentiles (as for 3-10b)
(<67, 67-133, 134-210, 211-366, 367-558, 559-843, 844-2388, >2388 ppm)



(c) STRMPLT map for strontium sub-populations
(light <656, dark >656 ppm)



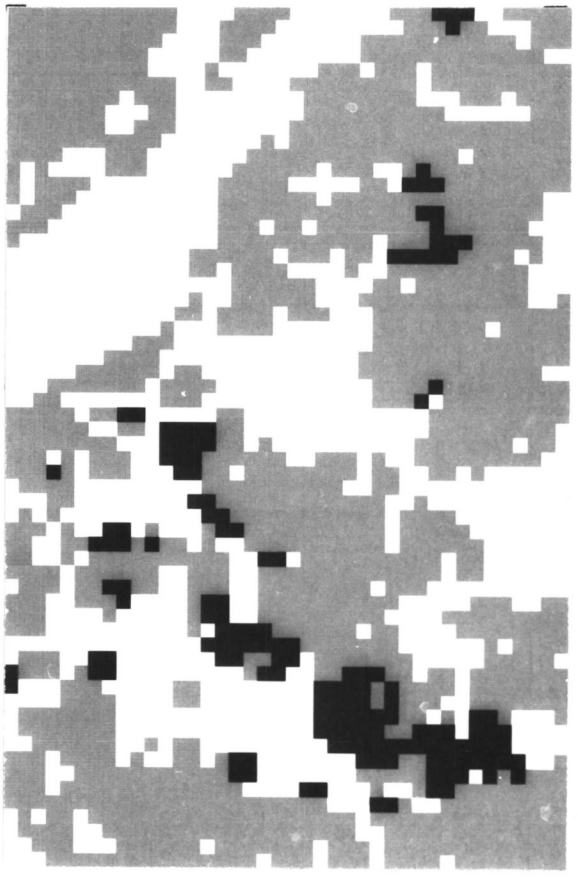
Figure 3-14
(a) Probability plot for ppm barium (as for 3-11b)



(b) STRMPLT map for barium percentiles (as for 3-10b)
(<209, 209-308, 309-466, 467-978, 979-2189, 2190-3992, 3993-9769, >9769 ppm)



(c) STRMPLT map for barium sub-populations
(light <2000, dark >2000 ppm)



3-5.06 Copper

The copper data have been divided into two sub-populations, and although the lower one has been normalised, the upper one has an irregular distribution and will be treated as an inhomogenous anomalous sub-population (Figure 3-15 a and b). Very low concentrations are characteristic of the Old Red Sandstone and Jurassic limestone (Figure 3-15 c). Areas with anomalous copper concentrations include the Bristol conurbation and association industrial areas, the areas of lead-zinc mineralisation, and the poorly drained ground along the banks of the Severn and south of Mendip (Figure 3-15 d).

3-5.07 Lead

Like copper, the lead data are characterised by an inhomogeneous anomalous sub-population (Figure 3-16 a and b). Samples from within the upper 1 percentile are restricted to the Mendip area and Avonmouth, although some of those from within the anomalous group are from immediately east of Bristol (Figure 3-16 c and d). The most extensive area of enrichment is the poorly drained alluvial plain south of Mendip. The anomaly northeast of Bristol, near Cromhall (696 905), is within an area underlain by Carboniferous Limestone.

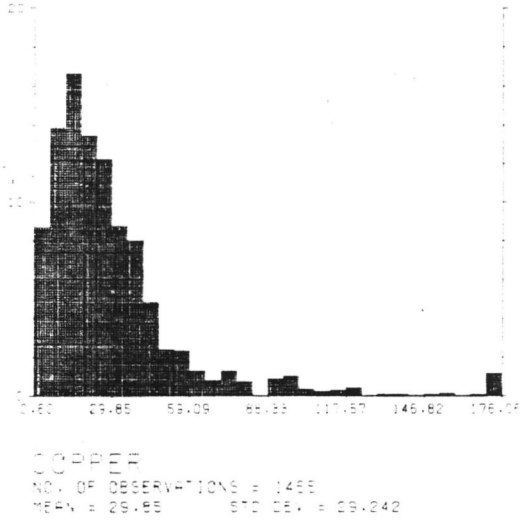
3-5.08 Zinc

The highly skewed zinc data are composed of two sub-populations (Figure 3-17 a and b). Consistently low values characterise the Old Red Sandstone (Figure 3-17 c). The upper 5 percent, and the data from the anomalous subset are confirmed to the Bristol, Mendip and Avonmouth areas, with some elevated values northeast of Bristol (Figure 3-17 d).

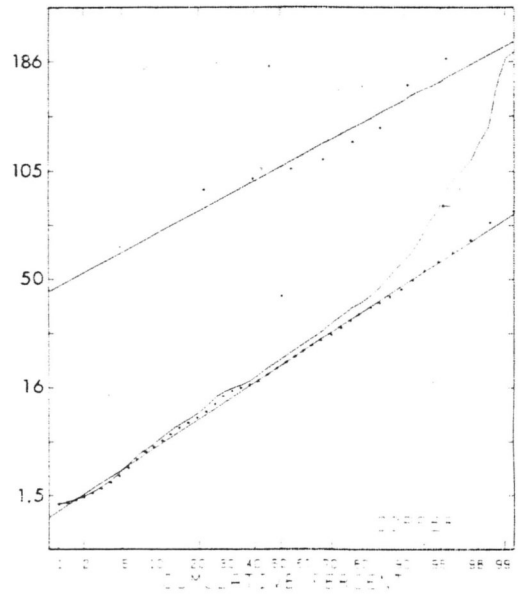
3-5.09 Cadmium

Over half of the samples have cadmium concentrations below the 0.1 ppm detection limit of the analytical method. The distribution of the remaining data is irregular, and although 4 skewed sub-populations have been identified, the fit between the model and the original data is poor, and the groups have not been plotted separately. The spatial distribution is similar to that for zinc, except that the Avonmouth enrichment is more extensive (Figure 3-18 b). High cadmium concentrations in poorly drained areas near Clevedon and southwest of Mendip are coincident with high copper concentrations.

Figure 3-15
(a) Histogram for ppm copper (as for 3-10a)



(b) Probability plot for ppm copper (as for 3-11b)



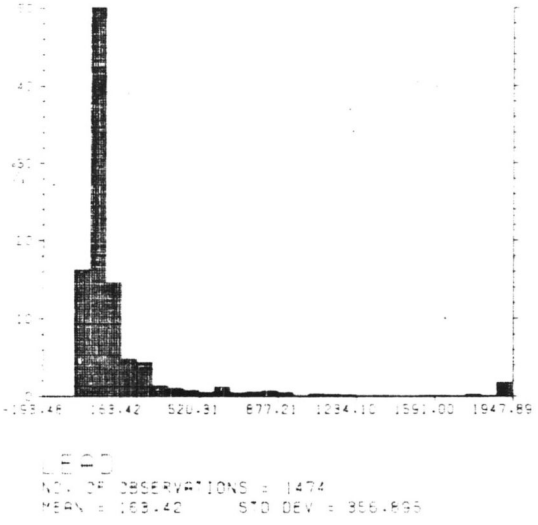
(c) STRMPLT map for copper percentiles (as for 3-10b)
(<11.7, 11.7-18.8, 18.9-26.6, 26.7-40.5, 40.6-55.8, 55.9-83.7, 83.8-176, >176 ppm)



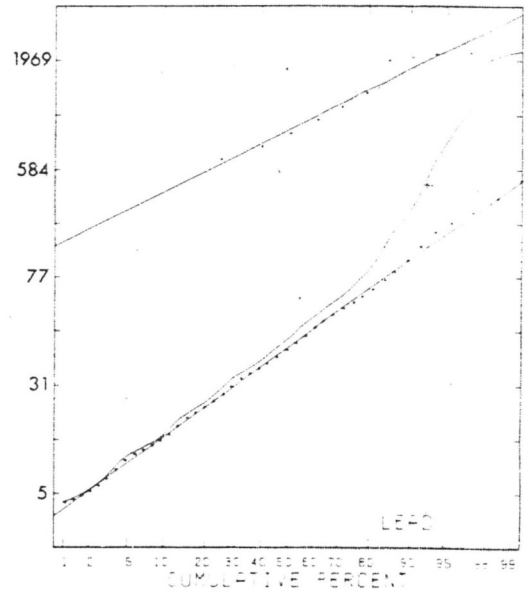
(d) STRMPLT map for copper sub-populations
(light <77, dark >77 ppm)



Figure 3-16
(a) Histogram for ppm lead (as for 3-10a)



(b) Probability plot for ppm lead (as for 3-11b)



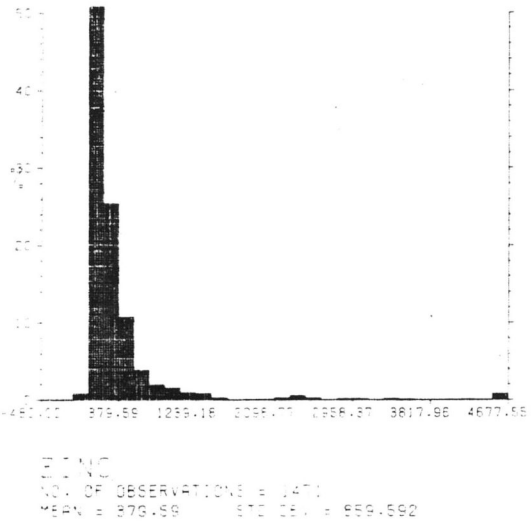
(c) STRMPLT map for lead percentiles (as for 3-10b)
(< 24.5, 24.5-45.5, 45.6-79, 80-157, 158-307, 308-690, 691-2300, >2300 ppm)



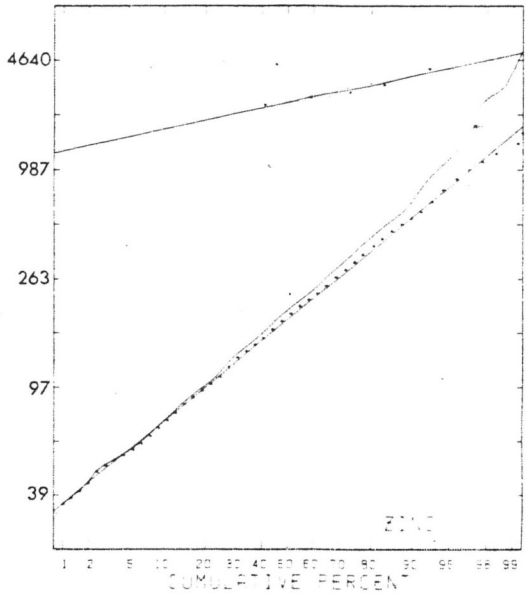
(d) STRMPLT map for lead sub-populations.
(light < 420, dark > 420 ppm)



Figure 3-17
(a) Histogram for ppm zinc (as for 3-10a)



(b) Probability plot for ppm zinc (as for 3-11b)



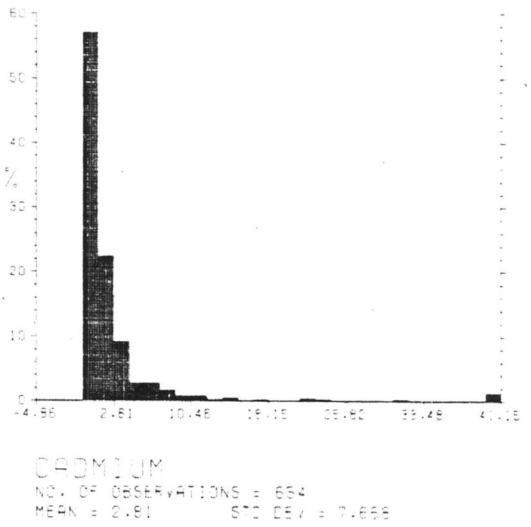
(c) STRMPLT map for zinc percentiles (as for 3-10b)
(< 103, 103-159, 160-243, 244-417, 418-627, 628-1088, 1089-3691, >3691 ppm)



(d) STRMPLT map for zinc sub-populations
(light <1590, dark >1590 ppm)



Figure 3-18
(a) Histogram for ppm cadmium (as for 3-10a)



(b) STRMPLT map for cadmium with subjectively chosen class intervals (<.4 (60% of data), .4-.8, .9-1.4, 1.5-2.9, 3.0-5.1, 5.2-7.9, 8-25, >25 ppm)



3-4.10 Arsenic

Although the arsenic data appear to consist of 3 skewed sub-populations (Figure 3-19 a and b), the distribution is largely controlled by discontinuities resulting from the analytical procedure (i.e., data were reported in multiples of 4), and the groups have not been plotted separately. The lower 80% has an even spatial distribution, except for lows in the upper Jurassic Oxford Clay and part of the Old Red Sandstone. The Lower Lias shows strong enhancement in arsenic southeast of Mendip and along the base of the Cotswold Scarp. Samples within the upper 5 percentile are from Avonmouth, Mendip and the Cotswold Scarp areas.

3-5.11 Iron

Three slightly skewed sub-populations have been identified in the iron population, but again these can be attributed to analytical discontinuities. Concentrations above 4% characterise most of the areas underlain by Coal Measures, especially northeast of Bristol and within the Radstock Basin. Iron enrichment is evident in areas underlain by the Lower Lias, along the Cotswold Scarp near Dundree (557 668) and southwest of Mendip (Figure 3-20 b). High iron concentrations are also evident in the lowlands along the banks of the Severn, particularly near Avonmouth.

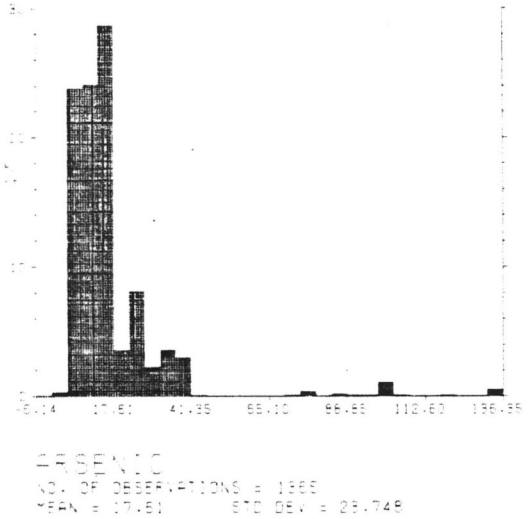
3-5.12 Molybdenum

The modybdenum data have been divided into 3 sub-populations (Figure 3-21 b). Data lying within the upper 10% of the population are entirely confined to areas underlain by the Lower Lias (Figure 3-21 c, d). Particular enrichment charcterises the base of the Cotswold Scarp, the area immediately north of Bristol, the base of Dundree Hill, and the area southwest of the Mendip Hills.

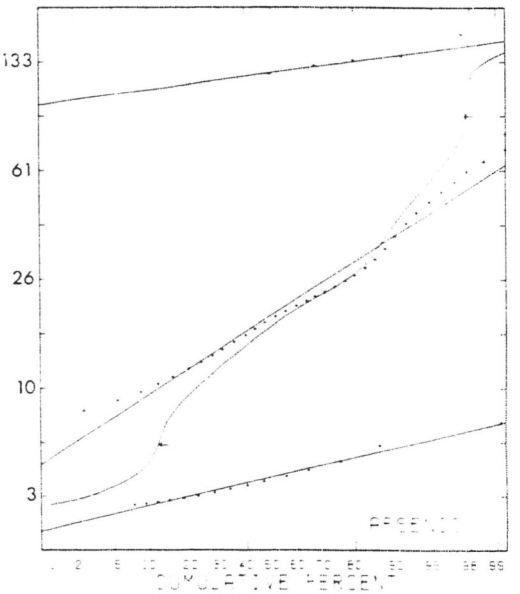
3-6 Principal Components Analysis of Stream Sediment Data

Principal components analysis was used to investigate elemental associations which are not readily apparent from studying the individual variables. The algorithm used is that of Mancey (1979), which is modified from the factor analysis routine of Davis (1973, program 7.12). The STRMPLT

Figure 3-19
(a) Histogram for ppm arsenic (as for 3-10a)



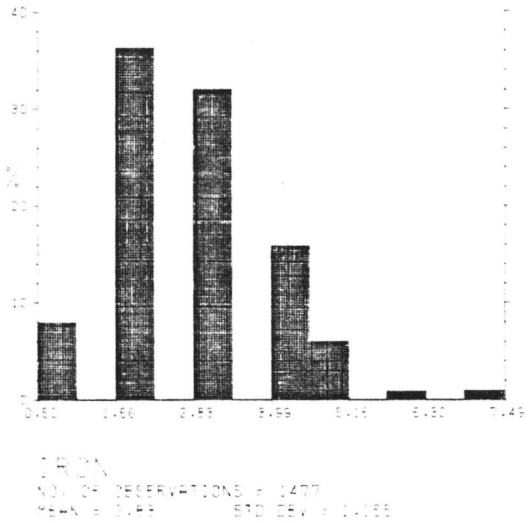
(b) Probability plot for ppm arsenic (as for 3-11b)



(c) STRMPLT map for arsenic percentiles (as for 3-10b)
(< 8.6, 8.6-12.3, 12.4-15.8, 15.9-22.0, 22.1-30.5, 30.6-38.1, 38.2-102, >102 ppm)



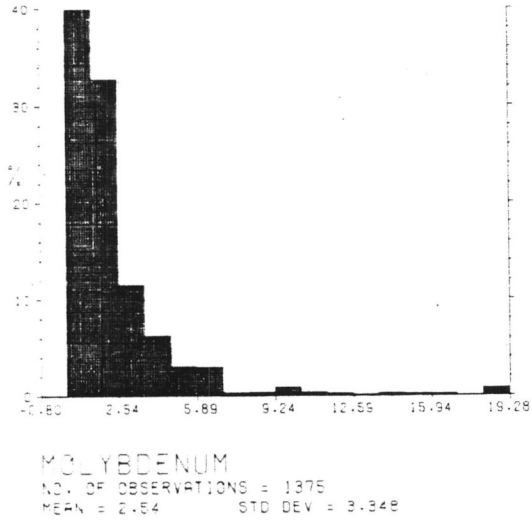
Figure 3-20
(a) Histogram for % iron (as for 3-10a)



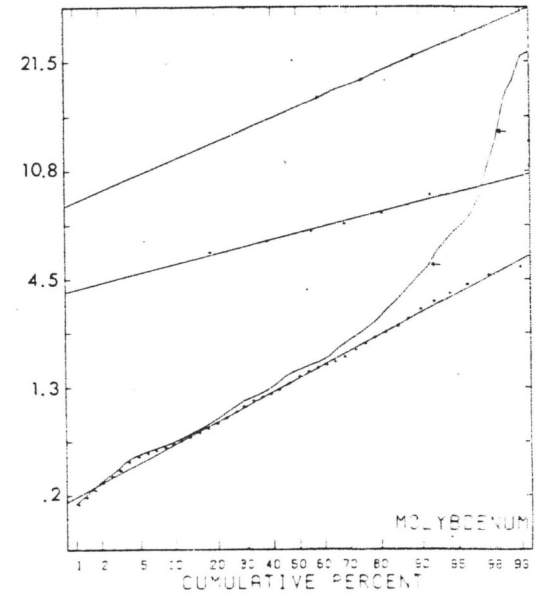
(b) STRMPLT map for iron with subjectively chosen class intervals (<1.5, 1.5-2.5, 2.6-3.5, 3.6-4.5, 4.6-5.5, 5.6-6.5, >6.5%)



Figure 3-21
(a) Histogram for ppm molybdenum (as for 3-10a)



(b) Probability plot for ppm molybdenum (as for 3-11b)



(c) STRMPLT map for molybdenum percentiles (as for 3-10b) (<1.0, 1.0-1.8, 1.9-2.0, 2.1-2.9, 3.0-4.1, 4.2-5.7, 5.8-17.6, >17.6 ppm)



(d) STRMPLT map for molybdenum sub-populations (light <4.9, medium 4.9-8.6, dark >8.6 ppm)



derived map-arrays, rather than the original data, were used as input because the sector averaging procedure accounts, to some extent, for sample representivity as a function of the size of the drainage basin (see Appendix C). Using this data also satisfies the "independence of observations" requirement for parametric statistical procedures (Box and Cox, 1964). For example, in cases where samples from two adjacent sites might be derived from largely the same drainage area the effective weighting would be reduced. To satisfy the normality requirement, the data were transformed by the generalised power technique (Howarth and Earle, 1979).

Models with from 4 to 7 components were investigated using the Varimax rotation technique. The components are summarised in Table 3-1, which lists only those variables with loadings greater than $\pm$ 0.3. Important associations as interpreted from the spatial distribution of the various factors (maps not shown) are as follows: (1) Cu-Pb-Zn-Ba As (with Sr-Mn-Fe) - areas of base metal mineralisation and probable industrial contamination, (2) Mn-Fe (with Mg and As) - areas underlain by the Coal Measures, and areas of poor drainage along alluvial flats, (3) Ca-Sr - areas underlain by calcareous strata and Keuper Marl, (4) Mo (with Cu-Fe) - areas underlain by the Lower Lias black shale and (5) Sr-Ba - areas underlain by the Keuper Marl.

3-7 Discussion

The Wolfson Geochemical Atlas of England and Wales (Webb et al, 1978) has revealed significant enrichment of strontium, barium, lead, zinc, cadmium, copper, calcium and molybdenum in parts of the region between Gloucester and the Central Somerset Basin. The current investigation is intended to provide geological explanation for the enrichment, and is concentrated on the area around Bristol and Mendip Hills. Part of the work has involved a re-evaluation of the existing stream sediment data based on a higher resolution plotting technique, and on various statistical procedures.

Geochemical variation appears to be dominantly controlled by lithology and mineralisation, although industrial activity is important for some elements, and it is difficult to estimate the real effect of former mining and processing. Lithologically, the Old Red Sandstone in the northwest and the Jurassic Limestone in the east have the most distinctive geochemical characteristics.

Table 3-1 Important loadings on principal components for the stream sediment data from the study area (Data from STRMPLT arrays, following transformation by the variable exponent technique)

No. components	7	6	5	4
% variance explained	89	84	79	72
Associations	Cu-Pb-Zn	Ba-Cu-Pb	Sr-Ba-Cu	Ba-Cu-Pb-Zn
		Zn-Mn-As	Pb-Zn-As	As-Mn-Sr
	Mg	Mg-Fe-Mn	Mg-Fe-Sr	Mg-Mn-Fe
	Ca-Sr	Ca-Mn-Sr	Ca-Sr	Ca-Sr
	Mo-Cu-Fe	Mo-Cu-Fe	Mo-Fe-Cu	Mo-Fe-Cu
	Mn-Fe	As-Fe-Mn	Mn-Fe-As	
	As	Sr-Ba		
	Sr-Ba			

(All loadings shown are greater than ± 0.3. Those underlined are greater than ± 0.5)

The relative heterogenity over other lithologies is probably a result of smaller areas for individual units, mineralisation and other alteration, and variations in secondary environment. Relative geochemical characteristics of the various lithologies can be summarised as follows:

(1) low concentrations (of all elements considered here) in the Old Red Sandstone,
(2) moderately high calcium concentrations but low magnesium concentrations over the Carboniferous Limestone,
(3) high magnesium and iron concentrations over the Coal Measures,
(4) high strontium, barium and magnesium concentrations over the Keuper Marl,
(5) high molybdenum, iron and arsenic concentrations over the black shales of the Lower Lias, and
(6) high calcium concentrations, but low concentrations of other elements over the Inferior Oolite.

These relationships are consistent with stream sediment lithological relationships for other parts of England and Wales, with the exception of the relative enrichment of barium and strontium in the Keuper Marl, and the general elevation of barium, strontium, lead and zinc throughout the study area. The lead and zinc are related to base metal mineralisation in the Carboniferous Limestone and Dolomitic Conglomerate, and the patterns are similar to those around other mining districts in England and Wales. Study of sediments in underground and surface streams in the Mendip area (Stenner, 1978) has shown that extremely high concentrations of lead, zinc, and to a lesser extent, cadmium and copper, can be archeologically related to mining and smelting activity. Samples of sediments which appear to pre-date mining activity have lower, but still anomalous heavy metal concentrations.

Barium also appears to be related to the base-metal mineralisation even though it is not a dominant constituent of the Mendip area ores. The area of barium enrichment seems disproportionately large in comparison to barite mining areas such as northern Wales, Derbyshire, the northern Pennines, and the Lake District (see Webb et al, 1978, page 24).

Much of the area of high strontium concentrations is related to the extensive celestite mineralisation in the evaporitic Triassic red-beds (see Chapter 6), however, the strontium enrichment extends well beyond the area underlain by the red-beds. In these latter areas the strontium is associated with calcium.

Enhanced levels of molybdenum near Bristol and in the central Somerset Basin are most likely related to shale beds within limestones of Lower mid-Jurassic age (Le Riche, 1959). The molybdeniferous strata are part of the Blue Lias Formation (Green and Welch, 1965) which forms the base of the Lias in the study area. Le Riche (1959) noted about 5% pyrite in one sample of the Lower Lias, and it is quite likely that pyrite is widely present in the black shales. Weathering of this pyrite may be the major factor contributing to the iron and arsenic anomalies, as pyrite is known to be enriched in arsenic (Boyle, 1974).

There are very significant cadmium, lead, zinc and copper anomalies in the area northeast of Avonmouth. The geochemical pattern follows the prevailing wind direction (Marples, 1979) and is probably a product of airborne contamination from smelter and chemical works. Allen et al (1974) have determined that silicate, sulphide and oxide compounds of zinc, lead and cadmium are present in roughly equal proportions of soluble and particulate material, whereas a smaller proportion of the lead is present in soluble form. Much of the soluble metal has probably been incorporated into iron and manganese oxides, where these are present.

Anomalously high copper, lead and zinc concentrations in the area immediately east of Bristol are probably a product of urban pollution. The most likely source of the lead is automobile exhaust (cf. Hem and Durum, 1973), although some of the contamination may originate at Avonmouth, or at smaller industrial operations nearby.

A consistent feature of the stream sediment geochemistry is enrichment of manganese and iron, and related elements including copper, lead, zinc and cadmium, in poorly drained areas of the alluvial lowlands. This feature is probably a function of spatial variation in oxidation-reduction potential which has resulted in oxidation and precipitation of dissolved iron and manganese. Metal contamination northeast of Avonmouth, and the extensive lead and zinc anomalies south of the Mendip Hills near Cheddar, may be partly related to the manganese and iron. Surface and sub-surface runoff from Mendip has relatively high lead and zinc concentrations (see Chapter 4), and it is likely that much of this dissolved metal has been adsorbed onto hydrous manganese oxides on the alluvial flats.

CHAPTER 4 GEOCHEMISTRY OF GROUND AND SURFACE WATERS OF THE MENDIP HILLS

4-1 Introduction

As noted in Chapter 1, mineral exploration based on stream sediment geochemistry is of limited use in karstic areas such as the Mendip Hills. This problem is of particular importance because many karstic formations are hosts to significant base metal mineral occurrences.

The application of hydrogeochemistry to mineral exploration in carbonate areas has been assessed by several workers. DeGeoffroy et al (1967) obtained apparently good results from a regional survey in the southwest Wisconsin zinc area, although they felt that in some cases analytical methods may not be sensitive enough for such a survey, and that deep sulphide ore may not be sufficiently oxidised to allow its detection in ground water. Based on a study of the Derbyshire Dome, Edmunds (1971) concluded that ground water geochemical surveys are useful in karstic terrains where surface drainage is limited. He expressed some reservations about seasonal variability and low metal solubility under high pH conditions, but pointed out that some associated non-metals, for example fluoride, can be useful indicators of mineralisation. Bertenshaw (1979, 1981) extended the work of Edmunds and concluded that zinc is a useful indicator of zinc-bearing deposits, provided that contamination can be recognized, and that fluoride is a useful indicator of fluorite-bearing deposits. Bertenshaw (1979) also showed that seasonal variations do not necessarily mask spatial variations. In a study of surface waters near zinc mineralisation in Tennessee, Perhac and Whelan (1972) compared dissolved metal concentrations with those of bottom sediment and colloidal sized suspended material. They found that the colloidal material showed the greatest contrast above and below a mineralised zone, and that dissolved metal showed virtually no contrast.

A programme of spring and stream water sampling has been carried out in the Mendip Hills area. Emphasis has been placed on using major element variations as a guide to interpreting hydrology and the behavior of the minor elements. The problem of distinguishing between spatial geochemical patterns and seasonal variation has been assessed on the basis of a series of periodic samples collected over 13 months.

4-2 Hydrology

The hydrology of the Mendip Hills has been summarised by Smith and Drew (1975). As steeply dipping carbonate rocks are dominant, and topographic relief is significant, underground drainage is well developed. The geology of the Mendip Hills is shown in Figure 4-1, and some aspects of the hydrology are shown in Figure 4-2. Sink-spring connections, taken from Drew (1967) and Smith and Drew (1975), are indicated where known.

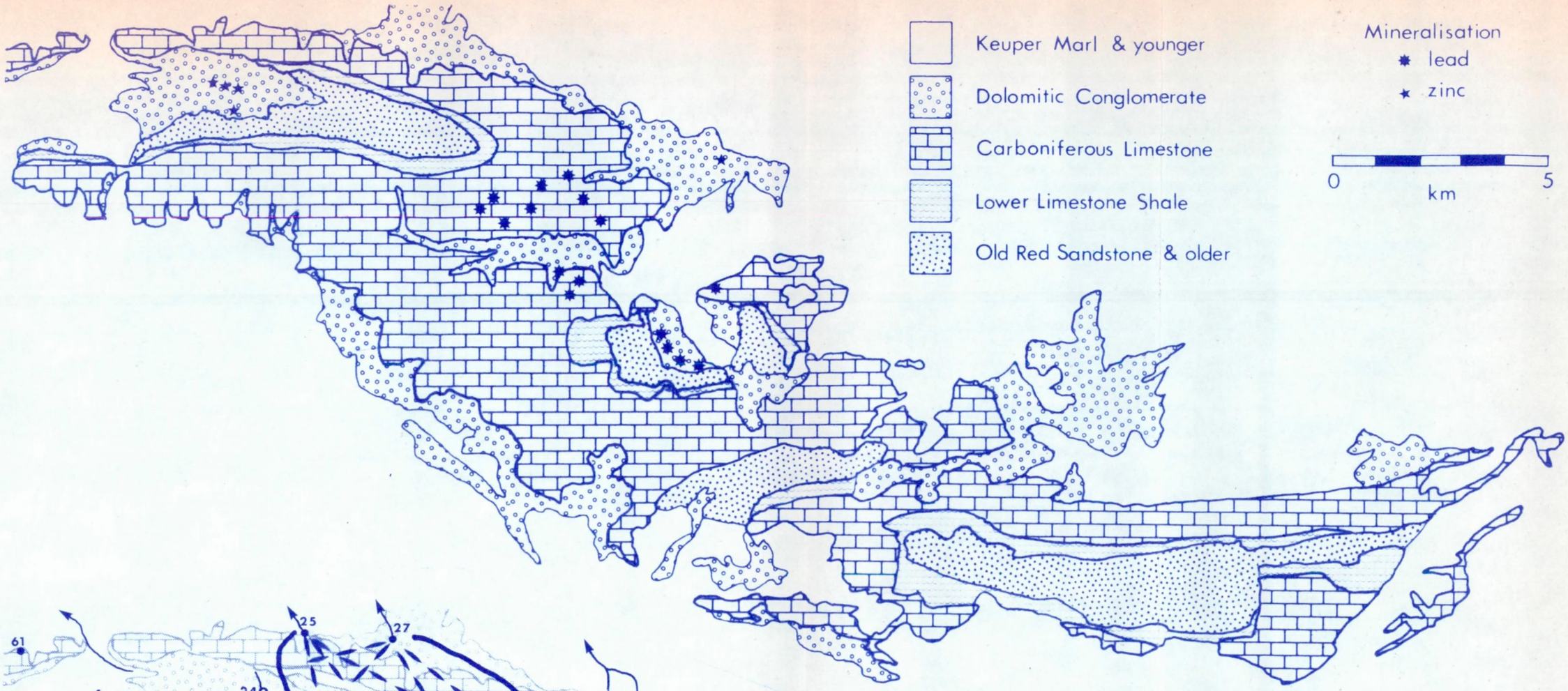
About 10% of the drainage is at surface, and in most cases this is over the Old Red Sandstone and Lower Limestone Shale. Most of these surface streams sink within a few tens of metres after crossing from the Lower Limestone Shale into the main Carboniferous Limestone. These swallet streams are virtually the only discrete recharges in the area, as more than 90% of the aquifer recharge is by percolation (Drew, 1967; Newson, 1970; Atkinson, 1977b). On the other hand, 60% to 80% of the ground water transmission is by conduit rather than diffuse flow (Atkinson, 1977a). Radically different flow rates for water from separate sinks discharging at one spring, or from one sink discharging at several springs, gives some idea of the complexity of the conduit flow (Smith and Drew, 1975). Several instances of crossing underground flow paths are documented, and some of these are shown in Figure 4-2.

Precipitation records covering the period from March 1976 to April 1977 for two sites in the Mendip area, and flow records for three Mendip Springs, are shown in Figure 4-3 and 4-4. Although Rickford and Langford flows are indicated as being nil during much of the summer of 1976, the springs did not run completely dry. All of the flow records are characterised by slow decay curves over the period of the dry 1976 summer. This is probably a result of gradual drainage of water stored in fine joints and fractures (Atkinson, 1977a). The response to rainfall in late August and early September 1976, after several weeks of drought, was initially very slight, presumably due to very low soil and ground water levels. The first rain was recorded in the last week of August and, of the springs documented here, none responded before late September.

4-3 Sample Collection, Preparation and Analysis

Samples were collected in 2 l polythene bottles which had been prewashed in 10% nitric acid. The bottles were rinsed three times at the sample site, and

Figure 4-1 Geological map of the Mendip Hills



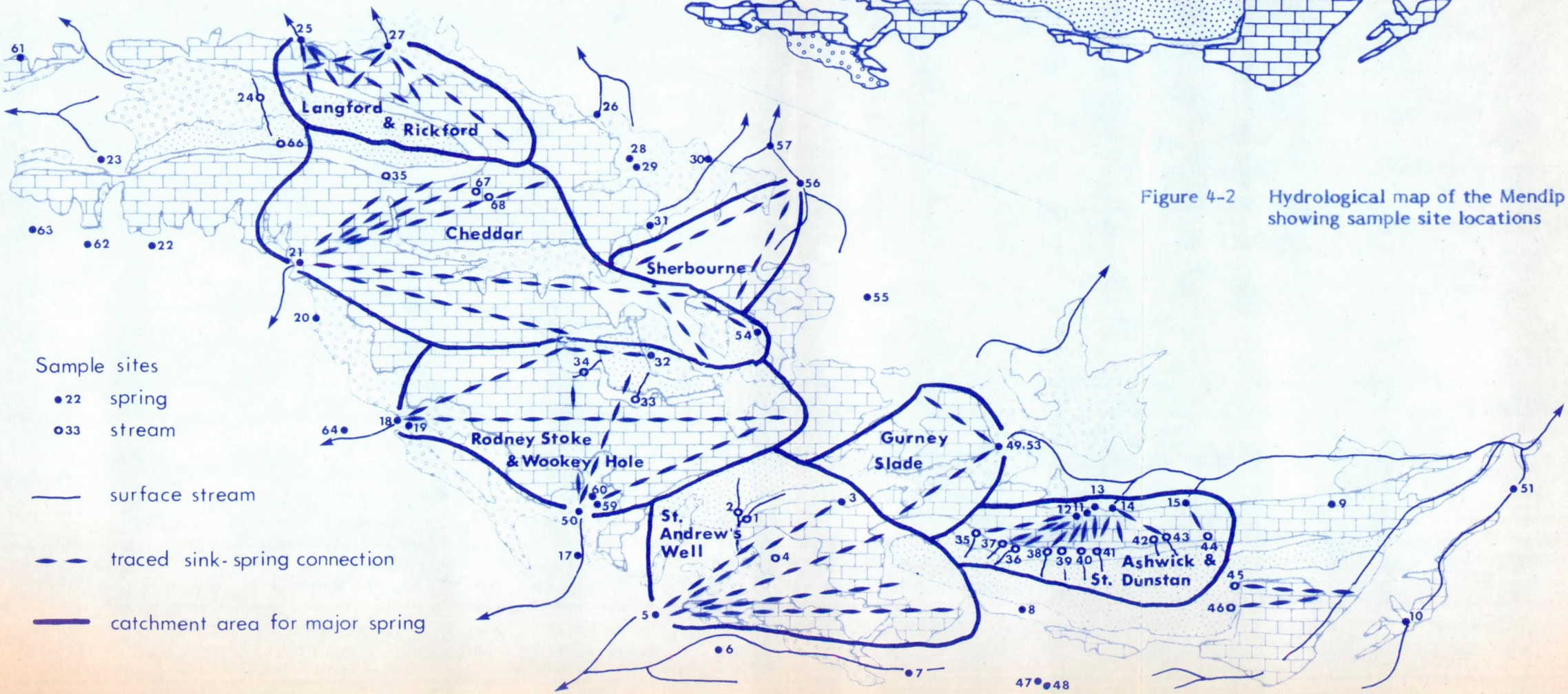
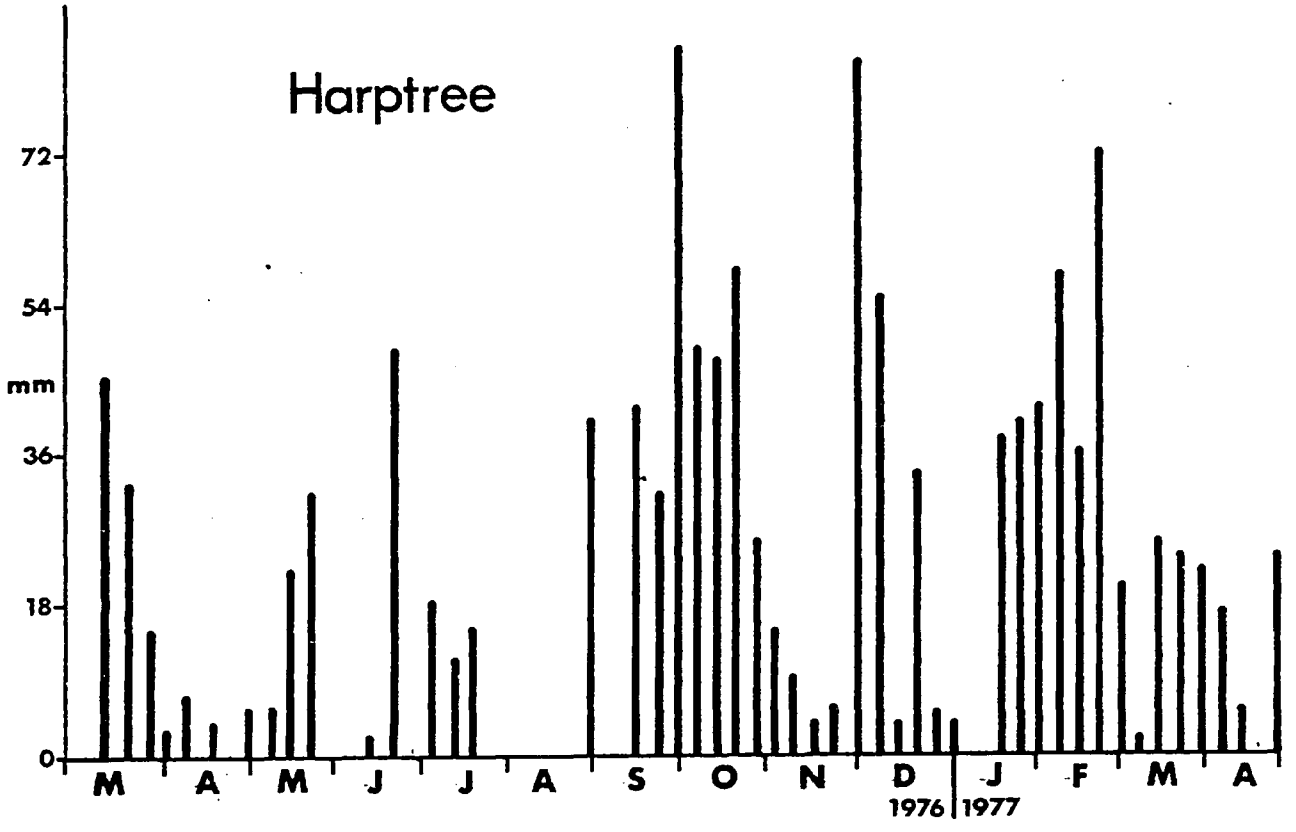


Figure 4-2 Hydrological map of the Mendip Hills showing sample site locations

Figure 4-3 Weekly precipitation records for Harptree (near site 30) and Charterhouse (near site 67) for the period March 1976 to April 1977



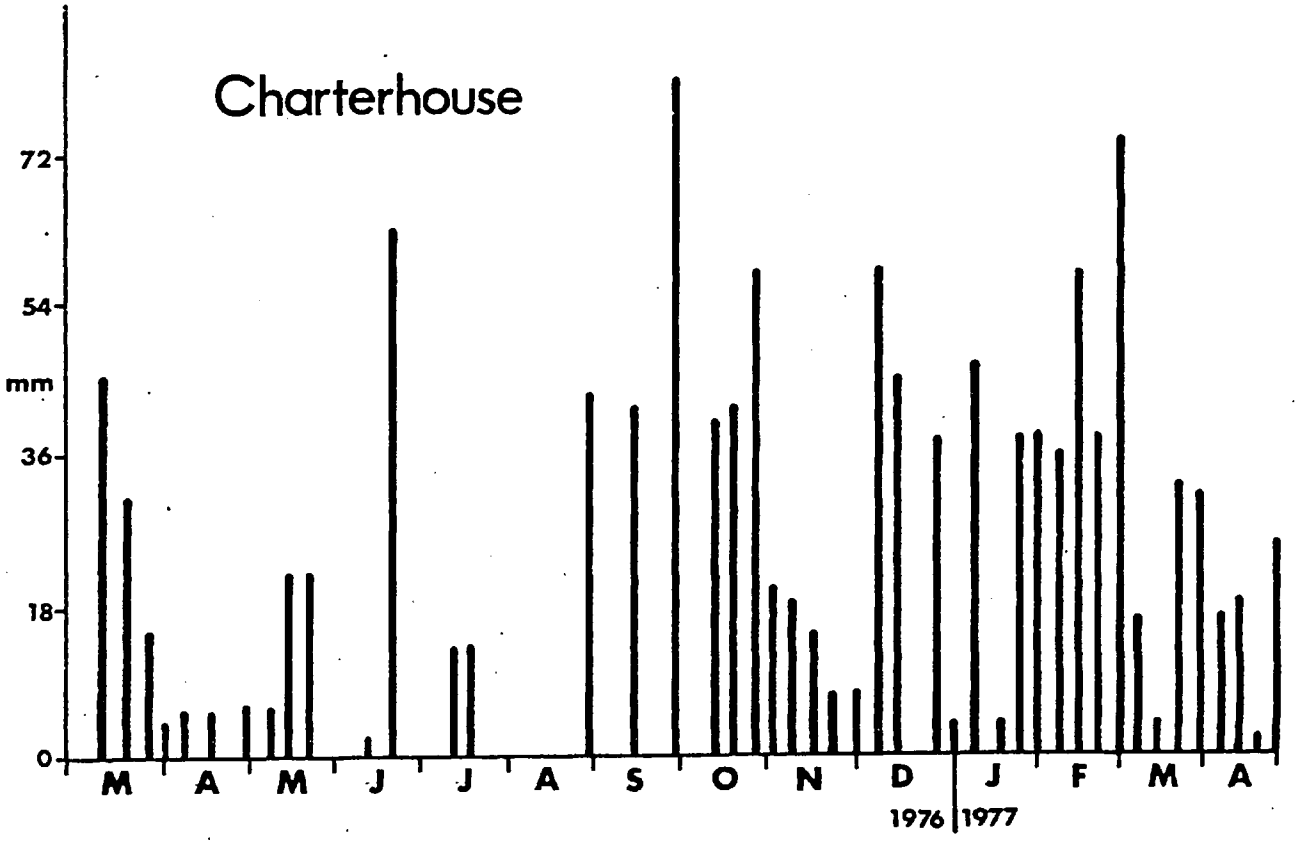
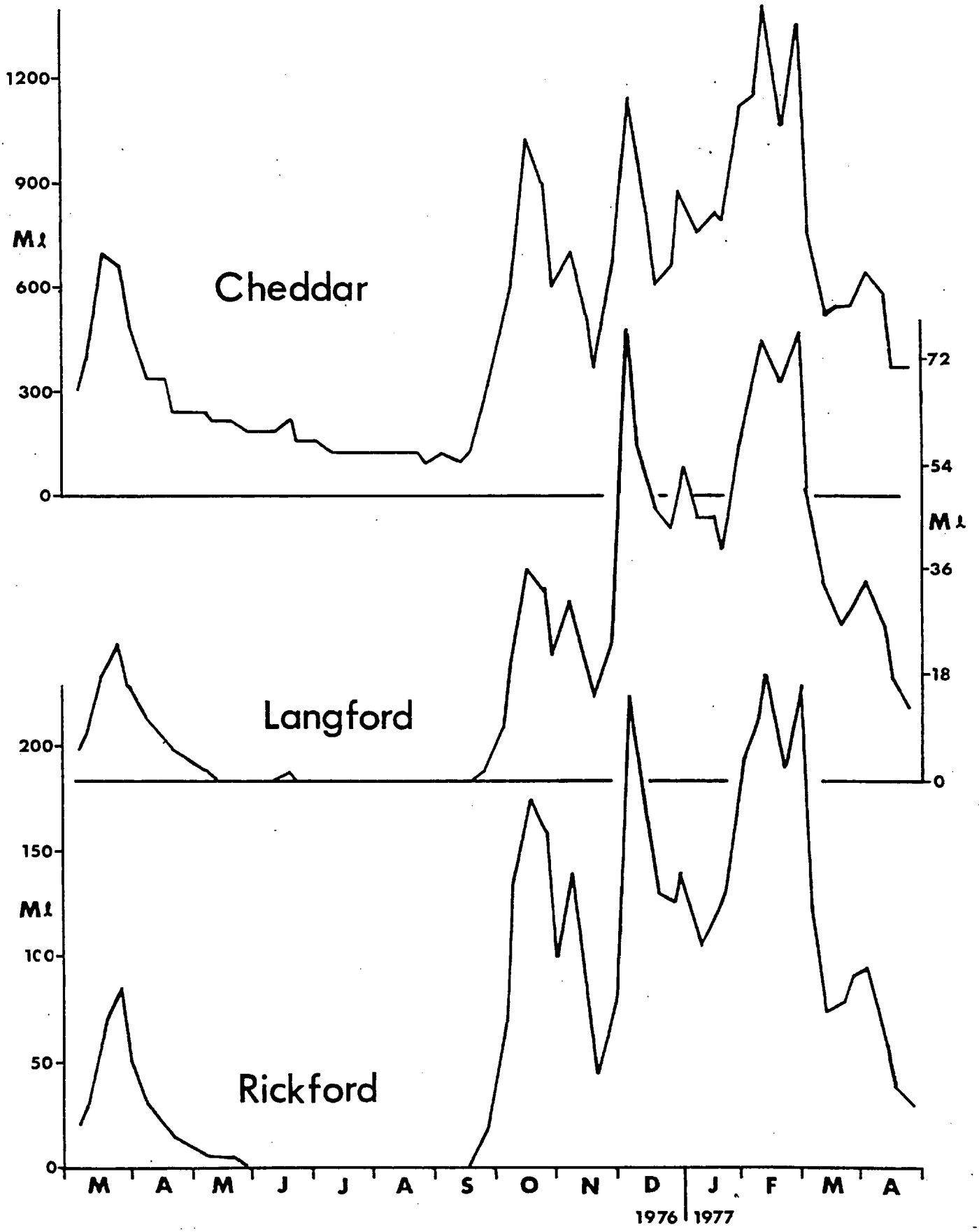


Figure 4-4 Flow records for Rickford (site 27), Langford (site 25) and Cheddar (site 21) for the period from March 1976 to April 1977 (data from Wessex Water Authority, Bristol)



filled underwater so as to avoid air bubbles. Water temperature and pH were determined in the field, the latter using a Pye-Unicam-293 pH meter which was calibrated several times each day with buffered solutions of pH 4.0, 7.0 and 9.2, and again at each sample site with the pH 7.0 solution. Springs were sampled as close to their source, and as free from apparent contamination as possible.

Within 12 hours of collection, bicarbonate concentration was determined by titration with hydrochloric acid (Appendix A). Samples were then vacuum filtered through G/F-C filter papers (nominal pore size .45 um) and split into 250 and 1 000 ml sub-samples. The 1 000 ml aliquot was acidified with 2 ml of concentrated nitric acid. Chloride and sulphate were determined titrametrically, and fluoride by specific ion electrode on the 250 mL unacidified aliquot (Appendix A). Calcium, magnesium, sodium, and potassium were determined by atomic absorption spectrophotometer, as were iron, manganese, cadmium, copper, lead, and zinc after complexation with Na-DDC and extraction into chloroform (Appendix A). At 10% of the sites duplicate samples were collected, and 10% of the fluoride, chloride, sulphate, bicarbonate, calcium, magnesium, sodium and potassium determinations were also duplicated. Estimates of sampling and analytical precision are given in Appendix A. Except at high concentrations, data for cadmium, lead and manganese are unreliable. For example, only 29% of the samples have lead concentrations above the detection limit.

A total of 79 sites was sampled, 66 of them over a period of 6 days during April 1976. Locations of these sites are given in Figure 4-2, and the data are listed in Table 4-1. Included are 42 springs, 21 streams and 3 wells. Average spring discharge varies from almost nil, to 500 l per second. Variation in discharge is discussed in Section 4-4. Nine sites were sampled at roughly monthly intervals over a period of 13 months. Data from these samples are given in Table 4-2. The sites were chosen to be representative of most of the different aquifer-types and flow conditions, although very small sources with only periodic flows were excluded.

4-4 Seasonal Fluctuations in Hydrogeochemistry

Data from five of the nine periodically sampled sites are shown graphically in Figures 4-5 to 4-9, including: Cheddar (Site 21 as shown on Figure 4-1),

Table 4-1 Analytical data for water samples from the Mendip Hills(T is in °C, HCO_3 to K are in mg/l, Cd to Zn are in ug/l)

SITE	DATE	T	PH	HCO3	F	SO4	CA	MG	NA	K	CD	CU	FE	MN	PB	ZN
001	15/04/76	8.5	8.0	302	0.06	22	90	5.0	9.9	11.0	0.40	1.50	105.00	52.0	4.0	30.50
002	15/04/76	8.5	7.2	82	0.06	23	37	4.0	10.6	1.9	0.35	0.75	10.00	1.5	1.2	20.00
003	15/04/76	9.5	7.3	302	0.44	18	86	4.6	8.6	1.9	0.85	1.45	16.00	20.0	2.2	215.00
004	15/04/76	8.5	8.3	334	0.08	33	118	4.0	6.5	1.4	0.05	1.15	15.00	2.5	1.2	1.95
005	15/04/76	11.0	7.2	315	0.16	29	100	9.5	9.2	2.8	0.15	0.65	7.50	1.0	0.5	30.00
005	15/04/76	11.0	7.2	315	0.17	26	93	8.8	8.2	2.7	0.35	0.85	9.50	1.0	1.2	37.00
006	15/04/76	10.0	8.0	252	0.16	35	75	23.8	10.5	2.3	0.05	0.90	8.50	1.0	3.0	6.10
007	15/04/76	11.5	7.2	252	0.14	17	88	6.5	6.1	1.8	0.15	0.60	4.00	0.5	1.2	42.00
008	15/04/76	10.0	6.2	19	0.07	10	9	1.5	8.7	1.6	0.15	0.80	15.00	6.5	1.2	55.00
009	15/04/76	11.0	6.7	271	0.12	28	80	7.3	10.6	8.4	0.20	3.15	75.00	12.0	1.2	30.00
010	15/04/76	11.5	6.8	364	0.15	26	93	6.8	7.6	2.1	0.25	1.10	4.00	6.0	1.2	90.50
011	15/04/76	13.0	6.8	158	0.14	20	123	6.6	7.9	2.6	1.50	1.10	5.50	0.5	1.2	35.50
012	15/04/76	13.0	6.7	284	0.11	18	86	8.8	.7.8	3.0	1.45	0.75	26.00	8.5	1.2	9.90
013	15/04/76	11.0	6.9	208	0.17	26	60	7.3	9.6	4.5	0.40	1.25	36.00	15.0	1.2	4.80
014	15/04/76	11.0	6.9	239	0.16	30	64	6.5	7.9	2.6	1.55	1.85	10.00	4.0	0.5	6.90
015	15/04/76	10.5	7.5	302	0.41	22	88	4.5	6.3	1.8	0.01	0.55	5.00	1.0	1.2	6.15
016	15/04/76	11.5	6.9	315	0.13	18	95	8.3	9.0	2.4	0.25	0.70	14.00	2.5	1.2	12.00
017	16/04/76	11.0	6.7	296	0.08	23	95	8.0	6.4	1.8	0.15	0.55	4.50	1.0	3.5	56.00
017	16/04/76	11.0	6.7	296	0.07	20	100	8.8	7.6	2.0	0.45	.	4.00	0.9	3.5	67.50
018	16/04/76	12.0	6.8	296	0.06	29	85	9.8	6.1	1.0	2.25	0.50	5.00	0.1	2.2	4.00
019	16/04/76	12.0	6.8	296	0.08	33	90	13.0	6.8	2.1	0.15	0.50	10.00	0.5	1.2	9.70
020	16/04/76	12.0	6.8	356	0.06	34	94	26.0	8.9	2.3	0.50	0.75	5.50	1.5	1.2	2.50
020	16/04/76	12.0	6.8	356	0.07	32	85	25.0	9.0	2.1	0.25	0.80	5.50	1.5	1.2	2.60
021	16/04/76	11.0	6.7	265	0.06	18	96	4.5	6.2	1.5	1.20	0.65	5.00	1.0	19.0	83.00
022	16/04/76	12.0	6.9	290	0.09	33	115	10.0	8.3	1.4	0.50	0.50	7.00	0.5	1.2	4.40
023	16/04/76	12.0	6.6	302	0.08	30	95	13.8	10.0	2.1	2.90	0.65	4.00	0.5	1.2	9.25
024	16/04/76	9.5	7.1	132	0.06	25	43	7.0	8.9	2.0	2.20	0.60	5.00	1.5	1.2	93.50
025	16/04/76	11.0	6.8	233	0.12	26	74	7.6	8.0	1.4	0.25	0.35	10.50	1.0	1.2	36.00
025	16/04/76	11.0	6.8	233	0.10	24	74	7.5	8.0	1.3	0.45	0.45	6.50	1.0	1.2	36.00
026	16/04/76	11.0	6.7	277	0.07	26	99	8.0	6.4	2.0	1.30	0.60	8.00	2.5	1.2	67.00
027	16/04/76	11.0	6.5	271	0.07	25	88	5.0	6.2	1.7	0.75	0.35	0.45	0.5	1.2	52.50
028	16/04/76	9.5	7.4	284	0.17	26	95	13.5	5.7	1.4	0.25	0.55	15.00	1.0	0.5	4.10
029	16/04/76	12.5	7.5	277	0.19	14	87	11.0	5.9	1.7	0.25	0.60	5.50	3.5	0.5	5.50
030	16/04/76	11.5	6.6	284	0.09	25	160	4.5	7.0	3.1	2.15	0.50	8.00	0.3	5.0	1010.00
031	16/04/76	11.0	7.4	126	0.07	16	37	5.0	4.7	1.4	0.50	0.95	16.00	3.0	8.0	42.50
032	17/04/76	.	6.2	13	0.10	15	7	2.4	5.0	1.8	0.70	0.85	155.00	125.0	46.0	31.00
033	17/04/76	.	7.4	132	0.08	17	48	2.0	6.6	1.6	0.10	0.45	110.00	23.5	18.0	44.00
034	17/04/76	11.5	7.7	214	0.07	23	82	5.4	6.4	2.1	0.10	0.85	16.00	1.5	3.0	3.65
034	17/04/76	11.5	7.7	214	0.08	21	80	5.3	7.2	2.0	0.15	0.70	51.00	1.5	5.0	3.80
035	18/04/76	9.0	6.8	202	0.06	22	71	4.5	9.4	2.1	0.25	0.70	28.00	85.0	0.5	2.85
036	18/04/76	12.5	7.2	176	0.23	5	47	7.0	7.7	2.5	0.30	0.35	15.00	2.0	1.2	2.30
037	18/04/76	12.5	7.5	239	0.14	19	83	6.0	6.9	2.4	0.05	1.10	7.50	1.5	2.2	1.60
038	18/04/76	12.5	7.5	126	0.20	17	36	4.5	5.5	1.9	0.55	1.40	125.00	7.5	2.2	5.65
039	18/04/76	12.0	7.3	113	0.09	24	36	3.8	6.1	4.0	0.60	1.55	85.00	25.0	1.2	5.70
039	18/04/76	12.0	7.3	113	0.08	24	44	4.3	6.8	4.7	0.60	1.60	85.00	25.0	1.2	5.50
040	18/04/76	13.0	7.4	44	0.05	24	21	2.5	6.3	3.1	0.30	1.45	31.00	4.0	1.2	3.50
041	18/04/76	14.0	7.9	94	0.14	11	30	5.2	6.6	2.0	0.15	0.75	41.00	11.0	1.2	3.50
042	18/04/76	14.0	8.4	176	0.19	19	51	7.4	9.3	6.9	1.25	1.15	17.00	3.5	0.5	2.50
043	18/04/76	13.0	7.8	107	0.11	17	28	5.5	10.4	5.7	.	.	.	.	.	.
044	18/04/76	14.0	7.8	189	0.17	20	50	8.5	10.2	10.3	0.40	1.05	135.00	65.0	1.2	5.35
044	18/04/76	14.0	7.8	189	0.19	20	46	7.5	9.4	8.9	0.35	1.10	105.00	51.0	1.2	4.60
045	18/04/76	12.5	7.8	120	0.53	6	32	4.6	6.5	1.9	0.75	0.50	20.00	4.0	1.2	2.20
046	18/04/76	12.5	7.7	145	0.20	10	40	7.5	6.5	1.5	0.25	0.85	13.00	13.0	1.2	2.60
047	18/04/76	15.0	7.9	221	0.09	37	100	2.5	8.0	1.9	0.40	0.50	20.00	15.0	1.2	1.15
048	18/04/76	11.0	7.9	221	0.07	45	86	2.5	9.6	6.4	0.25	0.70	7.00	0.5	1.2	2.50
049	18/04/76	11.0	7.0	328	0.17	35	98	7.5	9.0	2.2	0.40	0.60	8.50	7.5	1.2	86.00

Table 4-1 cont.

SITE	DATE	T	PH	HCO3	F	SO4	CA	MG	NA	K	CD	CU	FE	MN	PB	ZN
050	18/04/76	.	7.1	283	0.07	18	86	7.0	6.3	1.40	0.60	0.75	6.0	27.00	23.0	93.00
051	20/04/76	11.5	6.9	334	0.19	26	110	8.5	7.4	1.90	0.50	0.85	6.5	1.00	2.2	245.00
052	20/04/76	13.0	7.2	321	0.34	39	116	9.5	10.5	2.90	1.10	8.45	5.0	1.00	4.5	510.00
053	20/04/76	11.5	7.1	315	0.15	34	102	7.8	9.7	2.30	0.70	1.10	5.5	1.00	2.2	125.00
054	20/04/76	10.0	7.3	120	0.07	20	35	6.7	9.4	2.20	0.01	0.50	4.0	1.00	0.5	12.50
054	20/04/76	10.0	7.3	120	0.07	18	38	7.0	8.8	2.20	0.30	0.80	4.5	1.00	0.5	13.00
055	20/04/76	11.0	6.8	113	0.08	25	120	1.5	6.9	2.90	0.50	0.75	6.0	1.00	0.5	19.00
056	20/04/76	12.0	6.8	302	0.29	28	102	10.0	7.3	2.90	1.45	0.75	5.5	0.50	15.5	900.00
057	20/04/76	11.0	6.7	328	0.23	48	117	17.0	9.5	2.80	.	.	.	.	.	.
058	20/04/76	10.5	7.2	347	0.06	16	70	4.5	6.4	1.80	0.20	0.85	3.0	1.00	0.5	4.10
059	20/04/76	11.0	7.3	214	0.07	7	50	7.0	6.9	2.20	0.15	0.40	6.5	0.50	1.2	3.70
060	20/04/76	10.5	7.1	176	0.09	40	95	5.0	9.2	1.40	0.01	0.40	7.0	.	1.2	3.65
060	20/04/76	10.5	7.1	176	0.10	37	83	5.0	9.4	1.40	0.01	0.50	5.0	1.00	1.2	2.20
061	20/04/76	12.0	7.0	246	0.09	24	68	1.5	10.2	2.00	0.90	0.60	4.0	0.45	1.2	85.50
062	20/04/76	13.0	7.0	296	0.12	46	78	20.5	9.9	1.80	0.45	1.30	3.5	0.50	0.5	3.30
063	20/04/76	13.0	7.2	277	0.09	39	95	24.0	50.0	3.00	0.25	1.40	5.0	1.00	1.2	5.30
064	20/04/76	12.5	7.5	296	0.06	27	100	14.5	8.4	1.80	0.60	10.20	6.5	1.00	1.2	10.70
065	21/04/76	10.5	6.9	189	0.06	18	64	4.8	9.0	2.20	0.10	0.40	3.0	0.50	0.5	1.45
066	23/05/76	.	7.5	138	0.05	20	58	5.5	8.6	1.75	1.30	0.35	15.0	4.00	3.0	51.50
067	23/05/76	.	6.5	126	0.05	18	50	4.2	6.8	0.55	0.30	0.65	380.0	345.00	1.2	27.00
068	23/05/76	.	7.0	189	0.10	15	77	4.0	8.8	0.90	0.40	0.60	175.0	70.00	2.5	63.00
068	23/05/76	.	7.0	195	0.09	15	75	4.1	8.9	1.03	0.50	0.40	150.0	65.00	1.2	58.00

Table 4-2 Analytical data for water samples from the monthly sampling stations in the Mendip Hills area (T is in °C, HCO_3 to K are in mg/l, Cd to Zn are in ug/l)

SITE=005

DATE	T	PH	HCO3	F	SO4	CL	CA	MG	NA	K	CD	CU	FE	MN	PB	ZN
27/03/76	.	7.6	.	.	.	.	105	9.0	.	.	0.35	1.90	22.0	4.50	3.0	24.5
15/04/76	11.0	7.2	315	0.16	29	.	100	9.5	9.20	2.80	0.15	0.65	7.5	1.00	0.5	30.0
15/04/76	11.0	7.2	315	0.17	26	.	93	8.8	8.20	2.70	0.35	0.85	9.5	1.00	1.2	37.0
23/05/76	.	7.0	302	0.18	26	20	111	11.8	10.00	4.40	0.30	0.95	60.0	1.00	3.5	25.0
17/07/76	11.0	7.0	325	0.19	24	19	114	12.2	9.35	4.45	1.00	1.60	12.0	0.50	1.2	27.0
23/08/76	11.5	6.8	323	0.16	23	18	114	13.2	18.50	4.15	.	.	.	.	.	.
26/09/76	11.4	6.7	269	0.16	32	25	132	10.0	23.00	7.70	1.50	2.00	46.5	5.50	2.5	27.0
16/10/76	10.4	.	297	0.17	31	19	120	9.2	.	.	0.70	1.50	17.0	1.50	2.5	27.5
24/11/76	10.7	6.9	318	0.17	27	18	116	10.6	.	.	0.30	0.70	8.0	0.50	1.2	23.5
19/12/76	.	6.9	256	0.15	27	19	110	7.0	8.00	3.70	1.80	1.60	43.0	1.50	2.5	22.0
23/01/77	10.0	7.0	271	0.15	27	20	120	8.0	9.10	4.00	2.60	1.30	31.5	1.50	1.2	22.5
23/01/77	10.0	7.0	274	0.15	27	20	124	8.0	9.25	4.10	0.50	1.30	40.0	1.50	1.2	22.5
19/02/77	9.2	6.9	246	0.15	25	15	130	8.0	9.25	4.00	1.80	1.60	70.0	2.00	1.2	20.0
22/03/77	9.6	6.9	280	0.20	25	14	104	6.8	7.00	2.80	0.35	1.10	16.5	1.00	1.2	20.5
21/04/77	10.3	7.1	293	0.20	22	13	121	9.9	7.55	2.99	0.30	0.55	10.0	0.25	1.2	21.5

SITE=007

DATE	T	PH	HCO3	F	SO4	CL	CA	MG	NA	K	CD	CU	FE	MN	PB	ZN
27/03/76	11.5	7.2	252	0.14	17	.	88	6.5	6.10	1.80	0.15	0.60	4.0	0.50	1.2	42.0
15/04/76	11.5	7.2	252	0.14	17	.	88	6.5	6.10	1.80	0.15	0.60	4.0	0.50	1.2	42.0
23/05/76	.	7.0	296	0.13	18	16	112	8.0	7.40	2.45	0.35	0.40	5.0	0.50	1.2	22.5
17/07/76	10.7	7.1	322	0.18	19	16	120	8.8	7.45	2.50	0.30	0.50	6.0	0.50	1.2	22.0
17/07/76	10.7	7.1	322	0.17	20	15	118	9.0	7.80	2.65	0.20	0.70	4.5	0.50	1.2	22.0
23/08/76	13.0	7.5	324	0.14	26	18	138	9.2	18.00	2.55	0.20	1.30	13.0	4.00	1.2	19.0
26/09/76	11.8	6.8	330	0.16	25	19	155	10.6	.	4.50	0.40	1.05	14.0	3.50	2.5	22.0
16/10/76	10.8	.	321	0.13	21	13	120	8.0	.	.	.	1.50	5.0	1.00	1.2	40.0
16/10/76	10.8	.	321	0.15	20	14	119	9.0	.	.	0.75	1.75	4.0	1.00	1.2	33.5
24/11/76	10.4	7.0	322	0.17	14	13	120	8.4	.	.	0.70	0.40	6.0	0.25	1.2	23.5
19/12/76	.	7.1	302	0.12	17	13	106	6.0	6.60	2.40	0.25	0.75	8.5	0.25	1.2	27.5
23/01/77	10.3	7.0	313	0.12	16	15	128	7.0	7.25	2.50	4.00	0.75	0.7	0.25	4.0	29.0
19/02/77	10.3	7.0	304	0.12	18	14	138	6.6	7.55	2.75	0.50	0.50	14.0	0.25	1.2	35.0
22/03/77	10.0	7.0	304	0.15	15	12	104	5.2	6.00	2.00	0.30	0.40	4.0	0.50	1.2	29.5

SITE=014

DATE	T	PH	HCO3	F	SO4	CL	CA	MG	NA	K	CD	CU	FE	MN	PB	ZN
23/05/76	.	7.3	252	0.24	37	18	100	8.4	9.70	4.10	0.40	0.50	7.0	2.50	1.2	3.70
17/07/76	10.0	7.4	288	0.26	38	17	118	5.8	8.95	3.20	0.40	0.80	7.5	1.50	1.2	6.00
23/08/76	10.5	7.0	296	0.22	27	16	118	5.5	16.30	3.03	0.10	0.40	8.0	0.25	1.2	6.10
26/09/76	11.6	7.2	173	0.35	93	25	100	6.8	39.50	9.80	0.30	1.90	46.0	12.50	1.2	6.60
16/10/76	10.8	.	186	0.15	41	19	74	7.3	.	.	0.65	1.60	38.0	32.00	1.2	19.50
24/11/76	10.0	7.1	264	0.19	44	16	110	9.0	.	.	0.40	0.45	7.0	75.00	0.5	4.20
19/12/76	.	7.0	184	0.11	41	20	94	5.8	8.50	5.10	0.85	0.74	37.0	69.00	1.2	4.70
23/01/77	10.0	7.2	197	0.12	38	17	88	6.0	8.55	4.50	1.40	0.80	35.0	33.50	1.2	4.25
19/02/77	8.2	7.2	177	0.11	37	14	96	6.6	5.00	9.10	1.35	0.95	46.5	25.00	1.2	3.90
19/02/77	8.2	7.2	177	0.11	37	13	86	5.7	4.25	8.15	1.60	0.95	38.0	22.50	1.2	3.90
22/03/77	8.5	7.0	194	0.15	33	13	82	5.0	6.70	3.65	0.30	0.75	24.5	18.00	1.2	3.20
22/03/77	8.5	7.0	195	0.16	35	13	82	5.2	6.80	3.55	0.40	0.75	23.5	17.50	1.2	3.65
21/04/77	9.8	7.4	246	0.20	30	11	108	8.3	8.06	3.64	0.40	0.95	16.0	5.50	0.5	3.40

Table 4-2 cont.

SITE=018

DATE	T	PH	HCO3	F	SO4	CL	CA	MG	NA	K	CD	CU	FE	MN	PB	ZN
26/09/76	12.2	6.8	292	0.04	22	14	118	9.8	15.00	1.00	0.35	0.70	3.5	0.25	1.2	3.80
16/10/76	10.6	.	283	0.06	20	17	119	8.9	.	.	0.40	1.20	8.0	0.25	1.2	17.00
24/11/76	11.0	7.1	303	0.05	28	15	128	11.0	.	.	0.45	0.40	7.5	0.25	1.2	2.30
24/11/76	11.0	7.1	300	0.05	27	14	116	11.0	.	.	0.30	0.40	6.0	0.25	1.2	3.00
19/12/76	.	7.1	288	0.04	26	16	112	8.6	6.30	1.10	0.25	0.40	7.0	0.25	1.2	2.60
23/01/77	10.6	7.2	296	0.06	26	16	120	10.0	7.00	0.95	3.75	0.50	3.5	0.25	1.2	3.40
19/02/77	10.2	7.0	282	0.05	27	13	124	10.4	7.00	0.90	0.30	0.45	8.0	0.25	1.2	2.25
22/03/77	10.3	7.1	282	.	25	13	111	8.3	6.03	1.00	0.60	1.00	15.5	0.25	1.2	3.80
22/03/77	10.3	7.1	280	0.05	25	13	112	8.0	5.90	1.00	0.55	0.40	3.0	0.25	1.2	1.75
21/04/77	10.6	7.1	287	0.06	24	11	112	10.4	7.15	1.16	0.25	0.25	6.0	0.25	1.2	6.00

SITE=021

DATE	T	PH	HCO3	F	SO4	CL	CA	MG	NA	K	CD	CU	FE	MN	PB	ZN
27/03/76	.	7.0	.	.	.	.	95	4.00	.	.	0.70	0.95	14.00	1.50	24.5	60.0
16/04/76	11.0	6.7	265	0.06	18	.	96	4.50	6.20	1.50	1.20	0.65	5.00	1.00	19.0	83.0
23/05/76	.	7.0	245	0.05	14	16	98	5.00	6.50	2.05	0.45	0.50	11.00	1.00	21.5	85.5
23/05/76	.	7.0	245	0.05	14	16	97	5.00	6.40	2.00	0.40	0.45	7.00	0.50	21.0	82.0
17/07/76	12.0	7.0	260	0.09	16	16	102	4.80	6.40	2.00	0.75	0.80	10.00	1.00	19.5	86.0
23/08/76	10.5	6.9	266	0.06	13	14	102	5.40	12.00	1.83	0.50	0.80	7.50	0.25	22.5	90.0
26/09/76	10.8	6.8	259	0.07	15	15	102	5.20	15.50	2.50	0.75	0.75	12.50	0.25	22.5	87.0
16/10/76	10.2	.	249	0.07	23	16	104	4.30	.	.	0.70	1.15	6.25	1.50	17.0	83.0
24/11/76	10.4	7.0	272	0.06	19	14	109	5.10	.	.	1.70	0.30	5.00	0.50	13.5	.
19/12/76	.	7.0	254	0.05	18	16	100	4.20	6.10	1.50	0.70	0.35	12.00	0.50	14.5	69.0
23/01/77	10.2	7.1	250	0.05	17	16	104	4.30	7.00	1.80	0.45	0.40	21.00	1.00	14.0	75.0
23/01/77	10.2	7.1	249	0.05	17	15	104	4.50	7.25	2.00	0.50	0.50	27.00	1.00	15.0	72.0
19/02/77	9.7	6.9	247	0.06	18	13	106	4.40	6.75	1.50	0.75	0.35	17.00	1.00	14.5	74.0
22/03/77	9.8	6.9	240	0.07	16	12	93	3.50	5.70	1.45	0.50	0.50	17.50	1.00	15.0	84.0
21/04/77	10.3	6.9	249	0.07	15	10	108	4.50	6.45	1.63	0.70	0.30	22.00	0.25	15.0	79.0
21/04/77	10.3	6.9	250	0.07	15	10	106	4.55	6.54	1.63	0.55	0.25	9.50	0.25	16.0	78.5

SITE=023

DATE	T	PH	HCO3	F	SO4	CL	CA	MG	NA	K	CD	CU	FE	MN	PB	ZN
27/03/76	12.0	6.6	302	0.08	30	.	95	13.8	10.0	2.10	2.90	0.65	4.0	0.50	1.2	9.25
16/04/76	12.0	6.6	302	0.08	30	.	95	13.8	10.0	2.10	2.90	0.65	4.0	0.50	1.2	9.25
23/05/76	.	7.0	296	0.07	26	22	100	16.0	10.5	2.40	0.25	0.40	8.5	0.50	1.2	5.40
17/07/76	11.5	7.2	332	0.09	30	20	110	20.0	10.0	2.85	0.50	0.65	6.0	2.00	1.2	5.60
17/07/76	11.5	7.2	333	0.09	30	20	108	20.0	10.0	2.75	0.50	0.75	7.0	2.00	1.2	5.60
23/08/76	12.5	6.8	337	0.09	31	20	110	21.2	23.0	3.35	0.50	0.80	20.0	210.00	1.2	12.00
26/09/76	11.8	7.0	283	0.07	27	20	96	14.4	24.5	2.70	0.25	0.05	24.0	0.50	1.2	7.25
16/10/76	10.8	.	277	0.08	32	20	98	14.8	.	.	0.70	0.95	6.0	0.50	1.2	22.50
24/11/76	11.0	6.9	312	0.07	29	17	107	16.4	.	.	0.85	0.25	12.5	0.25	0.5	6.25
19/12/76	.	6.9	281	0.06	27	25	102	12.4	13.0	2.40	0.85	0.30	7.5	0.25	2.5	6.00
23/01/77	10.8	6.9	295	0.06	28	22	110	15.0	13.0	2.40	0.30	0.45	7.0	0.50	1.2	6.15
19/02/77	10.4	7.1	279	0.06	28	21	120	15.0	12.0	2.80	0.70	0.35	15.0	0.25	1.2	5.55
19/02/77	10.4	7.1	276	0.06	28	21	136	15.0	13.0	2.90	0.65	0.50	15.0	0.50	5.0	6.50
22/03/77	10.7	7.0	283	0.07	28	18	86	10.8	8.4	1.90	0.30	0.35	6.0	0.50	1.2	4.80
21/04/77	11.0	7.0	288	0.08	26	14	112	15.6	.	2.56	0.30	0.25	8.5	0.25	1.2	4.65

Table 4-2 cont.

SITE=025

DATE	T	PH	HCO3	F	SO4	CL	CA	MG	NA	K	CD	CU	FE	MN	PB	ZN
27/03/76	.	7.1	.	.	.	.	80	8.0	.	.	0.50	0.60	8.0	1.00	1.25	31
16/04/76	11.0	6.8	233	0.12	26	.	74	7.6	8.00	1.40	0.25	0.35	10.5	1.00	1.20	36
16/04/76	11.0	6.8	233	0.10	24	.	74	7.5	8.00	1.30	0.45	0.45	6.5	1.00	1.20	36
23/05/76	.	7.0	233	0.08	23	20	88	8.5	7.90	1.65	.	.	.	.	.	.
17/07/76	10.5	7.2	252	0.10	23	17	92	8.4	8.30	1.70	0.50	0.75	10.0	1.00	1.20	40
23/08/76	11.5	7.2	252	0.09	22	17	96	9.0	15.00	1.68	0.50	0.30	11.0	8.50	2.50	30
26/09/76	11.6	7.1	241	0.08	23	18	94	8.1	19.50	1.80	0.40	0.70	4.5	0.25	1.20	26
26/09/76	11.6	7.1	239	0.08	23	18	92	10.0	20.00	1.70	0.40	0.60	4.5	0.25	1.20	32
16/10/76	10.2	.	189	0.09	24	15	73	6.6	.	.	0.70	1.00	7.5	0.50	1.20	41
16/10/76	10.2	.	186	0.08	24	16	74	6.6	.	.	0.35	0.60	9.0	0.50	1.20	29
24/11/76	10.5	7.0	250	0.09	24	16	92	9.6	.	.	1.50	0.50	8.5	0.25	1.20	39
19/12/76	.	7.2	225	0.08	23	19	86	7.2	7.90	1.40	0.50	0.40	7.0	0.25	1.20	31
23/01/77	10.0	6.9	235	0.07	24	19	90	8.0	8.55	1.40	0.40	2.05	9.5	0.50	1.20	38
19/02/77	10.1	7.1	233	0.07	23	17	100	8.0	8.50	1.20	0.70	0.50	9.5	0.50	1.20	35
22/03/77	10.7	7.0	283	0.07	28	18	86	10.8	8.40	1.90	0.30	0.35	6.0	0.50	1.20	34
21/04/77	10.2	7.1	249	0.09	22	13	96	8.8	8.61	1.69	0.40	0.45	12.0	0.25	1.20	49
21/04/77	10.2	7.1	249	0.10	23	13	100	8.8	8.56	1.68	0.50	0.35	9.0	0.25	1.20	38

SITE=027

DATE	T	PH	HCO3	F	SO4	CL	CA	MG	NA	K	CD	CU	FE	MN	PB	ZN
28/03/76	.	7.0	.	.	.	.	112	6.0	.	.	0.55	0.43	6.75	0.75	3.0	53.0
16/04/76	11.0	6.5	271	0.07	25	.	88	5.0	6.20	1.70	0.75	0.35	0.45	0.50	1.2	52.5
23/05/76	.	7.0	283	0.21	18	18	109	6.0	7.50	2.35	.	.	.	.	.	.
23/05/76	.	7.0	283	0.06	19	19	140	6.0	8.10	2.30	0.45	0.35	5.50	0.50	4.5	55.0
17/07/76	10.5	7.0	301	0.09	20	18	117	6.4	7.67	3.10	0.60	1.65	9.00	0.50	4.5	57.5
23/08/76	11.0	6.8	300	0.07	19	16	118	6.8	14.50	2.65	0.70	0.80	6.00	0.25	2.5	50.0
26/09/76	10.6	6.9	295	0.07	21	20	130	6.4	22.50	3.40	0.50	0.75	12.50	0.25	2.5	56.0
16/10/76	10.4	.	293	0.07	27	19	128	5.0	.	.	0.50	0.80	5.50	1.00	1.2	65.0
24/11/76	10.4	6.9	303	0.06	22	16	124	6.5	.	.	2.00	0.35	5.00	0.25	1.2	53.5
19/12/76	.	7.0	286	0.06	23	19	120	5.4	7.00	1.90	0.70	0.35	6.00	0.25	1.2	39.5
23/01/77	10.1	6.7	284	0.05	22	18	126	6.0	7.55	2.00	0.70	0.65	24.00	0.50	1.2	52.5
19/02/77	10.0	6.9	273	0.05	23	15	120	5.4	7.20	1.80	1.20	0.50	17.50	0.50	3.0	50.0
22/03/77	10.0	6.9	272	0.07	22	15	110	4.6	6.20	1.85	1.00	0.45	9.50	0.25	1.2	34.0
21/04/77	10.4	7.1	279	0.08	20	11	124	6.2	8.60	1.97	0.45	0.30	10.50	0.25	1.2	49.0

SITE=042

DATE	T	PH	HCO3	F	SO4	CL	CA	MG	NA	K	CD	CU	FE	MN	PB	ZN
27/03/76	14.0	8.4	176	0.19	19	.	51	7.4	9.3	6.90	1.25	1.15	17	3.5	0.5	2.50
18/04/76	14.0	8.4	176	0.19	19	.	51	7.4	9.3	6.90	1.25	1.15	17	3.5	0.5	2.50
23/05/76	.	7.7	170	0.24	19	15	56	8.5	10.0	8.75	0.95	0.90	24	4.5	1.2	2.85
23/05/76	.	7.7	176	0.23	19	15	54	8.0	10.0	8.70	0.60	0.85	24	4.0	1.2	2.45
17/07/76	18.0	8.1	204	0.28	19	14	64	9.0	8.8	9.45	0.80	1.15	24	1.5	1.2	4.90
23/08/76	15.0	8.0	189	0.15	15	14	52	11.8	39.5	6.23	.	.	.	.	.	.
23/08/76	15.0	8.0	183	0.15	15	15	52	12.0	33.5	6.02	1.20	1.00	23	1.0	1.2	1.50
26/09/76	15.0	8.0	147	0.17	30	15	54	9.2	27.5	12.70	0.35	2.25	220	16.0	1.2	6.00
16/10/76	11.9	.	107	0.15	30	18	46	6.2	.	.	3.20	2.30	80	3.0	1.2	19.00
24/11/76	8.0	7.9	171	0.15	18	17	53	10.0	.	.	0.75	1.40	40	4.0	1.2	4.50
19/12/76	.	7.7	93	0.10	23	17	37	5.5	9.8	4.20	1.05	2.10	240	17.5	1.2	6.30
23/01/77	7.8	7.9	128	0.11	20	15	48	8.0	13.0	4.85	0.40	1.25	110	11.0	1.2	2.50
19/02/77	7.5	7.9	98	0.10	22	13	48	7.0	11.0	4.60	0.55	1.70	90	13.5	1.2	22.00
22/03/77	7.5	7.8	115	0.16	20	12	42	4.6	7.9	4.05	0.20	1.25	60	12.5	1.2	2.15
21/04/77	10.2	8.3	165	0.21	16	10	60	8.2	11.0	5.53	0.55	1.30	80	55.0	1.2	1.95

Figure 4-5 Temporal geochemical variations for Cheddar spring (site 21)

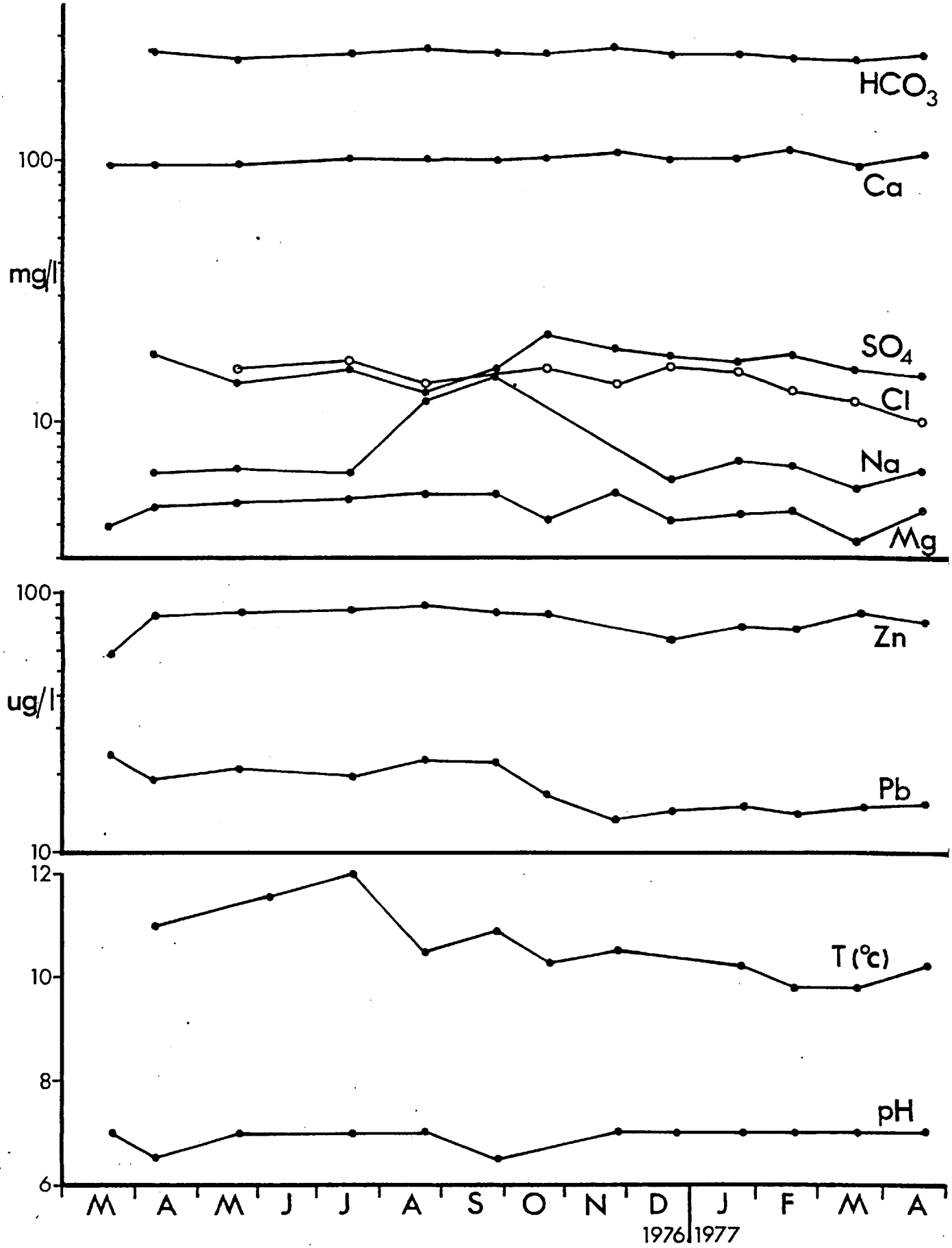


Figure 4-6 Temporal geochemical variations for Eastwell spring (site 23)

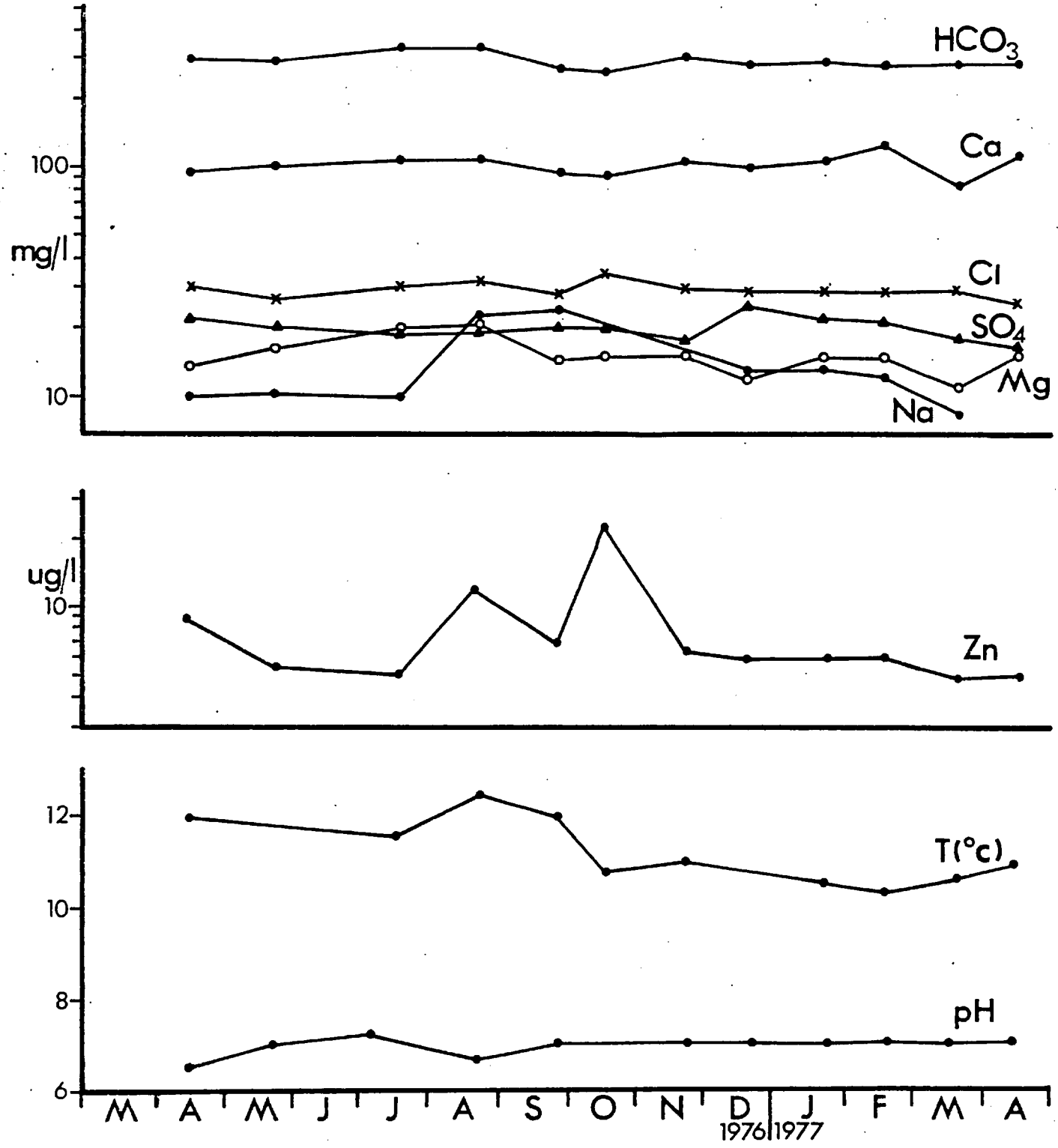


Figure 4-7 Temporal geochemical variations for Rickford spring (site 27)

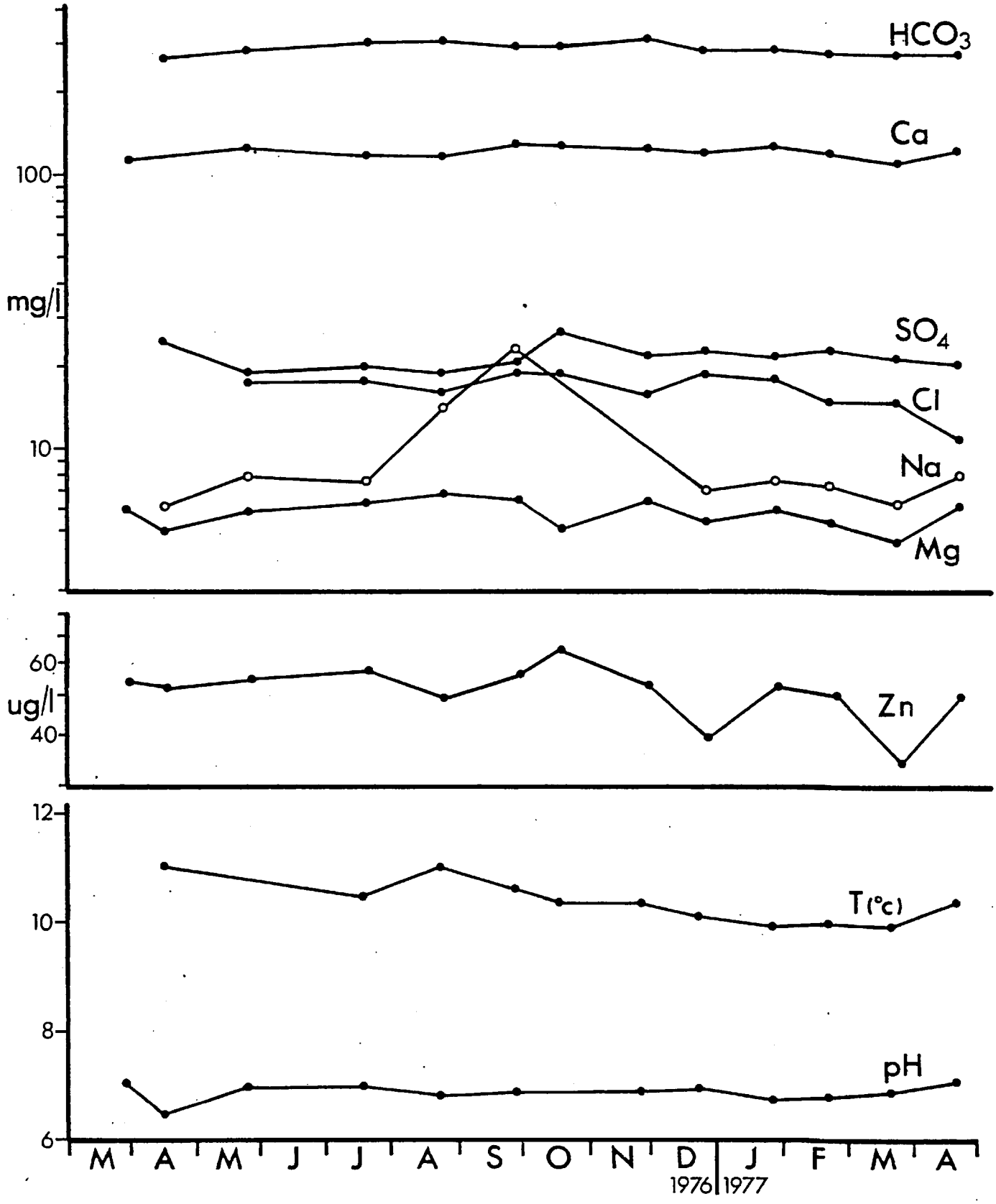


Figure 4-8 Temporal geochemical variations for Lycopodium Hole spring (site 14)

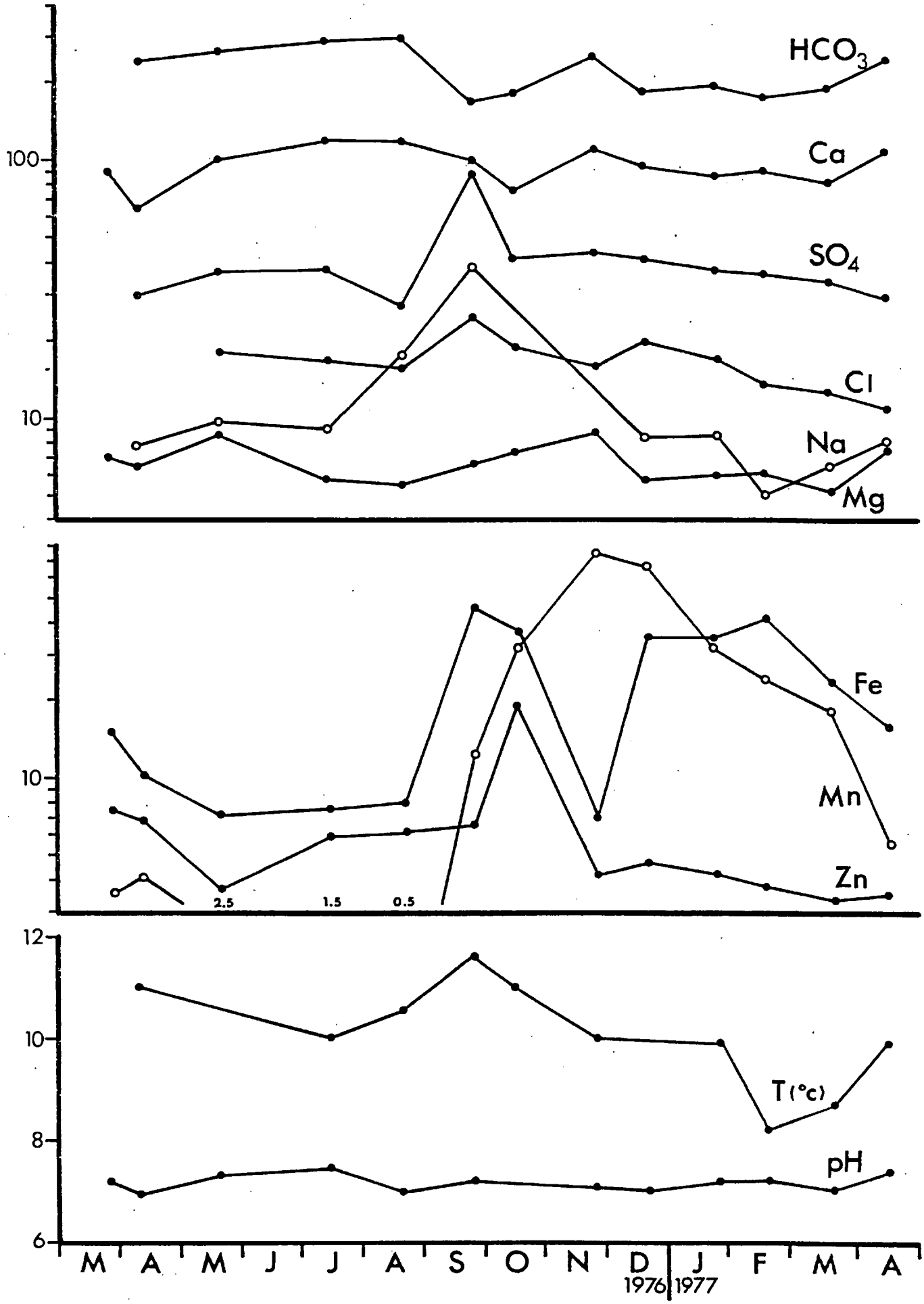
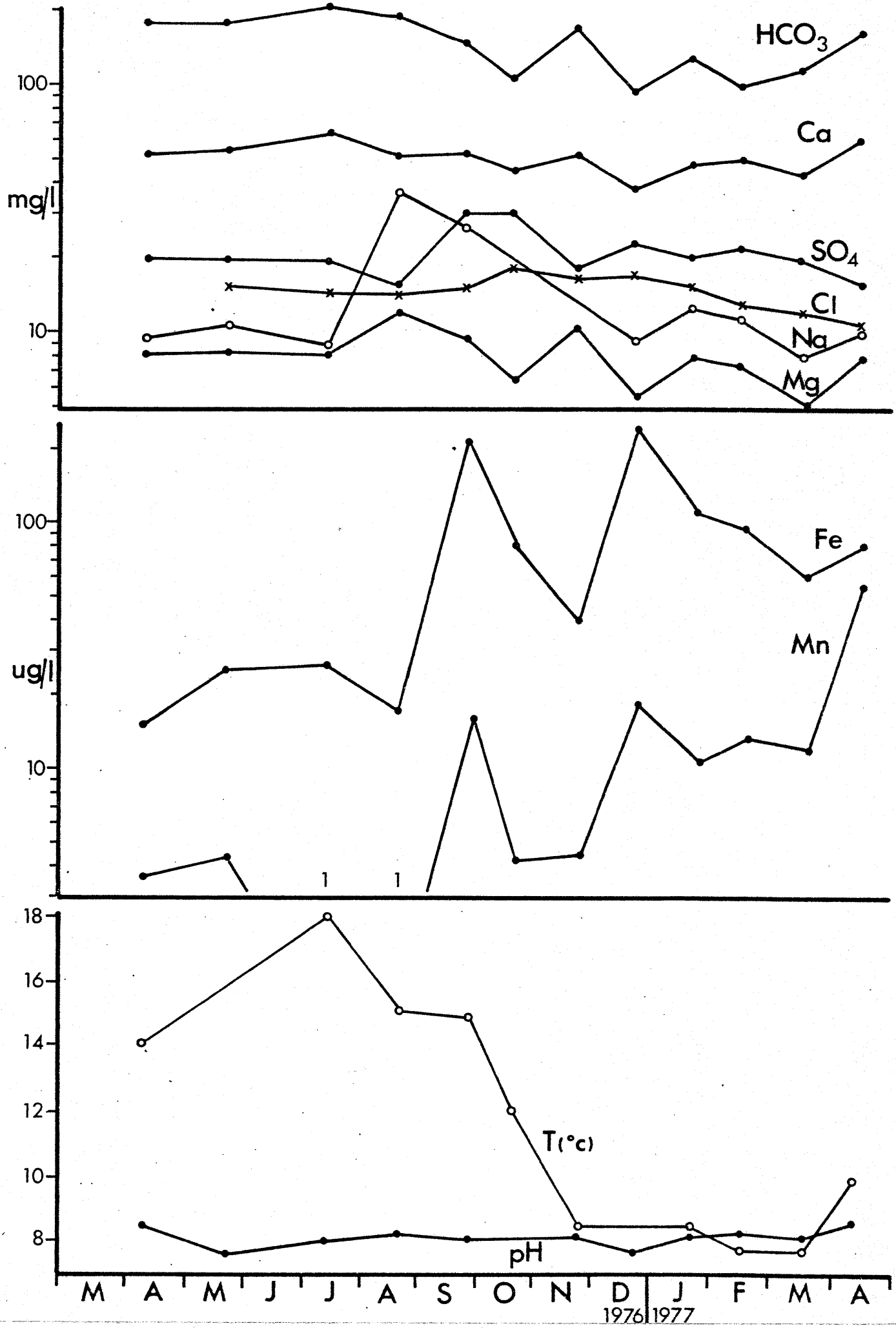


Figure 4-9 Temporal geochemical variations for Stoke Lane Slocker stream (site 42)



a very large spring flowing the Carboniferous Limestone; East Well (23), a small spring originating in the Old Red Sandstone and Carboniferous Limestone, but emerging through the Kueper Marl; Rickford (27), a moderately large spring flowing through the Carboniferous Limestone and Dolomitic Conglomerate; Lycopodium Hole (14), a small spring flowing through the Carboniferous Limestone; and Stoke Lane Slocker (42), a stream flowing over the Old Red Sandstone and Lower Limestone Shale. Part of the flow at Lycopodium Hole may be directly derived from Stoke Lane Slocker.

There is only a one or two degree range in ground water temperature throughout the year, with highs of 11 to 12.5°C in July and August and low of about 10° in February and March. An exception is Lycopodium Hole which dropped to 8.2° in February. Surface water at Stoke Lane reached 18° in July and dropped to 8° in February and March. Very little temporal variation was recorded in pH. Bicarbonate increased during the dry period and then dropped at the first increase in flow (cf. Figure 4-4). Calcium and magnesium showed little variation, although at East Well, where magnesium concentration is quite high, it followed the same pattern as bicarbonate.

Sulphate dropped slightly in response to the first rain in late August 1976, but increased sharply as flow rates peaked in October. In several cases the high concentrations persisted well into 1977. Sodium, and to a lesser extent, chloride and potassium responded similarly to the increase in flow rate.

At Stoke Lane and Lycopodium Hole, where the amount of suspended material is often considerable, iron, and less noticeably manganese, increased with increasing flow. Other sites showed similar trends. At some locations copper, cadmium, zinc and lead corresponded with peaks in iron and/or manganese, however the relationships are not consistent.

At Eastwell, Rickford and Lycopodium Hole zinc concentrations decreased with increasing flow, and at Cheddar both lead and zinc concentrations decreased with increasing flow. Despite these variations, however, concentrations at Cheddar and Rickford were anomalously high throughout the study period, while concentrations at Eastwell and Lycopodium Hole remained consistently low.

In summary, most hydrogeochemical constituents responded to significant changes in run-off rates during the drought of 1976. As might be expected,

surface drainage showed the greatest variation. Concentrations of bicarbonate and various trace elements generally decreased with increasing flow whereas sulphate, fluoride, chloride, sodium, potassium, iron and manganese increased at first, and then in most cases decreased as the flow rates stabilised. The geochemical increase at the initial flood was coincident with an increase in the amount of suspended material because not all of the material in suspension would have been removed by the .45 um GF/C filter.

4-5 Major Element Hydrogeochemistry

Cumulative frequency curves for data from 68 sample sites are shown in Figure 4-10. As would be expected in a limestone terrain, calcium and bicarbonate are dominant. Interestingly, however, bicarbonate molar equivalents are consistently higher than calcium molar equivalents. Chloride, sodium, magnesium and sulphate all have similar molar concentrations whereas potassium is almost an order of magnitude lower, and fluoride is an order of magnitude lower still.

Although most of the drainage systems sampled are underlain by more than one major rock type, it is possible to recognize differences in water chemistry based on bedrock type. Lithologies considered include the Old Red Sandstone, Carboniferous Limestone, Dolomitic Conglomerate and Keuper Marl, and Jurassic Limestone. Classification for this comparison is based on estimation of the dominant lithology for each drainage area. Where there are two dominant lithologies, the sample has been included in both sets. Group means and standard errors are presented in Figure 4-11. For comparison, data is shown for 12 samples draining Carboniferous Limestone exclusively, and for 59 samples draining Carboniferous Limestone and some other lithology. In most cases the other lithology is the Old Red Sandstone.

Water derived from the Old Red Sandstone is low in calcium, bicarbonate, and sulphate, and has much lower TDS (total dissolved solids) than that from other lithologies. The Triassic and Jurassic rocks generate waters with high TDS, but whereas those from the former have high magnesium concentration and low pH, those from the latter have relatively high pH, calcium and sulphate, and low magnesium. The mean pH of the 21 streams sampled, mostly flowing over Old Red Sandstone, is considerably higher than that of the 42 springs resurging from

Figure 4-10 Cumulative frequency curves for hydrogeochemical data from 68 sample sites in the Mendip Hills area

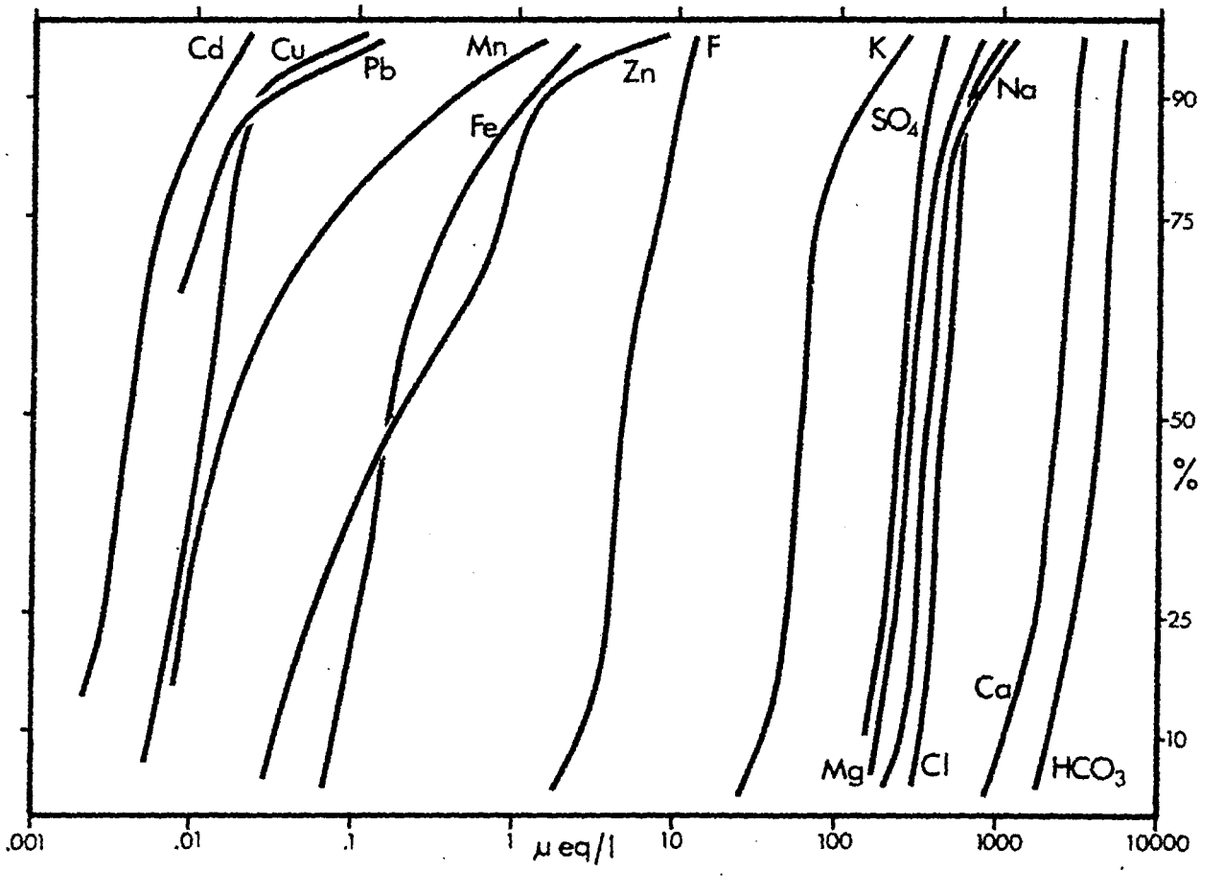
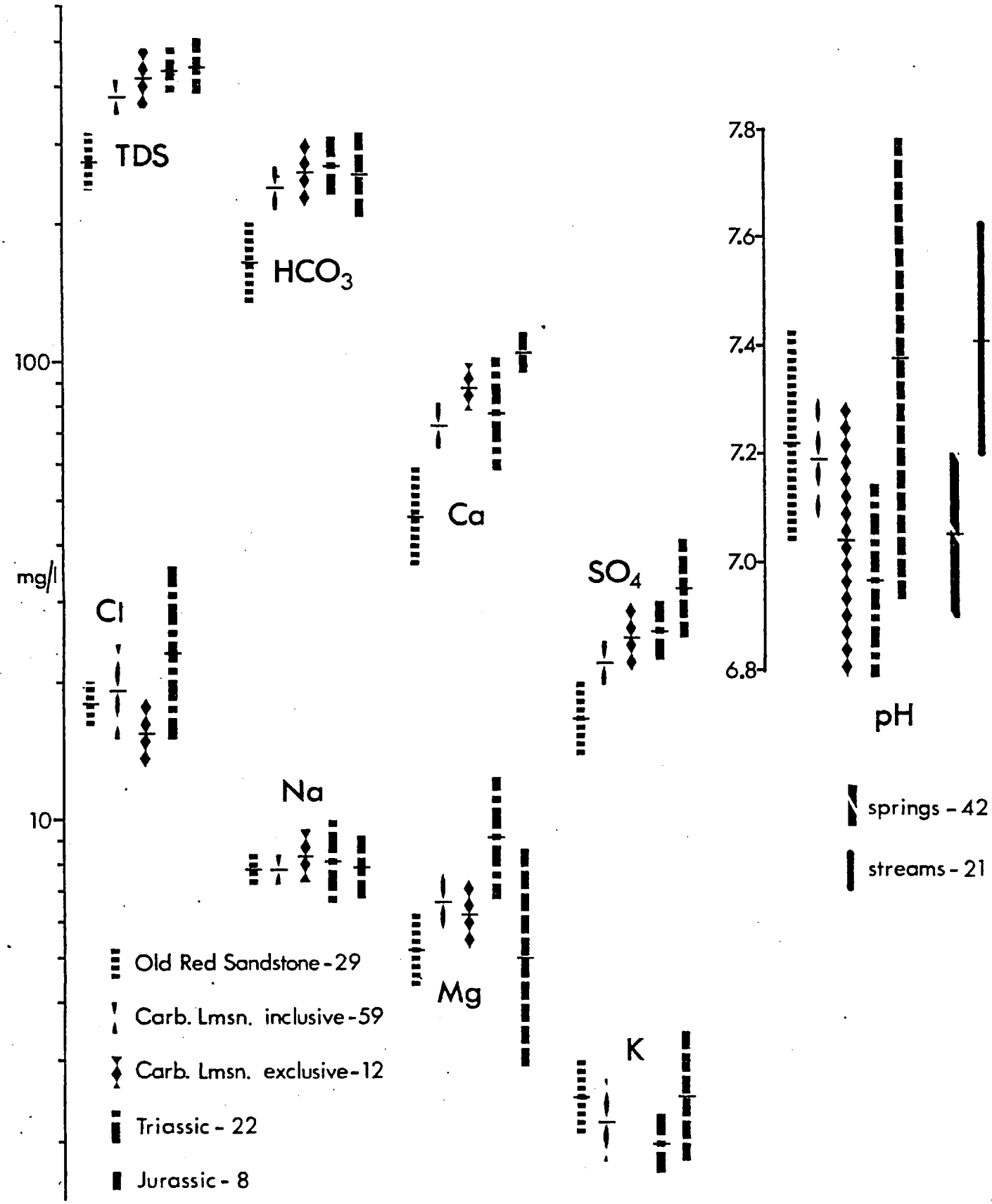


Figure 4-11 Means and standard errors (± 2 s.e.) for various lithological groups for the hydrogeochemical data from the Mendip Hills



Carboniferous Limestone, Dolomitic Conglomerate and Keuper Marl. There is very little variation in sodium, potassium and chloride amongst the lithological groups. Variations amongst the groups are emphasized in the CaMg-(Na+K) triangular diagram (Figure 4-12). The most important distinguishing constituent is magnesium, which is high in the Triassic derived waters, low in the Jurassic derived waters, and intermediate in waters from the Carboniferous Limestone and Old Red Sandstone.

Because virtually all of the samples have calcium and bicarbonate as their major ions, equilibrium calculations based on the system CO_2-$CaCO_3$-H_2O should account for most of the variation in the species Ca++, HCO_3- and H+. Variation of bicarbonate versus pH is shown in Figure 4-13. The straight-line reaction paths are taken from Deines et al (1974), and are valid under open system behavior, that is with constant pCO_2 as the reaction progresses. In a closed system, the reaction paths will curve over to the right as calcite saturation is approached, and for an initial pCO_2 of $10^{-1.5}$ the pH at saturation will be over 7.5 (Deines et al, 1974). Calcite saturation indeces have been determined using a modification of the algorithm described by Bath (1975), (cf. Jacobson and Langmuir, 1972). Only 14 samples exceed calcite saturation, and less than half of the samples are more than 40% saturated. In comparison to other karstic areas, these waters have high bicarbonate concentrations and low pH (cf. Harmon et al, 1972), and it is apparent that most of the species are in equilibrium with a gas phase which has a pCO_2 of approximately $10^{-1.5}$.

4-6 Trace Element Hydrogeochemistry

From Figure 4-10 it is clear that zinc is the dominant trace element in the Mendip ground waters. The shape of the cumulative curve for zinc suggests a multi-modal population, and it is likely that the samples with the higher concentrations have been in contact with zinc mineralisation. The curve for copper is bi-modal, and the part of the lead curve which is known is also bi-modal.

The map distributions of the lead and zinc data are shown in Figures 4-14 and 4-15. Lead and zinc are the only elements which show consistent spatial relationships with the distribution of mineral occurrences. All of the major drainage basins with lead mineralisation are characterised by anomalous lead

Figure 4-12 Ca-Mg-(Na+K) ternary plot for data from the various lithological groups from the hydrogeochemical data from the Mendip Hills (The data have been converted to molar equivalents, and the Ca data have been divided by 5 to maximise group distinction)

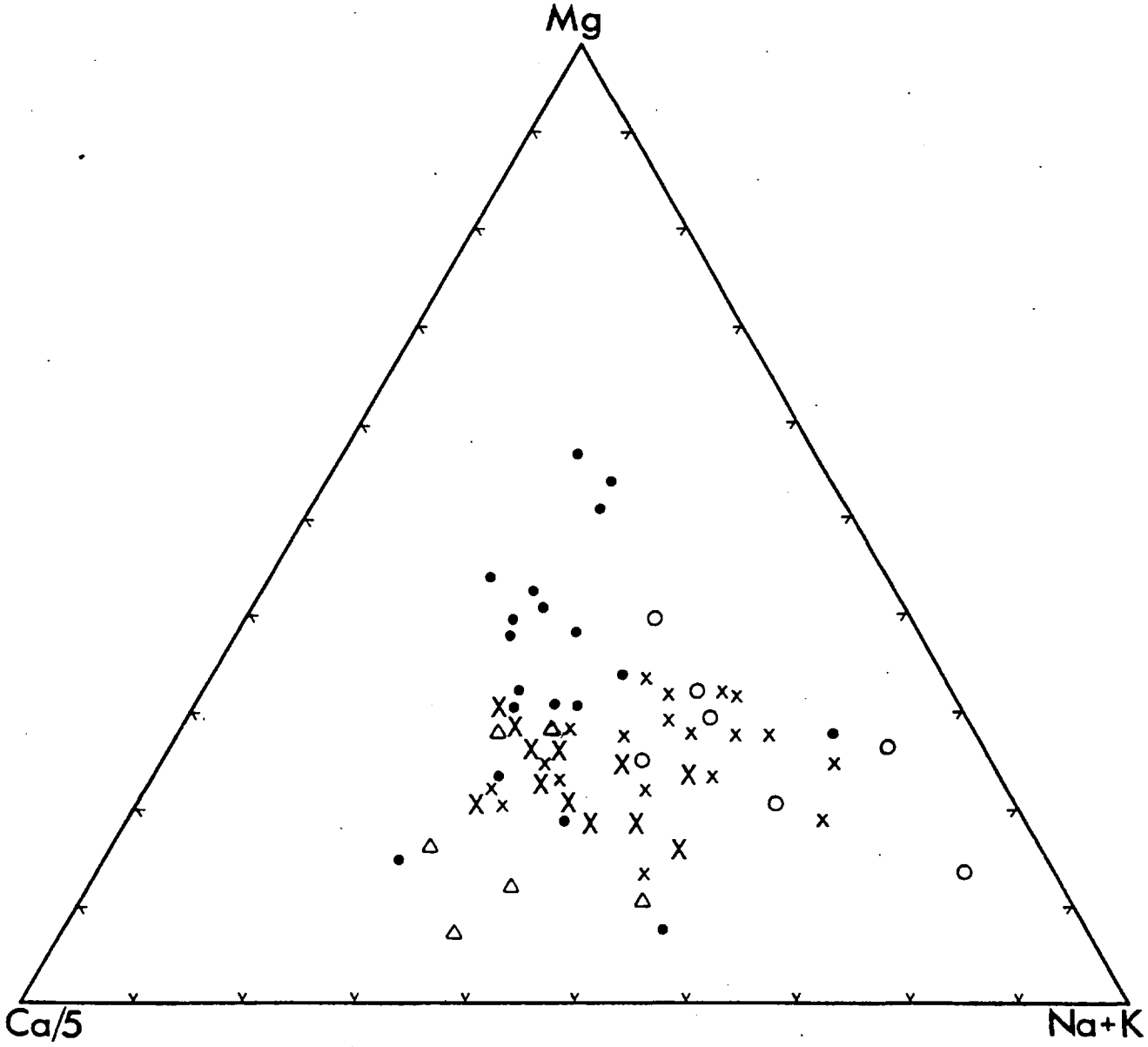


Figure 4-13 Calcite saturation characteristics for the Mendip Hills hydrogeochemical data, as shown on a plot of HCO_3 vs pH.

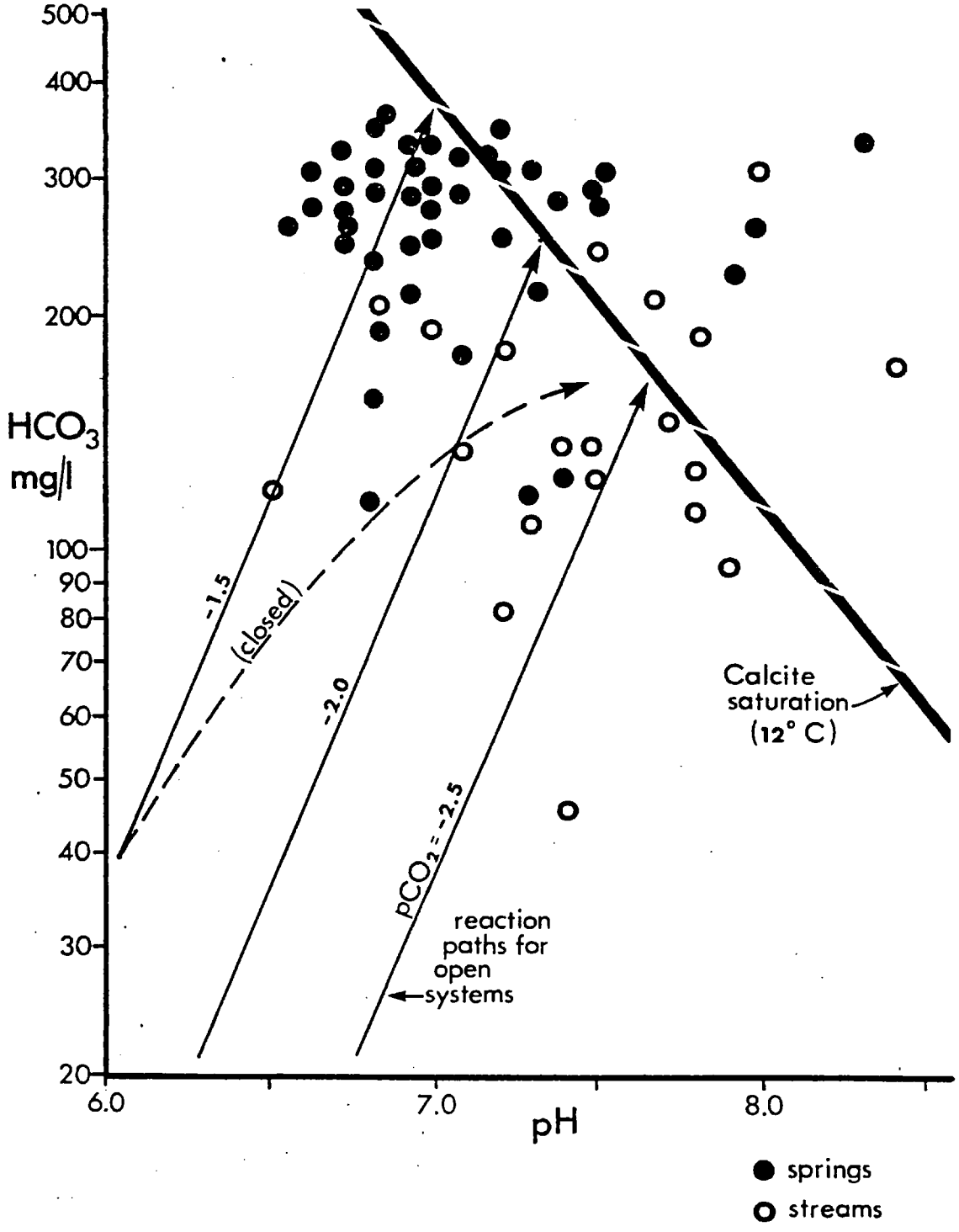


Figure 4-14 Map of lead concentrations in ground and surface water samples from the Mendip Hills

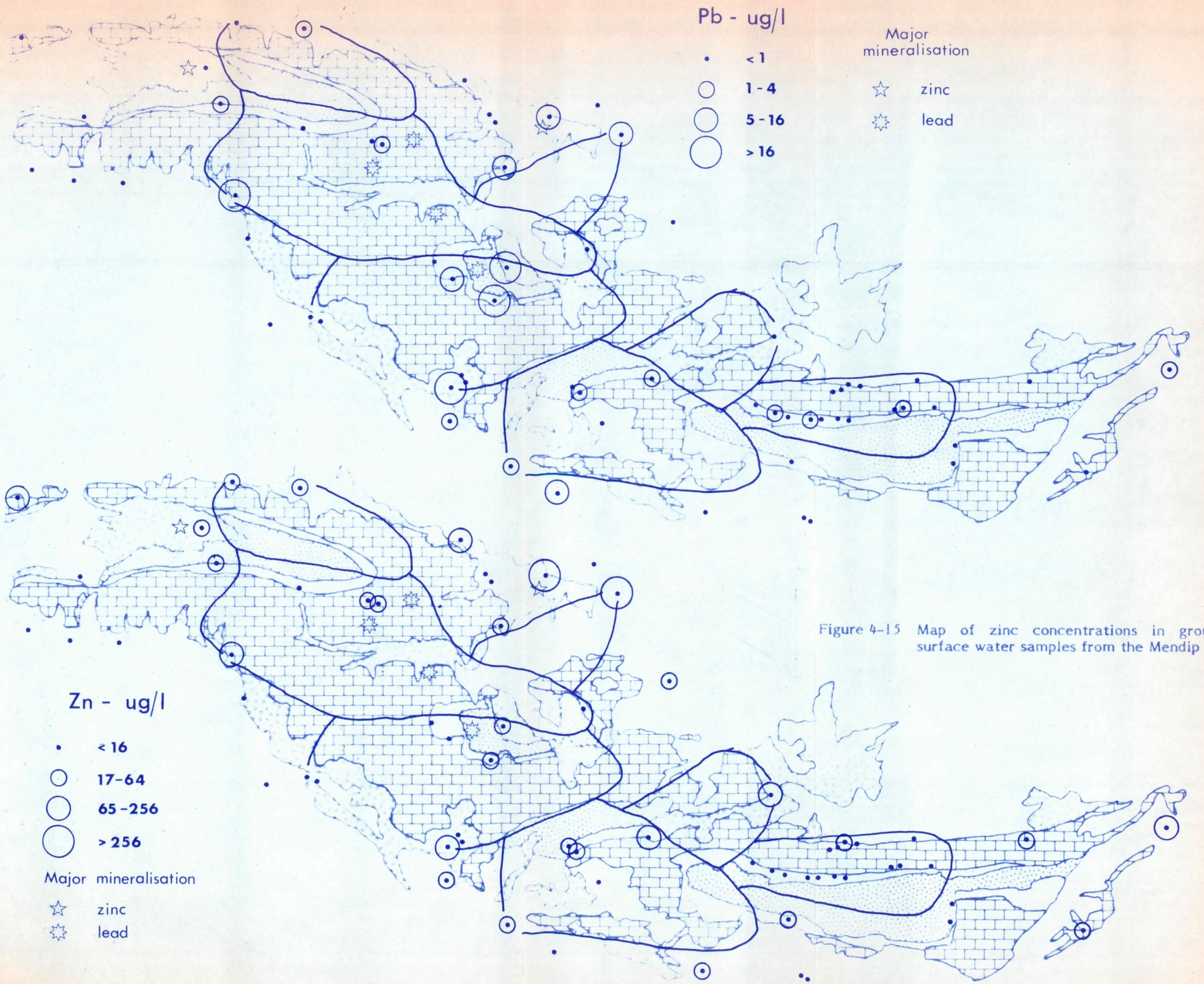


Figure 4-15 Map of zinc concentrations in ground and surface water samples from the Mendip Hills

concentrations, and there are no significant anomalies in areas where lead mineralisation has not been reported. There are two cases, however, where samples from small drainages in the vicinity of mineralisation do not have enhanced lead concentrations. Samples 28 and 29, near Compton Martin on the north side of Mendip (Figure 4-2), have lead concentrations below the detection limit, even though they appear to drain an area of lead mineralisation. These are very small springs, however, and it is possible that their drainage areas do not extend very far up the hill. Sample 67, which does not have a detectable concentration of dissolved lead, was collected from the outlet stream of a pond immediately adjacent to the pile of lead-bearing slag at Blackmoor (507 560), and slightly upstream from known mineralisation. The glassy nature of the slag probably inhibits lead solubility.

All areas with important zinc mineralisation have associated zinc anomalies, and areas of lead mineralisation are also characterised by enhanced zinc concentrations. Samples 3, 49 and 51, from Slab House, Gurney Slade and Egford, have relatively high zinc concentrations, although there is no documented zinc mineralisation in any of these areas.

Many types of mineral deposits have fluorite as an accessory mineral (Boyle, 1974), and considerable success has been achieved using fluoride as a pathfinder constituent (Edmunds, 1971; LaLonde, 1976; Boyle, 1977). In the Mendip area there does not appear to be a relationship between the distribution of fluoride in ground waters and the major areas of mineralisation (Figure 4-16).

Hoag and Webber (1976) have demonstrated the usefulness of sulphate geochemistry in exploration for sulphide deposits. Their data is from an area of volcanogenic massive sulphides, however, where oxidation of sulphide minerals, largely pyrite, and generation of acidic ground waters are complimentary processes. In Mendip ground waters sulphate concentrations are highest where water flows through Triassic and/or Jurassic strata rather than in areas of lead-zinc mineralisation (Figure 4-17).

Figure 4-16 Map of fluoride concentrations in ground and surface water samples from the Mendip Hills

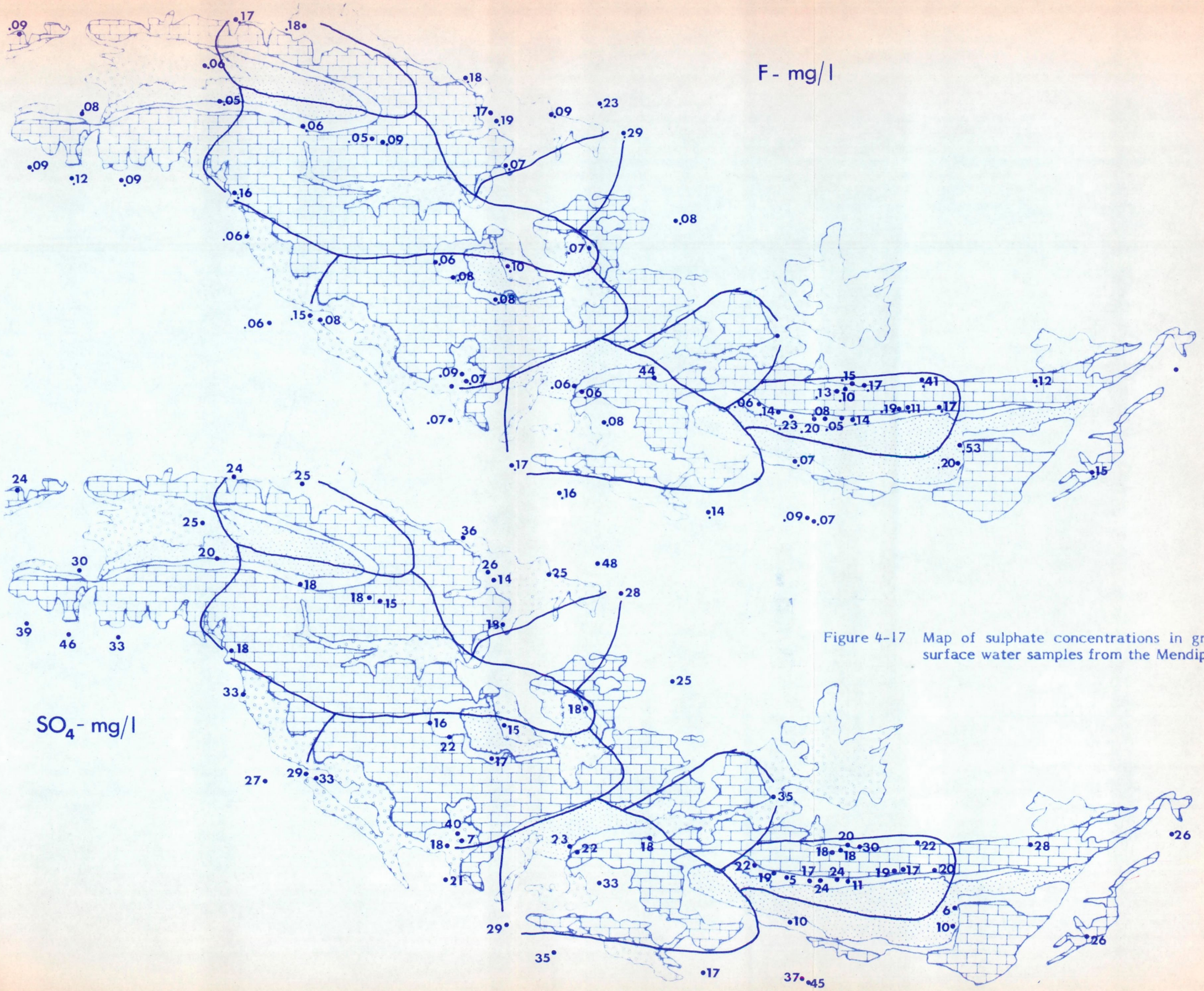


Figure 4-17 Map of sulphate concentrations in ground and surface water samples from the Mendip Hills

4-7 Discussion

4-7.1 Seasonal Fluctuations

A considerable body of research exists concerning variations in surface water geochemistry as a function of seasonal and storm variations in run-off. It has been shown that although most constituents are diluted by increasing flow (Glover and Johnston, 1974), significant increase in flow following an extended dry period will usually result in increased concentrations of some constituents due to flushing of previously deposited salts (Walling and Foster, 1975; Miller and Drever, 1977). Edwards (1973) has shown that sulphate, nitrate, sodium and potassium are particularly affected by the flushing effect, and he postulates that these constituents are leached from the soil.

Very little information is available concerning temporal variations in ground water geochemistry, however, and it can only be assumed that the above observations would apply, in part, to ground waters. The present data supports this assumption in general terms, in that there is a dilution affect for most elements, with an initial increase in concentrations of sulphate, sodium, chloride, potassium, iron and manganese. For iron and manganese, and perhaps for some of the other constituents, the increase may be due in part to increased sediment load (Mill, 1978; Marsh and Lloyd, 1981). Much of the iron may be present as very fine particles rather than dissolved ions. The fact that elevated sulphate levels persisted for several months in some cases suggests that there is a significant supply of sulphate salt which is unavailable to ground water under low flow conditions.

Lead and zinc, which appear to be useful for mineral exploration in the Mendip area, were significantly diluted by the dramatic increase in run-off during September 1976, but the magnitude of the variation is such that the distinction between anomalous and non-anomalous drainages is only obscured in borderline cases.

4-7.2 Major Elements

Like many other limestone regions, the Mendip area is characterised by underground drainage in solutionally enlarged conduits. Water-rock interaction in such systems can be accounted for by studying the system CO_2-$CaCO_3$-H_2O, in which the most important variable is pCO_2 of the gas phase. Such systems are

described as "open" if the pCO_2 remains constant during calcite dissolution or, more commonly, "closed" if the initial CO_2 is consumed during dissolution and not replenished. In the latter case calcite solubility will become restricted due to a lack of free carbon dioxide.

The pH-HCO_3 relationship for the Mendip waters suggests that equilibrium has taken place with a relatively high initial pCO_2 (ca. $10^{-1.5}$), which has been maintained during dissolution (i.e., open system behaviour, cf. Atkinson, 1977b).

In many karstic areas the soil atmosphere is the main source of carbon dioxide for ground waters, and after the water has passed through the soil, closed conditions prevail. The pCO_2 of the soil atmosphere on Mendip is generally less than $10^{-2.0}$ (Atkinson, 1977b), and although this would account for the bicarbonate levels in stream waters, it is too low to explain that of ground waters. Atkinson suggests that most of the carbon dioxide is derived from decaying organic matter in the unsaturated zone of the bedrock, and he presents data showing considerably higher pCO_2 values in small fissures adjacent to caves, than in the soil. The presence of a large carbon dioxide reservoir is supported by the high molar ratio of bicarbonate to calcium, as shown in Figure 4-10. Although closed system behaviour is the norm for most karstic regions (Deines et al, 1974; Drake and Wigley, 1975), open systems have been proposed for the Bruce Peninsula and Nahanni River areas of Canada (Brook et al, 1977).

Two important implications arise due to the existence of open system behaviour. Firstly, "erosion will be distributed throughout the unsaturated zone and perhaps in the phreatic zone as well" (Atkinson, 1977b). In other words, erosion will take place to a considerable depth. Secondly, the pH will remain low and the solubility of metals will not be as restricted as in other limestone regions.

4-7.3 Trace Elements

The distribution of both lead and zinc anomalies corresponds well with the known distribution of mineralisation. Zinc is considerably more soluble than lead, and hence may be a more useful hydrogeochemical indicator in this environment.

Zinc concentrations of samples from the East Harptree area (samples 30 and 56) are higher than might be expected considering the magnitude of known

mineralisation in the area. On the basis of several additional samples collected from near East Harptree, it is apparent that the mineralisation in Harptree Coombe, near Richmont Castle (562 558), is responsible for the elevated concentrations in sample 30. It seems unlikely, however, that the lead and zinc mineralisation in the vicinity of Eaker Hill farm (566 529) is solely responsible for the zinc anomaly in Sherbourne Spring. Instead, it is possible that the source of this zinc lies underneath the Keuper Marl cover rocks south of Sherbourne.

The zinc concentration of water from Egford Well, (site 51) is also somewhat higher than would be expected based on the known mineralisation in the vicinity. The major element chemistry of water from Egford Well (high calcium - low magnesium) indicates derivation from the Carboniferous Limestone rather than from the Dolomitic Conglomerate, suggesting that if buried mineralisation is present in this area, the host-rock is likely to be the Carboniferous Limestone.

Other zinc anomalies which cannot be explained by the presence of known mineralisation are at Slab House (site 3) and Gurney Slade (site 49). Both of these springs drain the area of probable mineralisation defined by the soil sampling programme (see Chapter 5).

Neither fluoride nor sulphate, which have been shown to be useful base metal pathfinders elsewhere, appear to be particularly helpful in the Mendip area. Although fluorite exists on Mendip, it is not known to be closely associated with sulphide mineralisation (see Chapter 7). Nor is pyrite an important gangue mineral, and assuming that on oxidation of lead and zinc sulphides, sulphate would be released in roughly equal proportions to lead and zinc, even the most anomalous waters would have sulphate additions of less than one milligram per litre.

4-7.4 Analytical Problems

As noted above, there are some inadequacies in the techniques used for analysis of natural waters. For instance, the data for lead, cadmium and manganese are unreliable for background levels, even though a twenty-fold pre-concentration step was carried out.

Chelation/solvent extraction and resin extraction techniques are well established in water analysis (see for example - Brown et al, 1970, Sachdev and

West, 1970, Kinrade and VanLoon, 1974, Korkish and Sorio, 1975), and they have the advantage of combining concentration with removal of some interfering constituents. These techniques are expensive, time consuming, and prone to contamination, however, and as we have seen here, are not always adequate for certain metals.

Recent refinements in analytical techniques have created some new alternatives for water analysis. For example plasma source emission spectrophotometry has been shown to be a sensitive technique for many elements (Greenfield et al, 1975; Thompson et al, 1978). Two elements for which emission spectrophotometry is not sufficiently sensitive are lead and cadmium.

Electroanalytical methods have been improved significantly in the past few years. Specific ion electrodes are available for lead, zinc, copper and cadmium, but according to Florence and Batley (1977) the zinc, lead and cadmium electrodes are unsuitable for use in natural waters because of interference problems and slow response. Anodic stripping voltammetry has been widely used for analysis of lead, zinc, copper and cadmium (Zirino and Healy, 1972; Florence and Batley, 1977), but for natural waters this technique is limited by the presence of organic and other impurities (pers. comm., G. Hall, Geol. Surv. Can.).

More optimistic results have been achieved by using thermal atomization devices for atomic absorption spectrophotometry, such as the graphite furnace or Delve's cup. These techniques have been used for analysis of various heavy metals in natural waters, including lead and cadmium (Kirkbright, 1971; Pickford and Rossi,1972; Dolinsek and Stupar, 1973; Maines et al, 1975).

Two other promising techniques, which have had limited application for analysis of heavy metals in waters, include neutron activation (Salbu and Pappas, 1975) and X-ray fluorescence (Marsh and Lloyd, 1976).

CHAPTER 5 SOIL GEOCHEMISTRY OF THE MENDIP HILLS

5-1 Introduction

Virtually all of the Mendip mining operations have been abandoned for well over 100 years and are now overgrown. There are very few good examples of mineralisation in outcrop and there is very little direct evidence of the nature of the deposits. Green (1958) based a description of the Mendip mineralisation on material found in waste piles, but even the waste piles have been re-worked and few specimens can be found. The representivity of these specimens is doubtful, and their value in characterising the mineralisation is limited.

A study of soil geochemistry has been undertaken to gain some information on the geochemical characteristics of mineralisation in different parts or the area, to reveal regional patterns of metal zonation, and to locate previously unknown mineral occurrences. The study has included research into optimisation of sample intervals for soil geochemical surveys, the results of which are given in Appendix E.

5-2 Soils of the Mendip Hills

Like other limestone upland areas, the soils over most of the Mendip Hills are well-drained brown earths. Gleyed soils are present where parent material is rich in clay. Although the soils are largely residual, much of the central Mendip area has a sparse cover of loessal material, which, according to Findlay (1965), is incorporated with the weathering residues of the underlying rocks.

Neutral to acid, shallow, brown and reddish brown, silty and loamy soils are present over the Carboniferous Limestone (Figure 5-1). Locally, particularly in mined areas, the soil is very stony. Where loessal drift is present, a thick, brown, silty and clay rich soil is developed. Limited areas of peaty gleyed podsol are related to thin horizons of iron enrichment developed over the loessal drift.

Soils over the Dolomitic Conglomerate are similar to those over the limestone, although rubbly sub-soil is present, and the colour is a strong reddish brown.

Acid, stony, brown to grey-brown, sandy and loamy soils are developed over the Old Red Sandstone. On level sites a clay iron pan is present and the overlying soils are gleyed.

Figure 5-1 Map of soil-type distribution for the central part of the Mendip Hills

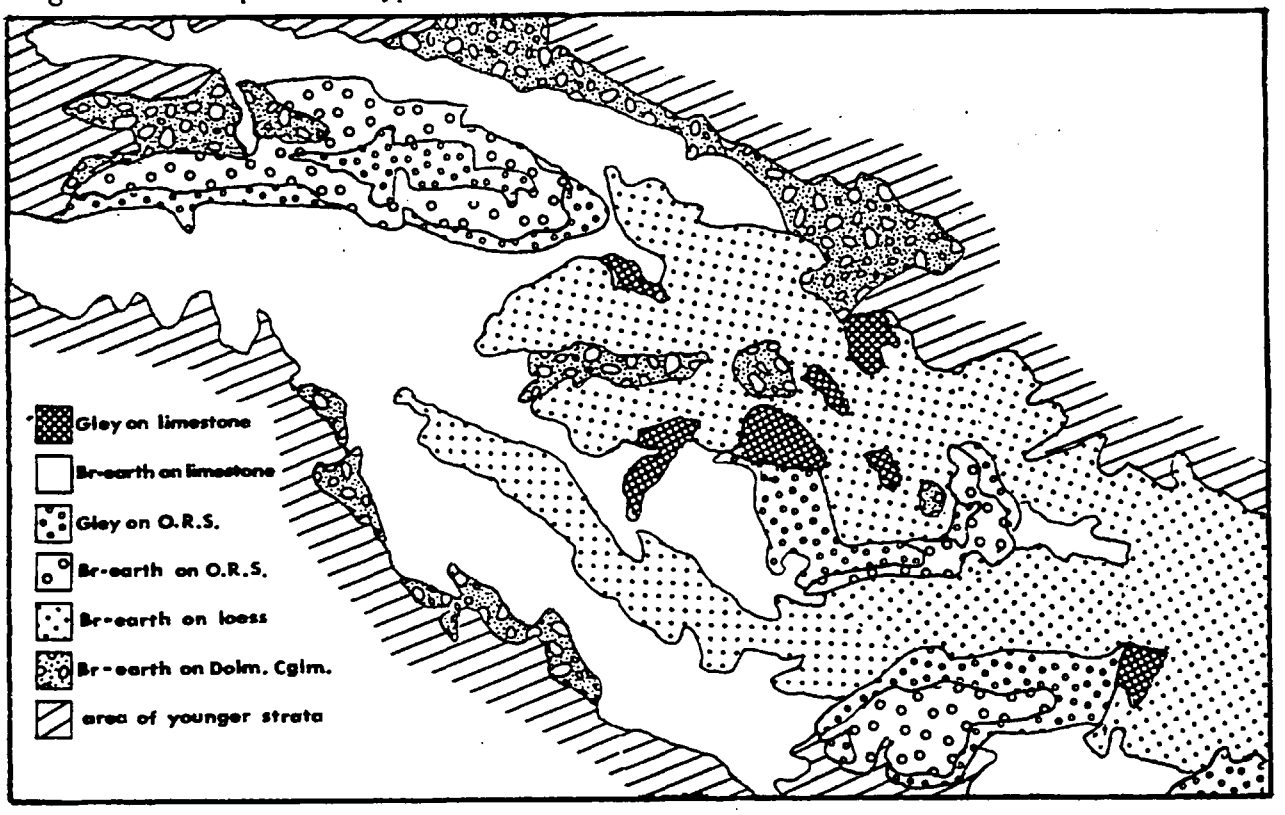
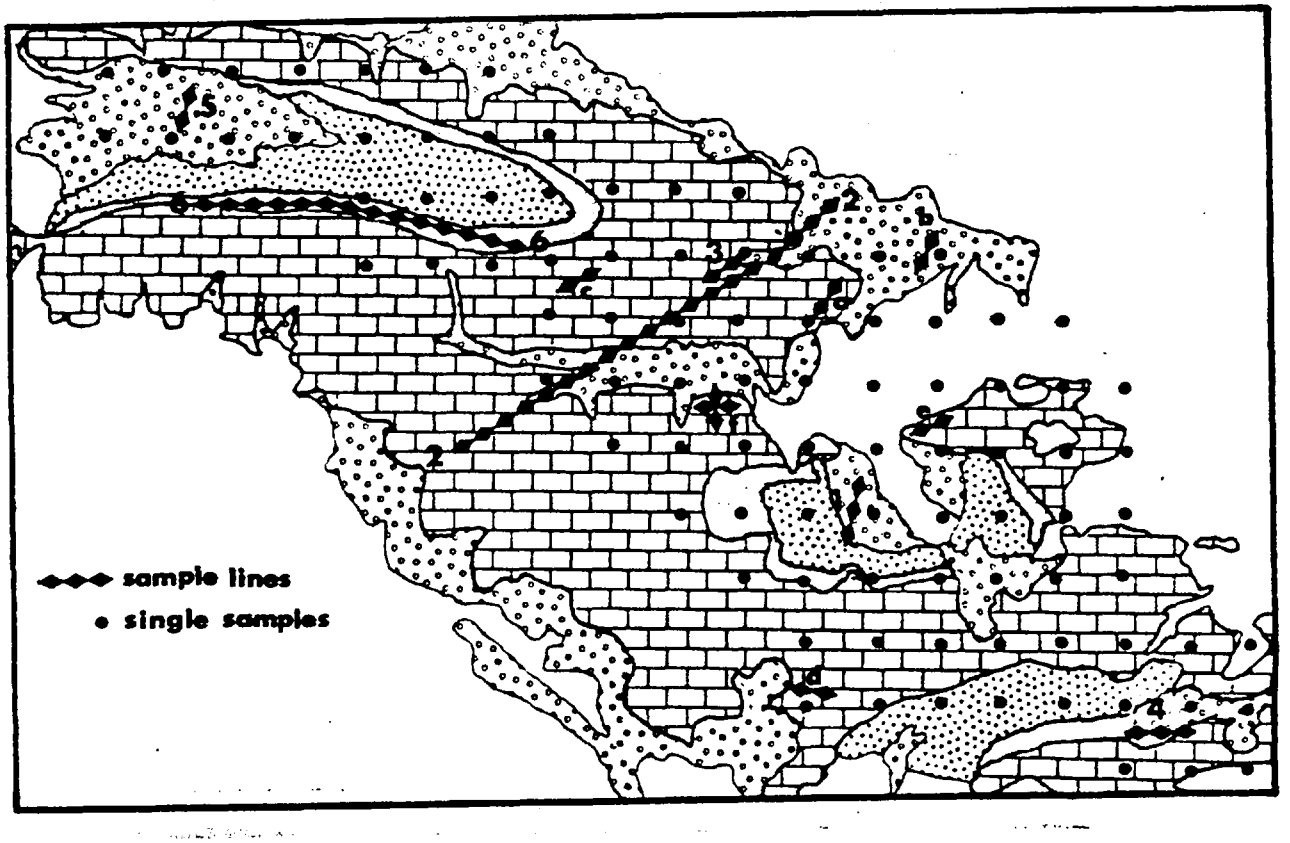


Figure 5-2 Location of soil grids and traverse lines. (see text for key to numbers and letters)



In the brown earths of well drained areas a grey-brown to brown A horizon of about 10 centimetres thickness is commonly developed over the brown to reddish-brown B horizon. Findlay (1965) suggests that this is due to leaching of carbonates from the surface horizon and translocation of clay, and not due to dissolution of hydrolyzates, as is characteristic of podsols.

5-3 Sample Collection and Analysis

As part of the study involved geostatistical determination of optimum sample spacing for soil surveys, samples were collected along lines at even intervals. The traverses, shown in Figure 5-2, were chosen to represent (1) lead-mineralised conglomerate, (2) lead-mineralised and unmineralised limestone across strike, (3) the same belt of lead mineralisation as line 2, but in an unploughed and un-levelled field*, (4) unmineralised conglomerate, (5) zinc-mineralised conglomerate, and (6) unmineralised limestone along strike. Although line 4, east of Slab House (592 483), was intended to represent an unmineralised area, there are distinctive anomalies near the western end of the traverse, indicating the possible presence of previously unknown lead and zinc enrichment.

In addition to the samples representing mineralisation at Chewton Warren (line 1), Longwood (2, 3), and Shipham (5), samples have been collected in the vicinity of mineralisation at Lamb Leer (a), East Harptree (b), Charterhouse (c), Rookham (d), Eaker Hill (e), and Stow Barrow (f), (Figure 5-2). Some 300 samples were collected from these nine areas. The data set also includes 167 samples of soils over unmineralised limestone, and 56 samples over unmineralised conglomerate. Some of these are from the traverses mentioned above, and the remainder comprise a grid covering most of the western end of Mendip at a one kilometre spacing (see Appendix E on choice of grid spacing).

Samples were collected from the B horizon, at 15 to 30 cm depth, using a 2 cm diameter auger. Where the soil was less than 30 cm thick, samples were taken

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* In many fields the linear pits left by the miners have been levelled and ploughed so as to make them more suitable for grazing.

at the greatest possible depth. At each site at least 3 auger holes were drilled, equally spaced at about 1 metre, so as to obtain a composite sample. The soils were dried at 80°C in kraft bags, disaggregated, and sieved to retain the minus-80 mesh (less than 0.18 mm) material. 250 mg sub-samples were digested in nitric and perchloric acids. Calcium, magnesium, manganese, cadmium, copper, lead, zinc, sodium, potassium, cobalt and nickel were determined by atomic absorption spectrophotometer. For most elements, analytical precision was better than 15% at the 95% confidence level. Comparison of field duplicates (pairs of 3-hole composite samples collected within several metres of each other) indicates high sampling variability, especially for calcium. For lead and zinc the sampling variability is in the order of 20%, however these two elements show similar behaviour in duplicate samples, and the variability of the lead to zinc ratio is not significantly higher than the analytical variability. Descriptions of the analytical procedures and estimates of analytical and sampling precision are given in Appendix A.

5-4 Results

5-4.1 Data From Mineralised Areas

Means for 12 elements for 11 sub-sets of the data are summarised in Table 5-1. For all elements except potassium and sodium it was found that the data are more closely approximated by logarithmic than arithmetic distributions, and log-transformations have been applied in order to estimate means. Groups A and B represent samples from unmineralised background areas of the Carboniferous Limestone and Dolomitic Conglomerate. Manganese, lead, zinc, and barium, and to a lesser degree, calcium, iron and cadmium are enriched in the conglomerate relative to the limestone. There is no significant difference in calcium to magnesium ratios for the two groups.

Groups C to K represent samples from nine different mineralised areas. The most striking enrichment is in lead, which is elevated to several times background levels in every area of mineralisation. Zinc is similarly enriched in six areas and cadmium in three. Although there is no background data for comparison, the variability of cobalt and nickel is small, and significant

Table 5-1 Means for major and minor elements for various subsets of the Mendip soil data. (All are geometric mean except K and Na, which are arithmetic mean. All are ppm except where noted)

Group	Mineralised area	Underlying Lithology	n	Ca%	Mg%	Fe%	K%	Na
A	un-min	C. Lmsn	125	.27	.42	3.06		
B	un-min.	D. Cglm	48	.32	.44	3.85		
C	Chewton	D. Cglm	57	.06	.36	4.74	.85	251
D	Longwood	C. Lmsn	39	.42	.41	4.16	.75	289
E	Shipham	D. Cglm	29	1.37	1.14	4.22	.88	322
F	Lamb Leer	C. Lmsn	24	.50	.43	6.93	.90	415
G	Harptree	D. Cglm	16	.37	.32	7.70	.77	344
H	C'house	C. Lmsn	34	1.15	.49	3.58	1.08	454
I	Rookham	C. Lmsn	14	2.72	.61	3.15	1.02	460
J	Eaker Hill	C. Lmsn	15	.71	.34	4.08	.73	365
K	Stow Barrow	C. Lmsn	81	.33	.45	3.04	.83	270

Group	Mn	Cd	Cu	Pb	Zn	Ba	Co	Ni
A	950	2.0	16.7	347	240	170		
B	1500	2.8	17.0	514	552	524		
C	2099	1.6	18.6	4325	578	602	19.4	39.6
D	1757	3.2	28.1	6209	1153	310	22.3	52.8
E	4227	137.0	37.4	4265	15381	584	25.3	65.2
F	2432	7.2	25.5	4786	1816		18.7	73.5
G	1005	36.0	18.0	2624	14655		25.8	75.0
H	1279	4.6	30.6	13868	1442		19.4	60.5
I	2032	2.9	32.4	8933	502		20.5	50.1
J	1545	2.8	19.9	2352	790		19.7	42.7
K	937	2.0	17.8	3221	346		25.1	38.6

enrichment seems unlikely. Calcium is enriched in six areas and strongly depleted in one. Both iron and manganese are enriched in seven areas, and magnesium is enriched in two.

Lead to zinc ratios for several of the mineralised areas are shown in Figure 5-3. Data are presented as ratios rather than absolute values, because the ratios are less dependent on variability caused by mining disturbance. The lead to zinc ratios are significantly higher on the top of the Mendip, than on the northern and western flanks especially at East Harptree and Shipham. Furthermore, there is a consistent trend on the northern slope, as can be seen in the data from East Harptree (Pb/Zn = 0.15), Lamb Leer (3.5), Longwood (7.1) and Charterhouse (9.8). This trend can easily be seen with lead to zinc ratios plotted against distance along a cross section through the mineralised areas (Figure 5-4). The north to south increase in lead to zinc ratio across the 500 m traverse at Chewton Warren (Figure 5-5), indicates that the trend also applies on a local scale.

Correlation coefficients have been calculated for the mineralised and unmineralised subsets in order to study relationships between the ore elements and the elements present in gangue minerals. For the unmineralised areas lead and zinc are correlated with calcium, and zinc is correlated with manganese and iron (Table 5-2). The various mineralised areas have strikingly different characteristics. At Chewton Warren, for example, lead and zinc are strongly correlated with magnesium, iron and manganese, but only weakly with calcium. At Longwood, Charterhouse and Stow Barrow, lead and zinc are correlated with calcium, iron and manganese, but not with magnesium. At Shipham lead and zinc are correlated with calcium and magnesium only. Correlations are generally weak in the other mineralised areas.

5-4.2 Data From Wide Spaced Grid

The most important observation made above is that there is a pronounced variation in the lead to zinc ratio from one area of mineralisation to another. Furthermore, there is a consistent decrease in lead to zinc ratio from north to south, from the plateau to the flanks of the Mendip Hills.

A regional soil grid of 100 samples at 1 km centres was established covering areas of known mineralisation on the plateau and on the northern slope,

Figure 5-3 Lead to zinc ratios for groups of soil samples from various mineralised areas in the central Mendip Hills (number of samples in small figures)

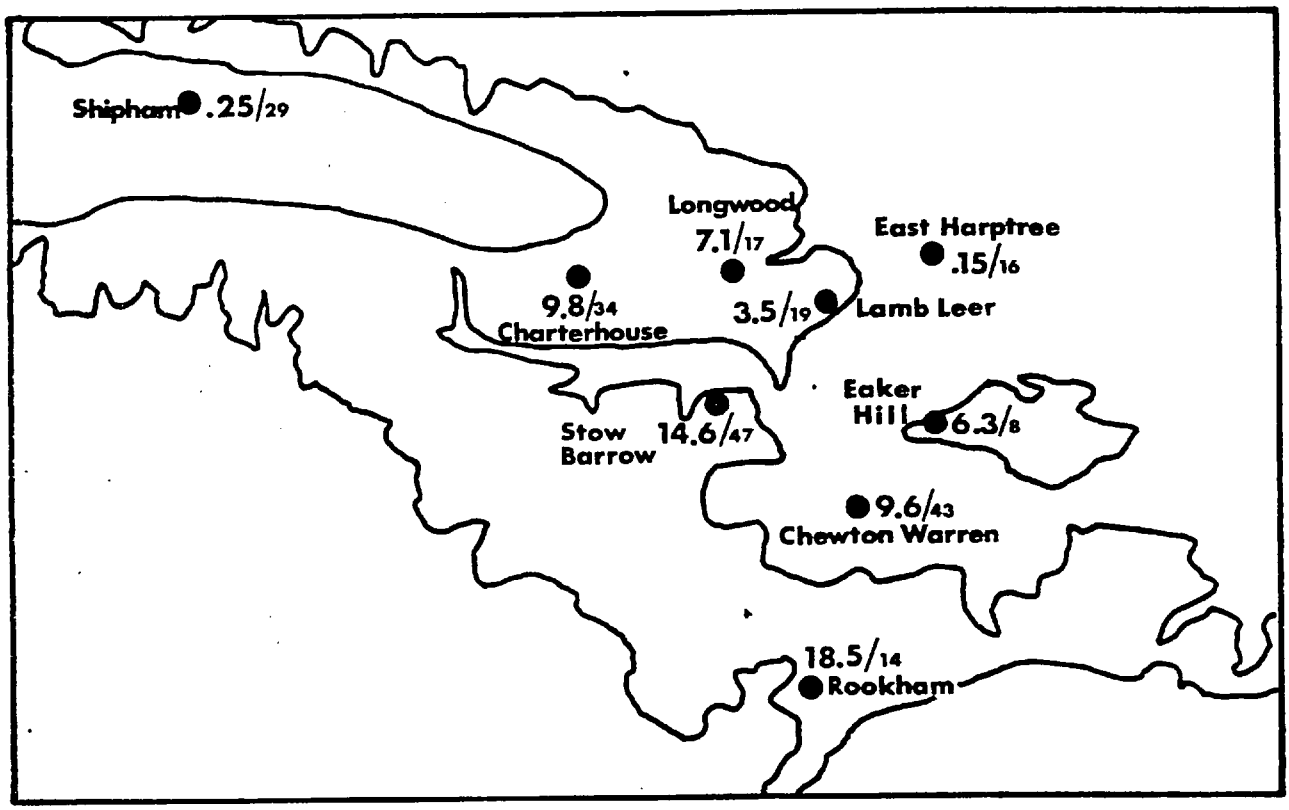
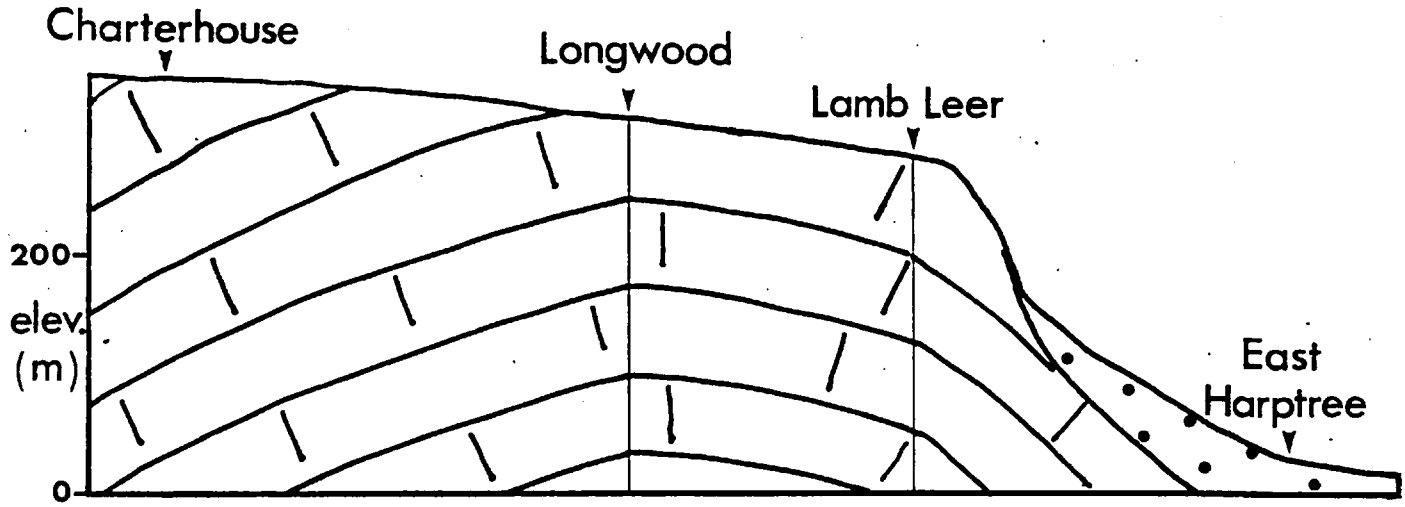


Figure 5-4 Variation in lead to zinc ratio along a line from the Mendip plateau at Charterhouse, to the base of the northern slope at East Harptree



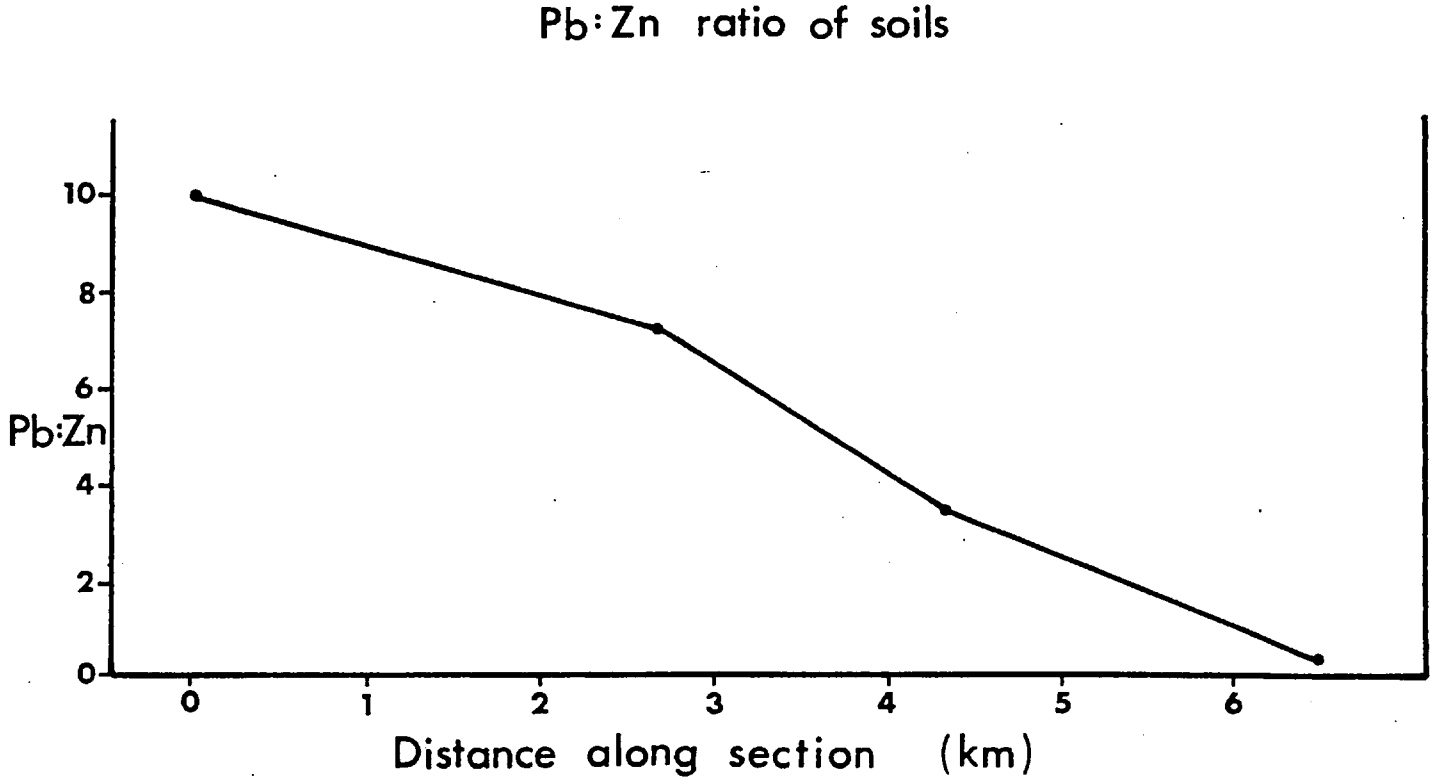


Figure 5-5 Variation in the lead to zinc ratio along a 500 m line across mineralisation at Chewton Warren

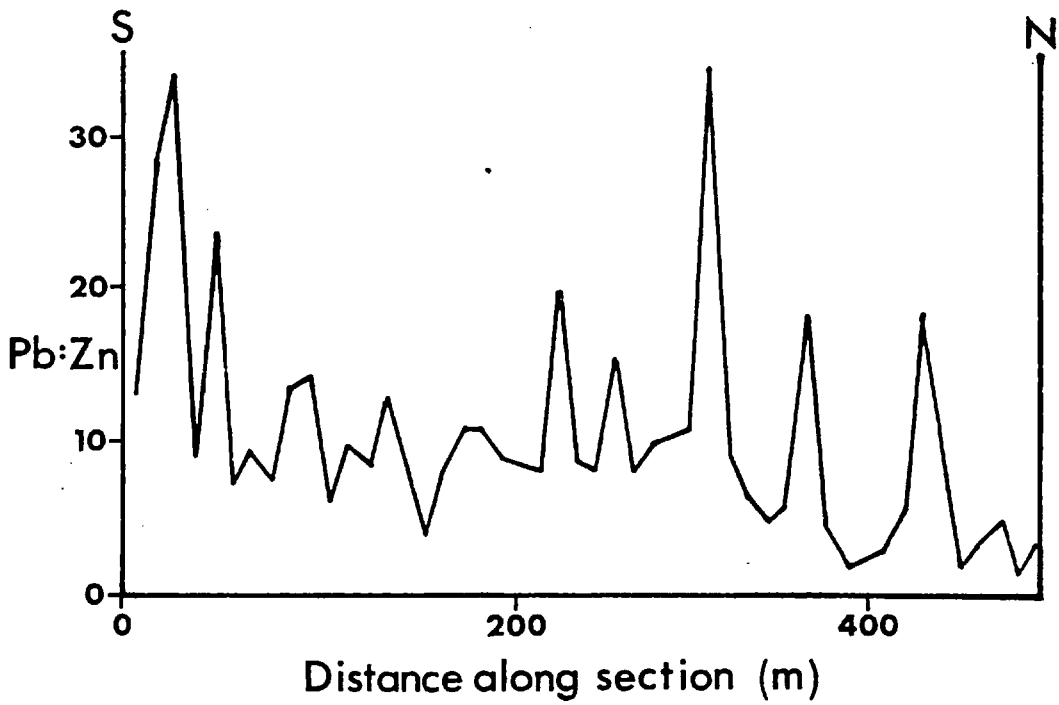


Table 5-2 Correlations between lead and zinc and the major elements for various subsets of the Mendip Hills soil data*

GROUP	n	Pb:Ca	Zn:Ca	Pb:Mg	Zn:Mg	Pb:Fe	Zn:Fe	Pb:Mn	Zn:Mn
Unmineralised Limestone	125	.42	.53	-.22	.20	.22	.43	.27	.61
Unmineralised Conglomerate	48	.32	.45	.10	.46	.30	.50	-.02	.54
Chewton Warren	57	.37	.38	.49	.55	.63	.73	.67	.57
Longwood	39	.64	.81	-.09	-.42	.68	.96	.68	.96
Shipham	29	.69	.88	.52	.76	-.12	-.15	-.44	-.52
Lamb Leer	24	-.05	.60	.09	.17	.23	.35	.19	.18
Harptree	16	-.02	-.28	-.34	.14	.56	.20	-.50	.37
C'house	34	.68	.42	-.20	.22	.17	.79	.49	.87
Rookham	14	.42	.35	.14	.24	.61	.54	.78	.63
Eaker Hill	15	-.23	.37	-.43	.21	-.98	.74	-.65	.50
Stow Barrow	81	.40	.47	.19	.24	.08	.53	.78	.77

*Correlations above the 95% significance level are underlined. (The data were normalised by the exponential transformation technique prior to calculation of correlation coefficients)

in central and western Mendip. The purpose of collecting this set of samples was to better define the spatial variation in lead and zinc concentrations. Cadmium and zinc (Figure 5-6, 5-7) are markedly enriched along the northern and north-eastern flanks of the uplands. There is some enrichment of lead in these areas, but the highest lead concentrations are restricted to the plateau (Figure 5-8). The lead to zinc ratio (Figure 5-9) shows zonation from zinc-rich soils on the northern slopes, including the areas near Slab House, East Harptree, Burrington and Shipham, to lead-rich soils on the west-central part of the plateau.

5-4.3 Effects of Industrial Contamination

The possibility of contamination of soils in the Mendip area by mining and refining activities is vividly expressed in a 17th century quotation in Gough (1967, page 140). Referring to one of the Mendip smelting operations it was observed that "... there is a flight in the smoak, which falling upon the grass, poysons those cattel that eat on it...". It is probable that the poisonous material was lead, and if it collected on the grass, it is likely that it also accumulated in the underlying soil. A soil sample collected within 300 metres of the smelter site at Waldegrave (544 506) where no mineralisation is known, has a lead concentration of 12 000 ppm, and a lead to zinc ratio of 30. (Most soils over unmineralised Carboniferous Limestone have lead to zinc ratios between 0.8 and 3). The distribution of lead in soils in the Chewton Warren area is shown in Figure 5-10. Several samples have high lead concentrations (greater than 400 ppm), but most of these can be related to adjacent mineralisation. Elevated lead concentrations in the samples 1 200 metres north and 800 metres east of the lead works may be due to airborne contamination.

A series of soil samples was collected along the line crossing the dry stream valley west of the Waldegrave lead works (Fig. 5-10, section a-a'). The lead and zinc concentrations of these samples are shown in Fig. 5-11. For at least 25 metres on either side of the stream bed soils are signficantly enriched in both elements. Ford and Stanton (1978) have discussed the paleo-geography of the Mendip Hills, and have suggested that a tributary of the Pliocene-aged Cheddar drainage system flowed through this east-west valley. Such a stream would probably have originated in the mineralised area around Chewton Warren.

Figure 5-6 Grey-scale map for cadmium in soils from the central Mendip Hills. (map cells are 1 km squares)

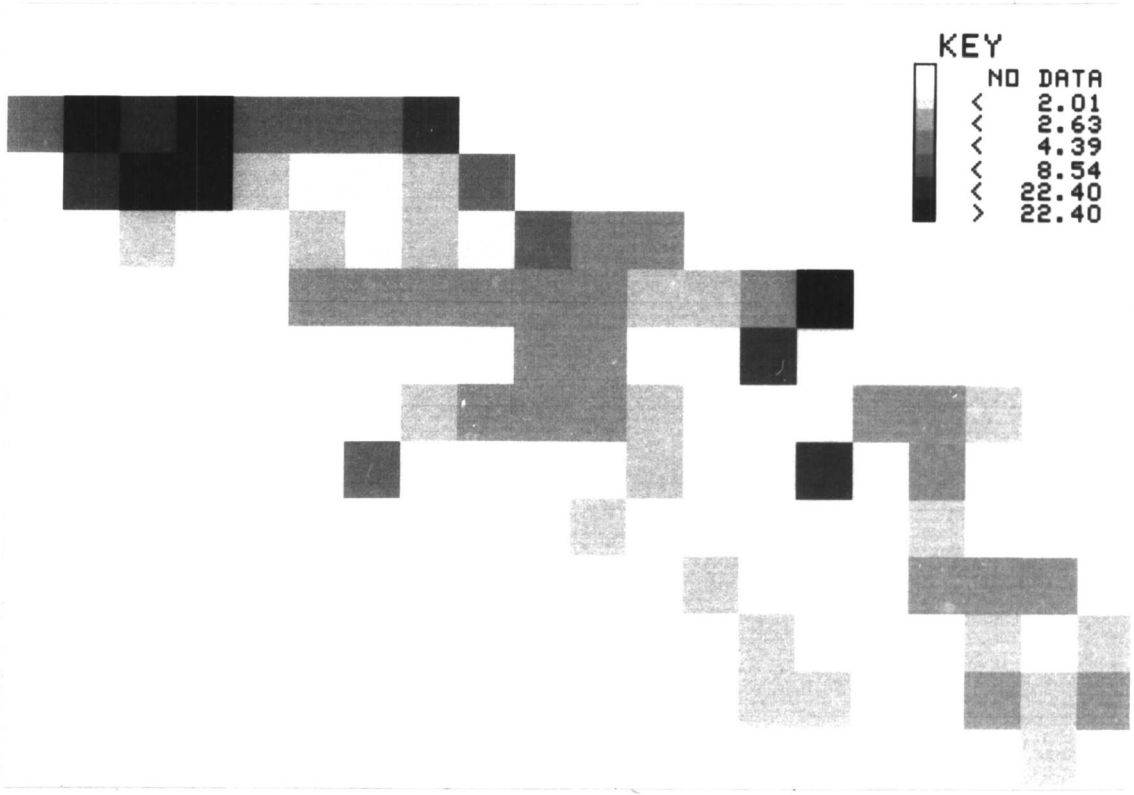


Figure 5-7 Grey-scale map for zinc in soils from the central Mendip Hills

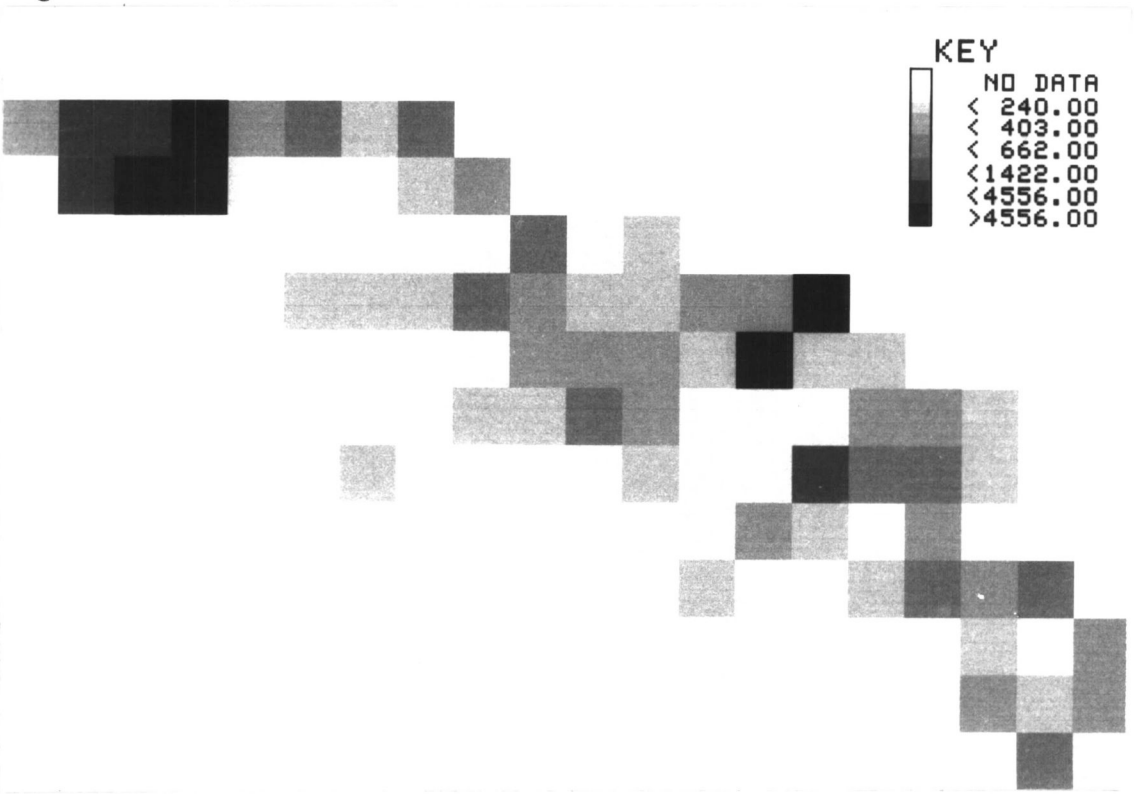


Figure 5-8 Grey-scale map for lead in soils from the central Mendip Hills. (Map cells are 1 km squares)

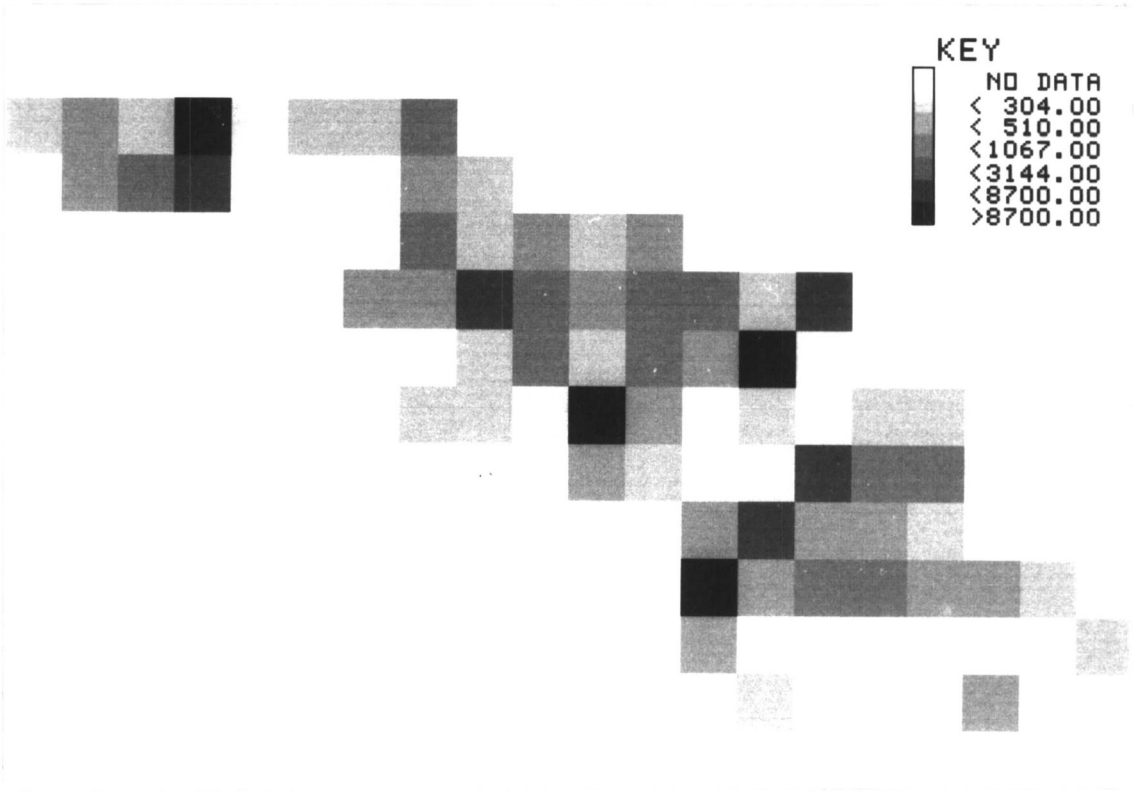


Figure 5-9 Grey-scale map for lead to zinc ratio in soils from the central Mendip Hills

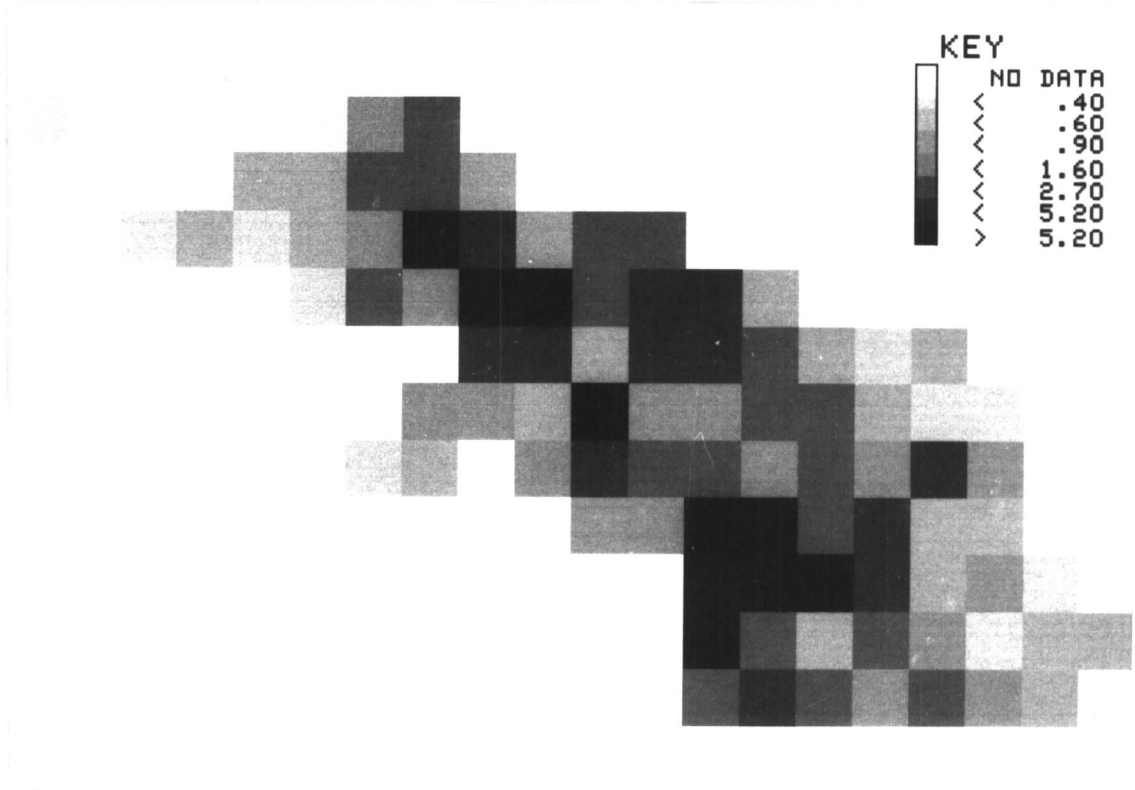


Figure 5-10 Lead distribution in soils in the vicinity of the former lead workings at Waldegrave in the central Mendip Hills

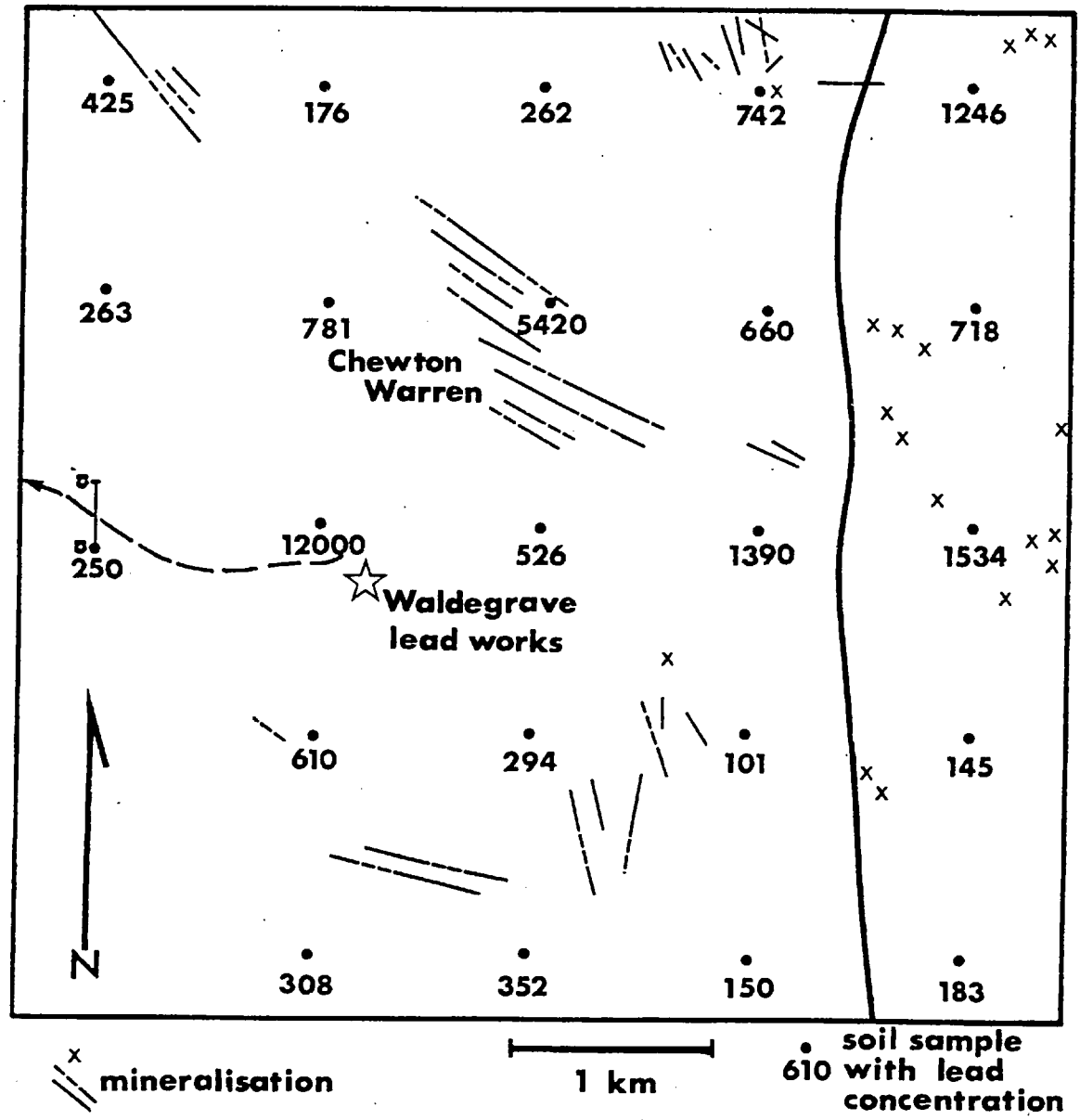
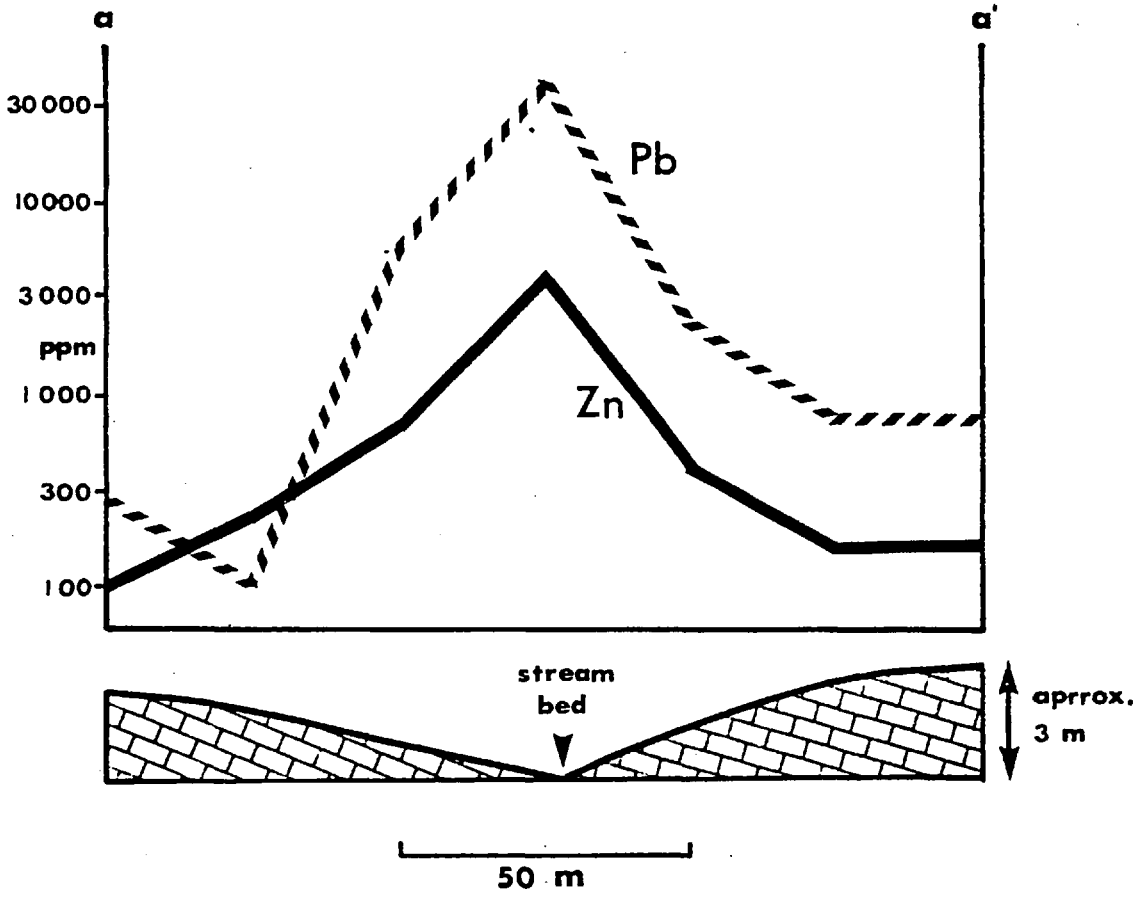


Figure 5-11 Lead and zinc distribution in soil samples collected at 25 m intervals across a stream bed, roughly one kilometre down-drainage from the former lead workings at Waldegrave in the central Mendip Hills. (the location of section a-a' is given on Figure 5-10)



Alternatively it is possible that the anomaly is derived from waste material from around the old workings at Waldegrave, a little over 1 km upstream.

Smelter works were also situated near Charterhouse (607 560), Smitham's Hill (556 547) and Priddy (exact location unknown) (Green, 1958). Two samples from near Charterhouse and one from the Smitham's Hill area appear to be affected by contamination, but there is no evidence of contamination near Priddy. In each case, contamination of greater than 1 000 ppm lead is restricted to the area within a few hundred metres of the smelter site, and some of that may be explained by near-by mineralisation. With the exception of the Charterhouse area, all of the mineralised zones are at least 1 000 metres from any of the smelters

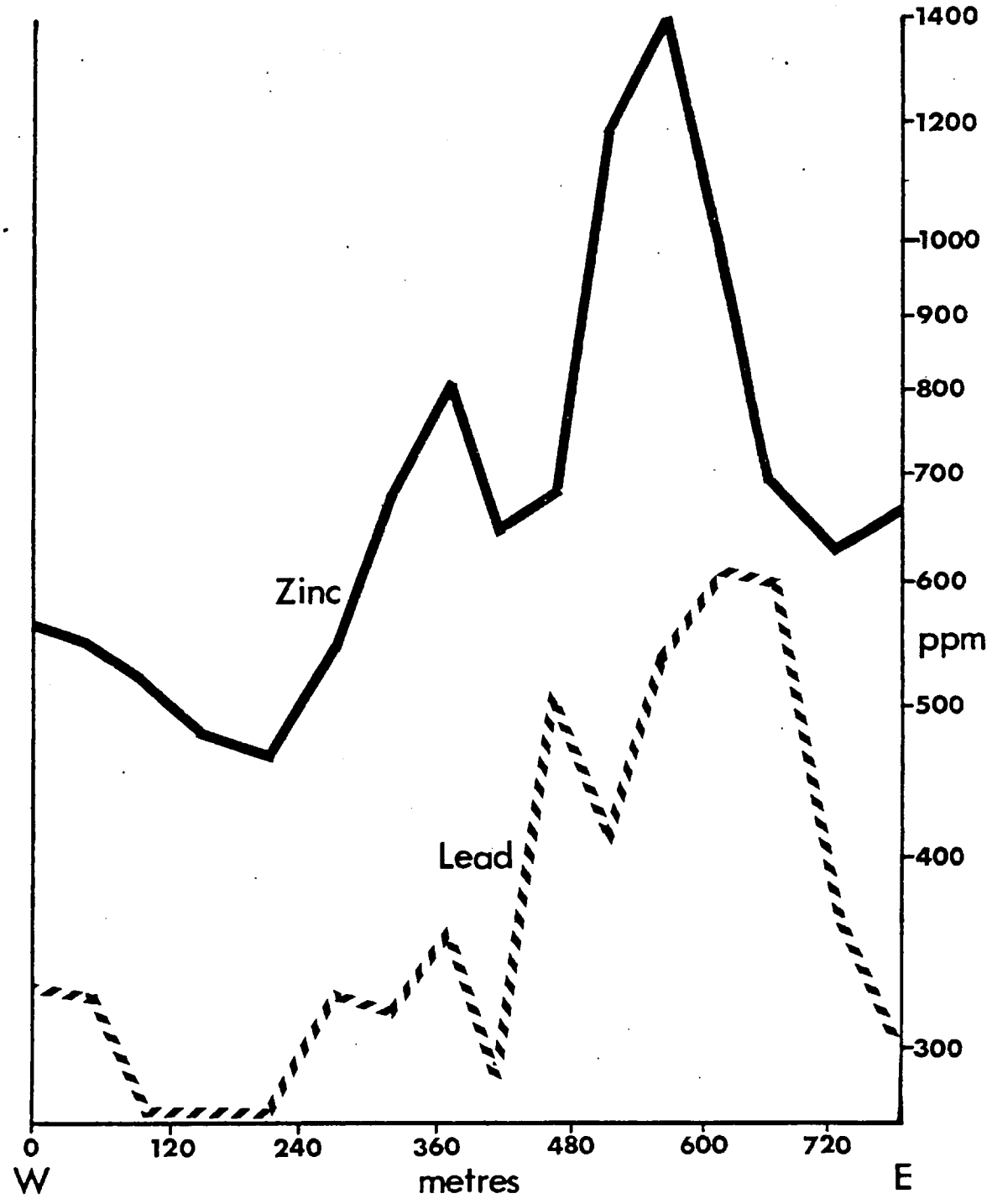
An interesting example of contamination from mining activities is revealed in the cadmium data from the samples collected near Shipham. Here the mean cadmium concentration is 137 ppm, (some 65 times background levels), and the maximum concentration is 691 ppm. This discovery of extreme cadmium levels, has since caused considerable alarm in medical circles, and several surveys and epidemiological studies have been carried out (Carruthers and Smith, 1979; Hughes and Stewart, 1979; Anon., 1982a; Iniskip and Beral, 1982; Anon., 1982b).

Cadmium enrichment is also evident at East Harptree, and as can be seen from Figure 5-6, there may be other areas of enrichment, particularly on the northern slope of the Mendip Hills.

5-4.4 Soil Anomalies in Areas of no Known Mineralisation

As noted above, a soil geochemical anomaly has been detected in an area underlain by the Dolomitic Conglomerate near Slab House. Zinc and lead data for the Slab House area are presented in profile form in Figure 5-12. The levels are low compared to other mineralised areas. The most obviously anomalous element is zinc. There is also enrichment of calcium, magnesium, iron, potassium, manganese and cadmium over a width of about 100 metres.

Figure 5-12 Smoothed profile of lead and zinc concentrations in soil samples from the Slab House area in the central Mendip Hills. (smoothing was by a 3-point moving average technique)



5.5 Discussion

It can be argued that soil geochemistry cannot be used as a means of characterising underlying bedrock mineralisation unless three criteria are met, namely:

1) the soils are locally derived,
2) the primary geochemical features are not significantly distorted by soil-forming processes, and
3) the effects of contamination, if any, can be identified and accounted for.

Although loessal drift of Quarternary age is present in the area, all of the important mineralised zones have been worked at least once, and possibly several times during the past millenia and the soil in the area of these workings must be derived largely from material excavated from beneath the loess.

Draining systems developed during the Tertiary appear to have promoted dispersion of metals from the mineralised areas. It is also possible that some fluvial dispersion has occurred more recently, involving waste products from the ore processing sites.

Correlation coefficients calculated for samples from unmineralised areas reveal relationships between the base metals and calcium, iron and manganese which could be a function of similar relationships in the underlying rock, or of processes taking place during soil formation. If the soil forming processes do exert a strong influence on metal behaviour, one would expect these relationships to be evident in the data from the mineralised areas as well. There is, in fact, a great diversity in the relationships between base metals and major elements, with very strong correlation in some cases, and virtually no correlation in others. It follows that the correlations are more likely to be controlled by differing ore-mineral versus gangue-mineral relationships in the different areas, than by secondary processes taking place within the soil.

Contamination from air- and water-borne waste products of the ore processing activities is an obvious problem in areas near former smelter works. Based on the limited evidence given above, the contamination is not severe beyond a few hundred metres from each smelter site. In the mineralised areas, where lead concentrations in soils commonly exceed 10 000 ppm, the contamination is unlikely to affect the lead to zinc ratios of the soils.

Assuming, then, that the soil geochemistry does adequately reflect the bedrock geochemistry the following points can be made:

1) The Dolomitic Conglomerate has higher background concentrations of manganese, lead, zinc, barium, calcium, iron and cadmium than the Carboniferous Limestone.
2) The magnesium content of the conglomerate is not significantly higher than that of the limestone.
3) Although all of the major zones of mineralisation on Mendip are characterised by enrichment of lead, both lead-rich and the zinc-rich end members can be identified, and there is an apparent gradation from lead-rich to zinc-rich mineralisation on both regional and local scales. The lead to zinc ratios are the lowest on the northern and western flanks of the plateau, and highest on top of the plateau.
4) Soil samples collected from within a few hundred metres of one of the former ore processing sites have distinctively high lead concentrations, which are probably a product of airborne contamination. Soil samples collected from a dry valley "downstream" from one of the former smelters have anomalous lead concentrations. During the Pliocene this valley may have channelled drainage originating in a heavily mineralised area, but it is also possible that the anomalies are due to contemporary drainage from the former smelter.
5) The mineralised areas appear to be composed of distinct "veins" separated by zones of lower grade or barren ground.
6) Near Slab House a 100 metre wide zone is characterised by anomalous concentrations of zinc and cadmium and several other elements. It seems likely that this anomaly is related to the presence of previously unknown mineralisation in the underlying Dolomitic Conglomerate.

A possible explanation for high background concentrations of various elements in the Dolomitic Conglomerate, as compared with the limestone, is that the intergranular porosity of the conglomerate is greater and more evenly distributed than the fracture porosity of the limestone, hence the process of mineralisation has affected the conglomerate over wide areas.

Concerning the calcium to magnesium ratios of the conglomerate and limestone, Campain (1979) has shown that the conglomerate is only sporadically dolomitic, and that parts of the limestone are also dolomitic. The calcite to dolomite ratios of the Lower Limestone Shale and Black Rock Limestone, for example, vary from 1 to 1 for impure carbonate (70 to 80% carbonate minerals) to more than 100 to 1 for pure carbonate. The dolomitic conglomerate varies from 75 to 100% carbonate purity, and from almost pure dolomite to almost pure limestone, the latter being dominant. The interstices of the conglomerate have

been filled with hematite, pyrolusite, calcite, dolomite and quartz, along with associated trace elements, and it is the dolomitic part of this alteration which gives its name to these rocks, although the amount of dolomite present is limited.

Variations in the lead and zinc composition of the mineralisation suggest that there were spatial variations in the composition of the mineralising fluids, or in the conditions which promoted mineral deposition in the various areas. This feature will be addressed in a more comprehensive geological context in Chapter 7.

CHAPTER 6 SOIL GEOCHEMISTRY IN THE LATTERIDGE AREA

6-1 Introduction

Over the past 100 years the celestite deposits in the Bristol area have provided more than half of the world's needs for strontium sulphate (Nickless et al, 1976). The ores are comprised of celestite bearing nodular evaporite beds within the Keuper Marl, and celestite veins and infillings in the underlying Silurian and Upper Carboniferous strata. Nickless et al (1975, 1976) have suggested that the celestite is a diagenetic replacement of gypsum and/or anhydrite formed under sabka conditions. Wood and Shaw (1975), on the other hand, favour direct precipitation of celestite from strontium-enriched groundwater in an arid basin.

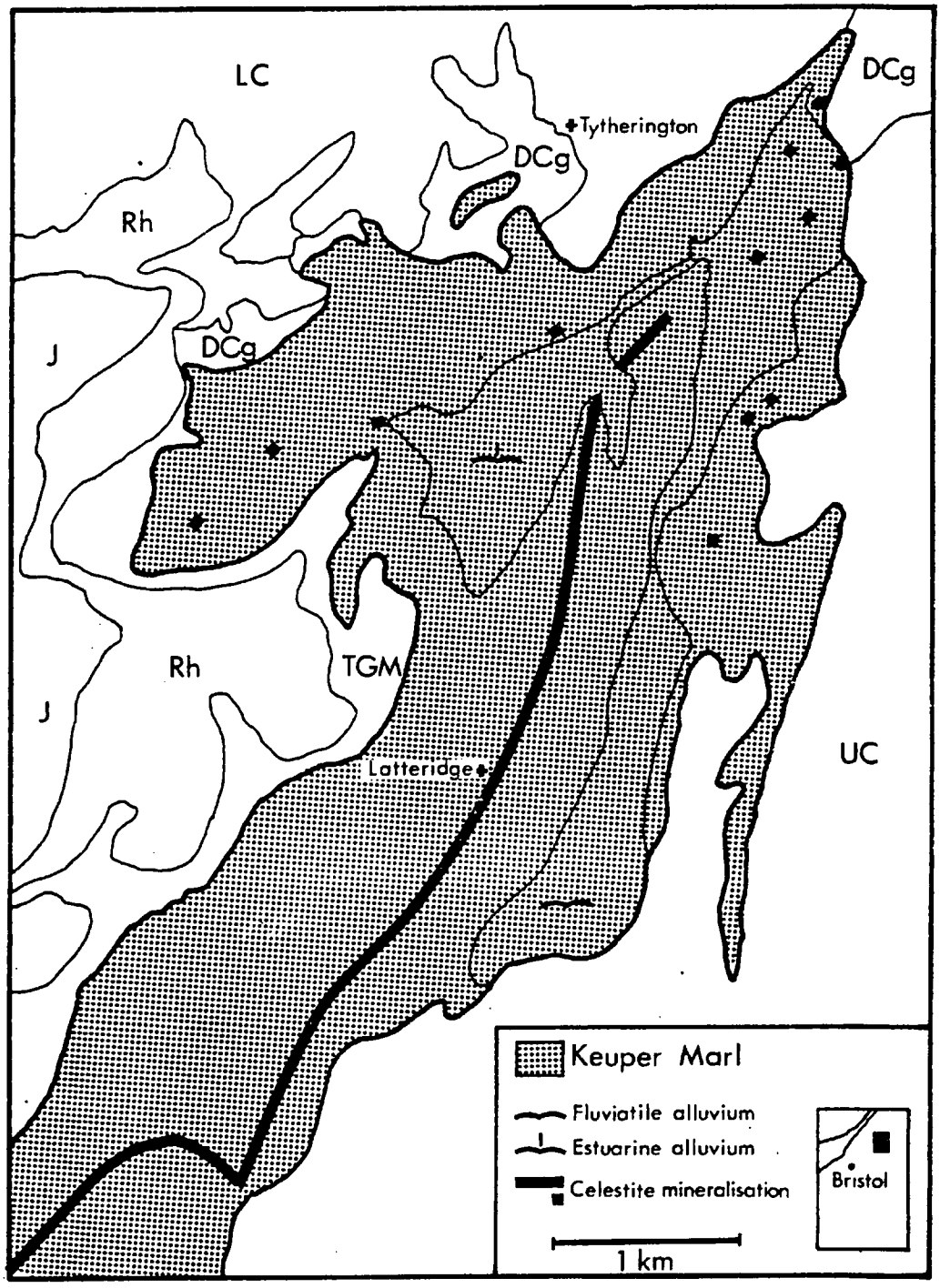
Between 1970 and 1973 the Institute of Geological Sciences conducted an evaluation of the celestite resources within the study area. The work, which included examination of mineral occurrences, soil and vegetation geochemical studies, and large diameter (1 metre) coring, is described by Nickless et al (1976). This chapter includes a discussion of geochemical analyses carried out on samples acquired from the Institute of Geological Sciences. The present study also includes a geostatistical analysis, which is described in Appendix E.

6-2 Geological Setting

The most important celestite bearing strata is the Keuper Marl calcareous red mudstone. A persistent evaporite bed lies some 5 to 20 metres below the top of the marl. Originally called the upper gypsum bed (Kellaway and Welch, 1948), it has been informally re-named the Severnside Evaporite Bed (SEB) by Nickless et al (1975). The stratigraphy of these upper Triassic rocks is well defined northeast of Bristol, near Latteridge (666 847) (Figure 6-1). Here the strata dip gently towards the northwest, with the SEB forming a ridge. A similar ridge marks the passage upward into the Tea Green Marl, as is shown in the generalised section across the strike of the Triassic strata (Figure 6-2).

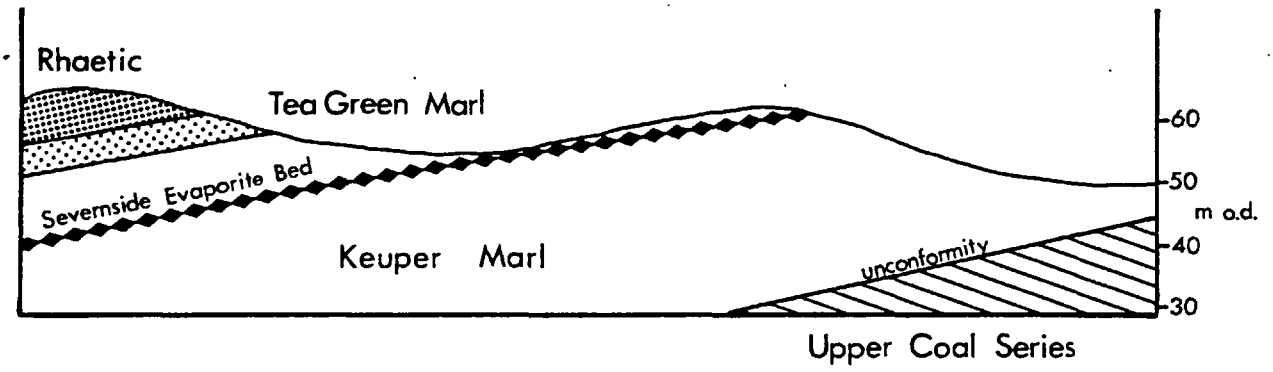
Much of the Keuper Marl is covered with up to 2 metres of blue-grey silty clay, which has been mapped as fluviatile and estuarine alluvium (Kellaway and

Figure 6-1 Geological map of the Latteridge area



(LC-Lower Carboniferous, UC-Upper Carboniferous, DCg-Dolomitic Conglomerate, KM-Keuper Marl, TGM-Tea Green Marl, Rh-Rhaetic, J-Jurassic)

Figure 6-2 Generalised cross-section showing the Triassic strata and their relationship to topography in the Latteridge area. (section is approximately 2 km long)



Welch, 1948). Where present, these drift deposits obscure the mineralised beds, even though they have been observed to include some isolated celestite fragments. Argillic brown earths are developed over the marl, with alluvial gley soils on the alluvium (Avery et al, 1975).

6-3 Sampling and Analysis

Some 850 soil samples were collected by the Mineral Assessment Unit of the Institute of Geological Sciences at 50 metre spacings along lines 200 to 500 metres apart (Figure 6-3). Strontium was determined by X-ray fluorescence (XRF) and isotope fluorimetry after grinding by pestle and mortar. Sampling, preparation and analytical methods are described in more detail by Nickless et al (1976). On the basis of geostatistical analysis (Appendix E), it was found that a similar amount of information could have been obtained using a sampling interval of 250 metres rather than 50 metres. A 250 metre square grid was used to select a sub-set of some 212 samples for further analysis. These samples were borrowed from the Institute of Geological Sciences.

Following digestion in nitric and perchloric acids, sodium, magnesium, calcium, strontium, barium, titanium, vanadium, manganese, iron, calcium, zinc, aluminum and lead were determined by direct reading emission spectrophotometry, with an inductively coupled plasma source (ICP). Although the XRF values are two to three times higher than those from the ICP, the correlation between the two methods is good. It appears that the nitric-perchloric digestion dissolves strontium in a constant proportion to its total concentration in the sample.

The analytical method is described in Appendix A which also includes estimates of analytical precision. For most elements, precision is better than 10% at the 95% confidence level.

6-4 Results

The distribution of strontium based on the 850 original samples is shown in Nickless et al (1976, 1980) and reproduced in Figure 6-4. The distribution for strontium as determined by ICP on the 212 sample data-set (Figure 6-5) is similar to that for the original data. There is a distinctive zone of strontium enrichment, which generally coincides with the trace of the SEB, although the

Figure 6-3 Locations of sampling traverses for soil samples collected by the Institute of Geological Sciences in the Latteridge area

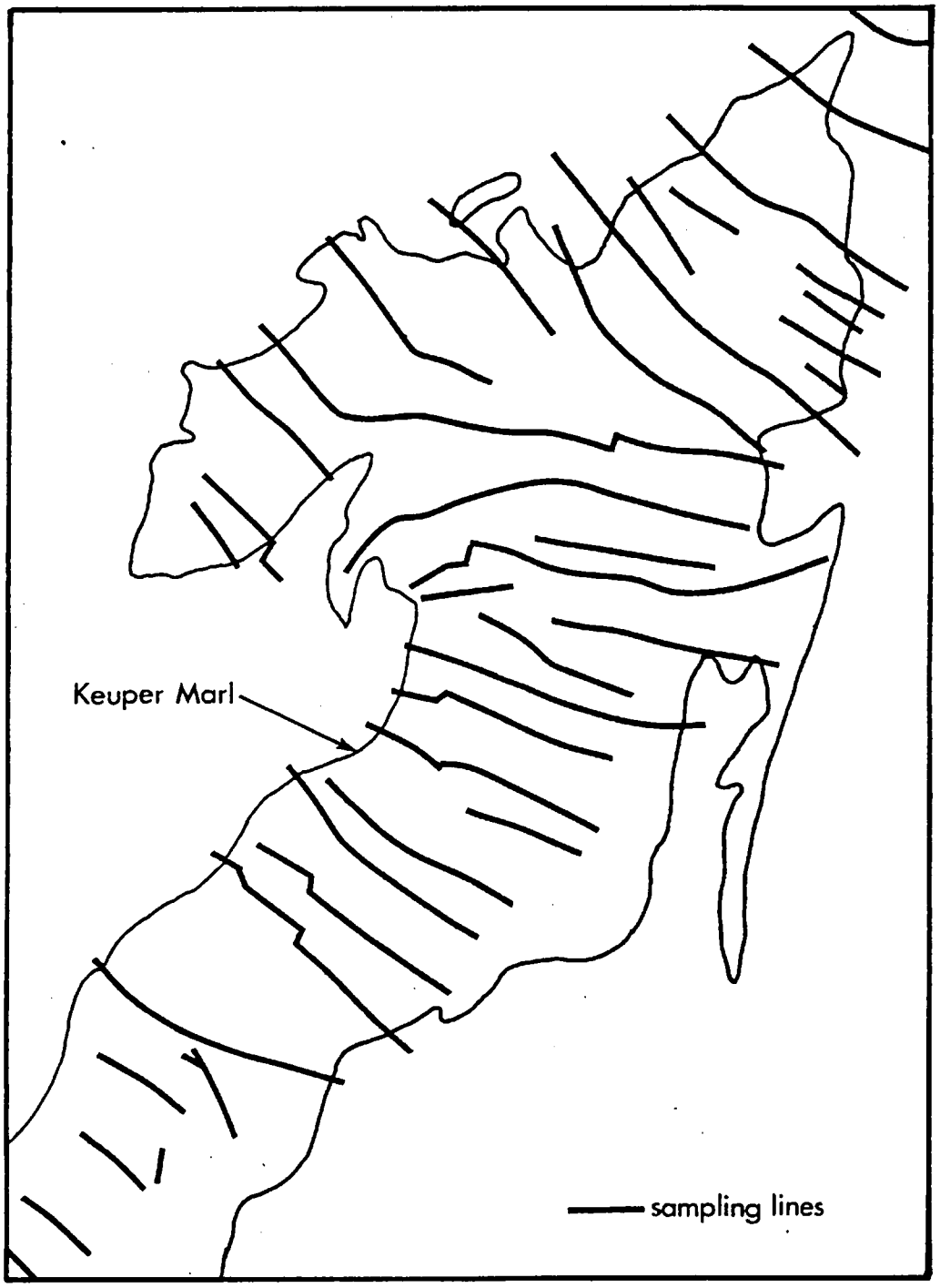
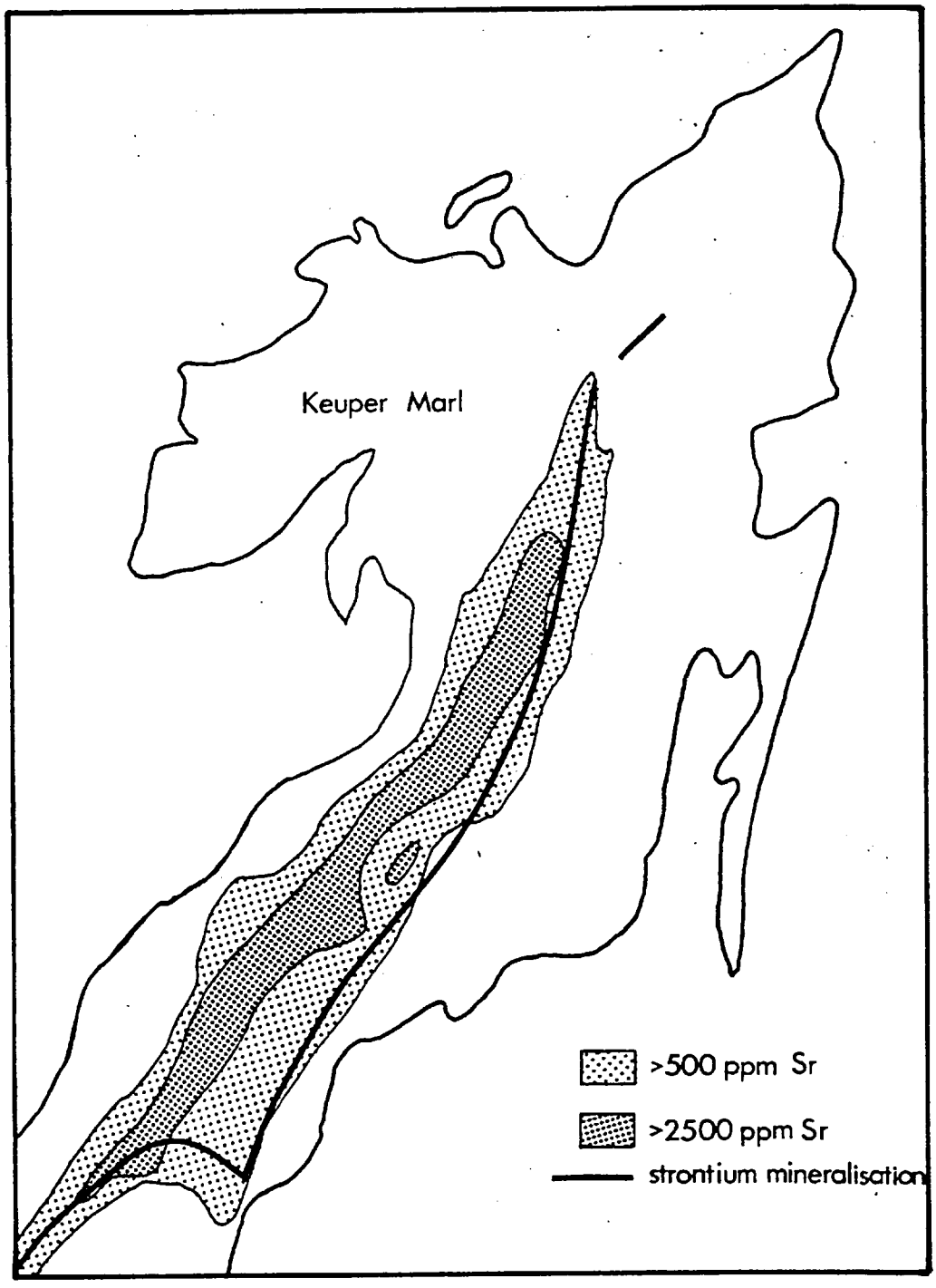
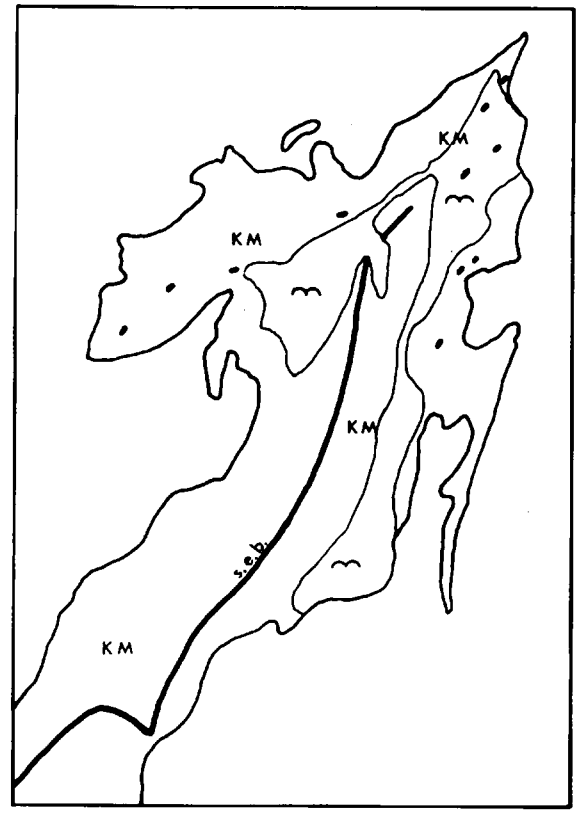


Figure 6-4 Map of strontium concentrations based on 850 soil samples collected in the Latteridge area (from Nickless et al, 1976)





Geological overlay for
Figures 6-5 to 6-15

Figure 6-5 Map of strontium concentrations in soils from the Latteridge area (Concentration levels for the 20, 40 ,60, 80, 90 and 95th percentiles are as follows, from light to dark: < 60, 60-106, 107-205, 206-612, 613-1582, 1583-4265, >4265 ppm. (each map cell is 250 by 250 m)



Figure 6-6 Map of barium concentrations in soils from the Latteridge area. (<246, 246-318, 319-399, 400-586, >587-813, 814-1270, 1270 ppm)



Figure 6-7 Map of sodium concentrations in soils from the Latteridge area. (<.032, .032-.056, .057-.078, >.079-.104, .105-.15, .16-.26, .26%)



Figure 6-8 Map of magnesium concentrations in soils from the Latteridge area. (<.77, .77-1.09, 1.1-1.5, 1.6-2.0, 2.1-2.8, 2.9-4.9, >4.9)



highest concentrations are on the dip-slope to the northwest. Moderate enrichment is also characteristic of the belt of fluviatile alluvium deposits in the valley to the east. The barium distribution (Figure 6-6) is similar to that of strontium although the trend along the SEB is less distinct. Enrichment is evident within the fluviatile alluvium, and sporadically within the Coal Measures.

Sodium (Figure 6-7) also shows a pattern similar to that of strontium. Magnesium, on the other hand, is strongly enriched directly along the SEB, and only slightly enriched along the dip-slope to the west (Figure 6-8). The calcium distribution (Figure 6-9) follows that of magnesium, but is less well defined. Aluminium (Figure 6-10) reaches its highest concentrations over the alluvial deposits, and in this respect is similar to vanadium, zinc, and, to a lesser extent, titanium (Figure 6-11 to 6-13). Aluminium, vanadium and titanium are also higher to the west of the SEB outcrop and to the east, although for vanadium and titanium this trend is indistinct and may not be significant. Copper, lead (Figure 6-14, 6-15) and zinc are distinctly enhanced along the trace of the evaporite bed, although there are high values elsewhere.

Iron (not shown) is characterised by high concentrations within the Coal Measures, but there are no other patterns which can be related to geology. Manganese is similarly irregular.

In summary, magnesium, calcium, copper, zinc and lead concentrations are enhanced along the trace of the SEB, whereas strontium, barium, sodium and aluminium concentrations are highest on the dip-slope to the west. A generalised profile of the behavior of some of the elements across the SEB is shown in Figure 6-16. Because of the relationship between topography and the dip of the beds, the SEB comes very near to the surface on the dip-slope west of the ridge. Here strontium, barium, and sodium concentrations are highest. On the steeper slope east of the ridge, calcium and magnesium concentrations are highest, and strontium and barium concentrations are at background levels.

The elemental associations described above in a spatial sense, are reflected in the inter-element relationships summarised in Table 6-1. Correlations amongst magnesium, calcium, copper, zinc and lead are virtually all high, as are those amongst strontium, barium, sodium and aluminium.

Figure 6-9 Map of calcium concentrations in soils from the Latteridge area. Levels are as follows, from light to dark: <.30, .30-.40, .41-.64, .65-2.6, 2.7-4.8, 4.9-7.5, >7.5 %. (each map cell is 250 by 250 m).



Figure 6-10 Map of aluminum concentrations in soils from the Latteridge area. (< 4.0, 4.0-4.6, 4.7-5.5, 5.6-6.1, 6.2-6.9, 7.0-7.7, >7.7 %)



Figure 6-11 Map of vanadium concentrations in soils from the Latteridge area. (< 56, 56-65, 66-73, 74-82, 83-92, 93-103, >103 ppm)



Figure 6-12 Map of zinc concentrations in soils from the Latteridge area. (< 112, 112-154, 155-203, 204-331, 332-457, 458-534, >534 ppm)



Figure 6-13 Map of titanium concentrations in soils from the Latteridge area. Levels are as follows, from light to dark: <632, 632-755, 756-900, 901-1077, 1078-1192, 1193-1303, >1303 ppm) (each map cell is 250 by 250 m)

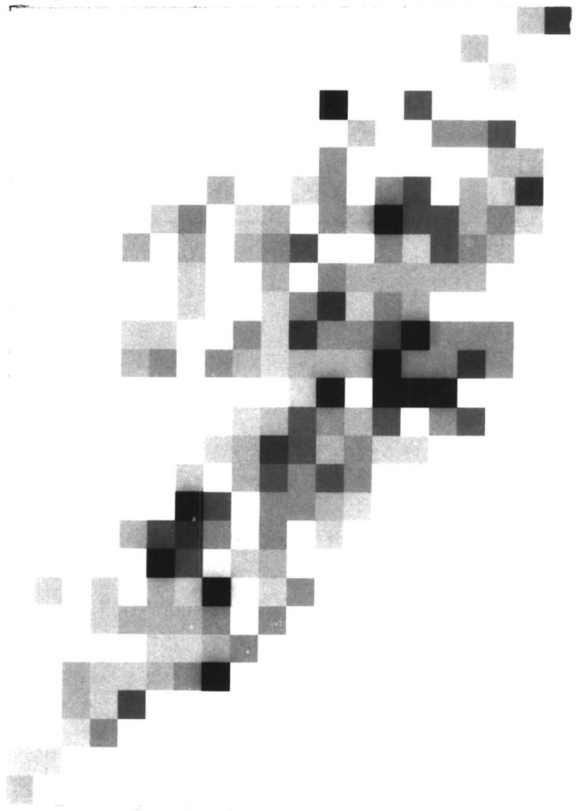


Figure 6-14 Map of copper concentrations in soils from the Latteridge area. (<20, 20-25, 26-30, 32-40, 41-49, 49-65, >65 ppm)



Figure 6-15 Map of lead concentrations in soils from the Latteridge area. (<121, 121-161, 162-239, 240-342, 343-468, >468 ppm)



Figure 6-16 Generalised profile of soil geochemical variations across the Severnside Evaporite Bed

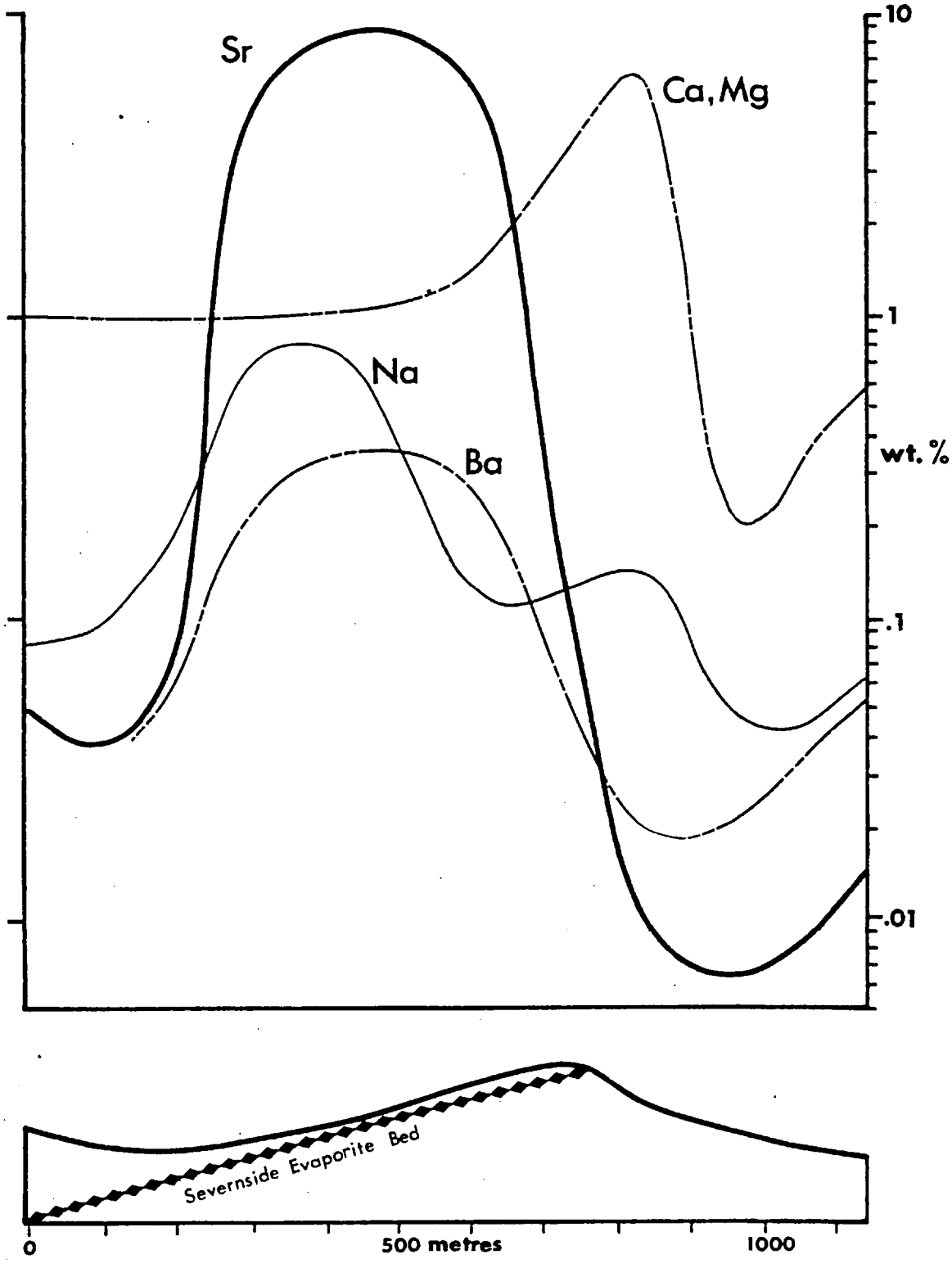


Table 6-1 Correlation coefficients for 212 soil samples from the Latteridge area

	Mg	Ca	Cu	Zn	Pb	Sr	Ba	Na	Al
Mg	1.0								
Ca	.67	1.0							
Cu	.56	.51	1.0						
Zn	.29	.34	.48	1.0					
Pb	.29	.37	.51	.17	1.0				
Sr	.39	.14	.15	.05	-1.0	1.0			
Ba	.12	.01	.08	.17	-.01	.63	1.0		
Na	.35	.20	.20	.00	.06	.54	.33	1.0	
Al	.41	.21	.29	.17	.26	.35	.41.	.29	1.0

6-5 Discussion

The weathering characteristics of the SEB and adjacent Keuper Marl have led to the situation where the evaporatic unit is exposed along the crest of a gentle scarp. As a result rock fragments from above and below the evaporite have been dispersed in opposite directions and there is a clear distinction, in the soils, between the geochemistry of the lower and upper parts of the evaporite unit. The lower part is rich in calcium and magnesium, whereas the upper part is rich in strontium, barium, and sodium. These observations may have important implications regarding the sedimentary and/or diagenetic environment during the accumulation of the deposits. This aspect will be discussed further in Chapter 7.

Another feature of the soil geochemistry is the enrichment of barium, aluminium, vanadium, zinc and titanium in areas of fluviatile alluvium. These alluvial deposits are down-slope from areas of relatively resistant rocks, including the Keuper Marl, and it seems likely that the anomalies are related to accumulation of chemically resistant minerals and/or clay minerals, during fluvial and related sedimentation.

CHAPTER 7 HISTORY OF ORE DEPOSITION IN THE BRISTOL-MENDIP HILLS AREA

7-1 Introduction

Many different theories have been advanced to explain the origin of ore deposits in the Bristol - Mendip Hills Region. The most important study of the lead and zinc mineralisation in the Mendip Hills was carried out by Green (1958), who implied that the mineralising solutions originated at depth, presumably as juvenile waters. This view is shared by Evans and Maroof (1976). Several other workers favoured deposition from waters derived in the sedimentary strata of the adjacent Central Somerset Basin (Ford, 1976; Worley and Ford, 1977; Emblin, 1978) following the stratafujic model of Jackson and Beales (1976).

The favoured theory for the origin of the iron ores of the area is that proposed by Trotter (1942) for similar deposits to the north. Iron released during weathering of the Coal Measures strata, was deposited in fractures in the underylying carbonates and in the intersticies of the Dolomitic Conglomerate (Kellaway and Welch, 1948; Green and Welch, 1965).

The celestite occurrences have been studied by Nickless et al (1975, 1976) and by Wood and Shaw (1976). These authors agree on an evaporitic origin for the deposits.

In an important study based on a deep borehole near Bristol, Kellaway (1967) remarked on the spatial coincidence of the various deposits within the Bristol and Mendip Hills area, and raised the question originally asked by Etheridge (1870), as to whether this spatial relationship also implies a genetic one. Evidence which supports and expands on this inference is cited in this chapter. The available information from within the region, including inferences from the geochemical data presented in Chapters 3 to 6, are compared with information on other similar deposits. A comprehensive genetic model for the three types of mineral deposits is developed. The model can be summarised as follows:

1) During the Hercynian orogeny, the Carboniferous and older strata were folded along east-west axes such as the Mendip axis.

2) Erosion of the emergent anticlinoria under hot and arid conditions, resulted in accumulation of coarse alluvial fans grading outward into fine-grained playa deposits.
3) Metals, such as lead and zinc, were dissolved at the weathering surface and then reprecipitated, as sulphides and carbonates, within fractures and fissures in the calcareous rocks, under carbon dioxide- and oxygen-poor conditions. With continued erosion the accumulations became enriched and a regional zonation developed because of the greater mobility of zinc versus lead.
4) Iron and manganese oxides precipitated within the alluvial fans where the relatively reduced deep ground waters discharged.
5) Sulphates and carbonates, including celestite and barite, accumulated within sediments of the playa, as groundwater originating in the uplands, was concentrated by evaporation.
6) All of the mineralising processes were abruptly terminated by the onset of marine conditions during Rhaetian times.

Information on Permian to Rhaetian climate and depositional environments is summarised in Section 7-2. The mineral occurrences are described in Section 7-3 and a review of the literature on similar deposits is included in Section 7-4. Details of the genetic model are presented in Section 7-5.

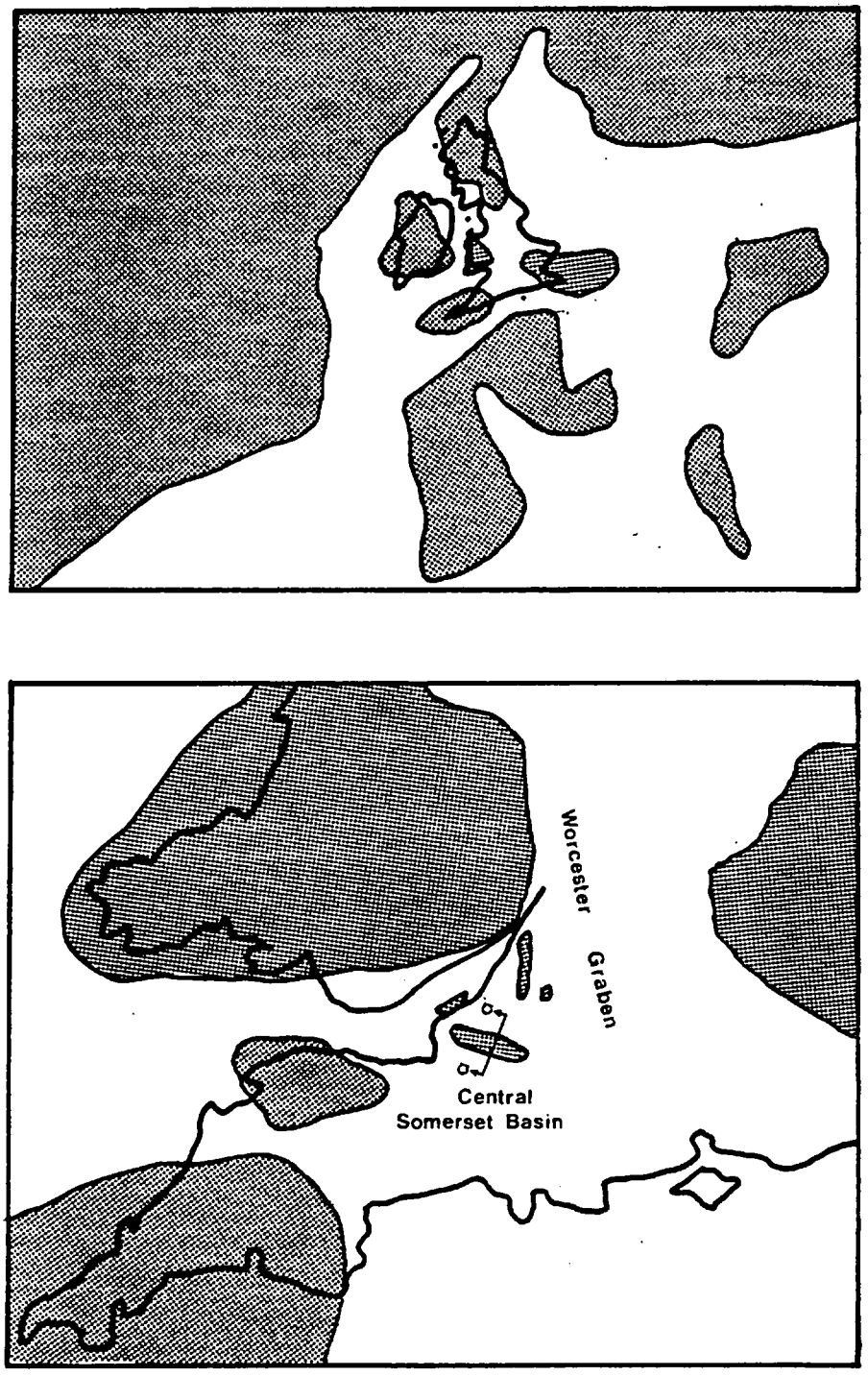
7-2 Permian to Jurassic Climate, Depositional Environments and Stratigraphy.

There are no known rocks of Permian age within the study area, and there is no direct evidence of what climatic conditions prevailed during that time. Significant folding and faulting took place after deposition of the late Carboniferous coal-bearing strata, and it is likely that erosion had been in progress long before the first accumulation of the upper-Triassic Dolomitic Conglomerate. Jones (1931) has suggested that the Permian erosion products were transported to the north and east. The Permian climate was probably hot and arid in the Bristol Mendip area, as it was in Devonshire and Yorkshire (Dewey, 1948; Smith, 1974).

As noted in Chapter 2, the red Triassic conglomerate deposits represent alluvial outwash fans or wadi sediments. The deposits are comparable to those of nearby South Wales (Tucker, 1977), and were probably deposited under conditions similar to those found in modern high relief deserts (Glennie, 1970).

Possible land-sea relationship for southwestern Britain during the Norian (middle-upper-Triassic) are shown in Figure 7-1. Although it is widely

Figure 7-1 Probable land-sea relationships during the middle and upper Triassic (after Audley-Charles, 1970)



accepted that the fine-grained Triassic strata are of continental origin (Klein, 1962; Dumbleton and West, 1966; Audley-Charles, 1970; Warrington, 1970; Wills, 1970; Meigh, 1976; Tucker, 1978), there is some controversy over whether the deposits products are of sub-aerial or sub-aqueous deposition. The two points of view are considered by Wills (1970), who proposes a model of periodic flooding of the land areas by storm runoff, followed by gradual evaporative drying. Regarding the Triassic strata of South Wales, Tucker (1978) describes various environments in which the fine-grained sediments may have accumulated. He suggests that:

1) the thin sandstones which grade from gravel to fine sand are a product of sheet flooding;
2) the fine sandstones and siltstones with wave-formed ripples and dessication cracks were deposited in and around ephemeral lakes;
3) the massive structureless silt and sand may be of aeolian origin;
4) the structureless dolomitic mudstone is an offshore lacustrine deposit.

On the basis of Tucker's work in the area of the Severn Estuary, it would appear that the Triassic sedimentary environment east of the Severn ranged from sheet-flood to off-shore lacustrine. By analogy with modern examples of evaporites in deserts (Durrell, 1953; Glennie, 1970; Twidale, 1972; Jones et al, 1977; Kendall, 1978; Hardie et al, 1978) one can assume that the discontinuous evaporite horizons in the Severnside Evaporite Bed were formed in an inland sabka environment (Wood and Shaw, 1976, Nickless et al, 1976). Following the coastal evaporite model of Shearman (1966), and observations of inland sabkas in California (Durrell, 1953), and Libya (Goudazi, 1970), the nodular evaporites probably accumulated during diagenesis, when the water table was maintained just below surface. The wide distribution of the main evaporite, and its 2 m thickness, suggests a stabilisation of water levels for a relatively long period. The 75 m variation in the present elevation of the evaporite could be explained by post-Triassic warping (Kellaway and Welch, 1948), or alternatively the evaporite may have been time-transgressive.

Towards the end of the Triassic, depositional conditions appear to have become less oxidising due to a wetter climate and a strengthening marine

influence (Kellaway and Welch, 1948; Audley-Charles, 1970). Deposition of mud, silt and sand continued during Tea Green Marl times, but the deposits differ from the Keuper Marl in their colour, and in the fact that sulphide minerals are present. Marine fossils have been identified in rare instances in the Tea Green Marl, in Somerset, (Green and Welch, 1965) and more commonly in Nottinghamshire (Elliott, 1961), but there is still some question as to whether the depositional environment of the green marl was significantly different from that of the red marl. In the Mendip area evaporite minerals, including celestite, have been observed in several outcrops of the Tea Green Marl (Green and Welch, 1965), and northeast of Bristol there is very little textural difference between the green marl and the sub-adjacent red marl (Nickless et al, 1976). According to Elliott (1961), the green colouration and the presence of sulphides might be a diagenetic feature of the Tea Green Marl.

The marine influence strengthened into the Rhaetian with transgression over most of the study area. The Rhaetic strata consists of dark pyritic mudstone and limestone, and pale silty mudstone and limestone. Both types contain abundant marine fauna, both vertebrate and invertebrate. Moore (1867) and Robinson (1957) have described evidence of marine and terrestrial vertebrates of Keuper, Rhaetic and Liassic age in Carboniferous Limestone fissures near Mendip. A conglomeratic facies of the Rhaetic at Butcombe, north of the Mendip Hills, may be the product of deposition in a littoral environment (Kellaway and Welch, 1948). Here the base of the Rhaetic is some 170 metres below its highest point in Central Mendip, hence, although a littoral facies may have developed at Butcombe during the early Rhaetic, it must have been submerged later on.

The Rhaetic strata are sequentially followed by White Lias and Blue Lias limestone and calcareous mudstone. On parts of the Mendip Hills and Broadfield Down, however, a conglomeratic littoral facies of Lias rests directly on the pre-Rhaetic rocks. In these areas the Rhaetic was either not deposited, or it has been removed as a result of a late Triassic or early Jurassic erosion on the uplands.

7-3 Description of Mineral Occurrences

7-3.1 Celestite

All of the important celestite deposits are either within, or else spatially associated with the Severnside Evaporite Bed of the Keuper Marl. The evaporite bed is a widespread feature, and includes up to four evaporitic horizons, within a total thickness of up to 2 m. Calcite, gypsum and celestite are the dominant minerals. Evaporitic minerals are also present throughout the Keuper Marl as scattered crystals, veinlets, nodules and distinct beds.

In most areas the evaporite is underlain by a significant thickness of mudstone and sandstone. Near the margins of the basin however, the evaporite oversteps the clastic strata and lies directly on the up-turned Coal Measures (Nickless et al, 1976). This feature is particularly important between the Bath and Severn anticlinal axes near Yate (714 828), where evaporite minerals are present in shale-bottomed depressions between sandstone ridges (Nickless et al, 1976). Much of the celestite recovery to date has been from this area.

The mineralisation consists mainly of celestite nodules, although disseminations and veins are also present. A common textural feature is that of celestite replacing anhydrite or gypsum. The proportions vary from almost pure gypsum to almost pure celestite, and there is an apparent increase in the celestite to gypsum ratio towards the margin of the basin. Other minerals present include quartz and calcite with minor amounts of hematite and illite. Pyrite, galena and sphalerite are present, but are very uncommon.

The soil geochemical data presented in Chapter 6 provide some insight into geochemical variations across the Severnside Evaporite Bed. For example, it was shown that the lower part of the bed, and perhaps part of the immediately underlying mudstone, is enriched in calcium and magnesium, as well as copper, lead and zinc. The upper part of the bed is enriched in strontium and barium. These geochemical differences indicate that the lower part of the bed is dominated by gypsum or anhydrite (with calcite) and a magnesium bearing mineral such as magnesite or dolomite (although neither of these minerals has been observed in any quantity). The upper part of the bed is dominated by celestite, barite and possibly halite.

7-3.2 Fluorite

Fluorite is uncommon in the study area. The most significant occurence is the fracture filling mineralisation in the Avon gorge (Loupekine, 1951). Here the fluorite is present in areas of dolomitisation, and is associated with hematite, calcite and bitumen. Green (1958) observed that traces of fluorite are associated with some of the sulphide deposits in the Mendip Hills. Much of the fluorite on Mendip is remote from other mineralisation however, and occurs in solution cavities within the Carboniferous Limestone (Kingsbury, 1941; Smith, 1974), in association with quartz, calcite and dolomite and in some instances with minor amounts of hydrocarbons and sphalerite. These occurrences appear to be restricted to the particularly bituminous and siliceous Black Rock Limestone series. A fluid inclusion homogenisation temperature of 85°C has been determined for fluorite within the Black Rock Limestone at Halecombe Quarry (701 457) in the eastern Mendip Hills (Smith, 1974). Assuming a geothermal gradient of 15°C per kilometer, and a surface temperature of 25°C, this temperature indicates a burial of about 4 kilometers.

7-3.3 Iron and Manganese

Accumulations of hematite, limonite and wad are known throughout the study area, particularly within the Dolomitic Conglomerate outwash fan deposits surrounding the Paleozoic uplands. Etheridge (1870) noted that the iron-ores are most common where the conglomerate rests on Carboniferous Limestone, Pennant Sandstone or Millstone Grit, and that the ores also occur within fractures and pockets in the underlying rocks. Within the conglomerate, the mineralisation is present as irregular lenses conformable to bedding, as non-conformable cavity fillings and as disseminations (Woodward, 1876; Green and Welch, 1965).

At Higher Pitts Farm (534 492) in the Mendip Hills, a 2-metre-thick lens of the Dolomitic Conglomerate is impregnated with hematite. Many uncommon minerals are present, including oxides, hydroxides and carbonates of manganese, lead, copper and molybdenum. Most other occurrences have simple mineralogy including hematite, limonite and goethite, with accessory calcite or quartz. Manganese oxides and hydroxides are almost invariably associated with the iron deposits.

Fragments of iron ore, sometimes siliceous, are common features of waste piles in most of the areas where lead or zinc mining has been carried out. Several authors have observed that iron oxides line the walls of lead and zinc veins on Mendip (Glanvil, 1668; Pooley, 1693; Green and Welch, 1965). With reference to manganese ore, Neri (1662 in Gough, 1967, p. 233) noted that "...wherever the lead-ore men find it, they certainly conclude that lead-ore lies under it." Paleomagnetic age determinations were carried out on iron minerals from Higher Pitts Farm (534 492) and from near Lamb Leer (545 555), (Evans and Evans, 1977). Samples from both locations show pole positions which corresponded to upper-Triassic ages.

7-3.4 Lead and Zinc

Because of the limited exposure of base metal occurrences Green (1958), based a study of their distribution on the locations of former workings, and of their mineralogy on examination of spoil tip material. Locations of some of the more important areas of mineralisation are given in Figure 4-2. The lead and zinc mineralisation is almost exclusively confined to the Carboniferous Limestone and Dolomitic Conglomerate. Exceptions include small occurrences of pyrite, galena, smithsonite and sphalerite in the middle-Jurassic Inferior Oolite in eastern Mendip (Alabaster, 1976); and galena and sphalerite in silicified Lower Lias and Inferior Oolite strata (Harptree Beds) near Harptree north of Mendip (Hamilton, 1966). Green (1958) has discussed the distribution of lead and zinc veins with respect to their host rocks, and suggests that within the Carboniferous Limestone of the Mendip area there is no obvious stratigraphic control to the mineralisation. Lead-rich veins are observed in both Carboniferous Limestone and Triassic conglomerate, whereas zinc-rich veins are almost exclusively restricted to the conglomerate. None of the areas of mineralisation, lead or zinc, is more than a few hundred meters away from a deposit of the Triassic conglomerate. From Figure 4-2 and from observations based on the soil geochemical data presented in Chapter 5, it is apparent that there is a regional zonation to the Mendip base-metal mineralisation. All of the occurrences which have lead as the dominant metal are confined to the top of the plateau, whereas

those in which zinc is more abundant are situated on the flank of the plateau. In some cases there is a gradation between the lead-rich and zinc-rich types.

Although the morphology and mineralogy of the deposits is not readily evident now, some information can be derived from the many first hand descriptions which were recorded during the 17th and 18th centuries. Many of these observations have been summarised by Gough (1967).

An important and recurring observation is that the ore was found within fissure-like openings in the limestone. These fissures thin downward, and the workings within them only rarely exceed a depth of 100 m (Gough, 1967 pp.72, 118, 138, 141, 226, 228; Moore, 1867; Green, 1958; Kellaway and Welch, 1965; Kellaway, 1967). There is a possibility that the depth limit was a product of the inability to pump water from deep workings (Woodward, 1876).

The mineralised fissures appear to be controlled by bedding planes: "...frontier's below ground were determined not by imaginary vertical lines but by the natural slope of the limestone strata..." (Gough, 1967, p 119). Offshoots at some angle to these steep veins were also mineralised.

The main veins reached well over a metre in width and were commonly separated by several metres of barren rock. In one case, two workings several metres apart at surface were observed to merge at a depth of about 10 m (Gough, 1967, p 118). Catcott (1768) noted solutional features along faults and bedding planes. Mineralisation within the conglomerate was seen to be present as a network of small veins up to a few centimetres in width, or in some cases as disseminations through the rock (Woodward, 1876; Gough, 1967, p 141, 226).

The intimate association of clastic fragments with the ore is a common feature, and in the examples decribed in Gough (1967), all of the fragments appear to be derived from the surrounding limestone or conglomerate. At Wick Rocks (709 737), east of Bristol, there is evidence of multiple mineralising periods interrupted by collapse of late Triassic mudstone debris (Kellaway, 1967). At Sandford Quarry (421 591), in western Mendip, one 5 m wide fissure is filled with a deposit of thinly bedded clay, whereas another less than fifty metres away is lined with a 10 cm layer of drusy calcite and filled with silty debris and angular blocks of Carboniferous Limestone.

Moore (1867) was the first to recognize post-Triassic fissure in-fillings. He described a 4 m thick deposit of "blue or greenish clay" at a depth of about 90 m in a mining shaft near Charterhouse (505 553). The clay contained abundant Lower Liasic marine fossils and about 7% galena. Robinson (1957) observed several similar occurrences, and others are mentioned by Green and Welch (1965). Mineralisation at Merehead Quarry (695 440) comprises iron and manganese oxides with minor secondary lead and copper, and collapsed fissure material ranging in age from late Triassic to early Jurassic (Alabaster, 1975, 1976, 1977). Symes and Embrey (1977) and Alabaster have attributed the presence of oxide and oxy-chloride minerals to alteration by Rhaetian and later sea waters. An occurrence with similar features has been discovered near Bristol (Alabaster, 1978).

The main ore minerals in the Mendip Hills are galena, cerrusite, smithsonite and sphalerite. One sample from the Central Mendip area is characterised by 5 mm bands of colloform galena alternating with .5 mm bands of sphalerite. Samples from a waste tip at Shipham (445 582) comprised calcite, galena and banded colloform sphalerite and pyrite in interstices in the conglomerate.

Both galena and smithsonite have been observed to occur in large masses almost free from gangue material (Glanvil, 1668; Billingsley, 1795). This situation was not universal, as is cited in Gough (1967), "...the ore runs sometimes in a vein, sometimes dispers'd in banks. It lies many times between rocks. Some of it is hard, some milder. They never find any perfect, but it must be refined. Many times they have branched ore in the sparr." Ore-bearing veins accompanied by columnar concretions of calcite extending from the wallrock have been described by Weaver, (1819). Similar, but non-metalliferous, occurrences are exposed in quarries at Whatley (729 481) and Sandford (421 591), and elongated calcite crystals have been seen in waste tips near Charterhouse (505 553). Woodward (1728) wrote that fissures filled only with calcite and rock fragments, alternated with ore-filled fissures.

There are igneous rocks known in the study area, but the youngest of these are the ash beds within the Carboniferous Limestone on Broadfield Down. It is

highly unlikely that the igneous activity associated with these deposits is related in any way to the apparently later base metal mineralisation. Based on a study of regional magnetic patterns, Evans and Maroof (1976) have postulated the existence of a buried granitic body to the east of the Mendip Hills. They suggest a link between this supposed pluton and the Mendip lead-zinc mineralisation.

To summarise, the Bristol-Mendip Hills lead-zinc mineralisation has the following important characteristics:

1) The ores occur at shallow depths as veins and replacements in limestone and dolomite;
2) enhanced porosity, due to brecciation (conglomerate) tectonic forces and solutional processes, is evident;
3) the deposits are spatially related to positive structural and paleogeographic features;
4) there is no apparent igneous source rock;
5) the mineralogy is simple with galena, sericite, smithsonite, sphalerite, pyrite, calcite, dolomite and barite;
6) there is a spatial association between base metal deposits and iron and manganese oxide deposits.

Clearly, these deposits fit within the classification "Mississippi Valley Type" as defined by Jackson and Beales (1967).

7-4 Theoretical Background for the proposed Model of Ore Deposition

7-4.1 Lead, Zinc and Iron Deposits

Callaghan (1967) has established a classification for the "Mississippi Valley Type" lead-zinc deposit based on paleophysiographic settings, in which most of the typical examples are situated immediately above, or immediately below an unconformity. Within the latter group one of the most important features is the presence of karstic openings or collapse structures related to solutional erosion.

Some examples of the deposits which are situated below an unconformity are: the Friedensville District of Pennsylvania, the East Tennessee District, the Tri-State District, the Southwest Wisconsin District and a number of others in the United States (Callaghan, 1967), the Pine Point District in Canada (Beales and Jackson, 1967), the Malines District of France (Foglierini and Bernard, 1967), the lead and zinc deposits in Belgium (De Magnee, 1967), the lead-zinc, barium and iron deposits in Sardinia (Padalino et al, 1973, Moore, 1972), many of the deposits of

the eastern-Alpine District (Dzulynski and Sass-Gustkiewicz, 1977), the Angouran and Lakin Districts in Iran (Pereira, 1967), the Yunnan Area of China (Searls, 1952), the Pennine District of England (Ford, 1976) and of course, the Mendip Hills Area. The genetic histories of these various deposits have been discussed at great length, with very little concensus being reached.

Although most geologists recognize the existence of karstic and solutional collapse features in the districts noted above, the possibility that the karstic-forming meteoric water could also be the mineralising solution, which has been advocated by several European geologists (including Bernard, Leleu, Rouvier, Lagny, Zuffardi, Bechstadt and others), has been rejected by most North American and British geologists. The most serious objection to the theory of meteoric origin is comprised in the data of fluid-inclusion studies, much of which suggests deposition from hot (100 - 150^{o}C), and dense (15 - 20 weight percent salt) brine (Roedder, 1967). Not all fluid inclusion studies show high salinities and homogenisation temperatures, however, and furthermore, it is probable that post-mineralisation burial would promote re-crystallization of ore and gangue minerals at elevated temperatures and in equilibrium with high salinity connate water (Zuffardi, 1968; Bernard, 1973; see also discussion to Roedder, 1967).

The question of whether karstic meteoric water can be a mineralising solution has been answered, of course, by the many examples of ore minerals precipitating in modern caves (Hill, 1976; Bradbury, 1959). Minerals observed include carbonates, sulphates, sulphides, and phosphates of copper, lead and zinc, plus various iron oxides and barite and fluorite. A recent study at a limestone quarry in Ontario provides some convincing support for the meteroric water argument (Haynes and Mostaghel, 1982). Lead and zinc minerals, including galena and sphalerite, are present in black sludges and as botryoidal encrustations, at the orifice of a spring 28 m below the top of the quarry face. The spring water has a temperature of around 3^{o}C, and lead and zinc concentrations below 1 mg/l. Based on lead-isotope determinations, Haynes and Mostaghel suggest that the metals are derived from carbonate rocks 10 to 15 m stratigraphically above the spring horizon.

The source of the metals which make up residual deposits in karstic terrains is the rock which the water flows over or through before entering the Karst system. The metal could be that originally present within the rock, as suggested by Collins and Smith (1972); Bechstade (1975); Rouvier (1971) and Haynes and Mostaghel (1982), or that within previous epigenitic mineralisation as suggested by Zuffardi (1968) and Hill (1976).

Deposition of sulphide minerals takes place under reducing conditions and possibly in the presence of bacteriogenic H_2S, within the phreatic zone (Bernard and Leleu, 1967; Bernard, 1973; Devignee, 1977a and 1977b; Amouri et al, 1978). Deposition of carbonate minerals follows from depletion of the carbon-dioxide reservoir (Holland ,1967; Krauskopf,1967).

Although a variety of barite occurrences within karst systems have been observed to be of meteoric origin (Walker, 1919, Bradbury, 1959, Hurlbut, 1968, Hill, 1976), and many others have been interpreted as being of meteoric origin (Zuffardi and Salvadori, 1963, Huvelin, 1976, Padalino et al, 1973), none of these authors has proposed a chemical mechanism which would result in barite deposition within a karstic aquifer. The solubility of barite is controlled by the temperature and ionic strength of the water in which it is dissolved (Holland, 1967; Krauskopf, 1967). A temperature difference between surface water and groundwater of up to 10 or 15^{o}C could exist during hot seasons, because groundwater temperatures change very little. Similarly, a decrease in ionic strength, which would accompany precipitation of carbonate or sulphide minerals, could be responsible for barite precipitation. Bolze et al (1974), have studied the possibility of biogenic barite mobilisation, and conclude that microbial sulphate reduction can account for enhanced barium solubility. It is possible that the reversal of such a process could occur within a karst system.

Bicarbonate is normally the dominant anion in the groundwater of carbonate areas, and where metal enrichment has taken place it follows that carbonate ore-minerals should be present. This is the case in modern caves (Hill, 1976). Lead and zinc carbonates are also present in many Mississippi Valley Type deposits, in North America (Callaghan, 1968; Brockie et al, 1968; Heyl, 1968;

Radabaugh et al, 1968; Tweto, 1968; Loughlin and Koshman, 1942) and in Europe and Asia, (Pereira, 1967; Sainfield, 1956; Padalino et al, 1973; Amouri et al, 1978; Rickard, 1924). Most of the above authors have suggested that the carbonate minerals are weathering products. However, in many cases the weathering is a process of concentration rather than dispersion, which might more accurately be described as supergene enrichment (Zuffardi, 1968; Haynes and Mostaghel, 1982). Furthermore, this supergene enrichment is not always strictly residual, in that the metals can be transported some distance before being redeposited. A good example of this phenomenom is the Goodspring Area of Nevada, where most of the ore bodies are of presumed supergene origin. In this area the metals which constitute the rich secondary ore bodies are observed to have migrated as much as 50 m from a sulphide source (Hewett, 1931).

Since it is possible for a rich secondary ore body to form as a result of supergene concentration of metal from existing sulphide mineralisation, it should be possible for a primary ore deposit to form as a result of supergene concentration of metals present at background concentrations in normal rocks. Such supergene ore need not always be present as carbonate minerals, as has been observed in Sardinia by Zuffardi (1968). There, supergene accumulations include both carbonates and sulphides, depending on the oxidation potential and the CO_2 and H_2S fugacities in the depositional environment.

7-4.2 Celestite Deposits

The strontium to calcium ratio of sea water is less than 1:50, and normal evaporative processes favour the precipitation of sulphate as a calcium salt rather than a strontium salt (Braitsch, 1971). Although calcium-sulphate precipitation could increase the strontium to calcium ratio to the point of celestite stability, there is always a ready supply of calcium in marine environments, and celestite deposits are rare in marine evaporite sequences, and in modern marine evaporite basins (Braitsch, 1971, Wood and Shaw, 1976). The only significant modern celestite accumulations are in continental evaporite basins, such as in California (Durrell, 1953) and Libya (Goudazi, 1970). In keeping with the accepted continental depositional environment for the Keuper Marl itself (see Section 7-2), it is thus postulated that the Severnside Evaporite Bed was

deposited in an inland playa or sabka complex (see for example, Glennie, 1970), where diagenesis of the playa sediments in the presence of brine, led to accumulation of evaporite minerals just below the surface (Durrell, 1953; Hardie, 1968).

During evaporative concentration, various minerals become unstable at successive stages, and the eventual mineral assemblage is a function of the composition of the incoming solutions. In virtually every case the first phases to reach saturation are low-magnesia calcite, followed by high-magnesia calcite or dolomite (Eugster and Hardie, 1978; Hardie, 1968). As the sulphate to calcium ratio increases, the stability of the calcium-sulphate salts is exceeded, and either gypsum or anhydrite is precipitated. The remaining brine normally contains sodium and chloride along with a number of minor constituents.

Precipitation of celestite, or replacement of anhydrite by celestite, depends on the strontium to calcium ratio and on the sulphate to calcium ratio. The latter factor is due to the higher solubility product of $CaSO_4$ versus $SrSO_4$, because a limited supply of sulphate will more severely limit the precipitation of gypsum or anhydrite, as opposed to celestite (Wood and Shaw, 1976).

Although the strontium to calcium ratio is low in marine environments, the source water for a continental evaporite may be relatively rich in strontium. Of the sedimentary rocks, carbonates have the highest strontium concentrations, but shales have the highest strontium to calcium ratios (Hem, 1967).

In the evaporation of sea water the strontium to calcium ratio reaches a critical point for celestite deposition at about the same point that the solubility of halite is exceeded (Braitsch, 1971; Sass and Starinsky, 1979). Under continental conditions, where higher original ratios of strontium to calcium, to sodium and to chloride, are possible, celestite saturation might be reached earlier.

7-5 History of Mineralisation

In the following section, the late Carboniferous to Jurassic geological history of the study area will be summarised with particular emphasis on those factors which have had some influence on mineralisation. The model for the genesis of the Bristol-Mendip Area mineralisation will be described.

7-5.1 Upper Carboniferous

While deposition of the shales and sandstones of the Coal Measures continued, the early stages of the Hercynian Orogeny resulted in the localised folding and uplift of the Carboniferous and older strata. There is evidence of Carboniferous uplift along the Lower Severn and Bath axes (Kellaway and Welch, 1948), and it is possible that some early warping took place along the Mendip axis (see Figure 2-5).

7-5.2 Lower Permian

The Marine environment of the Carboniferous gave way to desert conditions during the Permian, and erosion began in the already elevated anticlinal areas. In the Mendip area, uplift took place along the Mendip axis (Figure 7-2). At this stage the Carboniferous Limestone was buried under up to 3 000 metres of Coal Measures strata. The pressure and temperature were high enough that segregations of quartz, calcite and fluorite were formed from migrating connate water.

7-5.3 Lower Through Upper Permian

Continued Hercynian folding and uplift heightened topographic relief and accelerated the process of denudation. Deposits of angular rock debris, sand and mud collected on steeper slopes (Figure 7-3).

Permeability within the anticlinal massifs was enhanced by further folding and radial fracturing (Figure 7-4), thus promoting groundwater flow through the Coal Measures and limestone. Metals dissolved in the weathering zones were re-precipitated at depth, forming a diffuse zone of supergene enrichment.

7-5.4 Lower and Middle Triassic

With continued erosion, the Coal Measures strata were largely removed from the upland areas (Figure 7-5). Eventually the Carboniferous Limestone became exposed (Figure 7-6), allowing solutional erosion along fractures in the limestone, and resulting in a change in the composition of the scree deposits, from a mixture of shale and sandstone fragments, with a high proprtion of mud and sand, to a framework of limestone fragments with much less matrix material.

Figure 7-2 Idealised cross-section through the Mendip anticlinorium during lower Permian times (looking west) (The location of section a-a' is given on Figure 7-1)

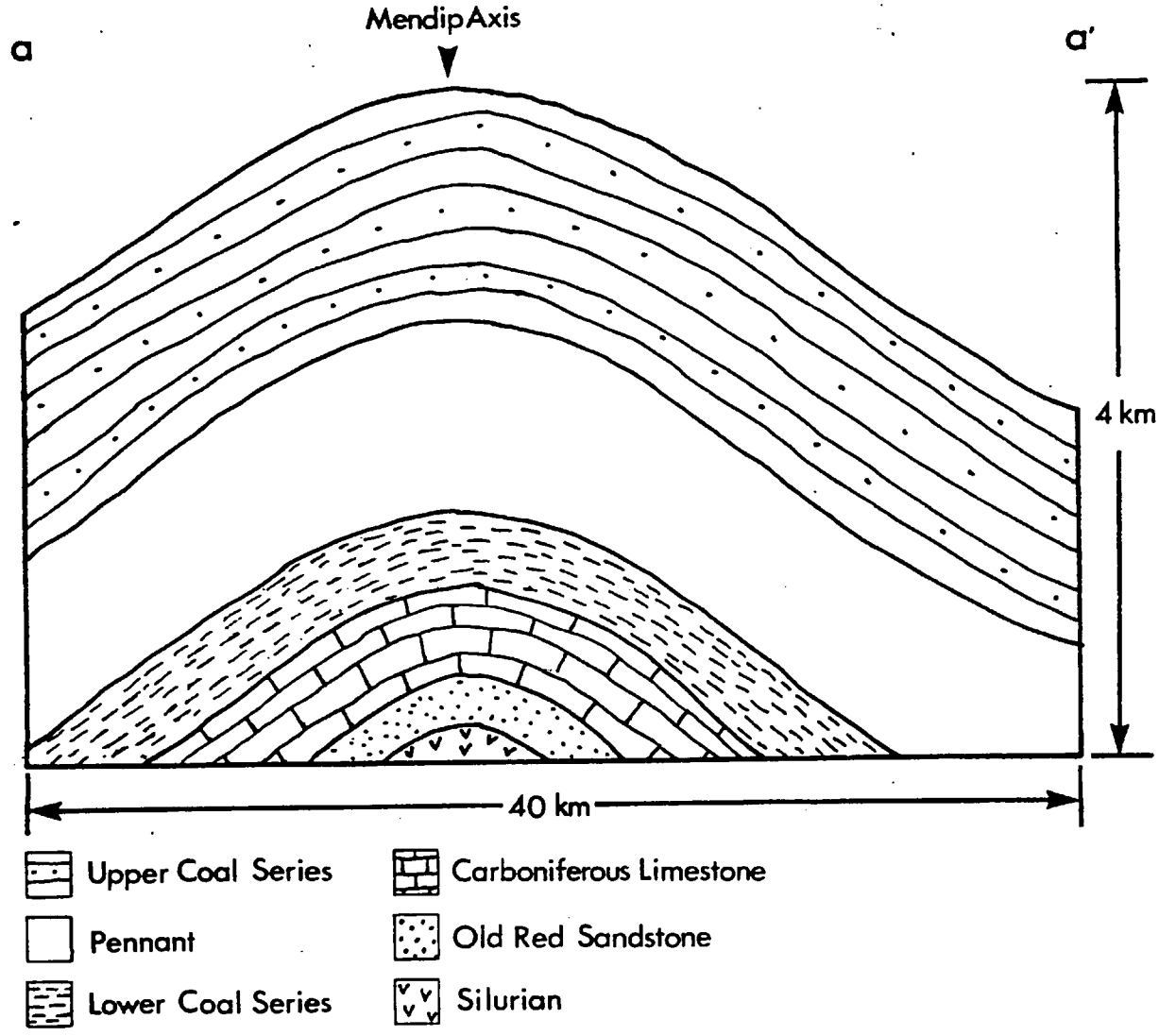


Figure 7-3 Idealised cross-section through the Mendip anticlinorium during lower to middle Permian times

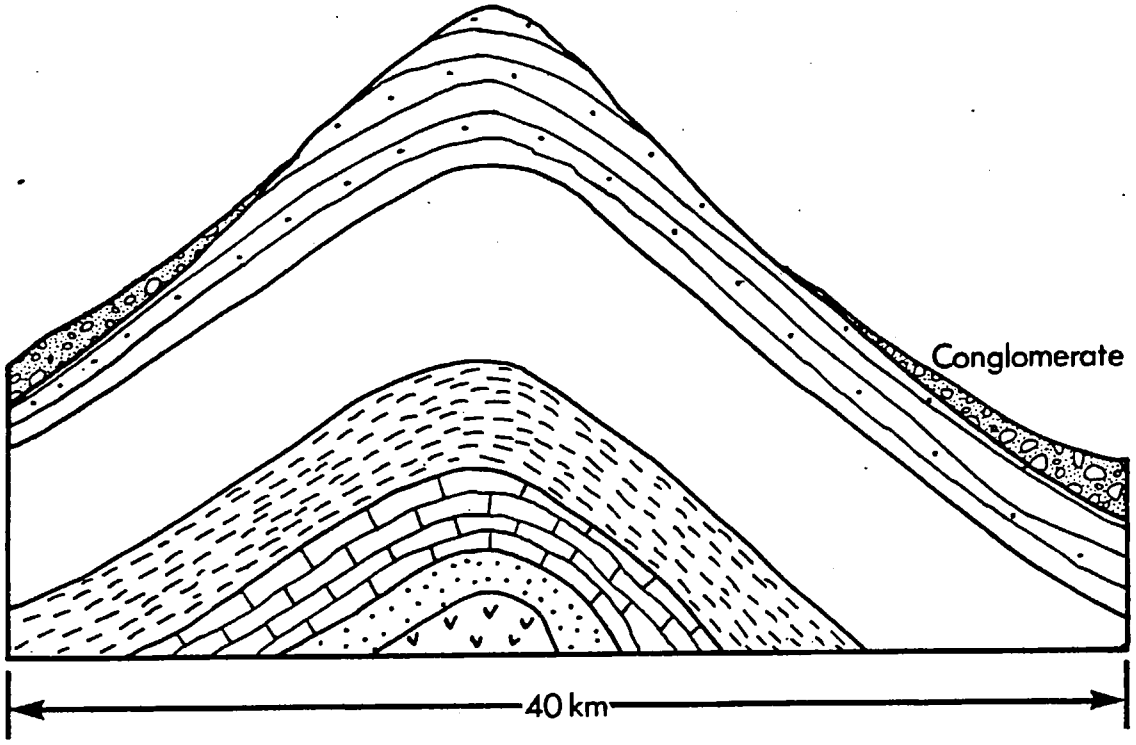


Figure 7-4 Idealised cross-section throught the Mendip anticlinorium during upper Permian times

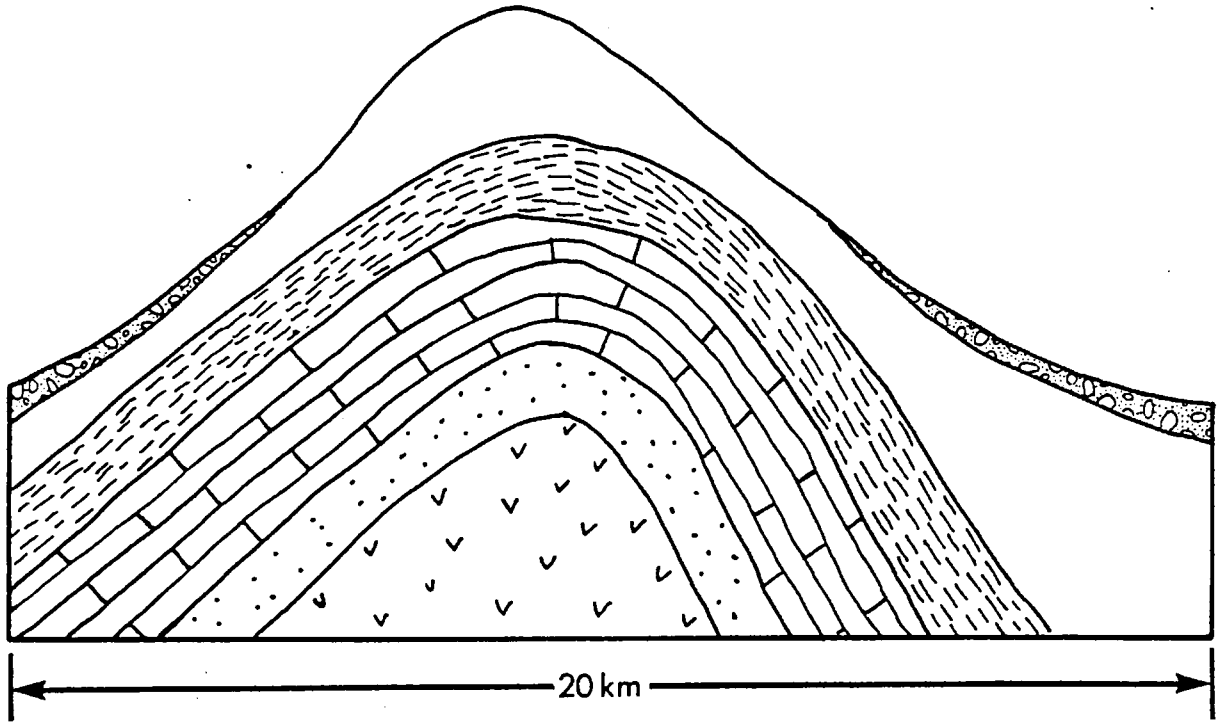


Figure 7-5 Idealised cross-section through the Mendip anticlinorium during lower Triassic times

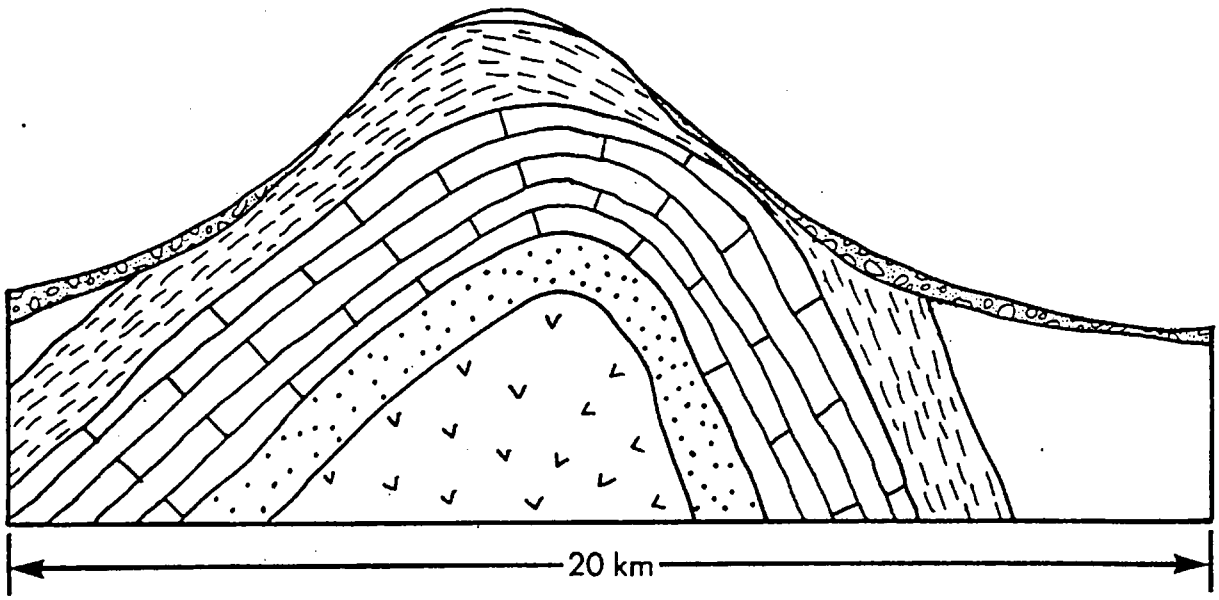
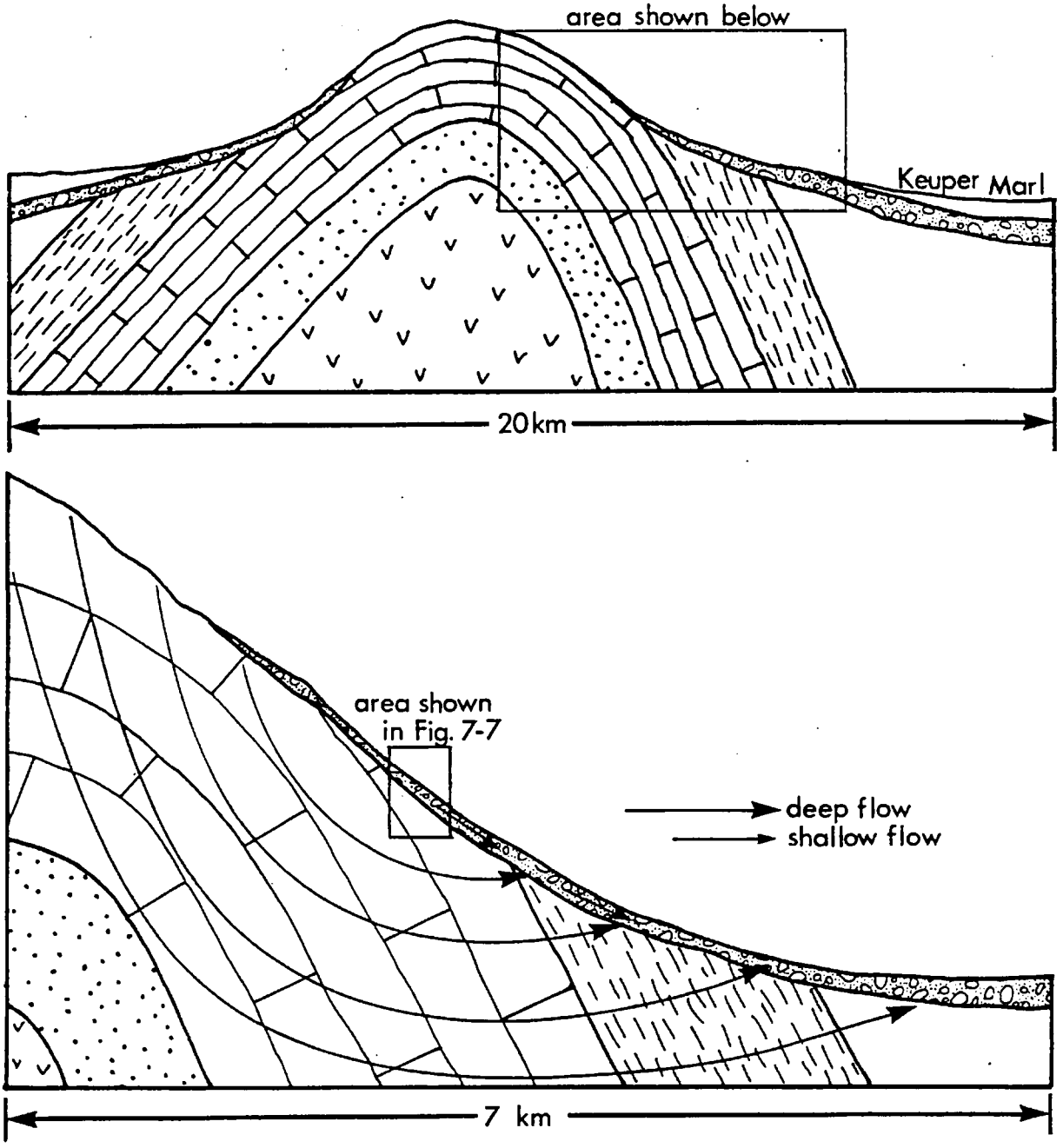


Figure 7-6 Idealised cross-section through the Mendip anticlinorium during middle Triassic times



Below surface, two important hydro-geochemical transitions existed as the water became isolated from the atmosphere. The carbon dioxide supply was depleted as the limestone was dissolved, and the oxidation potential was lowered as bacteriogenic H_2S was evolved and various minerals were oxidized (Figure 7-7). Within the oxygen and carbon dioxide rich upper zone, sulphide and carbonate minerals, mainly calcite or dolomite, but possibly also cerussite and smithsonite, were precipitated. Within the reducing and H_2S rich zone, galena, sphalerite and pyrite, along with further calcite or dolomite were precipitated.

In places where water from deep flow system discharged into the scree deposits, iron and manganese oxides were deposited.

7-5.5 Carnian to Norian

The minerals deposited by the mechanism described above were repeatedly removed and redeposited as the erosion surface was lowered. A process of fractionation took place due to the greater solubility of the zinc over lead (Figure 7-8). Near to the top of the system, lead was preferentially deposited due to its lower solubility. As the lead to zinc ratio of the solutions decreased, the lead to zinc ratio of the resultant mineralisation decreased. In the lower parts of the hydrological system, the lead to zinc ratio of the ground water would have been low enough to result in deposition of zinc-dominant mineralisation.

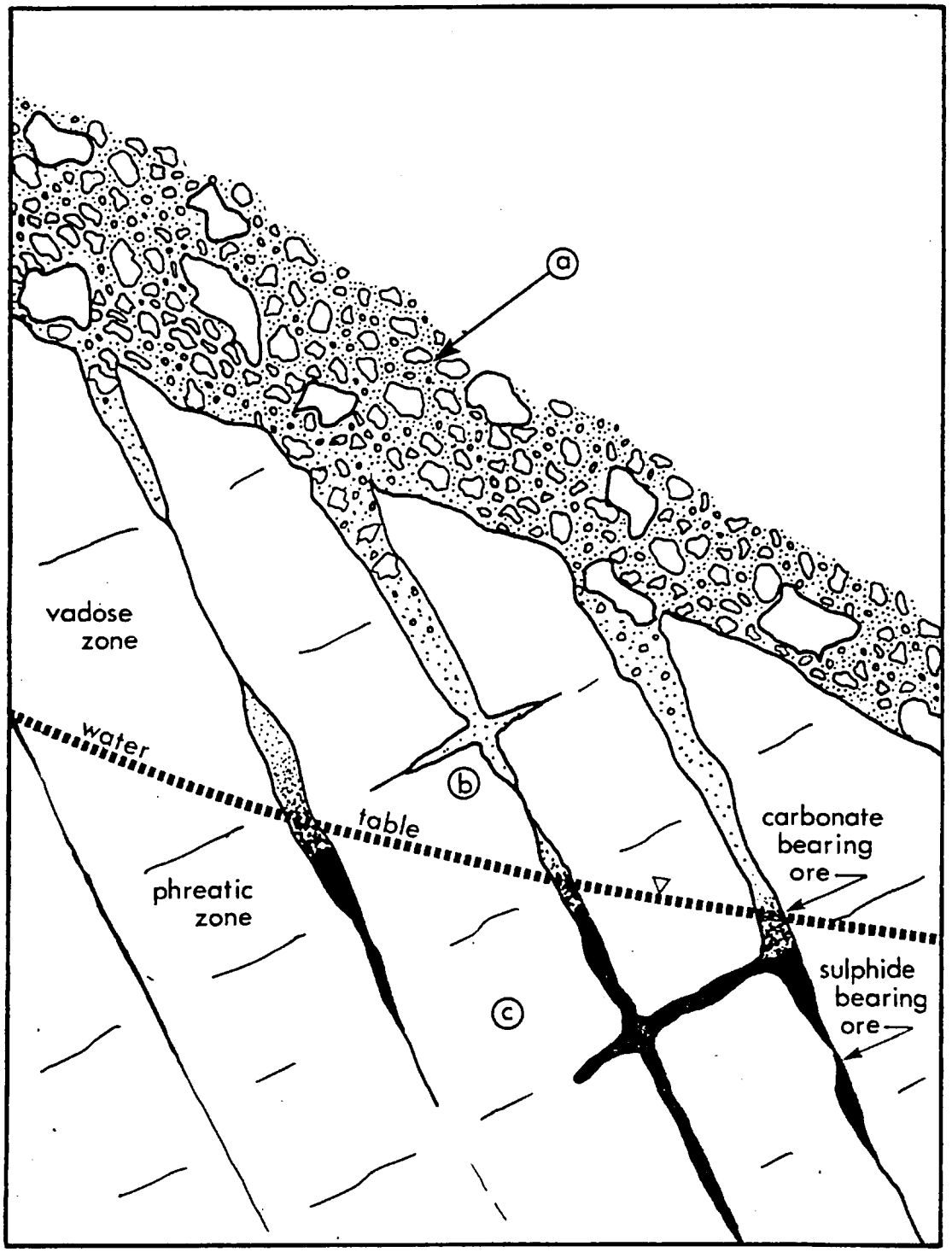
In areas where the conglomerate was overlain by the Keuper Marl mudstone, isolation from the atmosphere again resulted in the depletion of oxygen and carbon dioxide, and precipitation of sulphide and carbonate materials.

7-5.6 Norian

The ore forming process carried into the Norian with little change. The mineralisation continued to be eroded and redeposited as the anticlinal uplands were worn down.

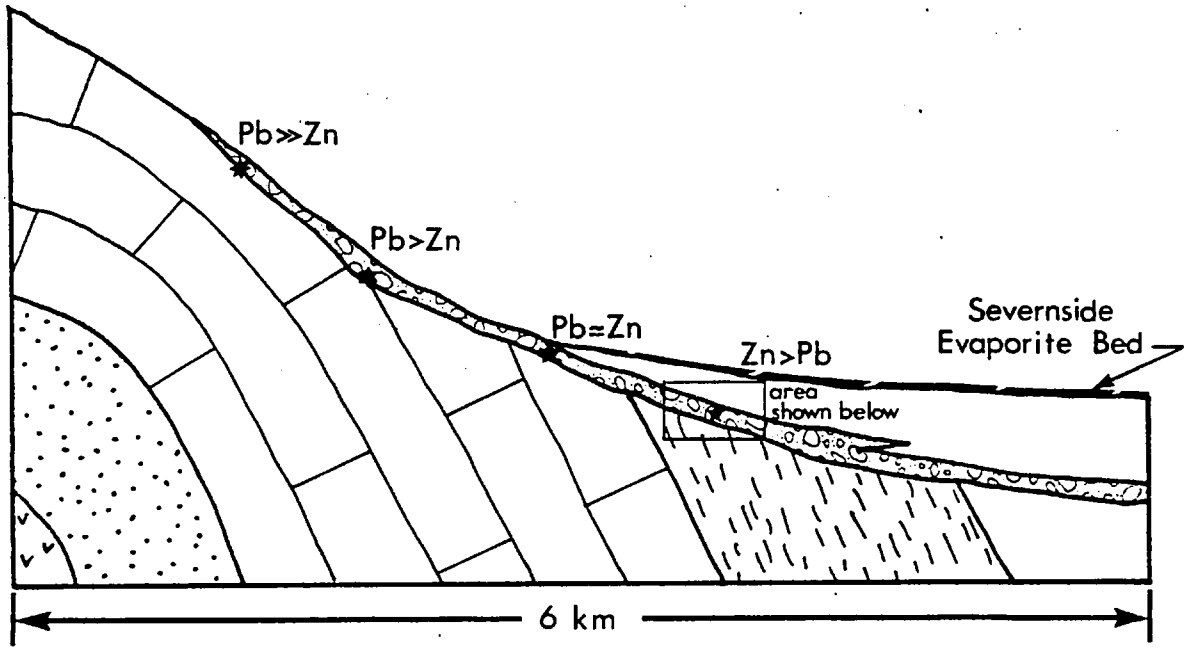
In the synclinal lowlands, where the Keuper Marl mudstone and sandstone were being deposited, a variety of environments existed, as descrbied in Section 7-2. The existence of alternating mudstone and sandstone layers suggests that the area was repeatedly flooded by a large lake or inland sea. Whenever the

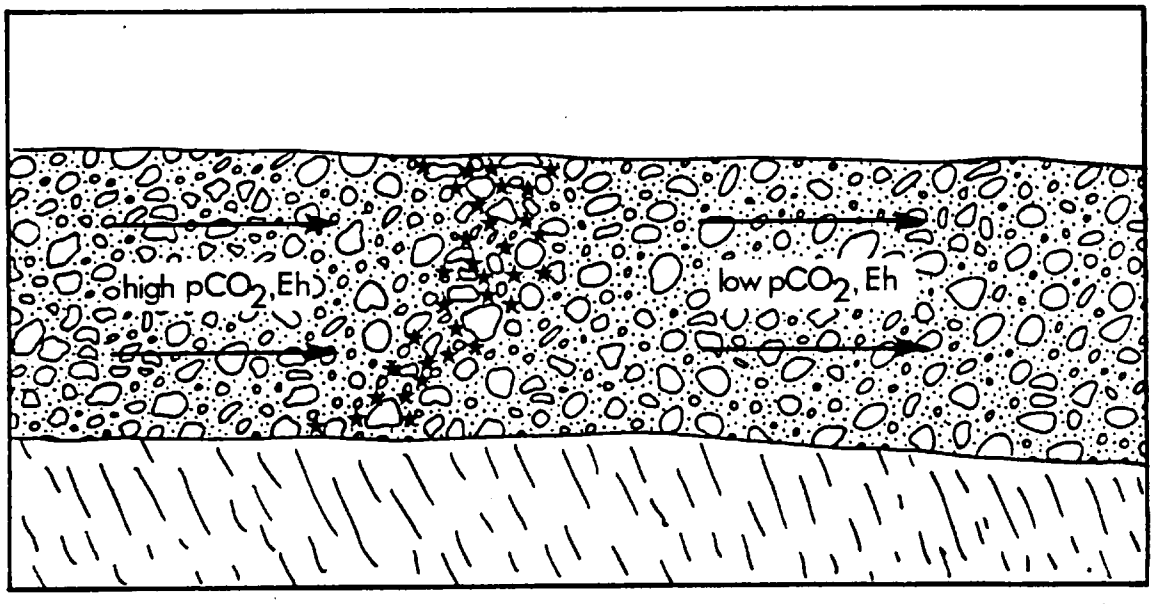
Figure 7-7 Possible geochemical conditions at the erosion surface of the Carboniferous Limestone during Triassic times



(a - zone of metal depletion, b - zone of metal-carbonate accumulation, c - zone of metal-sulphide accumulation)

Figure 7-8 Idealised cross-section through the northern flank of the Mendip anticlinorium during Carnian (early upper Triassic) and Norian (middle upper Triassic) times (looking west)





water table was within a few tens of centimetres of surface, diagenetic evaporite minerals were formed within, but near to the surface of the sediment. At some point the water level was sufficiently stable to allow the widespread accumulation of evaporite minerals in what is now the Severnside Evaporite Bed (Figure 7-8, 7-9).

As various minerals, including calcite and gypsum, precipitated, the brines evolved to the point at which the solubilities of strontium sulphate and sodium chloride were reached. Deposition of celestite and halite ensued, the former either by replacement of pre-existing gypsum or anhydrite (Nickless et al, 1976), or by direct precipitation (Wood and Shaw, 1976).

Since ground water flow was towards the centre of the basin, and the supply of strontium was limited, most of the celestite deposition took place near the margin of the basin. With subsequent flooding, much of the more soluble halite was redissolved.

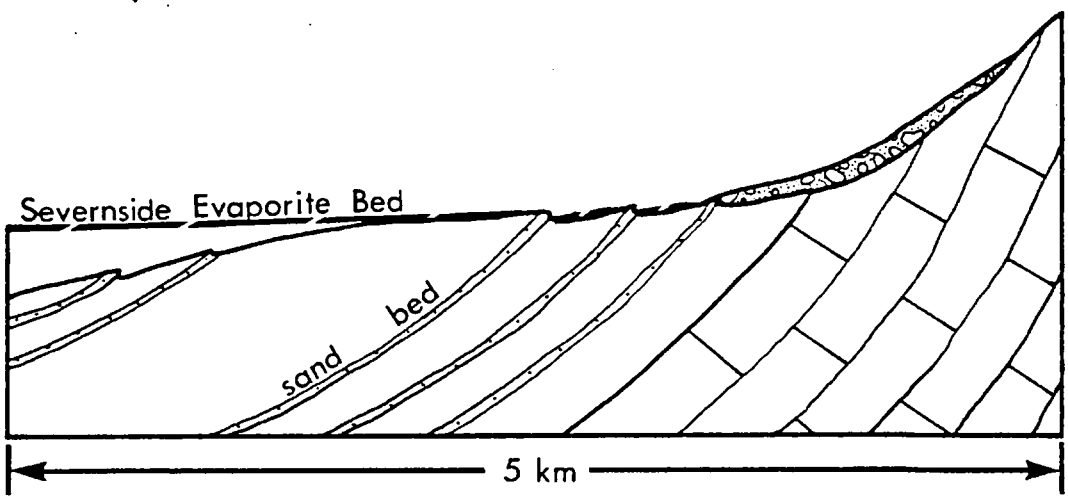
The rising sea level towards the end of the Norian, is reflected in a change of colour of the clastic sediments from red to green. The marine influence must have been intermittent however, as the depositional conditions do not appear to have been significantly altered.

7-5.7 Rhaetian and Liassic

The Rhaetian and Liassic seas covered most of the area and resulted in deposition of limestone and mudstone, with development of shallow water facies near the anticlinal highs. As the upland areas became submerged, any exposed fissures were filled with marine and terrestrial debris, and the mineralising process was essentially stopped. In some cases the incursion of the Rhaetian marine waters resulted in alteration of the existing metaliferous minerals .

The rugged relief of the anticlinal areas was probably preserved through the Jurassic, as is suggested by Ford and Stanton (1968), who present evidence that the planation of the Mendip Plateau took place during the Pliocene. During this period, many of the lead-rich occurrences in the top of the Mendip Hills were either partly or completely eroded.

Figure 7-9 Idealised cross-section through the Bath axis northeast of Bristol, showing the effects of topography on the distribution of the Severnside Evaporite Bed (looking north). (After Nickless et al, 1976, Figure 3)



7-6 Summary

The eighty-million-year period from the end of the deposition of Coal Measures sand and shale, until the beginning of deposition of Rhaetian marine shale and limestone, was extremely important from the point of view of ore deposition in the Bristol and Mendip Hills area.

Hercynian compressive forces generated a series of east-west folds, the largest being the Mendip anticlinorium, and reactivated north-south Caledonian folds along the Bath and Lower Severn axes. Erosion of the anticlinal uplands in a hot desert climate resulted in accumulation of coarse alluvial fans grading into fine-grained deposits in playas. Soluble minerals were dissolved by surface and ground waters, which either flooded into the basin or percolated through fractures in the rock.

Calcite, dolomite, cerussite, smithsonite, galena, sphalerite, pyrite and barite were reprecipitated from descending ground water in response to changes in carbon dioxide fugacity and oxidation potential. With continued erosion these residual accumulations developed into discrete zones of mineralisation along solutionally enlarged bedding planes and fractures, and within the porous alluvial fans. Because of differences in solubility, a regional zonation developed from lead-rich veins in the upper parts of the hydrological system, to zinc-rich veins in the lower parts.

Oxides of iron and manganese were precipitated where relatively reducing deep ground waters discharged into the alluvial fans near the base of the uplands.

Calcite, dolomite, gypsum, anhydrite, quartz and celestite accumulated within the sediments of the playa, as ground waters, derived from the upland areas, evolved into brines due to evaporitic concentration.

CHAPTER 8 SUMMARY AND CONCLUSIONS

8-1 Stream Sediment Geochemistry

Data from the Wolfson Geochemical Atlas of England and Wales (Webb et al, 1978) have been studied in order to identify factors which influence geochemical patterns in the Bristol-Mendip Hills Area. Most regional geochemical features can be attributed to lithological characteristics which are essentially consistent throughout Britain. For example, areas underlain by the arenaceous Old Red Sandstone are represented by low concentrations of all of the more soluble elements. Areas underlain by Carboniferous, Jurassic and Cretaceous limestone have high calcium and strontium concentrations but low concentrations of most of the other elements studied. The black Lower Liassic shales are associated with high concentrations of molybdenum, iron and arsenic.

In addition to these normal lithological variations, there are a number of geochemical features which are related to mineralisation, and others which can be attributed to industrial activities.

The base metal deposits within the Carboniferous and Triassic carbonate rocks are the source, both directly and indirectly, of much of the enrichment of lead, zinc, copper, cadmium and barium in stream sediments. The most direct link is through chemical and mechanical weathering of currently exposed deposits by surface and ground water. Two previous erosional periods which may have played a role in dispersal of the metals include the Pleistocene, during which Head deposits were derived by solifluction from the slopes surrounding the uplands, and the Pliocene, during which a significant volume of material was eroded from the upland areas. It is not clear which of these erosional episodes is most important in terms of generating the anomalies north of Mendip, except to say that mechanical processes must have been important to explain the abundance of barium in stream sediments. To the south of Mendip, all of the previous deposits are overlain by Holocene, clay, sand and peat-bearing estuarine alluvium, and the extensive lead anomaly in this area is very likely to be of recent origin. A probable mechanism is that lead has been scavenged from the metal rich spring waters emerging at Cheddar and elsewhere.

An indirect link between the ore deposits and stream sediment anomalies lies in human endeavours to extract and refine the metals. The mining activities have promoted mechanical and chemical erosion of the deposits, and the refining activities have resulted in the introduction of a large quantity of lead, zinc, copper and cadmium to ground and surface water, and to the atmosphere. In more recent times, importation of ores has contributed to the amount of metal introduced by refining activities. Lead, zinc, copper and cadmium anomalies which can be related to industrial activities include those near Avonmouth and around Bristol. The anomalies north and south of the Mendip Hills have probably been accentuated by industrial activities.

The mineral accumulations associated with the evaporative horizons of the Keuper Marl have had a significant effect on the distribution of strontium and barium in stream sediments. Strontium and barium anomalies are evident in areas where celestite-bearing evaporites have been observed. There is little question that in the process of accumulation of strontium, barium has also been enriched. Furthermore, the intense chemical weathering of the Permo-Triassic probably led to the enrichment of essentially insoluble barite in mechanically derived sediments. There is an extensive area of strontium enrichment extending beyond the limits of the Keuper Marl, from well south of the Mendip Hills to well north of Gloucester. Outside of the area underlain by Triassic strata all areas of strontium enrichment also have high calcium concentrations, and the strontium to calcium ratios in these areas are within the expected limits for limestones.

Chemical processes which take place at the interface between stream water and shallow ground water have also affected stream sediment geochemistry, especially on the alluvial flats where the water level is relatively high, and flow is sluggish. Iron and manganese, occurring as hydrated oxide coatings on clastic fragments, are the most obviously affected, but it is likely that lead, zinc, and cadmium have been co-precipitated with, and adsorbed onto these hydroxides.

8-2 Mendip Hills Ground Water Geochemistry

Geochemistry of the Mendip ground waters can be studied on the basis of equilibrium relationships within the system CO_2- $CaCO_3$-H_2O, in which the supply

of free carbon dioxide is an important factor in controlling dissolution of calcite. In most similar regions the main source of carbon dioxide is the soil atmosphere. In this case, however, an important additional supply is the decaying organic matter within fractures in the unsaturated zone of the bedrock. Steep radial fractures at the surface of the limestone outcrop, related to anticlinal folding, may be responsible for the presence of the sub-surface organic matter. Due to this supply of carbon dioxide, the water-rock system is effectively "open" with respect to carbon dioxide, with the result that erosion occurs to considerable depth, and the pH is relatively low.

Concentrations of dissolved lead and zinc range up to 40 and 1 000 ug/l respectively. All of the major discharges with base metal mineralisation in their catchment basins have anomalous zinc concentration, and some are considerably higher than would be expected from the magnitude of mineral occurrences. Contamination is not suspected, and it is assumed that these situations represent anomalies from previously undetected mineralisation. Owing to its higher concentrations and relative ease of analysis, zinc is considered to be a more suitable element than lead for hydrogeochemical exploraion in this terrain.

Unlike some other base metal districts, sulphate and fluoride concentrations are not anomalously high in waters draining mineralisation. This is probably due to the lack of fluorite, and non-ore sulphide minerals associated with the deposits.

Seasonal changes in the flow rates of springs and streams have a considerable effect on the geochemistry. At the beginning of a flood following a long period of drought, the concentrations of sulphate, sodium chloride, potassium, iron and manganese increased markedly, probably as a result of dissolution of previously deposited salts, and because of an increased sediment load. Following this initial peak, the concentrations of most constituents dropped to well below those of the low-flow period. Lead and zinc were affected by this dilution, but in most cases the magnitude of the anomalies was great enough such that they were not obscured by the seasonal variation. Nonetheless, it is recommended that surveys of this type be carried out within as short a time as possible to avoid seasonal variations.

8-3 Mendip Hills Soil Geochemistry

The base metal mineralisation of the Mendip Hills is so well reflected in the overlying soils (which sometimes contain several percent of lead or zinc), that soil geochemistry has been used as a means for mapping the metal ratios of the various deposits. On this basis it can be shown that there is a consistent regional zonation in the lead to zinc ratios of the various mineralised zones. On the top of the plateau the deposits are lead-rich. The lead to zinc ratio decreases towards the basin, and near the base of the slope the deposits are zinc-rich. This variation in the proportions of lead and zinc applies on a local scale as well.

Lead and zinc zonation has some important implications regarding the flow direction of the ore forming solutions and the source of the metals. Based on the fact that zinc is more soluble than lead, the observed fractionation could only result from solutions flowing from the upland areas towards the basin. The metal, therefore, must be derived from the upland area.

Samples collected from near to one of the former smelting operations have revealed the existence of contamination from air-borne and water-borne waste products. It is apparent that lead, because of its relatively high volatility, is the dominant heavy metal constituent from the air-borne wastes. The contamination has not significantly affected the results of the detailed soil sampling in mineralised zones, but it has affected data from the regional grid.

A soil traverse in an area underlain by Dolomitic Conglomerate near Slab House in east-central Mendip, has indicated the existence of previously unknown mineralisation. The mineralised zone has an apparent width of 80 metres, and is geochemically similar to the zinc-rich mineralisation at Shipham and East Harptree.

8-4 Latteridge Area Soil Geochemistry

A soil survey over an area of strontium enrichment in the Keuper Marl has enabled a geochemical distinction to be made between the upper and lower parts of the Severnside Evaporite Bed. The lower part of the bed, and the immediately underlying mudstone are rich in calcium and magnesium. The upper part of the bed, and the immediately overlying mudstone, are rich in strontium, barium and

sodium. These geochemical variations likely reflect the relative proportions of various minerals, including calcite, dolomite, gypsum/anhydrite, celestite (plus barite), and halite, at different levels in the evaporite bed. The association between strontium and sodium suggests that the brine from which these minerals precipitated became saturated with celestite and halite at roughly the same time.

8-5 Model for the Genesis of the Ore Deposits

Derivation of a model for the genesis of lead, zinc, iron and strontium deposits of the Bristol-Mendip area has been based on previous descriptions of the deposits, observations made by the writer, and the results of the various geochemical surveys carried out.

The major points of the model are that the ores were ultimately derived from the lower and upper Carboniferous strata which have now been eroded from the Mendip anticlinorium, and that mineralisation took place during this erosional episode.

During the Permian and Triassic periods, the Carboniferous rocks were folded and uplifted, and physically and chemically eroded. Some of the soluble constituents were selectively concentrated at various positions within the hydrological system, in response to changing chemical conditions. Accumulation of lead and zinc took place within open spaces in the Carboniferous Limestone, and its Triassic derivative the Dolomitic Conglomerate, by a mechanism which is similar to those proposed for base metal deposits in karstic carbonate rocks elsewhere, and similar to the observed phenomena of deposition of metalliferous minerals in limestone caves and quarries. Carbonate and sulphide minerals precipitated due to changes in pH and oxidation potential and to changes in the partial pressures of CO_2 and H_2S. These geochemical changes are the natural consequences of the flow of meteoric waters through carbonate rocks.

Accumulation of iron and manganese took place at a lower level in the hydrological system, within the Dolomitic Conglomerate, at points of discharge of ground water flowing through fractures in the Carboniferous and older rocks. The iron and manganese, dissolved in the relatively reducing waters, were precipitated as oxides and hydroxides in response to higher oxidation potential.

Accumulation of strontium took place at the base level of the hydrological system, where water derived from the surrounding uplands was being concentrated by evaporation within an enclosed basin. The eventual saturation with respect to celestite was dependent on the degree of concentration of the brine between episodes of flooding. Accumulation of a significant amount of celestite required a relatively long period free from extensive flooding.

Thus, it is clear that the origin of all of the economic mineral deposits of the Bristol and Mendip Hills area can be explained without having to speculate about hydrothermal solutions originating from imagined igneous bodies, or about upward moving brines derived from the adjacent sedimentary basins. Huge volumes of material were eroded from the anticlinal areas, and there is little doubt that this material contained enough metal to form the existing deposits. The observed distribution and nature of the deposits are consistent with the theory that the metals were derived from solutions migrating towards the basin, as is the existence of an extensive geochemical anomaly in the basinal area.

APPENDIX A ANALYTICAL PROCEDURES AND ESTIMATES OF SAMPLING AND ANALYTICAL PRECISION

A-1 Analytical Procedures for Water Samples

A summary of the procedures used in sampling, preparation and analysis of water samples is given in Chapter 4. In this section the specific procedures for preparation and non-instrumental analysis will be presented.

A-1.1 Carbonate Species

Carbonate species were determined by titration with hydrochloric acid (AGRG, 1962). Since only one of the samples had pH greater than 8.3, the concentration of carbonate was assumed to be negligible, and only bi-carbonate was determined.

Analysis was carried out as soon as was practical after collection of the samples. For the 68 regional samples bi-carbonate was determined within about six hours of collection. For the periodic samples, analysis was carried out within about twelve hours of collection. Care was exercised in ensuring that sample containers remained sealed between the times of collection and analysis.

Reagents

a) Screened Indicator Solution - 125 mg methyl red and 83 mg methylene blue dissolved in 100 ml 90% ethyl alcohol
b) 0.01 N hydrochloric acid - prepared by diluting concentrated HCl
c) 0.01 N sodium-carbonate - 530 mg dried hydrosodium carbonate diluted to 1 000 ml with de-ionized water

The exact normality of the hydrochloric acid solution was determined periodically by titration with the sodium carbonate solution.

Procedure

Two drops of the screened indicator solution were added to a 10 ml aliquot of sample. Hydrochloric acid was then added until the blue-grey end point was reached. Bi-carbonate concentration was determined as follows:

$$HCO_3^- \text{ (mg/l)} = (T \times 61 \times N \times 1\,000)/V$$

where T is the volume of HCl used (ml), 61 is the molecular weight of HCl (g), N is the normality of the HCl used, and V is the volume of sample used (ml).

A-1.2 Fluoride

Fluoride was determined by specific ion electrode following the method of Frant and Ross (1968) and the American Society for Testing and Materials (ASTM, 1979b). Analysis was carried out within several days of sample collection on waters which had been passed through 0.45 um GF/C filters.

Reagents

a) Standards - 50, 100 and 200 ug/l standards were prepared using weighed amounts of dried sodium chloride mixed with de-ionised water.

b) Buffer Solution - (a concentrated version of the solution described by Frant and Ross, 1968). 30 g sodium chloride, 57 ml glacial acetic acid, 0.3 g tri-sodium-citrate, and 150 ml de-ionised water, adjusted to pH 5.0 to 5.5 with 5 N sodium hydroxide solution.

Procedure

The specific ion metre (Orion - Model 407A) with fluoride electrode (Orion 94-09) and single juction reference electrode (Orion 90-01)was calibrated using 25 ml standards mixed with 5 ml of buffer. (The sample to buffer ratio was changed to 5 to 1 from the recommended 1 to 1 to avoid diluting the samples any more than was necessary. The effect of the buffer was maintained by increasing its strength.) Fluoride concentration in the samples was then read directly from the logarithmic concentration scale on the instrument.

For both standards and samples the instrument output was connected to a chart recorder in order to monitor the progress of stabilisation, which commonly took ten to fifteen minutes, especially for samples with low fluoride concentration.

A-1.3 Sulphate

Sulphate was determined by titration with barium perchlorate using thorin as an indicator (Fritz and Yamamura, 1955). Analysis was carried out within several days of sample collection on waters which had been vacuum filtered through 0.45 um GF/C filters.

Reagents

a) Standards - 5, 10, 20 and 40 mg/l sulphate standards were made up from dried Na_2SO_4 and de-ionised water.
b) 0.2% thorin solution - 0.2g thorin or thoron (2(2-hydroxy-3, 6-disulfo-1-naphthylazo) benzenearsonic acid) in 100 ml de-ionised water
c) Dowex-50 cation exchange resin
d) Absolute ethyl alcohol
e) 1% ammonium hydroxide solution - 1 ml concentrated ammonium hydroxide plus 9 ml de-ionised water
f) 1% hydrochloric acid solution - 1 ml concentrated hydrochloric acid plus 99 ml de-ionised water
g) 0.005 M barium perchlorate solution - 2.0 g barium perchlorate tri-hydrate dissolved in 200 ml de-ionised water and 800 ml of absolute ethyl alcohol, adjusted to apparent pH 3.5 with perchloric acid
h) 3 N hydrochloric acid

Procedure

Approximately 25 ml of standard or sample was passed through a 3 cm by 10 cm column of Dowex-50 resin. The first 15 to 20 ml was discarded and a 5 ml aliquot was combined with 20 ml of absolute alcohol and 1 drop of thorin indicator. The pH was adjusted by adding ammonium hydroxide solution until a pink colour was detected, and then hydrochloric acid solution until the pink colour disappeared. (According to Fritz and Yamamura, 1955, the apparent pH should be about 3.5 after the sample has passed through the ion exchange resin. For the low ionic strength samples used here, this was not the case and adjustments had to be made.) Standards and samples were titrated with a 0.005 M barium perchlorate solution until the colour changed from yellow to pink. Sulphate concentrations of samples were determined from a calibration curve.

The resin column was periodically re-generated by passing through several hundred ml of 3 N HCl.

A-1.4 Chloride

Chloride was determined by titration with silver nitrate according to the method of ASTM (1979a). Analysis was carried out within several days of sampling, on waters which had been vacuum filtered through 0.45 um GF/C filters.

Reagents

a) Standards - 0, 5, 10 and 20 mg/l chloride standards were made up from dried (600°C) NaCl and de-ionised water.
b) Calcite solution - an excess of ground $CaCO_3$, was equilibrated with de-ionised water in the presence of air, and then one part of this solution was mixed with 90 parts of de-ionised water.
c) Potassium chromate indicator solution - 50 g of K_2CrO_4 was added to 100 ml de-ionised water and $AgNO_3$ was added until a slight red precipitate was observed. After standing for 24 hours in darkness the solution was filtered and diluted to 1 000 ml with de-ionised water.
d) 0.25 N silver nitrate solution - 4.2473 g of dried $AgNO_3$ was diluted in 2 l with de-ionised water.

Procedure

25 ml of sample (or standard) was mixed with 25 ml of calcite solution and 8 drops of indicator solution. Silver nitrate solution was added until a persistent brick-red colour was observed. Chloride concentrations of samples were determined from a calibration curve after making appropriate corrections for the chloride content of the water used, as determined from the 0 mg/l standard.

A-1.5 Chelation/Solvent Extraction Concentration Procedure

Dissolved cadmium, copper, lead, zinc, iron and manganese were isolated by chelation with diethyl-dithiocarbamate and extraction into chloroform (AGRG, 1975). The procedure serves the dual function of separation from possible interfering constituents, and twenty-fold concentration for subsequent analysis.

Reagents

a) Sodium-diethyl dithiocarbamate (Na-DDC) buffer solution - 250 g of sodium acetate trihydrate were dissolved in 500 ml de-ionised water, and 6 ml of glacial acetic acid were added and mixed thoroughly. 50 g of Na-DDC were added. The solution was diluted to 1 000 ml in a 2 l separating funnel, any metal-DDC complexes were removed by successive extractions in 30 ml aliquots of chloroform, until consecutive extracts were colourless.
b) Ammonia solution - approximately 100 ml of 0.88 sg. reagent grade ammonia was allowed to equilibrate in a closed system with a similar volume of de-ionised water.
c) 16 M nitric acid (ultra pure grade)
d) Narrow range pH test paper (range 5-7)
e) Chloroform (ultra pure grade)
f) 1 M hydrochloric acid (ultra pure grade diluted with de-ionised water)

Procedures

1 000 ml of sample and 20 ml of Na-DDC/buffer were placed in a 2 l separating funnel. The pH was adjusted to 5.8 - 6.1 by addition of ammonia solution or nitric acid. 30 ml of chloroform were added and the flask was shaken vigorously for five minutes. The phases were allowed to separate, and the chloroform layer was removed. A further 20 ml of chloroform were added, shaken and removed in the same manner. The combined 50 ml of chloroform were gently evaporated to dryness, and the salt residue was dissolved in 5 ml of 1 M hydrochloric acid.

De-ionised water blank samples and multi-element spiked samples were also processed to test for blank contamination and the efficiency of the extraction.

A-1.6 Calcium and Magnesium

For calcium and magnesium analyses, samples were vacuum filtered through 0.45 um GF/C filters and acidified with 0.2 volume percent of concentrated hydrochloric acid. A 5 ml aliquot was diluted with an equal volume of a solution containing 0.45% lanthanum as $LaCl_2$. The addition of lanthanum to the solutions suppressed the interference effect of aluminum and phosphate during analysis by atomic absorption spectrophotometry.

A-2 Preparation Procedures for Soil Samples

Soil samples collected from the Mendip Hills Area, by the author, and from the Latteridge Area, by the Mineral Assessment Unit of the Institute of Geological Sciences, were digested in nitric and perchloric acids prior to analysis by atomic absorption or plasma emission spectrophotometry.

4 ml of concentrated nitric acid and 1 ml of concentrated perchloric acid were added to each tube and the contents were thoroughly mixed before placing the tubes in an airbath. The samples were digested at approximately 130°C for ten to fifteen hours, at which point the light yellow residue in each tube was dry. 6 ml of 2 N hydrochloric acid were added, and the contents were mixed thoroughly before being placed in a sand bath at 80°C for one hour. A further 6 ml

of water were added and the contents mixed thoroughly again. The insoluble residue was allowed to settle for several hours before the solutions were analysed by atomic absorption spectrophotometry (Mendip samples), or inductively coupled plasma emission spectrophotometry (Latteridge samples).

A-3 Estimates of Sampling and Analytical Precision.

A-3.1 Introduction

Precision of geochemical analytical data has traditionally been estimated as the co-efficient of variation of the results of a number of analyses of one sample (see for example, Rose et al, 1979, p.63). Using this definition it is possible to predict the absolute range about the mean within which the data are expected to fall. This technique is useful for determining the analytical variability of the replicate sample, but it is not necessarily adequate to determine the variability for the other samples in a batch. For example, the physical and chemical characteristics of the replicated sample may differ from those of the other samples, as may the preparation and analytical procedures. Another important consideration is that the precision determined for the replicate sample may not apply across the range of concentration of the other samples.

Thompson and Howarth (1973, 1976, 1978) have dealt with the problem of estimation of precision at some length, and have developed a procedure based on duplicate analysis of randomly selected samples. Their method involves determination of analytical variability as a function of concentration.

The main purpose of estimating analytical precision for the data presented in this thesis is to determine which data are analytically reliable, and at what concentration levels. All sample batches have incluced duplicates and standards, and have been sorted into random order. A computer program for automatic randomisation (Howarth, 1977) was used to generate the random sequence, and to allow insertion of duplicates and standards at the rate of one per ten samples.

For some of the data sets in the study, however, there are too few pairs of duplicate samples to use the methods of Thompson and Howarth. A modified version of their procedure has been devised where the difference in concentration between a pair of samples is expressed as a percentage of the average

concentration of the pair. For example, for two duplicate values 95 and 105, the difference is 10 and the average is 100, hence the "precision" is 10%. Where a number of pairs of duplicates are available the median "precision" is used as an estimate of overall precision. This technique does not allow determination of precision as a function of concentration.

A-3.2 Mendip Area Soils

The program DUPAN3 (Thompson, 1978) was used to study the variation in analytical precision, as a function of concentration, in 70 duplicate analyses of soil samples from the Mendip Hills. The regression parameters for the precision versus concentration relationships, as output from the program, have been used to estimate precision levels for various concentrations. The estimates are summarised in Table A-1. For most of the elements the data follows the expected trend of improving relative precision with increasing concentration. The departure from this trend, for magnesium and lead, is difficult to explain. The problem may lie in the fact that a first order regression curve is used to estimate the precision versus concentration function, thus not allowing for a possible flattening of the curve at low concentrations (see example shown in Thompson and Howarth, 1973). For magnesium and lead, therefore, the estimated precisions are not reliable. It is probable however, that the precision levels quoted for the higher concentrations (i.e. 12% at 1.6% Mg and 9% at 4 000 ppm Pb) are upper limits to the precision levels for these elements.

For the lower end of the expected range of concentrations, the estimated precision levels are better than 10% for iron, and better than 15% for zinc and calcium. For manganese, cadmium and copper, the precision levels are better than 20% at concentrations of 400, 4 and 10 ppm respectively, but worse than 20% at lower concentrations.

The analytical precision of the Mendip soil data was also estimated by determining the co-efficient of variation of replicate analyses of two control samples. The results, shown in Table A-2, are similar to those calculated by the duplicate analysis method (Table A-1), except that precision estimates for magnesium, manganese and copper are lower as determined by the co-efficient of variation method.

Table A-1 Analytical precision (in%) as a function of concentration, for 70 pairs of duplicate soil samples from the Mendip Hills

Ca%	Mg%	Fe%	Mn	Cd	Cu	Pb	Zn
.1-14%	.2-8%	1-10%	100-69%	1-78%	5-38%	300-4%	40-12%
.5-12%	.4-10%	2-8%	200-36%	2-40%	10-18%	500-6%	80-10%
1.0-11%	.6-11%	4-8%	400-20%	4-20%	20-10%	1000-8%	160-9%
2.0-11%	.8-12%	8-7%	800-12%	8-11%	40-4%	2000-9%	320-9%
4.0-11%	1.6-12%	16-7%	1600-8%	16-6%	80-2%	4000-9%	640-9%
			3200-6%	32-4%	160-1%		
			6400-4%	64-2%	320-.5%		

(All in ppm, except for Ca, Mg and Fe)

Table A-2 Analytical precision for two bulk soil samples from the Mendip Hills, expressed as the the coefficient of variation of replicate analyses

	RED[1]		BROWN[2]	
	Mean	Precision	Mean	Precision
Ca%	.15	16.2%	.10	33.3%
Mg	3998	6.4%	4154	8.3%
Fe%	4.02	3.2%	2.67	4.7%
Mn	1624	3.2%	415	6.3%
Cd	2.1	21.5%	1.2	40.2%
Cu	16.6	5.0%	10.7	7.8%
Pb	1958	8.2%	30.5	18.9%
Zn	470	3.4%	95.6	11.6%

1) Red soil derived from the Dolomitic Conglomerate (n=24)
2) Brown soil derived from the Carboniferous Limestone (n=21)

Variation between field duplicates (i.e. samples collected adjacent to each other) has been studied by computing ratios of pair-differences to pair-averages, as described in Section A-3.2. Precision estimates, based on the median of 25 ratios, are given in Table A-3. In comparing these with the estimates of analytical precision given in Table A-3, it is apparent that there is substantial sampling variability for calcium, iron, manganese, lead and zinc.

One of the "Association of Exploration Geochemists" standard soil samples was used to test for the accuracy of the analytical procedure. Although there are no definitive estimates of geochemical abundance in the samples, a report on their homogeneity (Alcott and Lakin, 1974), includes the analytical data for 50 random sub-samples. Analyses were carried out by several methods, including atomic absorption following a nitric acid digestion, using the procedure described by Ward et al (1969). Of the elements of interest here, only cadmium, copper, lead and zinc were determined by this method. Comparison of the results for sample GXR-2 is given in Table A-4.

The data from the present study are obviously higher than the Alcott and Lakin data, however this may be due to the stronger digestion used (nitric-perchloric as opposed to nitric). Taking this into account, the accuracy is acceptable.

A-3.3 Latteridge Area Soils

There are only 11 pairs of analytical duplicates from the Latteridge soil data, hence the pair-difference versus pair-average method has been used to estimate precision. The estimates are given in Table A-5.

Precision is 5% or better for barium, manganese, titanium and vanadium, 10% or better for strontium and zinc, 15% or better for copper and magnesium, and worse than 15% for calcium, sodium, aluminum, iron and lead.

A-3.4 Mendip Area Groundwaters

Again, because of the limited number of duplicate pairs, the pair-difference versus pair-average method has been used to estimate analytical

Table A-3 Estimates of sampling precision based on analysis of 25 field-duplicate soil samples from the Mendip Hills

	Mean[1]	Precision[2]
Ca	.36	35%
Mg	4656	8%
Fe	3.2	7%
Mn	1104	13%
Cd	2.5	21%
Cu	18.3	4%
Pb	2554	19%
Zn	522	22%

1) Mean of all duplicate samples
2) Precision calculated from pair-difference to pair-average ratios

Table A-4 Comparison of analyses in this study with those compiled by Alcott and Lakin (1974) for the reference sample GXR-2

	This study (n=11)			Alcott & Lakin(n=50)		
	Min.	Max.	Mean	Min.	Max.	Mean
Cd	4.22	4.79	4.61	2.7	4.5	3.4
Cu	69.8	78.1	73.6	52	74	66
Pb	616	698	668	460	700	600
Zn	472	529	505	420	570	490

(All in ppm)

Table A-5 Estimates of analytical precision for soil samples from the Latteridge area

	Mean	Precision[1]	Range in data[2]
Ca%	.87	22%	.25-7.5
Mg%	1.0	13%	.59-2.8
Na%	.07	40%	.01-.15
Al%	5	19%	3.4-6.9
Ti	830	5%	523-1192
Sr	1028	9%	43-1582
Ba	355	3%	199-813
Fe%	3.1	28%	2.9-6.9
Mn	780	4%	348-1839
Cu	32	12%	15-49
Pb	258	26%	86-407
Zn	27	9%	92-457
V	66	5%	49-92

1) Expressed as median of pair-difference to pair-average ratios for 11 duplicate pairs.
2) From 10th to 90th percentiles.

precision for the Mendip groundwater samples. The estimates are given in Table A-6. Precision is very good for all of the major elements, the worst being magnesium at 4%. For the minor elements, fluoride has the best precision, at 5%, followed by zinc at 9%, manganese at 10% and lead at 14%. Cadmium, copper, and iron are all worse than 15%.

Table A-6 Estimates of analytical precision for water samples from the Mendip Hills

	Mean	n	Precision[1]	Range in data[2]
HCO_3	249	21	1%	126-321
Cl	15	18	3%	13-20
SO_4	23	22	2%	15-35
Ca	106	27	3%	47-120
Mg	8.1	29	4%	4.4-13.5
F	.09	25	7%	.06-.20
Cd	.42	23	29%	.15-1.4
Cu	.70	23	18%	.35-1.6
Fe	9	24	23%	4.5-68
Mn	1.0	24	10%	.25-22
Pb	1.1	24	14%	1-14
Zn	17	24	9%	2.6-82

1) Expressed as median of pair-difference to pair-average ratios.
2) From 10th to 90th percentiles

APPENDIX B DESCRIPTION AND DISCUSSION OF THE STREAM DATA MAPPING ALGORITHM 'STRMPLT'

B-1 Introduction

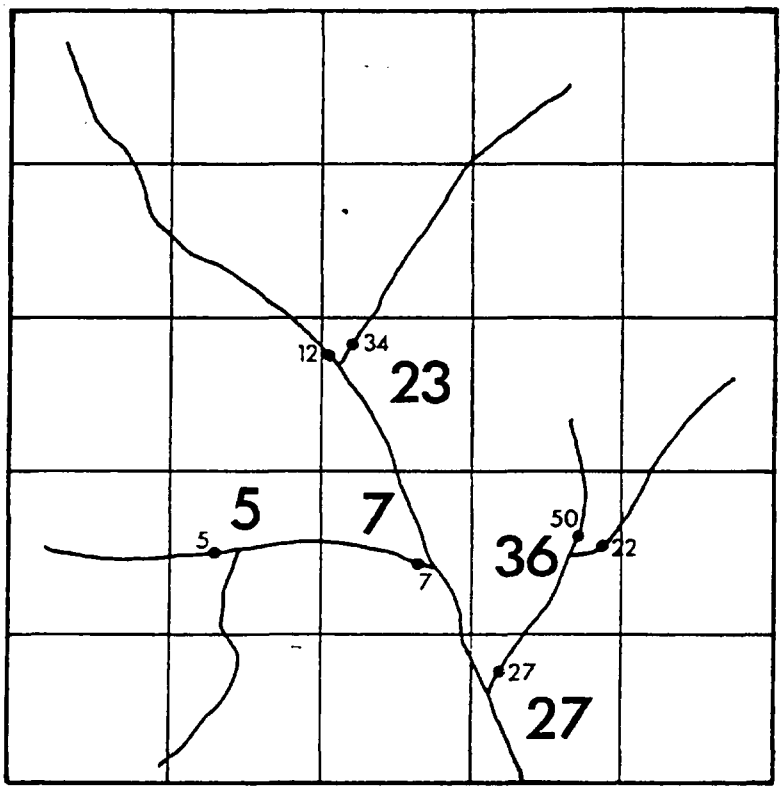
In a geochemical context, mapping involves the description of the spatial distribution of certain chemical constituents in surficial materials. In many parts of the world stream sediments, or other fluvial media, are routinely used for geochemical mapping because representative samples can be collected quickly and economically.

Stream-borne erosion products, including water and active sediments, are useful in surveys over large areas because they represent material derived from an area much larger than the immediate vicinity of the sample site. This feature can present problems in interpretation of the data however, because it is difficult to estimate the actual area represented by any individual sample. For example, the contribution is likely to be inversely related to the distance from the sample site, but this relationship is affected by features of the secondary environment, including mineral solubility in the zones of weathering, transport and deposition, and the characteristics of mechanical erosion.

One of the most widely used methods for the presentation of stream data involves plotting concentration values, or symbols that represent concentrations, at the appropriate sites on drainage patterns. This simple procedure avoids the problems inherent in explicit interpolation between data points, and facilitates isolation of obvious anomalous areas, but does not promote rapid visual recognition of the general characteristics of geochemical spatial distributions.

Contour maps and concentration versus shading intensity (grey-scale) maps represent improvements over point mapping techniques if the purpose of the survey is to show the general nature of the geochemical surface, instead of accurately indicating areas for follow-up work. For stream data, however, these methods can be inaccurate and misleading because they assume point source data in an isotropic medium. The hypothetical example shown in Figure B-1 illustrates the problems that can be encountered with superimposition of a grid network on to a drainage pattern. Samples are not necessarily representative of the map cell from within which they are collected because the sample material is derived

Figure B-1 Hypothetical stream data illustrating the problems inherent in mapping by simple cell averaging based on direct superimposition of a grid network. Small numbers are orginal data. Large numbers are 'averaged' data.



from upstream of the sample site. Direct surface representation (i.e., simple cell averaging) of stream data can only be realistically applied if the number of samples per map cell is high. In this case, regional patterns will be enhanced at the expense of local detail.

B-2 Stream Data Mapping Algorithm

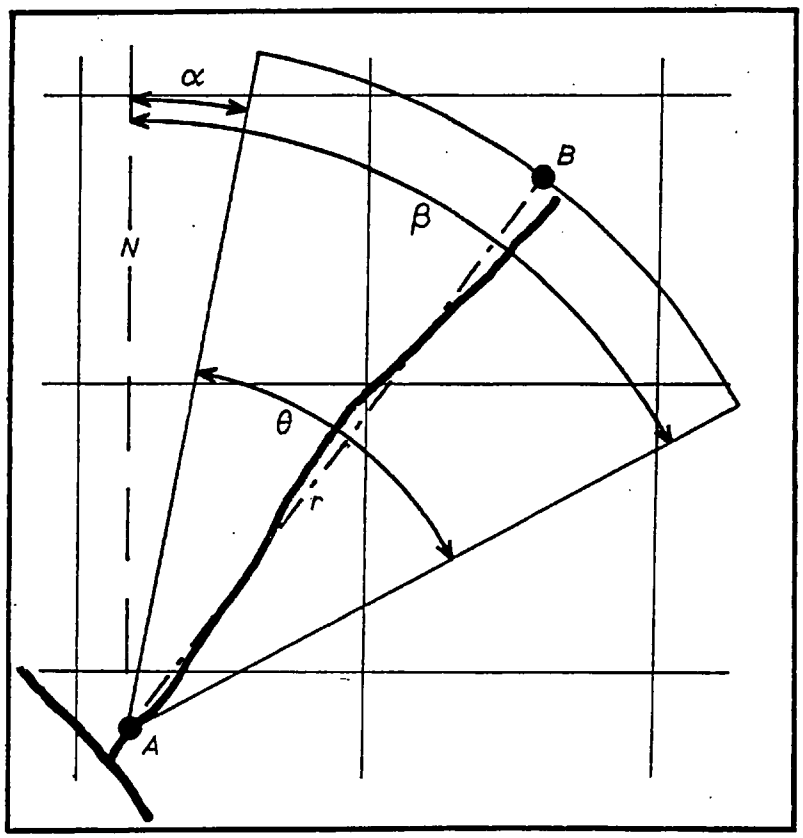
The mapping procedure involves the choice of a geometric shape to represent the catchment area of a sample. For each member of an array of square cells the relative areal contribution of the source area, or drainage basin, of each sample is estimated. A concentration value for each cell is then calculated to satisfy the concentrations of all samples whose drainage basins lie within that cell.

The choice of geometrical representation of a catchment area is important. Some alternatives are triangles, sectors of circles, ellipses and polygons. It is likely that a polygon would provide the best fit to a drainage basin, but, because of the ease of both data input and calculation of intersecting areas, a sector of a circle is considered the optimum shape.

A sector can be uniquely defined by its radius and a pair of angles α and β, which correspond to its left and right arms respectively, or similarly, by a radial line of length r and orientation $(\alpha+\beta)/2$ and an angle θ (Figure B-2). The latter method is simpler to use because it is only necessary to input the sample site co-ordinates (A), the co-ordinates of the distal end of the radial line bisecting the sector (B), and the sector angle θ (Figure B-2).

The radius, orientation and enclosing angle are chosen to obtain an optimum fit of the sector to the effective drainage area of the sample site. If mobility is limited and the dispersion distances of the various constituents can be estimated, it is desirable to limit the sector radius. A radius limit can be established when the program is executed. It is common to have considerable overlap between sectors, but this is not a problem because, as described below, the area and distance weighting factors strongly emphasize the contribution of samples that are most relevant to each cell. The choice of an appropriate sector is, of course, subjective, and although some drainage basins do not lend themselves to sector representation, a reasonable fit can be acheived in most situations.

Figure B-2 Detail of sector representation of a drainage basin. See text for explanation of symbols.



A weighted value is calculated for each member of a matrix of square cells that covers the area to be mapped. The value for any cell depends on the contributions of all samples whose sectors intersect that cell. Two area-weighting factors are used that take into account the ratio between the total area of a sector and its area within the cell, and the ratio between the contribution of each sector to the cell and the sum of the contributions of all sectors that intersect the cell. A third factor involves the distance between the sample site and the centre of each cell. In this case the reciprocal of the distance squared is used because the area represented by a stream sample is usually roughly proportional to the second power of the stream distance above the sample site. If stream length is doubled, for example, the area available for erosion will be quadrupled.

Calculation of the weighting factors AWT1, AWT2 and DWT is summarised in equations 1 to 3, where AXY_i is the area of sector i in cell xy, ATXY is the sum of all AXY_i for cell xy, A_i is the total area of sector i and DXY_i is the distance between the site of sample i and the centre of cell xy, or one-half the cell width if the sample site is within the cell.

$$AWT1 = (AXY_i/A_i)/\Sigma(AXY_i/A_i) \quad (1)$$

$$AWT2 = (AXY_i/ATXY)/\Sigma(AXY_i/ATXY) \quad (2)$$

$$DWT = (1/DXY_i)^2)/\Sigma(1/(DXY_i)^2) \quad (3)$$

The aggregate weighting factor is calculated as shown in equation 4, and for any cell the sum of WT_i is equal to 1.0.

$$WT_i = (AWT1 + AWT2 + DWT)/3 \quad (4)$$

The final calculation of a value for each cell is summarised in equation 5 :

$$VXY = \Sigma Z_i WT_i \quad (5)$$

where Z_i is the concentration of a constituent in sample i.

The results of sector averaging and distance weighting by the method just described are shown in Figure B-3. This distribution can be compared with the distribution derived from simple cell averaging shown in Figure B-1.

The sector technique was used to determine the distributions of stream sediment data for the study area, as is discussed in Chapter 3. A map showing the shapes of the sectors used in this application is given in Figure B-4. Two other examples of the use of the sector technique are presented in Earle (1978).

Figure B-3 Results of cell-averaging by the STRMPLT method. (The data are the same as portrayed in Figure B-1, and the small numbers are those derived from the STRMPLT algorithm.)

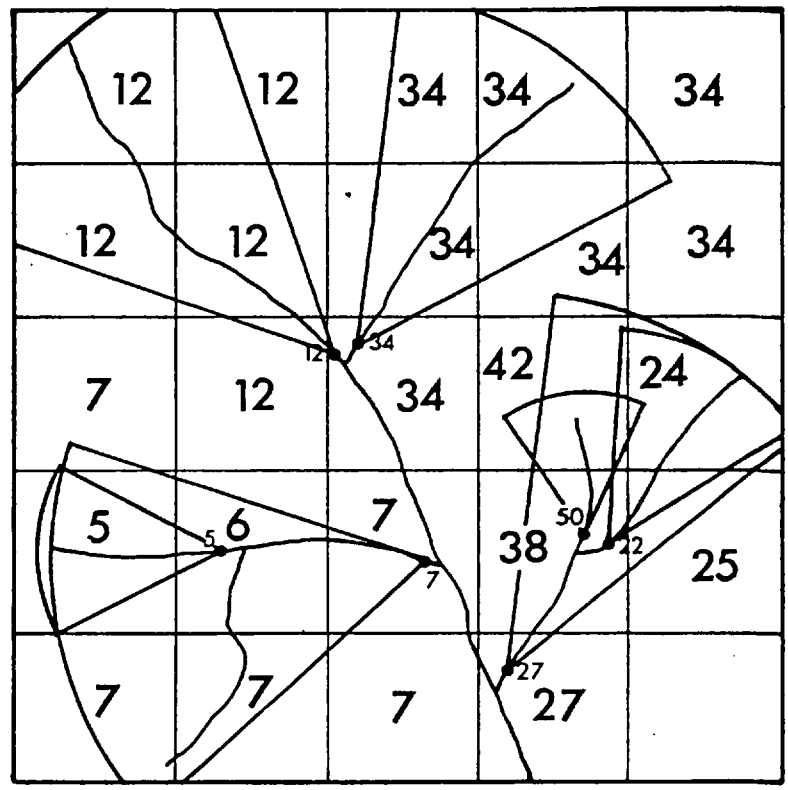
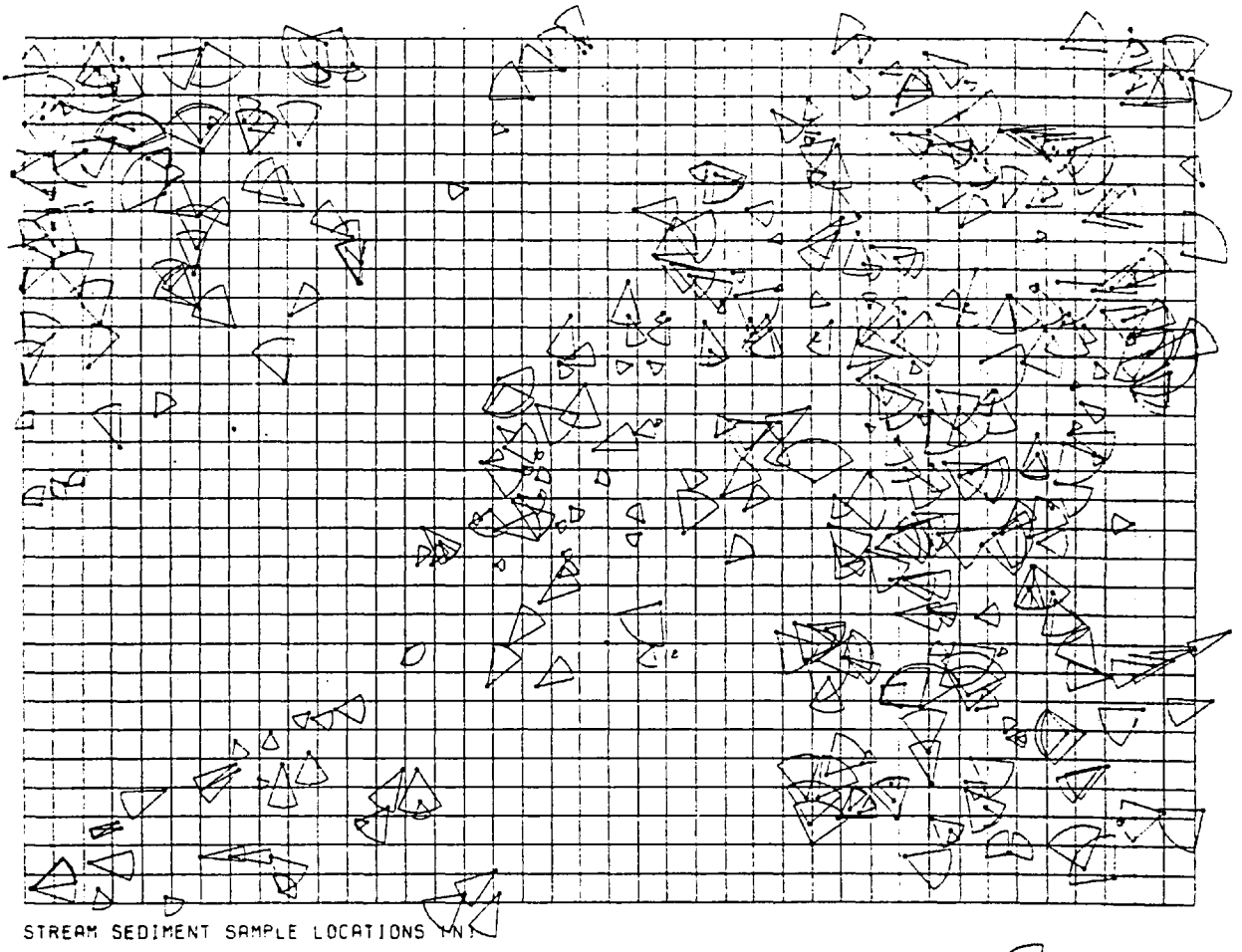


Figure B-4 Map showing the shape of sectors used for the data discussed in Chapter 3



B-3 STRMPLT Program

A FORTRAN computer program, STRMPLT, written to accept data and calculate the weighting factors described above, is listed below. Input to this program includes the co-ordinates of the southwest and northeast corners of the area to be mapped, the size of map-cell desired, and for each sample, the co-ordinates of points A and B and the sector angle (see Figure B-2), plus data for up to five elements. If desired, a dispersion distance limit, or maximum sector radius can be defined. Coding 100 samples for input to the STRMPLT routine would normally take about 2 hours. Output from the program is an array of map-cell values for each variable.

Running time depends mainly on the number of occupied cells, that is, cells which have intersections with sectors. Calculation of arrays for map areas comprising 350, 315, 240, 200 and 90 occupied cells required 71, 56, 35, 26 and 14 central-processing-unit seconds respectively on a CDC 6400 computer. The program is structured so that 5 variables can be processed in roughly the same length of time as one variable.

LISTING OF THE PROGRAM STRMPLT

```
C-----------------------------------------------------------------------MAIN   2
C                                                                       MAIN   3
C                    * * *   S T R M P L T   * * *                      MAIN   4
C                                                                       MAIN   5
C      ROUTINE TO PRODUCE A MAP-CELL ARRAY OF STREAM SAMPLE DATA,       MAIN   6
C      TAKING INTO ACCOUNT THE ANISOTROPY OF THE SAMPLING MEDIUM        MAIN   7
C      AND THE DISTANCE BETWEEN A SAMPLE AND THE CENTRE OF A MAP CELL   MAIN   8
C                                                                       MAIN   9
C-----------------------------------------------------------------------MAIN  10
C                                                                       MAIN  11
C  AUTHOR                                                               MAIN  12
C     STEVEN EARLE, DEPARTMENT OF GEOLOGY, IMPERIAL COLLEGE, LONDON     MAIN  13
C  DATE                                                                 MAIN  14
C     NOVEMBER 1975   (MODIFIED   MAY 1976)                             MAIN  15
C  LANGUAGE, COMPUTER                                                   MAIN  16
C     FORTRAN IV  -  CDC 6500  -  IMPERIAL COLLEGE COMPUTER CENTRE      MAIN  17
C  METHOD                                                               MAIN  18
C     A SECTOR OF A CIRCLE IS CHOSEN TO REPRESENT THE CATCHMENT AREA    MAIN  19
C     OF A STREAM, AND FOR EACH MAP CELL THE CONTRIBUTION OF EACH       MAIN  20
C     SAMPLE IS ESTIMATED ON THE BASIS OF THE AREA OF INTERSECTION      MAIN  21
C     BETWEEN THE SAMPLE AND THE CELL.  WEIGHTING FACTORS ARE           MAIN  22
C     CALCULATED BY TAKING INTO ACCOUNT THE RATIO BETWEEN THE AREA      MAIN  23
C     OF THE SECTOR OF A SAMPLE IN A CELL, AND THE TOTAL AREA OF        MAIN  24
C     THAT SECTOR;  THE AREA OF THE SECTOR OF A SAMPLE IN A CELL        MAIN  25
C     AND THE TOTAL SECTOR AREA IN THAT CELL;  AND THE DISTANCE         MAIN  26
C     BETWEEN A SAMPLE SITE AND THE CENTRE OF THE CELL BEING            MAIN  27
C     CONSIDERED.                                                       MAIN  28
C                                                                       MAIN  29
C     SECTORS ARE REPRESENTED BY SPECIFYING THE COORDINATES OF THE      MAIN  30
C     SAMPLE SITE (X1,Y1), THE SECTOR ANGLE (THTA), AND THE             MAIN  31
C     COORDINATES OF THE DISTAL END OF THE LINE SEGMENT WHICH           MAIN  32
C     BISECTS *THTA* (X2,Y2).                                           MAIN  33
C                                                                       MAIN  34
C-----------------------------------------------------------------------MAIN  35
C                                                                       MAIN  36
C      CONTROL CARDS                                                    MAIN  37
C                                                                       MAIN  38
C     CARD 1                                                            MAIN  39
C  COLS  1-80   HEADING INFORMATION                                     MAIN  40
C                                                                       MAIN  41
C     CARD 2 (FREE FORMAT)                                              MAIN  42
C              NUMBER OF VARIABLES (MAX. 5), INPUT DEVICE (4 OR 5),     MAIN  43
C              COORDINATES OF SW AND NE CORNERS OF MAP AREA,            MAIN  44
C              CELL SIZE - IN COORDINATE UNITS, SECTOR RADIUS           MAIN  45
C              LIMIT - IN COORDINATE UNITS, OUTPUT OPTION (0 FOR        MAIN  46
C              PRINTED O/P, 1 FOR PRINTED AND TAPE5 O/P), DISTANCE      MAIN  47
C              WEIGHTING FACTOR ( I - WHERE WEIGHTING IS 1/D**I)        MAIN  48
C                                                                       MAIN  49
C     CARD 3                                                            MAIN  50
C  COLS  1-80   INPUT FORMAT FOR READING *X1* *Y1* *X2* *Y2* AND       MAIN  51
C              *THTA* (*THTA* IS READ AS A NUMBER BETWEEN 1 AND 9       MAIN  52
C              AND IS EQUIVALENT TO THE ANGLE IN DEGREE DIVIDED         MAIN  53
C              BY 20.0), AND UP TO 5 DATA VALUES.                       MAIN  54
C                                                                       MAIN  55
C     CARD 4                                                            MAIN  56
C  COLS  1-25   VARIABLE NAMES (5A5)                                    MAIN  57
C                                                                       MAIN  58
C     CARD 5 (ONLY NECESSARY IF TAPE5 O/P IS REQUESTED)                 MAIN  59
C  COLS  1-80   OUTPUT FORMAT (LINE BY LINE) ENCLOSED IN PARENTHESES    MAIN  60
C                                                                       MAIN  61
C-----------------------------------------------------------------------MAIN  62
C                                                                       MAIN  63
C                                                                       MAIN  64 -
C                                                                       MAIN  65
      DIMENSION X1(360),Y1(360),X2(360),Y2(360),THTA(360),Z(5,360),     MAIN  66
     + AREA(360),PHIA(360),PHIB(360),ZEDL(5,20,20),JAY(15),AIC(15),     MAIN  67
     + RDSQ(360),ITITLE(8),NAME(5),IFMT(8),JFMT(8)                      MAIN  68
C                                                                       MAIN  69
C     *JAY*     TEMPORARY STORE FOR NUMBER OF SECTORS INTERSECTING     MAIN  70
C               ANY CELL                                                MAIN  71
C     *AIC*     TEMPORARY STORE FOR AREA OF EACH SECTOR WITHIN CELL     MAIN  72
C     *ITITLE*  80 CHARACTER HEADING INFORMATION                        MAIN  73
C     *NAME*    VARIABLE NAMES                                          MAIN  74
C     *IFMT*    INPUT FORMAT                                            MAIN  75
C     *JFMT*    OUTPUT FORMAT                                           MAIN  76
C     *ZEDL*    ARRAY OF MAP CELL CONCENTRATION VALUES                  MAIN  77
C                                                                       MAIN  78
C       THE DIMENSIONS OF THE FOLLOWING ARRAYS MUST BE CHANGED IN       MAIN  79
C       ORDER TO INCREASE THE MAXIMUM NUMBER OF SAMPLE SITES            MAIN  80
C                                                                       MAIN  81
C     *X1*      LIST OF SAMPLE SITE X-COORDINATES                       MAIN  82
C     *Y1*      LIST OF SAMPLE SITE Y-COORDINATES                       MAIN  83
C     *X2*      LIST OF DISTAL X-COORDINATES                            MAIN  84
C     *Y2*      LIST OF DISTAL Y-COORDINATES                            MAIN  85
C     *THTA*    LIST OF SECTOR ANGLES                                   MAIN  86
C     *Z*       DATA ARRAY                                              MAIN  87
C     *AREA*    LIST OF SECTOR AREAS                                    MAIN  88
C     *PHIA*    LIST OF SECTOR LEFT ARM ANGLES                          MAIN  89
C     *PHIB*    LIST OF SECTOR RIGHT ARM ANGLES                         MAIN  90
C     *RDSQ*    LIST OF SQUARED SECTOR RADII                            MAIN  91
C                                                                       MAIN  92
C       TO INCREASE THE MAXIMUM NUMBER OF VARIABLES THE ARRAYS *NAME*   MAIN  93
C       *Z* AND *ZEDL* MUST BE RE-DIMENSIONED. TO CHANGE THE MAXIMUM    MAIN  94
C       SIZE OF MAP PROCESSED THE ARRAY *ZEDL* MUST BE RE-DIMENSIONED   MAIN  95
C                                                                       MAIN  96
      DIMENSION AOT(15),DWT(15)                                         MAIN  97
      DATA ZEDL/2000*0./                                                MAIN  98
      DATA NTOT/360/                                                    MAIN  99
C                                                                       MAIN 100
C                                                                       MAIN 101
C       INITIALIZE PI AND NUMBER OF SAMPLES COUNTER                     MAIN 102
C                                                                       MAIN 103
      DATA PI,NUM/3.14159265358,0/                                      MAIN 104
C                                                                       MAIN 105
C       INPUT CONTROL CARDS                                             MAIN 106
C                                                                       MAIN 107
      READ(5,101) ITITLE                                                MAIN 108
  101 FORMAT(8A10)                                                      MAIN 109
      READ(5,*) NCL,MT,XSW,YSW,XNE,YNE,CLSZ,RMAX,RDPF,IDWF              MAIN 110
      READ(5,101) IFMT                                                  MAIN 111
      READ(5,102) NAME                                                  MAIN 112
  102 FORMAT(5A5)                                                       MAIN 113
      IF(RDPF.EQ.1.) READ(5,101) JFMT                                   MAIN 114
C                                                                       MAIN 115
      WRITE(6,104) ITITLE                                               MAIN 116
  104 FORMAT(1HX,8A10/)                                                 MAIN 117
      WRITE(6,105) NCL,(NAME(M),M=1,NCL)                                MAIN 118
  105 FORMAT(1HX,I1,1X,12HVARIABLES -,5(A5,2X)/)                        MAIN 119
      WRITE(6,106) MT,IFMT                                              MAIN 120
  106 FORMAT(1HX,19HDATA READ FROM TAPE,I1,1H, BY FORMAT,8A10/)         MAIN 121
      IXSW=XSW                                                          MAIN 122
      IYSW=YSW                                                          MAIN 123
      IXNE=XNE                                                          MAIN 124
      IYNE=YNE                                                          MAIN 125
      WRITE(6,107) IXSW,IYSW,IXNE,IYNE,CLSZ                             MAIN 126
  107 FORMAT(1HX,20HSOUTH-WEST CORNER - (,I5,1H,,I5,1H)/                MAIN 127
     1       1HX,20HNORTH-EAST CORNER - (,I5,1H,,I5,1H)/                MAIN 128
     2       1HX,12HCELL SIZE = ,F6.1,17H COORDINATE UNITS/)            MAIN 129
      WRITE(6,108) IDWF                                                 MAIN 130
      IF(RDPF.EQ.1) WRITE(6,108) JFMT                                   MAIN 131
  108 FORMAT(1HX,31HTAPE5 OUTPUT REQUESTED - FORMAT,8A10)               MAIN 132
  109 FORMAT(1HX,34HDISTANCE WEIGHTING FACTOR IS 1/D**,I1/)             MAIN 133
C                                                                       MAIN 134
C       SET RMAX AND 2*RMAX IN TERMS OF SQUARED DISTANCES               MAIN 135
C                                                                       MAIN 136
      RMX=(RMAX+RMAX)*(RMAX+RMAX)                                       MAIN 137
      RMAX=RMAX*RMAX                                                    MAIN 138
C                                                                       MAIN 139
C       INPUT DATA                                                      MAIN 140
C                                                                       MAIN 141
      DO 202 I=1,NTOT                                                   MAIN 142
C                                                                       MAIN 143
      READ (MT,IFMT) X1(I),Y1(I),X2(I),Y2(I), THTA(I),(Z(L,I),L=1,NCL)  MAIN 144
      IF(EOF(MT)) 203,201                                               MAIN 145
  201 NUM=NUM+1                                                         MAIN 146
C                                                                       MAIN 147
C       ESTABLISH RADIUS AND ORIENTATION OF SECTOR                      MAIN 148
C                                                                       MAIN 149
      X=X2(I)-X1(I)                                                     MAIN 150
      Y=Y2(I)-Y1(I)                                                     MAIN 151
      IF(X) 1,1,2                                                       MAIN 152
    1 IF(Y) 5,9,6                                                       MAIN 153
    2 IF(Y) 5,10,7                                                      MAIN 154
    5 PHI=ATAN(Y/X) + PI                                                MAIN 155
      GOTO 11                                                           MAIN 156
    6 PHI=ATAN(Y/X) + 2. *PI                                            MAIN 157
      GOTO 11                                                           MAIN 158
    7 PHI=ATAN(Y/X)                                                     MAIN 159
      GOTO 11                                                           MAIN 160
    9 PHI=1.5 * PI                                                      MAIN 161
      GOTO 11                                                           MAIN 162
   10 PHI=.5 * PI                                                       MAIN 163
   11 TH=THTA(I)/18. * PI                                               MAIN 164
      PHIA(I)=PHI-TH                                                    MAIN 165
      PHIB(I)=PHI + TH                                                  MAIN 166
C                                                                       MAIN 167
      RADSQ=X*X+Y*Y                                                     MAIN 168
      IF(RADSQ.GT.RMAX) WRITE(6,151) I                                  MAIN 169
  151 FORMAT('0**CAUTION SECTOR OF SAMPLE ',I3,*IS VERY LARGE*/*POSSIBLEMAIN 170
     + MISPUNCH OF COORDINATES*)                                        MAIN 171
      IF(RADSQ.GT.RMAX) RADSQ=RMAX                                      MAIN 172
C                                                                       MAIN 173
C       CALCULATE AREA OF SECTOR(I)                                     MAIN 174
C                                                                       MAIN 175
      AREA(I)=PI*RADSQ*THTA(I)/18.                                      MAIN 176
      RDSQ(I)=RADSQ                                                     MAIN 177
  202 CONTINUE                                                          MAIN 178
C                                                                       MAIN 179
C       DETERMINE NUMBER OF CELLS IN X AND Y DIRECTIONS                 MAIN 180
C                                                                       MAIN 181
  203 M=AINT((XNE-XSW)/CLSZ+0.5)                                        MAIN 182
      N=AINT((YNE-YSW)/CLSZ+0.5)                                        MAIN 183
C                                                                       MAIN 184
C       START IN SW CORNER                                              MAIN 185
C                                                                       MAIN 186
      DO 1100 MX=1,M                                                    MAIN 187
      DO 1000 NY=1,N                                                    MAIN 188
C                                                                       MAIN 189
C       DEFINE CENTER OF CELL (MX,NY)                                   MAIN 190
C                                                                       MAIN 191
      CENX=FLOAT(MX)*CLSZ-CLSZ*0.5  + XSW                               MAIN 192
      CENY=FLOAT(NY)*CLSZ-CLSZ*0.5 + YSW                                MAIN 193
C                                                                       MAIN 194
      J=0                                                               MAIN 195
      SAOT=0.                                                           MAIN 196
      SAIC=0.                                                           MAIN 197
      SDWT=0.                                                           MAIN 198
C                                                                       MAIN 199
C       SCAN LIST OF DATA FOR EACH MAP CELL                             MAIN 200
C                                                                       MAIN 201
      DO 400 I=1,NUM                                                    MAIN 202
C                                                                       MAIN 203
C       CALCULATE DISTANCE OF SAMPLE(I) FROM CELL (MX,NY)               MAIN 204
C                                                                       MAIN 205
      DSQ=(CENX-X1(I))**2+(CENY-Y1(I))**2                               MAIN 206
      DIST=SQRT(DSQ)                                                    MAIN 207
      RD=SQRT(RDSQ(I))                                                  MAIN 208
C                                                                       MAIN 209
C       IF CELL LIES OUTSIDE SECTOR, GO ON TO NEXT SAMPLE               MAIN 210
C                                                                       MAIN 211
      IF(DIST-SQRT(.5*CLSZ*CLSZ)-RD.GT.0.) GOTO 400                     MAIN 212
C                                                                       MAIN 213
C       IF SAMPLE IS WITHIN CELL SET DISTANCE TO 1/2 CELL SIZE          MAIN 214
C                                                                       MAIN 215
      IF(DIST.LT.(CLSZ*0.5)) DIST=CLSZ*0.5                              MAIN 216
C                                                                       MAIN 217
C       CALCULATE AREA OF SECTOR(I) WITHIN CELL (MX,NY)                 MAIN 218
C                                                                       MAIN 219
      ARE=0.                                                            MAIN 220
      CALL INTRSCT(CENX,CENY,CLSZ,PHIA(I),PHIB(I),RD,X1(I),Y1(I),ARE)   MAIN 221
      IF(ARE.EQ.0.) GOTO 400                                            MAIN 222
      J=J+1                                                             MAIN 223
      AIC(J)=ARE                                                        MAIN 224
      JAY(J)=I                                                          MAIN 225
C                                                                       MAIN 226
C       SUM AREAS OF ALL SECTORS WITHIN CELL                            MAIN 227
C                                                                       MAIN 228
      SAIC=SAIC+ARE                                                     MAIN 229
C                                                                       MAIN 230
C       DIVIDE AREA(I) WITHIN CELL BY AREA(I) TOTAL, AND SUM            MAIN 231
C                                                                       MAIN 232
      AOT(J)=ARE/AREA(I)                                                MAIN 233
      SAOT=SAOT+AOT(J)                                                  MAIN 234
C                                                                       MAIN 235
C       CALCULATE DISTANCE WEIGHTING FACTOR AND SUM ALL FACTORS         MAIN 236
C                                                                       MAIN 237
      DWT(J)=1./DIST**IDWF                                              MAIN 238
      SDWT=SDWT+DWT(J)                                                  MAIN 239
  400 CONTINUE                                                          MAIN 240
C                                                                       MAIN 241
      IF(J.LT.1) GOTO 1000                                              MAIN 242
      IF(J.GT.15) WRITE(6,9999) J,MX,NY                                 MAIN 243
 9999 FORMAT(1X,11H****CAUTION,3I4)                                     MAIN 244
C                                                                       MAIN 245
C       CALCULATE WEIGHTING FACTORS AS FRACTIONS OF TOTAL WEIGHTINGS    MAIN 246
C                                                                       MAIN 247
      DO 516 JJ=1,J                                                     MAIN 248
      FDWT=DWT(JJ)/SDWT                                                 MAIN 249
      FAOT=AOT(JJ)/SAOT                                                 MAIN 250
      FAIC=AIC(JJ)/SAIC                                                 MAIN 251
C                                                                       MAIN 252
      II=JAY(JJ)                                                        MAIN 253
C                                                                       MAIN 254
      WEIGHT=(FDWT+FAOT+FAIC)/3.                                        MAIN 255
C                                                                       MAIN 256
```

```
C                                                                       MAIN 257
C       CALCULATE ELEMENTAL VALUES FOR CELL (X,Y)                       MAIN 258
C                                                                       MAIN 259
      DO 515 L=1,NEL                                                    MAIN 260
  515 ZEDL(L,MX,MY)=ZEDL(L,MX,MY)+WEIGHT*Z(L,II)                        MAIN 261
  516 CONTINUE                                                          MAIN 262
C                                                                       MAIN 263
C                                                                       MAIN 264
 1000 CONTINUE                                                          MAIN 265
 1100 CONTINUE                                                          MAIN 266
C                                                                       MAIN 267
C       OUTPUT MAP ARRAYS                                               MAIN 268
C                                                                       MAIN 269
      DO 540 L=1,NEL                                                    MAIN 270
      WRITE(6,520) NAME(L)                                              MAIN 271
  520 FORMAT(1H1/1HO,/1HT,13HMAP ARRAY FOR,A5)                          MAIN 272
      DO 530 MY=1,M                                                     MAIN 273
      MM=M+1-MY                                                         MAIN 274
C                                                                       MAIN 275
      WRITE(6,525) (ZEDL(L,MX,MM),MX=1,M)                               MAIN 276
  525 FORMAT(1H ////1X,25F5.0)                                          MAIN 277
      IF(KBPF.EQ.1) WRITE(3,JFMT) (ZEDL(L,MX,MM),MX=1,M)                MAIN 278
C                                                                       MAIN 279
  530 CONTINUE                                                          MAIN 280
  540 CONTINUE                                                          MAIN 281
      STOP                                                              MAIN 282
      END                                                               MAIN 283
      SUBROUTINE INTRSCT(CENX,CENY,CLSZ,PHA,PHB,RAD,X1,Y1,ARE)          ISCT   2
C-----------------------------------------------------------------------ISCT   3
C                                                                       ISCT   4
C                                                                       ISCT   5
C     ROUTINE TO ESTIMATE THE AREA OF INTERSECTION OF A SQUARE          ISCT   6
C     AND A SECTOR OF A CIRCLE                                          ISCT   7
C                                                                       ISCT   8
C                                                                       ISCT   9
C        ARGUMENTS                                                      ISCT  10
C     *CENX*  X COORDINATE OF CELL CENTRE                               ISCT  11
C     *CENY*  Y COORDINATE OF CELL CENTRE                               ISCT  12
C     *CLSZ*  CELL SIZE IN COORDINATE UNITS                             ISCT  13
C     *PHA*   ANGLE OF LEFT SIDE OF SECTOR WRT NORTH=0 DEGREES          ISCT  14
C     *PHB*   ANGLE OF RIGHT SIDE OF SECTOR WRT NORTH=0 DEGREES         ISCT  15
C     *RAD*   SECTOR RADIUS IN COORDINATE UNITS                         ISCT  16
C     *X1*    SAMPLE SITE X COORDINATE                                  ISCT  17
C     *Y1*    SAMPLE SITE Y COORDINATE                                  ISCT  18
C     *ARE*   AREA OF THE SECTOR WITHIN THE CELL, EXPRESSED AS A        ISCT  19
C             PERCENTAGE OF THE CELL AREA                               ISCT  20
C                                                                       ISCT  21
C                                                                       ISCT  22
C     ALGORITHM - THE SQUARE IS REPRESENTED BY A GRID OF 100 POINTS,    ISCT  23
C     AND EACH POINT IS TESTED TO DETERMINE IF IT IS WITHIN THE         ISCT  24
C     SECTOR.  THE NUMBER OF POINTS WITHIN THE SECTOR IS PROPORTIONAL   ISCT  25
C     TO THE AREA OF THE SECTOR WITHIN THE SQUARE                       ISCT  26
C                                                                       ISCT  27
C     WRITTEN BY STEVEN EARLE - IMPERIAL COLLEGE - NOVEMBER, 1975       ISCT  28
C                                                                       ISCT  29
C-----------------------------------------------------------------------ISCT  30
C                                                                       ISCT  31
      DATA PI/3.14159265358/                                            ISCT  32
      IPCT=0                                                            ISCT  33
C                                                                       ISCT  34
C       LOCATE POINTS                                                   ISCT  35
C                                                                       ISCT  36
      C=CLSZ/9.                                                         ISCT  37
      RM=CENX-C*4.5                                                     ISCT  38
      RN=CENY-C*4.5                                                     ISCT  39
      PHIA=PHA                                                          ISCT  40
      PHIB=PHB                                                          ISCT  41
      RD=RAD                                                            ISCT  42
      DO 110 I=1,10                                                     ISCT  43
      XI = FLOAT(I-1) * C + RM                                          ISCT  44
      DO 100 J = 1,10                                                   ISCT  45
      YJ = FLOAT(J-1) *C +RN                                            ISCT  46
C                                                                       ISCT  47
C       ESTABLISH POLAR COORDINATES                                     ISCT  48
C                                                                       ISCT  49
      XX=XI-X1                                                          ISCT  50
      YY=YJ-Y1                                                          ISCT  51
      R=SQRT(XX*XX+YY*YY)                                               ISCT  52
C                                                                       ISCT  53
C       CHECK IF WITHIN RADIUS OF SECTOR                                ISCT  54
C                                                                       ISCT  55
      IF(R.GT.RD) GOTO 100                                              ISCT  56
C                                                                       ISCT  57
C       CHECK IF WITHIN ANGLE OF SECTOR                                 ISCT  58
C                                                                       ISCT  59
      IF(XX) 1,1,2                                                      ISCT  60
    1 IF (YY) 5,8,6                                                     ISCT  61
    2 IF (YY) 5,9,7                                                     ISCT  62
    5 PHI= ATAN(XX/YY) + PI                                             ISCT  63
      GOTO 20                                                           ISCT  64
    6 PHI= ATAN(XX/YY) +(2. * PI)                                       ISCT  65
      GOTO 20                                                           ISCT  66
    7 PHI= ATAN(XX/YY)                                                  ISCT  67
      GOTO 20                                                           ISCT  68
    8 PHI= 1.5 * PI                                                     ISCT  69
      GOTO 20                                                           ISCT  70
    9 PHI= 0.5 * PI                                                     ISCT  71
   20 IF(PHIA) 13,10,10                                                 ISCT  72
   10 IF((2. * PI) - PHIB) 14,11,11                                     ISCT  73
   11 IF(PHIB-PHI) 100,16,16                                            ISCT  74
   13 IF((2. * PI) + PHIA - PHI) 17,17,15                               ISCT  75
   14 IF(PHIB -(2. * PI)- PHI) 16,17,17                                 ISCT  76
   15 IF(PHIB-PHI) 100,17,17                                            ISCT  77
   16 IF(PHIA-PHI) 17,17,100                                            ISCT  78
   17 IPCT = IPCT + 1                                                   ISCT  79
  100 CONTINUE                                                          ISCT  80
  110 CONTINUE                                                          ISCT  81
C                                                                       ISCT  82
C       EXPRESS INTERSECTION IN TERMS OF PERCENT OF THE  CELL AREA      ISCT  83
C                                                                       ISCT  84
      ARE= 0.01* FLOAT(IPCT)                                            ISCT  85
C                                                                       ISCT  86
      RETURN                                                            ISCT  87
      END                                                               ISCT  88
                                                                        ISCT  89
                                                                        ISCT  90
```

APPENDIX C DESCRIPTION AND DISCUSSION OF THE INTERACTIVE FREQUENCY DISTRIBUTION ANALYSIS ALGORITHM 'GIRAF'

C-1 Introduction

The use of probability scale cumulative frequency plots to simplify the portrayal of normal distributions was initiated early in this century for application to data pertaining to engineering problems. The method was subsequently applied to data from various scientific disciplines, including Sedimentology (Krumbein and Pettijohn, 1938) and Geochemistry (Tennant and White, 1956). More recent applicants and developments include those of Williams (1967), Lepeltier (1969), Sinclair (1974) and Parslow (1974). Sinclair (1976) has published a manual describing a procedure which represents a refinement of the use of probability graphs from the point of view of defining sub-populations, and separating anomalous from background groups. The procedure is laborious, however, especially if several trial and error attempts are made to fit subdivisions of varying proportions. Celenk (1972) devised a computer algorithm employing graphical output in an interactive mode to assist in interpretation of probability plots. A similar algorithm was developed by McCammon (1976) (see also McCammon et al, 1979), and algorithms for numerical solutions to the problem were devised by McCammon (1969), and Clark and Garnett (1974) (see also Clark, 1977). A review of the subject of analysing multi-modal distributions has been compiled by Clark (1976).

The following is a description of an algorithm developed by the author, which allows graphical separation of multi-modal populations with the facility for transformation to normality by the variable exponential technique.

C-2 Frequency Distribution Analysis Algorithm

The frequency distribution analysis algorithm, GIRAF, is in the form of a FORTRAN program designed to be used on the interactive graphics facility at the Imperial College of Science and Technology (Raby, 1976). The program is run at a Tektronix graphical terminal, and hard-copy output can be obtained from the Tektronix hard-copy unit, or via microfilm. Execution is controlled from the terminal keyboard, and data is input from a binary disk-file. Creation of the binary disk-file is facilitated through the use of a separate interactive FORTRAN

program called START. As presently written, START is dimensioned for 15 variables and 500 observations. GIRAF is dimensioned for 20 variables and 2 500 observations. Documented listings of START and GIRAF are included below.

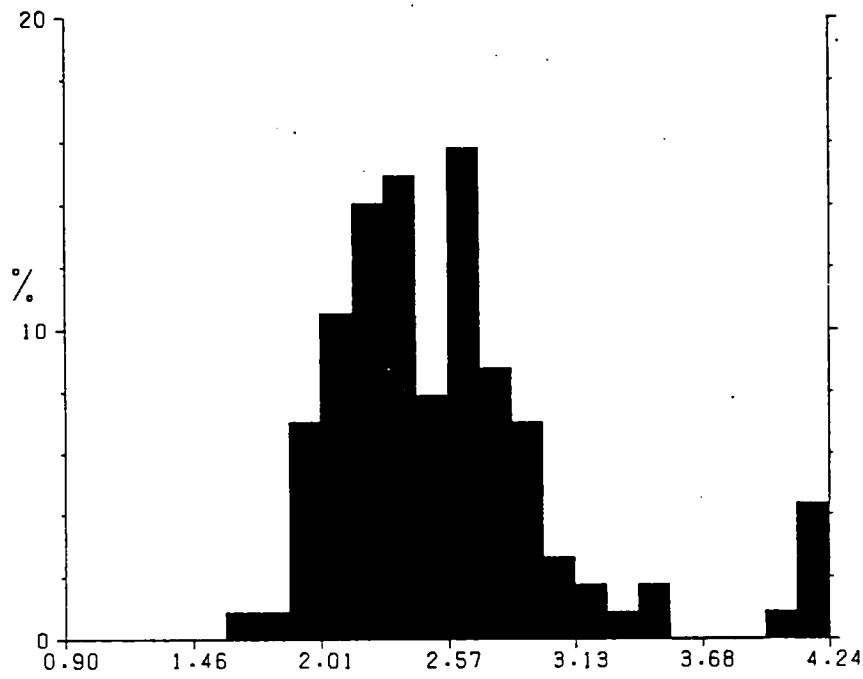
The program enables graphical representation of the data, either as a histogram (Figure C-1), or as a probability scale cumulative frequency plot (Figure C-2), or both. Prior to construction of the histogram or probability plot, it is possible to transform the data by taking the base-ten logarithm, or by using the variable exponential transformation technique described by Box and Cox (1964), and by Howarth and Earle (1979).

The range of values for the histogram is determined as the mean plus and minus three standard deviations, except in cases of strongly positively skewed distributions, where the minimum interval is set to the highest value possible which avoids truncation. The first and last bins hold values below the minimum and above the maximum respectively. The number of classes can be selected as a multiple of 6, from 6 to 72. The cumulative percentages for the probability plot are based on the histogram percentages, hence the ability to select the number of classes is an important feature. With a small number of classes, the cumulative curve will be smooth, and small inflections will not be apparent. With a large number of classes, small, and sometimes insignificant inflections will be preserved. When a probability plot is requested without a histogram, 30 classes are used.

For probability plots the cumulative curve is defined by 55 points evenly spaced along the probability axis. The first step in defining the 55 points is to fit a 250-point smooth curve to the cumulated histogram percentage curve. In this case the 250 points are evenly distributed along the cumulative frequency array, and the corresponding concentration values are calculated by piece-wise fitting of third-degree polonomials (Akima, 1972). In the second step the 55-point concentration array is derived from this smooth curve by linear interpolation between the 250 cumulative frequency points. The probability plot is then displayed, and if desired, the user initiates the process of defining sub-populations.

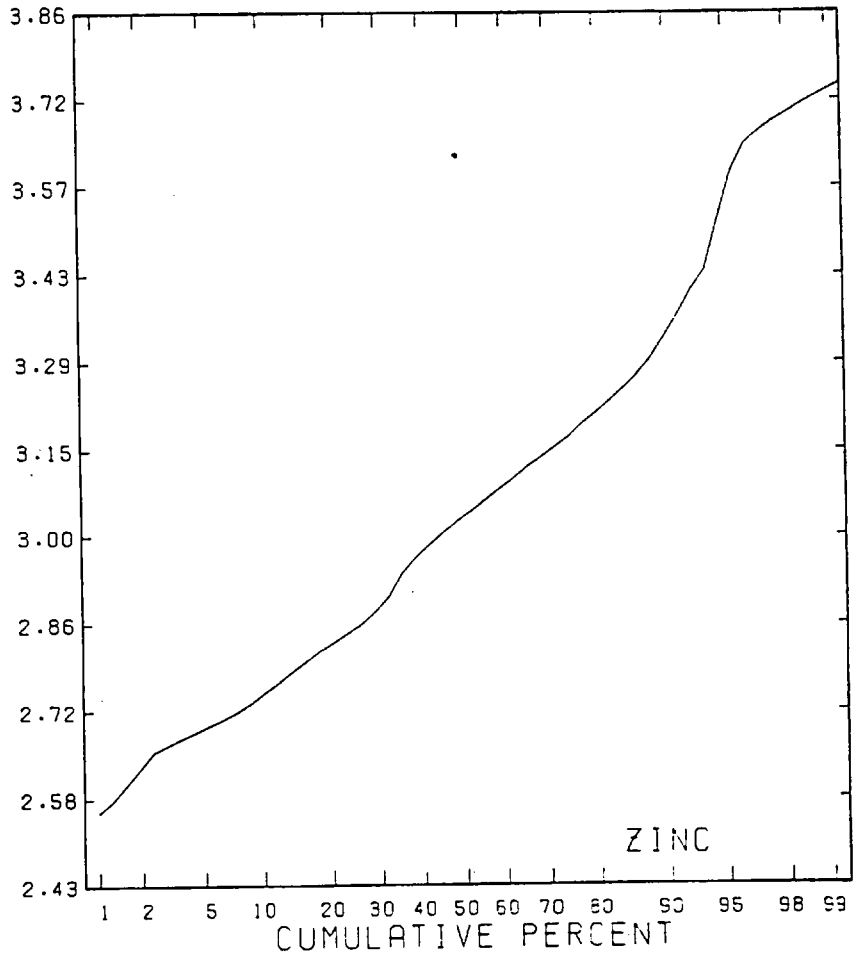
Populations can be divided into from 2 to 5 sub-populations using the procedure described by Sinclair (1976). The basis for defining sub-populations is the sigmoidal inflection point, that is, where the steepness of the curve reaches

Figure C-1 Example of a histogram generated by the program GIRAF



ZINC
NO. OF OBSERVATIONS = 114
MEAN = 2.57 STD DEV = 0.556
NO. OF LOG10 TRANSFORMS = 1

Figure C-2 Example of a probability-plot generated by the program GIRAF



a maximum. Using the Tektronix crosswires, the user selects from 1 to 4 inflection points, and the program derives the percentile and concentration values for points which define the sub-populations. Straight lines representing the sub-populations are fitted to the derived points by linear regression (Figure C-3). During the process of the selection of inflection points, the marks and numbers along the axes are not displayed so as to avoid bias. Selection of inflection points and calculation of the distribution of sub-populations can be repeated as often as is desired.

The closeness of fit between the model and actual data can be determined by combining the straight-line sub-populations (Sinclair, 1976). The resultant curve can be compared visually to the original curve, or the two curves can be compared statistically by calculating the Kolmogrov-Smirnov statistic. A similar facility is also available for testing a unimodal population for normality.

C-3 The Effect of Transformation on Multi-Modal Distributions

Maclean et al (1976), have discussed the implications of skewness on the apparent multi-modality of populations. They point out that skewness can be caused by non-normality or by multi-modality, or some combination of these two effects, and they advocate use of the exponential transformation (Box and Cox, 1964) to enable a close approximation to normality before assessing multi-modality. They also suggest that it is desirable to be conservative on the side of not claiming multi-modality, where skewness can be corrected by transformation.

Whether multi-modality should be suppressed, or even enhanced, by transformation, will not be discussed here, although it is important to realize that skewness and multi-modality are not necessarily independent characteristics.

The main reason for using probability plots in this study is to aid in recognition of sub-populations, from the point of view of establishing "anomalous" versus "background" groups. As mentioned in Howarth and Earle (1979), optimum results have been obtained by minimising the skewness of the potential sub-population rather than that of the parent population. Sinclair (1976) has suggested that in the case of overlap between the ranges of two sub-populations,

Figure C-3 Example of a probability-plot from GIRAF, showing decomposition into constituent sub-populations

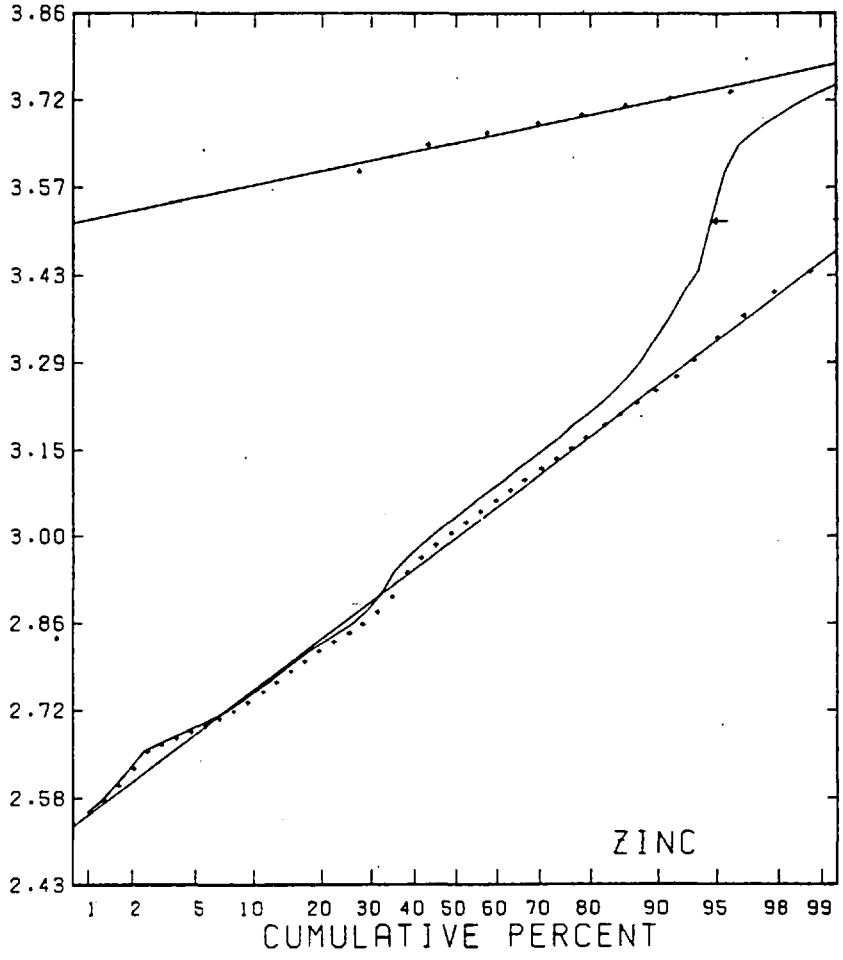
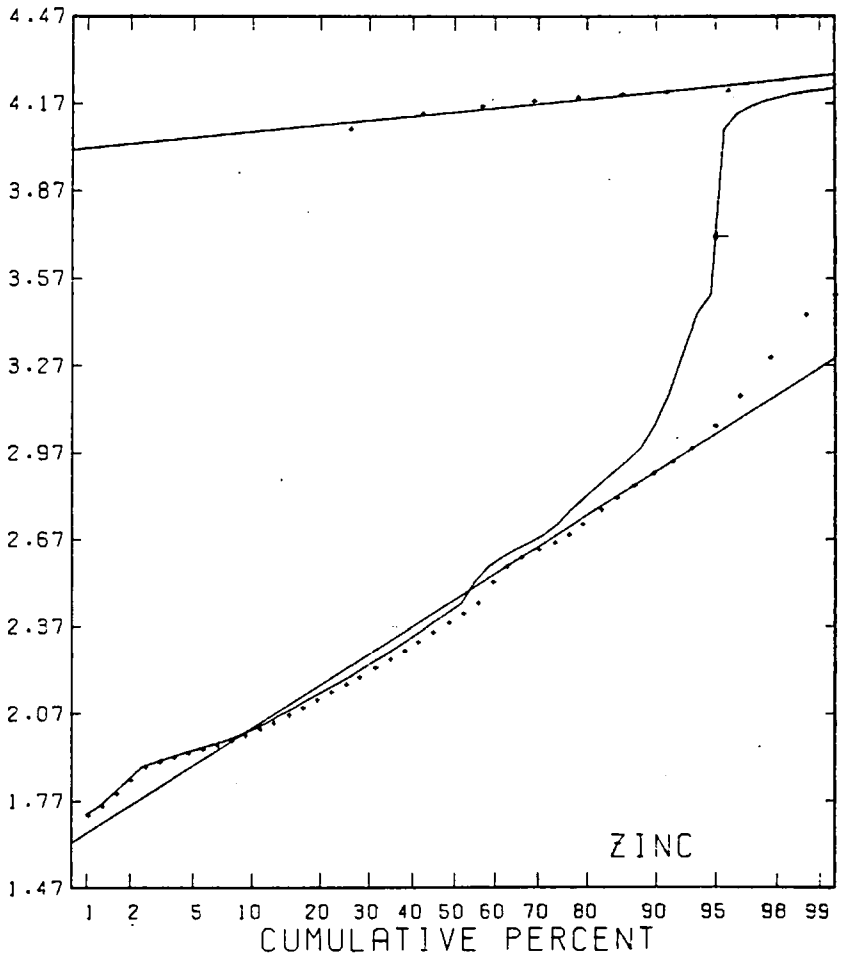


Figure C-4 Example of a subdivided population, with the lower sub-population positively skewed



the higher or "anomalous" group can be most efficiently separated by excluding data from below the 99th percentile of the lower group. Commonly, however, the lower sub-population is positively skewed to the extent that graphical estimation of its 99th percentile level is unreliable (Figure C-4). Exponential transformation can correct this feature, even though the parent population remains skewed.

The above discussion emphasizes the necessity for careful consideration of the contributions of both non-normality and multi-modality to the generation of skewed distributions. The danger of not reducing skewness and perceiving false multi-modality is no more important than the danger of completely removing skewness and concealing multi-modality. Without a facility for frequency distribution analysis which allows repeated emperical modelling of sub-populations with varying transformations, a truly adequate population analysis would be inhibitively laborious.

LISTING OF THE PROGRAM GIRAF

```
C
C                                                                      MAIN   2
C                                                                      MAIN   3
C                          *** G I R A F ***                           MAIN   4
C                                                                      MAIN   5
C                                                                      MAIN   6
C      GEOLOGICAL  INTER-ACTIVE FREQUENCY DISTRIBUTION ANALYSIS AND    MAIN   7
C      -           - -   -      -            -                       MAIN   8
C      DECOMPOSITION BASED ON PROBABILITY SCALE CUMULATIVE CURVES -    MAIN   9
C      FOLLOWING THE METHOD OUTLINED BY SINCLAIR - (APPLICATIONS       MAIN  10
C      OF PROBABILITY GRAPHS IN MINERAL EXPLORATION - ASSOC. OF        MAIN  11
C      EXPLORATION GEOCHEMISTS - SPEC. VOL. 4 - 1976)                  MAIN  12
C                                                                      MAIN  13
C----------------------------------------------------------------------MAIN  14
C                                                                      MAIN  15
C  AUTHOR                                                              MAIN  16
C     STEVEN EARLE. DEPARTMENT OF GEOLOGY. IMPERIAL COLLEGE. LONDON    MAIN  17
C  DATE                                                                MAIN  18
C     MAY 1977  (MODIFIED SEPT. 1977 AND FEB. 1978)                    MAIN  19
C  LANGUAGE:COMPUTER                                                   MAIN  20
C     FORTRAN-IV - CDC 6500 - (IMPERIAL COLLEGE COMPUTER CENTRE)       MAIN  21
C                                                                      MAIN  22
C  METHOD                                                              MAIN  23
C     THE DATA FOR ONE VARIABLE IS STORED AS A SINGLY DIMENSIONED      MAIN  24
C     ARRAY.  THE FREQUENCY DISTRIBUTION IS ANALYSED USING A HISTO-    MAIN  25
C     GRAM, AND A CUMULATIVE CURVE IS PLOTTED WITH A PROBABILITY       MAIN  26
C     SCALE AXIS.  DECOMPOSITION IS ACHEIVED BY SELECTING INFLECTION   MAIN  27
C     POINTS, THE CUMULATIVE PERCENT OF WHICH WILL BE A FUNCTION OF    MAIN  28
C     THE RELATIVE PROPORTIONS OF SUB-POPULATIONS PRESENT.             MAIN  29
C                                                                      MAIN  30
C----------------------------------------------------------------------MAIN  31
C                                                                      MAIN  32
C     THE PROGRAM IS ARRANGED AS OVERLAYS SO AS TO REDUCE CENTRAL      MAIN  33
C     PROCESSOR UNIT STORAGE REQUIREMENTS. THE MAIN OVERLAY INCLUDES   MAIN  34
C     SELECTION OF RECORDS TO BE INPUT.  WITHIN THE FIRST PRIMARY      MAIN  35
C     OVERLAY THE -ISTOGRAM IS PLOTTED AND POINTS ON THE CUMULATIVE    MAIN  36
C     CURVE ARE CALCULATED.  THE SECOND PRIMARY OVERLAY INCLUDES       MAIN  37
C     ROUTINES FOR DECOMPOSITION OF THE CUMULATIVE CURVE.              MAIN  38
C                                                                      MAIN  39
C----------------------------------------------------------------------MAIN  40
C                                                                      MAIN  41
C  OVERLAY(4,1,PPB,C,D)                                                MAIN  42
C                                                                      MAIN  43
C  PROGRAM GIRAF(INPUT=131B,OUTPUT=131B,TAPE5=INPUT,TAPE6=131B         MAIN  44
C +  TAPE7=131B,TAPE20=131B,TAPE21=131B,TAPE61=131B,TAPE66=131B)      MAIN  45
C                                                                      MAIN  46
C----------------------------------------------------------------------MAIN  47
C                                                                      MAIN  48
C  LOGICAL UNITS USED                                                  MAIN  49
C     TAPE5   INPUT FROM TERMINAL                                      MAIN  50
C     TAPE6   OUTPUT TO TERMINAL                                       MAIN  51
C     TAPE7   FILE FOR STORAGE OF STATISTICAL DATA WHICH CAN BE SAVED  MAIN  52
C             OR PRINTED BY THE USER                                   MAIN  53
C     TAPE20  FILE WHICH INCLUDES *NVAR*, THE NUMBER OF VARIABLES FOR  MAIN  54
C             WHICH DATA IS WRITTEN ON TAPE21, PLUS A 10 CHARACTER     MAIN  55
C             NAME FOR EACH VARIABLE.  (EG. (FROM COL. 1)) -           MAIN  56
C             CU                                                       MAIN  57
C             COPPER                                                   MAIN  58
C             LEAD                                                     MAIN  59
C             MAGNESIUM                                                MAIN  60
C                                                                      MAIN  61
C     TAPE21  FILE WITH A SINGLE BINARY RECORD FOR EACH VARIABLE       MAIN  62
C             INCLUDING THE NUMBER OF SAMPLE SITES *NSIT*, THE NUMBER  MAIN  63
C             OF OBSERVATIONS *NOBS*, AND THE ACTUAL DATA.  EACH       MAIN  64
C             ---------------------------------------------------------
C             RECORD WOULD THUS BE WRITTEN USING THE FOLLOWING STATE-  MAIN  65
C             MENT -                                                   MAIN  66
C                   WRITE(21) NSIT,NOBS,(DAT(I),I=1,NOBS)              MAIN  67
C             IF THERE IS NO MISSING DATA *NOBS* WILL EQUAL *NSIT*.    MAIN  68
C             OR, TAPE20 AND TAPE21 CAN BE WRITTEN USING THE ROUTINE   MAIN  69
C             *STAT3*. AS DESCRIBED BELOW                              MAIN  70
C                                                                      MAIN  71
C     TAPE61 AND TAPE66 ARE FILES USED BY ROUTINES IN THE *SIMPLE*     MAIN  72
C             LIBRARY. (SEE I.C.C.C. BULL. 6.3/6).  TAPE61 CONTAINS    MAIN  73
C             INSTRUCTIONS FOR GENERATION OF MICROFILM PLOTS.          MAIN  74
C                                                                      MAIN  75
C----------------------------------------------------------------------MAIN  76
C                                                                      MAIN  77
C  EXECUTION PROCEDURE                                                 MAIN  78
C                                                                      MAIN  79
C    THE *GIRAF* ROUTINE CAN BE STORED AS A BINARY FILE CREATED WITH   MAIN  80
C    THE FOLLOWING CONTROL STATEMENTS -                                MAIN  81
C                                                                      MAIN  82
C    MAP(N=GIRAFB)                                                     MAIN  83
C    REPLACE(G=GIRAFB)                                                 MAIN  84
C                                                                      MAIN  85
C    EXECUTION OF THE PROGRAM AT A TEKTRONIX TERMINAL WOULD THEN BE    MAIN  86
C    CARRIED OUT USING THE FOLLOWING CONTROL STATEMENTS (ASSUMING      MAIN  87
C    THAT TAPE20 AND TAPE21, AS DESCRIBED ABOVE, ALREADY EXIST AS      MAIN  88
C    LOCAL FILES: -                                                    MAIN  89
C                                                                      MAIN  90
C    GET(G=GIRAFB)                                                     MAIN  91
C    LIBFILE(S=SIMPLE7)                                                MAIN  92
C    -SIMPLE7(L=G=GIRAFB,CALFBR=EPL)                                   MAIN  93
C                                                                      MAIN  94
C    FOLLOWING EXECUTION,  MICROFILM PLOTTING INSTRUCTIONS GENER-      MAIN  95
C    ATED CAN BE PROCESSED USING THE CONTROL STATEMENTS -              MAIN  96
C                                                                      MAIN  97
C    LIBFILE(PROC61)                                                   MAIN  98
C    -PROC(61)                                                         MAIN  99
C                                                                      MAIN 100
C    A ROUTINE FOR GENERATION OF TAPE20 AND TAPE21, AND SUBSEQUENT     MAIN 101
C    EXECUTION OF *GIRAF* IS AVAILIABLE, AND CAN BE EXECTUTED AT A     MAIN 102
C    TEKTRONIX TERMINAL USING THE CONTROL STATEMENTS -                 MAIN 103
C                                                                      MAIN 104
C    GET(TAPE=* (USER'S DATA FILE NAME=*))                             MAIN 105
C    GET(START2/UN=UFBCDB)                                             MAIN 106
C    -START2                                                           MAIN 107
C                                                                      MAIN 108
C    THE PROCEDURE *START2* WILL ALLOW UP TO 500 SAMPLE SITES FOR UP   MAIN 109
C    TO 15 VARIABLES.  DATA SETS WITH UP TO 1600 SAMPLE SITES CAN BE   MAIN 110
C    PROCESSED USING THE PROCEDURE *START3* IN THE SAME MANNER.        MAIN 111
C                                                                      MAIN 112
C    IF, WITHIN ANY SESSION, EXECUTION IS TERMINATED AND THE USER      MAIN 113
C    WISHES TO CONTINUE WITH THE SAME DATA, THE FOLLOWING CONTROL      MAIN 114
C    STATEMENTS CAN BE USED -                                          MAIN 115
C                                                                      MAIN 116
C    REWIND(TAPE20,TAPE21)                                             MAIN 117
C    -SIMPLE7(L=G=GIRAFB,CALFBR=EPL)                                   MAIN 118
C                                                                      MAIN 119
C----------------------------------------------------------------------MAIN 120
C                                                                      MAIN 121
C     GRAPHICAL SUBROUTINES CALLED BY *GIRAF* ARE DESCRIBED IN ICCC    MAIN 122
C     BULL. 6.3/E AND 6.3/G.  INCLUDED ARE - START,SWITCH,SCALE2,      MAIN 123
C     PROMPT,BUFFEM,HARDCPY,NEWPAGE,PLOT,LIMAX,SYMBOL,NUMBER,XWIRES.   MAIN 124
C                                                                      MAIN 125
C----------------------------------------------------------------------MAIN 126
C                                                                      MAIN 127
C                                                                      MAIN 128
C                                                                      MAIN 129
      COMMON/AREA2/ FRED(72),CL55(72),CONC(55),PCTL(55),CPCL(250),     MAIN 130
     + CPTR(250),NTRAN,NCLL,NAME,CMND                                  MAIN 131
C                                                                      MAIN 132
C        *FRED*    PERCENTAGES FOR HISTOGRAM BINS                    MAIN 133
C        *CL55*    CONCENTRATION LOWER LIMITS FOR HISTOGRAM BINS     MAIN 134
C        *CONC*    CONCENTRATIONS FOR EACH PERCENTILE OF PROB. PLOT  MAIN 135
C        *PCTL*    PERCENTILES FOR PROB. PLOT (SEE BLOCK DATA)       MAIN 136
C        *CPCL*    CONCENTRATIONS INTERPOLATED IN EVEN INTERVALS FROM MAIN 137
C                  *CONC*                                            MAIN 138
C        *CPTR*    PERCENTILES INTERPOLATED FROM *PCTL*              MAIN 139
C        *NTRAN*   NUMBER OF LOG10 TRANSFORMATIONS OR -(NUMBER OF 10*MAIN 140
C                  TRANSFORMATIONS                                   MAIN 141
C        *NCLL*    NUMBER OF HISTOGRAM CLASSES                       MAIN 142
C        *NAME*    NAME OF CURRENT VARIABLE                          MAIN 143
C        *CMND*    CURRENT VALUE OF CONTROL COMMAND (SEE  STAT5)     MAIN 144
C                                                                      MAIN 145
      COMMON/AREA3/ NSIT,NOBS,XMEN,STDV                                MAIN 146
C                                                                      MAIN 147
C        *NSIT*    NUMBER OF SAMPLE SITES (INCLUDING MISSING DATA)   MAIN 148
C        *NOBS*    NUMBER OF OBSERVATIONS                            MAIN 149
C        *XMEN*    POPULATION MEAN                                   MAIN 150
C        *STDV*    POPULATION STANDARD DEVIATION                     MAIN 151
C                                                                      MAIN 152
      COMMON/AREA4/ NBIN,CLS1,XINC,XLM                                 MAIN 153
      DIMENSION NAMES(15)                                              MAIN 154
C                                                                      MAIN 155
C        *NBIN*    NUMBER OF HISTOGRAM CLASSES                       MAIN 156
C        *CLS1*    LOWER LIMIT OF FIRST CLASS                        MAIN 157
C        *XINC*    CLASS INTERVAL                                    MAIN 158
C        *XLM*     VALUE OF LAMBDA FOR GENERAL POWER TRANSFORM       MAIN 159
C        *NAMES*   LIST OF VARIABLE NAMES                            MAIN 160
C                                                                      MAIN 161
C                                                                      MAIN 162
      DATA NUMREC/0/                                                   MAIN 163
C                                                                      MAIN 164
C        INITIATE GRAPHICS AND LIST COMMAND OPTIONS                    MAIN 165
C                                                                      MAIN 166
      CALL START(2)                                                    MAIN 167
      CALL SWITCH(0,HARDCPY,0)                                         MAIN 168
      CALL SCALE2(1.5)                                                 MAIN 169
      CALL HELP                                                        MAIN 170
C                                                                      MAIN 171
C        INPUT INFORMATION FROM TAPE20                                 MAIN 172
C                                                                      MAIN 173
      READ(20,100) NVAR,(NAMES(J),J=1,NVAR)                            MAIN 174
  100 FORMAT(12/(A10))                                                 MAIN 175
C                                                                      MAIN 176
C        INCREMENT RECORD COUNTER, OR INITIALISE AS 1                  MAIN 177
C                                                                      MAIN 178
  110 NUMREC=NUMREC+1                                                  MAIN 179
C                                                                      MAIN 180
C        CHECK FOR END OF TAPE21 AND REWIND IF NECESSARY               MAIN 181
C                                                                      MAIN 182
      IF(NUMREC.LE.NVAR) GOTO 120                                      MAIN 183
      REWIND 21                                                        MAIN 184
      NUMREC=1                                                         MAIN 185
C                                                                      MAIN 186
C        LIST CONTENTS OF TAPE21 AND CURRENT RECORD NUMBER             MAIN 187
C                                                                      MAIN 188
  120 WRITE(6,130) NVAR                                                MAIN 189
  130 FORMAT(/16H TAPE21 CONTAINS ,I2,8H RECORDS:/)                    MAIN 190
      DO 150 J=1,NVAR                                                  MAIN 191
  150 WRITE(6,160) J,NAMES(J)                                          MAIN 192
      ---------------------------------------------------------------
  160 FORMAT(8H RECORD ,I2,3X,A10)                                     MAIN 193
      WRITE(6,170) NUMREC                                              MAIN 194
  170 FORMAT(/27H THE NEXT RECORD IS NUMBER ,I2/)                      MAIN 195
      CALL BUFFEM(-6)                                                  MAIN 196
C                                                                      MAIN 197
C        SELECT VARIABLE - OR STOP                                     MAIN 198
C                                                                      MAIN 199
C                                                                      MAIN 200
      CALL PROMPT(78HTYPE 0 TO READ THIS RECORD, OR -1 TO STOP EXECUTIOMAIN 201
     1, OR ENTER A NEW RECORD NO.:,78)                                 MAIN 202
      READ(5,*) NREC                                                   MAIN 203
      IF(NREC.EQ.0) GOTO 190                                           MAIN 204
      IF(NREC.LT.0) STOP                                               MAIN 205
C                                                                      MAIN 206
C        ADVANCE TAPE21 TO APPROPRIATE RECORD                          MAIN 207
C                                                                      MAIN 208
      REWIND 21                                                        MAIN 209
      IF(NREC.EQ.1) GOTO 185                                           MAIN 210
      DO 180 N=2,NREC                                                  MAIN 211
  180 READ(21)                                                         MAIN 212
  185 NUMREC=NREC                                                      MAIN 213
  190 NAME=NAMES(NUMREC)                                               MAIN 214
C                                                                      MAIN 215
C        LOAD HISTOGRAM OVERLAY AND BEGIN EXECUTION                    MAIN 216
C                                                                      MAIN 217
      CALL OVERLAY(5H4IPPB,1,0)                                        MAIN 218
C                                                                      MAIN 219
      IF(CMND.EQ.4HNEXT) GOTO 110                                      MAIN 220
C                                                                      MAIN 221
C        LOAD PROB. PLOT OVERLAY AND BEGIN EXECUTION                   MAIN 222
C                                                                      MAIN 223
      CALL OVERLAY(5H4IPPB,2,0)                                        MAIN 224
C                                                                      MAIN 225
      GOTO 110                                                         MAIN 226
C                                                                      MAIN 227
      END                                                              MAIN 228
      SUBROUTINE HELP                                                  MAIN 229
C                                                                      MAIN 230
C                                                                      MAIN 231
C        ROUTINE TO LIST EXECUTION CONTROL COMMANDS AND THEIR ACTION   MAIN 232
C                                                                      MAIN 233
      WRITE(6,100)                                                     MAIN 234
  100 FORMAT(                                                          MAIN 235
     A 34H COMMANDS FOR  *** GIRAF ***  ROUTINE//                      MAIN 236
     B 34H HELP  -  DISPLAY THIS BANNER      /                         MAIN 237
     C 34H END   -  STOP EXECUTION           /                         MAIN 238
     D 34H NEXT  -  SKIP TO NEXT VARIABLE    /                         MAIN 239
     E 34H LOGT  -  LOG(10) TRANSFORM DATA   /                         MAIN 240
     F 34H ALOT  -  10**X TRANSFORM DATA     /                         MAIN 241
     F 34H BTRN  -  XNEW=(XOLD**LAMBDA-1)/LAMBDA  /                    MAIN 242
     G 34H HIST  -  DRAW HISTOGRAM           /                         MAIN 243
     H 34H TEST  -  KOLMOGOROV-SMIRNOV TEST  /                         MAIN 244
     H 34H PROB  -  DRAW PROBABILITY PLOT    /                         MAIN 245
     I 34H AXES  -  LABEL PROB-PLOT AXES     /                         MAIN 246
     J 34H SUBD  -  PROCEED WITH SUBDIVISION/                          MAIN 247
     J 34H          OF PROBABILITY PLOT      /                         MAIN 248
     J 34H STAT  -  D/P STATISTICS TO TAPE7  /                         MAIN 249
     K 34H HCPY  -  GENERATE MICROFILM COPY  /                         MAIN 250
     K 34H          OF SCREEN CONTENTS       //)                       MAIN 251
C                                                                      MAIN 252
      CALL BUFFEM(-6)                                                  MAIN 253
      RETURN                                                           MAIN 254
      END                                                              MAIN 255
                                                                       MAIN 256
```

```
      BLOCK DATA                                                        MAIN 257
C                                                                       MAIN 258
C       CONTAINS DATA FOR XPCTL= - PERCENTILES FOR PROBABILITY PLOT     MAIN 259
C       (VALUES ARE SELECTED SUCH THAT WHEN EVENLY SPACED ALONG         MAIN 260
C       AN AXIS THEY WILL DEFINE A PROBABILITY SCALE)                   MAIN 261
C                                                                       MAIN 262
      COMMON/AREA2/ FREQ(72),CLSS(72),CONC(55),PCTL(55),CPCL(250),      MAIN 263
     + CPFR(250),NTRAN,NCLL,NAME,CMND                                   MAIN 264
C                                                                       MAIN 265
      DATA PCTL  /.796,1.006,1.272,1.568,1.963,2.445,3.073,3.794,4.587, MAIN 266
     1 5.422,6.488,7.636,8.094,10.592,12.394,14.168,16.327,18.681,      MAIN 267
     2 21.273,23.762,27.056,30.004,32.988,36.101,39.7,43.289,46.808,50.,MAIN 268
     3 53.382,56.711,60.3,63.899,67.013,69.896,72.945,76.238,78.727,    MAIN 269
     4 81.319,83.673,85.832,87.851,89.408,90.906,92.362,93.511,94.578,  MAIN 270
     5 95.413,96.206,96.927,97.555,98.038,98.432,98.728,98.994,99.204/  MAIN 271
C                                                                       MAIN 272
      END                                                               MAIN 273
      OVERLAY(HIPP0,1,0)                                                STAT   2
C=====================================================================  STAT   3
C                                                                       STAT   4
C       PRIMARY OVERLAY 1 - CALCULATION OF STATISTICAL PARAMETERS       STAT   5
C       FOR INITIAL POPULATION - DATA TRANSFORMATION - HISTOGRAM -      STAT   6
C       CALCULATION OF CUMULATIVE PERCENTAGES                           STAT   7
C                                                                       STAT   8
C=====================================================================  STAT   9
C                                                                       STAT  10
      PROGRAM STAT                                                      STAT  11
      COMMON/AREA1/ DAT(2500),CHISTO                                    STAT  12
C                                                                       STAT  13
C       *DATX     DATA ARRAY                                            STAT  14
C       *CHISTO=  FLAG INDICATING IF HISTOGRAM DISTRIBUTION HAS BEEN    STAT  15
C                 CALCULATED  (1 = YES, 0 = NO)                         STAT  16
C                                                                       STAT  17
      COMMON/AREA2/ FREQ(72),CLSS(72),CONC(55),PCTL(55),CPCL(250),      STAT  18
     + CPFR(250),NTRAN,NCLL,NAME,CMND                                   STAT  19
      COMMON/AREA3/ NSIT,NOBS,XMEN,STDV                                 STAT  20
      CALL STATS                                                        STAT  21
      RETURN                                                            STAT  22
      END                                                               STAT  23
      SUBROUTINE STATS                                                  STAT  24
C=====================================================================  STAT  25
C                                                                       STAT  26
C       A VECTOR OF DATA IS READ FROM TAPE21 AND KEY WORDS ARE USED     STAT  27
C       TO SELECT CONTROL OPTIONS                                       STAT  28
C                                                                       STAT  29
C=====================================================================  STAT  30
C                                                                       STAT  31
      COMMON/AREA1/ DAT(2500),CHISTO                                    STAT  32
      COMMON/AREA2/ FREQ(72),CLSS(72),CONC(55),PCTL(55),CPCL(250),      STAT  33
     + CPFR(250),NTRAN,NCLL,NAME,CMND                                   STAT  34
      COMMON/AREA3/ NSIT,NOBS,XMEN,STDV                                 STAT  35
      COMMON/AREA4/ NBIN,CLS1,XINC,XLM                                  STAT  36
C                                                                       STAT  37
      XLM=-100.0                                                        STAT  38
      CHISTO=0.                                                         STAT  39
      NTRAN=0                                                           STAT  40
C                                                                       STAT  41
C       READ CURRENT RECORD FROM TAPE21                                 STAT  42
C                                                                       STAT  43
      READ(21) NSIT,NOBS,(DAT(I),I=1,NOBS)                             STAT  44
      WRITE(6,80) NOBS,NAME                                             STAT  45
   80 FORMAT(14,24H OBSERVATIONS INPUT FOR ,A10)                        STAT  46
      CALL BUFFIN(-6)                                                   STAT  47
C                                                                       STAT  48
C       LIST CONTROL SELECTIONS AND BRANCH ON SELECTED OPTION           STAT  49
C                                                                       STAT  50
   90 CALL PROMPT(45HLBGT,ALGT,BTRN,HIST,PROB,HCPY,NEXT,END,HELP),45)   STAT  51
      READ(5,110) CMND                                                  STAT  52
  110 FORMAT(A4)                                                        STAT  53
C                                                                       STAT  54
      IF(CMND.EQ.4HEND ) STOP                                           STAT  55
      IF(CMND.EQ.4HELP) CALL HELP                                       STAT  56
      IF(CMND.EQ.4HHCPY) CALL HARDCPY                                   STAT  57
      IF(CMND.EQ.4HNEXT) RETURN                                         STAT  58
      IF(CMND.EQ.4HPROB) GOTO 150                                       STAT  59
      IF(CMND.EQ.4HLBGT) GOTO 120                                       STAT  60
      IF(CMND.EQ.4HALGT) GOTO 130                                       STAT  61
      IF(CMND.EQ.4HHIST) CALL HISTB(1)                                  STAT  62
      IF(CMND.EQ.4HBTRN) GOTO 140                                       STAT  63
      GOTO 90                                                           STAT  64
C                                                                       STAT  65
C       PERFORM APPROPRIATE TRANSFORMATION AND RETURN TO CONTROL        STAT  66
C                                                                       STAT  67
  120 CALL TLBG(NOBS)                                                   STAT  68
      NTRAN=NTRAN+1                                                     STAT  69
      GOTO 90                                                           STAT  70
C                                                                       STAT  71
  130 CALL TRLBG(NOBS)                                                  STAT  72
      NTRAN=NTRAN-1                                                     STAT  73
      GOTO 90                                                           STAT  74
C                                                                       STAT  75
  140 CALL BPTRAN(OLM,NOBS)                                             STAT  76
      GOTO 90                                                           STAT  77
C                                                                       STAT  78
C       IF HISTOGRAM HAS NOT BEEN PLOTTED, CALL HISTOGRAM ROUTINE       STAT  79
C       (TO CALCULATE FREQ. DIST.) WITH NO-PLOT FLAG                    STAT  80
C                                                                       STAT  81
  150 IF(CHISTO.EQ.0) CALL HISTB(0)                                     STAT  82
C                                                                       STAT  83
C       CALCULATE CUMULATIVE PERCENTAGES                                STAT  84
C                                                                       STAT  85
      CLSS(1)=CLS1                                                      STAT  86
      DO 160 I=2,NBIN                                                   STAT  87
      CLSS(I)=CLS1+FLOAT(I)*XINC                                        STAT  88
  160 FREQ(I)=FREQ(I)+FREQ(I-1)                                         STAT  89
C                                                                       STAT  90
C       CALCULATE CONCENTRATION FOR 250 INTERPOLATED VALUES             STAT  91
C                                                                       STAT  92
      DELCON=(CLSS(NBIN)-CLS1)/249.                                     STAT  93
      DO 170 I=1,250                                                    STAT  94
      PI=I-1                                                            STAT  95
  170 CPCL(I)=CLS1+PI*DELCON                                            STAT  96
C                                                                       STAT  97
C       CALCULATE PERCENTILE FOR 250 INTERPOLATED VALUES                STAT  98
C                                                                       STAT  99
      CALL INTRPL(55,NBIN,CLSS,FREQ,250,CPCL,CPFR)                      STAT 100
C                                                                       STAT 101
C       LINEAR INTERPOLATION OF 55 EVENLY SPACED PERCENTILES            STAT 102
C                                                                       STAT 103
      DO 180 I=1,55                                                     STAT 104
  180 CALL LINTRP(CPFR,250,CLS1,DELCON,PCTL(I),CONC(I))                 STAT 105
      RETURN                                                            STAT 106
      END                                                               STAT 107
      SUBROUTINE TLSG(NOBS)                                             STAT 108
C                                                                       STAT 109
C       LOG(10)  TRANSFORMATION                                         STAT 110
C                                                                       STAT 111
C                                                                       STAT 112
      COMMON/AREA1/ DAT(2500),CHISTO                                    STAT 113
C                                                                       STAT 114
      MBS=NOBS                                                          STAT 115
      DO 100 I=1,MBS                                                    STAT 116
C                                                                       STAT 117
C       REPLACE VALUES .LE. 0.0 WITH 0.001                              STAT 118
C                                                                       STAT 119
      IF(DAT(I).LE.0.) DAT(I)=0.01                                      STAT 120
  100 DAT(I)=ALOG10(DAT(I))                                             STAT 121
      RETURN                                                            STAT 122
      END                                                               STAT 123
      SUBROUTINE TRLBG(NOBS)                                            STAT 124
C                                                                       STAT 125
C       INVRX TRANSFORMATION                                            STAT 126
C                                                                       STAT 127
      COMMON/AREA1/ DAT(2500),CHISTO                                    STAT 128
      MBS=NOBS                                                          STAT 129
C                                                                       STAT 130
      DO 100 I=1,MBS                                                    STAT 131
  100 DAT(I)=10.0**DAT(I)                                               STAT 132
      RETURN                                                            STAT 133
      END                                                               STAT 134
      SUBROUTINE BPTRAN(OLM,NOBS)                                       STAT 135
C                                                                       STAT 136
C       GENERAL POWER TRANSFORMATION USING METHOD OF BOX AND COX        STAT 137
C       (SEE J. R.STAT. SOC (B) - VOL. 26)                              STAT 138
C                                                                       STAT 139
      COMMON/AREA1/ DAT(2500),CHISTO                                    STAT 140
      DATA SMALL/1.0E-20/                                               STAT 141
C                                                                       STAT 142
      MBS=NOBS                                                          STAT 143
C                                                                       STAT 144
C       READ VALUE FOR LAMBDA                                           STAT 145
C                                                                       STAT 146
      CALL PROMPT(12HENTER LAMBDA,12)                                   STAT 147
      READ(5,*) XLM                                                     STAT 148
C                                                                       STAT 149
C       IF LAMBDA=0. PERFORM LOG TRANSFORMATION                         STAT 150
C                                                                       STAT 151
      IF(ABS(XLM).GT.SMALL) GOTO 100                                    STAT 152
      CALL TLBG(NOBS)                                                   STAT 153
      XLM=XLM                                                           STAT 154
      RETURN                                                            STAT 155
C                                                                       STAT 156
  100 FXLM=1.0/XLM                                                      STAT 157
      DO 200 I=1,MBS                                                    STAT 158
      X=DAT(I)                                                          STAT 159
C                                                                       STAT 160
C       IF X IS 0 OR LESS DO NOT TRANSFORM                              STAT 161
C                                                                       STAT 162
      IF(X.LT.SMALL) GOTO 200                                           STAT 163
      DAT(I)=(X**XLM-1.0)*FXLM                                          STAT 164
  200 CONTINUE                                                          STAT 165
      XLM=XLM                                                           STAT 166
      RETURN                                                            STAT 167
      END                                                               STAT 168
C                                                                       STAT 169
      SUBROUTINE HISTB(IPLT)                                            HIST   2
C=====================================================================  HIST   3
C                                                                       HIST   4
C       ROUTINE TO CALCULATE LIMITS OF HISTOGRAM CLASSES AND            HIST   5
C       ASSIGN DATA VALUES TO APPROPRIATE BINS                          HIST   6
C                                                                       HIST   7
C       ARGUMENT                                                        HIST   8
C         *IPLT=    SWITCH INDICATING IF HISTOGRAM SHOULD BE DRAWN      HIST   9
C                   (1=YES, 0=NO)                                       HIST  10
C                                                                       HIST  11
C=====================================================================  HIST  12
C                                                                       HIST  13
      COMMON/AREA1/ ZED(2500),CHISTO                                    HIST  14
      COMMON/AREA2/ FREQ(72),CLSS(72),CONC(55),PCTL(55),CPCL(250),      HIST  15
     + CPFR(250),NTRAN,NCLL,NAME,CMND                                   HIST  16
      COMMON/AREA3/ NSIT,NOBS,SMEAN,STDV                                HIST  17
      COMMON/AREA4/ NBIN,CLS1,XINC,XLM                                  HIST  18
C                                                                       HIST  19
      CHISTO=1.                                                         HIST  20
      XMIN=1.0E20                                                       HIST  21
C                                                                       HIST  22
C       CALCULATE MEAN AND STANDARD DEVIATION                           HIST  23
C                                                                       HIST  24
      SUMX=SSQX=0.                                                      HIST  25
      DO 100 I=1,NOBS                                                   HIST  26
      DATT=ZED(I)                                                       HIST  27
      IF(DATT.LT.XMIN) XMIN=DATT                                        HIST  28
      SUMX=SUMX+DATT                                                    HIST  29
  100 SSQX=SSQX+DATT*DATT                                               HIST  30
C                                                                       HIST  31
      OBS=NOBS                                                          HIST  32
      SMEAN=SUMX/OBS                                                    HIST  33
      STDV=SQRT((OBS*SSQX-SUMX*SUMX)/(OBS*(OBS-1.)))                    HIST  34
C                                                                       HIST  35
C       SET DEFAULT OF 30 CLASSES FOR NO-PLOT MODE                      HIST  36
C                                                                       HIST  37
      NBIN=24                                                           HIST  38
      IF(IPLT.EQ.0) GOTO 101                                            HIST  39
C                                                                       HIST  40
C       INPUT NO. OF CLASSES DESIRED AND CHECK FOR ALLOWABLE VALUES     HIST  41
C                                                                       HIST  42
      CALL PROMPT(45HENTER NO. OF HISTOGRAM CLASSES (5,12,18,..,72),45) HIST  43
      READ(5,*) NBIN                                                    HIST  44
C                                                                       HIST  45
  101 XNCL=NBIN                                                         HIST  46
      XNCL=AINT((XNCL/6.)*6.                                            HIST  47
      IF(XNCL.GT.72.) XNCL=72.                                          HIST  48
      IF(XNCL.LT.6.) XNCL=6.                                            HIST  49
C                                                                       HIST  50
C       CALCULATE INTERVAL FOR RANGE OF 6 STANDARD DEVIATIONS           HIST  51
C                                                                       HIST  52
      XINC=STDV*6./XNCL                                                 HIST  53
C                                                                       HIST  54
C       FIRST CLASS IS MEAN MINUS 3 STANDARD DEVIATIONS                 HIST  55
C                                                                       HIST  56
      CLS1=SMEAN-3.0*STDV                                               HIST  57
C                                                                       HIST  58
C       SHIFT FIRST CLASS FOR POSITIVELY SKEWED DISTRIBUTIONS           HIST  59
C                                                                       HIST  60
      XLIM=SMEAN-2.0*STDV                                               HIST  61
      IF(XMIN.GE.XLIM) CLS1=XLIM                                        HIST  62
      XLIM=SMEAN-STDV                                                   HIST  63
      IF(XMIN.GE.XLIM) CLS1=XLIM                                        HIST  64
      XLIM=SMEAN-STDV                                                   HIST  65
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      IF(XMAX.GE.XLIM) CLS=XLIM                                         HIST  66
      MB=MBIN                                                           HIST  67
C                                                                       HIST  68
C        ASSIGN VALUES TO CLASSES                                       HIST  69
C                                                                       HIST  70
      DO 102 K=1,MB                                                     HIST  71
  102 FREQ(K)=0.                                                        HIST  72
      DO 103 I=1,NOBS                                                   HIST  73
      MCLS=INT((XRED(I)-CLS1)/XINC)+1.                                  HIST  74
      IF(MCLS.GT.MBIN) MCLS=MBIN                                        HIST  75
      IF(MCLS.LT.1) MCLS=1                                              HIST  76
  103 FREQ(MCLS)=FREQ(MCLS)+1.                                          HIST  77
C                                                                       HIST  78
C        CALCULATE PERCENT FREQUENCY MIDPOINT FOR EACH CLASS            HIST  79
C                                                                       HIST  80
      CLS1=CLS1-XINCR0.5                                                HIST  81
      DO 104 K=1,MB                                                     HIST  82
      FREQ(K)=100.*FREQ(K)/NOBS                                         HIST  83
  104 CLSS(K)=CLSS1+FLOAT(K-1)*XINC                                     HIST  84
C                                                                       HIST  85
C        PLOT HISTOGRAM IF REQUESTED                                    HIST  86
C                                                                       HIST  87
      IF(IPLT.EQ.1) CALL GHIST                                          HIST  88
C                                                                       HIST  89
      RETURN                                                            HIST  90
      END                                                               HIST  91
      SUBROUTINE GHIST                                                  HIST  92
C                                                                       HIST  93
C        HISTOGRAM PLOTTING ROUTINE                                     HIST  94
C                                                                       HIST  95
C                                                                       HIST  96
      COMMON/AREA2/ FREQ(72),CLSS(72),CONC(55),PCTL(55),CPCL(250),      HIST  97
     + CPF(250),XTRAN,NCLL,NAME,CMND                                    HIST  98
      COMMON/AREA3/ NSET,NOBS,SMEAN,STDV                                HIST  99
      COMMON/AREA4/ MBIN,CLS1,XINC,XLM                                  HIST 100
C                                                                       HIST 101
C        CALCULATE NUMBERING INTERVAL AND LOWER LIMIT OF FIRST BIN      HIST 102
C                                                                       HIST 103
      XOINC=FLOAT(MB/5)*XINC                                            HIST 104
      SVALC=CLSS(1)-0.5*XINC)                                           HIST 105
C                                                                       HIST 106
C        FIND MAXIMUM FREQUENCY PERCENT                                 HIST 107
C                                                                       HIST 108
      YFREQ=0.0                                                         HIST 109
      DO 100 I=1,MBIN                                                   HIST 110
      IF(FREQ(I).GT.YFREQ) YFREQ=FREQ(I)                                HIST 111
  100 CONTINUE                                                          HIST 112
C                                                                       HIST 113
C        READ MAXIMUM HISTOGRAM PERCENT, OR CALCULATE DEFAULT VALUE     HIST 114
C        AS NEXT HIGHEST MULTIPLE OF 10                                 HIST 115
C                                                                       HIST 116
      WRITE(5,99) YFREQ                                                 HIST 117
   99 FORMAT('MAXIMUM FREQ. IS ',F6.2/                                  HIST 118
     + 'ENTER MAX. HIST. PCT. OR 0.0 FOR DEFAULT MAX.')                 HIST 119
      CALL BUFFER(-6)                                                   HIST 120
      READ(5,*) YFRQ                                                    HIST 121
      IF(YFRQ.GT.0.1) YFREQ=YFRQ                                        HIST 122
C                                                                       HIST 123
  101 YFRQ=INT(YFREQ/10.)                                               HIST 124
      IF((YFRQ*10.).NE.YFREQ) YFRQ=YFRQ+1.0                             HIST 125
      INTY=YFRQ                                                         HIST 126
      ALNY=10./YFRQ                                                     HIST 127
C                                                                       HIST 128
C        ADVANCE FRAME AND MOVE TO START OF HISTOGRAM                   HIST 129
C                                                                       HIST 130
      CALL NEWPAGE                                                      HIST 131
      CALL PLOT(0.5,4.0,-3)                                             HIST 132
C                                                                       HIST 133
C        DRAW AXES                                                      HIST 134
C                                                                       HIST 135
      CALL AXIS(0.0,0.0,12.0,0,SVAL,XOINC,1,1,1,2,1)                    HIST 136
      CALL AXIS(12.0,0.0,2,ALNY,INTY,0.,10.,5,-1,1,-1,1)                HIST 137
      CALL AXIS(0.0,0.0,2,ALNY,INTY,0.,10.,5,2,2,-1,1)                  HIST 138
      CALL SYMBOL(-0.8,5.5,0.49,27,0.0,-1)                              HIST 139
      CALL PLOT(0.0,0.0,-3)                                             HIST 140
C                                                                       HIST 141
C        DETERMINE NUMBER OF SCANLINES FOR EACH BAR AND BAR INTERVAL    HIST 142
C                                                                       HIST 143
      NSCAN=600./MBIN                                                   HIST 144
      XINT=12.0/FLOAT(MBIN*NSCAN)                                       HIST 145
      XOINT=XINT*FLOAT(NSCAN)                                           HIST 146
C                                                                       HIST 147
C        CALCULATE BAR HEIGHT IN INCHES AND THEN DRAW BAR               HIST 148
C                                                                       HIST 149
      DO 102 M=1,MBIN                                                   HIST 150
      FRQ=FREQ(M)/YFRQ                                                  HIST 151
      IF(FRQ.LT.1.0E-3) GOTO 104                                        HIST 152
      DO 103 M=1,NSCAN                                                  HIST 153
      CALL PLOT(0.0,FRQ,-2)                                             HIST 154
  102 CALL PLOT(XOINT,-FRQ,-2)                                          HIST 155
      GOTO 103                                                          HIST 156
  104 CALL PLOT(XOINT,0.0,-2)                                           HIST 157
  103 CONTINUE                                                          HIST 158
      CALL PLOT(-12.0,-2.0,-3)                                          HIST 159
C                                                                       HIST 160
C        LABEL HISTOGRAM                                                HIST 161
C                                                                       HIST 162
      CALL SYMBOL(0.0,0.0,.49,NAME,0.0,10)                              HIST 163
      CALL SYMBOL(0.0,-0.50,.28,22HNO. OF OBSERVATIONS = ,0.0,22)       HIST 164
      NOBS=NOBS                                                         HIST 165
      CALL NUMBER(5.2,-0.50,.28,NOBS,0.0,-1)                            HIST 166
      CALL SYMBOL(0.0,-1.00,.28,28HMEAN =                STD DEV = ,0.0,28) HIST 167
      CALL NUMBER(1.98,-1.0,.28,SMEAN,0.0,2)                            HIST 168
      CALL NUMBER(7.8,-1.0,.28,STDV,0.0,3)                              HIST 169
C                                                                       HIST 170
C        INDICATE TRANSFORMATION USED                                   HIST 171
C                                                                       HIST 172
      IF(NTRAN) 201,204,202                                             HIST 173
C                                                                       HIST 174
  201 CALL SYMBOL(0.0,-1.5,0.28,26HNO. OF Z**10 TRANSFORMS = ,0.0,26)   HIST 175
      GOTO 203                                                          HIST 176
  202 CALL SYMBOL(0.0,-1.50,.28,26HNO. OF LOG10 TRANSFORMS = ,0.0,26)   HIST 177
C                                                                       HIST 178
  203 TRANS=ABS(FLOAT(NTRAN))                                           HIST 179
      CALL NUMBER(7.28,-1.5,.28,TRAN,0.0,-1)                            HIST 180
      RETURN                                                            HIST 181
C                                                                       HIST 182
  204 IF(NLM.EQ.-100.) RETURN                                           HIST 183
      CALL SYMBOL(0.0,-2.25,0.35,16HTRANSFORM IS X**,0.0,16)            HIST 184
      CALL NUMBER(5.6,-2.25,0.35,XLM,0.0,2)                             HIST 185
      RETURN                                                            HIST 186
      END                                                               HIST 187
      SUBROUTINE INTPL(IU,L,X,Y,N,U,V)                                  HIST 188
C                                                                       INTP   2
C-----------------------------------------------------------------------INTP   3
C                                                                       INTP   4
C     INTERPOLATION OF A SINGLE VALUED FUNCTION                         INTP   5
C                                                                       INTP   6
C     THIS SUBROUTINE INTERPOLATES, FROM VALUES OF THE FUNCTION         INTP   7
C     GIVEN AS ORDINATES (Y-VALUES) OF INPUT DATA POINTS IN AN X-Y PLANE INTP   8
C     AND FOR A GIVEN SET OF ABSCISSAS (X-VALUES), THE VALUES OF        INTP   9
C     A SINGLE VALUED FUNCTION Y = Y(X)                                 INTP  10
C                                                                       INTP  11
C     AUTHOR -                                                          INTP  12
C           H. AKIMA                                                    INTP  13
C     REFERENCE -                                                       INTP  14
C           ALGORITHM 433, COMM. A.C.M., 15 (10), 914, 1972)            INTP  15
C     METHOD -                                                          INTP  16
C           A SMOOTH CURVE WILL PASS THROUGH ALL THE GIVEN DATA POINTS   INTP  17
C           AND WILL APPEAR SMOOTH AND NATURAL.  IT IS BASED ON PIECEWISE INTP  18
C           FITTING OF 3-RD DEGREE POLYNOMIALS.  IT IS INVARIANT UNDER A INTP  19
C           LINEAR SCALE TRANSFORMATION OF THE COORDINATE SYSTEM.       INTP  20
C     ARGUMENTS -                                                       INTP  21
C           IU = LOGICAL UNIT NUMBER OF OUTPUT UNIT                     INTP  22
C           L = NUMBER OF DATA POINTS (MUST BE AT LEAST 2)              INTP  23
C           X = ARRAY OF DIMENSION L, STORING THE X VALUES OF INPUT DATA INTP  24
C               POINTS (IN ASCENDING ORDER)                             INTP  25
C           Y = ARRAY OF DIMENSION L STORING THE Y VALUES OF THE INPUT  INTP  26
C               DATA POINTS                                             INTP  27
C           N = NUMBER OF POINTS AT WHICH INTERPOLATION OF THE Y-VALUE   INTP  28
C               (ORDINATE) IS DESIRED (MUST BE AT LEAST 1)              INTP  29
C           U = ARRAY OF DIMENSION N STORING THE X-VALUES (ABSCISSAS)   INTP  30
C               OF THE DESIRED POINTS                                   INTP  31
C           V = ARRAY OF DIMENSION N CONTAINING THE INTERPOLATED POINTS  INTP  32
C     NOTE -                                                            INTP  33
C           WHEN THE FUNCTION TO BE INTERPOLATED IS PERIODIC, AND A SET  INTP  34
C           OF L (P) DATA POINTS COVERS THE WHOLE PERIOD, 2 ADDITIONAL   INTP  35
C           DATA POINTS SHOULD BE ADDED AT EACH END AND A SET OF L(P) + 4 INTP  36
C           DATA POINTS SHOULD BE GIVEN AS THE INPUT DATA POINTS TO THIS  INTP  37
C           SUBROUTINE.                                                 INTP  38
C                                                                       INTP  39
C-----------------------------------------------------------------------INTP  40
C                                                                       INTP  41
C                                                                       INTP  42
C                                                                       INTP  43
      DIMENSION X(L),Y(L),U(N),V(N)                                     INTP  44
      EQUIVALENCE (P0,X3),(Q0,Y3),(Q1,T3)                               INTP  45
      EQUIVALENCE (UK,DX),(H1,X2),(A1,H1),(H2,X4),(A2,H2),(H3,X5),(H4,X6),INTP  46
     + (Y2,W2),(H4,Q2),(Y5,W3),(Q3,W4)                                  INTP  47
      REAL M1,M2,M3,M4,M5                                               INTP  48
C                                                                       INTP  49
   10 LO = L                                                            INTP  50
      LM1 = LO-1                                                        INTP  51
      LM2 = LM1-1                                                       INTP  52
      LP1 = LO + 1                                                      INTP  53
      MO = M                                                            INTP  54
      IF (LM2 .LT. 0) GO TO 90                                          INTP  55
      IF (MO .LE. 0) GO TO 91                                           INTP  56
      DO 11 I=2,LO                                                      INTP  57
      IF (X(I-1)-X(I)) 11,95,95                                         INTP  58
   11 CONTINUE                                                          INTP  59
      IPV = 0                                                           INTP  60
      DO 80 K=1,MO                                                      INTP  61
      UK = U(K)                                                         INTP  62
C     LOCATE THE DESIRED POINT                                          INTP  63
   20 IF (UK2 .EQ. 0) GO TO 27                                          INTP  64
      IF (UK .GE. X(LO)) GO TO 26                                       INTP  65
      IF (UK .LT. X(1)) GO TO 25                                        INTP  66
      IMN = 2                                                           INTP  67
      IMX = LO                                                          INTP  68
   21 I = (IMN + IMX)/2                                                 INTP  69
      IF (UK .GE. X(I)) GO TO 23                                        INTP  70
C-----------------------------------------------------------------------INTP  71
   22 IMX = I                                                           INTP  72
      GO TO 24                                                          INTP  73
   23 IMN = I+1                                                         INTP  74
   24 IF (IMX .GT. IMN) GO TO 21                                        INTP  75
      I = IMX                                                           INTP  76
      GO TO 30                                                          INTP  77
   25 I = 1                                                             INTP  78
      GO TO 30                                                          INTP  79
   26 I = LP1                                                           INTP  80
      GO TO 30                                                          INTP  81
   27 I = 2                                                             INTP  82
   30 IF (I.EQ.IPV) GO TO 70                                            INTP  83
      IPV = I                                                           INTP  84
C     PICK UP NECESSARY X AND Y VALUES AND ESTIMATE THEM IF NECESSARY   INTP  85
   40 J = I                                                             INTP  86
      IF (J .EQ. 1) J=2                                                 INTP  87
      IF (J .EQ. LP1) J=LO                                              INTP  88
      X3 = X(J-1)                                                       INTP  89
      Y3 = Y(J-1)                                                       INTP  90
      X4 = X(J)                                                         INTP  91
      Y4 = Y(J)                                                         INTP  92
      A3 = X4 - X3                                                      INTP  93
      M3 = (Y4 - Y3)/A3                                                 INTP  94
      IF (LM2 .EQ. 0) GO TO 43                                          INTP  95
      IF (J .EQ. 2) GO TO 41                                            INTP  96
      X2 = X(J-2)                                                       INTP  97
      Y2 = Y(J - 2)                                                     INTP  98
      A2 = X3 - X2                                                      INTP  99
      M2 = (Y3 - Y2)/A2                                                 INTP 100
      IF (J .EQ. LO) GO TO 42                                           INTP 101
   41 X5 = X(J + 1)                                                     INTP 102
      Y5 = Y(J + 1)                                                     INTP 103
      A4 = X5 - X4                                                      INTP 104
      M4 = (Y5 - Y4)/A4                                                 INTP 105
      IF (J .EQ. 2) M2 = M3 + M3 - M4                                   INTP 106
      GO TO 46                                                          INTP 107
   42 M4 = M3 + M3 - M2                                                 INTP 108
      GO TO 46                                                          INTP 109
   43 M2 = M3                                                           INTP 110
      M4 = M3                                                           INTP 111
      IF (J .LE. 3) GO TO 46                                            INTP 112
      A1 = X2 - X(J-3)                                                  INTP 113
      M1 = (Y2 - Y(J-3))/A1                                             INTP 114
      GO TO 47                                                          INTP 115
   46 M1 = M2 + M2 - M3                                                 INTP 116
   47 IF (J .GE. LM1) GO TO 48                                          INTP 117
      A5 = X(J+2) - X5                                                  INTP 118
      M5 = (Y(J+2) - Y5)/A5                                             INTP 119
      GO TO 50                                                          INTP 120
   48 M5 = M4 + M4 - M3                                                 INTP 121
C     NUMERICAL DIFFERENTIATION                                         INTP 122
   50 IF (I .EQ. LP1) GO TO 52                                          INTP 123
      W3 = ABS(M4 - M3)                                                 INTP 124
      W2 = ABS(M2-M1)                                                   INTP 125
      SW = W2 + W3                                                      INTP 126
      IF (SW .NE. 0.0) GO TO 51                                         INTP 127
      W2 = 0.5                                                          INTP 128
      W3 = 0.5                                                          INTP 129
      SW = 1.0                                                          INTP 130
   51 T3 = (W2*M2 + W3*M3)/SW                                           INTP 131
      IF (I .EQ. 1) GO TO 54                                            INTP 132
   52 W3 = ABS(M5-M4)                                                   INTP 133
      W2 = ABS(M3 - M2)                                                 INTP 134
      SW = W3 + W4                                                      INTP 135
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      IF (X .NE. C.0) GO TO 53                                          INTP 135
      A = 0.5                                                           INTP 136
      B = 0.5                                                           INTP 137
      C = 0.0                                                           INTP 138
   53 A = 0.5*C + (Y-YC)/SX                                             INTP 139
      IF (I .NE. LP1) GO TO 60                                          INTP 140
      A4 = A                                                            INTP 141
      A3 = B + A3                                                       INTP 142
      A2 = 0.5*(M4+M5-A2*(A2-A3)*(M2-M3)/(SA*SA))                       INTP 143
      A1 = A                                                            INTP 144
      A4 = A4                                                           INTP 145
      A3 = A3                                                           INTP 146
      A2 = A2                                                           INTP 147
      A1 = A1                                                           INTP 148
   54 A = 0.5*C + B4                                                    INTP 149
      A4 = 0.5*(M2-A4*(A3-A4)*(M3-M4)/(SA*SA)) - B4                     INTP 150
      A3 = A3 - M2*A4                                                   INTP 151
      A2 = A2                                                           INTP 152
      A1 = A1                                                           INTP 153
C     DETERMINATION OF THE COEFFICIENTS                                 INTP 154
   60 Q1 = (2.0*(M3-T3) + M3 - T4)/A3                                   INTP 155
      Q2 = (-M3-M3+T3+T4)/(A3*A3)                                       INTP 156
C     COMPUTATION OF THE POLYNOMIAL                                     INTP 157
      DX = UX - PC                                                      INTP 158
      V(K) = Q0 + DX*(Q1 + DX*(Q2 + DX*Q3))                             INTP 159
      RETURN                                                            INTP 160
C     ERROR EXIT                                                        INTP 161
   90 WRITE (IU,2090)                                                   INTP 162
      GO TO 99                                                          INTP 163
   91 WRITE (IU,2091)                                                   INTP 164
      GO TO 99                                                          INTP 165
   95 WRITE (IU,2095)                                                   INTP 166
      GO TO 97                                                          INTP 167
   96 WRITE (IU,2096)                                                   INTP 168
   97 WRITE (IU,2097) I,X(I)                                            INTP 169
   99 WRITE (IU,2099) LD,MD                                             INTP 170
      RETURN                                                            INTP 171
 2090 FORMAT(1X,22H ****   L = 1 OR LESS./)                            INTP 172
 2091 FORMAT(1X,22H ****   N = 0 OR LESS./)                            INTP 173
 2095 FORMAT(1X,27H ****   IDENTICAL X VALUES./)                       INTP 174
 2096 FORMAT(1X,23H ****   X VALUES OUT OF SEQUENCE./)                 INTP 175
 2097 FORMAT(5H    I =,I7,10X,6HX(I) =,E12.3)                          INTP 176
 2099 FORMAT(5H    L =,I7,10X,3HN =,I7/36H ERROR DETECTED IN ROUTINE   INTP 177
     +INTRPL)                                                           INTP 178
      END                                                               INTP 179
      SUBROUTINE LINTRP(CPR,MM,CLS1,DELTA,PTLE,CONC)                    INTP 180
C     ------------------------------------------------------------------INTP 181
C                                                                       INTP 182
C                                                                       INTP 183
C        LINEAR INTERPOLATION OF PERCENTILE LIST                        INTP 184
C                                                                       INTP 185
C                                                                       INTP 186
C                                                                       INTP 187
C        *CPR*    ARRAY OF PERCENTILES TO BE INTERPRETED FROM          INTP 188
C        *MM*     LENGTH OF *CPR*                                      INTP 189
C        *CLS1*   FIRST VALUE OF CORRESPONDING ARRRAY OF CONCENTRATIONS INTP 190
C        *DELTA*  INCREMENT OF CONCENTRATION ARRAY                     INTP 191
C        *PTLE*   PERCENTILE VALUE TO INTERPOLATED                     INTP 192
C        *CONC*   CORRESPONDING CONCENTRAION VALUE                     INTP 193
C                                                                       INTP 194
C     ------------------------------------------------------------------INTP 195
C                                                                       INTP 196
      DIMENSION CPR(MM)                                                 INTP 197
      MMM=MM                                                            INTP 198
      PCTL=PTLE                                                         INTP 199
C                                                                       INTP 200
C        TEST FOR *PTLE* OUTSIDE RANGE OF *CPR*                         INTP 201
C                                                                       INTP 202
      IF (PCTL.LT.CPR(1)) GOTO 201                                      INTP 203
      IF (PCTL.GT.CPR(M)) GOTO 301                                      INTP 204
C                                                                       INTP 205
C        LOCATE UPPER BOUNDING ELEMENT OF *CPR*                         INTP 206
C                                                                       INTP 207
      DO 101 I=2,M                                                      INTP 208
      IF (CPR(I).LT.PCTL) GOTO 101                                      INTP 209
      INDX=I                                                            INTP 210
      GOTO 102                                                          INTP 211
  101 CONTINUE                                                          INTP 212
      INDX=CPR(INDX                                                     INTP 213
      CPO=CPR(INDX-1)                                                   INTP 214
C                                                                       INTP 215
C        DETERMINE PERCENT INCREMENT AND RELATIVE POSITION OF *PTLE*    INTP 216
C                                                                       INTP 217
      DEL_CP=CP1-CPO                                                    INTP 218
      FRACT=(PCTL-CPO)/DELCP                                            INTP 219
C                                                                       INTP 220
C        CALCULATE *CONC*                                               INTP 221
C                                                                       INTP 222
      WHOLE=INDX-2                                                      INTP 223
      CONC=CLS1+(WHOLE+FRACT)*DELTA                                     INTP 224
      RETURN                                                            INTP 225
C                                                                       INTP 226
C        SET FLAG FOR *PTLE* VALUE BELOW RANGE OF *CPR*                 INTP 227
C                                                                       INTP 228
  201 CONC=-99.                                                         INTP 229
      RETURN                                                            INTP 230
C                                                                       INTP 231
C        CALCULATE *CONC* FOR *PTLE* ABOVE RANGE                        INTP 232
C                                                                       INTP 233
  301 CP1=CPR(M)                                                        INTP 234
      INDX=1                                                            INTP 235
  302 CPO=CPR(M-INDX)                                                   INTP 236
      IF (CPO.LT.CP1) GOTO 303                                          INTP 237
      INDX=INDX+1                                                       INTP 238
      GOTO 302                                                          INTP 239
  303 DEL_CP=CP1-CPO                                                    INTP 240
      FRACT=(PCTL-CP1)/DELCP                                            INTP 241
      XMM=M-1                                                           INTP 242
      CONC=CLS1+XMM*DELTA)+(FRACT*DELTA)*FLOAT(INDX)                    INTP 243
C                                                                       INTP 244
      RETURN                                                            INTP 245
      END                                                               INTP 246
      OVERLAY(IPP8,2,0)                                                 INTP 247
C     ------------------------------------------------------------------INTP 248
C                                                                       PR08   2
C                                                                       PR08   3
C                                                                       PR08   4
C        PRIMARY OVERLAY 2.  DISPLAY PROBABILITY PLOT, ACCEPT INPUT OF  PR08   5
C        INFLECTION POINTS AND ESTIMATE DISTRIBUTION OF SUB-POPULATIONS PR08   6
C                                                                       PR08   7
C                                                                       PR08   8
C     ------------------------------------------------------------------PR08   9
C                                                                       PR08  10
      PROGRAM PR08                                                      PR08  11
      COMMON/AREA2/ FREQ(72),CLSS(72),CONC(55),PCTL(55),CPCL(250),      PR08  12
     + CPFR(250),NTRAN,NCLL,NAME,CMND                                   PR08  13
      COMMON/AREA3/ MSIT,MOBS,SMEAN,STDV                                PR08  14
      CALL OPR08                                                        PR08  15
      RETURN                                                            PR08  16
      END                                                               PR08  17
      SUBROUTINE OPR08                                                  PR08  18
C     ------------------------------------------------------------------PR08  19
C                                                                       PR08  20
C                                                                       PR08  21
C        ROUTINE TO ACCEPT INPUT OF CONTROL OPTIONS FOR POPULATION SUB- PR08  22
C        DIVISIONS, AND BRANCH AS REQUESTED                             PR08  23
C                                                                       PR08  24
C                                                                       PR08  25
      COMMON/AREA2/ FREQ(72),CLSS(72),CONC(55),PCTL(55),CPCL(250),      PR08  26
     + CPFR(250),NTRAN,NCLL,NAME,CMND                                   PR08  27
      COMMON/AREA3/ MSIT,MOBS,SMEAN,STDV                                PR08  28
      COMMON/AREA5/ PROP(5),SLOP(5),FIRST(5),CON(5,55),PC(5,55),KK(5),  PR08  29
     + FLEX(5),MSUB                                                     PR08  30
C                                                                       PR08  31
C        *PROP*   PROPORTIONS OF SUB-POPULATIONS                        PR08  32
C        *SLOP*   SLOPES OF LINES DEFINING SUB-POPULATIONS              PR08  33
C        *FIRST*  INTERCEPT WITH LEFT-HAND AXIS OF LINES DEFINING       PR08  34
C                 SUB-POPULATIONS                                       PR08  35
C        *CON*    CONCENTRATIONS OF POINTS DEFINING SUB-POPULATIONS     PR08  36
C        *PC*     PERCENTILES OF POINTS DEFINING SUB-POPULATIONS        PR08  37
C        *KK*     NUMBER OF POINTS DEFINING EACH SUB-POPULATIONS        PR08  38
C        *FLEX*   PERCENTILES OF INFLECTION POINTS                      PR08  39
C        *MSUB*   NUMBER OF SUB-POPULATIONS                             PR08  40
C                                                                       PR08  41
C     ------------------------------------------------------------------PR08  42
C                                                                       PR08  43
      MSUB=1                                                            PR08  44
C                                                                       PR08  45
C        DRAW PROBABILITY PLOT                                          PR08  46
C                                                                       PR08  47
  100 CALL PPLOT                                                        PR08  48
C                                                                       PR08  49
C        ACCEPT CONTROL COMMAND AND BRANCH ACCORDINGLY                  PR08  50
C                                                                       PR08  51
  105 CALL PROMPT(35HTEST,SUBD,PROB,AXES,NEXT,STAT,HCPY),36)            PR08  52
      READ(5,110) CMC                                                   PR08  53
  110 FORMAT(A4)                                                        PR08  54
C                                                                       PR08  55
      IF (CMND.EQ.4HEND ) STOP                                          PR08  56
      IF (CMND.EQ.4HPROB) GOTO 100                                      PR08  57
      IF (CMND.EQ.4HNEXT) RETURN                                        PR08  58
      IF (CMND.EQ.4HSTAT) GOTO 120                                      PR08  59
      IF (CMND.EQ.4HHELP) CALL HELP                                     PR08  60
      IF (CMND.EQ.4HAXES) CALL FRAME(1)                                 PR08  61
      IF (CMND.EQ.4HTEST) CALL KSTEST                                   PR08  62
      IF (CMND.EQ.4HHCPY) CALL HARDCPY                                  PR08  63
      IF (CMND.NE.4HSUB0) GOTO 105                                      PR08  64
C                                                                       PR08  65
      CALL FLEXX                                                        PR08  66
      GOTO 105                                                          PR08  67
C                                                                       PR08  68
  120 CALL STATBP(7)                                                    PR08  69
      GOTO 105                                                          PR08  70
      END                                                               PR08  71
      SUBROUTINE PPLOT                                                  PR08  72
C     ------------------------------------------------------------------PR08  73
C                                                                       PR08  74
C                                                                       PR08  75
C        ROUTINE TO DRAW PROBABILITY PLOT                               PR08  76
C                                                                       PR08  77
C                                                                       PR08  78
C                                                                       PR08  79
      COMMON/AREA2/ FREQ(72),CLSS(72),CONC(55),PCTL(55),CPCL(250),      PR08  80
     + CPFR(250),NTRAN,NCLL,NAME,CMND                                   PR08  81
      COMMON/AREA3/ MSIT,MOBS,SMEAN,STDV                                PR08  82
      COMMON/AREA5/ PROP(5),SLOP(5),FIRST(5),CON(5,55),PC(5,55),KK(5),  PR08  83
     + FLEX(5),MSUB                                                     PR08  84
      COMMON/AREA6/ SETMIN,YINC,IMIN,YSCALE                             PR08  85
C                                                                       PR08  86
C        *SETMIN*  LOWEST VALUE ON Y-AXIS                               PR08  87
C        *YINC*    Y-AXIS INCREMENT                                     PR08  88
C        *IMIN*    INDEX OF LOWEST DEFINED ELEMENT OF *CONC*            PR08  89
C        *YSCALE*  CONCENTRATION TO INCHES SCALER FOR Y-AXIS            PR08  90
C                                                                       PR08  91
C     ------------------------------------------------------------------PR08  92
C                                                                       PR08  93
      DO 50 I=1,55                                                      PR08  94
      IMIN=I                                                            PR08  95
C                                                                       PR08  96
C        DETERMINE FIRST DEFINED ELEMENT OF *CONC*                      PR08  97
C                                                                       PR08  98
      IF (CONC(I).NE.-88.0) GOTO 60                                     PR08  99
   50 CONTINUE                                                          PR08 100
C                                                                       PR08 101
C        INCREASE LENGTH OF Y-AXIS BY 10 PERCENT EITHER WAY             PR08 102
C                                                                       PR08 103
   60 DIFF=(CONC(55)-CONC(IMIN))*0.1                                    PR08 104
      SETMAX=CONC(55)+DIFF                                              PR08 105
      SETMIN=CONC(IMIN)-DIFF                                            PR08 106
C                                                                       PR08 107
C        SET PARAMETERS FOR Y-AXIS                                      PR08 108
C                                                                       PR08 109
      ALNY=1.4                                                          PR08 110
      NINT=10                                                           PR08 111
      YRNG=SETMAX-SETMIN                                                PR08 112
      YINC=0.1*YRNG                                                     PR08 113
C                                                                       PR08 114
C        DRAW OUTLINE OR AXES                                           PR08 115
C                                                                       PR08 116
      CALL NEWPAGE                                                      PR08 117
      CALL STATBP(6)                                                    PR08 118
      CALL PLOT(0.5,1.0,-3)                                             PR08 119
      CALL BUFFEM(-6)                                                   PR08 120
      CALL FRAME(0)                                                     PR08 121
C                                                                       PR08 122
C        PLOT TITLE AND MOVE TO START OF CURVE                          PR08 123
C                                                                       PR08 124
  110 CALL SYMBOL(3.0,-1.0,0.35,18HCUMULATIVE PERCENT,0.0,18)           PR08 125
      CALL SYMBOL(8.5,0.5,0.35,NAME,0.0,10)                             PR08 126
      YSCALE=14./YRNG                                                   PR08 127
      YPAGE=(CONC(IMIN)-SETMIN)*YSCALE                                  PR08 128
      XSCALE=0.21818                                                    PR08 129
      CALL PLOT(0SCALE,YPAGE,3)                                         PR08 130
C                                                                       PR08 131
C        DRAW CURVE                                                     PR08 132
C                                                                       PR08 133
      IMINP1=IMIN+1                                                     PR08 134
      DO 120 I=IMINP1,55                                                PR08 135
      YPAGE=(CONC(I)-SETMIN)*YSCALE                                     PR08 136
      XPAGE=FLOAT(I)*XSCALE                                             PR08 137
  120 CALL PLOT(XPAGE,YPAGE,2)                                          PR08 138
      CALL PLOT(0.0,0.0,-3)                                             PR08 139
C                                                                       PR08 140
C        DRAW LINES DEFINING SUB-POPULATIONS                            PR08 141
C                                                                       PR08 142
C                                                                       PR08 143
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      IF (MSUB.LE.1) RETURN                                             PROB 144
      DO 10 J=1,MSUB                                                    PROB 145
      SLOPE(J)=SLOPE(J)*YSCALE                                          PROB 146
      FIRST(J)=(FIRST(J)-SETMIN)*YSCALE                                 PROB 147
      SCND=FIRST-12.0*SLOPE                                             PROB 148
      XPOS=0.0                                                          PROB 149
      IF (FIRST.GE.0.0) GOTO 130                                        PROB 150
      XPOS=-FIRST/SLOPE                                                 PROB 151
      FIRST=0.0                                                         PROB 152
  130 CALL PLOT(XPOS,FIRST,3)                                           PROB 153
      XPOS=12.0                                                         PROB 154
      IF (SCND.LE.14.0) GOTO 140                                        PROB 155
      XPOS=12.0+(14.0-SCND)/SLOPE                                       PROB 156
      SCND=14.0                                                         PROB 157
  140 CALL PLOT(XPOS,SCND,2)                                            PROB 158
      CALL PLOT(0.0,0.0,3)                                              PROB 159
C                                                                       PROB 160
      RETURN                                                            PROB 161
      END                                                               PROB 162
      SUBROUTINE PROBAX(XPAGE,YPAGE,XLEN,IOPTN,IOPTT,IOPTS)             PROB 163
C                                                                       PROB 164
C                                                                       PROB 165
C     ROUTINE FOR CONSTRUCTION OF A PROBABILITY SCALE AXIS              PROB 166
C                                                                       PROB 167
C     ARGUMENTS                                                         PROB 168
C        XPAGE=    X COORD. OF L. END OF AXIS W.R.T. PRESENT POSITION   PROB 169
C        YPAGE=    Y COORD. OF L. END OF AXIS W.R.T. PRESENT POSITION   PROB 170
C        XLEN=     AXIS LENGTH IN INCHES                               PROB 171
C        IOPTN=    NUMBERING OPTION (1=BELOW AXIS, 2=ABOVE, 0=NO NO.)  PROB 172
C        IOPTT=    TICK MARK OPTION (AS FOR IOPTN)                     PROB 173
C        IOPTS=    SCALE DIRECTION OPTION (1 FOR INCREASING FROM LEFT  TPROB 174
C                  RIGHT, 2 FOR DECREASING FROM LEFT TO RIGHT)          PROB 175
C                                                                       PROB 176
C                                                                       PROB 177
      DIMENSION TICK(15),CPCT(15)                                       PROB 178
      INTEGER CPCT                                                      PROB 179
C                                                                       PROB 180
C     SET POINT POSITIONS FOR TICKS AND NUMBERING                       PROB 181
C                                                                       PROB 182
      DATA TICK/.019,.076,.158,.235,.325,.389,.446,.500,.554,.611,.677, PROB 183
     1.767,.844,.924,.981/                                              PROB 184
C                                                                       PROB 185
C     LABELLING FOR CUMULATIVE PERCENT AXIS                             PROB 186
C                                                                       PROB 187
      DATA CPCT/2H 1,2H 2,2H 5,2H10,2H20,2H30,2H40,2H50,2H60,2H70,2H80, PROB 188
     12H90,2H95,2H98,2H99/                                              PROB 189
C                                                                       PROB 190
C     MOVE TO STARTING POSITION                                         PROB 191
C                                                                       PROB 192
      CALL PLOT(XPAGE,YPAGE,-3)                                         PROB 193
      TLEN=.02*XLEN                                                     PROB 194
      IF (IOPTT-1) 201,101,102                                          PROB 195
C                                                                       PROB 196
C     DRAW TICK MARKS                                                   PROB 197
C                                                                       PROB 198
  101 TLEN=-TLEN                                                        PROB 199
  102 DO 103 I=1,15                                                     PROB 200
      XPOS=TICK(I)*XLEN                                                 PROB 201
      CALL PLOT(XPOS,0.0,3)                                             PROB 202
  103 CALL PLOT(XPOS,TLEN,2)                                            PROB 203
      CALL PLOT(XPOS,0.0,3)                                             PROB 204
  201 CALL PLOT(XLEN,0.0,2)                                             PROB 205
C                                                                       PROB 206
C     DETERMINE Y POSITION FOR NUMBERING AND NUMBER SIZE                PROB 207
C                                                                       PROB 208
      TLEN=.02*XLEN                                                     PROB 209
      IF (IOPTT.EQ.IOPTN) TLEN=TLEN+TLEN                                PROB 210
      IF (IOPTN-1) 301,202,203                                          PROB 211
  202 TLEN=2.0*TLEN                                                     PROB 212
  203 HEIGHT=AMIN1(0.02*XLEN)/0.035)*0.035                              PROB 213
C                                                                       PROB 214
C     PLOT NUMBERS                                                      PROB 215
C                                                                       PROB 216
      DO 204 I=1,15                                                     PROB 217
      XPOS=TICK(I)*XLEN-HEIGHT                                          PROB 218
      II=I                                                              PROB 219
      IF (IOPTS.EQ.2) II=16-I                                           PROB 220
  204 CALL SYMBOL(XPOS,TLEN,HEIGHT,CPCT(II),0.0,2)                      PROB 221
C                                                                       PROB 222
C     RETURN TO FORMER POSITION                                         PROB 223
C                                                                       PROB 224
  301 CALL PLOT(-XPAGE,-YPAGE,-3)                                       PROB 225
C                                                                       PROB 226
      RETURN                                                            PROB 227
      END                                                               PROB 228
      SUBROUTINE FRAME(IOPT)                                            PROB 229
C                                                                       PROB 230
C                                                                       PROB 231
C     ROUTINE TO PLOT FRAME OF PROBABILITY PLOT WITH OR WITHOUT         PROB 232
C     AXIS LABELLING                                                    PROB 233
C                                                                       PROB 234
C     IOPT=     LABELLING SWITCH (1=LABELS, 0=NONE)                     PROB 235
C                                                                       PROB 236
C                                                                       PROB 237
      COMMON/AREAS/ SETMIN,YINC,IMIN,YSCALE                             PROB 238
      DATA ALNY,NINT/1.4,10/                                            PROB 239
C                                                                       PROB 240
C     PLOT LABELLED AXES                                                PROB 241
C                                                                       PROB 242
      IF (IOPT.NE.1) GOTO 100                                           PROB 243
      CALL YAXIS(0.0,0.0,2.*ALNY,NINT,SETMIN,YINC,1.2,1.2,1)            PROB 244
      CALL PROBAX(0.0,14.0,12.0,0.1,2)                                  PROB 245
      CALL PROBAX(0.0,0.0,12.0,1.2,1)                                   PROB 246
      CALL YAXIS(12.0,0.0,2.*ALNY,NINT,SETMIN,YINC,1.,1.2,1)            PROB 247
      RETURN                                                            PROB 248
C                                                                       PROB 249
C     PLOT UNLABELLED AXES                                              PROB 250
C                                                                       PROB 251
  100 CALL PLOT(12.0,0.0,-2)                                            PROB 252
      CALL PLOT(0.0,14.0,-2)                                            PROB 253
      CALL PLOT(-12.0,0.0,-2)                                           PROB 254
      CALL PLOT(0.0,-14.0,-2)                                           PROB 255
      RETURN                                                            PROB 256
      END                                                               PROB 257
      SUBROUTINE LINREG(X,Y,N,SLOPE,FIRST)                              SPLT   2
C                                                                       SPLT   3
C     ROUTINE TO FIND THE SLOPE AND INTERCEPT OF A LINE USING           SPLT   4
C     LINEAR REGRESSION                                                 SPLT   5
C                                                                       SPLT   6
C     X=        X-ARRAY                                                 SPLT   7
C     Y=        Y-ARRAY                                                 SPLT   8
C     N=        LENGTH OF X= AND Y=                                     SPLT   9
C     SLOPE=    SLOPE OF LINE                                           SPLT  10
C     FIRST=    Y-INTERCEPT OF LINE                                     SPLT  11
C                                                                       SPLT  12
C                                                                       SPLT  13
      DIMENSION X(99),Y(99)                                             SPLT  14
C                                                                       SPLT  15
      M=0                                                               SPLT  16
C                                                                       SPLT  17
      NUM=N                                                             SPLT  18
C                                                                       SPLT  19
C        INITIALISE SUMS TO 0.0                                         SPLT  20
C                                                                       SPLT  21
      SUMX=SUMY=SUMXX=SUMXY=0.                                          SPLT  22
C                                                                       SPLT  23
C        CALCULATE SUMS                                                 SPLT  24
C                                                                       SPLT  25
      DO 100 I=1,NUM                                                    SPLT  26
      IF (X(I).EQ.0.0) GOTO 100                                         SPLT  27
      IF (X(I).EQ.12.0) GOTO 100                                        SPLT  28
      M=M+1                                                             SPLT  29
      XX=X(I)                                                           SPLT  30
      YY=Y(I)                                                           SPLT  31
      SUMX=SUMX+XX                                                      SPLT  32
      SUMY=SUMY+YY                                                      SPLT  33
      SUMXX=SUMXX+XX*XX                                                 SPLT  34
      SUMXY=SUMXY+XX*YY                                                 SPLT  35
  100 CONTINUE                                                          SPLT  36
C                                                                       SPLT  37
      IF (M.LT.2) GOTO 200                                              SPLT  38
      ZI=M                                                              SPLT  39
C                                                                       SPLT  40
C        CALCULATE AVERAGE XX= AND XY=                                  SPLT  41
      YBAR=SUMY/ZI                                                      SPLT  42
      XBAR=SUMX/ZI                                                      SPLT  43
      XXX=SUMXX-ZI*XBAR*XBAR                                            SPLT  44
      XY=SUMXY-ZI*XBAR*YBAR                                             SPLT  45
C                                                                       SPLT  46
C        CALCULATE SLOPE AND INTERCEPT, ASSUMING THAT XBAR= AND         SPLT  47
C        YBAR= LIE CLOSE TO LINE                                        SPLT  48
C                                                                       SPLT  49
      SLOPE=XY/XXX                                                      SPLT  50
      FIRST=YBAR-SLOPE*XBAR                                             SPLT  51
C                                                                       SPLT  52
      RETURN                                                            SPLT  53
C                                                                       SPLT  54
C        DISPLAY ERROR MESSAGE                                          SPLT  55
C                                                                       SPLT  56
  200 SLOPE=0.                                                          SPLT  57
      WRITE(6,210)                                                      SPLT  58
  210 FORMAT(38HTOO FEW POINTS FOR LINEAR REGRESSION)                   SPLT  59
      CALL BUFFEM(-6)                                                   SPLT  60
      RETURN                                                            SPLT  61
      END                                                               SPLT  62
      SUBROUTINE FLEXX                                                  SPLT  63
C                                                                       SPLT  64
C        ROUTINE TO ACCEPT INPUT OF INFLECTION POINT POSITIONS          SPLT  65
C        AND PLOT POINTS ON RESULTING SUB-POPULATIONS                   SPLT  66
C                                                                       SPLT  67
C                                                                       SPLT  68
      COMMON/AREAS/ PROP(5),SLOP(5),FIRST(5),CON(5,55),PC(5,55),KK(5),  SPLT  70
     + FLEX(5),MSUB                                                     SPLT  71
      COMMON/AREAS/ SETMIN,YINC,IMIN,YSCALE                             SPLT  72
C                                                                       SPLT  73
      PCT=0.0                                                           SPLT  74
C                                                                       SPLT  75
C        DISPLAY EXPLANATION OF INPUT PROCEDURE                         SPLT  76
C                                                                       SPLT  77
      WRITE(6,100)                                                      SPLT  78
  100 FORMAT(41HSUBDIVISION INVOLVES ENTERING INFLECTION /              SPLT  79
     1       41HPOINTS USING THE X-WIRES.  STARTING FROM /              SPLT  80
     2       41HTHE BOTTOM. TYPE P TO ENTER A POINT, OR  /              SPLT  81
     3       41HTO PROCEED, OR E TO ESCAPE AND RESTART.  /)             SPLT  82
  104 CALL BUFFEM(-6)                                                   SPLT  83
C                                                                       SPLT  84
  105 MSUB=0                                                            SPLT  85
C                                                                       SPLT  86
      DO 106 J=1,5                                                      SPLT  87
      PROP(J)=0.0                                                       SPLT  88
      SLOP(J)=1.0                                                       SPLT  89
  106 FIRST(J)=0.0                                                      SPLT  90
C                                                                       SPLT  91
C        ACCEPT COMMAND AND BRANCH ACCORDINGLY                          SPLT  92
C                                                                       SPLT  93
  110 CALL PROMPT(15HENTER A COMMAND:,15)                               SPLT  94
      READ(5,115) CMND                                                  SPLT  95
  115 FORMAT(A1)                                                        SPLT  96
C                                                                       SPLT  97
      IF (CMND.EQ.1HG) GOTO 130                                         SPLT  98
      IF (CMND.EQ.1HC) GOTO 105                                         SPLT  99
      IF (CMND.EQ.1HP) GOTO 120                                         SPLT 100
      GOTO 110                                                          SPLT 101
C                                                                       SPLT 102
  120 MSUB=MSUB+1                                                       SPLT 103
      IF (MSUB.GT.4 ) GOTO 140                                          SPLT 104
      WRITE(6,125) MSUB                                                 SPLT 105
  125 FORMAT(17H INFLECTION POINT ,I1)                                  SPLT 106
      CALL BUFFEM(-6)                                                   SPLT 107
C                                                                       SPLT 108
C        ACCEPT INPUT OF POINT POSITION AND PLOT INDICATOR ARROW        SPLT 109
C                                                                       SPLT 110
      CALL XWIRES(XPAGE,YPAGE)                                          SPLT 111
      CALL SYMBOL(XPAGE+0.21,YPAGE+0.42,BC,180.,-1)                     SPLT 112
      CALL PLOT(0.0,0.0,3)                                              SPLT 113
C                                                                       SPLT 114
      FLEX(MSUB)=PCTA(XPAGE)                                            SPLT 115
C                                                                       SPLT 116
C        REJECT INVALID POINTS, CALCULATE SUB-POPULATION PARAMETERS     SPLT 117
C        AND REQUEST NEXT POINT                                         SPLT 118
C                                                                       SPLT 119
      IF (FLEX(MSUB).LE.1.006) GOTO 150                                 SPLT 120
      IF (FLEX(MSUB).GE.98.994) GOTO 150                                SPLT 121
      PROP(MSUB)=FLEX(MSUB)-PCT                                         SPLT 122
      PCT=PCT+PROP(MSUB)                                                SPLT 123
      PROP(MSUB)=PROP(MSUB)*0.01                                        SPLT 124
      GOTO 110                                                          SPLT 125
C                                                                       SPLT 126
C        NO MORE POINTS, TEST FOR ASCENDING ORDER                       SPLT 127
C                                                                       SPLT 128
  130 MSUB=MSUB+1                                                       SPLT 129
      IF (MSUB.ED.1) RETURN                                             SPLT 130
      IF (MSUB.ED.2) GOTO 134                                           SPLT 131
      MSUB1=MSUB-1                                                      SPLT 132
      DO 132 M=2,MSUB1                                                  SPLT 133
      IF (FLEX(M).LE.FLEX(M-1)) GOTO 170                                SPLT 134
  132 CONTINUE                                                          SPLT 135
C                                                                       SPLT 136
C        CALCULATE SUBDIVISION DISTRIBUTIONS AND PLOT                   SPLT 137
C                                                                       SPLT 138
  134 CALL SPLIT                                                        SPLT 139
      DO 136 J=1,MSUB                                                   SPLT 140
      KJ=KK(J)                                                          SPLT 141
      DO 136 K=1,KJ                                                     SPLT 142
      XPAGE=POSA(PC(J,K))                                               SPLT 143
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      YPAGE=(CDM(J,K)-SETMIN)*YSCALE                                    SPLT 144
  135 CALL SYMBOL(OPAGE,YPAGE,0.07,3,0.0,-1)                            SPLT 145
      FRST=(FIRST(J)-SETMIN)*YSCALE                                     SPLT 146
      SLP=SLOP(J)*YSCALE                                                SPLT 147
      SCND=FRST+12.0*SLP                                                SPLT 148
      XPOS=0.0                                                          SPLT 149
      IF(FRST.GE.0.0) GOTO 137                                          SPLT 150
      XPOS=-FRST/SLP                                                    SPLT 151
      FRST=0.0                                                          SPLT 152
  137 CALL PLOT(XPOS,FRST,3)                                            SPLT 153
      XPOS=12.0                                                         SPLT 154
      IF(SCND.LE.14.) GOTO 138                                          SPLT 155
      XPOS=12.0+(14.0-SCND)*SLP                                         SPLT 156
      SCND=14.0                                                         SPLT 157
  138 CALL PLOT(XPOS,SCND,2)                                            SPLT 158
      CALL PLOT(0.0,0.0,3)                                              SPLT 159
      CALL STATOP(5)                                                    SPLT 160
      CALL BUFFEM(-6)                                                   SPLT 161
      RETURN                                                            SPLT 162
C                                                                       SPLT 163
C        DISPLAY ERROR MESSAGE                                          SPLT 164
C                                                                       SPLT 165
  140 WRITE(6,145)                                                      SPLT 166
  145 FORMAT(36HMAX. NUMBER OF POINTS IS 4 - RESTART)                   SPLT 167
      GOTO 104                                                          SPLT 168
C                                                                       SPLT 169
  150 WRITE(6,155)                                                      SPLT 170
  155 FORMAT(32HFIRST POINT IS TOO LOW - RESTART)                       SPLT 171
      GOTO 104                                                          SPLT 172
C                                                                       SPLT 173
  160 WRITE(6,165)                                                      SPLT 174
  165 FORMAT(32HLAST POINT IS TOO HIGH - RESTART)                       SPLT 175
      GOTO 104                                                          SPLT 176
C                                                                       SPLT 177
  170 WRITE(6,175)                                                      SPLT 178
  175 FORMAT(42HPOINT(I) MUST BE .GT. POINT(I-1) - RESTART)             SPLT 179
      GOTO 104                                                          SPLT 180
C                                                                       SPLT 181
      END                                                               SPLT 182
      SUBROUTINE SPLIT                                                  SPLT 183
C                                                                       SPLT 184
C        ROUTINE TO CALCULATE INITIAL DISTRIBUTION OF SUB-POPULATIONS   SPLT 185
C                                                                       SPLT 186
C                                                                       SPLT 187
      COMMON/AREA2/ FREQ(72),CLSS(72),CONC(55),PCTL(55),CPCL(250),      SPLT 188
     + CPFR(250),NTRAN,NCLL,NAME,CMND                                   SPLT 189
      COMMON/AREA5/ PROP(5),SLOP(5),FIRST(5),CDN(5,55),PC(5,55),KK(5),  SPLT 190
     + FLEX(5),NSUB                                                     SPLT 191
      COMMON/AREA6/ SETMIN,YINC,IMIN,YSCALE                             SPLT 192
C                                                                       SPLT 193
C        SET PARAMETERS FOR LAST SUB-POPULATION                         SPLT 194
C                                                                       SPLT 195
      FLEX(NSUB)=99.204                                                 SPLT 196
      PROP(NSUB)=((100.-FLEX(NSUB-1))*0.01                              SPLT 197
      I=IMIN                                                            SPLT 198
C                                                                       SPLT 199
      DO 300 J=1,NSUB                                                   SPLT 200
      K=0                                                               SPLT 201
C                                                                       SPLT 202
C        DETERMINE APPROPRIATE SUB-POPULATION INDEX NUMBER              SPLT 203
C                                                                       SPLT 204
  100 IF(PCTL(I).GE.FLEX(J)) GOTO 250                                   SPLT 205
      K=K+1                                                             SPLT 206
      CDN(J,K)=CONC(I)                                                  SPLT 207
      IF(J.GT.1) GOTO 200                                               SPLT 208
C                                                                       SPLT 209
C        CALCULATE PERCENTILES FOR SUB-POPULATION 1, IGNORING THE       SPLT 210
C        CONTRIBUTION OF THE HIGHER SUB-POPULATIONS                     SPLT 211
C                                                                       SPLT 212
      PC(J,K)=PCTL(I)/PROP(J)                                           SPLT 213
      KK(J)=K                                                           SPLT 214
      I=I+1                                                             SPLT 215
      GOTO 100                                                          SPLT 216
C                                                                       SPLT 217
C        DETERMINE CONTRIBUTION OF ALL LOWER SUB-POPULATIONS            SPLT 218
C                                                                       SPLT 219
  200 JM1=J-1                                                           SPLT 220
      P=0                                                               SPLT 221
      DO 225 JJ=1,JM1                                                   SPLT 222
  225 P=P+PROP(JJ)*PCTA((CONC(I)-FIRST(JJ))/SLOP(JJ))                   SPLT 223
C                                                                       SPLT 224
C        CALCULATE PERCENTILES FOR SUB-POPULATION NUM. IGNORING         SPLT 225
C        CONTRIBUTION OF HIGHER SUB-POPULATIONS                         SPLT 226
C                                                                       SPLT 227
      PC(J,K)=(PCTL(I)-P)/PROP(J)                                       SPLT 228
C                                                                       SPLT 229
      KK(J)=K                                                           SPLT 230
      I=I+1                                                             SPLT 231
      GOTO 100                                                          SPLT 232
C                                                                       SPLT 233
C        CALCULATE SLOPE AND INTERCEPT                                  SPLT 234
C                                                                       SPLT 235
  250 CALL SLOPE(J)                                                     SPLT 236
      IF(SLOP(J).EQ.0.0) RETURN                                         SPLT 237
  300 CONTINUE                                                          SPLT 238
C                                                                       SPLT 239
C        CALCULATE NEW POINTS, TAKING ACCOUNT OF THE CONTRIBUTION       SPLT 240
C        OF OTHER SUB-POPULATIONS                                       SPLT 241
C                                                                       SPLT 242
      CALL REFIT                                                        SPLT 243
C                                                                       SPLT 244
      RETURN                                                            SPLT 245
      END                                                               SPLT 246
      SUBROUTINE REFIT                                                  SPLT 247
C                                                                       SPLT 248
C                                                                       SPLT 249
C        ROUTINE TO RE-CALCULATE DISTRIBUTIONS FOR ALL BUT THE LAST     SPLT 250
C        SUB-POPULATION, TAKING INTO ACCOUNT THE AFFECTS WHICH THE      SPLT 251
C        OTHER SUB-POPULATIONS HAVE ON THE ORIGINAL CURVE               SPLT 252
C                                                                       SPLT 253
C                                                                       SPLT 254
      COMMON/AREA2/ FREQ(72),CLSS(72),CONC(55),PCTL(55),CPCL(250),      SPLT 255
     + CPFR(250),NTRAN,NCLL,NAME,CMND                                   SPLT 256
      COMMON/AREA5/ PROP(5),SLOP(5),FIRST(5),CDN(5,55),PC(5,55),KK(5),  SPLT 257
     + FLEX(5),NSUB                                                     SPLT 258
      COMMON/AREA6/ SETMIN,YINC,IMIN,YSCALE                             SPLT 259
C                                                                       SPLT 260
      DIMENSION PP(5),PCC(5,55)                                         SPLT 261
C                                                                       SPLT 262
      NSUBM1=NSUB-1                                                     SPLT 263
C                                                                       SPLT 264
C        CALCULATE PERCENTILES FOR 55 POINTS ALONG EACH LINE            SPLT 265
C                                                                       SPLT 266
      DO 100 I=1,55                                                     SPLT 267
      DO 100 J=1,5                                                      SPLT 268
      P=(CONC(I)-FIRST(J))/SLOP(J)                                      SPLT 269
      PCC(J,I)=PCTA(P)                                                  SPLT 270
      IF(P.GT.12.0) PCC(J,I)=100.                                       SPLT 271
      IF(P.LT.0.0) PCC(J,I)=0.0                                         SPLT 272
  100 CONTINUE                                                          SPLT 273
C                                                                       SPLT 274
C                                                                       SPLT 275
      LIM1=KK(1)                                                        SPLT 276
C                                                                       SPLT 277
C        RE-CALCULATE DISTRIBUTION FOR SUB-POPULATION 1                 SPLT 278
C                                                                       SPLT 279
      DO 200 I=IMIN,LIM1                                                SPLT 280
      PCT=PCTL(I)                                                       SPLT 281
C                                                                       SPLT 282
      DO 150 J=2,5                                                      SPLT 283
  150 PP(J)=PCC(J,I)*PROP(J)                                            SPLT 284
C                                                                       SPLT 285
      PC(1,I)=(PCT-PP(2)-PP(3)-PP(4)-PP(5))/PROP(1)                     SPLT 286
      IF(I.EQ.1) GOTO 200                                               SPLT 287
      IF(PC(1,I).LE.PC(1,I-1)) GOTO 230                                 SPLT 288
C                                                                       SPLT 289
  200 CONTINUE                                                          SPLT 290
C                                                                       SPLT 291
  230 IF(NSUB.LT.3) GOTO 290                                            SPLT 292
      LIM1=1                                                            SPLT 293
C                                                                       SPLT 294
C        RE-CALCULATE DISTRIBUTIONS OF OTHER SUB-POPULATIONS            SPLT 295
C                                                                       SPLT 296
      DO 280 J=2,NSUBM1                                                 SPLT 297
      JP1=J+1                                                           SPLT 298
      LIM1=LIM1+KK(J-1)                                                 SPLT 299
      LIM2=LIM1+KK(J)                                                   SPLT 300
      K=0                                                               SPLT 301
C                                                                       SPLT 302
      DO 250 I=LIM1,LIM2                                                SPLT 303
      P=0                                                               SPLT 304
      DO 240 JJ=JP1,NSUB                                                SPLT 305
  240 P=P+PROP(JJ)*PCTA((CONC(I)-FIRST(JJ))/SLOP(JJ))                   SPLT 306
      P=P+PROP(1)*PCTA((CONC(I)-FIRST(1))/SLOP(1))                      SPLT 307
      K=K+1                                                             SPLT 308
C                                                                       SPLT 309
      CDN(J,K)=CONC(I)                                                  SPLT 310
  250 PC(J,K)=(PCTL(I)-P)/PROP(J)                                       SPLT 311
C                                                                       SPLT 312
  280 CONTINUE                                                          SPLT 313
C                                                                       SPLT 314
C                                                                       SPLT 315
C                                                                       SPLT 316
  290 DO 400 J=1,NSUBM1                                                 SPLT 317
      II=0                                                              SPLT 318
C                                                                       SPLT 319
      K=KK(J)                                                           SPLT 320
      DO 300 I=1,K                                                      SPLT 321
      IF(PC(J,I).LT.0.796) GOTO 300                                     SPLT 322
      IF(PC(J,I).GT.99.204) GOTO 350                                    SPLT 323
C                                                                       SPLT 324
      II=II+1                                                           SPLT 325
  300 CONTINUE                                                          SPLT 326
C                                                                       SPLT 327
C        RECALCULATE SLOPES AND INTERCEPTS                              SPLT 328
C                                                                       SPLT 329
  350 KK(J)=II                                                          SPLT 330
      CALL SLOPE(J)                                                     SPLT 331
  400 CONTINUE                                                          SPLT 332
C                                                                       SPLT 333
      RETURN                                                            SPLT 334
      END                                                               SPLT 335
      SUBROUTINE SLOPE(J)                                               SPLT 336
C                                                                       SPLT 337
C        ROUTINE TO CALCULATE SLOPES AND INTERCEPTS OF LINES            SPLT 338
C        DEFINING SUB-POPULATIONS                                       SPLT 339
C                                                                       SPLT 340
C                                                                       SPLT 341
      COMMON/AREA5/ PROP(5),SLOP(5),FIRST(5),CDN(5,55),PC(5,55),KK(5),  SPLT 342
     + FLEX(5),NSUB                                                     SPLT 343
C                                                                       SPLT 344
      DIMENSION X(55),Y(55)                                             SPLT 345
      K1=KK(J)                                                          SPLT 346
C                                                                       SPLT 347
      DO 100 K=1,K1                                                     SPLT 348
C                                                                       SPLT 349
C        TRANSFER DATA TO LINEAR ARRAYS                                 SPLT 350
C                                                                       SPLT 351
      X(K)=POSA(PC(J,K))                                                SPLT 352
  100 Y(K)=CDN(J,K)                                                     SPLT 353
C                                                                       SPLT 354
      CALL LINREG(X,Y,K1,SLOP(J),FIRST(J))                              SPLT 355
      RETURN                                                            SPLT 356
      END                                                               SPLT 357
      FUNCTION CMBN(I)                                                  SPLT 358
C                                                                       TEST   2
C                                                                       TEST   3
C        ROUTINE TO COMBINE SUB-POPULATIONS                             TEST   4
C                                                                       TEST   5
C        *I*      INDEX OF ARRAY *CONC*                                 TEST   6
C        *CMBN*   PERCENTILE VALUE OF COMBINED SUB-POPULATIONS,         TEST   7
C                 CORRESPONDING TO *CONC(I)*                            TEST   8
C                                                                       TEST   9
C                                                                       TEST  10
      COMMON/AREA2/ FREQ(72),CLSS(72),CONC(55),PCTL(55),CPCL(250),      TEST  11
     + CPFR(250),NTRAN,NCLL,NAME,CMND                                   TEST  12
      COMMON/AREA5/ PROP(5),SLOP(5),FIRST(5),CDN(5,55),PC(5,55),KK(5),  TEST  13
     + FLEX(5),NSUB                                                     TEST  14
C                                                                       TEST  15
      CMBN=0.0                                                          TEST  16
C                                                                       TEST  17
      DO 100 J=1,NSUB                                                   TEST  18
      DX=CONC(I)-FIRST(J)                                               TEST  19
      IF(DX.LT.0.) DX=0.0                                               TEST  20
      POS=DX/SLOP(J)                                                    TEST  21
      IF(POS.GT.12.0) POS=12.0                                          TEST  22
  100 CMBN=CMBN+(PROP(J)*PCTA(POS))                                     TEST  23
C                                                                       TEST  24
      RETURN                                                            TEST  25
      END                                                               TEST  26
      SUBROUTINE KSTEST                                                 TEST  27
C                                                                       TEST  28
C        ROUTINE TO CARRY OUT KOLMOGOROV-SMIRNOV TEST OF DIFF-          TEST  29
C        ERENCE BETWEEN ACTUAL CURVE AND THEORETICAL CURVE              TEST  30
C                                                                       TEST  31
C                                                                       TEST  32
      COMMON/AREA2/ FREQ(72),CLSS(72),CONC(55),PCTL(55),CPCL(250),      TEST  33
     + CPFR(250),NTRAN,NCLL,NAME,CMND                                   TEST  34
      COMMON/AREA3/ NSIT,NOBS,XMEN,STDV                                 TEST  35
      COMMON/AREA5/ PROP(5),SLOP(5),FIRST(5),CDN(5,55),PC(5,55),KK(5),  TEST  36
     + FLEX(5),NSUB                                                     TEST  37
      COMMON/AREA6/ SETMIN,YINC,IMIN,YSCALE                             TEST  38
C                                                                       TEST  39
      DMAX=0.0                                                          TEST  40
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C
      CALL PROMPT(30,'TYPE 1 TO PLOT POINTS ON CURVE',30)
      READ(5,*) IPL
C
      IF(MSUB.GT.1) GOTO 50
C
C        CALCULATE PARAMETERS OF LINE FOR ONE POPULATION CASE
C
      SLOP(1)=(4.814*STDV)/12.0
      FIRST(1)=XMEN-2.412*STDV
      PROP(1)=1.0
C
C        CALCULATE COMBINED PERCENTILES
C
   50 DO 100 I=IMIN,55
      C=CMBN(I)
C
      IF(IPL.NE.1) GOTO 75
C
C        PLOT POINTS ON THEORETICAL CURVE
C
      XPAGE=POSA(C)
      YPAGE=(CONC(I)-SETMIN)*YSCALE
      CALL SYMBOL(XPAGE,YPAGE,0.07,9,0.0,-1)
C
C        CALCULATE MAXIMUM DIFFERENCE BETWEEN CURVES
C
   75 DIFF=ABS(PCTL(I)-C)
      IF(DIFF.GT.DMAX) DMAX=DIFF
  100 CONTINUE
      CALL PLOT(0.0,0.0,3)
C
C        CALCULATE KOLMOGOROV-SMIRNOV STATISTIC
C
      CALL KS(55-IMIN,DMAX,SIG,MSUB,DN)
C
      IF(SIG.LT.90.0) GOTO 210
C
      WRITE(5,200) MSUB,SIG,DN
  200 FORMAT(8HFOR THE ,I1,28H POP. CASE THE MODEL DIFFERS /
     1 35HFROM THE DATA AT A SIGNIFICANCE OF ,F4.1/
     2 31HKOLMOGOROV-SMIRNOV STATITSTIC = ,F5.3)
      CALL BUFFEM(-6)
C
  210 WRITE(5,220) MSUB,DN
  220 FORMAT('FOR THE ',I1,' POPULATION CASE, THE MODEL IS NOT'
     + /'SIGNIFICANTLY DIFFERENT FROM THE DATA AT THE 90 PCT.'
     + /'CONFIDENCE LEVEL, KOL-SMIR STATISTIC IS ',F5.3)
      CALL BUFFEM(-6)
C
      RETURN
      END
      SUBROUTINE KS(M,D,SIG,MSUB,DN)
C
C        ROUTINE TO CALCULATE KOLMOGOROV-SMIRNOV STATISTIC AND LEVEL
C        OF SIGNIFICANCE AT WHICH TWO POPULATIONS DIFFER
C
C
      REAL KSCRIT
      DIMENSION ALPHA(4),KSCRIT(8)
C
C        INITIALISE CONFIDENCE LIMITS AND CORRESPONDING K-S VALUES
C
      DATA ALPHA/90.0,95.0,97.5,99.0/
      DATA KSCRIT/1.224,1.358,1.480,1.628,0.819,0.895,0.955,1.035/
C
      WRITE(5,40) D
   40 FORMAT(29HMAXIMUM PERCENT SEPARATION = ,F4.1)
      MP=0
      X=M
      IF(MSUB.EQ.1) GOTO 50
C
C        CALCULATE KOLMOGOROV SMIRNOV STATISTIC
C
      XX=SQRT(X*X/(X+X))
      DN=(.001+0.12+0.11/XX)*D-0.01
      GOTO 60
C
   50 X=SQRT(X)
      DN=D*0.01*(X-0.21+0.85/X)
      MP=4
C
C        COMPARE WITH TABLE
C
   60 IF(DN.LT.KSCRIT(MP+1)) GOTO 160
      DO 100 J=1,4
      JJ=MP+5-J
      M=5-J
      IF(DN.GE.KSCRIT(JJ)) GOTO 150
  100 CONTINUE
C
  150 SIG=ALPHA(M)
      RETURN
C
  160 SIG=89.0
      RETURN
      END
      FUNCTION PCTA(PRSTN)
C
      COMMON/AREA2/ FREQ(72),CLSS(72),CONC(55),PCTL(55),CPCL(250),
     + CPFR(250),NTRAN,NCLL,NAME,CMND
C
C
C        ROUTINE FOR CONVERSION OF PLOT POSITION TO PERCENTILE
C
C        XPRSTN    X-COORDINATE POSITION IN INCHES
C        XPCTA=    CORRESPONDING PERCENTILE (RETURNED)
C
C
      WIDTH=12.0
C
C        CALCULATE POSITION IN TERMS OF INDEX OF PERCENTILES
C        ALONG THE X-AXIS
C
      POS=PRSTN/WIDTH*54.+1.
      IF(POS.GT.99.0) POS=55.0
      IF(POS.LT.1.0) POS=1.0
      TRUNC=INT(POS)
      FRACT=POS-TRUNC
C
C        FIND NEAREST MEMBER OF XPCTL= AND INTERPOLATE LINEARLY
C
      IPOS=TRUNC
      PCTA=PCTL(IPOS)
      IF(FRACT.EQ.0.0) RETURN
      DELP=PCTL(IPOS+1)-PCTA
      PCTA=PCTA+FRACT*DELP
      RETURN
      END
      FUNCTION POSA(PCT)
C
      COMMON/AREA2/ FREQ(72),CLSS(72),CONC(55),PCTL(55),CPCL(250),
     + CPFR(250),NTRAN,NCLL,NAME,CMND
C
C
C        ROUTINE FOR CONVERSION OF PERCENTILE TO PLOT POSITION
C
C        XPCT=     PERCENTILE VALUE
C        XPOSA=    CORRESPONDING X-AXIS POSITION IN INCHES
C
C
      PRCNT=PCT
      WIDTH=12.0
C
C        FIND INDEX OF NEAREST MEMBER OF XPCTL= AND INTERPOLATE LINEARLY
C
      IF(PRCNT.GT.PCTL(1)) GOTO 110
      POSA=0.
      RETURN
  110 IF(PRCNT.LT.PCTL(55)) GOTO 120
      POSA=WIDTH
      RETURN
  120 DO 150 I=2,55
      IF(PRCNT-PCTL(I)) 130,140,150
  130 DELT=PCTL(I)-PCTL(I-1)
      FRACT=(PRCNT-PCTL(I-1))/DELT
      POSA=((FLOAT(I-1)+FRACT)/54.0)*WIDTH
      IF(POSA.GT.WIDTH) POSA=WIDTH
      RETURN
  140 POSA=((FLOAT(I)-1.0)/54.0)*WIDTH
      RETURN
  150 CONTINUE
      RETURN
      END
      SUBROUTINE STATOP(MT)
C
C        ROUTINE TO OUTPUT STATISTICAL PARAMETERS FOR MAIN POPULATIONS
C        AND ALL SUB-POPULATIONS
C
C        MT=       OUTPUT DEVICE  (6 = TERMINAL, 7 = TAPE7)
C
      COMMON/AREA2/ FREQ(72),CLSS(72),CONC(55),PCTL(55),CPCL(250),
     + CPFR(250),NTRAN,NCLL,NAME,CMND
      COMMON/AREA3/ MSIT,NOBS,XMEN,STDV
      COMMON/AREA4/ NBIN,CLS1,XINC,XLM
      COMMON/AREA5/ PROP(5),SLOP(5),FIRST(5),CDN(5,55),PC(5,55),KK(5),
     + FLEX(5),MSUB
      COMMON/AREA6/ SETMIN,YINC,IMIN,YSCALE
C
      WRITE(MT,100) NAME,NOBS,XMEN,STDV
  100 FORMAT(/15HSTATISTICS FOR ,A10,22HNMB. OF OBSERVATIONS = ,I4/
     + 17HMEAN =            ,G8.2/17HSTD. DEVIATION = ,F8.3/)
C
      IF(NTRAN) 110,130,120
  110 WRITE(MT,115) -NTRAN
  115 FORMAT(12,22H 10**X TRANSFORMATIONS/)
      GOTO 135
  120 WRITE(MT,125) NTRAN
  125 FORMAT(12,24H LOG(10) TRANSFORMATIONS/)
      GOTO 135
C
  130 IF(XLM.LT.-99.0) GOTO 135
      WRITE(MT, 131) XLM
  131 FORMAT('X**(',F6.3,') TRANSFORMATIONS'/)
C
  135 IF(MSUB.LE.1) RETURN
      DO 150 J=1,MSUB
      XMEN=FIRST(J)+5.0*SLOP(J)/
      SDV=(SLOP(J)*12.0)/4.814
      WRITE(MT,140) J,NAME,PROP(J)*100.,XMEN,SDV
  140 FORMAT(9HSUB-POP. ,I1,5H FOR ,A10/F5.2,17H PERCENT OF TOTAL /
     + 7HMEAN = ,G9.3,8H STDV = ,G9.3/)
  150 CONTINUE
C
      RETURN
      END
```

LISTING OF THE PROGRAM START

```
C-----------------------------------------------------------------------
C
C                        * * *  S T A R T  * * *
C
C     INTERACTIVE ROUTINE TO CREATE AN INDEX FILE AND BINARY DATA
C     FILE FOR INPUT TO THE GRAPHICAL PROGRAMS *GEOSTAT* AND *GIRAF*
C
C-----------------------------------------------------------------------
C
C     AUTHOR
C        STEVEN EARLE, DEPARTMENT OF GEOLOGY, IMPERIAL COLLEGE, LONDON
C     DATE
C        MARCH 1976    (MODIFIED +)
C     LANGUAGE, COMPUTER
C        FORTRAN IV - CDC 6500 - IMPERIAL COLLEGE COMPUTER CENTRE
C     METHOD
C        THE PROGRAM IS EXECUTED AT A TERMINAL AND DATA IS READ FROM
C        A LOCAL FILE KNOWN AS TAPE4.  THE USER SUPPLIES THE NUMBER OF
C        VARIABLES, THE DATA TYPE (IE. WHETHER A LIST OR MAP ARRAY),
C        VARIABLE NAMES AND THE INPUT FORMAT.  *START* WRITES AN INDEX
C        FILE, CALLED TAPE20, CONTAINING THE NUMBER OF VARIABLE AND
C        VARIABLE NAMES, ALL ON SEPARATE LINES.  A SECOND FILE, TAPE21,
C        INCLUDES A SEPARATE RECORD FOR EACH VARIABLE, CONTAINING THE
C        NUMBER OF SAMPLE SITES AND THE DATA LIST.
C
C-----------------------------------------------------------------------
C
      PROGRAM START(INPUT,OUTPUT=131B,TAPE4,TAPE5=INPUT,TAPE6=OUTPUT,
     + TAPE20,TAPE21)
C
C     LOGICAL UNITS USED
C
C     TAPE4    FILE CONTAINING ORIGINAL DATA
C     TAPE5    INPUT FROM TERMINAL
C     TAPE6    OUTPUT TO TERMINAL
C     TAPE20   INDEX FILE OUTPUT
C     TAPE21   DATA FILE OUTPUT
C
C-----------------------------------------------------------------------
C
C     EXECUTION PROCEDURE
C
C     THE PROGRAM CAN BE STORED AS A RELOCATABLE BINARY FILE,
C     CREATED FROM THE CARD DECK USING THE CONTROL STATEMENTS -
C
C     MAP,OFF=$START8.
C     REPLACE,$START8.
C
C     EXECUTION AT A TERMINAL WOULD THEN PROCEED AS FOLLOWS, ASSUMING
C     THAT THE DATA FILE EXISTS AS A LOCAL FILE CALLED TAPE4 -
C
C     START8.
C
C     FOLLOWING EXECUTION, TAPE20 AND TAPE21 CAN BE SAVED, OR REWOUND
C     AND USED AS INPUT TO THE *GEOSTAT* OR *GIRAF* ROUTINES.
C     AS AN ALTERNATIVE, PROCEDURES FOR EXECUTING *START* AND THEN
C     EITHER *GEOSTAT* OR *GIRAF* ARE AVAILABLE AND CAN BE USED,
C     AT A TEKTRONIX TERMINAL, AS FOLLOWS -
C
C     GET,START1/UN=UPPBC08)      ... START2 FOR *GIRAF*
C     -START1
C
C
C-----------------------------------------------------------------------
C
      COMMON// MOBT,MVAR,MVPR,MOBR,IFMT(8),MTIP,MSIT,DAT(15,500)
      DIMENSION NAME(15)
C
C        *MOBT*    MAXIMUM NUMBER OF OBSERVATIONS
C        *MVAR*    NUMBER OF VARIABLES
C        *MVPR*    NUMBER OF VARIABLES PER INPUT RECORD (NORMALLY
C                  EQUAL TO *MVAR*)
C        *MOBR*    NUMBER OF OBSERVATIONS PER INPUT RECORD (NORMALLY
C                  EQUAL TO 1)
C        *IFMT*    INPUT FORMAT
C        *MTIP*    LOGICAL UNIT NUMBER FOR DATA INPUT
C        *MSIT*    NUMBER OF SAMPLE SITES
C        *DAT*     DATA ARRAY
C        *NAME*    LIST OF VARIABLE NAMES
C
C
C          TO INCREASE THE MAXIMUM NUMBER OF OBSERVATIONS OR VARIABLES
C          THE DIMENSIONS OF THE ARRAYS *DAT* AND *NAME* MUST BE
C          CHANGED, AND A NEW VALUE MUST BE ASSIGNED TO *MOBT*.
C
      MOBT=500
      MTIP=4
C
C-----------------------------------------------------------------------
C
C        DISPLAY HEADING AND REQUEST TYPE OF ANALYSIS
C
      WRITE(6,100)
  100 FORMAT(32H ROUTINE TO RE-FORMAT DATA FOR INPUT TO/
     1       29H GEO-STAT AND GIRAF ROUTINES.//
     2       35H TYPE 1 FOR GEO-STAT OR 2 FOR GIRAF.)
C
      READ(5,*) IBPT
      IF(IBPT.EQ.1) GOTO 400
C
C        ** GIRAF **   -   REQUEST NUMBER OF VARIABLES
C
      WRITE(6,120)
  120 FORMAT(33H ENTER NUMBER OF VARIABLES (1-15))
      READ(5,*)  MVAR
C
      WRITE(6,122) MVAR
  122 FORMAT(39H ENTER NO. OF VARIABLES PER INPUT ROW. ,I2,19H - UNLESS
     1GRID DATA)
      READ(5,*)  MVPR
C
      WRITE(6,124)
  124 FORMAT(33H ENTER NO. OF OBS. PER INPUT ROW (1 UNLESS GRID DATA))
      READ(5,*)  MOBR
C
      WRITE(6,130)
  130 FORMAT(41H ENTER VARIABLE NAMES (A10) ONE AT A TIME)
      DO 150 J=1,MVAR
      READ(5,140)  NAME(J)
  140 FORMAT(A10)
  150 CONTINUE
C
      WRITE(6,160)
  160 FORMAT(48H ENTER FORMAT FOR LINE-BY-LINE INPUT OF REAL DATA)
      READ(5,170)  IFMT
  170 FORMAT(8A10)
C
C        INPUT DATA INTO ARRAY *DAT*
C
      CALL INPUT
C
C        CHECK IF MISSING DATA SCAN IS REQUIRED
C
      IF(MSIT.LT.3) GOTO 300
      WRITE(6,200)
  200 FORMAT(29H TYPE 1 FOR MISSING DATA SCAN)
      READ(5,*)  MISS
C
      IF(MISS.EQ.0) GOTO 220
C
      WRITE(6,210)
  210 FORMAT(31H ENTER MISSING DATA CODE (REAL))
      READ(5,*)  CBOC
C
C        WRITE *MVAR* ON FIRST LINE OF TAPE20
C
  220 WRITE(20,221) MVAR
  221 FORMAT(I2)
C
      DO 240 J=1,MVAR
      IF(MISS.EQ.0) GOTO 230
C
C        TEST FOR MISSING DATA AND RE-ARRANGE *DAT*
C
      MOBS=0
      DO 225 I=1,MSIT
      IF(DAT(J,I) .EQ.CBOC)  GOTO 225
      MOBS=MOBS+1
      DAT(J,MOBS)=DAT(J,I)
  225 CONTINUE
C
      GOTO 231
  230 MOBS=MSIT
C
C        FOR EACH VARIABLE, WRITE NAME ON TAPE20 AND *MSIT*,
C        *MOBS*  AND DATA LIST ON TAPE21
C
  231 WRITE(20,140)  NAME(J)
      WRITE(21)  MSIT,MOBS,(DAT(J,I),I=1,MOBS)
  240 CONTINUE
C
C        INDICATE PROCESSING COMPLETE
C
      WRITE(6,250)  MVAR,MSIT
  250 FORMAT(32H DATA WRITTEN TO TAPES 20 AND 21/I2,14H VARIABLES AND,I4
     1,13H SAMPLE SITES)
      STOP
C
C        ** GEOSTAT **   -   REQUEST NUMBER OF VARIABLES
C
  400 WRITE(6,410)
  410 FORMAT(33H ENTER NUMBER OF VARIABLES (1-14))
      READ(5,*)  MVAR
      MVAR=MVAR+1
      MVPR=MVAR
      MOBR=1
C
C        REQUEST VARIABLE NAMES
C
      WRITE(6,130)
      DO 420 J=2,MVAR
  420 READ(5,140)  NAME(J)
C
C        REQUEST INPUT FORMAT
C
      WRITE(6,160)
      READ(5,170)  IFMT
C
C        INPUT DATA INTO ARRAY *DAT*
C
      CALL INPUT
      IF(MSIT.LT.3) GOTO 300
C
C        WRITE *MVAR* ON FIRST LINE OF TAPE20
C
      WRITE(20,221) MVAR-1
      DO 430 J=2,MVAR
C
C        FOR EACH VARIABLE, WRITE NAME ON TAPE20 AND *MSIT* AND
C        DISTANCE VECTOR AND DATA VECTOR ON TAPE21
C
      WRITE(20,140)  NAME(J)
      WRITE(21)  MSIT, DAT(1,I),DAT(J,I),I=1,MSIT)
  430 CONTINUE
C
C        INDICATE PROCESSING COMPLETE
C
      WRITE(6,440) MVAR-1
  440 FORMAT(10H DATA FOR ,I2,37H VARIABLES WRITTEN ON TAPES 20 AND 21)
      STOP
C
C        ERROR MESSAGE FOR TOO FEW SAMPLES
C
  300 WRITE(6,310) MSIT
  310 FORMAT(18H NO. OF SAMPLES = ,I2,13H TASK DROPPED)
      STOP
      END
      SUBROUTINE INPUT
C     ================================================================
C     *                                                              *
C     *              A GENERAL ROUTINE FOR DATA INPUT                *
C     *          ACCEPTS DATA IN LIST OR ARRAY FORM                  *
C     *              AND RETURNS IT IN LIST FORM                     *
C     *                                                              *
C     ================================================================
C
C        ARGUMENTS
C     MOBT-----MAXIMUM TOTAL NUMBER OF OBSERVATIONS (IE. ARRAY SIZE)
C     MVAR-----TOTAL NUMBER OF VARIABLES
C     MVPR-----NUMBER OF VARIABLES PER INPUT ROW
C     MOBR-----NUMBER OF OBSERVATIONS PER INPUT ROW. FOR EACH OF
C              THE MVPR VARIABLES
C     IFMT-----FORMAT FOR ROW BY ROW INPUT
C     MINT-----INPUT DEVICE OR TAPE NUMBER
C     MOBS-----TOTAL NUMBER OF OBSERVATIONS (RETURNED TO CALLING ROUTINE)
C     DAT ------DATA ARRAY (RETURNED TO CALLING ROUTINE)
C
C.....................................................................
C
      COMMON// MOBT,MVAR,MVPR,MOBR,IFMT(8),MINT,MOBS,DAT(15,500)
C
      MOBS=0
      NUM=0
      NUM1
      MV=MVPR
C
      DO 120 K=1,MVAR,MVPR
      NUM=NUM+1
      NI=1
      MB=MOBR
C
      DO 110 IX=1,MOBT
C
C        FROM EACH LINE OF DATA READ *MOBR* OBSERVATIONS FOR
C        EACH OF *MVPR* VARIABLES
C
      READ(MINT,IFMT)  ((DAT(J,I),I=NI,MB),J=K,MV)
      IF(EOF(MINT)) GOTO 115
C
      NI=NI+MOBR
      MB=MB+MOBR
  110 MOBS=MOBS+MOBR
  115 NUM=NUM+MVPR
      MV=MV+MVPR
  120 CONTINUE
C
      IF(NUM.GE.1) GOTO 140
      MOBS=0
      RETURN
C
  140 MOBS=MOBS/NUM
      RETURN
      END
```

APPENDIX D DESCRIPTION AND DISCUSSION OF THE INTERACTIVE GEOSTATISTICAL ANALYSIS ROUTINE 'GEOSTAT'

D-1 Introduction

The problem of fitting models to semi-variograms can be solved through the application of interactive graphical computer processing, where laborious calculations are avoided, while subjective decisions can be interjected. This appendix includes a brief description and discussion of an interactive graphical program for interpretation of semi-variograms. The application of geostatistics to mining and exploration problems is discussed in Appendix E.

D-2 Algorithm for Semi-variogram Modelling

The semi-variogram modelling algorithm, GEOSTAT, is in the form of a FORTRAN program which is designed to be used on the interactive-graphics facility at the Imperial College of Science and Technology (Raby, 1976). The program is run at a Tektronix graphical terminal, and hard-copy output can be obtained from the Tektronix hard-copy unit, or via microfilm. Execution is controlled from the terminal keyboard, and data is input from a binary disk-file. Creation of the binary disk-file is facilitated through the use of a separate interactive program START. As presently written, START is dimensioned for 15 variables and 500 observations, whereas GEOSTAT is dimensioned for 20 variables and 500 observations. A documented listing of START is included in Appendix C, and a documented listing of GEOSTAT is given below.

The program is limited to evenly spaced data in one dimension. Prior to construction of a semi-variogram, the data can be examined by plotting a profile of distance versus concentration. This step is important because although the semi-variogram does not require a normal distribution, it is very sensitive to extreme values (personal communication I. Clark, Imperial College). In some cases the author has obtained grossly misleading results with strongly skewed distributions. The program enables the user to delete extreme values, or to suppress their effect by applying a logarithmic transformation.

Semi-variograms are constructed by plotting $\gamma(h)$ against h - the distance between pairs. $\gamma(h)$ is defined as follows:

$$\gamma(h) = (1/2n)\left(\sum (f(x+h) - f(x))^2\right)$$

where f(x) and f (x+h) are the concentrations in samples separated by distance h, and n is the number of pairs of samples (Blais and Carlier, 1968; David, 1977) (Figure D-1). Modelling is based on the "spherical" or "Matheron" scheme as summarised in the following equations:

$$\gamma(h) = C(3h/2a - h^3/2a^2) + C_o \qquad H \leq a$$

$$\gamma(h) = C + C_o \qquad H > a$$

The modelling is initiated from the terminal keyboard by specifying values for C_o and A'. The calculated model curve is plotted (Figure D-2), and the calculated values for C and A are displayed. The user can then improve the fit by specifying new values for C, C_o and A. If desired, the user can request that the variogram curve be smoothed to assist in interpretation. Smoothing is performed by a moving average technique with a window of 3, 5, 7, or 9 samples.

Figure D-1 Example of a semi-variogram. (C_o is the variance of immediately adjacent samples, 'a' is the range, and $C+C_o$ is the variance at separations greater than 'a', or the sill variance.)

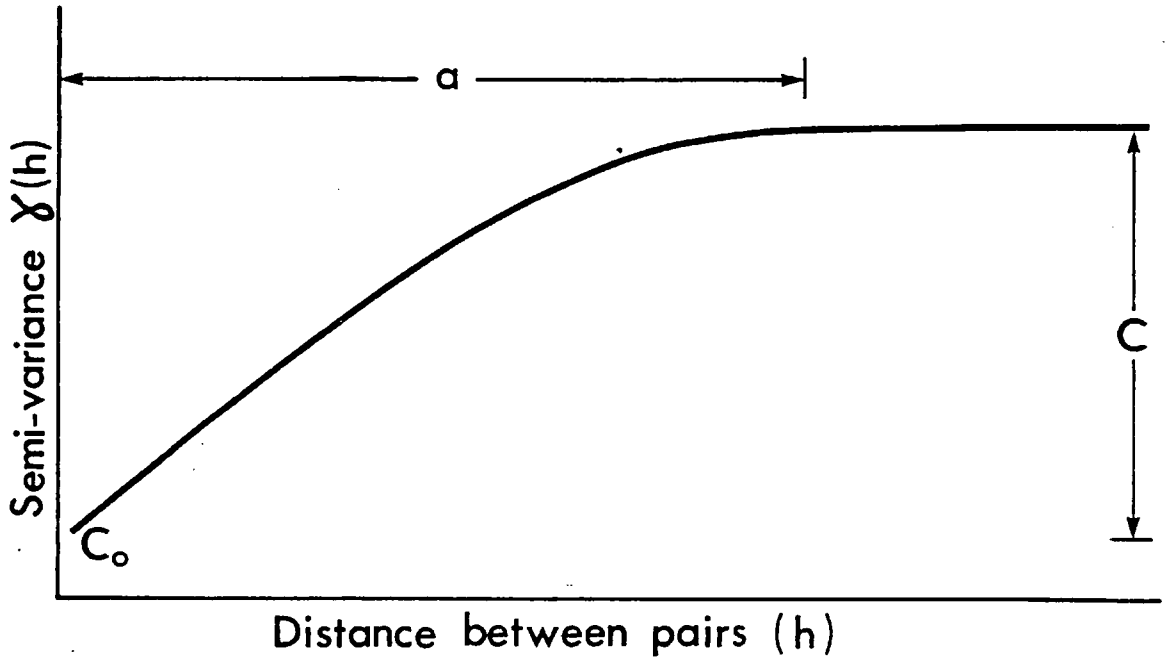
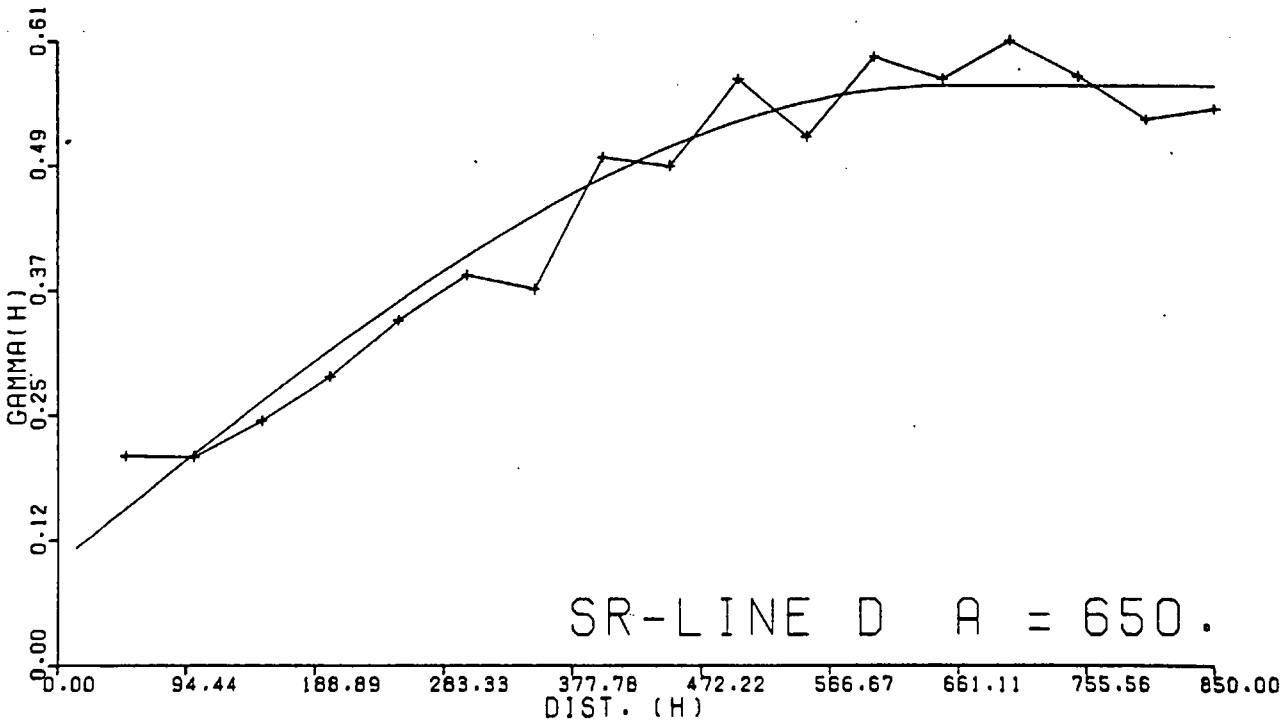


Figure D-2 Example of the output from the program GEOSTAT



LISTING OF THE PROGRAM GEOSTAT

```
C                                                                       MAIN   2
C                                                                       MAIN   3
C                        *** GEOSTAT ***                                MAIN   4
C                                                                       MAIN   5
C            INTERACTIVE-GRAPHICAL GEOSTATISTICAL ANALYSIS              MAIN   6
C                                                                       MAIN   7
C       CONSTRUCTION OF LINE PROFILES AND SEMI-VARIOGRAMS, AND          MAIN   8
C       CURVE FITTING ACCORDING TO THE SPHERICAL MODEL.  FOR AN         MAIN   9
C       OUTLINE OF THE METHOD SEE  BLAIS AND CARLIER- CAN. INST.        MAIN  10
C       MIN. AND METT., SPEC. VOL. 9                                    MAIN  11
C                                                                       MAIN  12
C-----------------------------------------------------------------------MAIN  13
C                                                                       MAIN  14
C   AUTHOR                                                              MAIN  15
C      STEVEN EARLE, DEPARTMENT OF GEOLOGY, IMPERIAL COLLEGE, LONDON    MAIN  16
C   DATE                                                                MAIN  17
C      MARCH 1976   (MODIFIED APRIL 1977, APRIL 1978)                   MAIN  18
C   LANGUAGE, COMPUTER                                                  MAIN  19
C      FORTRAN IV, CDC 6500  (IMPERIAL COLLEGE COMPUTER CENTRE)         MAIN  20
C   METHOD                                                              MAIN  21
C      A VECTOR OF DATA AND A VECTOR OF DISTANCES ARE STORED AS TWO     MAIN  22
C      PARALLEL ARRAYS.  DISTANCES ARE REAL, AND SAMPLES NEED NOT       MAIN  23
C      BE IN ORDER OF INCREASING DISTANCE.  INITIALLY, THE DISTANCES    MAIN  24
C      ARE CHECKED FOR A COMMON FACTOR BY WHICH THEY CAN ALL BE         MAIN  25
C      DIVIDED.  IF NONE IS FOUND, AND ANY DISTANCES EXCEED 500.0,      MAIN  26
C      THE ANALYSIS CANNOT BE COMPLETED.  AFTER THE VARIOGRAM IS        MAIN  27
C      PLOTTED, THE USER IS ASKED TO INPUT VALUES FOR THE FLATTENING    MAIN  28
C      POINT OF THE CURVE AND THE NUGGET EFFECT. A THEORETICAL CURVE,   MAIN  29
C      CONFORMING TO THE SPHERICAL MODEL IS PLOTTED.  THE FIT CAN BE    MAIN  30
C      IMPROVED BY CHANGING THE PARAMETERS DEFINING THE CURVE.          MAIN  31
C                                                                       MAIN  32
C-----------------------------------------------------------------------MAIN  33
C                                                                       MAIN  34
      PROGRAM GEOSTAT(INPUT=131B,OUTPUT=131B,TAPE5=INPUT,TAPE6=131B,    MAIN  35
     + TAPE20=131B,TAPE21=131B,TAPE61=131B,TAPE66=131B)                 MAIN  36
C                                                                       MAIN  37
C     LOGICAL UNITS USED                                                MAIN  38
C                                                                       MAIN  39
C     TAPE5   INPUT FROM TERMINAL                                       MAIN  40
C     TAPE6   OUTPUT TO TERMINAL                                        MAIN  41
C     TAPE20  FILE WHICH INCLUDES *NVAR* - THE NUMBER OF VARIABLES      MAIN  42
C             FOR WHICH DATA IS WRITTEN ON TAPE21, AND A 10 CHARACTER   MAIN  43
C             NAME FOR EACH VARIABLE.  ARRANGED EG. AS FOLLOWS          MAIN  44
C             (STARTING IN COLUMN 1)                                    MAIN  45
C                                                                       MAIN  46
C             03                                                        MAIN  47
C             COPPER                                                    MAIN  48
C             ZINC                                                      MAIN  49
C             MAGNESIUM                                                 MAIN  50
C                                                                       MAIN  51
C     TAPE21  FILE WHICH CONTAINS A SINGLE RECORD FOR EACH VARIABLE,    MAIN  52
C             INCLUDING THE NUMBER OF OBSERVATIONS *NOBS* FOLLOWED BY   MAIN  53
C             PAIRS OF DISTANCES AND DATA VALUES.  EACH RECORD WOULD    MAIN  54
C             THUS BE WRITTEN, IN A SEPARATE PROGRAM, USING THE         MAIN  55
C             STATEMENT                                                 MAIN  56
C                WRITE(21) NOBS,(DIST(J),DAT(J),J=1,NOBS)               MAIN  57
C             (TAPE20 AND TAPE21 CAN BE CREATED USING THE ROUTINE       MAIN  58
C             *START* - AS DESCRIBED BELOW                              MAIN  59
C                                                                       MAIN  60
C     TAPE61 AND TAPE66 ARE FILES USED BY ROUTINES IN THE SIMPLE        MAIN  61
C             LIBRARY. (SEE ICCC BULL. 6.3/6).  TAPE61 CONTAINS         MAIN  62
C             INSTRUCTIONS FOR GENERATION OF MICROFILM PLOTS.           MAIN  63
C                                                                       MAIN  64
C-----------------------------------------------------------------------MAIN  65
C                                                                       MAIN  66
C  EXECUTION PROCEDURE                                                  MAIN  67
C                                                                       MAIN  68
C     THE *GEOSTAT* ROUTINE CAN BE STORED AS A RELOCATABLE BINARY       MAIN  69
C     FILE CREATED FROM THE CARD DECK USING THE CONTROL STATEMENTS-     MAIN  70
C                                                                       MAIN  71
C     MAP(B=BSTATB)                                                     MAIN  72
C     REPLACE(BSTATB)                                                   MAIN  73
C                                                                       MAIN  74
C     EXECUTION OF THE PROGRAM AT A TEKTRONIX TERMINAL WOULD THEN       MAIN  75
C     BE CARRIED OUT USING THE FOLLOWING STATEMENTS (ASSUMING THAT      MAIN  76
C     TAPE20 AND TAPE21 AS DESCRIBED ABOVE ALREADY EXIST AS LOCAL       MAIN  77
C     FILES) -                                                          MAIN  78
C                                                                       MAIN  79
C     GET(BSTATB)                                                       MAIN  80
C     LIBFILE(SIMPLEF)                                                  MAIN  81
C     -SIMPLEF(L=BSTATB)                                                MAIN  82
C                                                                       MAIN  83
C     FOLLOWING EXECUTION, ANY MICROFILM PLOTS FILES GENERATED CAN BE   MAIN  84
C     PROCESSED BY USING THE STATEMENTS -                               MAIN  85
C                                                                       MAIN  86
C     LIBFILE(PROC61)                                                   MAIN  87
C     -PROC61                                                           MAIN  88
C                                                                       MAIN  89
C     A PROCEDURE FOR GENERATION OF TAPE20 AND TAPE21 AND SUBSEQUENT    MAIN  90
C     EXECUTION OF *GEOSTAT* IS AVAILIABLE, AND CAN BE USED AT A        MAIN  91
C     TEKTRONIX TERMINAL AS FOLLOWS -                                   MAIN  92
C                                                                       MAIN  93
C     GET(TAPE4=*USER'S DATA FILENAME* )                                MAIN  94
C     GET(START1/UN=UNFBCOB)                                            MAIN  95
C     -START1                                                           MAIN  96
C                                                                       MAIN  97
C     IF, WITHIN ANY SESSION, EXECUTION IS TERMINATED, AND THE USER     MAIN  98
C     WISHES TO CONTINUE WITH THE SAME DATA SET, THE FOLLOWING          MAIN  99
C     STATEMENTS CAN BE USED -                                          MAIN 100
C                                                                       MAIN 101
C     REWIND(TAPE20,TAPE21)                                             MAIN 102
C     -SIMPLEF(L=BSTATB)                                                MAIN 103
C                                                                       MAIN 104
C-----------------------------------------------------------------------MAIN 105
C                                                                       MAIN 106
C  LIMITATIONS                                                          MAIN 107
C     THE PROGRAM IS DIMENSIONED FOR UP TO 500 OBSERVATIONS AND UP      MAIN 108
C     TO 20 VARIABLES.  DISTANCES NEED NOT BE EVENLY SPACED AS LONG     MAIN 109
C     AS, AFTER DIVISION BY A COMMON FACTOR, ALL DISTANCES ARE LESS     MAIN 110
C     THAN OR EQUAL TO 500.  (BEST RESULTS, HOWEVER, WILL BE            MAIN 111
C     ACHIEVED WITH EVENLY SPACED DATA) THE PROGRAM MUST BE EXECUTED    MAIN 112
C     AT A TEKTRONIX GRAPHICAL TERMINAL.                                MAIN 113
C                                                                       MAIN 114
C-----------------------------------------------------------------------MAIN 115
C                                                                       MAIN 116
C     GRAPHICAL SUBROUTINES CALLED BY *GEOSTAT* ARE DESCRIBED IN        MAIN 117
C     ICCC BULL. 6.3/6.  INCLUDED ARE  -  START,SWITCH,PROMPT,          MAIN 118
C     BUFFEM,HARDCPY,NEWPAGE,FACTOR,PLOT,AXIS,INTENSE,SYMBOL,NUMBER     MAIN 119
C                                                                       MAIN 120
C-----------------------------------------------------------------------MAIN 121
C                                                                       MAIN 122
C                                                                       MAIN 123
      DIMENSION ZED(500),DIST(500),CC2(500)                             MAIN 124
      DIMENSION NAME(20)                                                MAIN 125
C                                                                       MAIN 126
      COMMON /VAR/ NV(551),CC(551),A,CEE,AEST,NOBS,MAXI                 MAIN 127
C                                                                       MAIN 128
      DIMENSION H(51),GAMM(51)                                          MAIN 129
C                                                                       MAIN 130
C        *NAME*    LIST OF VARIABLE NAMES                             MAIN 131
C        *A*       DISTANCE OF FLATTENING POINT OF CURVE              MAIN 132
C        *CEE*     VARIANCE VALUE OF SILL                             MAIN 133
C        *AEST*    ESTIMATED DISTANCE OF FLATTENING POINT OF CURVE    MAIN 134
C        *NOBS*    NUMBER OF OBSERVATIONS                             MAIN 135
C        *MAXI*    MAXIMUM DISTANCE                                   MAIN 136
C        *H*       DISTANCES ON THEORETICAL CURVE                     MAIN 137
C        *GAMM*    SEMI-VARIANCES ON THEORETICAL CURVE                MAIN 138
C                                                                       MAIN 139
C     THE FOLLOWING MUST BE CHANGE TO INCREASE THE NUMBER OF SAMPLES    MAIN 140
C                                                                       MAIN 141
C        *ZED*     LIST OF DATA VALUES                                MAIN 142
C        *DIST*    LIST OF DISTANCES                                  MAIN 143
C        *CC2*     LIST OF SEMI-VARIANCES AFTER SMOOTHING             MAIN 144
C        *X**      LIST OF DISTANCES BETWEEN PAIRS                    MAIN 145
C        *CC*      LIST OF AVERAGE SEMI-VARIANCES                     MAIN 146
C                                                                       MAIN 147
C                                                                       MAIN 148
      DATA YES,3HNO/3HYES,3HNO /                                        MAIN 149
C                                                                       MAIN 150
C                                                                       MAIN 151
C        ENABLE GRAPHICAL OUTPUT AND MICROFILM COPY                     MAIN 152
C                                                                       MAIN 153
C                                                                       MAIN 154
      CALL START(2)                                                     MAIN 155
      CALL SWITCH(8HHARDCPYON)                                          MAIN 156
C                                                                       MAIN 157
C        INPUT TAPE20, NUMBER OF VARIABLES AND VARIABLE NAMES           MAIN 158
C                                                                       MAIN 159
      READ(20,1) NVAR,(NAME(J),J=1,NVAR)                                MAIN 160
    1 FORMAT(I2/(A10))                                                  MAIN 161
      NUMREC=0                                                          MAIN 162
    2 NUMREC=NUMREC+1                                                   MAIN 163
      IF(NUMREC.LE.NVAR) GOTO 3                                         MAIN 164
      REWIND 21                                                         MAIN 165
      NUMREC=1                                                          MAIN 166
C                                                                       MAIN 167
C        ENABLE RECORD CONTROL                                          MAIN 168
C                                                                       MAIN 169
    3 WRITE(6,4)                                                        MAIN 170
    4 FORMAT(/40H      TAPE21 CONTAINS THE FOLLOWING DATA:-/)           MAIN 171
      DO 5 J=1,NVAR                                                     MAIN 172
    5 WRITE(6,6) J,NAME(J)                                              MAIN 173
    6 FORMAT(8H RECORD ,I2,3X,A10)                                      MAIN 174
      WRITE(6,7) NUMREC                                                 MAIN 175
    7 FORMAT(27H THE NEXT RECORD IS NUMBER ,I2)                         MAIN 176
      CALL BUFFEM(-6)                                                   MAIN 177
C                                                                       MAIN 178
C        SELECT VARIABLE FOR INPUT, OR STOP                             MAIN 179
C                                                                       MAIN 180
      CALL PROMPT(75HTYPE 0 TO READ THIS REC. OR -1 TO STOP EXECUTION.  MAIN 181
     1R ENTER A NEW RECORD NO.:,75)                                     MAIN 182
      READ(5,*) NREC                                                    MAIN 183
C                                                                       MAIN 184
C        CHECK POSITION OF TAPE21 AND REWIND IF NECESSARY               MAIN 185
C                                                                       MAIN 186
      IF(NREC.EQ.0) GOTO 9                                              MAIN 187
      IF(NREC.LT.0) STOP                                                MAIN 188
C                                                                       MAIN 189
      REWIND21                                                          MAIN 190
      IF(NREC.EQ.1) GOTO 9                                              MAIN 191
      NUMREC=NREC-1                                                     MAIN 192
C-----------------------------------------------------------------------MAIN 193
      DO 8 N=1,NUMREC                                                   MAIN 194
    8 READ(21)                                                          MAIN 195
      NUMREC=NUMREC+1                                                   MAIN 196
C                                                                       MAIN 197
C        INPUT THE DATA FOR THE CURRENT RECORD NUMBER                   MAIN 198
C                                                                       MAIN 199
    9 NCOUNT=0                                                          MAIN 200
C                                                                       MAIN 201
      READ(21) NOBS,(DIST(I),ZED(I),I=1,NOBS)                          MAIN 202
  101 FORMAT(A3)                                                        MAIN 203
C                                                                       MAIN 204
      WRITE(6,102) NAME(NUMREC),NOBS                                    MAIN 205
  102 FORMAT(24H DATA HAS BEEN READ FOR ,A10/28H THE NO. OF OBSERVATIONSMAIN 206
     1 IS ,I3)                                                          MAIN 207
      CALL BUFFEM(-6)                                                   MAIN 208
C                                                                       MAIN 209
      CALL PROMPT(63HENTER THE MINIMUM NO. OF PAIRS DESIRED FOR VARIANCMAIN 210
     1E CALCULATION,63)                                                 MAIN 211
      READ(5,*) NPAIRS                                                  MAIN 212
C                                                                       MAIN 213
C        CHECK DISTANCE ARRAY FOR COMMON FACTOR                         MAIN 214
C                                                                       MAIN 215
      FACT=1.0                                                          MAIN 216
      XFAC=COMFAC(DIST,NOBS,FACT)                                       MAIN 217
C                                                                       MAIN 218
C        CHECK FOR DISTANCES GREATER THAN 500.                          MAIN 219
C                                                                       MAIN 220
  103 DO 104 I=1,NOBS                                                   MAIN 221
      IF((DIST(I)/XFAC).GT.500.) GOTO 105                               MAIN 222
  104 CONTINUE                                                          MAIN 223
      GOTO 107                                                          MAIN 224
C                                                                       MAIN 225
C        REQUEST USER SUPPLIED COMMON FACTOR                            MAIN 226
C                                                                       MAIN 227
  105 WRITE(6,106)                                                      MAIN 228
  106 FORMAT(54H THE ARRAY NECESSARY TO CONTAIN ALL INTEGRAL DISTANCES/ MAIN 229
     1 48H BETWEEN 0 AND THE MAXIMUM DISTANCE IS TOO LARGE./,55H UNLESS MAIN 230
     2 HERE IS A COMMON FACTOR BY WHICH ALL DISTANCES,/,51H CAN BE DIVIDMAIN 231
     3ED, THE ANALYSIS CANNOT BE COMPLETED.)                            MAIN 232
      CALL BUFFEM(-6)                                                   MAIN 233
      CALL PROMPT(21HENTER A COMMON FACTOR,21)                          MAIN 234
      READ(5,*) FACT                                                    MAIN 235
      NCOUNT=NCOUNT+1                                                   MAIN 236
      IF(NCOUNT-3) 103,2,2                                              MAIN 237
C                                                                       MAIN 238
C        CHECK VALIDITY OF USER SUPPLIED FACTOR                         MAIN 239
C                                                                       MAIN 240
      XFAC=COMFAC(DIST,NOBS,FACT)                                       MAIN 241
      IF((DIST(NOBS)/XFAC).LE.500.) GOTO 107                            MAIN 242
C                                                                       MAIN 243
  107 CALL PROMPT(63HENTER A COMMAND (HELP,NEXT,END,LOGT,GRAF,SMTH,VAR,FMAIN 244
     1IT,FIX,HARD) ,63)                                                 MAIN 245
      READ(5,101) CMND                                                  MAIN 246
C                                                                       MAIN 247
C        BRANCH ON CONTROL OPTION                                       MAIN 248
C                                                                       MAIN 249
C                                                                       MAIN 250
      IF(CMND.EQ.3HEND) STOP                                            MAIN 251
      IF(CMND.EQ.3HNEX) GOTO 2                                          MAIN 252
      IF(CMND.EQ.3HFIT) GOTO 12C                                        MAIN 253
      IF(CMND.EQ.3HFIX) GOTO 15C                                        MAIN 254
      IF(CMND.EQ.3HHAR) GOTO 108                                        MAIN 255
      IF(CMND.EQ.3HSMT) GOTO 108                                        MAIN 256
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      IF (CMD.EQ.'$HELP') CALL HELP                                     MAIN 257
      IF (CMD.EQ.'$LOG') CALL TLOG(ZED,NOBS)                            MAIN 258
      IF (CMD.EQ.'$GRAF') CALL GRAFF(DIST,ZED,NOBS,NAME(NUMREC))        MAIN 259
      IF (CMD.EQ.'$HARD') CALL HARDCPY                                  MAIN 260
      GOTO 107                                                          MAIN 261
C                                                                       MAIN 262
C        CALCULATE SEMI-VARIOGRAM                                       MAIN 263
C                                                                       MAIN 264
  108 CALL VARIO(ZED,DIST,NPAIRS,XFAC,LEN)                              MAIN 265
      IF (CMD.EQ.'$VAR') GOTO 110                                       MAIN 266
C                                                                       MAIN 267
C        SMOOTH ARRAY OF SEMI-VARIANCES                                 MAIN 268
C                                                                       MAIN 269
      CALL PROMPT(40HENTER SMOOTHING WINDOW SIZE (3,5,7 OR 9):,40)      MAIN 270
      READ(5,*) ISMO                                                    MAIN 271
      CALL SMOOTH(CC,CC2,LEN,ISMO)                                      MAIN 272
      DO 109 I=1,LEN                                                    MAIN 273
  109 CC(I)=CC2(I)                                                      MAIN 274
C                                                                       MAIN 275
C        PLOT SEMI-VARIOGRAM                                            MAIN 276
C                                                                       MAIN 277
  110 CALL PLOTSV(NAME(NUMREC),HH,CC,LEN,LEN,1,A)                       MAIN 278
      GOTO 107                                                          MAIN 279
C                                                                       MAIN 280
C        REQUEST PARAMETERS FOR THEORETICAL CURVE                       MAIN 281
C                                                                       MAIN 282
  120 CALL PROMPT(75HENTER AN APPROXIMATION OF THE DISTANCE OF THE FLATTMAIN 283
     1ENING POINT OF THE CURVE:,75)                                     MAIN 284
      READ(5,*) REST                                                    MAIN 285
C                                                                       MAIN 286
C        CALCULATE HEIGHT OF SILL                                       MAIN 287
C                                                                       MAIN 288
      CALL SILL(LEN)                                                    MAIN 289
      A=REST*1.5                                                        MAIN 290
      CALL PROMPT(40HENTER A VALUE FOR THE NUGGET EFFECT, OR 0.0:,40)   MAIN 291
      READ(5,*) XNUG                                                    MAIN 292
C                                                                       MAIN 293
C        DETERMINE SHAPE OF THEORETICAL CURVE                           MAIN 294
C                                                                       MAIN 295
  130 CALL CURVE(A,CEE,H,GAMH,XNUG)                                     MAIN 296
      W(51)=MAXI                                                        MAIN 297
C                                                                       MAIN 298
      DO 140 I=1,51                                                     MAIN 299
      IPL=LEN+I                                                         MAIN 300
      CC(IPL)=GAMH(I)                                                   MAIN 301
  140 HH(IPL)=W(I)                                                      MAIN 302
C                                                                       MAIN 303
C        PLOT ACTUAL AND THEORETICAL CURVES                             MAIN 304
C                                                                       MAIN 305
      CALL PLOTSV(NAME(NUMREC),HH,CC,LEN+51,LEN,1,A)                    MAIN 306
C                                                                       MAIN 307
      GOTO 107                                                          MAIN 308
C                                                                       MAIN 309
C        REQUEST INPUT OF PARAMETERS TO IMPROVE FIT                     MAIN 310
C                                                                       MAIN 311
  150 WRITE(6,160) A,CEE,XNUG                                           MAIN 312
  160 FORMAT(15H AT PRESENT A= ,G10.4,5H, C= ,G10.4,11H AND XNUG=,G10.4)MAIN 313
      CALL BUFFEM(-6)                                                   MAIN 314
      CALL PROMPT(40HENTER NEW VALUES FOR 'A', 'C' AND 'XNUG':,40)      MAIN 315
      READ(5,*) A,CEE,XNUG                                              MAIN 316
      GOTO 130                                                          MAIN 317
C                                                                       MAIN 318
      END                                                               MAIN 319
      SUBROUTINE HELP                                                   MAIN 320
C                                                                       MAIN 321
C                                                                       MAIN 322
C        ROUTINE TO LIST CONTROL OPTION COMMANDS AND THEIR ACTION       MAIN 323
C                                                                       MAIN 324
C                                                                       MAIN 325
C                                                                       MAIN 326
      WRITE(6,100)                                                      MAIN 327
  100 FORMAT(//34H-COMMANDS FOR GEOSTATISTICS PROGRAM//                 MAIN 328
     $$OH HELP   DISPLAY THIS BANNER                          /         MAIN 329
     $$OH END    STOP EXECUTION                               /         MAIN 330
     $$OH NEXT   SKIP TO NEXT VARIABLE                        /         MAIN 331
     $$OH LOGT   LOG(10) TRANSFORMATION OF THE DATA           /         MAIN 332
     $$OH GRAF   PLOT A PROFILE OF THE DATA                   /         MAIN 333
     $$OH VAR    PLOT A VARIOGRAM OF THE DATA                 /         MAIN 334
     $$OH SMTH   SMOOTH THE VARIOGRAM                         /         MAIN 335
     $$OH FIT    FIT THE SPHERICAL MODEL TO THE VARIOGRAM     /         MAIN 336
     $$OH FIX    IMPROVE THE FIT OF THE MODEL                 /         MAIN 337
     $$OH HARD   CREATE MICROFILM COPY OF SCREEN CONTENTS     /)        MAIN 338
C                                                                       MAIN 339
      CALL BUFFEM(-6)                                                   MAIN 340
      RETURN                                                            MAIN 341
      END                                                               MAIN 342
      SUBROUTINE TLOG(ZED,NOBS)                                         MAIN 343
C                                                                       MAIN 344
C        ROUTINE FOR LOG(10) TRANSFORMATION OF DATA                     MAIN 345
C                                                                       MAIN 346
C                                                                       MAIN 347
C                                                                       MAIN 348
      DIMENSION ZED(*OB)                                                MAIN 349
C                                                                       MAIN 350
      NOBS=*OB                                                          MAIN 351
      DO 100 I=1,NOBS                                                   MAIN 352
  100 ZED(I)=ALOG10(ZED(I))                                             MAIN 353
      RETURN                                                            MAIN 354
      END                                                               MAIN 355
      FUNCTION COMFAC(DIST,NIBS,FAC)                                    FACT   2
C                                                                       FACT   3
C        ROUTINE TO FIND A COMMON FACTOR OF THE ELEMENTS OF *DIST*      FACT   4
C                                                                       FACT   5
C        *DIST*   INPUT ARRAY                                           FACT   6
C        *NIBS*   LENGTH OF DIST                                        FACT   7
C        *FAC*    A USER SUPPLIED COMMON FACTOR                         FACT   8
C                                                                       FACT   9
C                                                                       FACT  10
      DIMENSION DIST(NIBS),FACT(8)                                      FACT  11
C                                                                       FACT  12
C        INITIALISE POSSIBLE COMMON FACTORS FOR *DIST*                  FACT  13
C                                                                       FACT  14
      DATA FACT/1000.,500.,100.,50.,20.,10.,5.,2./                      FACT  15
C                                                                       FACT  16
      NOBS=NIBS                                                         FACT  17
      COMFAC=FAC                                                        FACT  18
C                                                                       FACT  19
C        CHECK FOR USER SUPPLIED FACTOR                                 FACT  20
C                                                                       FACT  21
      IF(COMFAC.LE.1.0) GOTO 102                                        FACT  22
      DO 101 I=1,NOBS                                                   FACT  23
      DIS=AINT(DIST(I)/COMFAC)*COMFAC                                   FACT  24
C                                                                       FACT  25
C        TEST FOR INTEGRAL QUOTIENT                                     FACT  26
C                                                                       FACT  27
      IF(DIS.NE.DIST(I))  GOTO 105                                      FACT  28
  101 CONTINUE                                                          FACT  29
      RETURN                                                            FACT  30
C                                                                       FACT  31
C        FACTOR NOT SUPPLIED - TRY VALUES IN *FACT*                     FACT  32
C                                                                       FACT  33
  102 DO 104 J=1,8                                                      FACT  34
      COMFAC=FACT(J)                                                    FACT  35
      DO 103 I=1,NOBS                                                   FACT  36
      DIS=AINT(DIST(I)/COMFAC)*COMFAC                                   FACT  37
C                                                                       FACT  38
C        TEST FOR INTEGRAL QUOTIENT                                     FACT  39
C                                                                       FACT  40
      IF(DIS.NE.DIST(I))  GOTO 104                                      FACT  41
  103 CONTINUE                                                          FACT  42
      RETURN                                                            FACT  43
C                                                                       FACT  44
  104 CONTINUE                                                          FACT  45
C                                                                       FACT  46
C        NON-INTEGRAL QUOTIENT - RETURN WITH FACTOR = 1                 FACT  47
C                                                                       FACT  48
  105 COMFAC=1.                                                         FACT  49
      RETURN                                                            FACT  50
      END                                                               FACT  51
      SUBROUTINE SMOOTH(DAT1,DAT2,LEN,NCLL)                             FACT  52
C                                                                       SMTH   2
C                                                                       SMTH   3
C        SMOOTHING ROUTINE FOR LINEAR DATA                              SMTH   4
C                                                                       SMTH   5
C        *DAT1*   UNSMOOTHED INPUT ARRAY                                SMTH   6
C        *DAT2*   SMOOTHED OUTPUT ARRAY                                 SMTH   7
C        *LEN*    LENGTH OF *DAT1* AND *DAT2*                           SMTH   8
C        *NCLL*   DIAMETER OF SMOOTHING WINDOW (ODD INTEGER BETWEEN     SMTH   9
C                 3 AND 9 INCLUSIVE)                                    SMTH  10
C                                                                       SMTH  11
C        DATA LESS THAN OR EQUAL 0.0 ARE CONSIDERED AS MISSING DATA     SMTH  12
C        AND WILL NOT BE FILLED IN OR USED IN OTHER CALCULATIONS        SMTH  13
C                                                                       SMTH  14
C                                                                       SMTH  15
      DIMENSION DAT1(LEN),DAT2(LEN)                                     SMTH  16
C                                                                       SMTH  17
      LN=LEN                                                            SMTH  18
C                                                                       SMTH  19
C        CHECK FOR ALLOWABLE VALUES OF *NCLL*                           SMTH  20
C                                                                       SMTH  21
      NCL=(FLOAT(NCLL)*0.5)*2.0+1.0                                     SMTH  22
      IF(NCL.GT.9) NCL=9                                                SMTH  23
C                                                                       SMTH  24
C        CALCULATE WINDOW RADIUS                                        SMTH  25
C                                                                       SMTH  26
      NCLR=FLOAT(NCL-1)*0.5                                             SMTH  27
C                                                                       SMTH  28
C        INITIALISE OUTPUT ARRAY                                        SMTH  29
C                                                                       SMTH  30
      DO 40 I=1,LN                                                      SMTH  31
   40 DAT2(I)=0.0                                                       SMTH  32
C                                                                       SMTH  33
      DO 100 I=1,LN                                                     SMTH  34
      IF(DAT1(I).EQ.0.0) GOTO 100                                       SMTH  35
C                                                                       SMTH  36
C        CALCULATE INDECES OF FIRST AND LAST POINTS IN WINDOW           SMTH  37
C                                                                       SMTH  38
      INF=I-NCLR                                                        SMTH  39
      IF(INF.LT.1) INF=1                                                SMTH  40
      INL=I+NCLR                                                        SMTH  41
      IF(INL.GT.LN) INL=LN                                              SMTH  42
C                                                                       SMTH  43
C        SUM DATA WITHIN WINDOW                                         SMTH  44
C                                                                       SMTH  45
      SUM=XN=0.0                                                        SMTH  46
      DO 50 J=INF,INL                                                   SMTH  47
      IF(DAT1(J).EQ.0.0) GOTO 50                                        SMTH  48
      SUM=SUM+DAT1(J)                                                   SMTH  49
      XN=XN+1.                                                          SMTH  50
   50 CONTINUE                                                          SMTH  51
C                                                                       SMTH  52
      IF(XN.EQ.0.0) GOTO 100                                            SMTH  53
C                                                                       SMTH  54
C        AVERAGE DATA WITHIN WINDOW                                     SMTH  55
C                                                                       SMTH  56
      DAT2(I)=SUM/XN                                                    SMTH  57
  100 CONTINUE                                                          SMTH  58
C                                                                       SMTH  59
      RETURN                                                            SMTH  60
      END                                                               SMTH  61
      SUBROUTINE VARIO(ZED,DIST,NPAIRS,XFAC,LEN)                        SMTH  62
C                                                                       SVAR   2
C        CALCULATES A SEMI VARIOGRAM FROM UNEVENLY SPACED DATA          SVAR   3
C                                                                       SVAR   4
C                                                                       SVAR   5
C        *ZED*      ARRAY OF DEPENDANT VARIABLES                        SVAR   6
C        *DIST*     ARRAY OF DISTANCES                                  SVAR   7
C        *NPAIRS*   MINIMUM NO. OF PAIRS FOR VARIANCE CALCULATION       SVAR   8
C        *XFAC*     A COMMON FACTOR FOR THE ELEMENTS OF DIST            SVAR   9
C        *LEN*      THE LENGTH OF THE O/P ARRAYS CC AND HH              SVAR  10
C                                                                       SVAR  11
      COMMON /VAR/ HH(551),CC(551),A,CEE,REST,NOBS,MAXI                 SVAR  12
      DIMENSION ZED(500),DIST(500),N(500)                               SVAR  13
C                                                                       SVAR  14
C        *N*      LIST OF NO. OF PAIRS AT EACH SEPARATION DISTANCE      SVAR  15
C                                                                       SVAR  16
      AXI=-1.0E20                                                       SVAR  17
C                                                                       SVAR  18
C        FIND MAXIMUM SEPARATION DISTANCE                               SVAR  19
C                                                                       SVAR  20
      DO 101 I=1,NOBS                                                   SVAR  21
      DIST(I)=DIST(I)/XFAC                                              SVAR  22
      IF(DIST(I).GT.AXI) AXI=DIST(I)                                    SVAR  23
  101 CONTINUE                                                          SVAR  24
      MAXD=AXI                                                          SVAR  25
C                                                                       SVAR  26
C        INITIALISE SEMI-VARIANCE AND NO. OF PAIRS ARRAYS               SVAR  27
C                                                                       SVAR  28
      DO 102 J=1,MAXD                                                   SVAR  29
      CC(J)=0.0                                                         SVAR  30
      N(J)=0                                                            SVAR  31
  102 CONTINUE                                                          SVAR  32
C                                                                       SVAR  33
      NIBS=NOBS-1                                                       SVAR  34
C                                                                       SVAR  35
C        COMPARE ALL POSSIBLE PAIRS                                     SVAR  36
C                                                                       SVAR  37
      DO 202 I=1,NIBS                                                   SVAR  38
      K=I+1                                                             SVAR  39
      DO 201 J=K,NOBS                                                   SVAR  40
C                                                                       SVAR  41
C        CALCULATE DISTANCE                                             SVAR  42
C                                                                       SVAR  43
                                                                        SVAR  44
                                                                        SVAR  45
                                                                        SVAR  46
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      XX=DIST(LO-DIST(I)                                                SVAR  47
      IF(XX.EQ.0.0) GOTO 201                                            SVAR  48
      L=L+1                                                             SVAR  49
C                                                                       SVAR  50
C        CALCULATE VARIANCE                                             SVAR  51
C                                                                       SVAR  52
      ZD=ZED(LO-ZED(I)                                                  SVAR  53
      CC(L)=CC(L)+ZD*ZD                                                 SVAR  54
      N(L)=N(L)+1                                                       SVAR  55
  201 CONTINUE                                                          SVAR  56
  202 CONTINUE                                                          SVAR  57
C                                                                       SVAR  58
C        CALCULATE AVERAGE SEMI-VARIANCE FOR EACH DISTANCE              SVAR  59
C                                                                       SVAR  60
      DO 204 J=1,MAXO                                                   SVAR  61
C                                                                       SVAR  62
C        DETERMINE MAXIMUM SEPARATION                                   SVAR  63
C                                                                       SVAR  64
      IF(N(L).GE.NPAIRS) GOTO 203                                       SVAR  65
      CC(L)=0.0                                                         SVAR  66
  203 CC(L)=CC(L)/FLOAT(N(L))*0.5                                       SVAR  67
C                                                                       SVAR  68
      HH(L)=FLOAT(L)*XFAC                                               SVAR  69
  204 CONTINUE                                                          SVAR  70
      AXI=-1.0E20                                                       SVAR  71
      LEN=NOBS-NPAIRS                                                   SVAR  72
      DO 205 I=1,LEN                                                    SVAR  73
      IF(HH(I).GT.AXI) AXI=HH(I)                                        SVAR  74
  205 CONTINUE                                                          SVAR  75
      MAXI=AXI                                                          SVAR  76
      DO 206 I=1,NOBS                                                   SVAR  77
  206 DIST(I)=DIST(I)*XFAC                                              SVAR  78
C                                                                       SVAR  79
      RETURN                                                            SVAR  80
      END                                                               SVAR  81
      SUBROUTINE SILL(LEN)                                              SVAR  82
C                                                                       SVAR  83
C        ROUTINE TO DETERMINE THE AVERAGE VALUE OF THE MEMBERS OF       SVAR  84
C        THE ARRAY *CC* WHERE VALUES OF THE ARRAY *HH* ARE              SVAR  85
C        GREATER THAN *REST*                                            SVAR  86
C                                                                       SVAR  87
C        *LEN*     LENGTH OF *HH* AND *CC*                              SVAR  88
C                                                                       SVAR  89
C                                                                       SVAR  90
      COMMON /VAR/ HH(551),CC(551),A,CEE,REST,NOBS,MAXI                 SVAR  91
C                                                                       SVAR  92
      SUM=0.                                                            SVAR  93
      NUM=0                                                             SVAR  94
      LEND=LEN                                                          SVAR  95
C                                                                       SVAR  96
      DO 100 I=1,LEND                                                   SVAR  97
      IF(HH(I).LT.REST) GOTO 100                                        SVAR  98
      SUM=SUM+CC(I)                                                     SVAR  99
      NUM=NUM+1                                                         SVAR 100
  100 CONTINUE                                                          SVAR 101
C                                                                       SVAR 102
      CEE=SUM/FLOAT(NUM)                                                SVAR 103
      RETURN                                                            SVAR 104
      END                                                               SVAR 105
      SUBROUTINE CURVE(AAA,CCC,N,GAMM,XNUG)                             SVAR 106
C                                                                       SVAR 107
C        A ROUTINE TO FIT A SPHERICAL CURVE TO A SEMI-VARIOGRAM         SVAR 108
C                                                                       SVAR 109
C                                                                       SVAR 110
C        *AAA*     ESTIMATED FLATTENING POINT OF CURVE                  SVAR 111
C        *CCC*     LEVEL OF SILL (FROM SUBROUTINE SILL)                 SVAR 112
C        *N*       OUTPUT ARRAY OF DISTANCES                            SVAR 113
C        *GAMM*    OUTPUT ARRAY OF VARIANCES                            SVAR 114
C                                                                       SVAR 115
C                                                                       SVAR 116
      DIMENSION N(51),GAMM(51)                                          SVAR 117
      A=AAA                                                             SVAR 118
      CEE=CCC                                                           SVAR 119
C                                                                       SVAR 120
      ACUBE=AAA*AAA*2.                                                  SVAR 121
      AT2=AAA                                                           SVAR 122
C                                                                       SVAR 123
C        CALCULATE FIRST 49 VALUES                                      SVAR 124
C                                                                       SVAR 125
      DO 102 J=1,49                                                     SVAR 126
      HJ=0.02*FLOAT(J)*AA                                               SVAR 127
      HCUBE=HJ*HJ*HJ                                                    SVAR 128
      GAMM(J)=CEE*((3.*HJ)/(AT2))-(HCUBE/ACUBE))                        SVAR 129
      GAMM(J)=GAMM(J)*((CEE-XNUG)/CEE)+XNUG                             SVAR 130
  102 N(J)=HJ                                                           SVAR 131
C                                                                       SVAR 132
C        50TH AND 51ST VALUE OF *GAMM* EQUAL LEVEL OF SILL              SVAR 133
C                                                                       SVAR 134
      N(50)=AA                                                          SVAR 135
      GAMM(50)=GAMM(51)=CEE                                             SVAR 136
      RETURN                                                            SVAR 137
      END                                                               SVAR 138
      SUBROUTINE PLOTSV(NAME,HH,CC,LENT,LEN,IOPT,A)                     SVAR 139
C                                                                       PLOT   2
C        ROUTINE TO CONSTRUCT A GRAPH OF 1 OR 2 VECTORS                 PLOT   3
C                                                                       PLOT   4
C        *NAME*    10 CHARACTER TITLE                                   PLOT   5
C        *HH*      INDEPENDENT OR VARIATE                               PLOT   6
C        *CC*      DEPENDENT (Y) VARIATE                                PLOT   7
C        *LENT*    TOTAL LENGTH OF ARRAYS HH AND CC                     PLOT   8
C        *LEN*     PART OF HH AND CC WHICH IS TO BE PLOTTED AS LINE     PLOT   9
C                  SEGMENTS (BEING X'S. THE REMAINING (LENT-LEN) ARRAY  PLOT  10
C                  ELEMENTS WILL BE PLOTTED AS A SINGLE CURVE.          PLOT  11
C        *IOPT*    PLOTTING OPTION (1 FOR VARIOGRAM, 2 FOR LINE PROFILE)PLOT  12
C                  WHEN *IOPT* = 1 MINIMUM Y VALUE WILL BE 0. AND *NAME*PLOT  13
C                  WILL BE PLOTTED IN THE LOWER RIGHT HAND CORNER.      PLOT  14
C        *A*       X VALUE FOR FLATTENING POINT OF CURVE                PLOT  15
C                                                                       PLOT  16
C                                                                       PLOT  17
C                                                                       PLOT  18
      DIMENSION HH(LENT),CC(LENT),RX(2),RY(2)                           PLOT  19
      DIMENSION N(53),GAMM(53)                                          PLOT  20
      DATA RX/10*DIST. 00  ,10H DISTANCE /,RY(1)/10H GAMMA 00  /        PLOT  21
     RY(2) *NAME                                                        PLOT  22
C                                                                       PLOT  23
C        INITIALISE PLOTTING PARAMETERS                                 PLOT  24
C                                                                       PLOT  25
      CALL NEWPAGE                                                      PLOT  26
      CALL FACTOR(2.0)                                                  PLOT  27
      CALL PLOT(0.25,0.5,-3)                                            PLOT  28
C                                                                       PLOT  29
C        CALCULATE AXIS INCREMENTS AND PLOT AXES                        PLOT  30
C                                                                       PLOT  31
      DELTRX=HH(LENT)/8.                                                PLOT  32
      AMAXX=-1.0E20                                                     PLOT  33
      AMINY=1.0E20                                                      PLOT  34
C                                                                       PLOT  35
      DO 100 I=1,LEN                                                    PLOT  36
      IF(CC(I).GT.AMAXX) AMAXX=CC(I)                                    PLOT  37
      IF(CC(I).LT.AMINY) AMINY=CC(I)                                    PLOT  38
  100 CONTINUE                                                          PLOT  39
C                                                                       PLOT  40
      FIRSTV=AMINY                                                      PLOT  41
      IF(IOPT.EQ.1) FIRSTV=0.0                                          PLOT  42
      DELTRY=(AMAXY-FIRSTV)/5.0                                         PLOT  43
C                                                                       PLOT  44
      CALL AXIS(0.0,0.0,0.0,HX(IOPT),-10.0,9.0,0.0,FIRSTV,DELTAX)      PLOT  45
      CALL AXIS(0.0,0.0,0.0,HY(IOPT),10.0,5.0,90.0,FIRSTV,DELTAY)      PLOT  46
C                                                                       PLOT  47
      CALL INTENSE(25)                                                  PLOT  48
C                                                                       PLOT  49
C        DRAW THEORETICAL CURVE IF CALCULATED                           PLOT  50
C                                                                       PLOT  51
      IF(LENT-LEN.EQ.0) GOTO 102                                        PLOT  52
      DO 101 I=51                                                       PLOT  53
      IPL=LEN+I                                                         PLOT  54
      GAMM(I)=CC(IPL)                                                   PLOT  55
  101 N(I)=HH(IPL)                                                      PLOT  56
C                                                                       PLOT  57
      N(52)=0.0                                                         PLOT  58
      GAMM(52)=0.0                                                      PLOT  59
      N(53)=DELTRX                                                      PLOT  60
      GAMM(53)=DELTRY                                                   PLOT  61
C                                                                       PLOT  62
      CALL LINE(N,GAMM,51,1,0,0)                                        PLOT  63
      CALL SYMBOL(7.0,0.25,0.28,4HR =  ,0.0,4)                          PLOT  64
      CALL NUMBER(8.0,0.25,0.28,A,0.0,0)                                PLOT  65
      CALL INTENSE(16)                                                  PLOT  66
C                                                                       PLOT  67
C        DRAW ACTUAL CURVE                                              PLOT  68
C                                                                       PLOT  69
  102 HH(LENT+1)=0.0                                                    PLOT  70
      CC(LENT+1)=0.0                                                    PLOT  71
      HH(LENT+2)=DELTRX                                                 PLOT  72
      CC(LENT+2)=DELTRY                                                 PLOT  73
      CALL LINE(HH,CC,LEN,1,1,3)                                        PLOT  74
C                                                                       PLOT  75
      IF(IOPT.EQ.1) CALL SYMBOL(4.0,0.25,0.28,NAME,0.0,10)              PLOT  76
      RETURN                                                            PLOT  77
      END                                                               PLOT  78
      SUBROUTINE GRAFT(DIST,ZED,NOBS,NAME)                              PLOT  79
C                                                                       PLOT  80
C        ROUTINE TO ENABLE REMOVAL OF EXTREME VALUES FROM *ZED*         PLOT  81
C                                                                       PLOT  82
C                                                                       PLOT  83
C        *DIST*    INDEPENDANT OR ARRAY                                 PLOT  84
C        *ZED*     DEPENDANT (Y) ARRAY                                  PLOT  85
C        *NOBS*    LENGTH OF *DIST* AND *ZED*                           PLOT  86
C        *NAME*    TEN CHARACTER TITLE                                  PLOT  87
C                                                                       PLOT  88
C                                                                       PLOT  89
      DIMENSION DIST(500),ZED(500)                                      PLOT  90
      NOB=NOBS                                                          PLOT  91
C                                                                       PLOT  92
C        PLOT GRAPH OF *DIST* AND *ZED*                                 PLOT  93
C                                                                       PLOT  94
   90 CALL PLOTSV(NAME,DIST,ZED,NOB,NOB,2,0.0)                          PLOT  95
C                                                                       PLOT  96
C        DETERMINE IF EDITING IS REQUIRED                               PLOT  97
C                                                                       PLOT  98
C                                                                       PLOT  99
  100 CALL PROMPT(42,*TYPE 0 TO CONTINUE, 1 TO EDIT, 2 TO REPLOT.*)     PLOT 100
      READ(5,*) IOPT                                                    PLOT 101
      IF(IOPT.EQ.0) RETURN                                              PLOT 102
      IF(IOPT.EQ.2) GOTO 90                                             PLOT 103
      J=0                                                               PLOT 104
C                                                                       PLOT 105
C        REQUEST THRESHOLD VALUE                                        PLOT 106
C                                                                       PLOT 107
      WRITE(5,110)                                                      PLOT 108
  110 FORMAT(51HIT IS POSSIBLE TO REMOVE ALL DATA ABOVE OR BELOW A THRESPLOT 109
     1HOLD.)                                                            PLOT 110
      CALL BUFFEM(-6)                                                   PLOT 111
      CALL PROMPT(76,*ENTER A THRESHOLD AND -1 TO REMOVE LOWER VALUES OR PLOT 112
     +1 TO REMOVE HIGHER VALUES.*)                                      PLOT 113
C                                                                       PLOT 114
      READ(5,*) THRSH,ITYPE                                             PLOT 115
      IF(ITYPE.EQ.-1) GOTO 140                                          PLOT 116
C                                                                       PLOT 117
C        REMOVE *ZED* VALUES ABOVE THRESHOLD                            PLOT 118
C                                                                       PLOT 119
      DO 120 I=1,NOB                                                    PLOT 120
      IF(ZED(I).GT.THRSH) GOTO 120                                      PLOT 121
      J=J+1                                                             PLOT 122
      ZED(J)=ZED(I)                                                     PLOT 123
      DIST(J)=DIST(I)                                                   PLOT 124
  120 CONTINUE                                                          PLOT 125
C                                                                       PLOT 126
  125 NOUT=NOB-J                                                        PLOT 127
      WRITE(5,130) NOUT                                                 PLOT 128
  130 FORMAT(I3,25H POINTS HAVE BEEN REMOVED)                           PLOT 129
      CALL BUFFEM(-6)                                                   PLOT 130
      NOBS=NOB=J                                                        PLOT 131
      GOTO 100                                                          PLOT 132
C                                                                       PLOT 133
C        REMOVE *ZED* VALUES BELOW THRESHOLD                            PLOT 134
C                                                                       PLOT 135
  140 DO 150 I=1,NOB                                                    PLOT 136
      IF(ZED(I).LT.THRSH) GOTO 150                                      PLOT 137
      J=J+1                                                             PLOT 138
      ZED(J)=ZED(I)                                                     PLOT 139
      DIST(J)=DIST(I)                                                   PLOT 140
  150 CONTINUE                                                          PLOT 141
C                                                                       PLOT 142
      GOTO 125                                                          PLOT 143
      END                                                               PLOT 144
```

APPENDIX E RESULTS OF GEOSTATISTICAL ANALYSIS OF GEOCHEMICAL SAMPLES

E-1 Introduction

Most variables studied by exploration geochemists can be considered to be "regionalised" in the sense that they demonstrate generally continuous spatial variation which cannot be adequately described by mathematical functions. The theory of "regionalised" variables" was developed by Matheron and co-workers in France, (Matheron, 1963) and has recently been summarised by David (1977). In mining problems, the theory and its basic tool, the semi-variogram, are used to characterise the spatial auto-covariance of ore grades (ie. the degree of variability between adjacent and sub-adjacent samples), in order to make reliable estimates of ore distributions and reserves. The method involves interpolation between points where grades are known. This application has been treated at length by David (1977) and Blais and Carlier (1968). A comprehensive summary of the English language literature on geostatistics as applied to mining problems, has been compiled by Bell and Reeves (1979).

The basic information which is provided by a semi-variogram is the distance at which two samples are independent of each other. An example is given in Figure D-1. In this case the average variance is low between pairs close to each other and increases as the distance between pairs increases. There is a distance "a" at which the variance no longer increases with increasing separation. This distance is called the range and it is an approximation of the minimum distance at which two samples are independent of each other. The idealised semi-variogram shown here conforms to the spherical, or Matheron model, which will be used throughout this discussion.

In exploration geochemistry the ultimate goal is different from that of mining. Instead of wishing to accurately interpolate between points where values are known, one attempts to define areas of metal enhancement which may be related to ore deposits, and to discern "regional" patterns of metal distribution which may reveal various features of geology, metallogeny, or secondary dispersion. One of the persisitent problems in exploration geochemistry is deciding what sample spacing will provide comprehensive cover at minimal cost. With knowledge of the spatial auto-covariance of the data, one can estimate such an optium sample spacing.

As stated above, the semi-variogram provides an estimation of the minimum distance at which two samples are independent of each other. With sample spacing greater than this minimum distance, one cannot gain complete information. With sample spacing less than the minimum distance, one is, to some degree, duplicating information. In the following discussion the minimum independence distance will be referred to as the "range".

In surficial sampling media there are two levels of "regionalisation" of geochemical variables. The "primary" range is a function of variations in the geochemistry of the bedrock, and can vary from a few metres to several kilometres. The primary range is obviously dependent on local geological features, and a range determined for one area or circumstance could not necessarily be applied in other circumstances. "Secondary" variation is caused by mixing during the erosional process. In soils, for example, the secondary range will be in the order of a few centimetres or a few metres. For other media such as stream sediments or glacial tills, mixing is more pronounced, and the secondary range could be hundreds or even thousands of metres. The secondary range is independent of bedrock geology, and hence a range determined for one area should be applicable in other areas.

To date, the application of geostatistics in geochemical sampling problems has been very limited. Dijkstra and Kubic (1975) have applied a similar technique (auto-correlation analysis) to stream sediment data, as have Hodgson (1972) and Webster and Cuanalo (1975) to soil data. Sinclair (1975) has discussed this use of serial correlations and has questioned its value because of the difficulty in relating test data to data from a real survey. Croissant (1977) and Howarth and Martin (1978) have discussed the application of semi-variograms in exploration geochemistry. Some of the geostatistical results presented in this section have been used by Earle (1978).

The objective of the present research is to further assess the applicability of geostatistical analysis to geochemical sampling problems. To this end, lines of evenly spaced soil samples and stream sediment samples were collected from both mineralised and unmineralised areas. Semi-variograms were constructed from the data and the indicated ranges were used in designing further sampling programs.

E-2 Data Sets

Soil geochemical data was acquired from an area of lead and zinc mineralisation in the Mendip Hills and from the strontium bearing area around Latteridge. These data sets have been described in Chapters 5 and 6. In the Mendip area, sample lines are both perpendicular and parallel to the geological strike, and are in both mineralised and unmineralised areas. In all cases considerable effort was made to avoid sampling across variations in soil type. At Latteridge, all of the lines are perpendicular to the strike of a zone of celestite mineralisation.

For stream sediment geochemical data, selection of suitable streams was based on criteria that they should be free from anthropogenic influences and should have no significant tributaries for at least 2 000 metres. Within the study area very few streams were found to meet these criteria, and even those which appeared to be suitable from a map, turned out to be less than ideal.

The first of the two sections sampled is within Mells Park, 6 kilometres west of Frome, between the National Grid coordinates (722 489) and (704 474). The area is underlain by lower-Carboniferous Limestone, middle-Carboniferous coal bearing shale and sandstone, and Triassic Dolomitic Conglomerate. Stream width averages about 1.5 metres, and depth is about .2 metres. Relief is low, with a drop of about 35 metres over a length of 2 800 metres. Sediment samples were collected and stream water and temperature were measured at 100 metre intervals. A 300-metre section was sampled at 10 metre intervals. At the time of sampling the stream did not flow at surface over the 1 200 metre portion underlain by Carboniferous Limestone. For part of this distance, sediment samples were collected from the dry stream bed.

The second stream flows over farm land near Pucklechurch, 10 kilometres east of Bristol, and is underlain predominantly by Jurassic clay and limestone. Triassic Keuper Marl mudstone is also present. The section sampled lies between the points (708 767) and (710 752). Relief is very low with a drop of about 20 metres in 2 500 metres. Average stream width is 1.7 metres and depth is 0.2 metres. A few hundred metres of the stream has been disturbed by ditching, and at one point effluent is introduced from a small water treatment plant. Temperature and pH were determined and samples were collected at 100-metre intervals.

Sediment samples were analysed for iron, manganese, copper, lead, zinc, magnesium, calcium, strontium, barium and potassium by emission spectrophotometry.

E-2.1 Mendip Area

The Mendip area data comprise samples along five lines in areas of mineralisation, and two regional lines, one across strike and crossing one of the mineralised areas, and another along strike and remote from mineralisation. The lines can be briefly described as follows:

1) Chewton Warren (550 520) - samples at 10 metre intervals over a length of 570 metres in an area of lead mineralisation;
2) Longwood A (530 555) - samples at 10 metre intervals over 200 metres in an area of lead mineralisation;
3) Longwood B (530 550) - samples at 10 metre intervals over 230 metres, adjacent to Longwood A, but in a levelled and ploughed field;
4) Shipham (445 580) - samples at 10 metre intevals over 250 metres in an area of zinc mineralisation;
5) Slab House (593 483) - samples at 20 metre intervals over 580 metres in an area of presumed zinc mineralisation;
6) Compton Martin (546 565) to Carscliff Farm (488 528) - samples at 50 and 100 metre intervals over 7 kilometres across strike, including a 200-metre zone with lead mineralisation;
7) Charterhouse (498 557) to Longbottom (446 566) - samples at 100 metre intervals over 6 kilometres along geological strike.

Some of the better fitting semi-variograms are shown in Figure E-1 and E-2 and a summary of the ranges is given in Figure E-3.

Representative ranges for the mineralised areas are 200 to 250 metres at Chewton Warren, 70 metres at Longwood A, 130 metres at Longwood B, 90 metres at Shipham, and 240 to 250 metres for some elements, and 325 to 375 metres for other elements at Slab House. For the Compton Martin to Carscliff Farm traverse, several of the variables show a nested structure (Figure E-2), which could be interpreted by using two models and hence two ranges (cf. Sinclair and Deraisme, 1974). Taking all the data for this line together, the two ranges are 800 to 1 000 metres, and 2 000 to 2 200 metres. For the Charterhouse to Longbottom traverse, along geological strike, the ranges vary from 1 300 to 1 600 metres.

E-2.2 Latteridge Area

Strontium data for 850 soil samples from the Latteridge area were provided by the Mineral Assessment Unit of the Institute of Geological Sciences.

Figure E-1 Representative semi-variograms from some of the Mendip Hills area soil sample lines

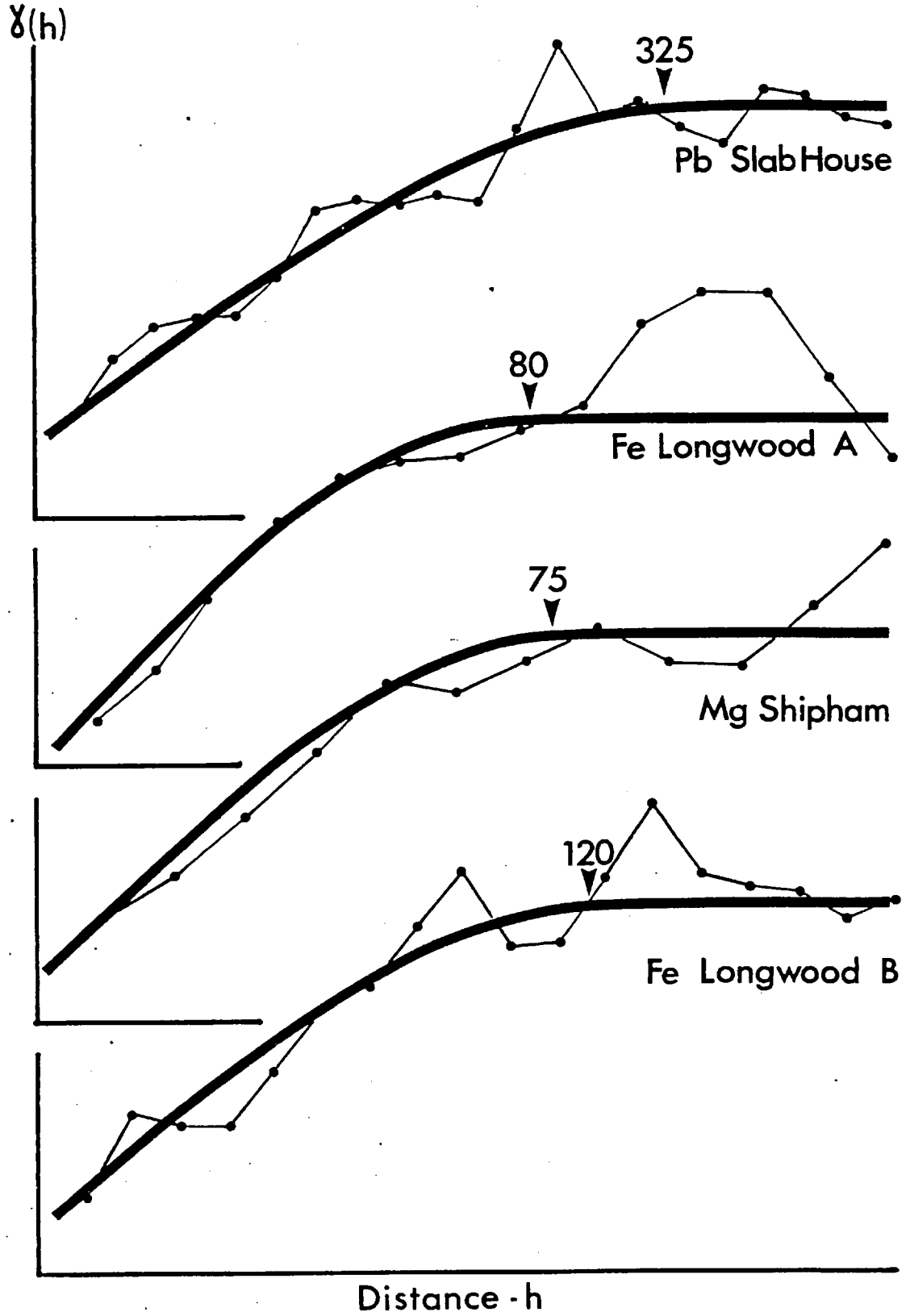


Figure E-2 Example of a nested semi-variogram

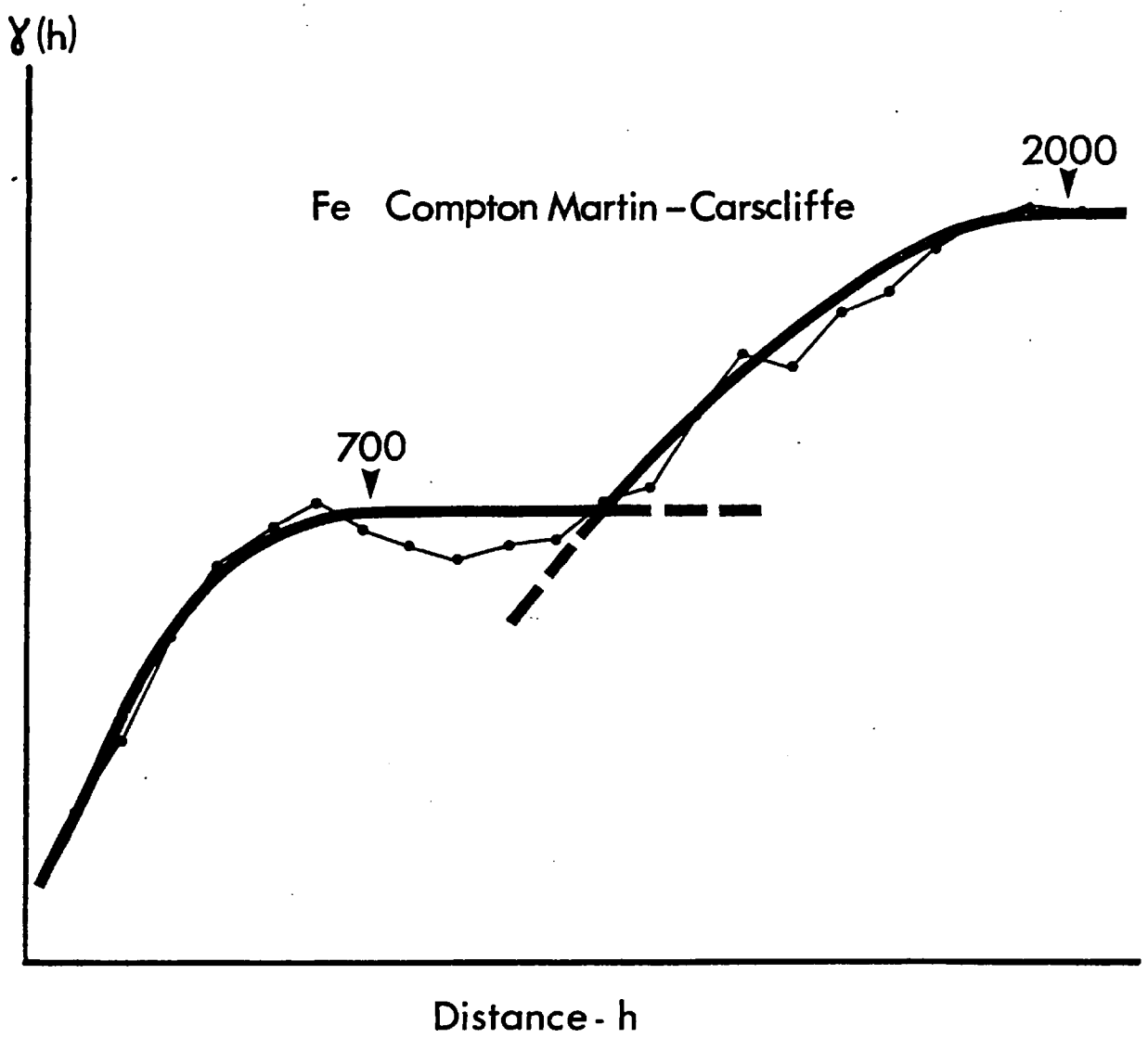
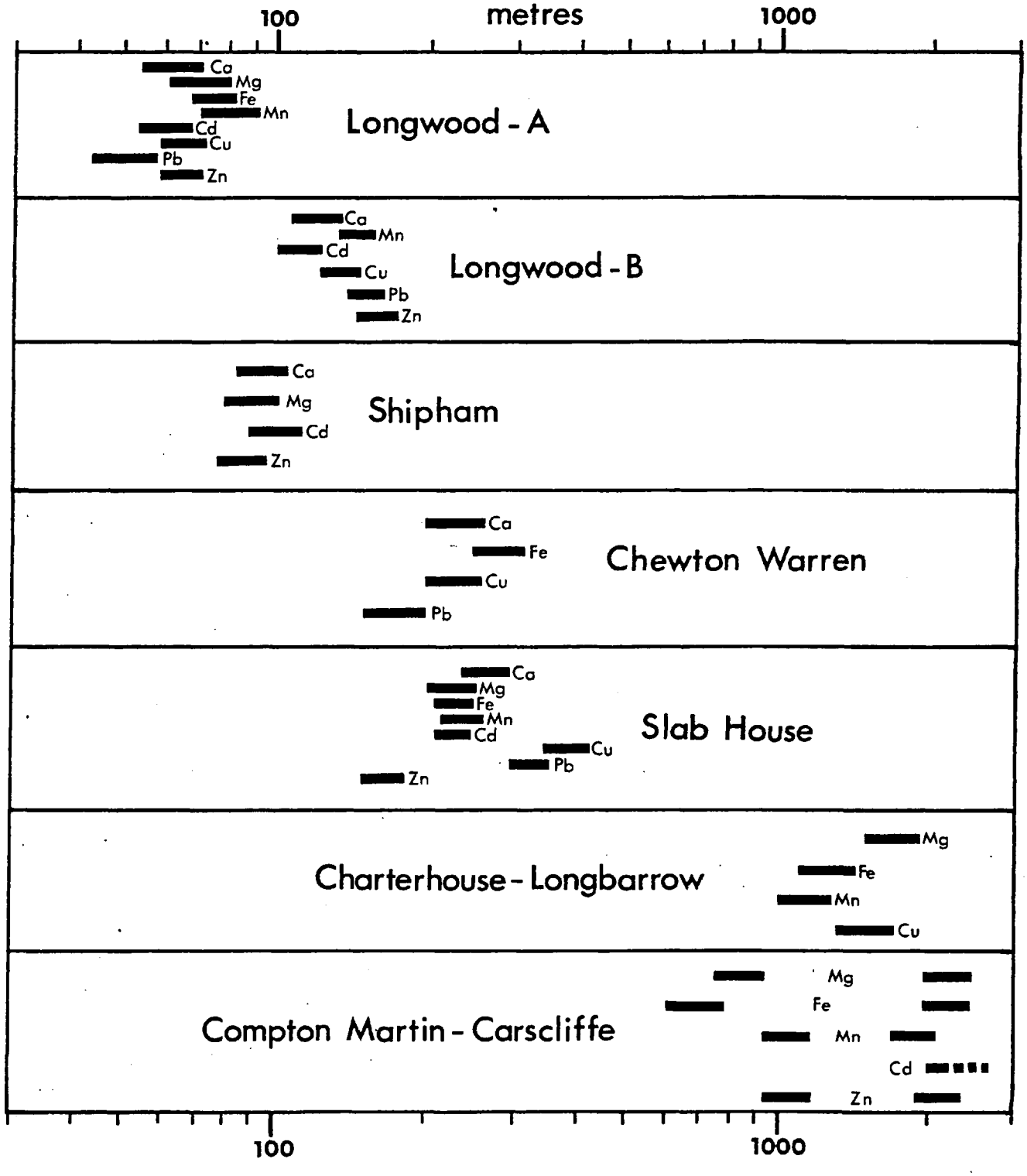


Figure E-3 Limits of ranges for various elements for the Mendip Hills sample lines. (Variables not shown do not correspond to the spherical model.)



Samples were collected at 50 metre intervals along lines across strike and across a zone of celestite mineralisation. Semi-variograms were constructed for 10 lines, 4 of which are shown in Figure E-4. The ranges vary from 400 to 750 metres, with an average of 550 metres.

E-2.3 Mells Park and Pucklechurch Areas

The data consists of geochemical analyses of stream sediments as well as temperature and pH of stream water, sampled at 10 and 100 metre intervals in the Mells Park stream, and at 100 metre intervals in the Pucklechurch stream. Results of the semi-variogram analyses are summarised in Table E-1. For most of the chemical parameters, the apparent range is in the order of 1 100 to 1 500 metres. Ranges for barium and potassium are shorter at 950 and 700 metres, and that for water temperature is 2 200 metres. Ranges for pH, iron, and copper are not given because the data do not fit the spherical model adequately.

E-3 Discussion

E-3.1 Mendip Area

The purpose of applying geostatistical analysis to the Mendip soil sampling problem was to establish maximum and minimum sampling intervals for regional soil surveys so that comprehensive coverage of a large area could be obtained with as few samples as possible, and so that statistically independent samples could be collected from individual mineralised area. Unfortunately it wasn't clear which geological features would be most useful to define. Part of the difficulty lay in the fact that the various mineralised areas are of differing sizes, and some appear to consist of a number of discrete zones.

The regional traverse from Compton Martin to Carscliff Farm crosses one major zone of mineralisation and several smaller zones, and it might be assumed that a range calculated from this data could be used as the maximum sampling interval for a regional grid to define mineralised areas. Many of the semi-variograms for these data show nested structures, and there are two apparent ranges - one at 700 to 1 000 metres and another at 2 000 to 2 200 metres (Figure E-2). The semi-variogram for lead, which is the main ore mineral in this area, has no sill, however, so it is questionable if either of the two ranges relate to mineralisation. The best fitting semi-variograms are for magnesium and iron,

Figure E-4 Representative semi-variograms for strontium in some of the Latteridge area soil sample lines

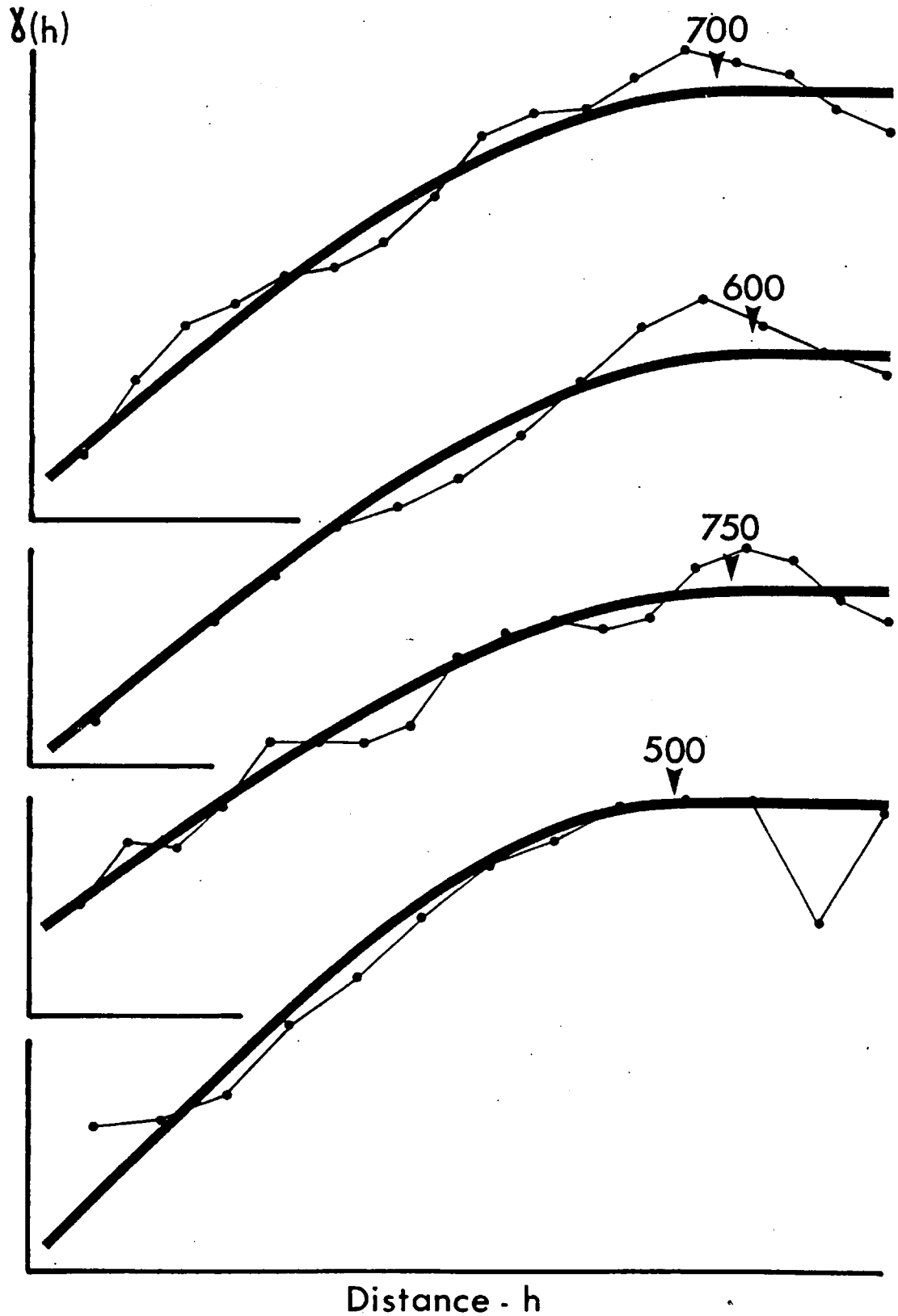


Table E-1 Dispersion distances as determined from semi-variograms for geochemical data from the Mells Park and Pucklechurch streams

Variable	Fit to model	Distance(m)
Temperature	Good	2200
Mn	Fair	1200
Pb	Good	1450
Zn	Good	1100
Mg	Fair	1500
Ca	Good	1350
Sr	Good	1200
Ba	Fair	950
K	Fair	700

and most of the variability in these elements is related to bedrock geology, that is, conglomerate versus limestone.

Ranges for the lines from individual mineralised areas vary from around 70 metres at Longwood A, to over 300 metres for some elements at Slab House. In most cases these ranges represent the widths of the individual mineralised zones. This can be seen in the data for the Longwood area. Longwood A and B are some 200 metres apart along the strike of the mineralisation. At longwood A there are two separate mineralised zones, each about 60 metres wide. Towards the east, at Longwood B, these two zones merge into one which is about 130 metres wide. These widths compare well with the ranges for these two lines (Figure E-3).

Semi-variograms from the long traverse from Compton Martin to Carscliff Farm were used in choosing the sample spacing for a regional soil grid, and the spacing of 1 000 metres was selected (see Chapter 5 for a discussion of the geochemistry of these samples). In retrospect, this may not have been a good decision for two reasons. Firstly, a sampling interval based on these semi-variograms should have been chosen at just less than the minimum range, (for example, 600 metres), rather than at the maximum range. Secondly, as pointed out above, it is doubtful if the structures identified by these semi-variograms actually relate to mineralisation, and hence they should not have been used to choose the sample spacing for a grid which was intended to identify mineralised zones.

The semi-variograms for traverses over mineralised areas appear to provide valid estimations of the width of the mineralised zones. On this basis one might select sample intervals varying from 50 metres (using the Longwood A data) to 200 metres (using the Chewton Warren or Slab House data) for grids to identify individual mineralised zones. A square grid with sample spacing of 70 metres in both directions was used in the Stow Barrow mineralised area. This survey was successful in identifying two separate mineralised zones, one about 200 metres wide and over 500 metres long, and a second 150 by 350 metres.

E-3.2 Latteridge Area

The strontium mineralisation in the Latteridge area is far less complex than the Mendip lead-zinc mineralisation, and the geostatistical results from this

area are relatively easy to interpret and apply. Ranges vary from 400 to 750 metres (Figure E-5). Since the original data were collected at 50 metre intervals, it was possible to simulate sample spacings of 250, 400 and 500 metres by replotting only part of the data. Maps for 50 and 250 metre spacings are included in Chapter 6 (Figure 6-4 and 6-5), and it is quite clear that very little information is lost with the 250 metre spacing. A map of the same data with 400 metre spacings (Figure E-5) also retains most of the information of the 50 metre map. From the 500 metre map (Figure E-6) much of the detail is lost, but the northeast striking zone of enrichment is still apparent, and this map could be reliably used to select an area for further sampling.

E-3.3 Mells Park and Pucklechurch Area

The reasoning behind applying geostatistical analysis to the study of sequential samples from streams lies in the possibility that the ranges determined might provide some insight into dispersion distances of constituents of the water or sediment. These would be the 'secondary' ranges referred to in the introduction, and would be controlled by a number of inter-dependent parameters, including: the rates of water flow and sediment transport, relative magnitude of physical and chemical variations along the course of the stream, the degree of mixing between transported material (ie. water or sediment with characteristics inherited from some point up stream) and local material (ie. water or sediment with characteristics derived from conditions prevailing at the sample site), and a tendency for transported material to disinherit previously acquired characteristics in favour of characteristics derived from local conditions. Although these various mechanisms would be difficult to describe using mathematical models, and almost impossible to predict, it may be practical to study them, in an empirical way, with the help of geostatistics.

From the data presented above it is apparent that of the parameters determined, water temperature, with a range of 2 200 metres, is the least sensitive to local changes in the environment. It could be interpreted, then, that the temperature of the water at any site is related to the conditions at that site, but is also related to conditions all along the stream bed for about 2 200 metres upstream. Although this may be a reasonable assumption, the significance of this

Figure E-5 Map of strontium concentrations in soils from the Latteridge area, based on a 400 m grid. Concentrations increase with intensity of shading

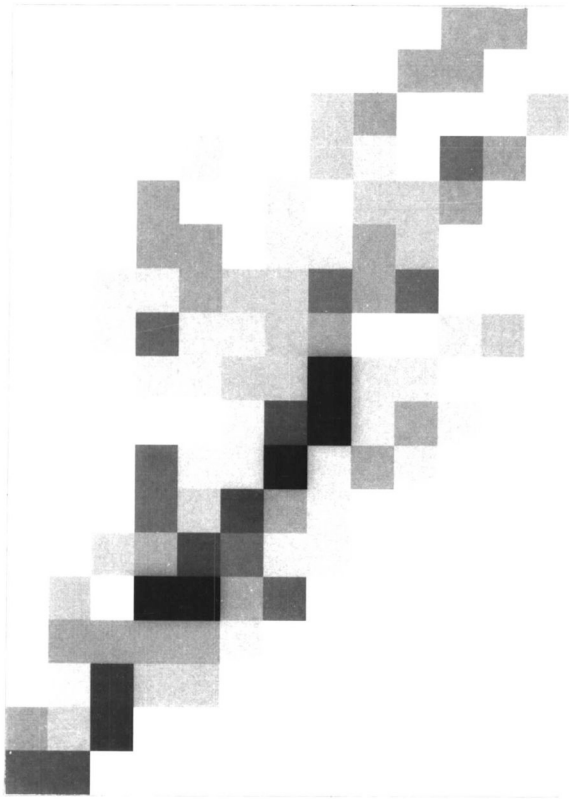
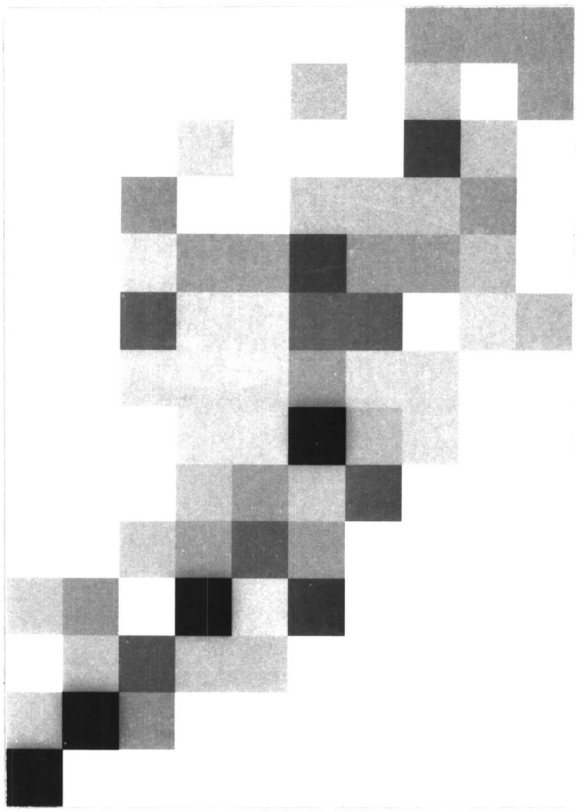


Figure E-6 Map of strontium concentrations in soils from the Latteridge area, based on a 500 m grid. Concentrations increase with intensity of shading



particular case must be viewed with caution. In the first place, the semi-variograms used are based on 2 800 and 2 500 metre traverses with 100 metre intervals, hence the variances for the longer lags are probably based on too few pairs of samples to be significant. Secondly, although care was taken to sample in the same part of the stream at each site, some of the variation may be a function of sampling irregularities.

The ranges for the stream sediment data vary from 700 to 1 500 metres. Taking manganese as an example, it could be interpreted that the effects of local geochemical variations are smoothed out, by physical mixing and a myriad of chemical exchange processes, over an average distance of 1 200 metres.

The most obvious application of this geostatistical information is in planning stream sediment surveys in areas similar to those studied here. Taking the ranges as estimates of dispersion distance, one would restrict sampling intervals along the streams to about 1 000 metres for the more mobile elements, and to perhaps 500 metres if the less mobile elements are of interest. Alternatively, in interpreting stream sediment data from this area, one would avoid extrapolating beyond 1 000 to 1 500 metres up stream from each sample site, as was suggested by Earle (1978).

E-4 Conclusions

Geostatistical analysis has been applied to soil geochemical data from two dissimilar areas of mineralisation in the Bristol area. The results have been used to provide some basis for establishing meaningful and statistically valid sample intervals in regional and local soil surveys.

The Mendip area is characterised by lead-zinc mineralisation in carbonate rocks. The size of the surface expression of the ore bodies is variable, as is their internal configuration. Semi-variograms calculated from a regional traverse crossing mineralisation, with 100 metre sample intervals, have not provided useful information concerning regional sample spacing. Semi-variograms for a number of short traverses with 10 to 20 metre intervals, across mineralised zones, have been more useful. Ranges, corresponding to individual mineralised zones, vary from 60 to over 300 metres. A survey intended to reveal the location of all

mineralised zones should have a sample spacing of 50 metres. To reveal the location of the larger zones, and some of the smaller zones, sample spacing could be increased to 200 metres.

The Latteridge area includes a north-east striking zone of celestite mineralisation within an evaporitic sequence. Semi-variograms have been calculated for strontium data with samples at 50 metre intevals. Ranges vary from 400 to 750 metres. Simulated sample spacings of 250, 400 and 500 metres using the data taken at 50 metre spacings, indicate that the sample interval could be increased to 250 metres without losing information. At 500 metres the trend of the anomalous zone is still evident, although some detail is lost. The optimum soil grid for this area may be one with 250 metre spacing across the strike of the evaporite bed.

Neither of these studies has dealt fully with the use of geostatistics in two dimensions, that is, both across and along the strike of the mineralisation. Such information would be useful from the point of view of determining optimum spacing between sampling lines, as well as optimum spacing betweeen the samples along the lines. In most geochemical exploration programmes assumptions are made about elongation of the target, either due to elongation in the host rocks, or due to linear dispersion processes. Based on such assumptions, sample grids with unit-cell elongations in the order of 10 to 1 (eg. 10 m spacings on lines at 100 m spacings) are commonly used. Results from such surveys can be highly misleading if the presumed elongation does not actually exist, especially if the data are to be contoured. In this connection, Olea (1974) has recommended the use of geostatistics and Universal Kriging for optimisation of a computer contouring algorithm.

Geostatistical analysis has also been used to assess dispersion distances in stream sediments and waters from two streams in the southeast and east-central parts of the study area. For the sediments, the ranges vary from 600 to 1 500 metres, and it is recommended that for stream sediment surveys the sample interval along streams should not exceed 1 000 metres. Similarly, in interpreting stream sediment data, one should not extrapolate beyond 1 500 metres upstream from any sample site.

APPENDIX F ALTERNATIVE EXPLORATION METHODS, AND SUGGESTIONS FOR FURTHER RESEARCH

F-1 Alternative Methods for Regional Geochemical Exploration in Karstic Terrains.

Since it is impractical to use stream sediment geochemistry for mineral exploration in most karstic areas, two alternative regional exploration techniques have been examined. These are hydrogeochemistry and soil geochemistry.

F-1.1 Hydrogeochemistry

In carbonate karstic systems, ground water flows through fractures and cavities that range in width from fractions of microns to tens of metres. Flow can be described as "diffuse" if there are very many small flow paths, or as "conduit" if most of the water is channelled along a few large flow paths.

The rate at which carbonate rock is eroded depends on the aggressiveness of the water towards minerals such as calcite, and the most important parameter in this regard is the partial pressure of carbon dioxide. The tendency for ore minerals to be dissolved depends on the pH and oxidation potential of the water.

From the perspective of mineral exploration one can envisage a "worst case" where most of the flow is through a few widely spaced conduits, and where the pH is too high and the oxidation potential too low to promote dissolution of ore minerals. The "best case" would be where diffuse flow predominates, and the waters are aggressive towards the ore minerals.

Water sampling in karstic areas is most effectively done at springs. This point raises another question, as to from whence the water in a given spring is derived. In some areas this may be well known, in others it may be unknown.

Water samples are normally analysed for any constituents which might reflect presence of ore or gangue minerals. In the case of the base metals, one often faces the problem that analytical techniques are not sufficiently sensitive to enable one to distinguish background from anomalous levels.

Seasonal variations in ground water flow rates can affect the concentrations of dissolved and suspended constituents. As a consequence, sampling programmes which extend over a period of changing flow rate are subject to temporal variations which may be confused as spatial variations.

Some of the potential problems associated with hydrogeochemical exploration in karstic areas have been summarised. The following points should be considered prior to conducting such programmes:

1) Flow Characteristics and Hydrology.
It is essential to have some knowledge of the ground water flow characteristics to assist in interpretation of hydrogeochemical data. If there is insufficient information from previous studies, some simple hydrogeological studies should be carried out, such as monitoring flow rates, determining major constituents and parameters such as pH, Eh and pCO_2, and estimating water budgets. A variety of general hydrology and hydrogeology textbooks are available to assist in planning and interpreting such studies (see, for example, Davis and DeWiest, 1966; Freeze and Cherry, 1979; Burger and Dubertret, 1975; Dilmarter and Csallany, 1977; Tolson and Doyle, 1977).
2) Source Area of Springs.
In many cases the type of rock through which ground water flows can be determined from the chemistry of the major constituents of the spring water. The actual source area of the spring can only be reliably determined by the introduction of tracing materials to discrete recharge streams, a difficult, laborious and often inconclusive process. Various techniques for flow path tracing have been summarised by Back and Zoetl (1975).
3) Analysis.
Most dissolved constituents which are useful for mineral exploration are present at levels of micrograms per litre, and their estimation is difficult both because of possible contamination, and because of the lack of sufficiently sensitive analytical techniques. Concentrating procedures are used to bring analyte levels into the range of routine analytical procedures, but recent improvements in instrumental analytic technology may provide a more satisfactory answer to the problem.
4) Temporal Variations.
Data from the present study has shown significant flushing and dilution effects as a function of changes in flow rate. These effects, which are most severe under flood conditions, are variable from one drainage system to another. During stable periods, when flow rates are at or below normal, the water chemistry is also stable and representative. Ground water sampling should always be completed in as short a time as possible, and should be carried out during a moderate to low flow period.

F-1.2 Soils

Water- or ice-related sampling media such as glacial drift, stream and lake waters and sediments, and ground water, are useful for regional geochemical exploration because a sample collected at a point may be representative of a large area. The same cannot be said of soil samples, because although mixing can

occur during soil formation it is unlikely that a soil sample is representative of material from more than a few tens of centimetres around the sample site. There is no reason to believe, for example, that a zone of mineralisation could be detected by a soil sample collected at a distance of ten or even five metres, unless, of course, there is a detectable envelope of primary dispersion in the rock adjacent to the mineralised zone.

It follows that in areas which are glaciated, and which have mineral deposits without extensive alteration halos, regional soil surveys should be designed such that there is a high probability that at least one sample will be collected from within a mineralised zone. In other words, spacing should be a function of the anticipated size of an economic deposit, as suggested by Sinclair (1975). Unfortunately, this principle does not apply to a partly buried deposit which has a surface expression smaller than the minimum size for an economic deposit. If it can be argued that even the smallest surface showing could lead to an economic deposit, then there is no minimum sample spacing which will guarantee detection of all deposits.

Geostatistical analysis has been shown to be useful in interpreting soil geochemical data from the perspective of choosing sample intervals. It is clear, however, that this tool must be used carefully, particularly in understanding how the results correspond with known geology. The application of geostatistics does not solve the problem that economically important deposits might have surface expressions of varying sizes, however, if it is used carefully, geostatistics should allow one to estimate the probability that the use of a particular sampling interval will lead to success.

F-2 Suggestions for Further Research

F-2.1 Research into the Genetic History of Mendip Lead-Zinc Deposits

The evidence provided to support the proposed theory of a residual/karstic origin for the Mendip deposits is only skeletal. The most likely avenue of success to either support or discredit this theory, would be to conduct a thorough geological examination of the mineral occurrences. Unfortunately, this would be a difficult, expensive and probably environmentally unacceptable undertaking. Other possibly fruitful areas of research include:

1) careful reconstruction of paleotopography and paleohydrology from the Permian to Jurassic periods,
2) further soil sampling of mineralised areas to better define metal zonation, and
3) thermodynamic assessment of the possible mineralising solutions and conditions for ore mineral accumulations under karstic conditions.

F-2.2 Comparison with Similar British Lead-Zinc Districts

If the residual/karstic theory for the genetic history of the Mendip lead-zinc mineralisation can be substantiated, it would be worthwhile re-examining data from some of the other British lead-zinc districts for evidence of a similar origin. Aspects which could be considered include:

1) paleotopography and paleohydrology,
2) ore textures and evidence for karstification, and
3) metal zonation.

F-2.3 Investigation into the Possible Existence of Further Unknown Lead and Zinc Deposits on the Mendip Hills.

Some of the results from the present study indicate the possible presence of previously unknown mineralisation. The application of modern mineral exploration techniques in the Mendip area might prove to be both geologically and economically rewarding. The following techniques are recommended:

1) extension and fill-in of the soil grid at intervals of about 500 metres,
2) follow-up soil sampling in anomalous areas at intervals of about 50 metres,
3) overburden drilling, with a hand-held drill and flow-through samplers in anomalous areas, and
4) diamond drilling with a small portable drill, in geologically favourable areas which are covered by Keuper Marl mudstone. Any such program should be combined with drill hole water sampling, and more detailed spring and well water sampling than has already been undertaken.

F-2.4 Geochemical Studies of the Keuper Marl

The geochemical characteristics of the Keuper Marl are probably related to the physical nature of the Severnside Evaporite Bed, and the presence or absence of celestite within it. A geochemical study of the Severnside Evaporite Bed horizon of the Keuper Marl on a regional scale, and of several vertical sections through the marl, could provide useful information as to the genesis and likely distribution of strontium-bearing material.

These research suggestions are seen only as logical extensions of the present study, and are not intended to cover the very many important and interesting research topics which could be based on the geochemistry of the Bristol and Mendip Hills Area.

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