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**CHLORIDE VARIATION IN SURFACE LAYERS
OF COLLIERY SPOIL HEAPS**

BY

SUSAN JUDITH BILLING, B.Sc. F.G.S.

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A Thesis presented for the degree of Doctor of Philosophy in the University
of Durham.

May 1987



13.11.1988

ABSTRACT

An investigation of chloride ion levels in coarse colliery discards was undertaken because modern British Coal practice is to restore discard tips and lagoon embankments at an early stage in construction, commonly before much leaching has taken place. High chloride ion concentrations result in physiological drought and the failure of vegetation cover.

Sites at two collieries were studied using grid and traverse (depth) sampling procedures. Results indicate downward leaching of chloride ions into the embankment during Winter months and an increase in chloride levels towards the surface of the discard during dry, summer months. Salt hotspots occur on embankment surfaces during Summer months. These high chloride/sulphate concentrations represent the desiccation of seepages, most of which are related to embankment construction inadequacies, rather than to lagoons incorporated into the structure.

Chlorides within the discard originate from formation waters intimately associated with Coal Measures sequences. In the eastern coalfields in particular, high chloride ion concentrations in the coal and waste rock from deep underground excavations are not removed by the coal washing processes. Consequently, they are retained in fresh colliery discards.

Seasonal movements of chloride ions are associated with an increase in (negative) suction pressures within the near-surface layers of a colliery embankment. Suction pressures were monitored experimtnally in two experimental tips and in the field at a third colliery site (Bilsthorpe Colliery). On an annual basis, suction pressures become operative early in April, reversing to residual negative or small positive pore pressures in mid-September.

The leaching of chlorides from discard embankments is a function of the drainage characteristics of the materials and in clayey discards leaching to low levels is shown to take 5 to 7 years. Hotspots do not decrease significantly.

The results of the present investigation can be applied to curent embankment restoration schemes. In particular, the sowing of an embankment during the Autumn window, when electrolytes move downwards into the structure, would enable young vegetation to become established before being subjected to the higher Summer chloride concentrations. Hotspots require individual field drainage treatment.

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To my Mother and Father.

Thank you for everything.

DECLARATION

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Susan J. Billing

May 1987

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CHAPTER 1

1.1 Introduction and Background

The mining of coal is an essential component in the economy of many countries. Current annual production from the British coal industry is approximately 100 Mt of bituminous coal, around 4.5% of the world total (Ward, 1984). With modern mechanised mining techniques, it is inevitable that a proportion of roof, floor or intra-seam discard is produced in association with the coal (run of mine, R.O.M.). A detailed study of the sources and quantity of colliery discard produced from coal mining activities, made by British Coal (formerly the National Coal Board) in 1980, revealed that for the period 1979/80 an average of 67 Mt of discard was produced in association with 109 Mt of saleable coal (Table 1.1). Of the discard, only 3 Mt were retained underground (Blelloch, 1983).

Year	Coal (Mt)	Waste (Mt)
1920	230	10
1950	205	10-15
1979/80	109	67

Table 1.1 Coal and Waste Production 1920-1980

Virtually all British coal produced is from Carboniferous strata. Other deposits include the Oligocene lignites of Bovey Tracey (Devonshire) and Loch Neagh (Northern Ireland), the Jurassic coals of Brora (Sutherland) and North Yorkshire. However, apart from Loch Neagh, these are of little economic significance. Ninety-five per cent of production is currently from the Westphalian beds, the remainder being produced from the Namurian



(Limestone Coal Group and Upper Limestone Group) of Scotland and in the Dinantian (Middle Limestone Group) of Northumberland.

The thickness of the coal-bearing strata varies greatly. The Westphalian A-C series exceed 1500m in parts of Lancashire and North Staffordshire, but thin away completely towards the South, that is, against the Wales-Brabant Island. The coal-bearing Carboniferous succession is essentially a cyclic depositional sequence of mudstones, silts, sands, seatearths and organic layers. These cyclothems show considerable lithological variation throughout the coalfields of the United Kingdom. The organic, or coal, beds are numerous in the sequences, but seldom exceed five per cent of the total thickness of sediments (Ward, 1984).

Most colliery discard produced during coal cutting operations is brought to the surface along with the coal as R.O.M. This is then generally pre-crushed to a top size of between 76mm and 203mm, before entering the coal preparation plant, where it is screened, washed and sorted into several size fractions, before the coal and discard are separated. Two categories of discard are produced: coarse discard and fine discard.

Coarse discard has a size distribution greater than 0.5mm. It is relatively free draining and may be dewatered in the coal preparation plant, or by gravity drainage on the tip. The coarse discard is relatively easy to handle and may be transported, placed and compacted at disposal sites as required.

The second category, fine discard, is carried in suspension from the washing process and can be classified into two types: slurry and tailings. Slurry is the fine material remaining in suspension, usually with a high coal content. Tailings are the fine reject from the froth flotation

process, now used in most preparation plants for cleaning the coal, and formed predominantly of argillaceous rock particles below 0.5mm in size (Taylor, 1984). Variations on the above processes include pressure filtration of tailings to produce tailings cake, which is then disposed of with coarse discard, super-thickening and other dewatering processes to reduce the volume of slurry and tailings, for example, some cement is added to tailings in South Wales.

In Great Britain the greatest proportion of coarse discard is disposed of by tipping above ground, usually within a few kilometres of the colliery (Glover, 1978). Coarse discard may also be used to construct lagoons, or confinement dams within the tip structure, to contain the fine discards. A very small proportion of coarse discard (possibly 7-8 Mt a year) may be used for engineering purposes, such as the construction of road and rail embankments and as a landfill material (Turnbull, 1983).

The principal rock types found in tips are the argillaceous rocks associated with the coal seams. These are predominantly roof materials of mudstone, shale, siltstone and small quantities of sandstone, and floor materials, including seatearths varying from plastic fireclay to carbonaceous mudstones and occasionally siliceous sandstones. Tips containing a high percentage of plastic seatearths (>50%) appear fine-grained and clayey and are commonly light grey in colour. Tips with a high proportion of roof materials have a darker appearance.

Some 50% of fine discards (slurry and tailings) are pumped into lagoons, where the solids begin to settle. The resultant supernatant water may be pumped from the lagoon and recycled to the preparation plant, or simply drained from the lagoon surface and discharged via the site drainage. Lagoon sediments may become highly stratified with alternate layers of

coarse-grained coal, silt and clay particles (Taylor, 1984).

Initially these deposits are of high porosity. Consolidation with water expulsion will occur over time and a surface crust develops due to desiccation. In some cases this will ultimately be overtipped with a cover of coarse discard and the whole lagoon structure will become an integral part of the tip. At any one time, colliery tip complexes may contain lagoons at several stages of development: lagoons being constructed, active lagoons, consolidating lagoons and old overtipped lagoons.

As well as the coarse and fine discards, some boulder-sized rock debris may be found in tips, originating from underground development and drivage work. These materials are customarily taken from the mine separately.

Before the Aberfan flowslide disaster in 1966, little was known about the physical, chemical and geotechnical properties of colliery discards, and little consideration was given to the construction of spoil tips, embankments and lagoon structures, or the long-term geotechnical behaviour of such structures. However, following the disaster, the coal industry commenced to look very carefully at the properties of colliery discards and the geotechnical implications of surface emplacement. As a consequence, British Coal, in 1970, produced a Technical Handbook providing design guidelines and some engineering properties used in the construction of spoil heaps and lagoons, in accordance with the Mines and Quarries (Tips) Act of 1969. Much research into the nature of colliery discards was initiated at this time, culminating in the publication by British Coal of the Composition and Engineering Properties of British Colliery Discards (Taylor, 1984). These new guidelines and detailed knowledge of the nature of colliery discards have resulted in a new generation of post-Aberfan

tips. Modern tips are now of low profile and are constructed in layers, or lifts, of up to 5m in thickness, to ensure stability and preclude spontaneous combustion. Safe tipping is now of prime consideration.

A composite, 'overtipped', lagoon structure (Fig. 1.1) has been developed in the last decade and is likely to become the common form of disposal structure in British Coal Areas which produce high quantities of fine discard. The lagoon banks are the flanks of the final tip profile, which is completed by overtipping the fine discards in thin layers. In this way a minimum tipping space is effectively utilised. The Maltby embankment (Chapter 3, Fig. 3.2a) which forms a major part of the present investigation is essentially a disposal structure of this type.

1.2 Influence of Legislation on Restoration

The tipping of large volumes of colliery waste can have a considerable long-term impact on the landscape and on the existing use of the land. A survey of derelict land by the Department of the Environment (1984) revealed that 45,000 ha, or 0.3% of the total land in England was classed as derelict: 48% of that total consists of spoil tips, excavations and old pits. Spoil tips alone account for 13,340 ha and altogether 20,130 ha have resulted from coal mining operations. Because mining has attracted other industries, this dereliction is now situated in areas of high population (Bradshaw and Chadwick, 1980).

Environmental considerations have become important issues in land reclamation schemes and new planning applications have to satisfy strict conditions, especially when associated with new mines and discard disposal.

Until 1969, when the Mines and Quarries (Tips) Act came into operation, followed in 1971 by the Town and County Planning Act, no guide-

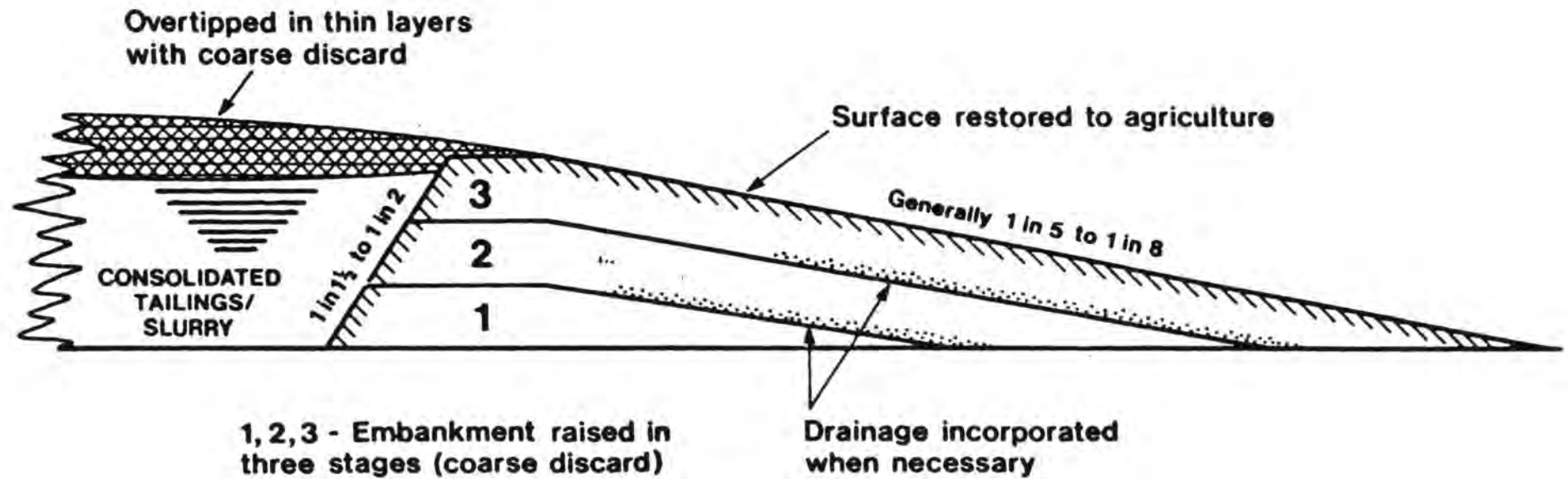


Figure 1.1 Composite disposal structure waste heap incorporating lagoon (After Taylor, 1984).

lines or regulations were set out for the siting, construction and general safety of spoil tips. Land used for tipping was not subject to any provisions for restoration or aftercare treatment. Before 1969, discard was generally transported to tips by aerial ropeways, conveyors and railways. Tipping took place at as high a point as possible, material being allowed to accumulate below in a loose state. Spoil tips tended to be high, steep sided, loose and conical. The restoration of the tips was not the responsibility of British Coal, but of the Local Authority. After the 1971 Act, however, the County Planning Authority, which controls planning permission, may require submission of a scheme for tipping waste which facilitates subsequent landscaping and restoration.

The Town and Country Planning (Minerals) Act, 1981 makes some important changes to the Town and Country Planning Act 1971, and is an extremely important piece of environmental legislation. It includes provision for the planning authorities to impose restoration and after-care conditions on applications for planning permission, stating; "Where planning permission for development consisting of the winning and working of minerals is granted, subject to a restoration condition, it may also be granted subject to any such after-care conditions, as the Mineral Planning Authority think fit." After-care conditions are steps to bring land to the required standard for use either for agriculture, forestry or amenity. The 1981 Act also covers sites where mineral workings have ceased permanently, have been temporarily suspended, or where tips are to be reworked (Widdowson, 1983).

Other recent legislation affects the use of land. The Local Government Planning and Land Act 1980 makes provision for the distribution of planning functions between Authorities. The Wildlife and Countryside

Act 1981 includes provisions for areas of special scientific interest and on public rights of way (Widdowson, 1983). The Derelict Land Act 1982 re-enacted legislation dealing with dereliction of all kinds, including coalfield dereliction and provides for investment by the Government into a national reclamation programme to be substantially increased. It also encourages joint schemes by local authorities and private developers for reclaiming land (Sampey, 1983).

The disposal of waste is now a significant environmental factor in the planning, development and operation of collieries. The Government White Paper (1981) on 'Coal and the Environment' concluded that local disposal of waste will remain predominant despite the application, where appropriate, of alternative disposal methods.

The above measures are intended to reduce the environmental impact of modern tipping sites, by the increased use of progressive restoration techniques, and by improvements in tip design. These will maximise the volume of spoil that can be tipped on a minimum acreage of land, consistent with landscaping and with contours which would allow the restored tip to blend into the surrounding landscape. Under the Town and Country Planning (Minerals) Act 1981, the subsequent responsibility and management of restored land will remain with British Coal, working to an agreed 5 year after-care programme with the local authority and the Ministry of Agriculture, Fisheries and Food (MAFF). The farmer will be acting as British Coal's agent or contractor in carrying out agricultural production, to ensure tipped land is restored to productive and beneficial use (Blelloch, 1983).

Planning applications for major industrial development, including new mine planning, are now subjected to a thorough examination of their

environmental implications. Environmental assessment of new mining development tries to identify the impact the new mine will have on the environment. These include visual impact, landscape quality before and after, agricultural loss, water pollution, dust generation, subsidence, safety and waste disposal (Allett, 1973).

British Coal has been involved in two major planning applications for new mines where environmental implications have been an important section of the application. These are the Selby Coalfield and the North East Leicestershire Prospect (Vale of Belvoir). These applications have involved three main stages. The first stage is a feasibility study, which is a commercial assessment primarily concerned with engineering, economic and environmental aspects. The second stage is a refinement of those plans and the third stage includes a Public Inquiry, with a final decision by the Secretary of State for the Environment.

The disposal of colliery discard is obviously one of the more important environmental issues connected with new mine development. Restoration and after-care conditions play a large part in any final successful planning application. The Vale of Belvoir Coalfield Inquiry Report, 1981, outlined detailed plans for the process of restoration and aftercare. These included the three tips being designed so that the maximum amount of spoil could be placed on the minimum land area. Details of top soil utilization, to enable successful progressive restoration to full agricultural production, had to be supplied together with a plan for future integration with the existing land use and landscape pattern. Nevertheless, all tips failed to meet either the inspector's yard-stick (Hose and Saltby), or the Secretary of State's (Asfordby). The latter was turned down on agricultural land merit, being opposed by MAFF. The tip

design which finally obtained permission at Asfordby was much more of a visual environmental intrusion, being higher and steeper than the one originally proposed. However, it did not sterilise agricultural land of reasonable local quality.

1.3 Mineralogy and Chemistry of Colliery Discard and Related Waters

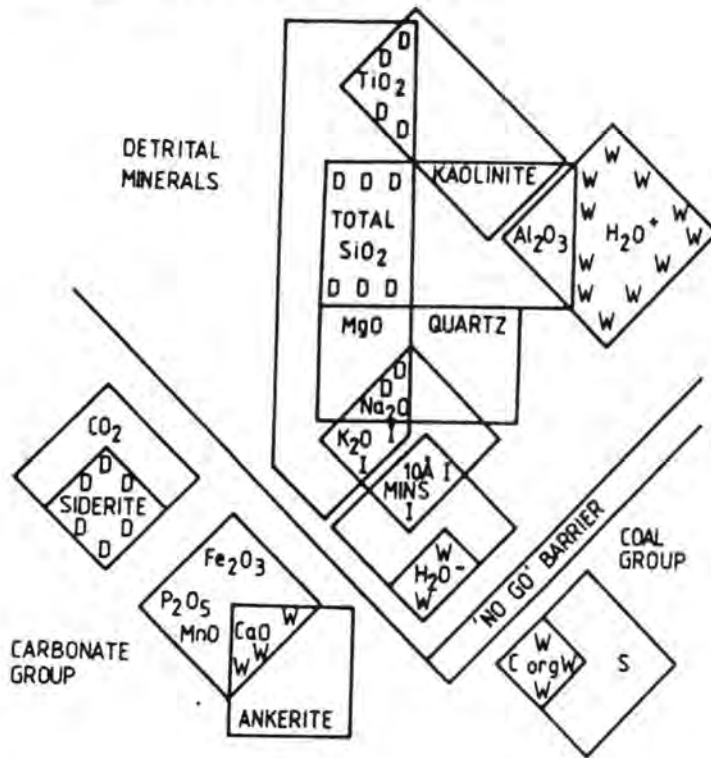
The reclamation of colliery tips for agricultural or recreational purposes is now common in all coal mining areas in Britain. However, vegetation establishment in some places is unsuccessful or impeded by the physical and chemical properties of the colliery discard (Kimber et al., 1978). After tipping, colliery discard is regarded as a highly unstable environment both physically and chemically (Down, 1974).

Research into the mineralogical and chemical properties of colliery discard has been carried out to investigate factors which might promote the breakdown and degradation of the discard. Interrelationships between the chemistry and mineralogy and the physical and mechanical properties of discards have been established over the past two decades (Taylor, 1984) (Figs. 1.2a, 1.2b).

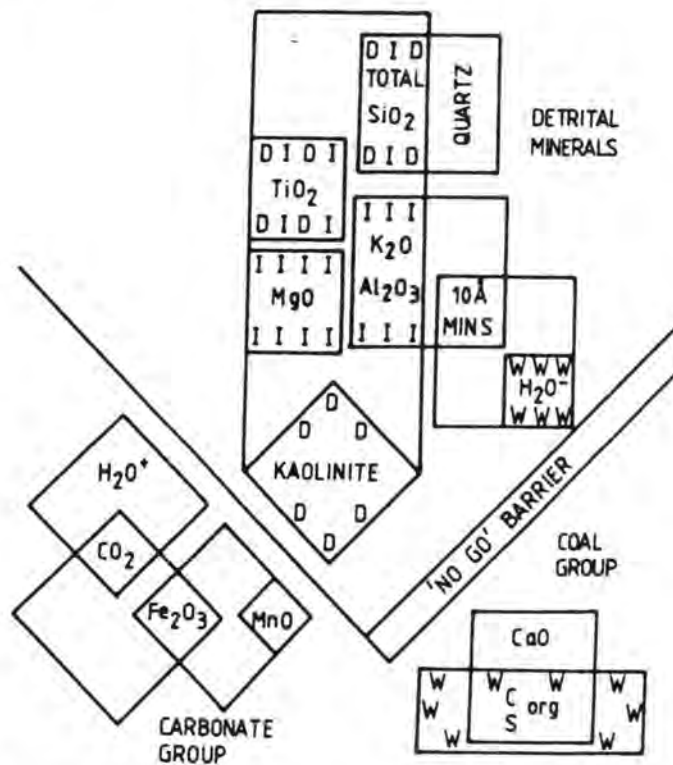
Three distinct groups of minerals were recognised as being associated with different engineering properties of the coarse discard. The three were classified as detrital, non-detrital and coal group minerals.

The detrital or transported minerals in discards are derived from land sources during the Carboniferous. This group includes quartz, clay minerals and titania. The clay mineral group is associated with bulk density and natural water content, correlating with the two water components of this group, H_2O^+ .

A. ENGLAND (25 analyses)



B. SOUTH WALES (45 analyses)



W = Water content D = Bulk density I = Plasticity index

Figure 1.2 Association of Minerals and fundamental properties in (a) English Tips, (b) Welsh Tips (After Taylor, 1984).

The non-detrital group represents the carbonate minerals, primarily calcite, dolomite and siderite.

Coal group minerals comprise mainly organic carbon and total sulphur. The total sulphur represents organic sulphur and pyrite minerals found in association with coal. A strong negative correlation has been shown between bulk density and coal content and a positive one between natural water content and coal.

Tables 1.2a and 1.2b show the average mineralogy of coarse and fine discards, (after Taylor, 1984). The discard fragments are predominantly argillaceous, dominated by the clay minerals illite, expandable mixed-layer clay, kaolinite and trace amounts of chlorite. Quartz is an important detrital mineral and smaller amounts of non-detrital carbonates and pyrite are also found. The national average coal content of tips is 11%, although some very old tips contain large quantities of coal, an average of 21% organic carbon being reported in three old County Durham tips. Lagoon sediments have a higher average coal content, 47%, due to periodic discharges (overflows, plant flushings etc.) from the preparation plant.

There is a distinct regional variation in the mineralogy of discards, especially in the clay mineral groups (Fig. 1.3). Kaolinite, a geotechnically more inert clay mineral, is dominant in the North East and Scottish Areas, whilst expandable mixed-layer clays, which have a greater tendency to promote breakdown and weathering of discard, are common in the Yorkshire coalfield and in the Doncaster British Coal Area in particular (Taylor and Spears, 1970). Coarse discard from the South Wales Area has a higher quartz content and the percentage of clay minerals is lower. The similarity in mineralogical properties of Scottish and North East Area discards is believed by Taylor (1984) to be a reason for their similar

	COARSE DISCARD (74 SAMPLES)				FINE DISCARD (54 SAMPLES)			
	Mean	Std.Dev.	Max.	Min.	Mean	Std.Dev.	Max.	Min.
SiO	46.23	7.77	61.42	23.86	32.68	8.90	46.19	10.74
Al O	19.74	2.74	26.24	13.92	16.42	5.49	29.91	5.45
Fe O	5.39	2.69	19.30	2.57	4.86	1.80	8.70	2.14
MnO	0.10	0.01	0.89	0.01	ND	ND	ND	ND
MgO	1.01	0.32	0.30	1.70	0.99	0.38	2.38	0.05
CaO	0.74	0.71	4.53	0.17	2.05	1.59	7.21	0.19
Na O	0.41	0.19	3.50	0.01	0.31	0.13	0.82	0.10
K O	3.40	0.55	4.56	1.76	2.83	0.88	4.40	0.74
TiO	0.88	0.10	1.11	0.56	0.78	0.13	1.06	0.46
S	0.96	0.72	3.67	0.05	2.89	1.54	7.85	0.44
P O	0.18	0.07	2.10	0.05	0.10	0.03	0.18	0.03
CO	1.81	1.60	9.00	0.00	ND	ND	ND	ND
C	13.30	8.16	40.48	0.01	ND	ND	ND	ND
H O	5.04	1.77	10.29	1.86	ND	ND	ND	ND
H O	1.15	0.27	1.83	0.74	ND	ND	ND	ND
Total	100.34				63.91			

ND = Not Determined

Table 1.2a). Average major geochemistry of discards (weight percent)
After Taylor, 1985.

	Coarse Discards 74 Samples	Fine Discards 47 Samples (72 Determinations)
Quartz	17.5	6.0
Illite	31.5	} 34.0
Mixed-layer clay	26.0	
Kaolinite	10.5	8.5
Chlorite	0.5	- (b)
Carbonates (a)	1.0	2.0
Pyrite	- (b)	2.0
Organic carbon (dom.coal)	13.0	47.4
Total	100.0	100.0

(a) Dominately siderite and some ankerite in tips, whereas ferroan dolomite (ankerite) in some fine discards.

(b) Small quantities in some samples.

Note: In coarse and fine discards, trace amounts of sulphates feldspar, rutile and phosphate total less than 2%.

**Table 1.2(b) Average (Proximate) Mineralogy of discards.
After Taylor, 1985 .**

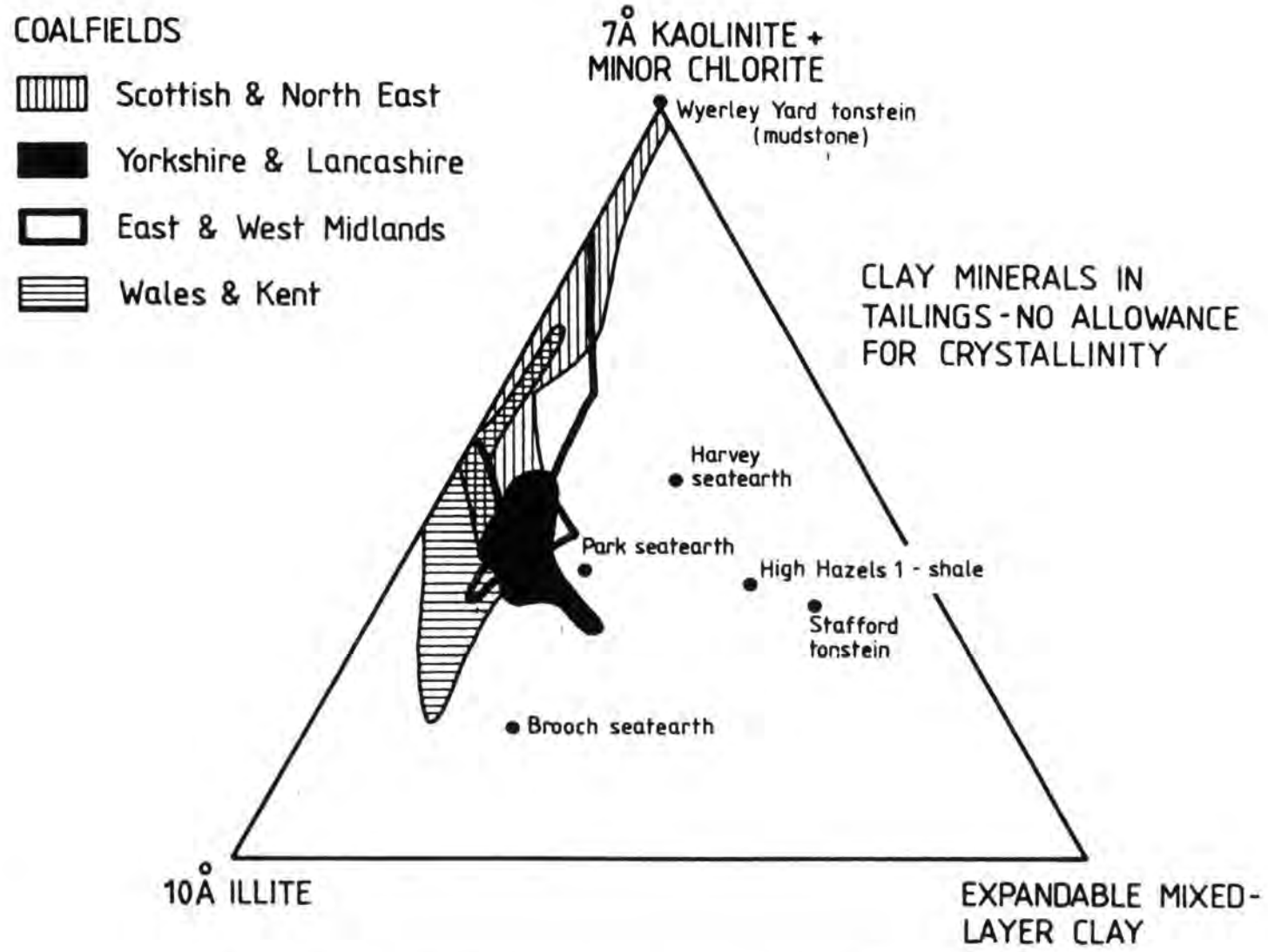


Figure 1.3 Clay Minerals present in fine discards (After Taylor, 1984).

drained shear strength, which is of the same order as discard from the more deeply buried (high rank) South Wales coalfield. Mineralogy and rank would seem to be important factors in determining shear strength differences in discards from British coalfields.

The chemical composition of colliery discard is also highly variable, both at individual tip sites and at a regional level (Table 1.2). This depends upon the mineralogical nature of the discard, treatment, preparation and disposal methods, and climatic conditions (Williamson, 1982).

Williamson concluded that some of the major chemical problems encountered by vegetation on colliery discard arise because of extremes in pH, an excess of toxic metals and salts, and a lack of essential nutrients.

Water and oxygen will affect the surface layers of a spoil tip first, initiating chemical and physical breakdown of the discard (Bradshaw, 1980). A major reclamation problem of many spoil tips is that of acid generation from weathering of sulphides, particularly pyrite. Pyrite oxidation occurs mainly in the surface layers where moisture and oxygen are present (Fig. 1.4). As a result of hydrolysis and oxidation, assisted by ferrous-ion oxidising bacteria such as Thiobacillus ferroxidans, pyritic wastes disposed of at a neutral or alkaline pH can weather within a few months or years to produce extreme acidity.

Various other factors influence the rate of production of acid. The natural carbonate content of the material, particularly ankerite and siderite, may neutralise some of the acidity produced on the tip. This process produces secondary minerals such as gypsum and jarosite. However, this natural neutralising potential is relatively small and free hydrogen ions accumulate, resulting in a drop in pH (Bradshaw and Chadwick, 1980).

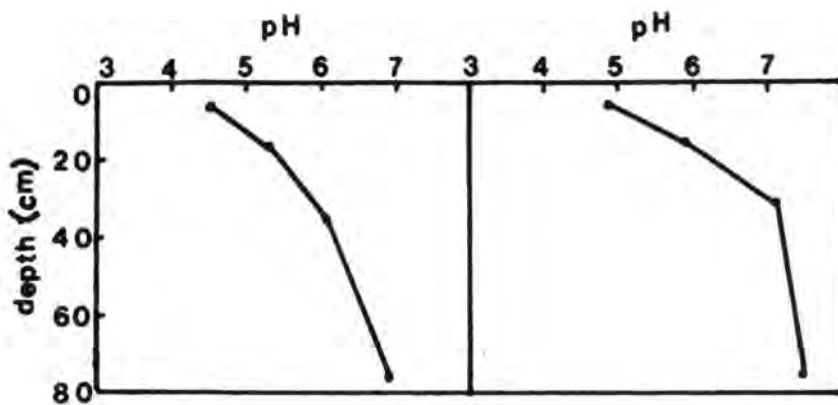


Figure 1.4 pH profiles of two colliery spoil tips (After Bradshaw & Chadwick, 1980).

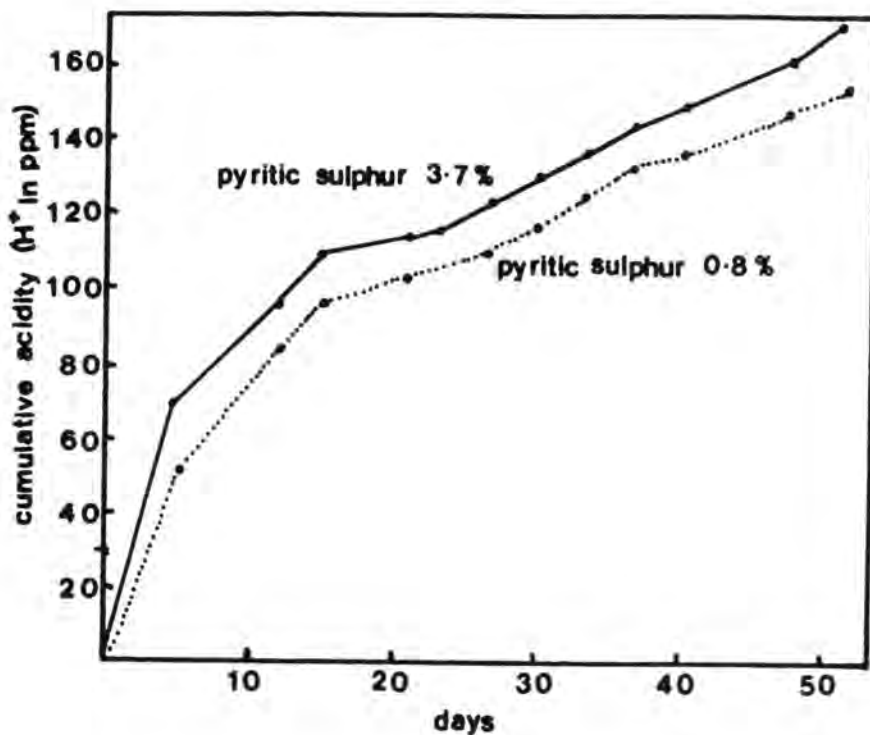


Figure 1.5 Acid production from contrasting samples of discard with different pyritic sulphur contents (After Bradshaw & Chadwick, 1980).

The size, morphology and type of pyrite present in the discard also influences acid production (Fig. 1.4). The smaller the grain size, the more reactive the pyrite; grains and framboids less than 0.25µm oxidising readily, whilst those greater than 50µm are fairly stable. The morphology of pyrite is also related to reactivity. The principle iron sulphides in order of reactivity are pyrrhotite, Fe_nS_{n+1} > marcasite, FeS_2 > pyrite, FeS_2 (Williamson et al., 1982). Samples with a relatively high pyritic sulphur content can produce acid at the same rate as samples with a much lower pyritic content (Fig. 1.5, after Bradshaw and Chadwick).

As the pH of colliery discard falls, toxicity to plants increases as potentially toxic elements, such as iron, aluminium and manganese, are mobilised. The availability of some essential plant nutrients, calcium and phosphorous for example, decreases as these elements form insoluble compounds, inhibiting cation exchange capacity.

Freshly deposited discard is initially alkaline or neutral and may display salinity problems, due to a high content of water soluble salts, which may accumulate in the surface layers of the discard. These concentrations result from the presence of indigenous salts in the discard material, interactions between the products of pyrite weathering and carbonates in the discard, and ground water associated with fresh discard. Natural levels of the salts, mostly calcium, magnesium and sodium sulphates and chlorides, are enhanced by the recycling of water to the coal preparation plant from tailings and slurry lagoons. Concentration also occurs around areas of natural drainage or seepages in lagoon and spoil tip embankments.

Little is known of the effects of salinity on the grass mixtures and tree species used in colliery discard reclamation schemes. However, some

studies have been conducted on the indigenous vegetation of saline soils and those of arid regions and also on crop plants such as wheat, barley, sugar beet and some vegetables. Salinity affects vegetation in several ways (York University publication, 1975):

- 1) The osmotic effect of high concentrations of soluble salts which may restrict the uptake of water by plants. This is known as 'physiological drought'.
- 2) Physiological disturbance within the plant which is caused by variations in the relative proportions, rather than the absolute amounts, of specific elements in the soil solution surrounding the plant roots.
- 3) The specific toxic effects of high concentrations of individual elements such as magnesium, sodium and chloride.

Opinion is divided as to the precise level at which the total soluble salt content of soil is likely to cause adverse effects on vegetation. The toxicity of different salts varies, for example, magnesium salts are more 'toxic' than sodium salts. There is also considerable variation between species in their ability to tolerate saline conditions and calculation of a relative salt toxicity index of plants is difficult.

The geochemistry of waters in the Coal Measures Strata has an important influence on the chemical and physical nature of both coarse and fine discard. Spears et al. (1971) concluded that the water chemistry of tips and lagoons was controlled mainly by the formation water released by the rock and (waste) coal components, with some dilution by recent meteoric water.

Saline ground waters in Carboniferous Strata have been studied from oil boreholes in the East Midlands (Downing and Howitt 1969), from under-

ground workings in Coal Measures Strata in Britain (Chamberlain and Glover, 1969) and from other European coalfields (Palys, 1971).

Fig. 1.6 indicates chloride ion trends in Coal Measures Strata waters. Data were obtained from various sources including British Coal, (Fellows, 1979). It will be observed that there is a concentration gradient towards the Eastern coalfields. Levels are not consistent within any one British Coal Area, or with depth at any one mine. The South Wales coalfield is almost free from saline waters.

In the past, cumulative problems have arisen from chloride levels, which at their minimum would satisfy World Health Organisation water supply standards (<200 mg/l). In terms of cumulative problems, the saline contamination of 27km² of chalk aquifer around Tilmanstone Colliery, Kent, is illustrative. Contamination resulted from direct minewater discharge with a chloride concentration ranging from 200-5000 mg/l (as Cl). According to Headworth et al. (1980) only about 15% of the estimated 318,000 tonnes of chloride discharged has so far been dissipated by stream flows from the aquifer. Chloride treatment is not a practical proposition, other than by dilution in rivers or discharge into the sea. In some parts of the country, it is necessary to pipe saline discharges over distances of about 20km (see Vale of Belvoir Coalfield Inquiry Report, 1981).

1.4 Aims of the Project

The aim of this research project is to gain an understanding of contained electrolyte concentrations, particularly chloride, in the surface layers of spoil tips whose constituents have been derived from coalmining operations. An assessment is made of their importance in terms of spoil tip morphology and restoration.

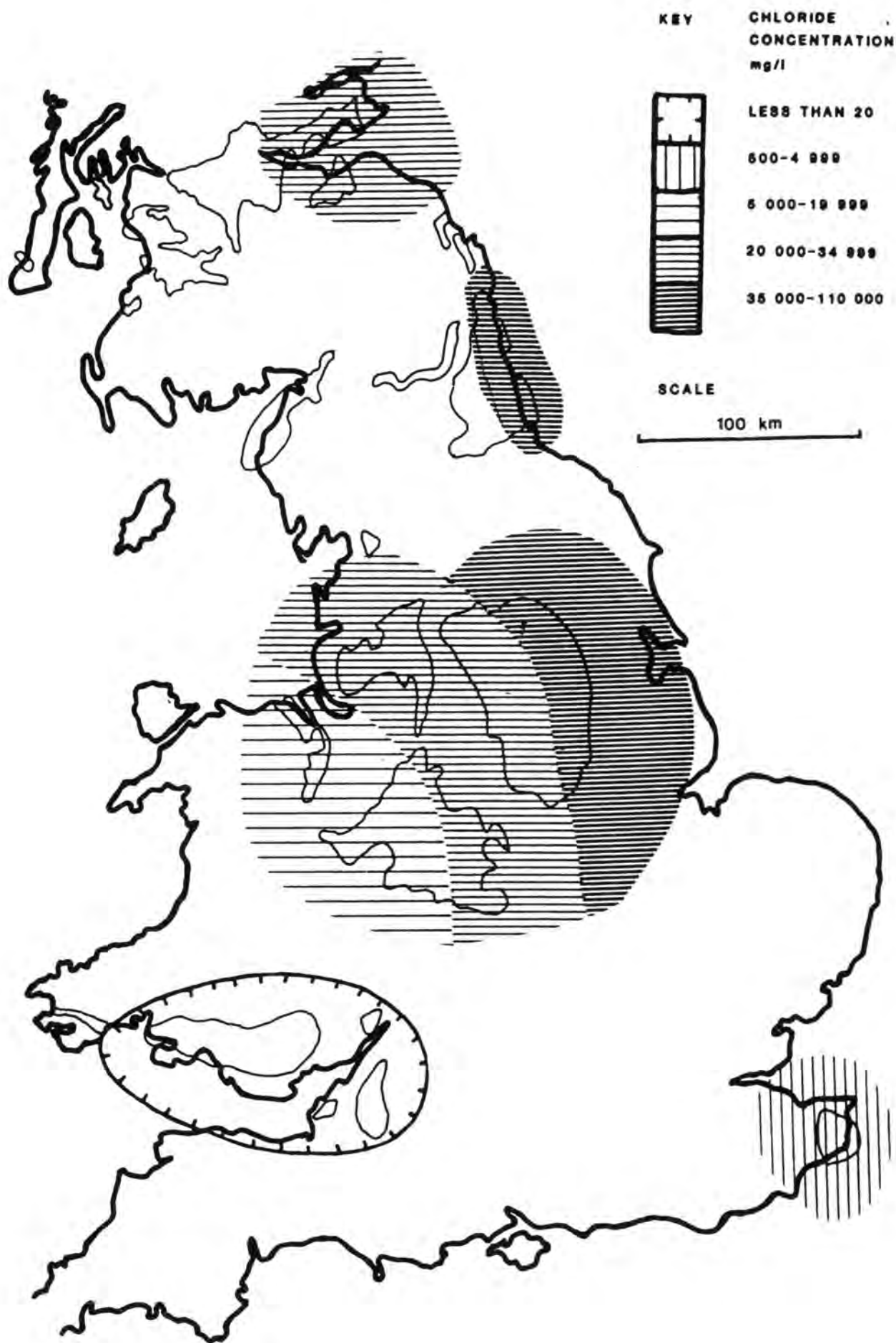


Figure 1.6 Chloride ion trends in Coal Measures strata water.

In earlier work (for example, Bradshaw and Chadwick, 1980), it was generally assumed that, when present, the chloride ion would be quickly leached from discard, in view of its high solubility. Previous to the last decade, however, the restoration of tips was not considered important, so any tip reclamation schemes generally concerned very old tips from which the chloride ion had been leached. Modern practice, required to fulfill the conditions of more recent legislation reviewed above, is to restore discard tips and lagoon embankments at an early stage of construction. The presence of high concentrations of electrolytes is likely to be detrimental to plant growth, so monitoring their presence and 'behaviour' is an important step in the planning of reclamation schemes for saline discards.

Investigations into the seasonal movement of electrolytes in the surface layers of coarse discard were initiated. These included the following:

- 1) How best to sample spoil tips for chloride movement.
- 2) The monitoring of chloride variations throughout the year.
- 3) The type of waste disposal structure in relation to chloride levels.
- 4) The nature and origin of saline seepages (hotspots) in embankments.
- 5) The physical and chemical nature of colliery discard associated with the salinity.
- 6) Variations in salinity levels in discard tips in different coalfields.

Mechanisms governing the movement of electrolytes in relation to soil suction variations were also studied. Soil moisture deficit in the surface layers is a response to evaporation of moisture from a tip. The moisture that remains in the surface layers develops a (negative) suction pressure

which equilibrates by drawing water (and salts) from deeper levels, or in response to precipitation. This phenomenon was first monitored in two experimental spoil embankments. Equipment was then installed in a lagoon embankment at a Nottinghamshire colliery and comparative results obtained. With these results, together with the results from chemical and physical investigations into the nature of saline discard, it is hoped to gain a better understanding of electrolyte release, relative concentrations and movement in colliery discards.

This information will also be used to produce guidelines, or a code of practice, for the reclamation and subsequent after-care of saline discards.

CHAPTER 2

ORIGIN AND DIAGENESIS OF FORMATION BRINES

2.1 Introduction

The origin of chlorides in the Coal Measures rocks, which were laid down mainly under non-marine conditions, is still a matter of debate. The chemistry of the brines must reflect their evolution within the sediments, from their initial incorporation and through diagenetic reactions with their host rocks.

Stratal waters have previously been recognised as originating from one or more of a number of possible sources. These include sea water, connate water (fossil sea water), present day meteoric water, fossil meteoric water, or water of igneous derivation in some special circumstances.

The evolution of subsurface saline waters is of interest for several reasons. They are associated with epigenetic metalliferous ore deposits in sediments, such as the Pennine Pb-Zn-Ba-F mineralisation. In this context, identification of the origin of the brine can make a large contribution to understanding the genesis of the deposit. Saline brines are also associated with petroleum deposits. Brines are further important in the identification of water emissions into mine workings, whether these be metalliferous mines or coal mines.

Research in these fields has led to various theories for the origins of such brines and the mechanisms by which they might evolve into their present day compositions.

Previous work by Downing and Howitt (1979), Edmunds (1975), Billings et al. (1969) and Bredehoeft (1963) has concluded that the saline waters in the Coal Measures originated from the diagenesis of original Carboniferous

marine or brackish pore water, that is from connate water and/or the incursion (flushing) of marine water into the Carboniferous aquifer at a later date. Downing and Howitt (1979) outlined the processes which may have influenced the composition of saline stratal water found in Carboniferous rocks of the East Midlands at the present time. The geological succession in the area comprises the Carboniferous Limestone sequence, deposited in a marine environment, overlain by Millstone Grit and Coal Measures sequences, the latter being in cyclic series, deposited in marine, brackish, to fresh water environments. The Namurian Millstone Grit is believed to have been deposited largely in a deltaic environment with occasional brief marine incursions. These incursions may have resulted in the Millstone Grit being flushed with more saline waters from time to time. During the Hercynian orogeny uplift, and erosion may have resulted in meteoric waters flushing Coal Measures rocks. Upper Permian marine transgressions could again have introduced saline water into the Coal Measures rocks. In the East Midlands, ingress of meteoric water could have occurred during post-Cretaceous uplift. Thus we can see that there may have been a very complex history of pore water compositional changes through geological time since deposition of the Carboniferous.

However, recent stable isotopic studies of saline subsurface waters from Permian and Coal Measures formations in North East England by Sheppard and Langley (1985) indicate the dominance of water of meteoric origin. Several of the sampled brines conformed to meteoric waters of recent origin, but fossil meteoric water, including probable Pleistocene water, was dominant in others. The δD and $\delta^{18}O$ data produced by Sheppard and Langley indicate that the brines cannot simply be derived from connate water by dilution with the recent or fossil meteoric waters. They conclude

that the chemistry of the brines must largely be controlled by exchange and/or filtration processes with the minerals of the host rocks.

Comparisons of the isotopic characteristics of oil field brines and present day sea water by Chilingarian and Ricke (1969) also suggest that the concentration of inorganic salts in the brines was due to compaction and ion filtration processes rather than to evaporation of trapped interstitial solutions.

Processes which may alter the chemistry of buried waters thus include the physical process of compaction and chemical processes involving reactions between rock minerals, organic matter and the interstitial solutions. These chemical processes include filtration through charged net clay membranes, adsorption, base exchange and biochemical processes.

Anion exclusion in clays and sediments has been proposed as a possible concentration mechanism for subsurface brines - see for example, White (1965), Hanshaw and Coplen (1973).

Clay particles in water develop a double layer structure consisting of a strongly bonded (Stern layer) made up largely of polar water and some cations, and a more diffuse part (Gouy layer) in which the ions are freer to move about (Drever, 1982). The diagrammatic model given by Taylor (1985) illustrates the relationship of the double layer to a negatively charged clay particle and to the free pore water in the larger capillaries (Fig. 2.1).

If the porosity of a sediment is high then the free pore water and dissolved salts will move through the larger pores. However, as consolidation and compaction occur negatively charged (clay) particles become so closely packed that the anions in solution are repelled and cannot escape. The double layer space between any two adjacent clay

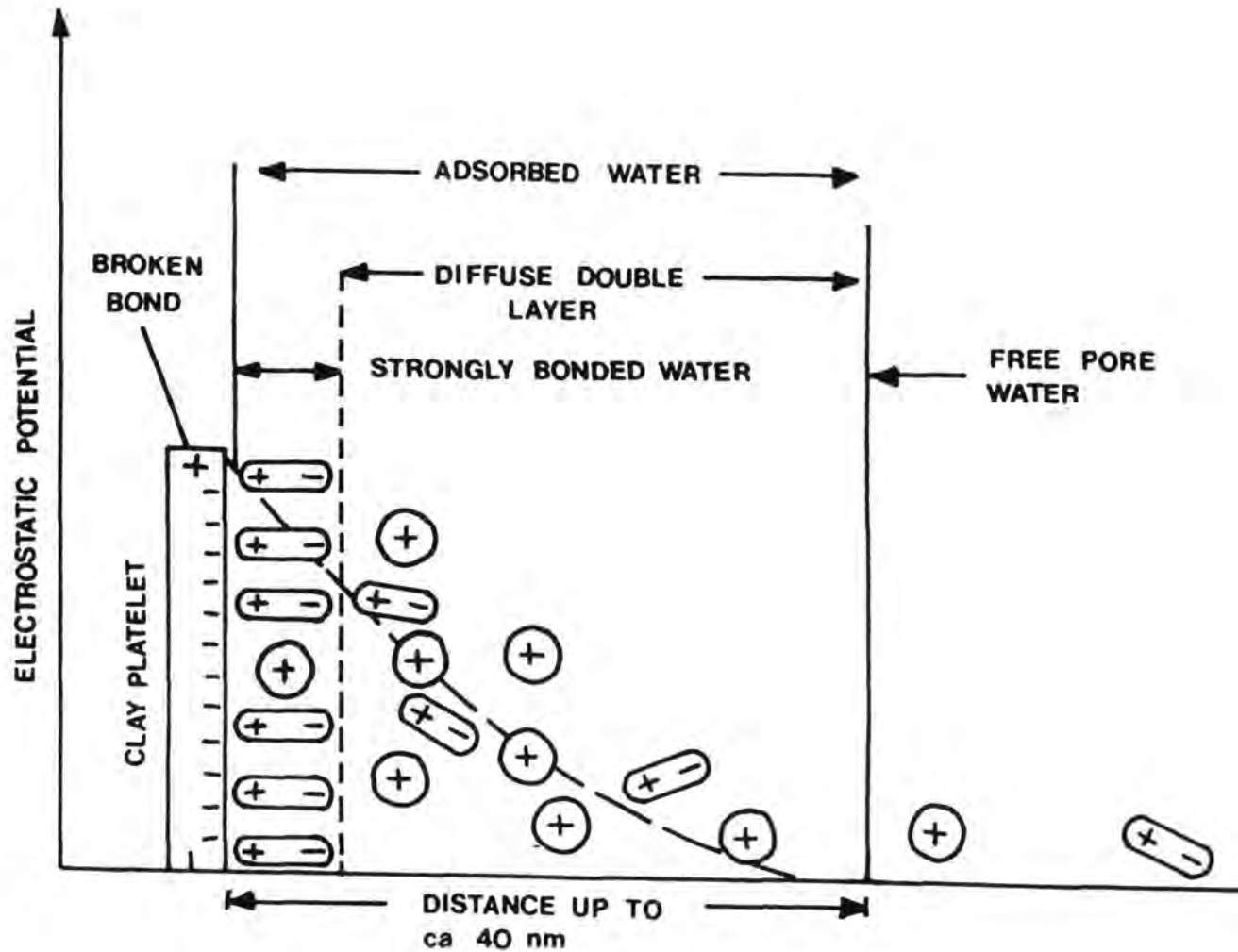


Figure 2.1 Schematic hydration of clay mineral surface showing cation/dipolar water satisfying charge deficiencies in clay mineral. +-, dipolar water; +, hydrated cations; -, anion.

particles can be regarded as a 'clay membrane'. The adsorbed cations can continue to move through the 'membrane' and between adjacent exchange sites to some extent but this leads to an electrical imbalance. Uncharged water molecules will continue to pass through the membrane towards areas of lower water pressure, that is usually towards the upper surface of the sediment. Consequently, there will be an increasing salt content on the 'input' side of the clay membrane filtration system. Long term water movements between permeable formations and less permeable strata will occur across semi-permeable membranes and brine concentrations will occur.

Retardation of cations and anions by geological membranes has been studied by Kharaka and Berry (1973). In laboratory experiments using sea water and chloride solutions flowing across a filtration cell of clay, the following retardation selectivity sequences were obtained:

1) cations

least retarded	Li < Na < NH ₃ < K < Rb < Cs	most retarded
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2) divalent cations

least retarded	Mg < Ca < Sr < Ba	most retarded
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monovalent cations are retarded with respect to divalent cations.

3) anions

least retarded	HCO ₃ < I < B < SO ₄ < Cl < Br	most retarded
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These sequences vary considerably with temperature and pressure, for example, at increased temperatures the passage of B, HCO₃, I and NH₃ are greatly increased.

Several other processes may affect the chemistry of buried waters.

They are, after Hitchon et al. (1971):

1. Solution of halite causing an increase in the proportions of sodium and chloride. (Increased salinities in formation waters may be related to the occurrence of known evaporite deposits as mentioned previously).
2. The dolomitization process may result in high calcium and low magnesium concentrations in formation waters, relative to sea water.
3. Bacterial sulphate reduction and anhydrite precipitation are important in removing sulphate from solutions.
4. Increased temperatures associated with burial, causing over pressuring and the conversion of smectite-type clay minerals to illite. This would be associated with an increased fixation of potassium, but addition of magnesium, calcium and some sodium to pore waters.

The water quality patterns from different coalfields exhibit remarkably similar characteristics, although there are some notable exceptions, such as the South Wales coalfield, which will be discussed later. Different water sources within a single mine may have extremely variable chemistries, as have waters from profiles taken through sequences of coal and associated strata. These chemical differences are in part a reflection of differences in the mineralogy and grain size and in the porosities and pore size distribution of the host rocks. Sandstones have higher porosities and lower relative concentrations of salts than coals. Mudstones have intermediate values (Cas/well et al., 1984).

As saline brines move up through Coal Measures sequences, they may pass through one or more clay layers. Water in the higher beds will thus be less mineralised because of filtration through charged net clay membranes. This could occur over depths of many metres, or on a much

smaller scale in individual coal/shale seams. These effects will give rise to discharges with differing salinities in any one mine.

2.2 Stratigraphical and Structural Controls of the Regional Distribution of Chloride Ions in British Coalfield Strata Waters

Saline groundwaters in Carboniferous Strata have been studied from oil boreholes in the East Midlands (Downing and Howitt, 1969), from underground workings in the Coal Measures Strata in Britain (Chamberlain and Glover, 1976), and from other European Coalfields (Palys, 1971). Fig. 1.6 incorporates data from a number of sources and shows chloride ion levels in Coal Measures stratal waters in United Kingdom coalfield areas. Higher chloride ion concentrations are apparently present in the Eastern coalfields. However, chloride levels are not uniform within any one British Coal Area, or with depth at any one mine. It is pertinent that in South Wales chloride levels are less than 20 mg/l.

The major source of chloride ions found in coal and coalbearing strata and thus in colliery discards, would appear to be the saline ground (or pore) waters with which the Coal Measures rocks have been associated. Elemental ratios of Na and Cl in coal and associated strata are directly related to the ionic concentration of the stratal waters.

The presence of saline ground waters in Coal Measures rocks implies that post-compaction diagenetic changes have occurred, since marine deposition was rare in this upper section of the Carboniferous, and coal is a terrestrial deposit.

Anderton et al., (1979) and Hollow, (1981) have suggested that there were two main marginal ocean basins covering the British Isles during the Carboniferous. These two basins were separated by the Wales-Brabant Island or high (Fig. 2.2). This high formed from primary structures and



Figure 2.2 Position of Wales-Brabant High and distribution of coalfields in NW Europe.

subsequent refolding events resulting from the Variscan thrust belt to the south. The thrust belt crosses Southern Ireland, Dyfed and Somerset, passing subsurface to the south of the London-Brabant high and reappearing in Holland, Belgium and N. Germany (see Fig. 2.2).

The British Isles lie at the northern edge of the Variscan orogenic belt. To the east and south of Great Britain the Precambrian and Palaeozoic rocks are affected by the Variscan deformation (Rast, 1981). The deformation is polyphase with radiometric dating indicating events in the late Devonian, and in the middle to late Carboniferous.

Very extensive drainage systems were established both to the north and south of the Wales-Brabant high. During the Namurian basin sedimentation ended and major river systems with extensive alluvial plains developed. Coal Measures (Westphalian) deposition comprised extensive shallow water deltaic and estuarine conditions. The Westphalian Coal Measures are the principal coal-bearing sequences in Britain and over much of North West Europe (Anderton et al., 1979).

The South Wales, Irish and small Bristol coalfields have all been linked using stratigraphic, palaeontological and sedimentological evidence. These basins were fed by rivers and delta systems draining the Southern landmasses.

The concealed Kent coalfield is the only British coalfield to lie within the French Basin. This was also fed from the south with sedimentation in a highly constructive, river dominated, environment (Bless et al., 1977).

The Wales-Brabant high separated the Southern basins from northern sedimentological sources (see Fig. 2.2). These northern sources yielded clastic sediments and turbidites, sedimenting towards the south and forming

the Midlands, Northern and Scottish coalfields.

Sequences obtained from boreholes located on the northern side of the Charnwood block (Fig. 2.3), on the northern edge of the Mercian highlands - an eastern prolongation of the Wales-Brabant high - suggest the presence of extensive Lower Carboniferous evaporite deposits, notably the Hathern Anhydrite sequence described by Llewellyn and Stabbins (1970).

These deposits are thicker than evaporites from the overlying Permian, Triassic and Jurassic sequences of the area, with anhydrite beds of 1-1.5m thick, over an interval of 97m, interbedded with dolomites, shales and some limestone. Anhydrite deposits also occur on the margins of the Derbyshire block, in the Edale Gulf, further supporting the general occurrence of evaporite deposits on the margins of topographic highs in the Lower Carboniferous. The Edale Gulf deposits were also cyclic, formed by successive marine transgressions throughout the Lower Carboniferous.

The Lower Carboniferous evaporites of the Midlands, described above, are believed to have been in contact with circulating meteoric groundwaters from the Westphalian Coal Measures. This probably took place in the Permo-Trias, during uplift, resulting from unloading in pre-Bunter times (Llewellyn and Stabbins, 1970). The dissolution of such evaporites may have been an important source of the salts currently found in the saline brines of the Coal Measures of the region. Such an origin would also conform, in a general way, with oxygen isotope studies on a variety of formation waters which demonstrate a meteoric origin, though not with Sheppard and Langley (1985), who established that the water constituting the brines in the Northumberland Coalfield is of much younger meteoric origin. Their evidence is, however, based on underground (colliery) sampling, and the possibility of considerable drawdown causing ingress of

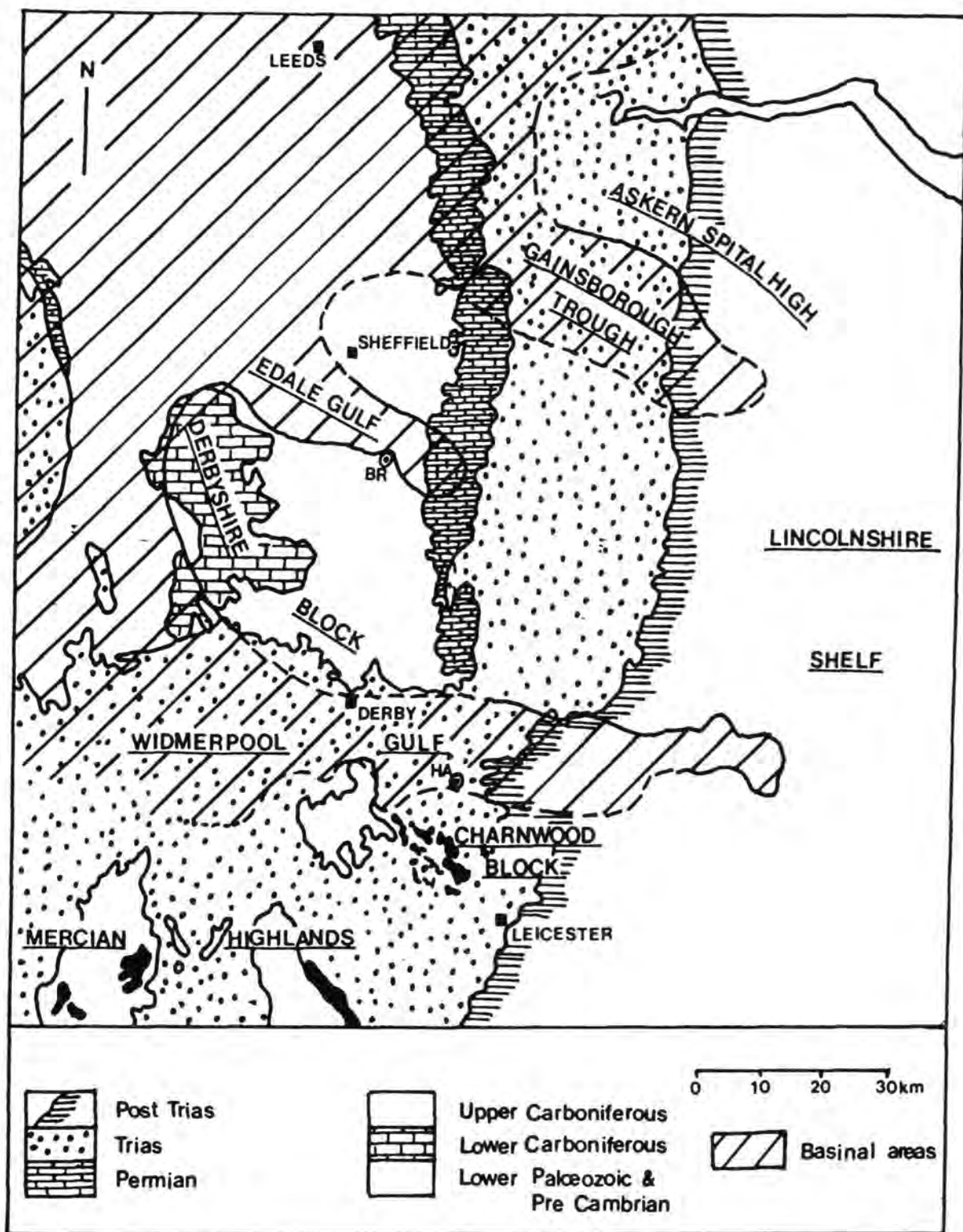


Figure 2.3 Block and gulf relationships in East Midlands Carboniferous rocks; showing locations of outcrops and boreholes. HA = Hathern No. 1, BR = Brimington.

recent meteoric water, due to pumping of the coastal pits, was not considered. Solution of Permian Zechstein evaporites is a realistic source of cations and anions of Na and Cl, respectively.

Bhatt (1975, 1976) has suggested that Lower Carboniferous evaporites were also deposited in limited amounts in the South Wales Coalfield basin, to the south of the Wales-Brabant high. However, recent work does not substantiate this view. Detailed stratigraphic, palaeological and geochemical analysis of the South Wales basin by Eustance (1981), Wright (1981) and Hird (1986) suggest that marginal basin environments and climatic constraints were not favourable for the deposition of evaporite sequences in the Lower Carboniferous in South Wales. No evidence has been found to verify their presence.

The absence of extensive evaporite sequences in South Wales, when compared with extensive deposits in the Lower Carboniferous of the East Midlands area, may thus go some way to explain the current absence of saline brines in the South Wales Coal Measures rocks, since the solution of evaporites is believed to be one of the main processes in brine formation.

Sections across the Kent coalfield (Trueman, 1954) also show no Lower Carboniferous evaporites which could influence the chemistry of the Coal Measures stratal waters.

During the Late Carboniferous and early Permian, the climax of the Variscan deformation resulted in the formation of numerous thrust faults and folds in the South Wales area. Basin sediments were compressed in a north-south direction. Two main factors influenced the structural evolution of the South Wales coalfield. They were:

- 1) The position between the rigid Wales-Brabant high to the North and the

main Variscan deformation belt to the south.

- 2) Regional northwards thinning of the Carboniferous sequence compared to older formations. Pre-Carboniferous strata thus had a greater influence to the north than to the south (Rast, 1981).

Mineralogical changes in carbonates, illite crystallinity, modifications in siliciclastic Carboniferous rocks and the development of diagenetic zones are mainly lateral in extent within the South Wales coalfield. There is little or no vertical variation in any of these properties with increase in the depth of burial. Coal rank and grade of metamorphism also increase progressively towards the west.

Associated faulting and sediment deformation will influence ground water movements and the setting up of brine sinks or reservoirs. Interference in groundwater circulation patterns might also affect the solution of any halite that may take place under unaffected groundwater flow conditions.

2.3 Vertical Variations in Groundwater Composition

The salinity of water commonly increases with depth below the surface, the composition of these subsurface brines alters with increasing depth and can be divided into three major zones. White (1965) and Cherbotarev (1955) identified these as near surface or shallow sulphate bearing waters, intermediate bicarbonate dominated waters and deeper chloride dominated zones (see Fig. 2.4).

Chamberlain and Glover (1979), identified a similar pattern of differing ionic compositions with depth for stratal waters taken from geological sequences of the Coal Measures of the United Kingdom.

The shallow sulphate zone, with Cl ions less than 100 mg/l, extends

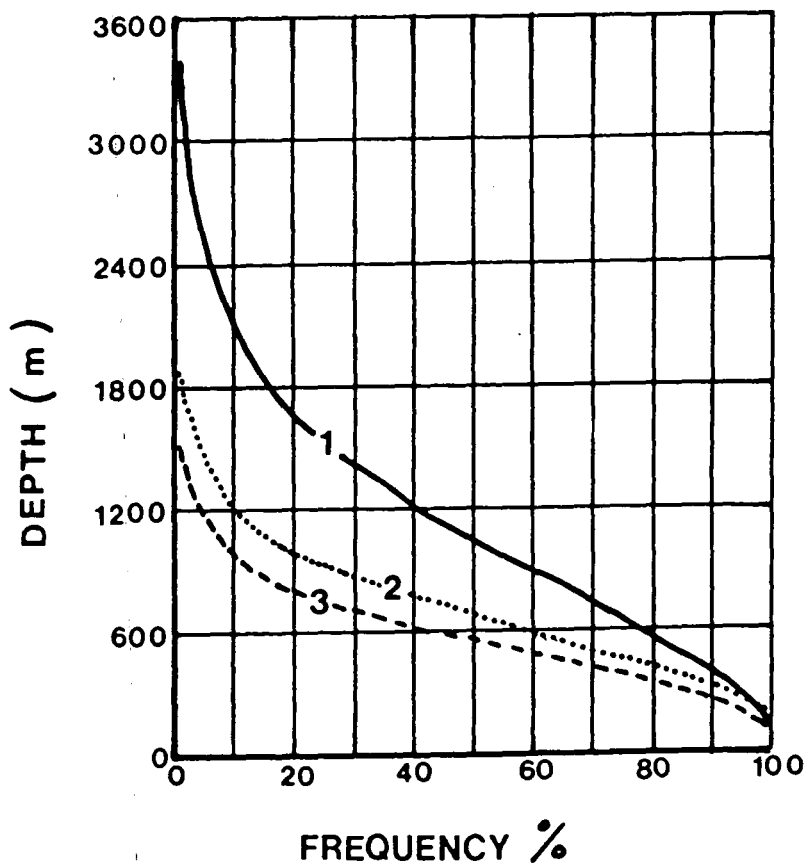


Figure 2.4 Frequency curves of depth of chloride (1), Bicarbonate (2), Sulphate (3) waters in oilfield areas (After Chebotarev, 1955).

from the surface to depths ranging from 50m to 200m . Calcium and magnesium sulphates occur in these near surface waters (see Table 2.1). This is a near surface phenomenon related to oxidation of pyrite in the vadose zone. In the underlying sulphate free zone, the calcium and magnesium sulphates are replaced by sodium bicarbonate as the principle solute. With increasing depth in the sulphate free zone, sulphate less than 5 mg/l as SO_4 , the concentrations of sodium, calcium and magnesium chlorides increase progressively. At the deepest levels, strontium and barium also occur, presumably as chlorides. Table 2.2 shows water compositions from the sulphate free zone. Water quality patterns from the British Coal Measures generally follow the above trends, although there are exceptions and local modifications. In the Kent coalfield, for example, no sulphate zone exists in the Coal Measures. This is because it is a concealed coalfield with no surface exposure. A typical coalfield aquifer may be represented by a progression from alkaline to less alkaline waters leading to more saline waters at depth.

Data given in Chamberlain and Glover (1976; Tables 2.1 and 2.2) are assembled in order of increasing depth [Mr. H.G. Glover, pers. comm.]. It will be noted from the tables that there is a progressive increase in the calcium/chloride ratio and a fall in the sodium/chloride ratio with depth. This converse behaviour of monovalent and divalent cations is not uncommon (see Downing and Howitt, 1969). This relationship itself suggests that some type of sediment/cation reaction must impede the upward migration of the monovalent cations in Coal Measures Strata.

SAMPLE REFERENCE	SPA	E. S11	P.H. WER	E. DRFT	N.G. KT
pH Value	5.8	7.5	6.8	8.2	7.8
Alkalinity to pH 4.5 mg/l CaCO ₃	85	370	500	160	570
Chloride mg/l Cl	45	40	90	100	40
Sulphate mg/l SO ₄	170	430	300	330	160
Sodium mg/l Na	40	65	70	100	340
Magnesium mg/l Mg	32	100	100	43	5
Calcium mg/l Ca	32	120	140	95	15
Strontium mg/l Sr	nd	0.5	< 1	nd	< 1
Barium mg/l Ba	nd	nd	<10	nd	<10
Manganese mg/l Mn	2.5	<0.1	0.4	nd	0.2
Ammonium mg/l N	nd	<0.1	<0.1	nd	0.3

"nd" signifies not determined.

Table 2.1 Water qualities found in the near surface, sulphate zone. (After Chamberlain and Glover, 1976).

SAMPLE REFERENCE	E. S10	W. PKG	O. S10	D. D08	M. P08
	8.4	8.3	8.4	7.5	6.4
alkalinity to pH 4.5 mg/l CaCO ₃	450	1730	410	200	60
Chloride mg/l Cl	45	100	6370	24800	135000
Sulphate mg/l SO ₄	< 5	<10	< 5	< 5	< 5
Sodium mg/l Na	240	830	4100	13420	57300
Magnesium mg/l Mg	0.2	13	46	410	3210
Calcium mg/l Ca	0.3	10	120	1680	20300
Strontium mg/l Sr	<0.1	< 1	4	49	660
Barium mg/l Ba	< 1	<10	12	85	1180
Manganese mg/l Mn	<0.1	<0.1	<0.1	0.3	15
Ammonium mg/l N	<0.1	0.2	2.0	8	108

**Table 2.2 Water qualities found in the deeper, chloride enriched zone.
(After Chamberlain and Glover, 1976).**

2.4 Chlorides in Coal and Coal Measures Rocks

The relationships between groundwater chloride concentration and depth have been studied in various sequences from the Coal Measures rocks of the United Kingdom, Germany and United States of America (Cas/well et al., 1984; Lehmann, 1952; Gluskoter and Rees, 1964).

The primary control on coal-chloride content would appear to be the salinity of the groundwaters with which the Coal Measures are associated, as is shown by a strong positive correlation between the two parameters. As ground water salinity generally increases with depth, so too does the chloride content of associated coals.

Chemical analyses of seam profiles through the Coal Measures show that coal samples have higher water soluble chloride levels than the associated mudrocks. Cas/well et al., (1984) found that a positive relationship exists between chloride levels and the organic matter contents of the sediments. Coals with a low ash content contain higher levels of chloride than mudrocks with a high ash content, where the chloride appears to be readily water soluble.

Figs. 2.5 and 2.6 show geological sections through two seams studied by the writer: the Parkgate and the Low Main Seams, from localities at Bilsthorpe Colliery, Nottingham. Each seam profile consists of roof materials, coal and associated intraseam dirt bands, and the floor seatearth. It can be seen that the chloride levels found from the above analyses follow those found by Cas/well et al., (1984).

2.5 Summary

It is unlikely that one single event or process is responsible for the chloride ion concentrations found in the formation waters, or for the

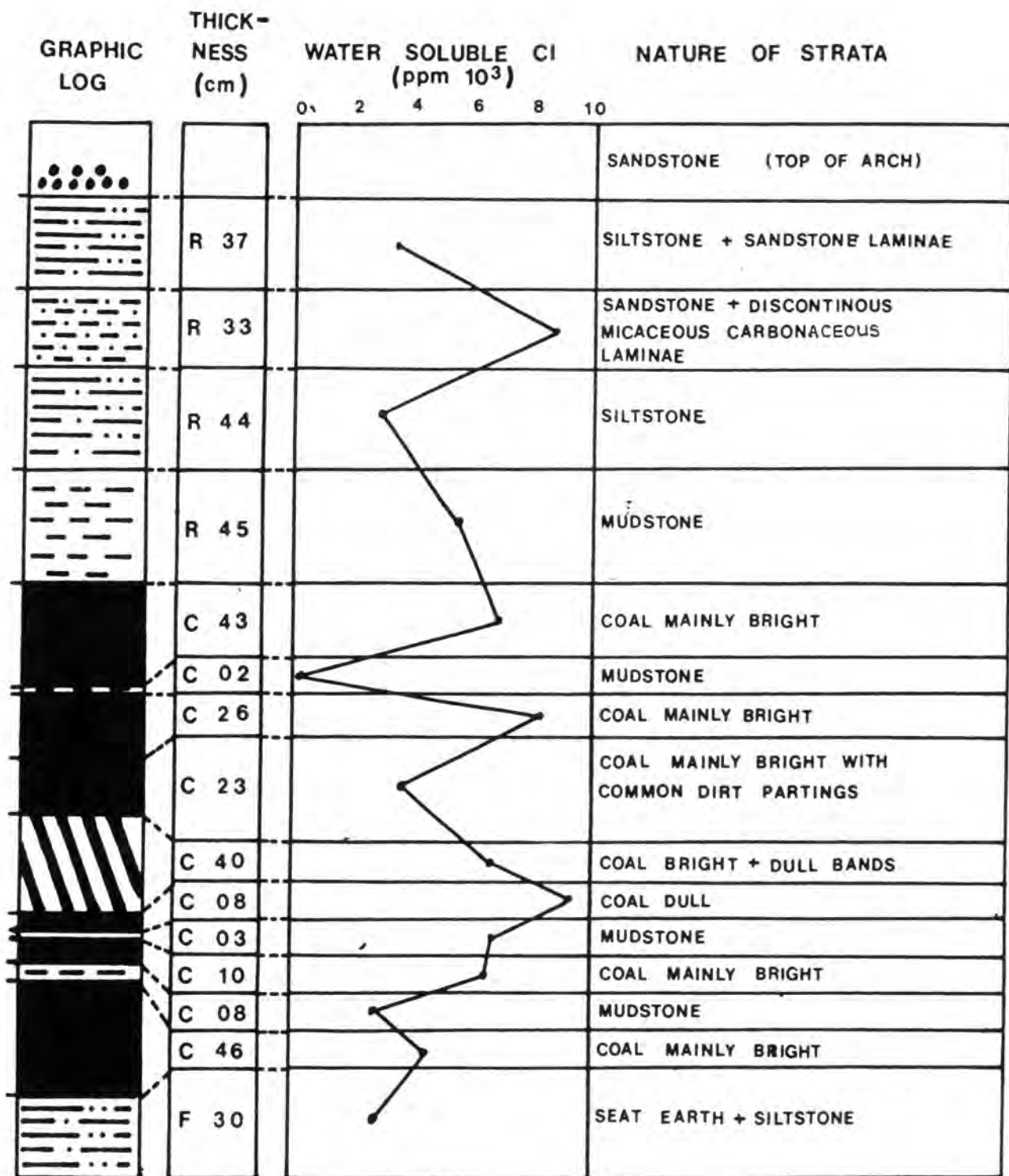


Figure 2.5 Water soluble chloride determinations on a section through Parkgate Coal Seam, Bilsthorpe Colliery. Sampling and lithological descriptions by P.S. Rees, British Coal.

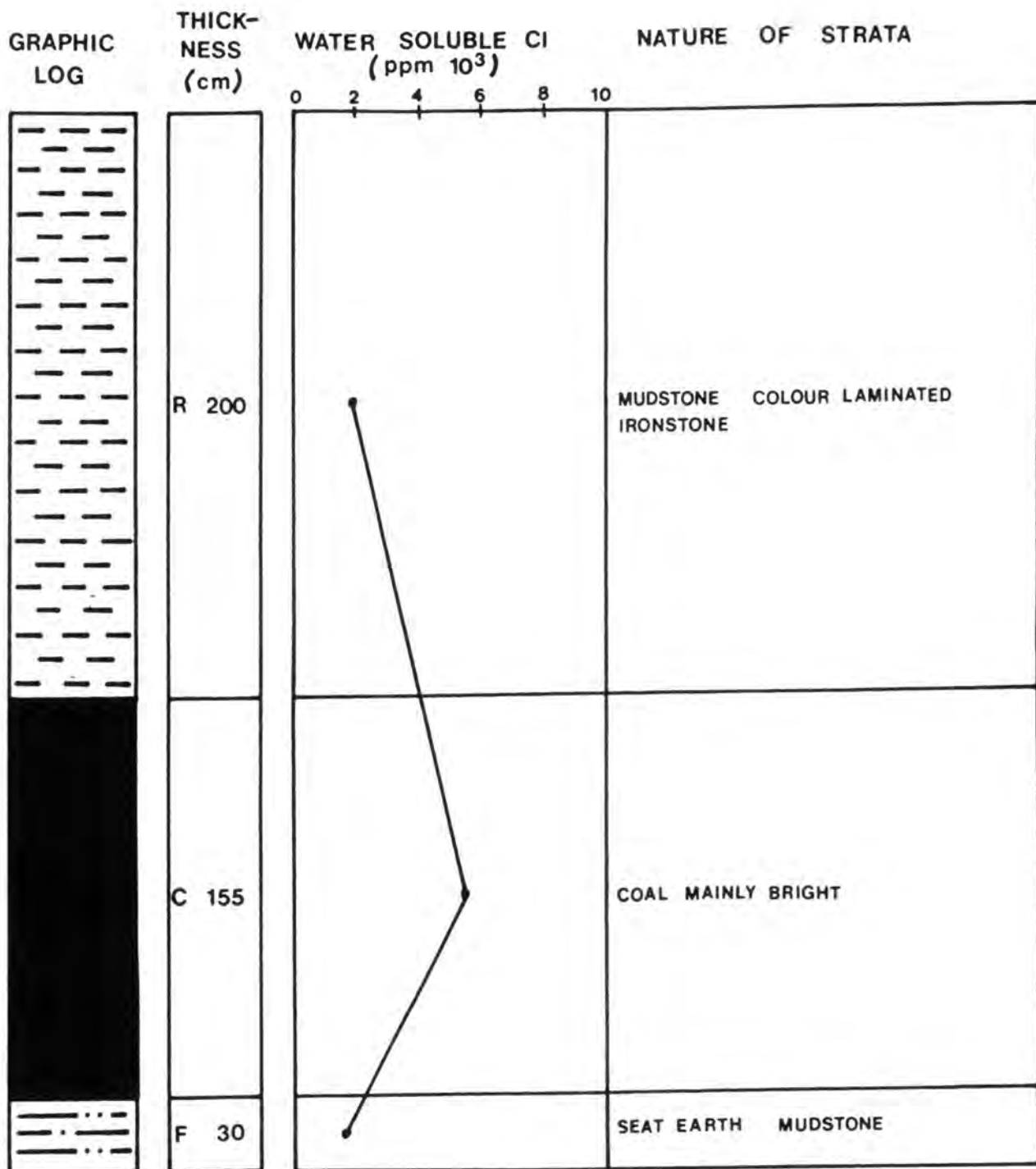


Figure 2.6 Water soluble chloride determinations on a section through Low Main Coal Seam, Bilsthorpe Colliery. Sampling and lithological descriptions by P.S. Rees, British Coal.

geochemical trends associated with depth and regional variation in the United Kingdom Coal Measures rocks. Mechanisms that would seem to have influenced the origin and diagenesis of the formation waters can be summarised as follows:

1. The Coal Measures are part of a cyclic sequence containing marine and brackish strata. The sequence may have been flushed with saline water soon after deposition.
2. There is evidence that Lower Carboniferous evaporite sequences were deposited around topographic highs to the north of the Wales-Brabant high. Typical is the Hathern Anhydrite, probably formed by a marine regression. These are believed to have been in contact with circulating groundwater from the Westphalian, during the Permo-Trias.
3. Composition of the groundwater of the Carboniferous would have been further altered and possibly concentrated by physical processes of compaction and by chemical processes involving reactions between rock minerals and interstitial solutions, filtration through clay membranes, adsorption, base exchange and biochemical processes.
4. Regional variation in groundwater chloride levels in the coalfields of Great Britain would appear to be linked to the geological history of the basin within which the Coal Measures were sedimented. During Carboniferous times, two main-drainage basins were established, to the north and south of the Wales-Brabant high. The South Wales, Irish and Bristol coalfields were sedimented from the south whereas the concealed Kent coalfield lies within the French Basin. The other main British coalfields were sedimented from northern sources. The South Wales basin has subsequently been deformed by the climax of Variscan deformation.

5. The absence of chloride ions in the groundwater of the South Wales coalfield may be explained in several ways:
 - i. The position of the basin to the south of the Wales-Brabant high creating a different sedimentary environment.
 - ii. The lack of evidence for Lower Carboniferous evaporite sequences in South Wales.
 - iii. The structural evolution of the basin in the late Carboniferous- Early Permian, influencing groundwater movements and groundwater flow conditions.
6. Groundwater ionic composition varies with depth through Coal Measures rocks. Three major zones can be identified, a shallow sulphate dominated zone, intermediate bicarbonate-rich and deep chloride dominated waters.
7. The chloride content of groundwaters influences the chloride content of the Coal Measures rocks. A positive relationship exists between organic matter content of sediments and chloride levels. Sequences taken through coal-bearing strata show high levels of chloride in coals and lower levels in associated mudrocks.

CHAPTER 3

BACKGROUND TO EXPERIMENTAL WORK

3.1 Site Selection Procedure

The sites selected for this project had to fulfill several criteria. They had to remain undisturbed for the duration of the project, the R.O.M discard had to have a chloride content (as Cl) greater than about 500 ppm (close to the crop spraying threshold damage value) and the discard had to be less than three years old and preferably freshly tipped.

Possible sample sites were suggested by British Coal, South Yorkshire Scientific Section. Maltby Colliery was chosen as it fulfilled all the above criteria and British Coal were already conducting top soiling experiments on part of the proposed embankment.

After approximately one year, it was decided to extend the sampling to another site that fulfilled all the criteria set out in paragraph 1, but unlike Maltby, had no lagoon incorporated into the tip structure. British Coal Western Region were approached and Wolstanton Colliery, Stoke-on-Trent, was selected.

To gather additional data on chloride distribution and to further study lagoon seepages and the effect of hot spots (areas of high salt concentration) on reclamation procedures, Bilsthorpe Colliery in Nottinghamshire was incorporated into the study. The three sites are shown in Fig. 3.1. Further details about the sites are given in the following sections.

3.1.1 Maltby Colliery

Maltby Colliery is situated approximately 16 km east of Rotherham and

M MALTBY COLLIERY
SOUTH YORKSHIRE REGION B

B BILSTHORPE COLLIERY
NOTTINGHAM REGION BC

W WOLSTANTON COLLIERY
WESTERN REGION BC

SCALE

100 km

N

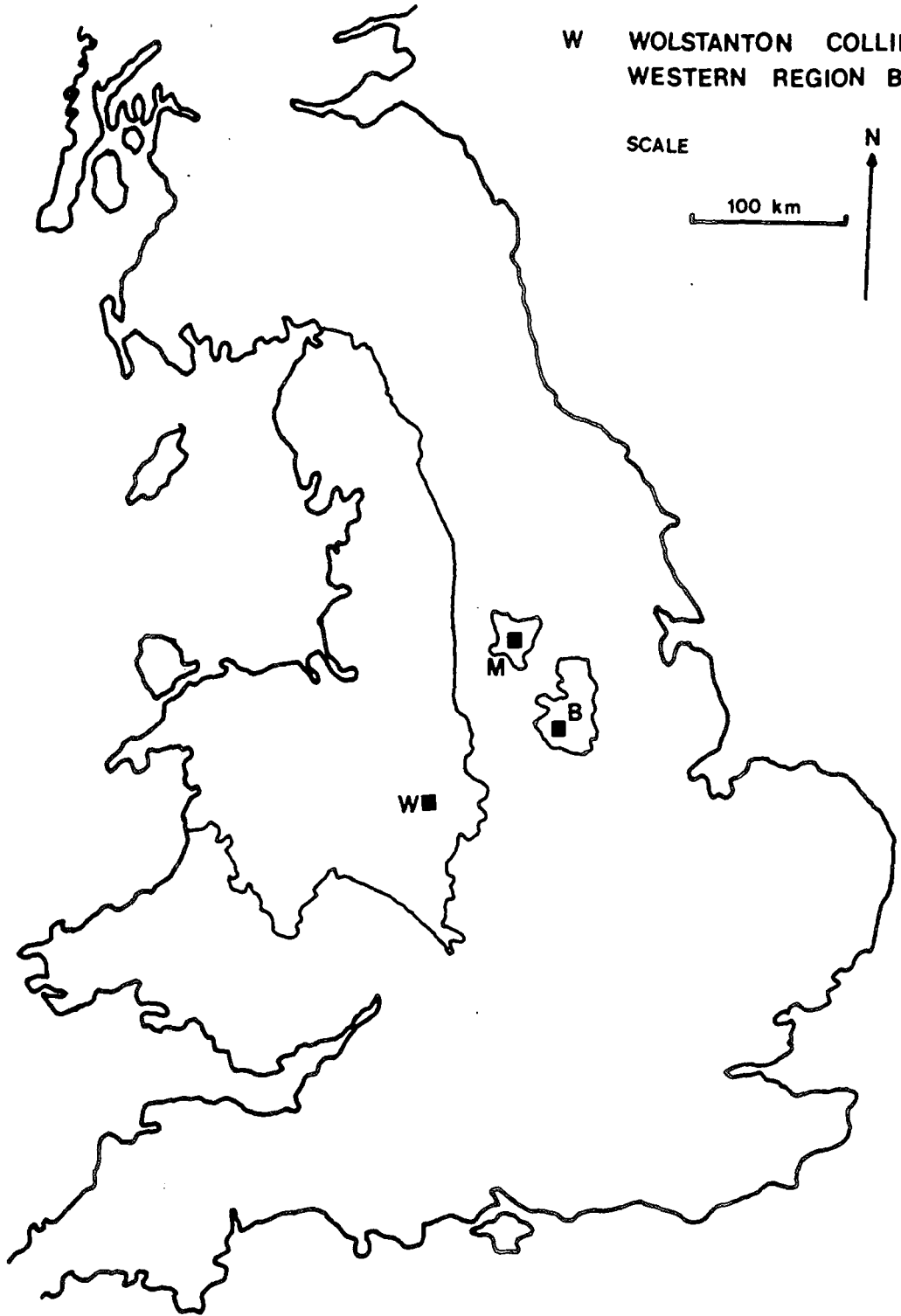


Figure 3.1 Site locations of collieries.

the same distance south of Doncaster, South Yorkshire.

The site is bounded by rough pasture and woodland to the north and east and by a housing estate and Maltby town to the west and south. The pit shafts were sunk in 1907, so tipping has been active since that date. The tip site now extends over several hectares. A successful area of tree planting can be seen on the north facing slope of the tip, whilst the rest of the tip remains bare apart from areas next to the Durham University (Engineering Geology) sample site, where experimental planting by British Coal has produced patchy grass/clover cover.

The tip structure has nine slurry lagoons incorporated into its design. Only two of these are active, receiving tailings from the coal preparation plant. The majority of the waste produced comes from the Swallow Wood seam with some from the Haigh Moor seam.

The sample site chosen was a west facing lagoon emplacement. The slope was completed and last graded to 14° some two years prior to the start of sampling and has been undisturbed since that time (5 years). The discard at the site was thus between three and five years old when sampled. This site was chosen because the discard was known to have high electrical conductivity and chloride levels (British Coal survey by Mr. H.G. Glover).

The lagoon embankment was constructed by the downstream method, in layers, in the conventional manner. Each lift would be expected to be less than 5m in thickness. The vertical distance between seepages, however, (Chapter 5) strongly suggests that the the compacted thickness of layers is in fact 3m. It is not known whether self-weight compaction has caused the reduction.

The site is underlain by Permian Magnesian Limestone and marls. This was identified in sample trenches at the toe of the embankment (Trench E,

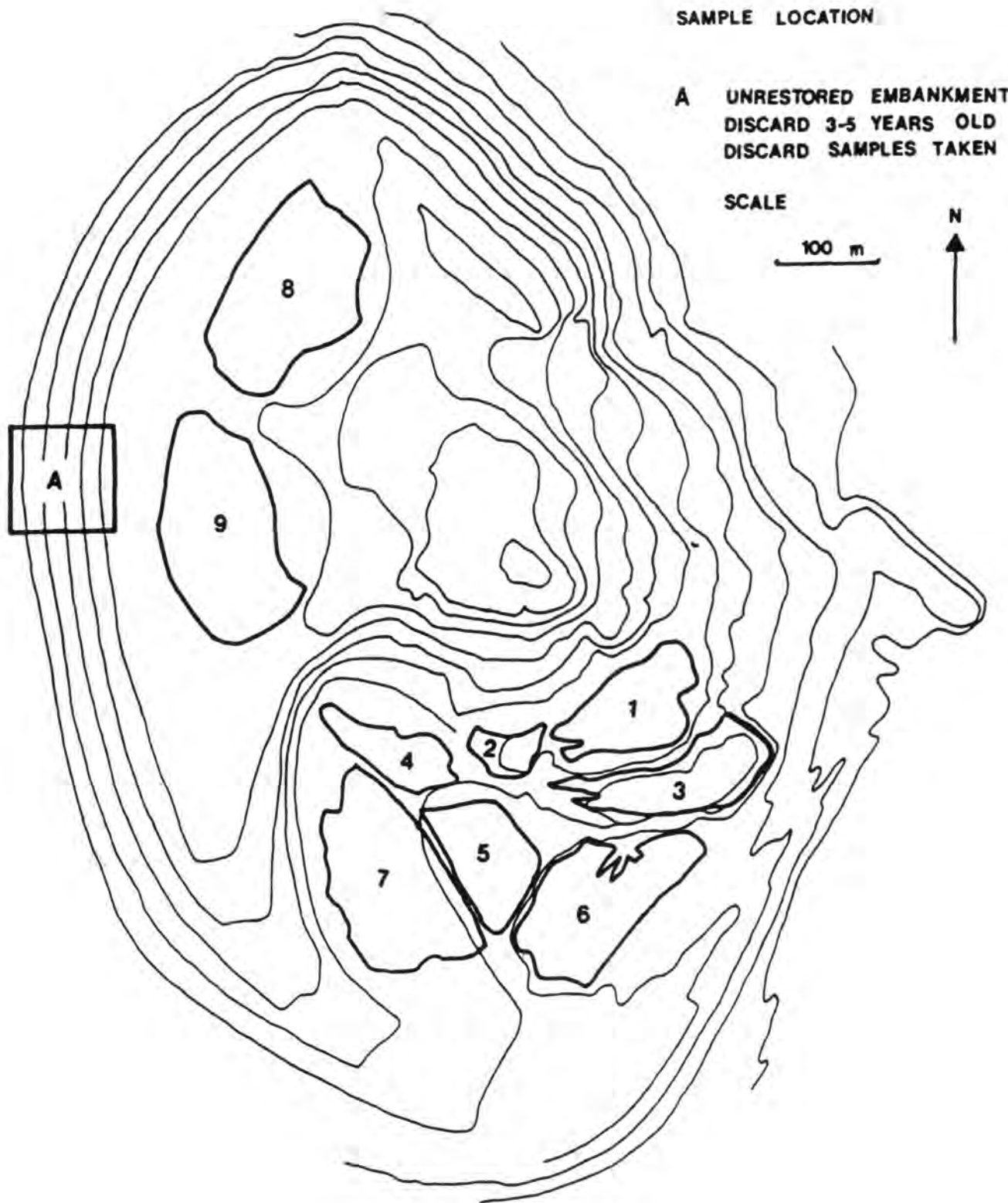


Figure 3.2a Maltby Colliery Plan showing location of sample site.



Figure 3.2b Sample site at Maltby Colliery.

Fig. 3.2a and b).

3.1.2 Wolstanton Colliery

The Wolstanton Colliery High Carr tipping site is situated approximately 5 km north of Newcastle-under-Lyme, Staffordshire. The site is bounded by rough pasture on the north, east and south sides, and by the A34 to the north. There is a slight gradient from west to east.

Prior to acquisition by British Coal, the site had various usages: rough grazing, a local authority domestic refuse tip, site of a small engineering works and there is evidence of mining activities from the previous century.

Tipping by British Coal commenced in 1975. Phase one comprised site levelling and was followed by phase two, involving the construction of a three-terraced tip. The upper plateau was completed in 1980 and tipping operations are currently in progress in the area of the intermediate and lower plateaus. Tipping is intermittent as discard produced at Wolstanton Colliery is often supplied to Local Authorities and private concerns for road construction and land reclamation uses. The slope between the intermediate and upper plateaus was seeded to grass and trees were planted in 1980. Grass has developed well and a substantial proportion of the trees planted have survived.

This site was chosen for research because the embankment was not a lagoon embankment and no lagoon structures were incorporated into the tip at any point, in direct contrast to the Maltby site. The tip could thus be used as a control to determine any influence the lagoon may have had on the distribution and movement of salts within the discard. Seepages and hotspots (although present) could not have arisen from lagoon seepages at

Wolstanton. Both the slope angle and discard age were comparable to those of the Maltby site. The sampling site (Fig. 3.3a and b) was the lowest slope of the three-tier terraced structure and was a large area of bare, undisturbed discard. Most of the discard originated from the Banbury and Cockshead seams.

The site is underlain by patchy drift consisting of red/brown and yellow/brown Boulder Clay. The drift lies on Etruria Marls which are present as bedrock beneath the whole of the tip site. They consist of red/brown mudstone with beds of coarse green and yellow grits and sandstones, and are relatively impermeable.

3.1.3 Bilsthorpe Colliery

Bilsthorpe Colliery is situated approximately 11 km east of Mansfield and was sunk in 1925.

The site is bounded by woodland and rough pasture to the north, east and south, and by the village of Bilsthorpe to the west. The tip structure has seven slurry lagoons incorporated into its design; two of them are active, receiving slurry from the washery. The slope chosen as a sample site forms the southern embankment of lagoon 6 and the dividing bank to lagoon 7 (Fig. 3.4a and b). The discard is approximately 3 years old, originating from the Parkgate and Low Main seams. The slope has been finished to a gradient of 14° .

The embankment was constructed in two phases. The first phase involved the construction of an embankment rising to a height of 78m A.O.D. whilst the second phase was completed by day-to-day tipping in 1981. A gravel toe drain was placed at the original toe of the first phase, with finger drains to the final toe of the embankment.

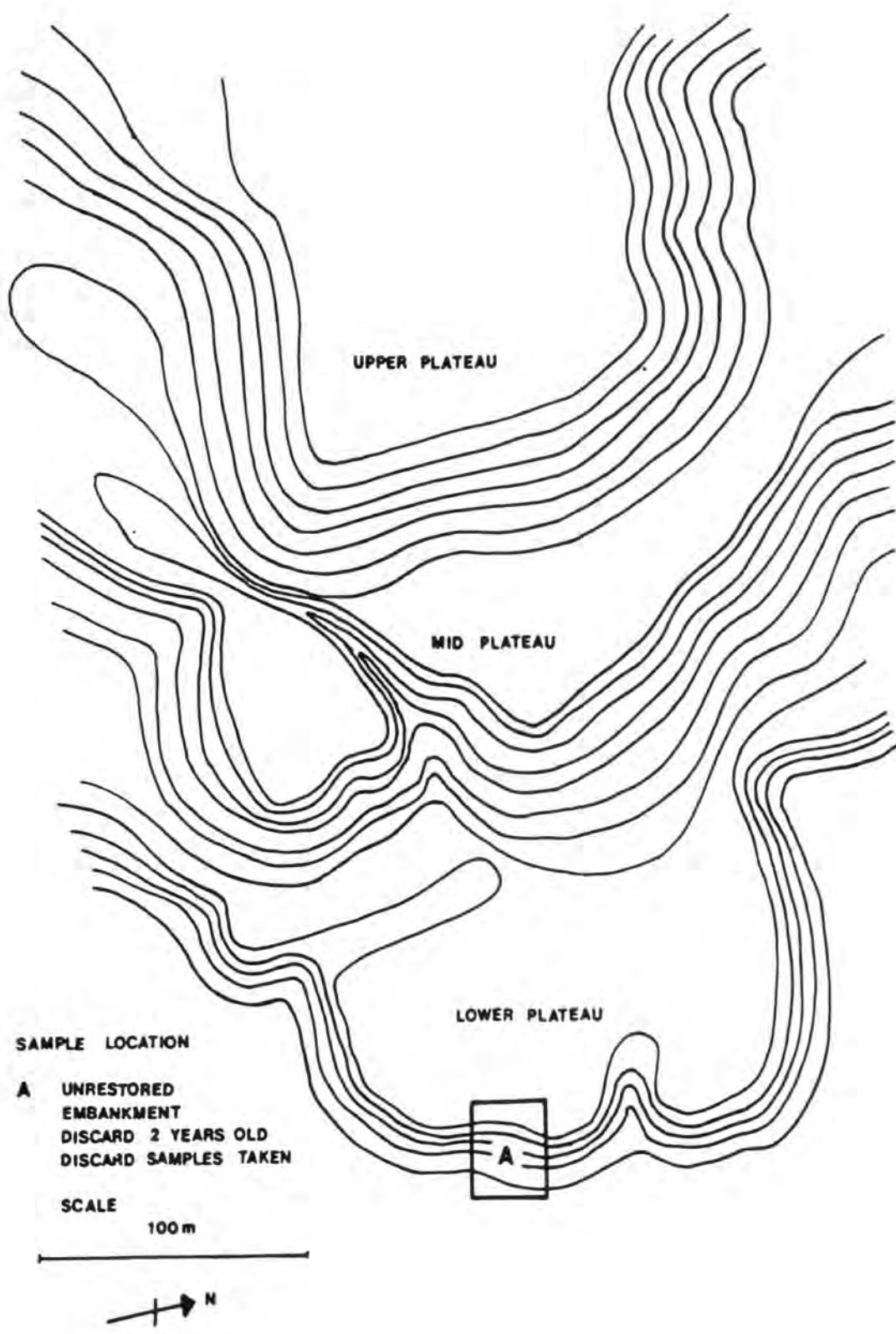


Figure 3.3a Wolstanton Colliery Plan showing location of sample site.



Figure 3.3b Sample site at Wolstanton Colliery.

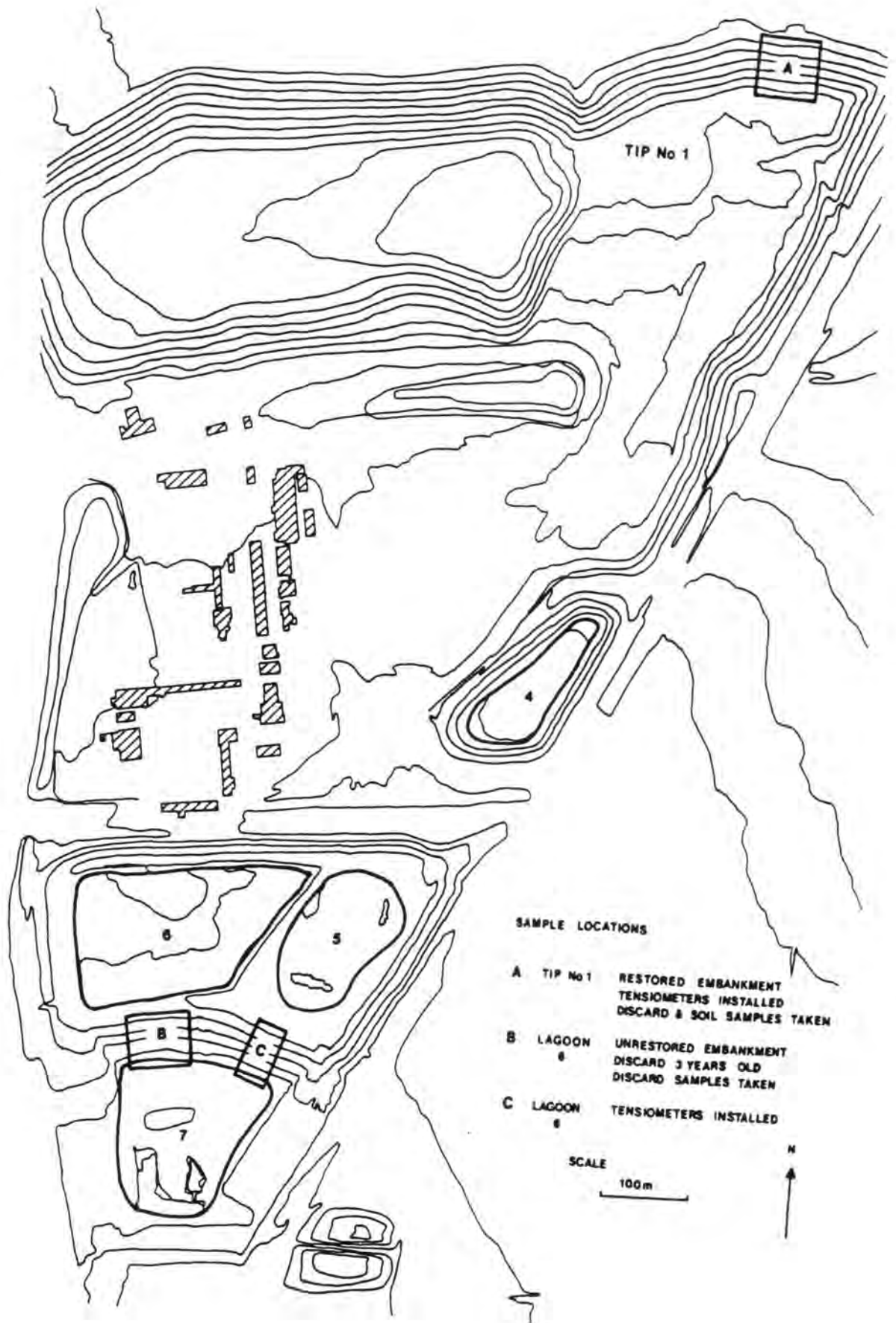


Figure 3.4a Bilsthorpe Colliery Plan showing locations of sample sites.



Figure 3.4b Sample site at Bilsthorpe Colliery.

Restoration work is progressing well on the north/northeast side of the tip (Tip No. 1, Fig. 3.4). An extensive area has been topsoiled, grassed and is now being let to a local farmer as rough grazing pasture. On some parts of this embankment restoration work has failed and seepage points or hotspots are visible where vegetation cover has failed to grow.

Tip No. 1, along with the southern embankment of lagoon 6 were sites of suction pressure measurements by tensiometers in the field (Chapter 6). Piezometers to monitor water tables were also installed in the lagoon embankment (see Bick, 1985) (Figs. 3.4a and b).

The site of lagoon 6 is underlain by Keuper Green Beds, comprising stiff clays and thin interbedded sandstones. On the western boundary, Bunter Sandstone lies immediately below the Green Beds, outcropping just beyond the colliery boundary. The impervious Keuper clays should provide an effective seal between the lagoons and the Bunter Sandstone aquifer.

3.2 Sampling Procedures

The sampling programme was initially carried out on the lagoon embankment at Maltby Colliery, South Yorkshire.

A survey of statistical sampling models led to the adoption of a regular grid. Sampling experience of contaminated land by the Environmental Advisory Unit of Liverpool University (1982) had previously shown that as the number of sampling points increased, a square grid proved to be more reliable than a random one for sampling hotspots or areas of contamination.

Two sampling procedures were established by the author. For assessments over a large surface area, and to locate possible seepage points or hotspots, a regular grid 5m x 5m, over a 50m x 25m area was

sampled in Spring 1983 (May), at two depths for each sample point; 0-100mm and 100-200mm. Based on preliminary results for this grid, a second, more limited grid, 10m x 10m, was sampled during Summer 1984 over the original grid area, to obtain a comparison of electrolyte variations with season.

To gather information on electrolyte movements within the spoil embankment at varying depths and through time, that is, from year to year and from season to season, a series of down-slope traverses, with sample points at the top, mid and toe of slope positions, were established. These traverses were sampled in Spring (May), Summer (August) and Winter (December), to a depth of 500mm, at intervals of 100mm (although at some sample points, samples were taken to a greater depth, depending on prevailing discard conditions). In addition, during the Summer of 1983, two machine-excavated trenches were sampled to depths of 1.8m and 3.9m, at the mid and toe slope positions respectively.

Detailed sampling of the surface of the colliery discard embankment was also undertaken at the top, mid and toe slope positions, at depths of 0-10mm, 10-20mm and so on, to 100mm, during Spring, Summer and Winter, from positions adjacent to the deeper sampling points on the slope.

A detailed spatial and chemical analysis of hotspot points on the embankments was also undertaken. This included sampling across hot spots at two depths; 0-100mm and 100-200mm, and detailed surface analysis of discard at depths of 0-10mm, 10-20mm and so on, to 100mm. Mineralogical investigations were undertaken on crystalline salt deposits recorded during summer months around hotspots on the embankment surface.

A total of 590 samples were taken at Maltby Colliery, including run-of-mine, washery and embankment materials, together with lagoon and seepage water.

After the first year, the sampling programme was extended to the other locations at the collieries described above. These exhibited variations in embankment and lagoon conditions compared with those at Maltby Colliery.

To enable direct comparisons to be made between Maltby and Wolstanton Collieries, an identical sampling regime was initiated at the latter site.

A total of 180 samples were taken at Wolstanton Colliery, including run-of-mine, washery and embankment materials. The analytical techniques used were identical to those listed for the Maltby Colliery samples.

3.3 Sample Preparation

For most samples, at least 0.5kg of discard was taken. This was sealed in air-tight plastic bags and weighed immediately on arrival in Durham. The discard was dried at a temperature of 30°C. After drying, the discard was reweighed and percentage moisture loss at 30°C calculated. Some samples were dried at 105°C, but no further appreciable water loss was recorded at this higher temperature. Drying at 30°C reduces the risk of volatilization of certain elements, or changing the physical structure of the discard (M.A.F.F., 1981).

The dried samples were then sub-sampled using a chute splitting riffle box. A sub-sample was sieved to obtain the less than 2mm fraction using a BS410 mesh sieve. It was presumed that this fraction would be more intimately associated with the establishment of vegetation on the surface of colliery tips than the large size grades, or 'whole' discard. There is evidence that it is this fine fraction which provides a plant's nutrient requirement (Russell, 1973). The less than 2mm fraction is also standard in most soil analysis texts (M.A.F.F., 1981).

3.4 Analysis

All samples have been analysed for moisture content (%), water soluble chloride (Cl^- ppm) and conductivity ($\mu\text{S}/\text{cm}$). Selected samples have been analysed for water and acid soluble sulphate (SO_4^{--} ppm). Analytical chemistry methods are shown in Appendix 1. Selected ions have also been determined by atomic absorption spectrometry. Total discard chemistries of selected samples have been determined by XRF spectrometry and mineralogical studies made using XRD techniques (including semi-quantitative estimates). Details of the above techniques are given in Appendix 2.

Initially, three different size fractions were analysed for water soluble chloride: the less than 2mm fraction, less than 2mm fraction tema-milled, and samples of whole or complete discard tema-milled. From Table 3.1, it can be seen that the less than 2mm tema-milled samples gave consistently higher results than the natural less than 2mm size and whole discard samples.

	WHOLE DISCARD TEMA-MILLED	LESS THAN 2mm TEMA-MILLED	LESS THAN 2mm
Maltby	1. 126	121	67
Discard	2. 121	210	121
	3. 191	244	204
	4. 291	368	318
	5. 187	248	152
	6. 336	348	238
	Parkside	1. 1216	1822
Discard			

Table 3.1 Variation in chloride concentration (ppm) in discard with size fraction used.

The tema-milled less than 2mm sample may be taken to represent a

potential maximum, as grinding to this fine grain size will release chlorides held in small pores in coaly fragments. This fraction was rejected, however, since natural leaching and weathering processes do not reduce all coal fragments and mudrocks to clay-sized grades.

All water soluble analyses were done using a 1:10 ratio of discard to deionised water suspension, agitated for 30 minutes. A 1:10 suspension creates obvious departures from the fluid concentrations experienced by plant roots. Cheng et al. (1983), however, suggest that for the evaluation of the total soluble salts of soil (and discard), and for the assessment of reclamation procedures, the 1:10 extract method is more suitable than other possible methods, such as the saturated paste extract method.

Advantages with the 1:10 extract method used are:

1. It gives a large quantity of extract for analysis.
2. Given the number of samples taken for analysis in this project, it is less time consuming than the saturated paste extract technique.
3. A smaller quantity of discard was needed, making laboratory handling easier.

The results shown were all based on this extract and thus information and inferences are internally consistent and can also be related to other published data on saline soils.

Precision for water soluble chloride, sulphate and conductivity was tested by analysing the same sample twenty times. The relative deviation of the specific ion electrode method for the determination of chloride was 4.1%, for the determination of water soluble sulphate 4.9%, and for electrical conductivity 1.3% (see Table 3.2).

	Cl (ppm)	SO ₄ (ppm)	Conductivity ($\mu\text{S}/\text{cm} \times 10^3$)
	1190	122	0.738
	1290	140	0.724
	1320	122	0.734
	1300	119	0.715
	1300	122	0.745
	1390	126	0.745
	1350	120	0.749
	1400	123	0.733
	1390	124	0.730
	1290	119	0.724
	1390	126	0.717
	1400	121	0.719
	1350	120	0.749
	1390	128	0.745
	1400	119	0.748
	1410	120	0.726
	1400	140	0.731
	1320	124	0.723
	1390		0.731
\bar{x}	1348	124	0.732
σ_n	56.4	6.1	0.01
relative deviation (%) *	4.1	4.9	1.3

* relative deviation = $\frac{\sigma}{\bar{x}} \times 100$

Table 3.2 Precision test for analytical methods used for water soluble chloride and sulphate and conductivity.

CHAPTER 4

THE CHEMISTRY AND MINERALOGY OF DISCARD FROM MALTBY, WOLSTANTON AND BILSTHORPE COLLIERIES

4.1 Introduction

The detailed chemistry and mineralogy of seven samples of coarse colliery discard was undertaken as part of this study. The discard came from three different colliery tips - Maltby in South Yorkshire, Bilsthorpe in Nottinghamshire and Wolstanton in Stoke-on-Trent, the details of which have already been discussed in Chapter 3. The analyses obtained form a comparative study of the broad mineralogical and chemical differences between coarse discard from the three sites.

Two samples were taken from each of the three colliery tip sites. These samples were surface samples from a 0-100mm depth, representing weathered material, samples from a 500mm depth from the Bilsthorpe and Wolstanton tips and samples from a 1.8m depth from an excavated trench location at Maltby Colliery. These sub-surface samples represent unweathered material. The seventh sample was also Maltby discard but was taken from the highly weathered surface of the 5 to 7 year-old discard, used to monitor suction pressures in an experimental tip, at the Durham University courtyard site (Chapter 6).

Comparison of dominant mineral groups and the chemistries of respective surface samples with those of deeper samples, allows the nature and extent of weathering to be evaluated. The presence or absence of weathering indicators such as pyrite, acid soluble sulphates and soluble carbonate minerals can be determined.

The presence of chloride/sulphate hotspots detected in desiccated

	Maltby Discard Experimental Tip	Maltby Discard 0-100mm	Maltby Discard 1.8m	Bilsthorpe Discard 0-100mm	Bilsthorpe Discard 500mm	Wolstanton Discard 0-100mm	Wolstanton Discard 500mm	Average Discard (Taylor, 1984)
SiO ₂	38.25	45.02	42.14	53.10	52.43	35.86	36.87	46.23
Al ₂ O ₃	17.22	21.79	20.31	19.86	19.92	13.40	13.93	19.74
Fe ₂ O ₃	5.19	7.27	4.43	3.90	4.20	5.10	6.07	5.39
MgO	1.69	2.03	1.45	1.32	1.33	0.90	1.00	1.01
CaO	2.50	2.57	0.89	0.91	0.91	2.00	2.65	0.74
Na ₂ O	0.32	0.44	0.62	0.45	0.45	0.31	0.51	0.41
K ₂ O	3.31	3.36	3.66	2.94	3.02	1.93	2.00	3.40
TiO	0.75	0.76	0.86	0.97	0.94	0.84	0.87	0.88
MnO	0.04	0.06	0.00	0.03	0.03	0.07	0.08	0.10
P ₂ O ₅	0.07	0.06	0.07	0.06	0.06	0.21	0.22	0.18
S	1.38	0.71	0.57	0.74	0.94	1.01	0.96	0.96
ORGANIC C	23.10	10.00	21.60	11.45	11.93	34.62	29.20	13.30
CO ₂ +H ₂ O+	3.10	3.05	2.07	2.98	3.07	1.68	4.28	6.85
H ₂ O-	1.56	1.65	1.89	1.74	1.96	1.41	1.25	1.15
TOTAL	98.48	98.77	100.56	100.44	101.19	99.34	99.89	100.34
QUARTZ	14.0	11.0	10.0	25.0	22.0	12.0	15.0	17.5
ILLITE	30.0	40.0	25.0	40.0	45.0	25.0	20.0	31.5
M.L.C.	22.0	20.0	20.0	15.0	10.0	15.0	15.0	26.0
KAOLINITE	6.0	8.0	8.0	10.0	10.0	7.0	10.0	10.5
CHLORITE	4.0		4.0		3.0			0.5
CALCITE	1.0	2.0	1.0	2.0	1.0	1.0		Average
DOLOMITE			5.0		1.0			1.0
SIDERITE	1.0		1.0		1.0	3.0	4.0	
ORGANIC C	23.0	16.0	22.0	11.0	12.0	35.0	27.0	13.0
TOTAL	101.0	97.0	97.0	103.0	104.0	98.0	91.0	100.0

Table 4.1

Total Chemistry and Mineralogy of Discard Samples from Maltby, Bilsthorpe and Wolstanton Sites.

surface discards at Bilsthorpe and Wolstanton Collieries is discussed in Chapter 5. Suction pressures generated in the near-surface, partly saturated, zone of a spoil heap (Chapter 6) are also pertinent to weathering, which includes oxidation within partly saturated discard.

In Chapter 1, brief mention was made of the three major mineral groupings revealed by a correlation matrix applied to a large number of samples of colliery discard from England and Wales (Taylor, 1984). The three groups are (a) detrital minerals, (b) non-detrital minerals and (c) the coal group. The detrital minerals are mainly quartz, clay minerals and minor rutile. Carbonates comprise the principal non-detrital minerals and are largely siderite and ankerite. Constituents of the coal group were established as coal, pyrite and probably gypsum and calcite, both of which are found in the cleat of coal (see for example, Spears et al., 1971). Superimposed on the three groups in Fig. 1.2 are engineering properties which correlate with particular mineral/chemical groups. These three groups are used as a framework for discussion in this Chapter.

4.2 Whole Rock Geochemistry

4.2.1 Method of Analysis

Chemical compositions of the whole rock and the less than 2mm fraction rock samples were analysed using a Phillips PW1212 Automatic Sequential X-ray Fluorescence (XRF) Analyser. Eleven major elements, expressed as elements or elemental oxides were analysed using pressed powders. They were; total Si, Al, Ti, Fe (as ferric oxide), Mg, Ca, Mn, Na, K, P and S. All constituents were expressed as percentages of the sample weight, the analyses being shown in Table 4.1. Moisture (as H_2O^-), H_2O^+ and organic

	Total SiO ₂	Combined SiO ₂	RATIOS WITH Al ₂ O ₃					WEIGHT %			Cl (ppm)	SO ₄ Water soluble (ppm)	SO ₄ Acid soluble (%)	Illite width at ½ peak height to peak height ratio
			Fe ₂ O ₃	MgO	CaO	NaO	K ₂ O	TiO ₂	P ₂ O ₅	S				
Maltby Discard Experimental Tip	2.22	1.41	0.30	0.09	0.14	0.02	0.19	0.04	0.07	1.38	130.0	303.0	0	0.23
Maltby Discard 0-100mm	2.06	1.56	0.33	0.09	0.11	0.02	0.15	0.03	0.06	0.71	565.0	228.0	0.14	0.26
Maltby Discard 1.8m	2.07	1.58	0.22	0.07	0.89	0.03	0.18	0.04	0.07	0.57	1113.0	128.0	0.1	0.21
Bilsthorpe Discard 0-100mm	2.64	1.40	0.19	0.06	0.04	0.02	0.14	0.04	0.06	0.74	298.0	372.0	0.49	0.30
Bilsthorpe Discard 500mm	2.63	1.52	0.12	0.06	0.04	0.02	0.15	0.04	0.06	0.94	70.0	480.0	0.10	0.24
Wolstanton Discard 0-100mm	2.67	1.78	0.38	0.06	0.15	0.02	0.14	0.06	0.21	1.01	22.0	23.0	0	0.48
Wolstanton Discard 500mm	2.64	1.56	0.43	0.07	0.19	0.03	0.14	0.06	0.22	0.96	32.0	0.0	0.05	0.44
Average Discard (Taylor, 1974)	2.34	1.45	0.27	0.05	0.04	0.02	0.17	0.04						

Table 4.2 Ratios with Al₂O₃. Chloride, acid and water soluble sulphates.

carbon contents were obtained by thermal treatment. Full details of the analytical procedures are given in Appendix 2.

4.2.2 X-ray Diffraction (XRD)

Details of the X-ray diffraction techniques used in this study are outlined in Appendix 2. Clay mineral reflection intensities, in the form of peak heights or peak areas measured from the diffraction charts cannot be compared quantitatively due to the inherent orientation and mass absorption problems. Moreover, species vary in chemical composition and crystal perfection. Consequently, the XRD analyses given in Table 4.2 are expressed on a semi-quantitative basis. Estimates are based on comparison with boehmite reflections used as an internal standard.

The platy character of most clay minerals gives some degree of preferred orientation of particles, particularly in the surface layer of diffraction mounts exposed to X-rays. However, because consistent preparation techniques were used, it is concluded that the influence of orientation on the intensities will be substantially constant. Initially, both distilled water and acetone were used as liquid mediums in the preparation of the mounts. The intensity diffracted by each clay mineral was nearly the same for both liquid media, so acetone was chosen because the mounts could be prepared much more quickly.

4.3 Detrital Group Minerals

4.3.1 Quartz (SiO_2)

The composition of quartz is normally very close to 100% SiO_2 . Being resistant to weathering, it is an abundant detrital mineral in Coal Measures rocks and is concentrated during the sedimentary process.

The range of quartz contents in the samples of discard analysed was

from 10% to 25% (Table 4.2). Materials from Bilsthorpe had the greatest percentage - 22% and 25%, then Wolstanton - 12% and 15%, followed by Maltby with relatively low levels of 10% and 11%. Surface samples do not appear to contain more quartz than the deeper samples and there is no indication that the Maltby discard is atypical. Average quartz found by Taylor (1984) for unburnt UK spoil heaps was 17.5%.

Although the total silica contents of Table 4.1 include combined silica, found largely in clay minerals, it will be observed that the Bilsthorpe specimens with the highest quartz contents (Table 4.2) also have the highest total silicas. However, low values of quartz are not identified so readily.

4.3.2 Clay Minerals

Clay minerals are hydrous silicates of aluminium and/or iron and magnesium. Their structure is based on groups built from composite sheets or layers of silica tetrahedra and aluminium or magnesium hydroxide octahedra, linked together by oxygen atoms common to both. The arrangement of these sheets and the degree of replacement of silica or aluminium ions by other elements, determines the clay mineral type.

The clay minerals identified in this study are outlined in Tables 4.1 and 4.2. They are kaolinite, illite, mixed layer clays and chlorite.

Variabilities in the ratios of various oxides to alumina in clay minerals are useful 'finger prints' for comparisons of the clay mineralogy of Coal Measures samples. These would include; Fe_2O_3 , MgO , CaO , Na_2O and K_2O in ratio with Al_2O_3 . Potassium oxide, and to a lesser extent, Na_2O , can be attributed to micaceous and mixed layer minerals, particularly illite, so the $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio can be interpreted as a measure of illite

content. Total Fe as Fe_2O_3 is also probably related to the illite group but the total includes iron which may be present as pyrite and siderite and as oxidation products, mostly limonite.

Total silica includes quartz, but if this is subtracted then the ratio of combined $\text{SiO}_2/\text{Al}_2\text{O}_3$ is a useful guide to clay mineral type. The following approximations can be made:

clay mineral group	combined $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio
kaolinite	1.06-1.37 (1.18 ideal kaolinite)
illite	1.45-2.40
smectite	2.14-3.45
chlorite	1.02-2.06

Ratios of combined SiO_2 to Al_2O_3 in Table 4.2 suggest that the dominant clay group in all samples studied is illite, as the ratios all fall within the range 1.45 to 2.40. The semi-quantitative mineralogy (Table 4.2) confirms the presence of illite and further indicates the importance of mixed-layer clays in these rocks. The average combined $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio for coarse discards from collieries in these areas is 1.45 (Taylor, 1984).

4.3.2.1 Kaolinite

Kaolinite is representative of a 1:1 clay mineral, each sheet being composed of one tetrahedral layer interlocked with one octahedral (gibbsite) layer. The ideal chemical composition is $\text{Si}_4\text{Al}_4\text{O}_{10}(\text{OH})_8$ and the mineral varies little from this. Kaolinite is a relatively stable clay mineral at normal temperatures and can be identified by its diagnostic

reflections at 7 \AA (001), 3.58 \AA (002) and 2.37 \AA (003) (J.C.P.D.S. index, 1974). Quantitative estimation is difficult because of variation in peak shapes. These are caused by differences in crystal size and by disorder, such as random displacement of the crystal lattices. Decreasing grain-size causes prominent basal reflections to become less sharp and less intense while increasing disorder is reflected by 'tails' to lower 'd' spacings on (hko) reflections.

When chlorite is present, the (002) reflection coincides with the 7 \AA (001) reflection of kaolinite, increasing the height and area of the kaolinite peak. To allow for this, the chlorite contribution to the 7 \AA reflection was sub/tracted following the method described by Smith (1978).

Kaolinite is third in order of clay mineral abundance in all of the discard samples analysed. The amounts range from 6% to 10%, compared with an average of 10.5% in United Kingdom spoil heaps. Bilsthorpe discard samples have the highest percentage of kaolinite, with the Maltby experimental tip the lowest. There is no evidence to suggest that the kaolinite content differs in shallow as opposed to deeper samples.

4.3.2.2 Illite

The term 'illite' is used for a wide range of the fine grain-size 10 \AA 'micaceous' minerals, sericites and hydrous micas. In the samples studied the illite has a 'tail' on the low 2θ angle side of the 10 \AA reflection. This represents an expandable mixed-layer clay component (see Section 4.3.2.3).

Illite is present in largest amounts in the deeper samples from Bilsthorpe - 45%, and is at a minimum of 20% in the deepest Wolstanton sample. It is of interest that the K_2O/Al_2O_3 ratio (Table 4.2) does not

reflect illite abundance alone in the samples, but does show some relationship with illite plus mixed-layer clay. The Wolstanton samples which have the lowest totals (35-40%) have the lowest ratios (0.14-0.14). At the other extreme, the Maltby sample from the 100mm depth has the highest illite plus mixed-layer clay content and this has a reasonably high ratio (0.154), although not the highest. Potassium is high in all the Maltby samples, as can be seen in Table 4.1, but an alternative site for K_2O , such as jarosite ($KFe_3(OH)_6(SO_4)_2$), is not indicated by the acid soluble sulphate values (Table 4.2).

Illite crystallinity was used as an indicator of weathering in the discard samples, following the method used by previous authors (for example, Taylor, 1971; Smith, 1978). Ratios of the width of the (001) illite reflection peak at half peak height, to the peak height are given in Table 4.2.

Wolstanton discard had the highest ratios, indicating least crystal degradation of the three discards from different sites. For each of the three discards, the surface samples from the 0-100mm depth had higher ratios than the samples from depth, showing a higher degree of weathering.

From the ratios given in Table 4.2, discard from Maltby would appear to be the most weathered of the three types.

4.3.2.3 Chlorite

Chlorite minerals, $Al_2Mg_{10}(Al_2Si_6)O_{20}(OH)_{16}$, have a 2:2 layered structure composed of two tetrahedral and two octahedral layers in each sheet. There is some substitution by Fe^{2+} for Al and Mg in the octahedral positions. The basal spacing produces a (001) reflectance at 14 \AA and the mineral is generally identified without much difficulty on diffraction

traces.

Chlorite was not identified in all the discard samples analysed. Maltby experimental tip discard and Maltby deep discard had about 4% present and Bilsthorpe deep discard, 3%. These values are of the same order of magnitude as those reported elsewhere for Upper Carboniferous strata, (Shaw, 1981).

4.3.2.4 Mixed-layer Clays

This is the term used for different types of sheet structure occurring in regular or random intergrowth. The 001 reflection shows the combined effects of the different types of layers in the structure. Thus a regular mixed-layer composed of 2 illite and 1 chlorite may have a (001) reflection of approximately 34 \AA . Qualitative identification and quantitative estimation are difficult and imprecise.

Expandable mixed-layer clays have smectite as a component and glycolation may be used to split the 'tail' on the 10 \AA reflection by expanding the smectite component to a higher d-spacing. Comparison of treated and untreated 10 \AA peaks can provide an indication of the mixed-layer component.

Table 4.2 indicates that mixed-layer clay is present in all samples. Estimates indicate a range from 10% to 22%, the latter figure being lower than the national average of 26.0%. The clayey discard from Maltby Colliery has the highest content.

4.4 Non-Detrital Minerals: Carbonate Group

The minerals identified from X-ray diffraction traces were calcite, dolomite and siderite.

Tables 4.1 and 4.2 show that calcite was identified in the shallow Maltby sample and in both Bilsthorpe samples. Since this is the most soluble of the carbonates, its absence might suggest that it has been removed from other samples. However, it is a cleat mineral of coal (Spears et al., 1971) and is not as common as, say, siderite in the dominantly non-marine mudrocks of Coal Measures age. Being a mineral associated with waste coal rather than the mudrocks, it may not be uniformly distributed. In other words, its absence in the deeper Maltby sample, and the reduced quantity in the deeper sample from Bilsthorpe, may not be indicative of weathering processes, but rather a crude measure of the amount of coal in the discard.

Siderite is the most resistant of the carbonate minerals in colliery discards (Taylor and Spears, 1970). It is present at the 3-4% level in the Wolstanton tip, where its presence is in accord with relatively high iron contents (Table 4.1) and the two highest Fe/Al ratios (Table 4.2).

A small amount of dolomite is present in the deepest Bilsthorpe material with quite a high percentage being present in the deeper Maltby discard. The latter sample has the highest CaO/Al₂O₃ ratio, but ratios involving magnesium and iron are not particularly high. Although the reflection measured (2.89 Å) is suggestive of essentially pure dolomite, it is likely that it is a ferroan type since the latter is more common in Coal Measures strata.

4.4.1 Coal Group Minerals

Colliery discards are different from conventional sediments and rocks by virtue of their high contents of waste coal, largely organic carbon, which thus forms an important constituent. At Wolstanton, organic carbon

accounts for between 29-35% of the constituents of the discard and at Maltby, levels vary from 22-23% (Table 4.1).

Total sulphur is high in the three samples with the highest coal content (Table 4.1), but no pyrite was identified in any of the samples. Whilst discussing the coaly constituents, it should also be noted that the highest P_2O_5 values follow high coal contents.

4.4.2 Sulphates

The distribution of water soluble sulphate in the discards follows that for acid soluble sulphates. The highest acid and water soluble sulphates are found in the Bilsthorpe samples, the deeper of the two having the highest levels. The Wolstanton discard has the lowest values for sulphates. In the Maltby and Wolstanton discards, the surface samples have higher sulphate contents than the samples at depth (Table 4.2).

4.5 Conclusions

Discard from three different collieries was studied using total chemistries, obtained by XRF analysis and semi-quantitative mineralogical analyses by XRD techniques.

A comparison of the results obtained by these methods shows that the discards fall into three groups, each having distinct characteristics.

The Maltby discard is predominantly clayey containing little quartz, below the average for British colliery discards (Taylor, 1984). The discard is dominated by illite and is probably the most highly weathered. In this respect, it should be recorded that in a surface sample taken from the experimental heap and in one tip specimen taken from the 0-100mm depth, 2% and 5% gypsum, respectively, were estimated. This additional evidence

of weathering was not found in samples from the other two colliery tips.

Discard from Bilsthorpe has a very high quartz content, but also a high clay content, compared to discards from Maltby and Wolstanton. This discard is dominated by illite and also has the highest mixed-layer clay content. This discard is probably more weathered than the Wolstanton discard.

Wolstanton discard is markedly different from that of the other two collieries, being a coal-rich material. Wolstanton discard, although being dominated by illite, has the lowest total clay and illite contents of the three discards. The highest siderite percentages were found in this discard and this, along with a high illite crystallinity ratio and low acid and water soluble sulphate content, would indicate that Wolstanton discard is the least weathered of the three studied.

CHAPTER 5

DISTRIBUTION OF CHLORIDES AND OTHER ELECTROLYTES IN THE NEAR SURFACE LAYERS OF COLLIERY EMBANKMENTS

5.1 Grid Sampling Results for Chloride

Figures 3.2a and 3.3a show the location of the grids sampled at the Maltby and Wolstanton High Carr sites. Sampling details have been outlined in Chapter 3 and at both sites a regular 5m x 5m grid was adopted.

The effects of changing the grid size on chloride distribution patterns over the tip surface, can be clearly demonstrated and are presented in Figs. 5.1 and 5.2. The loss of resolution in the plots when using larger sampling grids of 10m x 10m or 15m x 15m is considerable. Such widely spaced grids are clearly relatively useless in their ability to isolate areas of high chloride concentrations or hotspots on the tip surface.

Figures 5.3 (a) and (b), 5.4 (a) and (b), 5.5 (a) and (b) and 5.6 (a) and (b) are grid and contour plots of chloride levels at the Maltby and Wolstanton sites, for two different sampling depths of 0-100mm and 100-200mm. Sampling was carried out during Spring.

5.1.1 Maltby

Chloride 'highs' or hotspots occur at grid intersections A, B, C and D for material from 0-100mm depth as shown in Fig. 5.3(a) and photograph 5.7(a). These hotspots were not obvious on the ground in Spring and are not highlighted by a larger grid sampling plan. In material from the 100-200mm depth interval, most of these hotspots are still present, but are more subdued and dispersed (Fig. 5.3(b)).

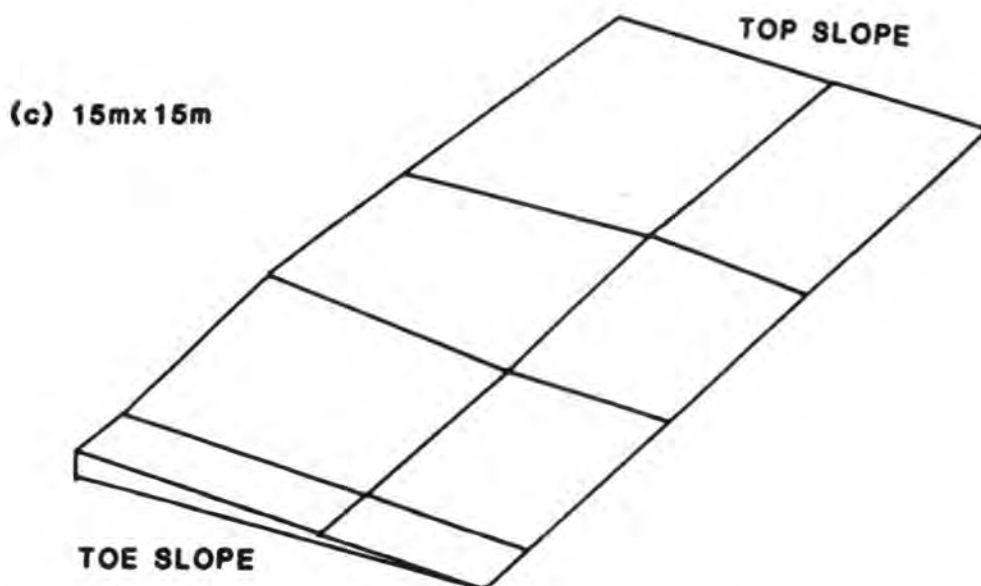
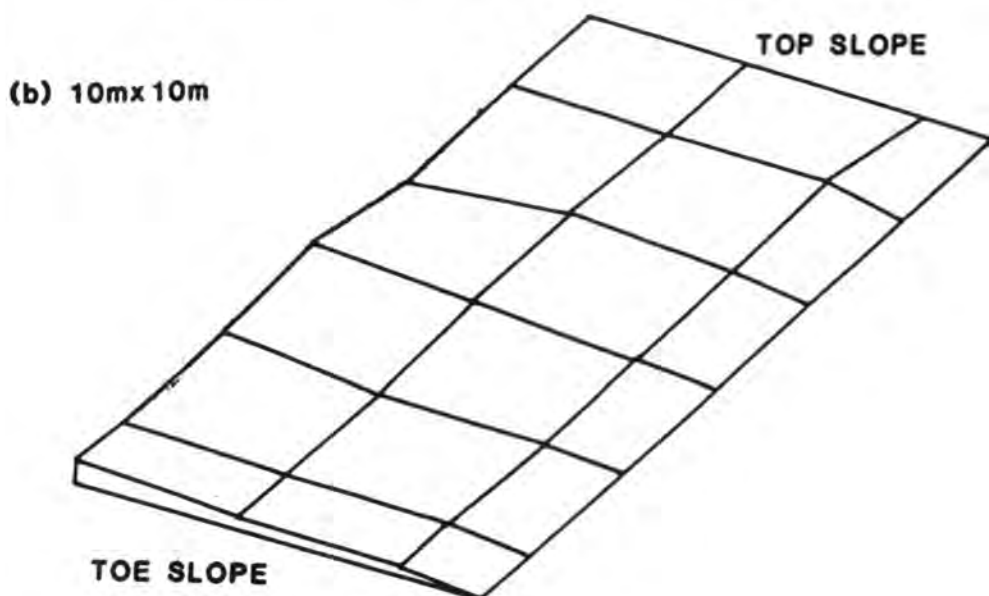
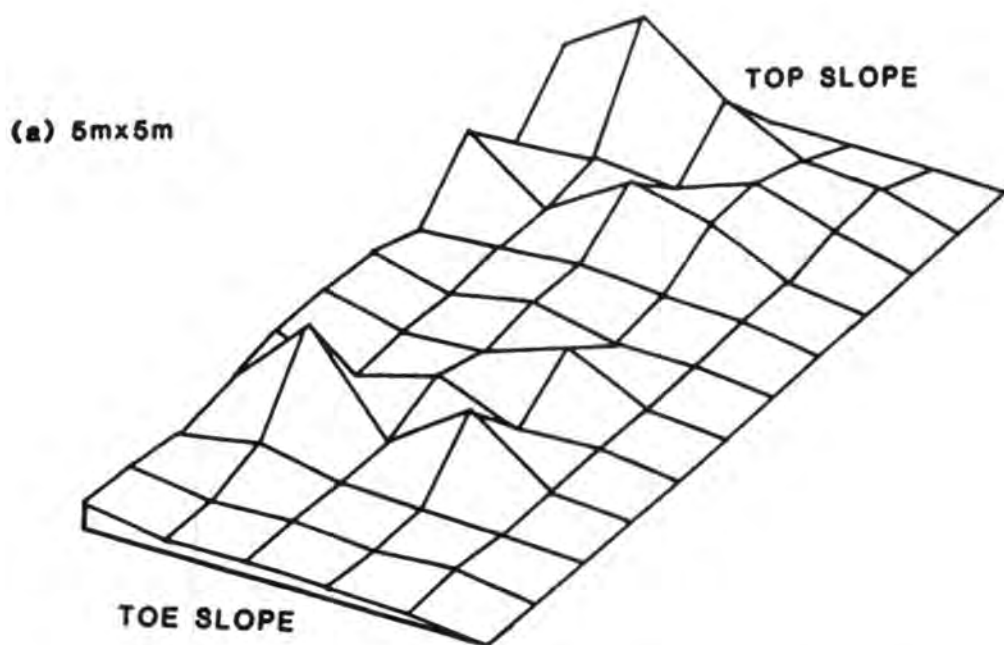
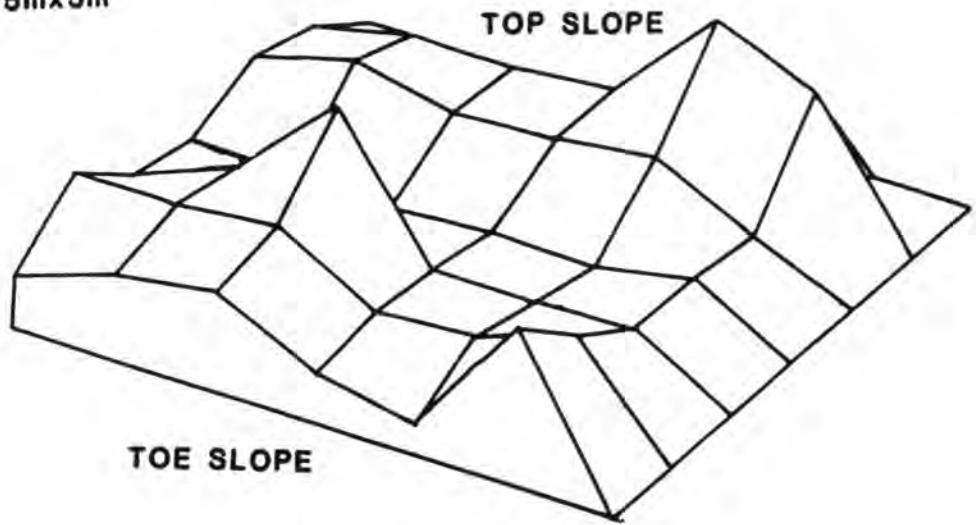
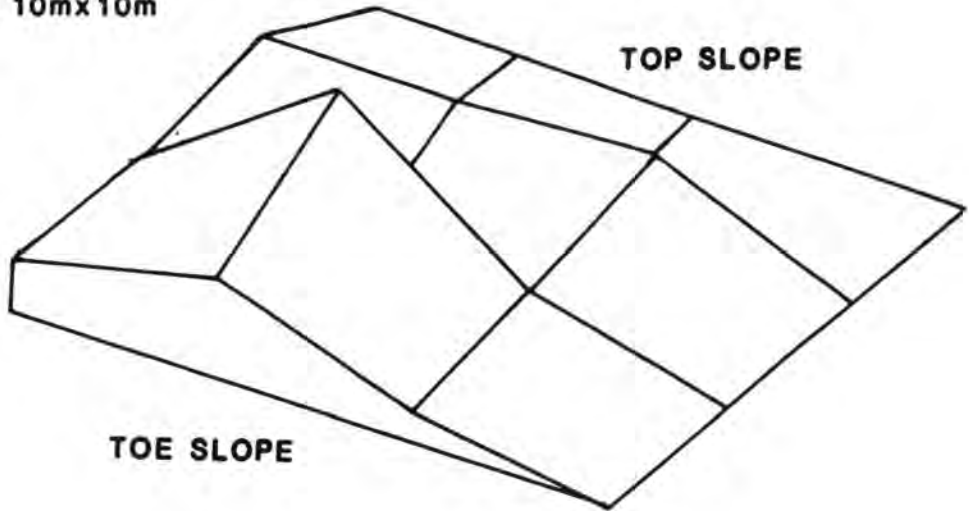


Fig. 5.1 Chloride distribution patterns on an embankment at Maltby Colliery using three different grid sizes: (a) 5m x 5m; (b) 10m x 10m; (c) 15m x 15m.

(a) 5m x 5m



(b) 10m x 10m



(c) 15m x 15m

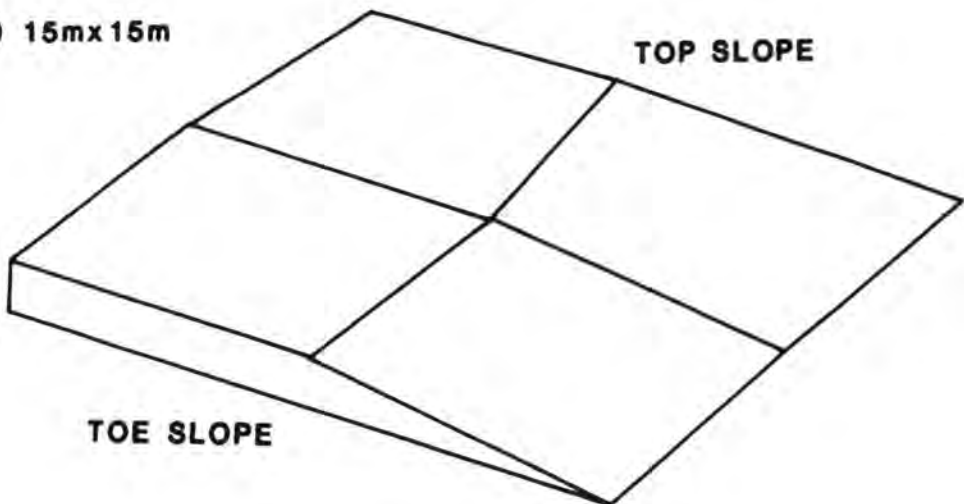


Fig. 5.2

Chloride distribution patterns on an embankment at Wolstanton Colliery using three different grid sizes: (a) 5m x 5m; (b) 10m x 10m; (c) 15m x 15m.

MALTBY SAMPLE GRID 5m x 5m

SPRING Cl ppm

DEPTH 0-100mm

CONTOUR INTERVAL 50 ppm

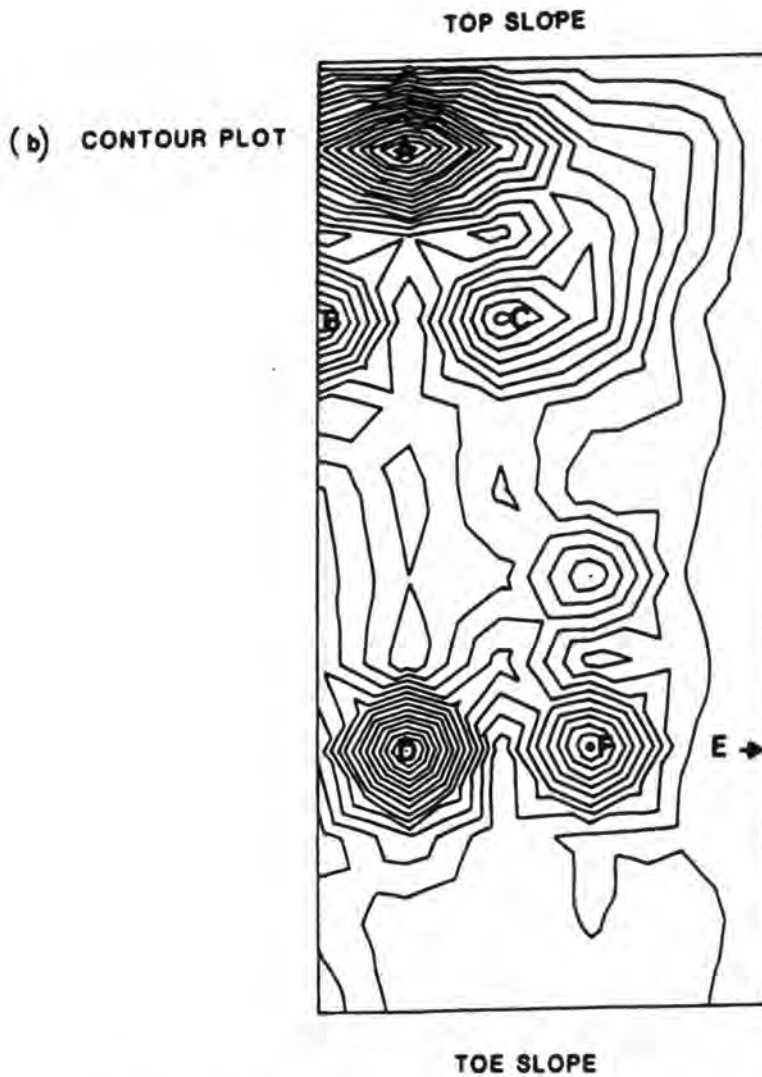
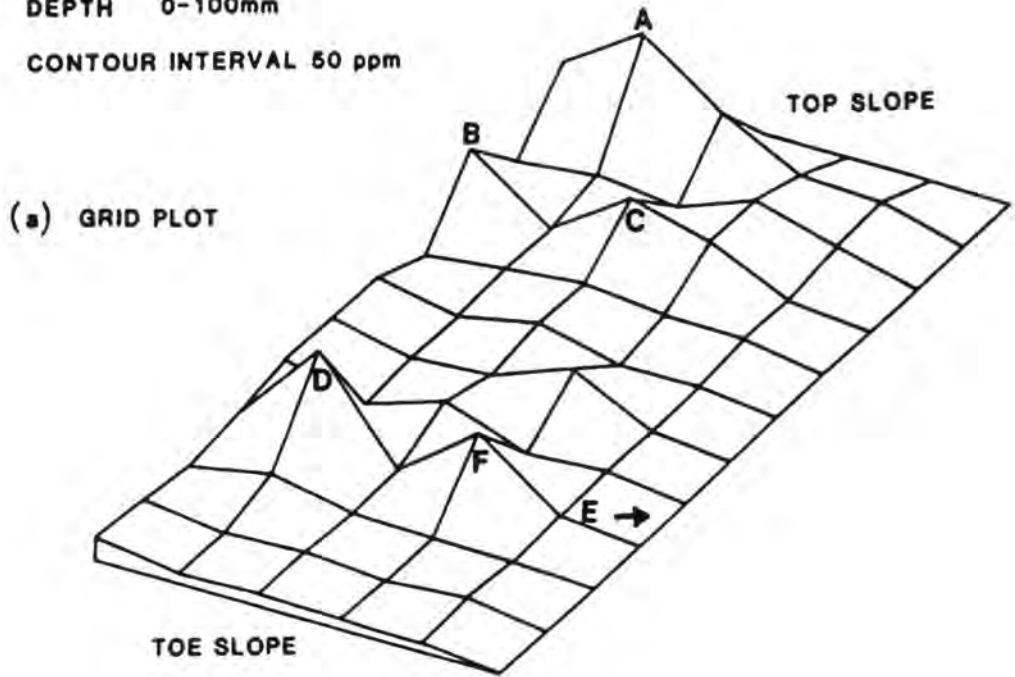


Fig. 5.3

Chloride ion distributions on Maltby embankment during Spring 1983 at a depth of 0-100mm, (a) grid plot; (b) contour plot.

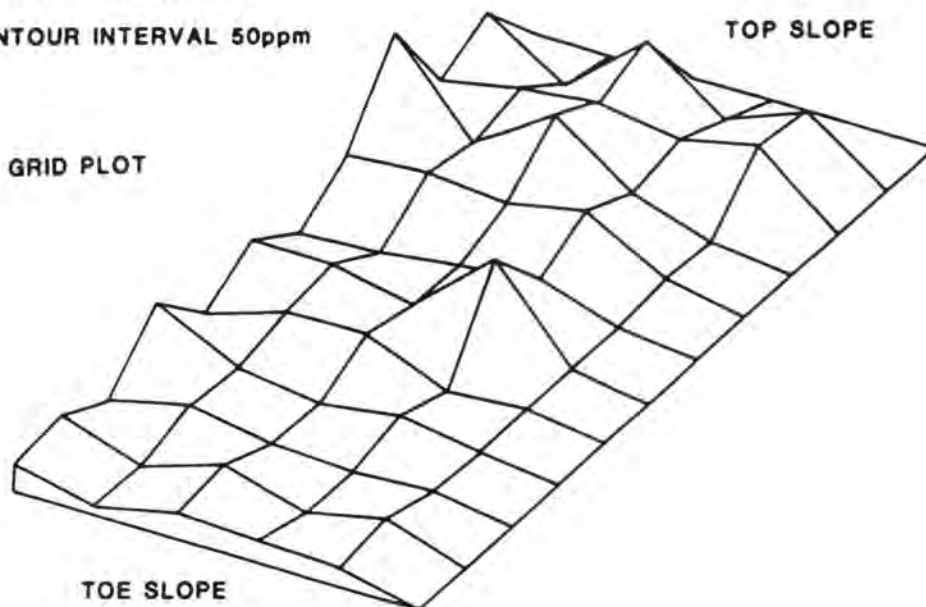
MALTBY SAMPLE GRID 5m x 5m

SPRING Cl ppm

DEPTH 100-200mm

CONTOUR INTERVAL 50ppm

(a) GRID PLOT



(b) CONTOUR PLOT

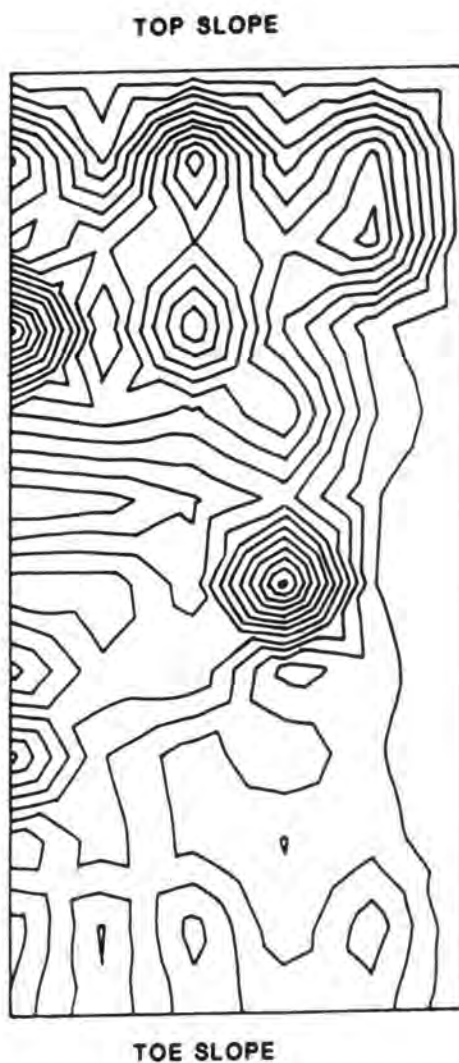


Fig. 5.4

Chloride ion distributions on Maltby embankment during Spring 1983 at a depth of 100-200mm, (a) grid plot; (b) contour plot.

WOLSTANTON SAMPLE GRID 5m x 5m

SPRING Cl ppm

DEPTH 0-100mm

CONTOUR INTERVAL 10ppm

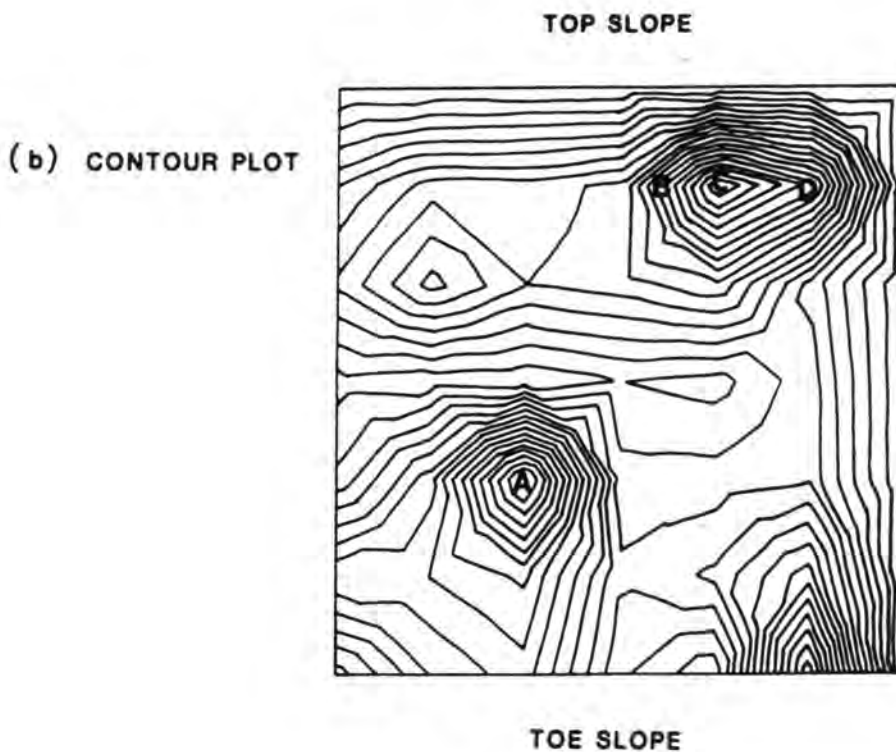
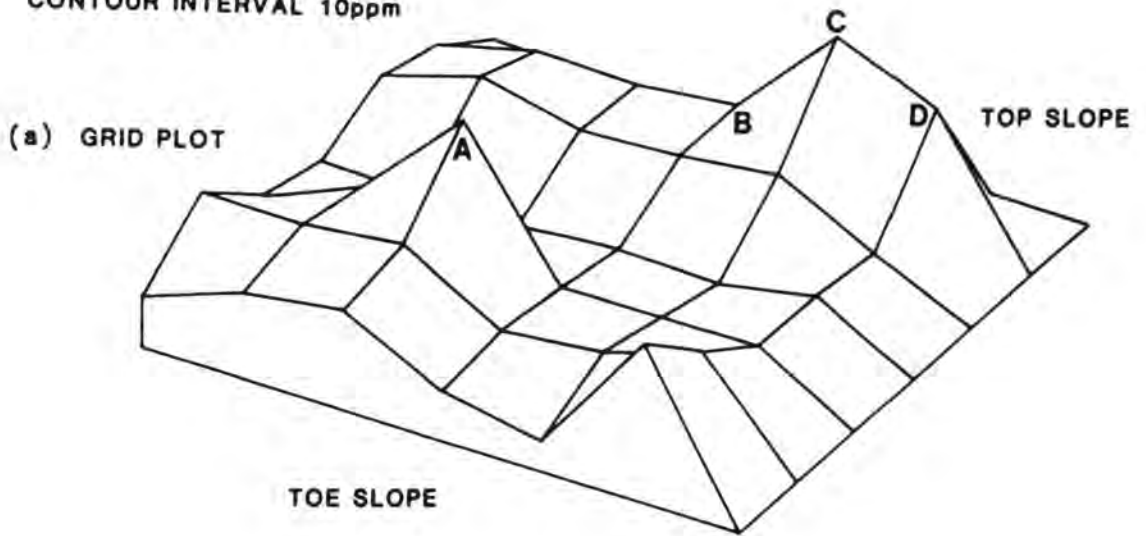


Fig. 5.5

Chloride ion distributions on Wolstanton embankment during Spring 1984 at a depth of 0-100mm, (a) grid plot; (b) contour plot.

WOLSTANTON SAMPLE GRID 5m x 5m

SPRING Cl ppm

DEPTH 100-200mm

CONTOUR INTERVAL 10ppm

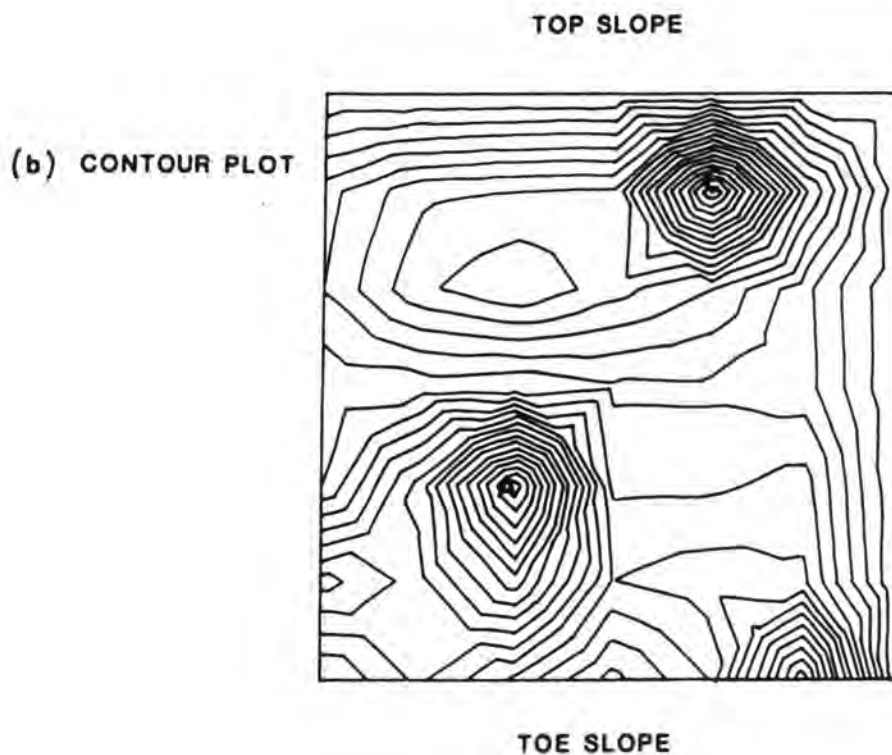
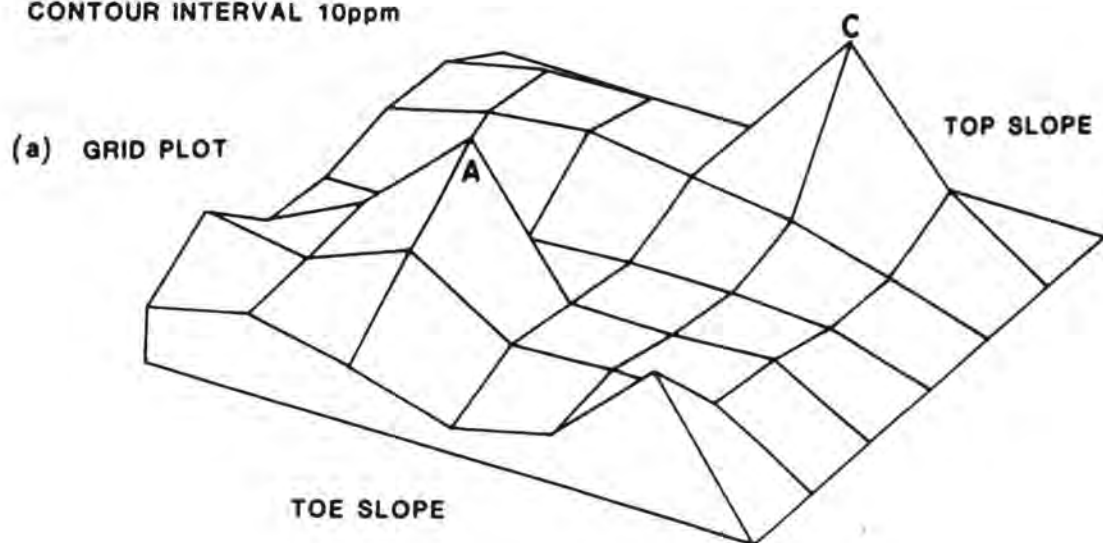
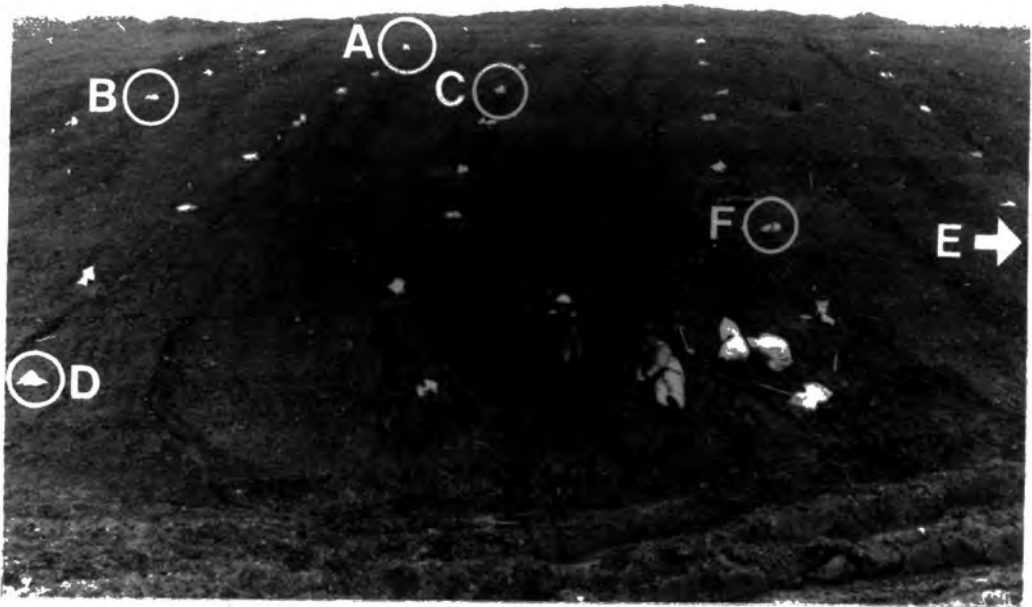


Fig. 5.6

Chloride ion distributions on Wolstanton embankment during Spring 1984 at a depth of 100-200mm, (a) grid plot; (b) contour plot.

(a)



(b)

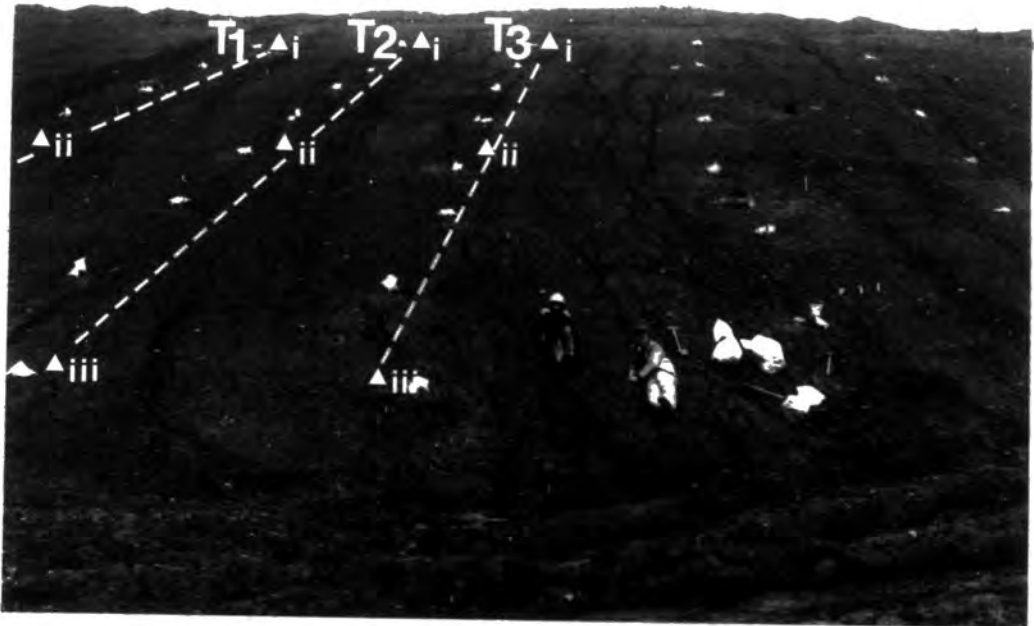


Fig. 5.7

- (a) Location of grid sampling on Maltby embankment, hotspots A, B, C and D and excavated Trenches E and F.
- (b) Location of three traverses on Maltby embankment with sampling positions indicated at top, mid and toe of slope.

During the Winter and Spring months the average chloride levels are higher in the depth interval 100-200mm (218ppm) than that from 0-100mm (189ppm). Chloride values fall in a downslope direction as might be expected because locations down-slope will progressively receive a greater volume of surface and shallow percolation runoff. This part of the tip will thus be subject to increased leaching and flushing of water soluble elements and to dilution of initial chloride concentrations.

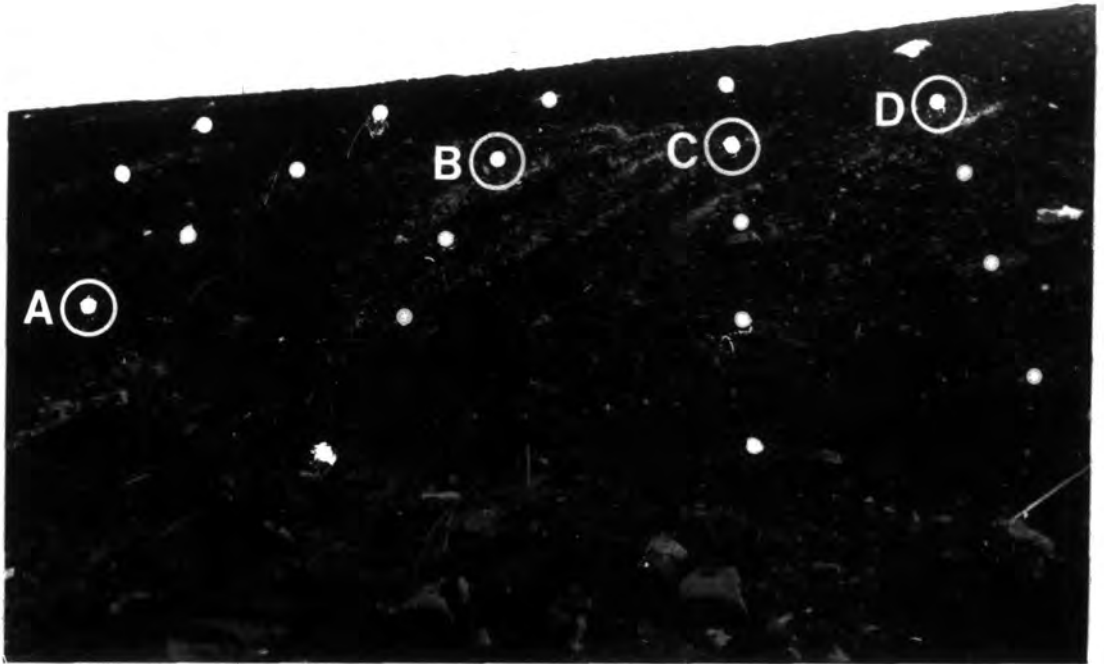
5.1.2 Wolstanton

Chloride hotspots occur at grid intersections A, B, C, and D in the discard from 0-100mm depth (Fig. 5.8(a) and (b)). These hotspots are of similar intensity in discard from the depth range 100-200mm (Fig. 5.5(a) and (b)).

During the Winter and Spring months the average chloride levels are slightly higher in the discard from the range 0-100mm (40ppm), than in that from 100-200mm (34ppm). No overall effects resulting from position on the slope can be seen and there is no overall decrease in chloride levels in a downslope direction.

A comparison between the Maltby and Wolstanton Winter and Spring grid patterns reveals basic differences in the level of chlorides in the two embankments. At Maltby the material from 0-100mm averages 189ppm Cl^- , compared to Wolstanton where the average is only 40ppm Cl^- . Discard from 100-200mm at Maltby averages 218ppm Cl^- whereas that from Wolstanton has an average of 34ppm Cl^- . Although hotspots are present at Wolstanton, the slope appears to be in equilibrium. Chlorides have probably reached a 'background' level and leaching is not a significant process affecting the chloride concentration in the discard. At Maltby, downslope leaching is

(a)



(b)

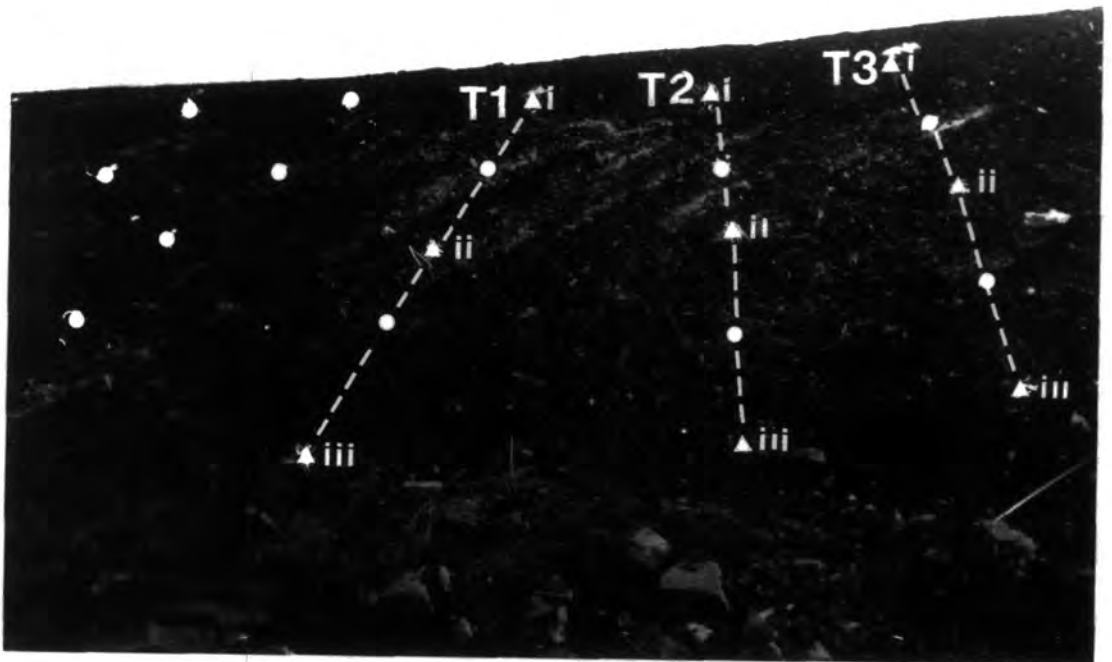


Fig. 5.8 (a) Location of grid sampling on Wolstanton embankment, hotspots A, B, C and D.
(b) Location of three traverses on Wolstanton embankment with sampling positions indicated at top, mid and toe of slope.

still an active process (see Fig. 5.9).

The differences may also be related in part to differences in the physical properties of the colliery discard at the two sites, as described in Chapter 4. The Maltby discard is predominantly a clayey discard, compared to a coal-rich discard at Wolstanton. Reference to Fig. 6.6 (Chapter 6) highlights differences in particle size distribution for discards of similar age at each colliery site. The degraded Maltby discard has a higher percentage of clay, silt and sand components, compared to the Wolstanton discard which has a higher percentage of coarser gravel, and would not appear to be as degraded as the Maltby material.

The coarser, less clayey discard of Wolstanton, would be relatively free draining, compared to that of Maltby. Natural leaching of chlorides from the discards would appear to progress at a faster rate, as shown by the relatively low background chloride levels for Wolstanton compared to Maltby. Conversely, the Maltby discard which is less coarse and has a higher clay fraction, would be less free draining and natural leaching of chlorides would be slower.

Table 5.1 shows chloride variation through time, from fresh ex-washery discard to a maximum of three years old. Comparison can be made with the Maltby discard, retaining its high chloride level, to that of Wolstanton, the three year old discard having reached a chloride level of less than 50ppm. Both discards had the same approximate initial chloride level.

	Fresh ex-washery discard	Tip	Leaching period
Maltby	810	44-830	3 years
East Hetton	283*	<20	1 year
Wolstanton	800	<50	3 years
Lea Hall	3200	<50	3 years

* mine water chloride content.

Table 5.1 Chloride (ppm) variation in coarse colliery discard with time.

5.2 Traverse data incorporating depth profiles with a sampling interval of 100mm

Figures 5.7(b) and 5.8(b) show the locations of several of the traverses sampled on the Maltby and Wolstanton High Carr sampling sites, respectively. Sampling details are as outlined in Chapter 3. In each traverse, three points were sampled, top of slope (i), mid slope (ii) and toe of slope (iii), referred to as top, mid and toe. Depth profiles, sampled at 100mm intervals, were obtained at each traverse position.

5.2.1 Chlorides

5.2.1.1 Maltby

A clear seasonal pattern of chloride movement in the discard embankment has emerged from the data. During Spring and Winter seasons, specifically 1983, there was a significant movement of chloride ions from the surface, down into the embankment, for all traverse positions; top ($r = 0.73$, $p = 0.05$), mid ($r = 0.97$, $p = 0.01$) and toe ($r = 0.99$, $p = 0.05$). During Summer and Autumn seasons the above trends disappear and no significant movement of chloride into the embankment can be measured.

However, there is an increase of chloride concentration towards the surface and a more uniform distribution of chloride in the top 500mm of the discard. These trends were repeated in data obtained for subsequent years.

The movement of chlorides into the embankment indicates that leaching has been an effective process in the colder and wetter months. Drier weather, in contrast, has resulted in increased evaporation and a general increase in chloride levels towards the surface (see also Chapter 6).

Comparison of average concentrations by the non-parametric Wilcoxon Rank Sum Test (Siegel, 1956) shows a significant decrease in chloride levels in the top 0-1m of discard from 1983 to 1984. This applies to top, mid and toe positions on the slope for all seasons, with $p = 0.01$ in all cases. This fall in chloride levels in the embankment from year to year can also be seen in Fig. 5.9, a graph of cumulative means for all positions on the spoil slope, for the period 1983-85. A continued decrease in chloride level in the discard embankment may be expected, as shown by the hashed black line on Fig. 5.9.

5.2.1.2 Wolstanton

Data obtained from traverse sampling at Wolstanton reveals no statistically significant seasonal pattern of chloride movement in the top 500mm of discard. However, data obtained did indicate that some leaching occurred during the wetter months, for example Winter 1984, chloride levels were 19ppm at a depth of 0-100mm and 35ppm at a depth of 500mm. A more uniform distribution occurs in the discard during the Summer months, for example during Summer 1984, chloride levels were 89ppm, 105ppm and 60ppm for depths 0-100mm, 100-200mm, 200-300mm and 300-400mm, respectively.

Analysis of the data by the Wilcoxon Rank Sum Test, showed a

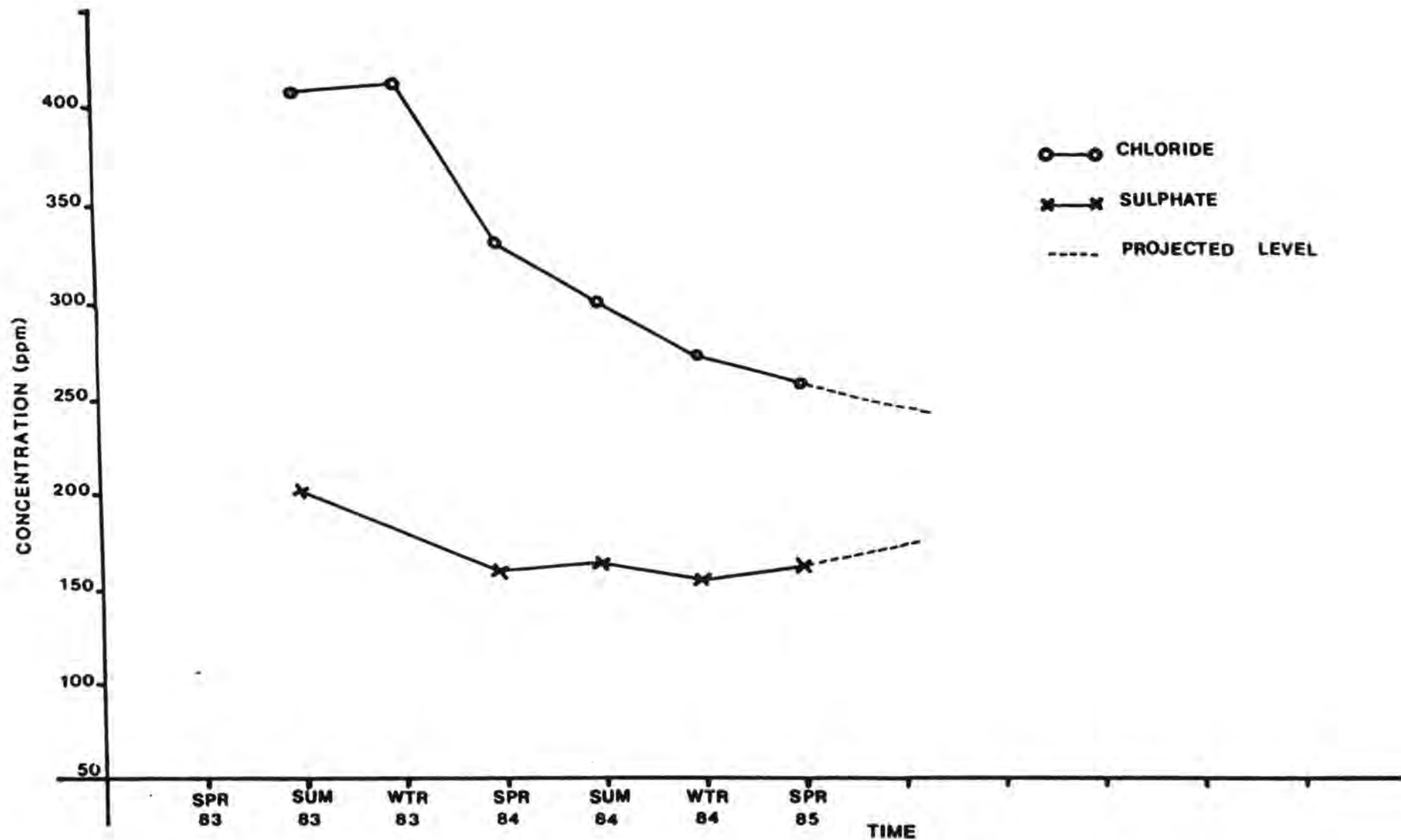


Fig. 5.9

Cumulative means for chloride and sulphate concentration in the Maltby embankment. Dashed lines indicating a projected fall (chlorides) and rise (sulphates) in concentrations.

significant increase in chloride levels from 1984 to 1985 for the Spring and Winter season, for the top of slope position ($p = 0.01$), but decreases for the mid and toe slope positions ($p = 0.01$). There were no significant changes for the Summer months.

Comparison of average chloride levels in the surface layers of discard from Maltby and Wolstanton shows that concentrations at Wolstanton are lower by a factor of up to x 6.4. The traverses at Wolstanton show no significant seasonal movement of chloride in the discard and can show both increased and decreased chloride levels with time, depending on slope position. Chloride levels in the Wolstanton discard are thus probably too low to fluctuate significantly and have reached equilibrium. The distribution of chlorides is thus unlikely to change significantly, unless in the immediate vicinity of a hotspot or seepage point.

5.3 Distribution of Sulphates and Patterns of Electrical Conductivity Within the Discard

Data for sulphate distribution within the discards also reveal a seasonal movement within the embankment at the Maltby site. During Spring 1983, for the top and mid slope positions, a positive correlation was obtained between sulphate concentration and depth reflecting movement into the embankment, ($r = 0.96$ and $r = 0.91$, $p = 0.01$ respectively). During the Summer of 1983, the top slope position gave a positive correlation between sulphate and depth into the embankment ($r = 0.78$, $p = 0.05$).

As with the chloride results for Wolstanton, only slight seasonal trends in sulphate concentration with depth were evident. These did not prove significant under statistical investigation.

5.3.1 Electrical Conductivity

The measurement of soluble salt contents in soils or discards is an essential component of agricultural studies and land reclamation practice. Under normal conditions total dissolved salts can be estimated accurately as a function of the electrical conductivity of soil moisture extracts. Such relationships between total dissolved salts and electrical conductivity may, however, be too simple and will not predict variations in any particular salt such as sulphate or chloride (Chang et al., 1982). Relationships between electrical conductivity and total dissolved salts may thus underestimate the role of any one particular salt and cannot monitor variations in the combinations of salts present in the discard or soil. Although conductivity may be used to indicate if the combination of salts is at a level harmful to the establishment of plants, it cannot be used to define which ions are contributing to the high conductivity levels.

Data obtained from Maltby Colliery show that relationships between electrical conductivity and chloride and sulphate concentrations within the embankment are not easily assessed. Seasonal distribution patterns are not as clearly defined in the embankment as for those of chloride and sulphate. However, electrical conductivity did increase towards the surface of the embankment during Summer 1983 ($r = 0.82$, $p = 0.05$). Large increases in electrical conductivity were noted around hotspots, Winter grid 1983 0.568×10^3 ; Summer grid 1984 $0.130 \times 10^4 \mu\text{S/cm}$. Although there seems to be some increase in electrical conductivity levels towards the surface during Summer months, it is not statistically significant.

From graph plots (Fig. 5.10) of chloride plus sulphate vs electrical conductivity, it would appear that the sulphate component has a greater effect on electrical conductivity than the chloride component. When

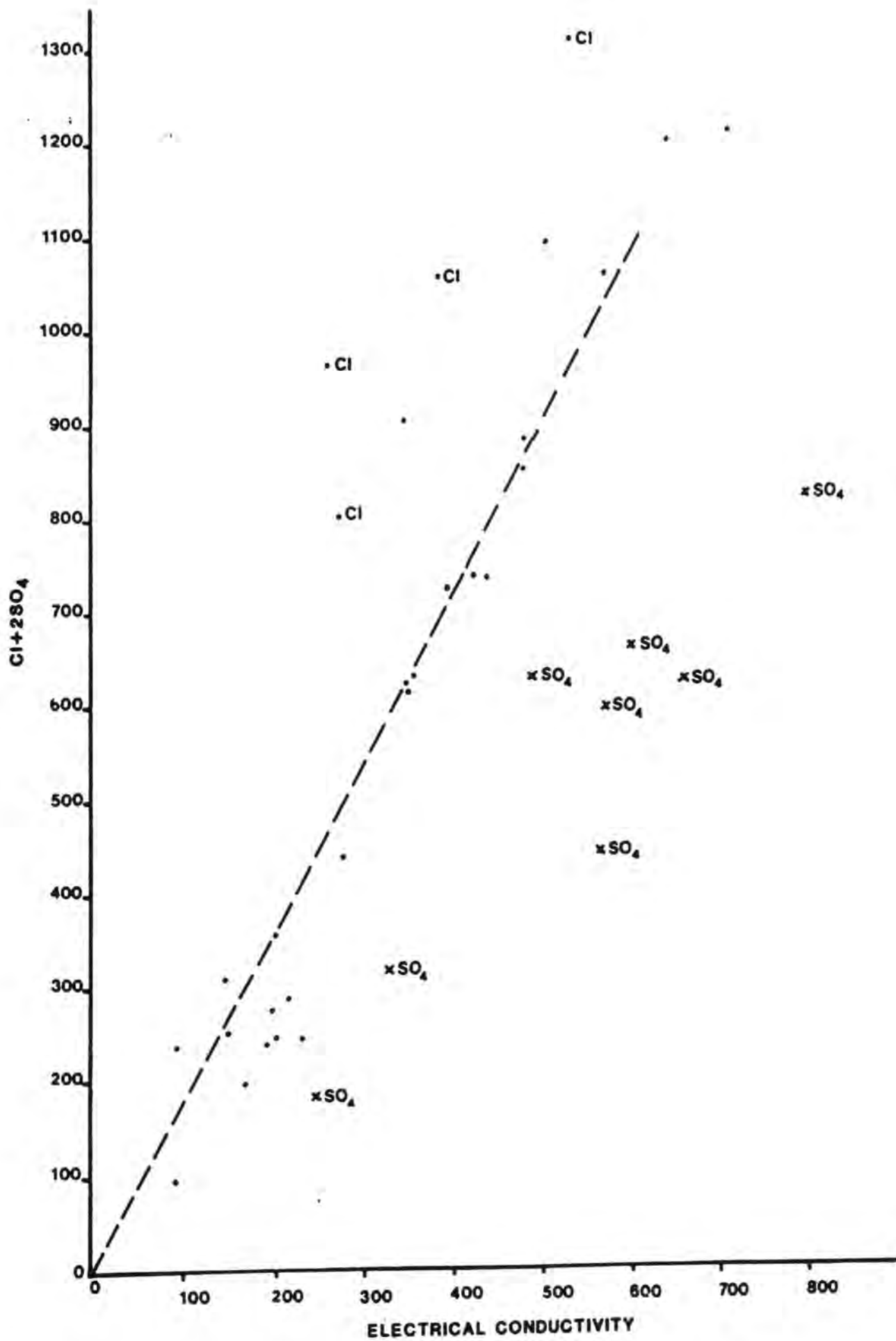


Fig. 5.10

Chloride plus two sulphate vs. conductivity, showing the greater effect of sulphates on conductivity.

conductivity is plotted against chloride and sulphate x 6, a better correlation is found. There would appear to be no ready explanation for this relationship. This may be especially true for surface discards where the oxidation of pyrite considerably increases the sulphate content in the top 100mm (see Section 5.5). Because of these findings it is unwise to rely on electrical conductivity as an accurate indicator of chloride levels in coarse discard, as a high electrical conductivity may not be indicative of high chloride levels.

No such trends were found for Wolstanton High Carr site. The figures for conductivity for Wolstanton discard compared to those of Maltby were very low and again may constitute a background level within the discard. Although fluctuations do occur, they are very slight and are not statistically significant.

5.4 Traverse data incorporating depth profiles with a sampling interval of 10mm

In section 5.2 three points were sampled, top, mid and toe of slope. Each position was sampled over the depth range 0-50mm at 10mm intervals. Samples were taken adjacent to positions used for the larger 100mm sampling interval. This enabled direct comparisons between these near-surface profiles and the deeper profiles described in Section 5.2

5.4.1 Chlorides

5.4.1.1 Maltby

The data reveal a clear seasonal pattern of chloride movement in the top 50mm of the embankment, for the top of slope position. In Summer 1984 a surface chloride concentration of 12,740ppm was recorded, falling to

1,540ppm at a depth of 50mm below the surface, a significant fall in concentration with depth ($r = 0.94$, $p = 0.05$). In contrast during the Spring of 1985, there was a significant downwards increase in chloride concentration reflecting leaching into the embankment ($r = 0.96$, $p = 0.01$).

5.4.1.2 Wolstanton

The data for Wolstanton confirm the results obtained over the greater depth range, in that only slight seasonal trends are evident. The only significant data concerned a build-up of chloride during Summer 1984 at the toe of slope position ($r = 0.95$, $p = 0.05$). This was presumably due to the presence of a hotspot (or a seepage) at this point.

No significant increases or decreases in chloride levels were noted from year to year, again indicating that discard had reached a background equilibrium level.

5.5 Distribution of Sulphates and Patterns of Electrical Conductivity within the Discard

In the Maltby discard a clear pattern of sulphate movement in the near-surface of the embankment emerges. During Winter 1984 there was significant movement of sulphates into the embankment for top and mid slope positions; $r = 0.87$, $p = 0.05$ and $r = 0.85$, $p = 0.05$ respectively. During the Summer of 1985, a surface accumulation of sulphate was noted, with a significant decrease in concentration with depth ($r = 0.95$, $p = 0.05$).

In contrast, at Wolstanton Colliery, only slight seasonal trends were evident. A build-up of sulphates during Summer 1984 was noted at the toe of slope position ($r = 0.91$, $p = 0.05$). This may reflect a surface hotspot as suggested by the chloride data.

5.5.1 Electrical Conductivity

During the summer of 1984 at Maltby, electrical conductivity in the near-surface layers (0-100mm) of discard increased towards the surface for tip and toe positions on the embankment; $r = 0.95$, $p = 0.05$; $r = 0.94$, $p = 0.05$ respectively. There was an increase of electrical conductivity downwards into the embankment during the Winter of 1985 ($r = 0.87$, $p = 0.05$).

At Wolstanton during the Spring of 1985, the top and toe of slope positions showed a significant increase in electrical conductivity with depth in the embankment ($r = 0.83$, $p = 0.05$). The lack of any other significant changes in conductivity levels reflect the overall low levels of electrolytes found in the Wolstanton discard compared to levels in the Maltby embankment.

5.6 Distribution patterns of chloride and sulphate in top soil over saline discard

Berg et al. (1980), studied the movement of salts into top soil cover, over previously desalinated mine spoil. The findings indicate that over periods of prolonged drought, under arid conditions or conditions where evaporation exceeds precipitation, the mine spoil may resalinate and top soil applications may also become saline.

Top soil samples were taken from Bilsthorpe Tip No. 1 site in July 1985, from patches of bare soil (seepage points). From table 5.2 it can be seen that an increase occurs in both chlorides and sulphates at the soil-discard interface. Some movement of electrolytes, particularly sulphates, into the topsoil has occurred.

Material	Depth (mm)	Cl (ppm)	SO ₄ (ppm)
Top soil	0-10	36	145
	10-20	35	84
	20-30	35	184
	30-40	45	345
	40-50	35	376
	50-60	51	314
Soil/discard interface			
discard		55	683

Table 5.2 Chloride and Sulphate Levels in Top Soil and Discard on Tip No. 1, Bilsthorpe Colliery.

5.7 Hotspots

As already mentioned in previous sections dealing with chloride and sulphate distributions in the discards from the three Colliery sites 'hotspots', or areas with a much higher salt concentration, were observed on the surface of embankments, particularly at Maltby and Wolstanton (Figs. 5.11a and 5.11b).

A surveyed cross section of the Maltby embankment showed the positions of the hotspots on the embankment to be equivalent to top water level in the lagoon. The supernatant water in the lagoon during that period, had a chloride concentration of 112 000 ppm. The top 3m of the embankment probably represents the final lift, with the seepage line representing the position of the previous crest. Similar observations made at the Wolstanton High Carr disposal site, with respect to hotspot distribution, again showed linear deposition of salts running parallel to the crest of the embankment. At Wolstanton there is no lagoon incorporated into the tip and so the possibility of direct lateral seepage from the lagoon as a possible mechanism for hotspot development (at Maltby) can be discounted.

(a)



(b)



Fig. 5.11

(a) Hotspots on the Maltby embankment.

(b) Hotspots on the Wolstanton embankment.

In July 1983, the hotspots A, B and C (Fig. 5.7a) were observed to form part of a linear surface deposition of salts running more or less parallel to the crest of the embankment. Their formation would appear to be associated with the layering of discard in 'lifts' of up to 5m in thickness (Chapter 3), influencing permeability. The raising of an embankment will usually mean that less dense discard is likely to be in contact with a more compacted and degraded underlying (older) surface, possibly of some years standing. In this way an old surface could act as a permeability barrier to water percolating downwards. This would result in the concentration of soluble salts along these less permeable surfaces eventually appearing as hotspots on the embankment surface.

Table 5.3 shows the distribution of chloride down two vertical faces excavated in August 1983 on the experimental embankment at Maltby Colliery. The positions of the two vertical faces are shown as E and F on Fig. 5.7a).

N.Flank haulage road			Below haulage road		
	Depth m	Cl in ppm		Depth m	Cl in ppm
surface	0.1-0.2	210	surface	1.9-2.0	35
	0.3-0.4	290		2.1-2.2	15
	0.5-0.6	<u>1016</u>		2.5-2.6	27
	0.7-0.8	125		2.7-2.8	76
	0.9-1.0	145		2.9-3.0	285
	1.1-1.2	245		3.1-3.2	555
	1.3-1.4	215		3.3-3.4	535
	1.5-1.6	325		3.5-3.6	106
	1.7-1.8	435		3.7-3.8	<u>1115</u>
				3.9-Bedrock	1085
				(Lr.Mag. L'st)	

Table 5.3 Showing distribution of chlorides in Trench E, sampled 31 August 1983.

The analyses demonstrate downward leaching in the discard. Chloride values in the embankment adjacent to the grid shown in Fig. 5.7(b) are generally intermediate between comparable traverse holes T2(ii) and

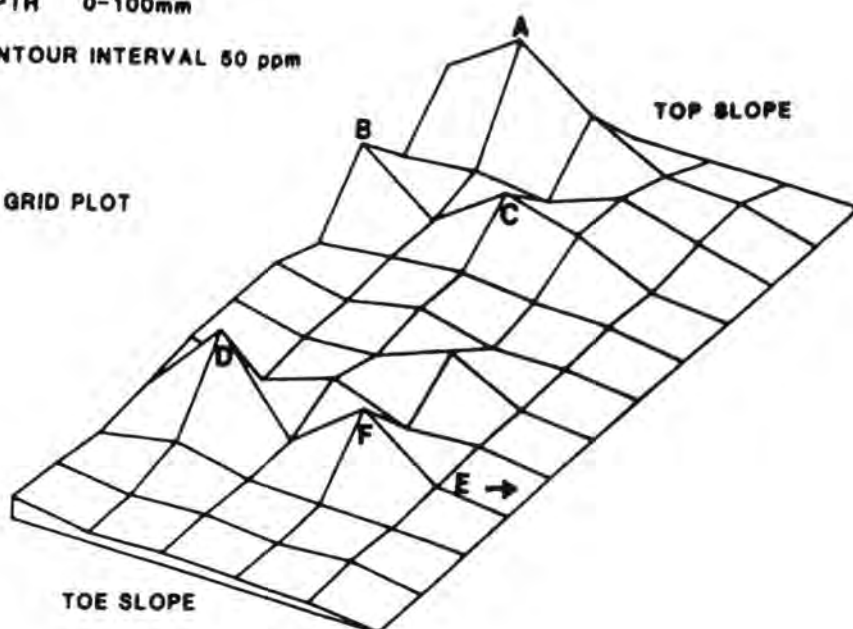
MALTBY SAMPLE GRID 5m x 5m

SPRING Cl ppm

DEPTH 0-100mm

CONTOUR INTERVAL 50 ppm

a) GRID PLOT



b) CONTOUR PLOT

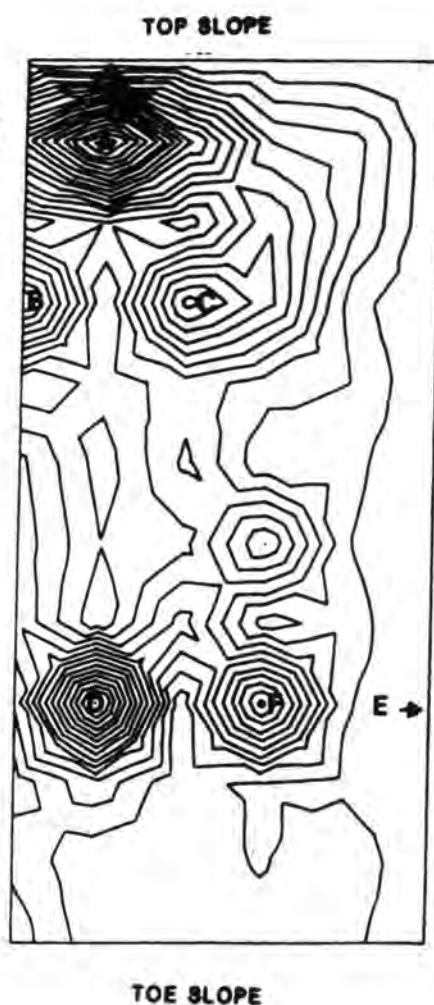


Fig. 5.13

Comparison of chloride distribution on Maltby embankment during Spring 1983 and Summer 1984 at a depth of 0-100mm; (a) grid plot; (b) contour plot.

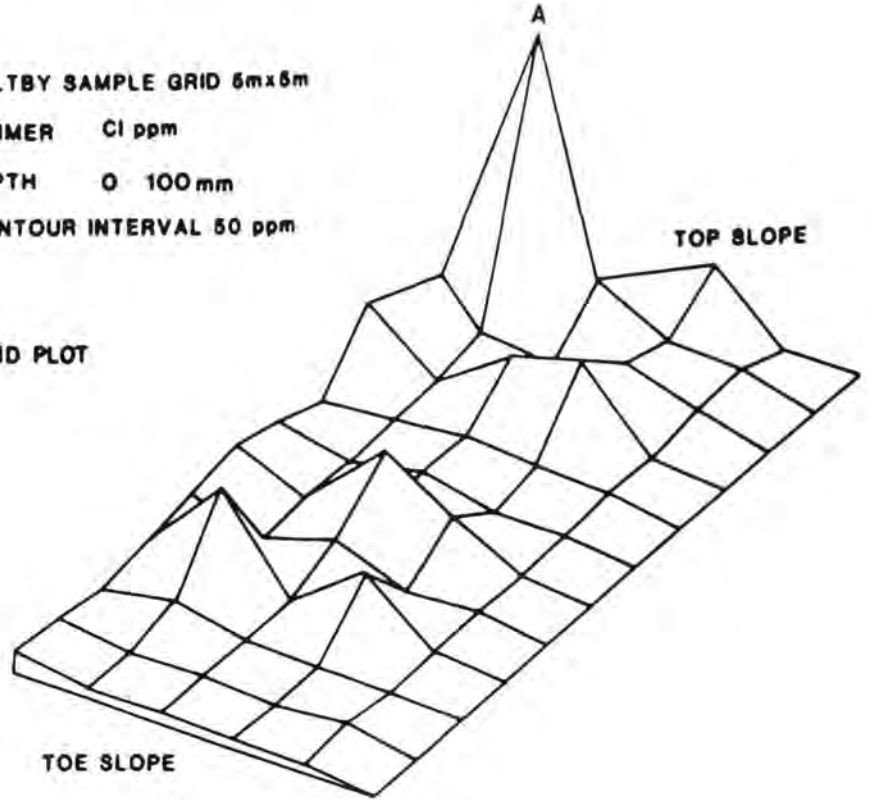
MALTBY SAMPLE GRID 5m x 5m

SUMMER Cl ppm

DEPTH 0-100 mm

CONTOUR INTERVAL 50 ppm

a) GRID PLOT



b) CONTOUR PLOT



T2(111).

The parting between the two high chloride values underlined in Table 5.3 is just over 3m in thickness, this may represent the position of the initial lift of the embankment. Indications from Maltby that seepages might be associated with impermeable surfaces of previous lifts were investigated further at Bilsthorpe Colliery (see Bick, 1985; Fig. 5.12). In addition to a definable phreatic surface being present, quite a high perched water table was measured in a lagoon embankment at Bilsthorpe. The perched water table was almost certainly supported by the the top of the initial lift, the present bank comprising two lifts. The old surface had been exposed to degradation for a period of 3 years prior to the construction of the second stage.

The Maltby site was also sampled on a grid basis during the Summer months of 1984. At this time hotspots could be seen on the discard surface forming damp patches surrounded by an efflorescence of crystalline salts. A comparison between Figs. 5.13(a) and 5.13(b) shows that all hotspots occur in both, but highlights seepage A in the Summer grid. There is clearly a large increase in chloride concentrations at, and around, seepage A. Average chloride concentrations for the entire sites at the 0-100mm depth in Summer are 724ppm Cl^- , compared to a 234ppm Cl^- Winter average. Seepage point A showed increased chloride concentration from 985ppm Cl^- in Winter to 2388ppm Cl^- in Summer, this was for discard of 0-100mm depth.

Samples of the crystalline salts from efflorescences on the discard embankments at Maltby and Wolstanton Collieries were analysed using XRD techniques. The main salt identified was thenardite (Na_2SO_4) with traces of halite (NaCl). The predominance of sodium sulphate over sodium chloride on the surface may be explained by the preferential crystallisation of



POSITION OF SURFACE SEEPAGE LINE →
 LEVEL OF SUPERNATANT WATER 25/7/85
 PERCHED WATER TABLE 25/7/85 - - - -
 PERCHED WATER TABLE 8/8/85 - - - -
 POSSIBLE POSITION OF INDURATED SURFACE — · — · —

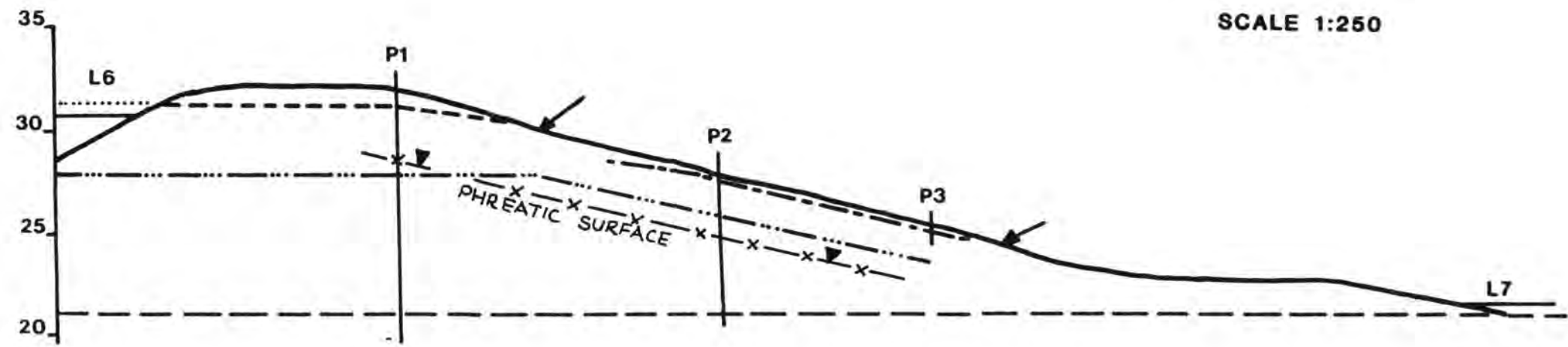


Fig. 5.12 Positions of perched water tables in lagoon embankment L.6, Bilsthorpe Colliery.

sulphate minerals over chloride types (see Weast and Astle, 1983). Analysis of depth profiles of a sampling interval of 10mm (Section 5.4) shows a much increased concentration of sulphate on and near the embankment surface.

5.8 Conclusions

Accurate sampling of colliery discard embankments is essential for investigating electrolyte distribution in such embankments. This process requires a grid of not less than 5m x 5m. A grid of this size can be used to locate hotspots and emissions from seepages. A grid size greater than 5m x 5m was found to be ineffective in terms of hotspot definition. By comparing electrolyte concentrations in samples taken from grids of an identical pattern, but for Winter and Summer seasons, a pattern of electrolyte movement and concentration over a wide area can be assessed.

Using data collected on a grid basis it can be seen that chloride levels are higher in to 100-200mm depth than the 0-100mm depth during the Winter/Spring months, whereas the converse is true during the Summer months when the surface discard has a higher chloride concentration (see also Chapter 6 in respect of suction pressure seasonal patterns).

Data from the depth traverses in the embankment (to at least 500mm), show that chloride levels increase in the surface layers of the discard during the summer months, and in certain areas salt efflorescences (or hotspots) appear, where salt concentrations are extremely high, and crystalline salts are visible on the surface. Seepages are not solely a symptom of seepage through the embankment from a lagoon. At Wolstanton, for example, seepage and chloride hotspots were identified in the absence of any encapsulated lagoon, or buried tailings within the tip. Further

investigations at Maltby and Bilsthorpe Collieries suggest that seepages and hotspots are associated with the impermeable surfaces of previous lifts during phased construction.

Seasonal variations in chloride distribution are not as obvious in the discard at the Wolstanton, High Carr, site. This is presumed to be a function of the much lower levels of chloride found in this discard than in the Maltby discard during the Summer and Winter months, less than 50ppm in most cases. This low level of chloride appears to represent a background level for chloride ions, so seasonal fluctuations are not obvious. Random samples were taken at two collieries not included in the main part of this project. Both sites were embankments of coarse discard older than three years, they were; East Hetton Colliery, County Durham and Lea Hall Colliery, Rugeley, Staffordshire. The discards both had chloride levels of less than 50ppm, suggesting that this discard has also reached a 'background' chloride level. Although hotspots do appear on the surface, these are assumed to be associated with embankment raising methods.

At Maltby seasonal movements of chlorides are statistically significant. During the Winter and Spring months, chlorides move down into the embankment. This trend is reversed during the Summer months, when chlorides accumulate in the surface layers of colliery discards.

Hotspots show little change in chloride levels over a two and a half year period, compared with the initial fresh discard levels. Background levels at Maltby have fallen to about 200ppm in about 6 years, and in the coarser discard from Wolstanton, to less than 50ppm in about 3 years. Three tonnes of fresh, coarse discard from Bilsthorpe Colliery, with an initial chloride level of 3438ppm for run-of-mine, which was used to construct the experimental (courtyard) tip at Durham University, gave

chloride levels of 287ppm after six months exposure. A leaching experiment simulating a further 5 years exposure to precipitation indicated a reduction in chlorides to about 50ppm (Bick 1985).

There is a slight seasonal pattern for both sulphates and electrical conductivity movement in the Maltby embankment, that is, a Spring increase with depth into the embankment, and a Summer increase in concentration towards the surface of the discard. Some patterns appeared at Wolstanton, but because levels of both sulphates and measurements of conductivity are low, these patterns were not statistically significant.

Sampling of embankments at both Maltby and Wolstanton with a much smaller depth interval (10mm), revealed increases in sulphates, particularly towards to surface of the discard. These sulphates make up the principal salt found in XRD analysis of the efflorescence hotspots on the discard surface, that is sodium sulphate in the form of thenardite.

CHAPTER 6

SUCTION PRESSURES IN COLLIERY EMBANKMENT SURFACES

6.1 Introduction

High electrolyte concentrations and, particularly, high chloride levels cause physiological drought in vegetation, young vegetation being particularly susceptible. The determination of salt concentrations and the movement patterns of electrolytes is thus important for restoration programmes. As chlorides and sulphates are relatively soluble, distribution patterns of these ions are likely to be governed by movement of water in the discard embankment. This section investigates such water movement, in particular soil suction and its effects on surface wetting and drying, and the possible formation of suction gradients within the surface layers of the embankments.

6.1.1 Physiological Drought

The effect of salinity on plant growth is to promote physiological drought, due to the osmotic effects of high salt concentration in reducing the availability of water to plants (Sutcliffe, 1976).

In saline soil solutions the matrix potential is decreased, and hence the attraction of water to soil particles, cell walls and organic matter is decreased. Continued dehydration causes disorganisation of the protoplasm and death of most organisms. Root tissue is especially susceptible so that their measured lengths (dry weights) decrease.

6.2 Soil Suction

Between compacted soil or spoil particles is an interstitial space,

which, above the water table, is occupied partly by soil solution and partly by soil atmosphere. This pore space is continuous, consisting of voids interconnected by narrower channels (capillaries). Randomly packed soils have a statistically normal 'distribution' of pore sizes, but coarse grained soils (and hence fills) have pores which are large relative to finer grained soils, such as silts and clays. Pore size distribution is a major control on the mechanical properties and total porosity of the soil. Thus soil texture is related to pore size distribution which is referred to by soil scientists as textural pore space. Pore size distribution is also important in the structural development characteristics, or aggregation of soils. This characteristic is known as the structural pore size distribution.

Water held in soil, the soil solution, can be categorised by its position in relation to the soil particles and type and size of pore. Gravitational water occurs in the larger pores of millimetre sizes, capillary water in those of intermediate size and adsorbed or hygroscopic water in the ca. 40nm (400Å) wide zone of strongly bonded water around clay sized and colloidal particles. Fig. 6.1 (after Buckman and Brady, 1969) illustrates the general zonation of water in relation to soil particles.

6.2.1 Gravitational Water

Following conditions in which the soil has become completely saturated with water, for example, after heavy rain, air is displaced from larger non-capillary pore spaces between soil particles. Under gravitational influence, this free water begins to percolate down through the soil towards the water table, the non-capillary spaces becoming refilled with air. This gravitational water is of little direct use to plants and may be

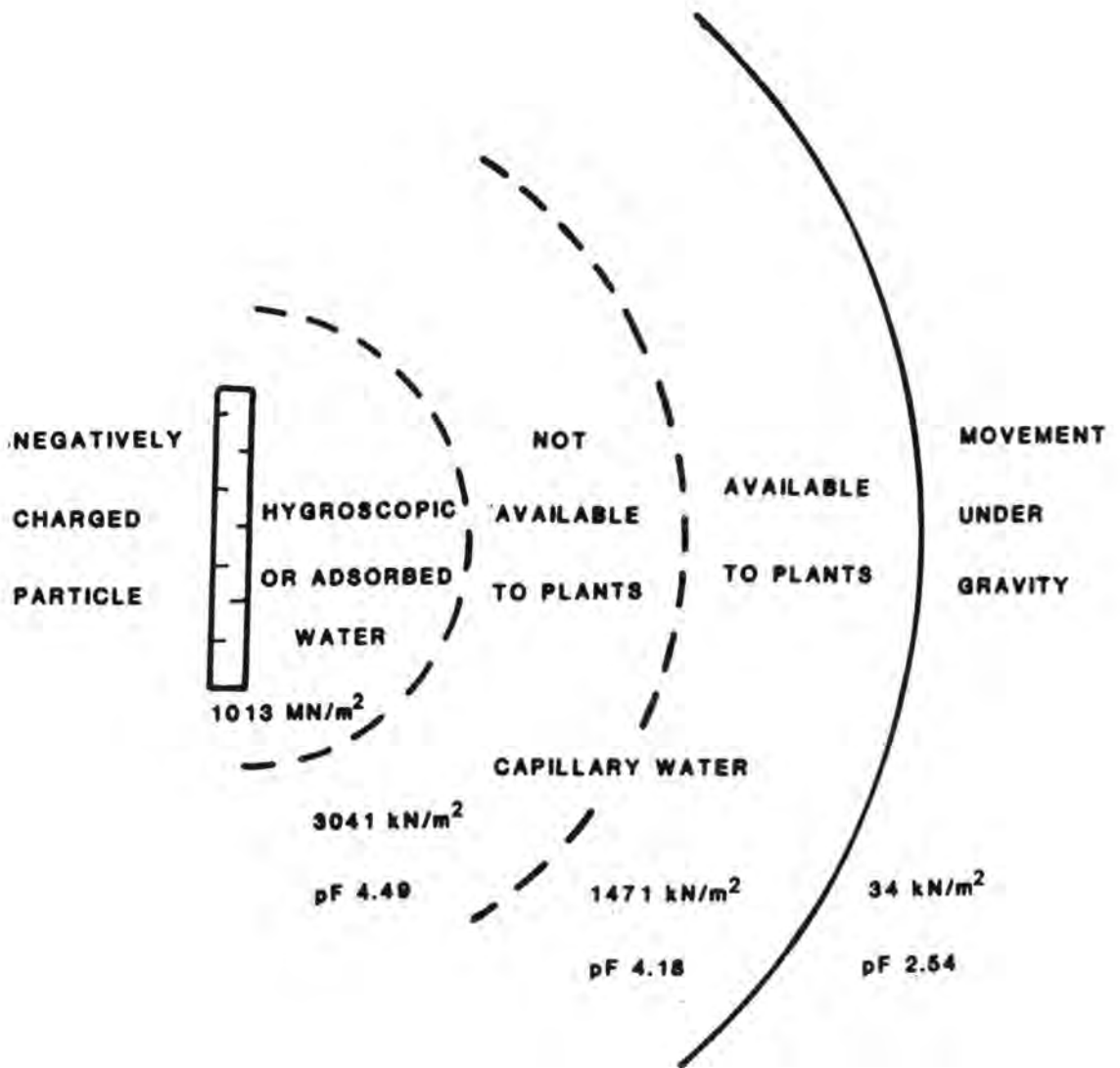


Figure 6.1 Illustrating relationship between water in soil and mineral particles. Suction requirements of vegetation shown (modified after Buckman & Brady, 1969).

detrimental if the soil remains saturated, causing injury to root systems through lack of oxygen, a build up of carbon dioxide and removal of nutrients.

6.2.2 Capillary Water

When gravitational water has drained away, a soil is said to be at field capacity. The remaining water in the soil exists as films around soil particles and in the smaller capillary pores. Most of this water is held loosely and is readily available to plants. However, some capillary water is firmly 'held' by colloidal material and, coupled with that in smaller pores, is relatively unavailable to plants. The finer the texture of the soil, the more surface area is exposed and the more capillary water it will hold.

6.2.3 Hygroscopic Water

Hygroscopic, or adsorbed, water is held in very thin films, 15 to 20 molecules thick, on the soil particles by surface forces exerted by those particles. It can be thought of as the capillary water remaining in the air dried soil. This water is held so firmly that it can only move in the form of vapour and thus is unavailable to plants. This water can only be quantitatively determined by oven drying at 105-110°C.

The relationships between soil water and plants is also illustrated in Fig. 6.1, indicating the range of root suction pressures which determine the water available to plants. In the requisite zone, the negative pore water pressure (suction pressure) is within the range 34-1471 kN/m². Gravitational water is unlikely to be acted on by pressures greater than 34 kN/m², whilst suction pressures greater than 1471 kN/m² preclude capillary

water being available to vegetation.

In agricultural studies, the water available to plants is described as the moisture content range between field capacity and permanent wilting percentage. Since field capacity is defined as the water content after drainage of gravitational water, as described earlier, the upper limit for plants is actually lower than the total 'field capacity' as is made clear in Fig. 6.2. Field capacity includes capillary water not available to plants as well as hygroscopic water. Strictly it is not a precise description. Permanent wilting percentage is the lower unit of soil water storage for plant growth. It is the soil water content at which plants remain permanently wilted unless water is added to the soil. This is also referred to as the wilting coefficient.

Continuous absorption of water is essential to the growth and survival of most plants. Plants absorb water through sections of the root intimately associated and in contact with capillary water films around soil particles.

If the water content is higher than field capacity, air is displaced from the non-capillary pores and absorption is hindered by poor aeration. If the moisture content is too low, water is held so firmly by the soil that it cannot move into plant roots.

The availability of soil moisture depends primarily on its tension, determined by gravitational, hydrostatic and surface forces, as mentioned above. Osmotic pressure which is determined by the concentration of solutes in the soil solution is also a factor.

The attraction of soil water to mineral particles is customarily described in terms of water tension or suction pressure (the negative pore water pressure).

EQUIVALENT HEIGHT OF WATER (h) (cm)	h (kN/m ²)	SCHOFIELD'S pF	CHARACTERISTIC SOIL MOISTURE CONTENT
10^7	$979090.0 \approx 10^6$	7	Oven dry soil
10^6	$97909.0 \approx 10^5$	6	Air dry soil
10^5	$9790.9 \approx 10^4$	5.6	
10^4	$979.0 \approx 10^3$	5	Permanent wilting percentage
		4.2	
10^3	$97.9 \approx 10^2$	4	Capillary water
		3	Readily available for growth
10^2	$9.79 \approx 10.0$	2.7	Moisture equivalent approximate field capacity
		2	
10	$0.979 \approx 1.0$	1	Gravitational water
0	0	0	

Figure 6.2 Soil suction characteristics.

6.3 Measurement of Suction

The measurement of soil suction in the field or in laboratory experiments can be achieved by using a tensiometer. Tensiometers usually take the form of a cylindrical, conical, pot of unglazed ceramic material connected to a measuring attachment, normally in the form of a mercury manometer. The tensiometer cone is inserted into a borehole in the soil material being tested. The borehole is of similar size to the cone, so a good contact between cone and soil material is achieved. Fig. 6.3 shows the system used in the experimental bunkers at Durham University. The following equations were used to calculate suction or positive pore water pressures.

$$[(h_2 + Dy) \rho_w - hm \rho_m]g < 0$$

$$[(h_2 + Dy) \rho_w - hm \rho_m]g > 0$$

$$Dy = Dp + Dt + hm_1$$

$$hm = hm_1 + hm_2$$

Dp = Depth of centre point of piezometer below discard tip surface

Dt = Height of datum above discard tip surface

hm_1 = Mercury head 'above datum' in piezometer arm

hm_2 = Mercury head 'below datum' in open arm

h_2 = Excess head of water in open arm

ρ_w = Density of water $\approx 1000 \text{ kg/m}^3$

ρ_m = Density of mercury $\approx 13,540 \text{ kg/m}^3$

g = acceleration due to gravity $\approx 9.81 \text{ m/s}^2$

A Fortran computer program was used in order to calculate the suction pressures at the centre point of each of the piezometers from the daily manometer readings, that is, hm_1 (m); hm_2 (m); and h_2 (m). A listing of

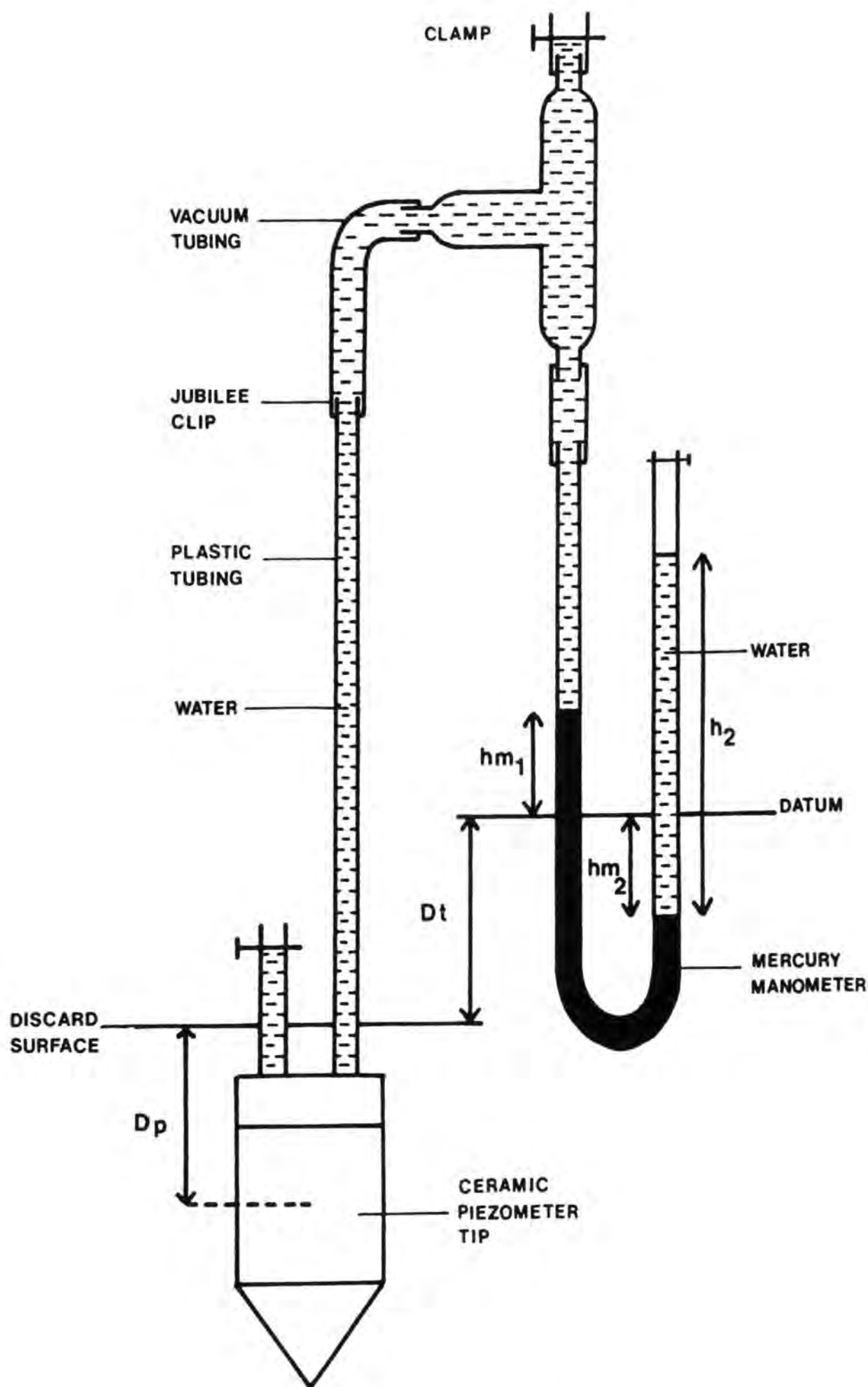


Figure 6.3 Suction Pressure recording system.

the program is given in Appendix 3.

The mercury manometer measuring system was later replaced by pressure transducers, calibrated for both pressure and tension. The electrical output from the transducers could then be converted into mercury head and thence kN/m^2 .

Relationships between suction pressure and soil moisture conditions, using conventional units or the logarithmic pF scale, are shown on Fig. 6.2.

A porous body such as soil does not contain pores of uniform size and shape which would all empty at the same suction pressure. Soils are characterised by a pore size distribution, thus pores with large channels of entry would empty at low suction pressures, whilst those with narrow channels of entry do not empty until larger suction pressures are imposed. As soil water suction pressure is progressively increased, the soil moisture content is progressively reduced. The plot of suction pressure against soil water content produces the curve known as the soil moisture characteristic.

When suction is relaxed in an attempt to refill the cell, the smaller pores will fill before the larger pores. The suction pressure at which each size group refills is less than that at which it empties. The curve obtained by plotting water content against suction pressure is similar in shape to that obtained during water removal, but is displaced in the direction of lower suction pressure. This deviation from perfect reversibility of the moisture characteristic, produces a hysteresis effect which is illustrated in Fig. 6.4 (Maltby discard less than 2mm grain size).

The drying curves shown in Fig. 6.4 are for Maltby and Bilsthorpe coarse colliery discards. Tensiometers were embedded in the discard, then

using a large coring shoe, the tensiometers and surrounding discard were taken and allowed to dry under laboratory conditions. These data can be compared with suction pressure water curves for material of less than 2mm size, separated from discard from a lagoon embankment at Maltby Colliery. These latter determinations were made by Simmonds (1984), using a laboratory suction plate apparatus. Suction pressures of up to $p^F 3$ can be measured with this equipment (Fig. 6.5). It can be seen that the coarse discard from Maltby and Bilsthorpe show a much more restricted water content range, than the less than 2 mm fines from Maltby. This size fraction displays the characteristic shape of curve for silty and argillaceous soils and fine grained mudrocks (see, for example, Taylor, 1978).

As previously mentioned, plants generally obtain their moisture and nutrient requirements from the smaller particle size fractions within a soil or discard. It can therefore be argued that the less than 2mm size of Maltby discard with its higher moisture content range in Fig. 6.3 is more ideal for plant growth than the in situ 'whole' discard sizes of Maltby and Bilsthorpe with lower moisture contents (Fig. 6.3). However, in the restoration procedure, scarifying is commonly used in the upper layer. This means that vegetation moisture requirements will be more nearly satisfied as in situ material is broken down. Weathering of the surface will, of course, help in producing smaller grain sizes if restoration is delayed for many months.

6.4 Design of Project

Two experimental discard tips were constructed in confined bunkers at Durham University. There were two reasons for conducting experiments in

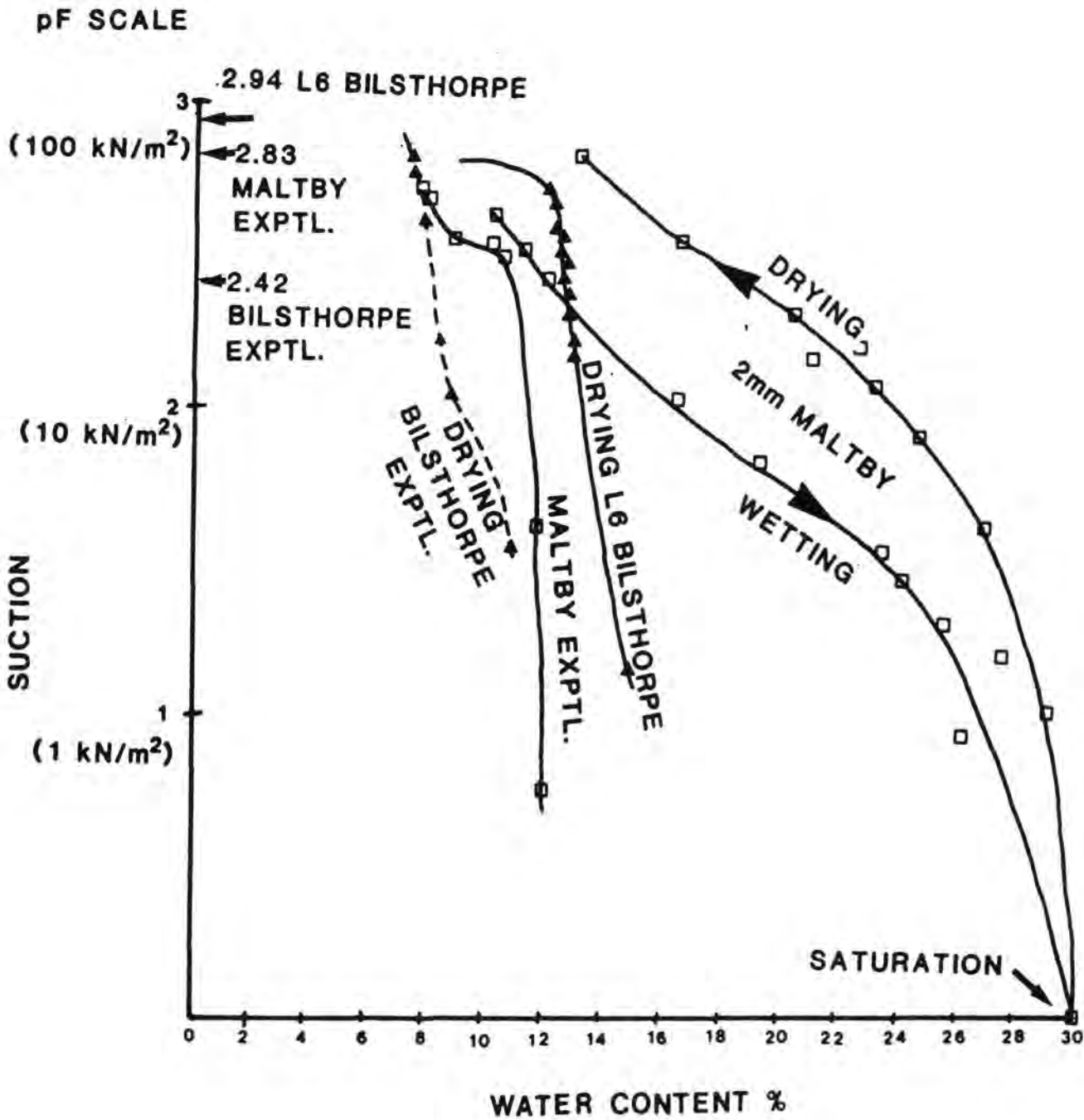


Figure 6.4 Suction pressure (pF) vs. moisture content relationships for coarse discards from Maltby and Bilsthorpe Collieries and less than 2mm size fraction (Maltby).

these experimental (courtyard) tips: (a) provision could be made for continuous data logging of tensiometer readings, and (b) research would not be interrupted by the Miner's Strike of 1984. Subsequently in 1985, measurements were made at two locations at Bilsthorpe Colliery, in the 3 year old embankment of lagoon 6, and below the 3 year old soil cover at a location devoid of grass on the restored part of Tip No. 1. The discard at the latter site was about 15 to 20 years old. Individual readings only could be made at Bilsthorpe since data logging was deemed to be too expensive.

The two experimental bunkers were of different construction. One used shuttering boards, reinforced with a vertical and horizontal framework of angular steel ("Dexion"), and the other was a more permanent structure made from breeze blocks. The base of each bunker had a 2-3° slope from back to front, to allow base flow and runoff into a plastic gutter. This water was channelled into a pyrex collecting beaker. A double lining of thick plastic was placed inside the bunkers to prevent any loss of water from the base or side wall intersections.

In June 1984, the first experimental tip was constructed using coarse discard from Maltby Colliery, believed to be about 7 years old. The particle size distribution of the material is shown in Fig. 6.6. About 2.2 tonnes of discard was used for the experimental tip. The structure shown in Fig. 6.7 was compacted in 3 layers to a nominal bulk density of 2.0 Mg/m³. The exposed face was given an inclination of 18°.

During Spring 1985, the second experimental tip was constructed using 3 tonnes of coarse discard from Bilsthorpe Colliery. This material was of considerably coarser grain size than that from Maltby, as seen in Fig. 6.6. Over a period of about 15 months, this discard degraded to a size range

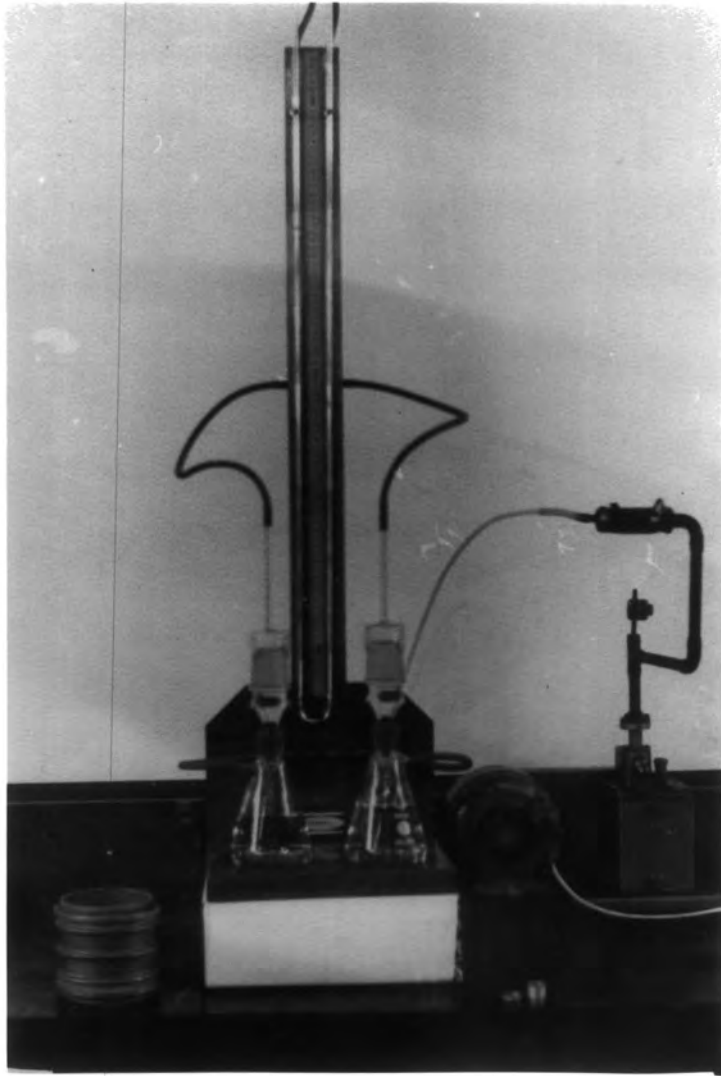


Figure 6.5 Suction plate apparatus.

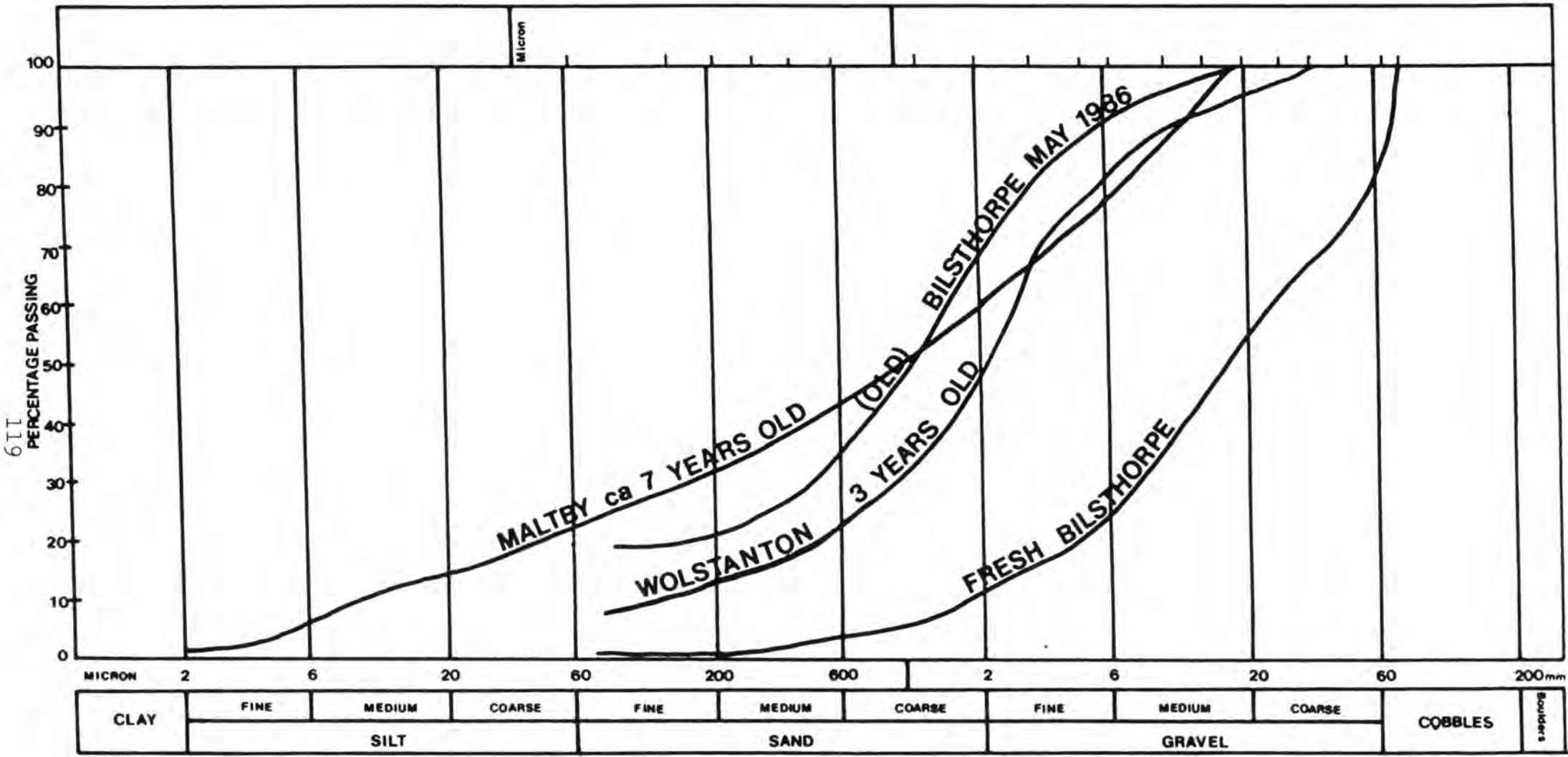


Figure 6.6 Particle size distributions of fresh and experimentally degraded coarse discard from Bilsthorpe Colliery and 5-7 year old discard from Maltby Colliery.

similar to that from Maltby. During this period, however, it was subjected to a leaching experiment simulating 5 years' rainfall.

6.4.1 Tensiometers

High air entry ceramic piezometers (Fig. 6.8) with a pore diameter of approximately 1 μm , an air entry value of approximately 1 atmosphere (ca. 100 kN/m^2) and a permeability of 2×10^{-8} m/s were modified as tensiometers. They consisted of a porous ceramic cylinder, sealed at one end, connected at the other to a sealed water reservoir and a suction measuring device (Fig. 6.8). In the initial stages of the Maltby experimental tip, standard mercury manometers were used to measure suction of positive pore water pressures as outlined previously. These were replaced to enable continuous monitoring by Schaevitz pressure transducers (No. P721/001) calibrated in both tension and compression. These were calibrated using a mercury manometer linked to a vacuum pump. The transducers were connected via a stabilised power supply to a data logger (CHRISTIE CD 248 DATA LOGGER). The transducers minimised the time lag in tensiometer response, since practically no water flow occurs as the instrument adjusts. The water inside the tensiometer assumes the same solute composition and concentration as the soil water and therefore it is the matric potential (suction) which is measured and not the osmotic suction. Measurements by tensiometers of this type are limited to suction pressures of below 1 atmosphere (101 kN/m^2). The highest measurement recorded in this study (see Fig. 6.11) was 86.7 kN/m^2 (pF 2.94) in Bilsthorpe Tip No. 1, but it was suspected that in dry weather higher suction pressures would apply.

Prior to installation of a tensiometer it is necessary to de-air the



Figure 6.7 Construction of Maltby experimental tip showing tensiometer ready for installing in hole made by cutter tube.

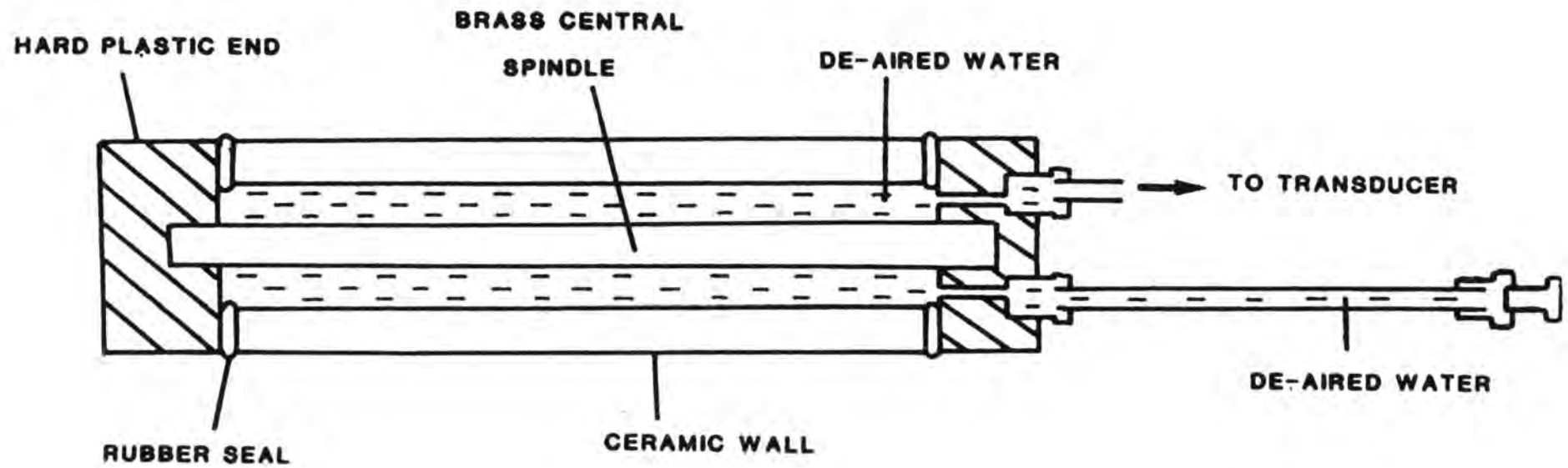


Figure 6.8 Cross section of tensiometer (piezometer).

ceramic cylinder and to ensure that it is not leaking after it has been filled by submergence in de-aired water and the top section assembled. In both experimental tips, tensiometers were installed at depths corresponding to shallow-100 mm; mid-200 mm; and deep-430mm (500 mm in the Bilsthorpe discard experimental tip). The depths correspond with the centre points of the ceramic cylinders and are indicated on Figs. 6.9-6.11.

The instruments were installed in narrow holes filled with water in the colliery discard material, any large cobbles or boulders having been previously removed. The discard was then tamped down around the tensiometer, the excess water helping to provide a good seal. However, after extended periods of high suction pressures, air did enter the tensiometers and they needed to be flushed and refilled with de-aired water. Some breaks in the record of individual tensiometer readings (Fig. 6.9) are a result of such system maintenance. The coarser material from Bilsthorpe was particularly troublesome in this respect. Breaks are indicated in the early Maltby readings highlighting the inadequacies of mercury manometers.

The tensiometers installed at Bilsthorpe Colliery had to be read individually by means of a sealed lead acid battery, a voltage regulator to ensure a constant excitation of 10v, and a battery-powered multimeter to display the output voltage. Considerable problems were encountered with these tensiometers because of water leakage. These tensiometers were largely manufactured in the laboratory workshops and difficulties were experienced with seals.

6.5 Suction Pressure Measurements

Output for the two experimental embankments is shown in Figs. 6.9 and

6.10, whilst field measurements at Bilsthorpe Colliery are shown in Fig. 6.11. Rainfall figures, maximum daily temperatures and wind speeds for the experimental tips were taken from the Durham University Observatory records, whilst those shown in Fig. 6.11 were supplied by the Nottingham Weather Station at Watnall.

The Maltby record commences in July 1984 and runs through to the end of August 1985. The Bilsthorpe experimental tip was monitored from early May to early August 1985, after which other experiments were carried out on the material (see Bick, 1985).

Maltby and Bilsthorpe records (Figs. 6.9 and 6.10) indicate that throughout the monitoring period, only small negative or positive pore pressures were measured in the deepest tensiometers (430mm Maltby, 500mm Bilsthorpe). Although the early Maltby measurements (Fig. 6.9, July 1984) were affected by air entering the measuring equipment, the technique of refilling and stabilising tensiometers was perfected within a few weeks. The Bilsthorpe discard experimental tip was about 6 months old when instrumented. Air entry difficulties were experienced throughout the monitoring period due to its coarseness.

The highest suction pressure reading in the experimental tips was recorded in July 1984, being 65 kN/m^2 for Maltby discard. In July 1985, the tensiometer at 100mm depth in the Maltby experimental tip registered a maximum of 59 kN/m^2 . This compares with a maximum of only 26 kN/m^2 for the shallowest tensiometer in the much coarser Bilsthorpe material. A comparison of the same time period in Figs. 6.9 and 6.10 illustrates the much lower suction pressures measured in the Bilsthorpe material.

The shallowest tensiometers at about 100mm depth recorded the highest suction pressures, although in more continuous wet periods there was a

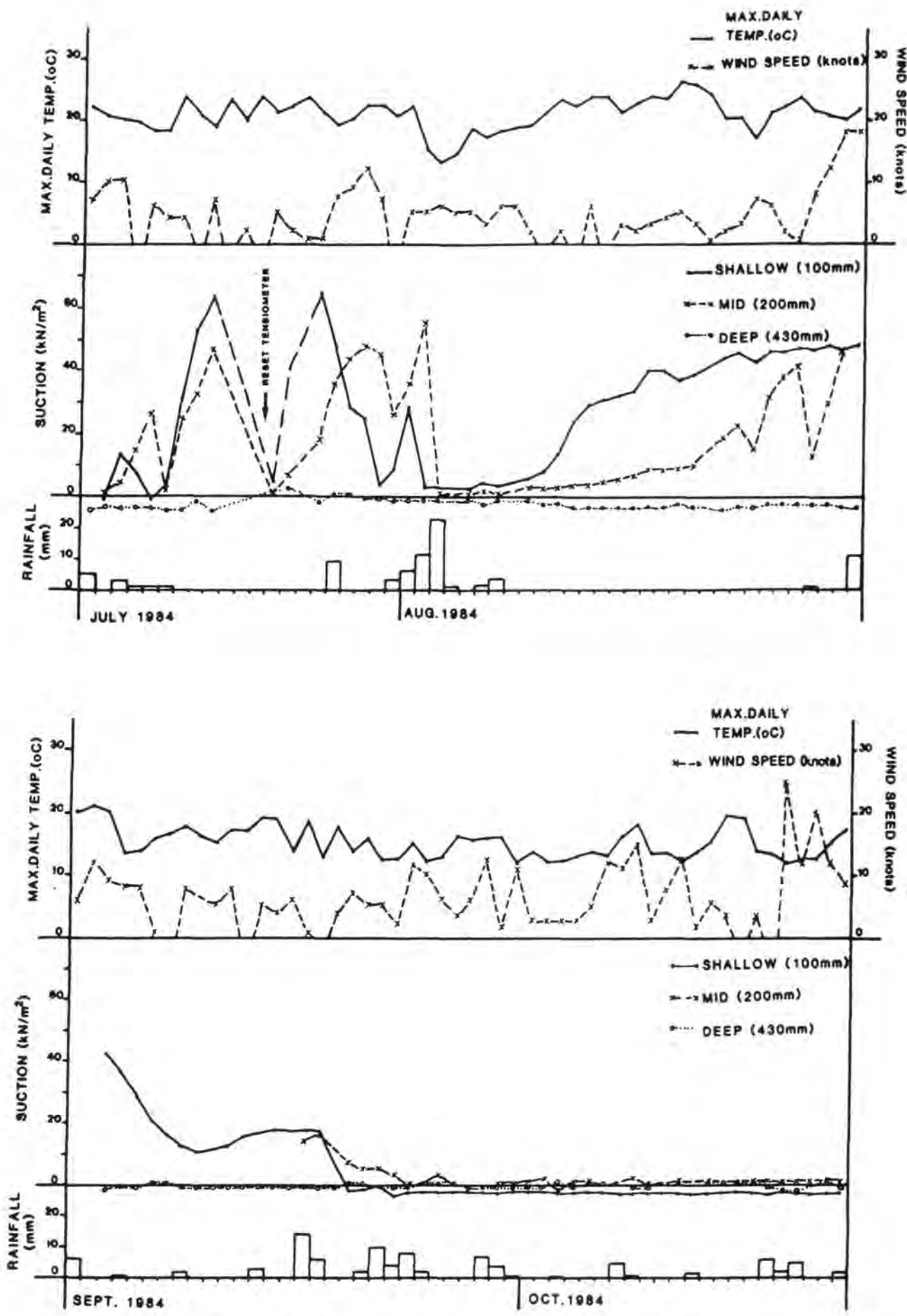


Figure 6.9 Record of suction pressure measurements from 3 tensiometers in Maltby experimental tip (1984-1985). Weather data from Durham University Observatory.

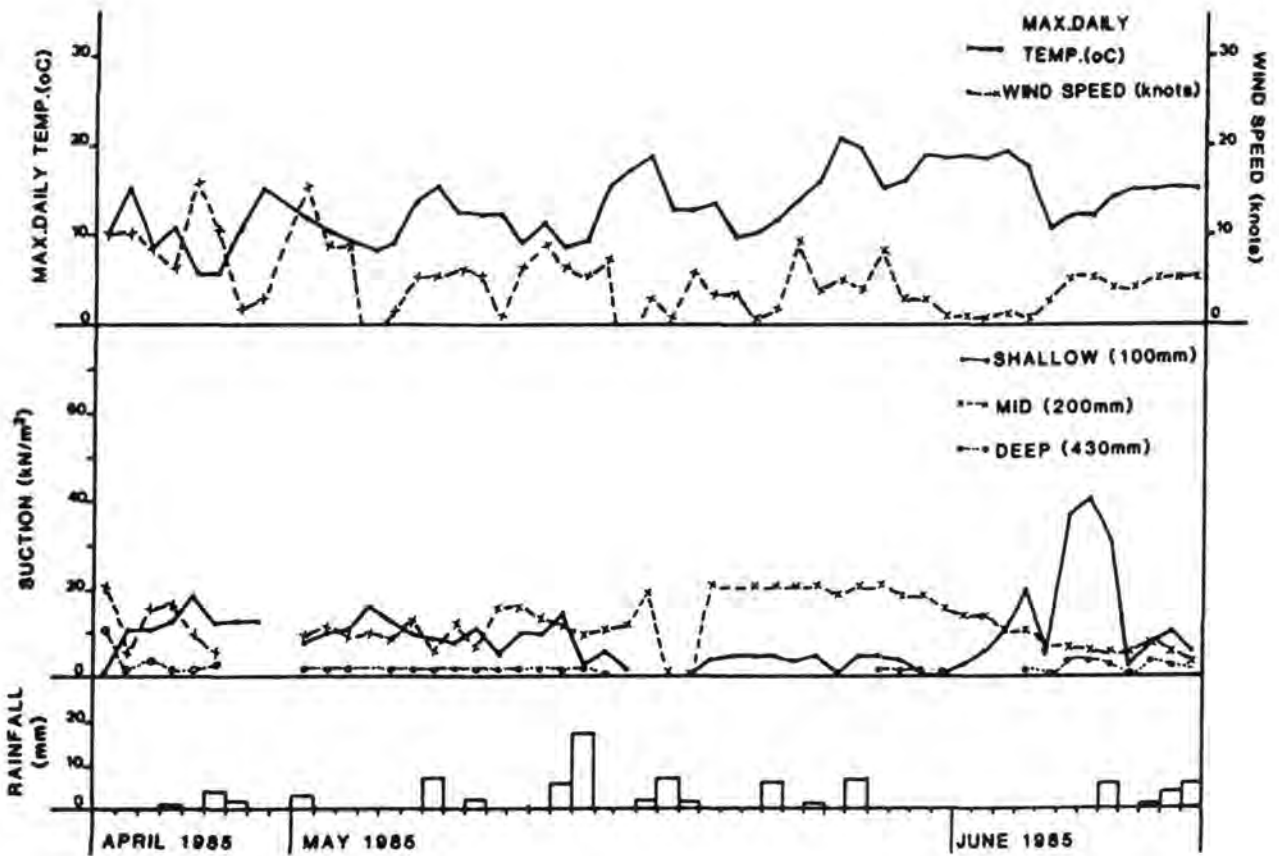
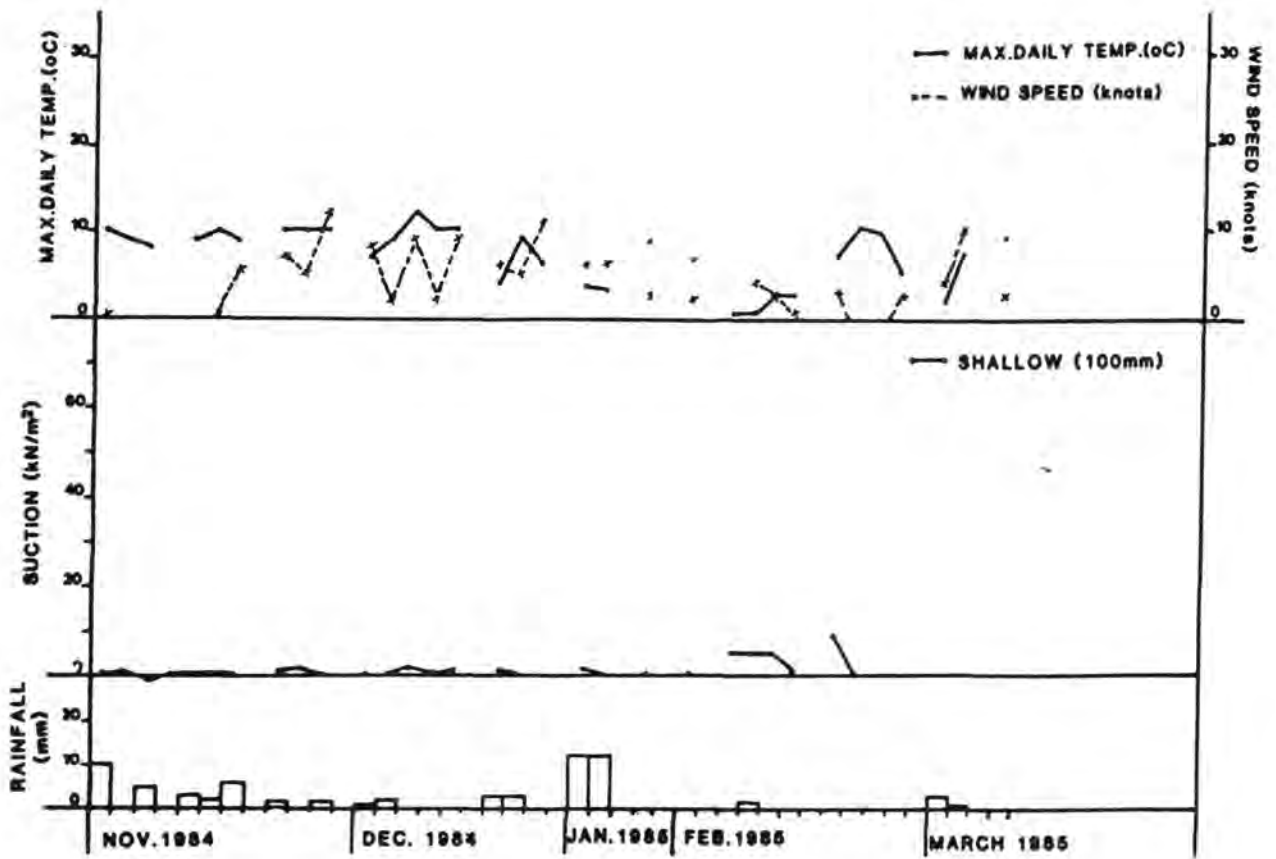


Figure 6.9 continued.

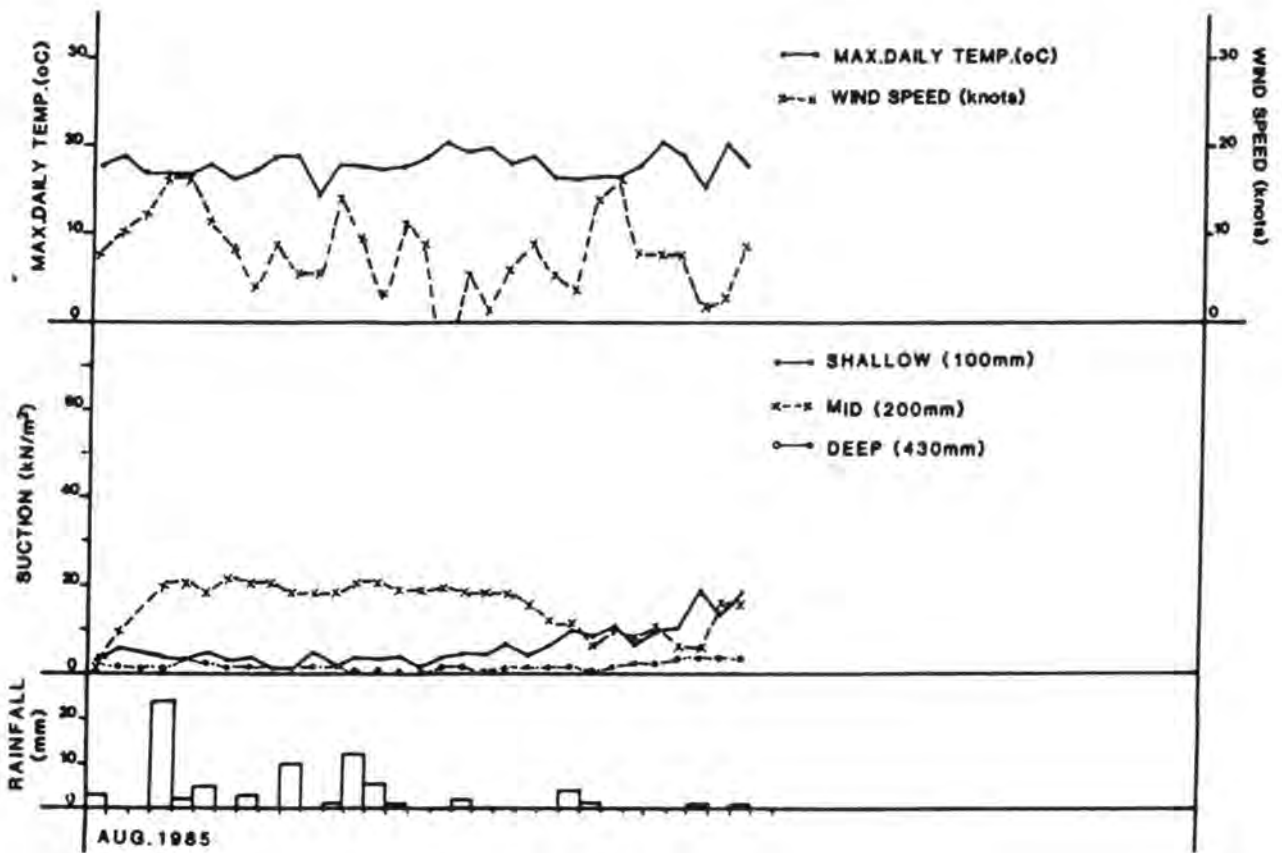
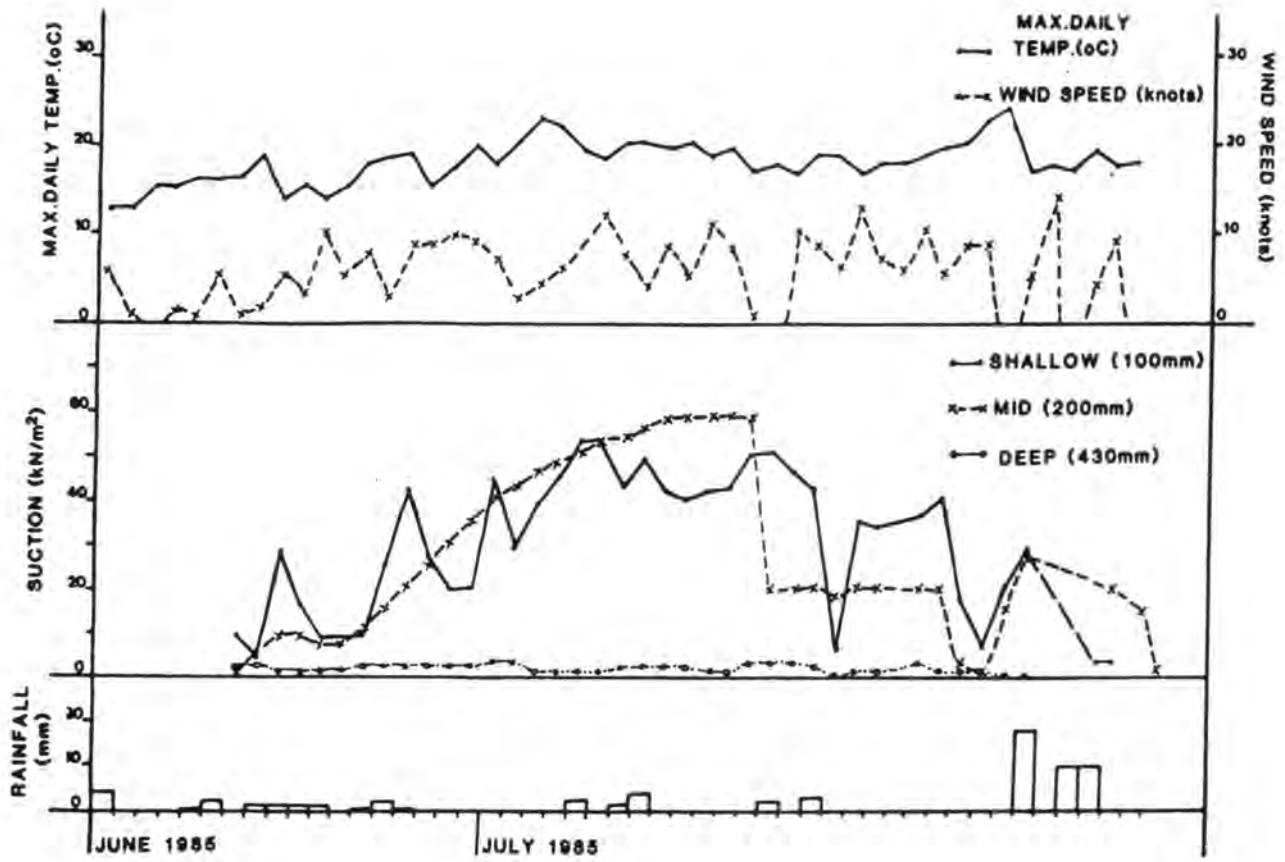


Figure 6.9 continued.

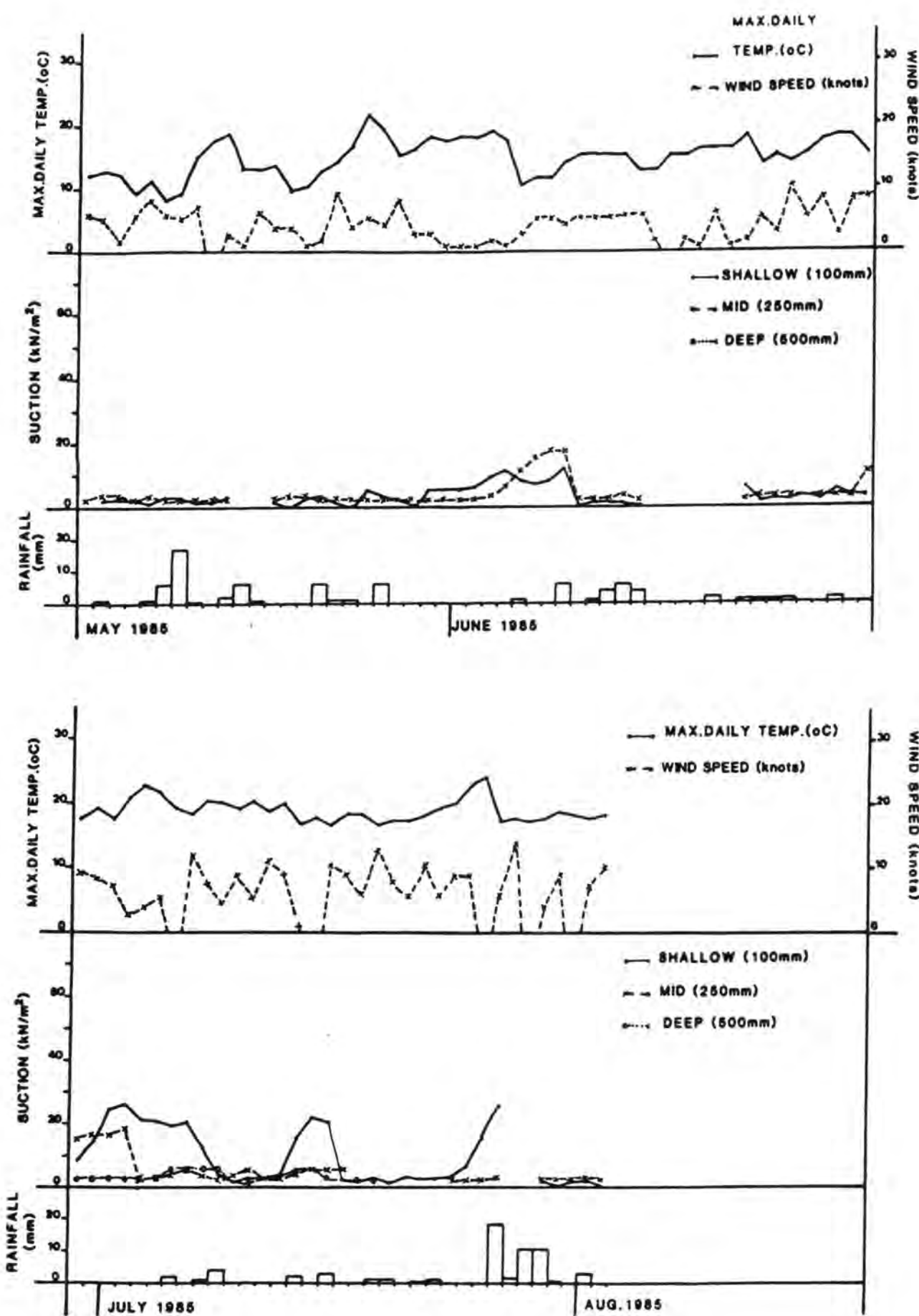


Figure 6.10 Record of suction pressure measurements from 3 tensiometers in Bilsthorpe experimental tip (1985). Weather data from Durham University Observatory.

tendency for the middle tensiometers to give the highest readings. Reference to Fig. 6.9 shows that, in August 1985, the middle tensiometer was recording suction pressures of about 20 kN/m^2 , as against values below 5 kN/m^2 for the shallowest instrument.

Examination of the records for both discards suggest that rainfall is the main control on suction pressure in the experimental tips. There is possibly some indication that wind speeds might have some influence on the Bilsthorpe readings. However, it was not possible to assess accurately the influence of wind and maximum temperature on these experimental heaps because they were to a large extent, protected by buildings.

The main findings of the monitoring programme are best illustrated by the Maltby record shown in Fig. 6.9. In mid September 1984, the suction pressures dropped in all tensiometers and remained at negligible levels throughout the winter months. By April 1985 they had started to rise although it was not until June that fluctuating, but sharp, increases occurred (see also Fig. 6.10). The highest suction pressures were measured in July and August in both 1984 and 1985.

The pattern described above suggests that sowing and planting of vegetation is best initiated during Autumn, starting in mid September. Results outlined in Chapter 5 and by Taylor et al. (1984) have indicated that the downward concentration of chlorides into an embankment commences in late Autumn. Spring sowing would mean that young vegetation might well be subject to the higher Summer suction pressures and thus to higher chloride and sulphate levels in new embankments constructed of saline discards.

6.5.1 Field Measurements

Fig. 6.11 is a record of the suction measurements taken in lagoon embankment L6 and within the grassed part of Tip No. 1 at Bilsthorpe Colliery. The 3 years old exposed coarse discard of embankment L6 forms the best comparison with the experimental tips, since Tip No. 1 has been top-soiled and seeded. The pattern of measurements in the L6 embankment agrees with this interpretation.

The maximum suction pressure readings shown both in Tip No. 1 and the lagoon embankment are notable at 89 and 86 kN/m² respectively. These values are more than 20 kN/m² higher than the maximum values measured in the Maltby experimental tip. Both field locations at Bilsthorpe Colliery are in open, exposed areas and will experience the drying effects of the wind to a greater degree than the experimental tip structures at the Durham University site. The lagoon 6 embankment is 11m high and Tip No. 1.17m high, compared to a height of under 1m for the experimental structures.

Fluctuations in the suction pressure measurements from the shallow tensiometers placed in both embankments at Bilsthorpe are very marked. It would appear from Fig. No. 6.11 that the high suction pressures measured on 23rd July 1985 (L6) and 26th July 1985 (Tip No. 1) corresponded to increasing daily temperatures, rather than to windspeed which is falling. The rapid response to rainfall of the shallow tensiometer in Tip No. 1 after 26th July is analogous to the tensiometer behaviour noted in the experimental tips. However, the weather station is not in the immediate site vicinity and slight discrepancies in weather and tensiometer response might be expected.

The overall tensiometer response in Tip No. 1 suggests that soiled and vegetated embankments may behave rather differently from untreated coarse

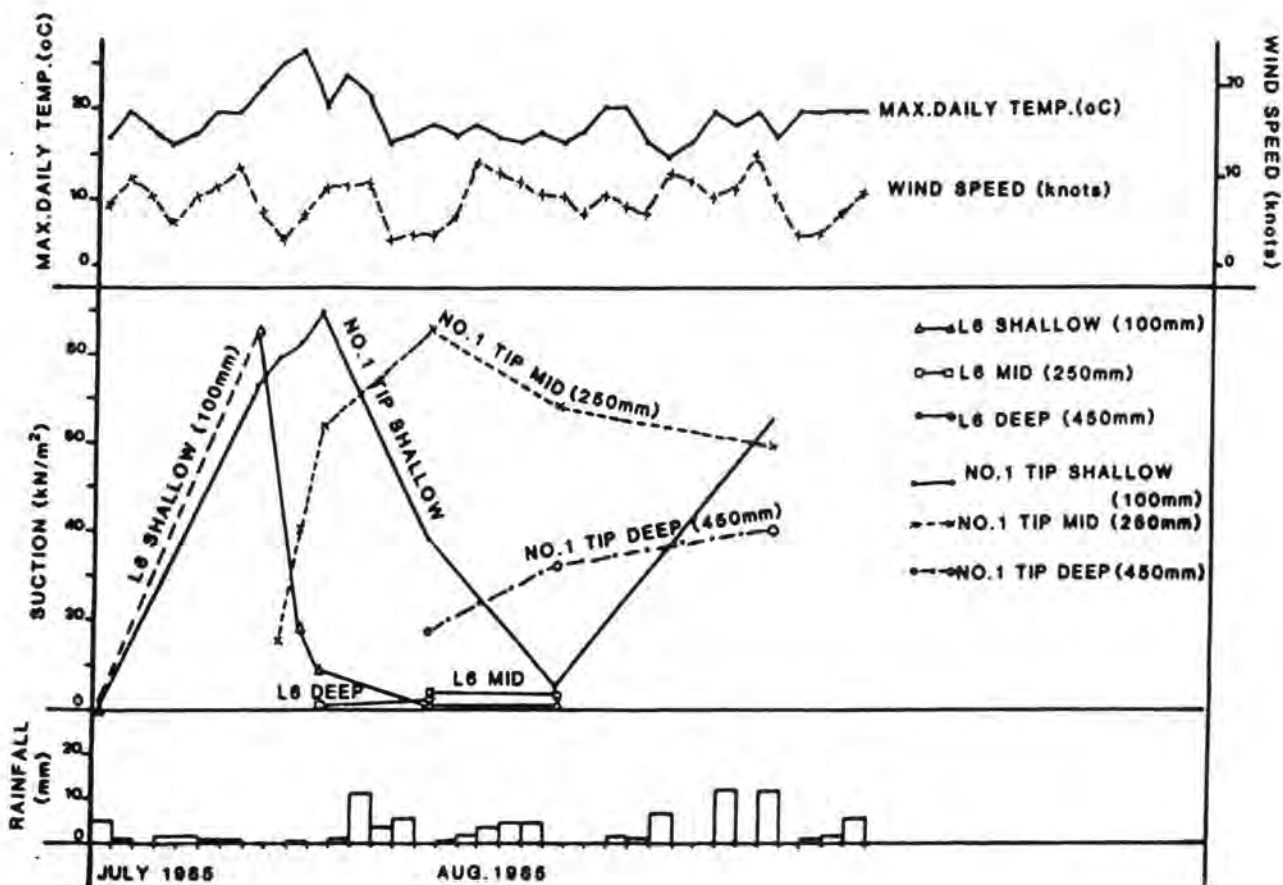


Figure 6.11 Suction pressure measurements in Lagoon 6 embankment and Tip No. 1, Bilsthorpe (1985). Weather data from Nottingham Weather Station, Wathall.

discard exposed in embankments. The middle and deepest tensiometers were apparently unaffected by fluctuations in rainfall, although the deepest instrument did show a gradual rise in suction pressure following installation. Embankment L6 is more comparable with the Durham experimental tips. Here the deepest tensiometer, at 450mm, registered negligible suction pressures in rainy periods. The response to rainfall for all 3 tensiometers over the period 26th July to 6th August 1985 suggests that the partly saturated zone of the embankment may be little more than a skin some 450mm in depth.

6.6 Conclusions

Soil suction pressures developed in the partly saturated zone of a waste embankment are of particular interest with respect to the early (progressive) restoration of saline colliery discards. Results to date (Taylor et al., 1984) suggest that 5 to 7 years of natural leaching may be necessary to reduce contained chlorides to acceptably low levels. Because chlorides can cause physiological drought in young vegetation, it is advantageous to assess their movement in colliery discard as precisely as possible. Monitoring of two experimental spoil banks by means of tensiometers connected to pressure transducers and a data logger has identified a number of important suction pressure characteristics.

The highest suction pressures were measured in the months of July and August, when, as shown in Chapter 5, desiccated chloride/sulphate hotspot measurements were also found to be at a maximum. Chloride ion levels in general are more evenly distributed through the partly saturated zone during this period. In mid September, suction pressures dropped to minimal levels, fluctuating around pF 0, until the following April, when they

started to rise again. It is suggested from this pattern of soil suction pressure variation that Autumn is the optimal sowing period for vegetation. At this time suction pressures are at a minimum and chloride ions are beginning to show a downward concentration into the embankment. In contrast, Spring sowing would subject young vegetation to enhanced suction pressures and the generally higher chloride levels of the Summer months.

Suction measurements made in the 3 year old lagoon embankment and the restored colliery tip at Bilsthorpe Colliery indicate a much higher maximum (x 1.5) and greater fluctuations in suction pressures than in the experimental tips. These differences are believed to be a function of the greater exposure to the weather in the case of the Bilsthorpe structures.

The pattern of suctions developed in the restored tip is rather different from that of the unrestored lagoon embankment, which shows certain similarities with the experimental tips. One similarity is the apparent depth of the partly saturated zone which suction measurements suggest is only about 450mm in thickness. Chemical oxidation is likely to be almost entirely restricted to the partly saturated zone in a shale embankment. In the older generation of unrestored loose tips, intense weathering is restricted to a depth of about 1m, and, for example, in the 50 year old Yorkshire Main tip, a low degree of weathering was detected even below this, to a maximum depth of 3.81m. Similarly, in discards placed in loose 1.5m layers at Gedling Colliery, suction pressures of between 6 and 17 kN/m² were noted to a depth of 4.5m. The present work suggests that a much thinner, partly saturated zone obtains in modern colliery embankments.

CHAPTER 7

CONCLUSIONS

High chloride ion concentrations found in freshly tipped coarse colliery discards are detrimental to the establishment and successful growth of vegetation. Chloride toxicity in agricultural crops has been reported by Parker et al. (1983) and high chloride and increased salt concentrations cause physiological drought and water stress to young vegetation.

Until 1981, with the introduction of the Town and Country Planning Act, problems of restoring highly saline discards did not occur. Most colliery tips were left undisturbed for many years after tipping and the soluble salts were allowed to leach naturally from the discards. Eventually, when reclamation did take place, high salt concentrations, detrimental to plant growth, were not found in these long-standing colliery discards. The problem was customarily low pH and high sulphates originating from surface pyrite oxidation (Bradshaw & Chadwick, 1980).

The 1981 Act made progressive reclamation practices compulsory within five years of discard disposal, that is, when the salt concentrations within the discard material are still sufficiently high to cause problems to plant establishment. British Coal, who now had to begin reclamation procedures, deemed it necessary to undertake a study of salinity in colliery tip surfaces. The work presented in this thesis is the result of the study commissioned by British Coal, and deals with the causes of salinity in discard material, distribution of salinity in freshly deposited discards, leaching patterns, seasonal fluctuations, possible effects of tipping practices and recommendations for restoration practices.

Problems of saline soils are not usually associated with British soil types, although such soils have been identified in South-east England, mainly on marshy land (South-east England Soils Discussion Group field meeting, May 1985). In other parts of the world, for example, western and central Europe, Africa, Asia, Australia, North and South America and Russia (Kovda, 1965), saline soils are common and can pose severe problems to agricultural production.

Saline salts generally contain large quantities of carbonate and bicarbonate salts of sodium and potassium and sodic salinity is often in combination with high concentrations of chlorides and sulphates. This gives rise to not only toxicity problems, but unfavourable soil physical conditions.

The top horizons of saline soils are very unstructured and are compacted and cemented. Horizons are strongly compressed and during the Summer months, with drying, become traversed by cracks and fissures that may extend through several horizons (Kovda, 1965). During wetter Seasons the soil swells and become^S particularly impermeable, giving rise to the ponding of surface water on the soil surface. During drying, these impermeable areas form hard crusts and salt efflorescences develop.

This 'primary' salinity, forming saline, sodic and alkaline soils is found mainly on alluvial plains and river terraces. Secondary salinity, following the installation of irrigation systems, is particularly common in arid countries. A decline in productivity in the Punjab, India because of secondary salinity amounted to 10-50% (Raychaudhuri, 1965).

The presence of saline soils in Great Britain is relatively unknown and so the reclamation problem of saline coarse colliery discard represents a pioneer study.

The need to study the origins of the salinity in colliery discards is obviously important and is discussed in Chapter 2. The primary control on coal chloride content and the chloride content of Coal Measures rocks, would appear to be the salinity of the groundwater with which the strata are intimately associated.

The areas most affected by saline groundwater are predominantly in the Eastern coalfields. Chloride ion in stratal waters varies from the low values of South Wales, with less than 20ppm Cl to the Eastern coastal coalfields and inland Nottinghamshire coalfields where Cl levels are higher than 100,000ppm in stratal waters.

Groundwater composition also varies with depth. Three major zones can be identified, a shallow sulphate dominated zone, an intermediate bicarbonate-rich zone, and deep chloride dominated waters.

It is unlikely that one single event or process is responsible for the chloride ion concentrations found in the formation waters, or for the geochemical trends associated with depth and regional variations in concentration, found in the United Kingdom Coal Measures rocks.

The composition of groundwaters circulating in the Coal Measures rocks, may have been influenced by solution of Lower Carboniferous evaporites and by subsequent uplift and erosion of overlying sediments during the Permo-Trias, allowing entry of meteoric water and/or sea water from subsequent marine transgressions. The composition would have been further altered by processes such as compaction by overlying sediments, chemical reactions and by clay minerals acting as filtration membranes.

After the discard has been tipped, an initial, relatively rapid physical breakdown occurs (Spears et al., 1970). This physical weathering appears to be confined to the surface layers of the tip or embankment. The

chemistry of the water in a spoil heap is thought to be controlled mainly by formation water, that is by entrapped water originating from a number of possible sources released by the rocks during weathering (Spears et al., op. cit.).

The whole rock chemistry and mineralogy of discards from three collieries, Maltby, Wolstanton and Bilsthorpe were studied using XRF analysis and semi-quantitative XRD mineralogical analysis. A comparison of the results obtained by these methods, shows that the discards fall into three groups, each having distinct characteristics.

Maltby discard is predominantly clayey, containing little quartz and the discard is dominated by illite. Discard from Bilsthorpe has the highest quartz content, but it also has a high clay content. Wolstanton discard is markedly different from the other two, being a coal-rich material, with a low total clay and illite content and is much more freely draining (See Chapter 5 and Chapter 6).

Within any embankment structure, movement of water will occur, and equilibrium flow nets will ultimately develop. As well as formation water released from the discards upon weathering, water in colliery embankments will contain a component from the coal preparation plant. That is, from washing and screening processes. This recycled water is generally saline, and is discharged along with the discard. Thus the salt content of a tip or embankment may increase.

Because of the soluble nature of most of the salts found in colliery discards, patterns of salt distribution and movement will be closely associated with water movement within the colliery embankment.

Chloride ion distributions within the near-surface zone of two colliery embankments at Maltby Colliery, South Yorkshire, and Wolstanton,

Stoke-on-Trent, have been investigated in an attempt to rationalise salt movement within tip surfaces. The detailed results have been presented in Chapter 5. The following principal factors have been identified:-

1. Following sampling methods developed by Liverpool University (1982), sampling on a grid pattern was used to locate hotspots and seepage emission areas. A grid size of greater than 5m x 5m, was found to be ineffective in terms of hotspot definition.
2. Depth sampling by means of traverses from crest to toe indicate downward leaching of chloride ions into the embankment in wet weather, that is in Winter and Spring seasons. An increase in chloride levels towards the surface with a more uniform distribution in the top 0.5m occurs in the relatively dry Summer months.

When sampling colliery discard for chloride ion content, careful consideration should be given to the season in which the sampling takes place. Differences in chloride levels from Winter to Summer are obvious (Chapter 5). Summer sampling should be used to indicate the maximum levels of salts which young vegetation will have to tolerate, because it is in these months that chloride levels are at their maximum near the surface with which such vegetation will be in contact.

3. Chloride ion levels generally decrease in a downslope direction throughout the year.
4. The 'background' level of chloride concentration in discard embankments falls from year to year through natural leaching (see Fig. 5.9). The data is from areas on the embankment not associated with hotspots.
5. Hotspots show little change in chloride levels over a two and a half

year period. Indeed at Wolstanton Colliery, where background chloride levels are less than 50ppm, hotspots still appear regularly on the embankment.

6. Crystalline salts sampled from seepage hotspots on the surface of saline heaps were identified, using X-ray Diffraction techniques, as sodium sulphate, calcium sulphate and sodium chloride. The predominance of sodium sulphate over sodium chloride on the surface may be explained by the preferential crystallisation of sulphate minerals over chlorides (Weast & Astle, 1983).
7. Seepages are not solely a symptom of leakage through a lagoon embankment. At the embankment studied at Wolstanton, seepages and hotspots were identified in the absence of any lagoon, or buried tailings being present in the heap. Evidence from the Maltby embankment indicates that seepages might be associated with impermeable surfaces of previous lifts. This was investigated further in an embankment at Bilsthorpe Colliery, near Mansfield, Nottinghamshire. Findings indicate that in addition to a definable phreatic surface being present, a perched water table was measured, almost certainly supported by the top of the initial lift, the embankment comprising two lifts.

Seasonal fluctuations in the soluble salt levels in discard embankments are associated with water movements. In order to study this phenomena, two experimental discard tips were constructed at Durham University. Each tip was made up of 3 tonnes of discard of two types:

1. Weathered 7 year old Maltby discard, and
2. Fresh Bilsthorpe discard.

Both tips had tensiometers installed at depths of 100mm, 200mm and 430mm below the tip surface. A continuous read-out system facilitated the measurement of both suction and small positive pore pressures for over 1 year in the case of the Maltby discard. Output has been compared with rainfall, wind and sunshine data. Detailed results are given in Chapter 6.

The highest suction pressure measured in the clayey Maltby discard was 65 kN/m^2 , this is compared with a value of 26 kNm^2 for the fresher, granular discard in the Bilsthorpe experimental tip. The upper tensiometers indicated that the highest suctions occur in the top, 100mm deep, tensiometer, during Summer months. In wet periods, the top tensiometer measured slight positive pore pressures, whilst the deeper tensiometers were still recording suction pressures. On an annual basis, suctions became operative early in April, reversing to a small positive pore pressure in mid-September.

Tensiometers installed in two embankments at Bilsthorpe Colliery measured much higher maximum suctions ($>85 \text{ kN/m}^2$) than those in the Durham Experimental tip. However, the exposed surface area and elevation was far greater at Bilsthorpe than at Durham. Results indicate that significant suctions are unlikely to be operative at depths greater than 1m, this is also equivalent to the depth of the superficial zone of major active physical and chemical weathering, previously determined in old spoil heaps (Taylor, 1984).

The build-up of salts in the surface layers of coarse discard during the summer months is associated with increased suction pressures in the embankment surfaces. Drying of the discard surface and increased evaporation, causes water to be drawn from deeper discard material within the tip or embankment. This already saline water, passes through saline

discard material. When the water reaches the surface, evaporation leaves salt deposits on the discard surface, and a build-up of salts through the near-surface profile. During the Winter (wetter season) the reverse process occurs. Salts are dissolved from the discard surface and as the wetting front travels down through the near-surface profile, the salts in solution are redistributed down the profile.

The clayey discards of Maltby and Bilsthorpe readily promote salt 'retention' within their degraded surface layers, salts are unable to drain or be leached quickly. Discards such as Wolstanton which have a lower clay content and appear less degraded are relatively free draining, allowing soluble salt levels to fall to a 'background' concentration within several years of tipping (see Table 5.2, Chapter 5).

The movement of salts in solution affects both top soiling and sowing, or indeed sowing directly onto unburnt discard.

Traditionally two sowing 'windows' operate in Spring and Autumn, when climatic conditions are favourable for vegetation establishment. The above data, combining salt and chloride distributions within the discard with measurements of suction pressures within the surface layers, indicate that the use of an Autumn sowing 'window' is advisable. Sowing in Spring will introduce young, newly established plants to high salt concentrations and high suction pressures relatively soon after sowing. The young plants may thus be affected by physiological drought and/or toxicity due to high salt concentrations. Young rooting systems are particularly at risk (Fransway and Wagenet, 1981). Sowing in Autumn would allow young plants a greater time to establish on tip surfaces, before facing the above hazards.

The problem of the disposal of saline wastes from mining operations also occurs in the United States (Fransway & Wagenet, 1981; Merrill et al.,

1983; Jurinak et al., 1984) and in Poland (Twardowskam, 1981).

In the United States the reclamation of saline soils and saline mine spoils, from spent oil shales has received much attention over the past 30 years (Bressler et al., 1982). Six major reclamation procedures are used depending on individual site conditions and the economic budget. Briefly, these are:

1. Reclaiming saline soils by leaching, this includes leaching by water ponded on the soil surface. For example, if the depth required for reclamation was 1m, then water would be ponded on the surface until a 1m depth had been infiltrated. This method usually precludes crop establishment whilst leaching is being carried out.
2. Leaching with water with a high salt content. Water with a high salt content is a source of divalent cations which act as flocculants maintaining soil structure and drainage. If the electrolyte concentration is lowered, the soils may become deflocculated and soil structure is lost.
3. Reclaiming sodic soils by the use of gypsum. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), is used as a source of Ca^{2+} to replace Na^+ on exchange sites on clay minerals. Surface applications of gypsum maintain or can increase infiltration rates. Gypsum can also be added to the soils in solution in the irrigation water.
4. Sulphuric acid treatments for reclaiming sodic soils. The addition of acid on calcareous soils provides Ca^{2+} to exchange with Na^+ . But this method requires specialist handling.
5. Deep mixing sodic soils for reclamation, such as ploughing and ripping.
6. The use of mulches and surface management to enhance salt leaching.

As water evaporates from the soil surface, or is transpired from plants, soluble salts accumulate on the soil surface. Surface mulches and, for example, the application of straw onto the soil surface effectively reduces evaporation and the accumulation of surface salts.

7. The use of topsoil to cover salt affected soils. Studies by Berg et al. (1980), indicate that under semi-arid conditions, or prolonged drought, previously leached mine spoil can resalinate, and topsoil applications may also become saline due to upward movement of groundwater as a result of evaporation exceeding precipitation (see Table 5.2, Chapter 5).

Most of the above methods are unsuitable as reclamation procedures for coarse colliery discard. Methods 1 and 2, involving prolonged leaching are impracticable because of the need to dispose of the runoff (leachate), with its high salt content. Disposal of the leachate into a water course, large enough to dilute the salts to an acceptable level, would then be necessary - see provisions for the disposal of saline discharges, Vale of Belvoir Coal Inquiry Report (1981). This generally is economically unviable.

Reclamation methods 3 and 4 are unacceptable because of the use of sulphate in various forms. Although when first tipped, saline discard is pH neutral to alkaline, pyrite oxidation occurs rapidly, lowering the pH of the discard (see Figs. 1.4 and 1.5, Chapter 1). Sulphates can also be the end result of this reaction and the addition of further sulphates would not be conducive to plant growth.

Method 5 is already used by British Coal. Deep mixing, or ripping, of embankment surfaces prior to either top soiling or the planting of vegetation, is common practice.

Experimentation with the addition of surface mulches to colliery

discard is now being undertaken by British Coal. Mulches such as sewage sludge have been applied as a fertilizer, as a source of organic matter, to increase spoil structure and cation exchange properties (Bradshaw and Chadwick, 1980).

Covering spoil with topsoil is already a practice of British Coal, where economically feasible. Observations made as to the success of this procedure, indicate that where seepages, saline or non-saline, appear on the embankment surface, topsoil is dislodged and moved further down the slope, leaving a bare patch showing the location of the seepage.

Natural leaching for between 5 to 7 years would appear to lower chloride levels in the Maltby embankment to an acceptable level (see Fig. 5.3, Chapter 5), but hotspots remain a surface problem. These hotspots appear to be a function of impermeable layers between successive lifts during the construction of the embankment. An obvious answer would be to drain each of these hotspots independently, as they appear on the embankment surface, using downslope tile drains with dilution in the perimeter site drains.

Restoration applications

1. Individual seepage hotspots require standard land drainage treatment. Chloride/sulphate levels are unlikely to reduce to ambient values in these areas so vegetation will not thrive without specific drainage measures.
2. A large number of seepages in staged embankments can almost certainly be eliminated if the previous surface is properly scarified (ripped) prior to emplacement of the next lift. If this is not done then the individual hotspot drainage treatment is expensive.

3. The addition of surface mulches may reduce evaporation from the discard surface as well as promoting good soil physical conditions for plant growth.
4. Background chloride ion levels in saline discard would seem to be reduced significantly on exposure over a period of 5 to 7 years. This suggests that resotation of clayey discards should be left until the end of the legislative period.
5. Sowing an embankment is best initiated during the period of 'downward flow' of electrolytes into the heap. Suction pressure measurements favour an Autumn window, starting in mid-September. In contrast, Spring sowing will mean that young vegetation could be subject to the higher Summer chloride levels in embankments constructed from saline discards.

The monitoring of electrolyte concentrations, particularly chlorides and sulphates, in coarse discard embankments is an essential procedure before considering the restoration of such embankments.

The importance of a structured sampling programme, such as the use of a regular grid, not less than 5m x 5m, over a complete top to toe of slope section of the embankment, has already been stressed. This should be done when the embankment is first completed, then, say repeated three to four years later to assess to what extent natural leaching has reduced electrolyte levels. Samples should always be taken during the Summer months, when electrolyte levels are at their highest.

This need not necessarily be a complicated or costly procedure. Only surface, 0-100mm samples, would be taken and an individual sample weight of less than 0.25 kg would be sufficient.

Methods of sulphate and chloride analysis are not complicated. The use of a chloride specific ion electrode is an acceptable and accurate analytical procedure. Electrical conductivity analysis of coarse discard is not a reliable indicator as to absolute levels of chloride, because the sulphate content of discards has a greater influence on electrical conductivity than the chloride content.

Note could be made of discard 'type', that is, clay or coal dominated. Chloride and sulphate concentrations are likely to take longer to reduce to acceptable levels in clayey discard.

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APPENDIX 1

A1.1 Sample Preparation

1. Oven dry the sample at 30°C.
2. Sub-sample using a Chute splitting riffle box, retaining one half.
3. Obtain the less than 2mm fraction of the sample using BS Sieve.

A1.2 Water Soluble Determinations

Reagents

1. Deionized water.

Apparatus

1. Screw top plastic bottles, 125ml volume.
2. Shaking machine.
3. Glass filtering funnels.
4. Whatman Number 2, 125mm filter papers.

Method

1. Weigh 10g of less than 2mm fraction discard into the plastic bottles.
2. Add 100ml deionised water and stopper securely.
3. Shake rigorously for 30 mins.
4. Filter into a second set of plastic bottles using the glass funnels and Whatman No. 2 filter paper.
5. Retain the clear filtrate for analysis.

A1.3 Water Soluble Chloride

Reagents

1. Standard solutions: 100 ppm chloride stock solution 1.65g Analar NaCl made up to 1 litre with deionized water. Standards used:- 1.0 ppm, 10.0 ppm, 100.0 ppm chloride, made up using 0.1ml, 1.0ml, and 10.0ml of 1000 ppm chloride stock solution respectively.
2. Ionic strength adjuster; 5M NaNO₃, 42.5g Analar NaNO₃ made up to 100ml with deionised water.

Apparatus

1. 50ml volume glass beakers.
2. Kent EIL 7055 pH meter.
3. Orion combination chloride electrode.

Method

1. Calibrate the Kent EIL 7055 pH meter, using the Orion combination chloride electrode and standard solutions of 10 ppm and 100 ppm chloride with ionic strength adjuster added (2 ml 5M NaNO₃ to each 100 ml of solution).
2. Pipette 25ml of the clear filtrate, obtained in (A1.2) above, into a 50ml glass beaker.
3. Add 0.5ml 5M NaNO₃ and mix thoroughly.
4. Place the chloride electrode into the solution and when the meter has stabilised, take the reading.

A1.4 Water Soluble Sulphates

Reagents

1. Acetone.
2. Sulphonazo III indicator. 0.1 sulphonazo diluted to 100ml with deionized water.
3. 0.01M barium perchlorate. 3.426g anhydrous $\text{Ba}(\text{ClO}_4)_2$ made up to 1 litre with deionized water.

Apparatus

1. 50ml conical flasks.
2. Graduated glass burette with 0.2ml divisions.

Method

1. Pipette 25ml of the clear filtrate obtained in (A1.2) above, into the 50ml conical flask.
2. Add 2ml acetone and mix thoroughly.
3. Add one drop of the sulphonazo III indicator. The solution turns purple.
4. Add one drop of the 0.01 M $\text{Ba}(\text{ClO}_4)_2$ solution. The solution turns sky blue.
5. Add further 1ml of acetone upon which the solution turns back to purple.
6. Filtrate to end point with the 0.01 M $\text{Ba}(\text{ClO}_4)_2$ solution, until the solution turns sky blue.

A1.5 pH Determinations

Reagents

1. Deionized water.
2. Buffer solutions pH 4, 7 and 9.

Apparatus

1. 50ml glass beakers.
2. Glass stirring rods.
3. Kent EIL 7055 pH meter.
4. pH Electrode.

Method

1. Weight 10g of discard into a glass beaker.
2. Add 25ml deionised water and leave to stand for one hour, stirring occasionally.
3. Calibrate the Kent EIL 7055 pH meter and electrode using the buffer solution.
4. Test the discard/water mix using the electrode.

Al.6 Conductivity Determinations

Apparatus

1. Kent EIL 5003 portable conductivity measuring set.

Method

1. Use clear filtrate as obtained in (Al.2) above in conjunction with the above apparatus.

Al.7 Determination Of The Total Sulphate Content Of Soil-(BS1377:1975)

Reagents

1. Barium chloride, 5% solution. Dissolve 50g of barium chloride in 1 litre of distilled water.
2. Dilute hydrochloric acid. Dilute 100ml of concentrated hydrochloric acid (relative density 1.18) to 1 litre with distilled water.
3. Dilute ammonia solution. Dilute 500ml of ammonia (relative density 0.880) to 1 litre with distilled water.
4. Litmus paper (blue).
5. Silver nitrate, 5% solution. Dissolve 0.5g of silver nitrate in 10ml of distilled water.
6. Bromine water. Shake 6ml of liquid bromine with 500 ml of distilled water.

Apparatus

1. Conical beakers, 500ml capacity with watch glasses to fit.
2. Glass filter funnels about 100mm diameter.
3. Porcelain or silica crucible, or porous porcelain or silica filter and ignition crucible.
4. Suitable means of igniting the precipitate preferably an electric muffle furnace, capable of reaching and maintaining 800°C.
5. Dessicator containing anhydrous silica gel.
6. Filter papers. Whatman No. 541, and No. 44, 110mm diameter.
7. Glass rods.

Method

1. Weigh 2.0g of the less than 2mm fraction discard into a 500 ml beaker.
2. Add 200ml of 10% hydrochloric acid, take care for any effervescence.
3. Cover with a watch glass and boil gently for 4 mins.
4. Rinse underside of watch glass back into beaker and whilst solution continues to boil add 3ml of bromine water.
5. Add ammonia solution (preferably from a burette) stir constantly, until sesquioxides are precipitated.
6. Filter suspension through a 110mm hardened Whatman No. 541 filter paper, into a conical 500ml beaker.
7. When filtering has stopped, place filter paper back into first beaker. Add 20ml of 10% hydrochloric acid and stir mixture.
8. Remove filter paper and wash with distilled water until all traces of yellow have been removed.
9. Remove filter paper and boil contents of beaker.
10. Add ammonia solution again, and filter suspension through a Whatman No. 514 filter paper into the conical beaker containing the first washings.

11. Test the combined extract with litmus and make slightly acidic by the addition of hydrochloric acid.
12. Bring extract to the boil and add 25ml of 5% barium chloride solution, drop by drop.
13. Cover the solution and keep hot but not boiling for at least one hour.
14. Add several more drops of barium chloride solution to ensure complete precipitation of barium sulphate. Keep solution hot for one hour.
15. Filter the solution with extreme care through a Whatman No. 44 filter paper, to retain precipitate.
16. Wash precipitate with hot distilled water until the washings are free from chloride, as indicated by the absence of turbidity when a drop is tested with silver nitrate solution.
17. Transfer the filter paper and precipitate to a previously ignited and weighed porcelain or silica crucible.
18. Place crucible and contents in a muffle furnace at room temperature. Raise the temperature to 800°C and leave for 15mins at 800°C .
19. When cool add a few drops of concentrated hydrochloric acid, then a few drops of concentrated sulphuric acid, ignite for a further 15 mins.
20. Cool in a dessicator. Weigh crucible and contents.

APPENDIX 2

A2.1 Atomic Absorption Spectrophotometry

In this technique the sample solution is delivered into the spray chamber as a fine mist in an air stream. It is then mixed in the burner, with fuel gas and the mixture is atomised on ignition. Pulsed light, from a hollow cathode lamp emitting the spectrum of the element to be determined; is passed through the flame and monochromator. The change in absorption of the light at an appropriate wavelength is detected electronically and recorded. The change in absorption is caused by the presence of free atoms of the element whose spectrum is being emitted and the degree of absorption is related to the number of atoms present (Beaty, 1978).

A2.2 X-ray Fluorescence Spectrometry

The rock samples were first crushed to a fine powder using a Tema swingmill with a tungsten carbide vial. Approximately 4.0g of powder were mixed with a few drops of PVA solution (MOWOIL) and pelletised in a hydraulic press at a pressure of 6 tons.

The pellets were introduced into a Phillips PW1400 X-ray fluorescence spectrometer. A Rhodium 3Kw X-ray tube was used, operating at 80 KV, 35mA.

Standardisation was achieved by means of a set of international sedimentary rock standards (Abbey, 1980) and a further selected set of sedimentary standards available at the University of Durham.

Corrections due to inter-element matrix effects were obtained from standards using a selected multiple regression technique. This was incorporated in a statistical package called MIDAS (Michigan Interactive

Data Analysis System), available from the University Computer Unit. These corrections were applied to the analysis of the unknown samples.

Trace elements were also analysed using X-ray fluorescence techniques. Standardisation was again achieved using a set of international rock standards (Abbey, 1980). Errors caused by matrix mass absorption and enhancement effects were minimised by correction for background radiation. The function used was peak/background minus one ($P/(B-1)$) (Anderman and Kemp, 1958), which was incorporated into a computer program available in the Geology Department, University of Durham, called TRATIO (XRF.TR). Both sides of the pelleted samples were analysed for major and trace elements to prevent any errors arising from the pelleting process, such as a build up of sodium on one side of the pellet. No such discrepancies were found.

A2.3 Semi-Quantitative X-Ray Mineralogy Analysis

Samples were prepared for X-ray analysis by mixing 0.9g of powdered rock sample with 0.1g of an internal standard, boehmite, in an agate pestle and mortar (Griffin, 1954). A little of the sample - boehmite mix was then smeared onto a glass slide using acetone.

This smear mount was placed in a Philips PW1130 2 kilowatt generator-diffractometer. Cobalt K radiation was used operating at 40 kV 20mA. The machine conditions used during analysis were from 2° to 18° , divergent slit 0.5° , receiving slit 0.1° , scatter slit 0.5° and from 13° to 45° divergent slit 1.0° , receiving slit 0.1° , scatter slit 1.0° . The goniometer scan speed was 1° of 20/min and the chart speed 10mm/min.

A scaled proportional detector was used together with pulse height analysis. X-ray diffraction scans were thus produced over the angular range 3° - 45° and the mineral phases present identified using the

standard J.C.P.D.S. index (Joint Committee for the Powder Diffraction Standards (1974)) and data from Thorey (1975) and Brindley and Brown (1980).

Semi-quantitative estimates were made on the clay minerals and on accessory minerals such as quartz and carbonates. These estimates utilized calibrations produced by Taylor (1971) and Smith (1978).

APPENDIX 3 PROGRAM TO CALCULATE SUCTION PRESSURES.

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DIMENSION HM1(100),HM2(200),HM(100),H2(100),DY(100),S(100)
LOGICAL*1 DATE(100,9),TIME(100,5)
WRITE(6,1010)
1010 FORMAT(/20X,' *** SUCTION PRESSURE CALCULATION. ***')
RHOM=13540
RHOW=1059.12
GRAV=9.81
WRITE(6,10)
10 FORMAT(20X,'SUCTION PRESSURE CALCULATION'//10X,'WHAT IS THE DEPTH O
1 INSTALLATION (IN METRES)'//10X,' OF THE PIEZOMETER TIP?:')
READ(5,20)DP
20 FORMAT(F5.2)
WRITE(6,30)
30 FORMAT(/10X,'GIVE HEIGHT OF DATUM ABOVE TOP OF SPOIL TIP (IN METRE
1S):')
READ(5,40)DZ
40 FORMAT(F6.3)
WRITE(6,50)
50 FORMAT(/10X,'HOW MANY SETS OF READINGS ARE THERE?')
READ(5,*)NREAD
NK=2
DO 100 I=1,NREAD
NK=NK+1
WRITE(6,60)I
60 FORMAT('10X,'FOR READING SET',I3,' GIVE DATE (EG 30-SEP-84)'//10X
1,' AND TIME (EG 22:35):')
READ(5,70)(DATE(I,J),J=1,9),(TIME(I,J),J=1,5)
70 FORMAT(9A1/5A1)
WRITE(6,80)
80 FORMAT('10X,'GIVE READUNGS IN METRES :')
IF(NK.NE.3)GOTO 85
NK=0
WRITE(6,82)
82 FORMAT(15X,'FIRST: MERCURY HEAD *ABOVE* DATUM IN PEIZOMETER ARM'
115X,' SECOND : HG HEAD *BELOW* DATUM IN OPEN ARM'//15X,' THIRD :
2 EXCESS HEAD OF WATER IN OPEN ARM')
85 READ(5,90)HM1(I),HM2(I),H2(I)
90 FORMAT(F6.3)
HM(I)=HM1(I)-HM2(I)
S(I)=GRAV*((H2(I)+DP+HM1(I)-DZ)*RHOW-HM(I)*RHOM)
S(I)=S(I)/1000.
100 CONTINUE
WRITE(6,200)
200 FORMAT('10X,'RES FROM P.W.P. MONITORING AT SHALLOW DEPTH'//10X,' IN
1 A MODEL COLLIERY SPOIL TIP.'//2X,'DATE',7X,'TIME',3X,'TOTOL HEAD
2 OF HG(M)',3X,'SUCTION PRESSURE (kN/m2)',3X,'POSITIVE P.W.P. (kN/m2
3)')
DO 300 I=1,NREAD
IF(S(I).GT.0.0)GOTO 230
WRITE(6,220)(DATE(I,J),J=1,9),(TIME(I,J),J=1,5),HM(I),S(I)
220 FORMAT(2X,9A1,4X,5A1,3X,F8.3,17X,F9.3)
GOTO 300
230 WRITE(6,240)(DATE(I,J),J=1,9),(TIME(I,J),J=1,5),HM(I),S(I)
240 FORMAT(2X,9A1,4X,5A1,3X,F8.3,51X,F9.3)
300 CONTINUE

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```
CALL FTNCMD('ASSIGN 8='PRINT*:',0)
WRITE(8,200)
DO 400 I=1,NREAD
IF(S(I).GT.0.0)GOTO 330
WRITE(8,220)(DATE(I,J),J=1,9).(TIME(I,J),J=1,5),HM(I),S(I)
GOTO 400
330 WRITE(8,240)(DATE(I,J),J=1,9).(TIME(I,J),J=1,5),HM(I),S(I)
400 CONTINUE
STOP
END
```

A4. DATA

KEY

NO. = SAMPLE NUMBER

POS. = SLOPE POSITION; 1= TOP, 2= MID, 3= TOE.

DEP. = SAMPLE DEPTH (CM)

MC. = MOISTURE CONTENT (%)

CL = CHLORIDE (ppm)

SO4 = SULPHATE (ppm)

EC = ELECTRICAL CONDUCTIVITY $\times 10^3$ US/CM

pH

SN = SEASON: 1, 4, 7= SPRING, 2, 5, 8= SUMMER, 3, 6, 9= WINTER

1-3= MALBY, 4-6= WOLSTANTON, 7-9= BILSTHORPE.

NO.	POS.	DEP.	MC.	Cl	S04	EC	pH	SN
5.	2.	2.00	12.8	258	14	.200	- .0	1.
6.	2.	2.00	12.2	258.	51.	.200	- .0	1.
7.	2.	3.00	14.7	713.	95.	.348	- .0	1.
8.	2.	4.00	13.2	513.	111.	.440	- .0	1.
9.	2.	5.00	11.2	870.	94.	.377	- .0	1.
20.	1.	1.00	10.3	430.	108.	.350	- .0	1.
21.	1.	2.00	6.7	-0.	194.	.730	- .0	1.
22.	1.	3.00	9.4	338.	146.	.490	- .0	1.
23.	1.	4.00	8.7	588.	148.	.480	- .0	1.
24.	1.	5.00	9.1	670.	194.	.570	- .0	1.
25.	1.	6.00	9.5	865.	223.	.530	- .0	1.
26.	1.	7.00	9.8	955.	221.	.600	- .0	1.
27.	1.	7.00	10.1	528.	235.	.638	- .0	1.
28.	1.	8.00	11.1	861.	261.	.649	- .0	1.
29.	1.	9.00	11.2	661.	274.	.710	- .0	1.
206.	1.	1.00	11.8	-0.	59.	2.65	7.4	1.
207.	1.	2.00	9.6	-0.	111.	4.30	7.4	1.
208.	1.	3.00	8.3	-0.	115.	3.04	7.4	1.
209.	1.	4.00	6.7	-0.	128.	.631	7.3	1.
210.	1.	5.00	8.5	-0.	88.	.448	7.5	1.
211.	1.	6.00	9.1	-0.	159.	.685	7.3	1.
212.	1.	10.00	12.5	-0.	151.	.440	7.1	1.
220.	2.	1.00	9.5	-0.	46.	.147	7.5	1.
221.	2.	2.00	11.6	-0.	89.	.245	7.4	1.
222.	2.	3.00	11.1	-0.	173.	.407	7.1	1.
223.	2.	4.00	10.3	-0.	59.	.162	7.6	1.
224.	2.	5.00	10.6	-0.	192.	.224	7.3	1.
225.	2.	6.00	10.6	-0.	111.	.251	7.3	1.
226.	2.	7.00	12.1	-0.	134.	.415	7.3	1.
227.	2.	8.00	10.4	-0.	119.	.519	7.2	1.
236.	3.	1.00	8.4	-0.	138.	.418	7.4	1.
237.	3.	2.00	12.1	-0.	78.	.269	7.5	1.
238.	3.	3.00	11.5	-0.	153.	.472	7.4	1.
239.	3.	4.00	9.2	-0.	172.	.562	7.1	1.
240.	3.	5.00	8.5	-0.	159.	.510	7.4	1.
241.	3.	6.00	8.8	-0.	145.	.463	7.3	1.
351.	1.	1.00	4.6	565.	228.	.708	- .0	2.
352.	1.	2.00	5.0	476.	226.	.615	- .0	2.
353.	1.	3.00	6.5	510.	224.	.612	- .0	2.
354.	1.	4.00	8.4	563.	258.	.775	- .0	2.
355.	1.	5.00	7.5	410.	261.	.65	- .0	2.
356.	1.	6.00	-0.0	525.	238.	.75	- .0	2.
357.	1.	7.00	-0.0	513.	295.	.78	- .0	2.
358.	1.	8.00	7.2	-0.	-0.	- .0	- .0	2.
359.	2.	1.00	-0.0	476.	188.	.54	- .0	2.
360.	2.	2.00	-0.0	356.	153.	.45	- .0	2.
361.	2.	3.00	-0.0	416.	229.	.65	- .0	2.
362.	2.	4.00	-0.0	523.	205.	.6	- .0	2.
363.	2.	5.00	-0.0	480.	197.	.75	- .0	2.
364.	2.	6.00	-0.0	395.	395.	- .0	- .0	2.
365.	3.	1.00	-0.0	365.	365.	- .0	- .0	2.
366.	3.	2.00	-0.0	113.	-0.	- .0	- .0	2.
367.	3.	3.00	8.3	115.	-0.	- .0	- .0	2.
368.	3.	4.00	10.5	135.	-0.	- .0	- .0	2.
369.	3.	5.00	9.7	153.	-0.	- .0	- .0	2.
370.	3.	6.00	8.6	265.	-0.	- .0	- .0	2.
371.	3.	7.00	8.9	545.	-0.	- .0	- .0	2.

NO.	POS.	DEP.	MC	Cl	SO4	EC	pH	SN
570.	1.	1.00	12.1	460.	-0.	-0	-0	3.
571.	1.	2.00	8.4	330.	-0.	-0	-0	3.
572.	1.	3.00	8.6	490.	-0.	-0	-0	3.
573.	1.	4.00	9.5	600.	-0.	-0	-0	3.
574.	1.	5.00	8.4	730.	-0.	-0	-0	3.
575.	1.	6.00	10.0	790.	-0.	-0	-0	3.
576.	1.	7.00	8.9	840.	-0.	-0	-0	3.
577.	2.	1.00	7.9	520.	-0.	-0	-0	3.
578.	2.	2.00	9.0	440.	-0.	-0	-0	3.
579.	2.	3.00	10.0	520.	-0.	-0	-0	3.
580.	2.	4.00	10.1	540.	-0.	-0	-0	3.
581.	2.	5.00	9.1	450.	-0.	-0	-0	3.
582.	2.	6.00	10.6	640.	-0.	-0	-0	3.
583.	2.	7.00	10.1	660.	-0.	-0	-0	3.
584.	2.	8.00	10.0	530.	-0.	-0	-0	3.
585.	2.	9.00	8.9	560.	-0.	-0	-0	3.
586.	2.	10.00	8.2	490.	-0.	-0	-0	3.
587.	2.	10.00	8.5	550.	-0.	-0	-0	3.
588.	3.	1.00	10.5	100.	-0.	-0	-0	3.
589.	3.	2.00	8.7	270.	-0.	-0	-0	3.
591.	3.	3.00	11.9	260.	-0.	-0	-0	3.
592.	3.	4.00	9.7	470.	-0.	-0	-0	3.
593.	3.	5.00	11.9	440.	-0.	-0	-0	3.
594.	3.	6.00	13.9	630.	-0.	-0	-0	3.
595.	3.	7.00	13.9	610.	-0.	-0	-0	3.
596.	3.	8.00	14.2	680.	-0.	-0	-0	3.
700.	1.	1.00	5.9	245.	117.	.339	6.9	1.
701.	1.	2.00	6.9	325.	160.	.468	6.9	1.
702.	1.	3.00	6.9	355.	91.	.498	6.9	1.
703.	1.	4.00	7.8	355.	71.	.438	7.0	1.
704.	1.	5.00	9.4	365.	96.	.522	6.9	1.
705.	1.	6.00	7.5	275.	98.	.479	6.9	1.
706.	2.	1.00	7.5	235.	81.	.360	6.8	1.
707.	2.	2.00	6.8	205.	61.	.315	7.0	1.
708.	2.	3.00	8.6	185.	71.	.395	7.0	1.
709.	2.	4.00	9.2	165.	65.	.323	7.2	1.
710.	2.	5.00	9.3	225.	61.	.359	7.2	1.
711.	2.	6.00	13.5	295.	111.	.501	6.9	1.
712.	2.	7.00	15.9	535.	113.	.575	7.0	1.
713.	2.	8.00	16.4	515.	132.	.638	6.8	1.
714.	3.	1.00	4.9	85.	46.	.225	7.1	1.
715.	3.	2.00	6.4	50.	49.	.238	6.9	1.
716.	3.	3.00	9.6	75.	59.	.253	7.0	1.
717.	3.	4.00	9.5	83.	84.	.396	7.0	1.
718.	3.	5.00	10.5	135.	66.	.298	7.1	1.
719.	3.	6.00	10.5	185.	81.	.382	7.1	1.
720.	3.	7.00	10.4	345.	109.	.535	6.9	1.
721.	3.	8.00	11.2	625.	92.	.528	7.0	1.
722.	3.	9.00	11.7	805.	92.	.501	7.1	1.
825.	1.	1.00	3.9	2138.	460.	1.31	-0	2.
826.	1.	2.00	4.9	538.	201.	1.52	-0	2.
827.	1.	3.00	5.6	468.	73.	.820	-0	2.
828.	1.	4.00	5.5	498.	97.	.857	-0	2.
829.	1.	5.00	4.6	92.	86.	.408	-0	2.
830.	2.	1.00	6.4	-0.	-0.	-0	-0	2.
831.	2.	2.00	8.6	128.	122.	.420	-0	2.
832.	2.	3.00	10.9	245.	236.	.707	-0	2.

NO.	POS.	DEP.	MC	Cl	SO4	EC	pH	SN
833.	2.	4.00	7.7	30.	326.	.354	-.0	2.
834.	2.	5.00	6.8	72.	102.	.284	-.0	2.
835.	3.	1.00	4.5	34.	92.	.318	-.0	2.
836.	3.	2.00	5.3	19.	108.	.329	-.0	2.
837.	3.	3.00	7.1	24.	120.	.315	-.0	2.
838.	3.	4.00	8.8	238.	216.	.659	-.0	2.
1000.	1.	1.00	8.2	350.	149.	.449	-.0	3.
1001.	1.	2.00	8.8	465.	255.	.690	-.0	3.
1002.	1.	3.00	6.9	1165.	224.	.703	-.0	3.
1003.	1.	4.00	7.7	925.	227.	.689	-.0	3.
1004.	1.	5.00	7.7	655.	179.	.572	-.0	3.
1005.	1.	6.00	8.2	665.	180.	.559	-.0	3.
1012.	2.	1.00	10.0	80.	58.	.177	-.0	3.
1013.	2.	2.00	9.2	120.	90.	.253	-.0	3.
1014.	2.	3.00	11.9	235.	21.	.369	-.0	3.
1015.	2.	4.00	11.5	425.	174.	.480	-.0	3.
1016.	2.	5.00	11.5	665.	182.	.570	-.0	3.
1017.	2.	6.00	9.3	545.	223.	.660	-.0	3.
1024.	3.	1.00	12.2	265.	90.	.236	-.0	3.
1025.	3.	2.00	10.7	105.	46.	.245	-.0	3.
1026.	3.	3.00	12.5	135.	61.	.221	-.0	3.
1027.	3.	4.00	15.1	135.	73.	.229	-.0	3.
1028.	3.	5.00	14.4	130.	68.	.226	-.0	3.
1029.	3.	6.00	16.2	60.	105.	.301	-.0	3.
1119.	1.	1.00	9.5	110.	165.	-.0	-.0	1.
1120.	1.	2.00	7.3	98.	268.	-.0	-.0	1.
1121.	1.	3.00	6.8	110.	182.	-.0	-.0	1.
1122.	1.	4.00	1.4	82.	105.	-.0	-.0	1.
1123.	1.	5.00	-0.0	115.	92.	-.0	-.0	1.
1124.	1.	6.00	8.5	120.	122.	-.0	-.0	1.
1125.	2.	1.00	10.3	180.	264.	-.0	-.0	1.
1126.	2.	2.00	10.6	250.	549.	-.0	-.0	1.
1127.	2.	3.00	4.9	370.	284.	-.0	-.0	1.
1128.	2.	4.00	6.4	390.	299.	-.0	-.0	1.
1129.	2.	5.00	6.7	470.	253.	-.0	-.0	1.
1130.	2.	6.00	6.6	510.	303.	-.0	-.0	1.
1131.	3.	1.00	7.3	75.	42.	-.0	-.0	1.
1132.	3.	2.00	8.8	70.	76.	-.0	-.0	1.
1133.	3.	3.00	8.4	904.	65.	-.0	-.0	1.
1134.	3.	4.00	7.3	140.	238.	-.0	-.0	1.
1135.	3.	5.00	7.2	250.	261.	-.0	-.0	1.
1136.	3.	6.00	8.7	330.	234.	-.0	-.0	1.
2100.	1.	1.00	2.0	22.	23.	.140	-.0	1.
2101.	1.	2.00	3.1	33.	19.	.140	-.0	1.
2102.	1.	3.00	-3.5	29.	34.	.171	-.0	1.
2103.	1.	4.00	3.3	29.	11.	.148	-.0	1.
2104.	1.	5.00	4.0	32.	-0.	.140	-.0	1.
2105.	1.	6.00	3.7	31.	-0.	.140	-.0	1.
2106.	2.	1.00	3.6	89.	59.	.259	-.0	1.
2107.	2.	2.00	13.6	105.	120.	.385	-.0	1.
2108.	2.	3.00	14.8	110.	159.	.420	-.0	1.
2109.	2.	4.00	13.1	60.	-0.	-.0	-.0	4.
2110.	3.	1.00	3.0	7.	-0.	-.0	-.0	4.
2111.	3.	2.00	3.4	15.	-0.	-.0	-.0	4.
2112.	3.	3.00	14.2	14.	-0.	-.0	-.0	4.
2113.	3.	4.00	8.0	13.	-0.	-.0	-.0	4.
2114.	3.	5.00	6.9	20.	-0.	-.0	-.0	4.

NO.	POS.	DEP	MC	Cl	SO4	EC	pH	SN
2115.	3.	6.00	5.1	9.	-0.	-0.	-0.	4.
2200.	1.	1.00	1.9	11.	-0.	-0.	-0.	5.
2201.	1.	2.00	2.5	9.	-0.	-0.	-0.	5.
2202.	1.	3.00	3.0	8.	-0.	-0.	-0.	5.
2203.	1.	4.00	3.1	17.	-0.	-0.	-0.	5.
2204.	2.	1.00	1.0	15.	-0.	-0.	-0.	5.
2205.	2.	2.00	2.0	13.	-0.	-0.	-0.	5.
2206.	2.	3.00	11.1	31.	-0.	-0.	-0.	5.
2207.	2.	4.00	8.6	32.	-0.	-0.	-0.	5.
2208.	3.	1.00	1.4	25.	-0.	-0.	-0.	5.
2209.	3.	2.00	1.5	20.	-0.	-0.	-0.	5.
2210.	3.	3.00	2.8	16.	-0.	-0.	-0.	5.
2211.	3.	4.00	3.8	17.	-0.	-0.	-0.	5.
2300.	1.	1.00	7.2	-0.	-0.	-0.	-0.	6.
2301.	1.	2.00	8.0	-0.	-0.	-0.	-0.	6.
2302.	1.	3.00	7.4	-0.	-0.	-0.	-0.	6.
2303.	1.	4.00	7.9	-0.	-0.	-0.	-0.	6.
2304.	1.	5.00	16.2	-0.	-0.	-0.	-0.	6.
2311.	2.	1.00	7.3	-0.	-0.	-0.	-0.	6.
2312.	2.	2.00	6.5	-0.	-0.	-0.	-0.	6.
2313.	2.	3.00	6.6	-0.	-0.	-0.	-0.	6.
2314.	2.	4.00	7.3	-0.	-0.	-0.	-0.	6.
2315.	2.	5.00	6.2	-0.	-0.	-0.	-0.	6.
2322.	3.	1.00	9.5	-0.	-0.	-0.	-0.	6.
2323.	3.	2.00	12.8	-0.	-0.	-0.	-0.	6.
2324.	3.	3.00	13.4	-0.	-0.	-0.	-0.	6.
2325.	3.	4.00	16.9	-0.	-0.	-0.	-0.	6.
2418.	1.	1.00	8.2	17.	84.	.227	6.8	4.
2419.	1.	2.00	13.3	24.	57.	.236	6.9	4.
2420.	1.	3.00	19.0	40.	176.	.241	7.0	4.
2421.	1.	4.00	14.1	46.	168.	.298	6.9	4.
2422.	1.	5.00	16.4	45.	203.	.487	7.0	4.
2423.	1.	6.00	16.3	53.	176.	.612	7.0	4.
2424.	2.	1.00	3.9	18.	-0.	.246	7.1	4.
2425.	2.	2.00	4.7	15.	-0.	.137	7.1	4.
2426.	2.	3.00	4.5	16.	-0.	.196	6.8	4.
2427.	2.	4.00	3.9	48.	-0.	.545	7.1	4.
2428.	2.	5.00	5.0	21.	78.	.210	7.1	4.
2429.	2.	6.00	4.7	19.	65.	.227	6.8	4.
2430.	3.	1.00	5.2	19.	-0.	.199	7.0	4.
2431.	3.	2.00	5.9	16.	-0.	.211	7.0	4.
2432.	3.	3.00	7.3	17.	-0.	.218	7.0	4.
2433.	3.	4.00	5.4	18.	-0.	.213	6.9	4.
2434.	3.	5.00	8.4	35.	85.	.294	7.1	4.
4025.	1.	1.00	-5.4	298.	-0.	1.02	-0.	8.
4026.	1.	2.00	3.7	57.	-0.	1.03	-0.	8.
4027.	1.	3.00	4.5	45.	-0.	2.01	-0.	8.
4028.	1.	4.00	4.0	65.	-0.	1.13	-0.	8.
4029.	1.	5.00	3.6	70.	-0.	1.43	-0.	8.
4030.	2.	1.00	3.8	32.	-0.	.608	-0.	8.
4031.	2.	2.00	4.5	54.	-0.	.398	-0.	8.
4032.	2.	3.00	6.5	36.	-0.	.345	-0.	8.
4033.	2.	4.00	6.3	56.	-0.	.520	-0.	8.
4034.	2.	5.00	8.5	52.	-0.	.442	-0.	8.
4035.	3.	1.00	4.3	589.	-0.	1.28	-0.	8.
4036.	3.	2.00	4.8	758.	-0.	1.20	-0.	8.
4037.	3.	3.00	4.8	818.	-0.	.970	-0.	8.

NO.	POS.	DEP	MC	Cl	SO4	EC	pH	SN
4300.	1.	1.00	15.9	-0.	-0.	-0	-0	9.
4301.	1.	2.00	14.0	-0.	-0.	-0	-0	9.
4302.	1.	3.00	12.7	-0.	-0.	-0	-0	9.
4303.	1.	4.00	12.2	-0.	-0.	-0	-0	9.
4304.	1.	5.00	10.3	-0.	-0.	-0	-0	9.
4311.	2.	1.00	13.6	-0.	-0.	-0	-0	9.
4312.	2.	2.00	10.6	-0.	-0.	-0	-0	9.
4313.	2.	3.00	11.4	-0.	-0.	-0	-0	9.
4314.	2.	4.00	11.7	-0.	-0.	-0	-0	9.
4315.	2.	5.00	11.1	-0.	-0.	-0	-0	9.
4322.	3.	1.00	14.8	-0.	-0.	-0	-0	9.
4323.	3.	2.00	12.8	-0.	-0.	-0	-0	9.
4324.	3.	3.00	22.8	-0.	-0.	-0	-0	9.
4325.	3.	4.00	12.6	-0.	-0.	-0	-0	9.
4326.	3.	5.00	15.1	-0.	-0.	-0	-0	9.
4418.	1.	1.00	12.0	1270.	604.	1.18	5.4	7.
4419.	1.	2.00	15.3	490.	422.	.822	4.8	7.
4420.	1.	3.00	13.5	280.	184.	.890	3.6	7.
4421.	1.	4.00	12.2	89.	816.	1.14	3.7	7.
4422.	1.	5.00	10.1	98.	600.	1.04	3.5	7.
4423.	1.	6.00	11.2	470.	782.	1.37	3.6	7.
4424.	2.	1.00	10.6	670.	225.	.620	3.7	7.
4425.	2.	2.00	10.8	680.	288.	.745	3.6	7.
4426.	2.	3.00	8.3	810.	201.	.510	4.8	7.
4427.	2.	4.00	11.2	890.	144.	.445	6.0	7.
4428.	2.	5.00	6.9	660.	105.	.354	6.3	7.
4429.	2.	6.00	5.5	640.	105.	.327	6.1	7.
4430.	3.	1.00	4.6	990.	134.	.578	4.5	7.
4431.	3.	2.00	15.9	990.	134.	.920	3.8	7.
4432.	3.	3.00	9.2	-0.	-0.	-0	-0	7.

NO.	POS.	DEP.	MC	Cl	SO4	EC	pH	SN
810.	1.	1.0	0.6	12740.	1056.	4.25	-.0	2.
811.	1.	2.0	1.9	11990.	734.	3.80	-.0	2.
812.	1.	3.0	2.3	6790.	755.	2.48	-.0	2.
813.	1.	4.0	3.4	690.	-0.	.671	-.0	2.
814.	1.	5.0	3.6	1540.	415.	1.10	-.0	2.
815.	2.	1.0	0.4	110.	276.	.599	-.0	2.
816.	2.	2.0	1.2	77.	261.	.570	-.0	2.
817.	2.	3.0	3.0	44.	290.	.655	-.0	2.
818.	2.	4.0	3.4	2590.	432.	1.35	-.0	2.
819.	2.	5.0	4.2	38.	298.	.719	-.0	2.
820.	3.	1.0	0.7	173.	324.	.794	-.0	2.
821.	3.	2.0	3.1	36.	210.	.565	-.0	2.
822.	3.	3.0	0.0	19.	151.	.329	-.0	2.
823.	3.	4.0	4.7	18.	134.	.240	-.0	2.
824.	3.	5.0	4.7	15.	86.	.245	-.0	2.
1006.	1.	1.0	12.1	125.	58.	.192	-.0	3.
1007.	1.	2.0	10.2	115.	67.	.201	-.0	3.
1008.	1.	3.0	10.2	155.	61.	.214	-.0	3.
1009.	1.	4.0	10.3	95.	89.	.197	-.0	3.
1010.	1.	5.0	10.9	205.	47.	.248	-.0	3.
1011.	1.	6.0	11.4	245.	96.	.277	-.0	3.
1018.	2.	1.0	17.1	195.	70.	.223	-.0	3.
1019.	2.	2.0	14.7	235.	106.	.332	-.0	3.
1020.	2.	3.0	12.4	185.	172.	.390	-.0	3.
1021.	2.	4.0	12.2	255.	362.	.750	-.0	3.
1022.	2.	5.0	11.9	235.	207.	.505	-.0	3.
1023.	2.	6.0	11.2	365.	386.	.840	-.0	3.
1030.	3.	1.0	11.8	75.	100.	.229	-.0	3.
1031.	3.	2.0	14.6	64.	87.	.214	-.0	3.
1032.	3.	3.0	10.1	45.	109.	.255	-.0	3.
1033.	3.	4.0	8.6	49.	91.	.233	-.0	3.
1034.	3.	5.0	10.4	39.	104.	.289	-.0	3.
1035.	3.	6.0	10.1	35.	213.	.495	-.0	3.
1101.	1.	1.0	9.8	90.	104.	.255	-.0	1.
1102.	1.	2.0	8.6	115.	94.	.232	-.0	1.
1103.	1.	3.0	7.0	150.	132.	.275	-.0	1.
1104.	1.	4.0	7.2	170.	78.	.270	-.0	1.
1105.	1.	5.0	5.5	200.	145.	.918	-.0	1.
1106.	1.	6.0	4.5	190.	188.	.290	-.0	1.
1107.	2.	1.0	15.1	50.	126.	.243	-.0	1.
1108.	2.	2.0	13.1	50.	86.	.213	-.0	1.
1109.	2.	3.0	10.5	45.	71.	.185	-.0	1.
1110.	2.	4.0	9.1	35.	163.	.331	-.0	1.
1111.	2.	5.0	8.9	37.	132.	.280	-.0	1.
1112.	2.	6.0	8.1	46.	105.	.229	-.0	1.
1113.	3.	1.0	10.6	42.	109.	.213	-.0	1.
1114.	3.	2.0	8.3	40.	236.	.421	-.0	1.
1115.	3.	3.0	6.6	62.	140.	.271	-.0	1.
1116.	3.	4.0	11.6	54.	126.	.213	-.0	1.
1117.	3.	5.0	10.1	45.	96.	.213	-.0	1.
1118.	3.	6.0	10.9	61.	57.	.171	-.0	1.
2212.	1.	1.0	0.2	21.	-0.	-0	-.0	5.
2213.	1.	2.0	0.6	20.	-0.	-0	-.0	5.
2214.	1.	3.0	1.1	19.	-0.	-0	-.0	5.
2215.	1.	4.0	1.5	18.	-0.	-0	-.0	5.
2216.	1.	5.0	1.9	20.	-0.	-0	-.0	5.
2217.	2.	1.0	0.5	32.	-0.	-0	-.0	5.
2218.	2.	2.0	0.8	31.	-0.	-0	-.0	5.

NO.	POS.	DEP.	MC	Cl	SO4	EC	pH	SN
2219.	2.	3.0	1.3	31.	-0.	-0	-0	5.
2220.	2.	4.0	1.6	160.	23.	.148	-0	5.
2221.	2.	5.0	0.6	155.	11.	.148	-0	5.
2222.	3.	1.0	0.3	450.	108.	.350	-0	5.
2223.	3.	2.0	0.8	410.	116.	.390	-0	5.
2224.	3.	3.0	1.4	300.	76.	.280	-0	5.
2225.	3.	4.0	2.0	270.	67.	.268	-0	5.
2226.	3.	5.0	2.4	260.	57.	.245	-0	5.
2305.	1.	1.0	10.3	-0.	-0.	-0	-0	6.
2306.	1.	2.0	8.9	-0.	-0.	-0	-0	6.
2307.	1.	3.0	9.8	-0.	-0.	-0	-0	6.
2308.	1.	4.0	10.4	-0.	-0.	-0	-0	6.
2309.	1.	5.0	18.6	-0.	-0.	-0	-0	6.
2310.	1.	6.0	4.7	-0.	-0.	-0	-0	6.
2316.	2.	1.0	8.5	-0.	-0.	-0	-0	6.
2317.	2.	2.0	7.5	-0.	-0.	-0	-0	6.
2318.	2.	3.0	6.4	-0.	-0.	-0	-0	6.
2319.	2.	4.0	7.5	-0.	-0.	-0	-0	6.
2320.	2.	5.0	7.3	-0.	-0.	-0	-0	6.
2321.	2.	6.0	7.4	-0.	-0.	-0	-0	6.
2326.	3.	1.0	8.0	-0.	-0.	-0	-0	6.
2327.	3.	2.0	8.1	-0.	-0.	-0	-0	6.
2328.	3.	3.0	7.9	-0.	-0.	-0	-0	6.
2329.	3.	4.0	7.4	-0.	-0.	-0	-0	6.
2330.	3.	5.0	8.0	-0.	-0.	-0	-0	6.
2331.	3.	6.0	7.4	-0.	-0.	-0	-0	6.
2400.	1.	1.0	4.8	57.	347.	.618	6.8	4.
2401.	1.	2.0	8.4	18.	253.	.360	7.0	4.
2402.	1.	3.0	8.4	16.	15.	.165	7.0	4.
2403.	1.	4.0	9.0	14.	46.	.170	7.0	4.
2404.	1.	5.0	8.8	13.	65.	.210	6.9	4.
2405.	1.	6.0	9.3	16.	-0.	.135	7.1	4.
2406.	2.	1.0	3.8	13.	-0.	.139	7.0	4.
2407.	2.	2.0	5.4	10.	-0.	.112	7.1	4.
2408.	2.	3.0	5.5	10.	-0.	.139	7.0	4.
2409.	2.	4.0	4.7	16.	-0.	.110	7.0	4.
2410.	2.	5.0	4.9	18.	-0.	.155	7.1	4.
2411.	2.	6.0	4.7	12.	-0.	.143	7.1	4.
2412.	3.	1.0	5.0	19.	-0.	.168	6.9	4.
2413.	3.	2.0	4.9	12.	-0.	.174	6.9	4.
2414.	3.	3.0	3.7	13.	-0.	.136	6.9	4.
2415.	3.	4.0	5.2	20.	-0.	.127	7.0	4.
2416.	3.	5.0	5.2	11.	-0.	.148	7.0	4.
2417.	3.	6.0	5.6	25.	-0.	.329	7.0	4.
4010.	1.	1.0	0.7	2668.	355.	1.24	-0	6.
4011.	1.	2.0	2.1	1188.	407.	1.08	-0	8.
4012.	1.	3.0	2.6	828.	357.	0.9	-0	8.
4013.	1.	4.0	3.5	758.	301.	.919	-0	8.
4014.	1.	5.0	4.3	468.	215.	.658	-0	8.
4015.	2.	1.0	0.3	83.	107.	.330	-0	8.
4016.	2.	2.0	2.3	25.	161.	.435	-0	8.
4017.	2.	3.0	3.4	19.	-0.	.521	-0	8.
4018.	2.	4.0	3.4	23.	-3.	.682	-0	8.
4019.	2.	5.0	4.7	20.	-0.	.630	-0	8.
4020.	3.	1.0	0.1	32440.	-0.	7.75	-0	8.
4021.	3.	2.0	2.0	11940.	-0.	3.22	-0	8.

NO.	POS.	DEP.	MC	Cl	SO4	EC	pH	SN
4022.	3.	3.0	3.2	6888.	-0.	2.00	-0.0	8.
4023.	3.	4.0	3.9	4488.	-0.	1.71	-0.0	8.
4024.	3.	5.0	5.4	2888.	-0.	1.57	-0.0	8.
4305.	1.	1.0	13.9	-0.	-0.	-0.	-0.0	8.
4306.	1.	2.0	16.4	-0.	-0.	-0.	-0.0	9.
4307.	1.	3.0	17.0	-0.	-0.	-0.	-0.0	9.
4308.	1.	4.0	16.1	-0.	-0.	-0.	-0.0	9.
4309.	1.	5.0	18.8	-0.	-0.	-0.	-0.0	9.
4310.	1.	6.0	17.1	-0.	-0.	-0.	-0.0	9.
4316.	2.	1.0	17.8	-0.	-0.	-0.	-0.0	9.
4317.	2.	2.0	14.2	-0.	-0.	-0.	-0.0	9.
4318.	2.	3.0	13.4	-0.	-0.	-0.	-0.0	9.
4319.	2.	4.0	13.4	-0.	-0.	-0.	-0.0	9.
4320.	2.	5.0	10.4	-0.	-0.	-0.	-0.0	9.
4321.	2.	6.0	-0.0	-0.	-0.	-0.	-0.0	9.
4327.	3.	1.0	18.2	-0.	-0.	-0.	-0.0	9.
4328.	3.	2.0	18.6	-0.	-0.	-0.	-0.0	9.
4329.	3.	3.0	17.8	-0.	-0.	-0.	-0.0	9.
4330.	3.	4.0	16.4	-0.	-0.	-0.	-0.0	9.
4331.	3.	5.0	14.2	-0.	-0.	-0.	-0.0	9.
4332.	3.	6.0	14.8	-0.	-0.	-0.	-0.0	9.
4400.	1.	1.0	6.7	2640.	552.	1.42	6.3	7.
4401.	1.	2.0	9.4	149.	449.	1.22	6.3	7.
4402.	1.	3.0	10.3	950.	468.	1.20	5.6	7.
4403.	1.	4.0	11.6	960.	833.	.098	5.8	7.
4404.	1.	5.0	12.7	780.	445.	1.00	5.2	7.
4405.	1.	6.0	12.7	720.	503.	1.10	4.4	7.
4406.	2.	1.0	5.3	280.	226.	.649	3.2	7.
4407.	2.	2.0	9.6	45.	-0.	1.80	2.8	7.
4408.	2.	3.0	10.4	72.	264.	.641	3.4	7.
4409.	2.	4.0	11.7	55.	464.	1.00	3.1	7.
4410.	2.	5.0	10.0	35.	695.	1.29	3.1	7.
4411.	2.	6.0	10.3	85.	779.	1.38	3.1	7.
4412.	3.	1.0	6.9	56.	220.	.680	3.0	7.
4413.	3.	2.0	12.6	50.	134.	.505	3.2	7.
4414.	3.	3.0	11.2	28.	307.	.755	3.0	7.
4415.	3.	4.0	10.6	36.	700.	1.23	3.0	7.
4416.	3.	5.0	11.6	75.	940.	1.51	3.1	7.
4417.	3.	6.0	11.3	52.	1526.	2.51	2.9	7.

