THE UNIVERSITY OF NOTTINGHAM

School of Chemical, Environmental and Mining Engineering

AN INVESTIGATION OF THE GEOCHEMISTRY AND PETROLOGY OF CANAL SEDIMENTS

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Abstract

Canals are artificial waterways, which are distinct from natural aquatic systems. As a result of their industrial heritage they have experienced high loadings of anthropogenic material, and consequently their sediments tend to have a bulk composition that is distinct from natural sediment. It is therefore expected that the geochemical behaviour of canal sediment may deviate significantly from that of natural sediment. This study investigates and contrasts the geochemistry and petrology of a rural and urban canal sediment, in order to determine the influence of anthropogenic material upon the urban sediment and to gain an understanding of the diagenetic processes operating within the sediments.

Sediment cores were collected from an urban canal in Birmingham and a rural canal in Leicestershire. The cores were analysed at 1cm intervals in order to build up 24cm depth profiles of their bulk chemistry, metal speciation and porewater chemistry. The petrology of both the sediments was analysed by CryoSEM in order to determine their *in situ* petrology.

The results have shown that the introduction of anthropogenic material to the urban canal has produced sediment that is chemically and mineralogically distinct from natural sediments. The bulk urban sediment contains elevated metal and organic matter loadings, and a significant proportion of its particulate matter is of anthropogenic origin (e.g. slag, fly ash, metal turnings) and is therefore not typical of clastic material in natural sediments. Rural sediment has not been subject to inputs of such material and therefore it has a bulk chemistry of natural materials such as clay, sand, silt and organic matter which is similar to that which is typically observed in natural sediments.

The petrological investigation of rural and urban canal sediment has shown that they have distinct authigenic mineralogies. The reduced iron phosphate, vivianite ($Fe_3(PO_4)_2.8H_2O$) is the most abundant authigenic mineral in urban sediment, as a result of its elevated organic matter and iron concentrations, while in the rural sediment, pyrite (FeS_2) is predominant.

In order to choose an appropriate scheme for the investigation of speciation in contaminated urban canal sediment, two different sequential extraction schemes were investigated by CryoSEM. The results revealed that they do not yield meaningful speciation results for urban canal sediment. In particular, the application of an oxalic acid buffer to extract oxides resulted in the formation of insoluble oxalates, and the exhaustion of the pH buffering capacity of the extraction reagents used to extract carbonates, resulted in the incomplete dissolution of calcite. The abundance of non-typical sediment components in urban canal sediment highlights the importance of investigating sediment mineralogy prior to the application of sequential extraction techniques.

The porewater chemistry was in broad agreement with the observed petrology and, in the case of the urban site, the data provides evidence of sediment disturbance. The periodic resuspension of the sediment by boat traffic results in a significant change to the surface porewater chemistry of iron and sulphate in the urban sediment and results in changes to the stability of certain authigenic phases, most notably vivianite. In the rural sediment, although physical disturbance of the sediment was observed, there was no chemical evidence in the porewater results. However, it does perhaps subtly enhance the organic matter degradation processes that are occurring, although this could not be confirmed by the results of this investigation.

The differences in the authigenic mineral assemblages of rural and urban canal sediment are the result of differences in their diagenetic paths. In the rural sediment, the relatively low organic matter and iron loadings result in a diagenesis dominated by sulphate and iron reduction; the abundance of pyrite in this sediment is evidence that sulphate reduction is the predominant process. In the urban sediment, the co-existence of vivianite and iron monosulphides implies that iron reduction is dominating the oxidation of organic matter in the sediment and occurring simultaneously with sulphate reduction.

The application of conceptual models of diagenesis, based on porewater studies of natural sediments, can be used to adequately describe the processes that are occurring in the rural canal sediment. However, the periodic physical disturbance and influx of material to urban canal sediment from pollution events prevents the development of steady state conditions. As a result of this, and the nature of the solid material, the diagenetic path observed in the urban sediment is quite distinct from that observed in natural sediments, and simple steady state models are inappropriate for its interpretation.

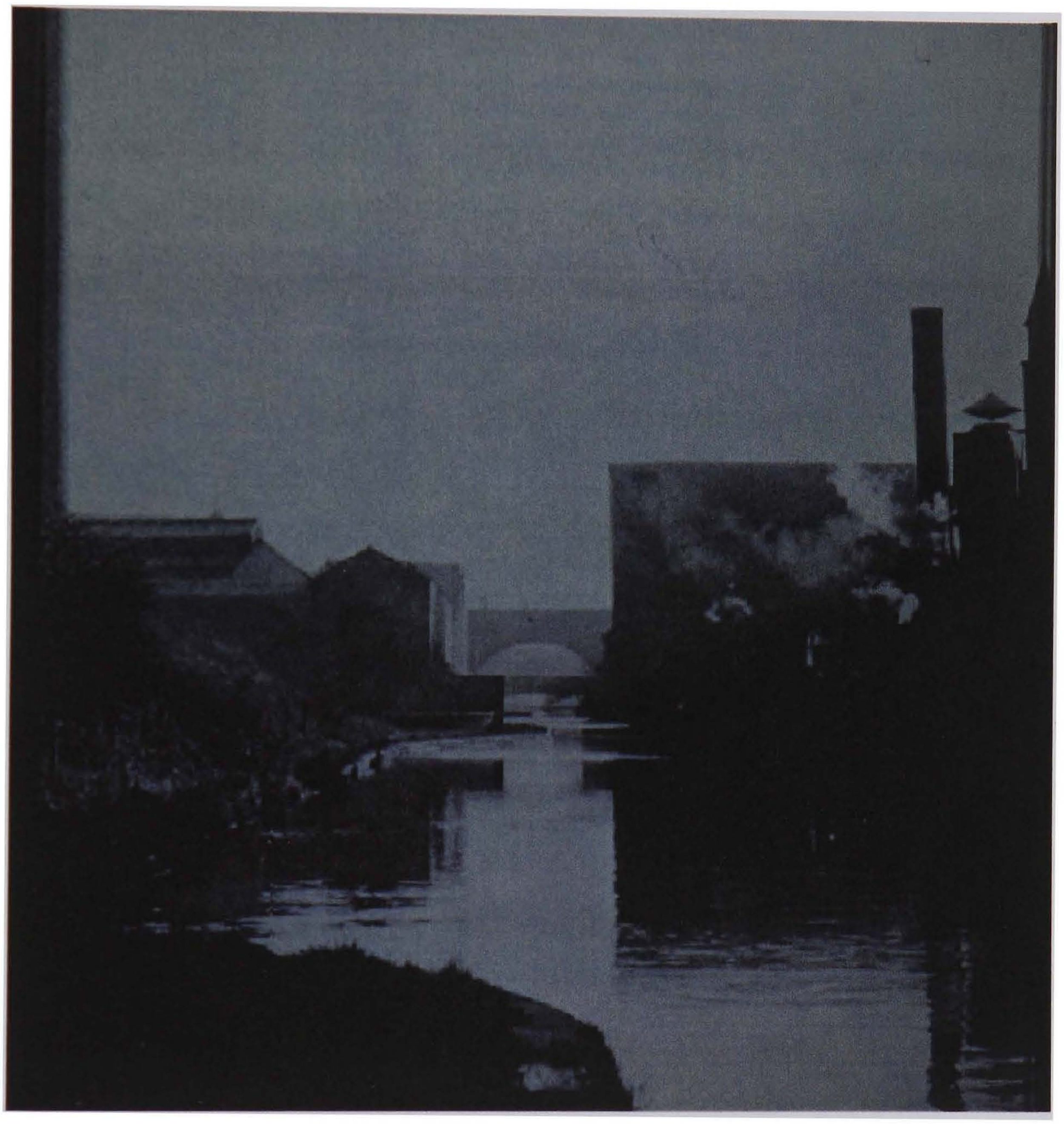

Figure 1.1: A photo of the Birmingham Maninline Canal, (Hadfield, 1969)

1. Introduction

Canals are defined as artificial waterways for inland navigation, and were first constructed in the United Kingdom during 18th century. The resultant canal network provided the backbone to Britain's industrial infrastructure until it was superseded by the railway system in the middle of the 19th century (Paget-Tomlinson, 1993). Industrial centres, like Birmingham and the Black Country, developed around their canal networks as industries located themselves along canal banks in order to take full advantage of the cheap transport they provided (Figure 1.1). Unfortunately, canals were also used as a repository for waste and sewage by bank side industries and this, together with the discards of the formerly intensive boat traffic, has led to the accumulation of contaminated sediments on the canal bed.

Today, few active industrial works remain close to canal banks, and canals are increasingly viewed as a land and water based leisure amenity. In city centres canals are often at the heart of urban renewal schemes, which are replacing canal side industry with pubs, restaurants, shops, parks and new residential estates. Outside cities, British Waterways are making considerable efforts to transform canals into leisure waterways, by improving towpaths and the surroundings in order to encourage their use for boating and fishing. The use of canals for such purposes depends principally upon their water quality, and a major threat to water quality comes from contaminated sediment.

Sediment geochemistry and petrology has been widely used as a means of assessing and characterising contamination (Carignan and Nriagu, 1985; Parkman et al., 1996; Salomons et al., 1987; Shaw et al., 1990). However, such studies have typically focused on the natural sediments of rivers, lakes, estuaries and oceans. Canal sediment is distinct from natural sediment because it is predominantly composed of anthropogenic and biogenic inputs. To begin an assessment of the threat posed to water quality by contaminated canal sediments, a greater understanding of the sediment is required, in particular:

- The processes operating between the sediment and the water column

- The nature of contamination within the sediment

1.1. Research Aims

This project investigates the inorganic geochemistry and petrology of canal sediment with the specific aims of:

1. Understanding the early diagenetic processes operating within the sediment. These processes are important because they reflect fluxes to and from the sediment.
2. Assessing the influence of anthropogenic material upon the geochemistry and petrology of canal sediment. This is a major component of urban canal sediment, and its nature and influence upon the geochemistry and petrology of sediments has not previously been investigated in detail.
3. Evaluating the applicability of techniques designed for use on natural sediments to canal sediments.

1.2. Research Objectives

In order to achieve the research aims the following objectives were set.

1. A combined petrographic and geochemical study of canal sediments' solid components.
2. An investigation of porewater chemistry over seasonal intervals as an indicator of the early diagenetic processes operating in canal sediment.
3. A site comparison between a relatively clean rural canal in Leicestershire and a highly contaminated urban canal in Birmingham, interpreted through comparison with existing studies of sediments.

1.3. Rationale for the Project

When this research was initiated in 1996 all previous research into canal sediments had used bulk chemical and physical analysis to assess the degree to which it was contaminated. In contrast to the work on canal sediment, studies of contaminated natural sediments had used petrographic analysis, porewater chemistry and applied more detailed chemical techniques to the sediment in order to assess the in-situ speciation of metals and the early diagenetic processes involved in their fixation. It was apparent that such an investigation of canal sediment could augment the existing studies and provide an interesting opportunity to investigate a predominantly anthropogenic sediment.

1.3.1. Previous Research

Geochemical research into urban canal sediment in the United Kingdom developed in the early 1990's in response the new 'Collection and Disposal of Waste Regulations 1988', which classified dredged sediments as "waste to be treated as industrial waste" for the first time. This required that dredged sediment be treated under the 'Control of Pollution Act 1974', which has now been superseded by 'The Environmental Protection Act 1990'. As a result of this legislation British Waterways, who manage the British canal network, are subject to a 'Duty of Care', which requires them to treat canal sediment in the following way:

1. Prior to disposal, dredged sediment needs to be chemically analysed.
2. The analysis has to be interpreted against existing guidance to assess it against the following Regulatory Requirements (based on guidance from the metropolitan waste authorities)
    a. If the waste does meet the requirements, it can be disposed of under exemption from waste licensing.
    b. If the waste does not meet the requirements, it is defined as "special waste" and has to be disposed of to a licensed site.
3. British Waterways then has to ensure deposits of "special waste" do not cause environmental harm and carry out limited site monitoring.

(Beckwith and Smith, 1999; Tromans, 1991)

Prior to the introduction of this legislation, most dredged sediment was spread onto the canal bank, at very low cost. The legal requirements introduced by the 'Duty of Care' legislation resulted in a massive increase to the cost of dredged sediment disposal. In response to this increase in cost, engineers working for, or in conjunction with, those responsible for the management and maintenance of the canal networks began to investigate the sediment. Their studies used bulk analysis of sediment sampled at intervals over entire canals or urban canal networks; in order to categorise the extent and nature of contamination, and to look for possible engineering solutions to the problem of disposal.

The highly contaminated nature of urban canal sediments has been established in several surveys. A study of Birmingham canals (Bromhead and Beckwith, 1994) showed that the sediments contained significant proportions of the heavy metals arsenic, lead, cadmium, copper, nickel, zinc and chromium and 65% of samples exceeded Dutch category C guideline values, for which clean-up is recommended. Studies assessing the extent and nature of heavy metal contamination in urban canal networks have also been conducted in Holland (Bijlsma et al., 1996; Jacobs and Sluis, 1993; Kelderman et al., 1991), Belgium (Seuntjens et al., 1995), Venice (Donazzolo et al., 1984) and Canada (Galvez-Cloutier and Dube, 1998a). These countries are experiencing similar pressures from environmental legislation to manage and improve canal sediment and water quality, and they also show that urban canal sediment is heavily enriched with heavy metals and organic contaminants.

The above studies have used total concentrations to assess the contamination of the sediment. They provide a good starting point for further analysis of the contamination. However, more detailed techniques for sediment analysis have been applied to natural sediments in order to assess the processes and phases of metal fixation (Froelich et al., 1979; Davison et al., 1997; Davison et al., 1991; Wersin et al., 1991; Parkman et al., 1996; Shaw et al., 1990; Williams, 1992; Morfett et al, 1988), these include:

- Sequential extraction
- Petrographic analysis coupled with sequential extraction
- Porewater analysis

Environmental scientists have begun to apply such techniques to canal sediment in an attempt to understand the environmental behaviour of the contaminants held within it (Boult and Rebbeck, 1999, Argese et al., 1997;

Boyd et al, 1999). These studies continue to focus on aspects of the sediment pertinent to the remediation and management of its contamination.

Sequential extraction schemes, such as that of Tessier et al., (1979), have been applied to canal sediments in order to determine the speciation of their contaminant metal content (Yong et al., 1995). The speciation results obtained by these studies quantified the distribution of each contaminant metal amongst its chemical forms, or species. They used this information to assess:

a. The bio-availability of the contaminant metals (Perin et al., 1997),
b. The probable response of the metal binding phases to changes in their physio-chemical environment (e.g. as a result of dredging) (Argese et al., 1997)
c. Optimum remediation or disposal mechanisms for the sediment (Galvez-Cloutier and Dube, 1998b).

Speciation studies of natural sediments have shown the importance of maintaining the ambient conditions of the sediment, in particular its redox status, in order to prevent changes to the in-situ pattern of speciation (Cauwenberg and Maes, 1997; Kersten and Forstner, 1986; Kersten and Forstner, 1987; Rubio and Rauret, 1996; Wallmann et al., 1993). To overcome these problems, extractions are conducted in oxygen-free conditions. To date, no sequential extraction of canal sediment has maintained anoxic conditions throughout the extraction procedure. The speciation of oxidised canal sediment is useful for assessing possible ex-situ disposal strategies for sediment, but cannot be used to accurately determine the in-situ behaviour of metals.

The results of sequential extraction schemes are subject to uncertainties for a number of reasons. The results can be difficult to interpret as the reagents used to selectively dissolve the various metal binding phases may dissolve sediment components other than those predicted (Forstner, 1993). The interpretation of speciation results can be greatly improved by petrographic analysis of the sediment (Dodd et al. (in press)). A study of the Venice Lagoon and canals by Perin et al. (1997), and an investigation of the Lachine Canal in Canada by

Galvez-Cloutier and Dube (1998b), have both combined petrological investigations of the sediments with a sequential extraction, to gain an insight into contaminant speciation for the improvement of remediation strategies.

Porewater analysis, in conjunction with investigations of sediment chemistry and petrology, is used to gain an insight into the diagenetic processes occurring near the sediment water interface. Porewater analysis is useful because nearly undetectable changes in sediment composition cause easily measurable variations in porewater concentrations. Investigations of natural lake and river sediment have used porewater chemistry to assess their early diagenesis and the flux of nutrients and metals from the sediment to the water (Morfett et al., 1988; Song and Muller, 1995; Williams, 1992). To date only two studies of canal sediment porewater have been conducted, both on the sediments of the Manchester Ship Canal and one of its docks (Boult and Rebbeck, 1999; Boyd et al, 1999). Boult and Rebbeck, (1999) apply a sequential extraction scheme in conjunction with the analysis of porewater chemistry to investigate the effects of canal sediment on water quality. They compared the sediments of the Manchester Ship Canal with the sediment of a dock basin, Salford Quays, which has been isolated from the polluting discharges of the canal and aerated for eight years. They found that the Quay sediment still exerts a high oxygen demand, which prohibits life in the Quay and facilitates the transfer of soluble reduced metal ions from the sediment to the waters. These findings highlight the importance of a detailed understanding of the in-situ sediment, if attempts to remediate canal sediment are to be successful. In a more recent study Boyd et al, (1999) have investigated the porewater-sediment interactions in Salford Quay sediment to determine their effect upon the quality and composition of the water column.

Comprehensive investigations of natural sediments have combined petrographic observations and the results of chemical analysis, with calculations from porewater data of ion activity product and log-log stability diagrams, to assess early diagenetic processes and the solid phases controlling the porewater chemistry (Emerson, 1976; Wersin et al, 1991). These studies have attempted to maintain the ambient anaerobic conditions of the in-situ sediment to prevent changes in the sediment and its porewaters between sampling and analysis. The information obtained from these studies has then been used to gain an understanding of the sediment's interaction with overlying water. A study of this nature of canal sediment could improve the understanding of the nature and behaviour of contaminants held within it, and has the potential to consolidate the management of canal sediment and water quality.

1.4. The Study Area

This study was conducted on canals in the Midlands, at urban localities in Birmingham and The Black Country, and a rural locality near Ashby de la Zouch in Leicestershire. The Birmingham and Black Country canals, known as the Birmingham Canal Navigations (BCN), were selected as a good example of an urban canal network because of their historical association with industry. Two sites were chosen for sediment sampling within the BCN. The first was on the Old Main Line at Smethwick (SP 019889) and the second a site on the Walsall Canal at Great Bridge (SO 978927). A rural locality on the Ashby Canal at the village of Snarestone (SK 343092) was selected because the canal sediment was known to be relatively uncontaminated, and it was close to the BCN.

1.4.1. The Birmingham Canal Navigations

The BCN extends over much of Birmingham and from its inception it opened up the region, which had been poorly served by roads, facilitating its industrial development. Throughout the 19th century the BCN was able to cater for all the material and distribution needs of the developing industries in the area, becoming the arteries of Birmingham and the Black Country, carrying the lifeblood of its commerce and wealth (Nicholson, 1989).

1.4.1.1. The Geology and Geography of Birmingham and The Black Country

Birmingham, The Black Country and Wolverhampton together form the industrial West Midlands conurbation. This conurbation is situated on high ground 100-400m above sea level, which initially made access to the area by road difficult. The urban canal network in the West Midlands is largely isolated from the natural fluvial systems of the Rivers Trent, Tame and Avon.

The western edge of the Midlands is underlain by Carboniferous Coal Measures, which consist of a mixed sequence of mudstones, siltstones, sandstones, coal and clay earths. Groundwater within this formation has naturally high levels of dissolved salts and metals which discharges into the surface watercourses as baseflow (NRA, 1996).

At the Smethwick site, Triassic Sandstones from the Sherwood Sandstone group dominate the underlying geology. The sandstone is an undifferentiated red, pebbly and micaceous rock, interbedded with mud in the upper part and a pebble conglomerate in the lower part. The overlying drift is a Quaternary age glaciofluvial deposit, comprised of sand, gravel and till.

The underlying geology at the Great Bridge site is older, being Upper Carboniferous Mudstone from the Etruria Formation. The mudstone is interbedded with conglomerate and sandstone in the upper part and thin coal seams in the lower part. The area is underlain by the Middle Coal Measures, which were formerly mined in the region. The overlying drift is Quaternary and of glaciofluvial origin.

The underlying geology of the sites chosen for investigation can be expected to have only a minimal impact upon the sediment geochemistry.

1.4.1.2. The History of The Birmingham Canal Navigations

The intricate nature of the BCN network that exists today resulted from the intense competition of three rival canal companies each seeking to capture traffic from the other. At its peak the Network was comprised of 157 miles of canal, on ten different levels ranging from 64m to 163m O.D. and connected by 191 locks. Water to work the system, which is isolated from local rivers, was supplied from seven reservoirs, lifted and re-circulated by 22 pumping stations (Weaver, 1971). In the 19th century the Birmingham Canal Navigation Company, responsible for the network described it in these terms:

> *" The Birmingham Canal with its immense local trade, with its numerous branches traversing in every direction the richest and most enterprising Mineral District in the Kingdom, is without parallel, and must be judged of solely, with reference to its own peculiar circumstances. "*

(General Assembly Minute Book of the BCN, 9th November 1838) (Broadbridge, 1974).

The history of Birmingham Canal Network began in 1768 when the Birmingham Canal Company was authorised to build a canal from Aldersley (SJ 903011) on the Stafford and Worcestershire Canal, to Birmingham, comprising of 22.5 miles of canal and 29 locks. The first section, engineered by James Brindley, ran from Birmingham to Wednesbury (SO 985955) and was opened in November 1769. The whole canal was completed by 1772. As the route traversed coal- fields and an area of developing industry it was immediately successful (Nicholson, 1989).

In the early 1780's a battle was fought, both inside and outside parliament, between the Birmingham Canal Company and a group of rival promoters, for the right to build a canal from Birmingham to Fazeley (SK 201020). The Birmingham Canal Company won, and bought the rival promoters' company to become 'The Birmingham and Fazeley Canal Company' a name which changed in 1794 to 'The Birmingham Canal Navigations Company'. At this time the pressure of traffic on the existing canal forced improvements to be made, through the removal of three locks from either side of the peak at Smethwick (SP 019889). The network was also extended to reach Walsall (SP 030985) via the Ryders Green Locks (SO983922).

Apart from the Birmingham Canal Navigations Company, there were two other rival companies instrumental in the creation of the BCN. The Dudley and Stourbridge Company set up a rival route to the Stafford and Worcestershire canal between 1785-1792. They then extended their canal further in order to link it with the recently authorised Worcester and Birmingham Canal at Selly Oak (SP045822), providing the means for them to avoid the severe tolls exacted on them by the Birmingham Company for the use of the junction at Tipton (SO 950977). However this new canal included two tunnels, one of which (the Lappal tunnel) was cut through rock and continuously suffered subsidence and roof failure resulting in its frequent closure, and placing the Dudley Company under financial strain.

In the North of Birmingham, the Wryley & Essington Company completed a canal from Wolverhampton to Wryley (SJ 996072) in 1795. The company grew quickly and expanded to the Coventry Canal, with several branches added to serve the coalfields of Brownhills (SK 055055) and Cannock (SJ 960099). The Birmingham Canal Navigations Company also spread their network northwards, but ill feeling between the two companies meant the logical link between their canals was not made until 1840, when the Walsall Branch was built.

From the late 1790's to 1840 all three companies were increasingly prosperous as the area they served developed into one of the world's industrial centres. Branches were built and old canal lines improved. The most ambitious of these was that of the Birmingham Canal Navigations Company, which between 1825 and 1838 built a completely new main line between Tipton (SO 950977) and Birmingham, under the guidance of Thomas Telford. This reduced James Brindley's original canal from 22.5 miles to a little over 15 miles, by cutting through the hill at Smethwick to construct a straightened canal at one level. These improvements, plus connections with what is now the Grand Union Canal in Birmingham, put added congestion onto the top end of the Birmingham and Fazeley Canal. To relieve this congestion the Tame Valley Canal opened in 1844, from Wednesbury to the Birmingham and Fazeley Canal at Salford Bridge (SP099902).

In 1840 the Birmingham and the Wyrley & Essington Companies amalgamated and in 1864 the Dudley Company also joined the Birmingham Canal Navigations Company. Soon after this, the concern came under railway control but internal traffic, within Birmingham, was still encouraged and only external trade suffered from competition with the railways. Trade on the system continued to increase, resulting in the continued expansion of the network. At the end of the 19th century, goods carried on the BCN had risen to over 8.5 million tons annually, but thereafter it fell slowly away, and although over a million tons were still moved in the early 1950's, by the end of the 1960's it had fallen to almost nothing.

Today the BCN remains as a complex network of used and disused canals weaving through a diversity of landscapes. Only 100 miles of canal remain as navigable water, although just over 30 years ago 90% of the network was threatened with closure. The injection of time and money by the Inland Waters Association and local authorities, along with the emergence and enthusiasm of canal societies, has left the BCN with a future as a pleasure craft waterway and leisure resource accessible to large numbers of the public (GEOprojects, 1996).

1.4.1.3. The Old Main Line at Smethwick

The Old Main Line at Smethwick was chosen as the principal site for the collection of urban canal sediment. The sampling site was 50m east the Brasshouse Lane Bridge (SP 019889) and is shown in Figures 1.2a and 1.3. Following consultation with British Waterways this stretch of canal was chosen for investigation for three reasons:

- This stretch of canal has a history of association with heavy industry
- In recent years it has suffered contamination from a combined sewage outlet
- Today the canal is used by leisure boat traffic.

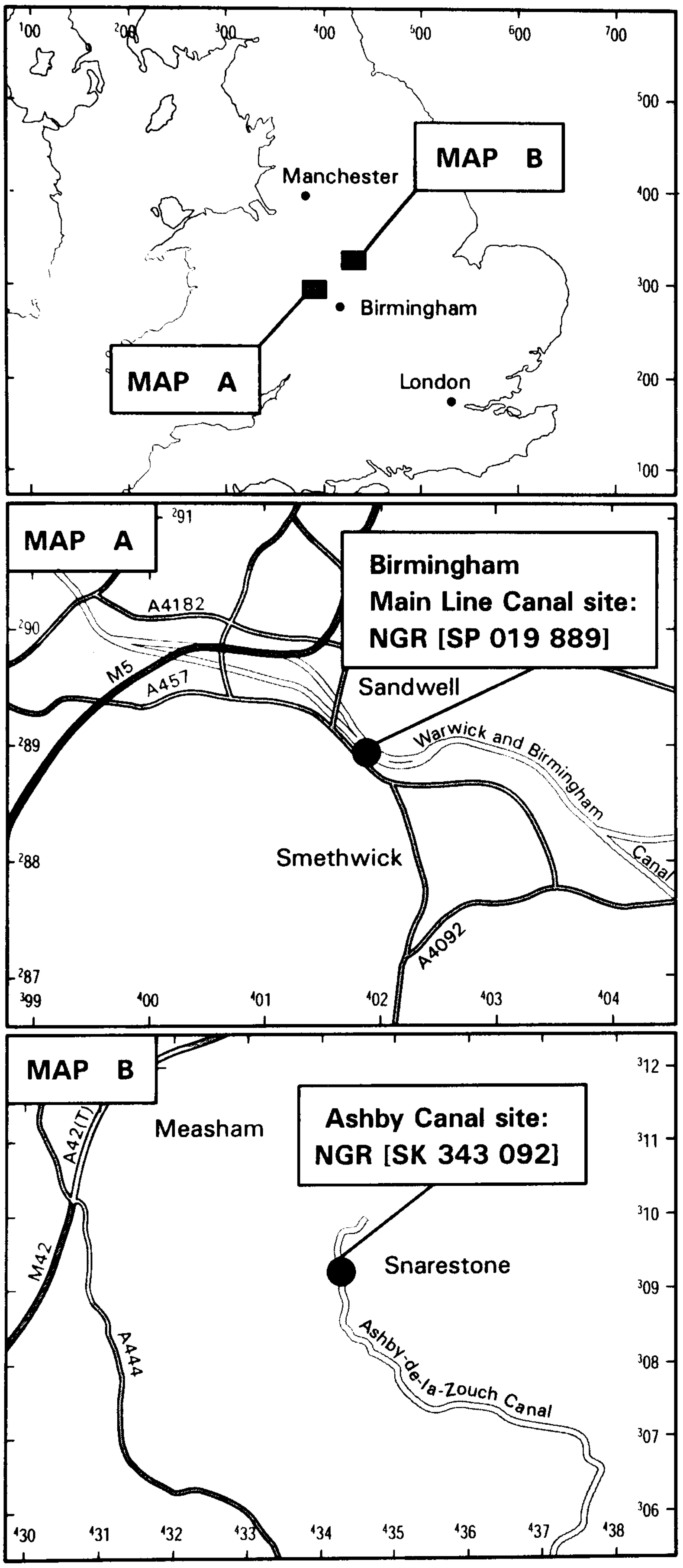

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Figure 1.2: Location map showing the location of the two canal sites in the UK. National Grid numbers are shown at the side of each figure and national grid references (NGR) are given for each site.

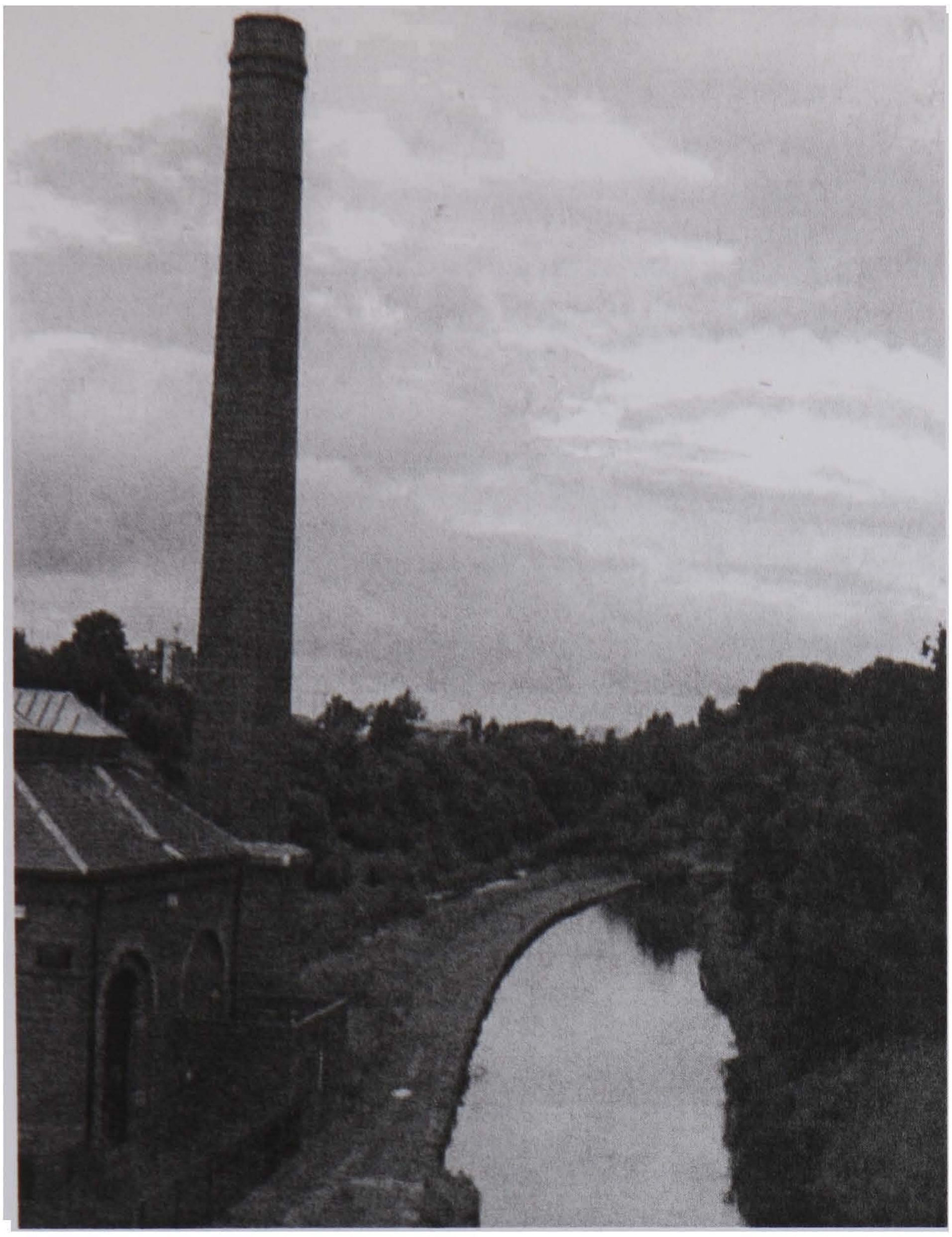


Figure 1.3: Image of Old Main Line Canal at the Smethwick sampling location

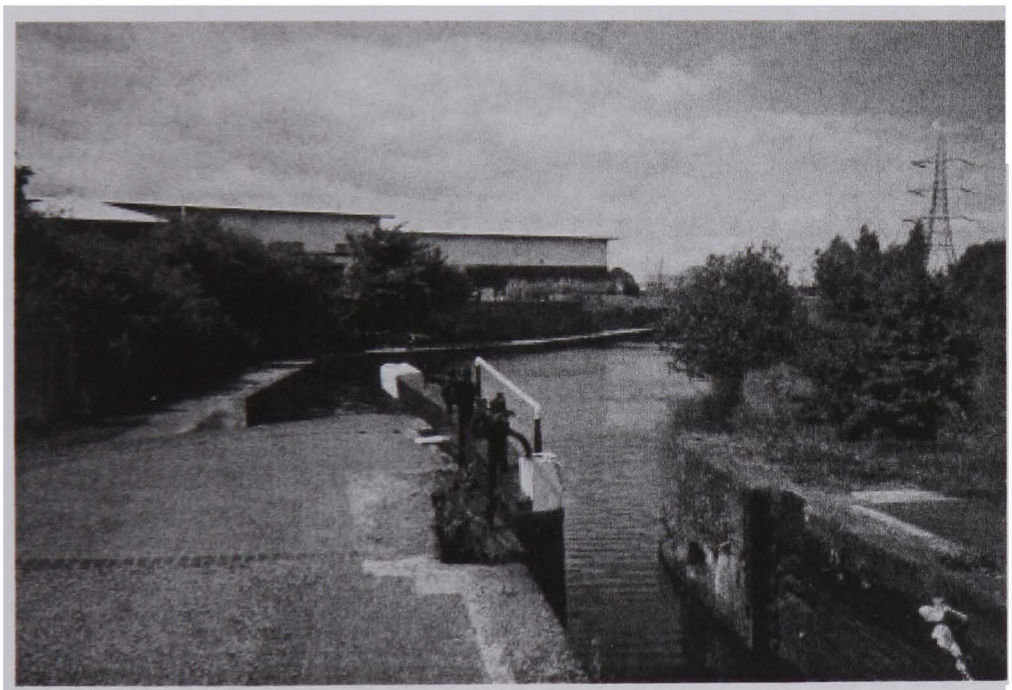


Figure 1.4: Image of The Walsall Canal at the Great Bridge sampling location

Figure 1.5: Image of The Ashby Canal at the Snarestone sampling location

Prior to the construction of Birmingham's first canal in 1769, Smethwick, three miles west of Birmingham, was a small hamlet (James Brindley's original canal was carried over the hill at Smethwick opening the area up to industry.)

Four years earlier in 1764, Matthew Boulton purchased a small mill in the portion of Smethwick known as Soho where he created his Soho Works, intended for the manufacture of small metal works. In 1774 James Watt joined Matthew Boulton as a partner at his Soho works, bringing with him the plans for an improved steam engine. Together they produced their first engine in 1775 and by 1796 demand for the engine was such that they built a foundry at the Soho site to produce the massive castings required for the engines.

By 1886 Smethwick was described in Kelly's Directory of Birmingham (1886) as an extensive and populous manufacturing district, containing various works and manufactories of great importance (Kelly, 1886). The industry in the area was largely either engineering, metal or glass works and the manufacture of lighthouse lights (Chapman, 1932). The first edition Ordnance Survey map of Smethwick, surveyed in 1886, shows the banks of the canal to the east of the sample site to be flanked by; four iron works, seven metal works (including brass and silver workings), a glass works, a gas works and an engineering works within a one mile radius. Many of these works had loading and unloading basins within their grounds. To the west, land use was predominantly residential. Today the residences are still there and a limited number of engineering works also remain in the area, most notably W. and T. Avery, Ltd. producing weighing appliances on the site of the former Soho Foundry.

The Environment Agency has classified the quality of canal water at Smethwick as poor, due to its high biological oxygen demand, low level of dissolved oxygen and high ammonia concentrations (Appendix 1.2, EA, 1997). This has resulted from a combined sewer overflow at Brasshouse Lane (SO 019889) supplying domestic and industrial effluent and road run off to the canal (EA, personal communication). The Environment Agency has assigned a

River Ecosystem (RE) Water Quality Objective (WQO) to all rivers and canals in England as a means of improving their water quality (Appendix 1.1); the stretch of canal at Smethwick has the lowest possible objective of RE5 (EA, 1997). The principal use of the canal today is for recreational boating.

1.4.1.4. The Walsall Canal at Great Bridge

The second site in the BCN was at Great Bridge, and this site was used in the initial stages of this study for both geochemical and petrological investigations of the sediment. The site is on the Walsall Canal down stream of Ryders Green Locks (SO 978927) and is shown in Figures 1.4. A first edition map of the area drawn in 1887 shows ten iron works and foundries at the canal side following its descent down the 8 locks, along with a substantial brick works, and immediately across from the sampling site there was a railway interchange (Ordnance Survey, 1887). This site was chosen for investigation following consultation with the principal engineer from the Black Country Development Corporation, because it was considered likely that contamination from the industries upstream of the eight locks would have been concentrated at the lowest level.

Today the canal is only used by leisure craft and the area surrounding the sample site has been completely reclaimed by the Black Country Development Corporation. Much of the heavy industry and the railway interchange have disappeared and have been replaced by light industry, in particular automotive component works. However stretches of this canal are still heavily industrialised. The Environment Agency has classified the water quality here as poor, with a River Ecosystem water quality objective of RE4 (Appendix 1.1 and 1.2, EA 1997).

1.4.2. The Ashby Canal, Leicestershire

The Ashby Canal in Leicestershire was chosen for the investigation of rural sediment, which was used to assess the differences between a relatively clean canal sediment and a heavily contaminated urban canal sediment.

1.4.2.1. The Geology and Geography of The Ashby Canal

The Ashby Canal runs through gently undulating land in Southern Leicestershire, used predominantly for arable and woodland, (NRA, 1996). The canal is largely isolated from the local natural fluvial systems of the Rivers Sence and Trent. However, at Snarestone the canal is dug into ground as it emerges from a tunnel and the sediment may therefore be affected by local fluctuations in the water table.

The underlying geology at Snarestone is Triassic sandstone from the Sherwood group, which dip below dolomitic silt and sandstone beds from the Merica Mudstone group. The overlying drift is a Quaternary glacial deposit of sand, gravel and boulder clay. The geology at Snarestone is broadly similar to that of the urban localities and would not be expected to have a significant effect upon the sediment chemistry.

1.4.2.2. The History of the Ashby Canal

The Ashby Canal was completed in 1802 and run by the Ashby Canal Company (Booth, 1973). Impetus to build the canal was provided by the owners of Leicestershire lime works and the new coalfields in Ashby de la Zouch (SK 356167), who wanted an outlet Southwards from their works. It was originally intended that the canal would join the River Trent at Burton to the Coventry Canal near Bedworth, but this plan was repeatedly shelved and never reached fruition. The Ashby Canal was constructed from the Coventry Canal to Moira (SK 166155) on one level. The canal did not make a profit for its first 20 years because while the canal was being built it was found that the new coalfields at Ashby Woulds were not as productive as had been hoped. This lack of income precluded the northward extension of the canal beyond Moira to the River Trent, which would have required expensive and complicated works including locks, reservoirs and pumping stations. A coal mine sunk at Moira in 1804 eventually produced coal of such high quality that it became widely demanded in London and the south of England, thus enabling the canal to go into profit (Nicholson, 1989).

In 1845 the Midland Railway bought the Ashby canal with the approval of all concerned, except the Coventry and Oxford Canal Companies who stood to lose a substantial amount of money in tolls from Moira's coal traffic. The two companies therefore negotiated a deal with the railway that enabled coal traffic from Moira to be maintained on the canal at a substantial level until the turn of the century.

Subsidence from the coal mines near Measham has caused great damage to the canal in this century, bringing about the abandonment of over 9 miles of canal. The canal now terminates just north of Snarestone and no longer carries any regular trade.

1.4.2.3. Snarestone

A site on the Ashby Canal at the village of Snarestone (SK 343092) (Figure 1.2b and 1.5) was selected for rural sediment sampling following consultation with British Waterways; their studies had shown that the sediment at this locality is clean, except for slightly elevated concentrations of zinc. The site chosen for sampling was 100m down stream of the Snarestone tunnel, 1km from the canal's terminus, at a stretch of bank that is in constant use for mooring of up to six boats.

The water quality at the site has been classified by the Environment Agency as fair, suitable for supporting coarse fish populations, with a long term objective to reach RE2, water of good quality suitable for all fish populations (Appendix 1.1 and 1.2, EA, 1997).

2. Methods

2.1. Methodology

This study investigates the geochemistry of metals in canal sediments through the chemical analysis of porewaters and sediments and petrographic analysis by Cryogenic Scanning Electron Microscope (CryoSEM). The chemical analysis of the sediments and porewaters was conducted at 1cm intervals on 25cm cores taken from a rural and urban canal over seasonal intervals producing depth concentration profiles. Nearly undetectable changes in sediment composition can produce easily measurable variations in porewater composition, and the depth profiles produced by the concentrations of ions in porewater are therefore useful in the interpretation of reactions occurring within the sediments. Sediment analysis provides quantification of the levels of metals in the sediments and semi-quantitative information on the sediment speciation. Information on the binding phases within the sediment was elucidated by direct petrographic analysis using CryoSEM.

Following a review of studies of natural sediments and consultation with the Institute of Fresh Water Ecology a sampling and analytical procedure was designed, and has been refined throughout this study. The procedure outlined below was considered a suitable compromise between the urgency of analysis, the nature and precision of analysis required, the availability of analytical techniques and the time and motion budget of the analyst.

2.2. Sampling Procedure

Two sampling sites were chosen for this study after consultation with British Waterways and the Black Country Development Corporation, and consideration of safety factors, accessibility and ease of sampling a 25cm long core:

1. The Birmingham Mainline Canal at Smethwick in Birmingham: an urban site known to be contaminated by both industrial and sewage effluents. (Grid reference: SP019889)
2. The Walsall Canal at Great Bridge between Birmingham and Wolverhampton: an urban site at the base of a suite of 8 locks called the Ryders Green Locks. (Grid reference: SO978927)
3. The Ashby Canal at Snarestone in Leicestershire: a rural site considered clean except for slight Zn contamination. (Grid reference: SK343092)

Sampling was conducted in the spring, summer, autumn and winter between the 11th May 1998 and 11th January 1999. On each occasion three 25cm cores were sampled; two separate cores for the analysis of anions and metals in their porewaters respectively, and a third reserve core used for additional sediment analysis. Due to the intensive nature of analysing the porewaters, and the time constraint placed upon analysis by the threat of oxidation, rural and urban samples were collected on consecutive weeks for seasonal porewater analysis. (Appendix 2)

2.2.1. Sampling Device

For the purposes of this study it was imperative that the sediment sampling method chosen resulted in minimal disturbance of the physical structure and properties of the sediment, and that the coring device itself could not cause contamination to the sediment or overlying water. With these criteria in mind and following an assessment of existing sediment coring devices, a corer was designed (Figure 2.1) with the following features:

- A top valve that allows water to escape as the core is taken and seals on removal setting up a vacuum which holds the sediment in the core and prevents mixing the waters.
- A choice of two bases;

  - A simple cutting edge for use with sediment consolidated enough to remain in the core by suction from the top valve alone, this usually sufficed.
  - A ball valve which could be closed prior to removal holding the sediment in the core while also preventing mixing with water and contact with oxygen (The use of the ball valve resulted in the loss of the lowermost 10cm of the sample).
- The corer was constructed from Perspex and P.T.F.E., materials that will not result in contamination of the sample.
- The corer incorporated a detachable Perspex tube which could be removed from the corer, sealed with bungs and used for storage prior to analysis.

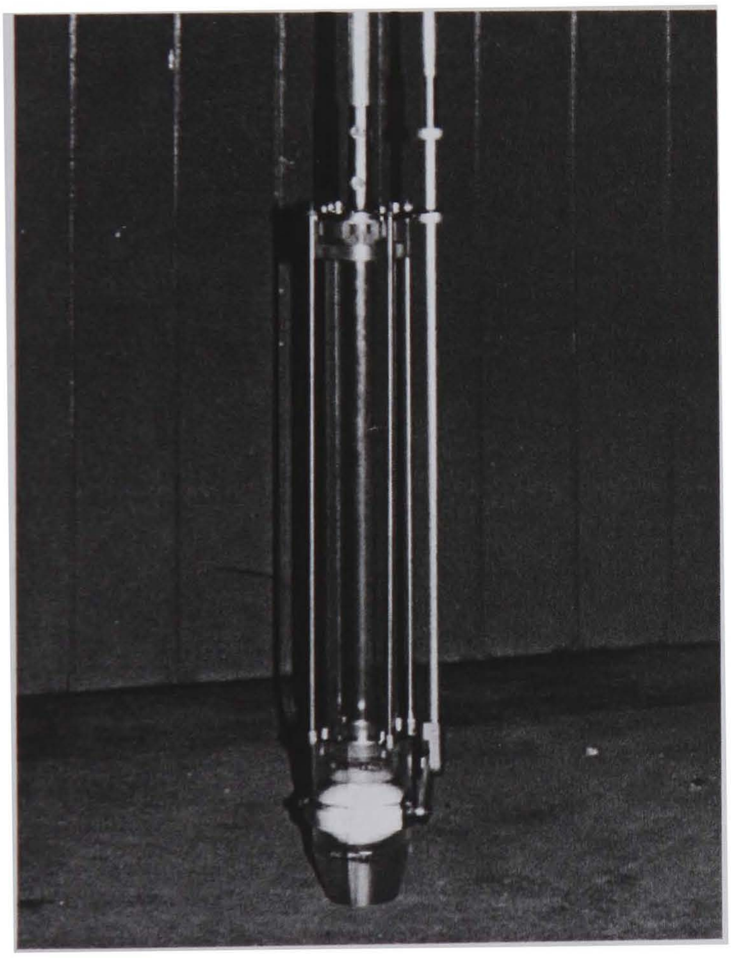


Figure 2.1: The Core Barrel Showing Upper Valve and Lower Ball Valve

2.2.2. Collecting the Sample

Before sampling the sediment, two water samples were collected in new 250ml polypropylene bottles that had first been rinsed several times with canal water.

The water temperature was recorded using a mercury thermometer, incorporating 1°C graduations from -10°C to 110°C.

The pH of the water was measured using a hand-held Jenway 3051 pH meter with a combination Gelplas electrode, calibrated at 20°C using buffers at pH 4.00±0.02 and pH7.00±0.02, during the measurement the temperature gauge on the pH meter was adjusted to the pre-measured canal water temperature.

Cores of sediment of at least 25cm in length were collected from the canal, by carefully lowering the corer into sediment from a standing position on the bank, ensuring the corer was vertical (Figure 2.2). Immediately upon removal, a bung was placed in the base of the Perspex core (Figure 2.3), the top valve was then removed and replaced with a bung; the sample was then sealed from ambient oxidising conditions for transport back to the laboratory. Cores were transported to the laboratory upright, in an insulated box. Once in the laboratory, samples were either processed immediately or stored at 4°C in a refrigerator prior to analysis.

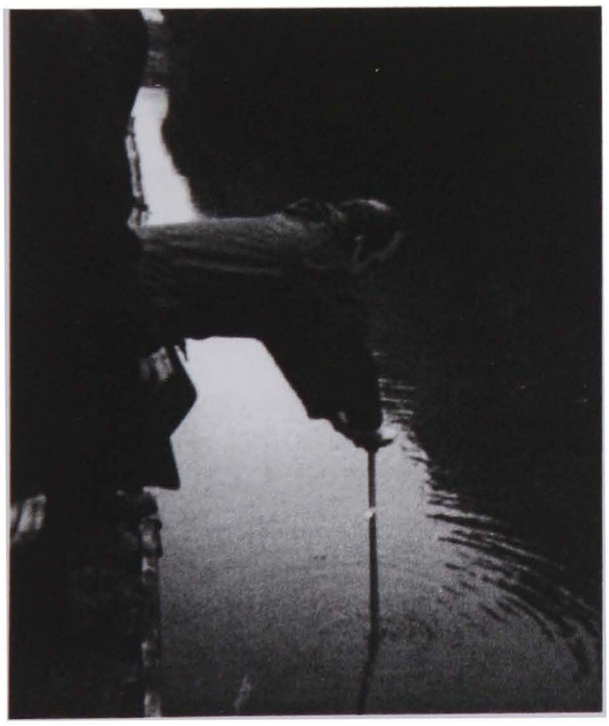


Figure 2.2: The Collection of a Sample at Snarestone.

Figure 2.3: A Core immediately after sampling, with its base sealed

2.3. Sample Processing

2.3.1. Anaerobic Handling

Canal sediment is chemically dynamic and is therefore prone to alteration between sampling and analysis. The principal problem is the risk of a shift in the redox status of the sediment. Previous workers have observed that Fe^{2+} in porewater can be readily oxidised which can lead to erroneously low results for Fe^{2+} determinations (Bray et al., 1973; Troup et al., 1974, Loder et al., 1978). Scavenging by freshly formed Fe^{3+} species can distort the analysis of trace metals, silica and phosphate (Loder et al., 1978). Studies of the effects of oxidation on metal speciation in anoxic sediments, determined by sequential extraction, have warned that contamination by oxidation must be avoided during sampling, storage and extraction in order to preserve the in-situ speciation of the sediments (Cauwenberg and Maes, 1997; Rubio and Rauret, 1996; Tack and Verloo, 1995).

Sediment samples can also become more reducing over time as a result of measures taken to maintain anaerobic conditions. By sealing sediment cores the sample becomes a closed system and the natural supply of oxygenated waters to its surface is cut off; thus over time oxygen in the sampled overlying water will be respired, and eventually exhausted by the sediment biota. If the oxygen is exhausted the oxic surface layer of the sediment (observed in rural samples) will be reduced, and the natural metal speciation depth profiles will be altered. This problem was observed through duplicate analysis of a rural sediment core one week after sampling showing an increase in the maximum Fe concentration of the porewaters from 4ppm to 6ppm. This suggested that iron oxides present in the sediment's oxic layer had been reduced, releasing Fe^{2+} to the porewaters.

In order to preserve the chemical quality at the time of sampling, the following steps were taken during sediment handling and sample preparation:

1. Time between sampling, handling and analysis was kept to a minimum.
2. Urban sediment cores were stored upright in airtight core tubes sealed with double sealing bungs prior to sub-sampling.

3. Rural sediment cores were stored upright in cores with the upper bung removed to prevent reduction of the oxic surface layer.
4. The cores were extruded into a nitrogen filled glove bag, which had been evacuated and flushed three times prior to use. The nitrogen used was passed over an oxygen removing catalyst (BASF R3-11) prior to use (Figure 2.4).
5. All centrifuge tubes used for storing the sediment and porewater extraction were stored under anaerobic conditions for at least 24hrs prior to analysis. This has been shown to minimise traces of dissolved oxygen in the plastic and thus prevent the reaction of porewaters with residual air in the plastic (Bray et al., 1973). It was also done in order to reduce the rate of diffusion of air through the tube walls during centrifugation.
6. Collection of porewaters and the preparation and handling of the early, oxidation sensitive steps, of the sequential extraction were conducted in a Don Whitley Mark Mark I Anaerobic Cabinet, under a 90% nitrogen/ 10% hydrogen atmosphere, <0.1% oxygen, verified using Becton Dickson Methylene Blue, dry indicator strips (Figure 2.5).
7. All reagents used for analysis were deoxygenated by flushing them with nitrogen which had been passed over an oxygen removing catalyst (BASF R3-11), for two hours (Figure 2.6). The reagents were then sealed in airtight vials and stored in the anaerobic cabinet prior to use.
8. Sediment sub-samples for analysis at other sites were transported in Oxiod® anaerobic jars, loaded in the anaerobic cabinet.

Figure 2.4: A Core Being Extruded, Under a Nitrogen Atmosphere, in a Glove Bag

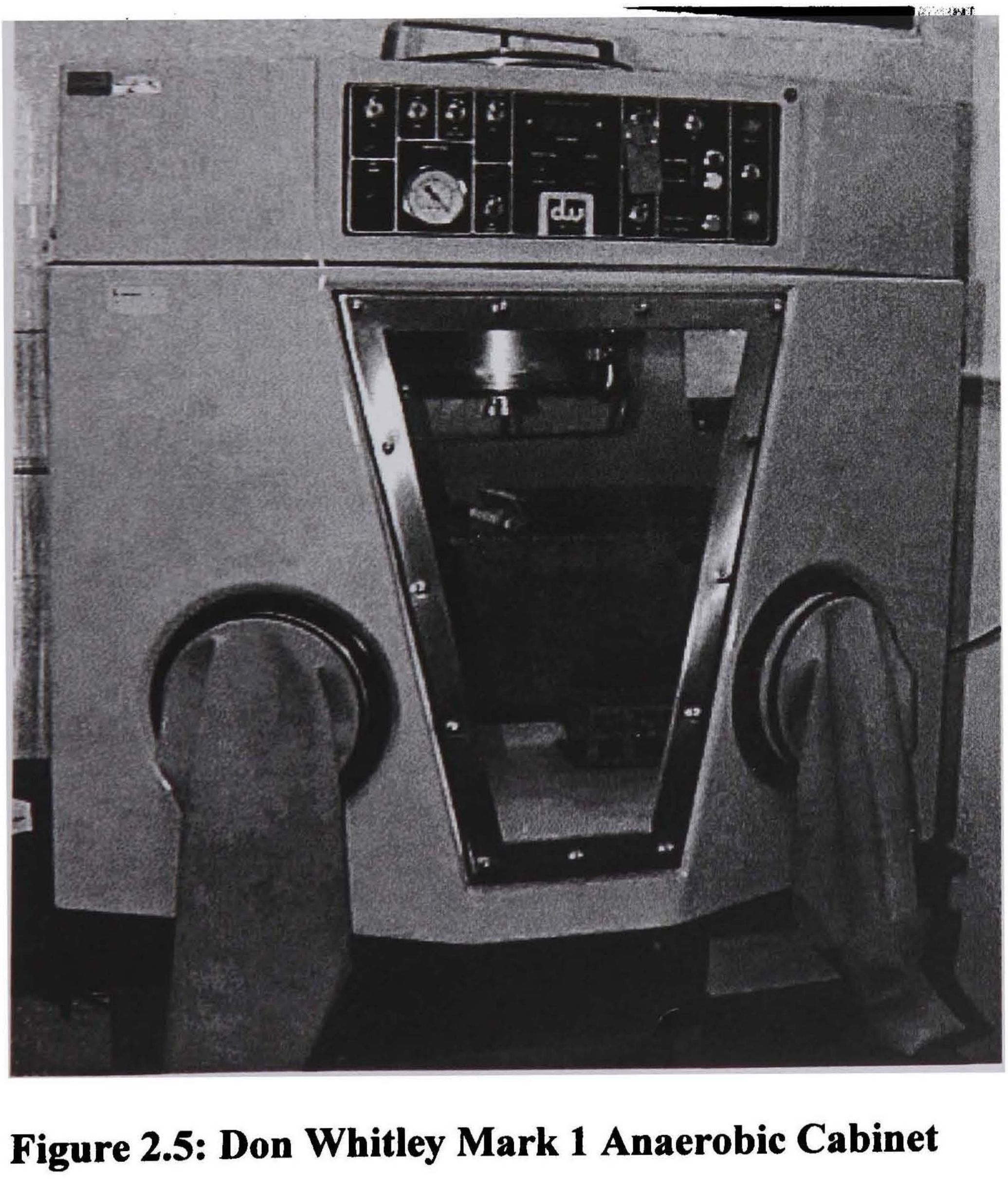


Figure 2.5: Don Whitley Mark 1 Anaerobic Cabinet

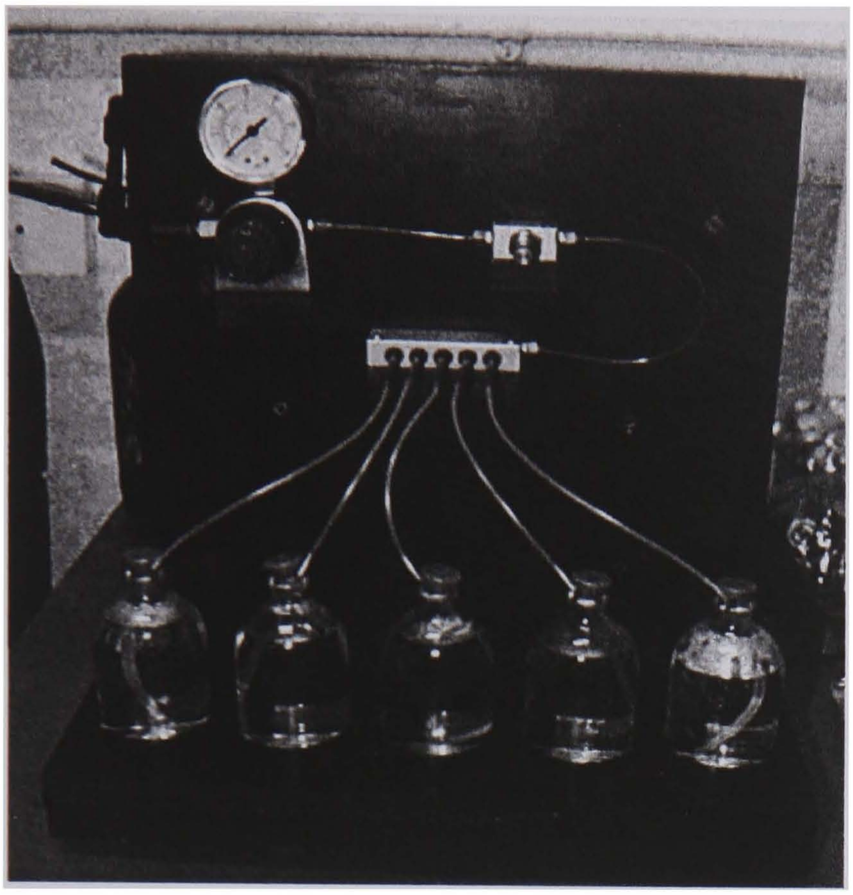


Figure 2.6: The Solution Deoxygenator

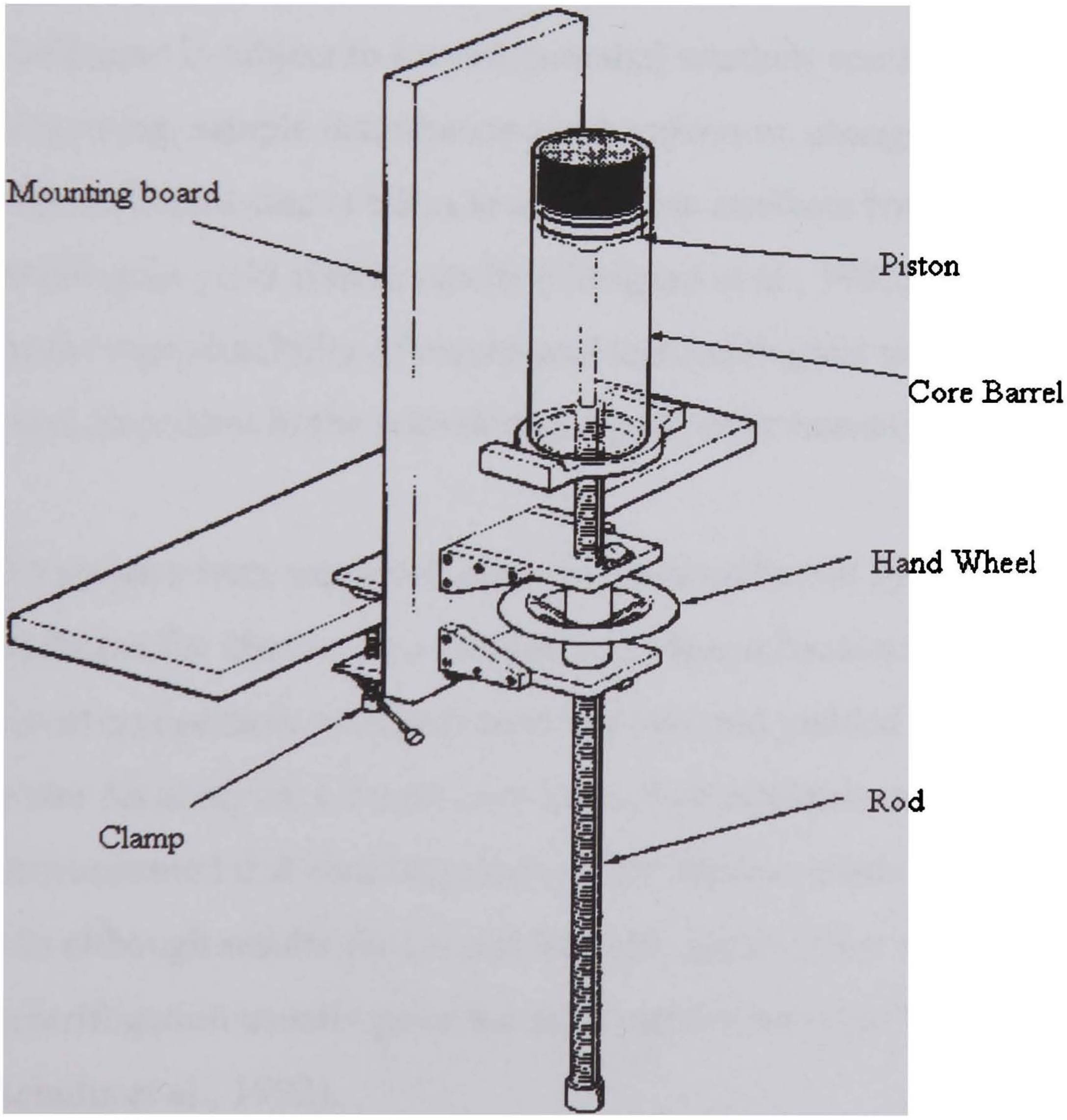


Figure 2.7: Mechanical Extruder – Lower Assembly (Ohnstad and Jones, 1982)

2.3.2. Extrusion

In the laboratory cores were extruded from the core barrel by means of an extruding device (Figure 2.7) (Ohnstad and Jones, 1982). The extrusion was conducted under a nitrogen atmosphere within a glove bag to prevent oxidation (Figure 2.4). The extruder was designed to accurately dispense a vertical section of core 1cm thick into the sample collection tray. Each 1cm of sample was then placed, using a perspex spatula, into a 50ml polypropylene centrifuge tube with an air tight cap seal (the tubes had been stored overnight in the anaerobic cabinet). Once the sediment was sealed in the centrifuge tube it could be removed from the glove bag for porewater extraction.

2.3.3. Porewater Extraction

Porewater can be extracted from sediments by a number of different techniques, including *in-situ* methods such as dialysis and the *indirect* methods of centrifugation, squeezing and suction (Mudroch and Azcue, 1995). Each technique is subject to several potential artefacts resulting from oxidation, CO_2 degassing, sample disturbance and temperature changes. However provided that sufficient care is taken to avoid these artefacts both indirect and *in-situ* techniques yield similar results (Carignan et al., 1985). Therefore factors such as the reproducibility of results and methodological simplicity were considered most important in the selection of a porewater extraction method for this study.

Porewaters were extracted from the canal sediment by centrifugation at 3200rpm for 20min. This method was chosen because it was simple, enabled direct comparison with sediment analysis and yielded a sufficient volume of water for analysis. Comparative studies of available extraction methods have demonstrated that centrifugation yields similar results to dialysis for Ca, Fe and Mn although results for Cu and Zn were higher, they also demonstrated that centrifugation usually gave the most precise results (Carignan et al., 1985; Schults et al., 1992).

2.3.3.1. Porewater Extraction for Analysis by ICP-AES

Sediment sub-samples were centrifuged 8 at a time; the samples were then placed into the anaerobic chamber where the porewater was decanted into Whatman Vectraspin 0.2μm filter-centrifuge tubes for filtration by re-centrifugation for 10min at 3200rpm. Filtered samples were then diluted by 50% with degassed Milli-Q and acidified with concentrated AnalR HNO_3 to 10% by volume. Studies have shown that once acidified, samples can be exposed to air without chemical losses (Loder et al., 1978). The extraction procedure was conducted on the day of sampling; samples were then stored at 4 °C prior to analysis at a later date (Section 2.4.4.1).

2.3.3.2. Porewater Extraction for Analysis by Ion Chromatography (IC)

Sediment sub-samples were centrifuged 2 at a time, as required (the remainder of the sub-samples were stored in the anaerobic cabinet prior to centrifugation). The supernatant was drawn into a 10ml plastic syringe and then passed through a Whatman 0.2μm Anotop filter and two Dionex preparatory sample pre-treatment cartridges. The cartridges called Onguard-RP and Onguard-H selectively remove organic molecules and transition metals respectively. These filters were used to prevent the porewaters from fouling the column of the Ion Chromatograph. The analysis of porewaters by IC was conducted as swiftly as possible following their extraction from the sediment (Section 2.4.5.). The extrusion and analysis by IC was begun one day after sampling, and required two days, due to 30min required for the analysis of each sample.

2.3.4. Sequential Extraction

Sequential extraction in conjunction with porewater analysis is a standard technique for the investigation of the chemical speciation of metals in soil and sediment. For a given element, the term speciation refers to its distribution amongst its chemical forms or species (Bourg, 1995). Sequential extractions are designed to determine this by measuring the proportions of elements in different chemical species and they depend on selective dissolution. Unfortunately, the results of sequential extractions can be difficult to interpret.

Conceptually, the solid material that constitutes a sediment can be regarded as being partitioned into specific fractions that can be extracted sequentially by a series of increasingly harsh 'selective' chemical extraction techniques that dissolve increasingly resistant fractions and their associated metals (Kersten and Forstner, 1995). The speciation derived from these techniques is therefore operationally defined by an element's reactivity, rather than an individual characterisation of each phase (Van Valin and Morse, 1982).

The results of sequential extraction schemes are subject to uncertainties for a number of reasons, namely:

- Reagents are not completely selective and may attack other sediment components than those predicted (Baffi et al., 1998; Baffi et al., 1995; Coetzee et al., 1995; Forstner, 1993; Martin et al., 1987; Tack and Verloo, 1995; Tack and Verloo, 1996; Ure et al., 1993)
- Handling prior to extraction can change the speciation of metals, in particular it can result in the oxidation of reduced species in anoxic sediments (Cauwenberg and Maes, 1997; Kersten and Forstner, 1986; Kersten and Forstner, 1987; Rubio and Rauret, 1996; Wallmann et al., 1993)
- Metals can be redistributed during the extraction procedure (Tipping et al., 1985; Wallmann et al., 1993)
- Most extraction schemes are based on a preconception of the types of minerals present in a sediment and may be wrong; canal sediment is particularly susceptible to this problem, because it is dominated by anthropogenic inputs giving it an unusual mineralogy.
- In organic rich anaerobic sediments, acid volatile sulphides are a dominant binding phase, these will be dissolved by the reagents used to extract oxides and carbonates applied prior to the extraction of sulphides and this could lead to the misinterpretation of results (Wallmann et al., 1993).

2.3.4.1. Methods for the Investigation of Two Sequential Extraction Schemes by CryoSEM

In order to choose an appropriate sequential extraction scheme for contaminated anaerobic canal mud two different sequential extraction procedures were investigated using a CryoSEM, with Energy Dispersive X-ray analysis (EDXA) (section 2.4.2). CryoSEM enabled complimentary petrographic observations to be undertaken in conjunction with two standard sequential extraction techniques for the assessment of the degree of reagent selectivity and any re-precipitation associated with the respective methods. The combination of these techniques has the potential to greatly improve the interpretation of the sequential extraction results.

The two extraction methods applied to the sediments were a 4-stage procedure modified by Kersten and Forstner (1986) from Tessier et al. (1979) for use on anaerobic sediments, and a new 3-stage procedure developed by the Bureau Communautaire de Reference (BCR) (1993) in order to harmonise the numerous sequential extraction procedures in use (Quevauviller, 1998) (Table 2.1).

The following procedures were observed for each sample. Initially a 1g sample of wet urban sediment was weighed under anaerobic conditions. A second 1g sample was also weighed and subsequently dried at 90°C in an oven to obtain a corrected dry mass.

All reagents were prepared using analytical grade chemicals and Milli-Q ultrapure water. The reagents were deoxygenated for two hours prior to extraction (Figure 2.7). The extraction was carried out following the procedures outlined in Table 2.1. To allow a fairer comparison of the two schemes, the easily reducible fraction of the Kersten and Forstner scheme was not performed. The fraction 3 extraction stage of both methods could therefore be expected to achieve total dissolution of amorphous and poorly crystalline Fe and Mn-oxyhydroxides present in the sediment. In addition to this it has been reported that there is a problem of metal redistribution between the easily and moderately reducible oxide fractions (Tipping et al., 1985). A sixth residual fraction is included in the Kersten and Forstner scheme as a control for comparison with total or bulk analysis. This fraction was not performed in this study because the important metal binding phases will be removed from the sediment by the earlier extractions and also because no similar step is included in the BCR scheme. Fraction 3 of the Kersten and Forstner scheme was extracted in the dark because when conducted in the presence of light the reagent will attack crystalline oxides. The Kersten and Forstner scheme was also carried out on a rural sample of relatively clean canal sediment in order to compare the affects of the oxalate buffer used in the extraction of the moderately reducible fraction (stage 3), on a metal-rich and a metal-poor sediment.

Table 2.1 Sequential Extraction Schemes Applied to the Sediment Samples

	Kersten and Forstner (1986)	BCR (1993)
Fraction 1: Exchangeable	20ml 1M ammonium acetate pH 7, 2hrs shaking.	-
Fraction 2: Bound as carbonates	20ml 1M sodium acetate pH 5, 5hrs shaking	40ml of 0.11M acetic acid, 16hrs shaking pH 2.7
Fraction 3: Bound as Fe/Mn oxides	Easily reducible: 20ml 0.01M hydroxyamine hydrocholride, with 0.01M nitric acid, 16hrs shaking*	40ml of 0.1M hydroxyamine hydrocholride, pH2 with HNO_3, 16hrs shaking.
	Moderately reducible: 20ml 0.1M ammonium acetate buffer, pH3 with oxalic acid, 24hrs shaking in the dark	
Fraction 4: Bound as sulphides or to organic matter	Two 10ml additions of 30% hydrogen peroxide, digested twice at 85°C to dryness, followed by 1M ammonium acetate pH 2 with HNO_3 shaking for 16hrs	Two 10ml additions of 30% hydrogen peroxide, digested twice at 85°C to dryness, followed by 1M ammonium acetate pH 2 with HNO_3 shaking for 16hrs

*The easily reducible fraction of the Kersten and Forstner scheme was not performed.

Following each stage of the procedures, the liquid extracts were separated from the solid residue by centrifugation (20 min at 3200rpm). The leachates were decanted into high-pressure polyethylene bottles; those from the Kersten and Forstner scheme were acidified with concentrated AnalR HNO_3 to 10% by volume, in order to prevent problems of precipitation. The samples were then sealed and stored at 4°C prior to analysis by ICP-AES. Between extraction steps the residue was washed with 10ml of degassed Milli-Q, shaking for 15min and centrifuging. Following washing one duplicate leached sample was kept back for CryoSEM analysis. Sample handling for the extraction of fractions 1 to 3 was conducted in the anaerobic cabinet; the fraction 4 extractions were conducted in air.

The results of this study showed the BCR scheme to give more meaningful results on the speciation of metals in urban canal sediment. These results are discussed in detail in Chapter 4.

2.3.4.2. B.C.R. Sequential Extraction Procedure

The BCR sequential extraction was applied to one rural and one urban core, when time permitted during the study. The procedure was conducted on a core from which the porewaters had been extracted for cation analysis, the interval between porewater extraction and sequential extraction was kept to a minimum of 3 days, (it could not be earlier due to the urgency of extracting porewaters for anion analysis, requiring 2 days).

1g samples of wet sediment were weighed, maintaining anaerobic conditions at all times, a second 1g sample was also weighed and subsequently dried at 90°C in an oven to obtain a corrected dry mass. Samples were taken every centimetre for the uppermost 10cm and then every 2cm for the remainder of the core, one duplicate and a certified reference material BCR CRM 601 (Quevauviller et al., 1997) were also sampled. All reagents were prepared using analytical grade chemicals, and Milli-Q ultrapure water, following the clear instructions outlined in (Quevauviller, 1998) and de-oxygenated for 2 hours prior to extraction (Figure 2.7). The extraction was carried out following the procedure outlined in Table 2.3, and covered in detail in (Quevauviller, 1998).

Following each stage of the procedure extracts were separated from the solid residue by centrifugation (20 min at 3200rpm) and decanted into a high pressure polyethylene bottles which were sealed at stored at 4°C prior to analysis by ICP-AES (Section 2.3.4.2.). Between steps the residue was washed with 10ml of degassed Milli-Q ultrapure water, shaking for 15min and centrifuging. All handling for steps 1 and 2 was conducted in the anaerobic cabinet and step 3 was conducted in air.

Table 2.2 BCR Sequential Extraction Experimental Procedure

	Reagent	**Procedure**	**Extracted Sediment Components inferred from CryoSEM results**
Step 1	0.11M acetic acid	40ml of reagent added to 1g of wet sediment in the anaerobic cabinet and extracted by shaking for 16 h at room temperature	Carbonates, partially dissolved Cu sulphides were absent
Step 2	0.1M hydroxyamine hydrocholride pH2 with HNO_3	40ml of reagent added to residue from step 1 in the anaerobic cabinet and extracted by shaking for 16 h at room temperature	Vivianite completely dissolved Fe oxides partially dissolved ZnS may also be partially dissolved by this fraction
Step 3	30% hydrogen peroxide, followed by 1M ammonium acetate pH 2 with HNO_3	10ml of reagent carefully added to the residue from step 2 to avoid looses due to violent reaction, digested at room temperature for 1h with occasional shaking, followed by 1h at 85°C in a water bath with the lid on. The lid was then removed and the volume reduced to a few ml. A further 10ml of reagent added and the sample again heated at 85°C for 1h followed by the removal of the cover to reduce the volume to a few ml. 50ml of 1M ammonium acetate then added to the cool moist residue and shaken for 16h at room temperature	Sulphides and most organic matter dissolved **NOT EXTRACTED** Crystalline Fe/Mn oxides and some amorphous Fe/Mn oxides, Barite, Barium Sulpide, Ti-oxide, silicate and slag particles

2.3.5. Sediment Drying and Crushing

The samples of sediment that remained after porewater extraction and sub sampling for sequential extraction were dried overnight at 90°C and subsequently crushed/disaggregated in a TEMA® agate swing mill to obtain samples <250μm. These samples were then analysed for parameters unaffected by oxidation by XRF, Aqua-Regia digest and carbon analysis.

2.3.6. Aqua Regia Digest

Aqua regia (three parts HCl + one part HNO_3) will leach many metals, notably base metals from sediments with considerable efficiency giving recoveries close to 60% for certain metals (Table 2.3). Aqua regia was chosen because it is less hazardous than alternative acids for total digestion (HF and perchloric acid), and the total concentration of dissolved solids in the resulting filtered solution is minimised, this is desirable for analysis by ICP-AES as it increases the efficiency of sample introduction to the plasma by nebulisation.

Table 2.3 Comparison of XRF Data with Aqua Regia Leachate Data

	Cr		Cu		Zn		Pb	
SAMPLE	XRF	Aqua regia	XRF	Aqua regia	XRF	Aqua regia	XRF	Aqua regia
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Urban 1cm	725	**404**	996	**633**	11838	**8079**	1569	**1173**
Urban 8cm	753	**418**	1028	**651**	13098	**9231**	1725	**1291**
Urban 16cm	826	**443**	1103	**701**	15474	**10656**	2093	**1586**
Urban 24cm	803	**469**	1131	**720**	15508	**10892**	2070	**1618**
Rural 1cm	96	**26**	61	**44**	533	**405**	97	**60**
Rural 8cm	70	**21**	46	**38**	348	**268**	75	**43**
Rural 16cm	45	**15**	29	**25**	180	**149**	50	**28**
Rural 24cm	40	**13**	29	**25**	87	**75**	38	**30**

The following procedure was conducted on each 1cm sub-sample of sediment, from which porewaters had been extracted for metal analysis. Samples of dried and crushed sediment were accurately weighed to 0.5g ±0.01g into a 100ml beaker, and 30ml aqua regia added (freshly prepared from three parts AnalR HCl + one part AnalR HNO_3). The samples were then digested at 80-95°C on a hot plate, until they reached near dryness, at which point they were removed from the hot plate and cooled. 30ml aliquots of 10% HNO_3 were subsequently added, before re-heating the samples for a further 30min. The samples were cooled and quantitatively transferred to a 100ml volumetric flask, with 70ml of 10% HNO_3. Each sample was then centrifuged twice to remove solid material, initially at 3200rpm for 10min, and then for a further 5 minutes following the addition of 0.5ml, 1% Brij-35, a surfactant which aids particle settling.

In order to assess the accuracy of this technique it was applied to a sample of the Nation Bureau of Standards, Standard Reference Material 1645, River Sediment, prepared from material dredged from the bottom of the Indiana Harbor Canal, near Gary, Indiana, USA. Duplicate analyses of samples and a laboratory standard were used to assess precision.

2.4. Analytical Methods

2.4.1 Accuracy and Precision

The accuracy of an analytical method is normally tested by analysis of samples of known composition. A river sediment standard (NBS SRM 1645) was used to assess the accuracy of the aqua-regia digest procedure and a new lake sediment standard (CRM 601) to assess the accuracy of the BCR sequential extraction procedure. They were included in the procedures as a normal sample, and the results of their analysis compared to certified values. However, the chemically dynamic nature of waters precludes their standardisation and unfortunately standard reference materials of canal waters do not exist. In order to assess the accuracy of the analytical techniques used for porewater analysis by both ICP-AES and IC, quality control standards were prepared from the quantitative dilution of Aldrich Atomic Absorption Spectroscopy Standards and BDH anion standards respectively. The results of these studies must be considered in the context of the standards being idealised samples without the interference and oxidation problems associated with natural waters. Consequently, accuracy estimates cannot be adequately made for techniques used to analyse waters in this study, however any bias introduced into the analyses should be the same for all samples since each sample was analysed by a standard procedure. It is therefore valid to relate the chemistry of different water samples here without a complete knowledge of accuracy.

Precision estimates were obtained by performing replicate analyses on samples of the same composition; precision was observed as 3 times the standard deviation. In the case of sediment studies duplicate analysis of sediment samples were conducted within each extraction, along with duplicates of previously analysed samples to give a measure of long-term precision. Duplicate analysis of waters was conducted when sample volumes permitted; however the small volumes of porewater extracted were generally equivalent to the volumes required for analysis. The ICP-AES automatically replicates the analysis of samples and this information was used to assess the precision of cation analysis. Ion Chromatography analysis requires 30 minutes per sample, therefore the urgency of analysis required for the prevention of oxidation precluded duplication, as it was deemed more important to analyse the samples in the shortest time possible. Attempts to re-analyse samples later proved impossible as redox sensitive anions had been altered. However the samples analysed were a depth sequence, and the analysis was not conducted in depth order, therefore the similarities in the concentrations of redox-stable anions such as chloride, in adjacent samples, can be used as an indicator of precision. Standard samples were run in sequence to assess the accuracy and detection limits of the instrument.

2.4.2. Cryogenic Scanning Electron Microscope (CryoSEM)

Petrographic analysis of the sediment was undertaken using a new CryoSEM technique at the British Geological Survey (BGS) (Figure 2.8). This technique allows samples to be viewed directly, without alteration to the texture or chemistry of the sediment.

Samples were taken from; the sediment interface and depths of 5cm, 15cm, and 30cm and placed into a two piece brass sample vessel. The vessel consisted of a basal cup and an upper tube fitted onto the lower cup and held together with a smear of Blu-Tak® (Figure 2.9). Once collected each sample was sealed in a separate 10ml glass jar and placed into an Oxiod® anaerobic jar for transport to the BGS.

Figure 2.8: LEO 435LV SEM with Cryogenic Stage.

Figure 2.9: Brass Sample Vessel Being Loaded With Sediment

Samples were prepared cryogenically immediately prior to analysis. The sample in the brass vessel was fixed to a special brass stage holder and plunged into a nitrogen slush (generated by the pressurisation of liquid nitrogen), rapidly freezing the sample, preventing ice crystal formation and hence disruption to the fabric of the sediment. The frozen sample was then transferred to the cryotransfer unit under vacuum and placed onto a liquid nitrogen cooled stage inside this unit (Figure 2.10).

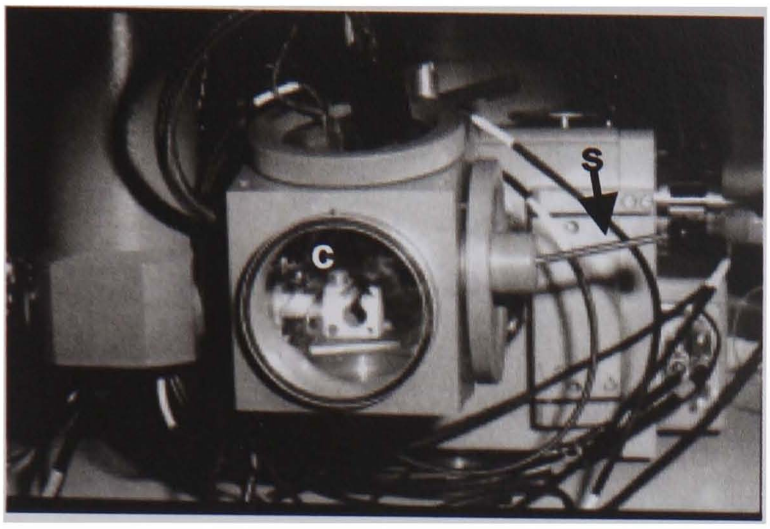


Figure 2.10: The Cryotransfer Unit (c) Showing Side Impact Chisel (s)

The upper part of the brass sample vessel was sheared off using a side impact chisel, to produce a near horizontal fracture surface of sediment that had neither been exposed to the atmosphere, nor directly to the nitrogen slush. The sample was then transferred under vacuum into the SEM chamber and mounted on the cold stage at approximately -140°C. By raising the temperature of the cold stage to -80°C the frozen porewater was sublimed revealing the undisturbed structure of the sample.

Analysis was carried out on the LEO 435LV variable pressure digital SEM, fitted with an Oxford instruments CT1500 cryogenic sample preparation and transfer system and cold stage. The CryoSEM was operated at a vacuum of 0.15 Torr which enabled observations to be made without the need to coat the sample in gold or carbon (as would be the case in a conventional SEM), by enabling the surface to be earthed through the atmosphere of the SEM chamber. Under low vacuum mode, SEM morphological images were recorded using a solid-state backscattered electron detector (accelerating voltage of 20kV and a beam current of 400pA). Spatial resolution was better than 1μm. Semi-quantitative analysis was carried out by Energy Dispersive X-Ray Analysis (EDXA) in order to determine the composition of individual particles and included the detection of light elements including C and O, using an Oxford Instruments ISIS1300 digital EDXA system fitted to the electron-microscope.

CryoSEM provides detailed information on canal sediment petrology and considerably augments the understanding of the geochemistry of sediments.

This technique is preferable to other SEM procedures that require sample drying and coating prior to analysis because rapid freezing of the sample's porewater prevents the formation of ice crystals and thus preserves the in-situ texture of the sediment. The cryogenic sample preparation also retains the anaerobic chemistry of the sediment. However this technique does have limitations:

- The relative abundance of a particular type of particle cannot be estimated precisely owing to the uneven sample surface, resulting from the loss of frozen porewater by sublimation that makes solid grains stand proud, the volume of pore spaces will therefore be under-estimated. Also efficient time management demands that the operator selects the particles to be examined, and therefore it is not always possible to get a representative view of the sediment (Fortey and Milodowski, personal communication).
- Because of the relatively high limits of detection of the X-ray analyser, CryoSEM cannot detect low, dispersed concentrations of adsorbed metals (Fortey and Milodowski, personal communication).
- It is difficult to reproduce exact observations because it is impossible to store the samples and therefore once examined a sample cannot be reanalysed (Fortey and Milodowski, personal communication).

From these considerations, it is readily apparent that CryoSEM observations should be viewed in the context of data provided by other analytical techniques.

2.4.3. X-Ray Diffraction (XRD) and Electron Micro-probe Analysis

The sediments were analysed by XRD and electron microprobe at the British Geological Survey. This analysis provided verification for the observations of major mineral phases made by CryoSEM (section 2.4.2).

XRD is a direct technique for the identification of minerals. The analysis is limited by a lack sensitivity, which prevents identification of trace components composing <5% of the sediment, it is also non-quantitative. XRD analysis was conducted on freeze-dried sediment samples that had been powdered in an agate pestle and mortar and back-loaded into standard aluminium sample holders for XRD analysis. The analysis was carried out using a Philips PW1700 series diffractometer fitted with a cobalt-target tube and operated at 45kV and 40mA. The sediment powders were scanned from 3-50° 2θ at 0.7° 2θ/minute. Diffraction data were analysed using Philips X'Pert software coupled to an International Centre for Diffraction Data (ICDD) database running on a Gateway personal computer system.

Polished thin sections of the sediment were prepared at the BGS by impregnation of freeze-dried sediment with resin. They were then mapped by the electron microprobe at the BGS to establish detailed spatial information on the major and trace elements in the sediment.

2.4.4. ICP-AES

An Inductively Coupled Plasma – Atomic Emission Spectrometer (ICP-AES) was used to analyse porewaters and sediment leachates from both aqua regia digests and sequential extractions. ICP-AES is a multi element technique applicable to over 70 elements with detection limits typically in the ppb range. Samples are introduced to a high temperature energy source, the inductively coupled plasma, resulting in the excitation (and/or ionisation) of the sample atoms. Excited species subsequently decay to lower more stable species resulting in the emission of excess energy as characteristic electromagnetic radiation. To determine the concentration of a particular element in a solution, the intensity of light at a wavelength characteristic to that element is measured. Quantification is achieved using a blank and multi-element standard solution to generate calibration curves. The intensity of radiation emitted by a sample at a particular wavelength is then measured and the calibration used to determine the concentration.

A Perkin Elmer Plasma 400® ICP-AES was used with a Gilson® 180 posistion sample changer to ascertain the concentration in mg/L of the elements; calcium, aluminium, iron, copper, zinc, manganese, magnesium, sodium, lead, chromium, cadmium, silicon, sulphur and phosphorus. The P400® is a sequential instrument, using a monochromator to locate spectra at a set of specific wavelengths in sequence, enabling the emissions from each excited species to be identified and its intensity to then be measured, without interference from emissions at other wavelengths. This type of instrument offers a choice of a number of wavelengths for an element; the careful selection of wavelengths with appropriate background corrections avoids interference from the presence of emission peaks of other species in the sample, near to the analyte wavelength. The disadvantage of this method is that each analysis requires at least 10ml of sample. The volume of sample required increases with the number of elements analysed, in this study the number elements analysed, particularly in the porewaters, was limited by the small volume of sample available. A simultaneous instrument using a polychromator would have had the advantage of achieving faster analysis with a small sample volume, but the choice of wavelength is limited with these instruments, increasing the risk of interference.

Suitable emission wavelengths for the elements of interest to this study were investigated for interference from other elements present in the samples. A set of wavelengths were selected which had maximum sensitivity, without suffering interference problems from other elements. Although the methods used for the analysis of porewaters and digest leachates varied, a standard procedure was followed for the operation of the instrument and this is outlined below:

1. A multi-element standard was prepared at concentrations just above those found in the particular set of samples to be analysed. The standard was prepared in the same solution (or matrix) as the samples to be analysed, minimising the physical interference caused by differences in the nebulisation efficiency of reagents of differing viscosity and dissolved solid content (section 2.4.3.3.)
2. Wavelengths were calibrated using the standard solution. This corrected for a drift in the location of spectral emission peaks that can occur between runs as a result of mechanical wear in the monochromator.

3. The instrument was calibrated using the multi element standard and a reagent blank.
4. The detection limits were determined for each element by conducting 10 replicate analysis of the reagent blank. The detection limit for each element to be analysed was then calculated to be three times the standard deviation of the 10 replicates.
5. The samples were analysed along with quality control standards, using QC Expert® software in conjunction with a Gilson® sample changer. The QC-Expert software was designed to run the analysis of the samples whilst ensuring the quality of analysis fell within programmed constraints by:
    a) Re-calibration of the instrument approximately every four to five samples to prevent drift.
    b) The analysis of a Quality Control (QC) standard at any particular point throughout the analytical run, usually every five or six samples, one greater than calibration in order to prevent their synchronisation. This tested the quality of analysis at differing points between calibrations.
    c) Setting limits for the QC standard, which if exceeded set the instrument to recalibrate and reanalyse the QC standard. If the limits are exceeded twice the analysis would immediately be aborted.
    d) Conducting 2 replicate analyses of each sample
    e) Setting a wash time of 20 seconds between each sample
    f) Increasing the wash time by an additional 20 seconds if upper concentration limits are exceeded
    g) Calculating the concentration of sample, by correcting for dilutions using information on sample weight or initial volume and the final volume.
6. The Quality of analysis was checked by a number of quality control measures: replicate analysis to assess precision, the analysis of quality control standards, replicate analysis of anomalous data.

A more complete account of the ICP-AES is given in (Laban, 1999).

2.4.4.1. Porewater Analysis by ICP-AES

Porewaters were analysed twice by the ICP-AES, initially for the determination of Ca, Al, Cu, Zn, Mn, Fe, Mg and Si concentrations in solution, on one occasion a third run was conducted for the analysis of Na, the data for this analysis is presented in Appendix 3. The concentration of these elements in the standard solutions used for calibration, their detection limits and uncertainties are shown in Table 2.4. The detection limits were calculated from 3 times the standard deviation of 10 replicate analysis of a 10% nitric acid blank and the uncertainties are three times the standard deviations from the mean concentration values of duplicate analysis of quality control standards, they represent a 99% confidence limit (Appendix 6.1).

The concentration of Cu in the porewaters was either beneath detection limit or subject to 3σ errors greatly in excess of 10% and therefore it is not considered further (Appendix 3.6). The concentration of Zn and Al were detectable in the porewaters. However, a number of readings were very low, and although the concentrations were above the detection limit of the instrument, the relative standard deviation from the mean of the two readings were often greater than 10%, putting some of the data into question (Appendix 3.1 and 3.7).

Table 2.4: Parameters Used in the Analysis of Porewaters by ICP-AES

Element	Wavelength (nm)	Standard concentration ppm	QC-standard Concentration ppm	Detection Limit ppm	3σ uncertainty
Ca	422.673	100	50	0.01	±5.0%
Al	396.152	5	2	0.063	±39.4%
Cu	324.754	1	0.5	0.0009	±3.9%
Zn	213.856	2	1	0.002	±8.2%
Mn	294.920	5	2	0.0064	±10.4%
Fe	273.955	10	5	0.0035	±8.3%
Mg	279.553	50	20	0.02	±9.3%
Si	251.61	20	2	0.005	±10.6%
Na	589.592	100	50	0.03	±3.1%

2.4.4.2. Aqua Regia

Aqua regia leachates were analysed twice by the ICP-AES, initially for the determination of Ca, Al, Cu, Zn, Mn, Fe, Mg, Cr, Cd and Pb concentrations in solution and subsequently for the analysis of S and P, the data for this analysis is presented in Appendix 4. The concentration of these elements in the standard solutions used for calibration, the detection limits and the uncertainty for each element are shown in Table 2.5. The uncertainties are calculated from 3 times the standard deviation of the mean concentrations derived from repeat analysis of a laboratory standard and account for both measurement and material variability, they represent a 99% confidence limit (Appendix 6.2).

Table 2.5: Parameters Used in the Analysis of Aqua regia Leachates by ICP-AES

Element	Wavelength (nm)	Standard concentration ppm	QC-standard concentration ppm	Detection limit ppm	3σ Uncertainty
Ca	422.673	350	100	0.015	±3.4%
Al	396.152	100	50	0.0033	±12.5%
Mn	294.920	15	5	0.0117	±5.3%
Cu	324.754	20	10	0.0033	±7%
Zn	213.856	75	25	0.0033	±7%
Fe	273.955	500	250	0.012	±6.5%
Cd	228.802	1	0.5	0.0057	±5.7%
Cr	267.716	5	2	0.0084	±11%
Pb	220.353	20	10	0.396	±16%
S –rural	180.73*	50	20	0.1	±40%
S-urban	180.73*	100	50	0.1	±37%
S-rural	182.037*	50	20	0.12	±40%
S-urban	182.037*	100	50	0.2	±38%
P-rural	178.283*	10	2	0.15	±6.9%
P-urban	178.283*	150	75	0.3	±10.5%
P-rural	178.769*	10	2	0.3	±11.7%
P-urban	178.769*	150	75	0.3	±10.6%

*These wavelengths are in the ultraviolet range, and therefore subject to absorption by oxygen, for this reason prior to analysis the spectrometer optics were purged with nitrogen.

Concentrations of metals measured following the digestion of a standard river sediment (NBS SRM 1645) by aqua regia were within the uncertainty tolerance limits of certified values (Table 2.6).

Table 2.6: Measured and Certified values in National Bureau of Standards Standard Reference Material 1645 (NBS SRM 1645)

	1st analysis of NBS SRM 1645	2nd analysis of NBS SRM 1645	Average	Certified Standard value*
Cd ppm	9.87	8.35	9.11	10.2 ±1.5
Cu ppm	110.52	102.72	106.6	109 ±19
Mn ppm	765.94	751.64	758.8	785 ±97
Pb ppm	722.32	688.26	705.3	714 ±28
Zn ppm	1706.14	1605.60	1655.9	1720 ±169
Cr %	2.75	2.72	2.7	2.96% ±0.28%
Fe %	10.71	10.19	10.45	11.3% ±1.20%

*The uncertainties of the certified values listed in the table include those associated with both material and measurement variability. They represent the 95% tolerance limit for an individual subsample.

2.4.4.3. Sequential Extraction

Each stage of the extraction produced leachates in different matrices. The affect of these matrices on analysis was investigated in order to ensure that the results obtained from the analysis of separate fractions were not affected by this difference. The analysis of these leachates is problematic because they contain dissolved salts at up to molar concentrations. This affects the efficiency of the sample nebuilisation as it enters the plasma, and over time it can also block the nebuliser by the formation of a solid crust, resulting initially in a decrease in the volume of sample reaching the plasma, and ultimately in the accuracy of the analysis.

In order to overcome this problem, standards were prepared in the reagents used for each stage of the extractions, thus minimising the physical interference caused by differences in the nebulisation efficiency. A test run of standards was then analysed using the Gilson® auto-sampler and QC-Expert software to assess the affect of each matrix upon the instrument over prolonged analysis. This test found that the acetic acid used in step 1 did not adversely affect analysis, therefore the method developed for the analysis of aqua-regia digests was adapted using standards prepared in an acetic acid matrix. The matrices used in step 2 and 3 1M hydroylamine-hydrochloride and 1M ammonium acetate did however adversely affect the analysis of the leachates over time, ultimately resulting in the failure of quality control measures. Consequently the nebuliser was changed to a 'high solid nebuliser' which is designed to overcome the problems outlined above. A repeat of the test analysis run showed that the accuracy of analysis was not significantly affected over time, however the 'high solid nebuliser' decreased the efficiency of nebulisation resulting in a decrease in the precision of the analysis. Therefore the analyses of leachates from fractions 2 and 3 was conducted with the high solid nebuliser. Calibrations were conducted every 4 samples and QC-standards every 5 samples, in order to ensure that this decrease in precision did not adversely affect the quality of analysis.

All the sequential extraction leachates were analysed twice by the ICP-AES, initially for the determination of Ca, Al, Cu, Zn, Mn, Fe, Mg, Cr, Cd and Pb concentrations in solution and subsequently for the analysis of S and P, the data for this analysis is presented in Appendix 5. The concentration of each of these elements in the standard solutions used for calibration were the same as those used for aqua-regia digests (Table 2.5). The detection limits and the uncertainty for each element are shown in Table 2.7. The uncertainties are calculated from 2 times the standard deviation of the mean concentrations derived from repeat analysis of matrix matched quality control standards, they represent a 95% confidence limit (Appendix 6.3a-c).

Concentrations of metals measured following the sequential extraction of the BCR certified reference material CRM 601 by the BCR scheme were not all within the uncertainty tolerance limits of certified values, in particular Zn in the first fraction showed very poor recovery (Table 2.8). This may have been due to the inefficiency of the shaker used for the procedure, which failed to keep the whole sample in suspension for the duration of the shaking.

Table 2.7: Precision of Sequential Extraction Leachate analysis

Element	Fraction 1		Fraction 2		Fraction 3	
	Detection limit ppm	2σ Error	Detection limit ppm	2σ Error	Detection limit ppm	2σ Error
Ca	0.021	5.80219	0.327	11.1508	0.057	14.9846
Al	0.021	6.117	0.174	10.4366	0.042	13.515
Mn	0.0081	5.85998	0.648	12.2278	0.0237	17.2486
Cu	0.0021	4.71732	0.0642	13.1602	0.0423	16.3991
Zn	0.0018	5.82318	0.0387	10.9793	0.0249	9.54699
Fe	0.015	5.92828	0.3672	11.5662	0.054	7.65216
Cd	0.0039	6.39241	0.0114	10.5275	0.0102	8.672
Cr	0.0066	6.61874	0.021	12.1352	0.0132	17.3205
Pb	0.0348	5.5966	0.1212	10.5119	0.0921	6.94343
S180*	0.0801	8.80811	0.198	13.3952	0.1611	9.29865
S182*	0.135	9.47533	0.1167	12.8391		
P178*	0.225	14.3968	0.666	14.0131	0.6459	11.6741
P179*	0.333	9.41008	0.3228	12.8165		

*These wavelengths are in the ultraviolet range, and therefore subject to absorption by oxygen, for this reason prior to analysis the spectrometer optics were purged with nitrogen.

Table 2.8: Measured and Certified values in the BCR Standard Reference Material CRM 601

	Fraction 1		**Fraction 2**		**Fraction 3**	
	certified	measured	certified	measured	certified	measured
Cd ppm	4.14 ±0.23	4.16 ±0.31	3.08 ±0.17	3.09 ±0.24	1.83 ±0.2	2.06±0.41
Pb ppm	2.68 ±2.68	1.77 ±0.97	33.1 ±10*	20.47 ±1.52	109 ±13	138.39 ±10.98
Zn ppm	264 ±5	173.6 ±14.16	182 ±11	167.74 ±3.7		
Cu ppm	8.32 ±0.46*	10.51 ±0.32				
Cr ppm	0.36 ±0.04	0.29 ±0.05				

* Indicative values, these values are not yet certified.

Measured values are given as the mean of the analysis of four leachates from the BCR extraction scheme applied to four duplicate samples of CRM 601.

The uncertainties of both the certified and measured values listed in the table include those associated with both material and measurement variability. They represent the 95% tolerance limit for an individual sub-sample.

Certified values quoted in (Quevauviller et al., 1997).

2.4.5. Ion Chromatography

The analysis of anions in porewater was undertaken using a Dionex DX500 Ion Chromatography system. Samples were introduced from a 25µl sample loop to an A611 guard column (pump size 4mm) and eluted by a gradient method with a starting concentration of 0.15mM and a maximum concentration of 40mM

(Table 2.9). Sodium hydroxide was used as the eluent with the gradient achieved from 3 solutions; A - Milli-Q ultrapure water, B - 200 mM sodium hydroxide and C - 5 mM sodium hydroxide.

Table 2.9: Gradient Programme used for inorganic anions

Time (min)	Injection Valve	Eluent A (%)	Eluent B (%)	Eluent C (%)
Initial	Off	84	16	0
0.0	Off	97	0	3
9.5	On	97	0	3
10.0	Off	97	0	3
17.0	Off	85	0	15
30.0	Off	84	16	0

Flow Rate 1.5ml/min

Concentrations of SO_4^{2-}, PO_4^{3-}, NO_3^- and Cl^- were determined by conductivity readings produced by the separated anions, following calibration by a standard solution (Table 2.10). Samples were injected to instrument manually following their preparation outlined in section 2.3.3.2.

Table 2.10: Standard Concentrations and 3σ Errors for the analysis of Porewaters by Ion Chromatography

Element	Standard-1 concentrations	Standard-2 concentrations	Detection Limit mM	3σ Error
SO_4^{2-}	1	100	0.000126	±2%
PO_4^{3-}	1	10	0.000329	±3.5%
NO_3^-	0.5	1	0.000231	±4%
Cl^-	10	100	0.00025	±2%

The accuracy of this analytical technique could not be tested by a standard reference material as no porewater reference materials exist. Duplicate analysis was also impossible due to the affect of oxidation on sampled porewaters (section 2.4.1). However a series of duplicate analyses of standard solution 2 was used to determine the 2σ errors shown in Table 2.10 (Appendix 6.1a).

Detection limits were calculated using the calibration line equations for each element and substituting in the minimum area threshold.

2.4.6. Alkalinity

Alkalinity is the capacity of a water to react with hydrogen ions. In natural waters of around pH7, alkalinity is primarily affected by the bicarbonate ion however because it may include reactions with small amounts of phosphate, borate and silicate as well as bicarbonate it is termed alkalinity. The alkalinity other than bicarbonate is deemed to be small enough to be negligible and alkalinity is thus virtually equivalent to the bicarbonate concentration.

One rural and one urban core were sampled in spring 1999 for the determination of alkalinity in their porewaters. Alkalinity of water samples was determined titrametrically by the addition of 0.02M H_2SO_4 using bromophenol blue as an indicator. In order to standardise the acid it was first titrated potentiometrically against a standard 0.008M solution of $NaCO_3$, in which pH was plotted against small increments of titrant. The resulting curve had two inflections the first due to the conversion of carbonate ions to bicarbonate and second due to the reaction;

$$H^+_{(ag)} + HCO_3^-{}_{(aq)} \rightarrow H_2O_{(aq)} + CO_{2(g)}$$

For waters at about pH 7 carbonate is absent and therefore the second inflection marks the end-point, this was within ±0.1ml of bromophenol blue colour change.

Titrations were conducted on water and porewater samples using the bromophenol blue colour change as the end point. Due to the small volumes of porewater extracted (between 5ml and 20ml), a 10ml micro-burette, with 0.02ml graduations was used to titrate against water samples of 5ml or 10ml measured into a 25ml conical flask by fini-pipette.

Duplicate analyses were carried out when volumes of porewater exceeded 10ml. Duplicate analysis of a 0.008M sodium carbonate standard showed the technique to be accurate to ±5% and duplicate analysis of samples with great enough volumes gave a similar figure for precision. Due to the high concentrations of dissolved species in the porewaters, it is likely that readings are affected by interferences from other anions particularly organic acids. It was not possible to quantify this affect.

2.4.7. pH

The pH of porewaters was measured prior to carbonate analysis using a hand-held Jenway 3051 pH meter with a combination Gelplas electrode, calibrated at 20°C using buffers at pH 4.00±0.02 and pH7.00±0.02.

2.4.8. Eh

The relative oxidising or reducing character of a natural solution is expressed in terms of its oxidation or redox potential, Eh, measured in volts (Gill, 1989). Eh was measured in the sediments in order to assess the exact depth at which the transition from oxic to anoxic conditions occurs and for use in thermodynamic calculations. Eh measurements were taken by placing a platinum electrode into a sample, and reading the voltage it develops against a standard hydrogen electrode. Standard hydrogen electrodes are fragile and expensive and therefore a saturated calomel electrode was used as a reference electrode in this study, readings consequently had to be corrected by +2.41V.

Eh was measured in duplicate rural and urban samples collected with the winter samples. Measurements were taken at each cm depth interval during extrusion, under a nitrogen atmosphere, by placing the platinum and calomel electrodes into the sediment and reading the resultant voltage on a hand held Voltmeter. Between readings the platinum electrode was placed into 10% HNO_3 in order to re-equilibrate it.

2.4.9. Carbon Coulometer

The carbon content of the sediments was measured using a UIC Inc® CO_2 Coulometer. This instrument measures total carbon released from combustion or inorganic carbon from acidification of samples, as CO_2 in a gas stream. The carbon coulometer solution contains ethanolamine and a colorimetric pH indictor. The CO_2 from the gas stream reacts with the ethanolamine forming a strong titratable acid, causing the indicator colour to fade. The coulometer's photometer recognises the condition and initiates the electrochemical generation of a base at a titration rate of up to 1800μg C/minute, returning the solution to its original colour. The current reading is then integrated and displayed as μgC (UIC Inc® promotional material). During analysis samples of standard $CaCO_3$ and blanks were routinely analysed in order to assess accuracy, and duplicate analysis was conducted for precision. Blank samples were also analysed for the determination of detection limits.

2.4.9.1. Total Carbon

Total carbon is analysed by combustion of a sample in a high temperature combustion furnace and a carbon coulometer. Dry sediment samples of between 8mg and 20mg were accurately weighed into ceramic sample boats. Each sample was then introduced into the combustion chamber, where oxygen passed through a precombustion tube to remove interfering substances, combusts the sample at a typical temperature of 950°C. The resulting CO_2 and other combustion products then pass through scrubbers to remove interfering halogens, sulphur, nitrogen oxides and water. The CO_2 then flows into the carbon coulometer for measurement. Analysis of standards show this method to be accurate to ±5%, duplicate analysis show the sample analyses to be precise to ±7.5%, the lower limit of detection was 30μM.

2.4.9.2. Inorganic Carbon

Inorganic carbon is analysed by acidification of samples with 5% HCl and a carbon coulometer. Dry rural sediment samples of between 100mg and 350mg were weighed into a weighing boat and carefully transferred to a reaction vessel with small amounts of Milli-Q ultra-pure water. The reaction vessel was then placed in a heating block and sealed into the acidification module where 5ml of 5% HCl was dispensed onto the sample. CO_2 evolved was purged from the vessel and carried through a condenser and a potassium iodide scrubber removing interfering sulphur to the carbon coulometer by an air pump.

This method was inadequate for the analysis of urban sediment for two reasons:

- The sediment was hydroscopic and would not mix with water, making the transfer of weighed sediment difficult and the addition of acid inaccurate.
- The high sulphur content of urban sediment spent the KI scrubber within two analyses, resulting in a large interference to the C reading.

For these reasons the method outlined above was modified for use on urban sediment. It was found that the sample would mix with 30% Industrial Methylated Spirits (IMS), a blank and standard analysis using IMS demonstrated that it did not affect the accuracy of the carbon coulometer. It was therefore used to introduce the sample to the reaction vessel and wet samples prior to acidification.

The KI scrubber was replaced with a 1M silver nitrate scrubber, this was found to effectively remove sulphur from the gas stream, provided that it was replaced on a daily basis. The analysis of standards gave an accuracy of ±5% for this method, duplicate analysis shown the precision of sample readings to be ±10%.

2.4.10. Malvern Mastersizer

The Malvern Mastersizer was used to ascertain the particle size distribution of the sediments by the laser diffraction of particles in suspension. The Malvern interprets particle size as the sphere that produces equivalent scattering to that of the particle being measured, which roughly corresponds to its actual volume.

The instrument samples scattered light passed through a sample cell at a range of clearly defined and accurately controlled angles. Each measurement is a10μs snapshot of the particles and 5000 such snapshots are obtained and summed to give a representative sampling of the whole range of sizes present. The scattered light data is transferred to Malvern Mastersizer V. 1.2b Software which transforms the scattered light data to a relative distribution of particle size.

Samples of wet sediment were put into suspension with distilled water using a propeller mixer and injected to the instrument with a 1ml plastic syringe. Duplicate analysis of a sample analysed previously at SChEME on a second Malvern instrument showed reproducibility to be good particularly in the lower size fractions (table 2.11). The poor reproducibility at the larger size range is probably caused by difficulties in putting larger grains into suspension homogeneously.

Table 2.11: Malvern Standard Data

	10% volume	50% volume	90% volume
SChEME Malvern	2.27μm	5.10μm	11.91μm
Second Malvern	2.04μm	5.04μm	13.26μm

2.4.11. X-Ray Fluorescence (XRF)

XRF is a multi-element technique applicable to elements with atomic number ≥9. It was used to determine the concentration of major elements in the sediments and to verify the results of the aqua-regia digests of the sediment.

Samples of dried and milled sediment were prepared as press pellets and analysed by XRF in order to obtain total concentrations of the major components; Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, MnO and Fe_2O_3 and the trace elements; V, Cr, Co, Ni, Cu, Zn, Pb, Rb, Sr, Y and Zr. The analysis was conducted at the Postgraduate Research Institute for

Sedimentology at Reading University using their Philips PW1408 XRF with Philips X40 analytical software.

Ten repeat analysis of the standard material GSP-1 shows the standard error at 3σ confidence to be <5% (Appendix 2.2). The lower limit of detection for trace metals is 5ppm and the calibration range for trace elements is of the order of a few hundred ppm, values that fall outside of his range should be treated with caution, as the lack of comparable standards precluded standardisation.

2.5. Summary

The sampling and analytical procedure outlined in this chapter is summarised in the flow chart Figure 2.11.

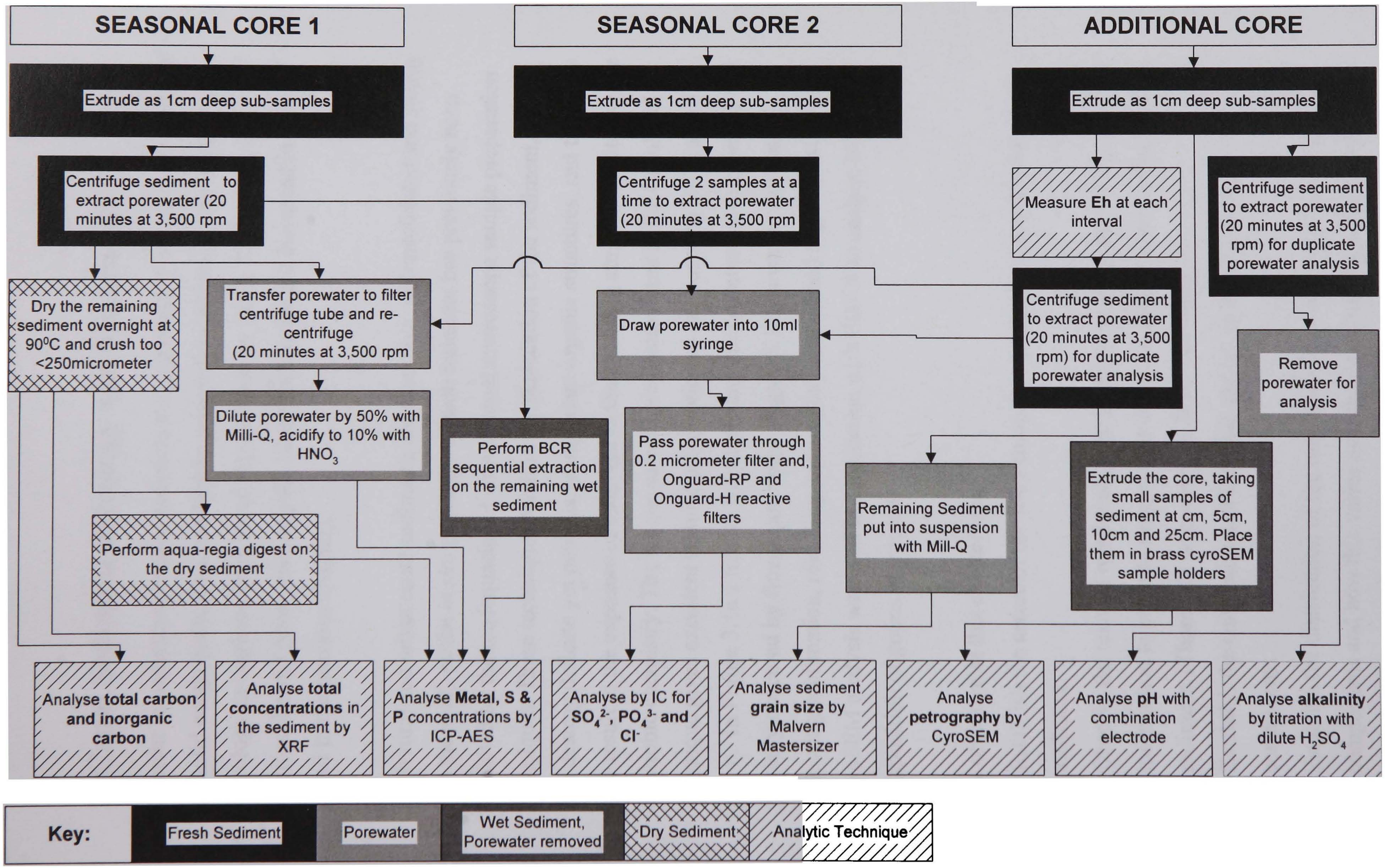


Figure 2.11: Summary of Sampling and Analytical methods

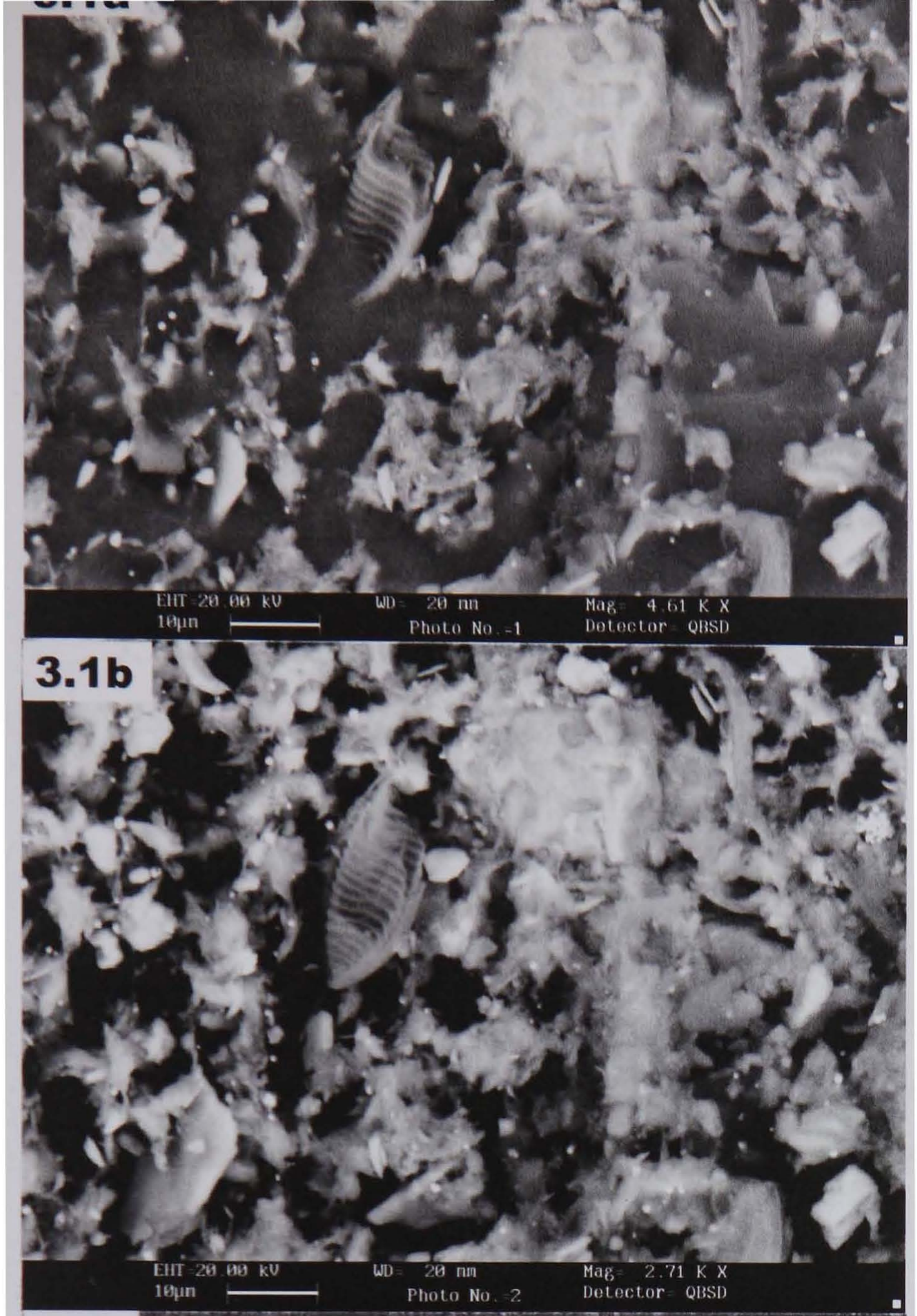
3. Canal Sediment Petrology and Mineralogy

In order to understand a canal sediment it is important to establish the nature of its solid components. This can best be achieved by observing the *in situ* petrology through the analysis of the sediment by SEM, XRD, electron microprobe and grain size analysis, (these techniques are discussed in some detail in the previous chapter).

Both rural and urban canal sediments are anaerobic, unconsolidated and sloppy and the study of the *in situ* petrology of such sediment has previously been inhibited by the inadequacies of conventional microscope sample preparation techniques. These techniques result in the desiccation of the sediment, which can destroy delicate yet potentially important organic structures, and they may also result in the exposure of sediment to the oxidising atmosphere altering the anaerobic chemistry. The unique sample preparation used in the CryoSEM technique gives excellent textural preservation as can bee seen in Figures 3.1a and b. In Figure 3.1a a freshly fractured sample of rural canal sediment is still partially obscured by frozen porewater, Figure 3.1b shows the sediment following sublimation, revealing undisrupted mineral and organic textures. CryoSEM analysis was used in conjunction with EDXA to analyse the composition of grains of interest.

The objective of this chapter is to:

- Establish the nature of the solid components of rural and urban canal sediment.
- Observe the textural relationships between these components, and use this information to begin to interpret the chemical processes operating in the sediment. (These will be covered in detail in chapter 5)
- Establish the composition of the rural and urban canal sediments constituents.
- Establish the distribution of the rural and urban canal sediments components and how this varies over the 24cm depth profile being investigated.



Figures 3.1a and b: CryoSEM Backscatter Electron (BSE) images of Snarestone sediment showing the progressive exhumation of the sample by the sublimation of frozen porewater.

Figure 3.2: A CryoSEM BSE image of Smethwick canal sediment from a depth of 15cm, showing the general fabric of the mud. Detrial and authigenic particles in the mud include: a large mass of Fe and S rich mineralised organic matter (a); an agglomerate of clay and Fe-oxide (b); coal particles (c); Zn sulphides (d); vivianite crystals (e); quartz particles (f) and a large agglomerate of clay particles (g)

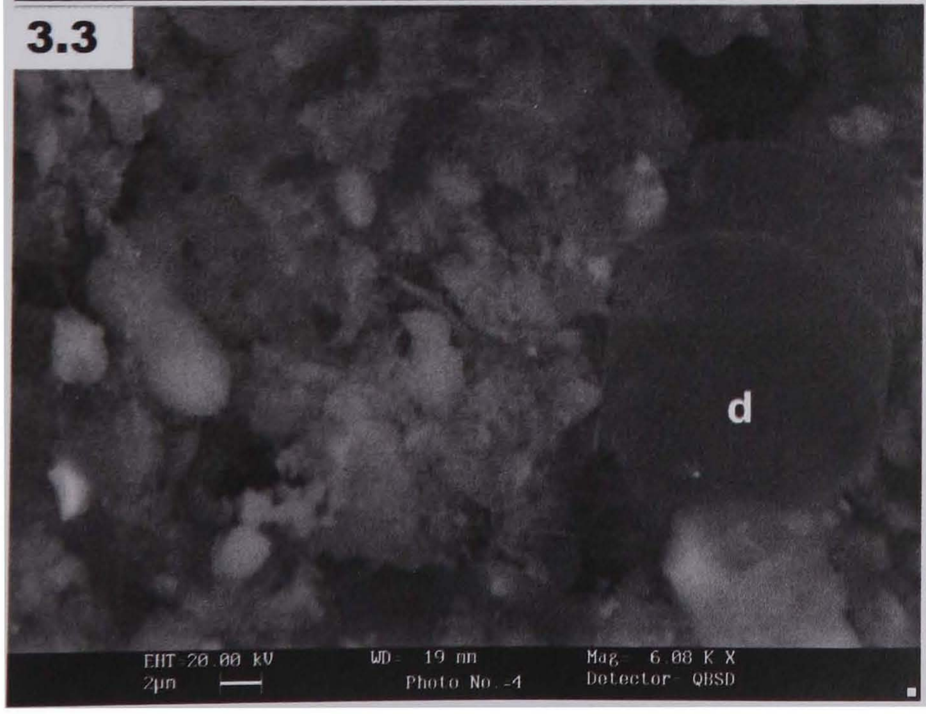


Figure 3.3: A CryoSEM BSE image of Great Bridge sediment showing fine floccular aggregates of clay, an organic biofilm and a diatom (d)

3.1. General Description of the Petrology of Rural and Urban Canal Sediment

CryoSEM analysis revealed that both rural and urban canal sediment have a porous structure predominantly composed of loosely packed aggregates of clay rich particles and to a lesser extent detrital, silt grade clasts (Figure 3.2 and 3.15a). Ubiquitous organic material such as biofilm, plant debris and siliceous diatoms can be identified within this matrix along with larger clastic detrital grains and authigenic mineral growths.

XRD analysis has shown that the major mineral components of both the rural Snarestone sediment and urban Smethwick sediment are quartz, calcite, feldspar and clays, including kaolinite and illite. In the urban sediment the reduced iron phosphate vivianite was also detected and the rural sediment contained dolomite (Appendix 7.1).

The fabric of both rural and urban sediment is broadly similar, however the high anthropogenic input into the urban sediment makes it quite distinct from the less contaminated rural sediment. The two sediment types will therefore be discussed separately in the results section.

3.2. Urban Sediment Results

Urban sediment from both Smethwick and Great Bridge was analysed by CryoSEM, a low magnification view of urban sediment is shown in Figure 3.2. The sediments are uniform on the scale of observation (up to 1mm), with no clear evidence of an oriented clay fabric. Well defined pore space, filled with water, is seen as a uniform dark grey material forming inter granular areas of 10μm or more in width and exhibiting an appreciable degree of inter-connection. Precise estimation of the proportion of this inter-granular water is hampered by the three-dimensional character of the ablated surface, in which solid particles stand proud. Compaction of the sediment with depth was observed as a decrease in pore size from approximately 10μm at the sediment interface to 1-2μm at 24cm.

3.2.1. Grain Size Analysis

Particle size analysis of sediment from Smethwick, by the Malvern Mastersizer®, found the sediment to be predominantly composed of silt sized grains. Between 3 and 6% of the sediment particles are clay sized (≤3.9μm), 65% to 80% of particles are silt sized (3.9-63μm) and the majority of the remaining sand sized grains are 63-250μm and therefore classified as fine sand (Figure 3.4a). The assessment of sediment samples at 1cm intervals over 24cm showed the sediment to have a small trend of decreasing particle size with increasing depth (Figure 3.4a and b). The fine-grained nature of the urban canal sediment size is reflected in the open matrix of clay and silt observed by CryoSEM analysis.

3.2.2. Allochthonous Components

The allochthonous or detrital components of urban sediment reflect the impact that 200 years of anthropogenic inputs have had upon the sediment. Along with the geologically derived material and organic matter, which are commonly observed in natural sediments, a variety of anthropogenic particles of industrial origin could also be identified throughout the sediment.

3.2.2.1. Clays

Clays were observed to form the bulk of the open floccular matrix of the sediment. EDXA analysis of clay particles found the majority of them to be composed of Al, Si, Ca, K and Fe suggesting that illite and kaolinite are the main clay species, an iron bearing species, possibly chlorite, was identified in one sample. The clay formed floccular aggregates with detrital material and biofilm (Figure 3.3).

Figure 3.4a: Cumulative Particle Size Distribution of Smethick Sediment

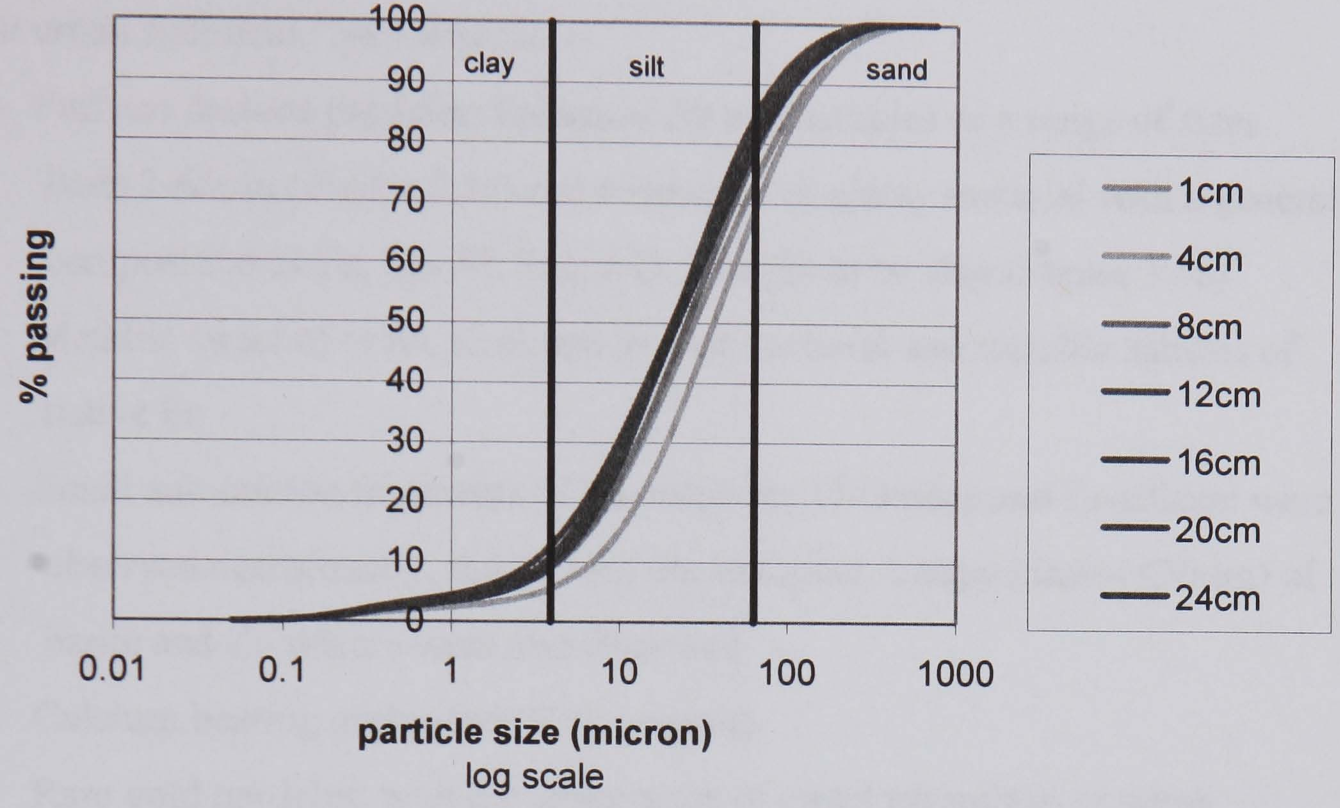
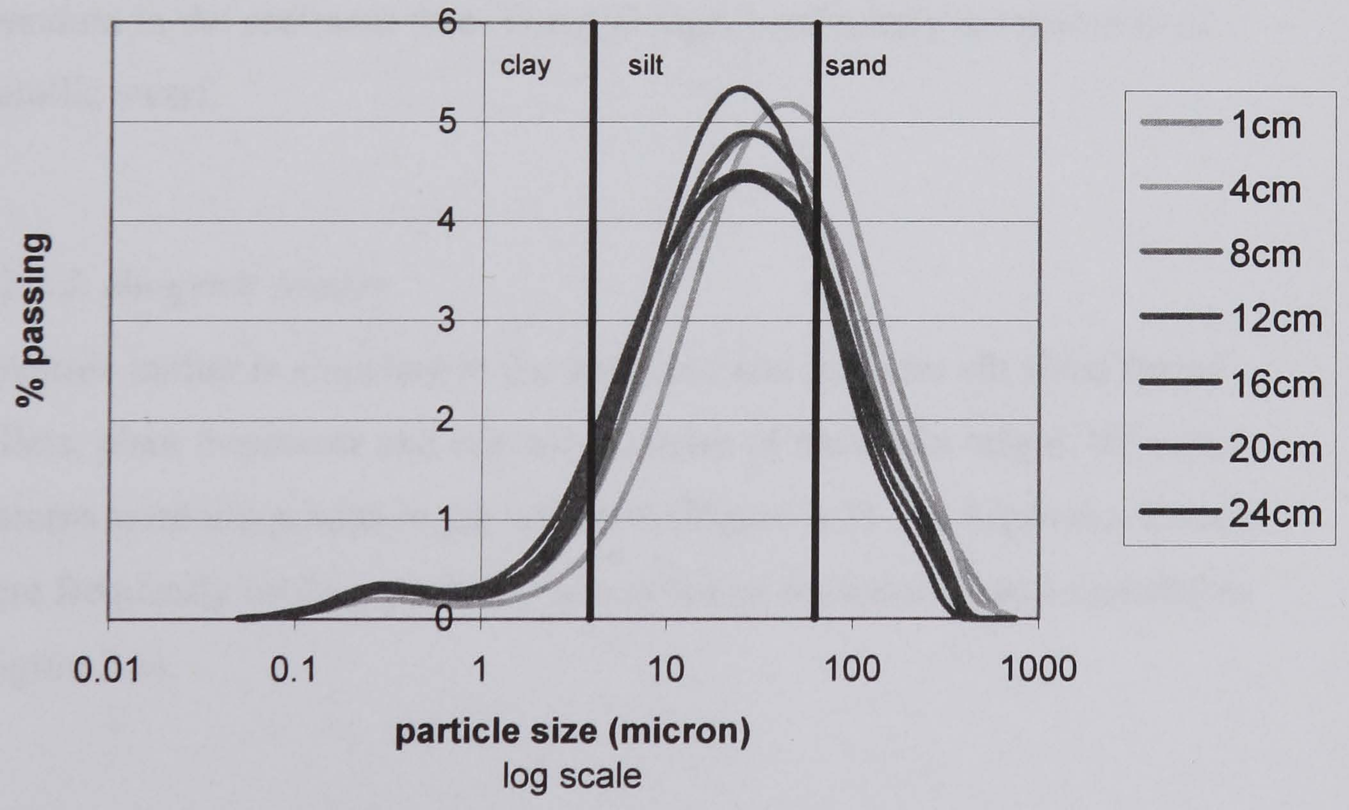


Figure 3.4b: Particle Size Distribution of Smethick Sediment



3.2.2.2. Anthropogenic Components

Anthropogenic components of industrial origin were commonly observed in the urban sediment. They include:

- Furnace derived particles: Spherical fly ash particles of a range of sizes from 2-65μm (Figure 3.5a) and fragments of glassy material with a general composition of Fe, Ca, Al, Si and O, thought to be slag (Figure 3.5b)
- Metallic swarf of brass, steel and Sn-rich material and metallic spheres of native Fe
- Small sub-micron fragments of Ba-sulphate, Ti-Oxides and Zr-silicate were observed occasionally, throughout the sediment. Larger clasts (≤30μm) of barite and Zr-silicate were also observed
- Calcium bearing grains (possibly cement)
- Rare gold particles, with the appearance of metal trimmings or wires (Figure 3.5c).

The anthropogenic particles were frequently observed in the sediment from both Great Bridge and Smethwick, although they appeared to be more abundant in the sediment from Great Bridge, particularly the particles of metallic swarf.

3.2.2.3. Biogenic Matter

Biogenic matter is abundant in the sediment and includes silt sized faecal pellets, plant fragments and organic particles of uncertain origin. Siliceous diatoms were ubiquitous in the sediment (Figure 3.3). At depth the diatoms were frequently broken, probably as a result of compaction and dissolution (Figure 3.6).

3.2.2.4. Clastic Material

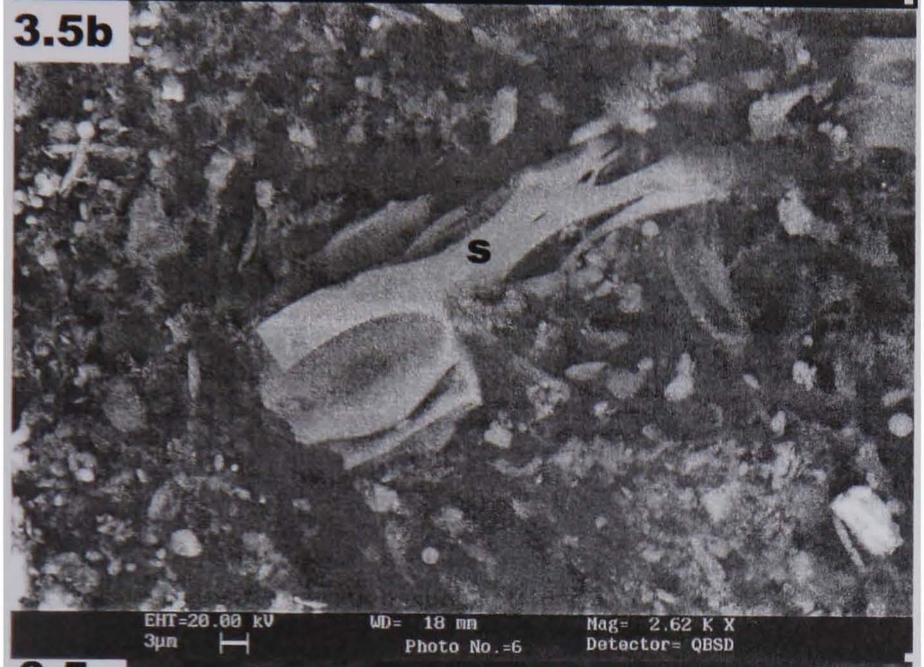
Silt sized quartz and detrital silt grains with similar compositions to plagioclase, potassium feldspar and mica were commonly observed in the

Figure 3.5: CryoSEM BSE images of detrital anthropogenic particles in Great Bridge canal sediment

3.5a

a: An Fe rich spherical particle of fly ash

3.5b



b: A porous particle of slicate slag material (s)

3.5c

c: Spongy reprecipitated gold on a detrital gold wire

3.6

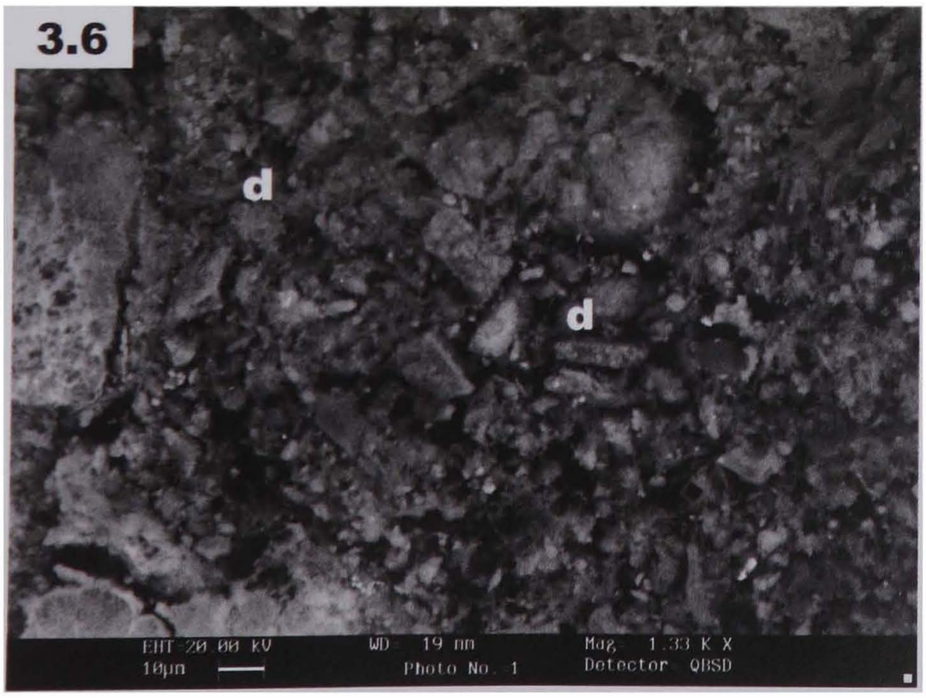


Figure 3.6: A CryoSEM BSE image of Great Bridge sediment from 25cm depth, containing two broken diatoms (d)

sediment, although they form only a volumetrically minor component. The presence of quartz and feldspar was confirmed by XRD analysis conducted on the Smethwick sediment.

3.2.3. Authigenic Components

Authigenic minerals are commonly observed throughout the sediment of both Great Bridge and Smethwick. Authigenic minerals were identifiable by their euhedral crystal faces or delicate amorphous structures; within the sediment they were commonly observed filling pore space or having nucleated upon detrital material. They are ubiquitous throughout the sediment profile and the most abundant forms are phosphates, carbonates and sulphides.

3.2.3.1. Phosphates

The most commonly observed authigenic mineral growths are euhedral bladed crystals of iron phosphate, interlocked in clusters, frequently in rosette or sheaf-like structures of up to 60μm across. X-ray diffraction analysis indicates the presence of the reduced iron phosphate vivianite ($Fe^{2+}{}_3(PO_4)_2.8H_2O$) (Nriagu and Moore, 1984), which is consistent with the form of crystals seen.

Clusters of vivianite crystals are present within 1cm of the sediment water interface, in the uppermost few centimetres of the sediment the majority of vivianite crystals are pristine or partially etched e.g. Figure 3.7a. With increasing depth the crystals become progressively more etched, with obvious corrosion on the edges of crystals and pitting along cleavage planes (Figure 3.7b). Although vivianite apparently becomes etched with depth most crystals show some sign of etching, partially etched crystals were seen in a sample taken from the sediment water interface and conversely pristine samples were also observed close to highly etched grains at depth. It is apparent however that at the surface the majority of grains are pristine or only slightly etched and that this balance shifts to predominantly etched grains at depths greater than 5cm. Micro-chemical maps of the sediment produced by the BGS, using an electron microprobe revealed a decrease in the volume of Fe and P rich grains in the sediment between a sample from 15cm and a sample from 30cm depth at Great Bridge (Figure 3.8). While this may be the result of the dissolution of vivianite, it could also be due to inhomogeneities in the sediment resulting from changes in the nature of inputs to the canal through time or from sample to sample variation.

Textural evidence suggests that a significant proportion of vivianite grains have nucleated upon the surface of detrital grains or organic matter. The composition of the grains upon which vivianite appears to be nucleated varies from that of quartz, calcite, and mixed sulphides (Figure 3.7c) to Fe, Ca, Al and Si rich grains that could be feldspar or slag. A number of the nucleation sites are Fe rich, and therefore may have provided a source of Fe for the growing vivianite grain, however the majority of grains have a composition that is completely unrelated to vivianite. In one example a cluster of vivianite is nucleated around a large particle of organic matter (Figure 3.7d).

At depths of 15 cm in the Smethwick sediment small spongy growths of Zn-rich FeS were observed surrounding a number of etched vivianite grains (Figure 3.7e). This textural relationship was not observed between Fe-rich sulphides and pristine vivianite grains, which suggests that these spongy growths may form as a result of the release of Fe during the dissolution of vivianite. This relationship was not observed in the Great Bridge sediment, although spheres of Fe-carbonate were observed coating a hollow sphere close to an etched vivianite grain in a sample from a depth of 20cm (Figure 3.7f).

Other phosphate minerals such as more thermodynamically stable calcium phosphates are rare. Small granules of calcium phosphate were observed in only one sample from Great Bridge, from 20cm deep, encrusting an etched vivianite grain (Figure 3.7g), showing a similar relationship to that observed above between vivianite and Zn rich Fe sulphide grains. Vivianite was the only phosphorous mineral detectable by XRD (Appendix 7.1)

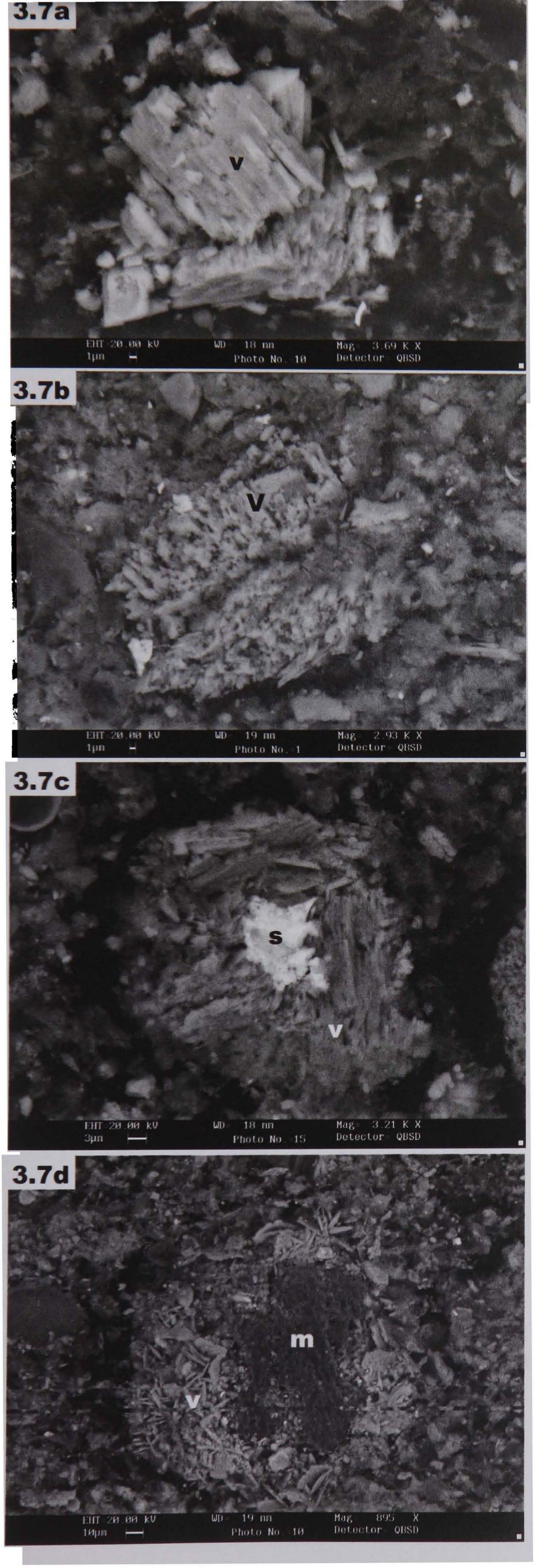


Figure 3.7: CryoSEM BSE images of vivianite textures in urban canal sediment from Great Bridge and Smethwick

a: A grain of vivianite (v) at a depth of 15cm in Great Bridge sediment, showing evidence of partial dissolution

b: A distressed grain of vivianite (v) from a depth of 30cm in Smethwick sediment, with obvious corrosion along the edges of crystals and pitting along cleavage planes.

c: A vivianite crystals (v) encrusting a central pocket of CuFe sulphide (s), from a depth of 15cm in Great Bridge sediment

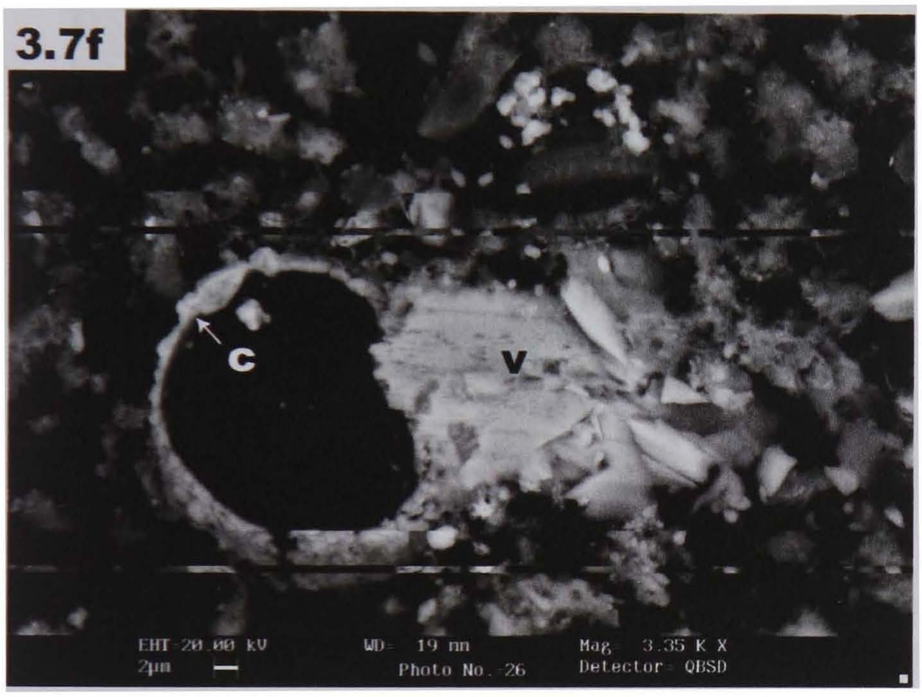
d: A large pocket of organic matter (m) encrusted by clusters of vivianite crystals (v) from a depth of 4mm in Great Bridge sediment

Figure 3.7 cont.

3.7e

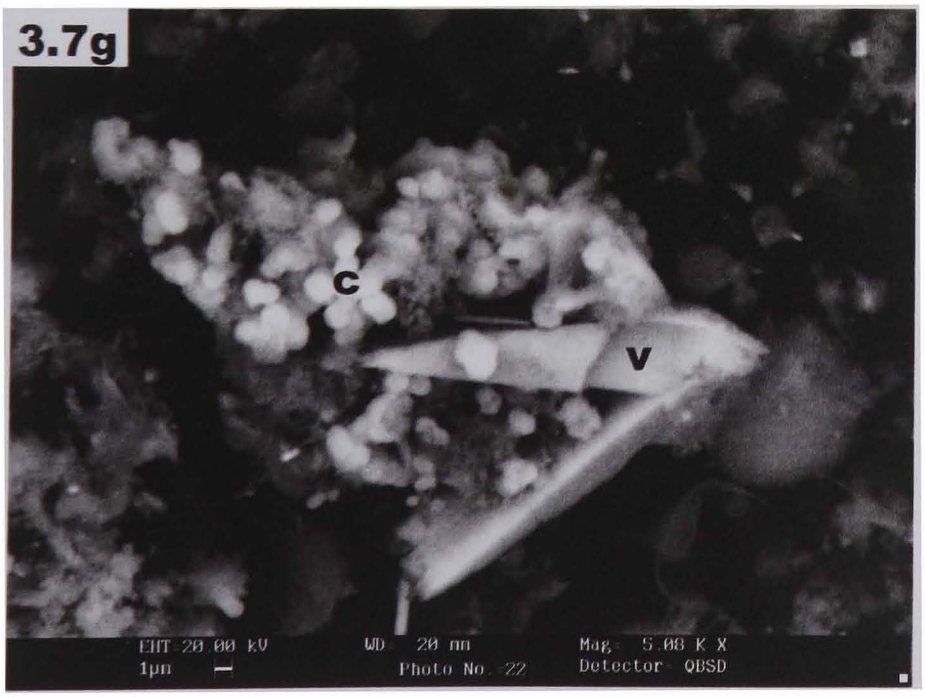
e: A partially etched grain of vivianite (v), adjacent to spongy grains of ZnFe-sulphide (z) from a depth of 25cm in Smethwick sediment

3.7f



f: A partially etched grain of vivianite (v) adjacent to a hollow object, coated in Fe- carbonate (c), from a depth of 20cm in Great Bridge sediment

3.7g



g: An intergrown cluster of vivianite blades (v) and sphereoids of Ca-phosphate (c) on a substrate of spongy clay. (from a depth of 20cm at Great Bridge)

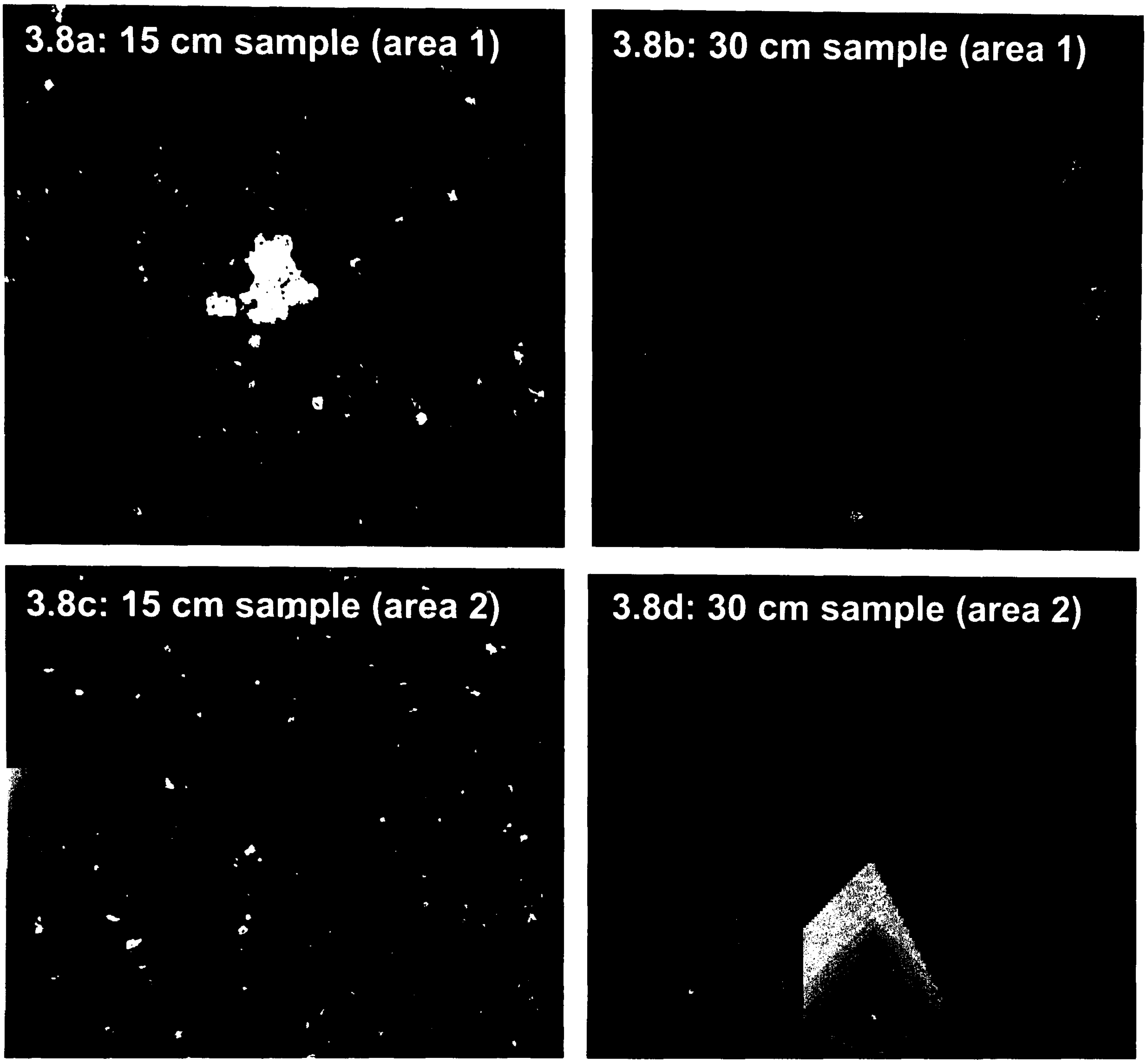


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Figure 3.8a-d: Micro-chemical maps showing the distribution of vivianite grains in four thin sections taken from area 1 and 2 (two different cores of Great Bridge Canal sediment) at depths of 15cm and 30cm

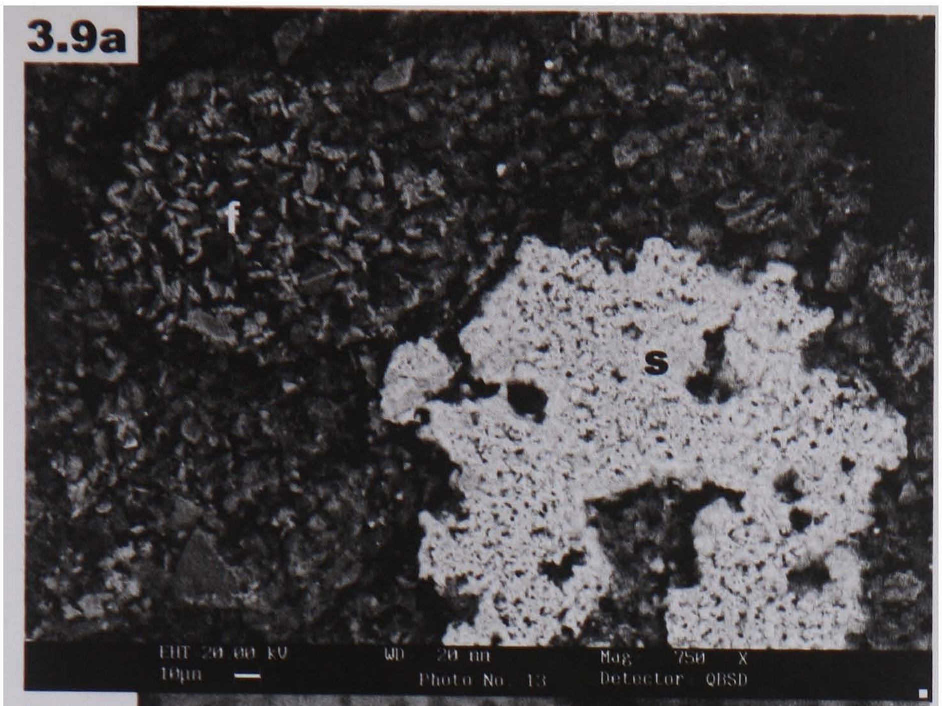
3.2.3.2. Iron Sulphide

Iron sulphide is widespread throughout the sediment, and is the second most abundant mineral in the sediment after vivianite. Iron sulphides occur in two different forms in the sediment:

1. **Film Coating Sulphides:** these have an obvious association with organic debris and biofilm. Film coating sulphides were present in the sediment from both Great Bridge and Smethwick, although they were more commonly observed and more diverse in form in samples from Great Bridge. These sulphides can be further subdivided into three forms:
   a) *Complex Cellular Aggregates:* A bright amorphous Fe and S rich aggregate 150μm in diameter was viewed in a sample from Great Bridge at a depth of 5cm. The Fe-sulphide appears to be acting as a cement, between densely packed 1μm cellular (Figure 3.9a) and rod shaped voids (Figure 3.9b), which appear to be the remnants of bacteria.
   b) *Coatings on Bacteria:* Spherical Fe and S rich grains were observed, they were approximately 1μm across, and appeared to be mineralised cells or bacteria (Figure 3.9c). Bright transparent spherical and rod shaped cells of 1-2μm in length were also observed close to most Fe-sulphide mineralised organic matter (Figure 3.9d).
   c) *Coatings on Other Organic Structures:* Large pieces of organic debris were also observed to be mineralised by Fe and S in sediment from both Great bridge and Smethwick. A sample from Smethwick at 15cm depth contained a fibrous mass of biogenic filament 440μm by 160μm, which has been mineralised to Fe-Sulphide and enclosed localised Fe-sulphides, one small pyrite framboid and a rod like structure which was interpreted as bacteria (Figure 3.2 and 3.9d). In one sample from a depth of 24cm at Smethwick, an organic structure 110μm by 50μm, containing a comb-like array of elongated tubular pods was observed (Figure 3.9e). Each pod appeared to contain framboid like clusters within its tip (Figure 3.9f).

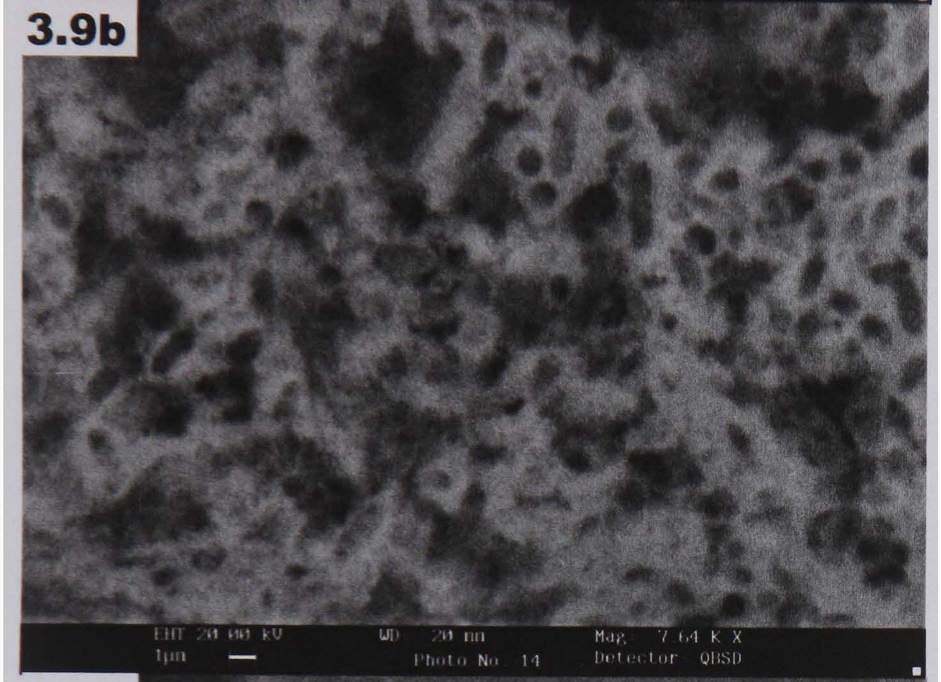
Figure 3.9: CryoSEM BSE images showing Fe sulphide textures in Urban Canal sediment

3.9a



a: A cellular precipitate of Fe-sulphide (s) resting on a faecal pellet of quartz silt with Fe-phosphate cement (f), (Great Bridge, 5cm depth)

3.9b

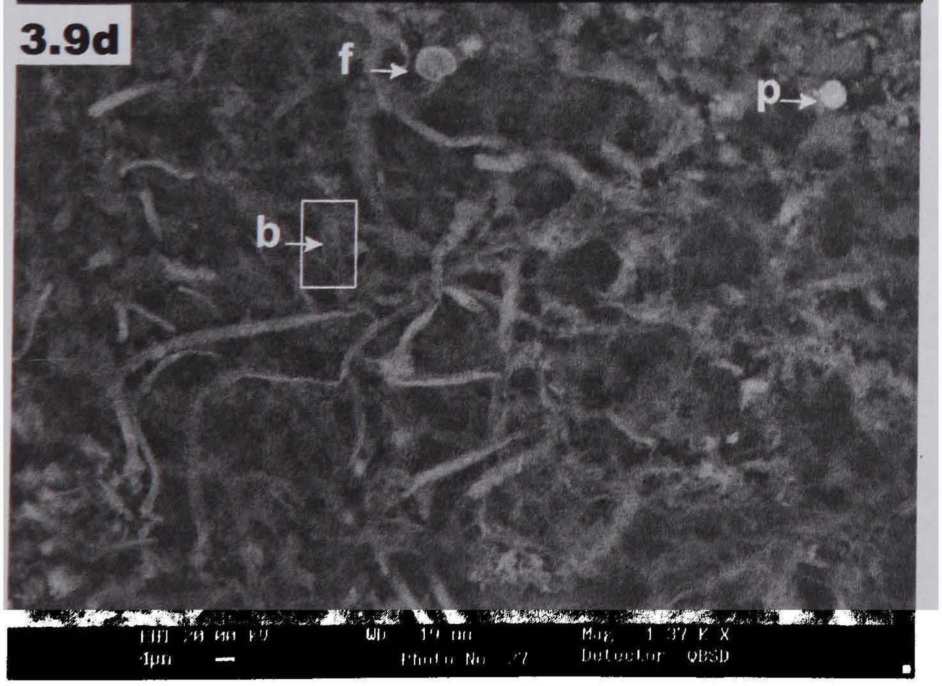


b: A close up of the Fe sulphide in Figure 3.9a illustrating the rod shaped bacterial bodies and their iron sulfide coating

3.9c

c: A water-filled plant cell with an area of Fe-S rich material (containing minor Zn, Cu) and small FeS rich cell-like structures that may be mineralized bacteria (b). (Great Bridge sediment, 5cm depth)

3.9d



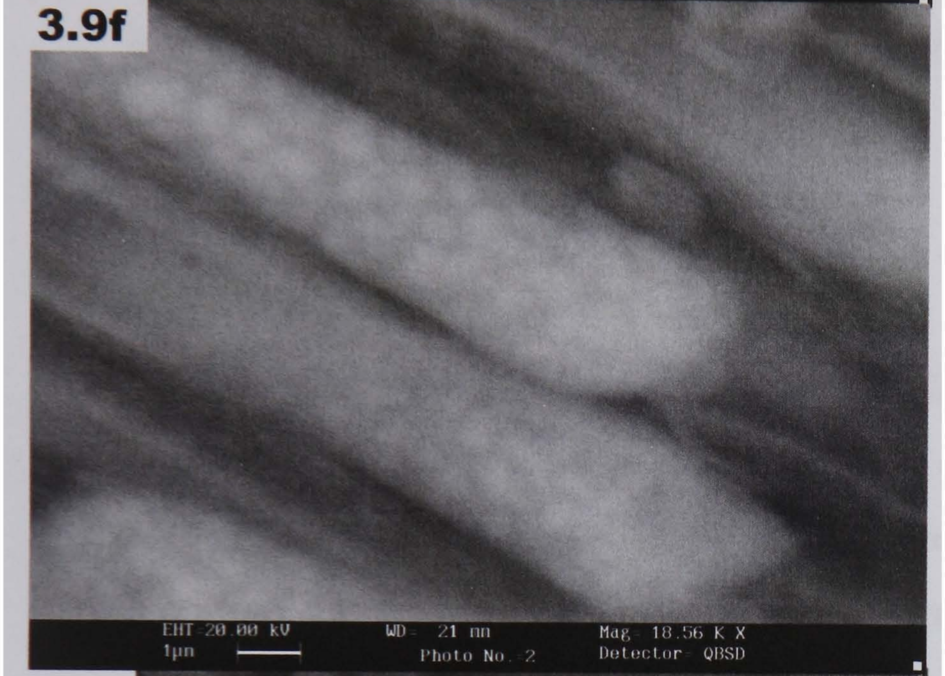
d: A filamnetous organic mesh mineralized to Fe-sulphide. Containing a pyrite framboid (p), an amorphous Fe sulphide (s) and a rod shaped bacteria (b). (overview in figure 3.2)

Figure 3.9 cont.

3.9e

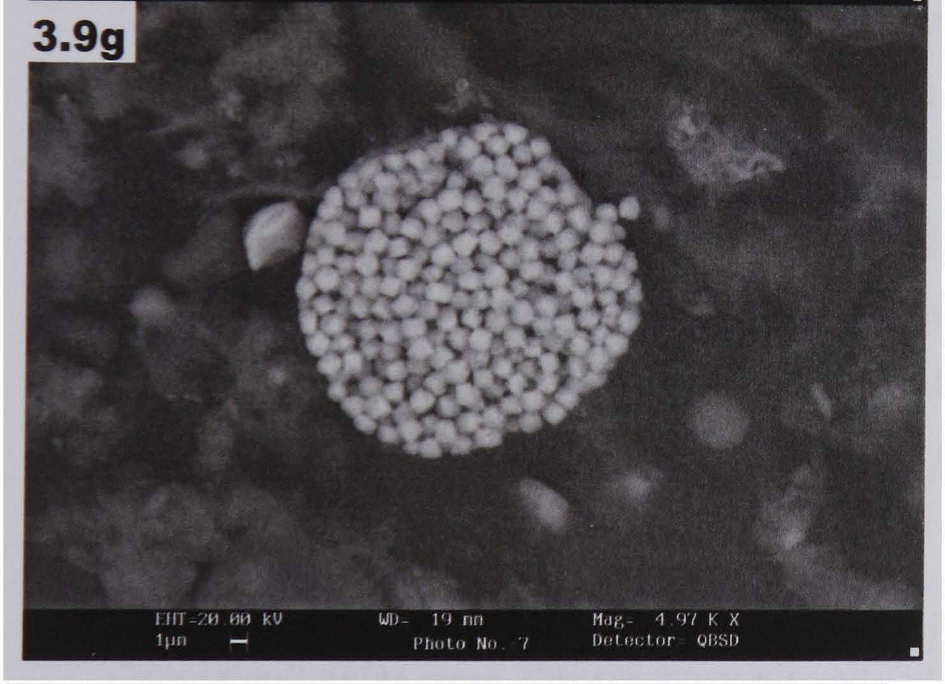
e. Framboid-like clusters in the ends of rod-like membranes forming a comb-like structure, from a depth of 24cm depth in Sandwell sediment

3.9f



f. A close up of the elongate cellular organic structures containing FeS microcrystals shown in 3.9e

3.9g



g. A well formed pyrite framboid that has been cleaved by the sample prepartion procedure, from a depth of 1cm in Smethwick sediment

3.10

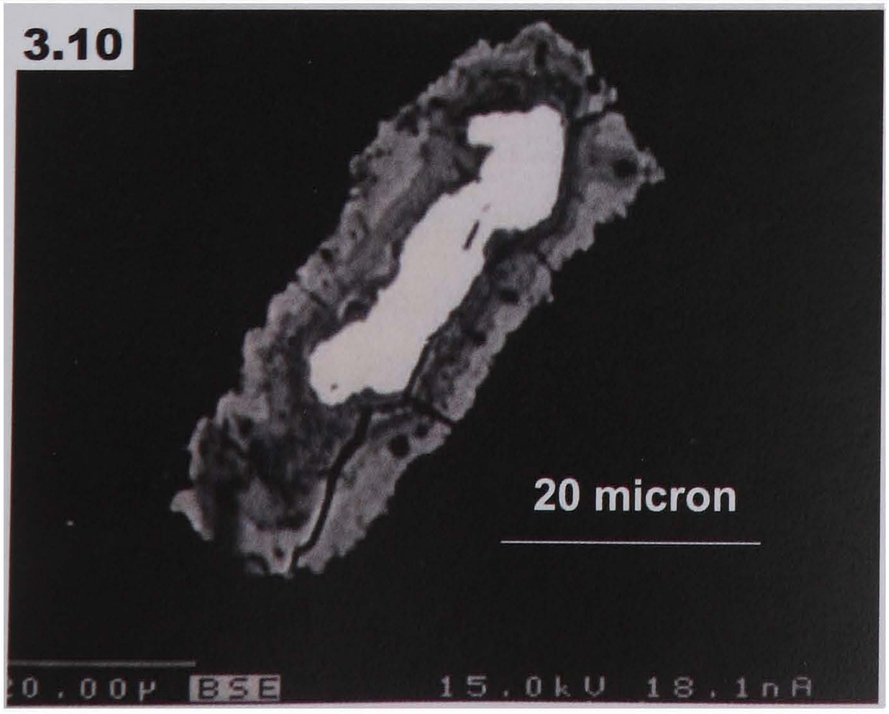


Figure 3.10: Backscatter SEM image of Great Bridge sediment showing a brass particle, altered to Cu-Fe sulphide at its edges

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Pyrite Framboids: these were observed as spherical clusters of iron sulphide held within a thin electron transparent film of probable organic origin (Figure 3.9g). Framboids were observed very occasionally in the sediment from both Great Bridge and Smethwick at all depths, they varied in diameter from 2-20μm.

Spherical granules of FeS approximately 1μm in diameter, were observed throughout the sediment, however it was impossible to discern the structure of these particles.

3.2.3.3. Base Metal Sulphides

Zinc sulphides were the second most common forms of sulphide in the sediment. They occur as a zinc-iron sulphide in several textural forms, most often as amorphous, spongy, floccular aggregates ranging in size from sub-micron to 20μm, with an almost organic appearance (Figure 3.11a). These sulphides were generally observed filling pore space with no association to other minerals or organic matter. One exception to this is the possible association with vivianite (Figure 3.7e). A Si, Al, Fe and Zn rich grain coated in Fe rich-Zn sulphide seen in Figure 3.11b, was interpreted to have resulted from the sulphidisation of fly ash through anaerobic degradation. Analysis of the zinc sulphides indicated that they have a wide compositional range with metal to sulphur ratios in the range 0.59 to 0.87 (Table 3.1) (Large et al., in press).

Copper sulphides were observed occasionally at all depths (1-24cm) in the sediment, they occurred more frequently in the sediment of Great Bridge than that of Smethwick. In both sediments copper occurs as a copper iron sulphide in several forms; amorphous grains from sub-micron size to 30μm in length (Figure 3.11c), coatings formed by the anaerobic degradation of fragments of native copper and brass (Figure 3.10) and coating possible biogenic structures (Figure 3.11d). Analysis revealed consistent Cu:Fe:S ratios of approximately 1:1:2 identical to that found in chalcopyrite (Large et al., in press) Table 3.1. This stoichiometry is in agreement with a previous study (Parkman et al., 1996)

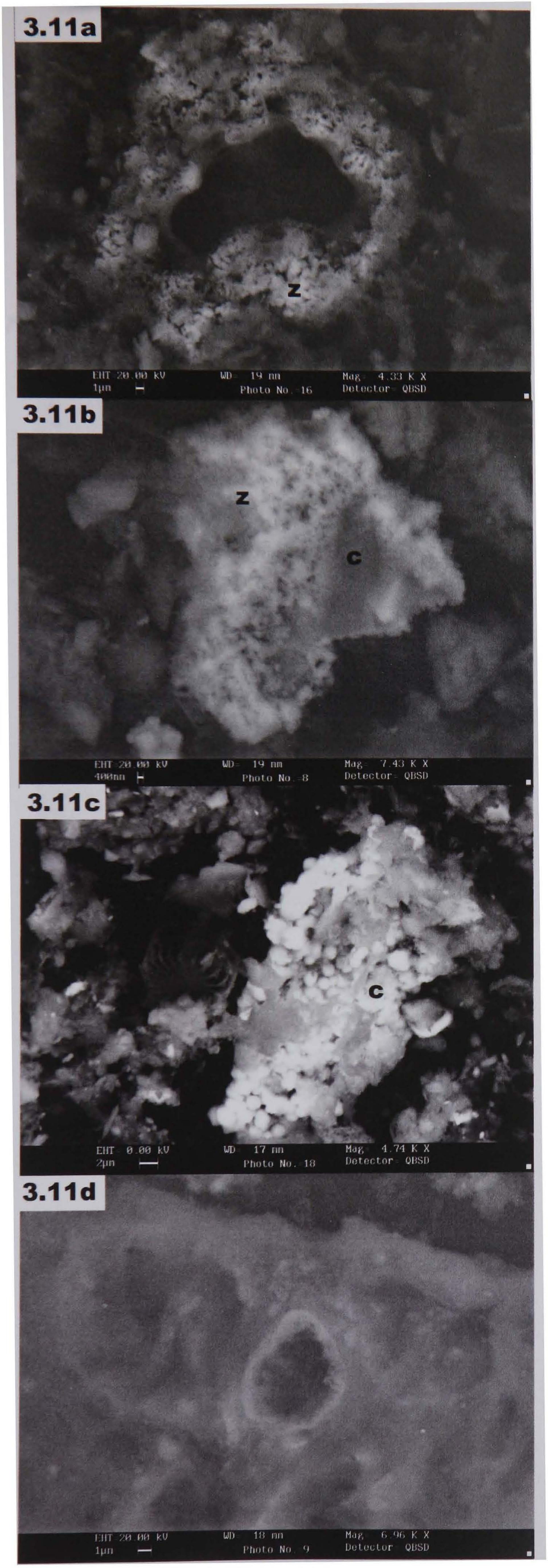


Figure 3.11: CryoSEM BSE images of base metal sulphides in urban canal sediment

a: An amorphous floccular zinc sulfide (z) filling pore space, from 5cm depth in Smethwick sediment

b: A Si, Al, Fe and Zn rich grain (c) (possibly clay), coated in Fe-rich Zn sulphide (z), from a depth of 1cm in Smethwick sediment

c: An aggregate of CuFe sulphide (c) (Fe:Cu approx. 1:1), at a depth of 8cm in sediment from Great Bridge

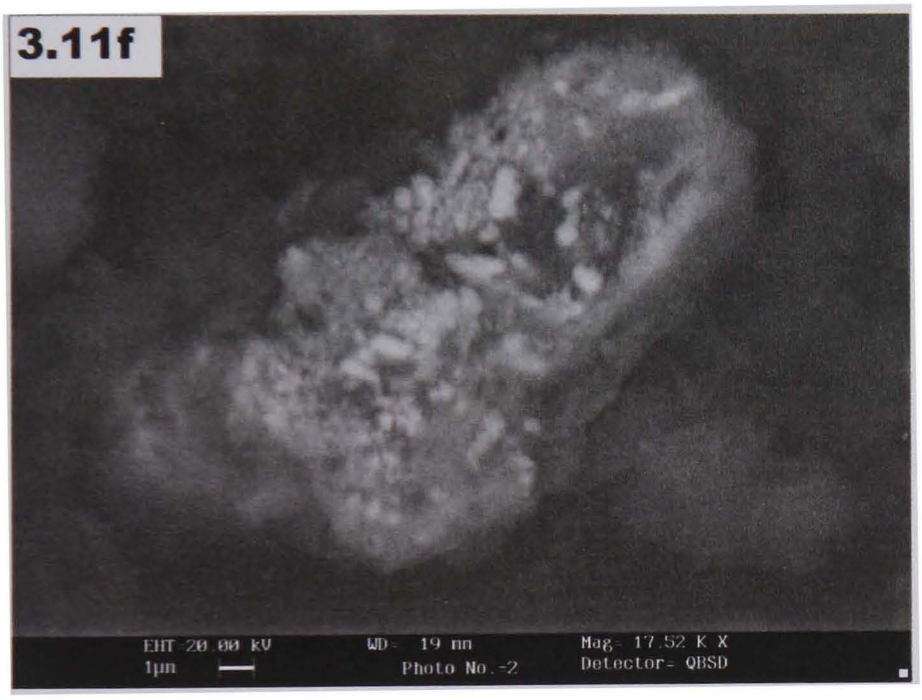
d: Plant material impregnated with Zn and Cu rich Fe-sulphide, from a depth of 15cm in Great Bridge sediment.

Figure 3.11 cont.

3.11e

e: Concentric bands of Cu-sulfides (bright) and Zn-sulfides (dark) around a bright Cu-rich particle. (5cm, Great Bridge)

3.11f



f: Spherical Pb Sulphide granules on an organic substrate. (15cm Great Bridge) in which authigenic copper sulphides were observed with chalcopyrite structure and stoichiometry.

Copper and Zn were only observed together as zoned Fe-rich sulphides. In one example concentric Cu and Zn rich bands enclosed a sub-micron Cu-rich nucleus (Figure 3.11e), in other examples the zoning was to too fine to be resolved by EDXA.

Lead sulphide was very occasionally observed in the sediment, Figure 3.11f shows a cluster of Pb and S rich spheres coating an organic substrate in the sediment from Great Bridge at a depth of 15cm.

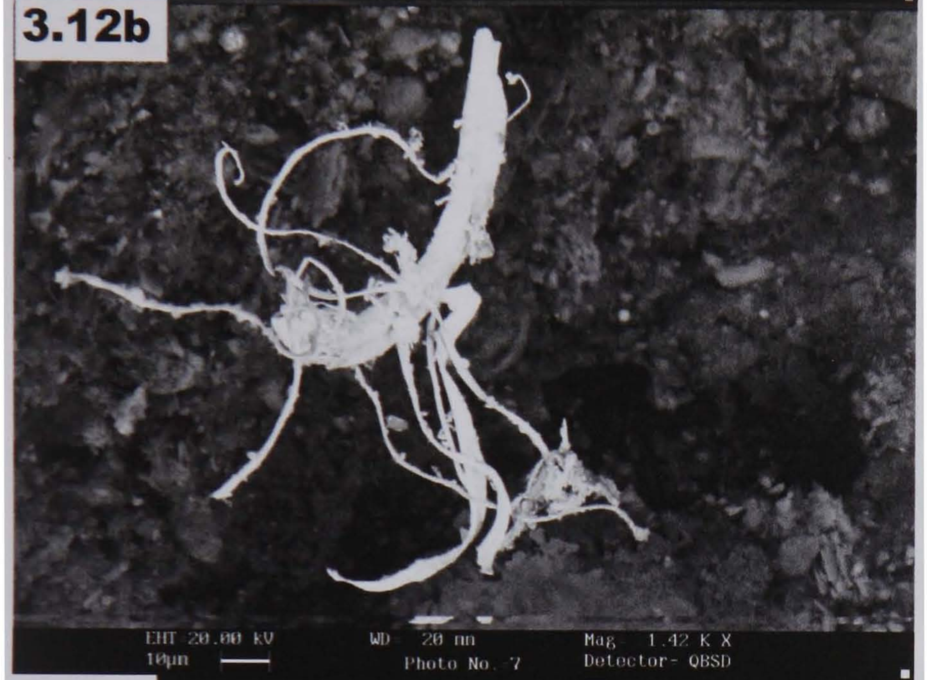
3.2.3.4. Authigenic Silver and Gold

Silver was observed in the sediment as a sulphide. Figure 3.12a shows as a cluster of silver sulphide needles, it is unclear whether these result from authigenic growth or the anaerobic degradation of detrital silver wires.

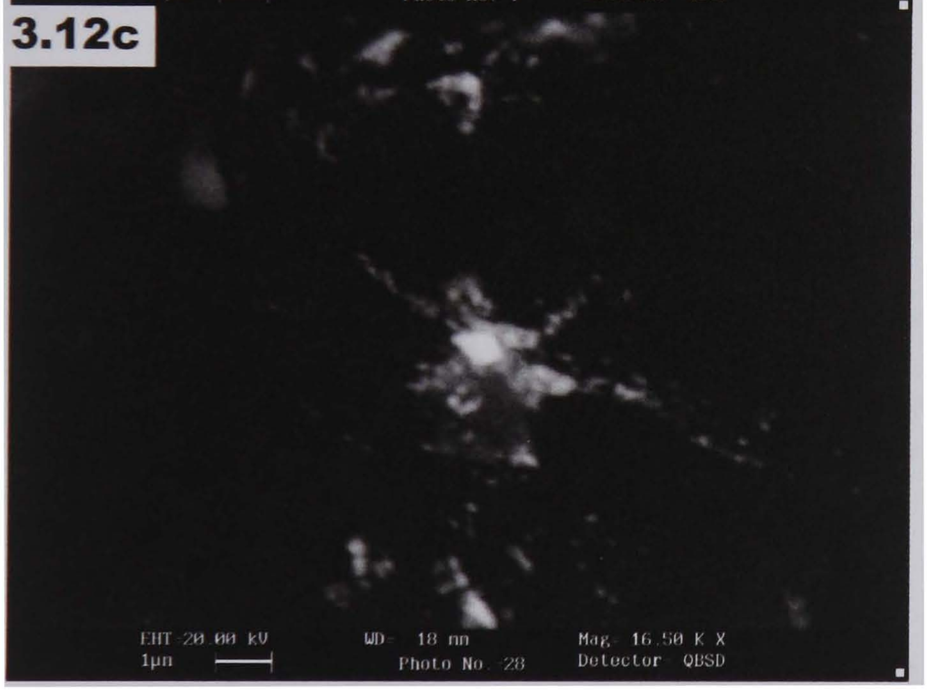
Some sediment samples suffered contamination by remnants of gold from coated samples in previous sample runs in the SEM, resulting in the occurrence of pure gold particles on the surface of the sediment. However gold was also observed in the sediment as amorphous spongy growths containing detectable Cu and Ni and it is assumed that this gold had been precipitated authigenically within the sediment. On one occasion Cu and Ni rich gold was on the surface of some plant debris (Figure 3.12c). Spongy Cu rich gold growths were also observed on the surface of unaltered pure gold shavings entangled with a piece of nickel wire (Figure 3.12b). The presence of Cu in the spongy gold growths on this detrital gold fragment suggests that they have been precipitated from solution onto the gold shavings.

Figure 3.12: CryoSEM BSE images of authigenic silver and gold particles in urban canal sediment

a: A cluster of Ag and S rich 'needles'. It is not possible to determine whether these are sulphitised detrital material or authigenic Ag-sulphide (5cm Great Bridge)



b: Spongy reprecipitated Cu-rich Au upon a detrital fragment of pure Au and Ni wires (Great Bridge 5cm)



c: The surface of a plant debris particle in which gold forms a minute replacement or adsorption, surrounded by a Ni-rich halo. (15cm deep, Great Bridge)

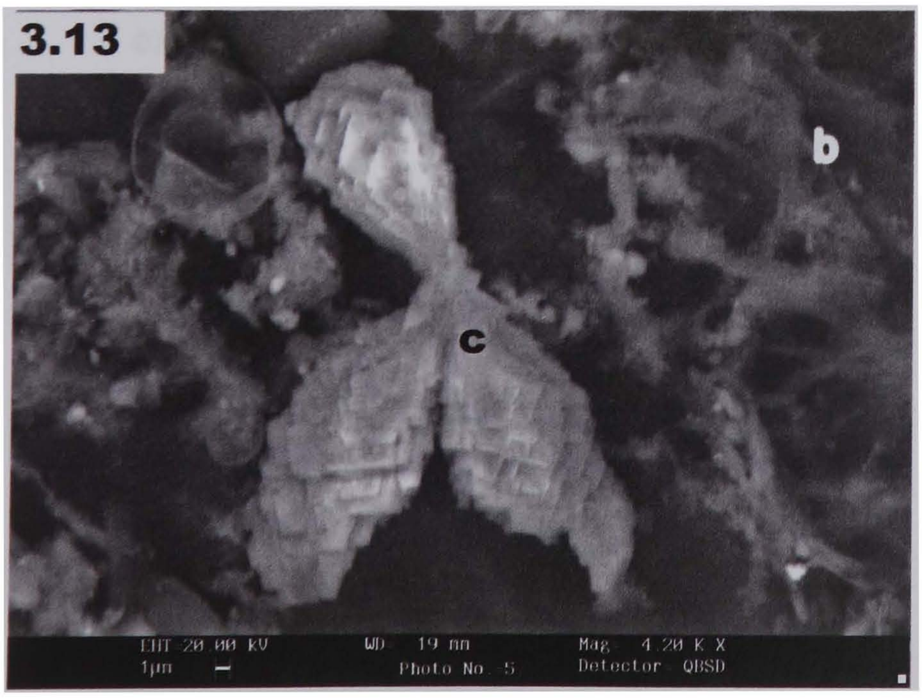


Figure 3.13: A CryoSEM BSE image of an authigenic calcite grain with a delicate stepped morphology (c) on a substrate of floccular clay and wispy biofilm (b), from the sediment water interface at Smethwick

3.2.3.5. Carbonates

Calcite is considerably less abundant than vivianite, but was commonly observed throughout the 1 to 30cm depth interval as individual crystals of up to 10μm in width. It is probably present in both detrital and authigenic forms. Calcite was observed as simple euhedral rhombic crystals, radial clusters and crystals with a delicate, minutely stepped morphology (Figure 3.13). Siderite, which is generally expected in freshwater organic rich sediments, was observed as a minor phase in only two relatively deep samples from Great Bridge, where it occurred as a botryoidal coating on coarse clastic particles and organic structures. Siderite is notable only by its absence, this has been observed in previous studies (Emerson, 1976) which suggest that in phosphorous rich environments the slow reaction kinetics of siderite formation results in the incorporation of Fe^{2+} into the less thermodynamically stable but more rapidly precipitated vivianite. Another factor may be growth kinetics that favour the precipitation of available HCO_3 as calcite.

3.2.3.6. Iron Oxides

Iron oxides are a widespread though minor constituent of the sediment, occurring as spherical grains which were generally no larger than 2μm. In some cases these oxides occurred in close proximity to iron-sulphide grains.

3.2.3.7. Organic Components

Authigenic biofilm was ubiquitous throughout the sediment. Biofilms are extracellular polymeric substances that are predominantly composed of polysaccharides (Geesey, 1982). Biofilm was observed as thin electron transparent filament (Figure 3.13). Biofilm is apparently playing an important role in loosely binding the fine particles of the sediment together. Biofilm is also observed close to the majority of iron sulphide particles (section 3.1.3.2) and it is thus interpreted as an important binding site for this mineral.

3.3. Rural Canal Sediment Results

Rural canal sediment from Snarestone was also analysed by CryoSEM and Figure 3.15a shows a low magnification view of the sediment from 5cm depth. As in the urban sediments an open clay matrix can be observed which is bound in places by organic biofilm. The sediment is massive on the scale of observation (up to 1mm), with no clear evidence of oriented clay fabric. The water filling pore space between the clay matrix is seen as a uniform dark grey colour and it exhibits a high degree of interconnection at the surface. However the sediment becomes more compact with depth with pore sizes decreasing from 10μm at the surface to 1-2μm at 24cm.

3.3.1. Grain Size Analysis

Particle size analysis of sediment from Snarestone, by the Malvern Mastersizer®, showed the sediment to be composed of predominantly clay, silt and fine sand sized grains (Figure 3.14a). This sediment shows a marked variation in grain size over the 24cm depth profile (Figure 3.14b). For the uppermost 13cm of the sediment ~10% of the particles are clay sized (≤3.9μm), ~60% of particles fall within the silt size range (3.9-63μm) and the remainder falls largely within the fine sand size range (63-250μm). However at depths greater than 13cm in the sediment, the proportion of clay sized particles increases to ~15-20% and the proportion of silt sized grains decreases to ~50%. Notably, at depths of between 14 and 18cm ~40% of particles are in the fine sand sized fraction, while at the surface this fraction accounts for only ~25% of particles. This increase in sand sized grains was observed by the CryoSEM analysis of a sediment sample from 15cm, which contained abundant large quartz clasts of 50-500μm in diameter (Figure 3.15b), such large grains were absent from shallower samples (Figure 3.15a). It must be noted that the increase in the percentage of clay sized particles with depth might not reflect an actual increase in the amount of clay in the sediment, but an analytical artefact. This is because the measurements are of the percentage of particles passing the laser, the increase in larger sand sized grains at depth will decrease the total number of particles in the sediment causing an apparent increase in the

Figure 3.14a: Cumulative Particle Size Distribution of Snarestone Sediment

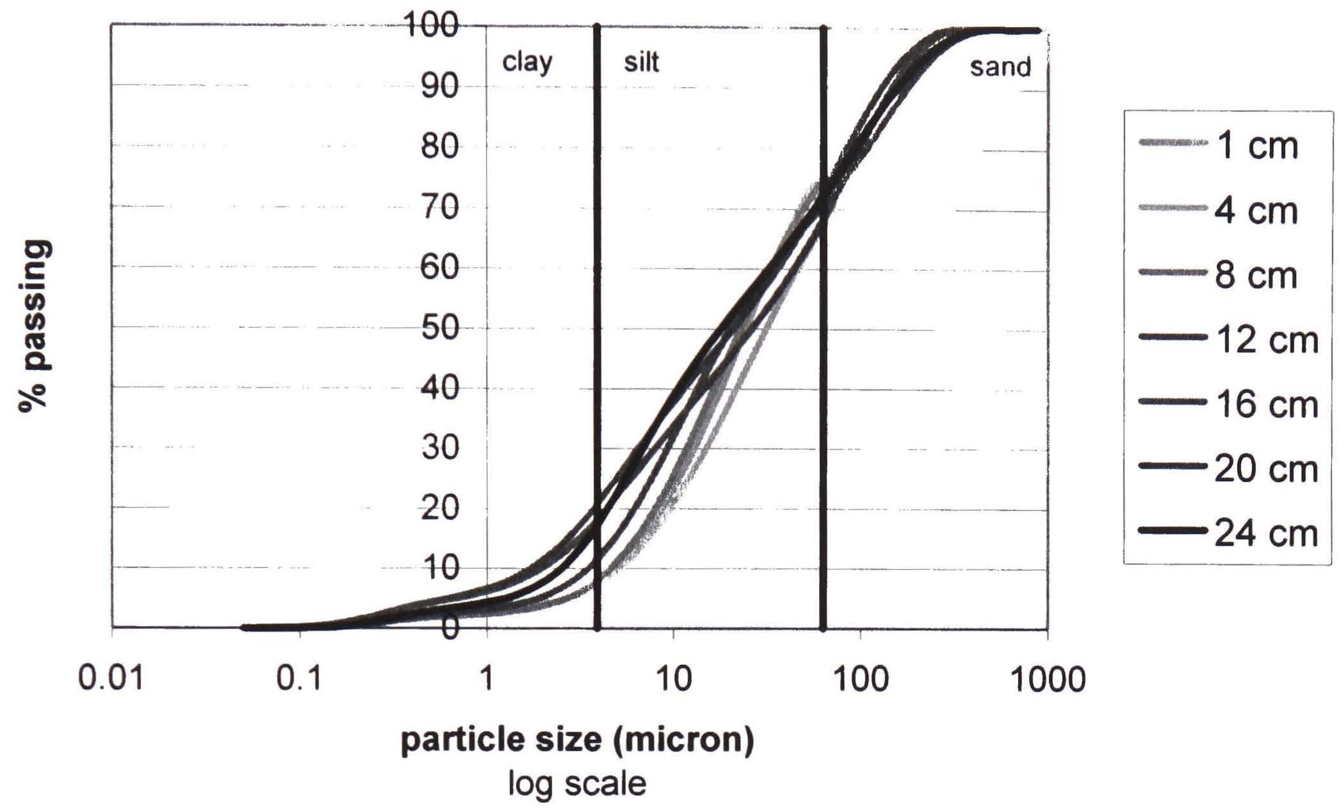
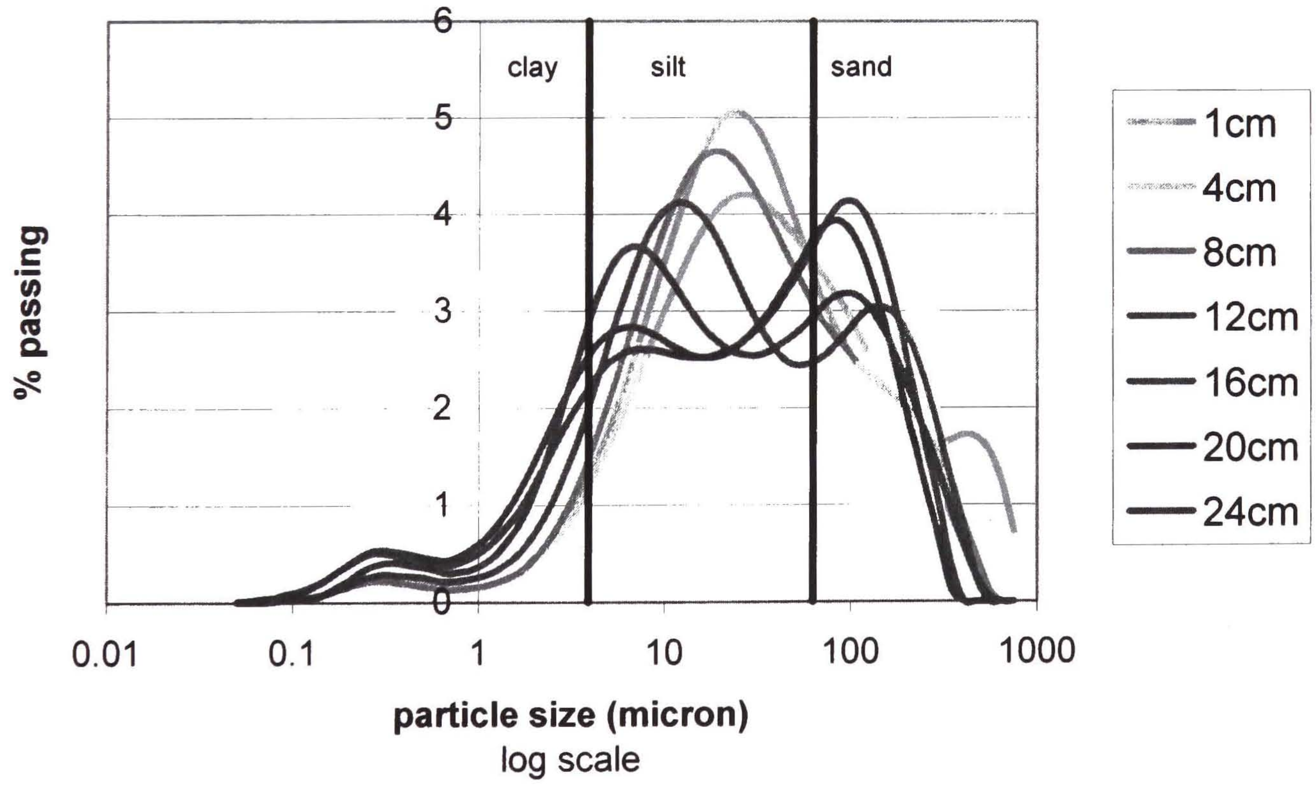


Figure 3.14b: Particle Size Distribution of Snarestone Sediment



proportion of smaller particles. The grain size was only analysed in one seasonal sample due to time constraints, although observations of the sediment made during sampling and crushing revealed that coarser grained sediment was present to varying degrees in all samples beneath depths of ~12cm.

3.3.2. Allochthonous Components

3.3.2.1. Clays

The large fine-grained fraction of this sediment is reflected in the abundance of clay observed by CryoSEM and analysis. Figure 3.15c is a high magnification image showing examples of the sediment's clay textures, EXDA data shows the matrix contains Al, Si, Ca, K and Fe and XRD analysis identifies the clays illite and kaolinite (Appendix 7.2).

3.3.2.2. Biogenic Matter

Biogenic matter is less commonly observed than in the urban sediment reflecting the presence of an aerobic zone at the sediment surface. Biogenic matter includes plant debris and diatoms (Figure 3.15c).

3.3.2.3. Clastic Material

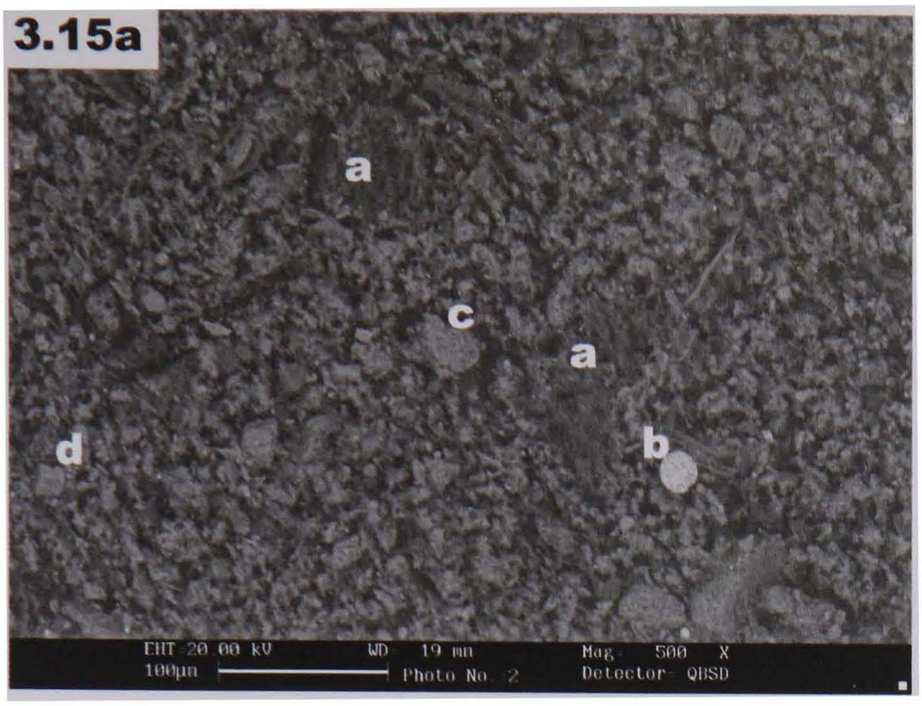
Detrital clasts include silt-sized particles of quartz, calcite, K-feldspar, mica, occasional dolomite and rare barite. The anthropogenic particles observed in the urban sediment were scarce, consisting of one occurrence of fly ash and occasional coal which had probably fallen in to the canal from barges. At depths of 15cm and below, larger sand sized (up to 500μm) rounded clasts of quartz were observed in the sediment (Figure 3.15b).

3.3.3. Authigenic Components

The rural sediment at Snarestone has not suffered from industrial pollution and therefore does not have a significant contaminant loading. This is reflected in the limited diversity of authigenic mineral phases. The only commonly

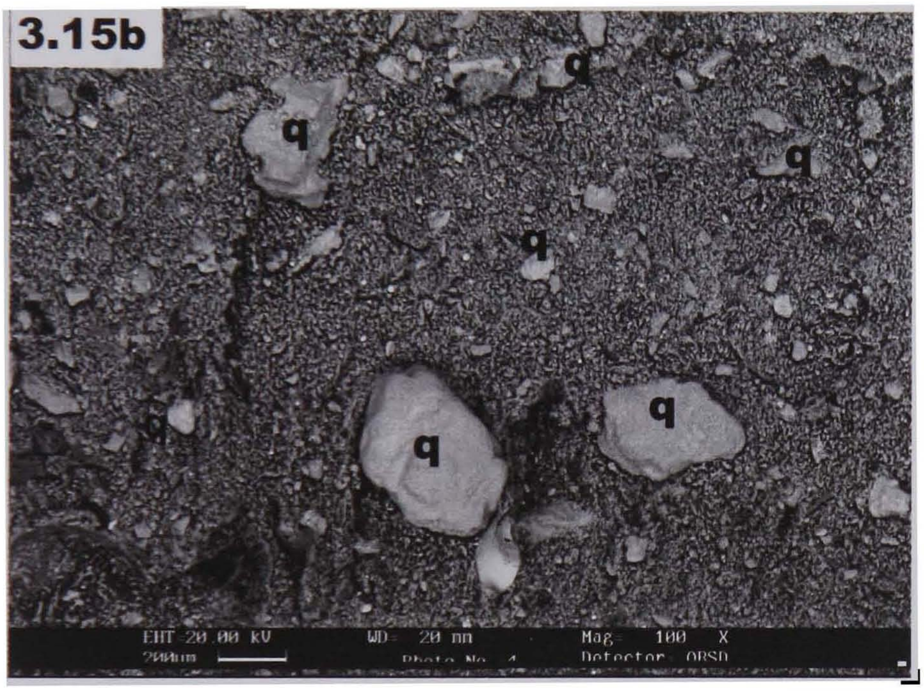
Figure 3.15: CryoSEM BSE images of rural canal sediment from Snarestone

3.15a



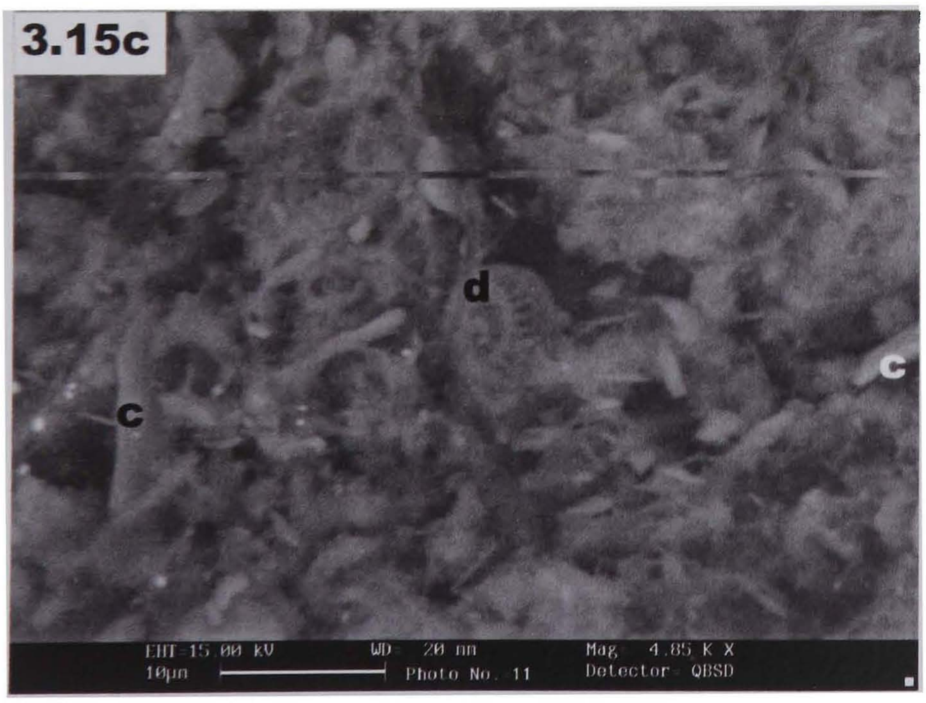
a: A low magnification view of the sediment from a depth of 1cm, showing the open porous matrix and clusters of organic matter (a), a pyrite framboid (b), an agglomerate of clay (c) and K-feldspar (d)

3.15b



b: A low magnification view of the sediment from a depth of 15cm, showing abundant quartz grains (q), ranging in size from 10-500 micron.

3.15c



c: A high magnification image of the sediment matrix showing a diatiom (d) and fine clay structures, including illite and kaolinite and some Fe-rich bladed particles, which could be chlorite (c).

observed authigenic phase was framboidal pyrite (FeS_2). In addition to pyrite, Zn-sulphide was also present in low abundance in the sediment.

3.3.3.1. Iron Sulphide

Two types of iron sulphide texture could be distinguished in rural canal sediment: amorphous Fe and S rich film coatings and framboids. The films were observed filling pore space, they have a similar appearance to biofilm and are probably of organic origin (Figure 3.15a). The more complex film coating sulphides and sulphidised organic matter observed in urban sediment were not observed in this rural sediment.

Pyrite framboids are relatively abundant in rural sediment in marked contrast to the urban sediments in which they are relatively scarce. Framboids occur from the sediment water interface downwards, this is noteworthy because the upper 5-10cm of the sediment were observed to be oxidised due to their brown coloration. The framboids range in diameter from 2-25μm, the crystallites that make up an individual framboid are equal in size, although between framboids they vary in diameter from 0.25-1μm. As in the urban sediment the framboids appear to be coated in a thin electron transparent film, which is probably biofilm. Two different forms of framboids were observed in the sediment:

1. Poorly formed 'proto-framboids', in which individual crystallites are indistinct (Figure 3.16b) and the overall surface texture is either smooth or 'cauliflower like' (Figure 3.16c). In these the film coating appeared to be thicker and brighter than those of well formed framboids.
2. Well formed framboids with clearly defined individual crystals (Figure 3.16d). In a few cases such framboids were split during the fracturing of samples revealing a cross section through the interior of the framboid structure. This showed the crystals to be ordered in concentric layers, and in one example the crystals displayed pentagonal symmetry (Figure 3.16e).

EDXA analysis of the iron to sulphur ratios revealed that framboids, proto-framboids and Fe-S rich films lie in discrete compositional ranges (Large et al., in press). Fe-S rich films have compositions between those expected for mackinawite (Fe-S). Proto-framboids and framboids to lie between Fe:S ratios expected for greigite (Fe_3S_4) and pyrite (FeS_2), with proto-framboids lying closer to greigite and framboids lying closer to pyrite (Table 3.1).

Table 3.1: Compositions of iron, zinc and copper sulphides measured by EDX analysis

Description	Atom %				
	S	Fe	Cu	Zn	S/Fe
Framboid	61.59	37.99	0.08	0.24	1.62
Framboid	64.10	35.05	0.13	0.29	1.83
Framboid	64.21	35.23	0.14	0.47	1.82
Framboid	61.13	38.67	0.00	0.17	1.58
Framboid	64.33	34.91	0.33	0.41	1.84
Framboid	63.59	34.95	0.82	0.36	1.82
Framboid	63.64	35.80	0.26	0.00	1.78
Protoframboid	60.00	40.28	0.00	0.04	1.49
Protoframboid	60.74	38.54	0.46	0.09	1.58
Film	53.88	46.50	0.00	0.10	1.16
Film	55.95	43.83	0.12	0.44	1.28
Film	57.48	40.95	0.66	0.30	1.40
	S	**Fe**	**Cu**	**Zn**	**S/Metal**
Zn-Fe-S	45.98	9.80	3.47	40.43	0.86
Zn-Fe-S	46.46	9.22	2.37	41.73	0.87
Zn-Fe-S	45.39	9.66	2.99	41.83	0.83
Zn-Fe-S	36.88	10.58	0.36	51.96	0.59
Zn-Fe-S	43.15	11.37	1.15	44.15	0.76
Cu-Fe-S	47.33	26.54	24.67	1.31	0.90
Cu-Fe-S	48.27	27.46	23.34	0.81	0.94

In one sample a large cluster of framboids were observed in which over 50 framboids were discernible, each one encased in a separate biofilm sheath (Figure 3.16f). The framboids within the cluster vary in diameter from 25μm to 3μm and the entire cluster has a diameter of 100μm. On the surface of the cluster a few individual crystallites are stuck to biofilm (Figure 3.16g), apparently as a result of the majority of the framboid being plucked away during the cleavage of the sample. The biofilm sheaths of individual framboids appear to be joined at triple junctions between 3 framboids (Figure 3.16g). One framboid shows the cauliflower texture attributed to proto-framboids, with roughly hexahedral clusters of poorly defined crystallites 1.7μm across. In some framboids the crystallites appear to be neatly packed, while others are less ordered, this is probably due to compaction by the close packing of the framboids and this is evidenced by flattened compacted contacts between some adjacent framboids.

A sample of rural sediment that had been shaken for two hours in 1M ammonium acetate was examined, as part of the CryoSEM investigation, into two sequential extractions (Section 2.3.4.1). In this sample any pyrite framboids had completely disassociated into individual pyrite crystals. This confirms the weak nature of bonds between pyrite crystals and the possible importance of biofilm in maintaining the structural integrity of a framboid.

Sub-micron single, FeS-rich, rounded grains were observed in the rural sediment, these were not generally observed close to framboids.

3.3.3.2. Base Metal Sulphides

Zinc rich iron sulphide was observed in the sediment on just two occasions and no other base metal sulphides were found reflecting the clean nature of the rural sediment. The two Zn sulphides observed were slightly different in form, at the sediment-water interface a sphere of Zn-Fe sulphide, 3μm diameter, was observed in open pore-space close to the clay matrix and sub-micron crystals of FeS (Figure 3.17a). At a depth of 10cm an amorphous Zn-Fe-S rich clay or film (20μm) was observed, again surrounded by bright specs of FeS (Figure 3.17b).

3.3.3.3. Iron Oxides

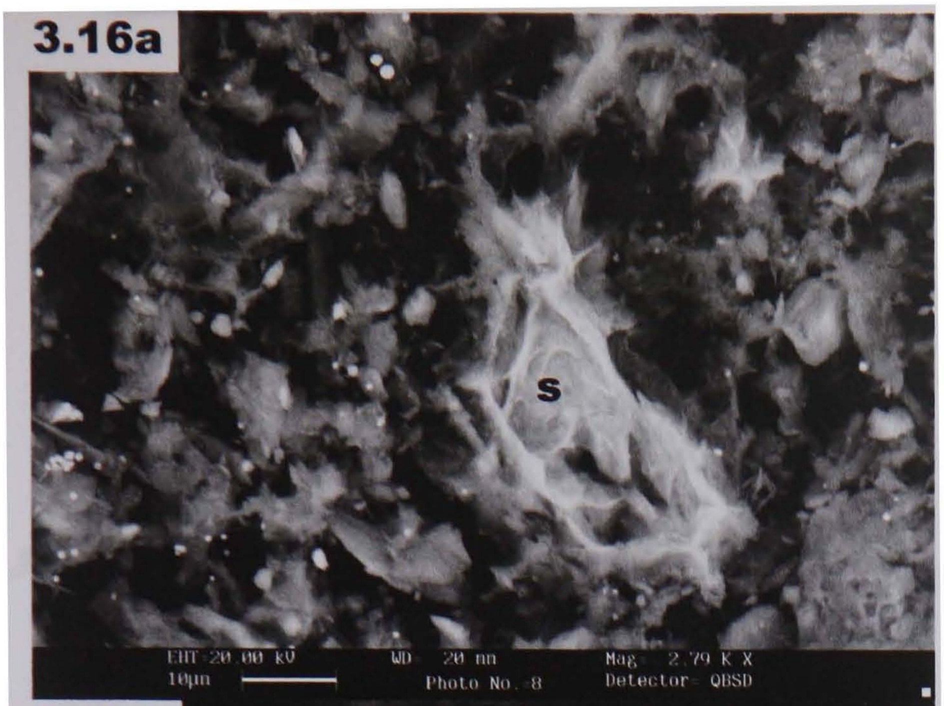
Iron oxides are a widespread, though minor, constituent of the sediment occurring as spherical grains which were generally no larger than 2μm.

3.3.3.4. Organic Components

Authigenic organic matter was widespread in the sediment, mainly in the form of biofilm. Mineralised organic matter and rod like bacteria such as those observed in the urban sediments were not observed.

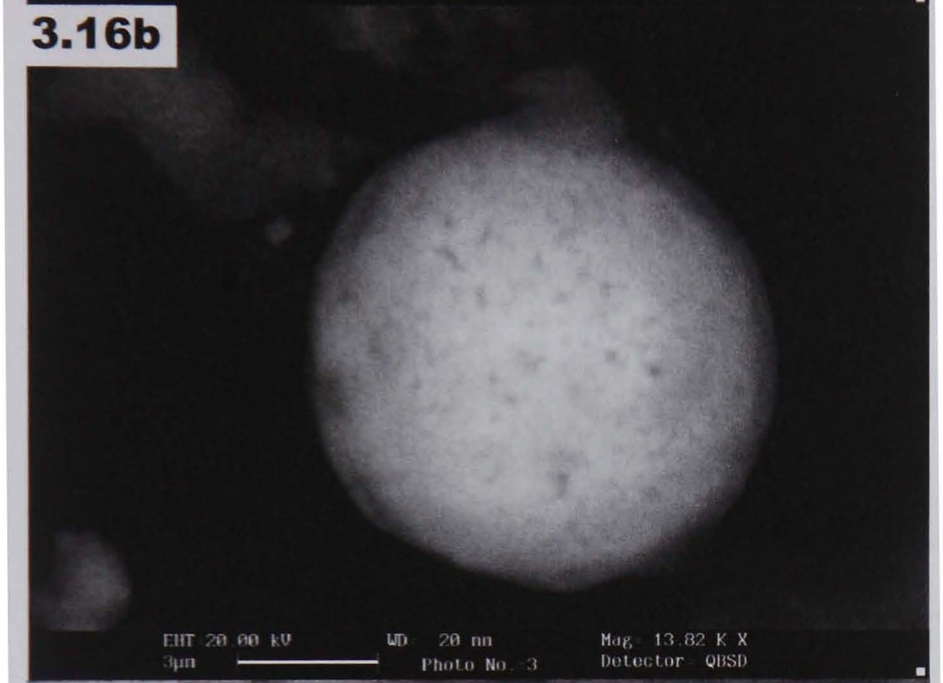
Figure 3.16: CryoSEM BSE images of iron sulphide textures in Snarestone canal sediment

3.16a



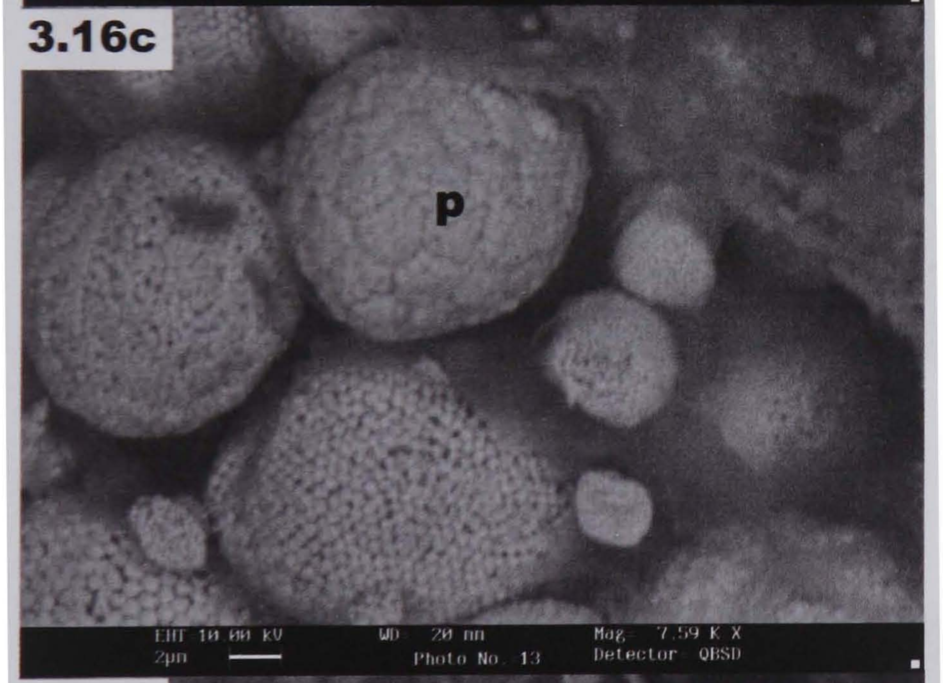
a: Pore filling iron coated sulphide films (s) from a depth of 15cm

3.16b



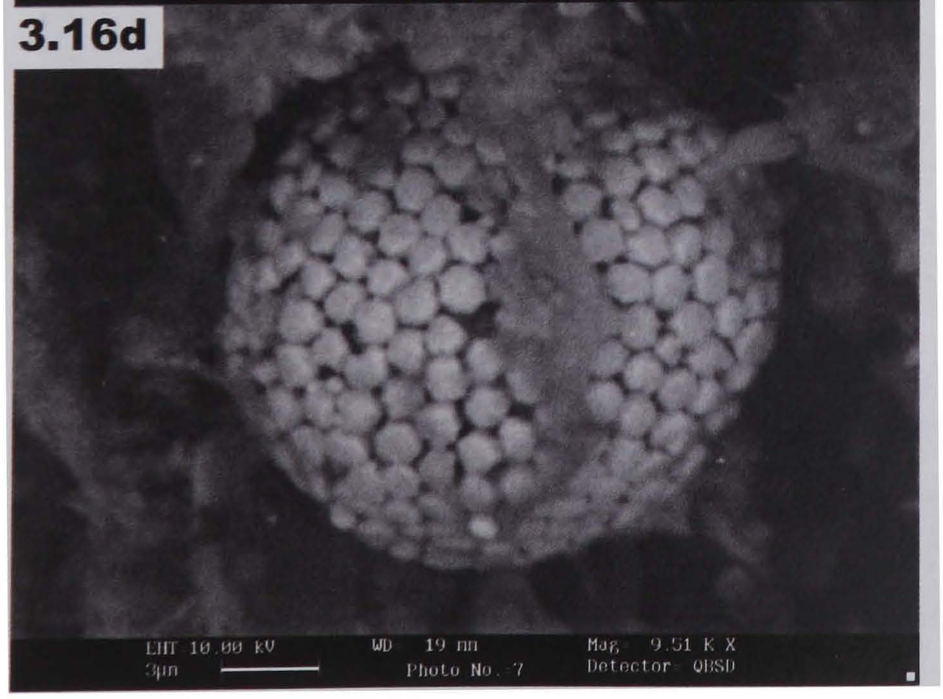
b: A protoframboid with barely visible crystallites, from a depth of 5cm

3.16c



c: A protoframboid (p) with a cauliflower like surface texture, from a depth of 15cm

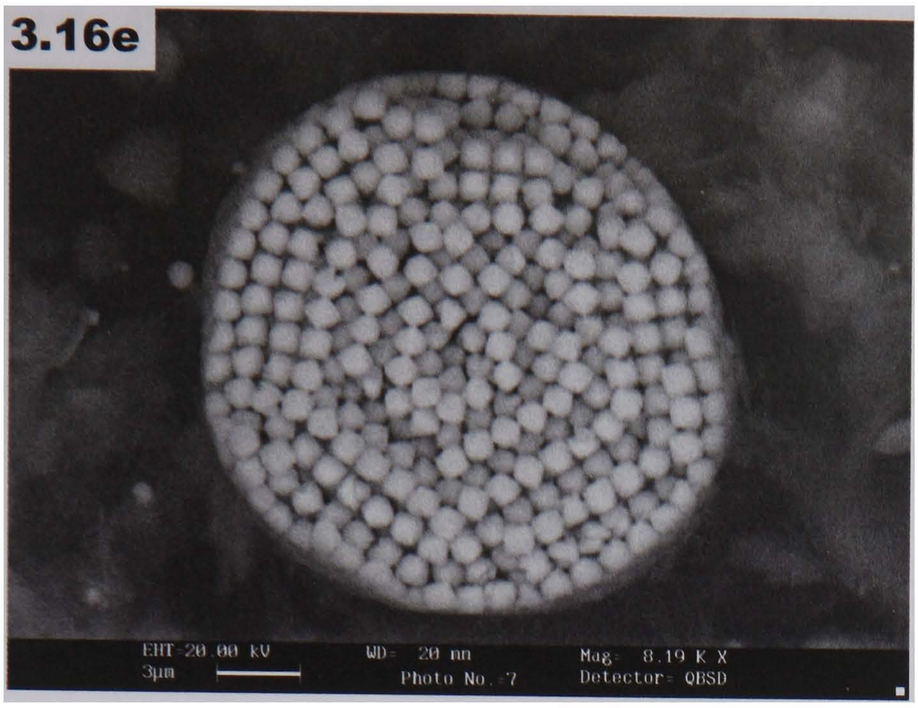
3.16d



d: A well formed framboid with clearly defined individual crystallites, covered by wisps of biofilm from a depth of 1cm

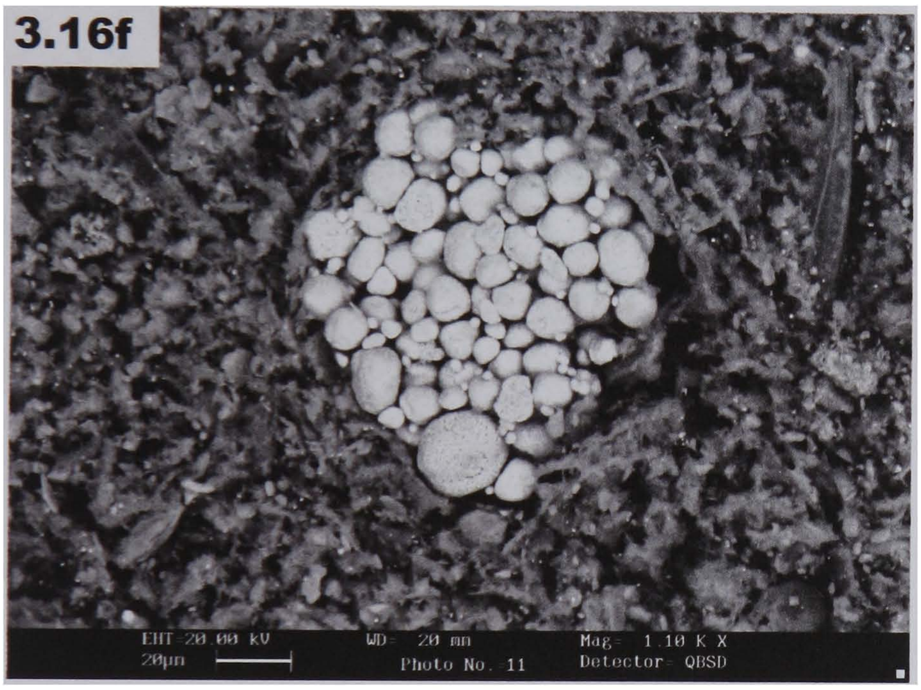
Figure 3.16 cont.

3.16e



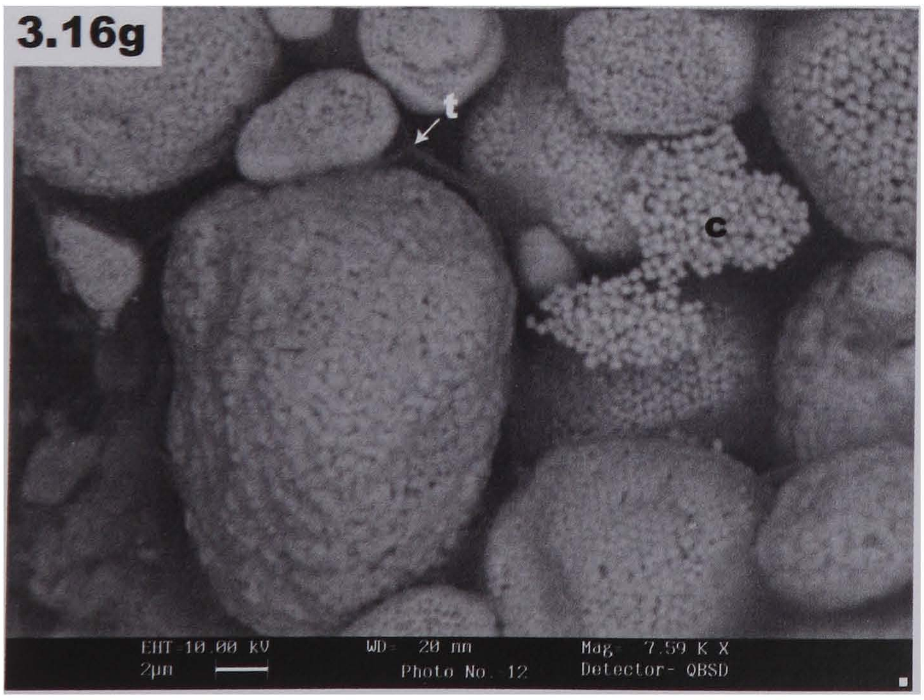
e: A cross section through a framboid displaying pentagonal symmetry. (15cm)

3.16f



f: A framboid cluster, from a depth of 15cm in Snarestone sediment

3.16g



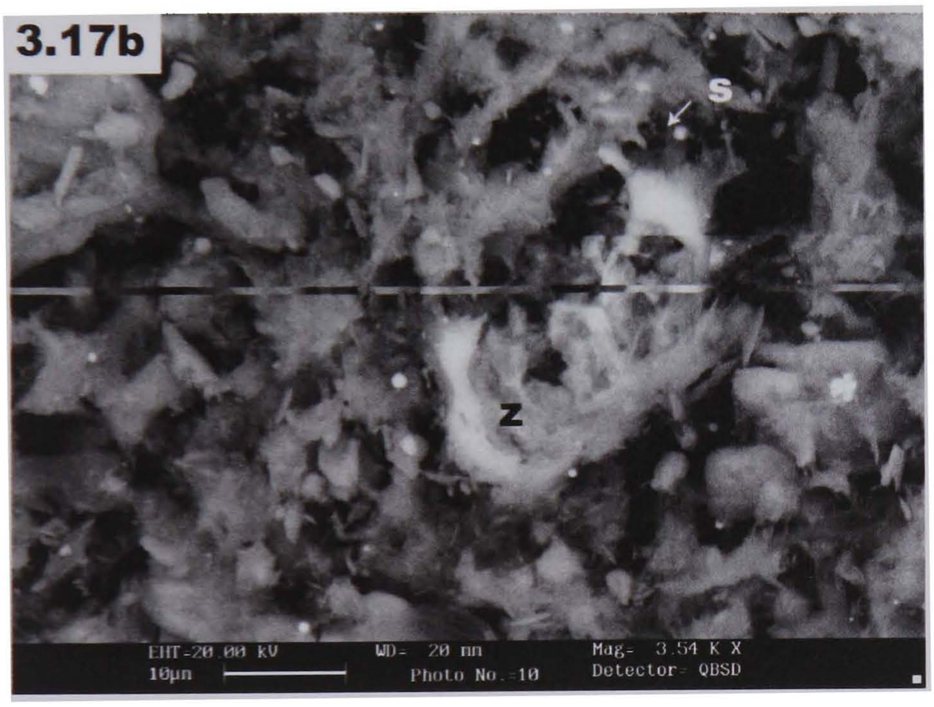
g: Biofilm coatings on individual framboids in a cluster. Interesting features include a triple junction (t) in the biofilm where 3 framboids meet and clusters of individual crystallites stuck to biofilm (c), apparently as a result of the majority of the framboid being plucked away by fracturing of the sample.

3.17a

Figure 3.17: CryoSEM BSE images of zinc sulphides in Snarestone sediment

a: An amorphous round Zn-sulphide (z) in open pore space, surrounded by a clay matrix containing sub-micron bright Fe-sulphides, from a depth of 1cm.

3.17b



b: A Zn-Fe S-rich particle (z), which might be an enriched clay particle or an amorphous sulphide. The surrounding clay matrix contains abundant, bright, sub-micron Fe-Sulphide particles (s)

3.4. Discussion

This investigation of canal sediment petrology and mineralogy by CryoSEM, XRD and particle size analysis has revealed broad similarities in rural and urban canal sediments. The sediments are both shown to consist primarily of a porous fabric of loosely packed clay aggregates and silt sized particles, held in an open floccular structure, in places by organic biofilms. The fabric is essentially massive at the scale observed, with no clear evidence of oriented clay fabric. Detrital minerals, biogenic particles, authigenic minerals and anthropogenic material occur scattered through this matrix to varying degrees of abundance in the two sediments. The common occurrence of coal, fly ash and metallic particles of industrial origin in the urban sediment suggest the incorporation of a combination of air-transported dust, run-off from industrial sites and material tipped from banks and passing boats. The comparative scarcity of such material in the rural sediment reflects the absence of heavy industry from the sampling locality and the canal's limited use for industrial freight.

The CryoSEM technique is limited particularly with regard to quantification of the relative abundance of metallic elements. Quantitative information about the abundance and speciation of metallic elements is obtained in this study through the application of a sequential extraction procedure to the sediment (Quevauviller et al., 1997). The results of the BCR sequential extraction and a CryoSEM investigation of this and a second sequential extraction procedure (Kersten and Forstner, 1986) are discussed in detail in chapter 4.

The mineralogy of urban and rural canal sediment is markedly different; the principal authigenic minerals in the sediments are summarised in Figure 3.18, which illustrates the importance of vivianite to urban sediment and its absence from rural sediment. The abundance of vivianite in the urban sediment is consistent with the incorporation of P-enriched sewage to the sediment (NRA, 1996). The stability of the authigenic minerals vivianite, calcite, iron oxides, calcium phosphate and siderite has been determined thermodynamically using the data obtained from the analysis of the Smethwick and Snarestone sediment

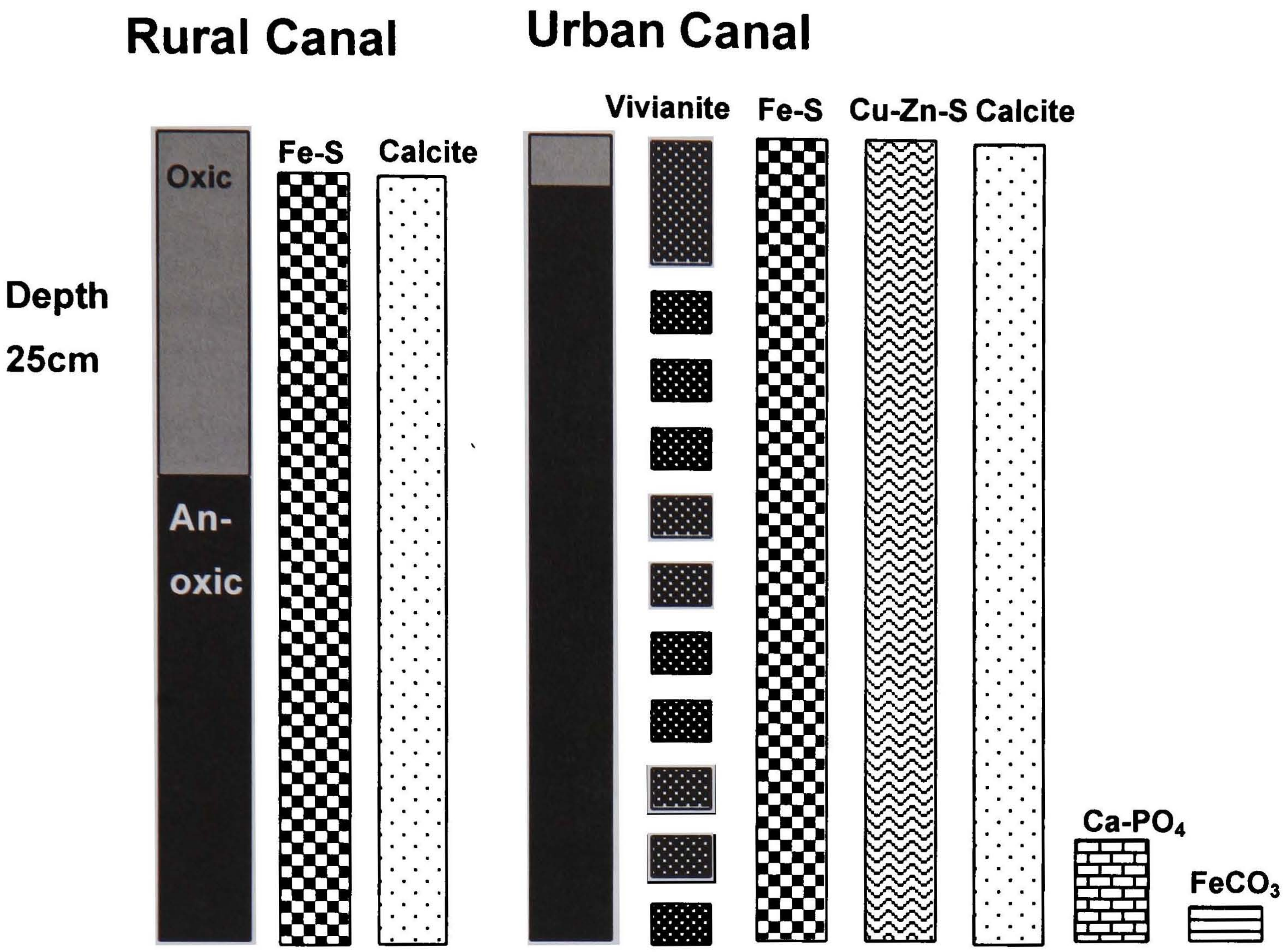


Figure 3.18: Diagram Summarising the Principal Authigenic Minerals Present in Rural and Urban Canal Sediment

porewaters. The results of this investigation and the implications they have upon the interpretation of the sediment petrology will be discussed fully in chapter 5. This discussion will include explanations for the following petrographic observations made in this chapter:

- The abundance of vivianite in urban sediment and its absence from rural sediment
- The observed dissolution of vivianite with depth in the urban sediment
- The absence of more thermodynamically stable phosphates than vivianite from the urban sediment
- The absence of siderite from both sediments
- The persistence of iron oxides in the anaerobic sediment

Figure 3.18 also reveals the abundance of FeS in both rural and urban sediment, however the concentration of sulphide was not measured in the sediment porewaters and therefore the solubility of Fe, Cu and Zn sulphides could not be determined. Also from the wide range of co-existing sulphides (mackinawite to pyrite) observed in the sediments it can be deduced that a geochemical investigation of porewater will only give an indication of the most soluble iron sulphides and will not give a true impression of all the co-existing sulphides. For these reasons the petrology of the sulphides will be discussed here.

3.4.1. Sulphide Authigenesis

Iron sulphides were observed in both the rural and urban sediments and their form is markedly different in the two sediments. In rural sediment pyrite framboids are the most abundant authigenic mineral, film coated sulphides are also present and these have the appearance of mineralised biofilm. In urban sediment framboids are scarce and film coated sulphides are commonly observed in a number of different forms including large particles of mineralised organic matter and mineralised cellular structures.

The observations of iron sulphides in the two sediments enable a number of interpretations to be made regarding sulphide diagenesis. The surface waters of both canals are shallow (1-1.2m deep) it is therefore reasonable to deduce that the water column is oxic and that the sulphides are formed in the sediment. Distinct differences exist between the pattern of the sulphide formation at the two sites. The scarcity of framboids in the urban sediment relative to the rural sediment is probably a function of the steepness of the redox gradient. It is well established (Wilkin and Barnes, 1997) that the formation of pyrite from a monosulphide precursor requires an oxidising agent and hence most pyrite forms in sediments or water columns at the oxic/anoxic interface. In the rural canal a more gradual transition from oxidised to reduced sediment is observed, indicated by a brown surface layer (section 4.1), and this will allow a longer time in which oxidising agents are able to promote the formation of pyrite. In addition to this, iron and sulphur may be less available at the urban site where the main sink for iron is vivianite, and chalcophile elements including Zn and Cu occur in relatively high concentrations (Chapter 4).

The common association of Fe-sulphides with biofilms is interpreted as an indication that biofilms are important sites for nucleation. The measured Fe:S ratios indicate that that biofilm coatings fall in the range makinawite (FeS) to greigite (Fe_3S_4) (Table 3.1). The association of Fe-sulphide with biofilm may indicate a strong affinity between Fe monosulphide and polysaccharide surfaces or that co-precipitation occurs in the same environment, possibly by the same bacterial processes (Large et al., in press). It is also possible that the biofilms developed under more oxidising conditions and were therefore sites where easily reducible Fe-hydroxides accumulated (Boult et al., 1997). Biofilms also appear to be playing an important role in stabilising framboid structures during sediment compaction or disturbance, although it has been proved experimentally that biofilm or other biogenic material is inessential to the formation of framboid structures (Berner, 1969).

The progression of protoframboid to framboid observed in the rural sediment enables deductions to be made about framboid formation. All framboids and protoframboids lie in the compositional range greigite to pyrite. This is in agreement with the observations of other workers (Sweeney and Kaplan, 1973; Wilkin and Barnes, 1997) that greigite (Fe_3S_4) and pyrite (FeS_2) form framboid structures but not makinawite (FeS). The textural transition from protoframboid to framboid corresponds to a compositional change from greigite to pyrite. Protoframboids are characterised as containing poorly defined crystallites and from this it can be deduced that the formation of distinct crystallites takes place after the formation of a spherical greigite protoframboid (Large et al., in press). The observations made in these sediments also indicate that the larger the framboid, the larger the crystallites from which it is composed. This correlation suggests that overall framboid size determines the crystallite size. Protoframboids tend to be smaller than framboids and this may indicate that the larger diameter framboids developed more quickly, or formed earlier and therefore have had longer to develop.

It is also interesting to note that no intermediate textures were observed between protoframboids and monosulphide biofilms e.g. spherical structures forming in a monosulphide biofilm. This may indicate the rapid formation of framboids under favourable conditions and possibly that framboid formation is hindered if the initial monosulphide is precipitated onto a biofilm (Large et al., in press). Rapid framboid formation is supported by Wilkin and Barnes, (1996) who predict from experimental evidence that only a rapid transformation from monosulphide to pyrite will result in framboid formation, and that is favoured by slightly oxidising conditions, such as those in the rural sediment. In the urban sediment, framboids are scarce and it is assumed that their formation has been inhibited, probably by the reduced state of the sediment. Thus, in the urban sediment monosulphide film coatings may have developed where under more oxidising conditions pyrite framboids would have formed (Large et al., in press).

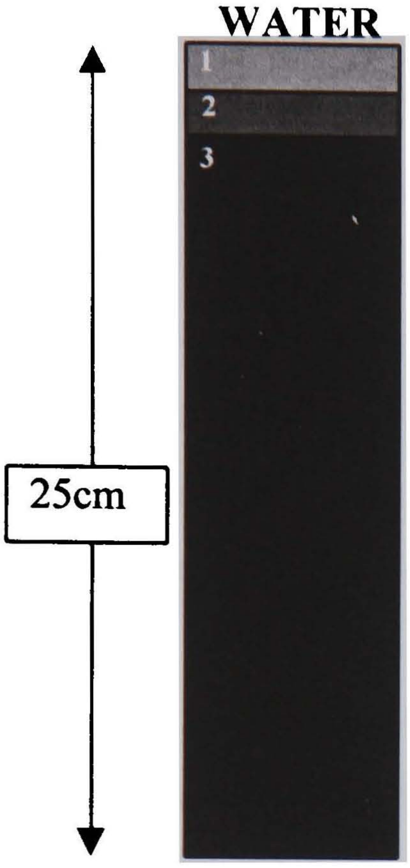
The most interesting feature of the copper sulphides observed in the urban sediment is their stoichiometry which is in agreement with previous studies (Parkman et al., 1996) that have observed copper sulphides with chalcopyrite stoichiometry. Parkman *et al.* (1996) did not however observe any iron in the zinc sulphides and reported compositions close to pure sphalerite. The presence of zinc sulphides in the rural as well the urban sediments indicates that their formation does not require very high concentrations of zinc in the sediment. The floccular appearance of the zinc sulphides in open pore space is interpreted as indicating that they are precipitated directly from solution. On the other hand the copper sulphides appear to nucleate on the surfaces of either organic particles or metal fragments and this may reflect differences in the adsorption behaviour of copper relative to zinc (Large et al., in press).

4. Sediment Chemistry

The solid component of canal sediment can be viewed as both the raw materials and end products of the processes occurring within it. An investigation of the solid chemistry therefore provides a quantitative foundation for the investigation of early diagenetic processes. In this chapter, the results of bulk chemical analysis and sequential extractions of rural and urban canal sediment are presented. The analysis was conducted over the 25cm depth profile of the sediments, to determine whether changes in inputs over time or depth dependant chemical changes, have altered their composition. The comparison of rural and urban bulk sediment chemistry is used to assess and quantify the difference in their contaminant loadings. Sequential extractions are used to quantitatively determine the speciation of metallic elements in the sediments. A CryoSEM investigation is used to assess the effectiveness of two different extraction schemes on urban canal sediment and to elucidate the interpretation of the results of the selected scheme.

4.1. Field observations of Canal Sediment

Observations of the sediment, made through the Perspex core barrel immediately after sampling, enabled a generalised sediment profile to be deduced. The profiles observed for urban and rural sediment show a transition from aerobic conditions at the surface to anoxia at depth. The profiles were different for both rural and urban sediment; they are summarised in figures 4.1a and 4.1b.

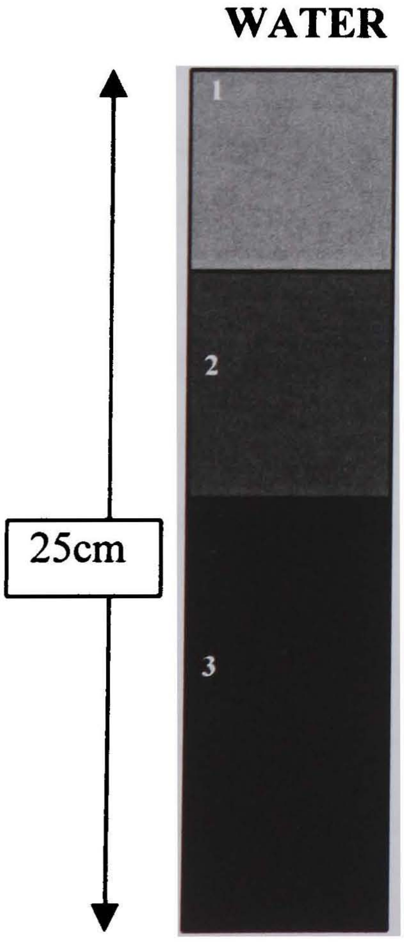


1. Aerobic section: This section is uniformly grey in colour (not brown), it was absent from all seasonal samples except the spring sample, where it was observed to be ~3cm thick and composed of floccular unconsolidated material. This layer showed no obvious evidence of bioturbation by either macrofauna or microfauna

2. Anaerobic interface: For the majority of the year the anaerobic interface is at the sediment water interface. In the spring when an aerobic section was present this section was marked by a change in colour from grey to black.

3. Anaerobic Section: This section is uniformly black in colour and contains numerous irregularly shaped gas bubbles, as evidence of methanogenesis.

Figure 4.1a Urban Sediment Profile



1. Aerobic section: This section is brown in colour, and composed of loose floccular material. This layer varied in thickness from 10cm in the spring to 2-3cm in the summer and autumn and was absent from the winter sample.

2. Anaerobic interface: Beneath the brown aerobic layer is a grey section that graded to black, this layer is more consolidated than the floccular material at the surface and can be up to 10cm thick.

3. Anaerobic Section: This section is black in colour gas bubbles are not obviously present in this section, as they were in the urban sediment. Patches of coarser grained sand and occasional gravel were observed in this section.

Figure 4.1b Rural Sediment Profile

The colour change in the sediments highlights the progression to anoxia that is occurring at differing rates in the two sediments. This is controlled by the rate of organic matter diagenesis and associated early diagenetic reactions involving the formation of authigenic minerals (this will be discussed in detail in chapter 5). The brown colour in the surface sediments is evidence of the presence of iron oxides and the grey or black coloration indicates the presence of metal sulphides (Emerson, 1976). This was confirmed by the CryoSEM analysis of the sediments, which found that sulphides are present at both sites but occur at the sediment water interface in the urban sediment.

Another significant field observation was the effect of passing boat traffic upon the sediment at both Snarestone and Smethwick. Observations of passing traffic during sampling trips revealed large plumes of sediment forced into suspension behind the barges. The continued passage of traffic results in the scouring of the sediment in the centre of the canal and its accumulation at the edges (Figure 4.2a-b). This disturbance will have a seasonal variation because boat traffic is greatest in the holiday season during spring and summer and minimal in the winter. The nature of boat traffic is slightly different at the two sites. The sampling site at Snarestone is at the end of the canal and therefore does not have much passing traffic, however it appears to be widely used for mooring, with up to five boats moored along the bank during sampling trips. At Smethwick the canal is apparently used quite extensively by passing leisure traffic, three boats passed during the summer sampling trip over a period of about 20 minutes. Conversely in the winter the canal was covered by ice which had not been broken by boat traffic prior to sampling which was conducted at ~10am in the morning.

Samples were collected from the bank; it is therefore probable that the uppermost portion of the core will be affected by seasonal variations in the net accumulation of sediment displaced by boat traffic, and by the distance from the bank at which the sediment was cored (0.5-1m). The disturbance will also have an effect upon sediment chemistry because it results in the mixing of the anoxic sediment with oxygenated canal water. This effect will be most marked upon urban sediment, because it is anaerobic from the sediment water interface.

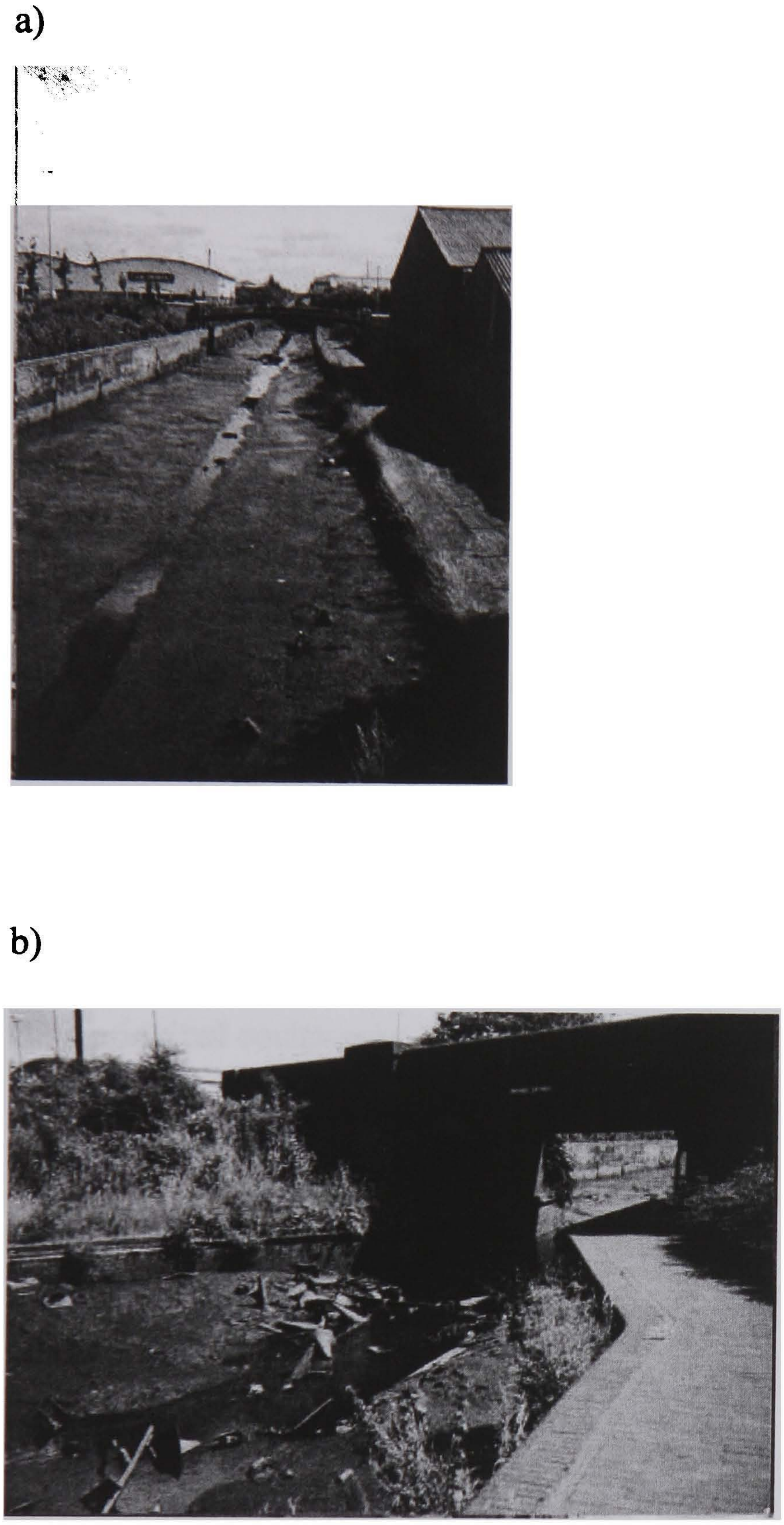


Figure 4.2. Photographs of The Walsall Canal at Great Bridge following its drainage through an open lock. Showing:

a) the profile of the canal basin, with scouring in the centre of the channel and sediment accumulation at the banks

b) the increase in the accumulation of sediment following the narrowing of a bridge, and the sort of debris found in canal basins close to roads

4.2. Bulk Sediment Composition

4.2.1. XRF Analysis Results

X-Ray fluorescence analysis was conducted upon samples of rural and urban canal sediment from Snarestone and Smethwick sampled during autumn 1998. The analysis was carried out on sub-samples taken at 8cm intervals. This analysis quantifies the major sediment constituents and is important because changes to the bulk sediment composition will affect the sediment's capacity to retain contaminants. The comparison of Snarestone's and Smethwick's bulk sediment composition will reveal the effects of anthropogenic influences upon the Smethwick sediment. The XRF results from both sediments are summarised in Table 4.1 a and b, these show each sediments' principal constituents excluding organic carbon (section 4.2.2-3).

Smethwick

The principal component of Smethwick sediment is SiO_2, which comprises 34% of the sediment throughout the depth profile. The sediment also contains significant quantities of Fe_2O_3 (16%), Al_2O_3 (10%), CaO (8%-7%) and P_2O_5 (6.5% to 5.9%). Generally the concentrations are constant with depth although both CaO and P_2O_5 decrease slightly.

Snarestone

Snarestone sediment is principally comprised of SiO_2, it contains 52.2% at the surface and this value increases to 68.9% at 24cm. The sediment also contains a high concentration of Al_2O_3, which decreases with depth from 13.2% at the surface to 9.2% at 16cm, rising again to 10.0% at 24cm. Snarestone sediment contains 5.9-3.3% Fe_2O_3, 7.5-3.6% CaO and 0.33-0.12% P_2O_5 and these concentrations all decrease over the depth profile of the sediment (table 4.1a).

Tables 4.1a and b: Results of the X-Ray Fluorescence analysis

a) Smethwick Sediment Results (sampled from the autumn core)

Depth	1cm	8cm	16cm	24cm
%-SiO2	33.53	34.26	34.31	33.92
%-Al2O3	9.49	9.74	10.10	9.90
%-Fe2O3	15.78	15.59	15.76	16.03
%-CaO	8.21	7.87	7.05	6.85
%-P2O5	6.45	6.38	6.38	5.86
%-K2O	1.33	1.36	1.30	1.33
%-MgO	2.16	2.02	1.89	1.87
%-Na2O	0.72	0.73	0.79	0.74
%-TiO2	0.57	0.59	0.59	0.59
%-MnO	0.52	0.49	0.53	0.50
Total*	78.79	79.02	78.70	77.59

b) Snarestone Sediment Results (sampled from the autumn core)

Depth	1cm	8cm	16cm	24cm
%-SiO2	52.16	55.49	63.26	68.9
%-Al2O3	13.17	11.90	9.24	10.01
%-Fe2O3	5.86	5.54	3.94	3.32
%-CaO	5.39	7.54	5.77	3.63
%-P2O5	0.33	0.18	0.18	0.12
%-K2O	3.46	2.94	2.46	3.12
%-MgO	2.93	3.90	4.57	2.49
%-Na2O	0.22	0.22	0.12	0.30
%-TiO2	0.77	0.60	0.46	0.50
%-MnO	0.09	0.10	0.09	0.06
Total*	84.38	88.40	90.09	92.44

*The remainder of the sediment can largely be accounted for by carbon (**Figure 4.3a and b**)

4.2.2. Urban Sediment Carbon Analysis Results

The urban canal sediment from Smethwick is rich in organic matter. Organic carbon comprises approximately 20% of the total sediment by weight throughout the profile (Figure 4.3a; Appendix 8.1), fluctuating by only 3% with depth and showing no systematic depth trend. Inorganic carbon is present, but comprises less than 1% of the dry sediment by weight. Petrographic observations suggest that inorganic carbon is principally present as calcite in the sediment of Smethwick and Great Bridge.

Figure 4.3a: Total, organic and inorganic carbon in Smethwick sediment

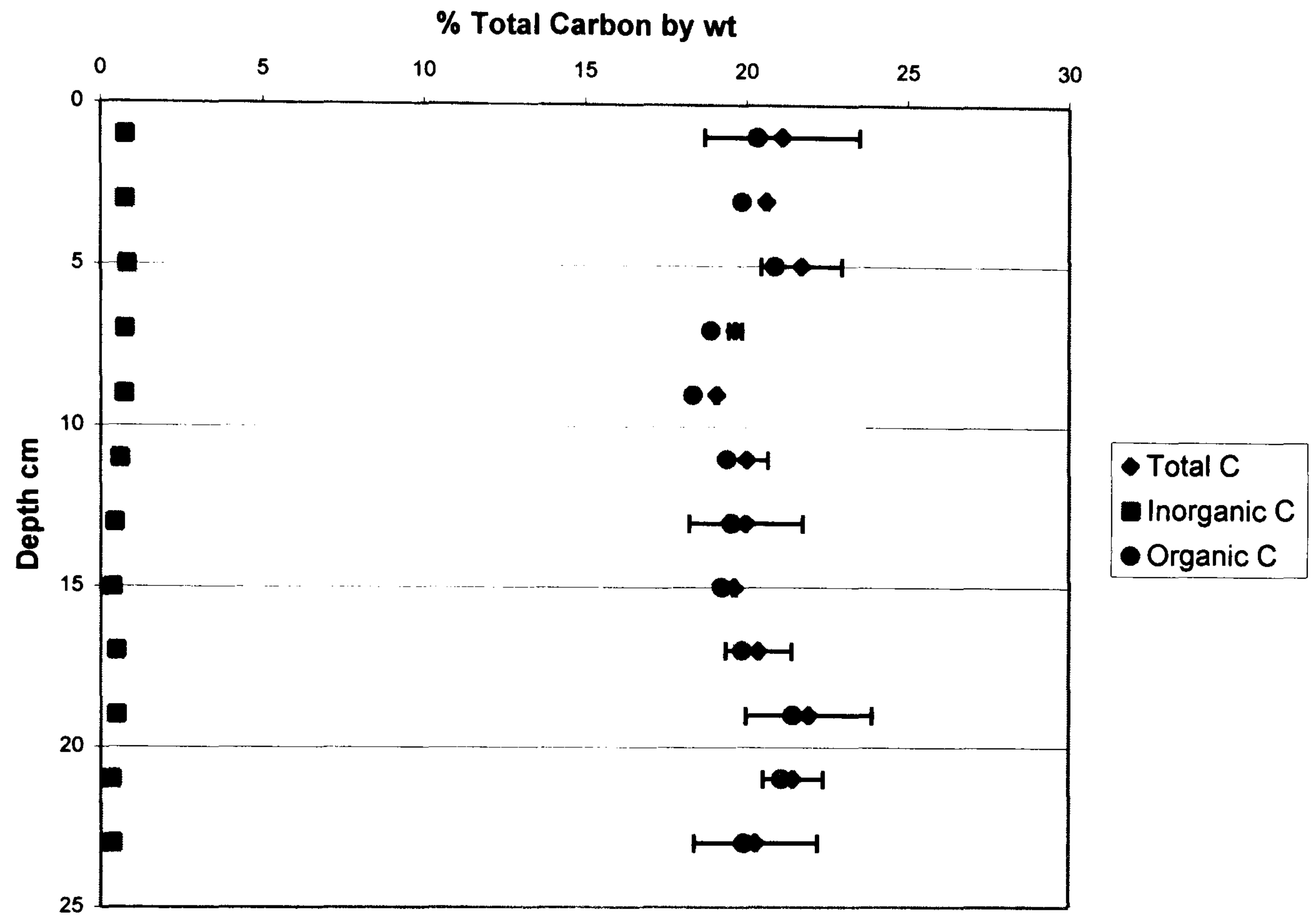
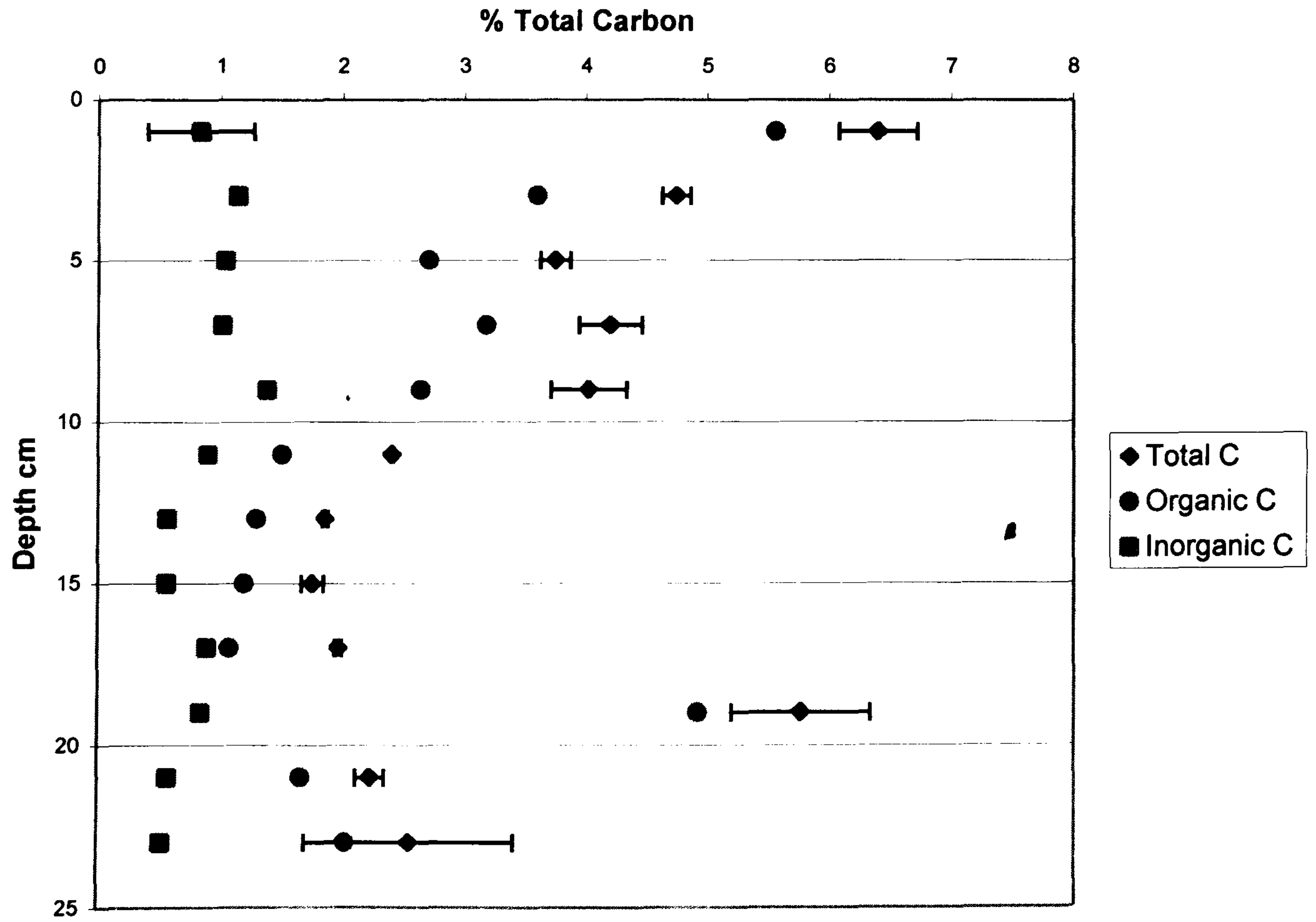


Figure 4.3b: Total, organic and inorganic carbon in Snarestone sediment



error bars show 3 times the standard deviation from the mean of two duplicate analysis

4.2.3. Rural Sediment Carbon Analysis Results

Rural canal sediment from Snarestone has a maximum organic carbon content at the surface of 5.6%, the level of organic carbon in the sediment then steadily decreases with depth to values of 1 or 2% (Figure 4.3b; Appendix 8.2). Inorganic carbon is constant in the sediment profile, comprising less than 1% of the total content, calcite and dolomite are the major sources of inorganic carbon in this sediment.

4.2.4. Aqua Regia Digest

The concentrations of Al, P, S, Ca, Cr, Mn, Fe, Cu, Zn, Cd and Pb were determined in the sediments by aqua-regia digest, over the depth profile and at seasonal intervals (Appendix 9 and Figures 4.4-4.14). These elements were selected because they are important in understanding the sediments' diagenesis, their bulk composition and contaminant loading. Depth and seasonal variations are used to assess changes in inputs to the canal through time, and the effect upon the solid chemistry of depth dependant chemical changes. The results are also important as a background against which porewater data can be considered and a means of ensuring that seasonal variations in porewater composition are not caused by anomalies in the composition of a particular sediment sample.

Duplicate analysis of two cores of Smethwick sediment and three cores of Snarestone sediment sampled in the spring; in order to assess the degree to which the sediment varies between samples (Appendix 10.1 and 10.2). These analyses reveal that there is greater sample to sample variability between the Snarestone sediment samples than between those from Smethwick. However, they show that trends in the variation of concentration with depth are in broad agreement in each duplicate core (Appendix 10.2)

4.2.4.1. Aluminium

Smethwick

From figures 4.4a-c it can be seen that the concentration of Al in the sediment is within the range of 14,110 - 17,790ppm in the spring, summer and autumn cores and shows no systematic depth variation. However the winter profile (Figure 4.4d) is markedly different due to a peak in concentration of 26,920ppm that occurs at 16cm and a subsequent fall in concentration to 11,620ppm between 20 and 23cm.

Snarestone

The concentration of Al in the rural sediment fluctuates between 4,413ppm and 16,685ppm. Figures 4.4 e-h show that concentrations are highest at the surface, sharply decreasing downwards in the top 5cm of the sediment, and continuing to decrease more gently for the remainder of the profile. This trend of decreasing Al content was also observed by XRF (Section 4.2.1).

4.2.4.2. Phosphorous

Smethwick

The concentration of P is between 23,127ppm and 17,701ppm in the spring, summer and autumn samples and does not show a systematic depth trend in all seasons (Figures 4.5 a-c). In the spring sample the P concentration is 19,841ppm at the surface and 19,267ppm at 24cm, and remains close to these values throughout the profile. In the summer profile the concentration decreases sharply downward from 23,127ppm at the surface to 20,677ppm at 5cm and then decreases more steadily reaching 18,479ppm at 24cm. In the autumn profile the concentration fluctuates over the profile between a maximum value of 22,771ppm at the 14cm and a minimum of 17,701ppm at 20cm. In the winter

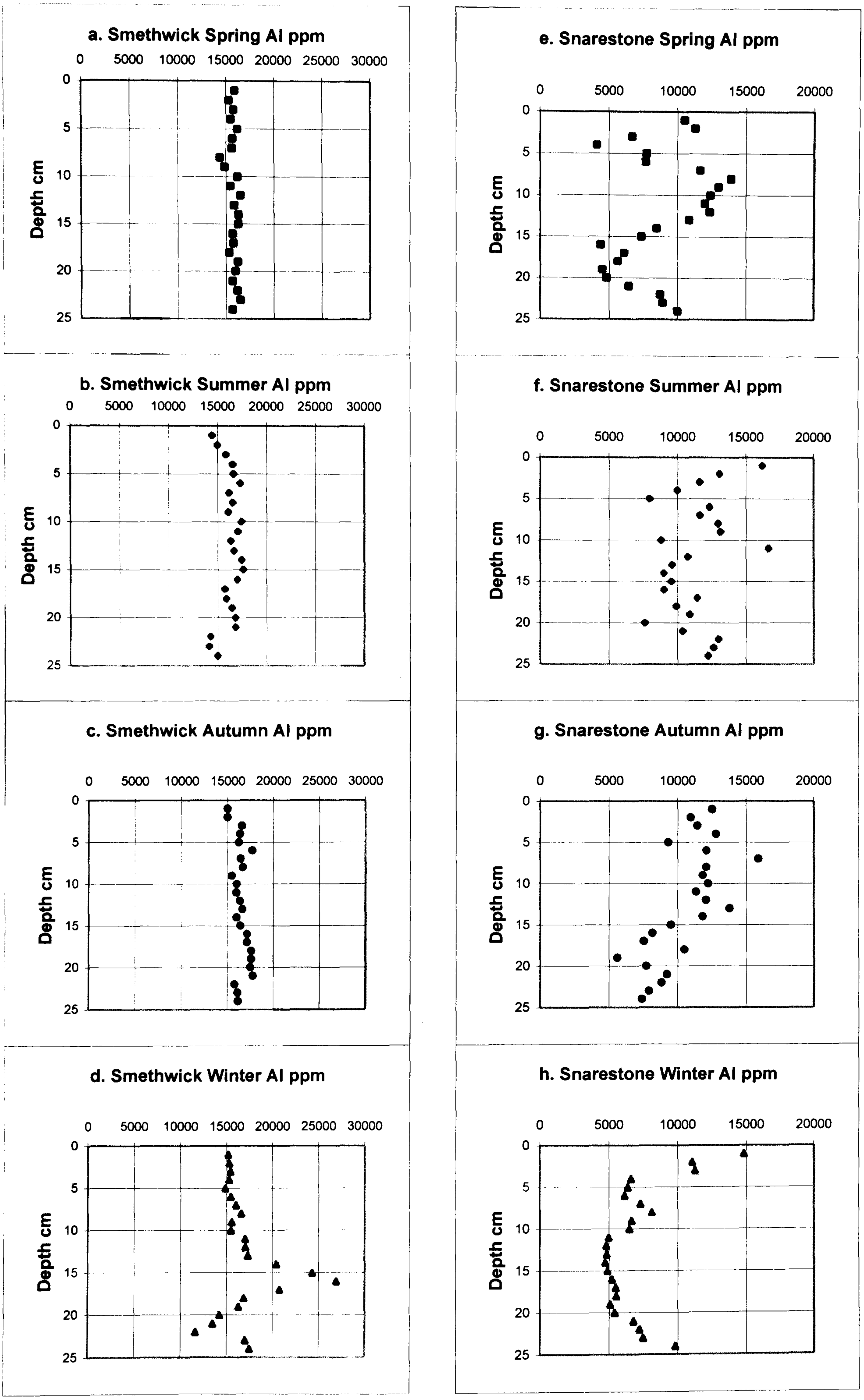
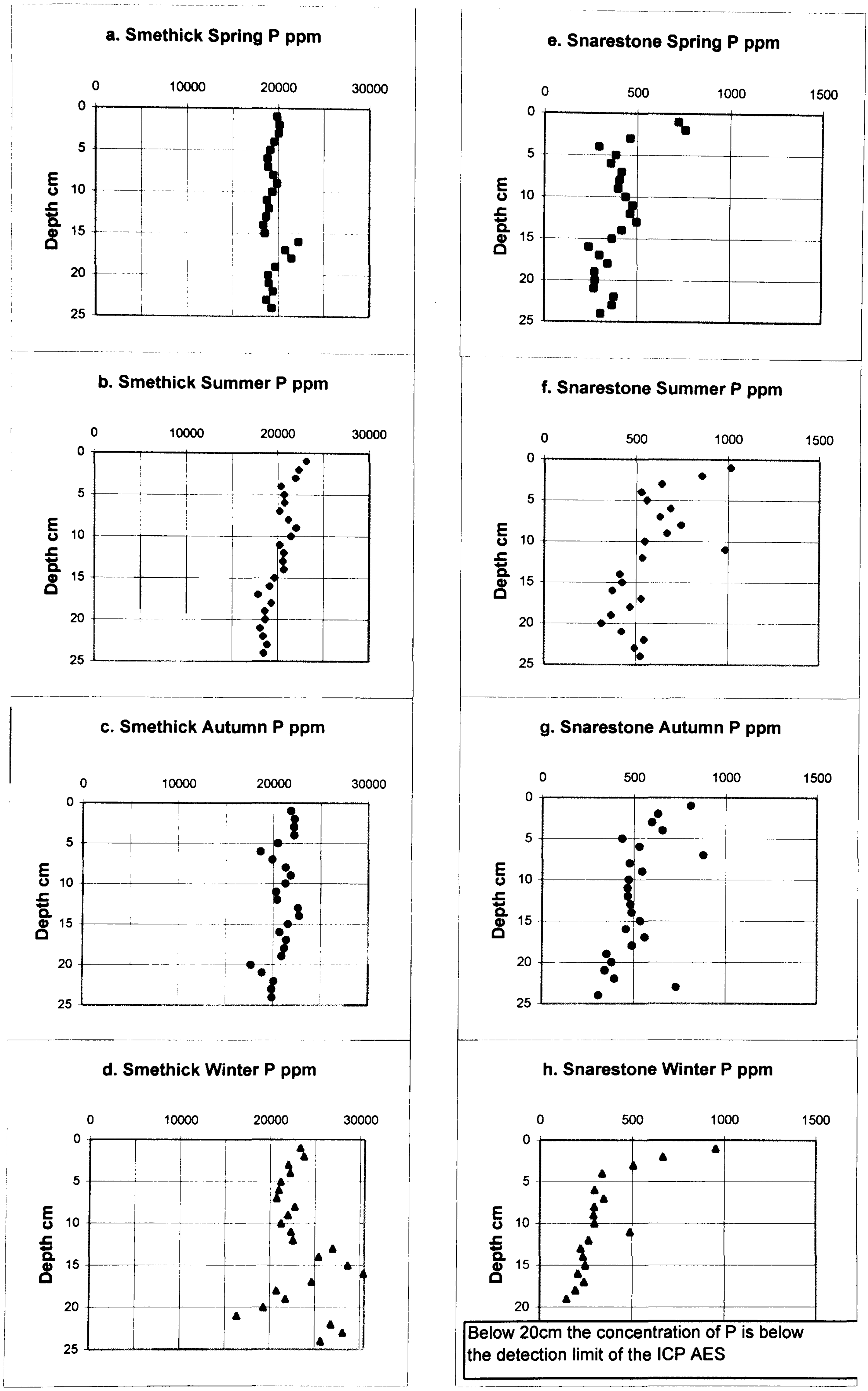


Figure 4.4a-f: Concentration of Al in Smethwick and Snarestone Sediment



Below 20cm the concentration of P is below the detection limit of the ICP AES

Figure 4.5a-f: Concentration of P in Smethwick and Snarestone Sediment profile the P concentration fluctuates over the depth profile, it increases steadily from 23,330ppm at the sediment surface to 30,422ppm at 16cm, below 16cm the concentration decreases to 16,342ppm at 21cm and then sharply increases to reach 26,813ppm at 23cm (Figure 4.5d).

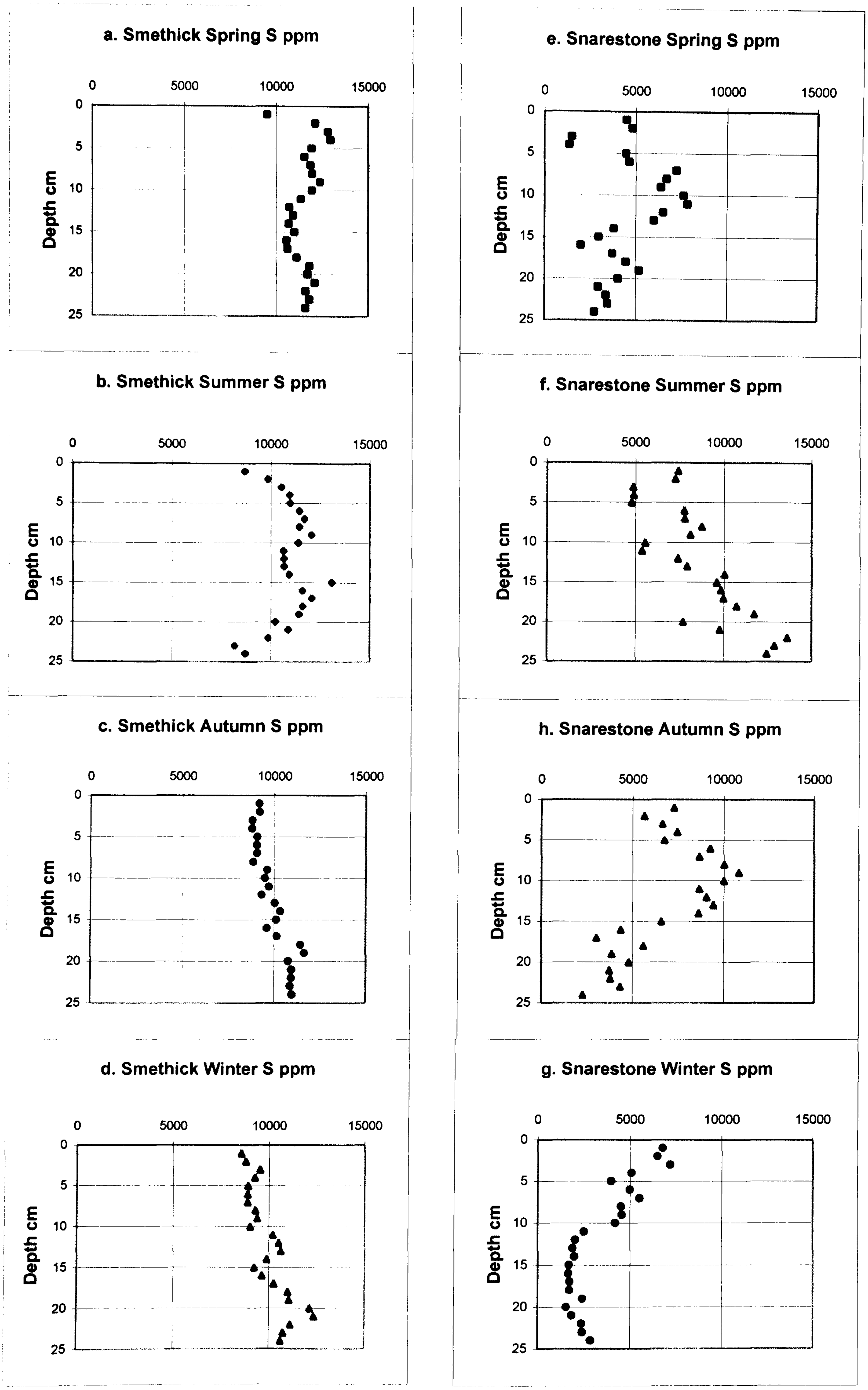
Snarestone

Phosphorous in the Snarestone sediment displays a clear trend of decreasing concentration with depth that is broadly similar in each seasonal sample (Figure 4.5e-h). Maximum values of between 780ppm and 1010ppm occur at the sediment surface, the concentration then sharply declines to between 293-526ppm within the uppermost 5cm of the profile and continues to decline more steadily for the remainder of the profile. The concentration of P declines most sharply in the winter when it falls close to the detection limit of 60ppm at depths greater than 20cm, and the uncertainty of the readings precludes their use, while in the summer elevated concentrations occur in the profile to a depth of 15cm (Figure 4.5h).

4.2.4.3. Sulphur

Smethwick

The concentration of S in the sediment is between 8,675ppm and 13,070ppm in all seasons (Figures 4.6a-d). Overall in the spring and summer profiles the concentration of S is higher than it is in the autumn and winter profiles. The concentration increases with depth in each season. In the spring and summer this increase occurs sharply over the uppermost 5cm of the sediment rising from 9,505ppm and 8,676ppm at the surface to 11,930ppm and 10,967ppm at 5cm respectively. The concentration then fluctuates around these values for the remainder of the profiles, except beneath 20cm in the summer profile where it sharply decreases from 11,425ppm to 8,707ppm at 24cm. In the autumn and winter profiles the concentration increases steadily from 9,177ppm and 8,547ppm respectively at the surface, to maximum values of 11,660ppm and


a. Smethick Spring S ppm

b. Smethick Summer S ppm

c. Smethick Autumn S ppm

d. Smethick Winter S ppm

e. Snarestone Spring S ppm

f. Snarestone Summer S ppm

h. Snarestone Autumn S ppm

g. Snarestone Winter S ppm

Figure 4.6a-f: Concentration of S in Smethwick and Snarestone Sediment

12,364ppm at 19cm and 21cm respectively, beneath these maxima the concentration remains high and relatively constant.

Snarestone

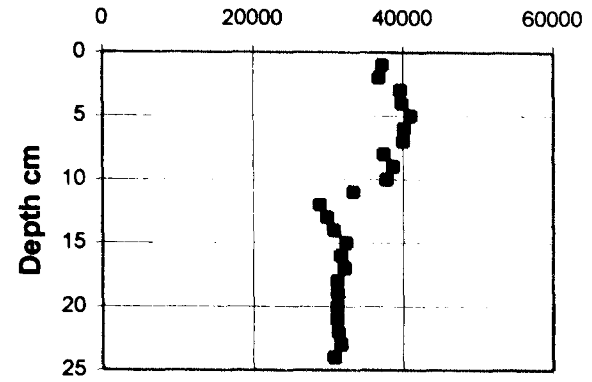
Figures 4.6e-h show the variability of S over the depth profile of the sediment and between seasonal samples to be large. In the spring and winter concentrations rarely exceed 5000ppm, whereas in the summer and autumn the majority of the depth profile contains S at levels in excess of 5000ppm. In the summer values of S increase with depth, while in the autumn, winter and spring they are greatest in the uppermost 10-15cm of the core. The large differences between S concentrations for each season might be added to by the uncertainty associated with the measurement of S using ICP-AES of 40%.

4.2.4.4. Calcium

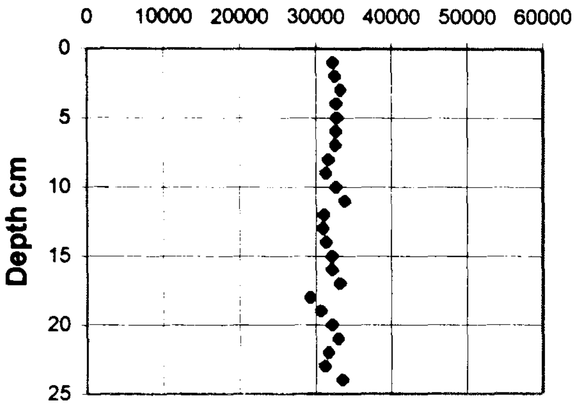
Smethwick

The concentration of Ca typically decreases with depth in the sediment, from values of ~40,000ppm at the surface to ~31,000ppm at 24cm, in the spring, autumn and winter cores (Figures 4.7 a, c and d). In the winter profile this decline in concentration with depth is most marked, the concentration falls from 39,422ppm at the surface to a minimum value of 20,060ppm at 22cm, before increasing to a more typical concentration of 30,799ppm at 23cm (Figure 4.7 d). In the summer profile the concentration shows no marked variation with depth, remaining constant at approximately 32,000ppm throughout the profile (Figure 4.7b). A decrease in Ca concentration with depth is also observed in the XRF results (Table 4.1a) in which the proportion of CaO decreases from 8.2% at 1cm to 6.8% at 24cm.

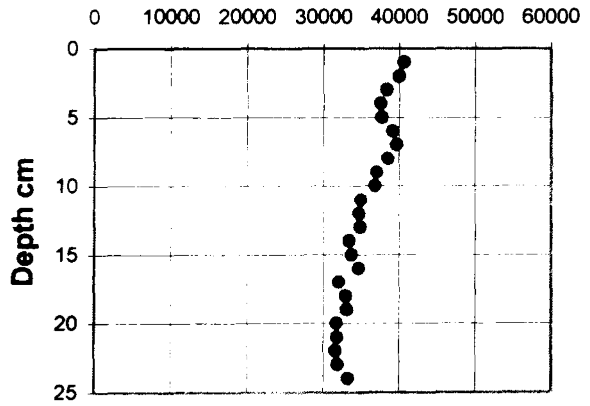
a. Smethwick Spring Ca ppm



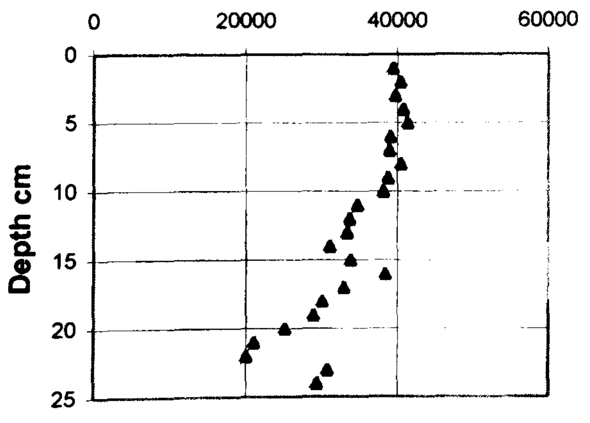
b. Smethwick Summer Ca ppm



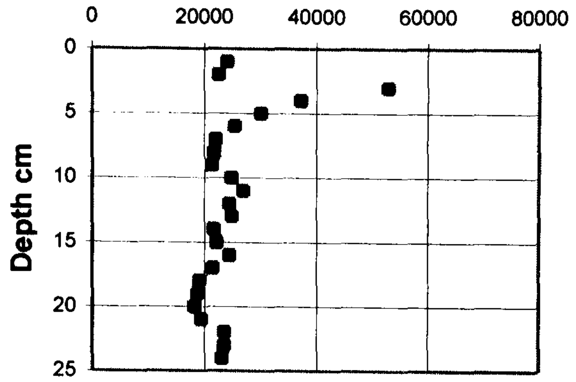
c. Smethwick Autumn Ca ppm



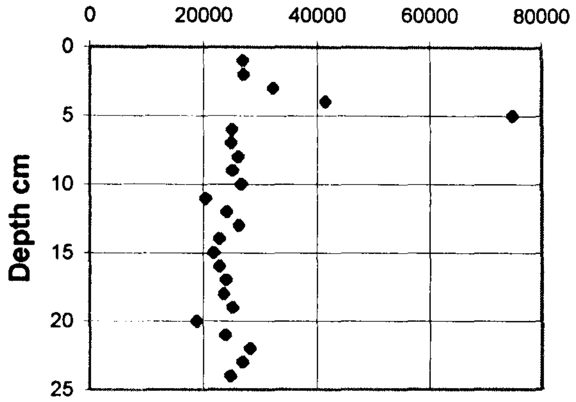
d. Smethwick Winter Ca ppm



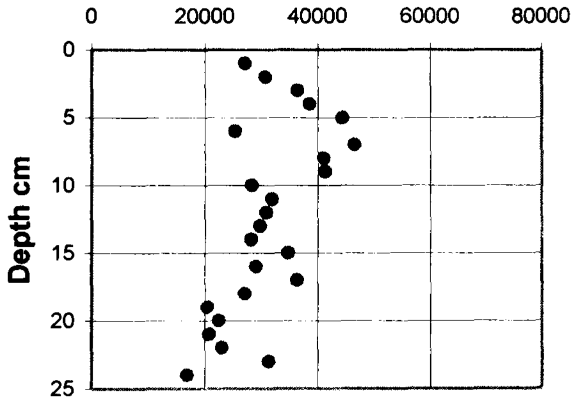
e. Snarestone Spring Ca ppm



f. Snarestone Summer Ca ppm



g. Snarestone Autumn Ca ppm



h. Snarestone Winter Ca ppm

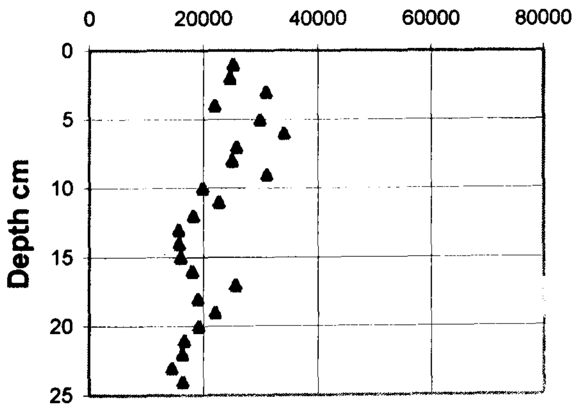


Figure 4.7a-f: Concentration of Ca in Smethwick and Snarestone Sediment

Snarestone

The concentration of Ca shows a seasonal variation between the summer and spring profiles and those of the autumn and winter. In the spring and summer cores the concentration is largely between 18,750ppm and 28,200ppm, with the exception of a peak in concentration at 3cm in the spring and 5cm in the summer of 52,847ppm and 74,764ppm respectively (Figures 4.7 e-h). In the autumn and winter cores the concentration of Ca is elevated over the uppermost 15cm of the profile. The concentration reaches a maximum value of 46,600ppm at 7cm in the autumn and of 34,118ppm at 6cm in the winter, it then declines to concentrations of 16,953ppm and 16,333ppm at 24cm in the autumn and winter respectively (Figure 4.7 f-h).

4.2.4.5. Chromium

Smethwick

The concentration of Cr increases with depth in all seasonal samples (Figures 4.8 a-d). In the summer sample the concentration increases sharply downwards in the uppermost 5cm of the core from 378ppm to 468ppm and then remains constant to a depth of 20cm where it decreases from 475ppm to 380ppm at 24cm. In the spring and autumn profiles the concentration is constant in the uppermost 10cm of the core at ~400ppm, between 10 and 15cm it increases to ~450ppm and remains close to this concentration for the rest of the profile. In the winter sample the concentration is again close to 400ppm in the uppermost 10cm of the core, but below this depth it increases sharply and reaches a maximum value of 570ppm at 22cm.

Snarestone

The concentration of Cr in the Snarestone sediment fluctuates over the profile between 7.6ppm and 31ppm and tends to decrease as depth increases in all seasons (Figures 4.8 e-h). The concentration at the surface is between 31ppm

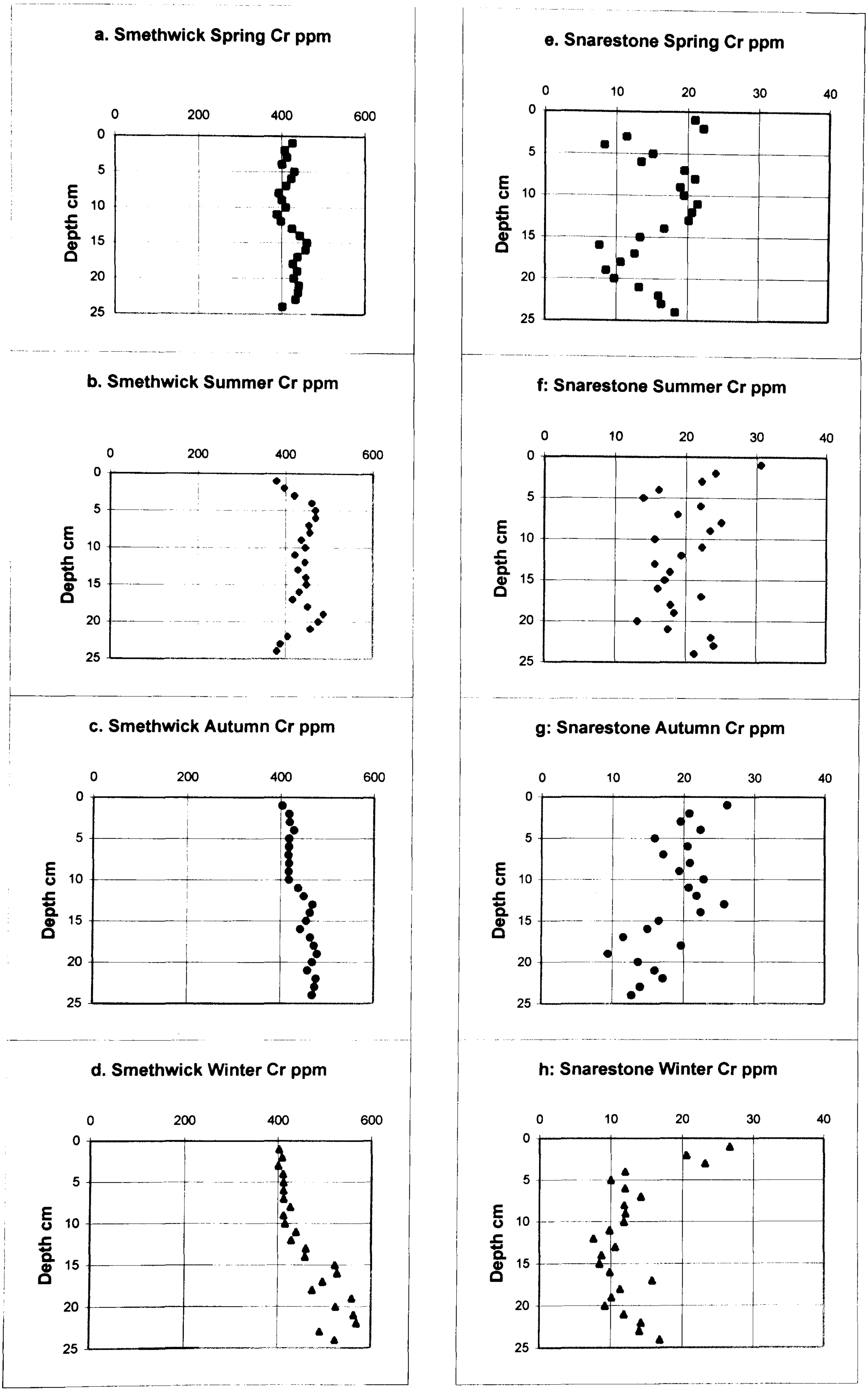


Figure 4.8a-f: Concentration of Cr in Smethwick and Snarestone Sediment

and 21ppm falling to between 13ppm and 9ppm at 20cm, beneath 20cm the concentration increases once more to between 13ppm and 21ppm.

4.2.4.6. Manganese

Smethwick

The concentration of Mn in the sediment is between 1875ppm and 2460ppm in all the seasonal Smethwick samples (Figures 4.9 a-c), except the winter sample in which values are greater than 2400ppm beneath 13cm and reach a maximum value of 3055ppm at 20cm (Figures 4.9d). With the exception of the winter sample the concentration of Mn shows no systematic depth trend.

Snarestone

In all of the seasonal profiles for Mn, the concentration fluctuates over the profile, but shows a general trend of decreasing concentration with increasing depth (Figures 4.9 e-h). Values at the surface are between 611ppm and 509ppm and fall to between 500ppm and 284ppm at depths greater than 20cm.

4.2.4.7. Iron

Smethwick

Iron is the most abundant metal in Smethwick sediment (Table 4.1a) and with the exception of the winter profile the concentration of Fe shows no systematic depth trend; it is present in the sediment at concentrations of between 64,886ppm and 77,465ppm (Figures 4.10a-c). Figure 4.10d shows the concentration profile for Fe in the winter core, and from this it can be seen that the concentration steadily increases below a depth of 10cm and then shows a marked peak of 14,2019ppm between 20cm and 22cm.

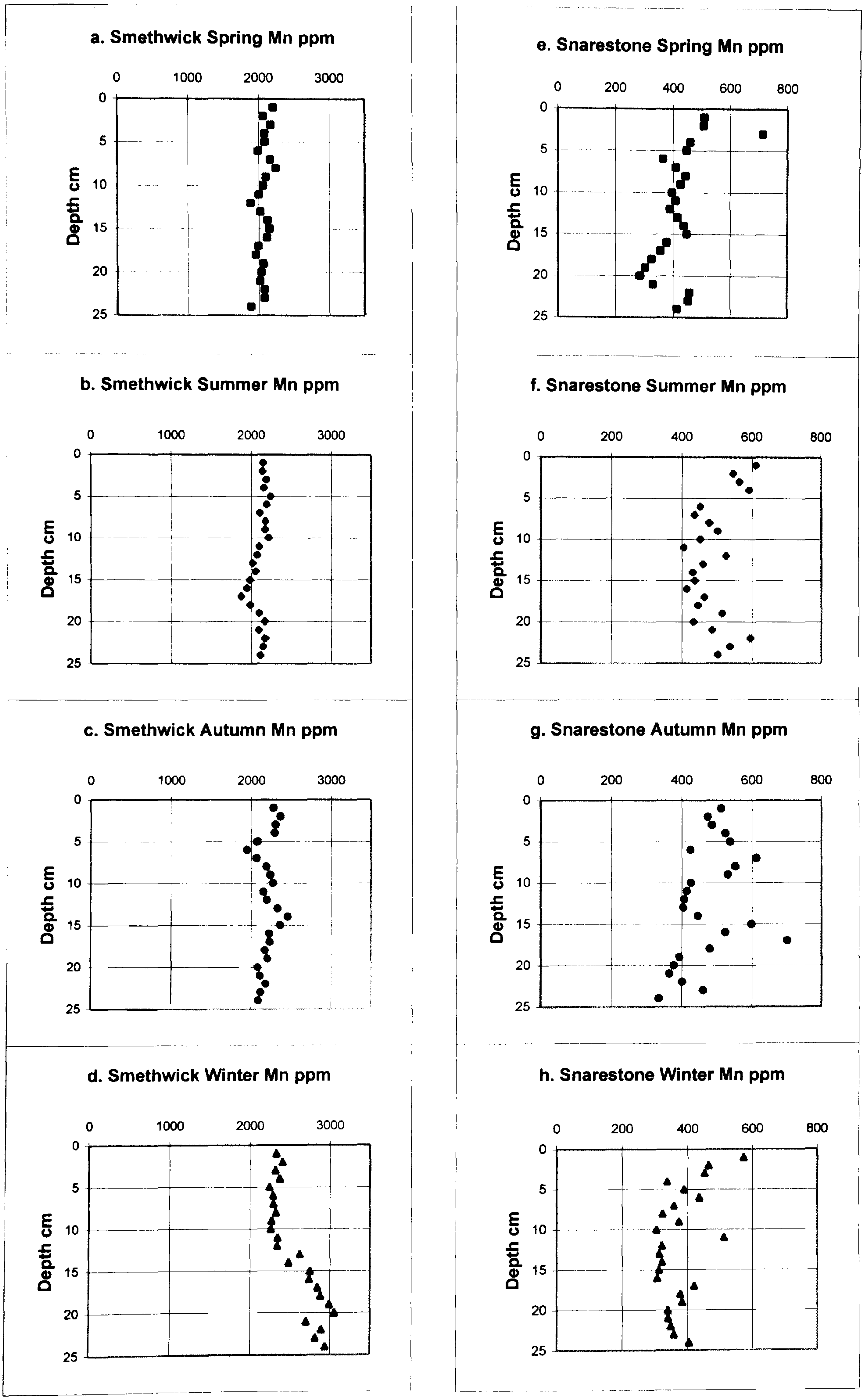


Figure 4.9a-f: Concentration of Mn in Smethwick and Snarestone Sediment

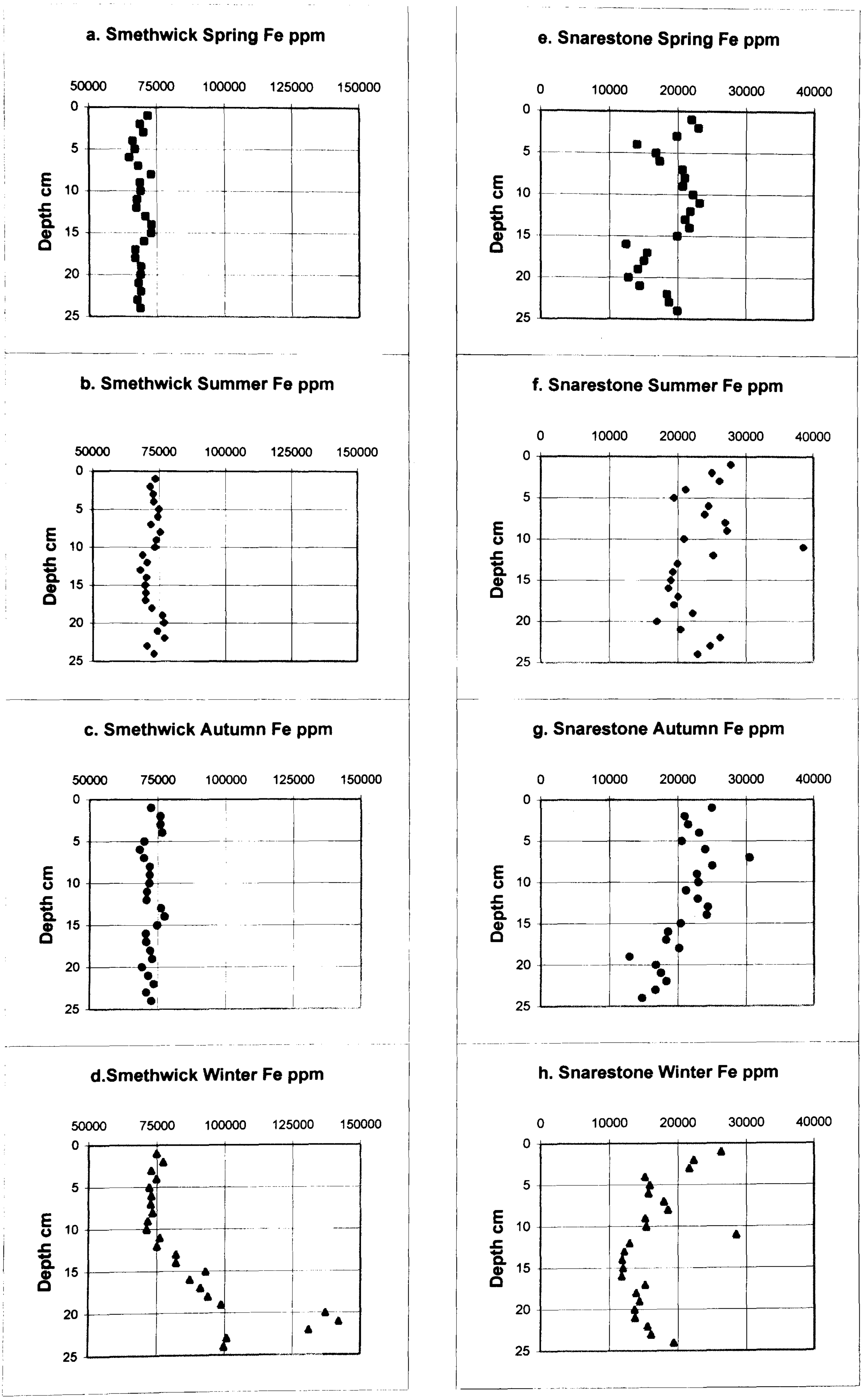


Figure 4.10a-f: Concentration of Fe in Smethwick and Snarestone Sediment

Snarestone

The total concentration of Fe in the sediment is close to 20,000ppm but ranges from 11,800ppm to values exceeding 30,000ppm (Figures 4.10 e-h). The Fe concentration decreases in the uppermost 5cm of the sediment by approximately 5000ppm in each season, which coincides with the observed colour change from brown to black caused by reduction of Fe-oxides. The concentration then continues to decline at much slower rate, reaching values of below 20,000ppm at different depths in each season, generally about 15cm.

4.2.4.8. Copper

Smethwick

Copper is present in the sediment at concentrations of between 600ppm and 800ppm in all seasons except the winter when it reaches a maximum value of 1320ppm at 21cm (Figure 4.11a-d). The Cu concentration tends to increase downwards over the depth profile in each season. This increase is most marked in the winter sample, although the trend is similar to that observed in the spring and autumn profiles in which the concentration gently increases by ~100ppm over the uppermost 15cm (Figure 4.11a,c and d). In the summer sample the concentration rises sharply from 604ppm at the surface to 750ppm by 5cm depth and then remains constant with depth until 20cm when the concentration begins to fall, reaching 628ppm at 24cm (Figure 4.11b).

Snarestone

The concentration of Cu decreases over the 25cm sediment profile, at the surface the concentration is between 50ppm and 36ppm, decreasing to between 25ppm and 20ppm at 20cm depth (Figure 4.11 e-h). In the winter the concentration declines most sharply in the uppermost 5cm of the profile from 50ppm to 22ppm and then remains constant, similar though less marked trends are observed in the spring and summer while in the autumn the concentration

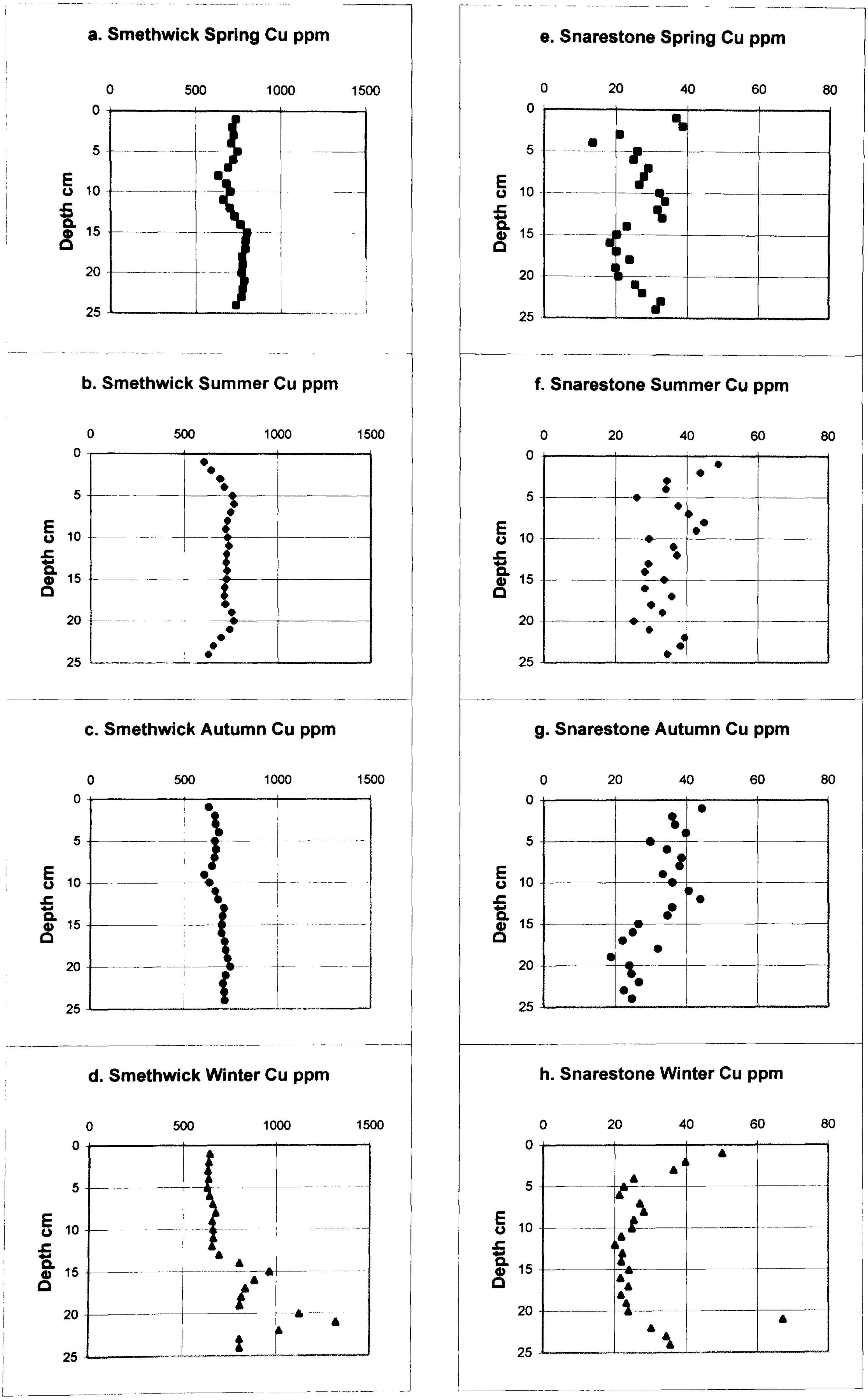


Figure 4.11a-f: Concentration of Cu in Smethwick and Snarestone Sediment

falls steadily over the entire depth profile.

4.2.4.9. Zinc

Smethwick

The concentration of Zn increases with depth in all seasons and this increase is most marked in the winter sample in which it rises from 7886ppm at the surface to 17,320ppm at 21cm. In the spring and autumn profiles the concentrations at the surface are 8,714ppm and 8,079ppm respectively, these concentrations steadily increase to 10,501ppm and 10,688ppm at 15cm and below this depth they remain relatively constant (Figure 4.12a and c). In the summer sample the concentration rises sharply from 8331ppm at the surface to 10,625ppm by 6cm depth and then remains constant with depth until 20cm when the concentration begins to decrease, reaching 8573ppm at 24cm (Figure 4.12b).

Snarestone

The concentration of Zn in the Snarestone sediment declines sharply in the uppermost 5cm of the sediment in all four seasons, from between 445-343ppm at the surface to between 235-155ppm at 5cm (Figures 4.12e-h). The concentration then stabilises but continues to decline slowly for the remainder of the profile reaching values of ~70ppm beneath 20cm.

4.2.4.10. Cadmium

Smethwick

The concentration of Cd increases with depth in all seasons; values are between 28ppm and 41ppm in the spring, summer and autumn sediment samples, while in the winter sample the concentration exceeds 40ppm at 15cm, reaching 70ppm at 21cm, before falling once more to 42ppm by 24cm (Figure 4.13a-d). In the spring and autumn profiles, the concentration gently increases from 30ppm to

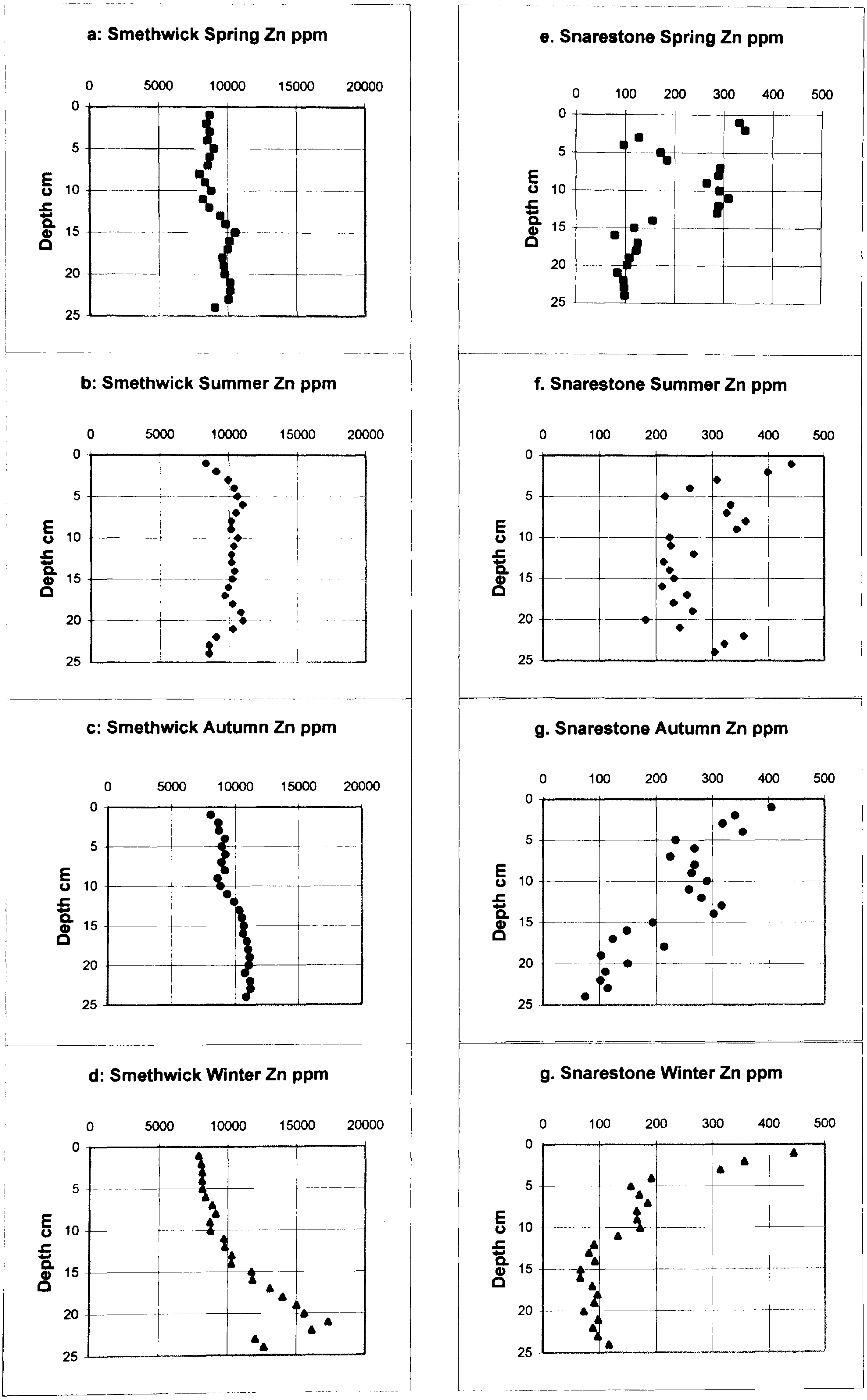


Figure 4.12a-f: Concentration of Zn in Smethwick and Snarestone Sediment

40ppm over the uppermost 15cm and then remains constant (Figure 4.13a and c). In the summer sample the concentration rises sharply from 29ppm at the surface to 40ppm by 6cm depth and then remains constant with depth until 20cm when the concentration decreases to 30ppm at 24cm (Figure 4.13b).

Snarestone

Cadmium was not detected in the Snarestone aqua-regia leachates; the detection limit of the ICP-AES is 1ppm, when corrected for the dilution used in this technique (x200) (Appendix 4.10b).

4.2.4.11. Lead

Smethwick

The concentration of Pb in the sediment is between 1135ppm and 1774ppm in the spring, summer and autumn samples. In all seasons the concentration increases over the depth profile. In the winter profile the concentration exceeds 1774ppm, rising sharply with depth and reaching 2340ppm at 21cm. In the spring and autumn profiles the concentration gently increases by ~350ppm over the uppermost 15cm and then remains constant (Figure 4.14a and c). In the summer sample the concentration rises sharply from 1206ppm at the surface to 1688ppm by 6cm depth and then remains constant with depth until 20cm when the concentration decreases to 1255ppm at 24cm (Figure 4.14b).

Snarestone

Lead was not detected in the Snarestone aqua-regia leachates; the detection limit of the ICP-AES is 80ppm, when corrected for the dilution used in this technique (x200) (Appendix 4.11b).

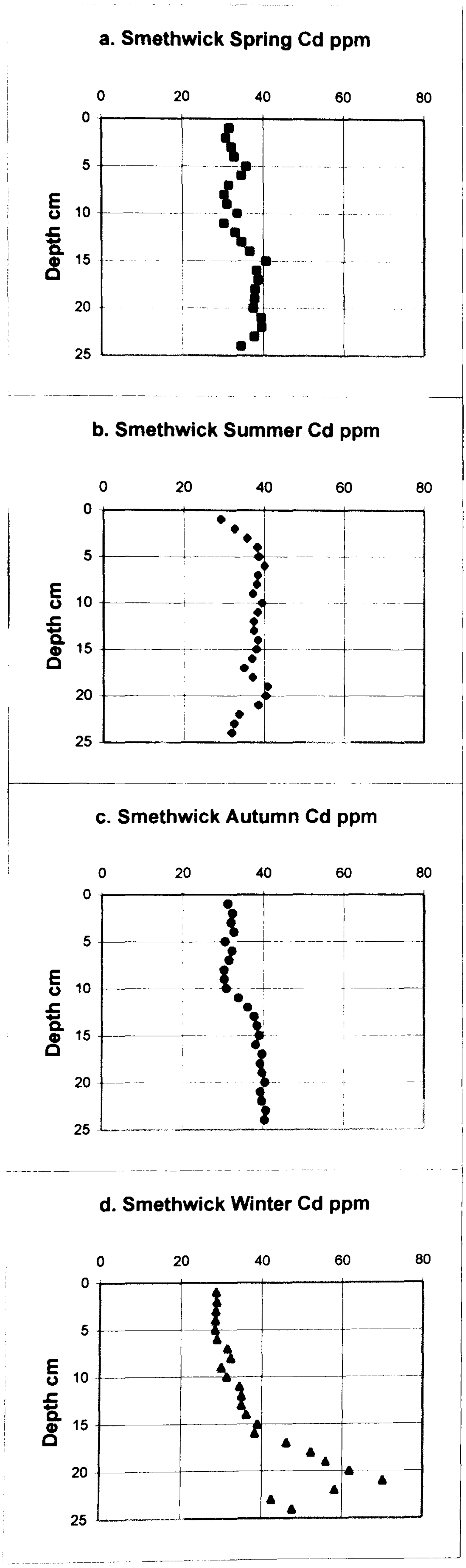


Figure 4.13a-d: Concentration of Cd in Smethwick Sediment

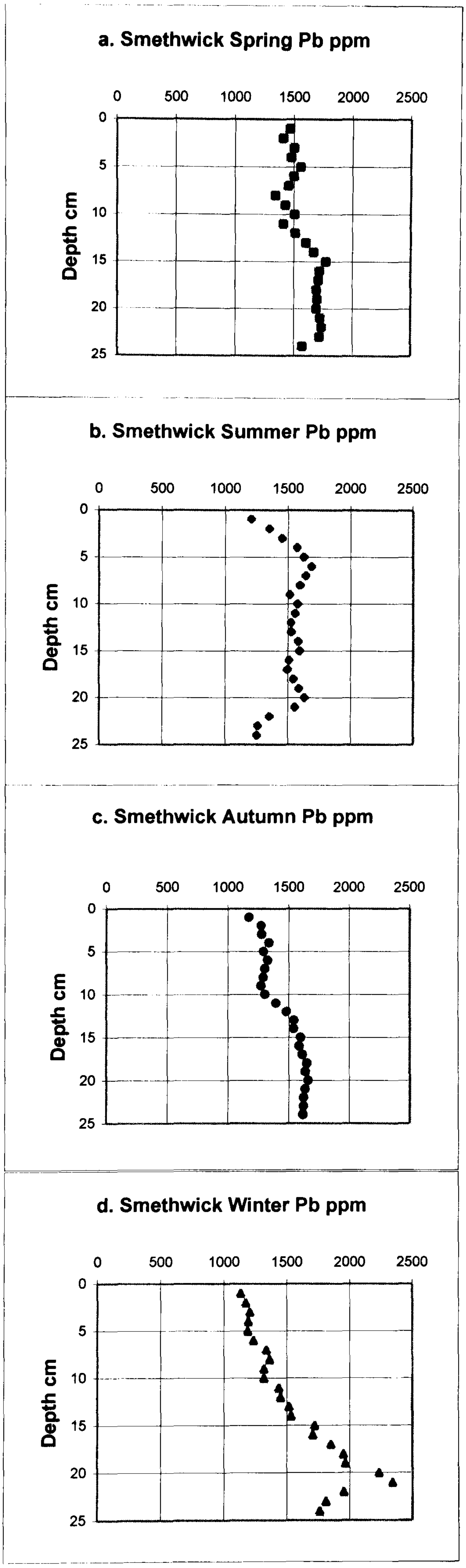


Figure 4.14a-d: Concentration of Pb in Smethwick Sediment

4.3. Results of the Sequential Extraction Investigation

Sequential extractions are designed to assess the solid speciation of trace metals in soils and sediments. It is recognised that they are important for understanding the particular environmental behaviour of metals present in a variety of forms and in a variety of matrices (Tack and Verloo, 1995). In this study a sequential extraction is potentially helpful in that it provides quantitative information about the solid phases in which metals are partitioned, which aids the interpretation of the sediments' petrology and diagenesis and how they have been affected by anthropogenic material. However, at present these extraction techniques are 'unsatisfactory operational tools and they have numerous associated conceptual and practical problems' (Kersten and Forstner, 1995) (Section 2.3.4). In order to assess the degree to which these problems affect the application of sequential extractions to canal sediment a petrographic investigation of the BCR sequential extraction procedure and a second extraction procedure designed for use on anaerobic sediments (Kersten and Forstner, 1986) was conducted using the CryoSEM (Section 2.3.4.1). The investigation focused upon urban sediment because it is very different from the natural sediments for which the schemes are designed. Certain urban sediment components, in particular vivianite, are not expected to be important metal binding phases in natural sediments and are thus not traditionally considered in the interpretation of the results of sequential extractions. Therefore it was important to assess how the sediment responded to the extractions and whether or not the unusual components could be separated by a particular fraction.

The sequential extraction of rural sediment was not investigated by CryoSEM because it has not received significant anthropogenic inputs, and its mineralogy and petrology reflect those of natural sediments for which the extraction schemes are designed. If however, irregularities were observed in the residues of the urban sediment, the rural residues were also examined in order to establish whether or not the problem was unique to the contaminated sediment.

Following this investigation of the two extractions, the BCR extraction was selected for assessing variations in element speciation over the depth profile of the sediment samples. The sequential extractions were conducted on the Snarestone autumn core and an additional Smethwick core sampled in Spring 1999, and the results of this analysis are also presented in this section. The concentrations of Al, P, S, Ca, Cr, Mn, Fe, Cu, Zn, Cd and Pb in the sequential extraction leachates are presented in Figures 4.17-4.26 (Appendix 11). The concentrations are given in units of milli Moles (mM) in order to assess whether elements have stoichiometric relationships to pure mineral phases.

Table 4.2 shows the average total concentrations in ppm of metals, sulphur and phosphorus in all three fractions of the BCR extraction scheme, and the corresponding average concentration derived from the aqua regia extraction of the sediment (average values for the 24cm core). These reveal that recoveries from the sequential extraction are consistently lower than the aqua regia digest, as would be expected, and that with the exception of Al and Fe the recovery is between 70% and 95%.

Table 4.2: The Total Concentrations in all Three Fractions of the BCR Extraction Scheme and the Corresponding Average Concentration Derived from the Aqua Regia Extraction of the Sediment (values are presented as an average for the 24cm core).

a) Smethwick

Smethick	a) Aqua Regia	b) Total, Sequential Extraction (SE)	Ratio
	a) Average ppm	b) Average ppm	b/a %
Al	15784	8304	52.61%
Ca	34402	32177	93.53%
Cd	35	30	85.71%
Cr	422	312	73.93%
Cu	736	563	76.49%
Fe	68971	44202	64.09%
Mn	2066	1961	94.92%
Pb	1578	1204	76.30%
Zn	9218	7860	85.27%
S	11514	8664	75.25%
P	19477	17162	88.11%

b) Snarestone

Snarestone	a) Aqua Regia	b) Total, Sequential Extraction (SE)	Ratio
	a) Average ppm	b) Average ppm	b/a %
Al	11263	2428	21.56%
Ca	27647	24325	87.98%
Fe	23180	6973	30.08%
Mn	491	349	71.08%
Zn	281	225	80.07%
S	8586	6978	81.27%
P	576	1249	216.84%

4.3.1. Selection of Sequential Extraction Method

CryoSEM analysis of the partially extracted residues from the two selected extraction schemes revealed one significant re-precipitation problem. The sediment leached by the oxide fraction of the Kersten and Forstner scheme, which uses acidified ammonium oxalate as an extractant, contained abundant iron oxalate crystals (Figure 4.15 a), the composition of which was confirmed by EDX analysis and by XRD (Appendix 12). No such precipitate was observed in the BCR residue that was extracted by hydroxyammonium-chloride. Vivianite was absent from the oxide residues of both schemes and it would appear that large quantities of iron released from the dissolution of vivianite in the Kersten and Forstner oxide extraction are being re-precipitated into the sediment as iron oxalate.

The application of acidified ammonium oxalate to extract the moderately reducible oxides has been observed to produce insoluble oxalate precipitates with Fe, Al and Ca (Pickering, 1986) and this study shows that the problem of iron oxalate precipitation must be kept in mind when dealing with iron-rich sediments. The formation of iron oxalate might have been avoided in this study had the easily reducible oxide fraction, which can be included in the Kersten and Forstner scheme, been extracted first. This would however only apply if the reagent used to extract the easily reducible oxides dissolved most of the vivianite, preventing the release of large quantities of Fe in the moderately reducible fraction.

In order to clarify the problem of Fe oxalate precipitation in the oxide fraction of the Kersten and Forstner procedure, the first three fractions were applied to a sample of Snarestone sediment. Analysis of the non-leached sample revealed that vivianite was absent from the sediment, and Fe was held largely as pyrite. In the leached sample there was no oxalate precipitation, suggesting Fe oxalate precipitation only occurred when Fe was released in large quantities.

The principal effect of this re-precipitation artefact upon iron speciation was an elevation in the proportion extracted in the sulphide fraction of the Kersten and Forstner scheme of 35% relative to the 10% extracted in the BCR extraction scheme (Figure 4.16 a-d). This elevation is the result of the dissolution of the iron oxalate generated in the oxide fraction. Iron concentrations measured in the final fraction of the BCR technique are therefore a better gauge of iron bound in sulphides.

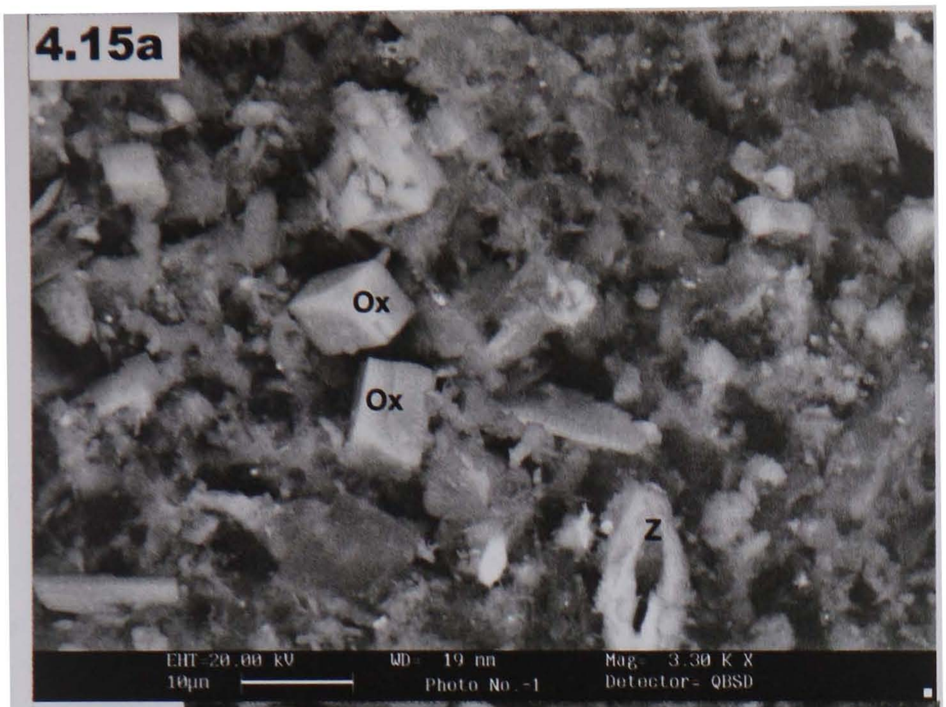
A precipitate of calcium phosphate was observed adhering to a sulphate rich organic grain in the residue from the oxide fraction of the Kersten and Forstner scheme (Figure 4.15b). This implied some re-precipitation of P might occur following the dissolution of vivianite in this fraction. The procedure used to extract the oxide fraction of the BCR scheme is different to that of Kersten and Forstner scheme, and although a high concentration of P was measured in the leachate of this fraction, no secondary P minerals were observed in the residue.

The BCR extraction technique was therefore selected as the most appropriate for application to canal sediment. The BCR technique consists of 3 extractions, for the selective dissolution of:

1. Carbonates
2. Oxides
3. Sulphide and organic matter

Figure 4.15: CryoSEM images of sequential extraction, Smethwick sediment residues

4.15a

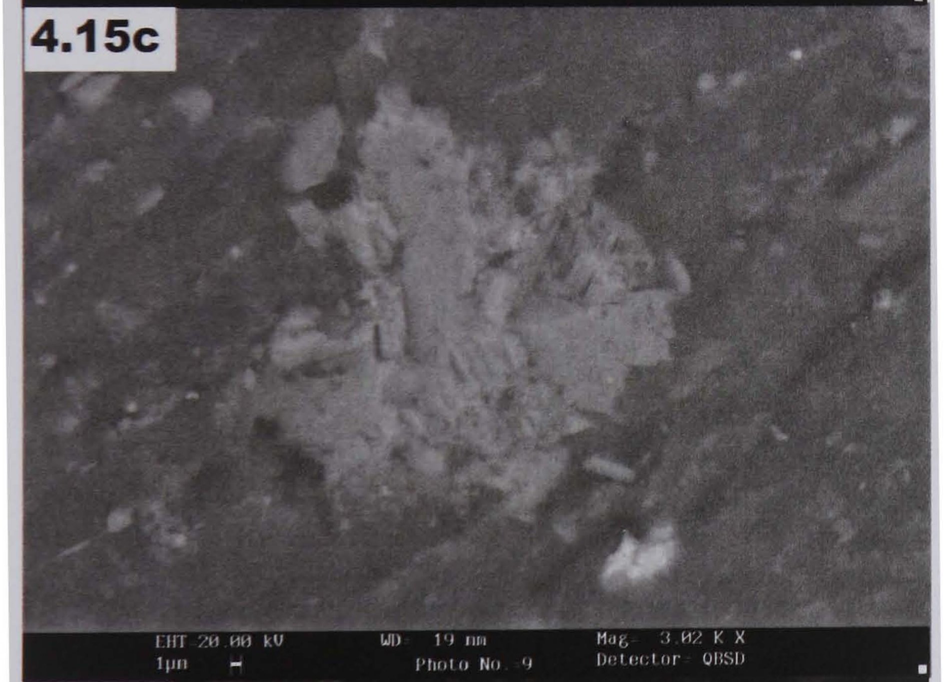


a: Sediment leached by the oxalate buffer in fraction 3 of the Kersten and Forstner scheme, showing cube shaped crystals of iron oxalate (Ox) and Zn sulphide (z)

4.15b

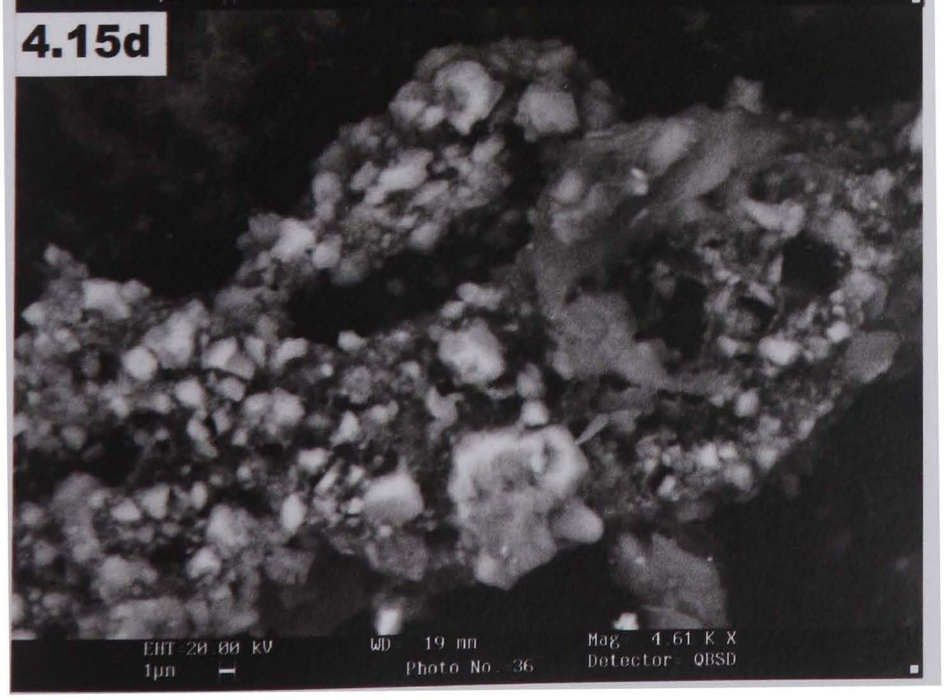
b: An S rich organic grain with calcium phosphate precipitated in its centre, following leaching by fraction 3 of the Kersten and Forstner scheme

4.15c



c: An etched vivianite grain, following leaching by fraction 2 of the BCR scheme

4.15d



d: Calcite grains in a clay-organic matrix, following leaching by fraction 1 of in the BCR scheme

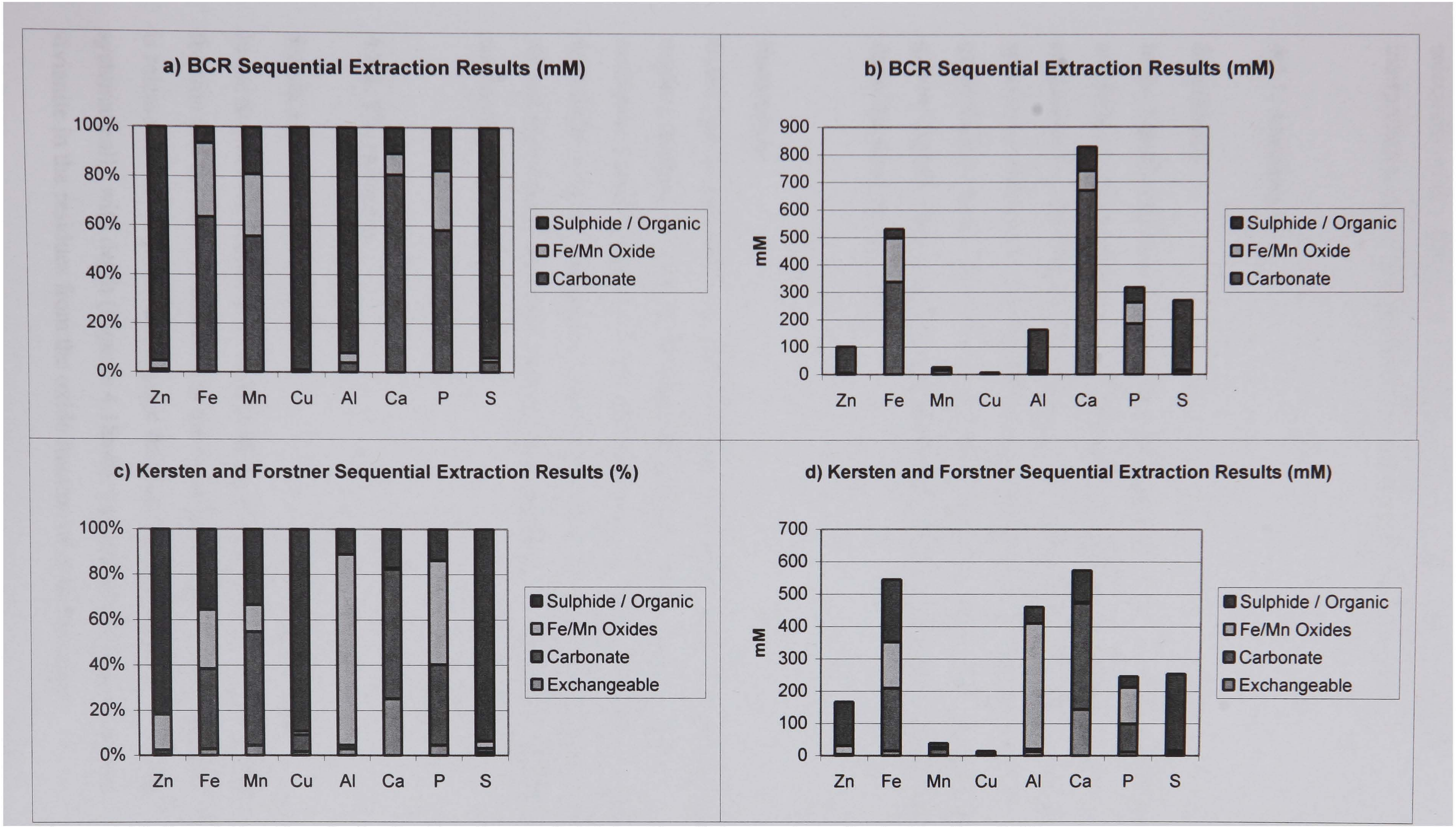


Figure 4.16: Speciation Results for the Two Sequential Extraction Schemes Investigated by CryoSEM

The CryoSEM investigation highlighted some problems related to the selectivity of this technique, which will be discussed along with the interpretation of the speciation results in Sections 4.4.2 and 4.5.3.

4.3.1. Aluminium

Smethwick

In the Smethwick sediment, between 55% and 80% of the Al is extracted in the sulphide and organic fraction, 20-40% in the oxide fraction and <5% in the carbonate fraction (Figure 4.17 a and b). The most significant variation in the speciation with depth is a decrease in the proportion of Al extracted in the oxide fraction from ~40% in the uppermost 10cm of the profile to 20-30% at greater depths. Clay minerals were observed in the residues from each of the three fractions by CryoSEM.

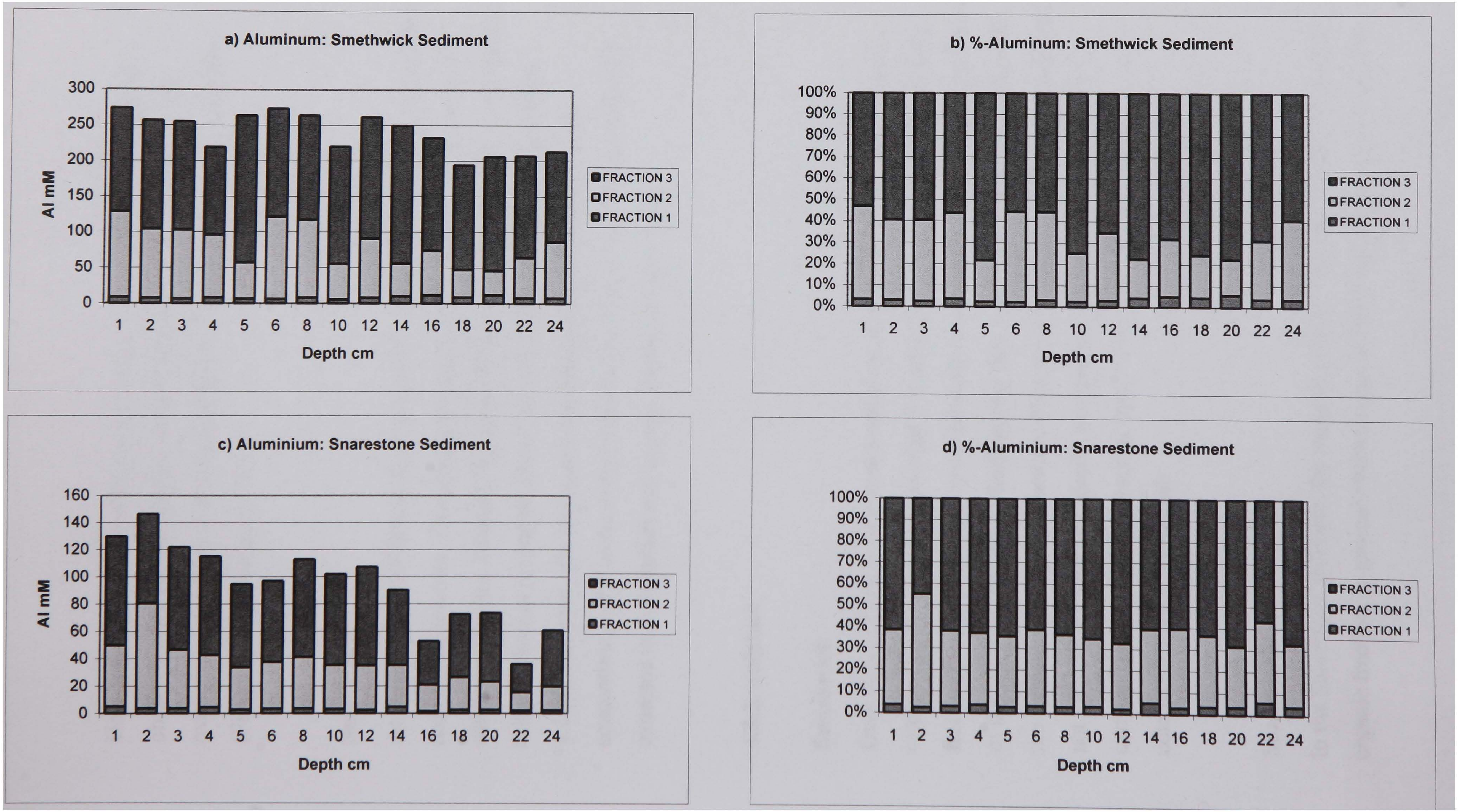
Snarestone

In the Snarestone sediment, 60-65% of the Al is extracted in the sulphide and organic fraction, 30-35% in the oxide fraction and <5% extracted in the carbonate fraction (Figure 4.17c). The speciation remains relatively constant with depth with the exception of the sample from 2cm deep in which 50% of Al was extracted in the oxide fraction, this sample also had the highest total Al concentration (Figure 4.17d).

4.3.2. Phosphorous

Smethwick

In the Smethwick sediment 35 to 55% of the P is extracted in the carbonate fraction and between 40 and 50% in the oxide fraction, the remaining 10-15% is released in the sulphide and organic fraction, the speciation does not vary systematically with depth (Figures 4.18a-b). CryoSEM analysis reveals no vivianite in the residues from the oxide fraction of either scheme.



a) Aluminum: Smethwick Sediment

b) %-Aluminum: Smethwick Sediment

c) Aluminium: Snarestone Sediment

d) %-Aluminium: Snarestone Sediment

Figure 4.17: The Sequential Extraction Results for Al in Smethwick and Snarestone Sediments

Unfortunately it is impossible to be certain whether the etched vivianite observed in the residues from the carbonate fraction is the result of the extraction procedures or if it was etched in the sediment prior to extraction (Figure 4.18c) (Section 3.2.3.1).

Snarestone

At Snarestone, 80-100% of the P is extracted from the sediment in the sulphide and organic fraction. Throughout the depth profile 0-10% is released in the carbonate fraction. Beneath 5cm some of the P is released in the oxide fraction, this increases in proportion from 5 to 10% with increasing depth (Figure 4.18d). However, this increase is not due to an actual increase in the concentration of P in the oxide leachate, but a fall in the concentration of P extracted in the sulphide and organic fraction (Figure 4.18c).

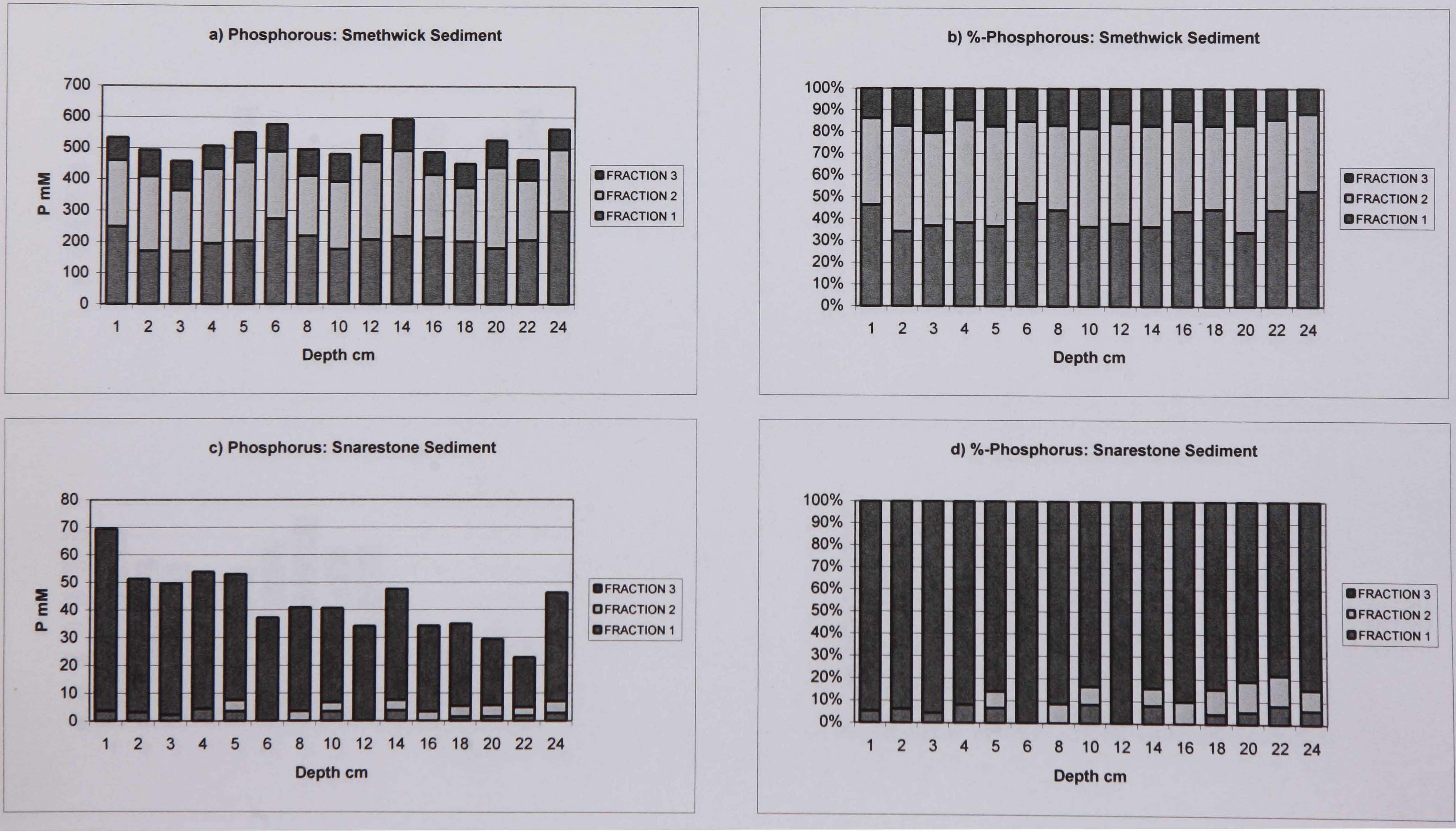
4.3.3. Sulphur

Smethwick

Over 90% of the S in Smethwick sediment is extracted in the sulphide and organic fraction and the remaining S is principally extracted in the carbonate fraction (Figure 4.19a-b). CryoSEM analysis revealed sulphides in the residues of the oxide and carbonate fractions but they were absent from the residues of the sulphide and organic fractions. Figure 4.19b reveals that the speciation does not vary significantly with depth, except for a decrease in the amount of S extracted in the carbonate fraction from ~10% in the uppermost 14cm of the core to ~5% below that depth.

Snarestone

In the Snarestone sediment, the majority of S is extracted in the sulphide and organic fraction, in general >90% (Figure 4.19d). The only marked change in



a) Phosphorous: Smethwick Sediment

b) %-Phosphorous: Smethwick Sediment

c) Phosphorus: Snarestone Sediment

d) %-Phosphorus: Snarestone Sediment

Figure 4.18: The Sequential Extraction Results for P in Smethwick and Snarestone Sediments

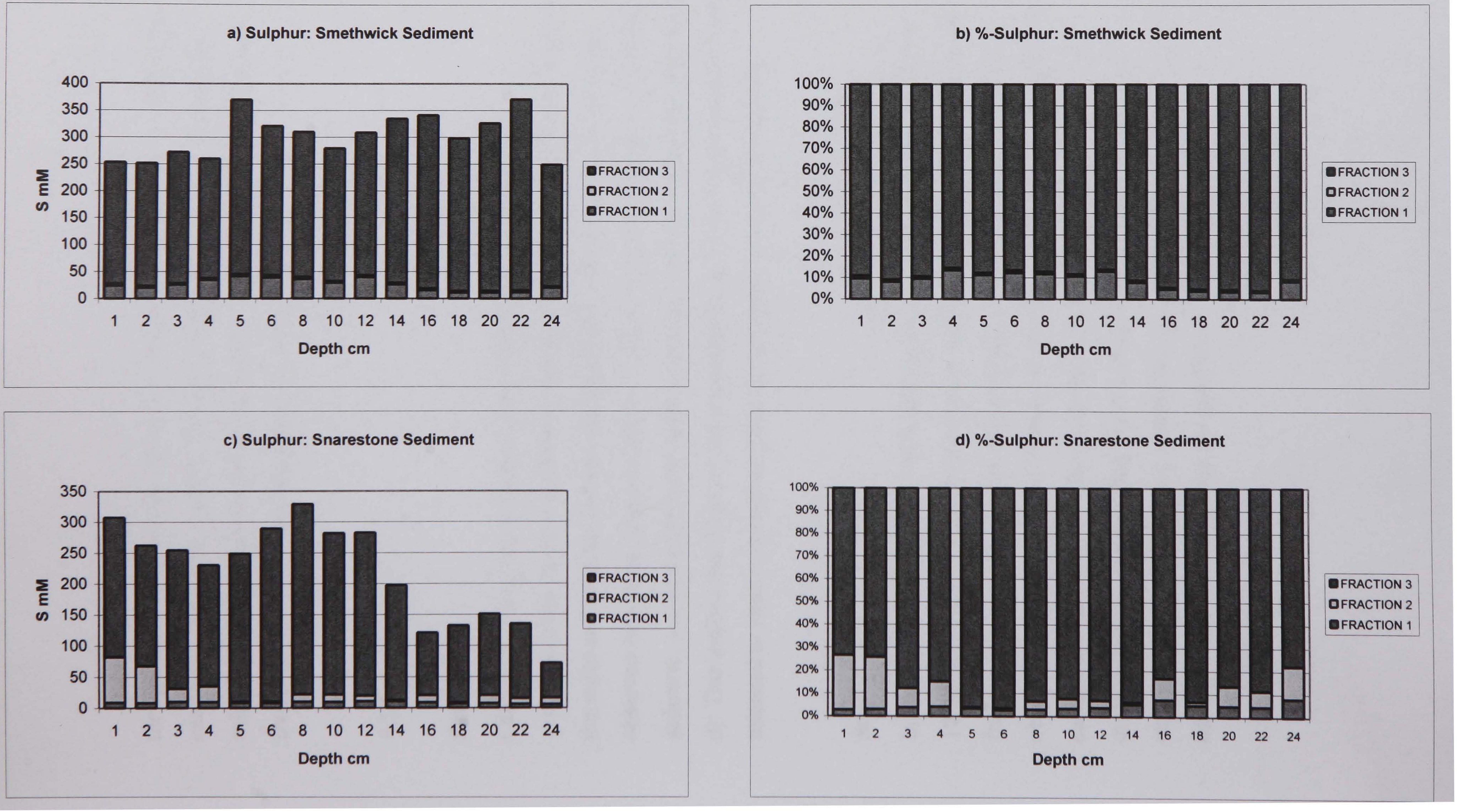


Figure 4.19: The Sequential Extraction Results for S in Smethwick and Snarestone Sediments

the speciation, occurs in the uppermost 3cm of the core, when 10-25% of S is extracted in the oxide fraction, with the remaining 75-90% extracted in the sulphide fraction (Figure 4.19c). The amount of S extracted in the carbonate fraction is low (<10mM) throughout the profile.

4.3.4. Calcium

Smethwick

Calcium is principally extracted in the carbonate fraction, 80% of Ca is extracted in this fraction and the remaining 20% is distributed evenly between the oxide and sulphide fraction. No significant variations in speciation were observed with depth (Figure 4.20a-b). Calcite, the principal sink for Ca in the sediment, was observed in the residue from the carbonate fraction (Figure 4.15 d). This implies that it has not been completely dissolved by the extraction step intended to remove carbonates from the sediment, as would be expected.

Snarestone

In the Snarestone sediment ~80% of Ca is extracted in the carbonate fraction, 10-20% is extracted in the oxide fraction and <5% in the sulphide and organic fraction (Figure 4.20c-d). The only exception to this pattern of speciation is observed in the sample from 22cm in which only 45% of Ca is extracted in the carbonate fraction, 30% in the oxide fraction and 25% in the sulphide and organic fraction (Figure 4.20d). In this sample the total concentration of Ca extracted is elevated, and this implies that an atypical Ca rich particle might be having a localised affect upon the speciation.

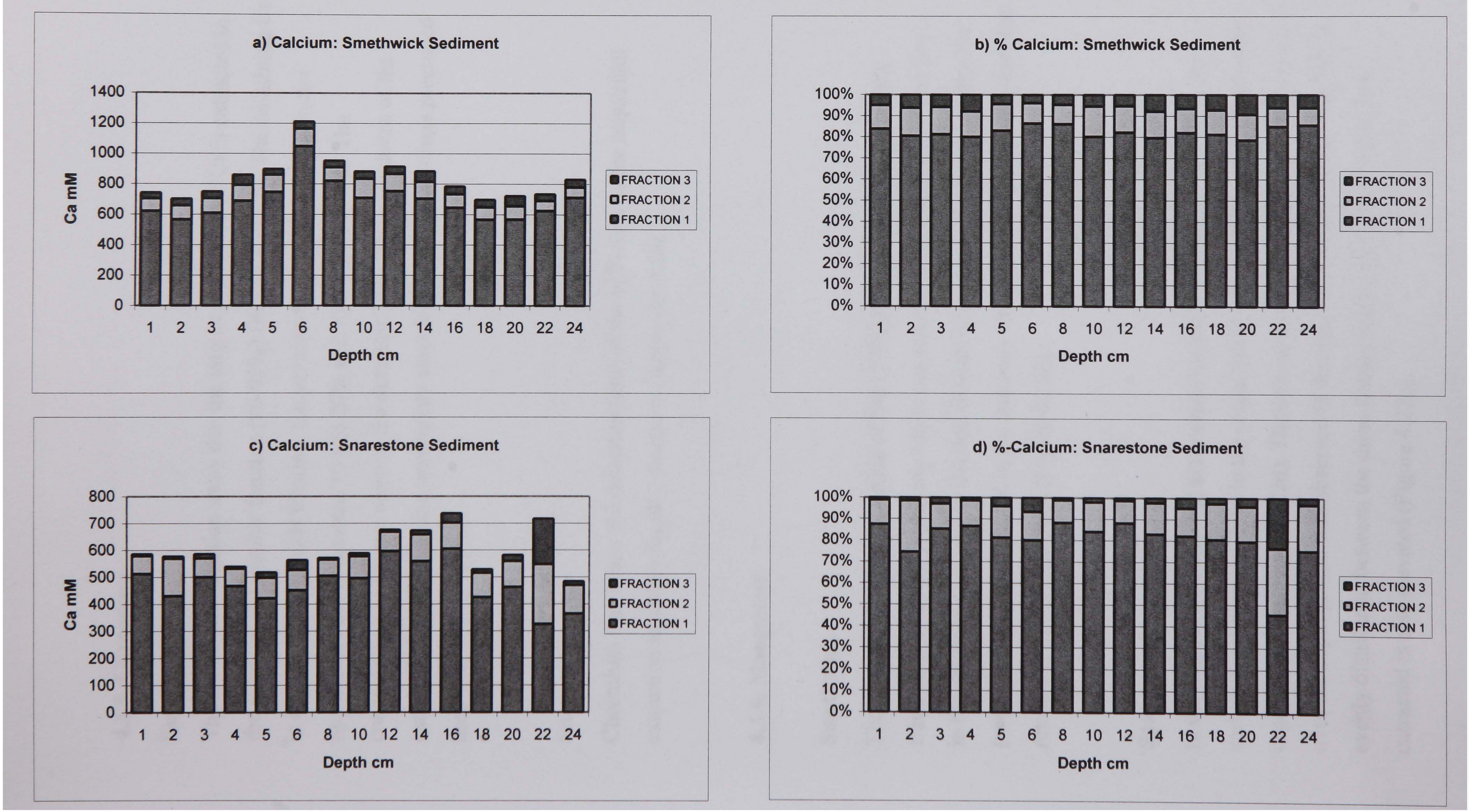


Figure 4.20: The Sequential Extraction Results for Ca in Smethwick and Snarestone Sediments

4.3.5. Chromium

Smethwick

The results of extraction show that the largest proportion of Cr is extracted in the sulphide and organic fraction (80-95%) (Figure 4.21a-b). The remaining Cr is extracted in the oxide fraction, the proportion of this is greatest in the uppermost 8cm at between 10 and 20% and <10% below 8cm. The concentration of Cr was close to the detection limit in the leachates of the carbonate fraction, and the uncertainty associated with the readings precluded their use.

Snarestone

Chromium was below the detection limit of the ICP-AES in the sequential extraction leachates for all 3 fractions (Appendix 5.5b).

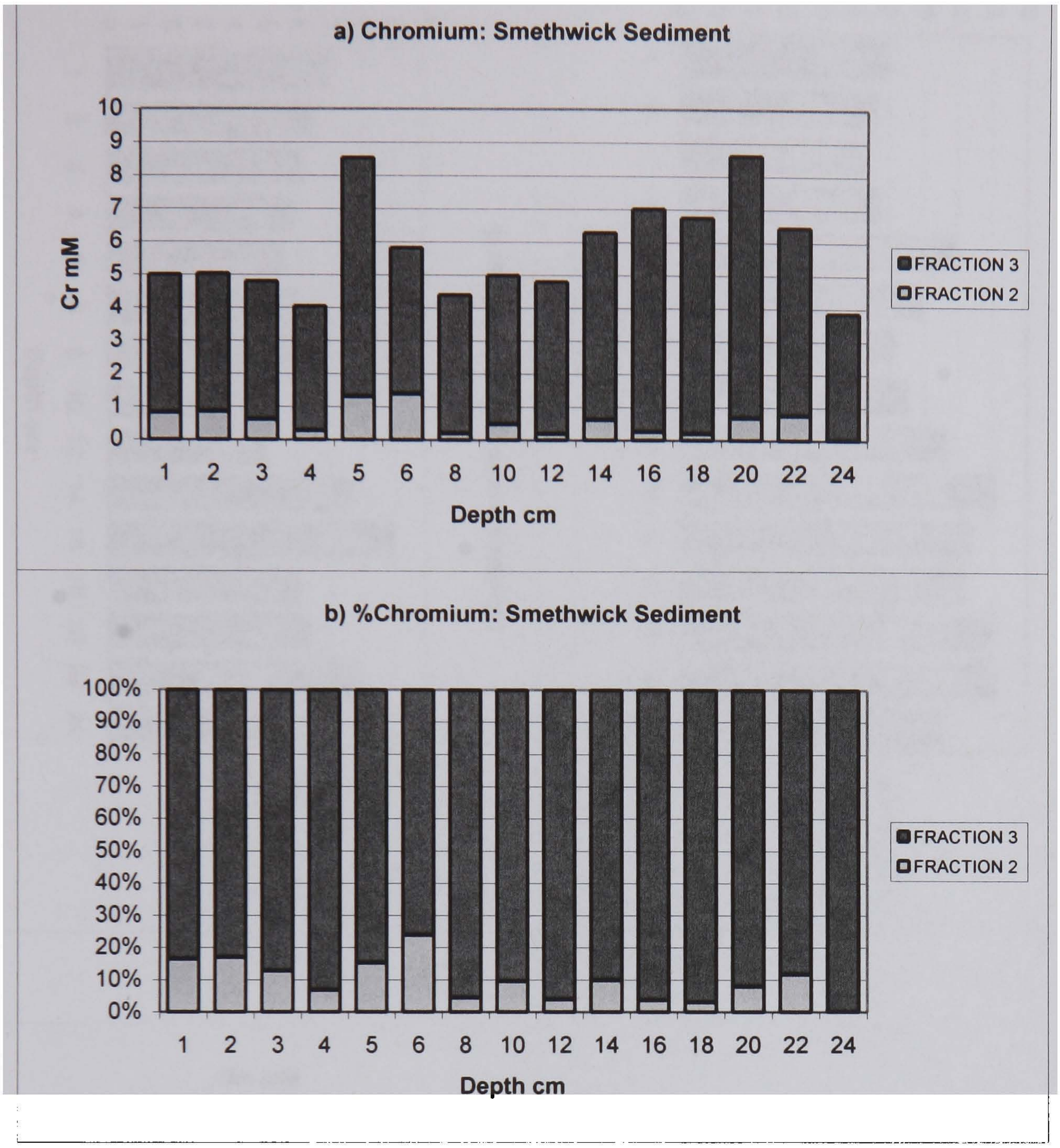
4.3.6. Manganese

Smethwick

The most significant proportion of Mn (55%) is released in the carbonate fraction; 25% of the remaining Mn is extracted in the oxide fraction and 20% in the sulphide and organic fraction (Figure 4.22a-b). In the depth profile, the proportions of Mn extracted in the fractions varies over the profile but does not reveal any systematic trend (Figure 4.22b).

Snarestone

In the Snarestone sediment, between 65 and 80% of Mn is extracted in the carbonate fraction, 10-25% in the oxide fraction and ~10% in the sulphide and organic fraction (Figure 4.22d). The only exception to this pattern of speciation over the depth profile was observed in the sample from 22cm, in which Mn is evenly distributed between the three fractions and the total concentration extracted is also elevated (Figure 4.22c).



a) Chromium: Smethwick Sediment

b) %Chromium: Smethwick Sediment

Figure 4.21: The Sequential Extraction Results for Cr in Smethwick Sediment

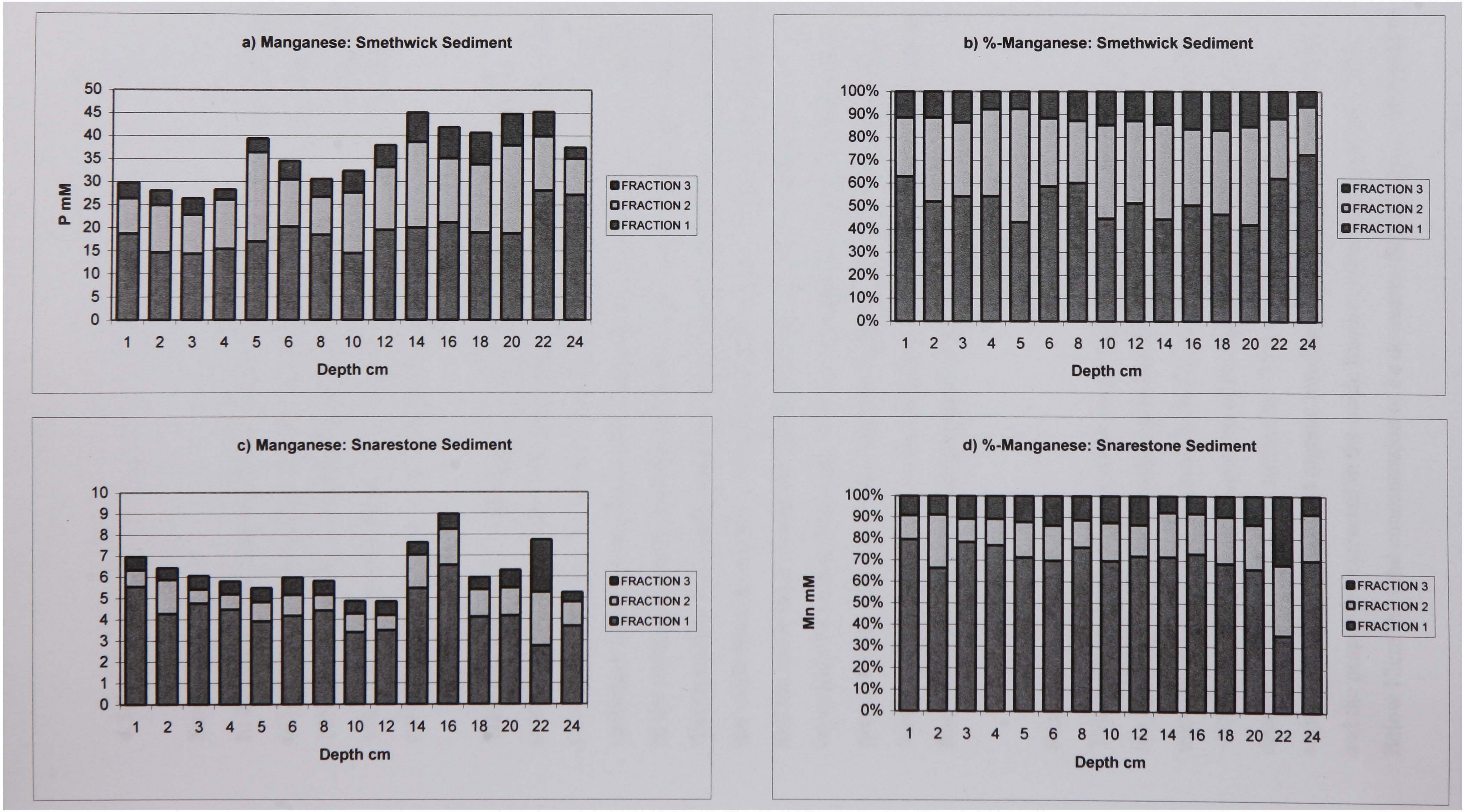


Figure 4.22: The Sequential Extraction Results for Mn in Smethwick and Snarestone Sediments

4.3.7. Iron

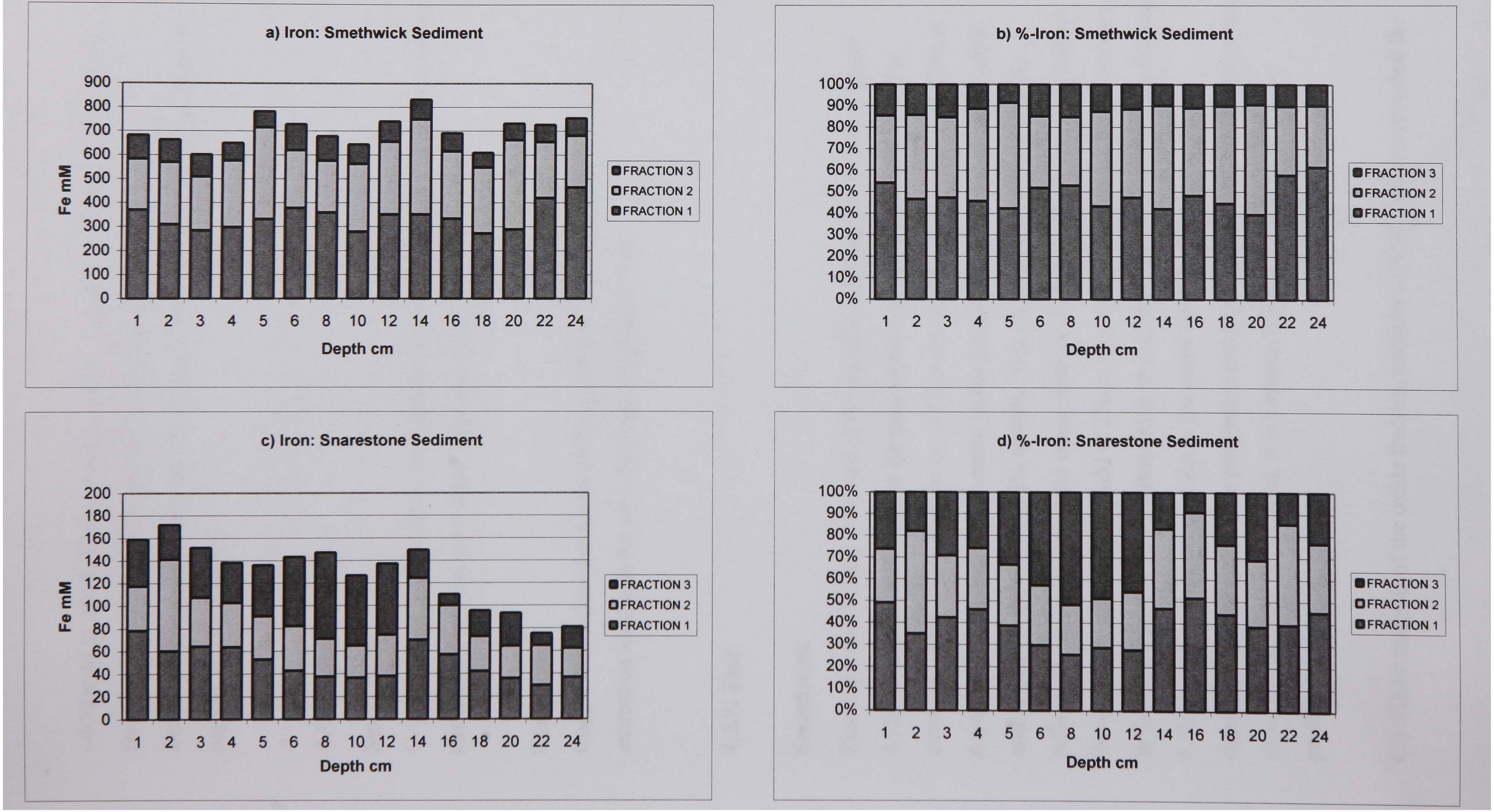
Smethwick

In the Smethwick sediment, Fe is principally extracted in the carbonate fraction (45-60%); of the remainder, 40-30% is extracted in the oxide fraction and 15-10% in the sulphide and organic fraction (Figure 4.23a-b). The proportion of Fe extracted in the carbonate fraction increases slightly with depth, while that extracted in the oxide and sulphide fraction declines slightly.

The CryoSEM analysis of the residues from the oxide extraction of both extraction schemes found vivianite to be absent. Unfortunately it is impossible to be certain whether the etched vivianite observed in the residues from the carbonate fraction is the result of the extraction procedures or if it was etched in the sediment prior to extraction (Figure 4.14b). The analysis also revealed that crystalline iron oxides persisted in all the sediment residues, most notably the oxide fraction residue, although crystalline oxides are known to be resistant and the oxide stage is only designed to extract amorphous and poorly crystalline Fe oxides (Pickering, 1986). Iron sulphides were also observed to persist in the sediment residues until the sulphide and organic residue, from which they were absent. The only notable change to Fe sulphides in the earlier fraction residues was the disaggregation of framboids.

Snarestone

The Fe speciation in Snarestone sediment shows a marked variation between the uppermost 12cm of the core and lower section (Figure 4.23c-d). In the uppermost 12cm the total concentration of Fe remains relatively constant at ~8000mM. However the proportion of Fe extracted in the carbonate fraction decreases from ~50% at the surface to ~30% at 12cm, while the proportion extracted in the sulphide and organic fraction increases from ~25% to ~45%, and the proportion extracted in the oxide fraction remains constant at ~25%. Below 12cm the total concentration of Fe decreases steadily from ~8000mM to



a) Iron: Smethwick Sediment

b) %-Iron: Smethwick Sediment

c) Iron: Snarestone Sediment

d) %-Iron: Snarestone Sediment

Figure 4.23: The Sequential Extraction Results for Fe in Smethwick and Snarestone Sediments

~4000mM at 24cm. The proportion of Fe extracted in the oxide and carbonate fractions increases to 50% and 30% respectively in these samples, simultaneously with a decrease in the proportion extracted in the sulphide and organic fraction to 20%.

4.3.8. Copper

Smethwick

Copper was only detected in the sulphide and organic fraction, and therefore no depth trend in speciation could be observed (Figure 4.24).

Snarestone

Copper was below the detection limit of the ICP-AES in the sequential extraction leachates for all 3 fractions (Appendix 5.8b).

4.3.9. Zinc

Smethwick

Zinc is predominantly extracted in the sulphide and organic fraction. Figure 4.25a reveals a depth trend in Zn speciation in which the proportion of Zn extracted in the oxide fraction is ~35% at the surface and decreases to 15% at depth, and a simultaneous increase in the proportion extracted in the sulphide and organic fraction from 55% to 80%. This change in speciation actually reflects an increase in the total concentration of Zn with depth from 111mM at the sediment surface to 229mM at 23cm, which is accounted for by an increase in the concentration of Zn extracted in the sulphide and organic fraction (Figure 4.25b). The concentration of Zn in the oxide fraction does not alter significantly with depth. The proportion extracted in the oxide fraction does not show a systematic depth trend, it is between 5% and 10% throughout the profile.

CryoSEM analysis of the oxide fraction residues of both schemes revealed the

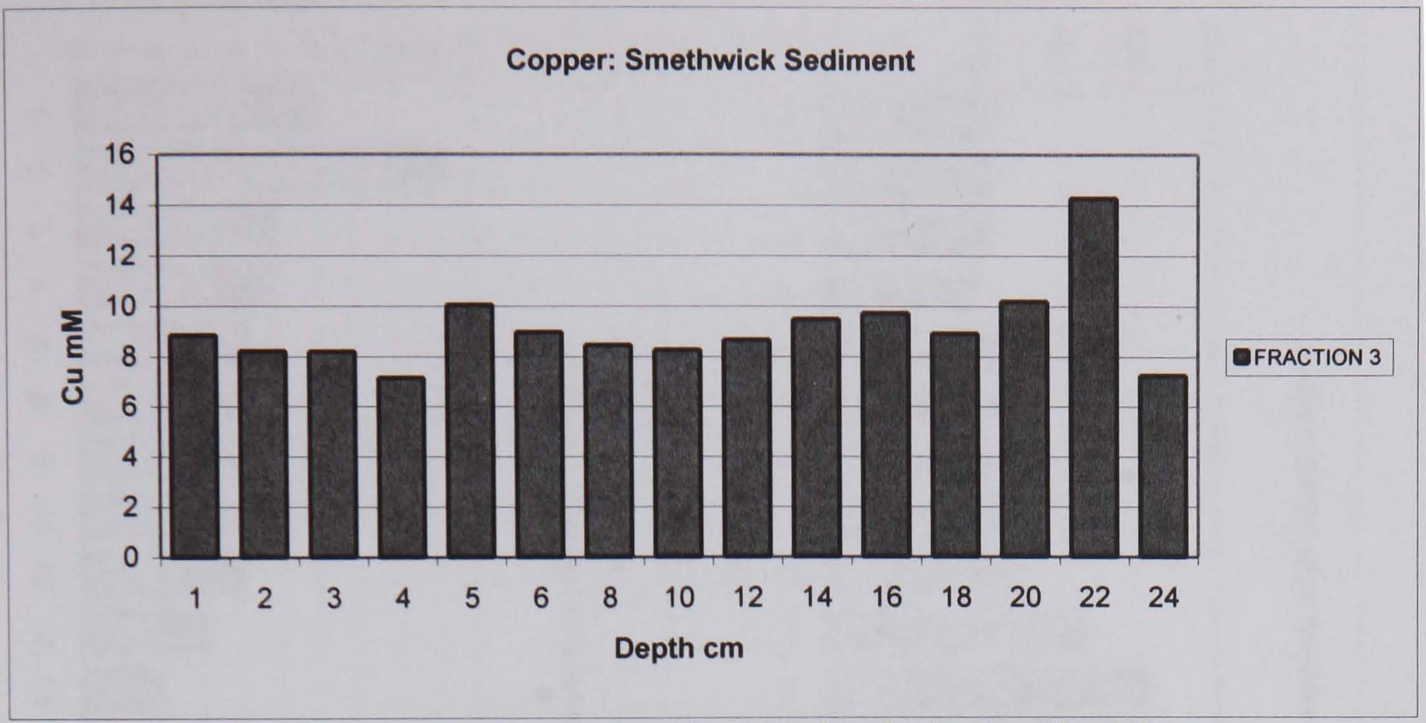
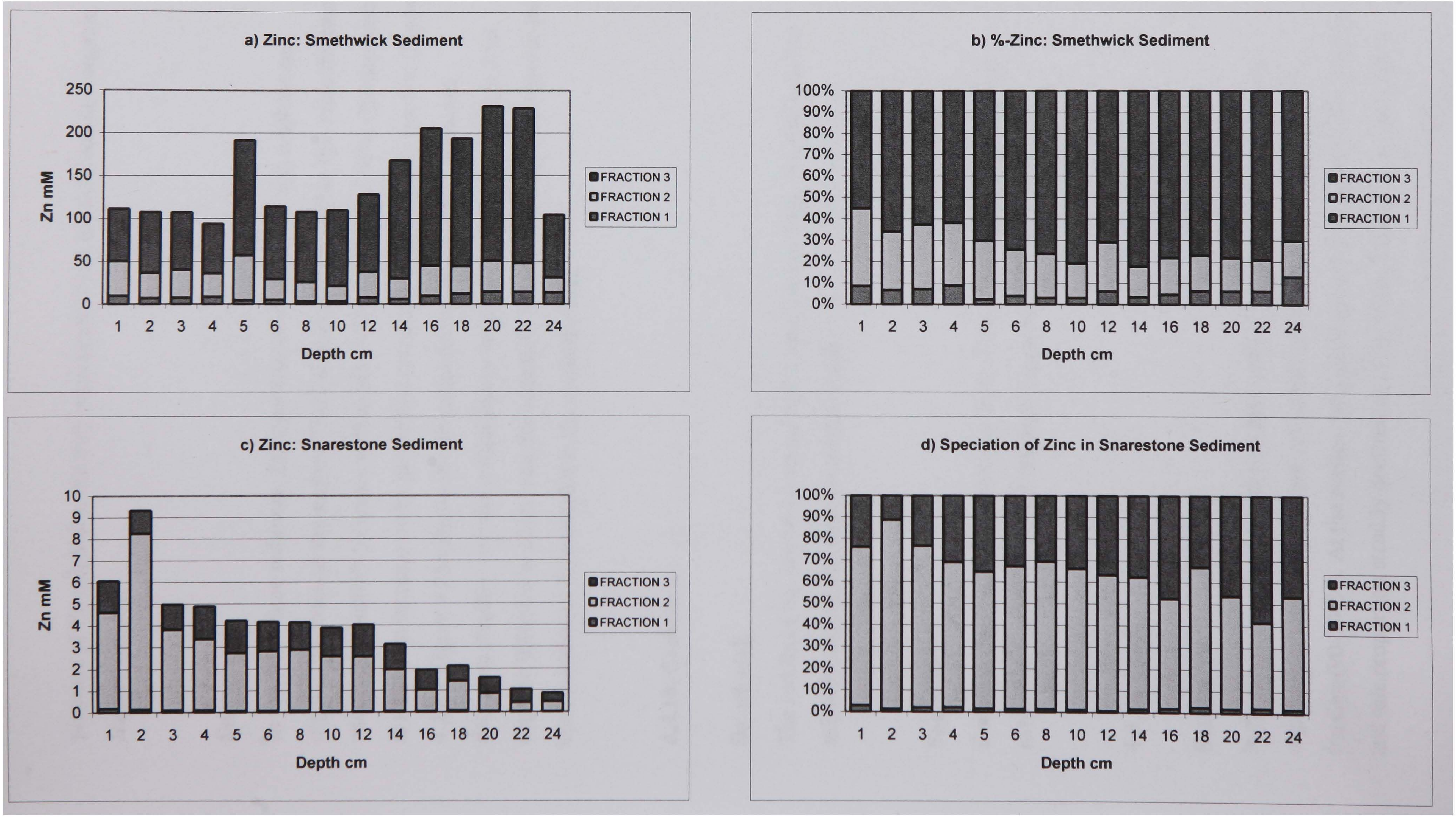


Figure 4.24: The Sequential Extraction Results for Cu in Smethwick Sediment



a) Zinc: Smethwick Sediment

b) %-Zinc: Smethwick Sediment

c) Zinc: Snarestone Sediment

d) Speciation of Zinc in Snarestone Sediment

Figure 4.24: The Sequential Extraction Results for Zn in Smethwick and Snarestone Sediments

presence of Zn sulphides, but they were absent from the sulphide and organic fraction residue.

Snarestone

In the Snarestone sediment, Zn is partitioned in the oxide and sulphide and organic fractions, at the surface 75-85% of Zn is extracted in the oxide fraction, and this proportion decreases with depth to between 40 and 50%; this decrease is met by an increase in the proportion extracted in the sulphide fraction (Figure 4.25c). Figure 4.25d shows that the total concentration of Zn extracted decreases steadily over the profile from a maximum value of 9.3mM at 2cm depth to 0.86mM at 24cm, and this is largely accounted for by a decrease in the concentration of Zn extracted in the oxide fraction.

4.3.10. Cadmium

Smethwick

The results of the extraction reveal that Cadmium was only detectable in the sulphide and organic fraction (Figure 4.26).

Snarestone

Cadmium was below the detection limit of the ICP-AES in the sequential extraction leachates for all 3 fractions (Appendix 5.10b).

4.3.11. Lead

Smethwick

In Smethwick, sediment lead was detectable in the oxide and sulphide and organic fractions of the scheme and predominantly bound in the sulphide fraction (90-100%). At the surface 10% of Pb is extracted in the oxide fraction and this proportion steadily declines to 1% at 12cm and Pb is not detected in

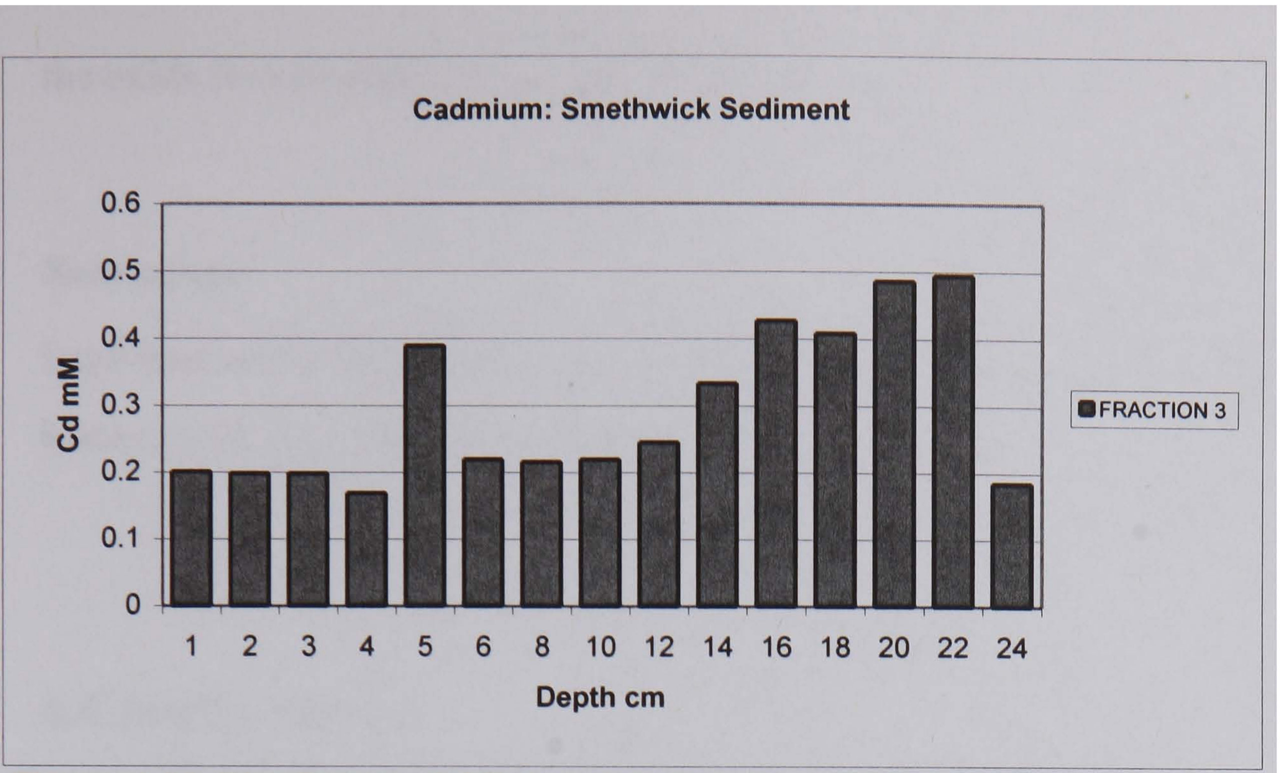
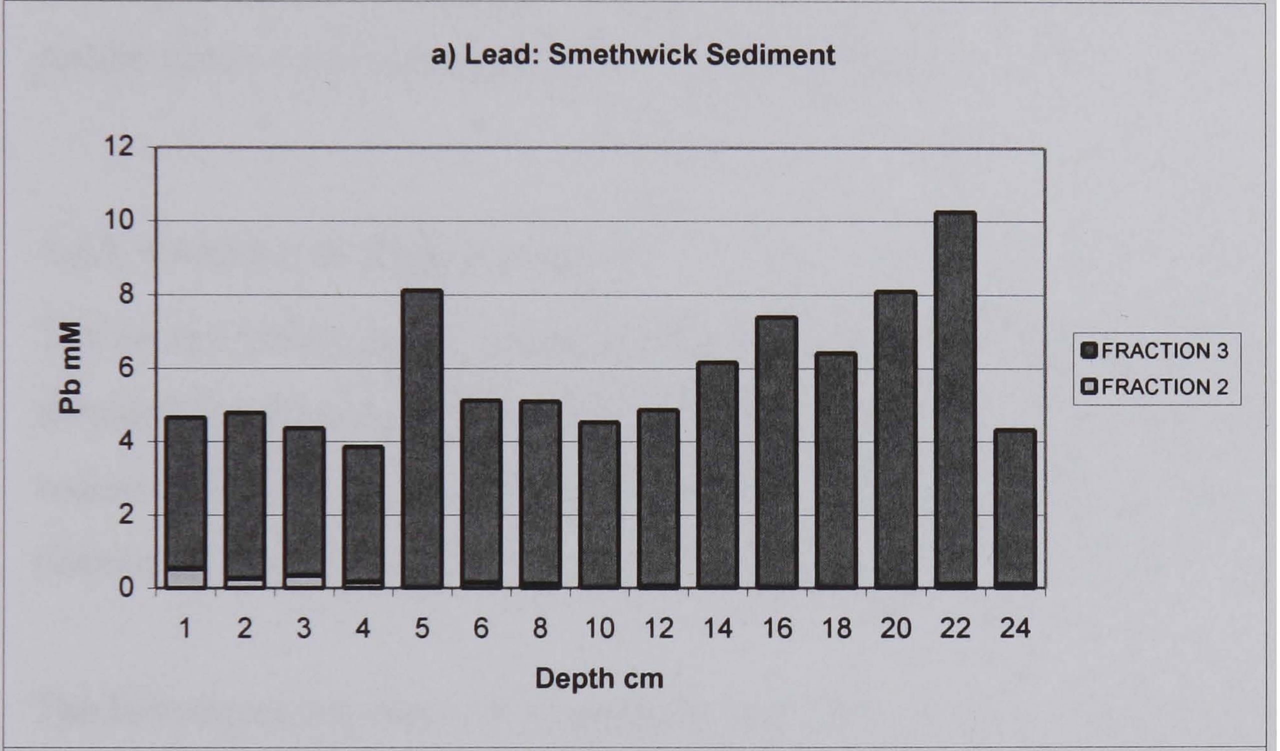


Figure 4.26: The Sequential Extraction Results for Cd in Smethwick Sediment



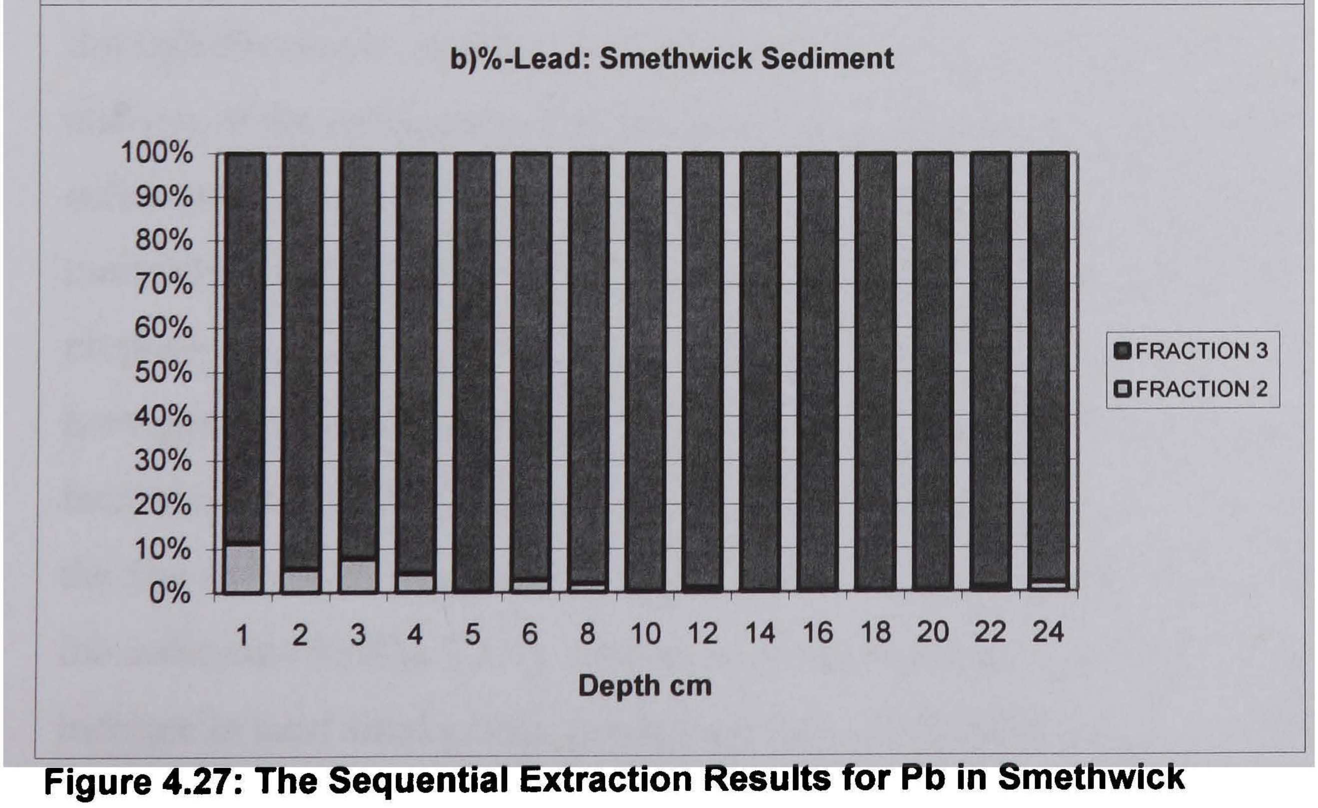


Figure 4.27: The Sequential Extraction Results for Pb in Smethwick an Snarestone Sediments

the oxide fraction below this depth (Figure 4.27a-b).

Snarestone

Lead was below the detection limit of the ICP-AES in the sequential extraction leachates for all 3 fractions (Appendix 5.11b)

4.4 Interpretation

The interpretation of the sediment chemistry is divided into two sections. Initially the bulk sediment chemistry will be interpreted and subsequently the results of the sequential extraction will be interpreted.

4.4.1. Changes in Bulk Chemistry

The analysis of the bulk chemistry of Snarestone and Smethwick sediment has revealed Smethwick sediment to be reasonably homogenous and Snarestone sediment to be heterogeneous, this difference must be considered before changes to the bulk sediment chemistry can be interpreted properly.

The heterogeneous nature of Snarestone sediment can be clearly observed through changes to its bulk chemistry observed over the depth profile. The bulk analysis of the sediment by XRF revealed SiO_2 to be the most abundant component of both rural and urban canal sediments although its distribution is markedly different in the two sediments. In the Smethwick sediment the proportion of SiO_2 varies by only 1% over the depth profile, reflecting its homogenous bulk composition. In Snarestone sediment the proportion of SiO_2 increases from 52% at the surface to 69% at 24cm, this mirrors the increase in the fine sand sized fraction with depth, observed through grain-size analysis of the sediment (Section 3.3.1). Although this increase could be unrelated to the increase in sand sized grains, petrographic observations of larger and more abundant quartz grains at depth appear to confirm the relationship.

Table 4.3 a and b show average aqua regia concentration values for the 24, 1cm interval samples of each seasonal core. They show the relative standard deviation (RSD) from the mean value, which gives an indication of the sample variability over the length of the core. From the RSD values it is clear that the urban Smethwick sediment, in which RSD values are generally less than 10%, is more homogeneous with depth than the rural Snarestone sediment, in which the majority of RSD values exceed 20%. However, the Smethwick winter core appears to be non-homogenous due to elevated concentrations at depths greater than 12cm that raise the average concentration and RSD (Table 4.3 a).

Duplicate analysis of two cores of Smethwick sediment and three cores of Snarestone sediment demonstrates that Snarestone sediment shows greater core to core variation than Smethwick sediment. However, it is important to not that variability between the duplicate cores from one season (Appendix 10.2) is less marked than that observed between different seasonal cores (Figures 4.4-4.14).

The heterogeneity at Snarestone is probably the result of variations in its bulk composition over the depth profile of the sediment and between cores. This variability in the Snarestone sediment composition makes the interpretations of any seasonal variations difficult, as seasonal samples are likely to be subject to a high degree of sample to sample variability, which might be unrelated to seasonal changes within the canal.

A comparison of the two sets of XRF results clearly illustrates the effects of anthropogenic inputs to the urban sediment. The abundance of SiO_2 in both rural and urban sediment reflects the frequent occurrence of silt sized quartz grains and to a lesser degree the other silicate minerals in the sediments which include feldspars, micas, zircon and some anthropogenic particles including slag. The rural sediment contains approximately twice as much SiO_2 as the urban sediment, and this presumably represents the dilution of natural clastic material in the urban sediment by anthropogenic material. The aqua regia analysis of rural and urban sediment revealed that the urban sediment is richer in the selected elements than the cleaner rural sediment, as would be expected. A comparison of the values in Table 4.3 a and b illustrates that the concentrations of metals, S and P in Smethwick sediment are generally an order of magnitude greater than in the Snarestone sediment for all metals except Ca.

Table 4.3 a and b: Average Concentrations of each 24cm long seasonal core, showing relative standard deviation as a measure of sample variability with depth

a)

Smethick	Spring		Summer		Autumn		Winter	
	Average ppm	RSD	Average ppm	RSD	Average ppm	RSD	Average ppm	RSD
Al	15784	**3.2%**	16209	**6.2%**	16505	**4.8%**	18072	**24.4%**
Ca	34402	**11.6%**	32113	**3.3%**	35466	**8.3%**	29600	**17.9%**
Cd	35	**9.5%**	37	**8.0%**	35	**11.3%**	49	**23.0%**
Cr	422	**4.7%**	436	**6.9%**	444	**5.6%**	514	**7.5%**
Cu	736	**6.1%**	714	**5.9%**	688	**5.2%**	906	**19.2%**
Fe	68971	**3.0%**	72499	**3.5%**	72542	**3.4%**	103208	**20.5%**
Mn	2066	**4.2%**	2106	**4.3%**	2207	**5.3%**	2811	**5.7%**
Pb	1578	**8.2%**	1508	**8.6%**	1462	**11.2%**	1861	**13.3%**
Zn	9218	**8.1%**	10036	**7.6%**	9939	**10.4%**	13336	**17.2%**
S	11514	**6.8%**	10810	**10.6%**	9922	**9.0%**	10001	**10.6%**
P	19477	**4.8%**	20124	**7.1%**	20853	**6.2%**	23349	**13.9%**

b)

Snarestone	Spring		Summer		Autumn		Winter	
	Average ppm	RSD	Average ppm	RSD	Average ppm	RSD	Average ppm	RSD
Al	8735	**34.6%**	11263	**20.4%**	10535	**22.9%**	6964	**35.9%**
Ca	24758	**29.0%**	27647	**39.5%**	30991	**25.1%**	21866	**26.0%**
Cr	15.6	**29.8%**	20	**20.9%**	18	**23.6%**	13	**36.2%**
Cu	26	**23.8%**	35	**17.8%**	32	**22.9%**	29	**37.8%**
Fe	18610	**18.3%**	23180	**19.6%**	20990	**18.3%**	16472	**26.8%**
Mn	420	**20.3%**	491	**12.4%**	475	**18.5%**	378	**18.2%**
Zn	186	**50.7%**	281	**23.9%**	227	**41.0%**	150	**64.3%**
S	4499	**41.5%**	8586	**29.8%**	6693	**37.7%**	3426	**53.0%**
P	399	**31.9%**	576	**32.1%**	521	**27.1%**	346	**57.1%**

In the absence of any appropriate UK sediment guidelines, the contamination of the two canal sediments is assessed in relation to criteria produced by the Dutch National Institute for Public Health and Environmental Protection (Table 4.4) (www.minvrom.nl, accessed 9/11/00). Comparison of the Cu, Cr, Pb, Cd and Zn concentrations in Smethwick sediment (4.3a) with the Dutch values in Table 4.4 reveals that they are greatly in excess of the 'intervention' limit for which remediation is necessary. At Snarestone (Table 4.3b) the values are close to or below the 'target' level for all metals except Zn, and elevated Zn concentrations have been noted at the Snarestone site (British Waterways, personal communication).

Table 4.4: Dutch Sediment Guideline List

Contaminant	**Soil Sediment** (ppm dry weight)	
Metals	Target	Intervention
Cadmium	0.8	12
Chromium	100	380
Copper	36	190
Lead	85	530
Zinc	140	720

4.4.1.1 Carbon

Smethwick

Smethwick sediment has a high organic carbon content, which reflects the high input of sewage to the canal from combined sewer overflows (NRA, 1996). The elevated concentrations of phosphorous in the sediment from sewage may also be contributing to the organic loading by increasing the organic productivity of the canal, i.e. the process of eutrophication. The increased rate at which organic matter is supplied to the sediment as a result of anthropogenic activities, must exceed the diffusive flux of the organic matter oxidants, oxygen and to a lesser extent sulphate into the porewaters. Therefore the sediment rapidly passes through shallow oxic and sulphate reduction zones, which are close to the sediment interface, to the methanogenesis zone where organic matter degradation is least intensive. It is interesting however; that the organic content of the sediment does not show any decrease with depth but remains at a constant value throughout the profile. This is noteworthy because the abundance of secondary ferrous minerals, particularly vivianite, is strong evidence that significant quantities of organic matter have been degraded, which should cause some decrease in its content with depth. The absence of a decrease suggests that the input of organic to the canal has declined in recent years.

Snarestone

The lower organic carbon content of Snarestone sediment reflects the absence of inputs of organic matter to the canal from outside sources such as sewage. The steady decline in organic matter content in the uppermost few centimetres of the sediment suggests that it is being efficiently broken down by respiration and sulphate reduction. This implies that the rate of organic matter accumulation does not outstrip the diffusive supply of these oxidants in this sediment, which is consistent with the observation of a brown oxic layer at the sediment surface (Figure 4.1b). Organic matter remaining in the sediment at depth is probably of a refractory nature e.g. coal particles.

4.4.1.2. Aluminum

Aluminium represents the clay content of the sediments, and can be viewed as part of the bulk sediment matrix.

Smethwick

Aluminium is present in the sediment in abundance reflecting the importance of clay in the bulk sediment matrix. The absence of any systematic variation in Al concentrations in the spring, summer and autumn sediment profiles and XRF samples suggests that it is largely unaffected by anthropogenic inputs and diagenetic effects. However in the winter profile a decline in Al concentration at 21cm coincides with a peak in the heavy metals Cu, Zn, Cd, Pb and Cr, which are indicative of anthropogenic inputs. It would appear a pollution event specific to the exact location of sampling has displaced the bulk sediment constituents, an upward displacement of clay in this sample could explain the peak in Al concentration at 16cm.

Snarestone

In Snarestone sediment the concentration of Al declines with depth in each seasonal sample and in the XRF results, which provides strong evidence that the proportion of clay in the sediment decreases over the depth profile. Therefore the results of grain size analysis that show an increase in the proportion of clay sized particles with depth in this sediment do not reflect an actual increase in clay content and are presumably the result of the analytical artefact discussed in section 3.3.1. This decrease in clay content with depth suggests that either the source of sediment to the canal has changed through time, or, that continual sediment disturbance by boat traffic is having a sorting effect on the sediment that results in the accumulation of fine grained particles at the sediment surface.

4.4.1.3. Phosphorus

The main source of phosphorous to natural sediments is organic matter; elevated phosphorous concentrations are associated with anthropogenic activities and this is reflected in elevated P concentrations in the Smethwick sediment relative to the Snarestone sediment. The mineralisation of organic matter results in the precipitation of authigenic phosphate minerals, most notably vivianite which constitutes ~1% of the Smethwick sediment. The sorption of P to amorphous ferric oxides is also an important P sink in aerated sediments (Emerson and Widmer, 1978; Nriagu and Dell, 1974).

Smethwick

The Smethwick sediment has high phosphorous concentrations throughout the sediment profile in each season and in the XRF samples. The high P concentrations reflect the elevated concentrations of organic carbon in the sediment and the abundance of authigenic vivianite. Phosphorous is a contaminant commonly associated with sewage and this stretch of canal has previously suffered from combined sewage overflows, most recently in 1996 (NRA, 1996). Some of the P may also be of industrial origin as the large chemical company Albright and Wilson have works located close to the Smethwick sampling site (Black Country Development Corporation, personal communication).

Elevated P concentrations at the surface of the summer sample probably reflect an increase in organic productivity, this is consistent with field observations that canal water was green at the time of sampling because of its high algal content. Fluctuations in the concentration of P over the winter and to a lesser extent, autumn depth profiles are probably caused by localised concentrations of organic matter or vivianite. The large peak in concentration at 16cm in the winter profile may represent a sewage pollution event. A sharp decrease in P concentration at 21cm corresponds to a peak in heavy metal concentration, which suggests that this sediment sample has been affected by a localised inorganic pollution event.

Snarestone

The decline in P concentration with depth implies that its major sinks are associated with the oxic surface sediments i.e. ferric oxides and organic matter. The absence of significant concentrations of P at depth suggests that it does not have a reduced authigenic phase in Snarestone sediment, which is consistent with petrographic observations. Its presence at low concentration is probably due to small quantities of residual organic matter and more resistant crystalline Fe oxides. Elevated P concentrations at the surface of the summer sample probably reflect an increase in organic productivity at this time, this is consistent with field observations that canal water was green at the time of sampling due to its high algal content.

4.4.1.4. Sulphur

Sulphur is present in the solid sediment as discreet metallic sulphides and mineralised organic matter. Detrital sources of S to the sediment include organic matter and S rich anthropogenic material such as smelting waste and building rubble. Authigenic sulphide formation results from the diffusion of sulphate from the overlying waters to the sediment and its subsequent reduction and precipitation as sulphides.

Smethwick

The concentration of S in Smethwick sediment is ~2 times that observed in Snarestone sediment. This implies that anthropogenic activities have increased the S content of the sediment, through the incorporation of S rich detrital anthropogenic material into the sediment and acid deposition from air pollution (Urban, 1994). Acid deposition would result in an increase in the concentration of dissolved sulphate in the overlying waters, in turn causing an increase in its diffusion to the sediment porewaters. However the retention of sulphate in the solid sediment is dependent upon its reduction and subsequent precipitation as a metallic sulphide (Urban, 1994). Urban, (1994) shows that an increase in the concentration of dissolved sulphate alone will not facilitate the formation of sulphides, but that concurrent increases in the concentration of organic matter and Fe do appear to increase S accumulation rates in sediments. CryoSEM analysis of the Smethwick sediment revealed that authigenic sulphides of Fe, Cu and Zn were common, which is evidence that elevated concentrations of organic matter, Fe and other chalcophile metals are important in retaining the high S concentration of this sediment (Table 4.3 a and Figure 4.3a).

The concentration of S varies markedly between seasonal samples and such large differences must be the result of sample to sample variation rather than seasonal changes within the canal. Sediment movement resulting from boat traffic disturbance would appear to be the most likely reason for a contrast between the profiles of spring and summer, when traffic is greater, and those of the autumn and winter, when traffic is minimal.

The most obvious change in S concentration is the sharp increase that occurs in the uppermost 5cm of the spring and summer samples. At this time two factors may result in lower surface concentrations of S:

1. The increased productivity of the canal and subsequent incorporation of fresh organic matter to the sediment might be causing the dilution of the surface sediment, which is consistent with an observed increase in surface P concentration at this time.
2. The mixing of the oxygenated canal waters and sediments as a result of the high levels of boat traffic may be oxidising the sulphides in the sediment, resulting in the loss of S as sulphate to solution.

It is not possible to establish further which of these factors is having the most marked effect upon the sediment at this time.

Snarestone

The profiles of S in Snarestone sediment are very different in each season, probably as a reflection of the heterogeneous nature of the sediment. In each season, however, a clear parallel can be seen between the S profiles and those of Fe, and the decrease with depth observed in spring, autumn and winter profiles also reflects the observed decline in organic matter. A study by (Carnigan and Tessier, 1988) of organic rich lake sediments also found a strong correlation between burdens of Fe and S, and suggested that Fe plays an important role in fixing S in the sediment. The common behaviour of Fe and S is consistent with petrographic observations that pyrite is the principal sink of both Fe and sulphide in Snarestone sediment (Section 3.3.3.1). However, in the surface oxygenated sediments organic matter is also likely to account for a significant proportion of the S concentration, this will be considered further in (Section 4.4.2.3.).

4.4.1.5. Calcium

Calcium is present in both rural and urban sediment at high concentration and to a great extent this can be accounted for by the common occurrence of calcite in both sediments.

Smethwick

Calcium is a bulk constituent of Smethwick sediment and this is reflected in the high concentrations observed in both the XRD and aqua regia results. Petrographic analysis has revealed calcite to be the principal authigenic host for Ca in Smethwick sediment. However slag and fly ash also contain high concentrations of Ca and their presence might explain the slightly elevated Ca concentration in this sediment relative to Snarestone sediment. In both the XRF and aqua regia results the concentration of Ca is greatest at the surface. Opposite the sampling site there was a recently demolished industrial building and this will have generated Ca rich dust that might have accumulated in the sediment surface producing this trend. However the absence of this trend in the summer suggests it could be the result of sample to sample variation.

Snarestone

In Snarestone sediment the Ca concentration is high throughout the depth profile reflecting the common occurrence of calcite. Large peaks in the Ca near the sediment surface might be the result of incorporation into the sediment of loose limestone chippings, which appear to have been recently used to cover the towpath at the locality. These chippings were occasionally observed in the surface sediment during crushing.

4.4.1.6. Chromium

Chromium was not observed in the petrological investigation of the sediment, except for one occurrence in the Smethwick sediment as a metallic detrital particle. Previous investigations of Cr in natural sediments have found it to be present in solution in two forms: the oxidised Cr (VI) which is an unreactive anion and the reduced Cr(III) which is a strongly hydrolysing cation with a tendency to bind to the surfaces of oxides and organic material (Johnson et al., 1992; Khun et al., 1994). It is therefore likely that Cr is principally held in rural and urban canal sediment as Cr(III) in association with organic matter and Fe oxides.

Smethwick

The principal trend observed in each seasonal sample, except the summer, is a gradual increase in Cr concentration with depth. It is probable that the decrease in the Cr concentration of the surface sediments has been caused by a change in the inputs to the canal in recent years, following the decline of heavy industry in the area and the implementation of new more stringent environmental regulations.

In the summer sample, the concentration of Cr is low at the sediment surface and it is probable that this is due to mixing with organic matter, accumulating in the sediment during this period of increased productivity. It is very unlikely that this decline in Cr concentration is contributed to by oxidation of Cr(III) resulting from the high levels of sediment disturbance by boat traffic at this time, because the oxidation has slow kinetics (0.4/yr) when compared to the reduction of Cr(VI) which occurs on a time scale of minutes to hours (Schroeder and Lee, 1975). However an investigation of the effects of sediment disturbance upon metal retention in Venice Canal sediments did find that the concentration of Cr in sediment that had been suspended was lower than that in undisturbed core samples by up to 24% (Argese et al., 1997). Therefore sediment disturbance may be a contributory factor in the low surface Cr concentration observed at the surface.

Snarestone

Chromium is present in Snarestone sediment at trace concentrations reflecting the limited anthropogenic influence upon this sediment. An observed decrease in its concentration with depth can best be accounted for by the reduction of Fe oxides close to the sediment surface and the decline organic matter with depth, as these are the principal sink of Cr(III).

4.4.1.7. Manganese

Manganese was not observed as a discrete phase in the petrological investigations of either rural or urban canal sediments. It is a natural component of sediments; its oxides act as an electron donor in the oxidation of organic matter in sediment following the exhaustion of oxygen. Manganese is used in industry as an alloy in steel and bronze, and the inputs of industrial material to the canal are likely to have resulted in the elevated concentrations of Mn in Smethwick sediment relative to Snarestone.

Smethwick

The concentration of Mn at Smethwick is relatively constant over the depth profile in each seasonal sample except winter. This suggests that anthropogenic influences or diagenetic effects have not affected the overall concentration of Mn. The seasonal profiles closely mirror those of Fe, which implies that Mn may enter the canal from the same sources as Fe and that following diagenesis its principal sink is in solid solution with secondary Fe minerals.

Snarestone

Manganese is present in Snarestone sediment at trace levels; its concentration profiles are similar to those of Fe suggesting that they have entered the sediment from a common source. Elevated concentrations at the sediment surface might represent the presence of Mn-oxides and the greater capacity of this organic and clay rich oxic layer to retain Mn. Although, the observed change in bulk sediment chemistry over the depth profile might reflect a change in the sources of material to the canal, that has resulted in an increase in the Mn content of the surface sediment.

4.4.1.8. Iron

Iron is a bulk constituent of Snarestone and Smethwick sediments; the reduction of Fe oxides and subsequent precipitation of secondary Fe minerals play an important role in the diagenesis of organic matter.

Smethwick

The concentration of Fe is high in the Smethwick sediment and does not change significantly with depth or between seasons. This suggests that anthropogenic influences or diagenetic transformations are masked by the high total concentrations of Fe. The concentration of Fe in Smethwick sediment is ~3 times that in Snarestone sediment, presumably as a result of the canals proximity to former heavy industry in Smethwick, which included numerous iron works. The peak in Fe concentration at 22cm in the sediment appears to represent a pollution event, as it is coincident with peaks in the contaminant metals Cu, Zn, Cd and Pb.

Snarestone

In the Snarestone sediment the concentration of Fe is highest in the surface sediment and decreases with depth. Elevated concentrations at the sediment surface presumably reflect the presence of Fe oxides in the surface oxic layer. However the observed change in bulk sediment chemistry over the depth profile suggests that inputs to the canal may have changed in recent years, resulting in an increase in the Fe content of the surface sediment.

4.4.1.9. Copper, Lead, Zinc and Cadmium

Elevated concentrations of Cu, Pb, Zn and Cd are typically associated with anthropogenic pollution. In both Smethwick and Snarestone sediments these metals display broadly similar depth dependant and seasonal changes in concentration and due to their chemical similarities they are discussed together here.

Smethwick

The heavy metals Cu, Pb, Zn and Cd are present in Smethwick sediment at elevated concentrations. They all display broadly similar seasonal and depth trends in Smethwick sediment, suggesting they enter the sediment from a common source. These heavy metals are chalcophile and petrographic observations have confirmed that Zn, Cu and Pb are present in the sediment as sulphide, Cd was not observed but is commonly associated with Zn sulphides at trace levels. Zn and Cu would normally be considered trace metals but Zn, in particular, which is present at concentrations of ~10,000ppm can no longer be considered as such for that reason. This is in marked contrast to the uncontaminated Snarestone sediment in which Cu and Zn are present at trace levels and Cd and Pb were beneath the ICP-AES detection limit.

Elevated concentrations of these metals are synonymous with anthropogenic contamination and pollution from the seven former metal works found in close proximity to the Smethwick sampling site has probably contributed to their high concentration in this sediment (section 1.4.1.3.). The decrease in heavy metal concentration in the surface sediments has perhaps been caused by a change in the inputs to the canal in recent years following the decline of heavy industry in the area and the application of new, more stringent environmental regulations. Such a decline in concentration is consistent with studies of heavy metal concentrations in the sediments of lake and rivers (Azcue et al., 1996; Song and Muller, 1995). However the variation in this trend between seasonal samples reveals that it is not constant, and has apparently been masked by the continual boat traffic disturbance of sediment.

In the summer profiles the concentration of these metals at the surface is low, sharply increasing to more typical values in the uppermost 5cm of each profile. This reduction in the concentration of predominantly sulphide bound metals at the sediment surface could have resulted from the increased input of organic matter at this time, which is consistent with an observed increase in concentration of P in the surface sediments. A study of a canal in Venice investigated the affect of sediment disturbance upon the retention of heavy metals by comparing the chemistry of sediment taken from cores and sediment collected in traps following its suspension (Argese et al., 1997). Within a canal of comparable depth to those sampled here (150cm), that is subject to tidal and boat traffic disturbance, they found significant losses (upto 50%) of Cu, Pb, Cd and Zn from the sediment caught in traps when compared to that sampled in the cores. They suggest that the amorphous sulphide phases in which the metals bound are being oxidised while in suspension with the oxygenated water column, resulting in their release to solution. It is possible that a similar process is occurring at Smethwick during periods of maximum boat traffic disturbance and contributing to the surface fall in concentration. However, the chemistry of the freshwater system at Smethwick will vary from that of the marine influenced Venice canal system.

Snarestone

In Snarestone sediment Cu and Zn are present at trace concentrations and both Cd and Pb are below the detection limit of the ICP-AES. A close similarity in the profiles of Cu and Zn probably reflects a common source for these metals to the sediment. The concentration profiles for these metals are similar to those of Fe, Al and organic carbon with a sharp decrease in concentration from the surface in each season. This suggests that Fe-oxides and organic matter are important as sorption sites for these metals (Kersten and Forstner, 1995) and might also reflect the importance of clay and biofilm as nucleation sites for sulphides.

It is important to note that the banks at the Snarestone sight are reinforced Zn galvanised panels and it is possible that these may also be responsible for the recent increase in the concentration of Zn at the sediment surface.

4.4.2. Sequential extraction

4.4.2.1. Aluminium

The speciation of Al is broadly similar in both Snarestone and Smethwick sediment. Aluminium's principal sink in the sediments is clay minerals although some Al will also be present as oxides. It is unlikely that this sequential extraction technique, which is designed for determining the speciation of trace metals in soils and sediments, will derive useful Al speciation information because it is a bulk sediment constituent. However, it is important to assess its operationally defined speciation in order to ensure that there are no artefacts associated with it.

In both sediments low concentrations of Al in the carbonate fraction indicate that the reagent is not attacking clays or Al oxides. The proportion of Al extracted in the oxide fraction can be accounted for in part by the dissolution of these Al oxides. The dissolution of clay minerals will probably also contribute to the Al concentration in this fraction because the reagent used in the oxide fraction will also attack some clay minerals (Pickering, 1986). The dissolution of clay minerals probably accounts for most of the Al extracted in the organic and sulphide fraction, although the reagent will not completely dissolve clay, as the observation of clay minerals in the residue from this fraction testifies.

The total concentration of Al extracted in all three fractions from the Smethwick sediment is about twice that extracted from the Snarestone sediment. In addition, the total amount of Al extracted from the Smethwick sediment is 50% that of the total aqua regia concentration, whereas in the Snarestone sediment it is only ~20% of the total aqua regia concentration. This suggests that Al is present in the Smethwick sediment in relatively more labile forms, possibly as amorphous oxides or a component of detrital anthropogenic material such as slag.

In the Snarestone sediment there is no systematic variation in the speciation of Al with depth, presumably because clay is the main sink for Al in the sediment and it is not subject to depth dependant chemical changes. In the Smethwick sediment, the proportion of Al extracted in the oxide fraction tends to decrease with depth. The reagent used to extract the oxide fraction dissolves amorphous Al-oxide and their dissolution might explain the high proportion of Al extracted in the oxide fraction from both sediments. Aluminium oxides remain stable under reducing conditions, and are therefore unlikely to be affected by depth dependant chemical changes, as the sediment becomes more reducing. The observed decrease with depth, in concentration of Al extracted from the oxide fraction at Smethwick, is thus likely to be the result of changes in inputs to the sediment. Possibly as a result of the incorporation of anthropogenic material, from a recent demolition site opposite the sampling site, into the surface sediments.

4.4.2.2. Phosphorous

The speciation of P is markedly different in Smethwick and Snarestone sediments. Petrographic observations have shown that authigenic vivianite is a major component of Smethwick sediment, while no secondary P minerals were observed in Snarestone sediment and this is likely to produce the observed differences in their speciations. Other sinks for P in sediments include sorption to Fe oxides and organic matter. This extraction technique has separate fractions for the extraction of metals associated with Fe oxides and organic matter and these could potentially separate P species. Vivianite is not considered to be a significant sediment constituent and is therefore not included in the design or interpretation scheme for this extraction.

In the Snarestone sediment the majority of P is extracted in the sulphide and organic fraction, which suggests that organic matter is the major sink for P in the sediment. In the Smethwick sediment the majority of P is extracted in the carbonate and oxide fractions, which indicates that vivianite is dissolving in the acidic reagents used for their extraction. Petrographic evidence revealed vivianite was removed from the sediment completely by the oxide fraction, but could not confirm its partial dissolution in the carbonate fraction (Figure

4.15c). However the relatively high proportion of Fe also released in both of these fractions would suggest that the dissolution of vivianite could account for the high concentrations of P. The absence of significant proportions of P in the oxide and carbonate fractions in the Snarestone sediment confirms petrographic observations that P does not have a significant reduced sink in this sediment.

The moderate P concentrations observed in the Smethwick leachates from the sulphide and organic fraction probably result from the dissolution of organic matter and primary phosphate minerals that are less soluble than vivianite. The concentration of P released in the sulphide and organic fraction is higher in the Smethwick leachates than in those from Snarestone. This reflects the elevated concentration of organic matter and, possibly, secondary phosphates produced during the previous extraction stage, when high concentrations of P were released by the dissolution of vivianite.

The P speciation at Smethwick does not vary significantly with depth, reflecting the uniform occurrence of vivianite and organic matter throughout the sediment. At Snarestone small amounts of P are extracted in the carbonate fraction beneath 5cm in the sediment and this corresponds to the depth at which the transition from oxic to anoxic conditions takes place. This implies that P, released to solution upon the reduction of amorphous oxides and degradation of organic matter in the surface sediment, might be precipitating to form a secondary P mineral such as apatite that is dissolving in this fraction. However, petrographic observations suggest that secondary P minerals are absent from Snarestone sediment. The change in speciation may therefore reflect a change in bulk sediment chemistry observed at this depth profile in Snarestone sediment.

The BCR method is not designed for determining P speciation and it therefore does not produce easily interpretable or especially useful results, particularly for Smethwick sediment. The speciation of P could be better determined by a sequential extraction scheme specifically for determining P speciation, such as that of Williams et al., (1976) designed for application to lake sediment. This technique separates P bound as organic P, non-apatite inorganic P and apatite P. The non-apatite organic P fraction would extract vivianite from the sediment, although P extracted in this fraction would also include orthophosphate adsorbed on Fe and Al oxides, the Al-P mineral variscite and Ca-P minerals other than apatite. As with any sequential chemical extraction the speciation determined will be operationally defined and subject to same conceptual and practical problems associated with all trace metal techniques (section 2.3.4).

Berner and Rao (1994) used the selective extraction technique of Ruttenberg (1992), designed for use on marine sediments, to determine P speciation in the Amazon River estuary. In order to overcome the inherent uncertainties of selective extraction techniques they developed an electron-probe technique for the micro-analysis of P and its possible association with Fe, Al, Mn, Ca and Ti in order to determine P speciation through the statistical analysis of microprobe maps (Rao and Berner, 1993; Rao and Berner, 1995). This technique, at present, uses carbon coated samples which preclude the determination of organic associated P. To date, this technique has largely been used as a means of validating selective extraction techniques and revealing correlative relationships among associated elements. The method has not been applied to freshwater sediments.

In order to apply either of these techniques successfully to canal sediment an investigation of their application and interpretation would have to be undertaken.

4.4.2.3. Sulphur

In both Smethwick and Snarestone sediments the majority of S is extracted in the sulphide and organic fraction, confirming the importance of authigenic sulphide as its sedimentary sink. The complete dissolution of sulphides in this fraction is supported by the CryoSEM observations that no sulphides were found in the residues. Organically bound S may also be contributing to the high

S concentration in this fraction, particularly in the urban sediment where sulphitized organic matter was commonly observed. However, when observed in the sediment, organically bound S was always closely associated with chalcophile metals and this blurs the boundaries between these species and makes their differentiation difficult even by direct observation.

Some S was released in the carbonate fraction from both sediments; this will have been contributed from residual pore water and possibly the dissolution of S rich biofilms and amorphous sulphides.

In Snarestone sediment significant quantities of S are extracted from the oxide fraction in the uppermost 3cm of the core. Iron monosulphides will dissolve in the acidic reagent used in this fraction (Parkman et al., 1996) and the significant S concentration could result from the dissolution of film coated sulphides. The low concentrations of S in the oxide fraction of Smethwick sediment is surprising as monosulphides were commonly observed in the petrographic investigation of this sediment. One possible explanation for this is the release of S, by the acidic reagent, as H_2S gas, which could not be captured by analysis of the solution (Parkman et al., 1996). It is also possible that the dissolution of more soluble phases such as vivianite is buffering the pH of the solutions and prohibiting the dissolution of monosulphides.

4.4.2.4. Calcium

As expected, most of the Ca, which was principally observed as calcite in the raw sediment from both Snarestone and Smethwick, is extracted in the carbonate fraction. Calcium adsorbed to surface sites may also account for some of the Ca extracted in the carbonate fraction, thermodynamic modelling of trace metal binding in sediments by Wallmann, *et al*, (1993) showed surface sites with strong affinities to be almost uniformly filled with Ca. Dissolved Ca present in the residual porewater of the wet sediment may also contribute to the high concentration in this fraction.

The procedure used for the extraction failed to completely remove calcite from the sediment in the carbonate fraction (Figure 4.15d). This is perhaps due to the rapid exhaustion of the acidic reagent used in the extraction by the high quantities of calcite in both sediments and vivianite in urban sediment. Calcite remaining after the carbonate fraction probably accounts for the Ca subsequently extracted in the oxide fraction. The higher Ca concentrations in the sulphide and organic fraction of Smethwick sediment is perhaps due to the reagents partially dissolving some detrital particles such as Ca-rich slag.

4.4.2.5. Chromium

The speciation of Cr could only be determined in the contaminated Smethwick sediment. It is likely that Cr is present in this anaerobic urban sediment in its hydrolysed reduced form Cr(III) bound to particles and organic matter. Speciation data for Cr in this sediment appear to confirm this. A small but significant proportion of Cr is released in the oxide fraction, and this is greatest in the uppermost 8cm (between 10 and 20%), suggesting that Cr is associated with some residual Fe-oxides in the sediment. The remainder is extracted in the sulphide and organic matter fraction, the abundance of organic matter in this sediment suggests that it may act as the principal sink for Cr(III). The dissolution of resistant iron oxides observed in the residues of the carbonate and oxide fractions by CryoSEM could also be contributing to the high concentration of Cr in this fraction.

4.4.2.6. Manganese

The speciation of Mn is different in rural and urban canal sediments. In Smethwick sediment the Mn speciation closely resembles that of Fe suggesting that Mn is principally bound in solid solution with vivianite. However in Snarestone sediment, Mn speciation does not resemble that of Fe but that of Ca, indicating that Mn is largely bound in this sediment in solid solution with calcite. In both sediments about 10% of Mn is extracted in the sulphide and organic fraction; Mn does not occur as a sulphide and therefore Mn, in this fraction, must be associated with organic matter or resistant oxides, not extracted in the oxide fraction. In the Smethwick sediment Mn extracted in this fraction may also be augmented by the dissolution of detrital anthropogenic particles such as metallic Fe.

4.4.2.7. Iron

The speciation of Fe is different in rural and urban sediment, reflecting petrographic observations that the principal sink for Fe in the Smethwick sediment is vivianite while in Snarestone sediment it is pyrite.

At Smethwick the largest proportion of Fe is extracted in the carbonate fraction but Fe carbonate was not observed in this sediment. It is therefore most likely that the high Fe concentrations in the carbonate leachate result from the partial dissolution of vivianite, which would be soluble at the pH of the extraction reagent. The relatively high proportion of P also released in this fraction supports this possibility. A significant proportion of Fe is again extracted in the oxide fraction, despite the relative scarcity of Fe oxides in the sediment. Some vivianite was still present in the carbonate residue but was absent from the oxide residue. This observation, coupled with the significant proportion of P also extracted in the oxide fraction, suggests that the majority of Fe in this fraction results from the dissolution of vivianite. Iron extracted in the organic and sulphide fraction is therefore likely to be a reasonable measure of Fe present in the sediment as sulphide. This will include Fe associated with mineralised organic matter. When observed in the sediment, organically bound Fe was always closely associated with sulphide, which blurs the boundaries between these species and makes their differentiation difficult even by direct observation.

In Snarestone sediment a significant proportion of Fe is extracted in the carbonate fraction. Iron carbonate was not observed in this sediment and nor was vivianite, however Fe-hydroxides and amorphous iron sulphides are also dissolved by the reagent used in this extraction (Parkman et al., 1996) so could account for the high Fe concentration in this fraction. The dissolution of Fe monosulphides in the form of FeS-mineralised biofilm is not supported by S speciation data, in which only relatively small amounts of S are extracted in the carbonate fraction. This suggests the dissolution of Fe hydroxides is the most feasible explanation for the high concentration of Fe in the carbonate leachates. This finding is also consistent with the decline in the proportion of Fe extracted with depth over the uppermost 12cm of the profile. The amount of Fe hydroxides in the sediment will decline with depth, as the sediment becomes more reducing.

A significant proportion of Fe in Snarestone sediment is also extracted in the oxide fraction and this proportion remains roughly equal over the entire profile. The dissolution of more resistant Fe oxyhydroxides and Fe monosulphides will probably account for most of the Fe in this fraction. Although significant, concentrations of S are only released in the uppermost 3cm of the profile, which suggests that the contribution of Fe from monosulphides declines with depth and is perhaps countered by an increase in the amount of more resistant oxides.

Fe released from Snarestone sediment in the sulphide and organic fraction is probably a good representation of Fe that is held as pyrite as the extraction procedure is known to dissolve it completely (Pickering, 1986). Organically bound Fe will also contribute to the concentration of Fe in this fraction, however, with the exception of mineralised biofilms that might be regarded as a sulphide, Fe rich organic matter was not commonly observed in the sediment.

In Smethwick sediment the Fe speciation does not vary significantly with depth, reflecting the uniform abundance of vivianite and Fe sulphides. At Snarestone the Fe speciation shows a transition over the uppermost 12cm of the profile from the carbonate fraction which appears to represent Fe present as oxides in the sediment, to the sulphide and organic fraction representing Fe present in the sediment as pyrite. This is presumably the result of the transition to anoxia, which occurs gradually over the uppermost 10cm of this sediment.

Beneath 12cm in the Snarestone sediment the total concentration of Fe extracted begins to fall, largely due to a decline in the amount of Fe extracted in the sulphide and organic fraction. This perhaps marks a change in the sediment composition, because it is coincident with a change in grain size and a fall in the total concentration of other reactive elements, most notably S and organic carbon.

4.4.2.8. Copper, Lead, Zinc and Cadmium

The speciation of Cu, Pb and Cd could not be determined in Snarestone sediment because the concentration of these metals in each fraction was below the detection limit of the ICP-AES. In Smethwick sediment Cu, Pb and Cd were only detectable in the sulphide and organic fraction, confirming their presence as sulphides and their association with mineralised organic matter in the sediment. The dissolution of metal rich anthropogenic particles such as brass may also contribute to the high concentrations in this fraction. Small amounts of Pb were extracted in the carbonate fraction in the uppermost 8cm of the sediment and this could represent Pb sorbed to Fe oxides.

The speciation of Zn was determined in both Snarestone and Smethwick sediment; it shows marked contrast from the speciation of the other chalocphile metals and between the two sediments. In Snarestone sediment the largest proportion of Zn is extracted in the oxide fraction and this proportion decreases with depth. This appears to suggest that Fe oxides are playing an important role in fixing Zn in the sediment particularly within the surface oxidising layer, although Zn sulphides will also dissolve in the reagent used in this fraction (Wallmann et al., 1993). In a study of the affects of aeration on the sediment of the Manchester Ship Canal, Boult and Rebbeck, (1999) found that the total concentration of trace metals, and in particular Zn, was greatly elevated in the uppermost 4-7cm of the core of aerated sediment, but no similar trend was detected in the sediment from the non-aerated canal. They suggest that this surface increase has resulted from the upward migration of Zn and its subsequent co-precipitation and/or sorption to $Fe(OH)_3$ at the oxic interface in the aerated sediment.

In Smethwick sediment it is notable that a significant quantity of Zn is extracted in the oxide fraction despite the limited occurrence of oxides in this reducing sediment. This probably reflects the greater solubility of Zn sulphides, known to dissolve in acidified reagents ≤pH5 (Wallmann *et al.,* 1993). Further evidence of this is the presence of low concentrations of S and a distinct smell of hydrogen sulphide from the reaction vessel. The relatively constant concentration of Zn extracted from this fraction suggests that buffering reaction might be taking place between the reagent and the Zn sulphides.

The differences in the speciation Cu and Zn in Smethwick sediment reflect observed differences in the form and composition of their sulphides. Copper was observed in the sediment as a sulphide with chalcopyrite stoichiometry while Zn is present as more amorphous Fe-rich sulphides which appear to be acid soluble. In a study of estuarine sediment by Parkman *et al.,* (1996) similar differences in the speciation and form of Cu and Zn were observed (section 3.4).

4.5. Discussion

4.5.1. Changes in bulk sediment chemistry

The two sites surveyed in this investigation are essentially similar shallow freshwater environments cut off from the natural hydrological networks in their localities. The only distinct contrast between them is that the canal at Smethwick has, throughout its history, received large quantities of anthropogenic waste, thus differences in the sediment's chemistry can largely be attributed to this influence. The principal effects of anthropogenic inputs to the urban sediment are elevated concentrations of metals, S, P and organic matter and the dilution of natural bulk sediment constituents, most notably SiO_2.

At Smethwick, periodic combined sewer overflows have supplied domestic waste, industrial effluent and road runoff to the canal. The canal has also received direct inputs of effluent from industries located along the bank. As a result, concentrations of Fe, Mn, Cu, Cd, Zn, Cr, Pb, P, S and organic matter are elevated relative to both Snarestone sediment and Dutch sediment 'action' limits (for which clean up is required). In Smethwick sediment the bulk sediment constituents SiO_2, Al, Fe, P and organic matter show very little variation over the 24cm depth profile of the sediment or between seasons. This reflects the homogenous nature of this sediment and the rapid transition to anoxia that occurs at, or immediately beneath, the sediment water interface which prevents significant changes in the chemistry over the depth profile and the efficient break down of organic matter. However the concentrations of contaminant metals Cu, Zn, Pb and Cd and S in Smethwick sediment appear to be declining at the surface. It is not clear if this is due to a change in the inputs to the canal in recent years following the decline of heavy industry in the area and new, more stringent, environmental regulations; or chemical changes induced in the uppermost 10cm of the sediment through its disturbance by boat traffic.

In both rural and urban canal sediment, the passage of boat traffic results in the mixing of the sediment with the overlying oxygenated canal waters. At Snarestone the surface sediments were observed to be oxic and this disturbance does not appear to affect the chemistry, although it could be important in maintaining the oxic status of the surface sediment. At Smethwick, the sediment becomes anoxic at the sediment water interface and boat traffic disturbance appears to affect the concentration profiles of metals held as sulphides, which might be oxidised during suspension in the oxygenated canal waters. As well as altering the chemistry of the surface sediment disturbance will be shifting quantities of the sediment around the canal because it has an unconsolidated and sloppy nature. Hence variations between samples may reflect changes resulting from the accumulation or scouring of the surface sediment. However, these changes are inferred to be the result of a seasonal increase in boat traffic in the spring and summer, and other factors, such as dilution of the sediment by fresh organic matter will also be affecting the sediment's chemistry at this time.

Snarestone sediment was heterogeneous and, with the exception of Ca, its constituents varied significantly over the depth profile. In this sediment the uppermost 10cm appear to have a different chemical composition than the lower section of the core. Most notably the concentrations of clay (Al) and organic matter are highest in the surface sediment and the concentration of SiO_2 increases with depth. This change in composition is partly a reflection of the gradual transition to anoxia in this sediment, which facilitates the decline the organic matter content with depth, by its efficient break down in the oxygenated surface sediments. This reflects the slower accumulation of organic matter in this sediment, from sources within the canal.

The surface sediment at Snarestone is enriched in trace metals, Fe and Mn. Other work on aerated canal sediment has found metal enrichment in the surface oxic layer in which Fe and Mn, liberated by the reduction of their oxides at depth, diffuse into the surface sediment and are re-precipitated as sulphides or oxides (Boult and Rebbeck, 1999). The speciation results for Fe and Zn in Snarestone sediment confirm that oxides and sulphides can account for elevated surface concentrations. The enrichment of Snarestone surface sediment is further augmented by a change in bulk chemistry over the sediment profile; because concentrations of clay and organic matter are elevated in the surface sediment and they are both important nucleation sites for sulphides and a sink for adsorbed metals.

In the Smethwick sediment, changes in Fe chemistry, which are important in understanding the diagenesis of sediments, are apparently masked by the high total concentration of Fe over the Smethwick sediment profile. Speciation results also are subject to uncertainties that preclude adequate interpretation. The chemistry of Fe and its role in diagenesis can therefore best be interpreted though porewater chemistry which is investigated in the following chapter.

4.5.2. The Value of Sequential Extractions

In general the petrological investigation of the application of sequential extractions to urban canal sediment revealed the importance of understanding the sediment mineralogy prior to and during a sequential extraction. Without the application of CryoSEM to directly investigate the sediment and extract residue petrology the relative contributions and nature of oxides, phosphates and sulphide would have been considerably more speculative, particularly where the volume percent of these minerals is close to or below the concentration detectable by X-ray diffraction. However, CryoSEM on its own cannot provide the quantitative results obtained by sequential extraction. It is instead a complimentary technique that can greatly improve the understanding of sequential extraction results.

In the carbonate fraction the extraction technique failed to completely remove calcite from the sediment. This could be due to the dissolution of high concentrations of calcite, and possibly also vivianite, in the Smethwick sediment that rapidly exhausted the acidic reagents used in the scheme. The ability of abundant authigenic or detrital minerals to exceed the pH buffering capacity of a solution is an important consideration and can potentially affect the quality of data obtained from a sequential extraction. To check for problems associated with buffering the pH of the solution could be measured before and after extraction. Tessier *et al.,* (1979) suggested longer leaching times and frequent adjustment of pH may be necessary, this would however increase the risk of oxidation if the extraction were being conducted under anaerobic conditions.

Rapin and Forstner (1983) investigated the reagent selectivity of the Tessier (1979) extraction scheme on a sample of vivianite collected from lake sediment. Their results showed that only a relatively small proportion of Fe from vivianite (<10%) was extracted in the carbonate fraction (1M sodium acetate pH 5), with the remaining Fe extracted in equal proportions in the oxide fraction (acidified 0.04M hydroxylamine hydrochloride, at 96°C) and residual fraction. The high value of Fe in the residual fraction cannot be verified by this study as it was not included in either extraction procedure applied to the sediment. However, the absence of vivianite from the residues of the oxide fractions and the high concentrations of Fe and P in the leachates is strong evidence that vivianite was removed from the canal mud in the carbonate and oxide fractions. It is difficult to make a comparison between these results and our own as the procedure they used differs slightly from that used in the BCR scheme investigated here, it is also important to note that their work was conducted in air and that oxidation may have affected the results.

Crystalline Fe oxides were not completely dissolved by the oxide fraction method, but the reagent used in the technique is reported to remove only Fe/Mn oxyhydroxides (Pickering, 1986). The BCR scheme has recently been modified, increasing the molarity of the hydroxyamine hydrocholride to 0.5M and decreasing the pH to 1.5 (Rauret, *et al.,* 1999) and it will be interesting to see if this facilitates the removal of crystalline oxides.

The results of the sulphide fraction extraction are encouraging as they confirm the importance of sulphide in the speciation of S and trace metals in the sediment. Copper and Zn are released in this fraction and from the petrographic observations it is known that they occur in the sediment as discrete Cu and Zn sulphides. The presence of discrete Cu and Zn sulphides has been established by others (Parkman, *et al.*, 1996) but more commonly Cu and Zn are considered to be bound as trace metals in Fe sulphides or in the case of Cu bound to organic matter. To decide on the relative proportions of metals bound to organic matter or sulphides requires some understanding of the likely stoichiometry of the sulphide minerals. Petrographic evidence can provide some of this information, but it also shows the wide range of co-existing Fe sulphide compositions such that it is extremely difficult to attribute Fe to any particular mineral. The high concentrations of Zn, Cu and S in the leachates extracted by this fraction coupled with petrographic evidence that sulphides persisted in the sediment throughout the carbonate and oxide fractions of the procedure suggests that the dissolution of these species in earlier fractions is not significant. Previous work has shown that sulphide dissolution in earlier fractions to be a problem (Rapin and Forstner, 1998; Lee and Kittrick, 1984; and Wallmann *et al.*, 1993). In the studies of Rapin and Forstner (1988) and Lee and Kittrick (1984) this could be due to oxidation of sulphides as the sediment was not handled anaerobically. The Wallmann *et al.* study was conducted anaerobically, but the sediment was estuarine and it would therefore be expected to have a different chemistry to the freshwater canal sediment and may thus have responded differently to the chemical changes imposed by the extraction.

The CryoSEM observations increase our awareness of non-typical components in the Smethwick sediment, particularly industrial wastes. For example detrital coal will significantly modify the perception of the organic content of the sediment and it is for example possible that some sulphides could be associated with coal. Native metals including Cu, Fe, Ag and alloys (mainly brass), although not abundant, were present as discrete particles. These are not expected in natural sediments and will contribute to the metal concentrations in many of the fractions. Some of the metals, particularly brass and Cu, were coated in sulphides and their dissolution would be inhibited until fraction 3. A wide range of slag particles, some glassy and others complex aggregates ,will add to the difficulties of interpretation and it would be worthwhile investigating the leaching behaviour of such particles in conjunction with sequential extraction studies of sediments containing industrial waste.

This study shows that direct CryoSEM petrographic investigation is a technique that, in conjunction with sequential extraction, provides a far better understanding of the sediment geochemistry and petrology. This is particularly important when dealing with sediments that have an unusual composition. Urban canal sediment is composed largely of anthropogenic and biogenic materials and therefore has a relatively small clastic component. Petrographic analysis by CryoSEM has revealed authigenic minerals to be the major sink for contaminants. The emphasis of sequential extractions applied to such sediments is therefore changed from the extraction of adsorbed substances and coatings, to the extraction of authigenic minerals. Unexpected high concentrations of minerals like vivianite present particular problems and care should taken to investigate the sediment mineralogy prior to extraction. The dissolution of high concentrations of vivianite can, for example, result in the precipitation of secondary phosphate minerals. Application of oxalic acid buffer to extract oxides in metal-rich sediments should be applied with caution and the risk of formation of insoluble oxalates should be considered. Care should also be exercised to check that the pH buffering capacity of the extraction reagents has not been exceeded as this may result in incomplete dissolution of certain components.

This investigation also highlights the danger of applying a sequential extraction as a means of comparing element speciation in two different sediments. Both rural and urban canal sediment respond differently to the chemical procedures of the extraction producing patterns of speciation that cannot be interpreted by a uniform scheme.

5. Porewater Chemistry

In this chapter the results of the porewater investigation of rural and urban canal sediment are presented. The analysis was conducted over a 25cm profile in samples from both sediment sites, in order to elucidate the chemical processes associated with the oxidation of organic matter and the fates of the nutrients, gases and metals released by these reactions during early sediment diagenesis. Furthermore, thermodynamic calculations of ion speciation and solubility products, calculated using porewater data, are used to assess the relative importance of different mineral equilibria in controlling porewater chemistry and ultimately sediment diagenesis. The interaction between the sediment and water are also investigated, to ascertain the sediment's role as both a potential source of, and sink for, contaminants.

5.1. Results

Figures 5.1-5.5 show single depth profiles for Eh, pH, alkalinity, Mg and Na in Snarestone and Smethwick porewaters (Appendices 13.1-13.2). Porewater concentration profiles for Ca, Si, Cl^-, SO_4^{2-}, Fe, Mn, Zn, Al and PO_4^{3-} are shown in Figures 5.6-5.14, and the data is shown in Appendices 13.3-13.11. The profiles for these ions are plotted for each season in order to assess the affects of seasonally induced factors upon their porewater profiles, and hence each sediment's diagenetic processes. It is important to note that porewaters for the analysis of anions by IC were extracted from a separate core to that from which the porewaters for cation analysis by ICP AES were extracted.

It is clear from figures 5.4-5.14 that the porewaters of the urban canal sediment contain significantly more dissolved solid than those of the less contaminated rural canal sediment. Overall, the profiles for Snarestone show greater seasonal variability than the Smethwick porewater. This probably reflects the lower total concentration of dissolved solids, the sample to sample variability highlighted in the previous chapter, as well as seasonally induced changes.

5.1.1. Alkalinity and pH

Smethwick

The pH at Smethwick decreases from 7.76 in the overlying canal water to 6.68 at the sediment water interface. For the remainder of the profile it stays relatively constant at between 6.42 and 6.96 (Figure 5.1a). Table 5.1 shows the pH values sampled in the canal water on each sampling trip and they reveal the variable nature of pH in the overlying waters (the profile readings were measured from the core taken in spring 1999).

The alkalinity increases sharply across the sediment water interface from 1.14mM in the canal water to 4.94mM at a depth of 2cm. Beneath 2cm the alkalinity rises more steadily to reach 7.81mM at 24cm (Figure 5.2a).

Table 5.1: Temperature and pH readings measured in the canal water on each sampling trip

	Temperature °C	*Ph*
Smethwick		
Spring 1998	18	8.20
Summer 1998	15	7.58
Autumn 1998	11	6.91
Winter 1998	2	7.44
Spring 1999	10	7.76
Snarestone		
Spring 1998	14	7.00
Summer 1998	16	7.13
Autumn 1998	10	Battery flat on meter
Winter 1998	3	7.67
Spring 1999	11	7.31

Snarestone

Figure 5.1b shows the pH of the canal water at Snarestone is 7.31 and it falls sharply in the porewaters reaching 6.45 at 3cm depth. Beneath 3cm the pH remains relatively constant, at values of between 6.23 and 6.65, to a depth of 20cm where it increases slightly to between 6.74 and 6.93 for the remainder of the profile. From Table 5.1 it can be seen that the pH fluctuates in the overlying canal water between sampling trips (the profile readings were measured from the core taken in spring 1999).

The alkalinity increases from 1.8mM in the canal and interface water samples to a peak value of 3.3mM at 1cm and then falls sharply to 2.45mM at 3cm (Figure 5.2b). Beneath 3cm the alkalinity remains relatively constant at values of between 2.18 and 2.98mM.

5.1.2. Eh

Smethwick

Figure 5.3a shows that in Smethwick sediment the Eh value falls from a positive value of +0.45V at the sediment water interface to a negative value of –0.06V at 1cm, it then declines more steadily to a value of -0.16V at 4cm. Beneath 4cm the Eh remains relatively constant at between –0.11V and –0.22V.

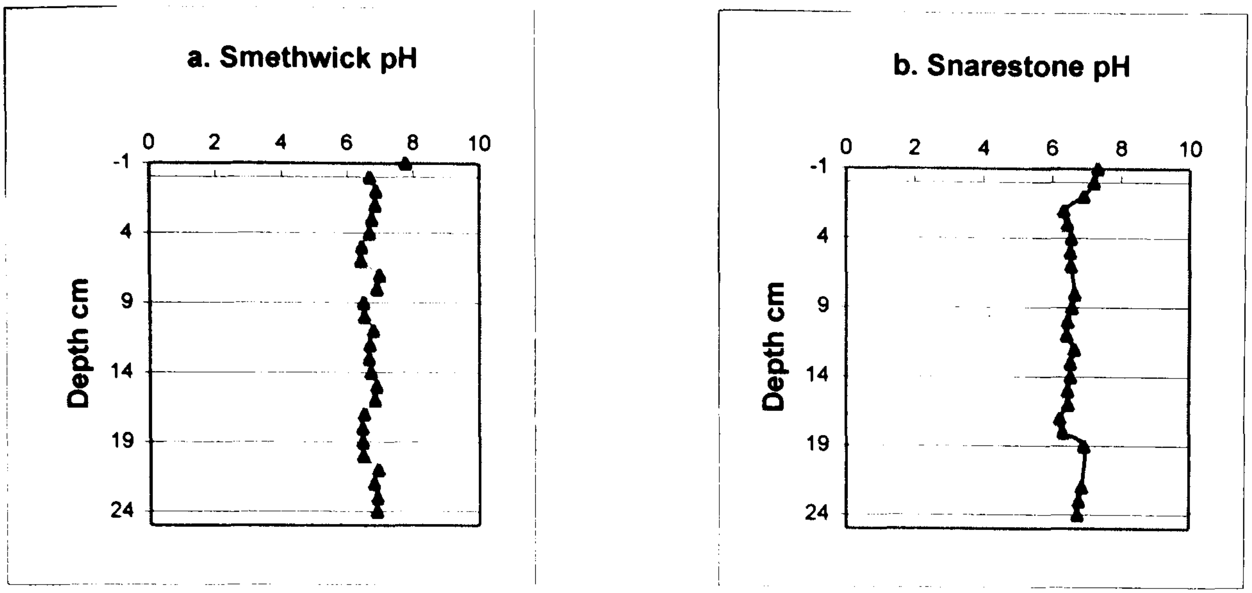
Snarestone

At Snarestone, the Eh at the sediment water interface is +0.30V; in the sediment it falls to a value close to 0V at 4cm and remains at this level to a depth of 7cm, where it falls once more to -0.04V; it then continues to fall and reaches a minimum value of -0.18V at 9cm (Figure 5.3b). Beneath 9cm the Eh increases to +0.04V at 10cm and fluctuates around 0V for the remainder of the profile.

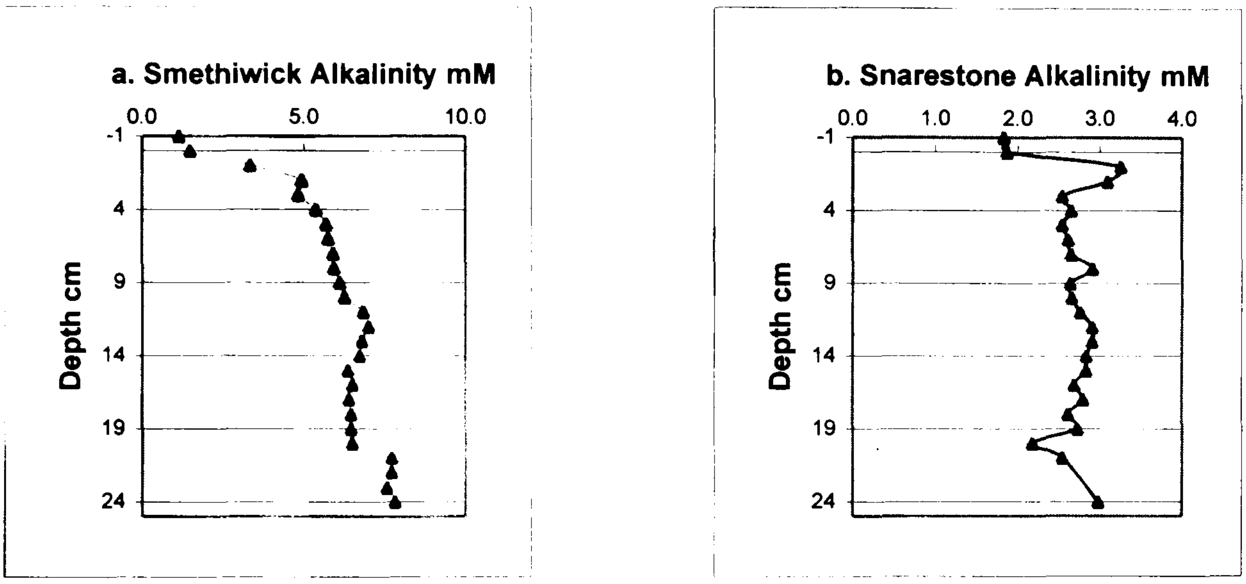
5.1.3. Sodium (Na)

Smethwick

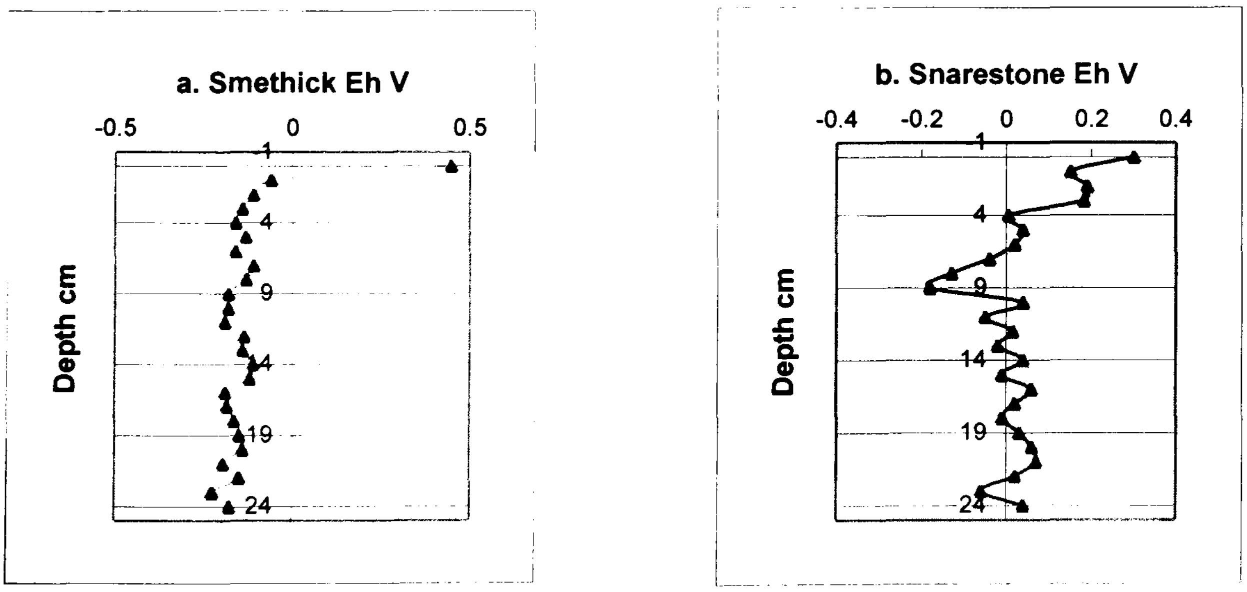
The concentration of Na increases steadily with depth in Smethwick porewaters, from 3.35mM in the overlying water to 4.69mM at 24cm (Figure 5.4a).



5.1 a and b: pH in Smethwick and Snarestone Porewaters



5.2 a and b: alkalinity in Smethwick and Snarestone Porewaters



5.3 a and b: Eh in Smethwick and Snarestone Porewaters

Snarestone

In Snarestone porewaters, the concentration of Na increases steadily downwards, from 0.67mM in the overlying canal waters, to 1.06mM at 19cm, which was the deepest reading taken (Figure 5.4b).

5.1.4. Magnesium (Mg)

Smethwick

The concentration of Mg rises very slightly from 1.23mM in the canal water to 1.26mM at 2cm, whereupon it increases sharply to a maximum value of 2.71mM at 8cm and then begins to decrease gently reaching 1.96mM at 24cm (Figure 5.5a).

Snarestone

The concentration of Mg in Snarestone sediment rises sharply from 0.052mM in the overlying canal water to 0.67mM at the sediment water interface, it then increases slightly over the profile to a concentration of 0.76mM at 24cm (Figure 5.5b).

5.1.5. Aluminium (Al)

Smethwick

The concentration of Al was measured in the Smethwick porewaters, but present at very low concentration <0.02mM, and occasionally fell beneath the detection limit of 0.0023mM (Figure 5.6a-d). The only notable exception to this is a large peak in concentration of 0.22mM at 2cm in the autumn sample, and a much smaller peak of 0.036mM at the sediment water interface in the winter sample (Figure 5.6d).

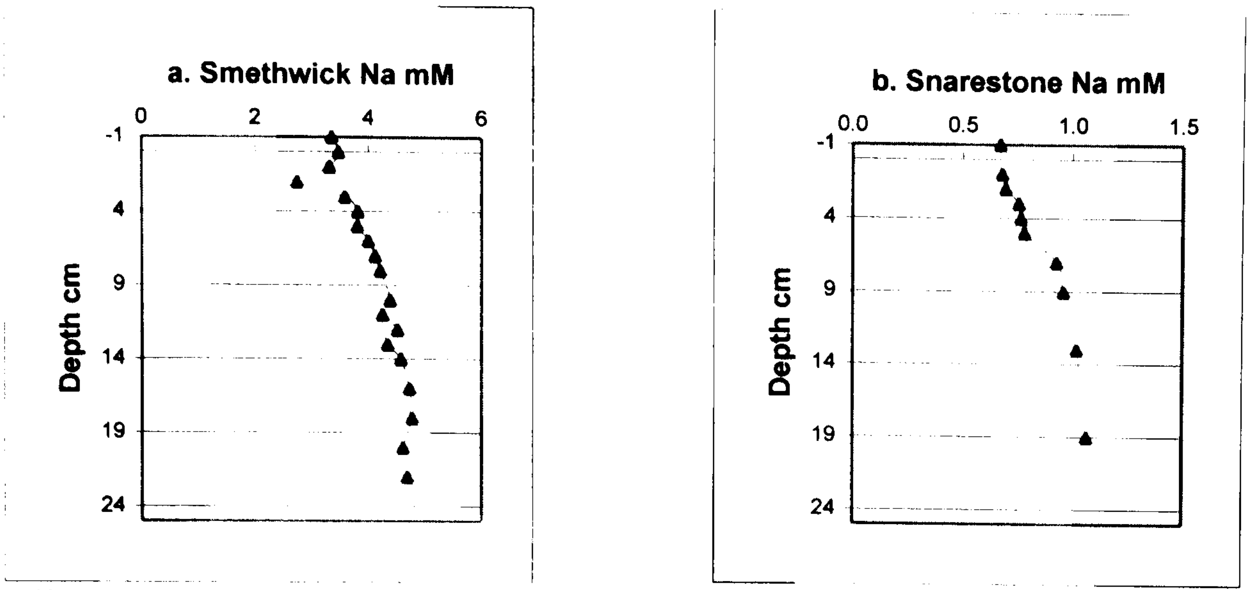


Figure 5.4 a and b: Concentration of Na in Smethwick and Snarestone Porewaters

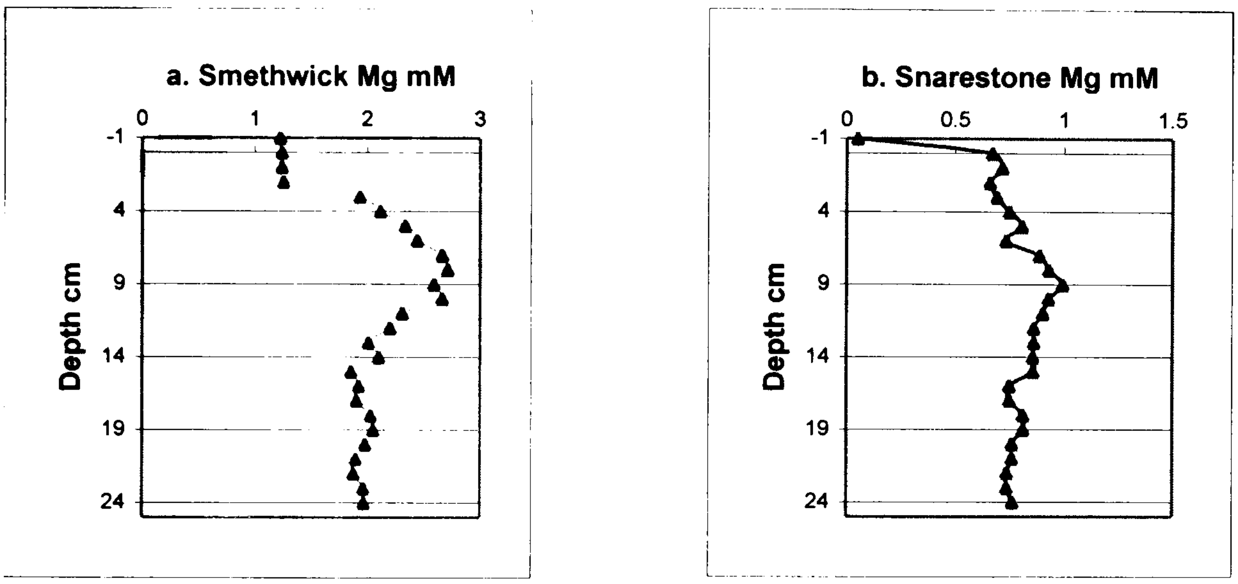


Figure 5.5 a and b: Concentration of Mg in Smethwick and Snarestone Porewaters

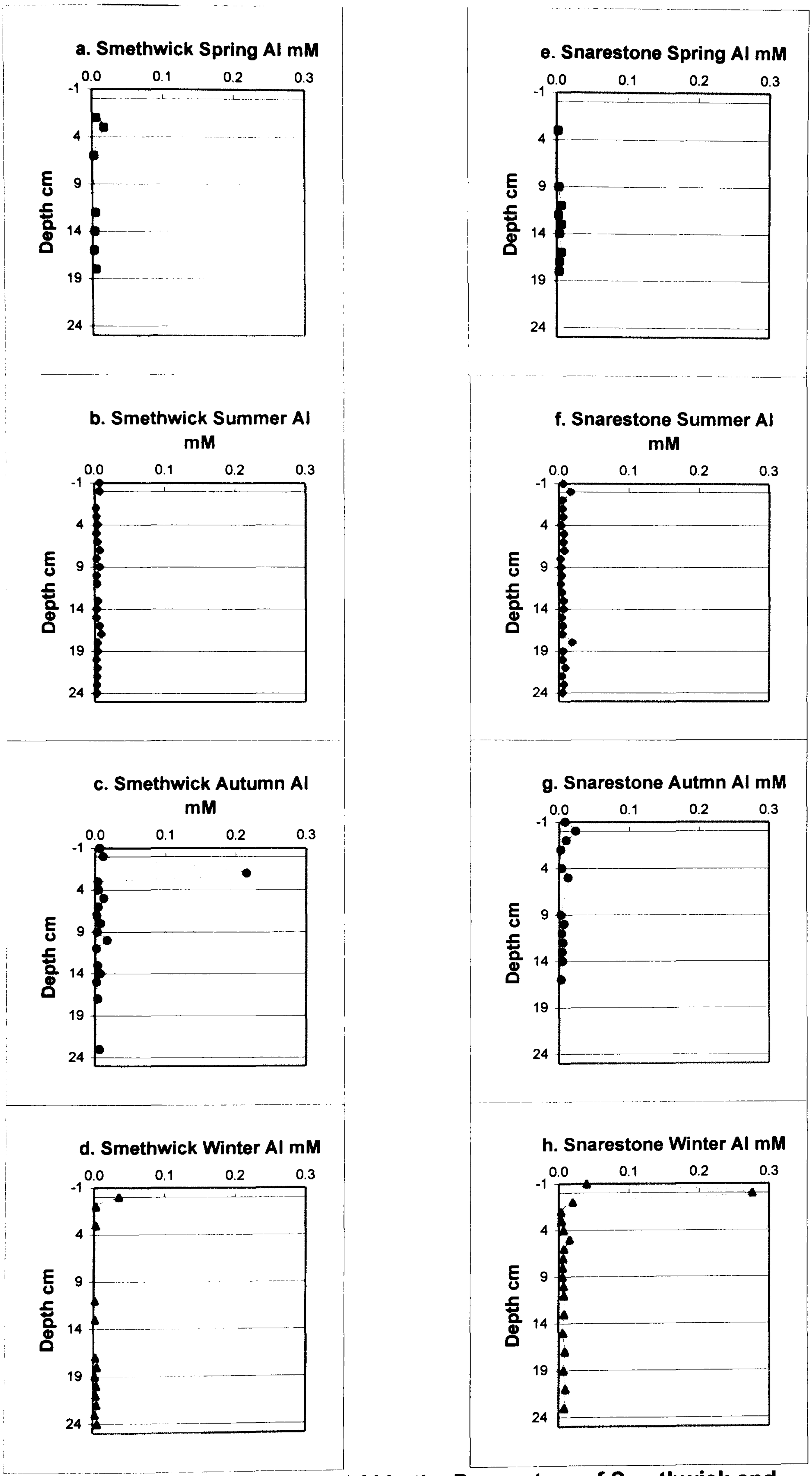


Figure 5.6a-h: Concentration of Al in the Porewaters of Smethwick and Snarestone

Snarestone

The concentration of Al was measured in the Snarestone porewaters but frequently fell beneath the detection limit of 0.0023mM, when detected it was present at very low concentrations of <0.01mM (Figure 5.6e-h, Appendix 3.1b). The only notable exception to this is a large peak in concentration of 0.28mM at the sediment water interface in the winter sample and a much smaller peak of 0.024mM at the sediment water interface in the autumn sample (Figure 5.6h).

5.1.6. Silicon

Smethwick

The concentration of Si in Smethwick porewaters increases sharply in the uppermost 5cm of each seasonal profile, and then continues to increase a small amount for the remainder (Figure 5.7a-d). The concentration of Si in the canal water is lowest in the spring sample at 0.003mM, and greatest in the winter at 0.145mM. By 5cm in each profile the concentration has increased to between 0.57-0.69mM, and for the remainder of the profile the concentration continues to increase slightly to between 0.76-0.84mM at 24cm.

Snarestone

At Snarestone, Si profiles show an overall trend of a sharp increase in concentration over the uppermost 3cm of the sediment, beneath 3cm the concentration shows a seasonal variation (Figure 5.7e-h). The concentration of Si in the overlying canal waters is greatest in the winter at 0.159mM and least in the spring at 0.005mM; in the winter there is also a marked peak in Si concentration of 0.54mM at the sediment water interface, which is not observed in the other seasons. At 3cm in the summer and winter, the concentration of Si is 0.29mM in both samples, and it increases gently to reach 0.54mM at 24cm in the summer profile and 0.40mM in the winter profile (Figure 5.7f and h). Between 10-13cm in the spring sample, the concentration peaks, reaching a maximum value of 1.00mM at 10cm; beneath 13cm the concentration falls to reach 0.63mM at 18cm (the

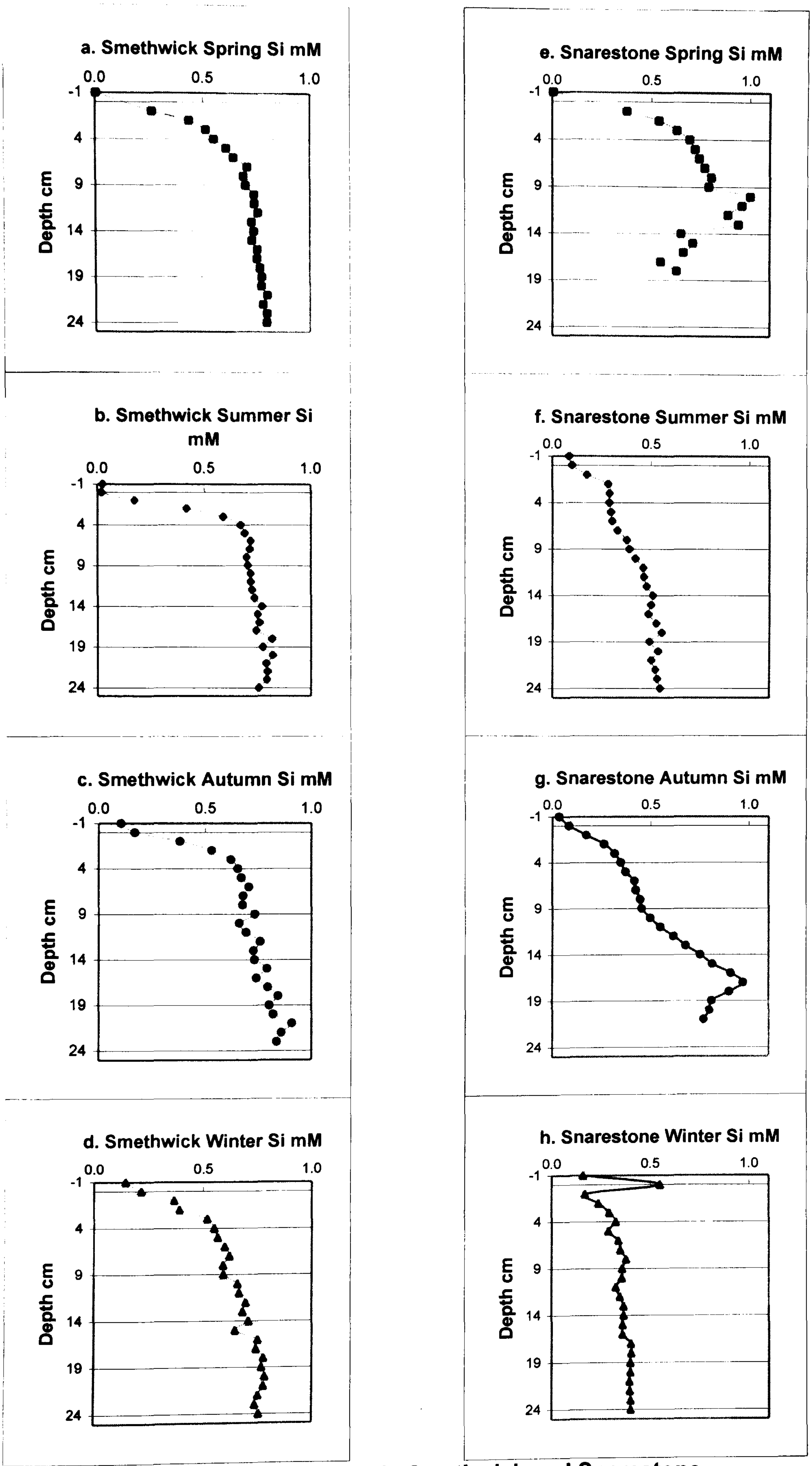


Figure 5.7a-h: Concentration of Si in Smethwick and Snarestone Porewaters

deepest sample) (Figure 5.7e). In the autumn sample the concentration of Si increases steadily over the profile reaching 0.97mM at 17cm; the concentration then falls to 0.77mM at 21cm (the deepest sample) (Figure 5.7g).

5.1.7. Phosphate (PO_4^{3-})

Smethwick

With the exception of the summer profile, the concentration of PO_4^{3-} peaks at between 0.28mM and 0.33mM at depths of between 2 and 7cm, then declines (Figure 5.8a-d). In the summer profile, the PO_4^{3-} concentration increases from 0.01mM at the sediment water interface to 0.07mM at a depth of 2cm; the concentration then fluctuates irregularly between 0.02mM and 0.14mM at greater depths in the sediment. Most notably in summer, the peak in PO_4^{3-} concentration observed in the other seasonal profiles is absent

Snarestone

Phosphate porewater concentration tends to increase from between 0.001mM and 0.004mM at the sediment water interface, to maximum values of between 0.08mM and 0.17mM (Figure 5.8e-h). This increase is most gradual in the spring core where a peak in PO_4^{3-} concentration is encountered at a depth of 13cm (Figure 5.8e). In summer and winter the porewater concentration remains relatively uniform below 5cm depth (Figure 5.8f and h). The autumn profile is very different; the concentration is below detection limit (<0.0003mM) in the water and interface samples, and remains low at between 0.01mM and 0.07mM in the upper 9cm of the sediment (Figure 5.8g). This is followed by a sudden downwards increase to 0.23mM at depths of between 9 and 13cm, and then by a gradual decline in PO_4^{3-} concentration to 0.04mM at 24cm depth.

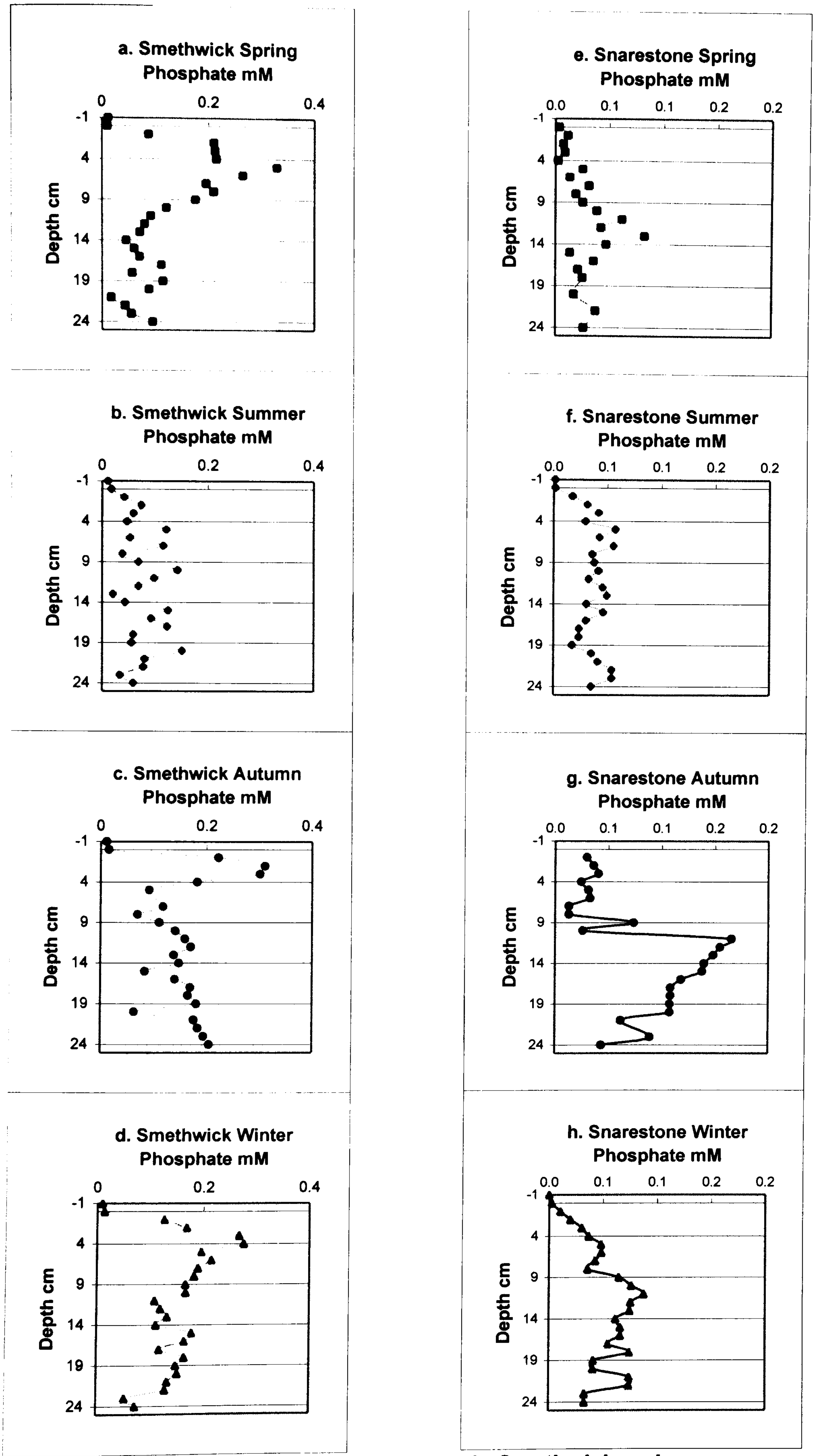


Figure 5.8a-h: Concentration of Phosphate in Smethwick and Snarestone Porewaters

5.1.8. Sulphate (SO_4^{2-})

Smethwick

The concentration of SO_4^{2-} in the Smethwick porewaters declines sharply from the sediment water interface downwards (Figure 5.9a-d). In the overlying canal waters the concentration ranges from a maximum value of 2.71mM in the spring, to a minimum value of 1.70mM in the winter. Beneath the sediment water interface, the concentration falls sharply in each season to concentrations close to the detection limit (0.0001mM) at depths of 3cm in the spring, 7cm in the summer and 2cm in the autumn and winter. In the winter sample the concentration of SO_4^{2-} falls from 1.70mM in the overlying canal water to 1.21mM in the sediment water interface sample (Figure 5.9d), whereas in the three other seasons it varies very little between the two water samples.

Snarestone

The concentration of SO_4^{2-} in Snarestone porewaters decreases sharply over the uppermost few centimetres of the core (Figure 5.9e-h). Concentrations in the overlying canal waters are between 0.76mM in the spring and 0.58mM in the winter. Beneath the sediment water interface, the concentration falls sharply in each season to concentrations close to the detection limit (0.0001mM) at depths of 2cm in the spring and summer, 3cm in the autumn and 5cm in the winter. In the spring sample, beneath 15cm the SO_4^{2-} concentration fluctuates between the elevated value of 0.76mM and 0.004mM; slightly elevated concentrations are also observed between 9 and 15cm in the summer profile and at 19cm in the winter profile.

5.1.9. Chloride (Cl^-)

Smethwick

The concentration of Cl^- remains relatively constant over the depth profile of Smethwick porewaters and does not show a systematic depth trend in each season

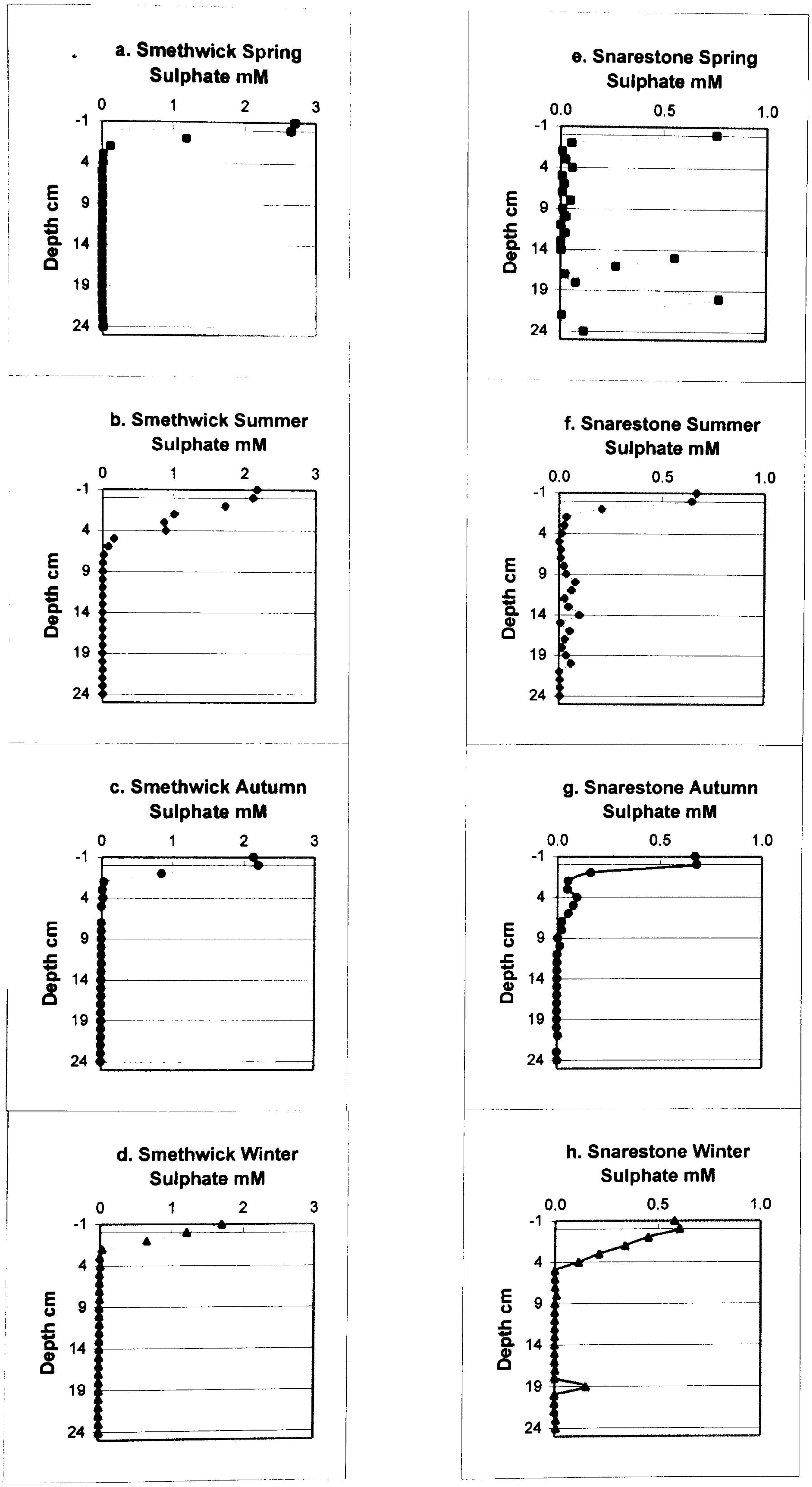


Figure 5.9a-h: Concentration of Sulphate in Smethwick and Snarestone Porewaters

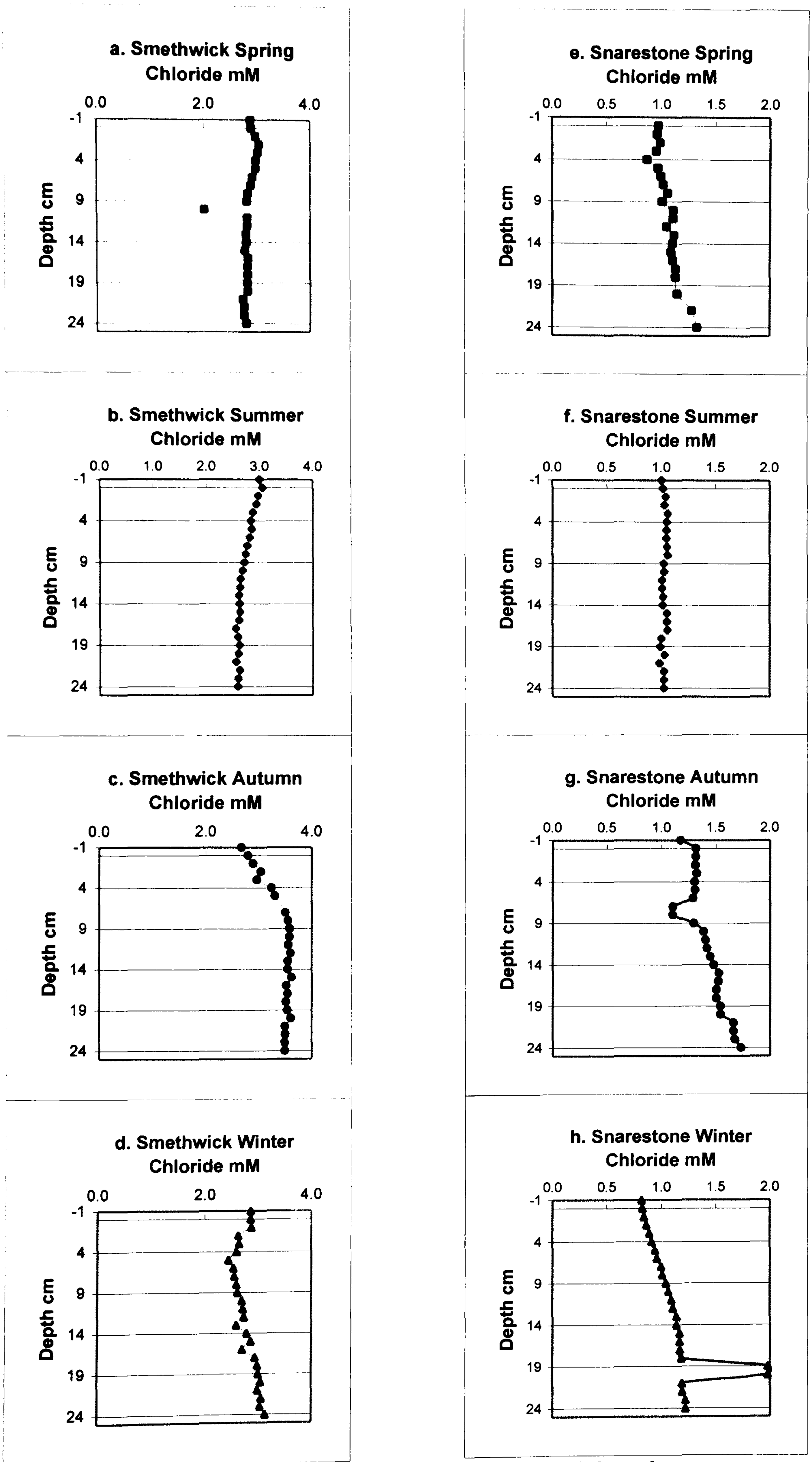


Figure 5.10a-h: Concentration of Chloride in Smethwick and Snarestone Porewaters

(Figure 5.10a-d). In the spring, the concentration is relatively constant over the profile, within the range 3.04-2.75mM, with the exception of the sample from 10cm in which the concentration falls to 2.01mM (Figure 5.10a). In the summer, the concentration decreases slightly with depth from 3.05mM at the surface to 2.59mM at 24cm depth (Figure 5.10b). In the autumn, the concentration rises from 2.67mM at the surface to 3.55mM at 8cm, beneath which depth it remains relatively constant at between 3.62mM and 3.50mM (Figure 5.10c). In the winter, the concentration is elevated in the water and interface samples at 2.86mM and subsequently falls to 2.44mM at 5cm, it then increases steadily downwards to reach 3.13mM at 24cm (Figure 5.10d).

Snarestone

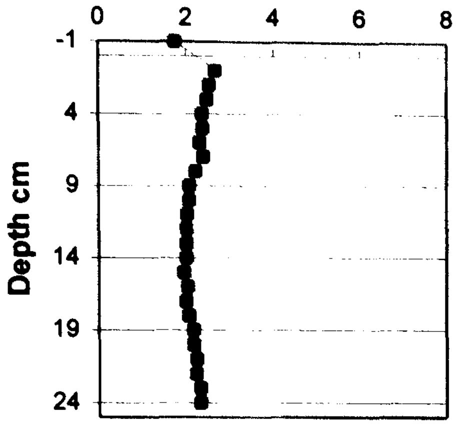
The concentration of Cl^- in Snarestone porewaters is relatively constant in the spring and summer profiles, fluctuating between 0.98-1.06mM (Figure 5.10 e and f). In the autumn profile, concentrations are elevated throughout, increasing from 1.17mM at the surface to 1.73mM at 24cm (Figure 5.10g). In the spring and winter profiles, the surface concentrations are low at 0.97mM and 0.81mM respectively, rising to 1.37mM and 1.22mM at 24cm; the samples from 18-19cm in the winter core have an elevated concentration of 1.98mM (Figure 5.10h).

5.1.10. Calcium (Ca)

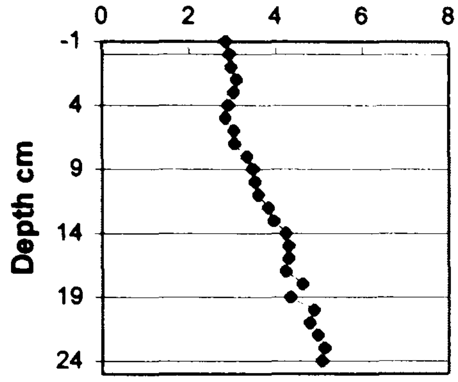
Smethwick

The concentration of Ca increases steadily with depth in Smethwick porewaters, and does not change sharply between the sediment water interface and the sediment porewater (Figure 5.11a-d). The increase is most marked in the winter profile, in which the concentration rises from 2.33mM in the canal water to 6.45mM at 25cm, and least marked in the spring where it only increases from 1.76mM in the water to 2.32mM at 24cm.

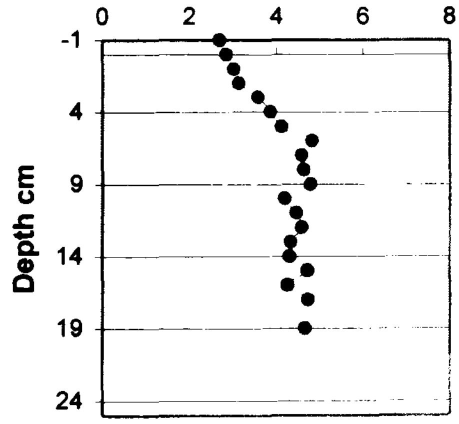
a. Smethwick Spring Ca mM



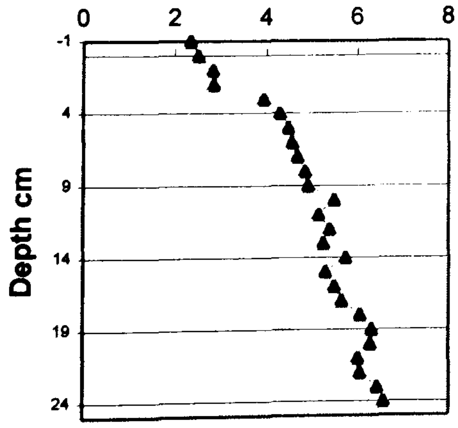
b. Smethwick Summer Ca mM



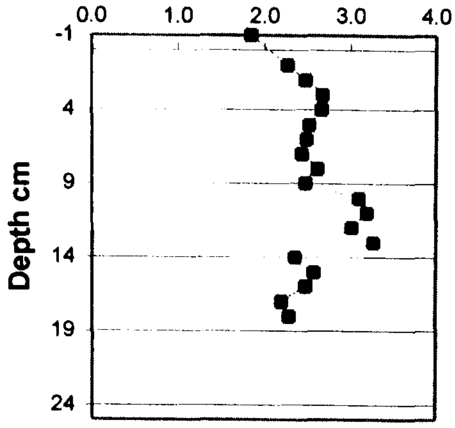
c. Smethwick Autumn Ca mM



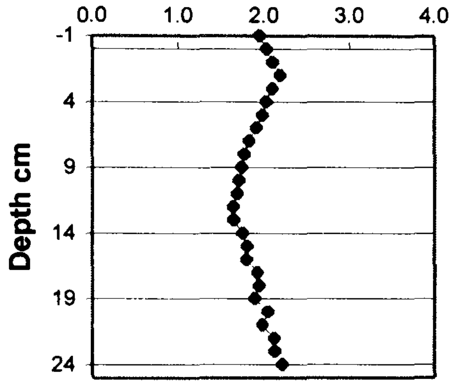
d. Smethwick Winter Ca mM



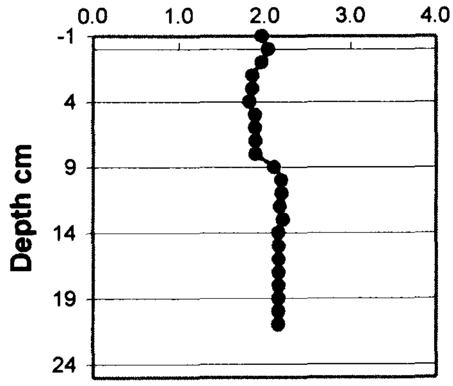
e. Snarestone Spring Ca mM



f. Snarestone Summer Ca mM



g. Snarestone Autumn Ca mM



h. Snarestone Winter Ca mM

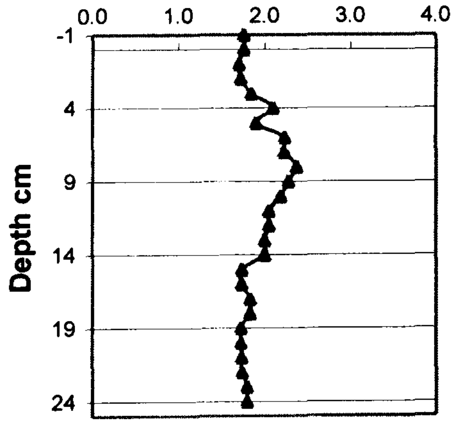


Figure 5.11a-h: Concentration of Ca in Smethwick and Snarestone Porewaters

Snarestone

The concentration of Ca in Snarestone porewaters is relatively constant over the depth profile, although it fluctuates somewhat within profiles and between seasonal samples (Figure 5.11e-h). The concentration ranges from a maximum value of 3.26mM in the spring sample to a minimum value of 1.64mM in the summer sample.

5.1.11. Manganese (Mn)

Smethwick

The concentration of Mn in the Smethwick porewaters increases downward with depth in each season, it increases most markedly in the winter and least in the spring (Figure 5.12a-d). In the spring, the concentration increases sharply from 0.0008mM in the water to 0.005mM at 1cm beneath the sediment water interface, it then increases very gradually over the remainder of profile to 0.009mM at 24cm. The summer and autumn profiles are broadly similar to that observed in the spring, although the concentrations are generally higher. The concentration again increases sharply over the sediment water interface, from 0.0005mM and 0.0006mM in the water to 0.007mM and 0.005mM at 1cm depth, in the summer and autumn respectively; the concentration then increases gently over both of the profiles, reaching 0.013mM at 24cm. In the winter profile the concentration in the overlying canal water is higher than in the other seasons at 0.002mM, it then increases markedly over the profile to a peak of 0.028mM at 20cm, before falling slightly to 0.024mM at 24cm (Figure 5.12d).

Snarestone

The concentration profiles for Mn show marked variations between seasonal samples (Figure 5.12e-h). In the summer and winter profiles, the Mn concentration peaks at a depth of 1cm reaching 0.03mM and 0.025mM respectively, the concentration then falls to 0.014-0.15mM at 5cm and is then relatively constant for the remainder of the profile (Figure 5.12e and h). In the autumn sample the Mn concentration again increases 1cm beneath the sediment water interface to

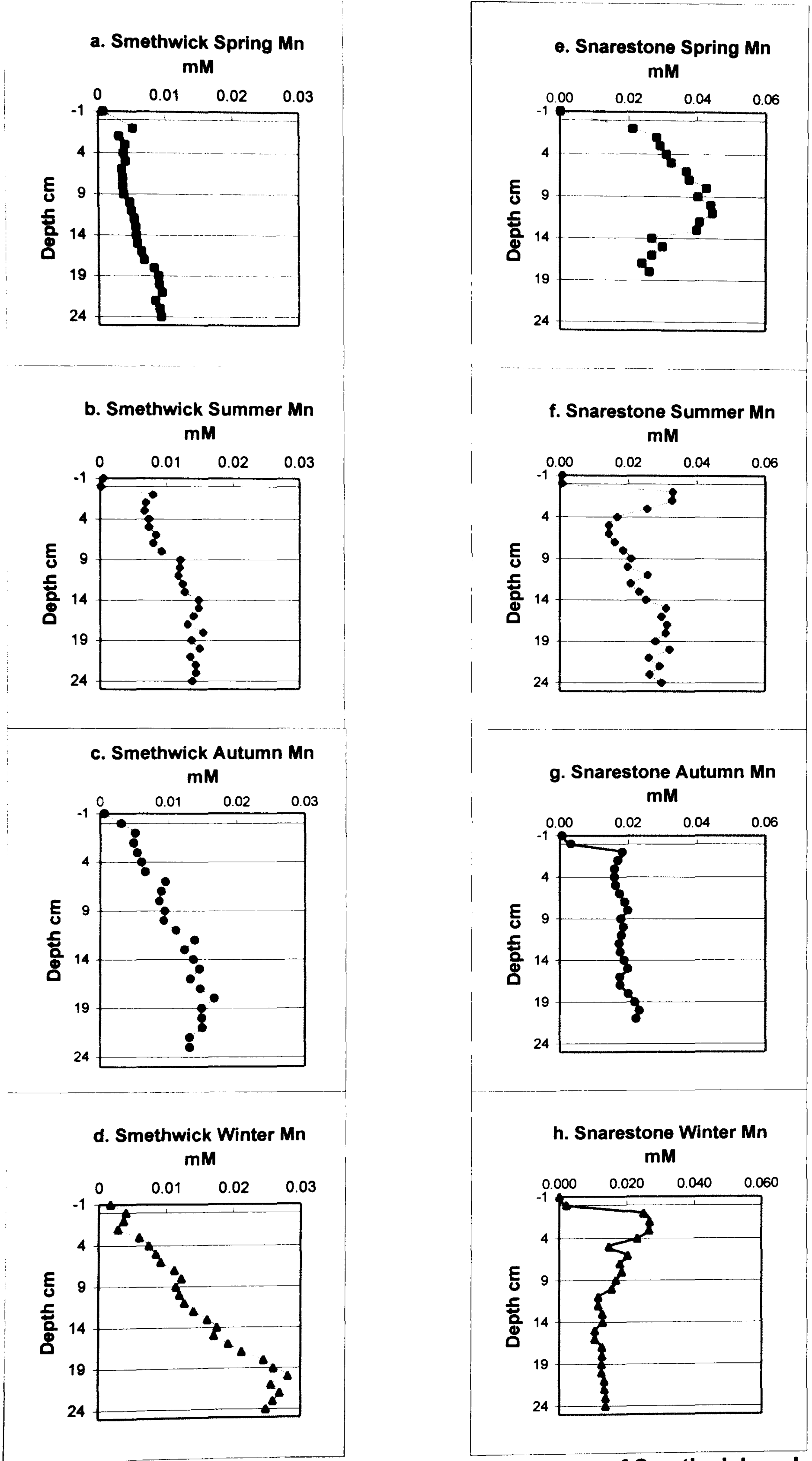


Figure 5.12a-h: Concentration of Mn in the Porewaters of Smethwick and Snarestone

0.018mM, however it then remains at about this level for the rest of the profile (Figure 5.12g). The spring core shows anomalously elevated Mn concentrations of up to 0.044mM (Figure 5.12e). It is however most probable that this has been caused by the storage of the core for 1week in a sealed vessel, prior to extrusion and sub-sampling, which induced increasingly reducing conditions as the oxygen and sulphate in the overlying water were depleted. Prior to storage this sample was observed to have a thick brown oxic layer rich in organic matter which had turned black at the time of extrusion. The absence of a similar anomalous trend in the sulphate profile, which was analysed in porewaters extracted from a separate core on the day of sampling, substantiates this theory (Figure 5.9e). Sample to sample variation will also be factor although it is unlikely that it could result in such a marked and anomalous variation.

5.1.12. Iron (Fe)

Smethwick

With the exception of the spring profile, the concentration of Fe shows a small peak at or 1cm beneath the sediment water interface, rising from values of 0.002-0.009mM in the canal water to between 0.018mM and 0.041mM (Figure 5.13a-d). In the spring no interface sample was collected and this probably explains the absence of the peak in this season (Figure 5.13a). Beneath the surface peaks the concentration falls back to a value similar to that observed in the water (0.002-0.007mM). In the spring sample, the concentration of Fe is low over the uppermost 8cm of the profile (0.002-0.005mM), it then steadily increases for the remainder of the profile reaching 0.09mM at 24cm. In the summer and autumn samples a second large peak in concentration of 0.038mM and 0.089mM respectively occurs at 7cm (Figure 5.13a and c). Beneath this peak in the summer, the concentration falls to 0.014mM at 11cm and then fluctuates over the remainder of the profile between 0.011-0.089mM. In the autumn the concentration falls to 0.008mM at 9cm and then fluctuates between 0.148 and 0.074mM for the remainder of the profile. In the winter the concentration falls to 0.02mM at 4cm but then steadily increases over the profile to a concentration of 0.099mM at 24cm

(Figure 5.13h).

Snarestone

In the Snarestone porewaters with the exception of the spring sample the concentration of Fe peaks at or just beneath the sediment water interface (Figure 5.13f-h). The concentrations in the water are between 0.004mM in the summer and 0.017mM in the winter; peaks in concentration of between 0.019mM in the autumn and 0.072mM in the winter occur at or 1cm beneath the sediment water interface. Beneath these peaks the concentration falls back to values close to those observed in the water; in the summer and winter they remain low at between 0.014mM and 0.001mM for the rest of the profile, while in the autumn they increase from 0.006mM at 10cm to 0.039mM at 24cm. In the spring the Fe concentration increases from 0.002mM in the water to an elevated concentration of 0.105mM at 8cm depth in the sample and then fluctuates over the remainder of the profile between 0.003-0.041mM (Figure 5.13e). As with Mn it is likely that storage of this core for one week prior to analysis has affected these results (section 5.1.12).

5.1.13. Zinc (Zn)

Smethwick

In Smethwick porewaters, Zn was detectable throughout the sediment profile in all seasons, although occasional values were close to the detection limit, and the relative standard deviation from the mean of the two analyses were greater than 10%, they were therefore excluded (Figure 5.14a-b; Appendix 3.7a). In the spring, the concentration of Zn is slightly elevated in the uppermost 10cm of the sediment at ~0.001mM, beneath 10cm the concentration is generally lower than this although it does fluctuate between the 0.0017mM and 0.0002mM (Figure 5.14a). In the summer, the concentration of Zn is uniformly low throughout the sediment profile, values range between 0.0016mM and 0.0005mM (Figure 5.14b). In the autumn profile the concentration of Zn is elevated in the water sample at 0.0021mM, it then falls to 0.0001mM and remains between this value and 0.001mM for the rest of the profile (Figure 5.14c). In the winter the

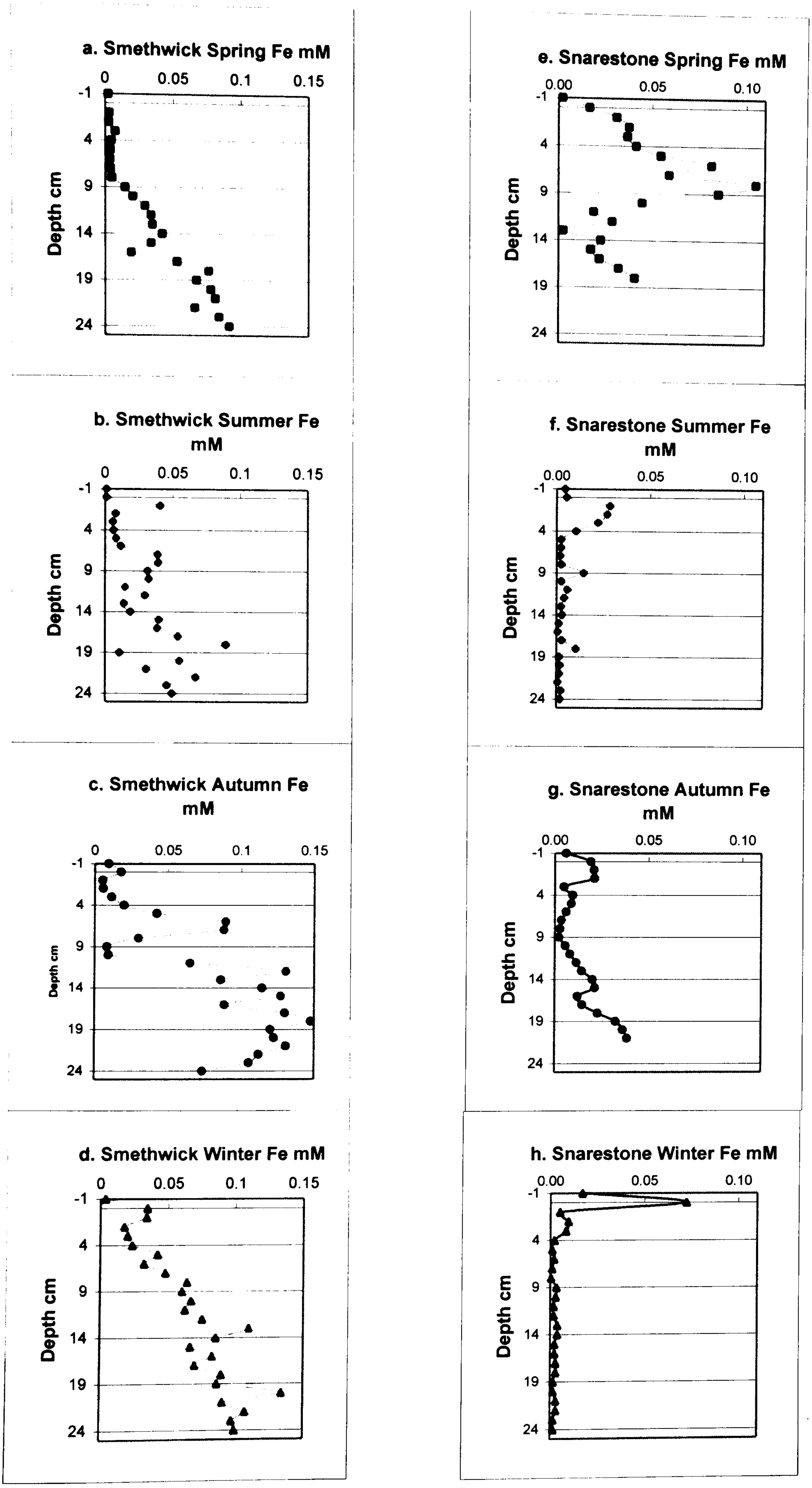


Figure 5.13a-h: Concentration of Fe in Smethwick and Snarestone Porewaters

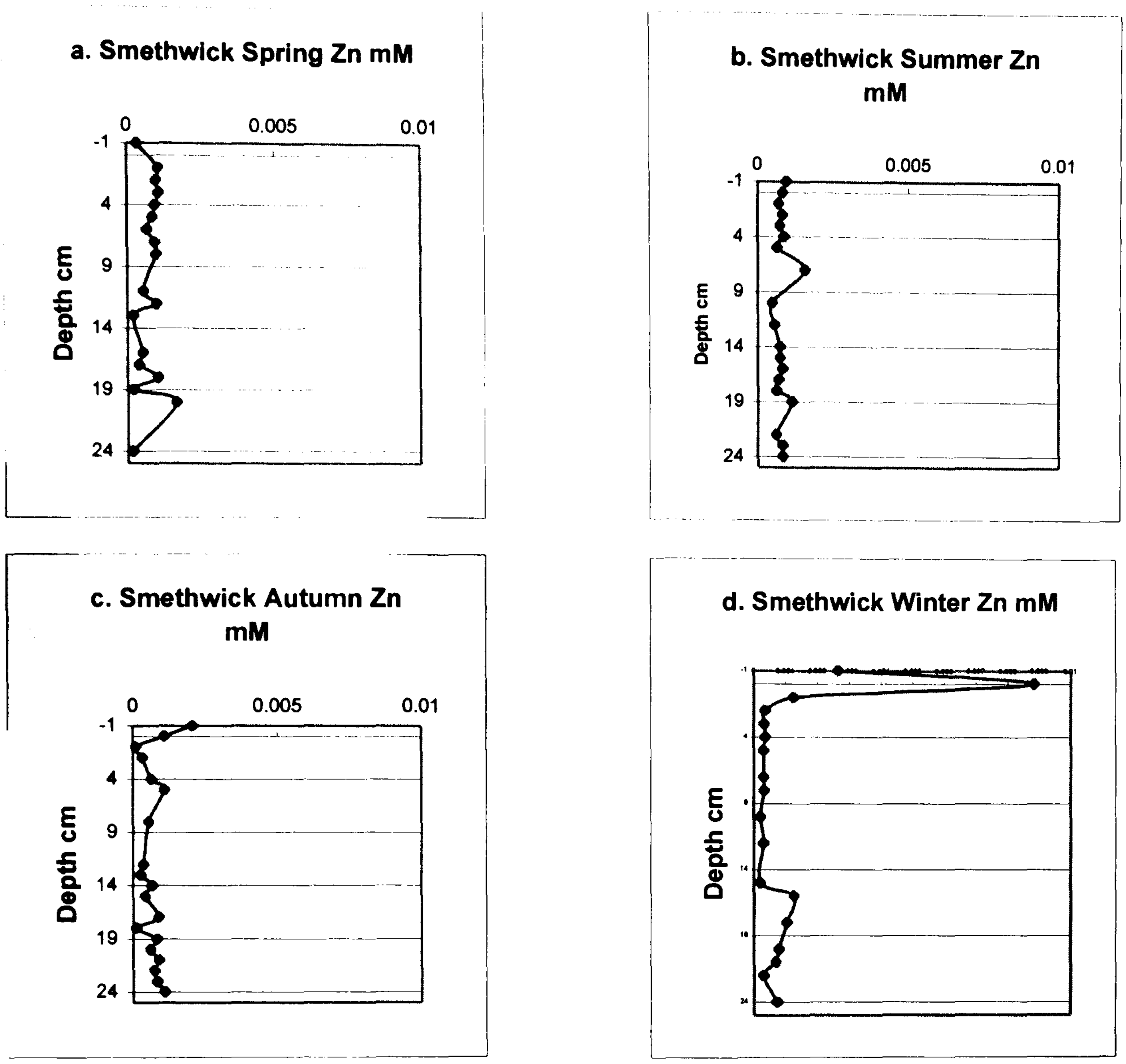


Figure 5.14a-d: Concentration of Zn in Smethwick Porewaters

concentration is again 0.002mM in the water and it increases to 0.0088mM in the interface sample, the concentration then falls to 0.0003mM at 3cm and remains between 0.0010mM and 0.0002mM for the rest of the profile (Figure 5.14d).

Snarestone

At Snarestone the concentration of Zn occasionally fell beneath the detection limit (0.00003mM). When Zn was detected, values were generally close to the detection limit, and the relative standard deviation from the mean of the two analyses were often greater than 10%. In some samples Zn was present at reasonably high concentrations (0.001mM) although no distinct trends could be observed from these measurements (Appendix 3.7b).

5.2. Interpretation

The chemistry of porewaters is primarily controlled by the mineralisation of organic matter (early diagenesis), which is in turn controlled by a series of bacterially mediated redox reactions (Table 5.2) (Froelich et al., 1979). The diagenesis of organic matter will exhaust certain species from the porewaters such as O_2 and SO_4^{2-} and release others including Fe^{2+}, HCO^{3-}, Mn^{2+} and PO_4^{3-}. The saturation of the porewaters in relation to mineral species is used to determine whether ions remain in solution or precipitate to form secondary minerals such as phosphates, sulphides and carbonates.

Table 5.2: Organic matter decomposition reactions and corresponding standard state free energy changes (Froelich *et al., 1979)*

OXIDANT	**REACTION**	**FREE ENERGY (ΔG°) (KJ/mol glucose)**
Oxygen	$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + \mathbf{138O_2} \rightarrow$ $106CO_2 + 16HNO_3 + H_3PO_4 + 122H_2O$	-3190
Manganese	$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + \mathbf{236MnO_2} + 472H^+ \rightarrow$ $236Mn^{2+} + 106CO_2 + 8N_2 + H_3PO_4 + 366H_2O$	-3090 (birnessite) -3050 (nsutite) -2920 (pyrolusite)
Nitrate	$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + \mathbf{94.4HNO_3} \rightarrow$ $106CO_2 + 55.2N_2 + H_3PO_4 + 177.2H_2O$ $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + \mathbf{84.4HNO_3} \rightarrow$ $106CO_2 + 42.2N_2 + H_3PO_4 + 148.4H_2O + 16NH_3$	-3030 -2750
Iron	$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + \mathbf{212Fe_2O_3} + 848\ H^+ \rightarrow$ $424Fe^{2+} + 106CO_2 + 16\ NH_3 + H_3PO_4 + 530H_2O$ $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + \mathbf{424FeOOH} + 848\ H^+ \rightarrow$ $424Fe^{2+} + 106CO_2 + 16NH_3 + H_3PO_4 + 742H_2O$	-1410 (hematite, Fe_2O_3) -1330 (limonitic goethite, FeOOH)
Sulphate	$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + \mathbf{53SO_4} \rightarrow$ $106CO_2 + 16NH_3 + 53S^{2-} + H_3PO_4 + 106H_2O$	-380
Methanogenesis	$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \rightarrow$ $53CO_2$ + 53CH4 + 16NH3 + H_3PO_4	-350

5.2.1. Saturation Indices

In order to test whether a solution or natural water is over- or under-saturated with respect to a particular mineral, it is possible to assess whether the free energy of dissolution is positive, negative or zero. The actual ion activity product (IAP) can be determined for a natural solution and compared with the equilibrium activity product (*K)* to define the state of saturation with respect to a solid as follows:

IAP > K (oversaturated)
IAP = K (equilibrium, saturated)
IAP < K (undersaturated)

By comparing IAP with K we can define a state of saturation for all reactions that involve a solid phase, this is expressed here in logarithmic terms as the *saturation index.* (Stumm and Morgan, 1996)

On the basis of measured concentrations of Fe, Mn, Ca, Mg, Na, Si, P, SO_4^{2-} and

Cl in the porewaters, species distribution and saturation with respect to pure phase minerals were calculated using the geochemical simulation programme PHREEQC (Parkhurst and Appelo, 2000), in order to determine weather reactions relating to observed mineral phases were at equilibrium. The thermodynamic database was taken from (Parkhurst and Appelo, 2000) and (Parkhurst et al., 1980).

The principal authigenic mineral phases observed in the petrological investigation of the sediment were vivianite, calcite, sulphides, iron oxides and silicates, and with the exception of the sulphides, their stability in the sediment will be discussed here. Other minerals such as hydroxyapatite and the iron carbonate siderite, which are typically observed in freshwater sediments, were notable by their scarcity in the canal sediments and therefore their stability will also be discussed in this section. The saturation index data is shown in Appendix 14 and presented in Figures 5.15-5.20.

It is important to note that certain parameters were not measured in all seasons, therefore mineral equilibria which, for example, are controlled to great degree by pH such as carbonates or Eh such as the oxides of Fe, cannot be adequately modelled to show the affects of seasonally induced factors. However the equilibrium of other authigenic phases such as vivianite and hydroxyapatite are controlled to a significant degree by the concentration of their constituent ions in solution and therefore seasonal profiles will be discussed for these minerals.

The petrological investigation of the sediment has revealed that the sulphides of Fe, Zn and Cu are important authigenic phases in both sediments. However, because the concentration of sulphide has not been measured in the porewaters the saturation indices of sulphide minerals in the sediment could not be determined (sulphide authigenesis is discussed in chapter 3).

5.2.2. Alkalinity and pH

The mineralisation of organic matter produces CO_2 and organic acids which will reduce the pH of porewater, this is compensated for by the simultaneous reduction of Fe-oxides which drastically modifies the alkalinity of porewater through the production of HCO_3^- by the following reaction:

$$2Fe_2O_3 + CH_2O + H_2O = 4Fe^{2+} + HCO_3^- + 7OH^-$$

(Curtis, 1987)

Smethwick

The sharp fall in pH between the canal water and sediment water interface at Smethwick indicates the occurrence of intense organic matter mineralisation at the sediment surface (Figure 5.1a). Beneath the sediment water interface the pH remains relatively constant in the porewaters, and this is consistent with a simultaneous increase in the concentration of bicarbonate with depth (Figure 5.2a). The concentration of bicarbonate in this sediment is about twice that observed in the Snarestone sediment, reflecting the greater abundance of both organic matter and Fe in the sediment which will facilitate organic matter degradation by Fe^{3+} reduction at depth.

The pH in the overlying canal water at Smethwick shows considerable seasonal variation, the lower values recorded in the autumn and winter may reflect heavy rainfall on the days preceding the trip (Table 5.1).

Snarestone

The pH declines at the sediment water interface of Snarestone sediment more gradually than it does at Smethwick and this can be accounted for by the lower concentration of organic matter in this sediment and a peak in alkalinity between 1 and 2cm (Figure 5.1b and 5.2b). The peak in alkalinity corresponds to the depth at which amorphous $Fe(OH)_3$ becomes under-saturated in the sediment (Figure 5.15b) and it is likely that this represents the depth of maximum Fe reduction. Beneath the surface sediments the fall in alkalinity to a constant level is likely to be the result of the precipitation of carbonate minerals, most notably calcite. A decline in the organic matter content of the sediment, coupled with the possible exhaustion of easily reducible amorphous oxides, will also prevent further Fe reduction.

5.2.3. Sodium

The sources of porewater Na include rock weathering products and, in urban areas, the extensive use of NaCl for road gritting. The incorporation of NaCl from road gritting into the canal via run off could account for the elevated concentration of Na in the Smethwick porewaters, which is 4 times that observed at Snarestone.

5.2.4. Magnesium

The principal source of Mg to the canal and porewaters will be rock weathering, elevated concentrations at Smethwick relative to Snarestone suggest that Mg is also introduced into sediment from anthropogenic waste.

Smethwick

At Smethwick the Mg porewater profile resembles that of Ca in the uppermost 10cm of the winter profile (Figure 5.5a and 5.11d). This suggests that they are both being released to the porewater from a common source, such as the dissolution of calcite or Ca and Mg rich anthropogenic particles, although no such particles were observed directly. Beneath 10cm the concentration of Mg begins to decrease downwards, while Ca continues to increase, which indicates that Mg is being lost from solution by precipitation to the solid sediment. Magnesium has a greater affinity for substitution into Fe minerals than Ca and is perhaps being incorporated into secondary Fe minerals such as vivianite or siderite; dolomite is unlikely to be a sink for Mg in this sediment, because it is under-saturated throughout the profile (Figure 5.19e).

Snarestone

The profile of Mg in Snarestone porewaters very closely resembles that of Ca in the winter porewaters at Snarestone (Figure 5.5a and 5.11h), suggesting that dolomite or Mg held in solid solution with calcite, are the major sources of Mg to the porewaters. Dolomite is highly under-saturated in the porewaters (Figure 5.19f) but was observed in the sediment by CryoSEM, which suggests that it occurs as a detrital grain rather than an authigenic phase and also that it is likely to be dissolving in the sediment.

5.2.5. Aluminium

The low concentration of Al in the porewaters at both Snarestone and Smethwick reflect its limited solubility (Al will only remain in solution at low pH). The similarity between the concentration of Al in both sediments indicates that its behaviour has not been affected by anthropogenic inputs to the sediment at Smethwick.

Smethwick

The only variation in the concentration of Al in Smethwick porewaters was a peak in concentration at the sediment water interface in the autumn and winter samples, which was most marked in the autumn sample. The autumn peak coincides with the minimum recorded pH and in the overlying waters and this could have increased the solubility of Al at sediment surface (Table 5.1). It is also possible that during these periods of minimal boat disturbance, a microbial mat is established at the sediment water interface producing large quantities of organic acid that might dissolve Al minerals.

Snarestone

At Snarestone, peaks in Al are observed at the sediment water interface in the autumn and winter samples, the peak in the winter is highly elevated. This might reflect the more rapid transition to anoxia in the sediment that occurs at the sediment water interface in the winter sample. It is also possible that, similarly to the Smethwick sediment, during these periods of minimal boat disturbance, a microbial mat is established at the sediment water interface producing large quantities of organic acid that might dissolve Al minerals.

5.2.6. Silicon

The main sources of Si to the porewaters are from the dissolution of detrital silicate grains, such as quartz, and diatoms. The growth of diatoms in the sediments photic zone will also act as a sink for Si from solution. An investigation of microbial mats at the surface of river sediment (Woodruff et al., 1999) revealed that they can influence the composition of overlying waters and the development of vertical concentration gradients of solutes in the porewaters, particularly with respect to Si. They suggest that diatom communities establish in these mats, causing a decrease in the concentration of Si and set up a diffusion gradient with Si from the underlying porewaters (Woodruff et al., 1999). Although it is not clear if such a film was present at the surface of the Smethwick or Snarestone sediment, abundant diatoms were observed at the sediment water interface, and throughout both sediment columns, by the CryoSEM. It is possible that benthic diatoms are controlling the diffusion of Si from both of these sediments. The activity of any biological community is likely to be greatest in the summer and least in the winter, and this could account for the low concentrations of Si at the surface in the spring and summer and elevated concentrations in the winter. With increasing depth in the sediment, diatoms were observed to be broken up, probably by compaction and dissolution, and it is likely that the constant concentration of Si with depth in both sediments is the result of equilibrium between the porewaters, diatoms, quartz and other Si minerals.

Smethwick

The silicates chalcedony and quartz are at equilibrium or over-saturated in the Smethwick canal water and rapidly become more saturated in Smethwick porewaters (Figure 5.20a). This suggests that one of the silica phases in the sediment is dissolving to a constant concentration close to equilibrium. It is likely that the dissolution of diatoms is the most significant source of Si to the porewaters. The slightly elevated concentrations of Si in the Smethwick porewaters relative to Snarestone may reflect the greater abundance of organic acids, produced by fermentation in this organic rich sediment. Diatoms are composed of opal-A silica and its saturation was not calculated in the porewaters.

Snarestone

Chalcedony and quartz are at equilibrium or under-saturated in the overlying and interface waters at Snarestone, and become more saturated within the sediment (Figure 5.20b). Similarly to the Smethwick sediment, it is likely that diatoms are dissolving as the pH decreases, to reach a constant concentration close to equilibrium, and that this is controlling the concentration of Si in the porewaters. However, diatoms are composed of opal-A silica and its saturation was not calculated in the porewaters.

5.2.7. Phosphate

The main sources of porewater phosphate are the mineralisation of organic matter, the dissolution of authigenic phosphate minerals and the reduction of amorphous Fe-oxides, which are an important adsorption site for PO_4^{3-}. Interpretation of the PO_4^{3-} pore water concentration profiles is best undertaken with reference to the saturation indexes for various phosphate minerals that are known to be stable in the sediment, which include vivianite (Figures 5.16a-d and 5.17) and hydroxyapatite (Figures 5.18a-h).

Smethwick

The main sources of phosphate in the Smethwick sediment are most probably a mixture of organic matter and P sorbed to iron oxides, which can account for its release to the porewaters as the sediment becomes reducing at the surface. Vivianite tends to become more saturated with increasing depth in the sediment and displays distinct seasonal variations. In winter, vivianite saturation is attained close to the sediment water interface and this is in agreement with the petrographic observations. In summer, autumn and spring significant under-saturation occurs in the upper 10cm of the sediment. This is probably due to sediment oxidation as a consequence of re-suspension and mixing by passing boat traffic. The fluctuating saturation state of vivianite is also supported by textural evidence of partially dissolved authigenic vivianite coexisting with pristine vivianite crystals.

Hydroxyapatite also tends to be oversaturated in Smethwick sediment (Figure 5.18a-d). Calcium phosphate minerals were observed but were not common, suggesting that its precipitation may in some way be inhibited. There are a number of possible reasons for the lack of calcium phosphate minerals. The nucleation kinetics of hydroxyapatite are such that the presence of other species e.g. organic acids and Mg^{2+}, may inhibit its formation (Martens and Harris, 1970). Nriagu and Dell, (1974) suggest that under the pH range encountered in many freshwater sediments anapaite ($Ca_2Fe(PO_4)_3.4H_2O$) may be more stable, although this argument would not explain the apparent absence of Ca-PO_4 minerals in the sediment. The control exerted upon PO_4^{3-} concentrations in the porewaters by vivianite might account in part for the large fluctuations in hydroxyapatite stability.

Snarestone

Given the very heterogeneous nature of the canal sediments at Snarestone, the large differences in PO_4^{3-} concentration between cores may only reflect this heterogeneity rather than any meaningful seasonal trends. Saturation indices indicate that vivianite approaches saturation close to the sediment water interface, and then with only a few exceptions is under-saturated at greater depths in the sediment (Figure 5.17). Similarly, hydroxyapatite approaches saturation at the sediment water interface and then remains under-saturated to depths below 19cm where it again approaches saturation or becomes over-saturated (Figure 5.18e-h).

The reason for the near surface approach to saturation of vivianite and hydroxyapatite is probably related to the near surface rise in pH which may relate to mixing with canal water or peak rates of iron reduction. The slight rise in pH below 19cm might also explain the over-saturation of hydroxyapatite below this depth, although the reason for this change in pH is not clear.

5.2.8. Sulphate (SO_4^{2-})

The depletion of SO_4^{2-} in the porewaters of the uppermost few centimetres of the sediment is typical of freshwater anaerobic organic rich sediments, in which SO_4^{2-} reduction occurs at or close to the sediment water interface rapidly exhausting it from the porewaters. The elevated concentrations of SO_4^{2-} in the overlying water at Smethwick are to be expected, as a result of the release of SO_2 into the atmosphere during the burning of fossil fuels and its subsequent incorporation into natural waters.

Smethwick

The deepest penetration of SO_4^{2-} at Smethwick occurs in the summer sample and this coincides with the peak period of holiday boat traffic on the canal. Boat traffic disturbs the sediment sending large clouds of it into suspension in its wake (section 4.1); it is probable that this results in the mixing of the overlying oxic canal water with the anaerobic surface sediments, increasing their porewater SO_4^{2-} concentration. In the winter, SO_4^{2-} reduction has clearly begun in the water column, resulting in the observed fall in SO_4^{2-} concentration between the water and interface sample. When the winter core was sampled the canal was covered by ice, and it was obvious that it had not been broken by boat traffic on that day. It is apparent that in this organic rich sediment the rate of sulphate depletion is limited by the rate at which sulphate can diffuse into the sediment.

It is interesting to note that the maximum concentration of SO_4^{2-} is recorded in the canal water in the spring, and the minimum value in the winter. This is consistent with an observed decline in the surface S concentration of the sediment in the spring and summer, and indicates that some oxidation of some amorphous sulphide phases might be occurring as a result of sediment mixing at this time.

Snarestone

At Snarestone, the seasonal variation in the depth to which SO_4^{2-} penetrates into the uppermost few centimetres of the sediment is similar to that which is typically observed in natural freshwater sediments, in particular seasonally anoxic lakes (Carignan and Lean, 1991; Morfett et al., 1988). The more rapid depletion of SO_4^{2-} in the spring and summer profiles probably results from the increased productivity of organic matter at this time, the diagenesis of which will rapidly exhaust first oxygen and then SO_4^{2-} from the porewaters. In the winter when the productivity of the canal is at a minimum, the exhaustion of SO_4^{2-} occurs less rapidly. In this less organic rich sediment the rate of organic matter input appears to determine the rate of sulphate depletion.

The elevated concentrations of SO_4^{2-} observed beneath 15cm in the spring profile, and between 9 and 15cm in the summer porewater, correspond to a change in sediment composition with a higher proportion of sand sized grains and a low organic matter content. It is possible that Snarestone porewaters are periodically influenced by groundwater flow, as this stretch of canal is cut into raised ground. Therefore a rise in the surrounding water table could have influenced the composition of porewaters, particularly in the more porous sandy sediments observed beneath 10cm. If oxidised water, containing SO_4^{2-}, were to penetrate to this depth the absence of non-refractory organic matter could prevent its reduction and peaks such as this would thus disperse slowly by diffusion controlled processes.

The concentration of SO_4^{2-} in the overlying water is significantly lower than that observed in the Smethwick waters, and also shows very little variation between the seasonal samples. This implies that the absence of sulphides from the sediment water interface sample, and the more crystalline nature of the sulphides observed in this sediment, are less responsive to periodic changes in the redox conditions of the sediment induced by the mixing of the sediment with the overlying waters.

5.2.9. Chloride

Sources of Cl^- to the porewater include rock weathering products and NaCl used in road gritting.

Smethwick

At Smethwick, the concentration of Cl^- in the porewater is over twice that observed at Snarestone, and elevated Cl^- concentrations are observed at the surface of the winter profile when road gritting is common-place, suggesting that it is the source of the elevated concentrations.

Snarestone

Concentrations of Cl^- are low at depth in the spring and summer samples relative to the concentrations observed at depth in the autumn and winter porewaters. If during the spring and summer, groundwater is mixing with the porewaters at depth, as the SO_4^{2-} data appears to suggest, the concentration of Cl^- might be diluted relative to the unaffected autumn and winter cores.

5.2.10. Calcium

Calcium is present in the porewater as a product of rock weathering; its concentration in the porewater will be controlled by the saturation of calcite in the sediments. Calcite is undersaturated in rural and urban sediments (Figure 19a-b), however XRD and CryoSEM investigations revealed the presence of calcite, and the fine stepped morphologies of a number of grains observed was strong evidence that they were authigenic.

It is possible that errors in the pH or alkalinity readings may have resulted in the underestimation of the calcite saturation indices in both sediments. The stability of carbonates in natural sediments is controlled to a great degree by the pH and alkalinity of the porewater. Porewater pH and alkalinity were only measured on one occasion and this limits the data set from which the saturation indices of carbonates have been calculated. The pH was measured in the overlying canal water on every sampling trip and showed large variations, and it is therefore possible that significant fluctuations in porewater pH may also occur temporally (Table 5.1). The technique used to establish the alkalinity of the porewaters is subject to interference from other anions in the porewater particularly organic acids, which may also have resulted in an underestimation of the concentration of CO_3^{2-}.

Smethwick

Figure 5.19a shows that calcite is largely under-saturated in the porewaters of Smethwick, although it tends towards equilibrium with depth. This is similar to the results of Wersin et al., (1991) who investigated lake sediment and found that the porewaters were at equilibrium or slightly under saturated with respect to calcite and also observed evidence of authigenic calcite, that did not appear to be dissolving. At Smethwick the increase in the porewater concentrations of Ca and alkalinity with depth is consistent with a decline in the concentration of Ca in the solid sediment, and observations of occasional calcite grains with textures that suggested they might be dissolving, such as etching. This evidence implies that calcite may be dissolving at depth in the sediment. Other workers have interpreted increases in the concentration of Ca and alkalinity with depth in porewaters, to be the result of the dissolution of calcite in the sediment in order to maintain equilibrium concentrations in the porewaters, or in response to a decrease in pH (Coleman, 1985; Emerson, 1976; Mayer et al., 1999). It is likely that organic acids are abundant at depth in the Smethwick sediment due to the fermentation of its high organic content, and if this is the case it could be causing the dissolution of calcite.

Snarestone

At Snarestone, calcite is under-saturated for the whole profile, and is closest to equilibrium at the surface and sediment water interface (Figure 5.19b). It is possible that calcite is precipitated at the sediment surface where intense Fe^{3+}

reduction appears to be producing a high bicarbonate concentration in the porewaters. Beneath the surface the concentration of Ca in the porewaters remains constant, and this indicates calcite may be closer to equilibrium than the saturation index predicts. Calcium will also be released by the dissolution of dolomite, which is apparently present in the sediment as a detrital grain, and is under-saturated in the porewaters (Figure 5.19f).

5.2.11. Manganese

Mn is released to porewaters following the reduction of Mn^{4+} to Mn^{2+}, this reaction will occur as soon as oxygen has been depleted from the porewaters. In both Snarestone and Smethwick sediment, the release of Mn at or immediately beneath the sediment water interface occurs concurrently with the near surface peak in Fe, as has been observed by previous workers (Froelich et al., 1979; Wersin et al., 1991).

Smethwick

In the Smethwick sediment the sequential extraction results for Mn indicate that it is very closely associated with Fe, occurring in solid solution with vivianite and as crystalline oxides which are able to persist under the reducing conditions of the sediment (section 4.4.2.6). The continued increase in Mn concentration in the porewaters with increasing depth can best be accounted for by the reduction of these oxides as the sediment becomes increasingly reducing. It could perhaps be related to the observed dissolution of vivianite, releasing both Fe and Mn into solution and the subsequent precipitation of a mineral such as mixed Fe Zn sulphides from which Mn is excluded. The increase in concentration with depth is greatest in the winter sample, possibly because more reducing conditions prevail at this time due to minimal boat disturbance. Although the increase may also be affected by the anomalously high metal concentrations observed in the aqua regia digest of this sample (section 4.4.1.7).

Figure 5.18g shows that the Mn carbonate rhodochrosite is under-saturated in the uppermost 20cm of Smethwick sediment, and becomes more saturated with depth, reaching equilibrium at 20cm. Rhodochrosite was not observed in the Smethwick sediment by CryoSEM and this is supported by its under-saturation at the surface, however its absence from the sediment at depth is less easily explained. It is possible that the slow kinetics of formation of rhodochrosite prohibit its formation in favour of less thermodynamically stable but more rapidly precipitated Fe-minerals such as vivianite, in which Mn appears to occur in solid solution.

Snarestone

At Snarestone the sequential extraction results revealed Mn to be associated with Ca in the solid sediment (section 4.4.2.6.). This suggests that following the reduction of Mn-oxides in this sediment, Mn is incorporated into the sediment in solid solution with calcite, accounting for the decline in Mn concentration following its near surface peak in summer and winter profiles. The Mn Carbonate rhodochrosite was not observed in the sediment during the CryoSEM investigation, and the saturation index data shows that with the exception of the sample immediately beneath the sediment water interface it is under-saturated (Figure 5.18h). Its absence from the sediment suggests that despite its saturation at the sediment surface it is not precipitating, perhaps due to the slow reaction time of its formation and the limited occurrence of saturated conditions.

5.2.12. Iron

The concentration profiles of Fe in the porewaters of Smethwick and Snarestone sediments are important indicators of their redox status. The Fe concentration values are similarly low in the surface waters of both sediments, however the values at depth in the Smethwick porewaters exceed those observed at Snarestone, which reflects the greater abundance of Fe and organic matter in the urban sediment. The interpretation of Fe porewater profiles is best undertaken with reference to the saturation indices for Fe oxides and the secondary Fe mineral vivianite which is the most abundant authigenic phase in the Smethwick sediment, comprising 1% of the sediment by volume.

Smethwick

The small peak in Fe concentration that occurs at or just beneath the sediment water interface at Smethwick (Figure 5.13b-d) will have resulted from the release of Fe^{2+} into solution following the reduction of amorphous Fe oxides. Saturation indices for amorphous Fe-oxides $Fe(OH)_3$ confirm that they are over-saturated in the overlying oxygenated waters of the Smethwick canal and rapidly become grossly under-saturated immediately beneath them, where the peak in porewater Fe was observed, they then remain under-saturated for the rest of the profile (Figure 5.15a).

The subsequent decline in Fe concentration beneath the near surface peak is less easy to explain. If the winter sample is taken as an example of equilibrium conditions within the sediment, it is clear that following the surface increase in Fe concentration the overall trend for the profile is of increasing Fe concentration with depth. This trend is consistent with the observations of other porewater investigations in lake sediment (Emerson, 1976; Nriagu and Dell, 1974; Wersin et al., 1991). The winter saturation index data for vivianite shows that, below the sediment water interface, vivianite is close to equilibrium to a depth of 5cm and then becomes over-saturated, by over an order of magnitude, for the remainder of the profile (Figure 5.16d). This suggests that vivianite will be precipitating from solution from the sediment water interface and is stable throughout the sediment in these undisturbed conditions.

In the spring and summer profiles below the sediment surface, the concentration of Fe in solution declines sharply and remains low until 8cm in the spring core and 6cm in the summer core. It is possible that this fall in concentration is caused by sediment disturbance by boat traffic, which has resulted in the oxidation of Fe^{2+} and its subsequent precipitation as an oxide. The abundance of FeS and vivianite observed in this sediment suggests that their precipitation must account in part for the loss of significant quantities of Fe^{2+} from the porewaters. The vivianite saturation index in the spring and summer profiles is largely under-saturated in the porewater to a depth of 10cm and then remains close to equilibrium for the rest of the profile (Figure 5.16a and b). This suggests that the presence of oxides in the uppermost 10cm of the sediment is perhaps resulting in the scavenging of Fe^{2+} and PO_4^{3-} from solution and preventing the precipitation of vivianite and possibly causing the dissolution of existing grains.

The large peak in concentration at 6-7cm in the autumn profile corresponds to the maximum depth of sulphate penetration in the summer core. This peak probably marks an interface between the disturbed surface sediments, which are being mixed with oxygenated waters, and the underlying sediment. If this is the case the peak may have resulted from the reduction of Fe oxides, which have accumulated at this depth, through the oxidation of Fe^{2+} supplied to this horizon by upward diffusion. A similar peak in Fe concentration was observed in the porewaters of the Salford Quay sediment investigated by Boyd et al., (1999). The uppermost 10cm of the Quay sediment is enriched with Fe as a result of oxide and sulphide precipitation, brought about by the mixing of the water column by a helixor pump system. Boyd et al., (1999) suggest that peak in Fe^{2+} observed in the Quay sediment, at the base of the enriched surface zone, results from the upward diffusion of metals to this horizon and their subsequent removal as oxyhydroxides or sulphides in the surface sediments. An alternative explanation might be that, in both Salford Quay and Smethwick sediment, the peak marks a transition from surface sediments, which are influenced by mixing with the overlying water column, and the unaffected underlying sediments.

The autumn Fe profile appears to represent a transition between the disturbed profile of the summer and the undisturbed profile of the winter (Figure 5.13c). The vivianite saturation indices for the autumn profile appear to confirm this; vivianite is at saturation/equilibrium in the uppermost 6cm, it then fluctuates from an over-saturated value at 7cm to an under-saturated value at 9-10cm and then recovers to an over-saturated value (Figure 5.16c).

The continued increase in Fe concentration at depth in all seasons suggests that some reduction of oxides is also occurring after the initial reduction of amorphous oxides at the surface. The more thermodynamically stable Fe-oxides goethite and hematite are over-saturated in the overlying canal waters and remain so to a depth of 3 and 4cm respectively in the Smethwick sediment (Figure 5.15c and e). They then appear to reach equilibrium and goethite becomes under-saturated for the majority of the profile while hematite fluctuates around the equilibrium value. The dissolution/reduction of these oxides, can account for the continued increase in Fe concentrations with depth which was most marked in the Smethwick winter profile, from which the data for these calculations were taken.

The continued increase in the concentration of Fe with depth is concurrent with an increase in bicarbonate concentration and the Fe carbonate siderite might be expected to precipitate at depth in the sediment. In the Smethwick porewaters, siderite is under-saturated in the uppermost 10cm of the core, but is then close to equilibrium/saturation for the remainder of the core (Figure 5.19c). This contradicts CryoSEM observations that siderite was observed on only one occasion in urban canal sediment from a depth of 24cm. Siderite has been found to be supersaturated in porewaters and absent during SEM investigations of organic rich anaerobic freshwater lake sediments (Emerson, 1976; Emerson and Widmer, 1978; Mayer et al., 1999; Wersin et al., 1991). Siderite has slow reaction kinetics, and therefore the precipitation of less thermodynamically stable but more rapidly precipitated Fe minerals, such as vivianite and amorphous Fe sulphides, may be controlling the Fe concentration in the porewaters (Emerson and Widmer, 1978).

Snarestone

Iron is released to the Snarestone porewaters following the reduction of amorphous Fe-oxides which become under-saturated immediately beneath the sediment water interface (Figure 5.15b), accounting for the peak in Fe concentration observed at or near the sediment water interface in the Snarestone profiles. The subsequent decline in concentration with depth can best be explained by the precipitation of Fe^{2+} from solution into the solid sediment as pyrite, following its reaction with H_2S produced during SO_4^{2-} reduction (there is no saturation index data for sulphides). The large peak in Fe concentration at the surface of the Snarestone winter core corresponds to the observation that no obvious oxic layer was present, suggesting it becomes reducing at the sediment water interface.

In the Snarestone porewaters, goethite is over-saturated in the overlying water and steadily becomes under-saturated 7cm beneath the sediment water interface; beneath 7cm it fluctuates around the equilibrium concentration although it is largely over-saturated in solution (Figure 5.15d). Hematite is also over-saturated in the waters and uppermost few centimetres of the sediment, although it becomes less saturated with depth and is under-saturated between 8-10cm depth, it then becomes saturated once more and remains close to equilibrium for the rest of the profile (Figure 5.15f). The saturation indices for goethite and hematite are closer to saturation in the Snarestone porewaters than the Smethwick porewaters, as would be expected in this less reducing environment in which organic matter, the sediments principal reducing agent, is largely oxidised in the uppermost 10cm of the sediment. The absence of an increase in Fe concentration with depth in all seasons except autumn appears to confirm that the reduction of stable oxides is not occurring.

The elevated Fe concentrations at depth in autumn profile might be the result of continued Fe^{3+} reduction, following the exhaustion of SO_4^{2-} from the porewater. Other authigenic Fe minerals, which might precipitate under these conditions such as siderite and vivianite, are under saturated in the porewaters and therefore Fe^{2+} will remain in solution (Figure 5.19d and 5.17). Over time the Fe^{2+} will either build up to a saturated concentration or probably diffuse upwards to the surface sediments where the precipitation of Fe oxides or sulphides will results in its removal from solution.

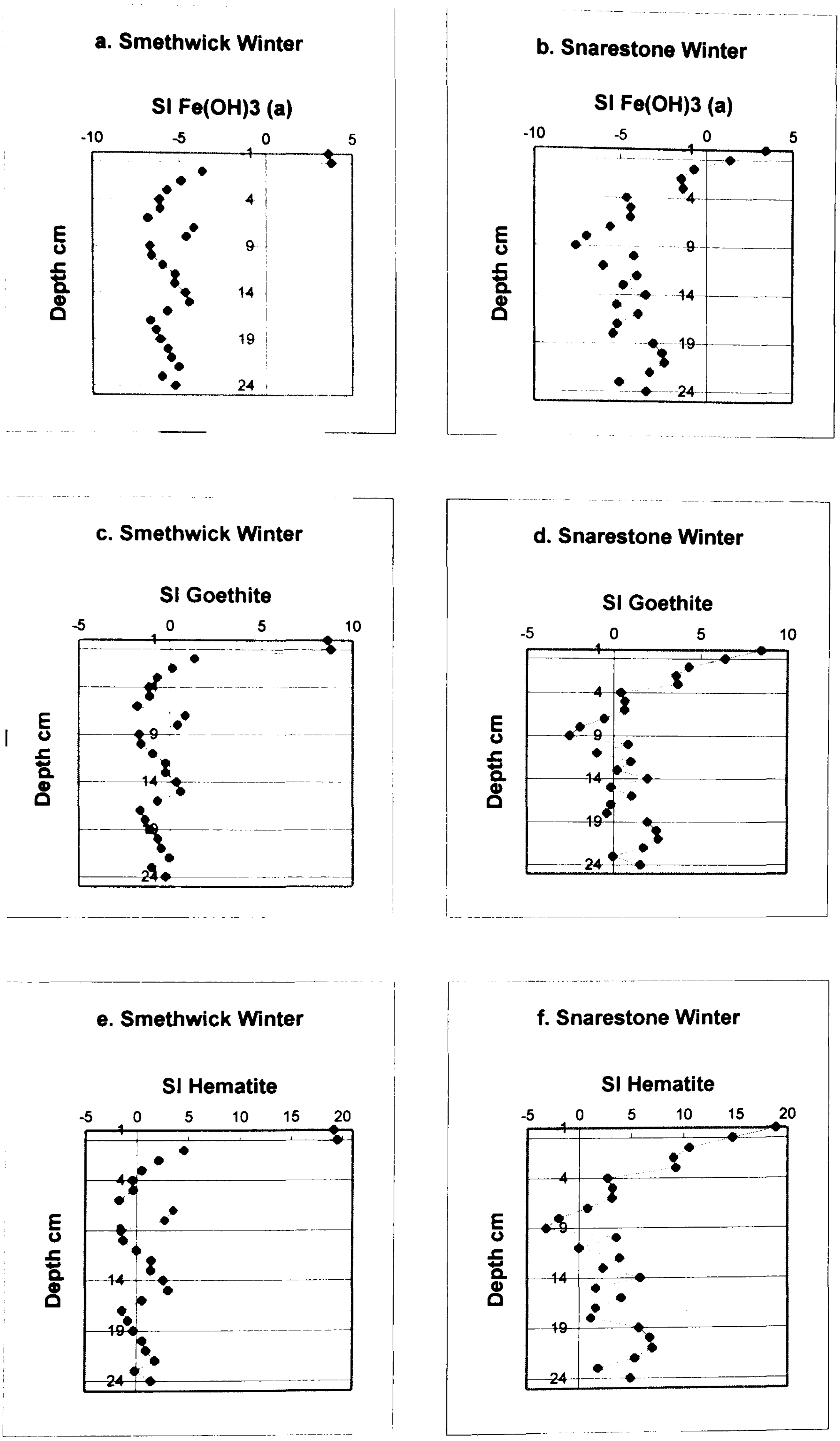


Figure 5.15a-f: Saturation indices for iron oxides in Smethwick and Snarestone porewaters

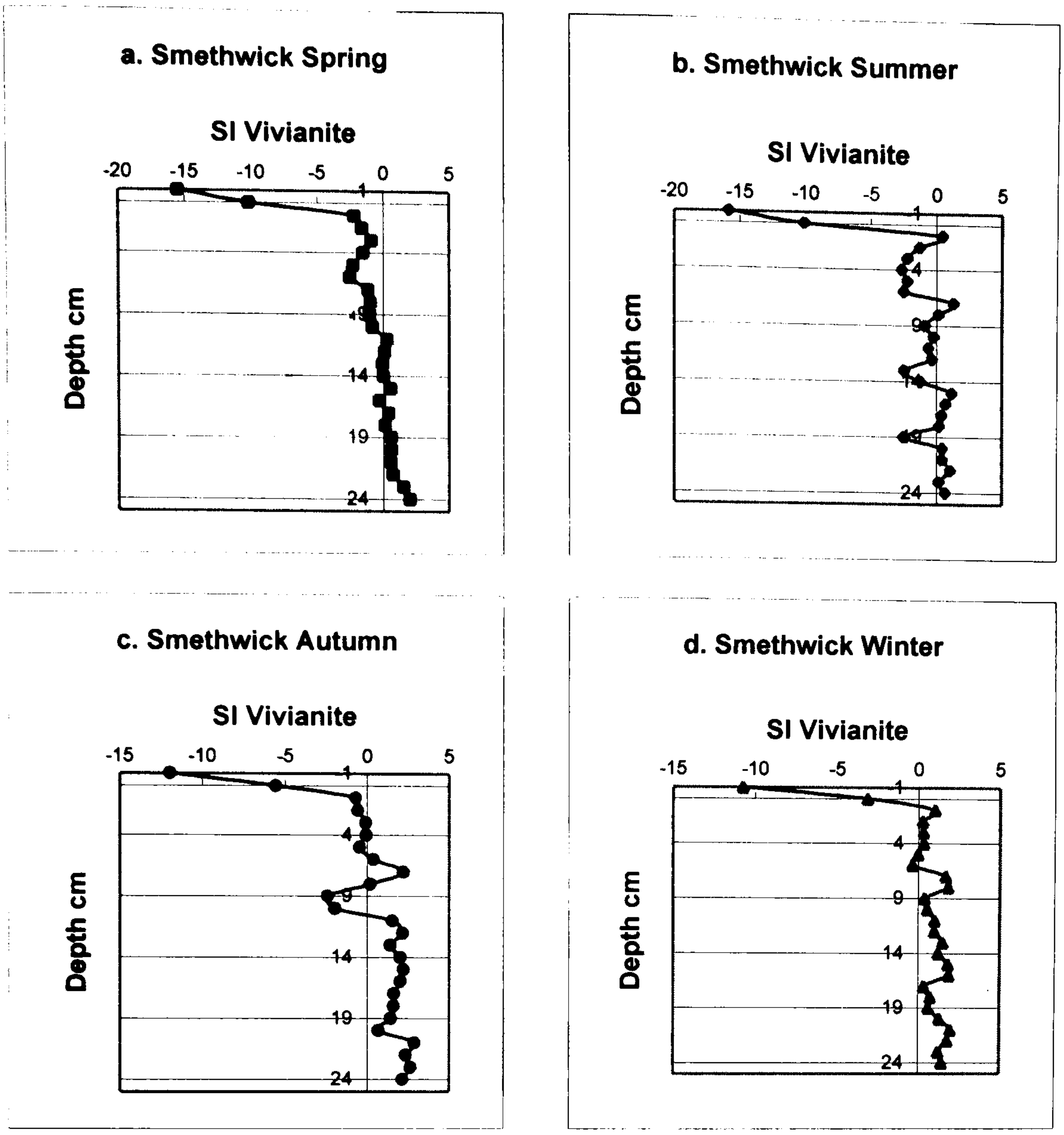


Figure 5.16a-d: Saturation indices for Vivianite in Smethwick porewaters

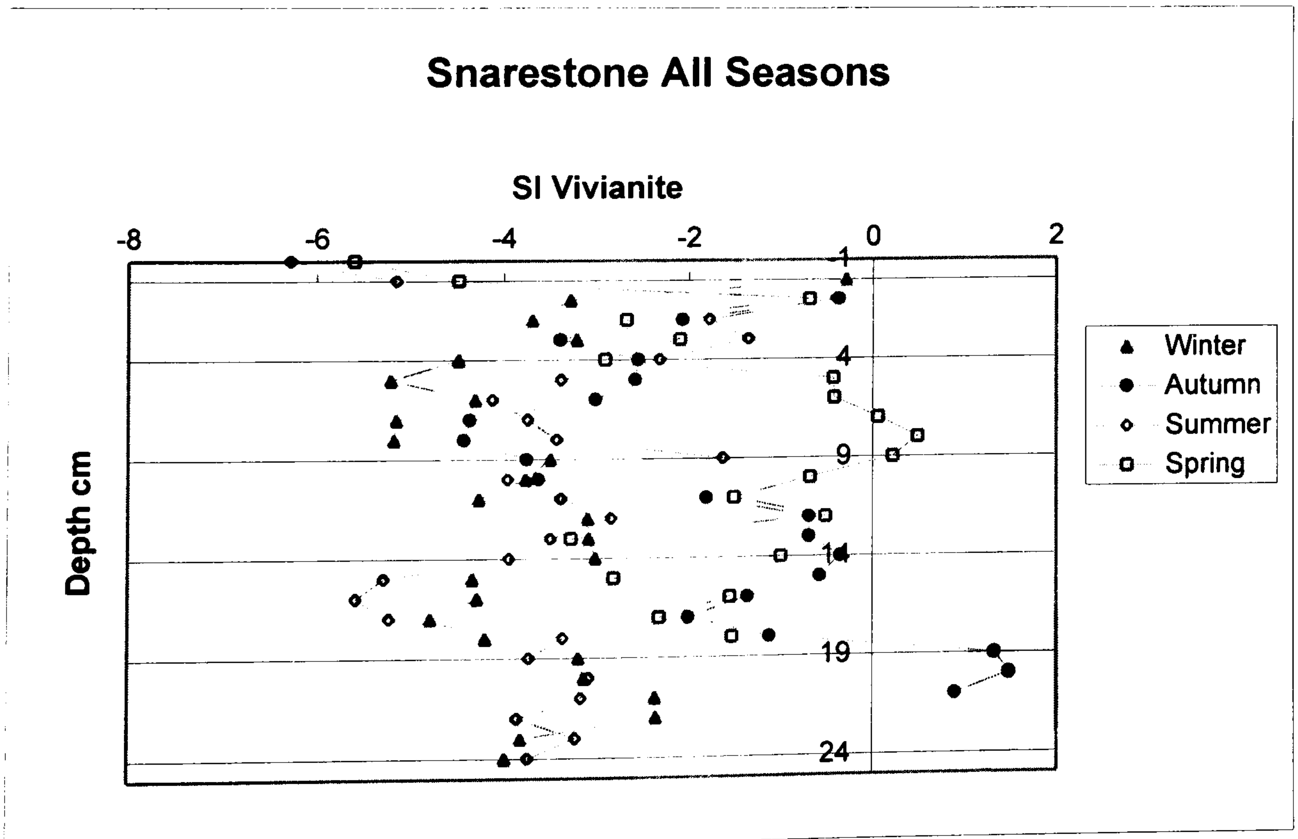
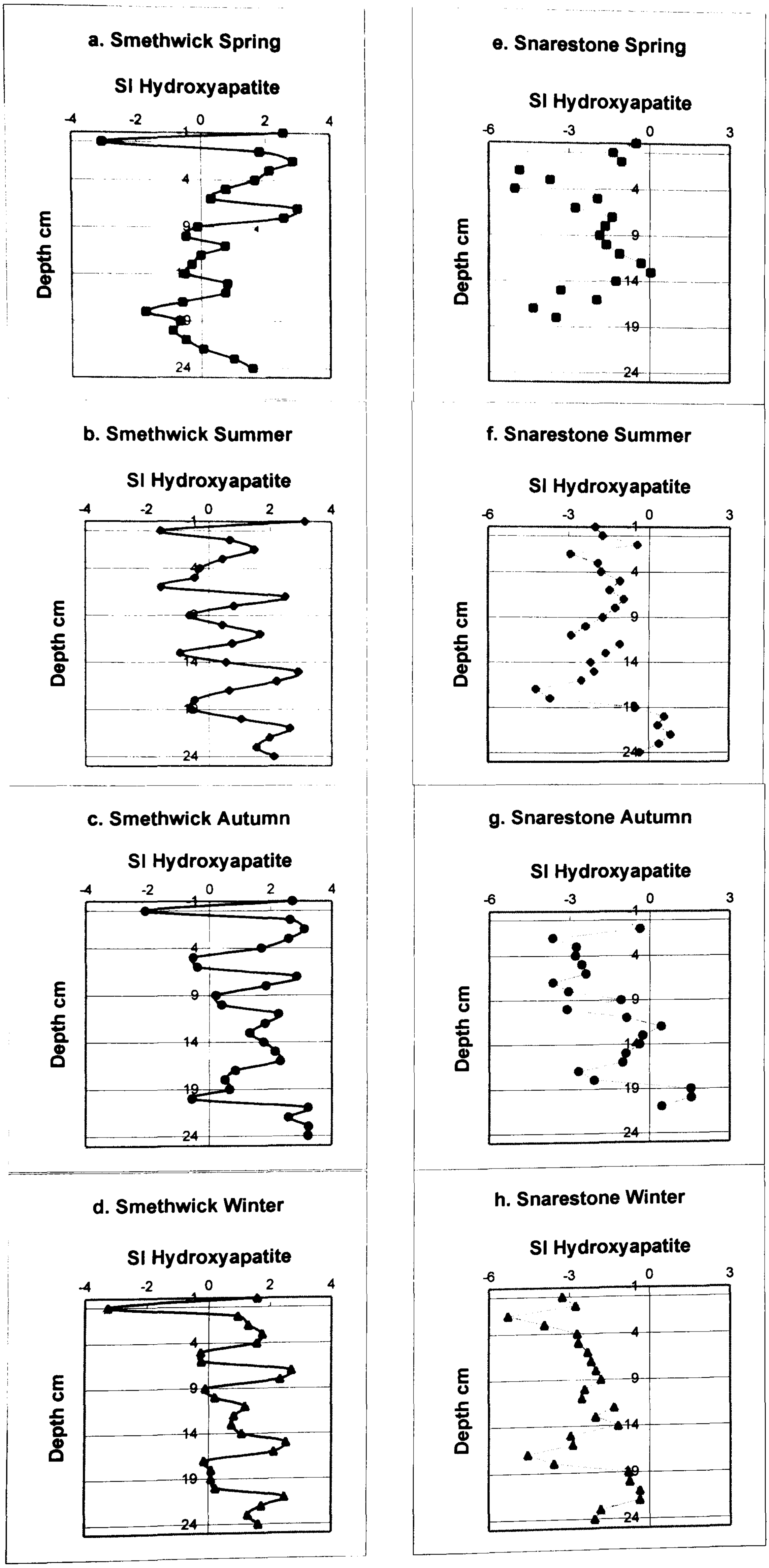


Figure 5.17: Saturation indices for Vivianite in Snarestone porewaters



a. Smethwick Spring

b. Smethwick Summer

c. Smethwick Autumn

d. Smethwick Winter

e. Snarestone Spring

f. Snarestone Summer

g. Snarestone Autumn

h. Snarestone Winter

Figure 5.18a-h: Saturation Indices for hydroxyapatite in Smethwick and Snarestone porewaters

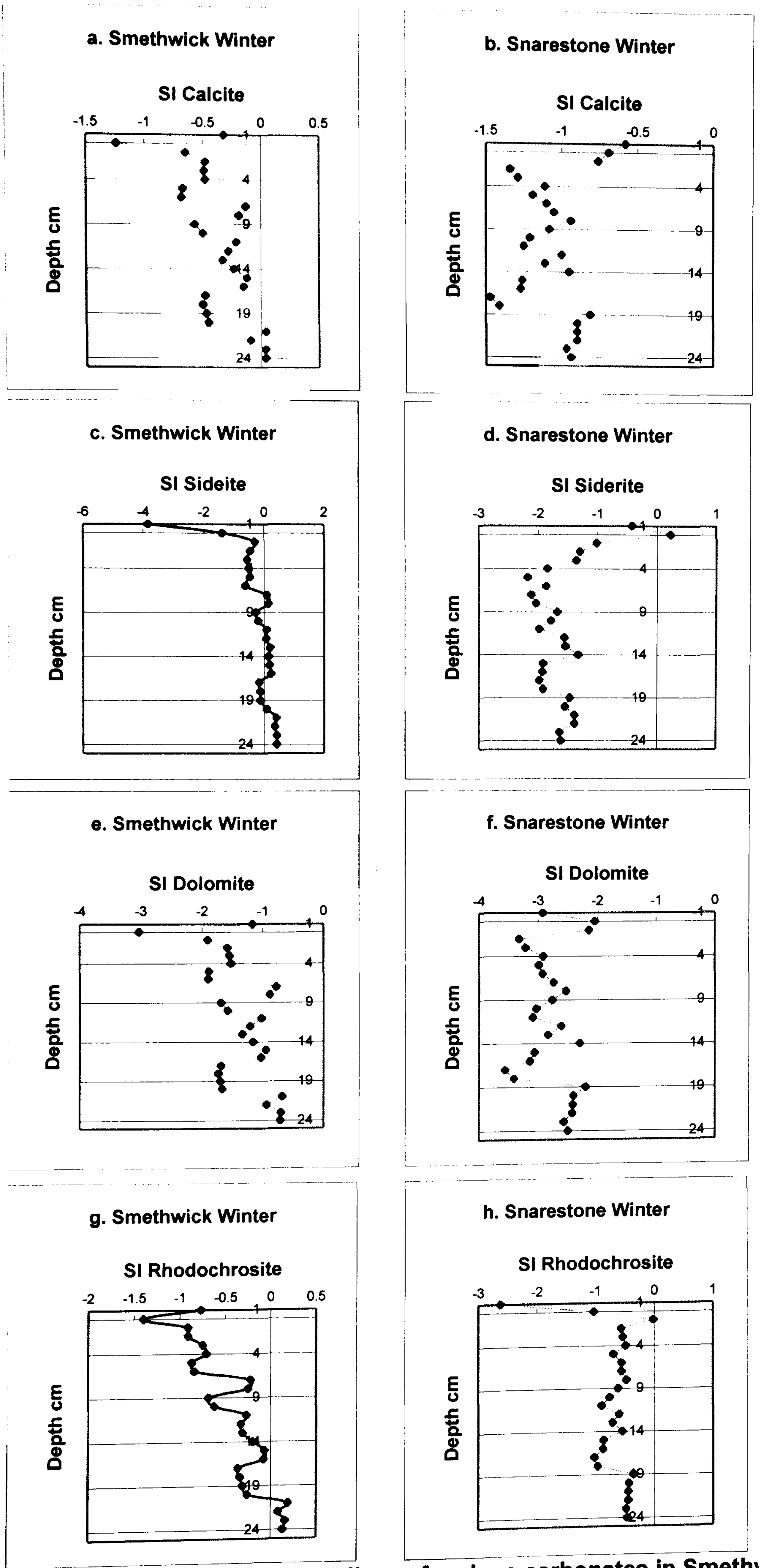


Figure 5.19 a-h: Saturation Indices of various carbonates in Smethwick and Snarestone porewaters

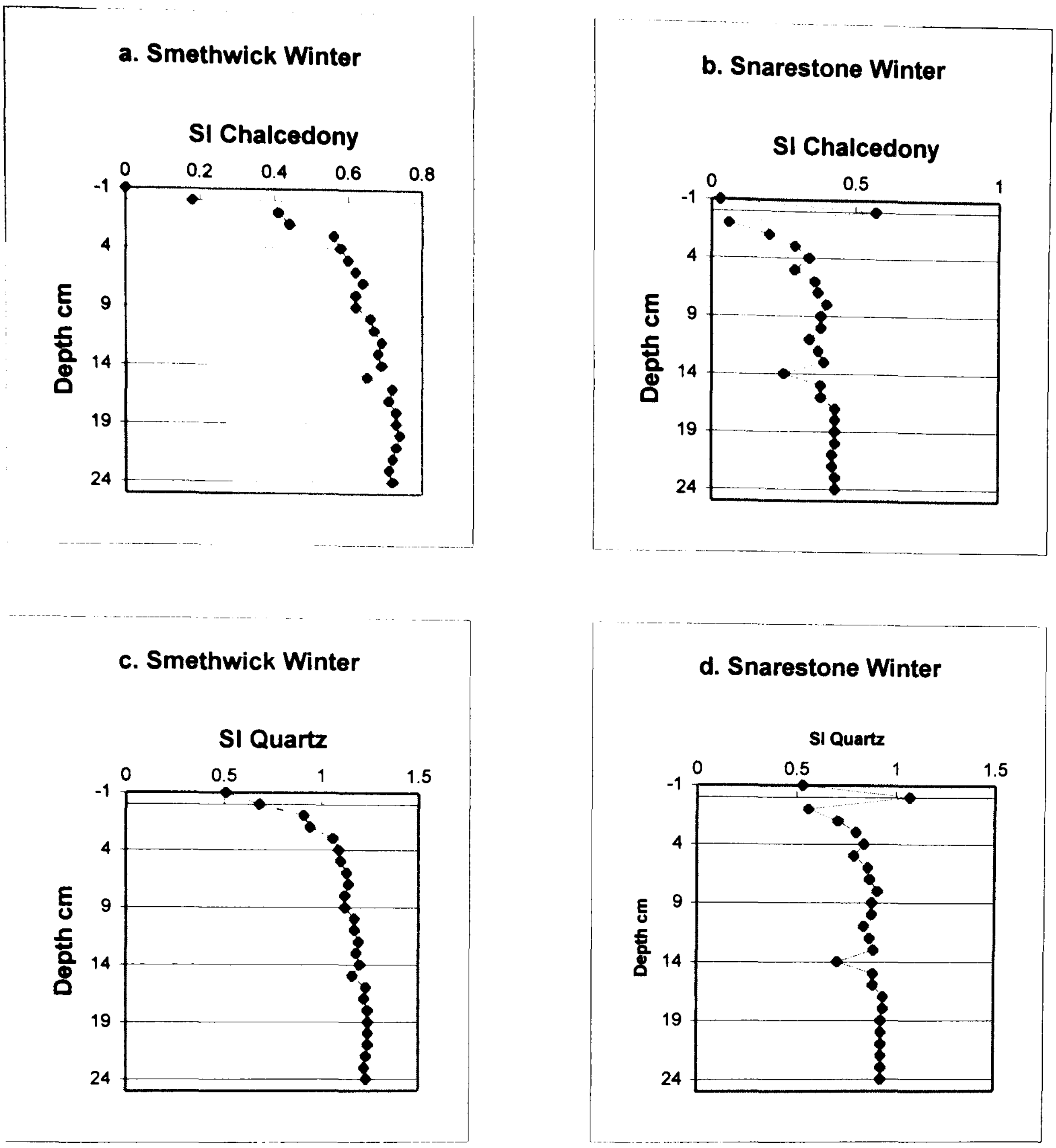


Figure 5.20a-d: Saturation Indices of silicates in the porewaters of and Snarestone

5.2.12. Zinc

It is known from petrographic evidence that Zn is present largely as an amorphous sulphide in Smethwick sediment and its low concentration in the porewaters can be accounted for by the limited solubility of sulphide minerals. However it is possible that during the spring and summer, Zn sulphides are oxidised following the disturbance of the sediment and some Zn goes into solution, accounting for the slightly elevated concentrations in the uppermost few centimetres of the spring profile. Amorphous Fe oxides will be precipitated in oxidising waters and can act as sink for Zn and prevent it from being lost to the overlying waters (Boult and Rebbeck, 1999). In the autumn and winter when the sediment becomes less disturbed and more reducing, Fe-oxides will be rapidly reduced, resulting in the loss of Zn to the overlying waters. These trends are consistent with those observed by Boult and Rebbeck, (1999) in the Manchester ship canal sediments. They observed that in non-aerated sediments with anoxic bottom waters (similar the conditions observed in the winter samples) Zn is lost from solution; whereas in aerated sediment (similar to boat disturbed sediment) the Zn concentration is low at the sediment surface. They assume that this is due to the trapping of Zn from solution by amorphous Fe oxides at the surface.

The elevated concentration of Zn, observed at the sediment water interface in the winter sample, might be the result of the ice cover on the canal at this time. Morfett et al., (1988) observed elevated Zn concentrations in interface water samples taken from the lake Esthwaite Water, during a period of ice cover. They suggest that the high concentration may result from a low rate of vertical transport. During periods of ice cover sediments will continue to accumulate settling particulate matter, and trace metals will probably be remobilized through decomposition and desorption at the sediment water interface. Most of the metal will be re-released to the water column because transport into the sediment by molecular diffusion is so slow. Usually the release of metals from the sediment is not apparent because it is diluted by the large body of overlying water, however during ice cover the mobility of Zn is reduced and the release of metal is observed as elevated bottom water concentrations.

5.3. Discussion

Given the nature of the data, particularly the fact that the anions, cations, pH and alkalinity were measured on different cores, it is dangerous to make too many deductions. What can be concluded however is that the porewater data is in broad agreement with the observed petrology and, in the case of the urban site, the data provides evidence of sediment disturbance.

Another striking feature is that the porewater profiles and associated diagenetic processes at the two sites are very different. The urban site is dominated by iron-phosphorus geochemistry whereas authigenesis in the rural site is dominated by iron-sulphur geochemistry.

5.3.1. Iron, Phosphorus and Sulphur Geochemistry

The main difference between Snarestone and Smethwick sediments can be summarised by their iron geochemistry and diagenesis, and can be attributed to their different iron, phosphorus and organic matter contents (chapter 4).

The domination of iron-sulphur geochemistry at Snarestone is typical of sulfidic sediments described by Berner (1981) in which sulphate reduction begins beneath the sediment water interface. The sulphide produced then reacts with Fe^{2+}, liberated by Fe^{3+} reduction (Lovely, 1991), or directly with detrital Fe oxide minerals initially to form iron-monosulphides i.e. film coated sulphides. In the presence of excess H_2S in the zone of sulphate reduction, iron monosulphides are converted to pyrite with depth by the addition of S (Rickard and Luther III, 1997). This is consistent with a tendency for protoframboids to be smaller than framboids, indicating that the larger diameter framboids formed earlier and therefore have had longer to develop. From the absence of vivianite and siderite in this sediment, and their under-saturation in the porewaters, it would appear that during the exhaustion of sulphate from the porewaters, all of the reactive Fe in the sediment is locked up as pyrite. The exhaustion of sulphate from the Snarestone porewaters corresponds to the depth at which the organic matter content of the sediment falls to a constant value of ~1% and the Eh of the porewaters reaches a constant value of close to 0V. This suggests that the remaining organic matter might be of a refractory nature (coal), and therefore methanogenesis and the reduction of less reactive Fe minerals such as goethite could be prevented by the lack of the sediment's principal reducing agent, organic matter. This is consistent with the absence of any notable gas bubbles in the anoxic section of the core, which might indicate methanogenesis was occurring, and other secondary Fe minerals such as vivianite and siderite which are associated with methanogenic zones in sediments (Berner, 1981). Therefore it would appear that the rate of accumulation of decomposable organic matter in Snarestone sediment is such that it does not outstrip the diffusive supply of sulphate to the sediment porewaters from the overlying canal water.

At Smethwick the pattern of diagenesis marked out by both porewater chemistry profiles and the authigenic mineral assemblages do not fit into any previously observed conceptual models of diagenesis (Berner, 1981; Froelich et al., 1979). The main discrepancy is the occurrence of vivianite at the sediment surface, suggesting that it is precipitated simultaneously with iron sulphides, which is contrary to a general assumption that vivianite does not precipitate until all the sulphate is exhausted from the porewaters (Berner, 1981). These observations imply that Fe^{2+} is being supplied to the porewater by Fe^{3+} reduction simultaneously with, and at a rate that exceeds, the supply of sulphide to the sediment by sulphate reduction. The concurrent release of phosphate as a waste product of the oxidation of organic matter, and from the reduction of iron oxides, appears to result in the saturation and precipitation of vivianite at the sediment water interface in the non-disturbed conditions of the winter sample. The increase in Fe concentration in the porewaters with depth suggests Fe reduction is also occurring simultaneously with methanogenesis in this sediment, following the exhaustion of sulphate from the porewaters, resulting in the continued saturation of vivianite throughout the profile.

The simultaneous occurrence of Fe^{3+} reduction with SO_4^{2-} reduction at the sediment surface and with methanogenesis at depth that is apparently occurring at Smethwick is in contrast to a general assumption that the processes of organic matter oxidation occur in a vertically separated sequence (Froelich et al., 1979). Froelich *et al* (1979) assumed that the different terminal electron accepting processes proceed from the reaction with the highest energy yield to that with the lowest (Table 5.2). The separation of these processes results from the competition of the bacteria that catalyse them. This is because the bacterial metabolic process that produces the greatest free energy will be at a competitive advantage and it will dominate the consumption of suitable organic matter until the supply of its oxidant is exhausted, at which stage it will be superseded by the next most efficient process (Coleman, 1985). Therefore the simultaneous reduction of Fe^{3+} with SO_4^{2-} reduction in the uppermost few centimetres of the sediment, and with methanogenesis at depth, would not be expected. However it has been noted previously in studies of freshwater lake and canal sediment (Boyd et al., 1999; Emerson, 1976; Wersin et al., 1991), in an aquifer (Jakobsen and Postma, 1999) and in salt marsh sediments (Coleman et al., 1993).

Lovley, (1991) states that "the different processes of organic matter oxidation will be separated in space or time or both in stable sedimentary environments, in which there is little sediment mixing and the rates of organic inputs are not excessively high". At Smethwick the sediment cannot be described in this way because it has received excessive organic matter from combined sewer overflows and is periodically mixed by boat traffic. It is most probable that these factors, coupled with the high Fe content of the sediment, have resulted in the pattern of diagenesis observed here, which appears to be dominated by Fe reduction throughout the profile. An alternative explanation is therefore required to interpret the diagenesis of Fe in Smethwick sediment.

Postma and Jakobsen (1996) suggest that the kinetics of the overall reactions between the terminal electron accepting processes (TEAP's) of organic matter oxidation cannot be predicted by their overall energy yield. This is because their rate is apparently controlled by the initial fermentation of organic matter, which produces H_2, acetate and formate that are subsequently consumed by the different TEAP's. Therefore the overall system could be described as a partial equilibrium process, where fermentation determines the overall rate, while TEAP's and their reaction products approach equilibrium. Using chemical equilibrium as an argument Postma and Jakobsen (1996) show that the simultaneous reduction of Fe^{3+} and SO_4^{2-} can occur in both Fe and S rich sediments if a wide range of Fe-oxides are present in the sediment. They find that iron oxide reduction is only energetically favourable to sulphate reduction with respect to the least stable iron oxides. These findings are consistent with the saturation indices for Fe oxides in the Smethwick sediment that show increasingly resistant oxides progressively becoming under-saturated with increasing depth (Figures 5.15 a, c and e).

Microbiological investigations of sediment diagenesis have found that the sequence by which organic matter is oxidised is affected by the concentration of the products of fermentation (H_2, acetate and formate) in the porewaters (Lovley and Goodwin, 1988; Lovley and Phillips, 1987). Although the concentrations of organic acids and H_2 have not been analysed in this investigation, the high organic matter content of the Smethwick sediment would imply that their supply to the sediment is not limited. Lovley and Phillips, (1987) show that the reduction of amorphic iron (III) oxyhydroxide proceeds at the expense of sulphate reduction and methane production by out-competing sulphate reducers and methanogens for fermentation products. However in the presence of excess H_2 and acetate the sediment retained its potential for sulphate reduction and methanogenesis. Lovley and Goodwin, (1988) found that in steady state conditions the predominance of a TEAP can be characterised by the concentration of H_2 in the porewaters. This occurs through competitive exclusion, whereby the most electrochemically positive electron acceptor can maintain lower H_2 concentrations than organisms using electron acceptors, which yield less energy from H_2 oxidation. Jakobsen and Postma (1999) investigated the concentrations of H_2 in an aquifer in which iron and sulphate reduction were active. They found that when sulphate and iron reduction are vertically separated, the concentrations of H_2 fell within the characteristic ranges determined by Lovley and Goodwin (1988). However, when they are proceeding simultaneously, the concentration of H_2 was found to be close to the maximum value for iron reduction and the minimum for sulphate reduction. An aquifer is very different to the organic and metal rich sediment at Smethwick, and therefore direct comparison of these results is highly speculative. However, if the rate at which fermentation products are supplied to the Smethwick porewaters exceeds the rate at which Fe reducing bacteria consume them, they will remain in the porewater at a level at which sulphate reduction can also proceed.

It is not possible to determine what is controlling the organic matter diagenesis in Smethwick sediment, but it is clear that high concentration of both organic matter and Fe in the sediment is causing the unusual pattern seen. From the predominance of iron phosphorus geochemistry in this sediment, it is clear that Fe reduction is the principal process by which organic matter is oxidised. The abundance of Fe sulphides in the sediment is evidence that sulphate reduction is also an important process, however the limited occurrence of pyrite in the sediment provides evidence that sulphide is rarely in excess of Fe^{2+} in the porewaters.

The consequence of the predominance of Fe reduction in organic matter diagenesis, and elevated phosphorous concentration resulting from anthropogenic sewage contamination, is the abundance of vivianite in the sediment. Vivianite was found to be close to equilibrium throughout the sediment profile, although was subject to seasonal variations in its stability, apparently caused by boat traffic disturbance of the sediment. Other workers suggest that concentrations of PO_4^{3-} in porewaters, produced by the diagenesis of organic matter, are governed by phosphate mineral equilibria, in particular vivianite (Emerson and Widmer, 1978; Mayer et al., 1999; Nriagu and Dell, 1974; Troup et al., 1974; Wersin et al., 1991). The absence of the more thermodynamically stable hydroxyapatite from the sediment, and the large fluctuations in its saturation index with depth, suggest that vivianite is controlling the concentration of PO_4^{3-} in the Smethwick porewaters. Siderite also is over-saturated in the porewaters but not common in the sediment. The absence of both hydroxyapatite and siderite in lake sediments is commonly attributed to their slow reaction kinetics or nucleation problems (Emerson and Widmer, 1978; Nriagu and Dell, 1974; Wersin et al., 1991). The over-saturation of the porewaters with respect to pure mineral phases may also be explained by the fact that thermodynamic calculations use solubility constants determined on pure phases in a laboratory. Sediment porewaters are complex mixtures and precipitated authigenic phases are likely to be chemically mixed, with their solubilites being different to those of pure phases. Another factor, resulting in the calculation of the over-saturation of these minerals, might be the over estimation of Fe available for inorganic precipitation, by ignoring the possibility that Fe may be organically bound in the porewaters and thus not available (Mayer et al., 1999).

It is clear from the observed seasonal variation in the profiles of Fe in Smethwick porewaters that the disturbance of the sediment by boat traffic is affecting the solid phase equilibria of certain minerals in the uppermost 10cm of the sediment. The absence of a full set of Eh data precludes the determination of the effect of this disturbance upon the redox conditions and iron oxide equilibria in the sediment. However the deeper penetration of sulphate and fluctuations to the Fe profile suggest that some oxidation of ferrous iron might be occurring and causing changes to the stability of reduced iron authigenic phases, most notably vivianite.

5.3.1.1. Dissolution of Vivianite in Smethwick Sediments

One of the most interesting petrological textures in the Smethwick sediment was that of etched vivianite grains that apparently became more common with depth. Consideration of the saturation index for vivianite revealed an intermittent variation in its stability, resulting from the sediment's disturbance by boat traffic. This suggests that in the relatively undisturbed winter sediment, vivianite is close to equilibrium and will precipitate throughout the sediment profile, whereas in the spring and summer, when sediment disturbance is at a maxima, vivianite is under-saturated at the sediment surface, and may begin to dissolve to re-establish equilibrium concentrations. When winter conditions return, etched grains might be preserved in the sediment alongside pristine grains, as was observed.

Other factors may also be influencing the stability of vivianite in the sediment. Figure 5.21 shows the stability relationships for vivianite in the Smethwick sediment. From this it is clear that at Fe^{2+} activities of $10^{-5.0}$ and HPO_4^{2-} activities of $10^{-4.5}$ the pH at which vivianite will begin to dissolve is 6.3. This is just beneath the pH recorded in the sediment (Figure 5.12b), and the buffering of pH by vivianite could account for its dissolution if the pH periodically falls beneath that which was measured. However, it is very unlikely that this would occur, as the pH of most sub-aqueous sediments rarely falls outside the range of 6.5-7.5 (Berner, (1981).

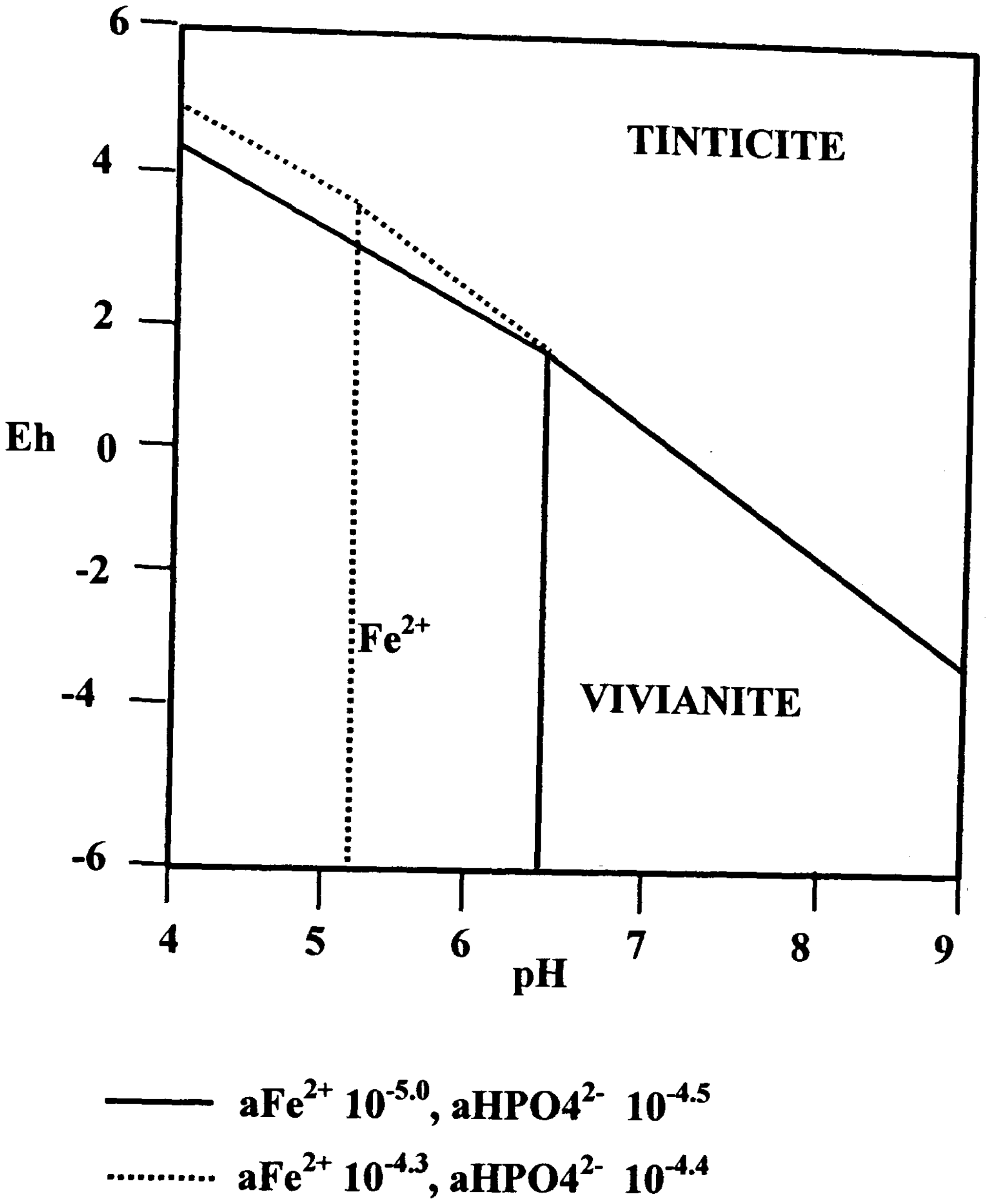


Figure 5.21: Stability relationships among ferric and ferrous phosphates, calculated from conditions in Smethwick sediment

Another factor, which might help to explain the occurrence of pristine and etched vivianite grains within the same horizons in the sediment, is the existence of microniches. The porewater profiles for this investigation were each composed from 24 samples of porewater extruded from a disk of sediment 1cm deep and 63mm in diameter, giving an average value. The assumptions made about sediment diagenesis from these profiles assume that processes are occurring in one dimension, as a result of horizontal and vertical diffusion. Harper et al. (1999) and Shuttleworth et al. (1999) have investigated porewater profiles on a 1mm scale in freshwater lake sediments using a new diffusive equilibrium in thin films technique (DET). They observed the redox zonation similar to that described in Table 5.2, on a fine scale, however they found that the reactions do not occur with lateral uniformity. They found quite different vertical profiles measured only 3mm apart on a horizontal axis, and suggest that microniches may play a significant role in metal remobilization. This suggests that sediments are not homogenous and small heterogeneties within the Smethwick sediment, set up by microniche reactions, perhaps in response to a localised concentration of organic matter, may explain the localised occurrence of vivianite dissolution.

5.3.2. Are the sediments a source of contamination to the waters?

The abundance of authigenic phases in the sediments confirms their importance as sinks for metals, and at Smethwick for the nutrient phosphorus. The sharp gradients of some porewater profiles at the sediment water interface, will result in upward diffusion set up by concentration gradients, and transport of ions in solution from the porewater to the water column by diffusion and advection and the resuspension of the sediment (Mayer et al., 1999). Of the ions in solution it is Zn and PO_4^{3-} that are most likely to result in deleterious effects to water quality upon release to the overlying waters, and their profiles in Smethwick porewaters suggest that they are being released from the sediment.

Phosphate is released to Smethwick porewaters in high concentration through solubilisation and decomposition, and a diffusion gradient is set up from the sediment to the PO_4^{3-} poor overlying water. The absence of a sharp gradient in the summer PO_4^{3-} profile (Figure 5.8b) may be the result of excessive loss of soluble P from the sediment, as a result of the mixing of canal and porewaters during sediment disturbance by boat traffic. Bray et al. (1973) found that following a catastrophic overturn of the top 20cm of Chesapeake Bay sediment, either by a storm surge, slumping or dredging, ten times the normal amount of PO_4^{3-} was liberated into the water column. No large increase in PO_4^{3-} concentration was observed in the summer water samples, although this may be the result of its rapid uptake from the water by the canal's biota and scavenging by Fe-oxides. Nriagu and Dell (1974) suggest that vivianite is controlling the PO_4^{3-} concentration in porewater and will therefore, indirectly, also influence its release to the overlying water, if P is being lost to the overlying waters in the summer at an increased rate, this would be supported by the dissolution of vivianite. If the sediment is releasing PO_4^{3-} to the overlying waters it may be maintaining the problems previously caused by P contamination of the canal from sewage overflow.

Zinc is also apparently being released to the canal water from the sediments, this is greatest in the winter when the near surface concentration is greatest and elevated concentrations are observed at the interface. It is not clear however, whether the lower gradients in the other seasons are the result of increased scavenging of Zn by Fe-oxides and sulphide at this time, (Emerson and Widmer, 1978; Mayer et al., 1999; Nriagu and Dell, 1974; Troup et al., 1974; Wersin et al., 1991) or because the mixing of the sediment and overlying waters has increased the rate at which Zn is diffused into the sediment and thus decreased the gradient.

Phosphate and Zn are being released from the sediment porewaters to the sediment by diffusion. It is unclear whether lower diffusion gradients in the summer are the result of the reduced mobility of these ions due to scavenging by amorphous Fe oxides or an increase in the rate of diffusion by sediment mixing, which has resulted in the dilution of the porewaters.

5.3.3. Summary

This discussion highlights that the two sites investigated have distinct diagenetic patterns. At the urban site, organic matter diagenesis is dominated by iron reduction and iron-phosphorus geochemistry; whereas diagenesis at the rural site is dominated by sulphate reduction and iron-sulphur geochemistry dominates the mineral authigenesis. The results also demonstrate that the disturbance of the sediment by boat traffic results in significant seasonal changes to the porewater chemistry of urban canal sediment, but does not have a noticeable effect upon that of rural canal sediment. In the concluding section, these observations are discussed in the broader context of sediment chemistry, in order to demonstrate the degree to which urban canal sediment is distinct from natural sediment.

6. Conclusions

This investigation has compared the geochemistry and petrology of two markedly different canal sediments, and interpreted the results through comparison with studies of natural sediment and the limited number of existing investigations of canal sediment. In this concluding section, the results of the investigation are taken and discussed as a means of illustrating whether anthropogenic material has made canal sediments distinct from other sediments. Comparisons are made with conceptual models of diagenesis in order to demonstrate the understanding of canal sediment diagenesis that has been gained from this investigation. In addition, the applicability of techniques and models, designed for use on natural sediments, to canal sediments is discussed.

6.1. Are canal sediments distinct from natural sediments?

Canals with their low water flow velocities, are essentially linear shallow freshwater lakes. However the physical conditions within the canal and the chemistry of the sediment produce features that make canal sediment distinct from lake sediment.

6.1.1. Differences in the Physical Environment

a. **Periodic sudden resuspension** of the sediment was observed to be caused by the passage of boat traffic; as a result the sediment chemistry is always in a state of change. This disturbance resulted in an increase in the depth to which sulphate penetrated into the urban sediment porewaters in the summer and spring, corresponding to the holiday period when traffic is greatest. The affects of the disturbance should in theory apply to both rural and urban sediment, however the results of this investigation did not reveal chemical evidence of disturbance in the rural sediment. This is apparently due to the difference in the organic matter loadings of the two sediments. In the urban sediment the high organic matter loading results in the rapid depletion of both oxygen and sulphate at or immediately beneath the sediment water interface. The lower organic matter content of the rural sediment results in a more gentle progression to anoxia and the presence of an oxic layer at the surface for much of the year. It has been shown that the mixing of oxygen and sulphate rich canal water with the sediments will cause a significant change to the surface porewater chemistry in the urban sediment. However, in the rural sediment it perhaps only subtly enhances the organic matter degradation processes that are occurring and this could not be confirmed by the results of this investigation. Natural lake sediments are unlikely to experience this degree of disturbance with such regularity, as they are generally deeper and not confined to narrow channels.

b. **Nature of input events:** The urban canal sediment investigated here differs markedly to natural sediments because it is subject to continuous inputs of anthropogenic material from road runoff, atmospheric fallout and licensed discharge. It has also received occasional inputs of large amounts of anthropogenic material, for example combined sewer overflows, which include domestic sewage, industrial effluent and road runoff. The rural canal is not affected by anthropogenic inputs and apparently receives natural material from within the canal system, such as weathering and erosion of the surrounding land and biological matter produced within the canal.

6.1.2. Bulk Chemical differences

The chemical investigation of solid canal sediment chemistry revealed that the different nature of sediment accumulation in the rural and urban canals has produced two chemically distinct sediments. The natural way in which the sediment has accumulated within the rural canal has produced a bulk chemistry of natural materials such as clay, sand, silt and organic matter, which is similar to that which is typically observed in natural sediments. The introduction of anthropogenic material to the urban canal has produced a sediment which is chemically and mineralogically distinct. The bulk urban sediment contains elevated metal and organic matter loadings, and a significant proportion of its particulate matter is of anthropogenic origin (e.g. slag, fly ash, metal turnings) and is therefore not typical of clastic material in natural sediments.

6.1.3. Differences in Authigenic Processes and the Applicability of Diagenetic Models

The petrological investigation of rural and urban canal sediment has shown that they have distinct authigenic mineralogies. The reduced iron phosphate, vivianite ($Fe_3(PO_4)_2.8H_2O$) is the most abundant authigenic mineral in urban sediment, as a result of its elevated organic matter and iron concentrations, while in the rural sediment pyrite (FeS_2) is predominant. Vivianite has also been observed in eutrophic lake sediments (Emerson and Widmer, 1978; Mayer et al., 1999; Nembrini et al., 1983; Nriagu and Dell, 1974), however certain distinctions can be made about its occurrence in urban canal sediment:

a. It occurs at the sediment water interface alongside iron and base metal sulphides.

b. Etched grains are observed close to freshly precipitated ones and this appears to be the result of a seasonal variation in its thermodynamic stability caused by the mixing of the sediment with the overlying waters.

The differences in the authigenic mineral assemblages of rural and urban canal sediment are the result of differences in their diagenetic paths. The porewater results show that in both rural and urban canal sediments, diagenetic organic matter oxidation reactions occur on a small vertical scale of a few centimetres. This is typical of what has been observed in freshwater lake sediments that are rich in organic matter (Davison et al., 1991; Wersin et al., 1991). It can be attributed to the relatively high rates of organic matter accumulation in freshwater sediment and low concentrations of dissolved sulphate, particularly when compared to sulphate rich marine sediment in which diagenetic processes are clearly separated over tens of centimetres (Froelich et al., 1979). In the rural sediment, the relatively low organic matter and iron loadings result in a diagenesis dominated by sulphate and iron reduction; the abundance of pyrite in this sediment is evidence that sulphate reduction is the predominant process. In the urban sediment the co-occurrence of vivianite and iron monosulphides implies that iron reduction is dominating the oxidation of organic matter in the sediment and occurring simultaneously with sulphate reduction. This is in contrast to traditional models of diagenesis (Berner, 1981; Froelich et al., 1979), which assume that iron reduction occurs prior to sulphate reduction. Other workers have found that iron reduction continues after the exhaustion of sulphate in organic rich and sulphate poor lake sediments (Emerson, 1976; Mayer et al., 1999; Wersin et al., 1991). Postma and Jakobsen, (1996) use a partial equilibrium approach to explain the segregation of iron and sulphate reduction and find that the dominant factor in determining which is most favourable is the stability of the iron oxides. The saturation indices of iron oxides in the urban canal sediment are consistent with this finding, illustrating that increasingly resistant oxides become progressively under-saturated with increasing depth.

Investigations of natural marine and freshwater sediments have shown that they tend towards steady state conditions (Emerson, 1976; Froelich et al., 1979; Lovely, 1991; Postma and Jakobsen, 1996; Wersin et al., 1991). Therefore conceptual models of sediment diagenesis are based on the assumption that steady state conditions apply. This investigation has revealed that rural canal sediment is very similar to natural sediment in this way. However the periodic physical disturbance and influx of material to urban canal sediment prevents the development of steady state conditions. As a result of this and the nature of the solid material, the diagenetic path observed in the urban sediment is quite distinct from that observed in natural sediments, and simple steady state models are inappropriate for its interpretation.

This study shows that significant short term changes are induced in the porewater chemistry by external factors such as sediment disturbance and not solely by diagenetic reactions. Most notably a peak in iron concentration observed a few centimetres beneath the sediment surface in the autumn and summer samples appears to mark an interface between the disturbed and undisturbed sediment. A similar peak in iron concentration has been observed in canal sediment which is subject to water column mixing by a helixor pump (Boyd et al., 1999), but no such peak has been observed in undisturbed natural sediments.

The seasonal variation in porewater geochemistry observed in the urban sediment is evidence that redox boundaries fluctuate as a result of the incorporation of oxidised canal water into the anoxic sediment. Most conceptual models assume that the organic matter oxidants oxygen and sulphate are supplied to the sediment by diffusion (Froelich et al., 1979), they therefore cannot account for the level of mixing observed in canal sediment. Numerical diagenetic models developed by Boudreau, (1996) can include limited biological disturbance at the sediment surface in diffusion models, but they can only be used if the rate of disturbance is small relative to the scale of observation. Such a model therefore cannot adequately describe canal sediment in which up to 10cm of the sediment is resuspended and mixed instantaneously. Steady state models can be used to interpret canal sediment diagenesis in undisturbed conditions. However, it is important to understand the effects of short term changes to canal sediment diagenesis, if the threat such changes pose to water quality are to be understood.

The predominance of iron reduction is widely observed in natural freshwater sediments and the work of Lovely, (1991) and Postma and Jakobsen, (1996) demonstrate both microbiological and thermodynamic mechanisms by which it can take place. While it is encouraging that the equilibrium processes occurring in the sediment can be described in this way, further work is required if the effects of sediment mixing and the diagenetic fates of anthropogenic material in sediments are to be fully understood.

6.1.4. Differences in the Interpretation of the Effects of Canal Sediments upon Water Quality

It is clear from this investigation that the addition of anthropogenic waste has had a very marked effect upon urban canal sediment petrology and geochemistry; however, comparison of the concentrations of dissolved ions in the canal water at both sites reveals the effects upon water quality are considerably less severe. It would appear that the predominance of iron reduction as a mechanism for the breakdown of organic matter results in the elevation of Fe^{2+} in the porewaters.

This reacts with the high levels of phosphorus in the sediment, locking it in a relatively insoluble form and possibly reducing the impact of eutrophication in the water column. In addition the contaminant heavy metals such as Zn are present in the waters at very low concentration. Petrographic evidence reveals that they are present in the sediment as authigenic sulphides. The only seasonal increase in Zn in canal waters occurs at the sediment water interface, in the winter. At this time the sediment was undisturbed due to ice cover, and the bottom waters of the canal appeared to be anoxic, it is therefore likely that the mobility of Zn at the sediment water interface was restricted. The absence of an increase in Zn in canal water in the summer sample does suggest that when oxidising waters are mixed with the sediment it does not result in an increase in the base metal concentration in the waters. This is perhaps because any metal released is rapidly adsorbed by Fe oxides formed at the same time, therefore any change to water chemistry will be short term and could subside within the sampling time of this investigation. It certainly would appear that the balance between the elevated concentration of organic matter and iron in sediment is preventing an excessive release of potential contaminants, which include contaminant metals and phosphate to the water column.

This study highlights the importance of investigating the processes operating within contaminated sediments through porewater geochemistry and the resultant petrology. Studies assessing the level to which a sediment is contaminated by examining the total metal concentrations (Bijlsma et al., 1996; Bromhead and Beckwith, 1994), or using a sequential extraction to determine speciation (Galvez-Cloutier and Dube, 1998; Perin et al., 1997; Zaggia and Zonta, 1997), might suggest that the urban sediment investigated here posed a greater threat to water quality than it in fact does.

6.1.5. Difficulties in the Application of Sequential Extraction Techniques Designed for use upon Natural Sediments to Canal Sediment

Sequential extractions are designed to investigate the resultant speciation of contaminant metals that have been incorporated into natural sediments. These methods give reasonable speciation results for the rural canal sediment, which is more analogous to natural sediment. However they perhaps cannot be expected to determine speciation within urban canal sediment which is comprised to a significant degree of anthropogenic material and in which metals such as Zn and Cu are present at highly elevated concentrations, precluding them from being considered as trace elements. The petrographic investigation of the application of sequential extraction schemes to urban canal sediment revealed that they do not yield meaningful speciation results for the following reasons:

1. Calcite is not completely removed from the sediment in the appropriate fraction.
2. Vivianite is extracted in both the carbonate and oxide fraction and therefore the interpretation of iron speciation in the sediment is impossible.
3. The presence of non-typical sediment components necessitate the investigation of sediment petrology prior to the application of a sequential extraction procedure

To adequately determine metal and phosphorus speciation in urban canal sediment an existing technique would have to be modified or a new one designed. This would perhaps improve the efficiency of the technique and the quality of the operationally defined speciation. However it would preclude comparison with investigations of speciation in natural sediment and this is an important reason for applying these techniques.

Speciation is considered important in understanding the environmental behaviour of metals in sediments (Bourg, 1995). This investigation has shown that it is of limited use for this purpose in a sediment that is largely comprised of anthropogenic material in the way that urban canal sediment is, because the response of anthropogenic waste to such procedures has not been comprehensively investigated.

6.3. Concluding Statement

This research has demonstrated that the physical environment of a canal and the nature of the material from which the sediment is accumulated, particularly in urban areas, has produced a sediment that is chemically and mineralogically distinct from natural sediments. Further research needs to be conducted if these distinctions are to be fully understood. In particular a greater understanding of diagenesis in canal sediment might improve models of diagenesis for use upon anthropogenic freshwater sediment and increase the understanding of sediment water interactions. This is important because urban canal sediment is composed almost exclusively of anthropogenic material, and therefore can provide greater insight into the behaviour of contaminants in natural sedimentary environments.

A number of recommendations for future work to improve the understanding of diagenesis in canal sediment are suggested:

1. The rates of organic matter oxidation reactions in the sediment should be determined as a means of assessing quantitatively their relative importance. This information could be used to quantify the level of iron and sulphur recycling in organic matter oxidation, which could increase the understanding of the role of sediment mixing in diagenesis.
2. The concentrations of organic acids should be analysed in the porewater in order to establish what control they are exerting upon the diagenetic processes in organic matter rich canal sediment
3. A high-resolution investigation of porewater chemistry, such as the gel probe method (Harper et al., 1999), could be undertaken to show both lateral and vertical concentration gradients. This would enable the role of processes occurring in microenvironments to be established and could help to explain the apparent simultaneous occurrence of normally separate processes. It would also improve the understanding of the effect of variations in the canal basin topography upon diagenesis.
4. A determination of the proportion of organic matter, in both rural and urban canal sediments, which is reactive, should also be undertaken. This is important because the nature of organic matter in canal sediment, which

includes anthropogenic sewage and coal particles, is not typical of natural sediment.

5. A further investigation of the diagenesis of anthropogenic components, for example the sulphidisation of native metals
6. An empirical and numerical investigation of the extent of sediment disturbance within the canal, and its effect on the sediment chemistry, could be undertaken in order to fully appreciate the degree to which canal sediment poses a threat to canal water quality.
7. In-situ analysis of porewater chemistry could be undertaken, using electrodes, to assess the short term changes to sediment chemistry imposed when the sediment is disturbed.

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Appendix 1: River Ecosystem Classification: Water Quality Objectives and Canal Water Quality at Sample Locations, Determined by The Environment Agency

Appendix 1.1. River Ecosystem Classification: Water Quality Objectives (EA, 1997)

The Surface Waters (River Ecosystem) (Classification) Regulations 1994, prescribe a system for classifying the quality of rivers and canals to provide the basis for setting statutory river water quality objectives (WQOs) under section 83 of the Water Resources Act 1991 in respect of individual stretches of water

The River Ecosystem classification comprises five hierarchical classes, in order of decreasing quality: RE1, RE2, RE3, RE4 and RE5. The criteria which samples of water are required to satisfy are set out in the table below.

River Ecosystem Class	Dissolved Oxygen % saturation 10 percentile	BOD* mg/l 90 percentile	Total Ammonia Mg/ N/I 95 percentile	Un-ionised Ammonia Mg/ N/I 95 percentile	pH lower limit as 5 percentile; upper limit as 95 percentile	Hardness mg/l Ca CO$_3$	Dissolved Copper µg/l 95 percentile	Dissolved Zinc µg/l 95 percentile
RE1	80	2.5	0.25	0.021	6.0-9.0	≤10	5	30
						>10 and ≤50	22	200
						>50 and ≤100	40	300
						>100	112	500
RE2	70	4.0	0.6	0.021	6.0-9.0	≤10	5	30
						>10 and ≤50	22	200
						>50 and ≤100	40	300
						>100	112	500
RE3	60	6.0	1.3	0.021	6.0-9.0	≤10	5	300
						>10 and ≤50	22	700
						>50 and ≤100	40	1000
						>100	112	2000
RE4	50	8.0	2.5	-	6.0-9.0	≤10	5	300
						>10 and ≤50	22	700
						>50 and ≤100	40	1000
						>100	112	2000
RE5	20	15.0	9.0	-	-	-	-	-

* as suppressed by adding allyl thio-urea

Appendix 1.2. Canal Water Quality at Sample Locations, Determined by The Environment Agency (EA, 1997)

Water Course	Stretch details	Grid References	Chemical* Grading 1990	Chemical* Grading 1997	River Ecosystem Class 1997	BOD mg/l	Total Ammonia Mg/ N/I	Dissolved Oxygen % saturation
Birmingham and Wolverhampton. Wolverhampton level. (Old Main Line)	Smethick Junction to Summit Tunnel (2km). At Brasshouse Lane	SP 029 890 to SP 012 898 At SP 019 889	F	E	RE5	7.47	2.74	101.6
Walsall Canal	Tame Valley to Birmingham Level Pudding Green Junction (2.2km) At Ryders Green Road	SO 997 935 to SO 989 906 At SO 983 917	F	F	RE4	23.39	2.37	69.03
Ashby Canal	Sutton Cheney Wharf to end at Snarestone (17.2km) At Market Bosworth	SP 4115 9940 to SK 3460 0995 At SK 392 032	D	D	RE2	3.93	0.05	90.26

*Chemical Grading for Rivers and Canals

Chemical Grading	Dissolved Oxygen % saturation 10 percentile	BOD (ATU) mg/l 90 percentile	Total Ammonia Mg/ N/I 95 percentile
A- Very good	80	2.5	0.25
B- Good	70	4.0	0.6
C- Fairly good	60	6.0	1.3
D- Fair	50	8.0	2.5
E- Poor	20	15.0	9.0
F- Bad	Does not meet requirements of Grade E in respect of 1 or more determinants		

The overall grade applied to a river or canal reach is determined by the worst of the three grades for the individual determinants.

Appendix 2: Sample Record

Appendix 2: Sampling Record

Spring Sample

Rural

Core number: JD08-Anions JD09-Cations
Date: 11 May 1998
pH: 7.00
Temperature: 14°C
Core description: Colour shows gradation from the interface downwards; from brown (oxic layer 10cm thick) through grey to black. Some gravel was visible at the top, possibly washed into the canal from the towpath. The surface is loose and floccular. Some streaking could be seen through the core, evidence of disturbance as a result of coring.
Comments on site: galvanised iron supporting the bank.
Date Cations Extruded: Monday 18th May, not ideal, from this core onwards always sampled on return from field, it is possible that this core became more anoxic over the week, changes in temperature might also affect results. On drying sample 15 was found to be sandy, sample 16 was lost when the centrifuge tube broke. This core contained a numerous chunks of coal at depth.
Date Anions Extruded: 11th May p.m. on return from field, actually analysed porewater for anions over Tuesday 12th to Wednesday the 13th May. On drying this core it was observed that the 16cm sample was very sandy in contrast to the rest of the core which was clay rich.

Urban

Core number: JD10A and JD10C (anions and cations)
Date: 19th May 1998
pH: 8.2
Temperature: Water: 17.5°C
Air: 16.5°C
Core description: Slightly lighter at surface, generally black in colour, a lot of gas is released when the core goes into the sediment.
Comments on site: Very sunny day, after three days of very warm weather. Boat went passed during sampling, and large clouds of sediment were released into the water column behind it.
Date Cations Extruded: 19th May 1998, 35cm long
Date Anions Extruded: 20th May 1998, 25cm long

Summer

These cores were also analysed at the BGS by CryoSEM in order to gain information on their mineralogy.

Rural

Core number: JD11A and JD11C
Date: 7th July 1998

pH: 7.13
Temperature: 16°C
Core description: Upper 3.5cm are red/brown (oxic) and floccular, 3.5-14cm grading to black, >13.5cm grey and contained gas bubbles. The water was green and contained macro-organisms.
Comments on site: The canal looks very green due to an apparent richness in algae. The banks are also covered in foliage from trees and shrubs. 3 Barges were moored along the bank (there are usually this many). A boat passed during sampling.
Date Cations Extruded: 7th July 1998, p.m. no problems, no really sandy samples observed on drying and crushing.
Date Anions Extruded: 8th July a.m. sample number 14 had no H-filter, and possible methanol contamination, sample 17 sandy, very little porewater. Had to calibrate using the previous calibration, as these samples were run in one day until 1am because the instrument had to be serviced the next day and there was no time to calibrate.

Urban

Core number: JD12A and JD12C
Date: 14th July 1998
pH: 7.58
Temperature: 15°C
Core description: Black at all depths, very soft and fine-grained (as usual), large amounts of gas released on coring. Fish recovered in one core, it was covered in lice and looked very unhealthy 7-8cm long.
Comments on site: Windy day, following very rainy weekend, overcast.
Date Cations Extruded: 14th July 1998 p.m. the water once extruded became muddy very easily. The pH of waters was measured using papers, at about 8.
Date Anions Extruded: 15th July, analysed over two days.

Sequential extraction carried out, but violent reaction on fraction 4, using H_2O_2 resulted in the loss of samples. An additional trip was therefore conducted for a study of sequential extractions by CryoSEM.

Urban

Core number: JD13U
Date: 18th August 1998
pH: 7.8
Temperature: 17°C
Core description: 30cm long, black for full length
Comments on site: Very sunny day, over the previous days it had been very wet.

Rural

Core number: JD13R
Date: 18th August 1998
pH: 7.47
Temperature: 18°C
Core description: Small oxic layer, getting darker with depth.

Comments on site: Very sunny day, over the previous days it had been very wet. A boat cruised passed during sampling

Autumn

Urban

Core number: JD14A and JD14C
Date: 6th October 1998
pH: 6.91
Temperature: 11°C
Core description: Uniformly black, gas released on sampling.
Comments on site: weather previous to rip had been wet. Construction work had obviously been carried out on the towpath, in usual sampling location (within 50m of the road) and the sediment obviously contained gravel, which hindered sampling, and was atypical. Because this was anomalous and apparently directly related to towpath work, samples were taken 50m further down the towpath.
Date Cations Extruded: 6th October 1998
Date Anions Extruded: 7th October 1998, analysed over the following two days.

Rural

Core number: JD15A-JD15C
Date: 13th October 1998
pH: Battery Flat
Temperature: 10°C
Air 12°C
Core description: Very difficult to get a sample due to high gravel content in sediment, less floccular material on the surface of the sediment, but oxic layer present, grading to darker anoxic sediment.
Comments on site: Previously wet weather and an unusually wet summer, 4-5 boats moored on canal bank, 2 moved off mooring during sampling.
Date Cations Extruded: 13th October 1998, large sand and clay lump which took up most of the core at 16-17cm. Some sandy samples form depths greater than 15 cm observed on drying. Sequential extraction carried out on this core.
Date Anions Extruded: 14th October 1998, contained large amounts of gravel, many samples had to be doubled up as the water just filled the pores again as soon as the samples were removed from the centrifuge.

Winter

Urban

Core number: JD16A (anions), JD16B (duplicate/Eh) and JD16C (cations)
Date: 7th December 1998
pH: 7.44
Temperature: 2°C

Core description: Black, as before.
Comments on site: 1cm of ice covering entire canal, the water was very clear, the corer could be seen very clearly to the sediment water interface. The surface of the ice looked very dirty and oily. 4 samples were taken 25m beyond pump house. An ice sample was taken in addition to the normal water sample and analysed in the same way.
Date Cations Extruded: 7th December 1998, sequential extraction conducted on this core.
Date Anions Extruded: 9th December, (10th and 11th December) analysis carried a day later than usual due to illness, and problems with IC.
Date Duplicate Extruded: 8th December 1998, Eh measured during extrusion had to stop for ½ an hour in the middle due to illness. I was unable to conduct anion analysis on the duplicate waters, due to time constraints. The cation porewater was not extruded until the 14th December. The sediment had been stored in the cabinet for a week, extruded into tubes. The cabinet is designed for bacterial studies, and therefore is insulated, and reaches temperatures of 30°C this will have affected porewater concentrations.

Rural

Core number: JD17A, B and C
Date: 11th January 1999, after Christmas holiday
pH: 7.67
Temperature: 3°C
Air 4°C
Core description: Clear anoxic layer up to 7cm thick, the water was cloudier than on previous trips. All cores were 30cm long, although some difficulty was experienced in sampling due to gravel in the sediment.
Comments on site: 0.5 – 1cm of ice covering the entire canal, no evidence of boat traffic having broken up the ice.
Date Cations Extruded: Extruded on 11th January, quite stony, very consolidated after 10cm, very little porewater, many samples from 10cm onwards had to be doubled up.
Date Anions Extruded: 12th January, 10 samples analysed on the first day, remainder on 13th. This core was also consolidated at depth, and again samples had to be doubled up.
Date Duplicate Extruded: 13th Eh measurements taken, this core was sandy at depth, and therefore there was very little porewater, samples 15-16 lost. Half the samples were analysed for cations and half for anions on the 14th January.

Carbonate Sampling Trip

Urban

Core number: JD18
Date: 22nd April 1999
pH: 7.76
Temperature: 10°C
Core description: Fig 2.4

Comments on site: Further down towpath than usual, sediment was only ~1m below the water surface and very easy to sample.
Date Extruded: 22nd April, begun analysis in the afternoon and completed it on 23rd April

Rural

Core number: JD19
Date: 22nd April 1999
pH: 7.31
Temperature: 11°C
Core description: Floccular layer on surface ~10cm thick and oxic
Comments on site: Oil on the surface, plant debris floating and very muddy water.
Date Extruded: 23rd April, begun analysis in the afternoon and completed it on 24th April

Appendix 3: The Mean Uncorrected Concentrations of Metals, Sulphur and Phosphorus in diluted Smethwick and Snarestone Porewaters, and the Relative Standard Deviation (RSD) of Two Duplicate Analyses

Appendix 3.1a: Uncorrected, mean concentration of Aluminium in diluted Smethwick porewaters (50% by volume), and relative standard deviation (RSD) from the mean of two duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
Water	**Concentration ppm**	0.032	0.104	0.09	0.019
	RSD%	15.47	2.72	25.14	66.99
Interface	**Concentration ppm**		0.099	0.156	0.48
	RSD%		2.14	1.36	2.36
1	**Concentration ppm**	0.018	0.011	0.025	0.044
	RSD%	39.28	38.57	5.66	19.28
2	**Concentration ppm**	0.084	0.028	2.905	0.028
	RSD%	1.68	0	0.85	7.58
3	**Concentration ppm**	0.232	0.035	0.065	0.041
	RSD%	0.3	6.06	13.05	10.35
4	**Concentration ppm**	0.03	0.058	0.073	0.028
	RSD%	11.79	23.16	5.81	60.61
5	**Concentration ppm**	0.018	0.039	0.175	0.025
	RSD%	23.57	18.13	2.02	11.31
6	**Concentration ppm**	0.043	0.056	0.067	0.03
	RSD%	19.73	11.36	9.5	16.5
7	**Concentration ppm**	0.005	0.106	0.037	0.021
	RSD%	98.99	2	5.73	20.2
8	**Concentration ppm**	0.011	0.041	0.11	0.028
	RSD%	0	6.9	1.93	35.36
9	**Concentration ppm**	0.01	0.098	0.049	0.018
	RSD%	7.07	3.61	11.54	27.5
10	**Concentration ppm**	0.016	0.04	0.237	-0.013
	RSD%	8.84	12.37	1.49	32.64
11	**Concentration ppm**	0.02	0.055	0.032	0.032
	RSD%	17.68	7.71	22.1	17.68
12	**Concentration ppm**	0.061	0.027	0.022	0.027
	RSD%	5.8	26.19	19.28	26.19
13	**Concentration ppm**	0.013	0.065	0.057	0.035
	RSD%	43.51	7.61	13.65	4.04
14	**Concentration ppm**	0.045	0.036	0.023	0.028
	RSD%	1.57	3.93		30.3
15	**Concentration ppm**	0.023	0.032	0.023	0.02
	RSD%	0	17.68		35.36
16	**Concentration ppm**	0.039	0.093	0.013	0.004
	RSD%	9.07	4.56	0	159.1
17	**Concentration ppm**	0.025	0.127	0.065	0.041
	RSD%	33.94	1.11	0	48.29
18	**Concentration ppm**	0.067	0.059	0.026	0.072
	RSD%	0	2.4	0	13.75
19	**Concentration ppm**	0.01	0.061	0.021	0.038
	RSD%	63.64	10.43	53.87	7.44
20	**Concentration ppm**	0.082	0.034	0	0.067
	RSD%	7.76	22.88	0	6.33
21	**Concentration ppm**	0.01	0.053	0	0.057
	RSD%	28.28	4	0	16.13
22	**Concentration ppm**	0.015	0.049	0	0.075
	RSD%	23.57	12.99	0	22.63
23	**Concentration ppm**	0.024	0.043	0.095	0.04
	RSD%	17.68	13.16	0	35.36
24	**Concentration ppm**	0.012	0.04	0	0.09
	RSD%	11.79	5.3	0	14.93

Detection limit: 0.063ppm

In the autumn sample the quantity of porewater extracted was insufficient for
2 analyses of every sample

Appendix 3.1b: Uncorrected, mean concentration of Aluminium in diluted Snarestone porewaters (50% by volume), and relative standard deviation (RSD) from the mean of two duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
Water	**Concentration ppm**	0.002	0.161	0.059	0.54
	RSD%	176.78	44.36	9.59	0.39
Interface	**Concentration ppm**		0.23	0.32	3.727
	RSD%		10.45	19.67	2.33
1	**Concentration ppm**	0.018	0.072	0.143	0.275
	RSD%	39.28	2.95	1.48	6.43
2	**Concentration ppm**	0.022	0.075	0.035	0.055
	RSD%	3.21	2.83	2.02	10.29
3	**Concentration ppm**	0.032	0.087	0	0.061
	RSD%	8.84	4.88	0	4.64
4	**Concentration ppm**	0.022	0.047	0.064	0.097
	RSD%	38.57	10.53	9.94	2.92
5	**Concentration ppm**	0.016	0.1	0.178	0.209
	RSD%	22.1	2.12	3.18	1.69
6	**Concentration ppm**	0.023	0.09	0	0.106
	RSD%	3.07	0.79	0	6.67
7	**Concentration ppm**	0.027	0.113	0	0.089
	RSD%	13.09	2.5	0	24.63
8	**Concentration ppm**	0.03	0.036	0	0.079
	RSD%	16.5	9.82	0	4.48
9	**Concentration ppm**	0.041	0.049	0.044	0.077
	RSD%	8.62	15.87	0	2.75
10	**Concentration ppm**	0.01	0.057	0.102	0.098
	RSD%	0	3.72	1.39	7.22
11	**Concentration ppm**	0.094	0.042	0.056	0.108
	RSD%	19.56	0	16.41	10.48
12	**Concentration ppm**	0.037	0.066	0.081	
	RSD%	7.64	4.29	10.48	
13	**Concentration ppm**	0.097	0.089	0.069	0.111
	RSD%	2.92	3.18	13.32	0.64
14	**Concentration ppm**	0.057	0.089	0.073	
	RSD%	3.72	0	1.94	
15	**Concentration ppm**	0.028	0.06	0	0.085
	RSD%	42.93	2.36	0	11.53
16	**Concentration ppm**	0.096	0.079	0.046	
	RSD%	21.36	7.16	0	
17	**Concentration ppm**	0.063	0.067		0.12
	RSD%	2.24	3.17		5.89
18	**Concentration ppm**	0.051	0.26		
	RSD%	4.16	10.61		
19	**Concentration ppm**		0.077		0.096
	RSD%		9.18		6.63
20	**Concentration ppm**		0.073		
	RSD%		4.84		
21	**Concentration ppm**		0.128		0.131
	RSD%		11.6		2.16
22	**Concentration ppm**		0.063		
	RSD%		6.73		
23	**Concentration ppm**		0.102		0.112
	RSD%		1.39		1.26
24	**Concentration ppm**		0.079		
	RSD%		1.79		

Detection limit: 0.063ppm

The sandy nature of the sediment at depth sometimes prevented the collection of a sufficient amount of porewater for analysis, in the winter consecutive sub-samples were mixed to enable analysis

Appendix 3.2a: Uncorrected, mean concentration of Silicon in diluted Smethwick porewaters (50% by volume), and relative standard deviation (RSD) from the mean of two duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
Water	Concentration ppm	0.082	0.361	1.481	2.04
	RSD%	9.49	0.2	0.33	0.35
Interface	Concentration ppm		0.282	2.396	3.03
	RSD%		1.25	0.09	0
1	Concentration ppm	3.698	2.433	5.365	5.15
	RSD%	1.47	1.34	1.11	1.92
2	Concentration ppm	6.139	5.838	7.466	5.51
	RSD%	1.14	0.29	0.91	0.26
3	Concentration ppm	7.236	8.256	8.735	7.28
	RSD%	0.51	0.45	0.45	0.87
4	Concentration ppm	7.755	9.399	9.197	7.74
	RSD%	1.12	0.64	1.83	0.18
5	Concentration ppm	8.556	9.677	9.421	7.97
	RSD%	0.6	1.83	0.74	1.24
6	Concentration ppm	9.041	10.061	9.933	8.43
	RSD%	1.23	0.48	0.82	2.18
7	Concentration ppm	9.941	10.02	9.554	8.73
	RSD%	0.18	0.43	0.69	0.73
8	Concentration ppm	9.694	9.798	9.527	8.32
	RSD%	0.58	0.4	0.26	1.02
9	Concentration ppm	9.818	9.889	10.318	8.33
	RSD%	0.47	0.41	0.94	0.68
10	Concentration ppm	10.372	10.071	9.29	9.26
	RSD%	0.05	1.65	0.43	0.69
11	Concentration ppm	10.399	10.09	9.732	9.36
	RSD%	0.35	0.39	0.54	0.68
12	Concentration ppm	10.631	10.182	10.679	9.78
	RSD%	0.05	1.4	0.45	0.29
13	Concentration ppm	10.221	10.318	10.225	9.6
	RSD%	0.08	0.53	0.55	1.18
14	Concentration ppm	10.355	10.8	9.426	9.96
	RSD%	0.68	0.31		1.63
15	Concentration ppm	10.227	10.52	9.341	9.08
	RSD%	1.13	0.54		0.78
16	Concentration ppm	10.593	10.651	10.42	10.54
	RSD%	0.19	0.48	1.2	0.27
17	Concentration ppm	10.567	10.435	11.176	10.44
	RSD%	0.66	1.33	0.1	1.35
18	Concentration ppm	10.764	11.474	11.864	10.92
	RSD%	0.66	0.78	0	0.26
19	Concentration ppm	10.897	10.863	11.289	10.8
	RSD%	0.33	0.44	0.69	0.33
20	Concentration ppm	10.836	11.528	11.524	11.01
	RSD%	0.63	0.08	0	1.09
21	Concentration ppm	11.238	11.091	12.769	10.91
	RSD%	0.41	0.87	0	0.45
22	Concentration ppm	10.958	11.177	12.061	10.56
	RSD%	0.82	0.34	0	0.07
23	Concentration ppm	11.218	11.121	11.745	10.37
	RSD%	0.12	0.72	0	0.27
24	Concentration ppm	11.207	10.614	0	10.62
	RSD%	0.59	0.42	0	1.33

Detection limit: 0.005ppm

In the autumn sample the quantity of porewater extracted was insufficient for 2 analyses of every sample

Appendix 3.2b: Uncorrected, mean concentration of Silicon in diluted Snarestone porewaters (50% by volume), and relative standard deviation (RSD) from the mean of two duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
Water	Concentration ppm	0.076	2.15	0.455	2.24
	RSD%	14.89	1.91	1.55	1.58
Interface	Concentration ppm		1.4	1.196	7.69
	RSD%		6.87	1.60	0.64
1	Concentration ppm	5.281	2.342	2.437	2.38
	RSD%	0.28	0.85	2.73	1.49
2	Concentration ppm	7.557	3.964	3.710	3.34
	RSD%	0.19	0.95	0.36	1.48
3	Concentration ppm	8.831	4.049	4.457	4.1
	RSD%	0.73	0.91	0	0.86
4	Concentration ppm	9.741	4.026	4.891	4.56
	RSD%	0.61	0.11	1.29	0.16
5	Concentration ppm	10.117	4.142	5.251	4.04
	RSD%	1.13	0.2	0.03	1.05
6	Concentration ppm	10.438	4.249	5.873	4.75
	RSD%	0.75	0.6	0	0.15
7	Concentration ppm	10.81	4.611	5.981	4.88
	RSD%	0.32	1.76	0	0.43
8	Concentration ppm	11.291	5.278	6.299	5.28
	RSD%	1.09	1.02	0	0
9	Concentration ppm	11.089	5.485	6.387	5.01
	RSD%	0.11	0.98	0	0.42
10	Concentration ppm	14.056	5.901	7.006	4.99
	RSD%	2.25	0.38	0.69	1.56
11	Concentration ppm	13.469	6.47	7.718	4.58
	RSD%	2.06	0.2	1.01	1.24
12	Concentration ppm	12.458	6.526	8.656	
	RSD%	0.97	1.47	0.52	
13	Concentration ppm	13.219	6.717	9.528	5.13
	RSD%	2.47	1.09	0.6	0.41
14	Concentration ppm	9.125	7.137	10.566	
	RSD%	0.67	0.92	0.98	
15	Concentration ppm	9.969	7.001	11.437	5.03
	RSD%	0.56	0.01	0	0.28
16	Concentration ppm	9.286	6.835	12.744	
	RSD%	1.17	0.11	0	
17	Concentration ppm	7.68	7.38	13.639	5.64
	RSD%	0.4	1.16	0	0.88
18	Concentration ppm	8.809	7.765	12.658	
	RSD%	0.45	1.78	0	
19	Concentration ppm		6.901	11.405	5.59
	RSD%		0.29	0	2.91
20	Concentration ppm		7.525	11.216	
	RSD%		0.86	0	
21	Concentration ppm		7.045	10.797	5.54
	RSD%		0.96	0	0.38
22	Concentration ppm		7.333		
	RSD%		0.83		
23	Concentration ppm		7.468		5.62
	RSD%		0.64		2.52
24	Concentration ppm		7.68		
	RSD%		0.3		

Detection limit: 0.005ppm

The sandy nature of the sediment at depth sometimes prevented the collection of a sufficient amount of porewater for analysis, in the winter consecutive sub-samples were mixed to enable analysis

Appendix 3.3a: Uncorrected, mean concentration of Calcium in diluted Smethwick porewaters (50% by volume), and relative standard deviation (RSD) from the mean of two duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
Water	Concentration ppm	63.369	57.312	54.012	46.861
	RSD%	0.83	0.08	0.2	0.4
Interface	Concentration ppm		58.717	57.209	50.209
	RSD%		0.79	0.55	0.2
1	Concentration ppm	53.64	59.491	60.27	56.727
	RSD%	0.06	1.01	0.87	0.62
2	Concentration ppm	50.842	62.036	62.791	57.017
	RSD%	0.21	0.78	0.69	1.2
3	Concentration ppm	50.005	60.617	71.749	79.024
	RSD%	0.13	0.64	1.62	0.24
4	Concentration ppm	47.789	58.375	77.469	86.105
	RSD%	1.2	0.43	0.45	0.36
5	Concentration ppm	47.742	56.982	82.627	89.859
	RSD%	0.58	0.6	1.48	1.66
6	Concentration ppm	46.415	60.934	96.835	91.394
	RSD%	1.32	1.36	1.2	0.8
7	Concentration ppm	48.19	61.345	91.911	93.663
	RSD%	1.31	1.04	0.15	0.78
8	Concentration ppm	44.501	66.74	92.939	97.143
	RSD%	0.36	0.23	0.66	0.37
9	Concentration ppm	41.67	69.437	96.018	98.42
	RSD%	0.04	0.55	0.24	0.39
10	Concentration ppm	41.764	70.445	84.128	110.105
	RSD%	0.64	0.63	1.77	1.07
11	Concentration ppm	40.821	71.979	89.335	103.235
	RSD%	1.65	1.9	1.76	1.18
12	Concentration ppm	40.275	76.727	91.913	108.176
	RSD%	1.09	1.12	0.58	1.26
13	Concentration ppm	40.402	79.266	86.735	105.226
	RSD%	0.64	1.05	1.05	1.28
14	Concentration ppm	40.371	84.779	74.178	115.049
	RSD%	0.02	0.24		0
15	Concentration ppm	39.053	86.219	74.909	106.051
	RSD%	1.52	0.44		0.56
16	Concentration ppm	40.929	86.236	85.252	110.129
	RSD%	0.57	0.58	0	1.03
17	Concentration ppm	40.101	84.619	94.848	113.205
	RSD%	0.54	0.36	0	1.53
18	Concentration ppm	41.591	92.341	0	121.388
	RSD%	0.03	0.18	0	0.69
19	Concentration ppm	43.647	86.934	93.343	126.641
	RSD%	1.15	0.94	0.5	0.15
20	Concentration ppm	43.602	97.925	0	126.074
	RSD%	0.87	0.51	0	1.44
21	Concentration ppm	44.854	95.843	0	120.277
	RSD%	0.96	2.3	0	0.52
22	Concentration ppm	44.795	99.643	0	121.216
	RSD%	1.3	0.53	0	0.31
23	Concentration ppm	46.755	102.867	0	128.827
	RSD%	0.47	1.12	0	0.51
24	Concentration ppm	46.659	101.578	0	131.728
	RSD%	0.47	1.26	0	0.52

Detection limit: 0.01ppm

In the autumn sample the quantity of porewater extracted was insufficient for 2 analyses of every sample

Appendix 3.3b: Uncorrected, mean concentration of Calcium in diluted Snarestone porewaters (50% by volume), and relative standard deviation (RSD) from the mean of two duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
Water	**Concentration ppm**	36.931	70.385	39.272	35.28
	RSD%	0.36	0.6	0.44	0.51
Interface	**Concentration ppm**		40.601	40.799	35.242
	RSD%		1.21	1.5	0.21
1	**Concentration ppm**	45.456	40.053	39.346	34.126
	RSD%	0.14	0.25	0.31	1.89
2	**Concentration ppm**	49.615	43.849	37.23	34.523
	RSD%	0.95	0.1	0.29	0.65
3	**Concentration ppm**	53.601	42.078	0	37.058
	RSD%	0.47	0.68	0	1.27
4	**Concentration ppm**	53.488	40.587	36.486	42.082
	RSD%	0.36	0.1	0.82	0.15
5	**Concentration ppm**	50.467	39.73	37.931	38.088
	RSD%	0.74	0.11	1.26	0.54
6	**Concentration ppm**	49.826	38.329	0	44.823
	RSD%	0.29	0.83	0	0.35
7	**Concentration ppm**	48.749	36.632	0	44.606
	RSD%	1.17	0.99	0	0
8	**Concentration ppm**	52.484	35.519	0	47.547
	RSD%	0.07	1.11	0	0.84
9	**Concentration ppm**	49.661	34.843	42.268	45.611
	RSD%	0.07	1.11	0	1.06
10	**Concentration ppm**	62.12	34.195	43.978	43.823
	RSD%	1.02	1.07	1.37	0.61
11	**Concentration ppm**	64.013	33.834	44.022	41.149
	RSD%	0.66	0.47	1.85	0.54
12	**Concentration ppm**	60.33	32.931	43.65	
	RSD%	0.86	0.32	0.45	
13	**Concentration ppm**	65.421	32.982	44.411	40.09
	RSD%	0.33	1.05	0.23	1.02
14	**Concentration ppm**	47.176	35.13	43.338	
	RSD%	0.81	0.29	0.63	
15	**Concentration ppm**	51.552	36.224	0	34.76
	RSD%	0.16	1.03	0	127.66
16	**Concentration ppm**	49.68	36.149	0	
	RSD%	0.16	1.13	0	
17	**Concentration ppm**	44.002	38.489	0	36.745
	RSD%	1.58	2.56	0	0.07
18	**Concentration ppm**	45.867	38.943	0	
	RSD%	1.16	0.83	0	
19	**Concentration ppm**		37.905	0	34.616
	RSD%		1.36	0	0.71
20	**Concentration ppm**		41.047	0	
	RSD%		1.1	0	
21	**Concentration ppm**		39.706	0	34.847
	RSD%		1.48	0	1.15
22	**Concentration ppm**		42.493		
	RSD%		1.73		
23	**Concentration ppm**		42.735		35.985
	RSD%		0.78		0.48
24	**Concentration ppm**		44.4		
	RSD%		0.36		

Detection limit: 0.01ppm

The sandy nature of the sediment at depth sometimes prevented the collection of a sufficient amount of porewater for analysis, in the winter consecutive sub-samples were mixed to enable analysis

Appendix 3.4a: Uncorrected, mean concentration of Manganese in diluted Smethwick porewaters (50% by volume), and relative standard deviation (RSD) from the mean of two duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
Water	**Concentration ppm**	0.038	0.015	0.017	0.047
	RSD%	14.89	0	0	13.54
Interface	**Concentration ppm**		-0.003	0.087	0.111
	RSD%		0	9.75	1.91
1	**Concentration ppm**	0.142	0.219	0.142	0.102
	RSD%	4.48	1.29	0.5	8.32
2	**Concentration ppm**	0.085	0.189	0.134	0.079
	RSD%	3.33	2.24	1.06	9.85
3	**Concentration ppm**	0.109	0.183	0.149	0.166
	RSD%	1.95	2.7	2.37	4.26
4	**Concentration ppm**	0.102	0.201	0.166	0.205
	RSD%	0	1.76	3.83	8.28
5	**Concentration ppm**	0.112	0.201	0.182	0.232
	RSD%	5.68	0.35	1.55	1.22
6	**Concentration ppm**	0.096	0.231	0.263	0.251
	RSD%	1.47	0	0.54	2.82
7	**Concentration ppm**	0.1	0.22	0.246	0.308
	RSD%	3.54	1.29	0.57	0.92
8	Concentration ppm	0.1	0.254	0.238	0.337
	RSD%	3.54	2.23	2.38	1.47
9	**Concentration ppm**	0.105	0.33	0.259	0.315
	RSD%	0.67	0.64	1.09	1.35
10	**Concentration ppm**	0.129	0.328	0.255	0.329
	RSD%	2.19	0	3.33	3.65
11	**Concentration ppm**	0.134	0.322	0.305	0.35
	RSD%	1.06	0.66	1.16	1.21
12	**Concentration ppm**	0.146	0.34	0.38	0.387
	RSD%	1.94	0.21	1.67	1.64
13	**Concentration ppm**	0.152	0.348	0.339	0.443
	RSD%	1.4	0.41	0.21	2.08
14	**Concentration ppm**	0.155	0.406	0.303	0.481
	RSD%	3.65	0.7		1.62
15	**Concentration ppm**	0.159	0.406	0.305	0.469
	RSD%	4.89	1.39		0.3
16	**Concentration ppm**	0.176	0.386	0.363	0.528
	RSD%	1.61	0.37	1.36	2.41
17	**Concentration ppm**	0.187	0.361	0.403	0.583
	RSD%	0.76	0.78	0.7	1.7
18	**Concentration ppm**	0.226	0.424	0.459	0.673
	RSD%	0.94	0.17	0	0.11
19	**Concentration ppm**	0.245	0.376	0.408	0.714
	RSD%	2.89	1.88	3.47	1.09
20	**Concentration ppm**	0.247	0.41	0.409	0.773
	RSD%	2.29	0.86	0	3.29
21	**Concentration ppm**	0.26	0.371	0.412	0.704
	RSD%	1.9	3.43	0	1.41
22	**Concentration ppm**	0.232	0.394	0.361	0.738
	RSD%	2.13	3.23	0	1.34
23	**Concentration ppm**	0.25	0.395	0.362	0.71
	RSD%	0.57	3.04	0	1.39
24	**Concentration ppm**	0.256	0.379	0	0.682
	RSD%	1.66	1.68	0	2.18

Detection limit: 0.0064ppm

In the autumn sample the quantity of porewater extracted was insufficient for 2 analyses of every sample

Appendix 3.4b: Uncorrected, mean concentration of Manganese in diluted Snarestone porewaters (50% by volume), and relative standard deviation (RSD) from the mean of two duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
Water	Concentration ppm	0.005	0.04	0.023	0.001
	RSD%	56.57	3.54	15.37	636.4
Interface	Concentration ppm		0.019	0.089	0.059
	RSD%		18.61	0.00	1.2
1	Concentration ppm	0.583	0.86	0.502	0.687
	RSD%	2.18	2.96	0.70	2.37
2	Concentration ppm	0.768	0.897	0.466	0.736
	RSD%	0.83	0.87	1.97	0.77
3	Concentration ppm	0.797	0.698	0.439	0.731
	RSD%	0	1.82	0	0.77
4	Concentration ppm	0.846	0.459	0.441	0.635
	RSD%	0.67	0.46	1.44	1.22
5	Concentration ppm	0.886	0.392	0.448	0.406
	RSD%	2.47	0.9	0.95	0.87
6	Concentration ppm	1.008	0.392	0.482	0.555
	RSD%	0.63	2.34	0	0.76
7	Concentration ppm	1.034	0.44	0.520	0.492
	RSD%	0.55	1.61	0	2.44
8	Concentration ppm	1.171	0.507	0.545	0.508
	RSD%	0.18	0.98	0	1.39
9	Concentration ppm	1.104	0.57	0.490	0.461
	RSD%	0.77	0.99	0	0.92
10	Concentration ppm	1.204	0.542	0.511	0.429
	RSD%	3.35	0.26	0.55	0.66
11	Concentration ppm	1.216	0.703	0.495	0.319
	RSD%	1.98	1.31	1	0.22
12	Concentration ppm	1.113	0.567	0.477	
	RSD%	0.19	0.62	2.52	
13	Concentration ppm	1.093	0.636	0.485	0.353
	RSD%	1.88	0.11	2.04	0
14	Concentration ppm	0.734	0.692	0.516	
	RSD%	2.31	1.23	0.69	
15	Concentration ppm	0.819	0.852	0.547	0.289
	RSD%	1.04	0.5	0	4.16
16	Concentration ppm	0.733	0.816	0.481	
	RSD%	0.96	2.08	0	
17	Concentration ppm	0.654	0.858	0.484	0.347
	RSD%	0.86	1.65	0	0.2
18	Concentration ppm	0.713	0.847	0.549	
	RSD%	1.69	0.25	0	
19	Concentration ppm		0.766	0.603	0.346
	RSD%		0.92	0	2.66
20	Concentration ppm		0.88	0.639	
	RSD%		0.72	0	
21	Concentration ppm		0.713	0.612	0.367
	RSD%		0.3	0	1.54
22	Concentration ppm		0.8		
	RSD%		0.44		
23	Concentration ppm		0.721		0.376
	RSD%		0.69		0.75
24	Concentration ppm		0.817		
	RSD%		0.17		

Detection limit: 0.0064ppm

The sandy nature of the sediment at depth sometimes prevented the collection of a sufficient amount of porewater for analysis, in the winter consecutive sub-samples were mixed to enable analysis

Appendix 3.5a: Uncorrected, mean concentration of Iron in diluted Smethwick porewaters (50% by volume), and relative standard deviation (RSD) from the from the mean of two duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
Water	**Concentration ppm**	0.111	0.035	0.265	0.105
	RSD%	2.55	2.02	0.27	2.02
Interface	**Concentration ppm**		0.032	0.501	0.967
	RSD%		4.42	1.55	2.19
1	**Concentration ppm**	0.085	1.136	0.156	0.949
	RSD%	3.33	2.8	6.8	0.52
2	**Concentration ppm**	0.077	0.217	0.165	0.495
	RSD%	6.43	1.96	0.43	0.57
3	**Concentration ppm**	0.205	0.159	0.322	0.559
	RSD%	0.34	1.78	2.64	3.16
4	Concentration ppm	0.128	0.176	0.559	0.657
	RSD%	1.1	1.61	1.64	0.32
5	Concentration ppm	0.107	0.227	1.183	1.182
	RSD%	1.32	0.93	1.61	0.72
6	Concentration ppm	0.098	0.324	2.494	0.902
	RSD%	0.72	3.27	1.11	0.31
7	Concentration ppm	0.11	1.083	2.467	1.34
	RSD%	1.93	0.98	0.2	2.01
8	Concentration ppm	0.139	1.095	0.835	1.79
	RSD%	1.53	1.29	0.59	1.78
9	Concentration ppm	0.404	0.878	0.236	1.682
	RSD%	3.15	0.24	0	2.23
10	Concentration ppm	0.57	0.897	0.265	1.876
	RSD%	0.37	1.97	2.94	0.9
11	Concentration ppm	0.814	0.411	1.819	1.75
	RSD%	0.78	1.72	1.09	0.04
12	Concentration ppm	0.938	0.825	3.657	2.101
	RSD%	0.53	0.69	1.74	1.45
13	Concentration ppm	0.967	0.388	2.407	3.067
	RSD%	1.83	2.55	1.23	0.09
14	Concentration ppm	1.168	0.52	1.476	2.384
	RSD%	0.48	0.27		1.19
15	Concentration ppm	0.94	1.11	1.454	1.854
	RSD%	1.05	1.21		0.38
16	Concentration ppm	0.535	1.077	2.474	2.308
	RSD%	0	1.84	0.17	0.34
17	Concentration ppm	1.471	1.499	3.635	1.949
	RSD%	0.87	0.99	1.32	1.23
18	Concentration ppm	2.127	2.495	4.129	2.498
	RSD%	0.9	0.82	0	0.23
19	Concentration ppm	1.872	0.296	3.352	2.405
	RSD%	0.08	0.48	1.48	0.71
20	Concentration ppm	2.167	1.534	3.421	3.743
	RSD%	0.59	0.32	0	1.11
21	Concentration ppm	2.263	0.847	3.657	2.519
	RSD%	0.12	0.25	0	0.28
22	Concentration ppm	1.837	1.868	3.129	2.993
	RSD%	0.62	1.78	0	0.4
23	Concentration ppm	2.337	1.273	2.945	2.71
	RSD%	0.91	0.06	0	0.47
24	Concentration ppm	2.552	1.379	2.056	2.775
	RSD%	0.53	0.46	0	0.38

Detection limit: 0.0035ppm

In the autumn sample the quantity of porewater extracted was insufficient for
2 analyses of every sample

Appendix 3.5b: Uncorrected, mean concentration of Iron in diluted Snarestone porewaters (50% by volume), and relative standard deviation (RSD) from the from the mean of two duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
Water	Concentration ppm	0.061	0.225	0.158	0.474
	RSD%	2.32	2.2	0.45	3.13
Interface	Concentration ppm		0.15	0.534	2.018
	RSD%		0	0.53	1.47
1	Concentration ppm	0.864	0.752	0.584	0.143
	RSD%	0.16	1.03	1.57	4.45
2	Concentration ppm	1.047	0.751	0.590	0.271
	RSD%	0.34	0.28	0.48	1.57
3	Concentration ppm	1.023	0.616	0.139	0.231
	RSD%	1.04	0	0	0.31
4	Concentration ppm	1.153	0.291	0.270	0.062
	RSD%	1.1	2.67	0.79	3.42
5	Concentration ppm	1.521	0.071	0.249	0.028
	RSD%	0.42	1	0.85	5.05
6	Concentration ppm	2.277	0.066	0.173	0.057
	RSD%	0.53	4.29	0	17.37
7	Concentration ppm	1.642	0.051	0.101	0.03
	RSD%	1.42	5.55	0	23.57
8	Concentration ppm	2.937	0.075	0.081	0.014
	RSD%	0.34	6.6	0	15.15
9	Concentration ppm	2.377	0.402	0.067	0.092
	RSD%	0.71	2.11	0	2.31
10	Concentration ppm	1.246	0.07	0.158	0.082
	RSD%	2.55	1.01	4.92	1.72
11	Concentration ppm	0.522	0.163	0.227	0.054
	RSD%	1.35	1.74	3.43	11.79
12	Concentration ppm	0.798	0.115	0.321	
	RSD%	4.96	7.38	0.44	
13	Concentration ppm	0.071	0.07	0.405	0.105
	RSD%	1	0	0.35	1.35
14	Concentration ppm	0.63	0.081	0.561	
	RSD%	1.01	2.62	0.88	
15	Concentration ppm	0.482	0.036	0.600	0.064
	RSD%	1.47	11.79	0	2.21
16	Concentration ppm	0.607	0.02	0.341	
	RSD%	2.8	10.61	0	
17	Concentration ppm	0.892	0.083	0.412	0.081
	RSD%	2.06	2.56	0	2.62
18	Concentration ppm	1.133	0.291	0.640	
	RSD%	0.87	2.92	0	
19	Concentration ppm		0.042	0.911	0.045
	RSD%		0	0	3.14
20	Concentration ppm		0.055	1.016	
	RSD%		2.57	0	
21	Concentration ppm		0.043	1.082	0.086
	RSD%		3.29	0	1.64
22	Concentration ppm		0.022		
	RSD%		3.21		
23	Concentration ppm		0.065		0.046
	RSD%		1.09		15.37
24	Concentration ppm		0.051		
	RSD%		2.77		

Detection limit: 0.0035ppm

The sandy nature of the sediment at depth sometimes prevented the collection of a sufficient amount of porewater for analysis, in the winter consecutive sub-samples were mixed to enable analysis

Appendix 3.6a: Uncorrected, mean concentration of Copper in diluted Smethwick porewaters (50% by volume), and relative standard deviation (RSD) from the mean of two duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
Water	Concentration ppm	0.003	0.012	0.007	-0.001
	RSD%	23.57	11.79	10.1	353.55
Interface	Concentration ppm		0.01	0.005	0.025
	RSD%		7.07	14.14	8.49
1	Concentration ppm	0.007	0.008	0.003	0.001
	RSD%	0	0	70.71	212.13
2	Concentration ppm	0.004	0.009	0.002	-0.003
	RSD%	53.03	7.86	35.36	23.57
3	Concentration ppm	0.101	0.008	0.004	-0.003
	RSD%	136.52	17.68	17.68	23.57
4	Concentration ppm	0.005	0.007	0.003	0.001
	RSD%	14.14	10.1	0	70.71
5	Concentration ppm	0.004	0.006	0.006	-0.002
	RSD%	17.68	0	0	0
6	Concentration ppm	0.004	0.008	0.005	-0.003
	RSD%	17.68	0	14.14	47.14
7	Concentration ppm	0.004	0.007	0.007	-0.002
	RSD%	0	0	20.2	70.71
8	Concentration ppm	0.006	0.007	0.003	-0.003
	RSD%	0	0	23.57	47.14
9	Concentration ppm	0.002	0.018	0.002	-0.002
	RSD%	0	7.86	0	35.36
10	Concentration ppm	0.001	0.005	0.004	0.001
	RSD%	70.71	0	0	141.42
11	Concentration ppm	0.006	0.006	0.003	0
	RSD%	11.79	23.57	23.57	0
12	Concentration ppm	0.002	0.005	0.003	0
	RSD%	70.71	28.28	23.57	0
13	Concentration ppm	0.002	0.007	0.004	0
	RSD%	35.36	0	17.68	0
14	Concentration ppm	0.001	0.007	0.002	0.001
	RSD%	141.42	20.2		70.71
15	Concentration ppm	0.001	0.006	0.002	-0.001
	RSD%	282.84	23.57		141.42
16	Concentration ppm	0.002	0.005	0.001	-0.002
	RSD%	70.71	14.14	141.42	0
17	Concentration ppm	0.002	0.007	0.003	0.001
	RSD%	106.07	10.1	23.57	212.13
18	Concentration ppm	0.004	0.006	0	0
	RSD%	35.36	11.79	0	0
19	Concentration ppm	0.003	0.008	0.002	0
	RSD%	23.57	26.52	35.36	0
20	Concentration ppm	0.004	0.006	0.004	0.002
	RSD%	17.68	11.79	0	106.07
21	Concentration ppm	0.004	0.005	0.007	0
	RSD%	53.03	28.28	0	0
22	Concentration ppm	0.002	0.007	0.005	0
	RSD%	35.36	0	0	0
23	Concentration ppm	0.002	0.007	0.008	-0.001
	RSD%	0	0	0	212.13
24	Concentration ppm	0.001	0.008	0	-0.001
	RSD%	70.71	8.84	0	0

Detection limit: 0.0009ppm

In the autumn sample the quantity of porewater extracted was insufficient for 2 analyses of every sample

Appendix 3.6b: Uncorrected, mean concentration of Copper in diluted Snarestone porewaters (50% by volume), and relative standard deviation (RSD) from the mean of two duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
Water	Concentration ppm	0.011	0.002	0.069	-0.002
	RSD%	6.43	70.71	2.05	35.36
Interface	Concentration ppm		0.002	0.073	0.006
	RSD%		35.36	0.00	11.79
1	Concentration ppm	0.003	0	0.083	-0.002
	RSD%	23.57	0	0.85	70.71
2	Concentration ppm	0.002	0.001	0.088	-0.002
	RSD%	0	70.71	0.80	0
3	Concentration ppm	0.004	0.003	0.001	0.002
	RSD%	17.68	0	0	70.71
4	Concentration ppm	0.002	0.001	0.090	-0.001
	RSD%	35.36	141.42	2.36	282.84
5	Concentration ppm	0.003	0.002	0.090	0.002
	RSD%	47.14	70.71	0.79	0
6	Concentration ppm	0.003	0.002	0.100	-0.001
	RSD%	23.57	35.36	0	70.71
7	Concentration ppm	0.003	0.002	0.050	-0.002
	RSD%	23.57	70.71	0	0
8	Concentration ppm	0.003	0.002	0.093	-0.002
	RSD%	0	70.71	0	0
9	Concentration ppm	0.005	0.002	0.091	-0.002
	RSD%	14.14	0	0	0
10	Concentration ppm	0.001	0.002	0.087	-0.001
	RSD%	0	0	0	0
11	Concentration ppm	0.001	0.002	0.090	-0.002
	RSD%	212.13	35.36	0.79	0
12	Concentration ppm	0.002	0.006	0.085	
	RSD%	35.36	0	0	
13	Concentration ppm	0.002	0.003	0.086	-0.002
	RSD%	35.36	23.57	0	35.36
14	Concentration ppm	0.004	0.003	0.092	
	RSD%	0	0	3.84	
15	Concentration ppm	0.007	0.003	0.091	-0.003
	RSD%	10.1	23.57	0	0
16	Concentration ppm	0.004	0.001	0.094	
	RSD%	17.68	282.84	0	
17	Concentration ppm	0.012	0.002	0.077	-0.003
	RSD%	5.89	0	0	47.14
18	Concentration ppm	0.008	0.002	0.090	
	RSD%	0	106.07	0	
19	Concentration ppm		0.002	0.086	-0.004
	RSD%		0	0	35.36
20	Concentration ppm		0.002	0.089	
	RSD%		70.71	0	
21	Concentration ppm		0.003	0.089	-0.005
	RSD%		47.14	0	42.43
22	Concentration ppm		0.001		
	RSD%		0		
23	Concentration ppm		0.004		-0.001
	RSD%		0		70.71
24	Concentration ppm		0.004		
	RSD%		35.36		

Detection limit: 0.0009ppm

The sandy nature of the sediment at depth sometimes prevented the collection of a sufficient amount of porewater for analysis, in the winter consecutive sub-samples were mixed to enable analysis

Appendix 3.7a: Uncorrected, mean concentration of Zinc in diluted Smethwick porewaters (50% by volume), and relative standard deviation (RSD) from the mean of two duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
Water	Concentration ppm	0.02	0.031	0.068	0.087
	RSD%	7.07	6.84	5.2	1.63
Interface	Concentration ppm		0.027	0.036	0.289
	RSD%		7.86	0	1.22
1	Concentration ppm	0.035	0.023	0.004	0.041
	RSD%	4.04	0	53.03	6.9
2	Concentration ppm	0.032	0.027	0.011	0.012
	RSD%	10.05	2.62	6.43	0
3	Concentration ppm	0.035	0.024	0.022	0.011
	RSD%	4.04	2.95	9.64	6.43
4	Concentration ppm	0.031	0.029	0.021	0.012
	RSD%	0	9.75	10.1	0
5	Concentration ppm	0.028	0.021	0.036	0.01
	RSD%	2.53	6.73	1.96	0
6	Concentration ppm	0.022	0.022	0.018	0.011
	RSD%	3.21	12.86	19.64	25.71
7	Concentration ppm	0.031	0.051	0.016	0.01
	RSD%	6.84	8.32	17.68	0
8	Concentration ppm	0.032	0.017	0.018	0.011
	RSD%	6.63	16.64	3.93	6.43
9	Concentration ppm	0.003	0.041	0.012	0.008
	RSD%	23.57	12.07	11.79	44.19
10	Concentration ppm	0.006	0.016	0.015	0.007
	RSD%	58.93	0	23.57	0
11	Concentration ppm	0.018	0.016	0.008	0.013
	RSD%	0	26.52	26.52	10.88
12	Concentration ppm	0.033	0.018	0.012	0.01
	RSD%	2.14	3.93	5.89	7.07
13	Concentration ppm	0.007	0.024	0.009	0.011
	RSD%	9.1	11.79	7.86	12.86
14	Concentration ppm	0.008	0.024	0.008	0.013
	RSD%	26.52	2.95		16.32
15	Concentration ppm	0.015	0.024	0.007	0.007
	RSD%	14.14	8.84		10.1
16	Concentration ppm	0.017	0.027	0.006	0.041
	RSD%	4.16	2.62	47.14	5.17
17	Concentration ppm	0.013	0.023	0.029	0.01
	RSD%	5.44	3.07	0	35.36
18	Concentration ppm	0.034	0.02	0.004	0.034
	RSD%	7.07	9.01	0	10.4
19	Concentration ppm	0.007	0.037	0.027	0.004
	RSD%	0	3.82	5.24	70.71
20	Concentration ppm	0.054	0.027	0.02	0.026
	RSD%	2.62	10.48	0	0
21	Concentration ppm	0.009	0.018	0.03	0.023
	RSD%	23.57	11.79	0	6.15
22	Concentration ppm	0.008	0.02	0.024	0.01
	RSD%	17.68	0	0	7.07
23	Concentration ppm	0.009	0.027	0.027	0.007
	RSD%	23.57	5.24	0	20.2
24	Concentration ppm	0.006	0.027	0.036	0.024
	RSD%	0	0	0	5.89

Detection limit: 0.002ppm

In the autumn sample the quantity of porewater extracted was insufficient for
2 analyses of every sample

Appendix 3.7b: Uncorrected, mean concentration of Zinc in diluted Snarestone porewaters (50% by volume), and relative standard deviation (RSD) from the mean of two duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
Water	Concentration ppm	0.012	0.007	0.004	0.011
	RSD%	5.89	10.1	1.22	6.43
Interface	Concentration ppm		0.008	0.004	0.038
	RSD%		26.52	0.94	7.44
1	Concentration ppm	0.042	0.005	0.004	0.001
	RSD%	1.68	14.14	0.85	141.42
2	Concentration ppm	0.046	0.007	0.004	0.006
	RSD%	0	0	0.33	23.57
3	Concentration ppm	0.047	0.006	0.005	0.018
	RSD%	1.5	0	0	0
4	Concentration ppm	0.049	0.004	0.004	0.01
	RSD%	4.33	35.36	10.96	7.07
5	Concentration ppm	0.048	0.005	0.044	0.002
	RSD%	2.95	14.14	0.97	70.71
6	Concentration ppm	0.06	0.005	0.047	0.005
	RSD%	1.18	0	0	0
7	Concentration ppm	0.053	0.006	0.043	0.001
	RSD%	8	0	0	0
8	Concentration ppm	0.04	0.006	0.003	-0.001
	RSD%	0	0	0	212.13
9	Concentration ppm	0.077	0.018	0.002	0.002
	RSD%	2.75	7.86	24.67	35.36
10	Concentration ppm	0.013	0.009	0.003	0.004
	RSD%	27.2	47.14	25.14	53.03
11	Concentration ppm	0.017	0.002	0.007	0.005
	RSD%	4.16	35.36	10.32	28.28
12	Concentration ppm	0.018	0.006	0.457	
	RSD%	15.71	58.93	10.93	
13	Concentration ppm	0.024	0.015	0.004	0.007
	RSD%	20.62	14.14	11.09	30.3
14	Concentration ppm	0.024	0.012	0.005	
	RSD%	5.89	11.79	12.52	
15	Concentration ppm	0.029	0.005	0.003	0.007
	RSD%	9.75	28.28	15.2	20.2
16	Concentration ppm	0.021	0.003	0.008	
	RSD%	0	70.71	0	
17	Concentration ppm	0.039	0.005	0.005	0.009
	RSD%	0	14.14	13.51	15.71
18	Concentration ppm	0.043	0.009	0.005	
	RSD%	9.87	0	0	
19	Concentration ppm		0.003	0.002	0.004
	RSD%		23.57	51.23	53.03
20	Concentration ppm		0.001	0.006	
	RSD%		282.84	0	
21	Concentration ppm		0.015	0.007	0.003
	RSD%		9.43	0	47.14
22	Concentration ppm		0.002		
	RSD%		35.36		
23	Concentration ppm		0.009		0.008
	RSD%		15.71		0
24	Concentration ppm		0.009		
	RSD%		7.86		

Detection limit: 0.002ppm

The sandy nature of the sediment at depth sometimes prevented the collection of a sufficient amount of porewater for analysis, in the winter consecutive sub-samples were mixed to enable analysis

Appendix 3.8a: Uncorrected, mean concentration of Sodium and Magnesium in diluted Smethwick porewaters (50% by volume), and relative standard deviation (RSD) from the mean of two duplicate analyses

Depth cm		Na	Mg
Water	Concentration ppm	38.51	14.9
	RSD%	0.92	0.24
Interface	Concentration ppm	39.92	15.06
	RSD%	0.16	0.28
1	Concentration ppm	38.05	15.09
	RSD%	1.47	0.89
2	Concentration ppm	31.55	15.29
	RSD%	0	1.02
3	Concentration ppm	41.19	23.51
	RSD%	0.82	1.5
4	Concentration ppm	43.85	25.71
	RSD%	0.13	1.21
5	Concentration ppm	43.79	28.42
	RSD%	0.53	3.13
6	Concentration ppm	45.98	29.69
	RSD%	0.2	1.5
7	Concentration ppm	47.31	32.38
	RSD%	0.61	1.29
8	Concentration ppm	48.41	32.98
	RSD%	0.03	1.39
9	Concentration ppm		31.52
	RSD%		1.21
10	Concentration ppm	50.43	32.37
	RSD%	0.76	0.66
11	Concentration ppm	48.81	28.1
	RSD%	1.32	1.81
12	Concentration ppm	51.89	26.72
	RSD%	0.46	0.29
13	Concentration ppm	49.91	24.43
	RSD%	1.33	0.03
14	Concentration ppm	52.63	25.52
	RSD%	1.57	0.25
15	Concentration ppm		22.52
	RSD%		1.98
16	Concentration ppm	54.38	23.35
	RSD%	0.65	0.88
17	Concentration ppm		23.13
	RSD%		0.52
18	Concentration ppm	54.87	24.67
	RSD%	1.01	0.26
19	Concentration ppm		24.94
	RSD%		0.57
20	Concentration ppm	53	24.07
	RSD%	1.25	0.24
21	Concentration ppm		23.02
	RSD%		1.81
22	Concentration ppm	53.93	22.82
	RSD%	0.76	0.43
23	Concentration ppm		23.88
	RSD%		0.74
24	Concentration ppm		23.93
	RSD%		0.98

Detection limit Na: 0.03ppm

Detection limit Mg: 0.02ppm

There was insufficient porewater to analyse for Na in every 1cm sub-sample

Appendix 3.8b: Uncorrected, mean concentration of Sodium and Magnesium in diluted Snarestone porewaters (50% by volume), and relative standard deviation (RSD) from the mean of two duplicate analyses

Depth cm		Na	Mg
Water	**Concentration ppm**	7.72	8.15
	RSD%	0.27	1.13
Interface	**Concentration ppm**	-0.1	8.7
	RSD%	7.07	0.49
1	**Concentration ppm**	7.81	8.01
	RSD%	0.54	0.79
2	**Concentration ppm**	7.97	8.41
	RSD%	0.53	1.01
3	**Concentration ppm**	8.68	9.11
	RSD%	1.47	0.08
4	**Concentration ppm**	8.79	9.8
	RSD%	0.4	0.22
5	**Concentration ppm**	8.96	8.93
	RSD%	0.55	0.4
6	**Concentration ppm**		10.79
	RSD%		0.46
7	**Concentration ppm**	10.65	11.32
	RSD%	0.07	0.62
8	**Concentration ppm**		12.09
	RSD%		0.23
9	**Concentration ppm**	11.01	11.29
	RSD%	0.26	0.88
10	**Concentration ppm**		10.98
	RSD%		0.19
11	**Concentration ppm**		10.49
	RSD%		1.95
12	**Concentration ppm**		
	RSD%		
13	**Concentration ppm**	11.72	10.44
	RSD%	0.91	1.35
14	**Concentration ppm**		
	RSD%		
15	**Concentration ppm**		9.11
	RSD%		1.63
16	**Concentration ppm**		
	RSD%		
17	**Concentration ppm**		9.87
	RSD%		0.29
18	**Concentration ppm**		
	RSD%		
19	**Concentration ppm**	12.22	9.27
	RSD%	1.5	1.14
20	**Concentration ppm**		
	RSD%		
21	**Concentration ppm**		8.98
	RSD%		0.47
22	**Concentration ppm**		
	RSD%		
23	**Concentration ppm**		9.28
	RSD%		0.53

Detection limit Na: 0.03ppm

Detection limit Mg: 0.02ppm

The sandy nature of the sediment at depth sometimes prevented the collection of a sufficient amount of porewater for analysis, where possible consecutive sub-samples were mixed to enable analysis

Appendix 4: The Mean Uncorrected Concentrations of Metals, Sulphur and Phosphorus in Smethwick and Snarestone Sediments Aqua Regia Leachates, and The Relative Standard Deviation (RSD) of Two Duplicate Analyses

Appendix 4.1a: The mean uncorrected concentration of Aluminium in the Smethwick sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
1	Concentration ppm	79.69	186.63	75.20	76.35
	RSD%	0.79	0.08	0.43	0.03
2	Concentration ppm	76.72	184.43	75.31	77.09
	RSD%	0.17	0.94	0.61	0.32
3	Concentration ppm	78.76	197.52	83.04	77.97
	RSD%	1.53	0.55	0.35	0.80
4	Concentration ppm	78.43	200.99	82.09	76.30
	RSD%	0.06	0.20	0.30	0.95
5	Concentration ppm	81.42	206.01	81.58	74.38
	RSD%	0.15	0.32	0.47	1.27
6	Concentration ppm	79.52	203.33	88.61	77.12
	RSD%	0.69	1.01	0.49	0.04
7	Concentration ppm	79.16	202.45	82.23	80.47
	RSD%	1.93	0.62	0.82	0.54
8	Concentration ppm	72.65	188.79	83.41	83.00
	RSD%	0.80	1.43	0.59	0.51
9	Concentration ppm	74.19	192.88	77.28	77.53
	RSD%	0.72	0.35	0.64	0.55
10	Concentration ppm	81.00	188.96	80.10	77.15
	RSD%	0.60	0.02	0.10	0.71
11	Concentration ppm	76.91	165.97	80.34	84.92
	RSD%	0.53	0.18	2.33	0.84
12	Concentration ppm	82.06	143.20	82.14	84.89
	RSD%	0.21	1.04	1.90	0.52
13	Concentration ppm	79.77	150.26	83.56	86.72
	RSD%	0.31	1.24	0.58	0.29
14	Concentration ppm	80.46	151.84	79.92	103.29
	RSD%	0.23	0.33	0.66	0.35
15	Concentration ppm	81.11	161.52	82.05	122.27
	RSD%	0.34	0.68	0.12	0.88
16	Concentration ppm	78.94	159.34	85.89	135.68
	RSD%	0.23	0.23	0.92	0.77
17	Concentration ppm	79.24	161.54	85.91	104.26
	RSD%	0.80	0.26	0.04	0.24
18	Concentration ppm	77.12	156.73	88.02	84.58
	RSD%	0.64	0.38	0.60	0.85
19	Concentration ppm	82.31	158.81	87.90	82.07
	RSD%	0.11	0.36	0.96	0.98
20	Concentration ppm	79.69	155.48	87.45	70.85
	RSD%	1.76	1.71	0.50	0.30
21	Concentration ppm	78.62	156.39	89.15	67.85
	RSD%	0.56	0.16	0.54	0.50
22	Concentration ppm	81.29	157.34	78.83	57.90
	RSD%	0.03	1.93	0.78	0.24
23	Concentration ppm	83.02	159.35	80.45	84.83
	RSD%	1.38	0.68	0.95	0.18
24	Concentration ppm	78.74	154.53	80.76	88.15
	RSD%	0.85	0.50	0.16	0.75

Appendix 4.1b: The mean uncorrected concentration of Aluminium in the Snarestone sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
1	Concentration ppm	52.62	81.10	62.69	74.56
	RSD%	0.16	1.18	0.42	0.98
2	Concentration ppm	56.42	65.40	54.75	55.28
	RSD%	0.12	0.79	0.34	1.09
3	Concentration ppm	33.89	58.04	57.13	56.75
	RSD%	0.42	0.76	0.79	0.27
4	Concentration ppm	20.79	50.13	63.95	33.04
	RSD%	0.49	0.44	0.14	1.17
5	Concentration ppm	39.03	39.96	46.77	31.98
	RSD%	1.10	0.09	0.17	0.42
6	Concentration ppm	38.73	61.95	60.58	30.80
	RSD%	1.27	0.83	1.29	0.16
7	Concentration ppm	57.89	58.03	79.54	37.01
	RSD%	1.23	0.37	0.49	0.16
8	Concentration ppm	69.54	64.72	60.76	40.96
	RSD%	0.55	0.02	0.97	0.50
9	Concentration ppm	65.18	65.55	59.27	33.54
	RSD%	0.66	1.32	0.65	0.28
10	Concentration ppm	62.49	44.00	60.99	32.89
	RSD%	0.25	0.47	0.93	1.70
11	Concentration ppm	60.77	83.74	56.95	24.78
	RSD%	0.15	0.82	0.06	0.76
12	Concentration ppm	61.82	53.82	60.29	24.14
	RSD%	1.25	1.28	0.59	0.45
13	Concentration ppm	54.30	48.00	69.11	24.17
	RSD%	0.65	1.41	0.60	0.47
14	Concentration ppm	42.58	45.17	58.97	23.37
	RSD%	1.47	0.09	0.27	0.24
15	Concentration ppm	37.49	47.63	47.61	24.50
	RSD%	0.72	0.92	0.06	1.69
16	Concentration ppm	21.97	44.99	40.97	26.45
	RSD%	0.22	0.22	0.42	1.34
17	Concentration ppm	30.60	57.20	37.82	27.95
	RSD%	0.04	1.32	1.33	0.41
18	Concentration ppm	28.25	49.52	52.75	27.89
	RSD%	0.07	1.04	1.27	0.40
19	Concentration ppm	22.70	54.50	28.18	25.29
	RSD%	1.67	0.26	0.64	1.30
20	Concentration ppm	24.29	38.18	38.58	27.06
	RSD%	1.12	0.09	0.83	1.40
21	Concentration ppm	32.20	52.10	46.08	33.79
	RSD%	0.46	0.33	1.00	1.28
22	Concentration ppm	43.40	64.88	44.26	36.48
	RSD%	1.41	0.97	0.77	0.21
23	Concentration ppm	45.39	63.07	39.78	37.31
	RSD%	0.29	1.69	0.81	0.73
24	Concentration ppm	50.72	61.09	37.25	49.44
	RSD%	0.46	1.39	0.39	0.70

Appendix 4.2a: The mean uncorrected concentration of Phosphorous in the Smethwick sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring		Summer		Autumn		Winter	
		P178	P179	P178	P179	P178	P179	P178	P179
1	Concentration ppm	101.76	97.73	116	115.73	110.86	107.6	117.19	117.13
	RSD%	1.74	0.48	0.46	0.1	0.7	0.64	0.95	0.97
2	Concentration ppm	98.21	98.19	111.45	111.78	110.16	112.75	120.22	119.1
	RSD%	1.03	1.51	0.16	0.5	0.8	0.95	0.15	0.13
3	Concentration ppm	96.98	96.47	108.2	111.35	110.21	112.06	111.26	110.92
	RSD%	0.56	2.49	1.42	0.23	0.89	0.73	1.49	0.91
4	Concentration ppm	91.44	92.92	100.86	102.1	110.73	112.15	111.02	110.55
	RSD%	0.77	1.7	1.11	1.2	0.12	0.11	2.1	0.6
5	Concentration ppm	88.22	90.34	102.4	104.17	102.32	103.24	106.19	105.51
	RSD%	0.43	0.46	1.1	0.72	0.58	0.08	1.27	1.06
6	Concentration ppm	87.7	87.72	108.68	106.5	93.51	92.94	103.82	105.2
	RSD%	0.69	1.23	0	0.23	0.05	0.44	0.75	0.29
7	Concentration ppm	98.77	97.1	102.89	104.11	99.94	99.49	102.76	105.14
	RSD%	0.14	1.33	1.16	0.86	0.04	0.33	0.58	0.46
8	Concentration ppm	102.3	104.98	101.23	100.81	106.6	106.19	113.53	114.42
	RSD%	2.82	0.26	1.26	0.13	0.89	0.63	0.11	0.21
9	Concentration ppm	91.66	92.71	104.82	106.02	108.34	109.52	109.57	109.61
	RSD%	0.59	0.79	1.19	1.82	0.74	0.22	0.03	0.03
10	Concentration ppm	88.1	89.69	110.46	110.2	105.8	106.69	106.16	105.35
	RSD%	0.31	0	1.29	0.06	0.07	0.95	0.89	0.94
11	Concentration ppm	89.75	91.29	107.49	107.02	101.68	102.08	107.9	106.22
	RSD%	0.45	0.85	0.46	0.8	0.1	1.3	0.45	1.74
12	Concentration ppm	88.08	87.36	104.02	102.61	103.37	101.35	110.73	112.02
	RSD%	0.85	0.53	0.4	3.11	0.07	0.63	0.55	1.26
13	Concentration ppm	93.55	93.53	101.22	101.37	112.23	114.36	111.67	113.05
	RSD%	1.03	0.63	0.75	1.23	0.6	1.68	0.39	0.19
14	Concentration ppm	93.69	93.9	103.82	103.1	114.73	112.67	135.19	134.68
	RSD%	0.41	1.69	1.63	0.86	0.54	1.22	0.39	0.51
15	Concentration ppm	95.63	94.62	103.36	102.93	107.27	108.58	128.63	128.61
	RSD%	1.86	0.39	1.87	0.38	0.21	0.59	0.54	1.54
16	Concentration ppm	87.74	87.03	103.21	103.94	104.4	102.69	144.62	143.88
	RSD%	1.85	0.36	0.88	0.57	0.98	0.78	0.76	0.15
17	Concentration ppm	84.14	83.52	97.5	98.84	107.39	106.86	151.27	146.48
	RSD%	0.71	1.4	0.3	0.08	0.01	1.34	0.84	2.3
18	Concentration ppm	82.56	83.05	95.82	95.51	105.39	105.51	152.74	153.91
	RSD%	2.25	1.11	0	0.1	0.39	0.03	0.63	0.25
19	Concentration ppm	89.83	88.32	89.75	89.08	106.87	105.42	122.65	125
	RSD%	0.31	0.04	0.69	0.81	0.16	0.42	0.96	2.02
20	Concentration ppm	88.78	86.89	95.96	96.62	104.39	104.87	103.86	104.03
	RSD%	1	1.46	0.3	0.31	1.73	0.49	0.5	1.17
21	Concentration ppm	86.08	85.43	93.28	92.9	88.2	88.57	109.38	109.63
	RSD%	0.61	0.18	0.42	0.47	0.43	1.04	0.58	0.09
22	Concentration ppm	89.55	90.02	93.51	92.79	89.85	88.82	96.88	95.78
	RSD%	0.33	0.49	0.36	0.4	1.36	0.88	0.58	1.2
23	Concentration ppm	91.4	92.21	91.53	90.25	94.6	94.56	82.29	82.18
	RSD%	1.09	2.21	0.16	1.35	0.52	0.43	1.31	1.6
24	Concentration ppm	78.02	79.47	93.07	91.83	99.63	101.09	135.95	131.21
	RSD%	0.18	0.07	1.22	1.89	0.45	0.76	1.36	2.54

Appendix 4.2b: The mean uncorrected concentration of Phosphorous in the Snarestone sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring		Summer		Autumn		Winter	
		P178	P179	P178	P179	P178	P179	P178	P179
1	Concentration ppm	3.6	3.61	5.08	5.05	4.27	3.84	4.78	5.06
	RSD%	2.55	4.9	5.15	2.1	0.5	1.47	2.96	*12.86
2	Concentration ppm	3.81	3.77	4.58	3.99	3.2	3.1	3.16	3.51
	RSD%	0.37	0.94	12.81	8.86	5.75	3.88	3.58	4.03
3	Concentration ppm	2.29	2.37	3.09	3.18	2.99	2.54	2.36	2.55
	RSD%	8.34	3.28	*11.67	9.12	7.8	*21.16	*10.49	1.11
4	Concentration ppm	1.43	1.51	2.64	2.68	3.28	3.28	1.69	1.71
	RSD%	12.36	10.3	4.55	*22.69	9.05	6.9	9.62	*13.23
5	Concentration ppm	1.88	1.97	2.84	2.73	2.19	2.09	1.61	1.62
	RSD%	1.88	4.67	4.23	9.32	3.88	*19.96	*15.81	*15.28
6	Concentration ppm	1.85	1.75	3.44	3.59	2.79	2.51	1.42	1.54
	RSD%	0.76	4.04	4.11	*10.64	6.08	2.25	2.49	5.05
7	Concentration ppm	2.07	2.06	3.14	3.18	4.4	4.53	1.76	1.35
	RSD%	1.02	3.43	2.48	*19.79	4.5	*13.27	8.03	*28.28
8	Concentration ppm	2.07	1.98	3.66	3.77	2.39	2.39	1.49	1.66
	RSD%	5.12	4.64	8.89	3.38	2.07	*15.39	0.95	*10.22
9	Concentration ppm	2.02	1.96	3.25	3.41	2.58	2.87	1.5	1.46
	RSD%	0.7	1.8	4.13	1.04	5.21	7.15	7.07	1.94
10	Concentration ppm	2.07	2.34	2.68	2.78	2.35	2.26	1.55	1.46
	RSD%	3.07	2.42	0.79	1.02	9.63	*13.14	14.6	9.69
11	Concentration ppm	2.29	2.53	4.99	4.88	2.23	2.45	2.39	2.47
	RSD%	0.93	0.84	0.43	1.3	0.63	8.95	4.14	4.58
12	Concentration ppm	2.06	2.55	2.56	2.79	2.33	2.41	1.33	1.26
	RSD%	1.37	5.82	2.21	1.01	4.55	*13.5	9.04	*14.03
13	Concentration ppm	2.45	2.53	1.79	1.92	2.43	2.41	1.11	0.69
	RSD%	2.02	4.47	*10.66	*23.2	*11.35	9.1	8.28	*24.6
14	Concentration ppm	2.15	2.05	1.85	2.29	2.36	2.51	1.16	1.31
	RSD%	8.88	3.79	8.79	5.25	2.1	3.38	1.83	*18.35
15	Concentration ppm	1.75	1.97	2.09	2.14	2.54	2.82	1.24	1.22
	RSD%	2.42	6.82	0	5.62	8.35	5.01	4.56	7.53
16	Concentration ppm	1.32	1.07	1.86	1.76	2.27	2.32	1	1.09
	RSD%	2.68	9.25	3.8	*13.26	3.43	1.22	7.78	0
17	Concentration ppm	1.59	1.39	2.46	2.82	2.83	2.78	1.21	1.22
	RSD%	2.22	4.07	5.17	5.27	2.25	5.09	*10.52	2.32
18	Concentration ppm	1.72	1.69	2.19	2.48	2.47	2.7	0.98	1.17
	RSD%	1.23	3.35	8.07	5.99	2.58	*10.21	2.89	*14.5
19	Concentration ppm	1.4	1.31	2.15	1.83	1.77	2.03	0.93	0.52
	RSD%	5.56	11.34	*22.04	1.54	0	*10.45	8.36	0
20	Concentration ppm	1.35	1.39	1.55	1.59	1.77	2.03	1.15	1.19
	RSD%	15.71	1.02	4.56	3.56	5.59	0	*60.26	*84.38
21	Concentration ppm	1.4	1.26	2.13	2.11	1.68	1.76	0.55	1.12
	RSD%	5.56	16.27	0	1.34	3.79	3.21	*42.43	*46.72
22	Concentration ppm	1.85	1.87	2.66	2.79	1.82	2.15	0.77	1.6
	RSD%	14.91	3.78	4.52	3.04	1.94	7.56	*88.16	*16.35
23	Concentration ppm	1.81	1.9	2.45	2.47	3.62	3.72	1.15	1.6
	RSD%	3.91	5.58	3.46	9.16	4.3	2.85	*35.05	*11.05
24	Concentration ppm	1.6	1.48	2.62	1.85	1.59	1.52	1.74	1.76
	RSD%	0	6.21	1.89	*17.58	4	8.84	*26.82	*71.11

*RSD is >10%, where this is the case the alternative concentration value was used, when both were >10% the data was not used

Appendix 4.3a: The mean uncorrected concentration of Sulphur in the Smethwick sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring		Summer		Autumn		Winter	
		S180	S182	S180	S182	S180	S182	S180	S182
1	Concentration ppm	51.24	49.62	43.43	43.48	46.25	45.45	42.87	42.98
	RSD%	1.71	0.88	0.75	0.16	1.47	0.73	0.84	2.48
2	Concentration ppm	51.81	49.35	49.67	48.85	46.2	46.13	44.61	43.91
	RSD%	0.29	0.49	0.36	0.38	0.09	0.09	2.95	1.05
3	Concentration ppm	56.94	54.56	53.12	52.33	44.86	43.36	48.08	48.1
	RSD%	1.37	0.16	1.34	0.82	0.82	0.33	0.66	0.62
4	Concentration ppm	57.99	55.87	55.93	53.32	44.48	43.76	46.38	45.91
	RSD%	0.1	0.15	0.75	0.42	1.56	0.82	0.81	0.77
5	Concentration ppm	64.51	61.76	55.55	54.02	45.57	45.54	44.97	44.14
	RSD%	0.25	0.96	1.13	0.09	0.54	0.67	0.22	0.74
6	Concentration ppm	62.54	61.49	57.28	56.29	45.68	44.78	44.66	44.01
	RSD%	0.12	0.37	2.9	0.46	1.1	0.93	0.22	1.48
7	Concentration ppm	58.46	56.89	57.98	56.21	46.4	44.54	44.97	44.1
	RSD%	1.26	0.27	0.05	0.29	0.38	0.56	0.63	0.48
8	Concentration ppm	66.76	67.63	59.03	57.97	45.13	43.31	46.99	46.12
	RSD%	0.51	1.1	3.16	0.15	1.43	0.31	0.41	0.72
9	Concentration ppm	65.76	64.38	57.49	56.55	48.87	47.09	47.22	46.29
	RSD%	0.39	0.89	0.97	0.31	0.45	1.05	0.18	0.08
10	Concentration ppm	65.96	64.5	61.46	59.47	47.07	47.63	45	44.87
	RSD%	0.39	0.88	2.45	0.04	0.26	1.28	0.33	0.44
11	Concentration ppm	57.98	56.82	56.67	57.19	48.75	48.7	46.35	45
	RSD%	1.45	0.82	0.76	0.21	0.25	0.01	0.17	1.23
12	Concentration ppm	54.88	54.31	56.99	56.39	46.86	46.36	51.52	50.26
	RSD%	0.58	0.62	0.19	0.03	0.48	0.34	0.1	0.07
13	Concentration ppm	64.85	63.19	53.89	52.8	50.4	50.12	52.59	52.14
	RSD%	1.98	0.04	0.72	0.09	0.43	1.2	0.3	0.04
14	Concentration ppm	62.62	60.95	53.82	52.93	52.22	51.14	53.58	52.71
	RSD%	0.63	1.48	1.27	1.63	0.37	0.32	0.59	1.78
15	Concentration ppm	72.57	70.71	54.34	52.84	51.12	49.99	50.41	49.38
	RSD%	0.99	0.9	0.07	1.83	0.83	0.13	1.82	0.79
16	Concentration ppm	64.62	62.56	55.27	54.17	48.77	47.41	47.16	45.72
	RSD%	1.13	0.75	0.45	0.42	0.87	0.07	0.63	0.45
17	Concentration ppm	65.5	63.53	65.34	65.25	51.34	50.48	49.2	48.78
	RSD%	1.2	0.6	2.43	1.17	0.06	0.91	1.32	1.71
18	Concentration ppm	65.38	62.86	58.48	57.59	51.09	50.9	49.16	48.06
	RSD%	1.19	0.83	1.8	1.31	0.6	0.58	0.89	0.47
19	Concentration ppm	71.41	69.42	60.7	59.96	57.64	57.1	51.43	51.55
	RSD%	0.39	0.58	0.16	0.67	0.56	1.02	1.44	1.78
20	Concentration ppm	65.56	63.78	57.55	58.27	59.23	57.35	55.14	54.87
	RSD%	0.23	1.04	1.03	1.08	0.21	0.84	0.77	0.32
21	Concentration ppm	61.98	62.85	57.34	56.94	54.68	52.89	55.81	55.56
	RSD%	0.56	0.36	0.84	0.31	0.57	1.52	0	0.15
22	Concentration ppm	61.26	61.67	51.83	50.38	55.3	53.8	59.7	61.3
	RSD%	0.93	0.22	0.94	1.02	0.46	0.67	1.2	1.67
23	Concentration ppm	60.66	60.54	55.53	53.7	55.31	54.47	62.06	62.38
	RSD%	0.41	0.36	0.45	0.14	0.31	1.22	0.66	0.26
24	Concentration ppm	63.42	64.02	50.01	48.85	55.39	53.83	55.98	54.88
	RSD%	0.97	0.51	2.09	0.33	0.49	0.87	1.36	1.84

Appendix 4.3b: The mean uncorrected concentration of Sulphur in the Snarestone sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring		Summer		Autumn		Winter	
		S180	S182	S180	S182	S180	S182	S180	S182
1	Concentration ppm	23.03	21.86	37.46	36.59	36.51	36.19	34.79	33.36
	RSD%	2.09	0.39	0.26	2.28	0.06	1.45	0.98	1.08
2	Concentration ppm	24.17	23.96	36.83	35.69	28.91	27.41	32.96	32.03
	RSD%	2.69	0.03	1.27	2.44	0.98	0.95	1.67	0.33
3	Concentration ppm	8.43	6.69	24.68	23.95	34.01	32.34	36.89	35.6
	RSD%	1.76	0.21	1.43	0.24	0.04	0.77	1.05	0.46
4	Concentration ppm	7.41	6.18	25.34	23.77	37.92	36.4	26.07	24.84
	RSD%	2.29	0.23	0.84	0.89	1.68	2.7	1.3	0.57
5	Concentration ppm	22.76	22.06	24.87	22.98	34.84	32.8	20.47	19.46
	RSD%	1.83	0.19	1.42	1.66	1.52	2.85	0.1	1.42
6	Concentration ppm	23.54	23.23	39.17	38.75	46.37	46.28	25.33	24.63
	RSD%	0.54	1.61	0.65	1.92	1.25	2.05	0.59	0.2
7	Concentration ppm	36.14	35.56	39.3	38.43	43.81	42.79	28.53	27.56
	RSD%	0.12	0.82	1.6	2.24	1.82	2.1	0.27	0.31
8	Concentration ppm	33.74	33.03	44.68	42.74	50.69	50.03	23.11	22.62
	RSD%	0.5	0.45	0.57	0.08	0.11	1.02	1.04	1.91
9	Concentration ppm	32.21	31.65	41.15	39.7	54.73	53.64	23.67	22.47
	RSD%	0.53	0.38	0.74	0.52	0.22	1.98	1.19	0.54
10	Concentration ppm	38.44	38.23	28.4	27.14	50.83	49.01	21.69	21.03
	RSD%	0.35	0.43	0.32	2.74	1.18	0.92	1.04	0.27
11	Concentration ppm	40.38	38.87	26.81	27.17	43.79	43.06	12.94	12.06
	RSD%	1.1	3.8	0.16	0.68	1.95	0.43	1.58	1.47
12	Concentration ppm	32.29	32.59	36.7	37.29	45.91	44.36	10.62	9.87
	RSD%	1.31	0.2	0.21	0.61	0.15	0.26	0.07	6.66
13	Concentration ppm	30.28	29.78	39.88	39.32	47.41	46.9	9.88	9.18
	RSD%	0.47	0.31	0.44	0.49	0.04	1	2.22	1.54
14	Concentration ppm	19.36	18.83	49.64	51.07	43.87	42.17	10.08	9.81
	RSD%	0.44	1.84	0.41	0.53	1.14	0.35	1.96	0.14
15	Concentration ppm	15.29	14.91	48.1	47.71	33.39	32.38	8.61	8.31
	RSD%	0.97	0.9	0.68	0.24	0.89	0.04	3.45	2.21
16	Concentration ppm	10.12	9.73	49.68	48.51	22.28	21.44	8.83	8.16
	RSD%	1.26	1.74	0.27	0.26	0.38	0.23	2.08	4.59
17	Concentration ppm	18.67	18.55	50.34	49.43	15.78	14.62	9.13	8.44
	RSD%	0.8	2.02	0.15	0.49	1.66	2.71	2.01	5.61
18	Concentration ppm	22.56	21.81	54.18	52.76	28.4	27.96	8.98	8.48
	RSD%	0.88	0.19	0.77	0.11	0.02	2.12	2.28	2.92
19	Concentration ppm	26.26	25.85	58.79	58.69	19.73	18.8	12.02	12.12
	RSD%	1.18	2.87	0.81	0.95	0.39	1.05	0.53	1.4
20	Concentration ppm	20.55	19.85	38.62	38.5	24.73	23.14	7.82	7.74
	RSD%	0.1	0.21	0.82	0.31	2.8	1.47	2.08	1.64
21	Concentration ppm	15.17	14.19	48.97	49.2	19.52	17.8	9.12	9.42
	RSD%	2.28	1	1.27	1.74	1.12	1.19	4.65	0.07
22	Concentration ppm	17.01	16.42	68.05	68	19.21	18.66	12.42	11.7
	RSD%	0.29	0.9	1.14	0.12	1.77	1.4	3.59	2.18
23	Concentration ppm	17.78	17.23	64.37	64.33	22.07	21.33	11.98	12.34
	RSD%	0.04	1.44	0.09	2.48	0.87	0.63	2.12	0.34
24	Concentration ppm	14.34	13.49	63.03	61.13	11.58	11.23	14.84	14.24
	RSD%	0.1	0.94	0.34	1.09	0.37	1.83	1.62	1.49

Appendix 4.4a: The mean uncorrected concentration of Calcium in the Smethwick sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
1	Concentration ppm	186.63	161.65	203.02	197.98
	RSD%	0.08	0.13	1.15	0.20
2	Concentration ppm	184.43	163.23	200.80	204.05
	RSD%	0.94	0.08	0.32	0.79
3	Concentration ppm	197.52	166.76	192.04	200.73
	RSD%	0.55	0.87	0.43	1.29
4	Concentration ppm	200.99	163.18	188.38	203.70
	RSD%	0.20	0.20	0.35	0.80
5	Concentration ppm	206.01	163.77	189.29	206.92
	RSD%	0.32	0.68	2.15	0.88
6	Concentration ppm	203.33	163.10	195.72	194.75
	RSD%	1.01	0.74	0.93	0.07
7	Concentration ppm	202.45	163.11	198.87	195.34
	RSD%	0.62	0.43	0.49	0.26
8	Concentration ppm	188.79	157.90	192.71	202.94
	RSD%	1.43	0.73	0.67	0.50
9	Concentration ppm	192.88	157.06	184.80	193.26
	RSD%	0.35	0.00	0.46	0.09
10	Concentration ppm	188.96	163.63	183.69	189.92
	RSD%	0.02	0.52	0.08	0.26
11	Concentration ppm	165.97	169.66	175.60	173.07
	RSD%	0.18	1.68	0.72	0.69
12	Concentration ppm	143.20	155.19	174.09	167.63
	RSD%	1.04	1.09	0.92	0.35
13	Concentration ppm	150.26	155.40	174.99	166.68
	RSD%	1.24	0.08	0.85	1.95
14	Concentration ppm	151.84	157.41	166.97	157.11
	RSD%	0.33	0.00	0.55	0.00
15	Concentration ppm	161.52	160.81	168.82	170.21
	RSD%	0.68	0.22	0.24	0.49
16	Concentration ppm	159.34	160.96	173.62	193.59
	RSD%	0.23	0.26	1.02	0.54
17	Concentration ppm	161.54	165.96	160.80	165.55
	RSD%	0.26	1.30	0.69	1.11
18	Concentration ppm	156.73	145.70	165.18	150.60
	RSD%	0.38	0.01	0.08	2.65
19	Concentration ppm	158.81	153.57	165.62	145.86
	RSD%	0.36	1.04	0.52	0.35
20	Concentration ppm	155.48	160.84	158.70	125.20
	RSD%	1.71	0.36	0.52	1.04
21	Concentration ppm	156.39	165.20	159.78	106.11
	RSD%	0.16	0.65	0.03	0.22
22	Concentration ppm	157.34	158.87	157.95	99.95
	RSD%	1.93	0.14	0.06	0.78
23	Concentration ppm	159.35	156.64	159.59	153.59
	RSD%	0.68	0.56	1.04	1.71
24	Concentration ppm	154.53	168.22	166.24	147.67
	RSD%	0.50	0.32	0.71	0.79

Appendix 4.4b: The mean uncorrected concentration of Calcium in the Snarestone sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
1	Concentration ppm	120.65	134.33	135.93	126.39
	RSD%	0.91	0.67	0.86	1.30
2	Concentration ppm	113.21	135.07	153.92	123.29
	RSD%	0.57	1.09	0.50	0.20
3	Concentration ppm	267.72	160.89	181.81	156.49
	RSD%	0.70	1.03	0.17	0.13
4	Concentration ppm	186.86	208.22	192.53	110.08
	RSD%	0.44	0.19	0.13	0.50
5	Concentration ppm	151.44	374.50	222.30	149.63
	RSD%	1.29	0.56	1.12	0.91
6	Concentration ppm	127.91	125.43	127.15	170.66
	RSD%	0.86	0.66	0.30	0.56
7	Concentration ppm	109.57	123.84	233.05	130.69
	RSD%	1.63	0.25	0.32	1.03
8	Concentration ppm	109.08	130.55	206.20	126.53
	RSD%	0.70	0.06	0.61	0.30
9	Concentration ppm	107.06	125.49	206.96	157.58
	RSD%	0.20	0.49	0.81	0.33
10	Concentration ppm	125.15	133.58	141.39	100.55
	RSD%	1.29	0.98	1.76	0.58
11	Concentration ppm	136.32	102.05	160.34	112.62
	RSD%	0.15	1.36	0.15	1.09
12	Concentration ppm	122.23	120.24	154.27	91.31
	RSD%	1.32	0.29	0.10	0.40
13	Concentration ppm	125.05	131.51	149.35	78.22
	RSD%	0.09	1.62	1.47	2.45
14	Concentration ppm	108.62	114.86	140.83	77.96
	RSD%	0.33	0.93	0.31	0.08
15	Concentration ppm	113.05	109.16	173.88	80.04
	RSD%	0.26	0.67	0.03	0.43
16	Concentration ppm	122.13	113.86	145.93	91.57
	RSD%	1.01	0.37	0.14	0.54
17	Concentration ppm	107.71	120.06	182.46	129.98
	RSD%	0.48	0.10	0.37	0.41
18	Concentration ppm	95.93	117.58	136.03	96.29
	RSD%	0.89	0.11	1.32	0.90
19	Concentration ppm	94.45	126.14	102.16	109.20
	RSD%	0.68	0.60	1.83	0.09
20	Concentration ppm	91.60	94.61	112.51	95.75
	RSD%	0.75	0.85	0.03	0.01
21	Concentration ppm	96.89	119.77	104.23	82.98
	RSD%	0.60	0.85	0.79	0.89
22	Concentration ppm	116.84	140.91	116.13	82.86
	RSD%	0.74	0.01	0.33	0.29
23	Concentration ppm	119.78	134.38	157.41	72.59
	RSD%	0.32	1.18	1.32	0.97
24	Concentration ppm	117.72	123.91	85.07	82.19
	RSD%	0.56	1.82	0.04	0.00

Appendix 4.5a: The mean uncorrected concentration of Chromium in the Smethwick sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
1	Concentration ppm	**2.13**	**1.90**	**2.02**	**2.02**
	RSD%	0.03	2.94	0.14	0.70
2	Concentration ppm	**2.04**	**1.99**	**2.10**	**2.06**
	RSD%	0.10	0.61	2.53	0.03
3	Concentration ppm	**2.06**	**2.11**	**2.10**	**2.02**
	RSD%	0.07	0.71	1.51	0.73
4	Concentration ppm	**2.03**	**2.30**	**2.15**	**2.05**
	RSD%	0.94	1.02	0.82	0.28
5	Concentration ppm	**2.16**	**2.34**	**2.10**	**2.06**
	RSD%	0.03	1.21	1.78	0.21
6	Concentration ppm	**2.14**	**2.34**	**2.09**	**2.05**
	RSD%	1.42	0.76	0.78	1.03
7	Concentration ppm	**2.08**	**2.27**	**2.09**	**2.07**
	RSD%	1.77	0.37	1.69	1.03
8	Concentration ppm	**1.98**	**2.27**	**2.09**	**2.14**
	RSD%	0.46	3.08	0.91	0.10
9	Concentration ppm	**2.00**	**2.19**	**2.08**	**2.05**
	RSD%	1.20	1.65	0.03	1.31
10	Concentration ppm	**2.05**	**2.23**	**2.09**	**2.07**
	RSD%	1.38	0.32	0.24	0.51
11	Concentration ppm	**1.93**	**2.12**	**2.20**	**2.19**
	RSD%	0.15	1.30	2.25	0.16
12	Concentration ppm	**1.98**	**2.22**	**2.25**	**2.13**
	RSD%	2.25	0.06	1.69	0.80
13	Concentration ppm	**2.13**	**2.15**	**2.35**	**2.30**
	RSD%	0.23	0.26	0.84	0.37
14	Concentration ppm	**2.19**	**2.24**	**2.32**	**2.32**
	RSD%	1.20	0.16	0.15	2.62
15	Concentration ppm	**2.29**	**2.23**	**2.28**	**2.63**
	RSD%	0.37	1.23	1.09	1.96
16	Concentration ppm	**2.30**	**2.16**	**2.22**	**2.66**
	RSD%	0.68	0.62	1.40	1.89
17	Concentration ppm	**2.20**	**2.08**	**2.33**	**2.49**
	RSD%	0.13	1.02	0.09	0.74
18	Concentration ppm	**2.14**	**2.25**	**2.37**	**2.37**
	RSD%	0.10	1.82	0.36	0.57
19	Concentration ppm	**2.22**	**2.44**	**2.40**	**2.81**
	RSD%	0.26	0.46	0.88	1.96
20	Concentration ppm	**2.14**	**2.38**	**2.34**	**2.61**
	RSD%	0.50	1.87	1.12	1.52
21	Concentration ppm	**2.21**	**2.29**	**2.30**	**2.84**
	RSD%	0.51	1.51	1.32	1.22
22	Concentration ppm	**2.21**	**2.04**	**2.38**	**2.84**
	RSD%	2.05	1.81	0.56	1.69
23	Concentration ppm	**2.18**	**1.95**	**2.36**	**2.45**
	RSD%	0.13	0.76	0.66	1.56
24	Concentration ppm	**2.01**	**1.91**	**2.34**	**2.63**
	RSD%	0.56	0.19	2.87	0.67

Appendix 4.5b: The mean uncorrected concentration of Chromium in the Snarestone sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
1	Concentration ppm	0.11	0.15	0.13	0.13
	RSD%	5.39	4.16	0.54	7.39
2	Concentration ppm	0.11	0.12	0.10	0.10
	RSD%	4.46	2.34	6.80	2.06
3	Concentration ppm	0.06	0.11	0.10	0.12
	RSD%	4.88	0.00	10.10	4.83
4	Concentration ppm	0.04	0.08	0.11	0.06
	RSD%	10.10	1.75	8.21	10.61
5	Concentration ppm	0.08	0.07	0.08	0.05
	RSD%	1.86	0.00	5.30	8.49
6	Concentration ppm	0.07	0.11	0.10	0.06
	RSD%	0.00	4.46	0.69	1.18
7	Concentration ppm	0.10	0.09	0.09	0.07
	RSD%	2.19	8.27	0.00	14.73
8	Concentration ppm	0.11	0.13	0.11	0.06
	RSD%	0.67	7.92	3.37	1.18
9	Concentration ppm	0.10	0.12	0.10	0.06
	RSD%	3.72	3.63	1.46	4.64
10	Concentration ppm	0.10	0.08	0.11	0.06
	RSD%	0.72	7.25	13.65	10.61
11	Concentration ppm	0.11	0.11	0.10	0.05
	RSD%	3.93	3.79	0.00	7.22
12	Concentration ppm	0.10	0.10	0.11	0.04
	RSD%	2.75	5.10	3.24	26.05
13	Concentration ppm	0.10	0.08	0.13	0.05
	RSD%	4.90	2.72	0.00	5.34
14	Concentration ppm	0.08	0.09	0.11	0.04
	RSD%	3.37	0.00	1.89	19.73
15	Concentration ppm	0.07	0.09	0.08	0.04
	RSD%	4.16	3.33	0.00	1.68
16	Concentration ppm	0.04	0.08	0.08	0.05
	RSD%	18.61	3.54	1.89	12.73
17	Concentration ppm	0.06	0.11	0.06	0.08
	RSD%	2.24	6.37	6.10	7.95
18	Concentration ppm	0.05	0.09	0.10	0.06
	RSD%	13.34	2.38	6.43	0.00
19	Concentration ppm	0.04	0.09	0.05	0.05
	RSD%	21.38	6.15	18.05	1.41
20	Concentration ppm	0.05	0.07	0.07	0.05
	RSD%	8.66	11.79	12.48	4.61
21	Concentration ppm	0.07	0.09	0.08	0.06
	RSD%	1.07	9.64	5.30	10.79
22	Concentration ppm	0.08	0.12	0.09	0.07
	RSD%	4.48	0.60	6.58	4.91
23	Concentration ppm	0.08	0.12	0.07	0.07
	RSD%	7.67	5.89	5.05	2.02
24	Concentration ppm	0.09	0.11	0.06	0.09
	RSD%	2.28	2.67	4.42	9.15

Appendix 4.6a: The mean uncorrected concentration of Manganese in the Smethwick sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
1	Concentration ppm	11.05	10.75	11.40	11.70
	RSD%	0.15	1.01	0.34	0.21
2	Concentration ppm	10.33	10.71	11.85	12.12
	RSD%	0.37	1.72	1.59	0.90
3	Concentration ppm	10.80	10.96	11.55	11.70
	RSD%	1.39	0.33	0.85	2.02
4	Concentration ppm	10.54	10.78	11.50	11.83
	RSD%	0.97	1.99	2.28	0.44
5	Concentration ppm	10.49	11.19	10.43	11.23
	RSD%	0.18	0.69	0.45	1.57
6	Concentration ppm	10.12	10.96	9.74	11.41
	RSD%	0.76	1.12	0.66	0.35
7	Concentration ppm	10.92	10.54	10.36	11.50
	RSD%	0.94	0.10	1.21	0.20
8	Concentration ppm	11.33	10.83	10.95	11.63
	RSD%	0.02	0.35	0.85	0.33
9	Concentration ppm	10.51	10.90	11.17	11.30
	RSD%	0.37	1.73	0.58	0.78
10	Concentration ppm	10.32	11.08	11.35	11.25
	RSD%	0.53	1.14	0.81	0.50
11	Concentration ppm	9.97	10.53	10.80	11.68
	RSD%	0.65	0.54	0.90	1.14
12	Concentration ppm	9.38	10.39	11.02	11.65
	RSD%	0.03	0.71	1.39	0.20
13	Concentration ppm	10.17	10.13	11.68	13.11
	RSD%	0.86	0.50	2.47	1.21
14	Concentration ppm	10.49	10.28	12.28	12.54
	RSD%	0.07	0.83	0.61	0.33
15	Concentration ppm	10.73	9.89	11.80	13.84
	RSD%	0.46	0.58	0.09	0.17
16	Concentration ppm	10.65	9.73	11.14	13.81
	RSD%	0.01	1.53	1.06	0.50
17	Concentration ppm	10.02	9.38	11.17	14.29
	RSD%	0.62	1.03	0.99	0.08
18	Concentration ppm	9.85	9.92	10.89	14.44
	RSD%	0.57	0.16	1.18	0.23
19	Concentration ppm	10.50	10.48	11.04	15.08
	RSD%	0.04	0.66	2.22	0.25
20	Concentration ppm	10.15	10.84	10.40	15.22
	RSD%	0.06	0.06	0.65	0.40
21	Concentration ppm	10.12	10.51	10.58	13.60
	RSD%	0.34	1.11	1.75	0.16
22	Concentration ppm	10.47	10.90	10.90	14.40
	RSD%	0.32	0.61	1.06	0.78
23	Concentration ppm	10.47	10.77	10.58	14.05
	RSD%	0.49	0.33	0.01	0.38
24	Concentration ppm	9.48	10.60	10.43	14.80
	RSD%	0.68	1.61	0.69	0.34

Appendix 4.6b: The mean uncorrected concentration of Manganese in the Snarestone sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
1	**Concentration ppm**	**2.55**	**3.06**	**2.56**	**2.87**
	RSD%	0.17	0.69	0.08	1.82
2	**Concentration ppm**	**2.53**	**2.73**	**2.37**	**2.32**
	RSD%	1.06	1.06	1.58	1.22
3	**Concentration ppm**	**3.62**	**2.82**	**2.43**	**2.28**
	RSD%	0.14	0.48	0.15	1.08
4	**Concentration ppm**	**2.31**	**2.97**	**2.62**	**1.69**
	RSD%	1.04	1.55	0.16	0.63
5	**Concentration ppm**	**2.25**	**13.61**	**2.70**	**1.95**
	RSD%	1.29	1.90	0.63	4.03
6	**Concentration ppm**	**1.84**	**2.27**	**2.12**	**2.18**
	RSD%	1.54	0.09	0.27	0.94
7	**Concentration ppm**	**2.04**	**2.17**	**3.07**	**1.82**
	RSD%	0.59	0.10	1.36	2.17
8	**Concentration ppm**	**2.22**	**2.39**	**2.78**	**1.63**
	RSD%	0.19	2.58	1.76	2.21
9	**Concentration ppm**	**2.14**	**2.51**	**2.66**	**1.89**
	RSD%	1.36	0.65	1.52	1.87
10	**Concentration ppm**	**2.00**	**2.26**	**2.13**	**1.54**
	RSD%	0.95	1.19	1.83	1.56
11	**Concentration ppm**	**2.07**	**2.04**	**2.08**	**2.55**
	RSD%	0.31	1.29	0.75	0.36
12	**Concentration ppm**	**1.95**	**2.64**	**2.03**	**1.61**
	RSD%	0.58	1.21	0.52	0.57
13	**Concentration ppm**	**2.08**	**2.30**	**2.02**	**1.56**
	RSD%	0.17	1.60	1.40	2.81
14	**Concentration ppm**	**2.20**	**2.16**	**2.23**	**1.59**
	RSD%	0.45	0.16	1.27	0.76
15	**Concentration ppm**	**2.28**	**2.18**	**3.00**	**1.56**
	RSD%	2.20	1.36	2.01	1.95
16	**Concentration ppm**	**1.89**	**2.07**	**2.62**	**1.56**
	RSD%	1.31	0.62	1.43	0.91
17	**Concentration ppm**	**1.79**	**2.32**	**3.52**	**2.13**
	RSD%	1.31	1.16	0.44	0.53
18	**Concentration ppm**	**1.62**	**2.23**	**2.41**	**1.91**
	RSD%	1.44	1.49	0.50	0.74
19	**Concentration ppm**	**1.53**	**2.58**	**1.96**	**1.90**
	RSD%	0.28	0.58	1.55	0.30
20	**Concentration ppm**	**1.43**	**2.17**	**1.89**	**1.70**
	RSD%	0.89	1.43	3.60	2.87
21	**Concentration ppm**	**1.65**	**2.44**	**1.83**	**1.70**
	RSD%	0.99	1.07	1.94	0.25
22	**Concentration ppm**	**2.27**	**2.98**	**2.01**	**1.76**
	RSD%	1.31	0.17	0.81	0.20
23	**Concentration ppm**	**2.31**	**2.69**	**2.32**	**1.79**
	RSD%	0.21	0.13	0.98	3.48
24	**Concentration ppm**	**2.10**	**2.51**	**1.68**	**2.04**
	RSD%	1.04	0.37	0.55	1.70

Appendix 4.7a: The mean uncorrected concentration of Iron in the Smethwick sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
1	Concentration ppm	359.47	367.93	362.61	376.28
	RSD%	0.86	0.36	3.05	2.86
2	Concentration ppm	344.83	358.55	380.98	388.87
	RSD%	0.16	0.51	0.25	1.40
3	Concentration ppm	349.42	364.66	380.63	368.07
	RSD%	0.23	0.05	1.09	0.45
4	Concentration ppm	334.62	364.35	384.09	372.73
	RSD%	0.89	1.00	0.45	0.46
5	Concentration ppm	337.26	373.50	351.43	361.14
	RSD%	0.02	0.46	0.41	1.14
6	Concentration ppm	329.23	371.28	341.98	363.65
	RSD%	0.42	2.84	0.37	0.47
7	Concentration ppm	344.91	359.31	350.59	364.16
	RSD%	0.52	0.12	0.47	1.58
8	Concentration ppm	368.26	375.56	360.05	367.35
	RSD%	0.56	1.28	0.34	1.31
9	Concentration ppm	343.98	370.69	359.50	356.27
	RSD%	0.62	1.80	0.05	1.14
10	Concentration ppm	346.06	367.21	359.26	354.59
	RSD%	1.36	1.13	0.17	0.16
11	Concentration ppm	337.05	344.68	356.31	378.89
	RSD%	0.10	0.47	0.86	0.19
12	Concentration ppm	335.37	351.98	355.39	373.38
	RSD%	0.25	0.42	2.86	1.23
13	Concentration ppm	355.34	340.37	381.32	410.05
	RSD%	0.36	0.48	2.16	0.19
14	Concentration ppm	360.10	351.42	386.79	414.63
	RSD%	0.30	0.06	0.40	0.38
15	Concentration ppm	363.36	347.55	373.80	467.33
	RSD%	0.10	0.14	0.50	1.12
16	Concentration ppm	353.49	350.09	353.56	439.23
	RSD%	0.52	0.91	1.71	1.42
17	Concentration ppm	336.84	349.31	354.59	457.29
	RSD%	0.25	1.23	0.16	0.23
18	Concentration ppm	337.13	360.22	362.21	469.82
	RSD%	0.58	0.76	0.31	0.76
19	Concentration ppm	350.88	380.21	365.40	496.89
	RSD%	1.17	1.55	1.14	0.01
20	Concentration ppm	343.70	383.89	345.84	683.01
	RSD%	0.69	0.32	0.64	0.64
21	Concentration ppm	341.82	372.24	358.36	714.64
	RSD%	0.14	1.11	0.97	0.63
22	Concentration ppm	347.02	385.56	366.83	652.37
	RSD%	0.25	0.85	1.41	0.42
23	Concentration ppm	340.49	352.77	353.07	502.75
	RSD%	0.28	0.17	2.27	0.49
24	Concentration ppm	345.21	365.95	363.05	501.68
	RSD%	0.76	0.70	0.65	0.94

Appendix 4.7b: The mean uncorrected concentration of Iron in the Snarestone sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
1	Concentration ppm	109.92	138.80	125.01	132.24
	RSD%	0.08	1.55	0.77	2.74
2	Concentration ppm	114.93	125.07	104.95	111.50
	RSD%	0.18	0.24	1.21	0.02
3	Concentration ppm	100.63	130.61	107.37	109.26
	RSD%	0.05	0.03	1.69	0.55
4	Concentration ppm	70.48	106.09	115.45	75.93
	RSD%	0.28	0.22	0.29	0.11
5	Concentration ppm	84.44	97.40	102.96	79.69
	RSD%	0.74	0.11	1.87	0.37
6	Concentration ppm	87.33	123.13	120.14	78.61
	RSD%	0.01	1.24	1.67	0.22
7	Concentration ppm	102.55	119.48	152.61	90.79
	RSD%	0.21	4.05	0.30	1.32
8	Concentration ppm	105.09	134.76	125.67	93.54
	RSD%	1.50	1.46	0.68	1.21
9	Concentration ppm	103.92	135.86	113.98	76.93
	RSD%	0.63	0.64	0.29	0.09
10	Concentration ppm	111.91	104.52	114.71	77.95
	RSD%	0.16	0.70	0.00	1.21
11	Concentration ppm	117.40	193.27	106.29	141.88
	RSD%	0.26	0.34	1.59	0.88
12	Concentration ppm	109.00	126.19	114.33	65.00
	RSD%	0.56	0.83	0.29	1.58
13	Concentration ppm	105.56	99.68	121.86	60.47
	RSD%	0.85	1.68	0.22	0.20
14	Concentration ppm	109.18	96.59	120.68	58.45
	RSD%	0.35	0.51	1.81	1.24
15	Concentration ppm	101.62	94.76	102.16	59.87
	RSD%	0.68	1.59	0.54	0.27
16	Concentration ppm	62.07	93.08	92.86	59.85
	RSD%	0.29	0.78	0.20	1.55
17	Concentration ppm	77.70	100.36	91.68	77.11
	RSD%	1.01	1.11	1.10	0.39
18	Concentration ppm	75.05	96.99	101.39	70.25
	RSD%	0.38	0.04	0.86	0.64
19	Concentration ppm	71.31	111.08	64.85	71.53
	RSD%	1.78	2.01	0.62	1.48
20	Concentration ppm	64.29	84.91	83.70	68.45
	RSD%	1.14	2.25	1.21	0.15
21	Concentration ppm	72.13	102.52	87.75	68.60
	RSD%	0.14	0.03	0.36	0.57
22	Concentration ppm	91.45	131.04	91.81	78.70
	RSD%	0.55	0.78	1.65	1.02
23	Concentration ppm	95.21	123.64	83.94	80.27
	RSD%	0.50	1.11	0.85	1.33
24	Concentration ppm	101.39	114.36	74.31	97.59
	RSD%	1.20	1.43	1.11	1.25

Appendix 4.8a: The mean uncorrected concentration of Copper in the Smethwick sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
1	Concentration ppm	3.69	3.03	3.16	3.24
	RSD%	0.15	1.73	2.57	0.72
2	Concentration ppm	3.58	3.22	3.34	3.21
	RSD%	1.05	1.21	1.21	0.33
3	Concentration ppm	3.61	3.47	3.34	3.20
	RSD%	0.18	0.14	0.17	0.66
4	Concentration ppm	3.59	3.56	3.44	3.17
	RSD%	0.45	1.49	1.36	0.58
5	Concentration ppm	3.75	3.78	3.34	3.15
	RSD%	0.34	0.52	0.53	0.25
6	Concentration ppm	3.66	3.83	3.36	3.20
	RSD%	0.43	1.66	0.17	0.57
7	Concentration ppm	3.48	3.73	3.32	3.31
	RSD%	0.26	0.78	1.09	0.77
8	Concentration ppm	3.19	3.63	3.26	3.38
	RSD%	1.71	0.08	1.56	0.57
9	Concentration ppm	3.39	3.62	3.03	3.27
	RSD%	0.38	0.53	0.84	1.02
10	Concentration ppm	3.52	3.66	3.17	3.29
	RSD%	0.44	0.95	2.77	0.86
11	Concentration ppm	3.30	3.70	3.35	3.30
	RSD%	0.96	0.42	1.61	0.56
12	Concentration ppm	3.48	3.63	3.42	3.27
	RSD%	0.57	0.04	1.43	0.48
13	Concentration ppm	3.66	3.64	3.58	3.47
	RSD%	0.10	0.62	0.49	0.33
14	Concentration ppm	3.76	3.66	3.52	4.05
	RSD%	0.30	0.41	1.40	0.10
15	Concentration ppm	3.99	3.62	3.51	4.85
	RSD%	0.28	1.23	0.30	0.03
16	Concentration ppm	3.99	3.58	3.51	4.46
	RSD%	0.09	0.10	1.98	0.27
17	Concentration ppm	3.97	3.57	3.60	4.19
	RSD%	1.58	0.18	1.20	0.67
18	Concentration ppm	3.88	3.59	3.62	4.08
	RSD%	1.42	0.32	1.64	0.45
19	Concentration ppm	3.93	3.76	3.67	4.05
	RSD%	0.49	2.24	0.37	2.06
20	Concentration ppm	3.84	3.82	3.73	5.60
	RSD%	0.42	1.30	0.02	1.16
21	Concentration ppm	3.94	3.72	3.62	6.64
	RSD%	0.83	0.49	0.62	1.34
22	Concentration ppm	3.89	3.49	3.54	5.07
	RSD%	0.33	2.21	0.30	1.94
23	Concentration ppm	3.86	3.28	3.57	4.01
	RSD%	0.77	0.60	1.78	0.35
24	Concentration ppm	3.68	3.15	3.59	4.05
	RSD%	0.63	0.34	1.12	1.14

Appendix 4.8b: The mean uncorrected concentration of Copper in the Snarestone sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
1	Concentration ppm	0.18	0.24	0.22	0.25
	RSD%	2.31	1.45	0.32	0.00
2	Concentration ppm	0.19	0.22	0.18	0.20
	RSD%	0.73	0.32	0.79	2.84
3	Concentration ppm	0.11	0.17	0.18	0.18
	RSD%	1.32	1.23	1.54	0.38
4	Concentration ppm	0.07	0.17	0.20	0.13
	RSD%	0.00	1.24	0.71	0.00
5	Concentration ppm	0.13	0.13	0.15	0.11
	RSD%	1.62	2.72	0.94	1.88
6	Concentration ppm	0.13	0.19	0.17	0.11
	RSD%	0.00	0.00	0.82	1.32
7	Concentration ppm	0.14	0.20	0.19	0.14
	RSD%	0.00	0.70	1.10	1.55
8	Concentration ppm	0.14	0.22	0.19	0.14
	RSD%	2.54	0.00	1.11	1.00
9	Concentration ppm	0.13	0.21	0.17	0.13
	RSD%	2.66	1.33	2.12	2.76
10	Concentration ppm	0.16	0.15	0.18	0.13
	RSD%	1.75	0.96	0.39	0.56
11	Concentration ppm	0.17	0.18	0.20	0.11
	RSD%	0.41	0.39	1.73	1.30
12	Concentration ppm	0.16	0.19	0.22	0.10
	RSD%	0.00	3.04	0.65	2.80
13	Concentration ppm	0.17	0.15	0.18	0.11
	RSD%	0.43	1.94	0.79	0.64
14	Concentration ppm	0.12	0.14	0.17	0.11
	RSD%	0.00	1.49	2.86	1.31
15	Concentration ppm	0.10	0.17	0.13	0.12
	RSD%	1.37	1.26	1.59	1.77
16	Concentration ppm	0.09	0.14	0.13	0.11
	RSD%	1.54	0.50	2.26	0.64
17	Concentration ppm	0.10	0.18	0.11	0.12
	RSD%	0.00	1.19	0.64	1.17
18	Concentration ppm	0.12	0.15	0.16	0.11
	RSD%	1.19	3.30	1.76	1.93
19	Concentration ppm	0.10	0.17	0.09	0.12
	RSD%	0.71	0.43	0.75	3.07
20	Concentration ppm	0.10	0.13	0.12	0.12
	RSD%	2.04	2.24	0.59	1.78
21	Concentration ppm	0.13	0.15	0.12	0.34
	RSD%	2.23	1.43	0.00	0.21
22	Concentration ppm	0.14	0.20	0.13	0.15
	RSD%	0.52	2.15	2.64	1.85
23	Concentration ppm	0.17	0.19	0.11	0.17
	RSD%	0.85	1.11	0.63	1.23
24	Concentration ppm	0.16	0.17	0.12	0.18
	RSD%	1.78	1.63	0.57	0.79

Appendix 4.9a: The mean uncorrected concentration of Zinc in the Smethwick sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
1	Concentration ppm	43.68	41.74	40.37	39.61
	RSD%	0.62	1.18	0.66	1.18
2	Concentration ppm	42.46	45.57	43.55	40.50
	RSD%	0.26	0.32	1.59	1.00
3	Concentration ppm	43.38	49.92	43.70	41.01
	RSD%	0.44	0.21	0.11	0.27
4	Concentration ppm	43.21	51.94	46.21	40.47
	RSD%	0.23	0.82	0.26	0.09
5	Concentration ppm	45.43	53.08	44.99	40.82
	RSD%	1.32	0.79	1.34	1.45
6	Concentration ppm	44.16	55.07	46.22	41.73
	RSD%	0.62	1.55	1.63	2.05
7	Concentration ppm	43.36	52.68	44.80	44.32
	RSD%	0.88	0.46	1.03	0.74
8	Concentration ppm	40.40	50.73	46.14	45.68
	RSD%	0.24	1.46	0.65	0.15
9	Concentration ppm	41.86	50.98	43.09	43.37
	RSD%	0.55	2.50	0.80	0.14
10	Concentration ppm	44.07	53.36	44.29	43.67
	RSD%	0.65	1.54	0.09	1.26
11	Concentration ppm	40.80	52.06	47.10	48.53
	RSD%	0.67	0.76	0.69	0.20
12	Concentration ppm	43.08	51.07	49.82	48.73
	RSD%	1.49	0.34	1.02	0.57
13	Concentration ppm	47.41	51.34	51.81	51.55
	RSD%	0.24	1.17	0.53	1.19
14	Concentration ppm	48.52	52.18	52.66	51.86
	RSD%	0.01	0.47	0.22	2.10
15	Concentration ppm	52.55	51.30	53.41	59.12
	RSD%	0.38	0.59	1.94	0.96
16	Concentration ppm	50.88	49.86	53.31	59.58
	RSD%	0.71	0.38	0.82	1.31
17	Concentration ppm	50.25	48.57	54.73	65.73
	RSD%	1.02	0.78	2.08	0.29
18	Concentration ppm	48.33	51.30	55.37	70.18
	RSD%	0.47	0.10	1.95	0.09
19	Concentration ppm	49.28	54.36	55.85	75.75
	RSD%	0.06	0.83	0.87	0.58
20	Concentration ppm	48.78	55.11	55.35	77.65
	RSD%	0.60	0.19	1.75	0.31
21	Concentration ppm	51.05	51.70	54.03	87.15
	RSD%	0.29	1.50	0.31	1.29
22	Concentration ppm	51.19	45.54	55.86	80.31
	RSD%	0.68	0.62	1.78	0.83
23	Concentration ppm	50.47	43.05	56.02	59.97
	RSD%	0.77	0.79	0.72	1.13
24	Concentration ppm	45.50	43.00	54.34	63.70
	RSD%	0.34	0.27	0.73	0.89

Appendix 4.9b: The mean uncorrected concentration of Zinc in the Snarestone sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
1	Concentration ppm	1.66	2.21	2.03	2.24
	RSD%	0.17	0.35	1.81	0.13
2	Concentration ppm	1.72	2.00	1.70	1.78
	RSD%	0.33	0.28	0.71	1.31
3	Concentration ppm	0.65	1.54	1.59	1.58
	RSD%	0.22	1.01	0.31	0.49
4	Concentration ppm	0.49	1.30	1.77	0.96
	RSD%	1.16	2.44	0.76	1.33
5	Concentration ppm	0.86	1.08	1.18	0.78
	RSD%	0.49	0.39	0.12	1.54
6	Concentration ppm	0.93	1.67	1.34	0.85
	RSD%	0.53	0.89	2.11	1.24
7	Concentration ppm	1.45	1.62	1.13	0.94
	RSD%	0.10	0.61	1.57	0.90
8	Concentration ppm	1.45	1.80	1.35	0.84
	RSD%	0.78	0.71	0.16	0.85
9	Concentration ppm	1.33	1.72	1.32	0.84
	RSD%	0.05	0.21	0.32	0.42
10	Concentration ppm	1.47	1.12	1.45	0.87
	RSD%	0.29	0.50	2.44	1.14
11	Concentration ppm	1.57	1.14	1.30	0.66
	RSD%	0.14	0.37	1.58	0.21
12	Concentration ppm	1.45	1.34	1.40	0.45
	RSD%	0.64	1.64	1.16	2.65
13	Concentration ppm	1.44	1.07	1.58	0.41
	RSD%	1.38	2.91	0.36	1.04
14	Concentration ppm	0.78	1.13	1.51	0.45
	RSD%	0.00	0.75	0.09	0.78
15	Concentration ppm	0.60	1.16	0.97	0.33
	RSD%	1.30	1.53	1.67	0.64
16	Concentration ppm	0.39	1.06	0.74	0.34
	RSD%	0.90	1.74	0.76	0.00
17	Concentration ppm	0.63	1.28	0.62	0.44
	RSD%	0.11	2.94	0.11	1.27
18	Concentration ppm	0.61	1.16	1.08	0.49
	RSD%	1.85	2.20	0.39	1.60
19	Concentration ppm	0.54	1.33	0.51	0.45
	RSD%	0.52	1.33	0.83	2.82
20	Concentration ppm	0.52	0.91	0.75	0.36
	RSD%	1.09	2.64	2.46	0.00
21	Concentration ppm	0.42	1.22	0.55	0.49
	RSD%	2.88	0.29	0.38	0.29
22	Concentration ppm	0.48	1.78	0.51	0.45
	RSD%	1.04	1.07	0.83	1.74
23	Concentration ppm	0.50	1.61	0.57	0.48
	RSD%	0.71	1.01	0.49	1.46
24	Concentration ppm	0.50	1.52	0.38	0.59
	RSD%	0.14	1.30	4.15	0.84

Appendix 4.10a: The mean uncorrected concentration of Cadmium in the Smethwick sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
1	**Concentration ppm**	**0.16**	**0.15**	**0.16**	**0.14**
	RSD%	2.24	0.97	0.45	1.47
2	**Concentration ppm**	**0.15**	**0.16**	**0.16**	**0.15**
	RSD%	0.92	2.17	2.62	0.98
3	**Concentration ppm**	**0.16**	**0.18**	**0.16**	**0.14**
	RSD%	1.77	1.19	1.33	2.46
4	**Concentration ppm**	**0.17**	**0.19**	**0.16**	**0.14**
	RSD%	0.43	0.37	2.16	0.00
5	**Concentration ppm**	**0.18**	**0.19**	**0.15**	**0.14**
	RSD%	1.96	0.37	0.00	0.50
6	**Concentration ppm**	**0.18**	**0.20**	**0.16**	**0.14**
	RSD%	0.80	1.06	1.32	4.91
7	**Concentration ppm**	**0.16**	**0.19**	**0.16**	**0.16**
	RSD%	1.33	2.95	0.90	3.58
8	**Concentration ppm**	**0.15**	**0.19**	**0.15**	**0.16**
	RSD%	0.46	0.00	2.81	0.44
9	**Concentration ppm**	**0.16**	**0.19**	**0.15**	**0.15**
	RSD%	1.82	3.42	0.00	0.47
10	**Concentration ppm**	**0.17**	**0.20**	**0.15**	**0.16**
	RSD%	0.00	2.87	4.59	0.00
11	**Concentration ppm**	**0.15**	**0.19**	**0.17**	**0.17**
	RSD%	1.40	0.00	2.50	2.06
12	**Concentration ppm**	**0.16**	**0.19**	**0.18**	**0.17**
	RSD%	0.43	1.13	0.78	1.22
13	**Concentration ppm**	**0.17**	**0.19**	**0.19**	**0.18**
	RSD%	0.81	1.50	2.62	0.40
14	**Concentration ppm**	**0.18**	**0.19**	**0.19**	**0.18**
	RSD%	0.39	2.21	1.47	1.16
15	**Concentration ppm**	**0.20**	**0.19**	**0.20**	**0.20**
	RSD%	1.04	3.35	2.90	0.00
16	**Concentration ppm**	**0.19**	**0.19**	**0.19**	**0.19**
	RSD%	2.93	0.00	4.44	1.10
17	**Concentration ppm**	**0.20**	**0.18**	**0.20**	**0.23**
	RSD%	2.54	3.23	1.78	0.30
18	**Concentration ppm**	**0.19**	**0.19**	**0.20**	**0.26**
	RSD%	1.48	2.68	0.36	0.27
19	**Concentration ppm**	**0.19**	**0.20**	**0.20**	**0.28**
	RSD%	2.95	2.77	0.71	1.76
20	**Concentration ppm**	**0.19**	**0.20**	**0.20**	**0.31**
	RSD%	1.13	0.35	0.00	2.30
21	**Concentration ppm**	**0.20**	**0.19**	**0.20**	**0.35**
	RSD%	3.21	2.20	0.00	1.80
22	**Concentration ppm**	**0.20**	**0.17**	**0.20**	**0.29**
	RSD%	3.55	0.42	0.71	0.24
23	**Concentration ppm**	**0.19**	**0.16**	**0.20**	**0.21**
	RSD%	0.00	0.43	0.35	0.33
24	**Concentration ppm**	**0.17**	**0.16**	**0.20**	**0.24**
	RSD%	2.86	3.09	1.05	0.00

Appendix 4.10b: The mean uncorrected concentration of Cadmium in the Snarestone sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
1	Concentration ppm	0.000	0.004	0.007	0.004
	RSD%	0.000	17.680	60.610	53.030
2	Concentration ppm	0.006	0.007	0.004	0.006
	RSD%	35.360	0.000	53.030	0.000
3	Concentration ppm	0.000	0.003	0.007	0.003
	RSD%	0.000	47.140	30.300	141.420
4	Concentration ppm	0.002	0.003	0.006	0.001
	RSD%	212.130	23.570	58.930	141.420
5	Concentration ppm	0.000	0.006	0.001	0.002
	RSD%	0.000	35.360	141.420	106.070
6	Concentration ppm	0.001	0.005	0.003	0.003
	RSD%	70.710	28.280	94.280	117.850
7	Concentration ppm	0.004	0.005	0.003	0.003
	RSD%	35.360	70.710	23.570	94.280
8	Concentration ppm	0.005	0.006	0.000	0.004
	RSD%	42.430	23.570	0.000	70.710
9	Concentration ppm	0.006	0.007	0.001	0.003
	RSD%	58.930	10.100	70.710	23.570
10	Concentration ppm	0.002	0.006	0.007	0.003
	RSD%	70.710	35.360	40.410	0.000
11	Concentration ppm	0.006	0.007	0.008	0.003
	RSD%	23.570	30.300	35.360	0.000
12	Concentration ppm	0.006	0.007	0.005	0.005
	RSD%	0.000	30.300	42.430	42.430
13	Concentration ppm	0.002	0.004	0.007	0.007
	RSD%	70.710	0.000	10.100	30.300
14	Concentration ppm	0.000	0.004	0.006	0.003
	RSD%	0.000	35.360	11.790	23.570
15	Concentration ppm	-0.001	0.004	0.001	0.002
	RSD%	70.710	53.030	70.710	70.710
16	Concentration ppm	-0.002	0.002	0.000	0.002
	RSD%	141.420	106.070	0.000	70.710
17	Concentration ppm	-0.002	0.006	0.001	0.001
	RSD%	0.000	23.570	70.710	0.000
18	Concentration ppm	0.004	0.007	0.000	0.000
	RSD%	88.390	10.100	0.000	0.000
19	Concentration ppm	0.004	0.007	0.003	0.001
	RSD%	0.000	20.200	70.710	141.420
20	Concentration ppm	0.001	0.006	0.002	0.002
	RSD%	70.710	11.790	0.000	176.780
21	Concentration ppm	0.004	0.006	0.001	0.002
	RSD%	35.360	47.140	70.710	0.000
22	Concentration ppm	0.002	0.009	0.002	0.006
	RSD%	106.070	7.860	35.360	11.790
23	Concentration ppm	-0.001	0.005	0.001	0.004
	RSD%	70.710	56.570	212.130	0.000
24	Concentration ppm	0.002	0.005	0.000	0.004
	RSD%	35.360	14.140	0.000	0.000

The dection limit for Cd in these solutions is 0.0057ppm, some values are just in excess of this, however the RSD values are all >10% and therefore this data is not used in the study

Appendix 4.11a: The mean uncorrected concentration of Lead in the Smethwick sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
1	Concentration ppm	7.34	6.04	5.86	5.70
	RSD%	1.45	0.08	0.99	1.57
2	Concentration ppm	7.06	6.76	6.39	5.91
	RSD%	0.67	0.62	2.53	1.26
3	Concentration ppm	7.49	7.28	6.40	6.09
	RSD%	0.27	0.34	0.66	0.35
4	Concentration ppm	7.47	7.85	6.72	5.95
	RSD%	1.42	0.36	0.04	1.29
5	Concentration ppm	7.84	8.13	6.49	5.95
	RSD%	2.16	0.07	1.43	2.83
6	Concentration ppm	7.61	8.43	6.64	6.15
	RSD%	0.68	2.37	0.45	1.63
7	Concentration ppm	7.35	8.21	6.53	6.70
	RSD%	0.44	0.28	1.02	0.81
8	Concentration ppm	6.78	7.95	6.45	6.82
	RSD%	1.75	1.64	1.52	0.33
9	Concentration ppm	7.13	7.60	6.36	6.55
	RSD%	0.24	2.78	0.62	0.30
10	Concentration ppm	7.54	7.88	6.52	6.56
	RSD%	0.12	0.40	0.18	0.69
11	Concentration ppm	7.03	7.80	7.01	7.16
	RSD%	1.90	0.78	0.33	0.12
12	Concentration ppm	7.51	7.63	7.43	7.20
	RSD%	0.18	0.28	0.76	0.84
13	Concentration ppm	8.05	7.66	7.72	7.57
	RSD%	0.18	1.18	0.04	0.80
14	Concentration ppm	8.25	7.93	7.70	7.73
	RSD%	1.32	0.21	0.85	1.98
15	Concentration ppm	8.85	7.95	7.99	8.66
	RSD%	0.28	1.00	0.75	0.47
16	Concentration ppm	8.65	7.55	7.94	8.60
	RSD%	2.32	0.86	0.20	3.26
17	Concentration ppm	8.60	7.48	8.08	9.29
	RSD%	0.51	0.67	2.06	2.30
18	Concentration ppm	8.51	7.71	8.28	9.76
	RSD%	0.33	1.75	1.77	0.46
19	Concentration ppm	8.64	7.93	8.20	9.90
	RSD%	0.16	1.93	1.07	1.11
20	Concentration ppm	8.45	8.17	8.28	11.12
	RSD%	2.14	0.48	0.20	0.05
21	Concentration ppm	8.65	7.80	8.19	11.78
	RSD%	0.20	0.56	0.71	1.00
22	Concentration ppm	8.73	6.79	8.11	9.73
	RSD%	0.56	1.50	0.53	0.26
23	Concentration ppm	8.64	6.33	8.09	9.03
	RSD%	0.50	1.90	0.11	1.14
24	Concentration ppm	7.87	6.29	8.07	8.86
	RSD%	1.18	0.11	0.68	1.79

Appendix 4.11b: The mean uncorrected concentration of Lead in the Snarestone sediment aqua regia leachates and the relative standard deviation (RSD) of 2 duplicate analyses

Depth cm		Spring	Summer	Autumn	Winter
1	Concentration ppm	0.26	0.32	0.30	0.32
	RSD%	17.88	3.34	7.00	9.60
2	Concentration ppm	0.29	0.30	0.23	0.25
	RSD%	11.66	0.95	6.37	10.51
3	Concentration ppm	0.18	0.24	0.24	0.35
	RSD%	3.84	7.69	8.98	2.45
4	Concentration ppm	0.09	0.41	0.26	0.13
	RSD%	15.21	8.75	0.54	11.51
5	Concentration ppm	0.17	0.18	0.19	0.11
	RSD%	13.55	0.00	10.05	10.73
6	Concentration ppm	0.17	0.24	0.24	0.13
	RSD%	4.18	2.32	6.48	24.83
7	Concentration ppm	0.21	0.24	0.20	0.24
	RSD%	2.41	10.43	7.86	0.00
8	Concentration ppm	0.21	0.25	0.22	0.16
	RSD%	5.67	1.71	9.73	0.88
9	Concentration ppm	0.19	0.26	0.24	0.14
	RSD%	0.00	1.09	5.39	14.54
10	Concentration ppm	0.27	0.21	0.25	0.57
	RSD%	5.74	1.37	2.82	2.87
11	Concentration ppm	0.26	0.14	0.22	0.18
	RSD%	4.88	18.66	7.26	8.16
12	Concentration ppm	0.24	0.24	0.25	0.14
	RSD%	3.55	4.21	8.59	9.09
13	Concentration ppm	0.42	0.17	0.25	0.06
	RSD%	2.01	3.31	3.91	19.71
14	Concentration ppm	0.24	0.23	0.28	0.08
	RSD%	7.86	0.61	7.38	33.12
15	Concentration ppm	0.20	0.28	0.18	0.08
	RSD%	0.71	0.51	2.41	2.59
16	Concentration ppm	0.10	0.19	0.14	0.08
	RSD%	12.02	16.04	5.56	14.84
17	Concentration ppm	0.19	0.25	0.14	0.08
	RSD%	9.08	8.35	13.83	2.53
18	Concentration ppm	0.17	0.22	0.21	0.08
	RSD%	0.84	11.03	2.02	56.57
19	Concentration ppm	0.21	0.21	0.12	0.08
	RSD%	17.25	2.04	16.92	13.43
20	Concentration ppm	0.22	0.13	0.19	0.06
	RSD%	5.57	3.39	5.86	8.11
21	Concentration ppm	0.16	0.20	0.15	0.09
	RSD%	0.87	0.00	1.95	47.14
22	Concentration ppm	0.16	0.25	0.13	0.09
	RSD%	3.19	1.41	14.80	33.41
23	Concentration ppm	0.17	0.25	0.14	0.11
	RSD%	4.23	1.95	14.14	22.26
24	Concentration ppm	0.16	0.24	0.15	0.11
	RSD%	20.72	9.55	3.26	32.25

The dection limit for Pb in these solutions is 0.396ppm and all the above values fall beneath it, therefore this data is not discussed in the study

Appendix 5: The Mean Uncorrected Concentrations of Metals, Sulphur and Phosphorus In Smethwick and Snarestone Sediments, Sequential Extraction Leachates, and The Relative Standard Deviation (RSD) From the Mean of Two Analyses

Appendix 5.1a: Mean corrected and uncorrected concentrations of Aluminium in the Smethwick sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1	Fraction 2	Fraction 3
1	**Uncorrected concentration ppm**	**2.235**	**29.765**	**36.195**
	Corrected concentration ppm	242.257	3226.305	3923.269
	RSD%	2.47	1.6	7.37
2	**Uncorrected concentration ppm**	**2.01**	**25.287**	**40.032**
	Corrected concentration ppm	207.02	2604.43	4123.089
	RSD%	1.2	4.79	2.19
3	**Uncorrected concentration ppm**	**1.792**	**26.971**	**42.372**
	Corrected concentration ppm	173.453	2610.598	4101.303
	RSD%	0.2	5.44	1.16
4	**Uncorrected concentration ppm**	**2.173**	**23.895**	**33.386**
	Corrected concentration ppm	216.342	2378.961	3323.875
	RSD%	1.3	0.44	1.01
5	**Uncorrected concentration ppm**	**1.579**	**12.112**	**49.305**
	Corrected concentration ppm	165.354	1371.385	5582.572
	RSD%	0.09	1.86	0.59
6	**Uncorrected concentration ppm**	**1.279**	**24.674**	**32.609**
	Corrected concentration ppm	161.248	3110.74	4111.134
	RSD%	0.06	1.42	1.24
8	**Uncorrected concentration ppm**	**1.771**	**23.902**	**32.342**
	Corrected concentration ppm	217.179	2931.115	3966.117
	RSD%	0.32	6.4	2.55
10	**Uncorrected concentration ppm**	**1.438**	**13.673**	**45.376**
	Corrected concentration ppm	141.035	1341.013	4450.362
	RSD%	2.51	1.58	0.33
12	**Uncorrected concentration ppm**	**1.928**	**20.471**	**42.289**
	Corrected concentration ppm	210.343	2233.369	4613.694
	RSD%	3.89	0.02	0.41
14	**Uncorrected concentration ppm**	**2.482**	**10.82**	**46.432**
	Corrected concentration ppm	279.801	1219.76	5234.37
	RSD%	0.97	3.93	2.56
16	**Uncorrected concentration ppm**	**3.08**	**16.686**	**42.571**
	Corrected concentration ppm	310.041	1679.656	4285.308
	RSD%	1.45	3.47	1.19
18	**Uncorrected concentration ppm**	**2.731**	**12.432**	**47.458**
	Corrected concentration ppm	228.428	1039.843	3969.504
	RSD%	0.36	2.09	1.24
20	**Uncorrected concentration ppm**	**3.297**	**9.575**	**44.958**
	Corrected concentration ppm	316.945	920.458	4321.877
	RSD%	0.13	2.35	0.42
22	**Uncorrected concentration ppm**	**2.006**	**14.87**	**37.475**
	Corrected concentration ppm	206.24	1528.809	3852.866
	RSD%	1.09	5.78	0.96
24	**Uncorrected concentration ppm**	**1.83**	**20.246**	**32.659**
	Corrected concentration ppm	207.202	2120.172	3420.068
	RSD%	3.21	2.8	1.83

Al Detection limits:

Fraction 1: 0.021ppm

Fraction 2: 0.174ppm

Fraction 3 0.042ppm

Appendix 5.1b: Mean corrected and uncorrected concentrations of Aluminium in the Snarestone sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1	Fraction 2	Fraction 3
1	**Uncorrected concentration ppm**	**1.202**	**10.662**	**15.224**
	Corrected concentration ppm	136.401	1209.907	2159.494
	RSD%	2.12	0.09	1.5
2	**Uncorrected concentration ppm**	**1.106**	**22.762**	**15.606**
	Corrected concentration ppm	100.762	2073.731	1777.23
	RSD%	0.26	9.59	0.39
3	**Uncorrected concentration ppm**	**1.069**	**12.183**	**17.277**
	Corrected concentration ppm	101.016	1151.238	2040.746
	RSD%	4.89	0.38	5.19
4	**Uncorrected concentration ppm**	**1.137**	**9.556**	**14.538**
	Corrected concentration ppm	122.332	1028.146	1955.21
	RSD%	6.84	1.31	1.99
5	**Uncorrected concentration ppm**	**0.879**	**9.791**	**15.466**
	Corrected concentration ppm	74.948	834.827	1648.381
	RSD%	0	1.29	1.4
6	**Uncorrected concentration ppm**	**1.019**	**10.694**	**14.865**
	Corrected concentration ppm	88.099	924.565	1606.468
	RSD%	0.56	3.42	4.08
8	**Uncorrected concentration ppm**	**0.908**	**9.998**	**15.264**
	Corrected concentration ppm	92.375	1017.147	1941.106
	RSD%	4.67	1.8	0.95
10	**Uncorrected concentration ppm**	**1.042**	**10.276**	**17.189**
	Corrected concentration ppm	87.503	862.94	1804.335
	RSD%	3.6	2.42	0.14
12	**Uncorrected concentration ppm**	**0.781**	**10.425**	**18.635**
	Corrected concentration ppm	65.623	875.949	1957.232
	RSD%	11.14	2.37	1.93
14	**Uncorrected concentration ppm**	**1.484**	**9.578**	**13.807**
	Corrected concentration ppm	127.813	824.931	1486.455
	RSD%	9.72	1.18	0
16	**Uncorrected concentration ppm**	**0.68**	**8.258**	**10.99**
	Corrected concentration ppm	42.867	520.576	865.998
	RSD%	2.29	1.28	0.33
18	**Uncorrected concentration ppm**	**1.104**	**10.098**	**15.659**
	Corrected concentration ppm	70.374	643.689	1247.713
	RSD%	0.38	0.03	0.27
20	**Uncorrected concentration ppm**	**1.238**	**9.798**	**19.209**
	Corrected concentration ppm	70.081	554.644	1359.227
	RSD%	3.08	0.07	1.66
22	**Uncorrected concentration ppm**	**1.128**	**7.056**	**8.68**
	Corrected concentration ppm	57.715	361.023	555.145
	RSD%	7.84	1.77	0.95
24	**Uncorrected concentration ppm**	**1.209**	**8.894**	**16.774**
	Corrected concentration ppm	63.696	468.581	1104.675
	RSD%	3.86	0.55	9.41

Al Detection limits:

Fraction 1: 0.021ppm

Fraction 2: 0.174ppm

Fraction 3 0.042ppm

Appendix 5.2a: Mean corrected and uncorrected concentrations of Phosphorous in the Smethwick sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1	Fraction 2	Fraction 3
1	**Uncorrected concentration ppm**	**70.922**	**60.533**	**21.189**
	Corrected concentration ppm	7687.418	6561.327	2296.73
	RSD%	3.23	0.16	8.64
2	**Uncorrected concentration ppm**	**50.979**	**71.932**	**25.707**
	Corrected concentration ppm	5250.574	7408.624	2647.688
	RSD%	1.04	2.27	1
3	**Uncorrected concentration ppm**	**54.102**	**62.532**	**30.148**
	Corrected concentration ppm	5236.683	6052.646	2918.108
	RSD%	1.14	1.03	5.9
4	**Uncorrected concentration ppm**	**60.556**	**74.346**	**23.142**
	Corrected concentration ppm	6028.892	7401.81	2303.993
	RSD%	5.51	0.96	4.5
5	**Uncorrected concentration ppm**	**59.831**	**69.143**	**26.35**
	Corrected concentration ppm	6265.535	7828.735	2983.486
	RSD%	0.71	1.99	1.54
6	**Uncorrected concentration ppm**	**67.138**	**53.176**	**21.713**
	Corrected concentration ppm	8464.329	6704.09	2737.436
	RSD%	1.77	2.02	6.23
8	**Uncorrected concentration ppm**	**55.106**	**48.795**	**21.433**
	Corrected concentration ppm	6757.679	5983.758	2628.341
	RSD%	1.94	11.73	1.65
10	**Uncorrected concentration ppm**	**55.542**	**68.447**	**28.062**
	Corrected concentration ppm	5447.417	6713.106	2752.249
	RSD%	7.89	2.06	1.67
12	**Uncorrected concentration ppm**	**58.659**	**70.904**	**24.766**
	Corrected concentration ppm	6399.647	7735.566	2701.949
	RSD%	2.95	2.1	2.06
14	**Uncorrected concentration ppm**	**59.728**	**75.369**	**28.145**
	Corrected concentration ppm	6733.254	8496.494	3172.841
	RSD%	7.59	3.68	1.53
16	**Uncorrected concentration ppm**	**65.529**	**62.223**	**22.447**
	Corrected concentration ppm	6596.32	6263.53	2259.574
	RSD%	1.04	0.41	2.78
18	**Uncorrected concentration ppm**	**74.194**	**64.132**	**28.658**
	Corrected concentration ppm	6205.769	5364.158	2397.026
	RSD%	1.54	5.4	7.62
20	**Uncorrected concentration ppm**	**57.687**	**83.487**	**28.513**
	Corrected concentration ppm	5545.534	8025.725	2740.995
	RSD%	1.98	4.05	5.11
22	**Uncorrected concentration ppm**	**61.774**	**58.059**	**19.91**
	Corrected concentration ppm	6351.086	5969.141	2046.98
	RSD%	1.6	3.46	0.62
24	**Uncorrected concentration ppm**	**81.363**	**58.959**	**19.352**
	Corrected concentration ppm	9212.348	6174.218	2026.552
	RSD%	0.22	17.21	0.26

P Detection Limits: Fraction 1: 0.225ppm Fraction 2: 0.666ppm Fraction 3: 0.646ppm

Appendix 5.2b: Mean corrected and uncorrected concentrations of Phosphorous in the Snarestone sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1		Fraction 2		Fraction 3	
		P178	P179	P178	P179	P178	P179
1	**Uncorrected concentration ppm**	**1.02**	**0.98**	**1.99**	**2.27**	**14.4**	**14.37**
	Corrected concentration ppm	115.75	111.21	75.1	142.87	2042.61	2038.36
	RSD%	9.79	41.13	11.74	52.41	1.18	0.54
2	**Uncorrected concentration ppm**	**1.08**	**0.73**	**3.37**	**2.85**	**12.97**	**13.2**
	Corrected concentration ppm	98.39	66.51	166.46	147.02	1477.04	1503.23
	RSD%	5.24	19.37	12.49	29.61	3.49	2.62
3	**Uncorrected concentration ppm**	**0.71**	**0.49**	**1.35**	**1.86**	**12.44**	**12.46**
	Corrected concentration ppm	67.09	46.3	127.57	175.76	1469.4	1471.77
	RSD%	2.99	70.71	16.24	10.64	2.05	1.36
4	**Uncorrected concentration ppm**	**1.34**	**1.18**	**1.03**	**0.84**	**11.47**	**11.31**
	Corrected concentration ppm	144.17	126.96	207.65	90.38	1542.6	1521.08
	RSD%	2.64	5.39	10.47	37.88	3.76	3.38
5	**Uncorrected concentration ppm**	**1.29**	**1.01**	**1.42**	**1.05**	**13.52**	**12.93**
	Corrected concentration ppm	109.99	86.12	121.08	89.53	1440.97	1378.09
	RSD%	5.48	11.2	6.47	22.22	7.48	6.78
6	**Uncorrected concentration ppm**	**1.21**	**1.06**	**1.36**	**0.88**	**11.01**	**10.35**
	Corrected concentration ppm	104.61	91.64	117.58	76.08	1189.86	1118.53
	RSD%	15.78	16.01	12.48	13.66	5.07	5.94
8	**Uncorrected concentration ppm**	**1.33**	**0.94**	**1.06**	**0.77**	**9.11**	**9.14**
	Corrected concentration ppm	135.31	95.63	107.84	78.34	1158.51	1162.32
	RSD%	15.95	23.32	0	56.02	3.03	2.63
10	**Uncorrected concentration ppm**	**1.33**	**1.18**	**1.2**	**0.98**	**10.25**	**9.82**
	Corrected concentration ppm	111.69	99.09	100.77	82.3	1075.95	1030.81
	RSD%	1.06	9.59	1.77	25.25	0.41	1.51
12	**Uncorrected concentration ppm**	**0.73**	**0.67**	**1.11**	**1.08**	**10.49**	**9.68**
	Corrected concentration ppm	61.34	56.3	93.27	90.75	1101.76	1016.69
	RSD%	21.31	20.05	17.2	47.8	2.63	4.53
14	**Uncorrected concentration ppm**	**1.55**	**1.19**	**1.31**	**1.3**	**11.62**	**11.44**
	Corrected concentration ppm	133.5	102.49	112.83	111.97	1251	1231.63
	RSD%	6.84	6.54	3.24	10.88	3.53	1.24
16	**Uncorrected concentration ppm**	**0.61**	**0.37**	**1.91**	**1.65**	**12.05**	**12.24**
	Corrected concentration ppm	38.45	23.32	120.4	104.01	949.52	964.5
	RSD%	39.41	42.04	10.37	6.43	5.69	9.99
18	**Uncorrected concentration ppm**	**0.85**	**0.6**	**2.04**	**1.75**	**11.45**	**11.58**
	Corrected concentration ppm	54.18	38.25	130.04	111.55	912.34	922.7
	RSD%	5.82	0	2.08	8.08	1.61	0.18
20	**Uncorrected concentration ppm**	**0.77**	**0.92**	**2.22**	**2.2**	**10.44**	**10.37**
	Corrected concentration ppm	43.59	52.08	125.67	124.54	738.73	733.78
	RSD%	3.67	8.45	4.78	11.25	1.49	0.89
22	**Uncorrected concentration ppm**	**1.13**	**1.03**	**1.95**	**1.78**	**8.76**	**8.63**
	Corrected concentration ppm	57.82	52.7	99.77	91.07	560.26	551.95
	RSD%	3.75	17.16	1.09	9.93	1.86	4.1
24	**Uncorrected concentration ppm**	**1.63**	**1.51**	**2.4**	**2.62**	**18.28**	**18.59**
	Corrected concentration ppm	85.88	79.55	126.44	138.03	1203.85	1224.27
	RSD%	4.34	11.71	5.3	2.43	3.67	3.08

P178 Detection Limits: Fraction 1: 0.225ppm Fraction 2: 0.666ppm Fraction 3: 0.646ppm

P179 Detection Limits: Fraction 1: 0.333ppm Fraction 2: 0.323ppm

The concentration of P is above the detection limit in all samples, however in some samples the concentration is low and when the RSD is >10% for both P178 and P179 and therefore the values are not used. When the RSD is <10% for only one of the P wavelengths, that value is used.

Appendix 5.3a: Mean corrected and uncorrected concentrations of Sulphur in the Smethwick sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1	Fraction 2	Fraction 3
1	**Uncorrected concentration ppm**	**7.189**	**0.942**	**66.871**
	Corrected concentration ppm	0.779	0.102	7.248
	RSD%	2.7	5.03	6.43
2	**Uncorrected concentration ppm**	**6.263**	**0.83**	**71.3**
	Corrected concentration ppm	0.645	0.085	7.344
	RSD%	2.43	0	3.74
3	**Uncorrected concentration ppm**	**8.526**	**0.84**	**80.832**
	Corrected concentration ppm	0.825	0.081	7.824
	RSD%	1.6	5.22	7.11
4	**Uncorrected concentration ppm**	**11.184**	**0.825**	**71.774**
	Corrected concentration ppm	1.113	0.082	7.146
	RSD%	1.22	6.6	0.37
5	**Uncorrected concentration ppm**	**12.718**	**0.967**	**92.128**
	Corrected concentration ppm	1.332	0.109	10.431
	RSD%	5.96	14.33	2.45
6	**Uncorrected concentration ppm**	**9.975**	**0.914**	**70.695**
	Corrected concentration ppm	1.258	0.115	8.913
	RSD%	4.76	9.36	1.19
8	**Uncorrected concentration ppm**	**9.529**	**0.748**	**70.721**
	Corrected concentration ppm	1.169	0.092	8.673
	RSD%	4.18	20.61	1.14
10	Uncorrected concentration ppm	**9.683**	**0.858**	**80.694**
	Corrected concentration ppm	0.95	0.084	7.914
	RSD%	0.43	4.29	3.69
12	**Uncorrected concentration ppm**	**11.722**	**0.733**	**78.204**
	Corrected concentration ppm	1.279	0.08	8.532
	RSD%	2.37	1.06	6.02
14	**Uncorrected concentration ppm**	**7.453**	**0.751**	**86.987**
	Corrected concentration ppm	0.84	0.085	9.806
	RSD%	5.07	1.04	1.72
16	**Uncorrected concentration ppm**	**4.992**	**0.877**	**102.81**
	Corrected concentration ppm	0.503	0.088	10.349
	RSD%	6.08	1.77	3.88
18	**Uncorrected concentration ppm**	**4.432**	**0.803**	**109.128**
	Corrected concentration ppm	0.371	0.067	9.128
	RSD%	2.23	9.16	3.66
20	**Uncorrected concentration ppm**	**3.862**	**0.895**	**104.082**
	Corrected concentration ppm	0.371	0.086	10.006
	RSD%	0.15	28.13	3.59
22	**Uncorrected concentration ppm**	**3.76**	**0.83**	**111.182**
	Corrected concentration ppm	0.387	0.085	11.431
	RSD%	9.48	11.33	4.61
24	**Uncorrected concentration ppm**	**5.844**	**0.656**	**69.332**
	Corrected concentration ppm	0.662	0.069	7.26
	RSD%	2.64	32.77	4.91

S Detection Limits: Fraction 1: 0.0801ppm Fraction 2: 0.198ppm Fraction 3: 0.161ppm

Appendix 5.3b: Mean corrected and uncorrected concentrations of Sulphur in the Snarestone sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1		Fraction 2		Fraction 3	
		S180	S182	S180	S182	S180	S182
1	**Uncorrected concentration ppm**	**2.48**	**1.4**	**27.09**	**25.64**	**50.42**	**51.73**
	Corrected concentration ppm	281.43	158.87	2436.38	2259.46	7151.98	7337.8
	RSD%	2	3.54	1.23	6.16	1.15	1.6
2	**Uncorrected concentration ppm**	**2.77**	**1.39**	**25.93**	**26.18**	**55.09**	**54.72**
	Corrected concentration ppm	252.36	126.64	1892	1931.9	6273.72	6231.58
	RSD%	3.06	0.51	4.73	2.04	2.25	2.52
3	**Uncorrected concentration ppm**	**3.37**	**1.88**	**7.35**	**6.99**	**60.15**	**61.32**
	Corrected concentration ppm	318.45	177.65	694.54	660.52	7104.87	7243.07
	RSD%	1.05	1.5	0.48	0.2	0.83	1.64
4	**Uncorrected concentration ppm**	**2.85**	**1.7**	**7.7**	**7.41**	**46.28**	**47.03**
	Corrected concentration ppm	306.64	182.91	828.46	797.25	6224.18	6325.05
	RSD%	0.99	4.58	1.01	5.25	1.47	2.48
5	**Uncorrected concentration ppm**	**3.18**	**1.78**	**0.62**	**0.51**	**71.22**	**72.7**
	Corrected concentration ppm	271.14	151.77	52.86	43.49	7590.7	7748.43
	RSD%	3.11	11.52	5.7	6.93	9.1	8.89
6	**Uncorrected concentration ppm**	**2.94**	**1.54**	**1.24**	**0.86**	**82.69**	**83.26**
	Corrected concentration ppm	254.18	133.14	107.21	74.35	8936.35	8997.95
	RSD%	0.72	5.05	13.69	1.64	0.35	1.4
8	**Uncorrected concentration ppm**	**3.14**	**1.68**	**3.77**	**3.66**	**77**	**78.11**
	Corrected concentration ppm	319.45	170.91	383.54	372.35	9792	9933.16
	RSD%	0.45	10.94	1.13	2.51	0.88	0.31
10	**Uncorrected concentration ppm**	**3.65**	**1.97**	**4.72**	**4.51**	**77.3**	**81.79**
	Corrected concentration ppm	306.51	165.43	396.37	378.73	8114.21	8585.52
	RSD%	1.55	12.56	1.95	1.1	1.29	2.33
12	**Uncorrected concentration ppm**	**4.14**	**2.07**	**3.37**	**3.38**	**77.87**	**82.91**
	Corrected concentration ppm	347.86	173.93	283.16	284	8178.68	8708.03
	RSD%	0.17	1.37	3.78	4.39	0.43	1.17
14	**Uncorrected concentration ppm**	**4**	**2.27**	**0.58**	**0.44**	**53.63**	**56.8**
	Corrected concentration ppm	344.51	195.51	49.95	37.9	5773.78	6115.06
	RSD%	0.53	6.54	0	16.07	0.15	2.07
16	**Uncorrected concentration ppm**	**4.55**	**1.53**	**6.06**	**5.49**	**39.7**	**42.35**
	Corrected concentration ppm	286.83	96.45	382.02	346.08	3128.31	3337.13
	RSD%	1.24	0.92	3.85	1.42	3.76	7.7
18	**Uncorrected concentration ppm**	**3.43**	**1.37**	**1.04**	**0.96**	**47.47**	**52.47**
	Corrected concentration ppm	218.64	87.33	66.29	61.19	3782.42	4180.82
	RSD%	5.77	8.77	12.92	2.21	12.29	0.67
20	**Uncorrected concentration ppm**	**4.07**	**1.66**	**7.77**	**7.17**	**59.16**	**59.32**
	Corrected concentration ppm	230.39	93.97	439.84	405.88	4186.16	4197.48
	RSD%	3.13	1.7	2.55	2.47	1.06	0.63
22	**Uncorrected concentration ppm**	**3.81**	**2.13**	**6.31**	**5.35**	**60.29**	**60.23**
	Corrected concentration ppm	194.94	108.98	322.85	273.73	3855.95	3852.12
	RSD%	2.23	2.99	0.11	3.44	3.45	0.85
24	**Uncorrected concentration ppm**	**3.57**	**1.7**	**6.45**	**6.07**	**27.04**	**27.93**
	Corrected concentration ppm	188.09	89.56	339.82	319.8	1780.76	1839.37
	RSD%	0.79	3.33	0.55	0.93	0.78	3.19

S180 Detection Limits: Fraction 1: 0.0801ppm Fraction 2: 0.198ppm Fraction 3: 0.161ppm

S182 Detection Limits: Fraction 1: 0.135ppm Fraction 2: 0.117ppm

Appendix 5.4a: Mean corrected and uncorrected concentrations of Calcium in the Smethwick sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1	Fraction 2	Fraction 3
1	**Uncorrected concentration ppm**	**229.638**	30.584	**14.009**
	Corrected concentration ppm	24891.052	3315.078	1518.471
	RSD%	0.54	5.31	7
2	**Uncorrected concentration ppm**	**219.941**	**36.124**	**17.251**
	Corrected concentration ppm	22652.786	3720.585	1776.764
	RSD%	1.21	4.08	4.21
3	**Uncorrected concentration ppm**	**252.076**	**40.041**	**18.163**
	Corrected concentration ppm	24399.135	3875.679	1758.047
	RSD%	0.88	0.24	2.59
4	**Uncorrected concentration ppm**	**277.397**	**41.685**	**27.358**
	Corrected concentration ppm	27617.355	4150.115	2723.734
	RSD%	1.83	0.98	0.4
5	**Uncorrected concentration ppm**	**285.7**	**40.239**	**13.942**
	Corrected concentration ppm	29918.658	4556.072	1578.587
	RSD%	0.87	0.08	0.27
6	**Uncorrected concentration ppm**	**333.212**	**36.904**	**15.44**
	Corrected concentration ppm	42009.235	4652.62	1946.576
	RSD%	1.18	0.34	0.04
8	**Uncorrected concentration ppm**	**268.345**	**28.75**	**14.782**
	Corrected concentration ppm	32907.294	3525.628	1812.725
	RSD%	0.57	1.05	0.01
10	**Uncorrected concentration ppm**	**289.226**	**51.638**	**20.018**
	Corrected concentration ppm	28366.545	5064.523	1963.314
	RSD%	1.78	0.39	2.3
12	**Uncorrected concentration ppm**	**276.499**	**41.87**	**18.176**
	Corrected concentration ppm	30165.803	4567.981	1982.986
	RSD%	0.75	0.16	1.27
14	**Uncorrected concentration ppm**	**250.354**	**39.393**	**24.894**
	Corrected concentration ppm	28222.894	4440.85	2806.349
	RSD%	1.07	1.18	1.37
16	**Uncorrected concentration ppm**	**256.07**	**35.648**	**20.781**
	Corrected concentration ppm	25776.675	3588.421	2091.87
	RSD%	1.34	3.15	2.28
18	**Uncorrected concentration ppm**	**271.192**	**38.919**	**24.361**
	Corrected concentration ppm	22683.167	3255.281	2037.614
	RSD%	1.24	4.51	1.97
20	**Uncorrected concentration ppm**	**236.197**	**36.668**	**28.303**
	Corrected concentration ppm	22705.956	3524.947	2720.808
	RSD%	0.31	1.28	1.94
22	**Uncorrected concentration ppm**	**243.181**	**25.83**	**17.556**
	Corrected concentration ppm	25001.838	2655.625	1804.961
	RSD%	0.31	2.99	1.35
24	**Uncorrected concentration ppm**	**251.598**	26.286	**19.592**
	Corrected concentration ppm	28487.254	2752.684	2051.685
	RSD%	1.41	19.89	4.3

Ca Detection limits

Fraction 1: 0.021ppm

Fraction 2: 0.327ppm

Fraction 3: 0.057ppm

Appendix 5.4b: Mean corrected and uncorrected concentrations of Calcium in the Snarestone sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1	Fraction 2	Fraction 3
1	**Uncorrected concentration ppm**	**180.885**	**23.492**	**2.042**
	Corrected concentration ppm	20526.54	2665.834	289.654
	RSD%	0.05	0.37	0.62
2	**Uncorrected concentration ppm**	**189.262**	**60.916**	**3.227**
	Corrected concentration ppm	17242.708	5549.751	367.495
	RSD%	0.48	11.52	0.75
3	**Uncorrected concentration ppm**	**212.074**	**29.453**	**5.783**
	Corrected concentration ppm	20040.019	2783.173	683.084
	RSD%	0.28	1.24	5.91
4	**Uncorrected concentration ppm**	**173.889**	**23.886**	**2.349**
	Corrected concentration ppm	18709.008	2569.935	315.916
	RSD%	0.34	0.22	0
5	**Uncorrected concentration ppm**	**197.971**	**35.749**	**7.978**
	Corrected concentration ppm	16879.949	3048.13	850.303
	RSD%	0.81	1.11	2.5
6	**Uncorrected concentration ppm**	**209.048**	**34.704**	**13.955**
	Corrected concentration ppm	18073.535	3000.383	1508.124
	RSD%	0.47	1.44	2.15
8	**Uncorrected concentration ppm**	**198.508**	**23.688**	**2.22**
	Corrected concentration ppm	20195.23	2409.901	282.315
	RSD%	1.72	1.3	2.1
10	**Uncorrected concentration ppm**	**236.381**	**39.021**	**4.599**
	Corrected concentration ppm	19850.396	3276.838	482.759
	RSD%	0.7	0.18	1.38
12	**Uncorrected concentration ppm**	**284.181**	**34.048**	**3.41**
	Corrected concentration ppm	23877.997	2860.846	358.152
	RSD%	0.88	4.05	0.15
14	**Uncorrected concentration ppm**	**259.995**	**46.079**	**5.808**
	Corrected concentration ppm	22392.755	3968.675	625.287
	RSD%	0.46	2.95	2.54
16	**Uncorrected concentration ppm**	**384.463**	**61.25**	**18.159**
	Corrected concentration ppm	24236.157	3861.138	1430.906
	RSD%	0.21	1.77	0.66
18	**Uncorrected concentration ppm**	**267.264**	**56.36**	**6.941**
	Corrected concentration ppm	17036.532	3592.624	553.061
	RSD%	0.6	0.53	0.62
20	**Uncorrected concentration ppm**	**327.535**	**67.88**	**13.307**
	Corrected concentration ppm	18541.073	3842.545	941.602
	RSD%	0.38	0.44	1.71
22	**Uncorrected concentration ppm**	**254.869**	**173.872**	**106.229**
	Corrected concentration ppm	13040.48	8896.234	6794.064
	RSD%	1.14	0.21	0.9
24	**Uncorrected concentration ppm**	**277.008**	**80.008**	**9.216**
	Corrected concentration ppm	14594.193	4215.229	606.932
	RSD%	0.43	0.31	8.88

Ca Detection limits
Fraction 1: 0.021ppm
Fraction 2: 0.327ppm
Fraction 3: 0.057ppm

Appendix 5.5a: Mean corrected and uncorrected concentrations of Chromium in the Smethwick sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1	Fraction 2	Fraction 3
1	**Uncorrected concentration ppm**	**0.026**	**0.7**	**2.007**
	Corrected concentration ppm	2.818	75.875	217.544
	RSD%	10.44	0.91	10.92
2	**Uncorrected concentration ppm**	**0.019**	**0.415**	**2.113**
	Corrected concentration ppm	1.957	42.743	217.628
	RSD%	14.89	0.85	3.08
3	**Uncorrected concentration ppm**	**0.014**	**0.46**	**2.251**
	Corrected concentration ppm	1.355	44.525	217.881
	RSD%	0	5.23	1.88
4	**Uncorrected concentration ppm**	**0.022**	**0.321**	**1.974**
	Corrected concentration ppm	2.19	31.958	196.529
	RSD%	25.71	7.05	4.62
5	**Uncorrected concentration ppm**	**0.018**	**0.128**	**3.322**
	Corrected concentration ppm	1.885	14.493	376.134
	RSD%	15.71	3.87	0.64
6	**Uncorrected concentration ppm**	**0.008**	**0.538**	**1.828**
	Corrected concentration ppm	1.009	67.828	230.463
	RSD%	35.36	1.71	3.21
8	**Uncorrected concentration ppm**	**0.02**	**0.592**	**1.785**
	Corrected concentration ppm	2.453	72.597	218.896
	RSD%	14.14	1.43	3.57
10	**Uncorrected concentration ppm**	**0.02**	**0.105**	**2.398**
	Corrected concentration ppm	1.962	10.298	235.19
	RSD%	14.14	4.71	1.5
12	**Uncorrected concentration ppm**	**0.026**	**0.226**	**2.202**
	Corrected concentration ppm	2.837	24.656	240.236
	RSD%	48.95	0	0.61
14	**Uncorrected concentration ppm**	**0.024**	**0.087**	**2.621**
	Corrected concentration ppm	2.706	9.808	295.47
	RSD%	38.3	2.44	0.16
16	**Uncorrected concentration ppm**	**0.043**	**0.32**	**3.493**
	Corrected concentration ppm	4.328	32.212	351.615
	RSD%	13.16	3.09	1.01
18	**Uncorrected concentration ppm**	**0.023**	**0.16**	**4.077**
	Corrected concentration ppm	1.924	13.383	341.01
	RSD%	13.07	7.51	4.18
20	**Uncorrected concentration ppm**	**0.051**	**0.109**	**4.296**
	Corrected concentration ppm	4.903	10.478	412.981
	RSD%	12.39	4.54	2.85
22	**Uncorrected concentration ppm**	**0.019**	**0.346**	**2.885**
	Corrected concentration ppm	1.953	35.573	296.612
	RSD%	11.44	15.12	1.45
24	**Uncorrected concentration ppm**	**0.015**	**0.374**	**1.915**
	Corrected concentration ppm	1.698	39.165	200.54
	RSD%	23.57	0.76	1.44

Cr Detection Limits
Fraction 1: 0.0066ppm
Fraction 2: 0.021ppm
Fraction 3: 0.0132ppm

Appendix 5.5b: Mean corrected and uncorrected concentrations of Chromium in the Snarestone sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1	Fraction 2	Fraction 3
1	**Uncorrected concentration ppm**	0	**0.008**	**0.051**
	Corrected concentration ppm	0	0.908	7.234
	RSD%	0	35.36	8.32
2	**Uncorrected concentration ppm**	**0.002**	**-0.146**	**0.053**
	Corrected concentration ppm	0.182	-13.302	6.036
	RSD%	388.91	196.63	9.34
3	**Uncorrected concentration ppm**	**-0.001**	**0.006**	**0.057**
	Corrected concentration ppm	-0.094	0.567	6.733
	RSD%	141.42	153.21	21.09
4	**Uncorrected concentration ppm**	**-0.003**	**0.01**	**0.05**
	Corrected concentration ppm	-0.323	1.076	6.724
	RSD%	23.57	42.43	8.49
5	**Uncorrected concentration ppm**	**0.002**	**0.009**	**0.06**
	Corrected concentration ppm	0.171	0.767	6.395
	RSD%	35.36	47.14	3.54
6	**Uncorrected concentration ppm**	**0.002**	**0.005**	**0.069**
	Corrected concentration ppm	0.173	0.432	7.457
	RSD%	106.07	240.42	4.1
8	**Uncorrected concentration ppm**	**0.001**	**-0.023**	**0.06**
	Corrected concentration ppm	0.102	-2.34	7.63
	RSD%	141.42	0	4.71
10	**Uncorrected concentration ppm**	**-0.002**	**-0.025**	**0.06**
	Corrected concentration ppm	-0.168	-2.099	6.298
	RSD%	176.78	28.28	8.25
12	**Uncorrected concentration ppm**	**-0.001**	**-0.027**	**0.07**
	Corrected concentration ppm	-0.084	-2.269	7.352
	RSD%	0	13.09	11.11
14	**Uncorrected concentration ppm**	**0.002**	**-0.005**	**0.049**
	Corrected concentration ppm	0.172	-0.431	5.275
	RSD%	35.36	212.13	12.99
16	**Uncorrected concentration ppm**	**0.004**	**-0.01**	**0.044**
	Corrected concentration ppm	0.252	-0.63	3.467
	RSD%	159.1	42.43	14.46
18	**Uncorrected concentration ppm**	**0.001**	**-0.001**	**0.053**
	Corrected concentration ppm	0.064	-0.064	4.223
	RSD%	494.97	141.42	0
20	**Uncorrected concentration ppm**	**0.003**	**0.013**	**0.075**
	Corrected concentration ppm	0.17	0.736	5.307
	RSD%	0	21.76	0.94
22	**Uncorrected concentration ppm**	**0.005**	**0.01**	**0.038**
	Corrected concentration ppm	0.256	0.512	2.43
	RSD%	28.28	42.43	1.86
24	**Uncorrected concentration ppm**	**0.01**	**0.01**	**0.055**
	Corrected concentration ppm	0.527	0.527	3.622
	RSD%	56.57	7.07	15.43

Cr Detection Limits

Fraction 1: 0.0066ppm

Fraction 2: 0.021ppm

Fraction 3: 0.0132ppm

Appendix 5.6a: Mean corrected and uncorrected concentrations of Manganese in the Smethwick sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1	Fraction 2	Fraction 3
1	**Uncorrected concentration ppm**	**9.479**	**3.875**	**1.721**
	Corrected concentration ppm	1027.453	420.021	186.544
	RSD%	0.83	1.31	2.84
2	**Uncorrected concentration ppm**	**7.794**	**5.478**	**1.711**
	Corrected concentration ppm	802.742	564.206	176.224
	RSD%	1.58	2.04	1.41
3	**Uncorrected concentration ppm**	**8.124**	**4.822**	**2.035**
	Corrected concentration ppm	786.344	466.735	196.973
	RSD%	0.42	3.4	2.57
4	**Uncorrected concentration ppm**	**8.497**	**5.897**	**1.227**
	Corrected concentration ppm	845.952	587.099	122.159
	RSD%	0.55	0.95	7.03
5	**Uncorrected concentration ppm**	**8.921**	**9.4**	**1.484**
	Corrected concentration ppm	934.212	1064.318	168.026
	RSD%	1.59	0.34	1.48
6	**Uncorrected concentration ppm**	**8.813**	**4.455**	**1.766**
	Corrected concentration ppm	1111.087	561.658	222.646
	RSD%	0.16	2.73	1.48
8	**Uncorrected concentration ppm**	**8.251**	**3.693**	**1.771**
	Corrected concentration ppm	1011.825	452.875	217.179
	RSD%	1.75	4.31	0.92
10	**Uncorrected concentration ppm**	**8.096**	**7.37**	**2.662**
	Corrected concentration ppm	794.035	722.831	261.082
	RSD%	4.49	6.64	2.1
12	**Uncorrected concentration ppm**	**9.821**	**6.869**	**2.458**
	Corrected concentration ppm	1071.463	749.402	268.166
	RSD%	0.04	0.48	0.55
14	**Uncorrected concentration ppm**	**9.75**	**9.077**	**3.164**
	Corrected concentration ppm	1099.136	1023.268	356.684
	RSD%	1.8	6.35	1.63
16	**Uncorrected concentration ppm**	**11.533**	**7.598**	**3.749**
	Corrected concentration ppm	1160.942	764.835	377.384
	RSD%	0.52	5.39	3.83
18	**Uncorrected concentration ppm**	**12.42**	**9.751**	**4.56**
	Corrected concentration ppm	1038.839	815.598	381.41
	RSD%	1.96	2.34	0.37
20	**Uncorrected concentration ppm**	**10.733**	**10.936**	**3.949**
	Corrected concentration ppm	1031.779	1051.293	379.623
	RSD%	1.23	2.08	3.94
22	**Uncorrected concentration ppm**	**15.003**	**6.307**	**2.876**
	Corrected concentration ppm	1542.483	648.433	295.686
	RSD%	0.69	10.29	0.22
24	**Uncorrected concentration ppm**	**13.172**	**4.116**	**1.306**
	Corrected concentration ppm	1491.403	431.03	136.765
	RSD%	0.67	2.73	0.43

Mn Detection Limits
Fraction 1: 0.0081ppm
Fraction 2: 0.648ppm
Fraction 3: 0.0237ppm

Appendix 5.6b: Mean corrected and uncorrected concentrations of Manganese in the Snarestone sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1	Fraction 2	Fraction 3
1	**Uncorrected concentration ppm**	**2.683**	**0.378**	**0.249**
	Corrected concentration ppm	304.463	42.895	35.32
	RSD%	1.95	2.81	0.57
2	**Uncorrected concentration ppm**	**2.57**	**0.968**	**0.276**
	Corrected concentration ppm	234.14	88.19	31.431
	RSD%	1.1	7.76	2.05
3	**Uncorrected concentration ppm**	**2.765**	**0.381**	**0.305**
	Corrected concentration ppm	261.28	36.003	36.026
	RSD%	0.08	13.92	7.88
4	**Uncorrected concentration ppm**	**2.278**	**0.363**	**0.257**
	Corrected concentration ppm	245.094	39.056	34.564
	RSD%	2.51	0.19	0.28
5	**Uncorrected concentration ppm**	**2.521**	**0.581**	**0.349**
	Corrected concentration ppm	214.952	49.539	37.197
	RSD%	0.2	1.83	0.61
6	**Uncorrected concentration ppm**	**2.648**	**0.623**	**0.423**
	Corrected concentration ppm	228.937	53.862	45.714
	RSD%	1.9	1.59	1.5
8	**Uncorrected concentration ppm**	**2.379**	**0.401**	**0.286**
	Corrected concentration ppm	242.028	40.796	36.37
	RSD%	0.12	3.35	3.46
10	**Uncorrected concentration ppm**	**2.218**	**0.567**	**0.32**
	Corrected concentration ppm	186.259	47.615	33.591
	RSD%	2.17	0.75	2.21
12	**Uncorrected concentration ppm**	**2.275**	**0.461**	**0.344**
	Corrected concentration ppm	191.154	38.735	36.13
	RSD%	1.52	5.52	5.76
14	**Uncorrected concentration ppm**	**3.478**	**1.007**	**0.305**
	Corrected concentration ppm	299.552	86.731	32.836
	RSD%	0	3.37	0.46
16	**Uncorrected concentration ppm**	**5.704**	**1.473**	**0.514**
	Corrected concentration ppm	359.574	92.856	40.503
	RSD%	0.51	3.98	1.79
18	**Uncorrected concentration ppm**	**3.528**	**1.115**	**0.402**
	Corrected concentration ppm	224.89	71.075	32.031
	RSD%	1.6	0.25	1.76
20	**Uncorrected concentration ppm**	**4.035**	**1.275**	**0.654**
	Corrected concentration ppm	228.413	72.175	46.277
	RSD%	1.23	5.6	0.76
22	**Uncorrected concentration ppm**	**2.946**	**2.694**	**2.14**
	Corrected concentration ppm	150.733	137.84	136.867
	RSD%	1.78	1.29	3.63
24	**Uncorrected concentration ppm**	**3.825**	**1.181**	**0.377**
	Corrected concentration ppm	201.52	62.221	24.828
	RSD%	1.74	1.92	0.75

Mn Detection Limits

Fraction 1: 0.0081ppm

Fraction 2: 0.648ppm

Fraction 3: 0.0237ppm

Appendix 5.7a: Mean corrected and uncorrected concentrations of Iron in the Smethwick sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1	Fraction 2	Fraction 3
1	**Uncorrected concentration ppm**	**190.237**	**109.982**	**51.518**
	Corrected concentration ppm	20620.276	11921.231	5584.168
	RSD%	0.53	2.81	3.51
2	**Uncorrected concentration ppm**	**167.717**	**140.956**	**51.383**
	Corrected concentration ppm	17273.984	14517.74	5292.183
	RSD%	0.7	1.96	5.06
3	**Uncorrected concentration ppm**	**163.845**	**129.77**	**53.436**
	Corrected concentration ppm	15859.012	12560.798	5172.219
	RSD%	1.14	1.78	0.07
4	**Uncorrected concentration ppm**	**166.63**	**156.311**	**41.668**
	Corrected concentration ppm	16589.508	15562.16	4148.422
	RSD%	1.67	4.8	4.37
5	**Uncorrected concentration ppm**	**176.309**	**189.726**	**32.993**
	Corrected concentration ppm	18463.174	21481.779	3735.642
	RSD%	2.02	0.53	3.38
6	**Uncorrected concentration ppm**	**167.143**	**107.446**	**48.218**
	Corrected concentration ppm	21072.319	13546.104	6079.017
	RSD%	1.93	1.24	0.84
8	**Uncorrected concentration ppm**	**163.379**	**98.334**	**47.291**
	Corrected concentration ppm	20035.256	12058.752	5799.321
	RSD%	1.07	3.66	4.32
10	**Uncorrected concentration ppm**	**158.815**	**161.24**	**46.909**
	Corrected concentration ppm	15576.168	15814.006	4600.714
	RSD%	4.38	0.77	2.19
12	**Uncorrected concentration ppm**	**179.366**	**155.978**	**43.965**
	Corrected concentration ppm	19568.677	17017.066	4796.544
	RSD%	1.16	0.49	0.24
14	**Uncorrected concentration ppm**	**173.578**	**197.516**	**41.317**
	Corrected concentration ppm	19567.786	22266.363	4657.746
	RSD%	0.02	3.46	1.02
16	**Uncorrected concentration ppm**	**184.843**	**156.18**	**42.575**
	Corrected concentration ppm	18606.779	15721.487	4285.711
	RSD%	2.35	2.6	1.48
18	**Uncorrected concentration ppm**	**181.29**	**184.294**	**41.509**
	Corrected concentration ppm	15163.542	15414.804	3471.915
	RSD%	0.27	3	2.76
20	**Uncorrected concentration ppm**	**167.554**	**217.262**	**40.241**
	Corrected concentration ppm	16107.206	20885.707	3868.425
	RSD%	4.15	0.8	0.28
22	**Uncorrected concentration ppm**	**227.965**	**127.026**	**40.206**
	Corrected concentration ppm	23437.456	13059.752	4133.645
	RSD%	1.09	3.89	0.94
24	**Uncorrected concentration ppm**	**228.816**	**115.592**	**39.576**
	Corrected concentration ppm	25907.755	12104.857	4144.42
	RSD%	1.81	0.06	0.52

Fe Detection Limits

Fraction 1: 0.015ppm

Fraction 2: 0.3672ppm

Fraction 3: 0.054ppm

Appendix 5.7b: Mean corrected and uncorrected concentrations of Iron in the Snarestone sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1	Fraction 2	Fraction 3
1	**Uncorrected concentration ppm**	**38.47**	**19.205**	**16.51**
	Corrected concentration ppm	4365.514	2179.353	2341.91
	RSD%	0.76	2	0.44
2	**Uncorrected concentration ppm**	**36.933**	**49.467**	**15.229**
	Corrected concentration ppm	3364.78	4506.689	1734.297
	RSD%	0.49	4.8	1.02
3	**Uncorrected concentration ppm**	**37.979**	**25.441**	**21.009**
	Corrected concentration ppm	3588.841	2404.058	2481.567
	RSD%	0.12	1.22	6.79
4	**Uncorrected concentration ppm**	**33.067**	**20.197**	**14.843**
	Corrected concentration ppm	3557.734	2173.029	1996.229
	RSD%	0.21	1.69	1.91
5	**Uncorrected concentration ppm**	**34.561**	**24.835**	**23.837**
	Corrected concentration ppm	2946.835	2117.55	2540.57
	RSD%	1.37	0.55	1.2
6	**Uncorrected concentration ppm**	**27.632**	**25.326**	**31.77**
	Corrected concentration ppm	2388.963	2189.595	3433.399
	RSD%	0.35	0.13	2.62
8	**Uncorrected concentration ppm**	**20.639**	**18.303**	**33.446**
	Corrected concentration ppm	2099.711	1862.057	4253.29
	RSD%	0.04	1.54	1.73
10	**Uncorrected concentration ppm**	**24.267**	**18.818**	**33.048**
	Corrected concentration ppm	2037.852	1580.266	3469.06
	RSD%	0.73	19	2.81
12	**Uncorrected concentration ppm**	**25.26**	**24.074**	**33.447**
	Corrected concentration ppm	2122.444	2022.791	3512.934
	RSD%	1.24	5.67	2.71
14	**Uncorrected concentration ppm**	**45.298**	**35.25**	**13.107**
	Corrected concentration ppm	3901.41	3035.999	1411.094
	RSD%	0.98	1.77	2.23
16	**Uncorrected concentration ppm**	**50.337**	**38.277**	**7.167**
	Corrected concentration ppm	3173.193	2412.943	564.75
	RSD%	0.11	1.27	0.25
18	**Uncorrected concentration ppm**	**36.98**	**26.672**	**16.165**
	Corrected concentration ppm	2357.261	1700.185	1288.031
	RSD%	1.5	2.66	1.93
20	**Uncorrected concentration ppm**	**35.45**	**28.048**	**22.938**
	Corrected concentration ppm	2006.75	1587.739	1623.09
	RSD%	0.55	1.43	3.63
22	**Uncorrected concentration ppm**	**32.45**	**38.079**	**9.595**
	Corrected concentration ppm	1660.318	1948.328	613.665
	RSD%	0.22	1.83	1.48
24	**Uncorrected concentration ppm**	**38.877**	**27.076**	**16.205**
	Corrected concentration ppm	2048.238	1426.502	1067.202
	RSD%	0	1.91	1.03

Fe Detection Limits

Fraction 1: 0.015ppm

Fraction 2: 0.3672ppm

Fraction 3: 0.054ppm

Appendix 5.8a: Mean corrected and uncorrected concentrations of Copper in the Smethwick sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1	Fraction 2	Fraction 3
1	**Uncorrected concentration ppm**	**0.001**	**-0.026**	**5.2**
	Corrected concentration ppm	0.108	-2.818	563.641
	RSD%	707.11	2.72	8.51
2	**Uncorrected concentration ppm**	**-0.006**	**-0.029**	**5.08**
	Corrected concentration ppm	-0.618	-2.987	523.214
	RSD%	0	14.63	7.04
3	**Uncorrected concentration ppm**	**-0.007**	**-0.034**	**5.388**
	Corrected concentration ppm	-0.678	-3.291	521.519
	RSD%	20.2	10.4	1.33
4	**Uncorrected concentration ppm**	**-0.008**	**-0.032**	**4.574**
	Corrected concentration ppm	-0.796	-3.186	455.383
	RSD%	8.84	11.05	0.96
5	**Uncorrected concentration ppm**	**-0.01**	**-0.044**	**5.648**
	Corrected concentration ppm	-1.047	-4.982	639.496
	RSD%	0	6.43	1.56
6	**Uncorrected concentration ppm**	**-0.008**	**-0.03**	**4.526**
	Corrected concentration ppm	-1.009	-3.782	570.609
	RSD%	8.84	2.36	1.08
8	**Uncorrected concentration ppm**	**-0.006**	**-0.031**	**4.389**
	Corrected concentration ppm	-0.736	-3.802	538.225
	RSD%	11.79	4.56	1.69
10	**Uncorrected concentration ppm**	**-0.005**	**-0.039**	**5.369**
	Corrected concentration ppm	-0.49	-3.825	526.578
	RSD%	14.14	3.63	1.11
12	**Uncorrected concentration ppm**	**-0.006**	**-0.032**	**5.056**
	Corrected concentration ppm	-0.655	-3.491	551.605
	RSD%	23.57	6.63	1.68
14	**Uncorrected concentration ppm**	**-0.006**	**-0.039**	**5.353**
	Corrected concentration ppm	-0.676	-4.397	603.454
	RSD%	23.57	7.25	2.5
16	**Uncorrected concentration ppm**	**-0.006**	**-0.036**	**6.143**
	Corrected concentration ppm	-0.604	-3.624	618.37
	RSD%	23.57	1.96	1.76
18	**Uncorrected concentration ppm**	**-0.007**	**-0.037**	**6.78**
	Corrected concentration ppm	-0.585	-3.095	567.096
	RSD%	20.2	3.82	0.45
20	**Uncorrected concentration ppm**	**-0.005**	**-0.033**	**6.742**
	Corrected concentration ppm	-0.481	-3.172	648.118
	RSD%	0	12.86	2.31
22	**Uncorrected concentration ppm**	**-0.012**	**-0.026**	**8.829**
	Corrected concentration ppm	-1.234	-2.673	907.724
	RSD%	17.68	8.16	4.28
24	**Uncorrected concentration ppm**	**-0.011**	**-0.028**	**4.409**
	Corrected concentration ppm	-1.245	-2.932	461.713
	RSD%	19.28	0	2.76

Cu Detection Limits

Fraction 1: 0.0021ppm

Fraction 2: 0.0642ppm

Fraction 3: 0.0423ppm

Appendix 5.8b: Mean corrected and uncorrected concentrations of Copper in the Snarestone sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1	Fraction 2	Fraction 3
1	**Uncorrected concentration ppm**	**-0.005**	**-0.012**	**0.037**
	Corrected concentration ppm	-0.567	-1.362	5.248
	RSD%	14.14	0	3.82
2	**Uncorrected concentration ppm**	**-0.005**	**-0.043**	**0.038**
	Corrected concentration ppm	-0.456	-3.918	4.327
	RSD%	14.14	9.76	10.02
3	**Uncorrected concentration ppm**	**-0.002**	**-0.014**	**0.007**
	Corrected concentration ppm	-0.189	-1.323	0.9331
	RSD%	35.36	10.1	30.43
4	**Uncorrected concentration ppm**	**-0.004**	**-0.761**	**0.033**
	Corrected concentration ppm	-0.43	-81.877	4.438
	RSD%	0	0.09	47.14
5	**Uncorrected concentration ppm**	**-0.003**	**-0.76**	**0.001**
	Corrected concentration ppm	-0.256	-64.801	0.15881
	RSD%	47.14	0.09	0
6	**Uncorrected concentration ppm**	**-0.004**	**-0.76**	**0.009**
	Corrected concentration ppm	-0.346	-65.707	0.9942
	RSD%	0	0.09	11.53
8	**Uncorrected concentration ppm**	**-0.003**	**-0.029**	**0.005**
	Corrected concentration ppm	-0.305	-2.95	0.8266
	RSD%	47.14	4.88	38.7
10	**Uncorrected concentration ppm**	**-0.004**	**-0.026**	**0.001**
	Corrected concentration ppm	-0.336	-2.183	0.10917
	RSD%	0	16.32	10.36
12	**Uncorrected concentration ppm**	**-0.004**	**-0.03**	**0.0011**
	Corrected concentration ppm	-0.336	-2.521	0.12183
	RSD%	0	4.71	14.27
14	**Uncorrected concentration ppm**	**-0.003**	**-0.014**	**0.006**
	Corrected concentration ppm	-0.258	-1.206	0.6567
	RSD%	47.14	30.3	0
16	**Uncorrected concentration ppm**	**-0.005**	**-0.024**	**0.009**
	Corrected concentration ppm	-0.315	-1.513	0.7092
	RSD%	0	5.89	29.43
18	**Uncorrected concentration ppm**	**-0.005**	**-0.023**	**0.003**
	Corrected concentration ppm	-0.319	-1.466	0.239
	RSD%	0	12.3	14.14
20	**Uncorrected concentration ppm**	**-0.005**	**-0.019**	**0.006**
	Corrected concentration ppm	-0.283	-1.076	0.4529
	RSD%	28.28	7.44	22.21
22	**Uncorrected concentration ppm**	**-0.006**	**-0.015**	**0.005**
	Corrected concentration ppm	-0.307	-0.767	0.3134
	RSD%	0	23.57	21.65
24	**Uncorrected concentration ppm**	**-0.008**	**-0.021**	**0.004**
	Corrected concentration ppm	-0.421	-1.106	0.3029
	RSD%	17.68	13.47	11.54

Cu Detection Limits

Fraction 1: 0.0021ppm

Fraction 2: 0.0642ppm

Fraction 3: 0.0423ppm

Appendix 5.9a: Mean corrected and uncorrected concentrations of Zinc in the Smethwick sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1	Fraction 2	Fraction 3
1	**Uncorrected concentration ppm**	**5.728**	**24.353**	**37.016**
	Corrected concentration ppm	620.873	2639.684	4012.259
	RSD%	1.04	0.79	7.07
2	**Uncorrected concentration ppm**	**4.551**	**18.637**	**45.071**
	Corrected concentration ppm	468.729	1919.515	4642.08
	RSD%	1.2	1	3.65
3	**Uncorrected concentration ppm**	**5.095**	**21.924**	**45.555**
	Corrected concentration ppm	493.159	2122.085	4409.395
	RSD%	1.6	0.14	1.88
4	**Uncorrected concentration ppm**	**5.417**	**18.115**	**38.188**
	Corrected concentration ppm	539.311	1803.51	3801.957
	RSD%	0.91	5.47	1.5
5	**Uncorrected concentration ppm**	**2.783**	**30.267**	**77.778**
	Corrected concentration ppm	291.437	3426.99	8806.436
	RSD%	1.12	1.11	0.35
6	**Uncorrected concentration ppm**	**2.361**	**12.704**	**44.206**
	Corrected concentration ppm	297.66	1601.639	5573.209
	RSD%	0.45	0.35	2.17
8	**Uncorrected concentration ppm**	**1.782**	**11.81**	**43.899**
	Corrected concentration ppm	218.528	1448.267	5383.358
	RSD%	0.56	3.32	3.26
10	**Uncorrected concentration ppm**	**2.272**	**11.698**	**59.135**
	Corrected concentration ppm	222.832	1147.31	5799.809
	RSD%	5.76	0.91	1.67
12	**Uncorrected concentration ppm**	**4.664**	**17.637**	**54.588**
	Corrected concentration ppm	508.838	1924.182	5955.504
	RSD%	0.29	0.45	1.13
14	**Uncorrected concentration ppm**	**3.347**	**13.868**	**80.178**
	Corrected concentration ppm	377.314	1563.367	9038.622
	RSD%	0.38	5.43	0.72
16	**Uncorrected concentration ppm**	**6.199**	**22.831**	**104.609**
	Corrected concentration ppm	624.008	2298.228	10530.215
	RSD%	1.49	2.16	2.26
18	**Uncorrected concentration ppm**	**9.405**	**25.14**	**116.88**
	Corrected concentration ppm	786.657	2102.771	9776.131
	RSD%	2.17	0.91	3.43
20	**Uncorrected concentration ppm**	**9.765**	**24.386**	**123.366**
	Corrected concentration ppm	938.723	2344.261	11859.35
	RSD%	0.97	0.88	0.52
22	**Uncorrected concentration ppm**	**8.971**	**21.346**	**115.39**
	Corrected concentration ppm	922.323	2194.617	11863.435
	RSD%	0.07	0.56	1.46
24	**Uncorrected concentration ppm**	**7.762**	**11.047**	**45.927**
	Corrected concentration ppm	878.855	1156.848	4809.5
	RSD%	0.13	0.14	0.16

Zn Detection Limits:
Fraction 1: 0.018ppm
Fraction 2: 0.0387ppm
Fraction 3: 0.0249ppm

Appendix 5.9b: Mean corrected and uncorrected concentrations of Zinc in the Snarestone sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1	Fraction 2	Fraction 3
1	**Uncorrected concentration ppm**	**0.103**	**2.553**	**0.673**
	Corrected concentration ppm	11.688	289.71	95.464
	RSD%	1.37	0.64	1.79
2	**Uncorrected concentration ppm**	**0.091**	**5.838**	**0.613**
	Corrected concentration ppm	8.291	531.871	69.809
	RSD%	0.78	7.42	4.04
3	**Uncorrected concentration ppm**	**0.067**	**2.57**	**0.648**
	Corrected concentration ppm	6.331	242.853	76.541
	RSD%	2.11	0.17	2.51
4	**Uncorrected concentration ppm**	**0.063**	**1.988**	**0.735**
	Corrected concentration ppm	6.778	213.892	98.85
	RSD%	1.12	0.71	0.48
5	**Uncorrected concentration ppm**	**0.051**	**2.043**	**0.919**
	Corrected concentration ppm	4.349	174.196	97.948
	RSD%	5.55	1.18	1.38
6	**Uncorrected concentration ppm**	**0.046**	**2.075**	**0.831**
	Corrected concentration ppm	3.977	179.397	89.807
	RSD%	6.15	5.08	2.13
8	**Uncorrected concentration ppm**	**0.039**	**1.81**	**0.651**
	Corrected concentration ppm	3.968	184.141	82.787
	RSD%	9.07	5.04	1.63
10	**Uncorrected concentration ppm**	**0.032**	**1.966**	**0.823**
	Corrected concentration ppm	2.687	165.097	86.391
	RSD%	11.05	7.19	2.92
12	**Uncorrected concentration ppm**	**0.02**	**1.967**	**0.924**
	Corrected concentration ppm	1.68	165.275	97.048
	RSD%	17.68	2.84	0.99
14	**Uncorrected concentration ppm**	**0.036**	**1.45**	**0.719**
	Corrected concentration ppm	3.101	124.885	77.407
	RSD%	1.96	3.71	0.69
16	**Uncorrected concentration ppm**	**0.038**	**1.021**	**0.77**
	Corrected concentration ppm	2.395	64.363	60.675
	RSD%	3.72	1.32	2.02
18	**Uncorrected concentration ppm**	**0.055**	**1.404**	**0.577**
	Corrected concentration ppm	3.506	89.497	45.976
	RSD%	3.86	3.22	3.8
20	**Uncorrected concentration ppm**	**0.034**	**0.954**	**0.683**
	Corrected concentration ppm	1.925	54.004	48.329
	RSD%	0	2.15	1.86
22	**Uncorrected concentration ppm**	**0.028**	**0.531**	**0.633**
	Corrected concentration ppm	1.433	27.169	40.485
	RSD%	7.58	0.13	0.78
24	**Uncorrected concentration ppm**	**0.019**	**0.56**	**0.408**
	Corrected concentration ppm	1.001	29.504	26.869
	RSD%	14.89	6.19	0.17

Zn Detection Limits:
Fraction 1: 0.018ppm
Fraction 2: 0.0387ppm
Fraction 3: 0.0249ppm

Appendix 5.10a: Mean corrected and uncorrected concentrations of Cadmium in the Smethwick sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1	Fraction 2	Fraction 3
1	**Uncorrected concentration ppm**	**0.003**	**0.005**	**0.209**
	Corrected concentration ppm	0.325	0.542	22.654
	RSD%	23.57	42.43	9.13
2	**Uncorrected concentration ppm**	**0.002**	**0.002**	**0.217**
	Corrected concentration ppm	0.206	0.206	22.35
	RSD%	212.13	70.71	3.26
3	**Uncorrected concentration ppm**	**0.004**	**0.005**	**0.231**
	Corrected concentration ppm	0.387	0.484	22.359
	RSD%	0	0	1.84
4	**Uncorrected concentration ppm**	**0.001**	**0.004**	**0.191**
	Corrected concentration ppm	0.1	0.398	19.016
	RSD%	212.13	0	4.07
5	**Uncorrected concentration ppm**	**0.001**	**0.002**	**0.387**
	Corrected concentration ppm	0.105	0.226	43.818
	RSD%	212.13	35.36	5.48
6	**Uncorrected concentration ppm**	**0.001**	**0.003**	**0.196**
	Corrected concentration ppm	0.126	0.378	24.71
	RSD%	424.26	47.14	6.13
8	**Uncorrected concentration ppm**	**-0.004**	**0.001**	**0.198**
	Corrected concentration ppm	-0.491	0.123	24.281
	RSD%	35.36	141.42	2.14
10	**Uncorrected concentration ppm**	**-0.001**	**0.001**	**0.252**
	Corrected concentration ppm	-0.098	0.098	24.716
	RSD%	212.13	212.13	3.09
12	**Uncorrected concentration ppm**	**-0.001**	**0.002**	**0.253**
	Corrected concentration ppm	-0.109	0.218	27.602
	RSD%	282.84	35.36	0.56
14	**Uncorrected concentration ppm**	0	**0.004**	**0.333**
	Corrected concentration ppm	0	0.451	37.54
	RSD%	0	53.03	0
16	**Uncorrected concentration ppm**	**0.001**	**0.003**	**0.477**
	Corrected concentration ppm	0.101	0.302	48.016
	RSD%	141.42	117.85	2.52
18	**Uncorrected concentration ppm**	**0.002**	**0.008**	**0.549**
	Corrected concentration ppm	0.167	0.669	45.92
	RSD%	106.07	17.68	3.35
20	**Uncorrected concentration ppm**	**0.004**	**0.003**	**0.569**
	Corrected concentration ppm	0.385	0.288	54.699
	RSD%	70.71	47.14	1.62
22	**Uncorrected concentration ppm**	**0.001**	**0.003**	**0.541**
	Corrected concentration ppm	0.103	0.308	55.621
	RSD%	353.55	0	1.18
24	**Uncorrected concentration ppm**	**0.002**	**0.003**	**0.199**
	Corrected concentration ppm	0.226	0.314	20.839
	RSD%	141.42	188.56	3.91

Cd Detection Limits
Fraction 1: 0.0039ppm
Fraction 2: 0.0114ppm
Fraction 3: 0.0102ppm

Appendix 5.10b: Mean corrected and uncorrected concentrations of Cadmium in the Snarestone sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1	Fraction 2	Fraction 3
1	Uncorrected concentration ppm	**0.001**	**-0.001**	**0.005**
	Corrected concentration ppm	0.113	-0.113	0.709
	RSD%	212.13	424.26	42.43
2	Uncorrected concentration ppm	**0.001**	**0.005**	**0.003**
	Corrected concentration ppm	0.091	0.455	0.342
	RSD%	282.84	388.91	164.99
3	Uncorrected concentration ppm	**0**	**-0.001**	**0.007**
	Corrected concentration ppm	0	-0.094	0.827
	RSD%	0	424.26	20.2
4	Uncorrected concentration ppm	**0**	**-0.001**	**0.007**
	Corrected concentration ppm	0	-0.108	0.941
	RSD%	0	212.13	30.3
5	Uncorrected concentration ppm	**0.001**	**0.002**	**0.01**
	Corrected concentration ppm	0.085	0.171	1.066
	RSD%	0	0	14.14
6	Uncorrected concentration ppm	**0.001**	**0.001**	**0.004**
	Corrected concentration ppm	0.086	0.086	0.432
	RSD%	70.71	141.42	17.68
8	Uncorrected concentration ppm	**0.004**	**0.002**	**0.002**
	Corrected concentration ppm	0.407	0.203	0.254
	RSD%	0	106.07	35.36
10	Uncorrected concentration ppm	**0.002**	**0**	**0.007**
	Corrected concentration ppm	0.168	0	0.735
	RSD%	35.36	0	30.3
12	Uncorrected concentration ppm	**0.004**	**-0.001**	**0.001**
	Corrected concentration ppm	0.336	-0.084	0.105
	RSD%	70.71	353.55	70.71
14	Uncorrected concentration ppm	**-0.001**	**0.001**	**-0.001**
	Corrected concentration ppm	-0.086	0.086	-0.108
	RSD%	70.71	141.42	141.42
16	Uncorrected concentration ppm	**0.001**	**0.002**	**0.002**
	Corrected concentration ppm	0.063	0.126	0.158
	RSD%	0	318.2	70.71
18	Uncorrected concentration ppm	**0.001**	**-0.002**	**0.003**
	Corrected concentration ppm	0.064	-0.127	0.239
	RSD%	282.84	70.71	47.14
20	Uncorrected concentration ppm	**0**	**-0.004**	**0.004**
	Corrected concentration ppm	0	-0.226	0.283
	RSD%	0	35.36	159.1
22	Uncorrected concentration ppm	**-0.003**	**-0.002**	**0**
	Corrected concentration ppm	-0.153	-0.102	0
	RSD%	0	141.42	0
24	Uncorrected concentration ppm	**-0.003**	**-0.005**	**0.003**
	Corrected concentration ppm	-0.158	-0.263	0.198
	RSD%	0	14.14	164.99

Cd Detection Limits
Fraction 1: 0.0039ppm
Fraction 2: 0.0114ppm
Fraction 3: 0.0102ppm

Appendix 5.11a: Mean corrected and uncorrected concentrations of Lead in the Smethwick sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1	Fraction 2	Fraction 3
1	**Uncorrected concentration ppm**	**0.058**	**1.002**	**7.907**
	Corrected concentration ppm	6.287	108.609	857.06
	RSD%	13.41	2.82	21.23
2	**Uncorrected concentration ppm**	**0.016**	**0.51**	**9.142**
	Corrected concentration ppm	1.648	52.527	941.579
	RSD%	35.36	5.27	2.85
3	**Uncorrected concentration ppm**	**0.003**	**0.717**	**8.649**
	Corrected concentration ppm	0.29	69.4	837.161
	RSD%	447.83	1.28	2.31
4	**Uncorrected concentration ppm**	**0.043**	**0.336**	**7.697**
	Corrected concentration ppm	4.281	33.452	766.305
	RSD%	16.44	0.21	1.29
5	**Uncorrected concentration ppm**	**0.007**	**0.07**	**14.872**
	Corrected concentration ppm	0.733	7.926	1683.886
	RSD%	414.16	21.21	0.15
6	**Uncorrected concentration ppm**	**-0.01**	**0.227**	**8.194**
	Corrected concentration ppm	-1.261	28.619	1033.047
	RSD%	42.43	4.98	7.2
8	**Uncorrected concentration ppm**	**-0.006**	**0.171**	**8.453**
	Corrected concentration ppm	-0.736	20.97	1036.596
	RSD%	223.92	8.68	0.86
10	**Uncorrected concentration ppm**	**0.026**	**0.018**	**9.582**
	Corrected concentration ppm	2.55	1.765	939.778
	RSD%	43.51	102.14	0.05
12	**Uncorrected concentration ppm**	**0.045**	**0.094**	**9.156**
	Corrected concentration ppm	4.909	10.255	998.912
	RSD%	9.43	7.52	1.25
14	**Uncorrected concentration ppm**	**0.021**	**-0.004**	**11.349**
	Corrected concentration ppm	2.367	-0.451	1279.395
	RSD%	33.67	406.59	1.13
16	**Uncorrected concentration ppm**	**0.014**	**0.111**	**15.241**
	Corrected concentration ppm	1.409	11.174	1534.199
	RSD%	50.51	0	4.29
18	**Uncorrected concentration ppm**	**-0.003**	**0.006**	**15.92**
	Corrected concentration ppm	-0.251	0.502	1331.588
	RSD%	94.28	47.14	4.54
20	**Uncorrected concentration ppm**	**0.028**	**0.043**	**17.45**
	Corrected concentration ppm	2.692	4.134	1677.493
	RSD%	174.25	36.18	0.38
22	**Uncorrected concentration ppm**	**0.022**	**0.193**	**20.487**
	Corrected concentration ppm	2.262	19.843	2106.302
	RSD%	45	8.43	2.23
24	**Uncorrected concentration ppm**	**0.026**	**0.176**	**8.382**
	Corrected concentration ppm	2.944	18.431	877.768
	RSD%	8.16	11.25	0.78

Pb Detection Limits

Fraction 1: 0.0348ppm

Fraction 2: 0.1212ppm

Fraction 3: 0.0921ppm

Appendix 5.11b: Mean corrected and uncorrected concentrations of Lead in the Snarestone sediment sequential extraction leachates and the relative standard deviation (RSD) from the mean of two analyses

Depth cm		Fraction 1	Fraction 2	Fraction 3
1	**Uncorrected concentration ppm**	**0.022**	**0.14**	**0.078**
	Corrected concentration ppm	2.497	15.887	11.064
	RSD%	6.43	1.52	18.13
2	**Uncorrected concentration ppm**	**0.01**	**0.148**	**0.078**
	Corrected concentration ppm	0.911	13.483	8.883
	RSD%	28.28	139.49	23.57
3	**Uncorrected concentration ppm**	**-0.02**	**0.1**	**0.09**
	Corrected concentration ppm	-1.89	9.45	10.631
	RSD%	88.39	7.07	24.36
4	**Uncorrected concentration ppm**	**-0.008**	**0.099**	**0.04**
	Corrected concentration ppm	-0.861	10.652	5.38
	RSD%	335.88	5	22.98
5	**Uncorrected concentration ppm**	**0.004**	**0.089**	**0.075**
	Corrected concentration ppm	0.341	7.589	7.994
	RSD%	176.78	2.38	12.26
6	**Uncorrected concentration ppm**	**0.016**	**0.082**	**0.091**
	Corrected concentration ppm	1.383	7.089	9.834
	RSD%	35.36	22.42	18.65
8	**Uncorrected concentration ppm**	**-0.017**	**0.082**	**0.082**
	Corrected concentration ppm	-1.729	8.342	10.428
	RSD%	95.67	28.46	22.42
10	**Uncorrected concentration ppm**	**-0.004**	**0.111**	**0.117**
	Corrected concentration ppm	-0.336	9.321	12.282
	RSD%	70.71	8.28	13.3
12	**Uncorrected concentration ppm**	**0.006**	**0.059**	**0.092**
	Corrected concentration ppm	0.504	4.957	9.663
	RSD%	94.28	58.73	31.51
14	**Uncorrected concentration ppm**	**0.004**	**0.081**	**0.054**
	Corrected concentration ppm	0.345	6.976	5.814
	RSD%	70.71	38.41	70.71
16	**Uncorrected concentration ppm**	**0.032**	**0.003**	**0.038**
	Corrected concentration ppm	2.017	0.189	2.994
	RSD%	79.55	471.4	65.13
18	**Uncorrected concentration ppm**	**0.006**	**0.074**	**0.087**
	Corrected concentration ppm	0.382	4.717	6.932
	RSD%	23.57	29.62	15.44
20	**Uncorrected concentration ppm**	**0.032**	**0.075**	**0.109**
	Corrected concentration ppm	1.811	4.246	7.713
	RSD%	92.81	29.23	13.62
22	**Uncorrected concentration ppm**	**-0.004**	**0.034**	**0.075**
	Corrected concentration ppm	-0.205	1.74	4.797
	RSD%	636.4	35.36	34.88
24	**Uncorrected concentration ppm**	**0.021**	**0.061**	**0.111**
	Corrected concentration ppm	1.106	3.214	7.31
	RSD%	121.22	3.48	21.02

Pb Detection Limits

Fraction 1: 0.0348ppm

Fraction 2: 0.1212ppm

Fraction 3: 0.0921ppm

Some values just exceed the detection limit in Fraction 3, but have an RSD >10%, and are thus not used

Appendix 6: The Results of Duplicate Analysis of Standards, Used to Determine the Precision of the Porewater, Sediment and Sequential Extraction Analytical Procedures

Appendix 6.1a: Results of dulpicate analysis of IC Standard Solution used to calculate the 3s error for porewater analysis

Sample Name	Chloride ppm	Sulphate ppm	Phosphate ppm
std 1	99.48	100.21	9.41
std 2	101.39	100.19	9.76
std 3	100.92	99.79	9.76
std 4	100.82	99.68	9.79
std 5	100.36	99.73	9.82
std 6	101.41	99.56	9.74
std 7	100.8	99.46	9.79
std 8	101.09	100.32	9.71
std 9	100.91	98.98	9.74
std 10	100.34	100.48	9.66
std 11	100.79	100.78	9.62
std 12	99.46	98.33	9.77
Average	100.65	99.79	9.71
Std Dev	0.64	0.68	0.11
% SD	0.64	0.68	1.14
% error	1.91	2.03	3.43

Appendix 6.1b: Results of Dulpicate analysis of ICP AES Quality Control Standard Solution used to calculate the 3s error for porewater analysis

	Al	Ca	Cu	Fe	Mn	Si	Zn
Std 1	1.95	50.40	0.52	4.97	1.97	2.03	0.97
Std 2	2.18	53.30	0.52	5.11	2.02	1.99	1.05
Std 3	1.98	50.47	0.52	5.01	2.01	2.08	0.99
Std 4	1.98	50.35	0.52	5.03	2.01	2.10	0.99
Std 5	1.96	50.77	0.52	5.05	1.99	2.07	0.99
Std 6	2.09	51.74	0.51	4.95	1.92	1.96	1.09
Std 7	1.98	50.09	0.52	5.25	2.08	2.13	1.03
Std 8	2.02	50.37	0.52	5.07	2.04	2.10	1.06
Std 9	2.75	51.72	0.52	5.20	2.01	1.98	1.02
Std 10	2.09	51.19	0.51	4.79	1.86	1.95	1.04
Std 11	2.01	51.40	0.52	5.30	2.10	2.11	1.04
Std 12	1.99	51.01	0.51	5.10	2.01	2.12	1.00
Std 13	2.08	51.98	0.51	4.85	1.87	1.95	1.00
Std 14	1.99	49.51	0.52	5.25	2.11	2.10	1.00
Std 15	2.12	51.80	0.51	5.05	1.91	2.01	1.02
Std 16	2.73	50.75	0.51	5.16	1.97	1.95	1.01
Std 17	1.98	50.56	0.53	5.26	2.06	2.15	1.04
Std 18	1.99	50.49	0.51	5.20	2.05	2.11	1.00
Std 19	2.68	51.62	0.51	5.14	2.02	1.96	1.01
Std 20	2.66	50.88	0.52	5.23	2.04	1.98	1.00
Average	2.16	51.02	0.52	5.10	2.00	2.04	1.02
Std Dev	0.29	0.85	0.01	0.14	0.07	0.07	0.03
3x Std Dev	0.86	2.54	0.02	0.42	0.21	0.22	0.08
% error	39.66	4.97	3.92	8.27	10.39	10.57	8.20

Appendix 6.2: The results of duplicate analysis of a laboratory sample, used to calculate the precision of the Aqua Regia procedure

Sample run	Al ppm	Ca ppm	Cd ppm	Cr ppm	Cu ppm	Fe ppm	Mn ppm	Pb ppm	Zn ppm
Spring-Sna (a)	24281.57	55304.51	50.98	60.98	105.49	28623.14	1923.14	6750.78	3891.18
Spring-Sna (b)	23961.23	54665.41	50.30	62.03	103.38	28919.48	1921.47	6608.95	3849.90
Spring-Sna (c)	25116.44	54448.47	51.53	62.16	103.86	29228.56	1956.73	6900.28	3925.26
Spring-Sme (a)	23205.64	54427.89	51.61	59.21	104.62	27781.96	1944.59	6641.13	3779.56
Spring-Sme (b)	24418.73	53054.45	49.83	63.29	101.87	27981.11	1917.02	6591.92	3701.83
Summer-Sna	26233.82	55044.61	52.98	62.14	101.18	29000.80	1887.47	5963.95	3891.26
Summer-Sme	25337.59	54842.88	50.91	64.68	99.22	28716.11	1928.33	5926.73	3991.02
Autumn-Sna	26180.07	54282.13	50.73	67.58	99.66	28070.78	1913.58	6029.88	3902.55
Autumn-Sme (a)	24218.46	55030.29	50.95	62.19	107.32	28815.25	1973.52	6150.85	3957.67
Autumn-Sme(b)	26847.49	53939.59	51.64	66.39	106.46	29969.30	2012.36	6169.46	3976.48
Winter-Sna	26041.82	53764.78	51.87	64.74	100.93	29181.75	1943.91	5957.58	4012.26
Winter-Sme	25375.42	53949.21	53.38	65.92	103.37	29476.60	1995.42	6119.90	4041.03
Duplicate	29222.40	55774.15	49.63	68.67	109.18	30066.03	2012.96	6928.30	3969.01
Duplicate	30318.31	54724.36	49.08	80.33	110.58	30245.39	1991.59	6736.58	3897.04
Duplicate	29318.96	54026.91	49.86	75.19	107.84	29082.91	1934.31	6679.46	3926.00
Average	**26005.20**	**54485.31**	**51.02**	**65.70**	**104.33**	**29010.61**	**1950.43**	**6410.38**	**3914.13**
Standard Deviation	**2122.26**	**684.90**	**1.20**	**5.61**	**3.46**	**736.45**	**38.62**	**370.46**	**88.43**
RSD %	**8.16**	**1.26**	**2.35**	**8.53**	**3.31**	**2.54**	**1.98**	**5.78**	**2.26**
3s error	**24.48**	**3.77**	**7.06**	**25.60**	**9.94**	**7.62**	**5.94**	**17.34**	**6.78**

Snarestone	P178	P179	S180	S182
Spring (a)	3268.63	3309.8	2549.02	2209.8
Spring (b)	3133.2	3284.29	2451.29	2265.61
Spring (c)	3351.18	3277.81	3063.65	2722.59
Summer	3441.55	3393.75	3216.49	2740.49
Autumn	3198.32	3302.59	3009.83	2648.89
Winter	3365.5	3586.65	3492.16	3162.44
Average	**3293.06**	**3359.15**	**2963.74**	**2624.97**
Standard Deviation	**114.72**	**119.00**	**397.45**	**350.38**
RSD %	**3.48**	**3.54**	**13.41**	**13.35**
3s error	**10.45**	**10.63**	**40.23**	**40.04**

Smethwick	P178	P179	S180	S182
Spring (a)	3419.73	3494.07	3232.87	2875.23
Spring (b)	3390.68	3382.68	2474.49	2074.41
Summer	3395.89	3501.7	2523.46	2253.94
Autumn (a)	3568.71	3640.92	2296.89	2069.91
Autumn (b)	3450.96	3337.32	2547.85	2338.52
Winter	3541.13	3387.77	2527.38	2232.62
Average	**3489.17**	**3466.93**	**2600.49**	**2307.44**
Standard De	**79.97**	**134.84**	**323.11**	**297.50**
RSD %	**2.29**	**3.89**	**12.42**	**12.89**
3s error	**6.88**	**11.67**	**37.27**	**38.68**

Appendix 6.3a: Results of Dulpicate analysis of ICP AES Quality Control Standard Solution used to calculate the 2s error for Fraction 1 sequential extraction leachates

	Al	Ca	Cd	Cr	Cu	Fe	Mn	P178	P179	Pb	S180	S182	Zn
Std 1	51.78	108.68	0.52	2.11	10.21	262.27	5.15	45.92	45.98	10.53	47.29	48.31	26.14
Std 2	51.99	108.45	0.53	2.05	10.14	260.58	5.13	44.54	45.68	10.51	47.19	47.53	26.67
Std 3	51.75	104.97	0.52	2.00	10.15	261.42	4.97	51.43	51.39	10.19	52.29	51.69	25.41
Std 4	51.46	107.20	0.51	2.01	10.24	255.47	5.07	51.10	50.18	10.07	51.22	52.63	25.29
Std 5	52.35	107.44	0.52	2.01	10.16	254.94	4.96	52.80	53.50	10.27	51.70	52.36	25.52
Std 6	52.88	109.18	0.51	2.04	10.28	254.44	4.84	52.78	51.73	10.34	50.37	51.69	25.67
Std 7	52.24	107.69	0.53	2.01	10.30	258.27	5.02	56.44	51.78	10.24	53.71	54.76	26.11
Std 8	52.14	106.35	0.51	2.00	10.08	257.62	5.02	55.55	50.88	10.27	51.97	54.53	25.45
Std 9	51.55	106.81	0.52	2.03	10.22	261.78	4.97	54.61	53.91	10.22	51.56	52.71	25.49
Std 10	51.44	106.94	0.50	2.00	10.11	251.03	4.88	53.14	53.21	10.15	52.01	53.67	24.45
Std 11	53.83	106.50	0.52	2.03	10.28	261.43	5.05	54.24	53.78	10.17	55.19	57.27	25.84
Std 12	53.11	105.83	0.53	2.03	10.32	261.09	5.08	52.84	53.71	10.46	56.17	57.30	26.57
Std 13	52.70	107.75	0.52	2.05	10.39	258.72	5.12	48.98	49.10	10.31	49.82	51.65	25.30
Std 14	53.45	110.98	0.52	2.03	10.32	255.64	5.05	49.63	49.54	10.27	50.58	52.45	25.89
Std 15	53.17	108.68	0.53	2.13	10.49	268.35	5.24	50.69	51.78	10.38	50.83	51.13	26.32
Average	**51.76**	**109.27**	**0.52**	**2.01**	**10.23**	**256.72**	**5.10**	**79.22**	**50.97**	**10.33**	**51.17**	**52.65**	**25.71**
Standard Deviation	**1.58**	**3.17**	**0.02**	**0.07**	**0.24**	**7.61**	**0.15**	**5.70**	**2.40**	**0.29**	**2.25**	**2.49**	**0.75**
2s error (%)	**6.12**	**5.80**	**6.39**	**6.62**	**4.72**	**5.93**	**5.86**	**14.40**	**9.41**	**5.60**	**8.81**	**9.48**	**5.82**

Appendix 6.3b: Results of Dulpicate analysis of ICP AES Quality Control Standard Solution used to calculate the 2s error for Fraction 2

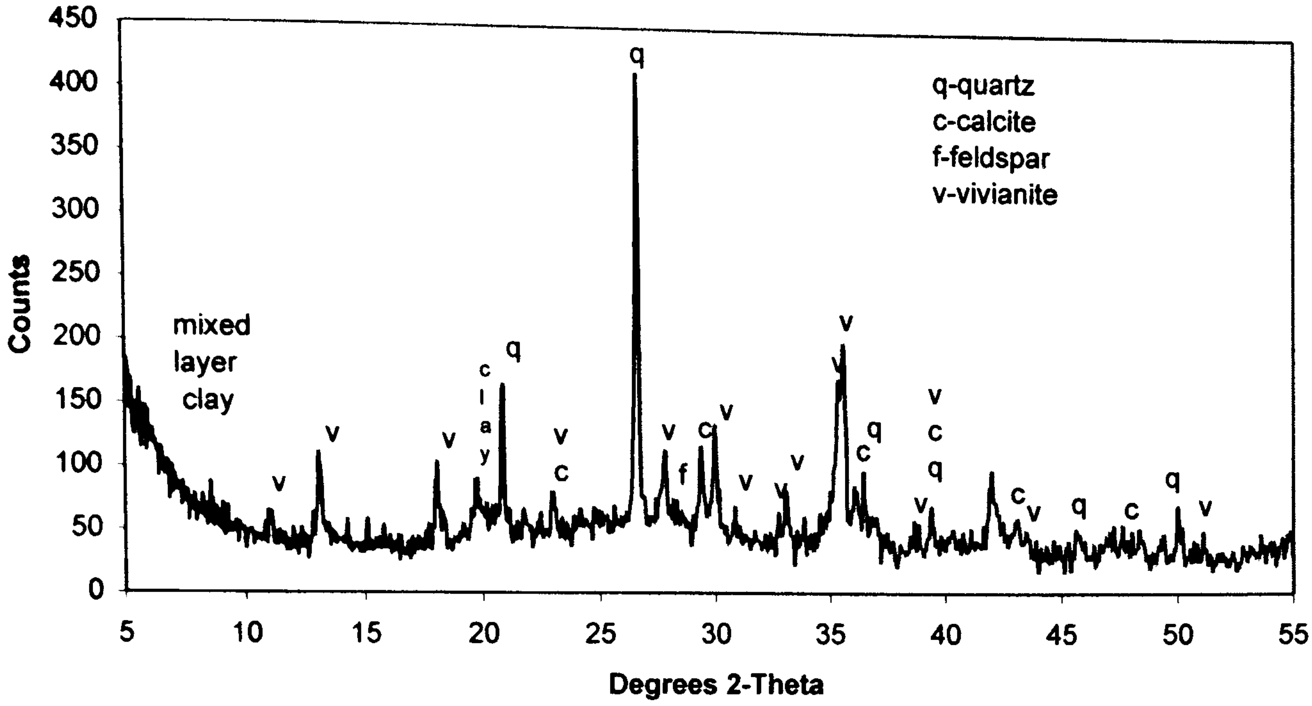
	Al	Ca	Cd	Cr	Cu	Fe	Mn	P178	P179	Pb	S180	S182	Zn
Std 1	51.69	107.80	0.49	1.94	10.13	268.39	5.17	8.10	8.72	9.79	47.27	44.56	25.55
Std 2	51.38	107.31	0.53	1.99	10.14	267.47	5.09	8.96	9.18	10.07	45.91	43.86	26.80
Std 3	51.68	103.59	0.56	2.10	11.10	270.20	5.68	9.87	10.48	10.67	58.37	56.44	27.77
Std 4	50.34	105.15	0.51	1.97	10.99	258.42	5.28	10.50	10.35	10.26	57.11	58.26	27.15
Std 5	54.84	110.31	0.58	1.92	10.77	287.61	5.51	9.59	6.58	11.11	49.84	48.49	30.28
Std 6	56.26	110.65	0.59	2.02	10.98	288.88	5.40	9.86	6.76	11.28	50.74	50.15	29.13
Std 7	48.67	102.88	0.49	1.92	9.94	253.49	5.37	9.26	10.57	9.44	49.50	46.80	25.54
Std 8	48.42	104.73	0.50	2.02	10.49	258.31	5.34	8.71	10.32	9.72	48.44	47.20	25.26
Std 9	51.71	106.76	0.53	1.98	10.39	259.60	5.24	52.79	51.76	9.87	50.49	52.72	26.03
Std 10	53.09	110.48	0.53	1.90	10.46	262.73	5.42	52.08	44.43	10.26	45.61	46.74	26.18
Std 11	53.72	111.15	0.54	2.02	10.84	276.06	5.45	48.53	50.21	10.27	49.88	49.76	27.74
Std 12	51.48	110.28	0.55	2.01	10.64	278.84	5.53	48.25	50.09	10.31	48.81	48.16	27.92
Std 13	52.82	106.87	0.54	2.02	10.21	273.84	5.52	50.33	49.71	10.38	46.35	48.73	27.82
Std 14	53.17	106.12	0.53	1.99	10.62	273.18	5.54	50.79	51.63	10.42	47.53	47.89	27.89
Std 15	49.30	103.88	0.54	1.89	10.25	254.53	5.00	50.77	51.03	10.38	49.25	47.73	26.57
Average	**51.04**	**106.29**	**0.52**	**1.99**	**10.39**	**261.49**	**5.25**	**78.02**	**49.93**	**10.22**	**49.56**	**49.31**	**26.73**
Standard Deviation	**2.66**	**5.93**	**0.03**	**0.12**	**0.68**	**15.12**	**0.32**	**5.47**	**3.20**	**0.54**	**3.32**	**3.17**	**1.47**
2s error (%)	**10.44**	**11.15**	**10.53**	**12.14**	**13.16**	**11.57**	**12.23**	**14.01**	**12.82**	**10.51**	**13.40**	**12.84**	**10.98**

Appendix 6.3c: Results of Dulpicate analysis of ICP AES Quality Control Standard Solution used to calculate the 2s error for Fraction 3 sequential extraction leachates

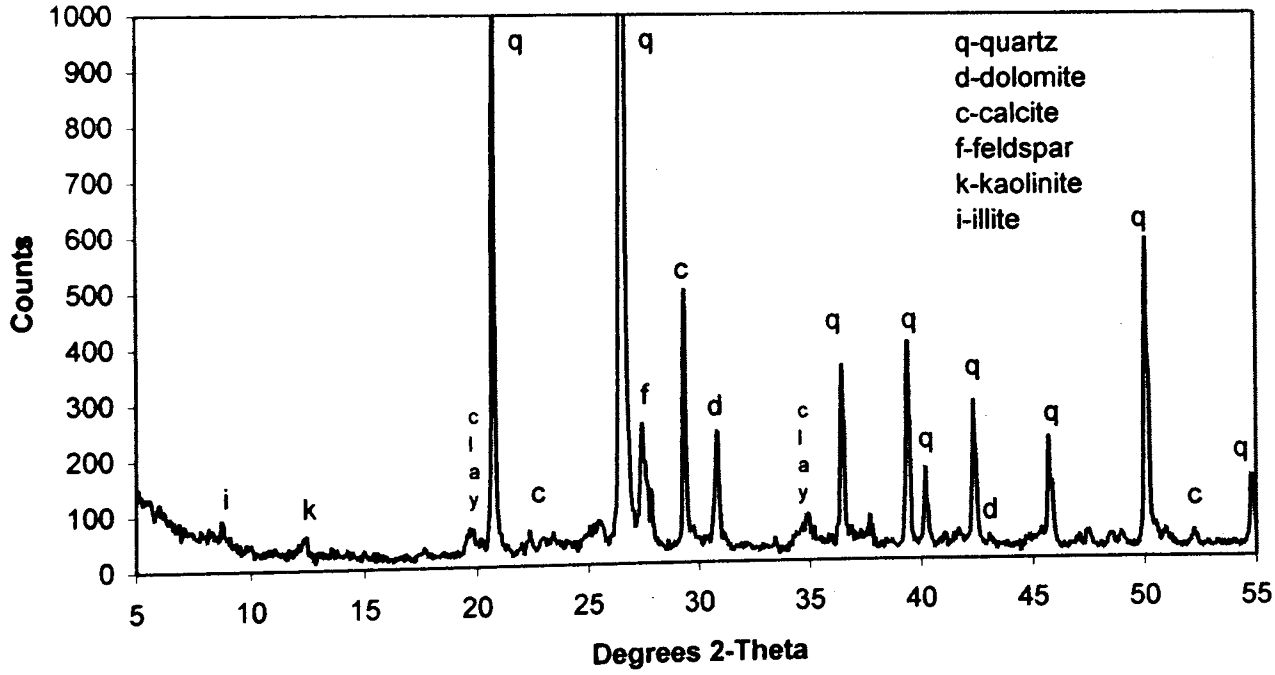
	Al	Ca	Cd	Cr	Cu	Fe	Mn	P	Pb	S	Zn
Std 1	55.56	108.52	0.49	1.97	10.94	276.63	5.31	51.75	10.48	52.41	26.84
Std 2	51.90	105.39	0.49	1.89	10.76	264.93	5.25	52.20	10.43	49.64	25.26
Std 3	49.29	99.98	0.45	1.75	9.68	259.44	5.10	45.72	9.82	47.76	24.80
Std 4	50.79	104.03	0.48	1.78	9.61	242.53	5.05	46.39	9.56	46.52	23.61
Std 5	48.62	106.72	0.52	1.80	9.88	253.40	4.82	55.14	10.18	52.49	26.44
Std 6	52.63	109.90	0.48	1.83	10.74	252.85	5.23	52.13	9.85	51.96	26.61
Std 7	50.28	99.44	0.47	1.77	9.76	249.31	4.92	49.36	9.19	44.53	22.72
Std 8	50.64	101.86	0.44	1.75	10.04	248.15	4.96	46.18	9.35	45.47	22.70
Std 9	51.18	104.58	0.49	1.81	10.00	263.65	5.06	47.57	10.02	50.02	25.64
Std 10	49.68	105.66	0.51	1.90	10.16	259.93	5.10	45.92	10.12	49.82	26.51
Std 11	49.53	100.61	0.51	2.08	10.87	257.57	6.33	71.42	10.15	52.33	
Std 12	64.42	130.79	0.50	2.62	14.06	280.29	7.19	69.70	9.98	49.17	24.55
Std 13	52.05	102.07	0.51	1.97	10.29	266.55	5.08	51.57	10.13	50.25	25.51
Std 14	50.86	99.31	0.51	1.95	9.98	261.56	5.18	50.11	9.90	51.26	26.29
Std 15	51.30	102.83	0.47	1.89	10.14	247.75	4.87	48.79	10.01	50.09	26.18
Average	**50.42**	**100.93**	**0.49**	**1.98**	**10.21**	**258.98**	**5.28**	**49.52**	**9.98**	**48.87**	**24.93**
Standard Deviation	**3.41**	**7.56**	**0.02**	**0.17**	**0.84**	**9.91**	**0.46**	**2.89**	**0.35**	**2.27**	**1.21**
2s error (%)	**13.51**	**14.98**	**8.67**	**17.32**	**16.40**	**7.65**	**17.25**	**11.67**	**6.94**	**9.30**	**9.70**

Appendix 7: XRD Traces for Smethwick and Snarestone Sediments

Appendix 7.1: XRD trace for Dry Smethwick Sediment (20cm)



Appendix 7.2: XRD trace for Dry Snarestone Sediment (20cm)



Appendix 8: The Concentrations of Carbon on Smethwick and Snarestone Sediments

Appendix 8.1: Carbon in Smethwick sediment

Depth cm	Inorganic Carbon (%)	3s Error (%)	Total Carbon (%)	3s error (%)	Organic C Carbon (%)
1	0.76	0.01	21.11	2.40	20.35
3	0.75	0.02	20.61	0.04	19.87
5	0.82	0.02	21.69	1.25	20.87
7	0.75	0.02	19.66	0.21	18.91
9	0.72	0.01	19.07	0.05	18.35
11	0.61	0.07	20.01	0.66	19.41
13	0.44	0.12	19.99	1.76	19.55
15	0.37	0.03	19.63	0.04	19.26
17	0.50	0.03	20.39	1.02	19.89
19	0.50	0.03	21.94	1.95	21.45
21	0.35	0.12	21.47	0.93	21.12
23	0.37	0.04	20.30	1.92	19.94

Appendix 8.2: Carbon in Snarestone sediment

Depth cm	Inorganic Carbon (%)	3s Error (%)	Total Carbon (%)	3s error (%)	Organic C Carbon (%)
1	0.84	0.44	6.40	0.32	5.56
3	1.14	0.06	4.74	0.12	3.60
5	1.04	0.02	3.75	0.12	2.71
7	1.02	0.05	4.20	0.26	3.19
9	1.38	0.01	4.03	0.31	2.65
11	0.90	0.03	2.41	0.01	1.51
13	0.57	0.01	1.86	0.02	1.30
15	0.56	0.04	1.76	0.09	1.20
17	0.89	0.04	1.97	0.03	1.08
19	0.84	0.04	5.77	0.57	4.93
21	0.57	0.04	2.23	0.12	1.66
23	0.52	0.02	2.55	0.86	2.03

Appendix 9: The Concentrations in ppm of Metals, Sulphur and Phosphorus in Smethwick and Snarestone Sediments

Appendix 9.1a: The concentrations in ppm of Aluminium in Smethwick sediment

Depth cm	Spring	Summer	Autumn	Winter
1	15899.04	14449.70	15051.44	15203.51
2	15300.36	14976.84	15022.34	15301.51
3	15800.00	15846.94	16574.05	15448.39
4	15502.27	16525.33	16371.96	15308.19
5	16190.50	16593.99	16261.11	14878.78
6	15672.25	17293.21	17742.69	15482.84
7	15635.00	16183.34	16422.81	16074.31
8	14377.00	16536.21	16689.48	16586.13
9	14839.97	16094.88	15490.68	15581.59
10	16178.15	17436.23	16042.46	15504.42
11	15446.68	17050.08	16013.36	17049.19
12	16521.84	16337.80	16407.91	17079.48
13	15868.11	16650.67	16689.44	17370.99
14	16288.26	17462.09	16006.41	20452.87
15	16253.91	17593.11	16419.65	24303.32
16	15690.92	16979.23	17168.30	26920.04
17	15779.37	15718.66	17160.61	20769.32
18	15340.56	15866.08	17575.68	16899.30
19	16205.16	16462.71	17582.52	16306.97
20	15963.94	16775.69	17515.32	14218.94
21	15661.16	16820.92	17789.86	13482.71
22	16179.34	14255.23	15798.20	11621.24
23	16514.22	14109.43	16141.65	17009.83
24	15703.83	15005.58	16188.21	17513.41
Average	**15783.83**	**16209.33**	**16505.26**	**18072.41**
Standard Deviation	**503.01**	**1012.64**	**789.34**	**4410.77**
RSD %	**3.19**	**6.25**	**4.78**	**24.41**

Appendix 9.1b: The concentrations in ppm of Aluminium in Snarestone sediment

Depth cm	Spring	Summer	Autumn	Winter
1	10516.19	16207.03	12516.27	14852.59
2	11283.20	13054.69	10952.19	11040.54
3	6689.89	11605.28	11433.46	11243.71
4	4142.91	9987.45	12799.84	6596.65
5	7767.91	7978.04	9336.79	6384.03
6	7694.48	12333.67	12120.05	6156.94
7	11647.69	11614.69	15905.02	7296.14
8	13905.42	12940.81	12092.95	8100.48
9	12996.61	13127.58	11849.26	6632.59
10	12409.45	8801.76	12230.20	6487.77
11	12015.42	16685.40	11356.53	4985.71
12	12369.75	10750.10	12091.66	4822.05
13	10834.00	9589.61	13821.20	4853.04
14	8464.61	8994.43	11822.17	4728.25
15	7355.90	9537.85	9510.79	4901.58
16	4401.84	9005.00	8179.88	5213.48
17	6102.09	11435.23	7552.43	5510.95
18	5653.99	9931.01	10502.99	5532.13
19	4501.39	10881.21	5644.63	5104.36
20	4816.94	7614.68	7724.53	5404.83
21	6437.43	10373.56	9213.16	6773.46
22	8735.91	12988.99	8833.73	7210.91
23	8919.04	12628.96	7930.42	7475.66
24	9975.02	12248.00	7423.48	9825.72
Average	**8734.88**	**11263.13**	**10535.15**	**6963.90**
Standard Deviation	**3018.16**	**2297.08**	**2412.08**	**2501.29**
RSD	**34.55**	**20.39**	**22.90**	**35.92**

Appendix 9.2a: The concentrations in ppm of Phosphorous in Smethwick sediment

Depth cm	Spring	Summer	Autumn	Winter
1	19841.255	23126.745	21863.49	23329.35
2	20110.405	22282.89	22233.195	23751.485
3	20040.98	21906.805	22182.635	22011.095
4	19544.815	20316.315	22225.765	22228.13
5	19088.26	20677.675	20486.345	21174.235
6	18800.48	20729.02	18667.4	20981.73
7	18868.09	20175.755	19915.12	20765.085
8	19452.27	21147.44	21287.515	22776.78
9	19857.425	21991.23	21834.035	22023.71
10	19363.855	21442.42	21278.795	21253.015
11	18752	20210.495	20306.955	22359.97
12	18971.88	20679.595	20447.465	22607.645
13	18674.625	20542.72	22627.32	27030.25
14	18366.36	20665.405	22771.88	25469.31
15	18529.585	19657.59	21597.96	28672.235
16	22233.625	19110.07	20696.58	30421.63
17	20771.54	17879.425	21399.32	24666.335
18	21449.13	19304.33	21195.09	20768.23
19	19629.295	18614.275	20930.19	21757.405
20	18839.62	18622.55	17701.78	19331.725
21	18929.63	18105.58	18874.475	16342.41
22	19376	18434.7	20112.225	26812.525
23	18677.905	18872.83	19899.68	28144.17
24	19267.93	18479.56	19930.85	25708.325
Ave	**19476.54**	**20123.9758**	**20852.7527**	**23349.4492**
Standard Deviation	**935.660359**	**1434.22939**	**1287.87607**	**3239.33508**
RSD	**4.80403788**	**7.12696835**	**6.17604827**	**13.8732827**

Appendix 9.2b: The concentrations in ppm of Phosphorous in Snarestone sediment

Depth cm	Spring	Summer	Autumn	Winter
1	720.42	1012.19	809.55	952.19
2	758.00	855.29	630.13	666.07
3	459.93	635.87	598.36	505.25
4	293.01	526.00	656.53	337.46
5	383.16	556.00	437.21	RSD >10%
6	357.57	684.85	530.21	295.89
7	415.50	628.50	879.82	347.00
8	404.92	742.85	475.72	294.70
9	396.81	666.94	544.78	292.67
10	437.85	546.11	471.23	296.85
11	476.48	983.27	466.60	488.94
12	461.18	534.36	467.31	265.63
13	496.81	RSD >10%	482.00	222.85
14	417.50	412.19	488.18	234.72
15	364.92	423.51	535.36	246.05
16	239.38	372.30	458.18	205.99
17	297.11	527.79	560.22	240.58
18	341.21	468.31	491.84	194.37
19	268.75	365.34	354.57	146.35
20	271.72	313.12	380.38	RSD >10%
21	265.90	422.14	343.93	RSD >10%
22	374.40	545.55	396.21	RSD >10%
23	364.51	492.59	731.66	RSD >10%
24	302.85	525.26	309.89	RSD >10%
Average	**398.74**	**575.67**	**520.83**	**346.31**
Standard Deviation	**127.35**	**184.28**	**141.24**	**197.60**
RSD	**31.94**	**32.01**	**27.12**	**57.06**

RSD >10%: These readings were close to the detection limit and the relative standard deviation of 2 analyses was greater than 10%, therefore they were not used in the study

Appendix 9.3a: The concentrations in ppm of Sulphur in Smethwick sediment

Depth cm	Spring	Summer	Autumn	Winter
1	9505.025	8673.65	9177.345	8547.39
2	12118.56	9834.3	9209.055	8785.23
3	12810.875	10521.855	8804.39	9528.43
4	12945.62	10935.935	8799.36	9258.63
5	11930.035	10967.965	9080.13	8912.785
6	11506.865	11435.01	9056.87	8900.825
7	11840.47	11683.64	9081.29	8896.325
8	11942.845	11438.315	8847.54	9303.56
9	12373.88	12052.025	9617.16	9396.1
10	11938.49	11381.45	9483.28	9030.345
11	11339	10643.455	9711.98	10216.82
12	10704.03	10668.6	9310.83	10536.22
13	10916.63	10673.175	10037.95	10646.03
14	10680.605	10917.795	10350.49	9880.2
15	10988.88	13074.69	10117.07	9230.77
16	10558.405	11593.085	9612.23	9644.84
17	10620.63	12063.585	10169.795	10256.97
18	11107.335	11609.865	11455.67	10990.01
19	11788.57	11425.715	11660.33	11063.975
20	11686.64	10216.915	10772.08	12141.28
21	12092.45	10879.48	10953.905	12364.865
22	11573.52	9856.43	10943.89	11126.055
23	11797.05	8179.195	10891.855	10753.96
24	11574.705	8707.875	10988.17	10611.965
Ave	**11514.2131**	**10809.7502**	**9922.19438**	**10000.9825**
Standard Deviation	**778.340525**	**1143.48975**	**891.240494**	**1059.26398**
RSD	**6.75982385**	**10.578318**	**8.98229223**	**10.5915992**

Appendix 9.3b: The concentrations in ppm of Sulphur in Snarestone sediment

Depth cm	Spring	Summer	Autumn	Winter
1	4485.42	7399.08	7256.94	6787.85
2	4813.00	7237.53	5633.13	6489.91
3	1492.30	4862.03	6638.98	7181.50
4	1354.40	4892.41	7437.95	5082.87
5	4460.59	4776.40	6751.85	3985.03
6	4645.41	7756.32	9268.71	4994.00
7	7213.28	7779.22	8658.27	5529.38
8	6675.67	8740.25	10023.89	4522.35
9	6366.90	8096.34	10832.67	4562.00
10	7612.19	5555.12	10010.03	4213.02
11	7834.13	5377.57	8659.02	2515.09
12	6490.60	7390.13	9052.35	2046.14
13	5991.62	7912.09	9431.00	1913.27
14	3796.23	10026.89	8624.70	2012.35
15	2962.53	9592.51	6569.12	1692.34
16	1988.18	9826.87	4364.15	1674.56
17	3710.87	9973.01	3035.75	1732.40
18	4439.67	10724.03	5611.31	1731.46
19	5167.59	11726.89	3859.18	2436.42
20	4006.35	7690.47	4791.79	1553.83
21	2934.83	9774.00	3731.26	1858.46
22	3364.53	13618.62	3779.44	2383.87
23	3439.77	12885.47	4326.16	2436.39
24	2736.48	12445.87	2272.82	2889.51
Average	**4499.27**	**8585.79**	**6692.52**	**3426.00**
Standard Deviation	**1866.05**	**2554.89**	**2523.14**	**1817.47**
RSD	**41.47**	**29.76**	**37.70**	**53.05**

Appendix 9.4a: The concentrations in ppm of Calcium in Smethwick sediment

Depth cm	Spring	Summer	Autumn	Winter
1	37235.63	32264.67	40636.11	39421.74
2	36782.01	32587.54	40055.66	40501.79
3	39622.07	33279.59	38330.74	39772.93
4	39729.20	32669.07	37570.20	40871.39
5	40964.61	32785.79	37730.32	41392.08
6	40072.72	32665.13	39190.43	39099.18
7	39985.38	32575.79	39718.99	39021.77
8	37362.75	31675.03	38557.22	40556.36
9	38584.12	31304.56	37041.69	38839.23
10	37738.57	32712.72	36789.91	38167.40
11	33334.40	33850.76	35001.60	34745.03
12	28830.08	31019.19	34776.47	33727.57
13	29889.60	30949.01	34949.07	33388.82
14	30737.04	31406.62	33441.42	31110.10
15	32368.54	32199.84	33783.47	33833.04
16	31670.84	32152.42	34702.38	38411.11
17	32166.07	33185.16	32120.86	32977.49
18	31178.04	29210.51	32983.23	30089.51
19	31268.16	30708.06	33130.83	28981.32
20	31145.63	32155.14	31783.70	25126.03
21	31152.79	32908.17	31886.25	21086.45
22	31316.88	31678.96	31653.11	20062.22
23	31698.03	31221.85	32020.87	30798.68
24	30820.50	33543.77	33322.11	29340.35
Average	**34402.24**	**32112.89**	**35465.69**	**29600.43**
Standard Deviation	**3993.02**	**1050.59**	**2948.57**	**5301.72**
RSD	**11.61**	**3.27**	**8.31**	**17.91**

Appendix 9.4b: The concentrations in ppm of Calcium in Snarestone sediment

Depth cm	Spring	Summer	Autumn	Winter
1	24110.71	26844.92	27137.55	25176.30
2	22642.20	26960.48	30789.56	24622.93
3	52846.82	32171.17	36383.03	31006.34
4	37246.16	41485.36	38537.63	21981.03
5	30142.32	74765.22	44380.72	29866.07
6	25408.62	24970.14	25439.38	34118.75
7	22047.08	24787.43	46600.08	25766.76
8	21811.24	26104.58	41043.79	25026.31
9	21347.36	25132.79	41375.25	31161.56
10	24850.08	26720.94	28351.11	19832.35
11	26951.56	20332.74	31972.28	22659.56
12	24456.18	24019.98	30941.44	18236.07
13	24949.72	26274.93	29869.00	15703.27
14	21595.23	22870.97	28234.36	15774.59
15	22179.32	21857.23	34733.32	16010.80
16	24465.14	22790.03	29133.56	18049.68
17	21477.17	24002.40	36441.78	25632.42
18	19196.52	23581.63	27086.62	19097.38
19	18731.65	25182.47	20464.94	22041.99
20	18166.40	18868.17	22523.52	19122.23
21	19370.45	23848.27	20842.03	16635.93
22	23517.51	28209.41	23180.04	16378.34
23	23537.04	26908.29	31381.18	14544.78
24	23149.85	24841.82	16953.17	16332.87
Average	**24758.18**	**27647.14**	**30991.47**	**21865.76**
Standard Deviation	**7176.95**	**10920.03**	**7764.13**	**5675.38**
RSD	**28.99**	**39.50**	**25.05**	**25.96**

Appendix 9.5a: The concentrations in ppm of Chromium in Smethwick sediment

Depth cm	Spring	Summer	Autumn	Winter
1	425.78	378.84	403.52	402.63
2	407.06	396.49	418.91	408.69
3	413.04	420.28	419.96	400.63
4	400.28	460.06	429.00	410.71
5	429.71	468.27	418.58	411.88
6	422.15	468.86	418.90	411.77
7	410.03	453.57	417.82	412.71
8	392.24	455.97	417.97	427.06
9	399.88	436.52	417.32	412.58
10	409.43	446.02	418.39	415.80
11	388.23	422.19	438.11	439.67
12	398.03	443.93	450.06	428.97
13	423.71	428.00	469.34	460.74
14	443.12	446.73	463.85	459.01
15	459.52	447.34	455.67	522.16
16	456.57	431.48	443.33	527.18
17	437.48	416.12	464.44	496.41
18	425.90	450.68	473.24	474.13
19	436.50	486.90	479.70	558.91
20	428.69	475.21	468.46	524.38
21	440.84	456.97	458.39	563.39
22	438.89	405.78	476.75	569.65
23	432.86	388.08	474.12	490.88
24	401.68	380.46	469.23	523.35
Average	**421.73**	**436.03**	**444.38**	**514.18**
Standard Deviation	**19.75**	**29.96**	**24.92**	**38.48**
RSD	**4.68**	**6.87**	**5.61**	**7.48**

Appendix 9.5b: The concentrations in ppm of Chromium in Snarestone sediment

Depth cm	Spring	Summer	Autumn	Winter
1	20.98	30.58	26.15	26.69
2	22.20	24.15	20.80	20.57
3	11.45	22.20	19.61	23.18
4	8.37	16.14	22.42	11.98
5	15.13	13.98	15.97	9.98
6	13.51	22.10	20.61	12.00
7	19.52	18.82	17.20	14.20
8	21.00	25.00	20.90	11.87
9	18.94	23.43	19.39	12.06
10	19.46	15.60	22.86	11.83
11	21.35	22.32	20.74	9.86
12	20.61	19.38	21.86	7.59
13	20.15	15.58	25.80	10.64
14	16.70	17.72	22.45	8.70
15	13.34	17.02	16.58	8.40
16	7.61	16.01	14.97	9.86
17	12.56	22.19	11.58	15.78
18	10.61	17.85	19.71	11.31
19	8.53	18.37	9.42	10.09
20	9.72	13.16	13.61	9.19
21	13.19	17.52	16.00	11.83
22	15.90	23.62	17.17	14.23
23	16.31	24.03	13.96	14.03
24	18.29	21.25	12.75	16.89
Average	**15.64**	**19.92**	**18.44**	**13.03**
Standard Deviation	**4.66**	**4.16**	**4.36**	**4.72**
RSD	**29.76**	**20.88**	**23.65**	**36.19**

Appendix 9.6a: The concentrations in ppm of Manganese in Smethwick sediment

Depth cm	Spring	Summer	Autumn	Winter
1	2205.11	2145.51	2281.43	2329.95
2	2059.83	2138.55	2363.46	2405.52
3	2166.90	2186.19	2304.79	2317.81
4	2083.02	2158.76	2294.18	2373.60
5	2086.10	2240.84	2077.94	2246.85
6	1995.27	2194.27	1949.54	2291.51
7	2156.82	2105.85	2068.11	2297.64
8	2242.23	2172.72	2190.48	2323.94
9	2102.82	2173.01	2237.92	2271.10
10	2061.31	2214.51	2272.38	2261.66
11	2002.41	2100.76	2153.48	2344.91
12	1888.46	2076.95	2200.76	2344.06
13	2022.28	2016.73	2332.73	2626.00
14	2122.67	2051.68	2458.44	2482.18
15	2149.30	1981.18	2362.22	2749.95
16	2115.88	1943.27	2227.26	2740.28
17	1996.02	1875.03	2231.32	2846.22
18	1958.42	1989.17	2174.12	2885.12
19	2067.34	2095.18	2209.24	2996.03
20	2033.45	2166.33	2083.32	3054.99
21	2016.33	2092.83	2110.76	2703.10
22	2083.60	2173.28	2183.57	2890.21
23	2082.55	2146.70	2121.79	2816.72
24	1890.91	2114.46	2090.60	2940.39
Average	**2066.21**	**2106.41**	**2207.49**	**2810.93**
Standard Deviation	**87.80**	**90.78**	**115.90**	**161.32**
RSD	**4.25**	**4.31**	**5.25**	**5.74**

Appendix 9.6b: The concentrations in ppm of Manganese in Snarestone sediment

Depth cm	Spring	Summer	Autumn	Winter
1	509.19	611.31	511.28	571.71
2	506.20	545.31	474.30	464.15
3	713.58	564.29	485.49	452.15
4	460.43	591.95	524.82	337.26
5	447.25	lost sample	538.03	389.22
6	365.91	452.72	424.97	436.03
7	409.46	435.15	612.88	359.03
8	443.51	477.70	552.75	323.18
9	426.32	501.90	531.59	373.15
10	397.14	452.49	426.51	304.34
11	409.25	405.46	415.16	512.27
12	389.16	526.77	407.34	321.15
13	414.80	459.54	404.60	313.39
14	436.98	430.31	446.07	321.53
15	447.91	435.92	598.68	312.06
16	378.00	414.13	523.86	306.92
17	356.33	464.61	702.62	420.43
18	324.79	446.65	480.29	378.22
19	302.86	514.47	393.43	383.53
20	284.41	433.19	377.38	339.13
21	329.87	486.46	365.13	339.82
22	456.32	595.60	401.20	348.49
23	452.94	537.65	461.52	358.45
24	412.98	503.01	335.39	404.61
Average	**419.82**	**490.72**	**474.80**	**377.93**
Standard Deviation	**85.42**	**60.83**	**87.93**	**68.90**
RSD	**20.35**	**12.40**	**18.52**	**18.23**

Appendix 9.7a: The concentrations in ppm of Iron in Smethwick sediment

Depth cm	Spring	Summer	Autumn	Winter
1	71722.27	73439.92	72579.86	74925.53
2	68773.23	71581.15	75998.01	77186.38
3	70094.08	72771.10	75974.45	72928.47
4	66143.90	72942.34	76602.91	74784.31
5	67063.03	74774.78	70048.64	72241.85
6	64885.49	74360.91	68477.37	73007.23
7	68124.23	71760.54	70020.37	72745.31
8	72879.68	75337.01	72039.42	73411.27
9	68810.56	73886.39	72058.13	71598.47
10	69114.24	73412.24	71952.13	71259.45
11	67694.12	68771.35	71021.33	76067.06
12	67518.62	70352.79	70992.21	75127.57
13	70686.29	67789.88	76157.78	82141.43
14	72894.53	70114.73	77465.45	82104.55
15	72818.24	69592.71	74804.68	92889.29
16	70262.77	69933.08	70668.80	87149.41
17	67073.68	69847.63	70832.60	91092.83
18	67063.66	72217.72	72325.88	93870.13
19	69083.68	76026.20	73094.62	98726.01
20	68850.36	76746.70	69264.97	137068.43
21	68091.04	74151.20	71513.67	142018.68
22	69072.45	76882.15	73513.23	130944.60
23	67731.45	70314.73	70840.29	100811.51
24	68848.82	72970.49	72770.70	99678.52
Average	**68970.85**	**72499.07**	**72542.40**	**103207.95**
Standard Deviation	**2099.51**	**2536.03**	**2465.14**	**21208.68**
RSD	**3.04**	**3.50**	**3.40**	**20.55**

Appendix 9.7b: The concentrations in ppm of Iron in Snarestone sediment

Depth cm	Spring	Summer	Autumn	Winter
1	21967.03	27736.81	24956.08	26341.83
2	22985.20	24964.67	20994.00	22268.62
3	19863.40	26116.78	21485.89	21647.51
4	14048.63	21136.68	23107.89	15161.74
5	16806.73	19444.80	20554.60	15905.99
6	17347.24	24512.84	24036.82	15716.31
7	20634.61	23915.13	30515.90	17900.83
8	21014.20	26945.81	25013.73	18501.58
9	20722.23	27209.09	22786.69	15212.58
10	22221.80	20908.98	23002.01	15374.56
11	23209.77	38508.27	21193.42	28546.68
12	21807.92	25207.35	22930.21	12981.83
13	21062.25	19915.88	24372.20	12140.53
14	21704.97	19233.37	24193.67	11827.80
15	19936.43	18975.17	20407.11	11975.60
16	12433.69	18630.91	18539.43	11798.54
17	15494.12	20062.98	18310.57	15206.67
18	15019.01	19451.46	20188.57	13932.77
19	14143.59	22175.68	12989.98	14439.24
20	12751.69	16934.78	16756.56	13670.46
21	14420.23	20413.58	17546.49	13753.41
22	18408.62	26234.03	18326.15	15556.63
23	18708.19	24757.91	16735.05	16082.95
24	19939.82	22927.83	14808.09	19394.48
Average	**18610.47**	**23180.03**	**20989.63**	**16472.46**
Standard Deviation	**3414.48**	**4546.50**	**3850.55**	**4406.90**
RSD	**18.35**	**19.61**	**18.35**	**26.75**

Appendix 9.8a: The concentrations in ppm of Copper in Smethwick sediment

Depth cm	Spring	Summer	Autumn	Winter
1	736.03	604.59	632.91	644.37
2	714.00	642.64	665.27	636.56
3	723.77	691.88	667.27	633.05
4	708.64	713.11	685.68	636.44
5	746.27	757.36	664.74	630.33
6	721.32	766.27	672.21	643.04
7	687.93	745.16	663.07	660.81
8	631.51	728.59	651.46	674.66
9	678.74	720.95	607.54	656.15
10	702.82	731.11	635.09	660.57
11	662.58	738.83	667.13	662.92
12	700.22	725.57	683.58	656.94
13	727.27	724.36	714.00	695.31
14	760.32	729.25	705.79	802.77
15	800.40	725.07	702.02	964.02
16	792.88	715.74	700.98	883.93
17	790.92	713.06	718.14	834.86
18	771.43	719.33	723.04	814.39
19	773.97	750.85	733.75	805.48
20	769.03	763.30	747.05	1123.02
21	784.46	741.43	723.01	1320.35
22	774.48	695.31	709.82	1016.66
23	767.06	654.57	716.09	804.29
24	734.74	628.32	719.58	804.29
Average	**735.87**	**713.61**	**687.88**	**905.78**
Standard Deviation	**44.54**	**42.06**	**35.52**	**174.30**
RSD	**6.05**	**5.89**	**5.16**	**19.24**

Appendix 9.8b: The concentrations in ppm of Copper in Snarestone sediment

Depth cm	Spring	Summer	Autumn	Winter
1	36.77	48.76	44.32	50.00
2	38.60	43.71	36.01	39.74
3	21.12	34.39	36.82	36.46
4	13.55	34.07	39.83	25.36
5	26.07	25.95	29.95	22.56
6	25.03	37.43	34.61	21.39
7	28.97	40.43	38.59	27.01
8	27.79	44.79	38.02	28.09
9	26.52	42.66	33.39	25.31
10	32.17	29.41	36.09	24.85
11	33.81	36.26	40.68	21.93
12	31.61	37.16	43.92	20.17
13	32.92	29.17	36.00	22.08
14	23.06	28.28	34.68	21.85
15	20.21	33.64	26.57	24.01
16	18.43	28.22	24.96	21.68
17	20.14	35.79	22.17	23.86
18	23.81	30.08	32.06	21.82
19	19.83	33.14	18.83	23.21
20	20.63	25.13	24.02	23.77
21	25.39	29.47	24.60	67.16
22	27.38	39.44	26.75	30.24
23	32.62	38.25	22.53	34.46
24	31.27	34.68	24.71	35.57
Average	**26.57**	**35.01**	**32.09**	**28.86**
Standard Deviation	**6.31**	**6.22**	**7.34**	**10.90**
RSD	**23.76**	**17.76**	**22.89**	**37.79**

Appendix 9.9a: The concentrations in ppm of Zinc in Smethwick sediment

Depth cm	Spring	Summer	Autumn	Winter
1	8714.09	8331.14	8079.46	7886.30
2	8467.69	9097.62	8686.81	8038.71
3	8702.51	9962.88	8723.15	8126.21
4	8541.61	10397.60	9216.79	8119.78
5	9032.81	10625.83	8966.91	8164.63
6	8702.80	11029.44	9254.91	8377.64
7	8564.68	10521.67	8946.68	8852.38
8	7995.84	10177.33	9230.89	9128.30
9	8373.87	10162.25	8636.60	8716.44
10	8801.28	10667.13	8870.82	8775.52
11	8193.41	10387.07	9388.48	9743.63
12	8673.85	10208.68	9951.26	9805.23
13	9431.87	10224.26	10347.51	10326.12
14	9822.06	10410.81	10547.37	10268.71
15	10531.86	10271.93	10688.81	11751.54
16	10114.09	9959.25	10655.61	11821.83
17	10005.38	9711.46	10933.08	13093.43
18	9614.88	10284.48	11055.71	14020.98
19	9703.29	10870.23	11172.03	15050.86
20	9771.83	11017.39	11085.32	15582.18
21	10168.53	10299.40	10783.08	17319.95
22	10188.50	9080.96	11193.59	16120.43
23	10040.58	8581.22	11239.17	12025.07
24	9073.99	8573.68	10891.96	12655.67
Average	**9217.97**	**10035.57**	**9939.42**	**13336.40**
Standard Deviation	**745.85**	**762.75**	**1034.88**	**2288.14**
RSD	**8.09**	**7.60**	**10.41**	**17.16**

Appendix 9.9b: The concentrations in ppm of Zinc in Snarestone sediment

Depth cm	Spring	Summer	Autumn	Winter
1	330.94	441.45	405.07	445.22
2	343.00	398.60	340.27	355.70
3	127.52	308.34	317.79	313.26
4	97.07	259.81	353.88	191.29
5	171.58	216.41	234.78	155.49
6	184.94	332.67	268.71	170.73
7	292.15	324.86	225.36	185.53
8	289.34	359.13	267.91	165.35
9	265.60	343.48	263.10	166.11
10	291.50	224.25	290.36	171.60
11	309.61	226.34	258.23	132.39
12	289.12	267.08	280.59	90.47
13	286.71	213.59	316.60	81.91
14	155.07	224.21	301.93	91.66
15	117.72	232.08	193.97	66.61
16	78.93	211.37	148.53	66.04
17	125.62	254.90	123.43	87.56
18	122.27	231.65	214.26	96.39
19	107.89	264.72	102.36	91.04
20	103.33	181.69	149.75	71.90
21	83.57	241.94	110.18	97.63
22	96.01	355.96	101.80	88.16
23	97.47	321.79	114.43	96.98
24	98.33	304.73	74.73	116.85
Average	**186.05**	**280.88**	**227.42**	**149.83**
Standard Deviation	**94.29**	**67.11**	**93.25**	**96.29**
RSD	**50.68**	**23.89**	**41.00**	**64.26**

Appendix 9.10a: The concentrations in ppm of Cadmium in Smethwick sediment

Depth cm	Spring	Summer	Autumn	Winter
1	31.52	29.14	31.23	28.67
2	30.71	32.54	32.32	28.78
3	32.10	35.72	31.94	28.53
4	32.81	38.24	32.71	28.49
5	35.79	38.64	30.50	28.41
6	34.69	40.06	32.24	28.91
7	31.40	38.35	31.56	31.56
8	30.28	38.11	30.21	32.37
9	31.01	37.07	30.27	29.94
10	33.55	39.38	30.84	31.35
11	30.33	38.31	33.89	34.53
12	33.02	37.38	36.16	35.01
13	34.61	37.44	37.75	35.06
14	36.64	38.31	38.45	36.24
15	40.68	38.05	39.02	38.96
16	38.36	36.96	38.18	38.29
17	38.83	34.99	39.75	46.22
18	37.99	37.09	39.34	52.35
19	37.80	40.79	39.81	56.03
20	37.46	40.38	40.46	61.81
21	39.44	38.45	39.31	70.15
22	39.61	33.70	39.68	58.21
23	37.80	32.49	40.73	42.51
24	34.50	31.90	40.49	47.69
Average	**35.04**	**36.81**	**35.70**	**48.63**
Standard Deviation	**3.34**	**2.94**	**4.03**	**11.20**
RSD	**9.53**	**7.99**	**11.28**	**23.03**

Appendix 9.11a: The concentrations in ppm of lead in Smethwick sediment

Depth cm	Spring	Summer	Autumn	Winter
1	1463.89	1206.39	1173.34	1135.80
2	1408.26	1349.97	1274.29	1172.89
3	1501.91	1453.40	1278.24	1205.67
4	1476.77	1571.17	1339.25	1194.62
5	1558.56	1627.63	1293.00	1189.24
6	1498.82	1688.36	1329.80	1235.29
7	1450.92	1639.51	1303.58	1339.19
8	1342.57	1594.18	1290.92	1361.91
9	1426.89	1513.85	1274.40	1317.12
10	1506.09	1575.57	1305.63	1317.52
11	1411.33	1557.06	1398.05	1437.06
12	1512.58	1525.69	1483.42	1449.10
13	1601.55	1525.79	1542.64	1517.23
14	1669.64	1581.21	1541.96	1530.50
15	1773.55	1592.31	1599.16	1720.93
16	1720.14	1507.59	1586.45	1705.75
17	1711.87	1495.90	1614.46	1849.60
18	1692.66	1546.31	1652.76	1949.85
19	1700.14	1585.68	1639.53	1966.62
20	1691.71	1632.55	1658.32	2232.39
21	1723.71	1553.79	1635.20	2340.62
22	1736.86	1354.34	1624.25	1952.23
23	1719.51	1261.31	1623.40	1810.91
24	1569.80	1255.04	1617.96	1760.98
Average	**1577.90**	**1508.11**	**1461.67**	**1861.47**
Standard Deviation	**130.06**	**129.93**	**163.60**	**248.47**
RSD	**8.24**	**8.62**	**11.19**	**13.35**

Appendix 10: The Results of Aqua Regia Digest Conducted Upon Duplicate Cores of Snarestone and Smethwick Sediment

Appendix 10.1a: Concentrations of Metals, S and P in Core 10A sampled from Smethwick in the Spring 1998

Sample no	Al ppm	Ca ppm	Cd ppm	Cr ppm	Cu ppm	Fe ppm	Mn ppm	Pb ppm	Zn ppm	P ppm	S ppm
JD10A01	15326.17	42155.59	30.76	409.19	694.73	74474.27	2292.84	1406.43	8619.21	19841.26	9505.03
JD10A02	15411.18	42244.88	32.42	409.39	687.69	75047.34	2357.67	1438.63	8724.89	20110.41	12118.56
JD10A03	15499.60	42738.90	32.19	406.04	691.72	76042.58	2370.65	1459.82	8757.50	20040.98	12810.88
JD10A04	14831.22	40353.07	29.61	393.35	640.68	71855.79	2214.70	1391.54	8165.76	19544.82	12945.62
JD10A05	14459.59	40930.44	32.17	415.16	673.50	70036.39	2179.94	1482.11	8683.76	19088.26	11930.04
JD10A06	15082.75	42113.59	30.83	415.16	674.36	68792.92	2201.71	1482.79	8608.32	18800.48	11506.87
JD10A07	14146.32	37300.64	32.43	402.92	666.13	68421.14	2183.15	1468.57	8531.63	18868.09	11840.47
JD10A08	15350.27	37146.66	33.54	411.39	680.69	70689.03	2221.67	1494.15	8623.93	19452.27	11942.85
JD10A09	14251.65	36786.84	31.31	405.18	682.75	68895.91	2188.63	1477.57	8805.58	19857.43	12373.88
JD10A10	14327.39	34300.54	31.06	397.52	675.02	71500.70	2113.60	1404.13	8494.89	19363.86	11938.49
JD10A11	14895.00	33961.20	31.80	394.00	674.40	71572.20	2146.20	1509.20	8860.20	18752.00	11339.00
JD10A12	15531.31	34347.83	35.10	430.59	727.96	72969.68	2176.31	1586.76	9355.01	18971.88	10704.03
JD10A13	16074.06	35014.97	34.80	423.51	729.87	71461.76	2176.85	1589.64	9447.79	18674.63	10916.63
JD10A14	15198.34	35660.99	34.67	425.60	706.95	70197.74	2191.80	1615.81	9560.53	18366.36	10680.61
JD10A15	15548.05	36496.82	36.93	433.08	723.79	71460.29	2222.99	1634.03	9617.55	18529.59	10988.88
JD10A16	13928.57	32354.58	28.81	390.29	611.68	75482.44	2351.82	1349.05	7996.25	22233.63	10558.41
JD10A17	15247.45	29248.25	33.58	409.75	693.38	73739.56	2212.07	1516.49	9169.90	20771.54	10620.63
JD10A18	14996.80	30384.17	37.98	452.53	747.35	75859.08	2332.60	1699.78	10241.66	21449.13	11107.34
JD10A19	14959.83	31858.71	39.97	457.03	805.96	73280.98	2262.99	1749.20	10408.07	19629.30	11788.57
JD10A20	15545.44	32075.09	38.35	443.98	794.29	72702.82	2216.50	1726.78	10196.13	18839.62	11686.64
JD10A21	13902.82	31900.85	40.21	440.37	789.47	72099.35	2167.55	1722.85	10077.27	18929.63	12092.45
JD10A22	15040.67	32455.93	38.46	434.70	766.03	72799.68	2230.97	1682.69	9989.78	19376.00	11573.52
JD10A23	14195.37	32568.95	37.72	413.89	752.15	68738.38	2136.90	1699.86	10019.76	18677.91	11797.05
JD10A24	14987.65	30390.24	38.84	441.24	740.44	68849.40	2059.56	1685.26	10013.94	19267.93	11574.71

Appendix 10.1b: Concentrations of Metals, S and P in Core 10C sampled from Smethwick in the Spring 1998

Sample no	Al ppm	Ca ppm	Cd ppm	Cr ppm	Cu ppm	Fe ppm	Mn ppm	Pb ppm	Zn ppm	P ppm	S ppm
JD10C01	15899.04	37235.63	31.52	425.78	736.03	71722.27	2205.11	1463.89	8714.09	19901.24	10061.85
JD10C02	15300.36	36782.01	30.71	407.06	714.00	68773.23	2059.83	1408.26	8467.69	19585.17	10087.76
JD10C03	15800.00	39622.07	32.10	413.04	723.77	70094.08	2166.90	1501.91	8702.51	19403.21	11183.55
JD10C04	15502.27	39729.20	32.81	400.28	708.64	66143.90	2083.02	1476.77	8541.61	18221.00	11253.21
JD10C05	16190.50	40964.61	35.79	429.71	746.27	67063.03	2086.10	1558.56	9032.81	17753.03	12554.19
JD10C06	15672.25	40072.72	34.69	422.15	721.32	64885.49	1995.27	1498.82	8702.80	17286.17	12222.11
JD10C07	15635.00	39985.38	31.40	410.03	687.93	68124.23	2156.82	1450.92	8564.68	19343.28	11391.47
JD10C08	14377.00	37362.75	30.28	392.24	631.51	72879.68	2242.23	1342.57	7995.84	20510.59	13298.04
JD10C09	14839.97	38584.12	31.01	399.88	678.74	68810.56	2102.82	1426.89	8373.87	18440.69	13016.61
JD10C10	16178.15	37738.57	33.55	409.43	702.82	69114.24	2061.31	1506.09	8801.28	17754.15	13027.77
JD10C11	15446.68	33334.40	30.33	388.23	662.58	67694.12	2002.41	1411.33	8193.41	18180.36	11528.42
JD10C12	16521.84	28830.08	33.02	398.03	700.22	67518.62	1888.46	1512.58	8673.85	17628.62	10971.67
JD10C13	15868.11	29889.60	34.61	423.71	727.27	70686.29	2022.28	1601.55	9431.87	18607.52	12735.23
JD10C14	16288.26	30737.04	36.64	443.12	760.32	72894.53	2122.67	1669.64	9822.06	18986.85	12507.09
JD10C15	16253.91	32368.54	40.68	459.52	800.40	72818.24	2149.30	1773.55	10531.86	19063.13	14356.72
JD10C16	15690.92	31670.84	38.36	456.57	792.88	70262.77	2115.88	1720.14	10114.09	17369.31	12639.63
JD10C17	15779.37	32166.07	38.83	437.48	790.92	67073.68	1996.02	1711.87	10005.38	16692.55	12846.48
JD10C18	15340.56	31178.04	37.99	425.90	771.43	67063.66	1958.42	1692.66	9614.88	16472.05	12755.13
JD10C19	16205.16	31268.16	37.80	436.50	773.97	69083.68	2067.34	1700.14	9703.29	17537.90	13863.95
JD10C20	15963.94	31145.63	37.46	428.69	769.03	68850.36	2033.45	1691.71	9771.83	17595.16	12954.73
JD10C21	15661.16	31152.79	39.44	440.84	784.46	68091.04	2016.33	1723.71	10168.53	17082.67	12433.27
JD10C22	16179.34	31316.88	39.61	438.89	774.48	69072.45	2083.60	1736.86	10188.50	17871.22	12234.28
JD10C23	16514.22	31698.03	37.80	432.86	767.06	67731.45	2082.55	1719.51	10040.58	18262.39	12054.91
JD10C24	15703.83	30820.50	34.50	401.68	734.74	68848.82	1890.91	1569.80	9073.99	15705.03	12708.42

This core is used in the investigation

Appendix 10.1c: Concentrations of Metals, S and P in Core 7 sampled from Snarestone in the Spring 1998

Sample no	Al ppm	Ca ppm	Cd ppm	Cr ppm	Cu ppm	Fe ppm	Mn ppm	Pb ppm	Zn ppm	P ppm	S ppm
JD0701	10907.11	23790.85	<0.0042	20.97	36.56	22770.68	414.50	57.93	292.45	593.29	8042.35
JD0702	8993.81	48986.02	<0.0042	18.77	23.16	19698.68	642.37	30.35	163.74	502.20	4040.54
JD0703	18492.81	42835.53	<0.0042	19.56	35.33	33519.76	640.52	127.94	154.09	485.03	2870.26
JD0704	7622.40	63011.12	<0.0042	10.51	23.45	17556.09	807.56	59.63	112.39	475.04	1968.87
JD0705	8771.68	49004.99	<0.0042	16.95	33.30	18204.59	592.42	64.21	189.63	484.55	4260.22
JD0706	8723.70	46516.67	<0.0042	20.16	30.94	21274.91	655.82	43.32	158.12	519.07	3222.20
JD0708	10857.28	26497.13	<0.0042	19.43	35.08	21749.85	404.16	59.27	292.17		
JD0709	13941.20	26856.97	<0.0042	24.63	42.51	24299.76	444.78	115.42	341.48	556.99	6722.50
JD0710	10837.13	25933.90	<0.0042	19.00	31.66	20742.73	451.02		236.10	654.55	7108.66
JD0711	12016.09	23671.37	<0.0042	27.62	35.37	24289.69	463.94	79.08	208.23	482.89	5221.65
JD0712	10187.03	20712.30	<0.0042	17.92	36.64	22421.99	424.20	60.80	178.78	510.63	6229.88
JD0713	7799.80	19306.02	<0.0042	14.61	24.09	17997.43	434.35	36.72	113.72	476.15	7082.75
JD0714	4553.63	22044.60	<0.0042	9.04	19.45	13033.60	332.42	19.45	80.75	389.93	4591.31
JD0715	4942.80	21953.25	<0.0042	10.45	22.88	15786.98	357.40	27.61	88.36	258.35	2610.02
JD0716	5122.46	23404.63	<0.0042	12.08	26.79	15276.54	407.85	35.05	90.03	303.75	4745.56
JD0717	5279.92	24530.83	<0.0042	9.53	27.79	14257.61	404.06	48.88	111.97	333.34	2985.90
JD0718	5790.42	21219.64	<0.0042	9.86	20.70	15030.95	362.78	34.70	103.12	313.39	3724.14
JD0719	5451.32	19318.83	<0.0042	10.18	22.15	14094.37	343.77	28.93	89.19	332.22	3308.36

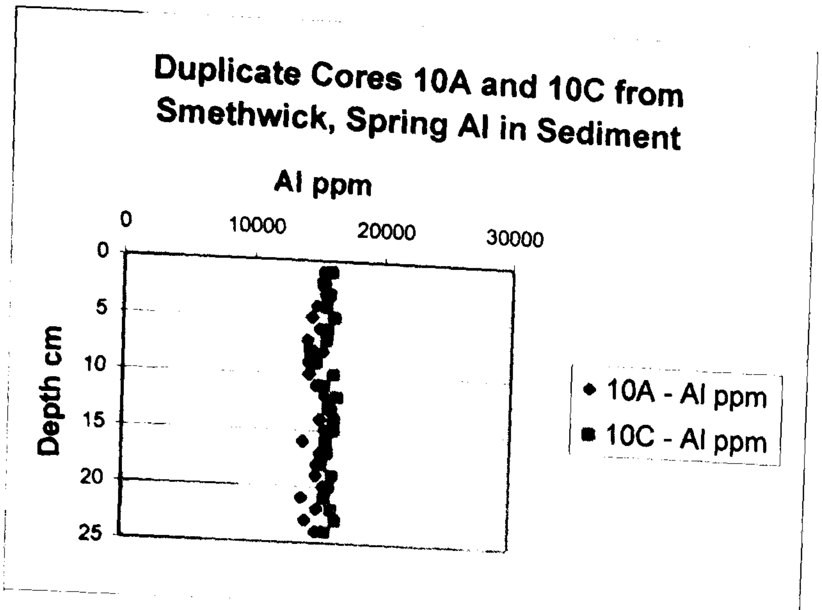
Appendix 10.1d: Concentrations of Metals, S and P in Core 8 sampled from Snarestone in the Spring 1998

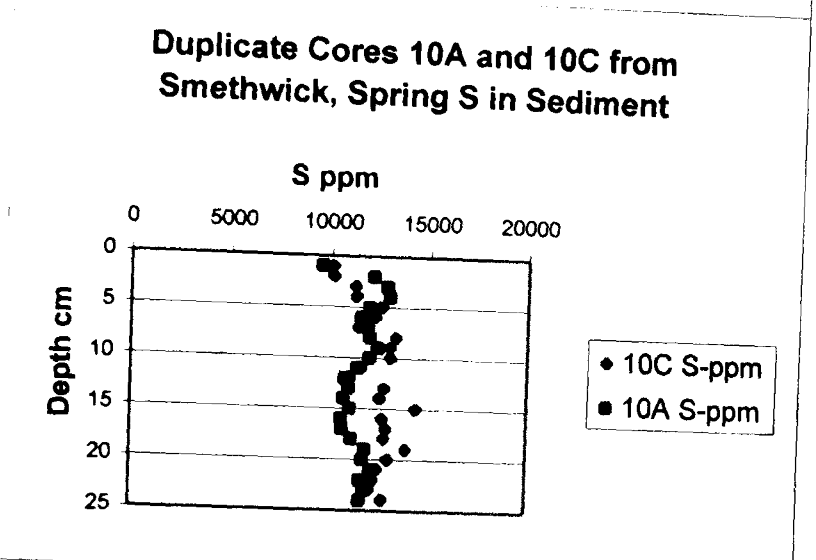
Sample no	Al ppm	Ca ppm	Cd ppm	Cr ppm	Cu ppm	Fe ppm	Mn ppm	Pb ppm	Zn ppm	8 P-ppm	8 S-ppm
JD0801	10516.19	24110.71	<0.0042	20.98	36.77	21967.03	509.19	51.36	330.94	720.42	4485.42
JD0802	11283.20	22642.20	<0.0042	22.20	38.60	22985.20	506.20	57.00	343.00	758.00	4813.00
JD0803	6689.89	52846.82	<0.0042	11.45	21.12	19863.40	713.58	36.32	127.52	459.93	1492.30
JD0804	4142.91	37246.16	<0.0042	8.37	13.55	14048.63	460.43	18.54	97.07	293.01	1354.40
JD0805	7767.91	30142.32	<0.0042	15.13	26.07	16806.73	447.25	33.24	171.58	383.16	4460.59
JD0806	7694.48	25408.62	<0.0042	13.51	25.03	17347.24	365.91	33.57	184.94	357.57	4645.41
JD0807	11647.69	22047.08	<0.0042	19.52	28.97	20634.61	409.46	41.25	292.15	415.50	7213.28
JD0808	13905.42	21811.24	<0.0042	21.00	27.79	21014.20	443.51	42.39	289.34	404.92	6675.67
JD0809	12996.61	21347.36	<0.0042	18.94	26.52	20722.23	426.32	37.89	265.60	396.81	6366.90
JD0810	12409.45	24850.08	<0.0042	19.46	32.17	22221.80	397.14	53.81	291.50	437.85	7612.19
JD0811	12015.42	26951.56	<0.0042	21.35	33.81	23209.77	409.25	51.60	309.61	476.48	7834.13
JD0812	12369.75	24456.18	<0.0042	20.61	31.61	21807.92	389.16	47.82	289.12	461.18	6490.60
JD0813	10834.00	24949.72	<0.0042	20.15	32.92	21062.25	414.80	84.20	286.71	496.81	5991.62
JD0814	8464.61	21595.23	<0.0042	16.70	23.06	21704.97	436.98	48.31	155.07	417.50	3796.23
JD0815	7355.90	22179.32	<0.0042	13.34	20.21	19936.43	447.91	39.04	117.72	364.92	2962.53
JD0816	4401.84	24465.14	<0.0042	7.61	18.43	12433.69	378.00	20.03	78.93	239.38	1988.18
JD0817	6102.09	21477.17	<0.0042	12.56	20.14	15494.12	356.33	37.29	125.62	297.11	3710.87
JD0818	5653.99	19196.52	<0.0042	10.61	23.81	15019.01	324.79	33.82	122.27	341.21	4439.67
JD0819	4501.39	18731.65	<0.0042	8.53	19.83	14143.59	302.86	41.45	107.89	268.75	5167.59
JD0820	4816.94	18166.40	<0.0042	9.72	20.63	12751.69	284.41	42.84	103.33	271.72	4006.35
JD0821	6437.43	19370.45	<0.0042	13.19	25.39	14420.23	329.87	32.39	83.57	265.90	2934.83
JD0822	8735.91	23517.51	<0.0042	15.90	27.38	18408.62	456.32	31.20	96.01	374.40	3364.53
JD0823	8919.04	23537.04	<0.0042	16.31	32.62	18708.19	452.94	32.82	97.47	364.51	3439.77
JD0824	9975.02	23149.85	<0.0042	18.29	31.27	19939.82	412.98	30.88	98.33	302.85	2736.48

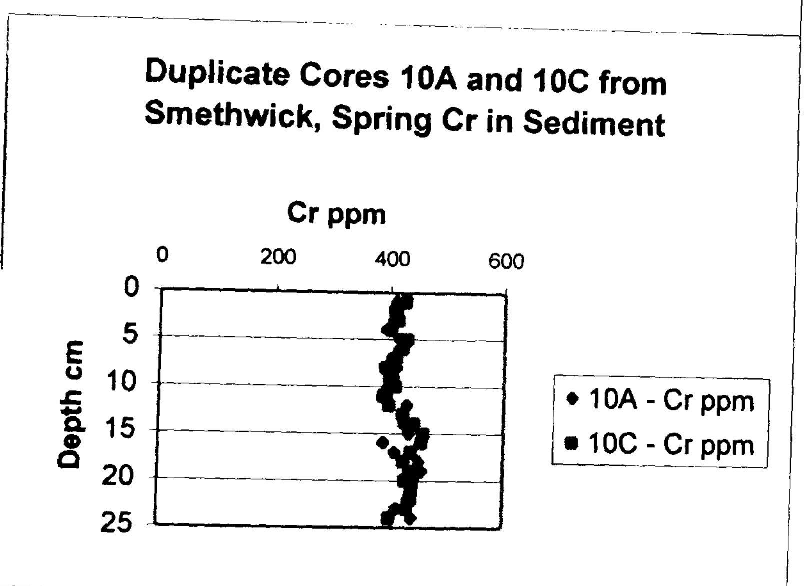
This core is used in the investigation

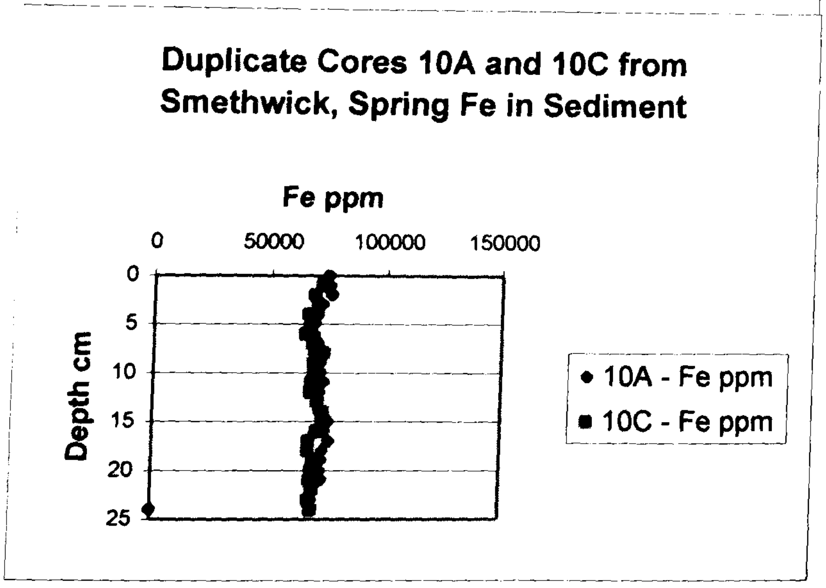
Appendix 10.1e: Concentrations of Metals, S and P in Core 9 sampled from Snarestone in the Spring 1998

Sample no	Al ppm	Ca ppm	Cd ppm	Cr ppm	Cu ppm	Fe ppm	Mn ppm	Pb ppm	Zn ppm	9 P-ppm	9 S-ppm
JD0901	11115.93	39442.33	<0.0042	21.20	42.21	22188.66	575.51	56.28	341.66	658.94	5210.07
JD0902	10132.65	45333.73	<0.0042	18.61	35.81	19940.78	545.62	44.62	297.32	639.26	4908.97
JD0903	10063.58	56402.34	<0.0042	19.07	36.56	19560.70	644.35	43.51	282.73	568.25	4929.47
JD0904	12149.91	29602.80	<0.0042	21.92	45.63	22572.19	472.64	55.70	344.06	708.08	6184.08
JD0905	14030.65	25567.71	<0.0042	25.44	45.27	24366.79	463.74	52.48	360.58	809.30	6452.33
JD0906	13841.78	27396.56	<0.0042	25.84	48.47	26448.03	516.92	63.69	405.97	894.25	7458.44
JD0907	14435.40	25760.87	<0.0042	26.39	46.83	25585.04	500.30	51.99	388.37	760.08	6950.79
JD0908	14828.26	26656.53	<0.0042	27.02	48.24	27325.66	530.42	64.45	402.72	801.64	7602.09
JD0909	14453.86	26222.18	<0.0042	24.95	43.17	26469.70	501.98	55.64	365.94	752.48	8172.28
JD0910	14281.11	26802.98	<0.0042	24.65	40.16	26368.99	466.00	66.00	340.16	587.48	9151.09
JD0911	11658.69	25609.81	<0.0042	21.34	36.51	23559.15	422.30	56.05	292.24	475.76	8678.44
JD0912	11171.74	24056.25	<0.0042	20.08	35.58	22959.25	413.04	58.44	270.13	438.29	7699.27
JD0913	7283.34	22791.65	<0.0042	14.44	24.34	17300.55	387.22	42.94	169.77	348.24	5340.33
JD0914	8746.32	26977.52	<0.0042	16.71	25.67	17947.87	439.71	38.20	172.90	382.87	5336.37
JD0915	7294.20	21102.90	<0.0042	13.51	22.45	17761.62	358.56	40.13	116.41	423.80	5019.90
JD0917	10617.75	23312.75	<0.0042	19.86	28.20	23158.26	436.26	37.73	107.63	353.60	3673.03
JD0918	9798.00	21259.32	<0.0042	19.04	24.25	21299.60	418.84	32.87	89.38	413.03	3890.99
JD0919	9797.46	19883.64	<0.0042	17.87	24.42	20423.55	404.49	31.57	89.95	369.74	3225.45
JD0920	9800.08	18712.06	<0.0042	17.76	23.09	20329.58	382.67	25.46	88.42	377.28	3173.16



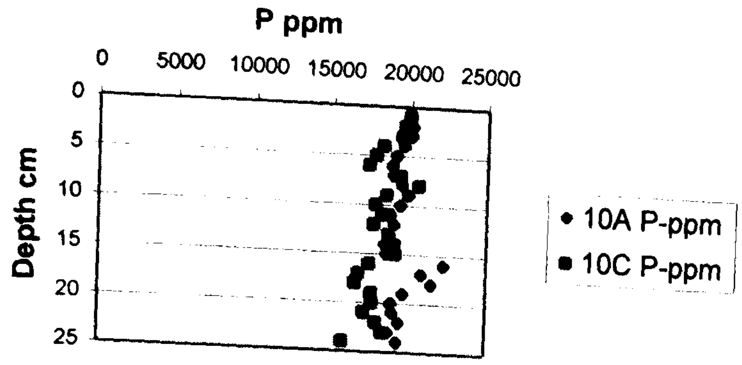




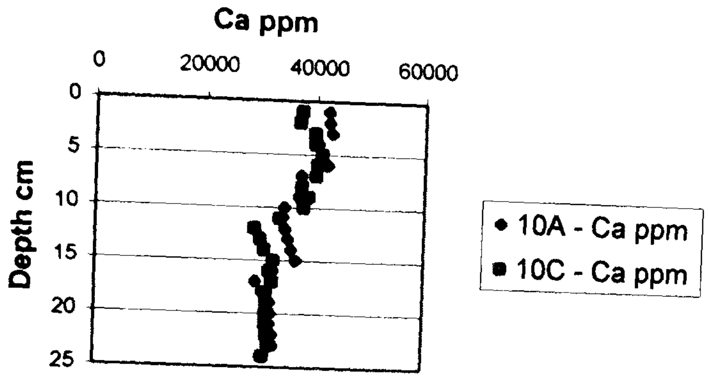


Appendix 10.2a: Duplicate depth concentration profiles for Al, S, Cr and Fe in Smethwick Sediment

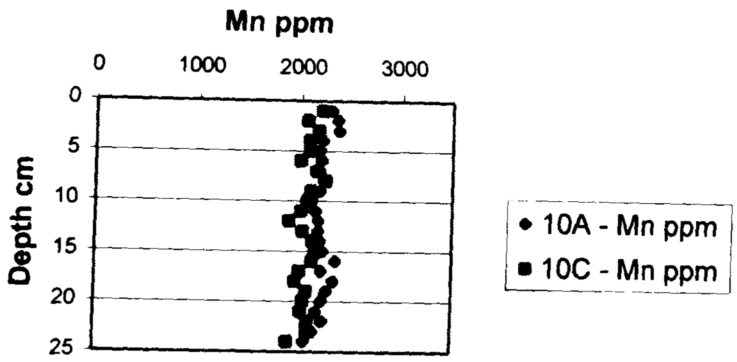
Duplicate Cores 10A and 10C
Smethwick, Spring P in Sediment



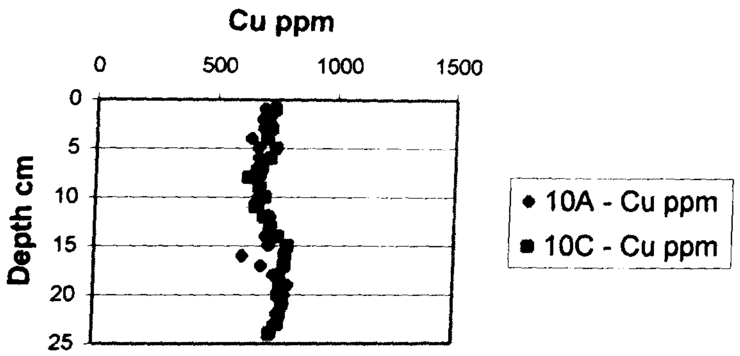
Duplicate Cores 10A and 10C from
Smethwick, Spring Ca in Sediment



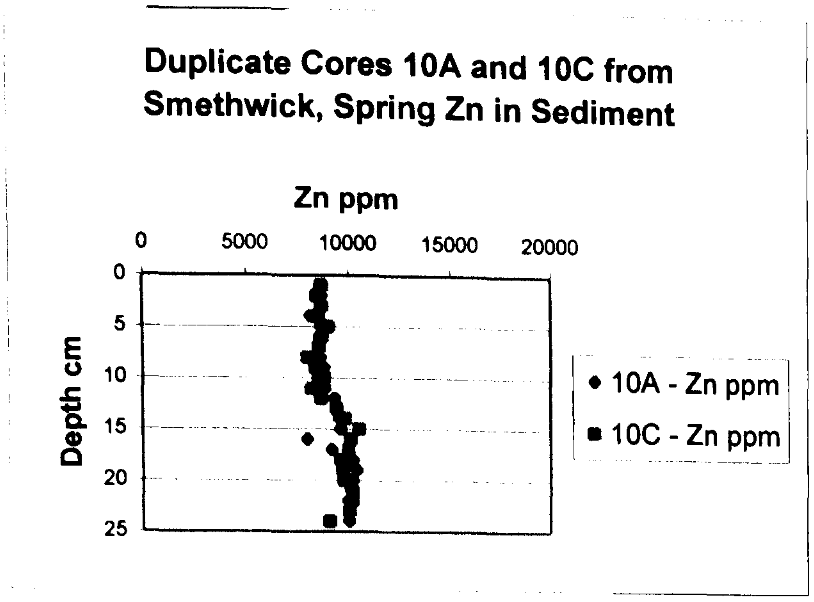
Duplicate Cores 10A and 10C from
Smethwick, Spring Mn in Sediment

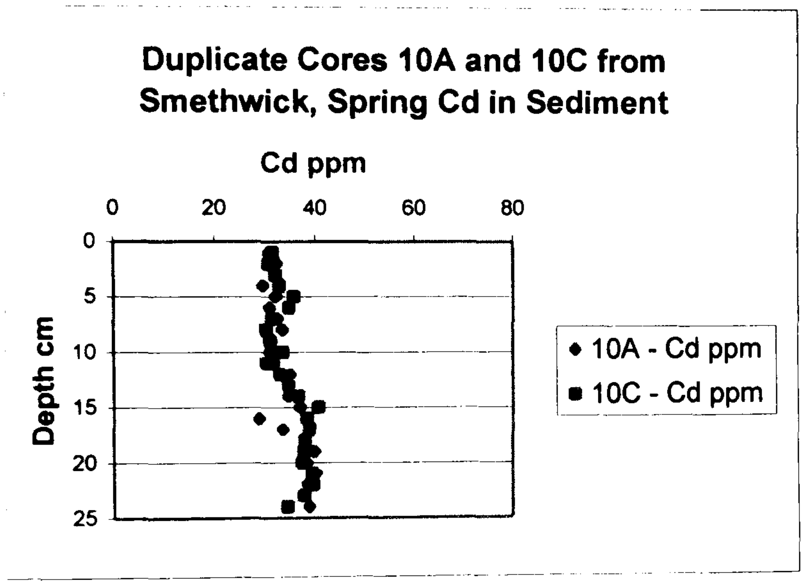


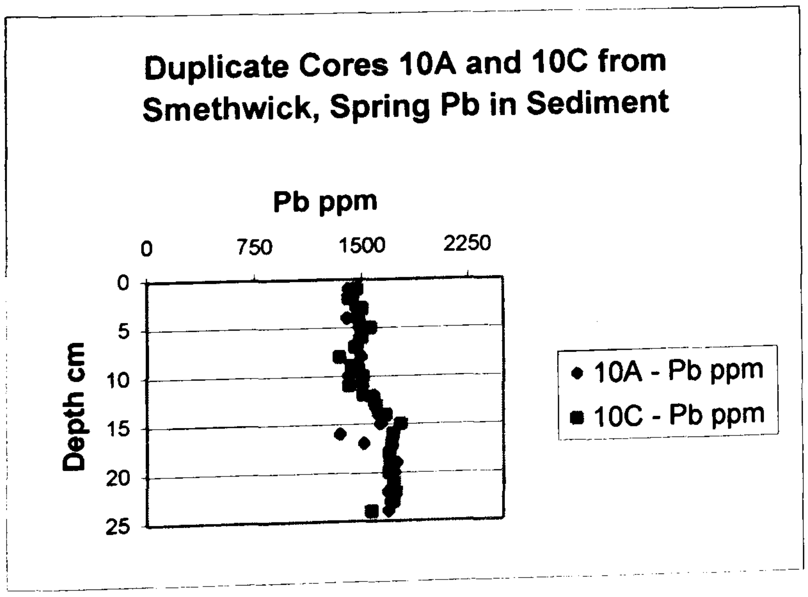
Duplicate Cores 10A and 10C from
Smethwick, Spring Cu in Sediment



Appendix 10.2b: Duplicate depth concentration profiles for P, Ca, Mn and Cu in Smethwick Sediment

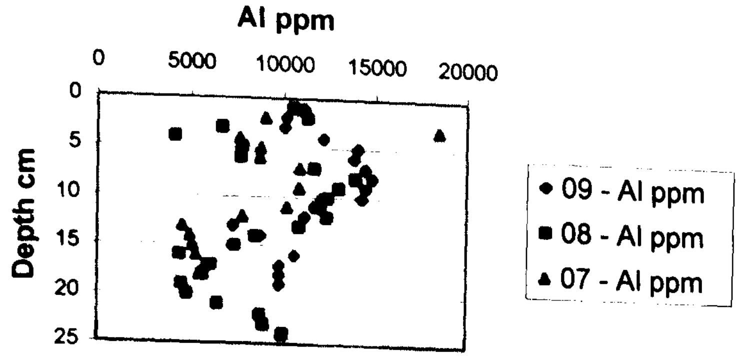




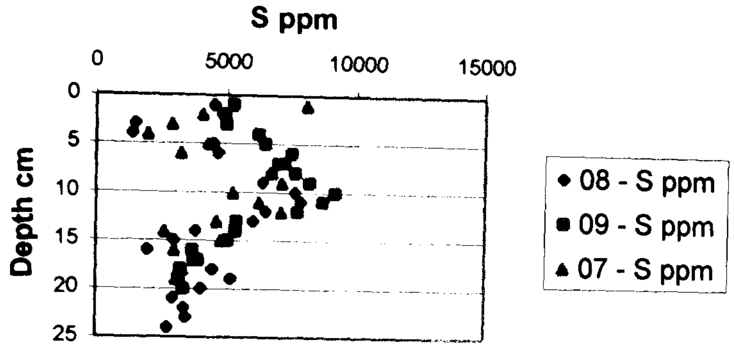


Appendix 10.2c: Duplicate depth concentration profiles for Zn, Cd and Pb in Smethwick Sediment

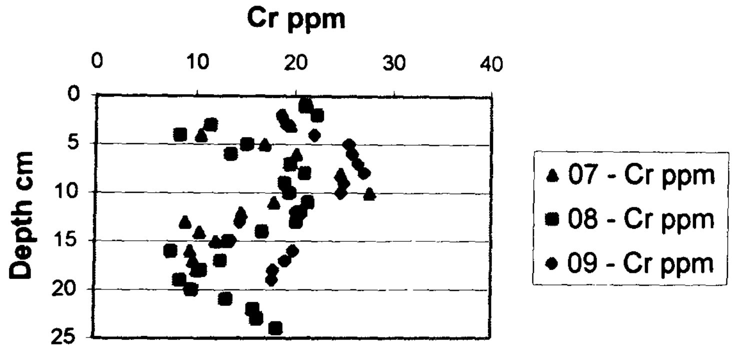
Duplicate Cores 7,8 and 9 from Snarestone, Spring Al in Sediment



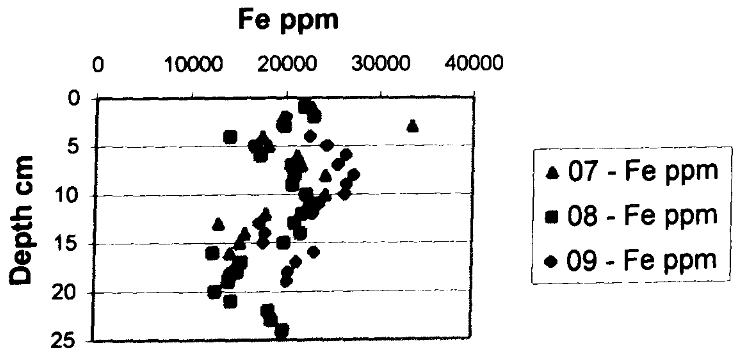
Duplicate Cores 7,8 and 9 from Snarestone, Spring S in Sediment



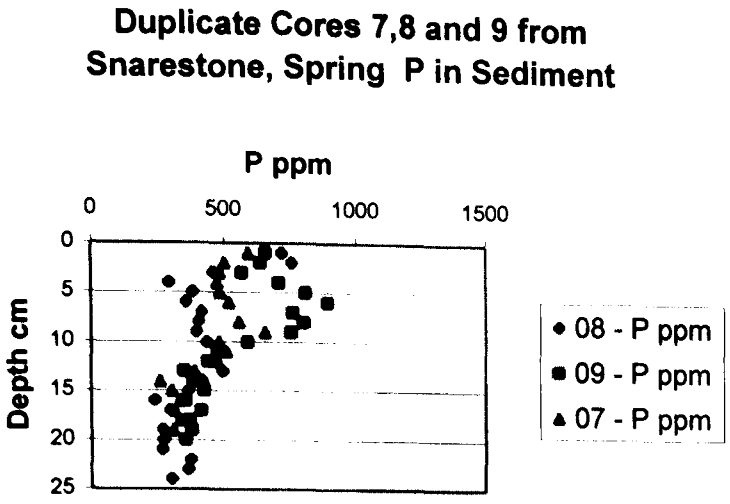
Duplicate Cores 7,8 and 9 from Snarestone, Spring Cr in Sediment

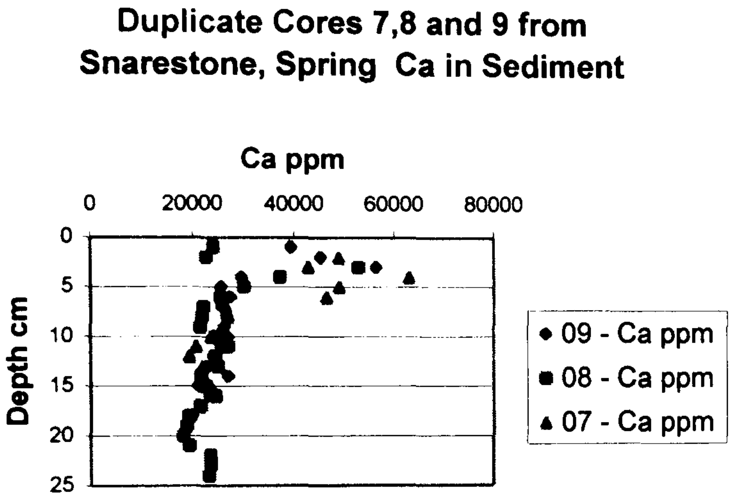


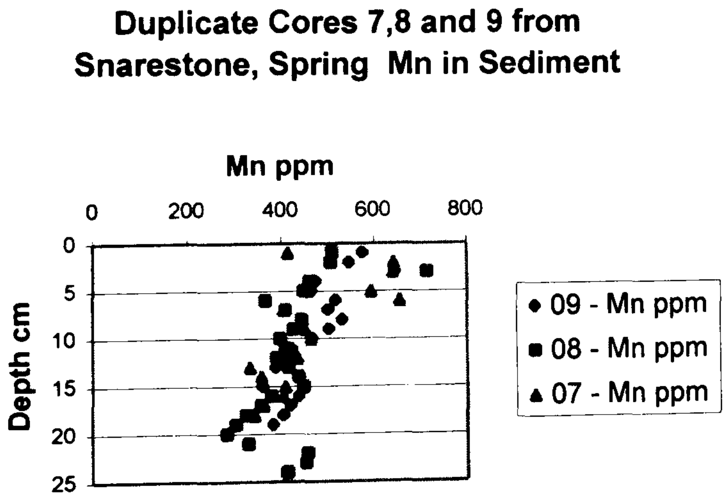
Duplicate Cores 7,8 and 9 from Snarestone, Spring Fe in Sediment

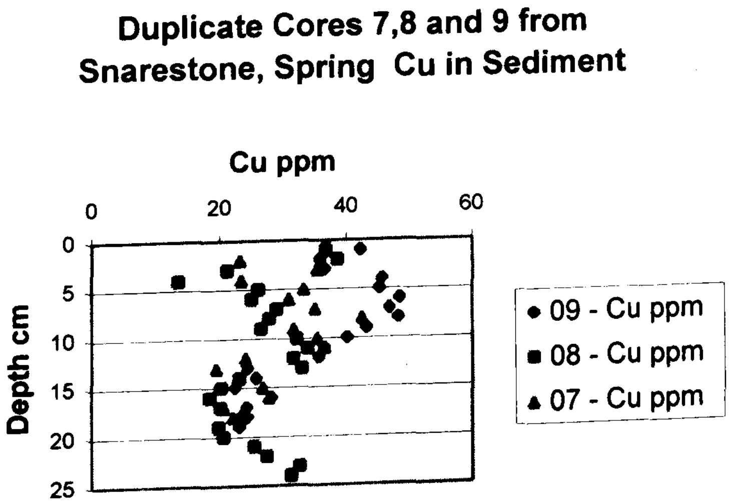


Appendix 10.2d: Duplicate depth concentration profiles for Al, S, Cr and Fe in Snarestone sediment

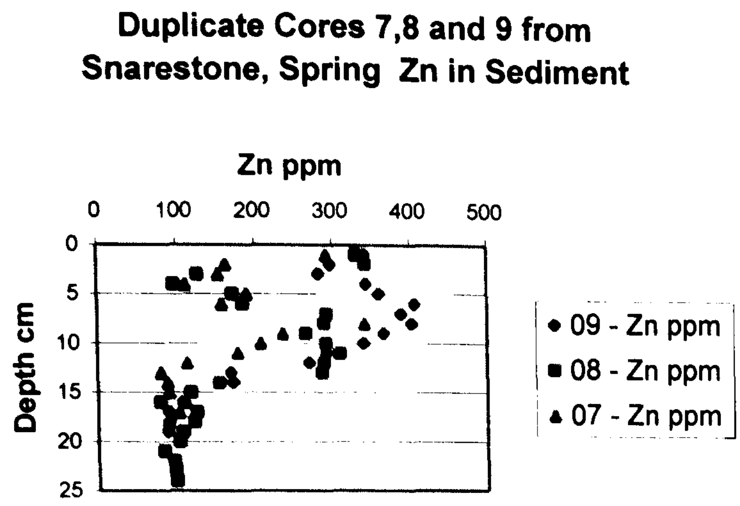








Appendix 10.2e: Duplicate depth concentration profiles for P, Ca, Mn and Cu in Snarestone sediment



Appendix 10.2f: Duplicate depth concentration profiles for Zn in Snarestone sediment

Appendix 11: The Concentrations in mM of Metals, Sulphur and Phosphorus, Extracted in Each Fraction of the Sequential Extraction, from Snarestone and Smethwick Sediments

Appendix 11.1a: The results in mM of Aluminium extracted in each fraction of the sequential extraction, from Smethwick sediment

Depth cm	Fraction 1	Fraction 2	Fraction 3
1	8.98	119.57	145.40
2	7.67	96.52	152.81
3	6.43	96.75	152.00
4	8.02	88.17	123.19
5	6.13	50.83	206.90
6	5.98	115.29	152.37
8	8.05	108.63	146.99
10	5.23	49.70	164.94
12	7.80	82.77	170.99
14	10.37	45.21	193.99
16	11.49	62.25	158.82
18	8.47	38.54	147.12
20	11.75	34.11	160.18
22	7.64	56.66	142.79
24	7.68	78.58	126.75

Appendix 11.1b: The results in mM of Aluminium extracted in each fraction of the sequential extraction, from Snarestone sediment

Depth cm	Fraction 1	Fraction 2	Fraction 3
1	5.06	44.84	80.03
2	3.73	76.86	65.87
3	3.74	42.67	75.63
4	4.53	38.10	72.46
5	2.78	30.94	61.09
6	3.27	34.27	59.54
8	3.42	37.70	71.94
10	3.24	31.98	66.87
12	2.43	32.46	72.54
14	4.74	30.57	55.09
16	1.59	19.29	32.10
18	2.61	23.86	46.24
20	2.60	20.56	50.38
22	2.14	13.38	20.57
24	2.36	17.37	40.94

Appendix 11.2a: The results in mM of Phosphorus extracted in each fraction of the sequential extraction, from Smethwick sediment

Depth cm	Fraction 1	Fraction 2	Fraction 3
1	248.19	211.83	74.15
2	169.52	239.19	85.48
3	169.07	195.41	94.21
4	194.64	238.97	74.38
5	202.28	252.75	96.32
6	273.27	216.44	88.38
8	218.17	193.19	84.86
10	175.87	216.73	88.86
12	206.61	249.74	87.23
14	217.38	274.31	102.44
16	212.96	202.22	72.95
18	200.35	173.18	77.39
20	179.04	259.11	88.49
22	205.05	192.71	66.09
24	297.42	199.34	65.43

Appendix 11.2b: The results in mM of Phosphorus extracted in each fraction of the sequential extraction, from Snarestone sediment

Depth cm	Fraction 1	Fraction 2	Fraction 3
1	3.66	RSD >10%	65.88
2	3.18	RSD >10%	48.11
3	2.17	RSD >10%	47.48
4	4.38	6.70	49.46
5	3.55	3.91	45.51
6	RSD >10%	RSD >10%	37.26
8	RSD >10%	3.48	37.46
10	3.40	3.25	34.01
12	RSD >10%	RSD >10%	34.20
14	3.81	3.63	40.08
16	RSD >10%	3.36	30.90
18	1.49	3.90	29.62
20	1.54	4.04	23.77
22	1.87	3.08	17.95
24	2.77	4.27	39.20

Appendix 11.3a: The results in mM of Sulphur extracted in each fraction of the sequential extraction, from Smethwick sediment

Depth cm	Fraction 1	Fraction 2	Fraction 3
1	24.29	3.18	226.03
2	20.11	2.65	229.03
3	25.73	2.53	244.00
4	34.71	2.56	222.85
5	41.54	3.40	325.30
6	39.23	3.59	277.96
8	36.46	2.87	270.47
10	29.63	2.62	246.80
12	39.89	2.49	266.08
14	26.20	2.65	305.81
16	15.69	2.74	322.74
18	11.57	2.09	284.66
20	11.57	2.68	312.04
22	12.07	2.65	356.48
24	20.64	2.15	226.41

Appendix 11.3b: The results in mM of Sulphur extracted in each fraction of the sequential extraction, from Snarestone sediment

Depth cm	Fraction 1	Fraction 2	Fraction 3
1	8.78	73.22	225.94
2	7.87	59.63	194.99
3	9.93	21.13	223.73
4	9.56	25.35	195.68
5	8.46	1.50	239.18
6	7.93	2.32	279.65
8	9.96	11.79	307.57
10	9.56	12.09	260.40
12	10.85	8.84	263.31
14	10.74	1.56	185.38
16	8.94	11.35	100.81
18	6.82	1.99	124.17
20	7.18	13.19	130.72
22	6.08	9.30	120.19
24	5.87	10.29	56.45

Appendix 11.4a: The results in mM of Calcium extracted in each fraction of the sequential extraction, from Smethwick sediment

Depth cm	Fraction 1	Fraction 2	Fraction 3
1	621.07	82.72	37.89
2	565.22	92.83	44.33
3	608.79	96.70	43.87
4	689.09	103.55	67.96
5	746.51	113.68	39.39
6	1048.19	116.09	48.57
8	821.08	87.97	45.23
10	707.78	126.37	48.99
12	752.68	113.98	49.48
14	704.20	110.81	70.02
16	643.16	89.54	52.19
18	565.98	81.22	50.84
20	566.54	87.95	67.89
22	623.83	66.26	45.04
24	710.80	68.68	51.19

Appendix 11.4b: The results in mM of Calcium extracted in each fraction of the sequential extraction, from Snarestone sediment

Depth cm	Fraction 1	Fraction 2	Fraction 3
1	512.16	66.52	7.23
2	430.23	138.47	9.17
3	500.03	69.44	17.04
4	466.81	64.12	7.88
5	421.18	76.05	21.22
6	450.96	74.86	37.63
8	503.90	60.13	7.04
10	495.29	81.76	12.05
12	595.79	71.38	8.94
14	558.73	99.02	15.60
16	604.72	96.34	35.70
18	425.08	89.64	13.80
20	462.62	95.88	23.49
22	325.38	221.97	169.52
24	364.14	105.18	15.14

Appendix 11.5a: The results in mM of Chromium extracted in each fraction of the sequential extraction, from Smethwick sediment

Depth cm	**Fraction 1**	**Fraction 2**	**Fraction 3**
1	0.05*	1.46	4.18
2	0.04*	0.82	4.19
3	0.03*	0.86	4.19
4	0.04*	0.61	3.78
5	0.04*	0.28	7.23
6	0.02*	1.30	4.43
8	0.05*	1.40	4.21
10	0.04*	0.20	4.52
12	0.05*	0.47	4.62
14	0.05*	0.19	5.68
16	0.08*	0.62	6.76
18	0.04*	0.26	6.56
20	0.09*	0.20	7.94
22	0.04*	0.68	5.70
24	0.03*	0.75	3.86

* these values are close to the detection limit the ICP AES and could not be used because the RSD from the mean of two analyses was >10%

Appendix 11.6a: The results in mM of Manganese extracted in each fraction of the sequential extraction, from Smethwick sediment

Depth cm	Fraction 1	Fraction 2	Fraction 3
1	18.70	7.65	3.40
2	14.61	10.27	3.21
3	14.32	8.50	3.59
4	15.40	10.69	2.22
5	17.01	19.38	3.06
6	20.23	10.22	4.05
8	18.42	8.24	3.95
10	14.46	13.16	4.75
12	19.51	13.64	4.88
14	20.01	18.63	6.49
16	21.13	13.92	6.87
18	18.91	14.85	6.94
20	18.78	19.14	6.91
22	28.08	11.80	5.38
24	27.15	7.85	2.49

Appendix 11.6b: The results in mM of Chromium extracted in each fraction of the sequential extraction, from Snarestone sediment

Depth cm	Fraction 1	Fraction 2	Fraction 3
1	5.54	0.78	0.64
2	4.26	1.61	0.57
3	4.76	0.66	0.66
4	4.46	0.71	0.63
5	3.91	0.90	0.68
6	4.17	0.98	0.83
8	4.41	0.74	0.66
10	3.39	0.87	0.61
12	3.48	0.71	0.66
14	5.45	1.58	0.60
16	6.55	1.69	0.74
18	4.09	1.29	0.58
20	4.16	1.31	0.84
22	2.74	2.51	2.49
24	3.67	1.13	0.45

Appendix 11.7a: The results in mM of Iron extracted in each fraction of the sequential extraction, from Smethwick sediment

Depth cm	Fraction 1	Fraction 2	Fraction 3
1	369.23	213.46	99.99
2	309.31	259.96	94.76
3	283.97	224.91	92.61
4	297.05	278.66	74.28
5	330.60	384.65	66.89
6	377.32	242.56	108.85
8	358.75	215.92	103.84
10	278.91	283.17	82.38
12	350.40	304.71	85.89
14	350.38	398.70	83.40
16	333.17	281.51	76.74
18	271.52	276.02	62.17
20	288.42	373.98	69.27
22	419.67	233.85	74.02
24	463.91	216.75	74.21

Appendix 11.7b: The results in mM of Iron extracted in each fraction of the sequential extraction, from Snarestone sediment

Depth cm	Fraction 1	Fraction 2	Fraction 3
1	78.17	39.02	41.93
2	60.25	80.70	31.05
3	64.26	43.05	44.44
4	63.71	38.91	35.74
5	52.77	37.92	45.49
6	42.78	39.21	61.48
8	37.60	33.34	76.16
10	36.49	28.30	62.12
12	38.00	36.22	62.90
14	69.86	54.36	25.27
16	56.82	43.21	10.11
18	42.21	30.44	23.06
20	35.93	28.43	29.06
22	29.73	34.89	10.99
24	36.68	25.54	19.11

Appendix 11.8a: The results in mM of Copper extracted in each fraction of the sequential extraction, from Smethwick sediment

Depth cm	Fraction 1	Fraction 2	Fraction 3
1	<0.0033	<0.101	8.87
2	<0.0025	<0.101	8.23
3	<0.0026	<0.101	8.21
4	<0.0027	<0.101	7.17
5	<0.0028	<0.101	10.06
6	<0.0029	<0.101	8.98
8	<0.0030	<0.101	8.47
10	<0.0031	<0.101	8.29
12	<0.0032	<0.101	8.68
14	<0.0033	<0.101	9.50
16	<0.0033	<0.101	9.73
18	<0.0033	<0.101	8.92
20	<0.0033	<0.101	10.20
22	<0.0033	<0.101	14.28
24	<0.0033	<0.101	7.27

Appendix 11.9a: The results in mM of Zinc extracted in each fraction of the sequential extraction, from Smethwick sediment

Depth cm	Fraction 1	Fraction 2	Fraction 3
1	9.49	40.37	61.36
2	7.17	29.35	70.99
3	7.54	32.45	67.43
4	8.25	27.58	58.14
5	4.46	52.41	134.68
6	4.55	24.49	85.23
8	3.34	22.15	82.33
10	3.41	17.55	88.70
12	7.78	29.43	91.08
14	5.77	23.91	138.23
16	9.54	35.15	161.04
18	12.03	32.16	149.50
20	14.36	35.85	181.36
22	14.10	33.56	181.43
24	13.44	17.69	73.55

Appendix 11.9b: The results in mM of Zinc extracted in each fraction of the sequential extraction, from Snarestone sediment

Depth cm	Fraction 1	Fraction 2	Fraction 3
1	0.18	4.43	1.46
2	0.13	8.13	1.07
3	0.10	3.71	1.17
4	0.10	3.27	1.51
5	0.07	2.66	1.50
6	0.06	2.74	1.37
8	0.06	2.82	1.27
10	0.04	2.52	1.32
12	0.03	2.53	1.48
14	0.05	1.91	1.18
16	0.04	0.98	0.93
18	0.05	1.37	0.70
20	0.03	0.83	0.74
22	0.02	0.42	0.62
24	0.02	0.45	0.41

Appendix 11.10a: The results in mM of Cadmium extracted in each fraction of the sequential extraction, from Smethwick sediment

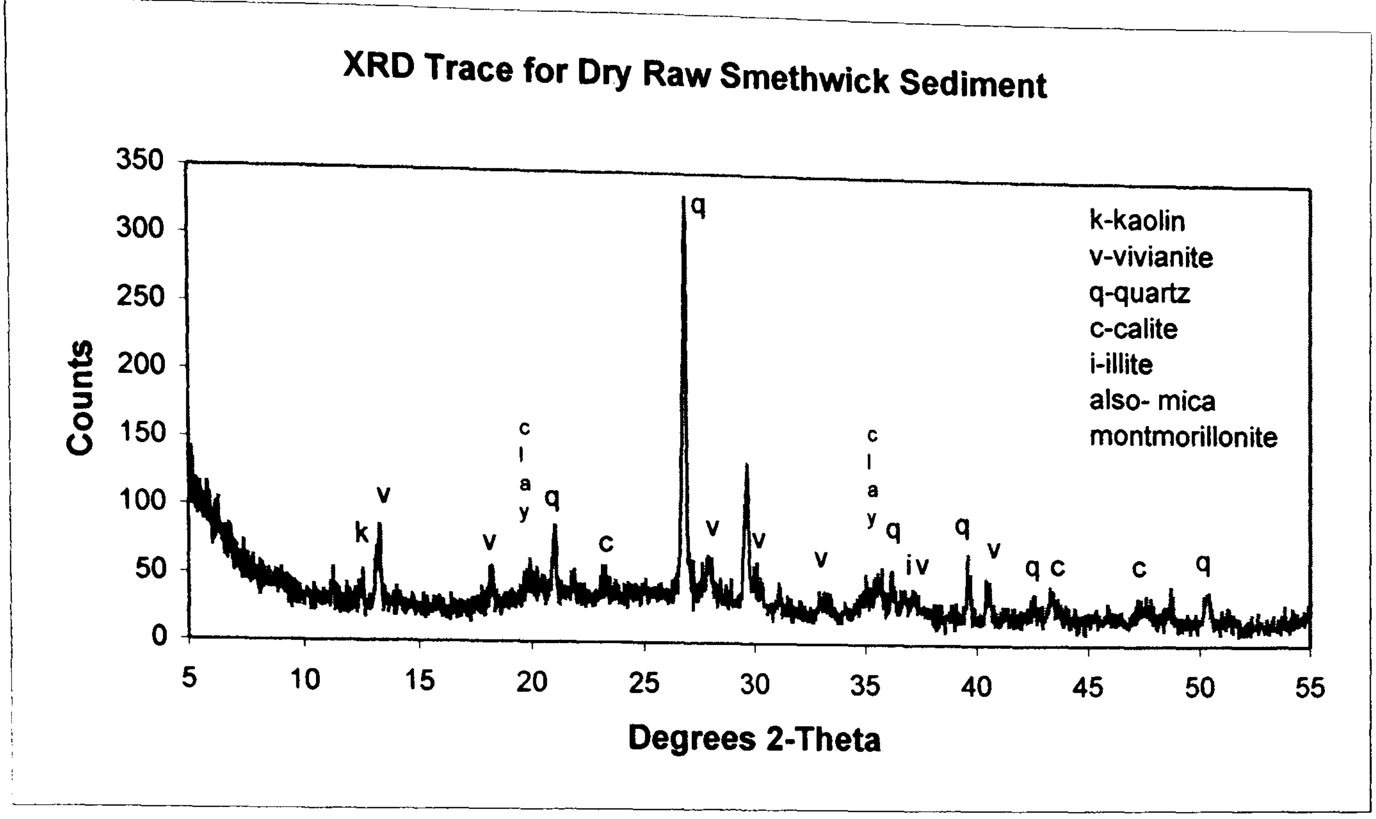
Depth cm	Fraction 1	Fraction 2	Fraction 3
1	<0.0035	<0.0101	0.20
2	<0.0035	<0.0101	0.20
3	<0.0035	<0.0101	0.20
4	<0.0035	<0.0101	0.17
5	<0.0035	<0.0101	0.39
6	<0.0035	<0.0101	0.22
8	<0.0035	<0.0101	0.22
10	<0.0035	<0.0101	0.22
12	<0.0035	<0.0101	0.25
14	<0.0035	<0.0101	0.33
16	<0.0035	<0.0101	0.43
18	<0.0035	<0.0101	0.41
20	<0.0035	<0.0101	0.49
22	<0.0035	<0.0101	0.49
24	<0.0035	<0.0101	0.19

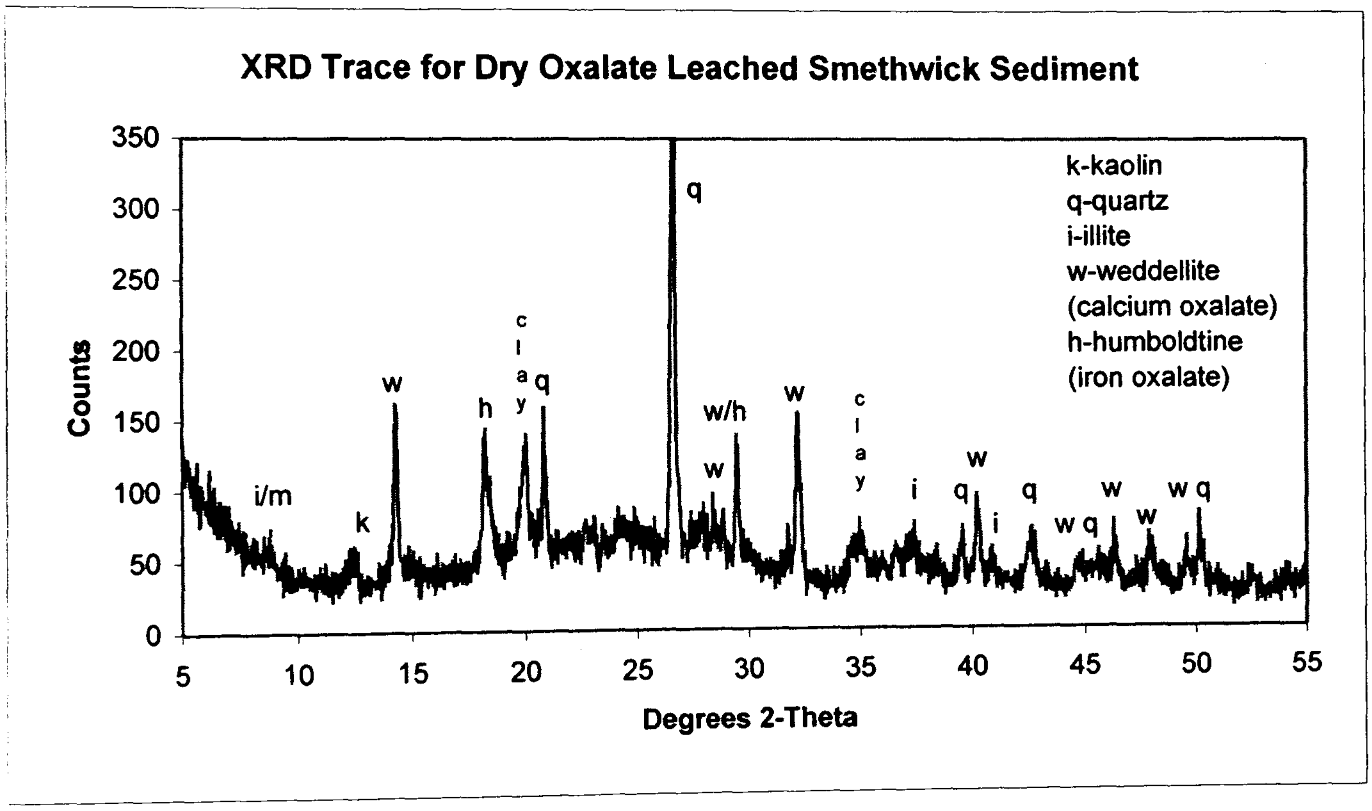
Appendix 11.11a: The results in mM of Lead extracted in each fraction of the sequential extraction, from Smethwick sediment

Depth cm	Fraction 1	Fraction 2	Fraction 3
1	<0.017	0.52	4.14
2	<0.017	0.25	4.54
3	<0.017	0.33	4.04
4	<0.017	0.16	3.70
5	<0.017	<0.059	8.13
6	<0.017	0.14	4.99
8	<0.017	0.10	5.00
10	<0.017	<0.059	4.54
12	<0.017	0.05	4.82
14	<0.017	<0.059	6.17
16	<0.017	<0.059	7.40
18	<0.017	<0.059	6.43
20	<0.017	<0.059	8.10
22	<0.017	0.10	10.17
24	<0.017	0.09	4.24

Appendix 12: XRD Traces for Raw and Oxalate Leached Smethwick Sediment

Appendix 12


XRD Trace for Dry Raw Smethwick Sediment
Counts
0
50
100
150
200
250
300
350
Degrees 2-Theta
5
10
15
20
25
30
35
40
45
50
55
k-kaolin
v-vivianite
q-quartz
c-calite
i-illite
also- mica
montmorillonite
k
v
v
clay
q
c
q
v
v
v
clay
q
i v
q
v
q c
c
q


XRD Trace for Dry Oxalate Leached Smethwick Sediment
Counts
0
50
100
150
200
250
300
350
Degrees 2-Theta
5
10
15
20
25
30
35
40
45
50
55
k-kaolin
q-quartz
i-illite
w-weddellite
(calcium oxalate)
h-humboldtine
(iron oxalate)
i/m
k
w
h
clay
q
q
w/h
w
w
clay
i
w
q
i
q
w q
w
w
w q

Appendix 13: Concentrations of Ions in Solution, in the Porewaters of Snarestone and Smethwick Sediments

Appendix 13.1a: Measurements of alkalinity, Eh and pH in Smethwick porewaters

Depth cm	Smethwick alkalinity mM	Smethwick pH	Smethwick Eh V
Water	1.145	7.760	
Interface	1.491	6.680	0.448
1	3.345	6.870	-0.059
2	4.946	6.850	-0.109
3	4.836	6.740	-0.139
4	5.382	6.680	-0.159
5	5.691	6.440	-0.129
6	5.764	6.420	-0.159
7	5.891	6.960	-0.109
8	5.927	6.890	-0.129
9	6.109	6.480	-0.179
10	6.255	6.500	-0.179
11	6.836	6.780	-0.189
12	7.018	6.680	-0.134
13	6.800	6.650	-0.139
14	6.727	6.720	-0.109
15	6.364	6.890	-0.119
16	6.509	6.830	-0.189
17	6.400	6.500	-0.184
18	6.473	6.450	-0.164
19	6.473	6.460	-0.149
20	6.509	6.480	-0.139
21	7.709	6.920	-0.194
22	7.709	6.790	-0.149
23	7.564	6.900	-0.224
24	7.818	6.880	-0.175

Appendix 13.1b: Measurements of alkalinity, Eh and pH in Snarestone porewaters

Depth cm	Snarestone alkalinity mM	Snarestone pH	Snarestone Eh V
Water	1.830	7.310	
Interface	1.873	7.210	0.301
1	3.255	6.910	0.152
2	3.091	6.340	0.191
3	2.545	6.450	0.183
4	2.655	6.560	0.006
5	2.545	6.540	0.041
6	2.618	6.550	0.021
7	2.655	6.600	-0.039
8	2.909	6.650	-0.129
9	2.636	6.570	-0.179
10	2.658	6.450	0.041
11	2.764	6.420	-0.049
12	2.909	6.650	0.016
13	2.909	6.540	-0.019
14	2.836	6.540	0.041
15	2.836	6.460	-0.009
16	2.691	6.470	0.061
17	2.800	6.230	0.021
18	2.618	6.320	-0.009
19	2.727	6.930	0.031
20	2.182	6.930	0.061
21	2.545	6.910	0.071
22	0.000	6.860	0.021
23	0.000	6.780	-0.059
24	2.982	6.740	0.041

Appendix 13.2a: Corrected concentrations of Sodium and Magnesium in Smethwick porewaters (mM)

Depth cm	Smethwick Na mM	Smethwick Mg mM
Water	3.350	1.226
Interface	3.473	1.239
1	3.310	1.242
2	2.745	1.258
3	3.583	1.935
4	3.815	2.116
5	3.810	2.339
6	4.000	2.443
7	4.116	2.664
8	4.211	2.714
9		2.594
10	4.387	2.664
11	4.246	2.312
12	4.514	2.199
13	4.342	2.010
14	4.579	2.100
15		1.853
16	4.731	1.921
17		1.903
18	4.773	2.030
19		2.052
20	4.611	1.981
21		1.894
22	4.692	1.878
23		1.965
24		1.969

Appendix 13.2b: Corrected concentrations of Sodium and Magnesium in Snarestone porewaters (mM)

Depth cm	Snarestone Mg mM	Snarestone Na mM
Water	0.052	0.672
Interface	0.671	0.676
1	0.716	0.679
2	0.659	0.693
3	0.692	0.755
4	0.750	0.765
5	0.806	0.779
6	0.735	0.853
7	0.888	0.926
8	0.931	0.942
9	0.995	0.958
10	0.929	0.989
11	0.904	0.989
12	0.863	0.989
13	0.861	1.020
14	0.859	1.041
15	0.804	1.041
16	0.750	1.041
17	0.781	1.041
18	0.812	1.041
19	0.787	1.063
20	0.763	1.063
21	0.751	1.063
22	0.739	1.063
23	0.751	1.063
24	0.764	1.063

Appendix 13.3a: Corrected concentrations of Aluminium in Smethwick porewaters (mM)

Depth cm	Spring AlmM	Summer Al mM	Autumn Al mM	Winter Al mM
Water	<0.0023	0.008	0.007	<0.0023
Interface	<0.0023	0.0073	0.0116	0.0356
1	<0.0023	<0.0023	<0.0023	0.0033
2	0.0062	0.0021	0.2153	<0.0023
3	0.0172	0.0026	0.0048	0.0030
4	<0.0023	0.004*	0.0054	<0.0023
5	<0.0023	0.003*	0.0130	<0.0023
6	0.0032	0.004*	0.0050	<0.0023
7	<0.0023	0.0079	0.0027	<0.0023
8	<0.0023	0.0030	0.0082	<0.0023
9	<0.0023	0.0073	0.0036	<0.0023
10	<0.0023	0.003*	0.0176	<0.0023
11	<0.0023	0.0041	0.0024	0.0024
12	0.0045	<0.0023	<0.0023	<0.0023
13	<0.0023	0.0048	0.0042	0.0026
14	0.0033	0.0027	0.0082	<0.0023
15	<0.0023	0.002*	0.0026	<0.0023
16	0.0029	0.0069	<0.0023	<0.0023
17	<0.0023	0.0094	0.0048	0.003*
18	0.0050	0.0044	<0.0023	0.005*
19	<0.0023	0.005*	<0.0023	0.0028
20	<0.0023	0.003*	<0.0023	0.0050
21	<0.0023	0.0039	<0.0023	0.004*
22	<0.0023	0.004*	<0.0023	0.006*
23	<0.0023	0.003*	0.0070	0.003*
24	<0.0023	0.0030	<0.0023	0.007*

* RSD >10%, therefore this value was not used

Appendix 13.3b: Corrected concentrations of Aluminium in Snarestone porewaters (mM)

Depth cm	Spring AlmM	Summer Al mM	Autumn Al mM	Winter Al mM
-1	<0.0023	0.0066*	0.0085	0.0400
0	<0.0023	0.017*	0.0237	0.2763
1	<0.0023	0.0056	0.0106	0.0204
2	<0.0023	0.0056	0.0026	0.0041*
3	0.0024	0.0064	<0.0023	0.0045
4	<0.0023	0.0035*	0.0047	0.0072
5	<0.0023	0.0074	0.0132	0.0155
6	<0.0023	0.0067	<0.0023	0.0079
7	<0.0023	0.0084	<0.0023	0.0066*
8	<0.0023	0.0027	<0.0023	0.0059
9	0.0030	0.0036*	0.0033	0.0057
10	<0.0023	0.0042	0.0076	0.0073
11	0.0070	0.0031	0.0042	0.0080*
12	0.0027	0.0049	0.0060	<0.0023
13	0.0072	0.0066	0.0051	0.0082
14	0.0042	0.0066	0.0054	<0.0023
15	<0.0023	0.0044	<0.0023	0.0063
16	0.0071	0.0059	0.0034	<0.0023
17	0.0047	0.0050	<0.0023	0.0089
18	0.0038	0.0193	<0.0023	<0.0023
19		0.0057	<0.0023	0.0071
20		0.0054	<0.0023	<0.0023
21		0.0095	<0.0023	0.0097
22		0.0047		<0.0023
23		0.0076		0.0083
24		0.0059		

* RSD >10%, therefore this value was not used

Appendix 13.4a: Corrected concentrations of Silicon in Smethwick porewaters (mM)

Depth cm	Spring Si mM	Summer Si mM	Autumn Si mM	Winter Si mM
Water	0.003	0.026	0.105	0.145
Interface		0.020	0.171	0.216
1	0.263	0.173	0.382	0.367
2	0.437	0.416	0.532	0.392
3	0.515	0.588	0.622	0.518
4	0.552	0.669	0.655	0.551
5	0.609	0.689	0.671	0.568
6	0.644	0.716	0.707	0.600
7	0.708	0.714	0.680	0.622
8	0.690	0.698	0.678	0.592
9	0.699	0.704	0.735	0.593
10	0.739	0.717	0.662	0.659
11	0.741	0.719	0.693	0.667
12	0.757	0.725	0.760	0.696
13	0.728	0.735	0.728	0.684
14	0.737	0.769	0.733	0.709
15	0.728	0.749	0.792	0.647
16	0.754	0.758	0.742	0.751
17	0.752	0.743	0.796	0.743
18	0.767	0.817	0.845	0.778
19	0.776	0.774	0.804	0.769
20	0.772	0.821	0.821	0.784
21	0.800	0.790	0.909	0.777
22	0.780	0.796	0.859	0.752
23	0.799	0.792	0.836	0.738
24	0.798	0.756		0.756

Appendix 13.4b: Corrected concentrations of Silicon in Snarestone porewaters (mM)

Depth cm	Spring Si mM	Summer Si mM	Autumn Si mM	Winter Si mM
Water	0.005	0.085	0.035	0.160
Interface	#N/A	0.100	0.085	0.548
1	0.376	0.175	0.174	0.169
2	0.538	0.282	0.264	0.238
3	0.629	0.288	0.317	0.292
4	0.694	0.287	0.348	0.325
5	0.720	0.295	0.374	0.288
6	0.743	0.303	0.418	0.338
7	0.770	0.328	0.426	0.348
8	0.804	0.376	0.449	0.376
9	0.790	0.391	0.455	0.357
10	1.001	0.420	0.499	0.355
11	0.959	0.461	0.550	0.326
12	0.887	0.465	0.616	0.346
13	0.941	0.478	0.678	0.365
14	0.650	0.508	0.752	0.365
15	0.710	0.499	0.814	0.358
16	0.661	0.487	0.908	0.358
17	0.547	0.526	0.971	0.402
18	0.627	0.553	0.901	0.402
19		0.491	0.812	0.398
20		0.536	0.799	0.398
21		0.502	0.769	0.395
22		0.522		0.395
23		0.532		0.400
24		0.547		0.400

Appendix 13.5a: Corrected concentrations of Phosphate in Smethwick porewaters (mM)

Depth cm	Spring Phosphate mM	Summer Phosphate mM	Autumn Phosphate mM	Winter Phosphate mM
Water	0.012	0.011	0.011	0.010
Interface	0.010	0.017	0.016	0.014
1	0.088	0.042	0.223	0.127
2	0.211	0.074	0.311	0.169
3	0.212	0.059	0.301	0.267
4	0.215	0.047	0.183	0.276
5	0.329	0.122	0.092	0.196
6	0.265	0.053		0.215
7	0.195	0.116	0.118	0.190
8	0.210	0.038	0.070	0.183
9	0.176	0.069	0.111	0.167
10	0.121	0.142	0.142	0.167
11	0.091	0.099	0.160	0.109
12	0.080	0.069	0.171	0.119
13	0.071	0.020	0.139	0.132
14	0.045	0.043	0.148	0.111
15	0.061	0.124	0.084	0.178
16	0.070	0.093	0.141	0.164
17	0.112	0.123	0.170	0.117
18	0.057	0.059	0.166	0.164
19	0.115	0.055	0.181	0.148
20	0.088	0.151	0.064	0.152
21	0.017	0.080	0.177	0.133
22	0.044	0.078	0.184	0.128
23	0.055	0.034	0.195	0.053
24	0.095	0.059	0.206	0.073

Appendix 13.5b: Corrected concentrations of Phosphate in Snarestone porewaters (mM)

Depth cm	Spring Phosphate mM	Summer Phosphate mM	Autumn Phosphate mM	Winter Phosphate mM
Water	0.004	0.001	<0.0003	0.000
Interface		0.002	<0.0003	0.002
1	0.011	0.017	0.030	0.010
2	0.007	0.031	0.036	0.020
3	0.009	0.042	0.041	0.030
4	0.002	0.029	0.025	0.037
5	0.025	0.057	0.031	0.048
6	0.013	0.042	0.033	0.048
7	0.031	0.055	0.013	0.043
8	0.019	0.036	0.013	0.036
9	0.025	0.038	0.074	0.065
10	0.038	0.042	0.026	0.076
11	0.061	0.032	0.166	0.088
12	0.042	0.045	0.155	0.075
13	0.082	0.050	0.148	0.075
14	0.047	0.030	0.140	0.062
15	0.013	0.046	0.138	0.066
16	0.035	0.030	0.118	0.066
17	0.021	0.024	0.108	0.055
18	0.025	0.023	0.108	0.075
19		0.017	0.108	0.041
20	0.017	0.035	0.108	0.041
21		0.041	0.062	0.074
22	0.037	0.054		0.074
23		0.054	0.089	0.033
24	0.026	0.035	0.044	0.033

Appendix 13.6a: Corrected concentrations of Sulphate in Smethwick porewaters (mM)

Depth cm	Spring Sulphate mM	Summer Sulphate mM	Autumn Sulphate mM	Winter Sulphate mM
Water	2.7064	2.1725	2.1381	1.7005
Interface	2.6486	2.1235	2.2065	1.2114
1	1.1767	1.7269	0.8453	0.6540
2	0.1187	1.0087	0.0346	0.0316
3	0.0158	0.8657	0.0129	<0.0001
4	0.0161	0.8901	0.0224	0.0136
5	<0.0001	0.1619	<0.0001	<0.0001
6	0.0052	0.0800	<0.0001	<0.0001
7	0.0058	0.0173	<0.0001	<0.0001
8	0.0070	0.0041	<0.0001	0.0025
9	0.0020	0.0023	<0.0001	<0.0001
10	0.0022	<0.0001	<0.0001	<0.0001
11	0.0022	<0.0001	<0.0001	0.0042
12	0.0018	<0.0001	0.0041	0.0037
13	0.0012	<0.0001	<0.0001	0.0028
14	0.0019	<0.0001	<0.0001	0.0056
15	0.0012	<0.0001	<0.0001	<0.0001
16	0.0014	<0.0001	<0.0001	<0.0001
17	<0.0001	<0.0001	<0.0001	<0.0001
18	0.0013	<0.0001	<0.0001	<0.0001
19	<0.0001	<0.0001	<0.0001	<0.0001
20	0.0011	<0.0001	0.0017	<0.0001
21	0.0019	0.0054	<0.0001	<0.0001
22	0.0020	<0.0001	<0.0001	<0.0001
23	0.0083	0.0026	<0.0001	0.0035
24	0.0098	0.0029	<0.0001	0.0081

Appendix 13.6b: Corrected concentrations of Sulphate in Snarestone porewaters (mM)

Depth cm	Spring Sulphate mM	Summer Sulphate mM	Autumn Sulphate mM	Winter Sulphate mM
Water	0.7552	0.6673	0.6714	0.5811
Interface		0.6433	0.6809	0.6068
1	0.0531	0.2055	0.1636	0.4540
2	0.0082	0.0345	0.0515	0.3417
3	0.0234	0.0259	0.0491	0.2154
4	0.0575	0.0120	0.0960	0.1157
5	0.0067	<0.0001	0.0796	0.0000
6	0.0182	0.0078	0.0544	<0.0001
7	0.0076	0.0062	0.0223	0.0017
8	0.0479	0.0238	0.0223	0.0085
9	0.0107	0.0342	0.0030	<0.0001
10	0.0264	0.0795	0.0134	<0.0001
11	0.0013	0.0608	<0.0001	<0.0001
12	0.0226	0.0272	<0.0001	<0.0001
13	<0.0001	0.0454	<0.0001	<0.0001
14	0.0023	0.0986	<0.0001	<0.0001
15	0.5534	0.0067	<0.0001	<0.0001
16	0.2697	0.0523	<0.0001	<0.0001
17	0.0222	0.0298	<0.0001	0.0022
18	0.0740	0.0166	<0.0001	<0.0001
19		0.0346	<0.0001	0.1517
20	0.7685	0.0585	<0.0001	<0.0001
21		0.0033	0.0048	<0.0001
22	0.0048	0.0055		<0.0001
23		0.0055	<0.0001	0.0068
24	0.1138	0.0055	0.0032	0.0070

Appendix 13.7a: Corrected concentrations of Chloride in Smethwick porewaters (mM)

Depth cm	Spring Chloride mM	Summer Chloride mM	Autumn Chloride mM	Winter Chloride mM
Water	2.880	3.000	2.672	2.861
Interface	2.898	3.054	2.797	2.861
1	2.977	2.968	2.895	2.878
2	3.038	2.937	3.043	2.630
3	3.016	2.872	2.969	2.647
4	2.976	2.835	3.247	2.595
5	2.974	2.851	3.312	2.442
6	2.914	2.814		2.540
7	2.884	2.770	3.503	2.554
8	2.828	2.737	3.551	2.596
9	2.812	2.710	3.583	2.617
10	2.015	2.677	3.582	2.699
11	2.816	2.637	3.566	2.722
12	2.816	2.632	3.604	2.740
13	2.794	2.612	3.555	2.593
14	2.798	2.622	3.555	2.787
15	2.770	2.633	3.622	2.864
16	2.835	2.617	3.523	2.704
17	2.822	2.547	3.551	2.946
18	2.830	2.587	3.517	2.989
19	2.820	2.618	3.541	3.008
20	2.822	2.601	3.610	3.054
21	2.729	2.555	3.504	2.990
22	2.755	2.625	3.507	3.060
23	2.755	2.596	3.497	3.040
24	2.802	2.587	3.496	3.132

Appendix 13.7b: Corrected concentrations of Chloride in Snarestone porewaters (mM)

Depth cm	Spring Chloride mM	Summer Chloride mM	Autumn Chloride mM	Winter Chloride mM
Water		1.003	1.174	0.820
Interface	0.972	1.013	1.316	0.827
1	0.962	1.039	1.316	0.842
2	0.986	1.030	1.314	0.863
3	0.952	1.059	1.325	0.890
4	0.866	1.050	1.307	0.914
5	0.965	1.049	1.310	0.943
6	0.993	1.048	1.291	0.959
7	1.017	1.055	1.104	0.999
8	1.059	1.059	1.104	1.008
9	1.005	1.020	1.296	1.044
10	1.109	1.026	1.387	1.066
11	1.106	1.006	1.405	1.094
12	1.047	1.010	1.420	1.109
13	1.116	1.018	1.451	1.142
14	1.101	1.013	1.483	1.138
15	1.089	1.053	1.528	1.167
16	1.104	1.054	1.523	1.167
17	1.131	1.058	1.506	1.170
18	1.130	1.002	1.506	1.185
19		0.991	1.544	1.983
20	1.144	1.032	1.544	1.983
21		0.984	1.666	1.192
22	1.278	1.025	1.666	1.192
23		1.025	1.678	1.220
24	1.328	1.025	1.732	1.220

Appendix 13.8a: Corrected concentrations of Calcium in Smethwick porewaters (mM)

Depth cm	Spring Ca mM	Summer Ca mM	Autumn Ca mM	Winter Ca mM
Water	1.757	2.860	2.695	2.338
Interface		2.930	2.855	2.505
1	2.677	2.969	3.007	2.831
2	2.537	3.096	3.133	2.845
3	2.495	3.025	3.580	3.943
4	2.385	2.913	3.866	4.297
5	2.382	2.843	4.123	4.484
6	2.316	3.041	4.832	4.561
7	2.405	3.061	4.586	4.674
8	2.221	3.330	4.638	4.847
9	2.079	3.465	4.791	4.911
10	2.084	3.515	4.198	5.494
11	2.037	3.592	4.458	5.151
12	2.010	3.829	4.586	5.398
13	2.016	3.955	4.328	5.251
14	2.015	4.230	4.312	5.741
15	1.949	4.302	4.728	5.292
16	2.042	4.303	4.254	5.495
17	2.001	4.223	4.733	5.649
18	2.075	4.608		6.057
19	2.178	4.338	4.658	6.319
20	2.176	4.886		6.291
21	2.238	4.783		6.002
22	2.235	4.972		6.049
23	2.333	5.133		6.428
24	2.328	5.069		6.573

Appendix 13.8b: Corrected concentrations of Calcium in Snarestone porewaters (mM)

Depth cm	Spring Ca mM	Summer Ca mM	Autumn Ca mM	Winter Ca mM
Water	1.843	1.951	1.962	1.760
Interface	#N/A	2.026	2.036	1.759
1	2.268	2.099	1.963	1.703
2	2.476	2.188	1.858	1.723
3	2.675	2.100	1.858	1.849
4	2.669	2.025	1.821	2.100
5	2.518	1.983	1.893	1.901
6	2.486	1.913	1.893	2.237
7	2.433	1.828	1.893	2.226
8	2.619	1.772	1.893	2.373
9	2.478	1.739	2.109	2.276
10	3.100	1.706	2.195	2.187
11	3.194	1.688	2.197	2.053
12	3.010	1.643	2.178	2.053
13	3.265	1.646	2.216	2.000
14	2.354	1.753	2.163	2.000
15	2.572	1.808	2.163	1.735
16	2.479	1.804	2.163	1.735
17	2.196	1.921	2.163	1.834
18	2.289	1.943	2.163	1.834
19		1.891	2.163	1.727
20		2.048	2.163	1.727
21		1.981	2.163	1.739
22		2.120		1.739
23		2.132		1.796
24		2.216		1.796

Appendix 13.9a: Corrected concentrations of Manganese in Smethwick porewaters (mM)

Depth cm	Spring Mn mM	Summer Mn mM	Autumn Mn mM	Winter Mn mM
Water	0.001	0.001	0.001	0.002
Interface	#N/A	0.000	0.003	0.004
1	0.005	0.008	0.005	0.004
2	0.003	0.007	0.005	0.003
3	0.004	0.007	0.005	0.006
4	0.004	0.007	0.006	0.007
5	0.004	0.007	0.007	0.008
6	0.003	0.008	0.010	0.009
7	0.004	0.008	0.009	0.011
8	0.004	0.009	0.009	0.012
9	0.004	0.012	0.009	0.011
10	0.005	0.012	0.009	0.012
11	0.005	0.012	0.011	0.013
12	0.005	0.012	0.014	0.014
13	0.006	0.013	0.012	0.016
14	0.006	0.015	0.014	0.018
15	0.006	0.015	0.015	0.017
16	0.006	0.014	0.013	0.019
17	0.007	0.013	0.015	0.021
18	0.008	0.015	0.017	0.025
19	0.009	0.014	0.015	0.026
20	0.009	0.015	0.015	0.028
21	0.009	0.014	0.015	0.026
22	0.008	0.014	0.013	0.027
23	0.009	0.014	0.013	0.026
24	0.009	0.014		0.025

Appendix 13.9b: Corrected concentrations of Manganese in Snarestone porewaters (mM)

Depth cm	Spring Mn mM	Summer Mn mM	Autumn Mn mM	Winter Mn mM
Water	0.000	0.001	0.001	0.000
Interface		0.001	0.003	0.002
1	0.021	0.033	0.018	0.025
2	0.028	0.033	0.017	0.027
3	0.029	0.025	0.016	0.027
4	0.031	0.017	0.016	0.023
5	0.032	0.014	0.016	0.015
6	0.037	0.014	0.018	0.020
7	0.038	0.016	0.019	0.018
8	0.043	0.018	0.020	0.018
9	0.040	0.021	0.018	0.017
10	0.044	0.020	0.019	0.016
11	0.044	0.026	0.018	0.012
12	0.041	0.021	0.017	0.012
13	0.040	0.023	0.018	0.013
14	0.027	0.025	0.019	0.013
15	0.030	0.031	0.020	0.011
16	0.027	0.030	0.018	0.011
17	0.024	0.031	0.018	0.013
18	0.026	0.031	0.020	0.013
19		0.028	0.022	0.013
20		0.032	0.023	0.013
21		0.026	0.022	0.013
22		0.029		0.013
23		0.026		0.014
24		0.030		0.014

Appendix 13.10a: Corrected concentrations of Iron in Smethwick porewaters (mM)

Depth cm	Spring Fe mM	Summer Fe mM	Autumn Fe mM	Winter Fe mM
Water	0.002	0.001	0.009	0.004
Interface		0.001	0.018	0.035
1	0.003	0.041	0.006	0.034
2	0.003	0.008	0.006	0.018
3	0.007	0.006	0.012	0.020
4	0.005	0.006	0.020	0.024
5	0.004	0.008	0.042	0.042
6	0.004	0.012	0.089	0.032
7	0.004	0.039	0.088	0.048
8	0.005	0.039	0.030	0.064
9	0.014	0.031	0.008	0.060
10	0.020	0.032	0.009	0.067
11	0.029	0.015	0.065	0.063
12	0.034	0.030	0.131	0.075
13	0.035	0.014	0.086	0.110
14	0.042	0.019	0.114	0.085
15	0.034	0.040	0.127	0.066
16	0.019	0.039	0.089	0.083
17	0.053	0.054	0.130	0.070
18	0.076	0.089	0.148	0.089
19	0.067	0.011	0.120	0.086
20	0.078	0.055	0.123	0.134
21	0.081	0.030	0.131	0.090
22	0.066	0.067	0.112	0.107
23	0.084	0.046	0.105	0.097
24	0.091	0.049	0.074	0.099

Appendix 13.10b: Corrected concentrations of Iron in Snarestone porewaters (mM)

Depth cm	Spring Fe mM	Summer Fe mM	Autumn Fe mM	Winter Fe mM
Water	0.002	0.004	0.006	0.017
Interface	0.017	0.005	0.019	0.072
1	0.031	0.028	0.021	0.005
2	0.037	0.027	0.021	0.010
3	0.037	0.022	0.005	0.008
4	0.041	0.010	0.010	0.002
5	0.054	0.003	0.009	0.001
6	0.082	0.002	0.006	0.002
7	0.059	0.002	0.004	0.001
8	0.105	0.003	0.003	0.001
9	0.085	0.014	0.002	0.003
10	0.045	0.003	0.006	0.003
11	0.019	0.006	0.008	0.002
12	0.029	0.004	0.011	0.002
13	0.003	0.003	0.015	0.004
14	0.023	0.003	0.020	0.004
15	0.017	0.001	0.021	0.002
16	0.022	0.001	0.012	0.002
17	0.032	0.003	0.015	0.003
18	0.041	0.010	0.023	0.003
19		0.002	0.033	0.002
20		0.002	0.036	0.002
21		0.002	0.039	0.003
22		0.001		0.003
23		0.002		0.002
24		0.002		0.002

Appendix 13.11a: Corrected concentrations of Zinc in Smethwick porewaters (mM)

Depth cm	Spring Zn mM	Summer Zn mM	Autumn Zn mM	Winter Zn mM
Water	0.0003	0.0009	0.0021	0.0027
Interface		0.0008	0.0011	0.0088
1	0.0011	0.0007	0.0001	0.0013
2	0.0010	0.0008	0.0003	0.0004
3	0.0011	0.0007	0.0007*	0.0003
4	0.0009	0.0009	0.0006	0.0004
5	0.0009	0.0006	0.0011	0.0003
6	0.0007	0.0007*	0.0006*	0.0003*
7	0.0009	0.0016	0.0005*	0.0003
8	0.0010	0.0005*	0.0006	0.0003
9	0.0001*	0.0013*	0.0004*	0.0002*
10	0.0002*	0.0005	0.0005*	0.0002
11	0.0006	0.0005*	0.0002*	0.0004*
12	0.0010	0.0006	0.0004	0.0003
13	0.0002	0.0007*	0.0003	0.0003*
14	0.0002*	0.0007	0.0007	0.0004*
15	0.0005*	0.0007	0.0004	0.0002
16	0.0005	0.0008	0.0002*	0.0013
17	0.0004	0.0007	0.0009	0.0003*
18	0.0010	0.0006	0.0001	0.0010
19	0.0002	0.0011	0.0008	0.0001*
20	0.0017	0.0008*	0.0006	0.0008
21	0.0003*	0.0006*	0.0009	0.0007
22	0.0002*	0.0006	0.0007	0.0003
23	0.0003*	0.0008	0.0008	0.0002*
24	0.0002	0.0008	0.0011	0.0007

* RSD >10%, therefore this value was not used

Appendix 14: The Saturation Indices of Observed Mineral Phases in the Porewaters of Snarestone and Smethwick

Appendix 14.1a: Saturation Indices of Amorphous Iron Hydroxide in Smethwick porewaters

	Spring	Summer	Autumn	Winter
Water	2.32	2.54	2.92	3.44
Interface	0.02	2.53	3.24	1.36
1	0.35	0.36	0.08	-0.73
2	-0.6	-0.7	-0.96	-1.47
3	-0.41	-0.58	-1.37	-1.36
4	-3.04	-3.59	-3.74	-4.64
5	-2.38	-3.58	-3.26	-4.4
6	-2.51	-4.07	-3.74	-4.42
7	-3.53	-4.94	-4.94	-5.59
8	-4.66	-6.14	-6.29	-6.97
9	-5.83	-6.55	-7.57	-7.58
10	-2.75	-3.85	-3.71	-4.21
11	-4.75	-5.17	-5.23	-6
12	-2.77	-3.56	-3.3	-4.04
13	-4.69	-4.61	-4.09	-4.83
14	-2.77	-3.59	-2.94	-3.52
15	-3.99	-5.15	-4.01	-5.2
16	-2.65	-3.93	-3.03	-3.97
17	-3.88	-4.85	-4.32	-5.2
18	-4.01	-4.57	-4.38	-5.44
19		-2.76	-1.72	-3.11
20		-2.25	-1.16	-2.58
21		-2.29	-1.17	-2.46
22		-3.45		-3.31
23		-4.75		-5.07
24		-3.17		-3.51

Appendix 14.1b: Saturation Indices of Amorphous Iron Hydroxide in Snarestone porewaters

	Spring	Summer	Autumn	Winter
Water	2.31	2.19	3.4	3.62
Interface	1.86	1.7	3.14	3.81
1	-4.31	-3.26	-4.21	-3.67
2	-5.25	-4.9	-5.15	-4.89
3	-5.72	-5.86	-5.68	-5.7
4	-6.4	-6.39	-5.98	-6.15
5	-6.72	-6.48	-5.86	-6.11
6	-7.28	-6.86	-6.11	-6.81
7	-4.82	-3.9	-3.66	-4.17
8	-5.28	-4.44	-4.67	-4.6
9	-6.9	-6.62	-7.32	-6.7
10	-6.68	-6.56	-7.22	-6.6
11	-5.86	-6.23	-5.7	-5.96
12	-5.15	-5.29	-4.77	-5.25
13	-5.31	-5.79	-5.12	-5.26
14	-4.51	-4.94	-4.28	-4.65
15	-4.26	-4.28	-3.88	-4.42
16	-5.88	-5.66	-5.41	-5.69
17	-6.34	-6.42	-6.15	-6.66
18	-5.99	-6.01	-5.9	-6.37
19	-5.76	-6.63	-5.71	-6.1
20	-5.47	-5.71	-5.46	-5.68
21	-5.08	-5.61	-5.09	-5.49
22	-4.8	-4.89	-4.51	-5.04
23	-5.64	-5.99	-5.75	-6.02
24	-4.84	-5.2	-5.14	-5.24

Appendix 14.2a: Saturation Indices of Goethite in Smethwick porewaters

	Spring	Summer	Autumn	Winter
Water	7.8	8.1	8.25	8.49
Interface	5.5	8.09	8.57	6.41
1	5.84	5.92	5.41	4.32
2	4.88	4.86	4.37	3.58
3	5.08	4.98	3.96	3.69
4	2.45	1.97	1.59	0.41
5	3.1	1.98	2.07	0.64
6	2.97	1.49	1.59	0.63
7	1.96	0.62	0.39	-0.54
8	0.82	-0.58	-0.96	-1.92
9	-0.35	-0.99	-2.24	-2.53
10	2.73	1.71	1.62	0.84
11	0.74	0.39	0.1	-0.96
12	2.71	2	2.03	1.01
13	0.8	0.95	1.24	0.21
14	2.72	1.97	2.39	1.96
15	1.49	0.41	1.32	-0.15
16	2.83	1.63	2.3	1.07
17	1.61	0.71	1	-0.15
18	1.47	1	0.95	-0.39
19		2.8	3.6	1.94
20		3.31	4.17	2.46
21		3.27	4.16	2.58
22		2.11		1.73
23		0.81		-0.03
24		2.39		1.54

Appendix 14.2b: Saturation Indices of Goethite in Snarestone porewaters

	Spring	Summer	Autumn	Winter
Water	7.95	7.72	8.77	8.63
Interface	7.49	7.22	8.51	8.81
1	1.32	2.27	1.16	1.33
2	0.38	0.62	0.22	0.12
3	-0.09	-0.34	-0.32	-0.7
4	-0.76	-0.86	-0.61	-1.15
5	-1.09	-0.95	-0.49	-1.11
6	-1.65	-1.34	-0.74	-1.8
7	0.81	1.62	1.71	0.83
8	0.36	1.08	0.7	0.41
9	-1.26	-1.1	-1.96	-1.69
10	-1.04	-1.04	-1.85	-1.59
11	-0.22	-0.7	-0.34	-0.95
12	0.48	0.23	0.6	-0.25
13	0.33	-0.26	0.25	-0.25
14	1.13	0.58	1.09	0.35
15	1.38	1.24	1.49	0.58
16	-0.24	-0.13	-0.04	-0.68
17	-0.7	-0.89	-0.78	-1.65
18	-0.35	-0.48	-0.54	-1.37
19	-0.13	-1.11	-0.34	-1.1
20	0.17	-0.19	-0.09	-0.68
21	0.55	-0.09	0.28	-0.49
22	0.84	0.64	0.86	-0.04
23	0	-0.46	-0.38	-1.01
24	0.79	0.33	0.23	-0.24

Appendix 14.3a: Saturation Indices of Hematite in Smethwick porewaters

	Spring	Summer	Autumn	Winter
Water	17.56	18.16	18.43	18.87
Interface	12.96	18.14	19.07	14.72
1	13.63	13.8	12.75	10.54
2	11.72	11.69	10.68	9.06
3	12.11	11.93	9.85	9.27
4	6.85	5.9	5.11	2.71
5	8.16	5.92	6.08	3.19
6	7.9	4.95	5.11	3.16
7	5.87	3.21	2.72	0.81
8	3.6	0.8	0.01	-1.95
9	1.26	-0.02	-2.54	-3.17
10	7.42	5.38	5.17	3.57
11	3.43	2.75	2.14	-0.02
12	7.38	5.97	5.99	3.91
13	3.55	3.87	4.42	2.32
14	7.39	5.91	6.71	5.88
15	4.94	2.78	4.58	1.59
16	7.62	5.23	6.54	4.04
17	5.17	3.38	3.94	1.59
18	4.9	3.96	3.84	1.12
19		7.56	9.14	5.77
20		8.59	10.27	6.82
21		8.5	10.26	7.06
22		6.19		5.37
23		3.58		1.84
24		6.74		4.97

Appendix 14.3b: Saturation Indices of Hematite in Snarestone porewaters

	Spring	Summer	Autumn	Winter
Water	17.87	17.39	19.47	19.15
Interface	16.96	16.4	18.96	19.52
1	4.62	6.5	4.26	4.56
2	2.74	3.21	2.38	2.13
3	1.8	1.29	1.31	0.5
4	0.45	0.23	0.72	-0.41
5	-0.2	0.06	0.96	-0.33
6	-1.32	-0.72	0.46	-1.71
7	3.6	5.2	5.36	3.55
8	2.69	4.13	3.34	2.71
9	-0.55	-0.23	-1.97	-1.49
10	-0.11	-0.11	-1.76	-1.29
11	1.54	0.55	1.27	-0.01
12	2.94	2.42	3.13	1.4
13	2.63	1.43	2.44	1.39
14	4.23	3.13	4.12	2.6
15	4.73	4.44	4.92	3.06
16	1.49	1.69	1.86	0.52
17	0.57	0.17	0.38	-1.41
18	1.27	0.99	0.87	-0.84
19	1.72	-0.25	1.25	-0.3
20	2.31	1.58	1.76	0.54
21	3.08	1.78	2.5	0.92
22	3.65	3.23	3.66	1.82
23	1.97	1.03	1.18	-0.13
24	3.56	2.61	2.4	1.41

Appendix 14.4a: Saturation Indices of Vivianite in Smethwick porewaters

	Spring	Summer	Autumn	Winter
Water	-5.6	-6.28		
Interface	-4.48	-5.15		-0.29
1	-0.69	-0.4	-0.37	-3.28
2	-2.68	-1.78	-2.07	-3.69
3	-2.1	-1.36	-3.39	-3.21
4	-2.91	-2.32	-2.55	-4.48
5	-0.43	-3.38	-2.58	-5.21
6	-0.42	-4.12	-3.01	-4.3
7	0.06	-3.74	-4.36	-5.15
8	0.49	-3.43	-4.42	-5.17
9	0.22	-1.63	-3.75	-3.49
10	-0.68	-3.95	-3.62	-3.76
11	-1.51	-3.38	-1.81	-4.26
12	-0.51	-2.84	-0.69	-3.09
13	-3.27	-3.49	-0.69	-3.08
14	-1	-3.94	-0.35	-3.01
15	-2.81	-5.28	-0.57	-4.33
16	-1.55	-5.58	-1.36	-4.28
17	-2.32	-5.22	-2	-4.78
18	-1.53	-3.36	-1.12	-4.19
19		-3.72	1.33	-3.19
20		-3.08	1.49	-3.13
21		-3.16	0.9	-2.36
22		-3.85		-2.35
23		-3.22		-3.81
24		-3.73		-3.98

Appendix 14.4b: Saturation Indices of Vivianite in Snarestone porewaters

	Spring	Summer	Autumn	Winter
Water	-15.52	-15.86	-11.97	-10.75
Interface	-10.18	-10.08	-5.56	-3.12
1	-2.2	0.48	-0.67	1
2	-1.6	-1.29	-0.56	0.27
3	-0.86	-2.22	-0.07	0.32
4	-1.51	-2.64	-0.04	0.34
5	-2.28	-2.24	-0.46	-0.02
6	-2.52	-2.5	0.4	-0.38
7	-1.15	1.31	2.23	1.69
8	-0.98	0.16	0.2	1.82
9	-1.03	-0.89	-2.39	0.39
10	-0.81	-0.2	-1.95	0.56
11	0.3	-0.63	1.55	1.02
12	0.09	-0.35	2.19	0.99
13	-0.04	-2.47	1.43	1.5
14	0.02	-1.22	2.05	1.22
15	0.56	1.16	2.23	1.84
16	-0.28	0.71	2.05	1.87
17	0.42	0.36	1.65	0.34
18	0.14	0.19	1.62	0.74
19	0.59	-2.53	1.46	0.63
20	0.63	0.45	0.69	1.29
21	0.56	0.41	2.9	1.98
22	0.74	1.04	2.36	1.79
23	1.55	0.16	2.64	1.23
24	2.04	0.65	2.16	1.45

Appendix 14.5a: Saturation Indices of Hydroxyapatite in Smethwick porewaters

	Spring	Summer	Autumn	Winter
Water	-0.5	-2.01		
Interface	-1.36	-1.73		-3.26
1	-1.04	-0.44	-0.36	-2.76
2	-4.84	-2.93	-3.62	-5.29
3	-3.7	-1.92	-2.74	-3.92
4	-5.01	-1.79	-2.77	-2.7
5	-1.95	-1.08	-2.55	-2.66
6	-2.78	-1.47	-2.39	-2.3
7	-1.4	-0.93	-3.63	-2.18
8	-1.66	-1.26	-3.04	-2
9	-1.86	-1.72	-1.07	-1.8
10	-1.62	-2.35	-3.09	-2.41
11	-1.12	-2.91	-0.86	-2.52
12	-0.32	-1.1	0.44	-1.32
13	0.05	-1.62	-0.25	-2.02
14	-1.25	-2.18	-0.37	-1.17
15	-3.32	-2.04	-0.88	-2.94
16	-1.98	-2.52	-0.99	-2.86
17	-4.36	-4.22	-2.64	-4.54
18	-3.5	-3.69	-2.07	-3.56
19		-0.5	1.55	-0.78
20		0.59	1.57	-0.74
21		0.36	0.46	-0.36
22		0.84		-0.36
23		0.39		-1.81
24		-0.34		-2.05

Appendix 14.5b: Saturation Indices of Hydroxyapatite in Snarestone porewaters

	Spring	Summer	Autumn	Winter
Water	2.55	3.14	2.71	1.58
Interface	-3.05	-1.56	-2.07	-3.26
1	1.82	0.69	2.65	0.95
2	2.85	1.48	3.11	1.29
3	2.12	0.45	2.6	1.75
4	1.67	-0.29	1.71	1.57
5	0.77	-0.46	-0.51	-0.25
6	0.3	-1.55	-0.38	-0.23
7	2.99	2.49	2.85	2.7
8	2.56	0.82	1.85	2.33
9	-0.11	-0.62	0.22	-0.1
10	-0.47	0.45	0.41	0.21
11	0.74	1.66	2.27	1.19
12	-0.01	0.75	1.83	0.82
13	-0.29	-0.94	1.33	0.74
14	-0.51	0.56	1.78	1.07
15	0.81	2.91	2.16	2.52
16	0.75	2.2	2.33	2.13
17	-0.59	0.66	0.87	-0.15
18	-1.73	-0.46	0.52	0.09
19	-0.66	-0.57	0.67	0.09
20	-0.89	1.06	-0.55	0.23
21	-0.49	2.65	3.23	2.48
22	0.05	1.98	2.59	1.73
23	1	1.54	3.25	1.28
24	1.58	2.12	3.23	1.62

Appendix 14.6a: Saturation Indices of Calcite in Smethwick porewaters

Depth cm	Spring	Summer	Autumn	Winter
Water	-0.39	-0.34	-0.43	-0.58
Interface	-0.5	-0.43	-0.52	-0.69
1	-0.47	-0.47	-0.59	-0.76
2	-1.03	-1.04	-1.19	-1.34
3	-0.97	-1.03	-1.17	-1.29
4	-0.85	-0.92	-1.05	-1.11
5	-0.91	-0.97	-1.08	-1.19
6	-0.89	-0.96	-1.05	-1.1
7	-0.85	-0.92	-1.05	-1.05
8	-0.74	-0.85	-0.91	-0.94
9	-0.88	-0.98	-1	-1.08
10	-0.91	-1.1	-1.09	-1.21
11	-0.91	-1.12	-1.11	-1.25
12	-0.68	-0.88	-0.87	-1
13	-0.76	-0.99	-0.97	-1.11
14	-0.89	-0.97	-0.99	-0.95
15	-0.95	-1.04	-1.07	-1.26
16	-0.97	-1.05	-1.08	-1.27
17	-1.23	-1.25	-1.3	-1.47
18	-1.16	-1.18	-1.24	-1.41
19		-0.57	-0.62	-0.81
20		-0.64	-0.72	-0.9
21		-0.65	-0.71	-0.9
22		-0.63		-0.9
23		-0.63		-0.97
24		-0.66		-0.94

Appendix 14.6b: Saturation Indices of Calcite in Snarestone porewaters

	Spring	Summer	Autumn	Winter
Water	-0.22	-0.05	-0.13	-0.32
Interface	-1.18	-1	-1.07	-1.24
1	-0.44	-0.45	-0.49	-0.65
2	-0.29	-0.27	-0.31	-0.48
3	-0.42	-0.4	-0.39	-0.49
4	-0.46	-0.44	-0.37	-0.48
5	-0.68	-0.65	-0.56	-0.67
6	-0.71	-0.64	-0.52	-0.68
7	-0.15	-0.09	0	-0.13
8	-0.25	-0.12	-0.06	-0.19
9	-0.67	-0.5	-0.44	-0.57
10	-0.63	-0.47	-0.46	-0.5
11	-0.32	-0.14	-0.13	-0.21
12	-0.42	-0.2	-0.2	-0.28
13	-0.45	-0.23	-0.26	-0.33
14	-0.39	-0.14	-0.2	-0.23
15	-0.25	0.01	-0.02	-0.12
16	-0.29	-0.04	-0.11	-0.15
17	-0.63	-0.38	-0.41	-0.48
18	-0.66	-0.4	-0.45	-0.5
19	-0.64	-0.41	-0.45	-0.47
20	-0.61	-0.34	-0.42	-0.45
21	-0.09	0.16	0.08	0.04
22	-0.22	0.04	-0.05	-0.09
23	-0.11	0.16	0.05	0.04
24	-0.12	0.15	0.05	0.04

Appendix 14.7a: Saturation Indices of Siderite in Smethwick porewaters

	Spring	Summer	Autumn	Winter
Water	-1.62	-1.42	-0.99	-0.42
Interface	-1.19	-1.22	-0.47	0.23
1	-0.02	-0.03	-0.26	-1.02
2	-0.52	-0.63	-0.84	-1.3
3	-0.5	-0.68	-1.42	-1.36
4	-0.33	-0.89	-1	-1.85
5	-0.25	-1.46	-1.08	-2.18
6	-0.04	-1.61	-1.24	-1.87
7	-0.14	-1.56	-1.41	-2.12
8	0.19	-1.3	-1.4	-2.04
9	-0.01	-0.74	-1.71	-1.68
10	-0.42	-1.53	-1.34	-1.79
11	-0.81	-1.24	-1.26	-1.98
12	-0.38	-1.17	-0.88	-1.56
13	-1.48	-1.4	-0.85	-1.54
14	-0.58	-1.41	-0.73	-1.33
15	-0.8	-1.97	-0.79	-1.92
16	-0.69	-1.98	-1.03	-1.93
17	-0.74	-1.72	-1.15	-1.98
18	-0.57	-1.14	-0.91	-1.92
19		-1.22	-0.14	-1.47
20		-1.31	-0.19	-1.55
21		-1.32	-0.15	-1.39
22		-1.63		-1.39
23		-1.35		-1.64
24		-1.38		-1.62

Appendix 14.7b: Saturation Indices of Siderite in Snarestone porewaters

	Spring	Summer	Autumn	Winter
Water	-5.28	-5.38	-4.14	-3.85
Interface	-3.45	-3.59	-2.12	-1.39
1	-1.06	0.02	-0.91	-0.31
2	-0.95	-0.57	-0.8	-0.47
3	-0.7	-0.81	-0.62	-0.57
4	-0.87	-0.83	-0.4	-0.52
5	-1.2	-0.93	-0.29	-0.48
6	-1.21	-0.76	0.01	-0.62
7	-0.67	0.27	0.54	0.09
8	-0.64	0.22	0.01	0.14
9	-0.57	-0.28	-0.96	-0.27
10	-0.38	-0.25	-0.88	-0.2
11	0.09	-0.27	0.28	0.09
12	0.07	-0.05	0.49	0.07
13	0.05	-0.41	0.28	0.2
14	0.19	-0.22	0.46	0.15
15	0.25	0.24	0.67	0.18
16	-0.06	0.18	0.45	0.23
17	0.05	-0.01	0.28	-0.17
18	0.17	0.16	0.29	-0.12
19	0.12	-0.73	0.21	-0.12
20	0.21	-0.03	0.26	0.09
21	0.72	0.2	0.75	0.41
22	0.5	0.42	0.56	0.36
23	0.7	0.36	0.63	0.42
24	0.72	0.38	0.46	0.42

Appendix 14.8a: Saturation Indices of Dolomite in Smethwick porewaters

	Spring	Summer	Autumn	Winter
Water	-2.36	-2.25	-2.53	-2.92
Interface	-1.47	-1.34	-1.62	-2.04
1	-1.46	-1.41	-1.71	-2.14
2	-2.65	-2.6	-2.93	-3.32
3	-2.56	-2.54	-2.86	-3.21
4	-2.27	-2.26	-2.58	-2.91
5	-2.34	-2.32	-2.62	-2.98
6	-2.34	-2.32	-2.61	-2.92
7	-2.16	-2.15	-2.52	-2.74
8	-1.95	-1.97	-2.23	-2.53
9	-2.18	-2.19	-2.42	-2.76
10	-2.37	-2.46	-2.66	-3.03
11	-2.4	-2.5	-2.71	-3.09
12	-1.93	-2.02	-2.23	-2.61
13	-2.13	-2.24	-2.44	-2.83
14	-2.25	-2.25	-2.47	-2.29
15	-2.4	-2.39	-2.63	-3.06
16	-2.48	-2.47	-2.71	-3.14
17	-2.95	-2.89	-3.15	-3.56
18	-2.79	-2.74	-3	-3.41
19		-1.5	-1.76	-2.19
20		-1.69	-1.98	-2.4
21		-1.71	-1.97	-2.41
22		-1.7		-2.42
23		-1.72		-2.56
24		-1.77		-2.49

Appendix 14.8b: Saturation Indices of Dolomite in Snarestone porewaters

	Spring	Summer	Autumn	Winter
Water	-0.56	-0.47	-0.68	-1.17
Interface	-2.47	-2.37	-2.57	-3.03
1	-1.17	-1.29	-1.45	-1.91
2	-0.84	-0.94	-1.1	-1.58
3	-0.92	-1.01	-1.13	-1.55
4	-0.93	-1.02	-1.08	-1.52
5	-1.33	-1.39	-1.45	-1.89
6	-1.35	-1.37	-1.41	-1.9
7	-0.22	-0.26	-0.31	-0.78
8	-0.38	-0.34	-0.43	-0.89
9	-1.2	-1.14	-1.23	-1.69
10	-1.12	-1.07	-1.2	-1.58
11	-0.55	-0.48	-0.61	-1.02
12	-0.76	-0.66	-0.81	-1.21
13	-0.87	-0.76	-0.94	-1.34
14	-0.72	-0.59	-0.8	-1.16
15	-0.49	-0.35	-0.52	-0.95
16	-0.56	-0.44	-0.64	-1.03
17	-1.25	-1.12	-1.28	-1.69
18	-1.3	-1.15	-1.35	-1.73
19	-1.26	-1.15	-1.33	-1.7
20	-1.23	-1.09	-1.29	-1.67
21	-0.22	-0.09	-0.31	-0.68
22	-0.48	-0.34	-0.57	-0.94
23	-0.25	-0.11	-0.35	-0.7
24	-0.27	-0.13	-0.36	-0.71

Appendix 14.9a: Saturation Indices of Rhodochrosite in Smethwick porewaters

	Spring	Summer	Autumn	Winter
Water	-1.8	-1.03	-1.11	-2.62
Interface	-1.9	-1.13	-0.74	-1.03
1	0.08	0.3	-0.04	-0.01
2	-0.38	-0.27	-0.64	-0.56
3	-0.33	-0.35	-0.63	-0.53
4	-0.18	-0.39	-0.51	-0.48
5	-0.2	-0.51	-0.55	-0.69
6	-0.12	-0.49	-0.47	-0.55
7	-0.05	-0.38	-0.45	-0.55
8	0.08	-0.25	-0.29	-0.47
9	-0.07	-0.3	-0.46	-0.61
10	-0.15	-0.43	-0.56	-0.75
11	-0.17	-0.33	-0.6	-0.89
12	0.05	-0.18	-0.38	-0.6
13	-0.08	-0.24	-0.46	-0.71
14	-0.23	-0.22	-0.44	-0.54
15	-0.28	-0.21	-0.5	-0.86
16	-0.33	-0.23	-0.55	-0.87
17	-0.59	-0.44	-0.77	-1.02
18	-0.49	-0.38	-0.67	-0.96
19		0.19	-0.02	-0.35
20		0.16	-0.08	-0.43
21		0.06	-0.1	-0.44
22		0.11		-0.44
23		0.04		-0.48
24		0.06		-0.46

Appendix 14.9b: Saturation Indices of Rhodochrosite in Snarestone porewaters

	Spring	Summer	Autumn	Winter
Water	-0.85	-0.89	-0.94	-0.77
Interface	-1.78		-1.4	-1.4
1	-0.57	-0.42	-0.67	-0.91
2	-0.66	-0.35	-0.54	-0.91
3	-0.65	-0.47	-0.67	-0.75
4	-0.68	-0.49	-0.62	-0.71
5	-0.9	-0.7	-0.77	-0.87
6	-1.04	-0.66	-0.64	-0.84
7	-0.39	-0.13	-0.16	-0.22
8	-0.45	-0.15	-0.22	-0.25
9	-0.83	-0.41	-0.61	-0.68
10	-0.71	-0.39	-0.58	-0.62
11	-0.41	-0.08	-0.19	-0.27
12	-0.49	-0.17	-0.18	-0.33
13	-0.45	-0.18	-0.28	-0.31
14	-0.39	-0.05	-0.15	-0.2
15	-0.24	0.09	0.03	-0.07
16	-0.29	0.01	-0.08	-0.08
17	-0.55	-0.34	-0.35	-0.36
18	-0.54	-0.33	-0.34	-0.34
19	-0.48	-0.35	-0.39	-0.31
20	-0.45	-0.3	-0.36	-0.26
21	0.01	0.14	0.11	0.19
22	-0.16	0.02	-0.08	0.08
23	-0.01	0.11	0.02	0.16
24	-0.02	0.1	0.01	0.13

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Appendix 14.10a: Saturation Indices of Chalcedony in Smethwick porewaters

	Spring	Summer	Autumn	Winter
Water	-1.62	-0.41	-0.72	0.03
Interface	-1.58	-0.34	-0.34	0.57
1	0.26	-0.1	-0.02	0.06
2	0.42	0.11	0.16	0.2
3	0.48	0.12	0.24	0.29
4	0.53	0.12	0.28	0.34
5	0.54	0.13	0.31	0.29
6	0.56	0.14	0.36	0.36
7	0.57	0.18	0.37	0.37
8	0.59	0.24	0.39	0.4
9	0.58	0.25	0.39	0.38
10	0.69	0.28	0.43	0.38
11	0.67	0.32	0.48	0.34
12	0.63	0.33	0.53	0.37
13	0.66	0.34	0.57	0.39
14	0.5	0.37	0.61	0.25
15	0.54	0.36	0.65	0.38
16	0.51	0.35	0.69	0.38
17	0.42	0.38	0.72	0.43
18	0.48	0.4	0.69	0.43
19		0.35	0.65	0.43
20		0.39	0.64	0.43
21		0.36	0.62	0.42
22		0.38		0.42
23		0.39		0.43
24		0.4		0.43

Appendix 14.10b: Saturation Indices of Chalcedony in Snarestone porewaters

	Spring	Summer	Autumn	Winter
Water	-1.89	-0.91	-0.26	0
Interface	-1.89	-1.03	-0.04	0.18
1	0.06	-0.09	0.31	0.41
2	0.28	0.29	0.45	0.44
3	0.35	0.44	0.52	0.56
4	0.38	0.5	0.54	0.58
5	0.42	0.51	0.55	0.6
6	0.45	0.53	0.57	0.62
7	0.49	0.53	0.56	0.64
8	0.47	0.52	0.56	0.62
9	0.48	0.52	0.59	0.62
10	0.5	0.53	0.55	0.66
11	0.51	0.53	0.56	0.67
12	0.52	0.53	0.6	0.69
13	0.5	0.54	0.59	0.68
14	0.5	0.56	0.59	0.69
15	0.5	0.55	0.62	0.65
16	0.51	0.55	0.59	0.72
17	0.51	0.54	0.63	0.71
18	0.52	0.59	0.65	0.73
19	0.53	0.56	0.63	0.73
20	0.52	0.59	0.64	0.74
21	0.54	0.57	0.68	0.73
22	0.53	0.57	0.66	0.72
23	0.54	0.57	0.65	0.71
24	0.53	0.55	0.65	0.72

Appendix 14.11a: Saturation Indices of Quartz in Smethwick porewaters

	Spring	Summer	Autumn	Winter
Water	-1.15	0.05	-0.24	0.53
Interface	-1.12	0.12	0.14	1.07
1	0.72	0.36	0.45	0.56
2	0.88	0.57	0.64	0.71
3	0.95	0.58	0.71	0.8
4	0.99	0.58	0.76	0.84
5	1.01	0.59	0.79	0.79
6	1.02	0.6	0.84	0.86
7	1.04	0.63	0.84	0.87
8	1.06	0.69	0.87	0.91
9	1.05	0.71	0.87	0.88
10	1.15	0.74	0.91	0.88
11	1.13	0.78	0.95	0.84
12	1.1	0.79	1	0.87
13	1.12	0.8	1.05	0.89
14	0.96	0.82	1.09	0.71
15	1	0.82	1.12	0.89
16	0.97	0.81	1.17	0.89
17	0.89	0.84	1.2	0.94
18	0.95	0.86	1.17	0.94
19		0.81	1.12	0.93
20		0.85	1.12	0.93
21		0.82	1.1	0.93
22		0.84		0.93
23		0.84		0.93
24		0.86		0.93

Appendix 14.11b: Saturation Indices of Quartz in Snarestone porewaters

	Spring	Summer	Autumn	Winter
Water	-1.44	-0.45	0.22	0.51
Interface	-1.44	-0.56	0.43	0.68
1	0.51	0.37	0.78	0.91
2	0.73	0.75	0.92	0.94
3	0.8	0.9	0.99	1.06
4	0.83	0.96	1.01	1.09
5	0.87	0.97	1.03	1.1
6	0.9	0.99	1.05	1.13
7	0.94	0.99	1.03	1.14
8	0.93	0.98	1.03	1.12
9	0.93	0.98	1.07	1.12
10	0.96	0.99	1.02	1.17
11	0.96	0.99	1.04	1.17
12	0.97	1	1.08	1.19
13	0.95	1	1.06	1.18
14	0.95	1.02	1.06	1.2
15	0.95	1.01	1.1	1.16
16	0.96	1.01	1.07	1.23
17	0.96	1.01	1.1	1.22
18	0.97	1.05	1.13	1.24
19	0.98	1.02	1.1	1.24
20	0.98	1.05	1.11	1.24
21	0.99	1.03	1.16	1.24
22	0.98	1.04	1.13	1.23
23	0.99	1.03	1.12	1.22
24	0.98	1.01	1.12	1.23