

CRANFIELD UNIVERSITY

INSTITUTE OF WATER AND ENVIRONMENT

PhD

ACADEMIC YEAR 2004-2005

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**THE BIOGEOCHEMICAL ORIGINS AND PLANT-
AVAILABILITY OF POTENTIALLY TOXIC ELEMENTS
IN SEDIMENT FROM THE THAMES ESTUARY**

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AUGUST 2005

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**THIS THESIS IS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF
PHD**

ABSTRACT

In this thesis I investigate the biogeochemical origins and plant availability of potentially toxic elements (PTEs) in sediments dredged from the Thames Estuary. The sediments were pumped from the Thames into silt lagoons on the Rainham Marshes between 1961 and the late 1970s. They are fine-textured and rich in organic matter.

The results show that PTE concentrations in the sediments are strongly positively correlated with nitrogen concentrations, and are highly inter-correlated. It is known that this distribution pattern is restricted to ancient and modern sediments from near coastal environments, and hence a link with estuarine processes is suggested. Subsequent investigation showed that the dredgings came from the Thames maximum turbidity zone, and that the lagoons represent a chronological record of changes in sediment quality during a period when dissolved oxygen in the water column rapidly increased. Analysis of one 5 m core from a lagoon showed that there were concurrent substantial changes in the relative proportions of clay, silt and sand in the sediment

A novel mechanism is proposed, whereby the textural changes and PTE/organic matter correlation result from mineral dissolution and re-precipitation within flocs in the water column of the maximum turbidity zone. This is mediated by microbial consortia, and is driven by the requirement for Fe(III) as a terminal electron acceptor by dissimilatory iron-reducing bacteria. Potentially toxic elements released from mineral carrier phases are subsequently complexed by various components of the organic fraction or incorporated into secondary minerals and evenly distributed throughout the sediment by tidal action. Published data from historical, geological, hydrological and microbiological science are presented in support of this hypothesis.

Foliar concentrations of PTEs in plants grown in the sediments were lower than those predicted by current models, probably because of strong sorption of these elements on sediment solids.

ACKNOWLEDGEMENT

I would like to express my thanks to the Cleanaway Havering Riverside Trust and Cranfield University at Silsoe for funding this work, and to Professor Guy Kirk for his invaluable help, encouragement and practical advice during the preparation of this thesis.

I would also like to thank Professor Jim Harris for giving me this opportunity for further study, and for emotional support during times of trial.

This Thesis is dedicated to the staff of the Water Pollution Research Laboratory, 1949-1964, in grateful recognition of the contribution their conscientious study of the Thames Estuary made to this research.

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CHAPTER 1 - INTRODUCTION

1.1. ESTUARINE SEDIMENTS AS A SINK FOR CONTAMINANTS

Most dredging occurs in estuaries. The most generally accepted definition of an estuary is that given by Pritchard (1967):

“An estuary is a semi-enclosed coastal body of water, which has a free connection with the open sea, and within which sea water is measurably diluted with fresh water derived from land drainage”.

Estuaries have played an important role in human economic development throughout history. Early man found it much easier to travel over water than land, and river mouths are natural access points for ships. As trading links between populations increased, estuaries provided sheltered places in which to build ports and harbours. With the advent of the industrial revolution, ports, as entry points for raw materials, became centres for manufacturing and food processing industries.

These industries were able to exploit the estuary as a convenient sink both for industrial effluents and for the excreta produced by human populations. Industry needs energy, and power stations need cooling towers. Estuaries provide a convenient source of cold water for cooling towers and a sink for the heated discharge water. As a consequence, most estuaries where there has been significant economic development suffer from thermal, organic and industrial pollution.

Contaminants discharged into an estuary may either be retained in estuarine sediments or flushed out to sea. Many studies (see, for example, McLusky, 1990) show that estuarine sediments act as a sink for potentially toxic elements (PTEs) and that only 25-50% of total metal inputs to rivers reach the sea.

The last three decades have seen substantial and increasingly effective legislative control over metal discharges to estuaries in developed countries, so there is a general

pattern of less polluted surficial sediments overlying historically contaminated material in Europe and North America.

1.2. DREDGING

There are two categories of dredging. Capital dredging is a one-off operation associated with major development projects, such as the creation of deep water navigation channels or the building of docks and quays. Maintenance dredging is the regular removal of sediment to maintain a navigation channel of a given depth. The size of ships, and consequently the depth required to clear a ship's hull, have steadily increased over time since steel replaced wood. The rate of increase has accelerated dramatically in recent decades.

Traditionally, most cargo was transported as break-bulk (i.e. transported as separate pieces). A revolution in transport began with the introduction of intermodal containers in the 1950s (Vigarié, 1999). These can be transported by road, rail or ship (Parola and Sciomachen, 2004), and are either 20 ft or 40 ft in length, to conform with the International Organisation for Standardisation (ISO) container manufacturing standards.

Buxton (2004) shows that the average size of a large freighter increased by 0.7% per annum between 1900 and 1950, and by 2.6% between 1950 and 1980. A typical, large bulk carrier specializing in the transport of 20 ft ISO containers had a volume of 15,000 t deadweight in the mid-fifties, whereas the most popular design is presently the Capesize, which is around 180,000 t deadweight (Buxton, 2004). The current fleet of containerships requires a depth of between 45 and 53 ft, while most general cargo vessel drafts are between 22 and 32 ft (Kiefer et al. 2000). The increase in world trade caused by globalization is expected to continue this trend.

This continuing increase in size of ships has had a major effect on port development, with the loss of those ports which could not provide deep water channels and quays (Palmer, 1999). In order to accommodate ever larger vessels and remain viable, port

authorities all over the world are competing to deepen and widen their navigation channels, causing a net increase in dredging activity.

Deep dredging mobilizes historical contaminants directly through the exposure of older sediments, and indirectly through its effects on the channel regime. Channel depth in an estuary is the result of a dynamic equilibrium between discharge rates and sediment supply (Dennis et al. 2000). This equilibrium state is known as an estuary's regime (Dennis et al. 2000). When an estuary is dredged below its equilibrium depth the area through which water moves is increased, leading to a decrease in frictional flow. Such changes in flow regime generally accelerate sediment deposition (Marine Board, 1985). Maintenance dredging of a navigation channel, once initiated, is thus a continuous operation (Marine Board, 1985).

1.3. DISPOSAL OF DREDGED MATERIAL

Dredged material was traditionally disposed of at sea, which was unregulated until 1969. Two incidents, the sinking of the Torrey Canyon in 1967 and an attempt by a Dutch coaster, the Stella Maris, to dump chlorinated hydrocarbons off the coast of Norway in 1971 convinced governments of the need for marine protection. This resulted in the introduction of domestic and international agreements to regulate waste disposal at sea.

The most important piece of marine legislation is the London Convention of 1972 (Murley, 2004), also known as the convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter. A review of the Convention resulted in the 1996 Protocol, which Britain ratified in 1998. The London Convention has been ratified by most seafaring countries (Howarth and McGillivray, 2001). There are additional regional agreements. Two conventions collectively known as OSPAR (also known as the Convention for the Protection of the Marine Environment of the North East Atlantic) form the European Regional Agreement (Bell and McGillivray, 2000).

In 1998, OSPAR introduced the Best Environmental Practice (BEP) concept to marine dumping. Dumping of dredged waste may lead to severe physical and

biological environmental impacts, so BEP is interpreted by OSPAR to mean the minimization of dredging activity, and a reduction in the amount of spoil disposed of at sea (<http://www.dredging.org/dmgs/ospardm.pdf>). The amount of dredged material produced globally each year is now in excess of 1 billion m³ (Förstner, 2004). The UK continues to dispose of almost all of its dredged waste to sea. This amounts to between 10 and 20 million tonnes of the 280 million tonnes still dumped at sea annually throughout the world (RLC and ABP Research, 1999).

The trend in international law is against dumping at sea, and there are likely to be greater restrictions against marine disposal in the future (Side and Jowitt, 2002). The 1996 Protocol of the London Convention represents a decisive move away from the previous policy of “dilute and disperse”. The Convention calls for a reduction of waste, an increase in waste recycling and the removal of all harmful components, as well as consideration of terrestrial waste disposal options (Howarth and McGillivray, 2001). The only contaminated material which can be dumped at sea under the OSPAR Convention is contaminated dredged material, and the third International North Sea Conference in 1990 has indicated that this should be phased out (Howarth and McGillivray, 2001).

The disposal of historically contaminated dredging spoil has become a major economic and environmental challenge. The large quantities involved preclude clean-up treatments such as solvent extraction, bioremediation, thermal desorption and vitrification (Förstner, 2004). Most ports in the US have accumulated large quantities of sediments. The Netherlands estimate that they will need to dispose of 200 Mm³ of contaminated dredged material between 2000 and 2015 (Laboyrie, 1998). They are constructing large scale Confined Disposal Facilities to store the material, while research on decontamination and beneficial re-use is carried out. Disposal of dredging spoil to landfill is not a realistic option because of the volume and physical characteristics of the dredged material. Most nations are now actively investigating beneficial re-use of dredged material.

1.4. BENEFICIAL RE-USE – OPTIONS AND IMPEDIMENTS

There are three main options for the beneficial re-use of dredged material: foreshore renourishment programmes; use in the construction industry; use as a soil forming substrate. Coastal erosion is a serious problem throughout Europe, where more than 20% of the coastline is actively retreating (Salman et al. 2004). Foreshore renourishment is the technical term for replenishing beaches which are losing sediment with sediment from another source. The risk of remobilizing contaminants into the water-column means that only clean dredged material can be considered for such programmes. A high organic matter content adversely affects material shear strength, so only dredgings low in organic matter are suitable for use in construction. The main obstacle to dredging re-use as a soil forming material is the possibility of bioaccumulation and biomagnification of contaminants. Additional impediments to beneficial re-use of dredgings are their high water and salt content.

Before any reuse is considered, dredged sediments require dewatering. Maintenance dredging removes surficial sediments, which are less consolidated than deeper sediments and have large water contents. The amount of water in dredged sediments is also a function of the dredging method used. Mechanically dredged sediment contains about 50% water, whereas hydraulically dredged sediment contains about 20% (Mulligan et al. 2001).

Estuarine water is saline, and the presence of salt may limit the use of the material as a soil-forming substrate. Soil salinity leads to a decreased water potential in the root zone of plants, and means that they will reach permanent wilting point at higher soil water contents. Salinity has a major impact on plant survival and productivity. Plant response to high levels of electrolytes in the soil solution is species specific, and, in the case of agricultural crops, cultivar specific. There are, in all cases, reductions in mesophytic plant performance over 2 dS m^{-1} , and this reduction increases with increasing EC (Ayers and Westcot, 1985).

Sodicity occurs where there is substitution of Ca^{2+} ions by Na^+ on clay interlayers. This substitution results in twice as many cations in the interlayer sheet, and has the

effect of pushing the sheets apart, leading to dispersion of the clay. Since it either causes or increases the swelling and dispersion of soil clay particles, sodicity leads to physical deterioration of soils. Sodic soils are vulnerable to waterlogging, crusting and hard setting. These features of the soil lead in turn to problems such as poor infiltration, reductions in plant available water capacity, poor seedling emergence and poor root development. Hydraulic conductivity of sodic soils is low, so leaching of toxic elements from the root zone is impeded (Shaw, 1999).

1.5. BIOAVAILABILITY OF POTENTIALLY TOXIC ELEMENTS

The main impediment to the re-use of dredged sediments as a soil forming substrate is the risk posed to human and ecosystem health from contaminants contained within the material, and our present inability to predict the bioavailability of those contaminants. There are two main classes of contaminant likely to be found in the dredgings. These are the persistent organic pollutants and the potentially toxic elements. This work will concentrate on the latter.

The expression “potentially toxic element” is used herein in preference to “heavy metals” or “trace elements”. The expression “heavy metal” is widely used and ill-defined (Duffus, 2002). By convention, a heavy metal is a metal with a density greater than 5 g cm^{-3} . This definition encompasses 59 elements in the period table, of which only 17 are considered very toxic and available at toxic levels (Reuther, 1999). The expression “trace element” is defined by Alloway (1990) as those elements making up between 0.01% and 1% of the Earth’s crust. These elements can be divided into three groups (Kaputaska et al. 2004). One group consists of essential elements such as Cu, Zn and Se, where both lack of exposure and over-exposure may cause adverse biological effects. Hopkins (1989) describes the optimal mid-range dosage for these elements as “the window of essentiality”.

That window may be very narrow as it is for selenium deficiency in animals, and for boron in plants. Selenium deficiency has led to cancer belts in China (Caussy et al. 2003). Selenium toxicity, caused by plants producing abnormal proteins where sulphur in cysteine is replaced by selenium, leads to “alkali disease” or the “blind

stagers” in animals grazing on plants where the selenium content is greater than 5 mg kg⁻¹ dry weight (Tinggi, 2003).

A second group of elements are those not considered essential, but which have a beneficial effect on metabolism. This group includes Ni in animals, and Co and Se in plants (Kaputska et al. 2004). The third group of elements consists of those widely distributed in living organisms, but having no known beneficial metabolic effect. This group includes the metals Pb, Hg and Cd, and the metalloid As.

Potentially toxic elements (PTEs) are of particular environmental concern because of their long residence time in soils and the implications of this for the food chain. McGrath (1987) cites residence times of thousands of years. Since they are elements, they cannot be degraded by biological, chemical or physical means to an innocuous bi-product. Additionally, anthropogenic releases of potentially toxic metals from industrial processes are steadily increasing background levels of these contaminants (Alloway, 1990).

There are three main routes by which PTEs, once present in a soil, can be removed. These are plant uptake, leaching through the soil profile, and volatilisation. Of the three elements, selenium, arsenic and mercury, which most commonly volatilise from soils, mercury is the best studied. In a review of the literature for the U.S. Army Corps of Engineers, Thibodeaux et al. (2002) cite flux rates of gaseous mercury from soils of 0.001 to 0.009 ng cm⁻² hr⁻¹ when soil mercury concentrations are \approx 10 μ g g⁻¹. Even at the upper rate, removal of mercury by this means would take many hundreds of years.

Concern in the early '70s over the increasing background levels PTEs led to most European countries setting threshold levels for agricultural land. This was associated with the widespread habit of applying sewage sludge to agricultural land, and was intended to protect the food chain (Giller et al. 1998).

The use of a single threshold level for a given PTE for all soils and in all contexts has limitations. In order to be toxic, a trace metal has to be both available (exist in the soil/sediment pore water as a free ion) and in an ionic form (its speciation) which causes damage to living organisms (Gleyzes et al. 2002). The ingestion of sodium metal is potentially fatal, whereas sodium chloride is essential in the diet (Duffus, 2002). Cr(VI) is a potent toxin, whereas Cr(III) is an essential nutrient. Chelation with low molecular weight organic ligands may increase or decrease toxicity. Inorganic mercury is much less bioavailable and toxic than methyl mercury, while the most toxic form of arsenic is the inorganic As(III) (Caussy et al. 2003).

In addition, most contamination is multi-elemental, and little is known regarding synergistic and antagonistic effects. A further complication is that soils are dynamic systems, and PTEs may move from one phase to another with temporal and spatial changes in pH, redox potential, moisture content, organic matter input, temperature, oxygen availability and salinity.

Tessier (1979) suggested that the use of sequential extraction procedures is a more meaningful way of estimating the remobilization potential of PTEs in soils and sediments. This was based on the principle that different environmental conditions are likely to release metals from different phases, and that the proportion of metals carried in each phase can be identified by using different extractants. He proposed that the five main binding phases for metals are the exchangeable phase; the carbonate phase; the Fe/Mn oxide or reducible phase; the organic/sulphidic or oxidisable phase, and the residual or mineral phase (Tessier, 1979).

Tessier's approach has been widely adopted. The choice of extractants is governed by the following considerations: metals in the exchangeable phase are those which are weakly sorbed, and may be removed by changes in interstitial water ionic composition; carbonates are susceptible to changes in pH; iron and manganese oxides are unstable under anoxic conditions; oxidising conditions lead to the degradation of organic matter and the oxidation of insoluble metal sulphides. Metals held in the residual phase are regarded as being unavailable under natural conditions.

Many problems have been encountered when sequential extraction (or fractionation) schemes have been practically applied (Gleyzes et al. 2002). The classification of the phases in soils and sediments in which PTEs occur is useful conceptually.

1.5.1. EVOLUTIONARY CONTEXT

Evolution is commonly misconceived as being driven by the fitting of organisms to their environment. This is not the case. Life and the planet Earth have co-evolved. The environment is shaped by living systems capable of adaptation and evolution.

As James Lovelock said “So closely coupled is the evolution of living organisms with the evolution of their environment that together they constitute a single evolutionary process.”

PTEs are common constituents of the Earth’s crust. Co-evolution has led to the development of strategies for maintaining PTE concentrations at a tolerable level. Most studies of plant PTE uptake have quantified shoot concentrations, so there is little information in the literature on root concentrations. Plants may be divided into three groups on the basis of the strategy they employ (Kaputaska et al. 2004). “Excluders” have the same shoot concentrations of PTEs over a wide range of soil metal concentrations. “Accumulators” will concentrate PTEs in shoots whether soil concentrations are high or low. The shoot concentrations of “indicators” will vary with variation in soil concentrations. Phytotoxicity will occur in all plants when PTE bioavailability is sufficient to overwhelm the individual species’ capacity for regulation of homeostasis.

Plant response to available PTEs is complex, varying between and amongst species, and with environmental stimuli. Due to the complex interaction of environmental factors, site factors and species populations, site of final use testing is increasingly becoming the standard method of assessment for projects involving the use or deposit of river dredgings where there is concern over possible contaminants.

1.5.2. REDOX REACTIONS IN SEDIMENTS

Redox reactions involve the transfer of one or more electrons from a donor atom or molecule to an acceptor atom or molecule. The donor is oxidised, and the acceptor reduced. Substances vary in their tendency to give up or receive electrons, their reduction potential. By convention, this tendency is defined with reference to the standard hydrogen electrode, which is arbitrarily assigned a value of zero for a reaction occurring at standard conditions of pressure, temperature and concentration.

The reduction potentials of many atoms and molecules of environmental importance have been experimentally derived under laboratory conditions. This is done using an electrochemical cell, where the donor couple and the acceptor couple are in separate reaction vessels, separated by a salt bridge. Platinum electrodes connected to a potentiometer link the reaction mixture in one cell to that of the other. This circuit allows the electrons to flow from one vessel to another in the direction of the gradient created by the free energy difference between one redox pair and another. The potentiometer measures the current generated.

The difference in reduction potential between an electron donor and an electron acceptor is a measure of how much energy the reaction is capable of generating. It is important to note that this measured energy difference tells us nothing about the likelihood of that reaction occurring, or the rate at which it will occur. The assumptions of classical thermodynamics are that reactions are reversible, that the system is closed and that the system is at equilibrium.

In natural systems, almost all biotic reactions and many abiotic reactions are redox reactions. The redox reactions in biological systems are coupled to energy requiring biosynthetic systems. Photosynthesis and respiration are complementary redox reactions which maintain life on Earth at present. In photosynthesis, solar energy is used to reduce the carbon in carbon dioxide, which has a valency of 4, to the carbon in carbohydrate, which has a valency of zero. The energy is stored in chemical bonds,

and can be used to satisfy plant metabolic demand. Utilisation of this stored energy involves many sequential redox reactions linked to metabolic pathways, until finally the carbon is re-oxidised and returns to the atmosphere as carbon dioxide. The relationship between photosynthesis and respiration, which in reality is made up of complex energy flows from high to low energy levels through an integrated series of sequential chemical oxidation reactions, can be simplified to the net equation



Sugar and oxygen are converted to water and carbon dioxide in energy yielding respiration, water and carbon dioxide are converted to sugar and oxygen in energy demanding photosynthesis. In aerobic respiration, electrons are passed down an electron transport chain till they reach the terminal electron acceptor, oxygen, which is reduced to water.

Though oxygen is needed as a terminal electron acceptor for all multi-cellular organisms, bacteria have the ability to use alternative electron acceptors. This happens when bacterial numbers and substrate concentration are large, and re-aeration fails to satisfy bacterial oxygen demand. Respiration then switches to other atoms and molecules that can accept electrons from reduced organic compounds. Many aerobic micro-organisms can completely oxidize organic matter to carbon dioxide and water, whereas anaerobic respiration frequently requires a consortium of different organism living syntrophically. Micro-organisms utilize many alternative terminal electrons acceptors when they oxidize reduced carbon in energy-yielding processes. The most important of these quantitatively, in order of decreasing energy yield, are NO_3^- , Mn(IV) , Fe(III) , SO_4^{2-} and CO_2 .

The energy yields of these sequential electron transfers were derived from abiotic reactions under controlled laboratory conditions in closed systems. Natural systems are characterized by being open to transfers of matter and energy, being far from equilibrium, and having many reactions that are irreversible (Prigogine and Stengers, 1984). Despite this difference, numerous studies of soils and sediments have

demonstrated the sequential utilization of terminal electron acceptors follows the predictions of equilibrium thermodynamics. The presence of an electron acceptor of a higher oxidation state tends to inhibit respiration of an electron acceptor of a lower oxidation state because the energy yield is lower (Killham, 1994).

The preferential use of alternative electron acceptors in sediments gives rise to a well characterized zonation in sediments (see, for example, Thamdrup et al. 2000). As organic matter is oxidized in the sediment, oxygen is depleted and microbial respiration switches to the next most energetic terminal electron acceptor. This gives rise to a horizontal zonation pattern of terminal electron utilization with depth in the sediment profile. Reduced iron and manganese diffuse into the pore water and are re-oxidised near the profile surface, leading to high concentrations of these elements close to the sediment surface. Metals released from the Fe/Mn oxide carrier phases react with reduced sulphur species diffusing through the profile from the sulphate reduction zone. Trace metal contaminants combine with the reduced sulphur, forming insoluble metal sulphides.

Oxygen diffusion is typically limited to the first couple of centimeters of the profile, though this can be complicated by bioturbation and oxygenation by benthic organisms. Dissimilatory nitrate reduction begins when oxygen concentration is reduced to a few $\mu\text{M l}^{-1}$, followed by Mn (IV) reduction, Fe(III) reduction, sulphate reduction and finally methanogenesis.

The large concentrations of sulphate in sea water and its diffusion from the overlying water into the sediment means that this is often the dominant terminal electron acceptor in marine sediments, and may account for as much as 90% of total organic matter mineralisation (Thamdrup and Canfield, 1996).

1.5.3. SEQUESTRATION OF ORGANIC MATTER IN SEDIMENTS

The concentration of oxygen in the atmosphere has remained fairly stable at around 21% for around two hundred million years. This is the result of dynamic equilibrium between the net rate of photosynthesis, which splits water, reduces carbon, and

releases oxygen, and the net rate of respiration which releases the energy stored in reduced carbon via oxidation. Any significant reduction in atmospheric oxygen concentrations would lead to bottom-water anoxia in the oceans, and the death of marine, benthic organisms. A significant increase would lead to run-away forest fires (Berner, 1989).

For the first two and a half billion years of earth's existence, oxygen was only present in trace amounts in the atmosphere. It was the evolution of oxygen releasing, photosynthetic cyanobacteria and subsequent sequestration of reduced organic carbon in sediments and soils which led to the gradual oxygenation of the atmosphere. Most of the excess organic carbon (Berner (1989) estimates a pool of $\approx 15,000 \times 10^{18}$ g C) is stored in sedimentary rocks as highly insoluble kerogen macromolecules (Hedges and Keil, 1995). A much smaller amount, estimated at 1.6×10^{18} g C is stored in soils as soil humus (Olsen et al. 1985), and only 0.95×10^{18} g C in terrestrial plants (Olsen et al. 1985).

There is generally a linear relationship between the amount of organic matter sequestered in the sediments and the surface area of the mineral component. This has been noted by a range of workers in estuarine and near coastal environments since the 1960s, and is frequently interpreted as representing the sorption of an organic matter monolayer to sediment particles (Hedges and Keil, 1995).

Organic-rich sediments with carbon contents in excess of 5% by weight are unusual, but receive disproportionate attention because it is assumed that the study of these sediments may elucidate the mechanisms by which petroleum source rocks were formed (Hedges and Keil). Though these sediments share a linear relationship with mineral surface area and percentage organic carbon, any associated organic layer would need to be 2 to 5 layers thick (Hedges and Keil).

Accumulation of high levels of organic matter in sediments is associated with anoxia in bottom waters of aquatic systems (Hedges and Keil, 1995). There is active debate on why this should be so, since, with the exception of oxygen poor, hydrolysis

resistant substrates such as lignins and photosynthetic pigments, the presence of oxygen has not been demonstrated to have any great effect on organic matter oxidation rates (Reeburgh, 1995). In a review of the literature, Hedges and Keil (1995) identified the most common reasons given.

- Anaerobic decomposition of organic matter is less efficient because of the lower free energy yield associated with alternative electron acceptors such as nitrate, Mn(IV), Fe(III), and sulphate;
- The varied microbial consortia required for the stepwise degradation of complex organic matter may not be present;
- The build-up of toxic substances such as H₂S may inhibit bacterial degradation of substrates;
- There is reduced activity by benthic fauna, so less sediment mixing by bioturbation, irrigation and predation occurs; and
- The insolubility and low oxygen content of some substrates renders them resistant to fermentative breakdown, though these substrates can be aerobically degraded by O₂ requiring oxidative enzymes

Despite being well studied, the mechanisms controlling organic matter preservation in sediments are still unclear. The two models most commonly invoked are the “polycondensation model” and the “selective preservation and natural vulcanization model” (Boussafir and Lallier-Vergés, 1997; Hedges and Keil, 1995).

“Natural vulcanization” occurs when reactive organic substances (e.g. polyunsaturated fatty acids and carotenoid pigments) combine with reduced sulphur compounds from microbial sulphate reduction (Sinninghe-Damsté et al, 1989). The end products are degradation resistant carbon macromolecules held together by polysulphide bridges (Adam et al. 1998). These molecules are found in recent sediments and are particularly common in evaporative basins such as the Messinian in Sicily, where they make up 80% of the organic matter (Adam et al. 1998). Their presence in sediments less than a thousand years old and the observation that functional groups were still present led Adam et al. to conclude that they were formed

at normal temperatures and pH, and to hypothesise that they may have been caused by a light induced radical reaction where there was photic zone anoxia. They demonstrated experimentally that good yields of low molecular weight organo-sulphur compounds and sulphur cross-linked macromolecules could be produced from simple hydrocarbons in the presence of elemental sulphur and reduced sulphur species in natural daylight, and that yield could be augmented when ketones were added.

There is not necessarily one universal mechanism for organic matter preservation in sediments.

1.6. ESTUARINE DYNAMICS

Estuaries have upper, middle and lower regions, defined by salinity. The upper estuary is tidal, but dominated by fresh river water, the middle estuary is the site of strong salt and fresh water mixing, and the lower estuary is the region in open connection with, and dominated by, the sea. The boundaries between these zones shift seasonally with changes in freshwater input, and weekly with spring and neap tides.

The Thames Estuary stretches from 109 km from Teddington Weir at the upper limit of its tidal rise to the former limit of the Port of London Authority (PLA). This limit is an imaginary line east of Shoeburyness between Havengore Creek on the Essex Coast to Warden Point on the Kent Coast, the mid-point of which is marked by the Sea Reach No 1 Buoy (see Figure 1.1).

Estuaries are divided into four general circulation types, based on salinity patterns within the water column. These are salt wedge, partially mixed, fully mixed, and negative circulation. The Thames is classified as either partially (Pethwick, 1984; Inglis and Allen, 1957) or fully mixed (DSIR, 1964; Turner et al., 1990). Estuarine circulation has a direct bearing on sediment transport and deposition processes within the estuary, so differences in classification lead to different assumptions over the causes of sedimentation in the river.

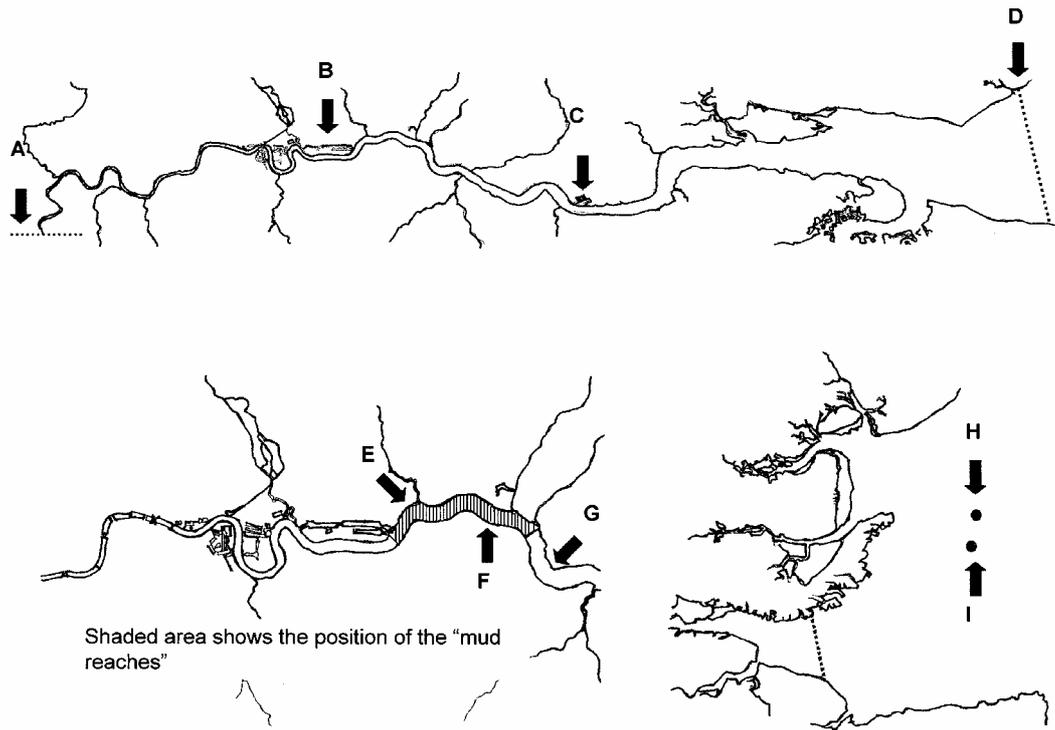


Figure 1.1 Diagram of the Inner and Outer Thames Estuary showing locations mentioned in the text. A shows the position of Teddington Weir, B the Royal Docks, C Tilbury Basin, D the limit of the Port of London Authority, E the Northern Sewage Outfall, F the Southern Sewage Outfall, G Coldharbour Point, H Barrow Deep and I the Black Deep. The stretch of the river comprising Gallions, Halfway and Barking Reach – the “mud reaches” has been shaded.

Partially mixed estuaries have a large tidal range and a small freshwater input. They vary in salinity from the river bed to the surface, with a gradation between salt water at the bottom, brackish water in the middle and fresh water at the top (Pethwick, 1984). This density distribution pattern leads to net seaward transport of surface freshwater with its load of suspended sediments, while there is a net landward movement of dense, saline near-bottom water and its suspended sediments. Zero velocity occurs at that point in the water column where the seaward movement of freshwater is balanced by the landward movement of sea-water. The point at which the landward and seaward flows converge at bed level is known as the null point, and is associated with a turbidity maximum and the localized sedimentation of fine material (Marine Board, 1985; Pethwick, 1984).

Fully mixed estuaries have strong tidal currents and weak river inputs. These have little vertical variation in salinity, though they may have a large variation across their width (Pethwick, 1984).

The Thames was the subject of intensive investigation by the Water Pollution Laboratory from 1949 to 1964 (DSIR, 1964). The salinity data collected by the laboratory show that the river has only very slight stratification, and that the Thames conforms most closely to the fully-mixed estuarine circulation model.

1.6.1. SEDIMENT TRANSPORT IN ESTUARIES

Studies of river sediments almost invariably use analytical techniques which lead to chemical dispersion of the mineral fraction. Hydrogen peroxide is used to break down organic linkages between particles; chemical agents are used to disperse colloidal clays.

Despite deriving particle size data using these aggressive procedures, most conventional transport models are based on calculations of the energy required to transport discrete particles (Droppo, 2001). In these models heavier material such as sand and gravel is assumed to move by saltation close to the river bed. The silt fraction is assumed to be lighter than sand, so that tidal energy above a certain limit will carry silt in suspension. Below this limit the silt will sediment out. Clay is considered to move as a colloid, and to flocculate due to ionic reactions at the limit of salt intrusion, causing the turbidity maximum (Pethwick, 1984). This aggregation is considered to alter the hydrodynamic qualities of the material by increasing the settling velocity.

The settling velocity of aggregated suspended sediments can be up to four orders of magnitude larger than for the constituent primary particles (Migniot, 1968, cited in van Leussen, 1999.) The increased sedimentation by fines (particles less than 65 μm) in the upper and mid reaches of estuaries are, in purely abiotic hydrological models, generally attributed to fine sorting of particles by transport processes and salinity mediated clay flocculation.

Laboratory experiments indicate that salinity should, indeed, cause clay mineral flocculation and increased sedimentation at low salinity (Kempe, 1988). The evidence that this occurs *in vivo* has never been convincingly demonstrated (Kempe, 1988). The Thames turbidity maximum occurs at the 10-19 psu isohaline (DSIR, 1964). The Weser has a salinity of 4‰ due to pollution with waste salts, and should, if the salinity/clay flocculation argument was true, have no turbidity maximum. It has a distinct turbidity maximum (Wellershaus, 1982, cited in Kempe, 1988).

There is a growing consensus that clay does not flocculate due to salinity in rivers subject to high organic matter input because the fine mineral fraction is not carried as separate fractions, but as aggregates, bound together by organic matter (Kempe, 1988). Schild and Prochnow (2001) make a distinction between sediment transport and deposition in large, oligotrophic rivers with high flow rates, and eutrophic rivers with low flow rates. They show that, though classic hydrological models based on channel morphology, flow velocity and shear strength can adequately describe the former, the latter is dominated by biological processes.

Working in a eutrophic section of the River Spree near Berlin, Schild and Prochnow found no significant correlation between river discharge in $\text{m}^3 \text{s}^{-1}$ and suspended sediment concentrations. There was, by contrast, a strong correlation ($r^2 = 0.54$) between phytoplanktonic concentrations and suspended sediments. Phytoplankton production was shown to alter suspended sediment deposition and resuspension rate.

The nature, origin and function of the organic matter associated with suspended sediments are highly pertinent to any study of maintenance dredgings, since these are largely surficial sediments, made up of clay and silts with lesser amounts of sand, and with moderate to high water and organic matter contents (Marine Board, 1985). The immediate origin of surficial sediments is the deposition of suspended sediments, and deposition rate is, *inter alia*, a function of settling velocity. Settling velocity is modeled by Stokes' Law, a mathematical equation which describes the relationship between particle density, particle diameter, and the viscosity and temperature of the fluid through which the particle is falling.

$$= 2/9[(\text{Density}_{\text{sphere}} - \text{Density}_{\text{fluid}})(\text{radius}_{\text{sphere}})^2 g] / \text{Viscosity}_{\text{sphere}}$$

Field results from settling tubes show an exponential relationship between settling velocity and suspended sediment concentration, such that

$$w_s = K C^m$$

Where w_s is the settling velocity, K is an empirically derived constant, and C is the concentration of suspended sediment. The exponent m varies over a wide range, both between and within estuaries (van Leussen, 1999). Examples cited in van Leussen (1999) have values for m of between 0.5 and 3.5 in different estuaries.

Van Leussen (1999) carried out a series of settling-tube experiments using water and dispersed suspended sediment from twelve locations along a transect of the highly eutrophied Ems estuary. Each column had the same initial suspended sediment concentrations (1000 mg l^{-1}). The physical conditions were the same for each column at the start of the experiment, but settling velocities varied by almost an order of magnitude. Van Leussen's experiments show that the empirical relationship between settling velocity and suspended sediment concentration is location specific, and that other factors must be involved in differential settling velocities.

Microscopic investigation of thousands of samples of cohesive, fine-grained suspended sediments showed them to be made up of flocs (Droppo, 2001). Estuarine flocs vary in size from microflocs, which are less than $100 \mu\text{m}$ to large fragile microflocs of several mm (van Leussen, 1999). Macroflocs result from collision events between microflocs (van Leussen, 1999). There are three possible processes mediating inter-floc collisions. These are random (or Brownian) motion, differential settling by larger particles resulting in their collision with smaller particles as they descend through the water column, and turbulence (Winterwerp, 2002). Extensive studies (cited in Winterwerp, 2002) show that turbulence is the dominant process in floc building with the other two processes having negligible effect. Turbulence may

increase inter-particle collisions, and so increase floc size, or decrease floc size through turbulent shear strength (van Leussen, 1999).

At high concentrations the settlement of individual floc particles (papers cited in Winterwerp, 2002) is impeded. This phenomenon, known as “hindered settlement” (Winterwerp, 2002), is caused by several different factors. Falling particles affect other particles in their vicinity by generating return flows and wakes, with the net effect of decreasing settling velocity. When suspended sediment descends through the water column, the increase in particle concentration increased the effective viscosity of the water. Empirical studies in the Netherlands (cited in Winterwerp, 2002) indicate that viscosity is increased by a factor of two to three relative to clear water. As the bulk density increases, an individual particle effectively becomes more buoyant (Winterwerp, 2002).

When the concentration of flocs in a given volume reaches a critical value, a gel of cohesive sediment is formed. This gel is referred to in the literature as “fluid mud”. Winterwerp cites a range of values for the gel state from the literature, ranging from 40 g l^{-1} to 120 g l^{-1} . Individual flocs are formed by collision events due to turbulence at relatively high flow velocities. At these periods suspended sediment is mixed throughout the water column. Fluid mud is formed at slack water. The gelling concentration, the mass per unit volume, varies with flow velocity, and requires a larger mass per unit volume at high flow velocities (Winterwerp, 2002).

The presence of “fluid mud” is specifically mentioned as occurring in a range of estuaries. Abril et al. (2000) noted its presence in the Loire and Gironde estuaries during neap tides. It is also found in the Scheldt estuary (Baeyens et al, 1998), the Ems (Winterwerp, 2002), and the Thames Estuary (Inglis and Allen, 1957). Droppo (2001) considers that it is a feature of all estuaries.

1.6.2. TIDAL EXCURSION AND RETENTION TIME

Estuarine tidal excursion is the horizontal distance along the estuary that a particle will move during one tidal cycle of ebb and flow. Average tidal excursion in the

Thames is 11-14 km in reaches more than 10 km seaward of Teddington, though matter discharged to the estuary will be dispersed upstream and downstream over considerably greater distances than this (DSIR, 1964).

Estuarine retention time is how long water remains in the system. Figures for the retention time in the Thames are given as between twenty and seventy five days (compared to a top retention time of forty days for the Humber and sixty days for the Scheldt in Turner et al., 1991). DSIR (1964) give a figure of ninety days for periods of low flow.

1.6.3. TIDAL RANGE

Estuaries are also classified according to their tidal range, the difference in water depth between high and low tide. A microtidal estuary has a wave amplitude of under two metres, and the tide has no great effect on physical processes. A mesotidal estuary has a tidal amplitude of between two and four metres, and the tide plays an important role in shaping the estuary. In estuaries with a tidal range which exceeds four metres the tide is the dominant influence on sediment transport, deposition and erosion.

The Thames has an average tidal range of 2 m at Teddington, 6 m at London Bridge and 4 m at Southend. Paleocological reconstruction shows that the Thames was naturally mesotidal with a tidal range of between 2 and 4 m (Juggins, 1992). In Central London the tidal amplitude in the 14th century was 2.7 m for spring tides. Modification of the channel through embankment in the intervening centuries has resulted in a much narrower river, and greatly increased the tidal amplitude. The present mean spring tidal range is 6.4 m (Juggins, 1992).

1.6.4. BED CHARACTERISTICS

For most of its length the bed texture of the Thames is hard; of gravel, stones, chalk and clay (Inglis and Allen (1957), DSIR (1964). Two areas are severely silted with fine black mud. One area which is prone to siltation is at the seaward end of

Gravesend Reach, and the other area consists of three consecutive reaches (Gallions, Barking and Halfway) in the mid-upper Thames (Figure 1.1).

1.7. THE RAINHAM DREDGINGS

The Port of London Authority (PLA) bought the Rainham Marshes in 1960 and disposed of dredgings there from 1961 (DSIR, 1964) until the late seventies. The disposal site was divided into seven narrow rectangular sections, each around 1000 m in length, and 100 – 120 m in width (Figure 1.2). Each section is bordered by a five metre high clay bank, with sluice boxes for drainage at either end. The base and banks of the lagoons are constructed from blue-brown clay found *in situ* (Inglis and Allen, 1957). The external sides of the clay banks are exposed to the atmosphere.

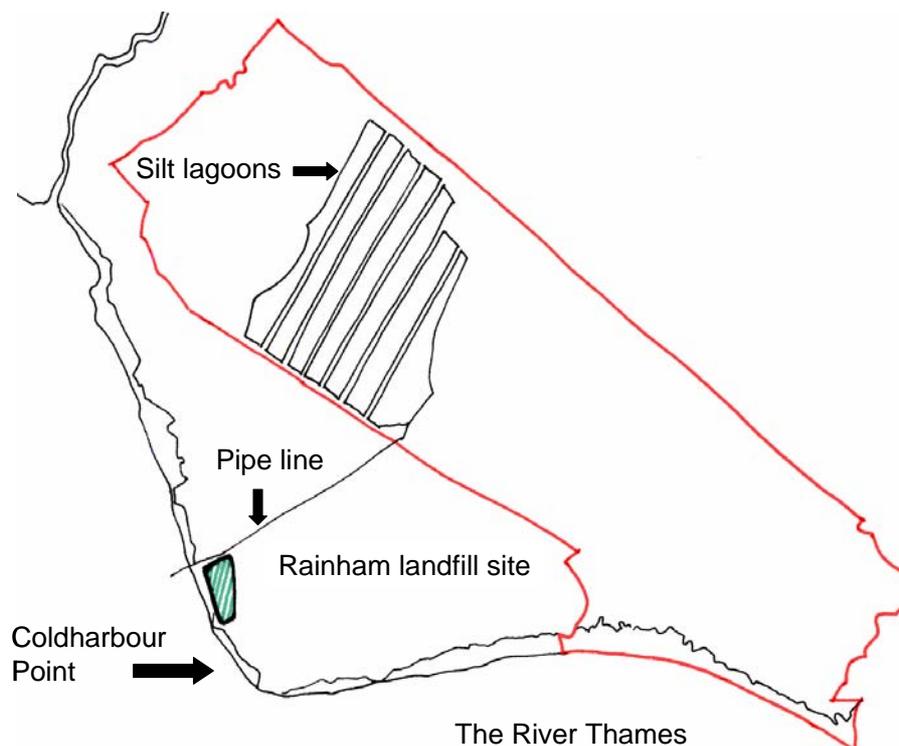


Figure 1.2 Diagram of The Rainham Marshes showing the location of the silt lagoons. The red line delineates the boundary of the Inner Thames Site of Special Scientific interest. The green shaded area shows the location of the experimental site.

The dredged material was discharged via a pipeline which runs across the middle of the lagoons. Sections were used in sequence. Each section was filled for three months then allowed to drain for the following eighteen months. The approximated

daily dredging rate when disposal began averaged 810 imperial tons (823×10^3 kg) dry weight a day (DSIR). The lagoons cover 120 ha (297 acres) and are estimated to hold 7.2×10^6 m³ of dredging spoil (UeL, 1999). They are now well-vegetated with *Phragmites australis*. This reed performs best in wet eutrophic regimes, and cannot survive when the water table is lower than 1 m (Rodwell et al. 1997).

Pedogenesis in soft, clayey, impermeable sediments is called soil ripening, and is well characterized from studies of reclaimed polders in the Netherlands (Rijniersce, 1984). Fine-textured, clay-rich, saturated sediments like the Rainham dredgings do not drain through the soil matrix, but through macropores, which result from cracks, worm channels or roots (Van Hoorn, 1984). Micropore water can only be removed by evapotranspiration (Van Hoorn, 1984).

As the material desiccates and de-waters it becomes denser and more compact as contractive capillary forces pull the particles together, resulting in a coarse, prismatic structure (Wilding and Hallmark, 1984). These structural changes can only be reversed by mechanical disturbance, and not by rewetting (Wilding and Hallmark, 1984). Once formed, planes open up in the same place in successive drying cycles (Brewer, 1964). Repeated cycles of wetting and drying augment this process, so aggregation is generally more developed at the soil surface. The individual aggregates produced are called peds, defined by Brewer (1964) as:

“individual soil aggregates, separated from adjoining aggregates by surfaces of weaknesses which are recognizable as natural voids, or by the occurrence of cutans.”

Cutans are coatings on soil peds, formed by illuviation or diffusion (Brewer, 1964). Cutans differ in structure from the soil bulk matrix, and may be composed of any of its component substances. These may be enriched or depleted relative to the matrix soil (Liu et al, 2002). Soluans is the general term for cutans made of crystalline salts such as carbonates and chlorides of magnesium and sodium (Brewer, 1964). Deposition of soil solution constituents on ped surfaces slows down diffusion from the ped interior (Wilding and Hallmark, 1984).

The climate in the Rainham area is one of the warmest and driest in the UK. Annual average rainfall is 630 mm and average potential evaporation is 540 mm (Armstrong et al. 1996). In general, the seasonal pattern is one of wet winters and dry summers, leading to a large soil water deficit during the summer months.

1.8. AIMS AND OBJECTIVES

Re-use of the material would be beneficial in several different ways. While dredging spoil was being deposited at Rainham, dewatering of the sludge created surface water which attracted a range of birds. This made Rainham nationally and internationally important from a conservation perspective, and led to the marshes being classed as a site of special scientific interest (SSSI). The lagoons are now well vegetated, drier and at capacity. They are, in consequence, less attractive to birds (UeL, 1999). The RSPB bought Rainham for £1 million in 1999.

The PLA have retained the option of using the site. Re-use would serve the dual functions of freeing capacity within the lagoons, thus satisfying the continuing need of the PLA for a silt disposal and dewatering site, and allowing the re-initiation of dewatering so that the former conditions were recreated. Finally, it could provide a soil forming material for use in the many post-industrial sites in East London where the natural soil cover has been lost.

Beneficial re-use of the dredged material would thus fulfill a range of functions: a disposal problem would become an asset; new capacity for dealing with dredging would be created; the conservation value of the Rainham Marshes would be improved; areas of derelict land could be restored. Contractors working on the A13 trunk road, which was constructed through the northern part of the lagoons, found that the material contained elevated levels of metals, raising concerns over its re-use.

An integral part of the present study was the establishment of a two hectare site at Coldharbour Point (Figure 1.2), where material from across the lagoons has been spread to a depth of one and a half metres. The material on the site is fine textured, and swells and shrinks markedly with changes in moisture content. Hydraulic

conductivity varies between winter and summer. It is dry, deep cracking and quick to drain in the summer months. As the dredgings dry, hexagonal cracking appears on the surface. In places, the sides of these cracks are covered with a white precipitate. The material forms large peds on drying, which are often black within a few millimeters of the ped surface, and is finely laminated. During winter, it becomes soft, impermeable and cohesive.

The primary aim of this research was to increase our understanding of those factors which determine PTE uptake in plant biomass when dredgings are used as a soil-forming material. This information was to be used as a cost effective means of screening material and providing guidance on the potential for its future re-use. At the beginning of the study the objectives were based on a preliminary study (UeL, 1999) which had generated the following hypotheses:

1. Hydraulic filling of the lagoons resulted in horizontal gradation of material based on sedimentation characteristics. Larger particulates and materials with a higher specific gravity would be found close to the inflow, and materials with a lower specific gravity towards the sluice box outflow.
2. Due to the known affinity of contaminants for organic matter (low specific gravity) and clay particles, higher contaminant levels would be found at either end of the lagoons compared to the mid-section discharge point.
3. Quality would vary in depth as a consequence of the short term rotational use of each lagoon, and the deposit of different materials at different times.
4. Quality would also vary with depth due to vertical migration of mobile contaminants. The preliminary study used surface (from the upper 30 cm of a lagoon) and subsurface (from 50 to 70 cm below the surface) samples from a transect along the lagoons, and had concluded that the material was only slightly contaminated with respect to PTEs.

Specific objectives were

1. To characterize the chemical and physical properties of silt samples from the trial site, and obtain information on its variability.
2. To determine the concentration of a range of potentially toxic elements in plant tissues grown on the dredgings in field and greenhouse vegetation trials.
3. To understand the mechanisms governing the fractionation of metals accumulated in the sediment.
4. To use these results to produce dredging quality criteria that can be simply assessed by routine field sampling and lab analysis, but that are robust enough to provide a realistic assessment of metal bioavailability.

The results of the chemical characterization of the silts did not support the original hypotheses. They did, however, strongly indicate that conditions in the river when the dredgings were removed had had a profound effect on biogeochemical cycling. The aim of the research was widened to include a search for an understanding of the effects of pollution on biogeochemical cycling in a highly modified estuarine environment. A fresh objective was created, that of producing a conceptual model of how coupled physical, chemical and microbiological processes affect sediment diagenesis in grossly polluted estuaries.

CHAPTER 2 - POLLUTION IN THE THAMES

ESTUARY

Until 1815 the sewer system in London used the natural river network in the Metropolitan area to carry away surface water. Draining domestic effluent into the sewers was prohibited by law, and the construction of cesspools, which were emptied by night-soil men and used as agricultural manure, was enforced. Though historical descriptions of the river show that this prohibition was often ignored, the Thames remained well-oxygenated until the beginning of the nineteenth century. This is known by the abundant presence of salmonids, an indicator of unpolluted and well oxygenated water (Porter, 1994). The survival of salmonids requires dissolved oxygen levels of at least 6mg l^{-1} (Spence et al, 1996). By 1850, all commercial fishing in the river had ceased (Porter, 1994).

There were two reasons for the deterioration in the condition of the river. One was undoubtedly population growth. The first census gives a figure of 900 000 inhabitants for the Metropolis in 1801, and this had more than doubled to two million in 1850. The main cause, however, is generally acknowledged to be the rapid spread of the flush toilet after 1830, facilitated by wider provision of piped water by London's private water companies (Porter, 1994). As the metropolis grew the distance from the city to agricultural land had increased, and disposal of human sewage had become increasingly difficult and expensive. In 1815 connection of cesspools and house drains to the sewers was permitted for the first time (Halliday, 1999).

Contamination of the river by sewage was exacerbated by the Metropolitan Buildings Act of 1844, which stipulated that all new buildings and all extensions of existing buildings should be drained to the sewer. An amendment to this Act in 1847 was made in reaction to news of yet another cholera epidemic. The legislation was widened to make the connection of all cesspools and privies to the sewers mandatory (Halliday, 1999).

By 1858 the stench from the Thames became so unbearable that every day tons of lime were dumped into the river outside the newly built Houses of Parliament, and the windows were hung with sheets soaked in chloride of lime as a disinfectant. On the 13th of June, the House of Commons was forced to adjourn, and a Bill to grant powers to the Metropolitan Board of works was rushed through Parliament (Halliday, 1999).

The Board's Chief Engineer, Sir Joseph Bazalgette, thought two courses of action were needed. One was to put the open sewers that disgraced the capital underground, and the other was to stop the sewers flowing directly into the central part of the Thames, which at that time still supplied most of London's water supply. The works cost six and a half million pounds, and serve the capital still. Thirteen hundred miles of sewers, including 83 miles of main sewers were built, intercepting the old sewers at right angles. The old sewers were retained as storm overflows (Halliday, 1999).

The Northern and Southern Sewage Outfalls (Figure 1.1) were completed and opened for use in 1864. The Chemical Advisor to the Board of Works had advised that "experience has shown that whenever putrifying organic matter comes into contact with soluble sulphates, it decomposes them and causes the evolution of sulpherreted hydrogen" (DSIR, 1964). The foul smell generated was believed to cause typhoid, cholera and malaria. Accordingly, it made sense to discharge sewage to water which was as fresh as possible. Barking, 43 kilometres seaward of the tidal head, had lower levels of tidal sulphate than the lower reaches of the Thames (DSIR, 1964).

There were also financial benefits. Had the discharge points been any lower, sewage could not discharge by gravity at any state of the tide, and there would have been a requirement for pumping equipment. The longer the sewers were, the more costly they would be. There were few mud banks at that point in the river, so deposition of sludge was deemed unlikely (DSIR, 1964).

The building of the outfalls did not solve the problems associated with sewage disposal, but displaced them from Central London. The first of many complaints

over the condition of the river in the vicinity of Barking Creek came from the vicar of Barking in 1868. In a letter to the Home Office, he and his parishioners complained that conditions in the river were “dangerous alike to navigation and to the health of the inhabitants of the parish of Barking and of all the populous and industrial towns below London” (DSIR, 1964).

By 1947 a large stretch of the river was anaerobic for three months of the year, and there were public complaints over H₂S evolution (DSIR, 1964). The government intervened, at the behest of the Chairman of the Port of London Authority (PLA), Lord Waverley. The PLA was particularly concerned by siltation in the vicinity of Barking (DSIR, 1964). Two major investigations were carried out by the Department of Scientific and Industrial Research. The Water Pollution Research Laboratory had the remit of investigating the capacity of the Thames to purify sewage and industrial effluent. The resulting report covers work carried out between 1949 and 1964 (and is here referenced as DSIR, 1964). This report included a great deal of raw data, and has been invaluable in the present study. The second study concentrated on the causes of siltation in the river. This was carried out by the Hydraulics Research Station (and is here referenced as Inglis and Allen, 1957).

2.1. ANALYSIS OF EXISTING DATA

There were significant differences between the two laboratories in the way they approached the problem, and in the conclusions they came to. The Hydraulics Research Station (HR) favoured a modelling approach, using, for example, the movement of celluloid balls on a 1/600 scale model of the Thames to validate observations made regarding the movement of radioactive tracers released into the river, whereas the conclusions of the Water Pollution Research Laboratory (WPRL) were based on empirical measurements. The HR approached the problem with a set of *a priori* assumptions regarding hydrological processes in the river. The WPRL amassed a large amount of data from all available historical sources, carried out a planned regime of intensive repeat sampling, and interpreted the data from the perspective of inductive reasoning. The HR concluded that dredging was the main problem in the river, the WPRL concluded it was the sewage outfalls.

2.1.1. CONCLUSIONS OF THE HYDRAULICS RESEARCH STATION

The main conclusions of HR were that the turbidity maximum in the Thames at Barking Creek had been caused by extension and deepening of the dredged navigation channel. This had upset the equilibrium of the estuary. Material deposited at the Black Deep dump site (Figure 1.1) was returning to Barking and being deposited in the navigation channel.

In 1947 siltation was so severe in three stretches of the river Thames (Gallions Reach, Barking Reach and Halfway Reach; Figure 1.1) that it was costing the Port of London Authority £500,000 per annum in dredging charges (Inglis and Allen, 1957). Inglis and Allen decided that the problem had been caused by the deepening of the navigation channel between 1909 and 1928. This had been done to provide access to King George V Dock, which was opened in 1921 and completed the Royal group of docks, the largest area of impounded water in the world. Inglis and Allen argued that this had upset the equilibrium of the estuary by causing a dense saline current, laden with material of marine origin, to come up the channel.

Inglis and Allen (1957) suggested that the fine texture of the material in the “mud reaches” was a result of dredged silt and mud dumped in the Black Deep (88 km from Barking in the Outer Estuary) finding its way to the estuary mouth and proceeding up the estuary as a concentrated suspension till it reached the point it had been dredged from. They explained the unique texture of the material by proposing that it became progressively finer and more difficult to dredge as it moved back up the estuary.

Careful reading of the Inglis and Allen paper shows that though they demonstrated that material of marine origin was entering the estuary, they produced no real evidence in support of their hypothesis that this material originated in the Black Deep. Monitoring of the Black Deep dump site by the Ministry of Agriculture, Fisheries and Food (Franklin and Jones, 1994) shows that the Black Deep is in fact a dispersive site, and PTEs from material dumped there are spread widely over the North Sea. Concentrations of PTEs are higher at the former dump site than in the surrounding area.

There is a wealth of circumstantial evidence connecting the high rates of sedimentation to discharges from the Northern and Southern Sewage Outfalls. The main driving force for the construction of the sewage works had been the stench from the river, and the presence of banks of black, stinking mud in Central London (DSIR, 1964). The appearance of these phenomena at Barking following the construction of the sewage works suggests that the problem had simply been moved seaward of the Metropolis. One of the reasons given by the Metropolitan Board of Works for choosing Barking rather than Erith as the site of the Northern Outfall was that the river was free of mud-banks at Barking, so deposition of sludge was considered less likely were they to be constructed there (DSIR, 1964).

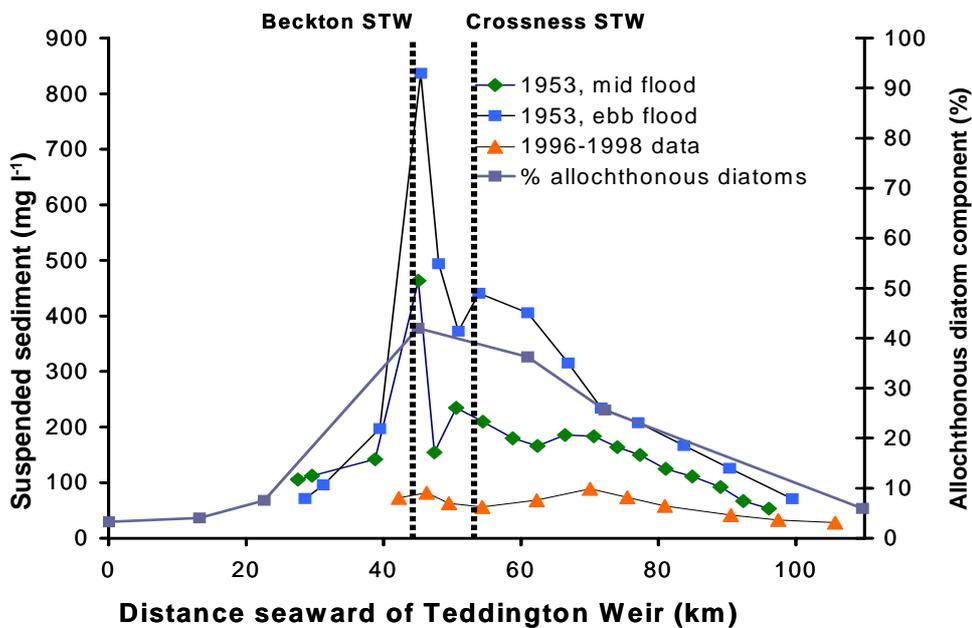


Figure 2.1 Suspended sediment levels in the Thames for 1953 and 1996-1998. The 1953 data are from Inglis and Allen (1957) and the 1996-1998 data from Trimmer et al. (2000). Data on allochthonous diatom composition is from Juggins (1992).

Inglis and Allen (1957) identified the stretch of the river into which the outfalls discharge as the turbidity maximum for the Thames. Trimmer et al. (2000) show that, though this is still a turbidity maximum, concentrations of suspended solids are much lower there than they were formerly, and that there was a second turbidity maximum at Tilbury Basin during the period 1996 - 1998. Suspended solids increase

downstream to the outfalls, then increase again until Tilbury. Figure 2.1 shows the change in suspended sediment levels between 1953 and 1996.

When Inglis and Allen presented their paper at the Maritime and Waterways Engineering Division (a branch of the Institution for Civil Engineers) meeting of 30th May, 1957, Mr. G.A. Wilson, Chief Engineer for the Port of London, asked if any account had been taken of the fact that the Northern and Southern Sewage Outfalls discharge into that stretch of the river. Inglis replied that the sewage works, far from contributing to the problem, had a scouring and cleansing effect on the river. The sewage outfalls were at that time discharging 180 tonnes a day of suspended matter with a concentration of 100 to 200 mg l⁻¹ (Inglis and Allen). The mid-depth average suspended solids concentration in the “mud reaches” was around 500 mg l⁻¹. Inglis and Allen argued that this was evidence that the outfalls diluted the concentration of suspended solids in the mud reaches.

The respective roles of sewage and dredging in the deteriorating condition of the Thames had been a matter of controversy for many years. This part of the river had been prone to siltation since the construction of the Northern and Southern Sewage Outfalls by the Metropolitan Board of Works. The Thames Conservancy, which was responsible for the condition of the river, first complained about siltation in a letter dated 29th July, 1877. The Board was informed of banks of deposits in Halfway Reach, a little down from the Outfalls. It replied, at the instigation of Bazalgette, the Chief Engineer, that the outfalls had not created the banks, but had conversely created “a positive scour and improvement in the depth of the river referred to, to the extent of three hundred thousand cubic yards, or in other words that part of the river is actually ten inches deeper than in 1867” (quoted in Halliday, 1999).

The discussion following the presentation of the paper by Inglis and Allen suggests there may have been a difference of opinion between HR and the WPRL over the hypothesis that dredged spoil returned to the Thames. Mr. Preddy, Chief Scientific Officer of the WPRL, refers to samples of dredged material and bottom deposits given by his laboratory to the University of Leeds for microscopic analysis. Leeds

University had concluded that around half the material had come from outside the estuary. Preddy suggested that this indicated that the landward drift of solids along the Thames may not be from the Black Deep Dump site. Sir Claude Inglis gave him very short shrift, commenting that the WPRL's own analysis showed that around 70% of the material from the mud reaches was either silica or oxides of iron and aluminium whose origin could not be determined either by microscopic or thermal analysis.

Juggins (1992) found that some 30-40% of surface sediment diatom assemblages in sediment cores from the mud reaches are robust marine species normally found in subaqueous (i.e. below the level of mean low water for spring tides), but shallow marine depositional environments in the outer estuary (Figure 2.1). If the assumption is made that diatoms are co-transported with sediment entering the estuary, this suggests that material from tidal flats rather than material from the Black Deep was the source of the marine component of the Thames dredgings. Figure 2.1 shows the distribution of allochthonous diatoms reaches a peak in the mud reaches, then declines rapidly in a landward direction.

From the perspective of the present study, the most important consequence of the report was its recommendation that dredged material should no longer be disposed of in the Black Deep, but should be pumped ashore. Lord Waverley, Chairman of the Port of London Authority, made a general statement following the presentation of the paper that, in the light of the proof presented by Inglis and Allen that dredged material was returning from the Black Deep to Barking Reach, the decision had been made to dispose of material from the "mud reaches" on shore at Rainham Marshes. The material was to be hydraulically raised via a fixed pump at Coldharbour Point, and the work was to commence as soon as the necessary equipment could be brought into action. Inglis and Allen did not expect that removal of the material from the river would yield results quickly, so he expected that Rainham would provide capacity for seven and a half years. After that, deposition on land would commence at Cliffe in Kent.

One of the preliminary hypotheses of the present study - that the material disposed of at Rainham came from all parts of the Thames - was now shown to be wrong. The provenance of material disposed of in the Rainham lagoons was now known, and, as will be shown below, came from a stretch of the river which had been the subject of an intensive scientific investigation.

2.2. THE REPORT OF THE THAMES SURVEY COMMITTEE

The WPRL did not publish their report for a further seven years. When they began their work there was no real knowledge of what biological reactions occur in a large polluted water body; there was no information on re-aeration rates in estuarine systems; there was no known method of calculating the distribution of a substance discharged into a system where the seaward flow of freshwater was superimposed on an oscillating tidal motion. By the time the laboratory reported its findings, they had established, through exhaustive field and laboratory studies, the role of nitrate and sulphate as terminal electron acceptors in estuarine systems; they had laid the foundation for current methods of modelling re-aeration; and they had developed a robust equation that corrected data for tidal movement.

2.2.1. THE OXYGEN SAG CURVE IN THE THAMES

When a large amount of organic matter is introduced to a body of water, the amount of dissolved oxygen starts to decline because of respiratory oxygen utilization by microbes consuming the organic matter. If this decline is plotted against distance, the resulting graph is called an oxygen sag curve.

Early records of pollution are much more detailed and complete for the Thames than they are for other estuaries. What may well be the world's earliest oxygen sag curve was drawn for the Thames in 1882 (Gameson and Wheeler, 1977). In 1885 the Metropolitan Board of Works introduced a programme for regular sampling of estuarine water off the Northern and Southern Sewage Outfalls for oxygen content. The sag curve minimum was always found at the Southern Outfall at low tide (Figure 2.2). There was no oxygen at this point 50% of the time in 1921; by 1934 this part of the river was anoxic at low water 96% of the time (DSIR, 1964).

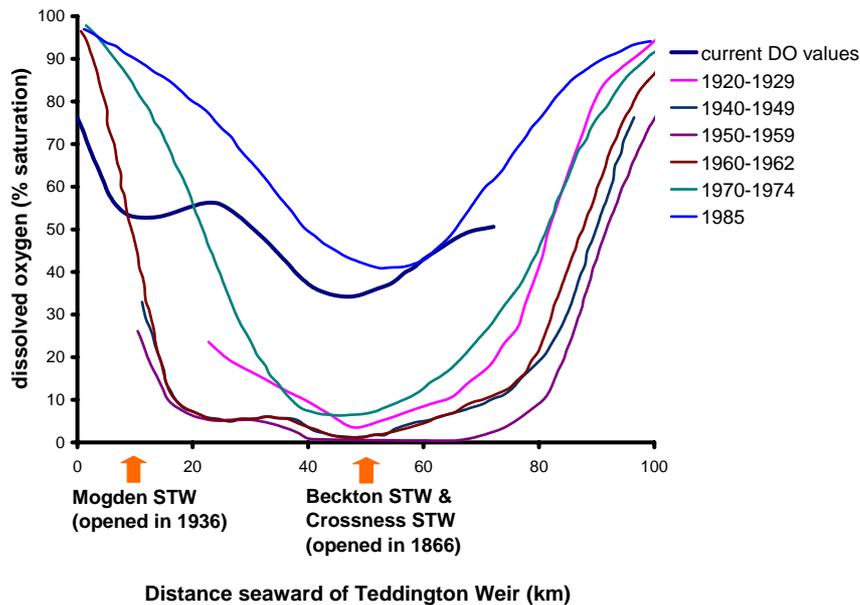


Figure 2.2 The historical trend in average dissolved oxygen in the tidal Thames.

Data until 1962 is from DSIR (1964). 1970-1974 data is from Gameson and Wheeler, 1978. The 1985 data is from Juggins (1992). “Current DO values” is taken from the EA website, and covers the period 1990 to 2000.

The data from DSIR (1964) and from Gameson and Wheeler (1978) in Figure 2.2 represent the dissolved oxygen status of the river during the third quarter of the year when the freshwater discharge at Teddington Weir is $13 \text{ m}^3 \text{ s}^{-1}$. Flow rates were below that level 20% of the time. The data from Juggins (1992) are the mean dissolved oxygen concentrations during the third quarter of the year. The EA data are the average dissolved oxygen concentrations from May till September for a ten-year period.

Oxygen sag curves vary in intensity and duration. If the re-aeration rate (the rate at which oxygen equilibrates across the water/atmosphere interface, also called the transfer coefficient) exceeds the microbial oxygen demand, then the sag is shallow and of short duration. The oxygen sag curve shows that during the 1940s – 1960s oxygen was absent from large stretches of the river (Figure 2.2). A particular problem in the immediate post war era was the introduction of synthetic detergents made from propylene tetramer benzene sulphonate. These made up well over half the world detergent market in the 1950s and 1960s. They reduced the transfer coefficient by

about 20% (DSIR, 1964). Once the problems associated with their use became known they were gradually phased out, and their use (in Britain) was finally banned in 1974. Comparing historical oxygen sag curves shows that dissolved oxygen in the river had been steadily declining before the river became anaerobic.

The remarkable increase in the dissolved oxygen content in recent decades is the result of improvements in sewage treatment works at Beckton and Crossness. The river ceased to evolve hydrogen sulphide in 1966, and by 1974 oxygen saturation was almost 10% in the zone affected by the sewage Outfalls when flow at Teddington Weir was $13 \text{ m}^3 \text{ s}^{-1}$ (Gameson and Wheeler, 1977).

The river is still susceptible to anoxia. Any significant rainfall in London causes the Combined Sewer Overflows (CSOs) to discharge into the Thames, leading to low dissolved oxygen, chemical and bacterial pollution (ENDs Report, 2004). Thames Water currently uses two boats, the Thames Bubbler and the Thames Vitality to pump air into the water. These boats can, between them, introduce 60 tonnes of molecular oxygen a day into the river. They are used on average about thirty days a year. The Environment Agency regularly uses hydrogen peroxide to prevent fish kills through hypoxia. Even so, dissolved oxygen levels can drop below 10% in summer, and fish kills occur four to eight times a year (ENDs Report, 2004).

The EU urban wastewater treatment and water framework directives are now forcing the British Government to find a solution to the problem. The EU Urban Wastewater Directive required member states to have adequate sewage collection systems in larger sewerage catchments by the end of 2000. By 2015, all waters will have to achieve good ecological status to meet the requirements of the Water Framework Directive (ENDs Report, 2004).

In a written answer to the House of Commons, the Environment Minister Elliot Morley revealed that an average of six million cubic metres of untreated sewage is being pumped into the tidal Thames every month (ENDs Report, 2005). Previous estimates from the Environment Agency were of 12 million cubic metres of storm

sewage each year, carrying 10 000 tonnes of plastic, needles and faecal matter. This discharge moves up and down the estuary for 15 km on the tide.

2.2.2. CORRECTING FOR TIDAL OSCILLATION

Using chloride as a conservative tracer, and integrating the changing volume of the river as it moves seaward, the WPRL developed a mathematical model for adjusting all data to the half tide condition, where half tide is defined as the instant that the volume of water to landward was equal to its average value over the average tidal cycle. In practical terms the sampling position was replaced with the position that the body of water sampled would occupy when the volume upstream was the mean value for the average tidal cycle. Using this method, the error in adjustment during high/low water at spring and neap tides is about half a mile.

By the end of the investigation they had established the conditions under which hydrogen sulphide generation would evolve, and developed and tested a fairly robust, predictive model of the effect on the oxygen status of known discharge volumes of organic matter into the Thames at given rates of freshwater flow and temperature.

As is probably inevitable in any project of this type, the WPRL carefully analysed, noted and recorded data, especially in the early stages of the investigation, which eventually proved to be irrelevant to their objectives. They decided to include this data in their report, in the hope that it would be of assistance to future researchers. This data has been an invaluable source of background information to the present study.

2.3. THE WATER POLLUTION RESEARCH LABORATORY DATA

2.3.1. DREDGING DATA

Amongst the unused data in the Thames Survey Committee Report is a breakdown of the dredging totals for 1935-1953 by position along the river. Figure 2.3 shows the average dredging rate in tonnes dry weight per day plotted against distance from the tidal head to the mid point of each stretch of the river. The variation in dredging

intensity along the estuary transect is clearly demonstrated. The next largest source of dredged material was the Royal Docks, which is in open connection with Gallion's Reach. Almost all the dredgings deposited at Rainham came from a discrete stretch of the river.

During the winter of 1949-1950, the WPRL took samples from the Thames bottom. The sampling strategy was to take three samples at one mile intervals. One sample was taken from the middle of the river, one from the south bank, and one from the north bank. The river bed was too hard to sample at various points, so a few data points are missing. The WPRL found nothing useful in the bottom sample data, but included it when they published.

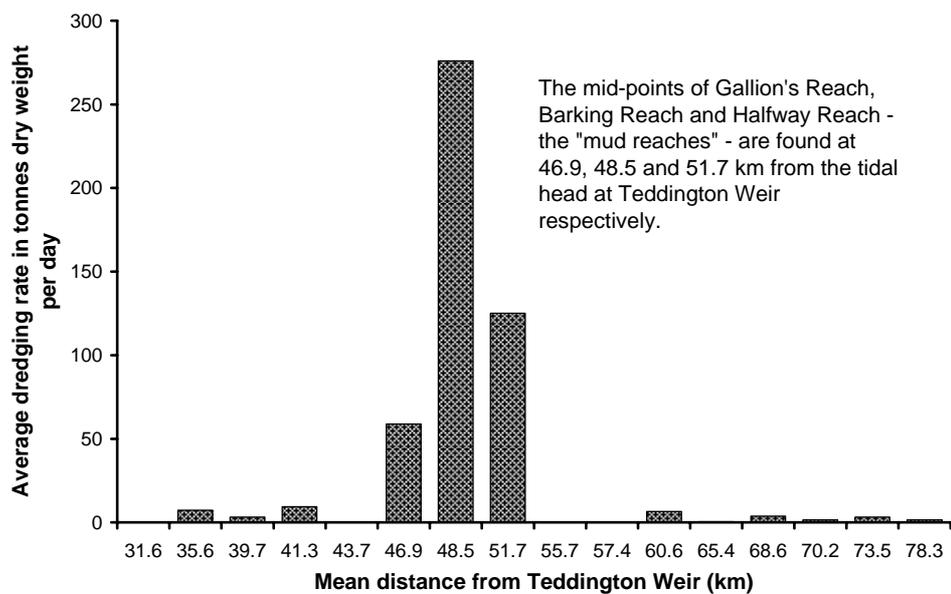


Figure 2.3 The variation in dredging intensity with distance from Teddington Weir for 1934-1953 (DSIR, 1964).

These data have also been analysed. A plot of particle size against distance from the tidal head, showed, contrary to expectations, that the greatest percentage of fines (particles smaller than 65 μm) was not found in the three reaches where the most intensive dredging had occurred. The greatest percentage of fines is found between 60 and 70 kilometers from Teddington Weir.

2.3.2. SILICA/SESQUIOXIDE RATIO AND REDOX POTENTIALS

Primary silicates, which make up most of the Earth's crustal material, weather in terrestrial ecosystems to produce secondary silicate minerals, the phyllosilicates or clays (Sposito, 1989). Estuaries contain material both from the sea and from the land. The material forming the sea bed is mainly sand, made up of primary silicate minerals. Material coming from the land will be richer in clays.

Phyllosilicates are richer in sesquioxides, oxides containing three atoms of oxygen, and two atoms of another element, generally iron or aluminium (Fe_2O_3 and Al_2O_3), than their primary mineral precursor because some silica is, in terrestrial systems, leached down the profile. A low silicate/sesquioxide ratio generally indicates an increase in the clay fraction. Under extreme weathering conditions, silicate clays derived from parent rocks may be dissolved and lost from the soil by leaching, leaving the sesquioxides behind in the soil.

The WPRL used soil science analytical methods from the Association of Official Agricultural Chemists (AOAC, 1950) to determine silica and sesquioxide content in the bottom samples. Silica was weighed as the acid-insoluble portion of the sample following fusion with sodium carbonate. Combined filtrates and washings from the silica determination were combined with ammonium hydroxide solution and the resulting precipitate ignited and weighed to determine sesquioxides. Bottom samples high in silica were assumed by the WPRL to contain a large amount of marine sand, while bottom samples high in sesquioxides were assumed to be rich in terrestrial clays (DSIR, 1964). When the aggregated mean values of silica and sesquioxides for three-mile stretches of the river are plotted against distance from the tidal head, a strong pattern of silica depletion and sesquioxide enrichment relative to the rest of the estuary is observed. These aggregated means were used to determine silica/sesquioxide ratios (Figure 2.4).

Dredging intensity can be used as a proxy for sediment deposition. The trough in the silica/sesquioxide ratio extended far beyond the discrete stretch of the river where there was intense dredging activity (Figure 2.3). This suggests that the change in

bottom sample mineralogy was not caused by deposition of clay from terrestrial sources.

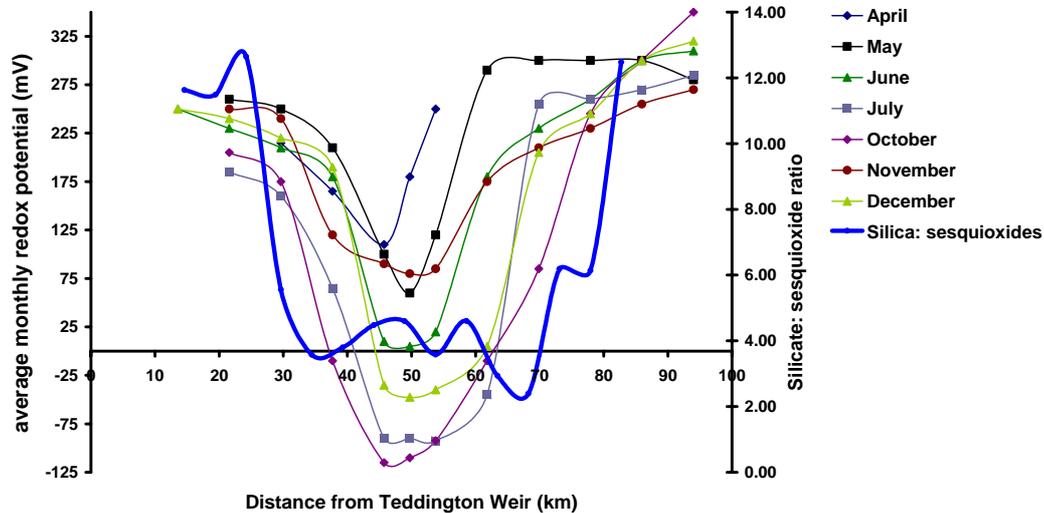


Figure 2.4 The variation in redox potentials and variation in silicate/sesquioxide ratios with distance from Teddington Weir in 1953. Data from DSIR (1964).

The main focus of the WPRL was on calculating the oxygen demand created by organic matter discharges into the Thames. Since the mid-upper stretches of the river were anaerobic for a large part of the year, this could not be achieved by measuring the decline in percentage oxygen saturation. In 1953, redox potentials were measured in the anaerobic part of the river to determine what changes were occurring in the water under anoxic conditions. These data are also presented in Figure 2.4.

Comparison between Figure 2.3 and Figure 2.4 shows that the lowest redox potentials correspond to the zone of highest dredging intensity. The lowest silicate/sesquioxide ratios are around 20 km seaward of this point, corresponding to that part of the river where average particle size was smallest. The decline in silicate/sesquioxide ratio precedes the sharp decline in redox potentials, and extends beyond the point where redox potentials begin to rise.

When tidal excursion is taken into consideration, the rapid drop in redox potential recorded in the water column by the DSIR (1964) and the contemporaneous changes

in the silicate/sesquioxide ratio in bottom samples appear to be almost perfectly correlated. It seems highly unlikely that the co-occurrence of low redox potentials and low sesquioxide ratios has occurred by chance, or is solely the result of depositional processes. It seems much more likely that this pattern is, at least in part, the result of the accelerated weathering of silicates under reducing conditions.

Dissolved silica is commonly regarded as being the result of the weathering of sedimentary and crystalline rocks on the land masses. This enters rivers through runoff, and is subsequently transported to the sea (Turner et al. 2003). The riverine input is balanced by diatom burial in marine sediments (Smetacek, 1999). The silica cycle is regarded as being independent of anthropogenic activity (Turner et al. 2003).

Microbially mediated dissolution of primary silicates, though never before suggested as a process occurring in estuaries, is known to occur in polluted subsurface environments. Bennett and Siegal (1987), for example, noted a strong linear correlation between dissolved silica and dissolved organic carbon in a petroleum contaminated aquifer at near neutral pH, and suggested that organic acids were complexing dissolved silica. In subsequent years microbially mediated dissolution of silicates and aluminosilicates associated with organic acids has frequently been demonstrated in both field and laboratory studies (Bennett et al., 1988; Welch and Ullman, 1992; Vandevivere et al., 1994).

2.3.3. PHYTOPLANKTON

The WPRL also measured the concentration of phytoplankton in the river, and identified the species present, since they were unsure whether phytoplanktonic blooms caused net oxygenation of the river through photosynthesis, or de-oxygenation through microbial decomposition of the phytoplanktonic biomass. When the data on phytoplankton numbers are plotted against distance from Teddington Weir (Figure 2.5), the highest concentrations are found seaward of the sewage outfalls (i.e. roughly co-incident with the zone where silicate levels are lowest in the bottom samples and the highest percentage of fines is found). The WPRL noted that cyanobacteria and

dinoflagellates were never observed in the Thames, and that the phytoplanktonic blooms were dominated by diatoms.

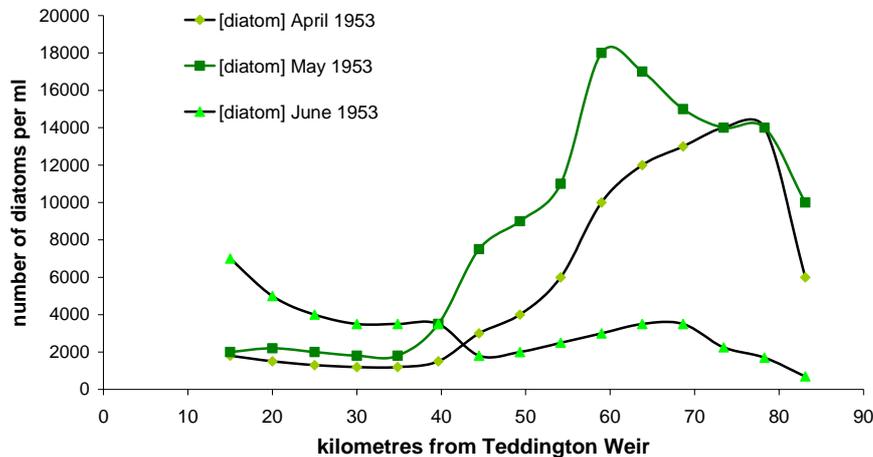


Figure 2.5 The variation in diatom distributions as function of distance from Teddington Weir for 1953 (DSIR, 1964).

A green algal bloom an order of magnitude lower (maximum densities were $\approx 2,000$ organisms per ml) peaked just above London Bridge, which is around 30 km from the tidal head (DSIR, 1964). Phytoplankton numbers were comparatively low in the “mud reaches”. Consideration of the suspended sediment concentrations shown in Figure 2.2 show that this was probably due to turbidity.

Phytoplankton growth in the turbidity maximum zone of an estuary is limited by two factors, light attenuation and water column mixing. Light attenuation with water column depth is described by the Beer-Lambert equation:

$$I_z = I_0 e^{-kz}$$

Where I_0 is light intensity at the surface, I_z is light intensity at z metres below the surface and k is the rate of attenuation. The rate of attenuation is a function of water turbidity.

Phytoplankton convert light energy to chemical energy, which is partitioned between cell growth and maintenance and respiration. Photosynthesis is light dependent and respiration occurs in both the light and the dark, so some carbon is stored to allow for dark period respiration. The point at which light is sufficient to supply the total carbon need of a plant is called the compensation point. The aquatic equivalent of the compensation point, i.e. the zone where light intensity is high enough to permit phytoplankton survival, is called the euphotic zone. Turbulent mixing means that photosynthetic organisms will spend only part of the time in the euphotic zone, and so effectively increases the dark period.

There was an almost complete absence of phytoplankton in the Outfall discharge zone. This shows that sewage rather than phytoplanktonic primary production was the source of fixed carbon. The very low redox potentials show that this part of the river was the site of intense activity by heterotrophic bacteria.

Diatom numbers gradually increased with distance from the turbidity maximum, presumably as light became less limiting for photosynthesis, until the maximum diatom concentration was reached above that part of the bed with the smallest silica/sesquioxide ratio.

In general, diatoms dominate the phytoplankton (Turner et al. 2003), since they take up nutrients faster than other phytoplankton (Libes, 1992). Redfield ratios are the elemental ratios required for sustained planktonic growth. Both the quality and quantity of phytoplankton growth change with changes in Redfield ratios (Turner et al. 2003). Diatoms have an absolute requirement for a 1:1 elemental dissolved silica/nitrogen ratio to form their frustules. In marine environments, dissolved silica fluxes from the sediment have been estimated to account for 30 – 50% of water column dissolved silica (Gehlen et al. 1995). The highest exchange rates are linked to the areas where there is the highest deposition of diatomaceous debris (Gehlen et al.). Given the magnitude of the annual diatom blooms in the Thames and the continual removal by dredging of large amounts of diatom-enriched sediments it is unlikely that

this requirement could be satisfied by either riverine inputs of dissolved silica or recycling of diatom frustules from either the benthos or the water column.

An increase in dissolved silica availability favours the growth of diatoms over non-diatomaceous phytoplankton (Tréguer and Pondaven, 2000). Conversely, the results of numerous field and laboratory studies show that the abundance of diatoms relative to other phytoplankton is reduced when the Si:N ratios drop below 1 (cited in Turner, 2003). The position of the algal and diatom blooms imply that dissolved silica was a limiting resource for diatom growth above the Sewage Outfalls but not below, in keeping with the hypothesis that silicate dissolution was occurring in the Sewage Outfall discharge zone.

2.3.4. PRESENCE OF ALTERNATIVE TERMINAL ELECTRON ACCEPTORS

The WPRL carried out an intensive survey of nitrate and sulphide contents of water in the estuary between 1953 and 1954 (Figure 2.6). The resulting map shows that, despite the Thames being a highly energetic and well mixed estuary, it was rare to find nitrate and sulphide together in the same water sample. Large areas of estuarine water were completely free of oxygen, but contained neither nitrate nor sulphide. The

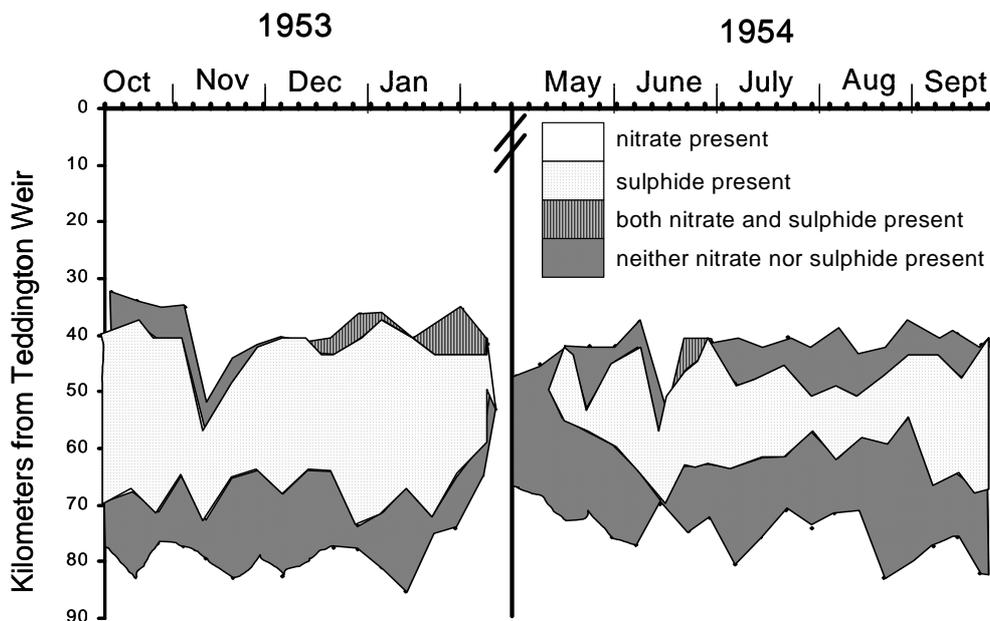


Figure 2.6 The maximum extent of nitrate and sulphide in the water column for the period October 1953 - September 1954. The data have been corrected for the half-tide position (DSIR, 1964)

distribution pattern is skewed, with zones which are free of both sulphide and nitrate tending to be much more extensive seaward of the sewage outfalls than they are in a landward direction. There is a strong seasonal element. By the beginning of February, 1954, nitrate was present in all stretches of the river.

Microbial use of alternative electron acceptors when oxygen is not available has already been discussed (1.5.2). Though the WPRL were unaware that manganese and iron oxides could be used as respiratory substrates, their data clearly show these to have been the most important alternative electron acceptors in those large volumes of anoxic water containing neither sulphide nor nitrate. Iron has a much higher crustal abundance than manganese, so Fe(III) would have played the more significant role.

Figure 2.6 represents the period when the rate of hydrogen sulphide evolution from the Thames was highest, and the anoxic stretch longest. The historical record shows that anoxia had been a feature of the Thames for some time before that, suggesting that Fe(III) availability had previously been high enough to prevent water column sulphate reduction. If silica depletion in bottom samples is linked to microbial processes in the overlying water column, then it is more likely to be associated with Fe(III) reduction than with sulphate reduction.

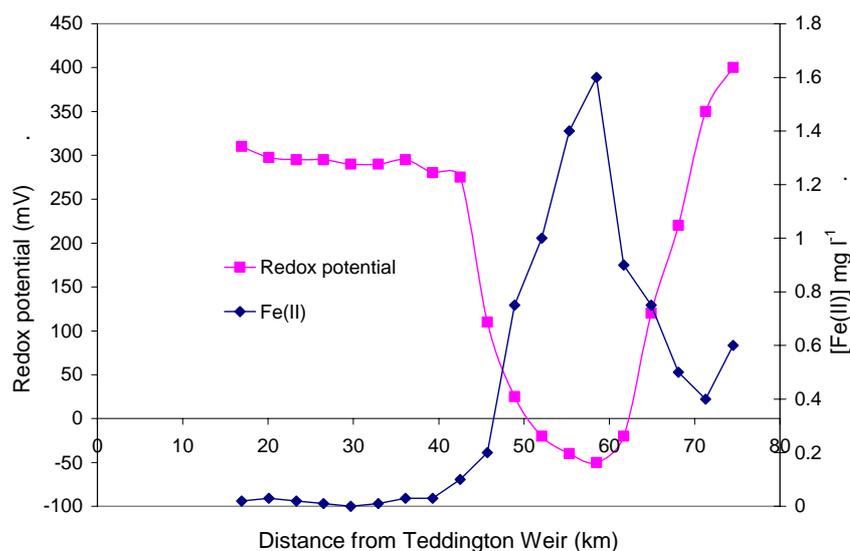


Figure 2.7 The variation in Fe (II) concentrations along a transect of the Thames Estuary, 27th June, 1952. Redrawn from DSIR (1964)

The remit of the WPRL was to determine the causes of hydrogen sulphide evolution, so their interest in dissolved iron only extended to the zone where sulphide was present in excess of ferrous iron. They did, however, measure dissolved iron on 27th June, 1952 along a transect to the start of the main depositional area at Tilbury (Figure 2.7).

There is frequently an implicit assumption in the literature that organic matter mineralisation in shallow environments occurs within the settled sediment. The “mud reaches” were characterized by turbulent mixing, cycles of deposition and re-suspension, and low settling velocities. Dredging alone would have created extensive plumes of re-suspended sediment. Sediment re-suspension is known to cause an increase in degradation rates, and an increase in water column mineralisation. In a review of the literature, Wainwright and Hopkinson (1997) showed that sediment re-suspension leads to water column degradation rates of total organic carbon that are over two orders higher than those in aerobic sediments. They also showed that sediment re-suspension causes a shift in mineralisation from the benthic to the pelagic environment.

Intuitively, one would expect the suspended solids in reaches of the river affected by the sewage outfall to be rich in organic matter. However, the converse is true. There is a marked negative correlation between loss on ignition and solids content. The WPRL found that, for samples taken from the stretch of the river between 10 to 14 miles below London Bridge, the proportion of solids volatilized at 800°C decreased as the concentration of suspended solids increased. When the suspended solids content was greater than 100 mg l⁻¹ the loss on ignition was between 30 – 40%, implying a high mineral content.

2.4. SUMMARY AND CONCLUSIONS

Research revealed that over 90% of the material disposed of in the lagoons at Rainham came from a discrete stretch of the Thames and the large complex of docks with which it was in open connection. During the 1940s to 1960s, this part of the river was anaerobic and evolving hydrogen sulphide. The immediate causes were the

construction of a navigation channel deeper than the natural river bed and a reduction in the re-aeration coefficient caused by the introduction of non-biodegradable detergents. The underlying cause was the presence of two large sewage Outfalls that discharged into the centre of the anaerobic zone. Siltation and problems associated with low concentrations of dissolved oxygen had been increasingly problematic since their construction in 1864.

The economic consequences of this for the Port of London led to Government intervention, and a subsequent scientific investigation. The Hydraulic Research Station concluded that the unusual texture of the dredged material was due to material deposited at the Black Deep returning to the sewage outfall discharge zone. The unique mineralogy of the sediment in the “mud reaches” has also been attributed to estuarine transport processes and enhanced sedimentation caused by salinity induced clay flocculation (Pethwick, 1984). There is no real evidence for either of these hypotheses. The decision was made to construct silt lagoons on the Rainham Marshes, so that the material could be permanently removed from the river.

Some aspects of the data - the strong correlation between redox potentials and the silica/sesquioxide ratio in bottom samples and the position and magnitude of the diatom bloom - are highly suggestive of silicate mineral dissolution under reducing conditions. It is here proposed that the source of the silica utilized by the diatoms is silicic acid released from the matrix of silicate minerals and that continual removal of precipitated diatoms by dredging led to the observed silicate depletion and sesquioxide enrichment of the bottom sediments. Silicate dissolution has been noted in terrestrial environments.

There were continual improvements in the quality of the discharge from the Outfalls during the depositional period. The lagoons at Rainham are a record of the physical effects of the transition between eutrophication driven anoxia and suboxia in a large water body. They represent what is perhaps a unique opportunity to study biogeochemical cycling within a grossly polluted estuary in the absence of

bioturbation and transport processes, which are common confounding factors in core studies of estuarine sediment.

CHAPTER 3 - CHARACTERISATION OF THE SILTS

3.1. INTRODUCTION

The field study experimental site was a two-hectare plot on a closed landfill site (map reference TQ 518 793) at Coldharbour Point, Rainham. The site was capped with silt dredgings from the lagoons to a depth of a metre and a half. Material had been removed from lagoons using a digger, piled up on the site, and then spread out with earth moving equipment. The precise source of any individual sample cannot, therefore, be determined.

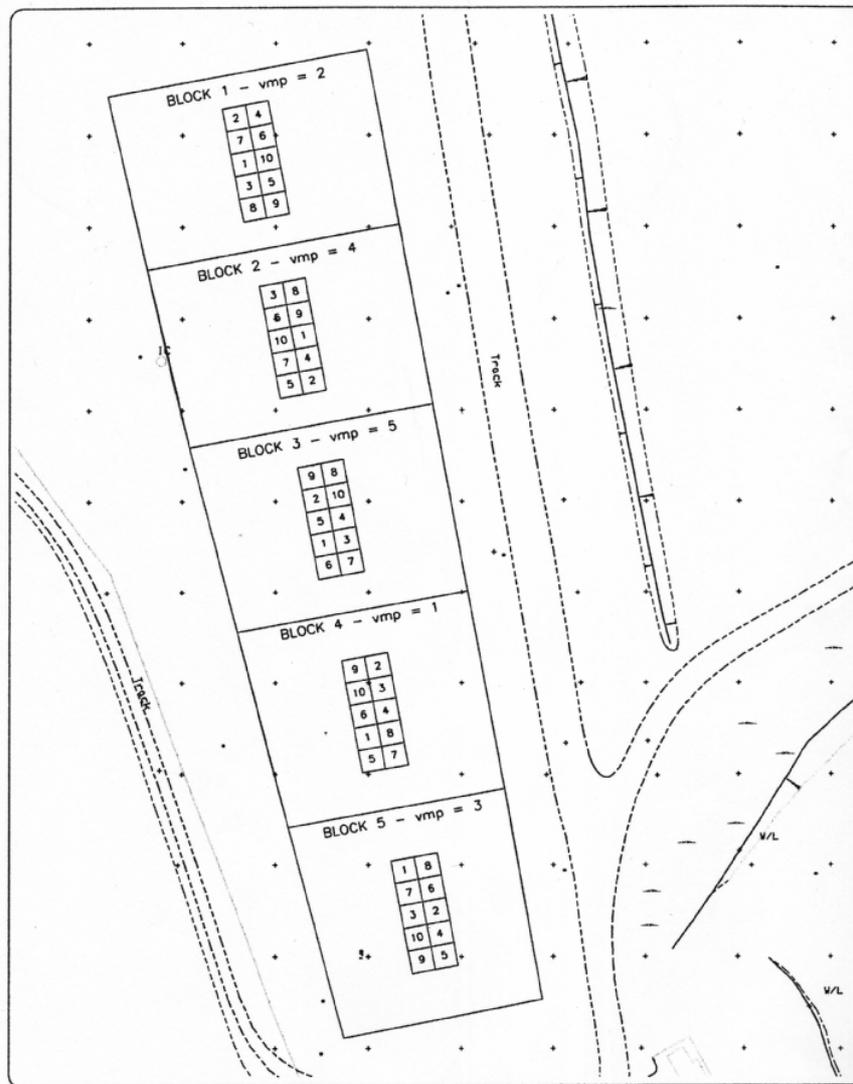


Figure 3.1 Diagram of the experimental site

As shown in Figure 3.1 the study site was divided into 5 sub-plots of roughly equal size. A block measuring 10 m by 25 m was laid out within each sub-plot. These blocks were further divided into 10 smaller 5 m by 5 m sections. The silts came from across the lagoons and from different depths within the lagoons. It was initially assumed that quality would be highly variable spatially because of short term rotational use, deposition of different materials at different times, and differences in contaminant loadings across the lagoon transect caused by the particle size driven differences in sedimentation characteristics. This experimental design was expected to represent the full range of variability in the dredgings.

Chemical and physical analyses were carried out on three sample sets from the experimental site. A limited range of parameters was quantified in ten preliminary silt samples from across site. This was followed by measurement of a more extensive range of attributes from 60 samples taken from within the experimental blocks. Hypotheses resulting from the initial analyses were tested by additional measurements on a core. All statistical analyses were carried out using Statistica 7 software. Sample material not used in the analyses has been stored in the National Soil Resource Institute's soil store, Cranfield University at Silsoe.

3.2. MATERIALS AND METHODS

3.2.1. PRELIMINARY SAMPLES

Ten preliminary samples, each weighing around one kilogram, were taken with a soil auger from within the rooting zone at the mid-point of the top and bottom end of each block in March, 2002 (see Figure 3.1).

3.2.2. EXPERIMENTAL SITE SAMPLES

Sixty samples, each weighing around 1 kg, were taken with a soil auger from the top 30 cm of the dredgings, in the plant rooting zone. Each sampling position was established using randomly generated co-ordinates.

One sample was taken from each of the 50 5m² sections (see Figure 3.1), and an additional ten samples from a section chosen at random. This sampling strategy was used to allow for the spatial variability both between and within the sections.

3.2.3. CORE SAMPLES

Intact cores were removed from the silt lagoons in the late 1990s using a 150 mm vibro-corer. These had been cut into 0.5 m sections, each of which was sealed top and bottom with petroleum jelly, labelled, placed in a rigid plastic sleeve, and sealed in polythene. No data are available on which part of the lagoons the cores were removed from. The cores were taken to Cranfield University at Silsoe in December 2002. The wrapping was removed from all cores, and the cores left to air dry in a greenhouse. A core which appeared to be in good condition, and for which all sections were available, was selected for study. Thirty sections of approximately 10 cm in length were sawed from the cores, avoiding areas which had been contaminated with petroleum jelly. The saw was washed down with de-ionised water and dried between cutting operations. The central portion of the 1.5 to 2 m section had crumbled, and was discarded.

3.2.4. SAMPLE PREPARATION

All 100 silt samples were air dried, ground in a mortar and pestle, and passed through a 2 mm. soil sieve to homogenise the material. A representative 100 g sub-sample of each sample was ground in an agate ball mill to 45 µm for subsequent analysis. The air-dried moisture content (Θ) was calculated using the mean of two replicate sub-samples oven dried to constant weight at 105°C.

3.2.5. ELEMENTAL COMPOSITION

Acid digests were prepared by adding 10 ml of nitric acid to 1.5 (± 0.01) g aliquots of 45 µm material, heating at 130°C for 30 minutes, adding 5 ml of H₂O₂, heating at 130°C for one hour, filtering through No. 40 Whatman paper and making up to 100 ml with deionised water. This strong acid digest is fairly aggressive, and is

considered to solubilise elements from all phases though it does not give a complete extraction (Zwolsman et al. 1996).

The acid digests from the ten preliminary samples were analysed for Zn, Cu, Ni, Pb, Fe, Mn, Ca, Mg and Al by ICP-AES. The acid digests from the 60 experimental site samples were analysed for Cu, Ni, Cr, Pb, Cd, Hg, As, Se, Mn and B. ICP-AES was used for Cu, Ni, Cr, Pb, Mn and B. AAS with graphite furnace was used for Cd, and AAS with hydride generation for As and Se. The ICP-AES was calibrated using a Merck multi-element standard solution, and a sample of the calibration solution was run every four samples.

Cu and Zn were measured in the acid digests from the core using a Hitachi AAS. All calibration curves had an R^2 term greater than 0.99.

3.2.6. PARTICLE SIZE ANALYSIS

Particle size analysis, using the pipette method, was carried out on the 2 mm material from the experimental site samples and the core samples. The pipette method involves removing organic matter with hydrogen peroxide and treating the material with sodium hexametaphosphate to disperse clays. Size fractions are calculated by a combination of wet sieving and (based on Stoke's Law governing the sedimentation rate of perfect spheres through a liquid) timed removal of suspended material at a certain height from measuring cylinders maintained at constant temperature. Data represent the means of three replicates.

3.2.7. CARBON, NITROGEN AND SULPHUR CONTENTS

An attempt was made to measure organic matter in the preliminary samples using loss on ignition. Air-dried ground soil was dried at 105°C, then burnt in an oven at 550°C. The results (not shown) were considered too high (in excess of 20%) to be credible.

Elemental analysis for C, N and S was carried out on those sub-samples from the experimental site samples and the core which had been milled and passed through a 42 µm sieve. Total carbon (TC), nitrogen (TN) and sulphur (TS) were measured

using an Elemental Vario El III CNS analyzer. Aliquots of each sample were pre-treated with HCl to remove carbonates and analysed for carbon and nitrogen. The fraction remaining after acid treatment was assumed to be organic carbon (C_{org}). The difference between total carbon and organic carbon was assumed to be inorganic carbon.

3.2.8. PH AND CEC

The cation exchange capacity (CEC) of the ten preliminary samples was measured using the centrifuge method (Soil Survey Laboratory Methods Manual, 1996). pH was measured in the preliminary samples in a 1:2.5 0.01M w/v CaCl₂ suspension of air-dried soil (Soil Survey Laboratory Methods Manual, 1996).

The pH of the within block samples and core samples was measured using air dried soil in a 1:2.5 de-ionised water suspension.

3.2.9. WATER SOLUBLE IONS AND ELECTRICAL CONDUCTIVITY

20 ± 0.01g of the 2 mm air-dried sediment from the experimental site and core samples was made up to 100 ml of solution with de-ionised water, and placed in a shaker for 24 hours. The electrical conductivity (EC) of the 1:5 aqueous extracts was measured at 25°C using a Camlab-CM-IIP EC meter.

It had been intended to measure the electrical conductivity of a saturation extract (USSL, 1954) as this more closely approximates EC in the plant rooting zone, but difficulties were encountered in removing a useful amount of soil solution from the extract. The saturation percentage (SP) was established for experimental site samples.

Extracts from the experimental site samples were filtered through No. 40 Whatman paper, then analysed for B, Na, K, Ca and Mg using ICP-AES, calibrated using Merck standard solutions. Phosphate was determined colorimetrically. Chloride was determined potentiometrically by titration against AgNO₃. All results were corrected for Θ . Quality control was ensured by running a standard solution every four samples.

The extracts from the cores were filtered through a 45 µm membrane filter. A x 50 dilution was prepared and analysed for chloride content. Chloride concentration was determined using a Technicon autoanalyser. The results of the chloride determinations were corrected for Θ .

3.2.10. SCANNING ELECTRON MICROSCOPY

Samples of the core material were sputtered with gold and examined under a scanning electron microscope. Elemental EDX mapping was used to determine the distribution of different elements, and BSE used to determine the chemical composition of discrete particles.

3.3. RESULTS : A. EXPERIMENTAL SITE

3.3.1. PRELIMINARY SAMPLES

The acid digest results from the preliminary samples are given in Table 3.1. The rationale for measuring these elements was as follows. Al, Ca and Mg were measured because the hydrolysis of Al is responsible for most soil acidity, while the base cations Ca and Mg have a neutralizing effect. These were measured since the mobility in soils of most potentially toxic elements increases with increasing acidity. Iron and manganese oxides were measured since they are common in most soils, are important binding phases for PTEs, and are redox sensitive. Finally, a range of PTEs was measured.

Table 3.1 Means, ranges and standard deviations of acid-extractable element concentrations in the preliminary samples (mg kg⁻¹ silt dry weight).

	Zn	Cu	Ni	Cr	Pb	Fe	Mn	Ca	Mg	Al
mean	581	198	65	124	257	23176	351	37864	6940	14634
max	731	234	73	143	301	30768	403	43107	8512	16364
min	208	71	53	73	108	19174	332	30499	5891	12264
stdev	148	49	7	22	58	3608	22	4025	869	1392

Principal components analysis (PCA) of the data from the preliminary samples shows two distinct groups of elements (Figure 3.2). Pb, Cu, Zn, Cr and Ni have a relatively wide range and are closely correlated to each other. Ca, Mg, Fe and Al form a second

group. Mn is not correlated with any of the other elements. The strength of individual inter-elemental correlations is shown in Table 3.2. The co-variance of the group of PTEs over the relatively wide ranges found is remarkable.

Analytical results vary with the procedures used to obtain them. Al, Ba, Cr, Fe, Mn, Ni and Va are known to have relatively low recoveries when strong acid digests are used (BCMELP, 2001). Cook et al. (1997) compared the reproducibility of different digestion techniques. They used ICP-MS to analyse sample digests from a number of different laboratories using a range of strong acid digest techniques and total (i.e. hydrofluoric acid) digestion. They found excellent comparability between all strong acid digests used. Recovery rates were higher for Cd, Ni and Cr when hydrofluoric acid was used. Data from other studies have only been referred to in the present work where strong acid digests were used to extract metals.

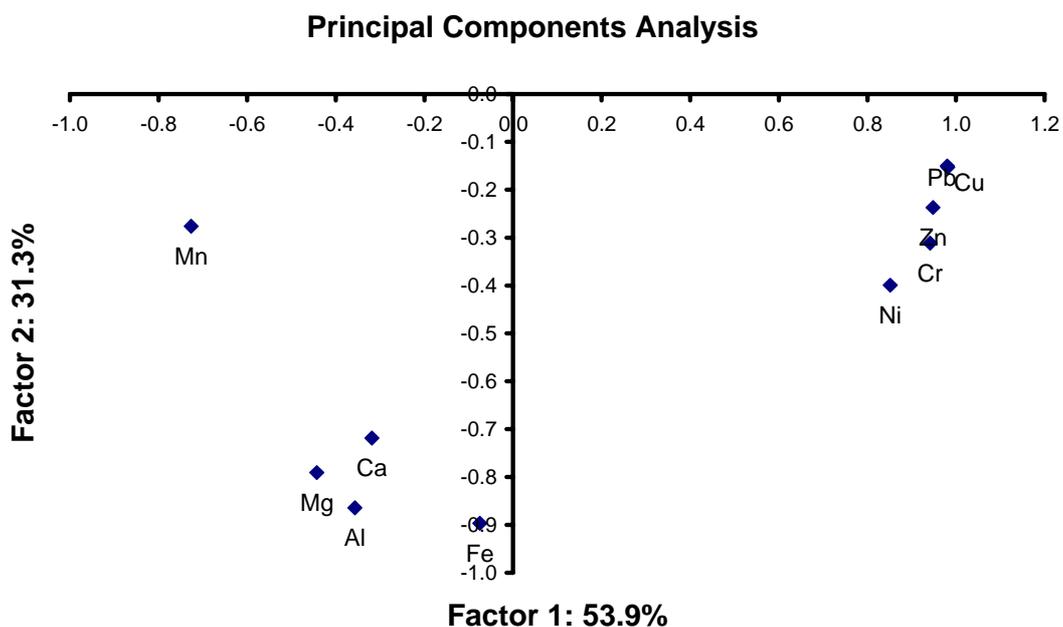


Figure 3.2 Principal Components Analysis of preliminary samples.

Attrill and Thomas (1995) used a nitric acid/hydrogen peroxide extraction to quantify sediment metal concentrations in the Thames. Their results should therefore be comparable with the results from the present study. The mean concentrations of a range of elements in 18 samples collected in 1989 from the Mid-Upper Thames differ

significantly from the data reported here. Aluminium concentrations are $21\,282 \pm 700 \text{ mg kg}^{-1}$ and iron $30\,626 \pm 733 \text{ mg kg}^{-1}$, an increase of 45% and 32% over the values found in the present study. Mn concentrations were also much higher, with a mean of $570 \pm 20 \text{ mg kg}^{-1}$. By contrast, their results for Zn, Cu, Ni, Cr and Pb were much lower at 244 ± 33 , 70 ± 6.1 , 36 ± 1.9 , 71 ± 6.1 and $149 \pm 11 \text{ mg kg}^{-1}$ respectively.

Table 3.2 Correlations between element concentrations from the preliminary samples

Marked correlations are significant at $p < 0.005$, $n=10$

	Zn	Cu	Ni	Cr	Pb	Fe	Mn	Ca	Mg	Al
Zn	1									
Cu	0.99	1								
Ni	0.85	0.88	1							
Cr	0.96	0.97	0.96	1						
Pb	0.98	0.99	0.89	0.97	1					
Fe	0.11	0.05	0.25	0.18	0.03	1				
Mn	-0.61	-0.64	-0.39	-0.53	-0.63	0.12	1			
Ca	-0.06	-0.16	0.12	-0.01	-0.15	0.52	0.61	1		
Mg	-0.23	-0.33	-0.13	-0.21	-0.32	0.84	0.34	0.61	1	
Al	-0.13	-0.21	0.04	-0.05	-0.18	0.74	0.59	0.68	0.80	1

Stevenson and Ng (1999) acid digested sediment samples taken at Beckton in November 1992. They found copper contents of 37.2 mg kg^{-1} , nickel contents of 21.5 mg kg^{-1} and zinc contents of 142 mg kg^{-1} . Power et al. (1999) state that, with the exception of Pb, metal loadings to the estuary decreased exponentially between 1980 and 1997. This decrease corresponds to the collapse of British manufacturing industry so these reductions in PTEs over a very short time span are entirely reasonable.

O'Reilly-Weise et al. (1997), in a study of cores at Tilbury Basin, 20 km seaward of the Sewage Outfalls, also used a strong acid digest (HCl/HNO₃) to extract metals. Cores were dated using PLA sounding charts. Concentrations of aluminium and iron are higher than those found either in the Rainham dredgings, or by Attrill and Thomas. Mean aluminium concentrations were $23\,946 \pm 5448 \text{ mg kg}^{-1}$, and iron concentrations $33\,904 \pm 6330$. They found little through-core variation in iron and aluminium ($n = 181$), but Mn was found to be 553 mg kg^{-1} in a core section deposited before 1966, and 1189 mg kg^{-1} in the section deposited after that date. The increase in Mn was strongly correlated with an abrupt decrease in PTEs. Cd decreased from a

mean of 6.25 to 1.88 mg kg⁻¹, copper decreased from 194 to 90 mg kg⁻¹, Hg from 6.65 to 2.32 mg kg⁻¹, Ni from 57 to 48 mg kg⁻¹, lead from 226 to 173 mg kg⁻¹ and Zinc from 573 to 345 mg kg⁻¹. Dissolved oxygen was < 5% at Tilbury in 1950, but had increased to 10 - 20% by 1960, and to around 20-50% by 1966 (O'Reilly-Weise et al. 1997).

When iron and manganese oxides are used as a respiratory substrate, the products are the highly soluble reduced forms Mn(II) and Fe(II) ions. Re-oxidation kinetics differ between Fe(II) and Mn(II). Fe(III) is usually regenerated from Fe(II) through biotic or abiotic re-oxidation at the oxic/suboxic interface. This allows the same ion to be used and reused as a terminal electron acceptor many hundreds of times before its eventual burial. Iron may be re-oxidised by oxygen, Mn(IV), nitrous oxide or nitrite (papers cited in Ratering and Schnell, 2000). None of these species would have been present in the mid-Upper Thames during its anoxic period. Fe(II) will also react with any hydrogen sulphide present, so buffering the release of free sulphide (Wijsman et al. 2002). The evolution of H₂S in the 1940s – 1960s shows that, during this period, reactive iron was limiting in the mid-Upper Thames.

Mn(IV) is reduced at higher redox potentials than Fe(III), but, in spite of similarities in redox chemistry, appears to be less amenable than Fe(II) to reoxidation. When Mn(II) is released into water, it may persist for days to months because of its slow oxidation kinetics (Sunda and Huntsman, 1998). Epping et al. (1998), for example, measured diffusive fluxes of iron and manganese from reduced sediment into an overlying oxic water column. All water-column manganese was present in the dissolved Mn(II) form, whereas most iron had oxidized and formed precipitates.

Iron is a marker for terrigenous material. It exhibits such distinctly non-conservative behaviour in estuaries, where it flocculates and precipitates, that the flux to the sea is depleted by 90% with respect to the riverine supply (Poulton and Raiswell, 2002). The data presented above suggest that the “mud reaches” were a zone of significant iron and manganese dissolution throughout the period that dredgings were disposed of to the Rainham lagoons. The increase in dissolved oxygen shown in Chapter 2 may

have led to less iron solubilisation, and so to the apparent increase in iron found by Attrill and Thomas a decade after the lagoons reached capacity.

O'Reilly-Weise et al. (1997) suggest that the marked increase in manganese in more recent sediments at Tilbury and the high degree of through core consistency for iron showed that dissolved oxygen had historically been low enough for manganese oxide dissolution, but not for iron oxide dissolution. Data from the WPRL (Figure 2.7) show that iron reduction did occur at Tilbury in the 1950s. Given the seaward position of Tilbury, it is also possible that a flux of dissolved iron from the “mud reaches” may have been carried down the Thames, and re-oxidised at Tilbury.

There appears to be an even more significant increase in aluminium. Aluminium is widely regarded as being unaffected by early diagenic processes and strong redox effects, allowing its use as a proxy for the clay fraction (Rowlatt et al. 1998). Aluminium may not behave in a conservative manner in all circumstances. Barker et al. (1998) showed that several bacterial strains can enhance the dissolution of Al, as well as Fe and Si, by up to two orders of magnitude over abiotic controls. Enhanced mineral dissolution is associated with the production of organic acids and extracellular polymers by the bacteria.

3.3.2. CATION EXCHANGE CAPACITY AND PH

The cation exchange capacity is a measure of the capacity of the negative electrical charge on clay particles and soil organic matter to remove positively charged cations from the soil solution and to retain them against gravitational pull. The CEC was very high, ranging between 33.2 and 41.4 cmol kg⁻¹, with a mean of 37.2 cmol kg⁻¹. The mean pH was 7.4.

3.3.3. POTENTIALLY TOXIC ELEMENTS

The potentially toxic elements selected for measurement in the experimental site samples are those for which, because of their potential toxicity, the Department of the Environment Food and Rural Affairs (DEFRA) has produced soil guideline values (SGVs) as a screening tool (Environment Agency, 2002). These are the metals Cr,

Hg, Ni, Pb, and Cd, and the metalloids As and Se. Cu, Zn and B were also measured. Although they are not considered to present a risk to humans, they are known to be phytotoxic. The means, ranges and standard deviations for the elements measured are given in Table 3.3.

The term “SGV” in the first line refers to the soil guideline values. The values for Cu and Zn are the United Kingdom Interdepartmental Committee for the Redevelopment of Contaminated Land (ICRCL) intervention values. The ICRCL provided guidance on the assessment and development of contaminated land for over two decades. The figures used are from ICRCL 59/83. DEFRA have formally withdrawn ICRCL values, but there are as yet no SGV values for Cu and Zn. These have been included to put the values for Cu and Zn found at Rainham into historical context.

Table 3.3 Mean, ranges and standard deviations of element concentrations (mg kg⁻¹ silt dry weight) in the experimental site samples. SGV denotes soil guidance levels, a denotes ICRCL values.

	Cu	Ni	Cr	Pb	Cd	Zn	Hg	As	Se	Mn	total B
SGVs	130a	50	130	450	2	300a	8	20	35		
mean	229	61	121	261	9.5	630	7.5	38	5	379	29
max	321	82	181	362	15.3	871	11.5	60	11	495	50
min	82	28	56	93	0.7	189	1.0	16	2	246	14
stdev	59	10	27	53	3.2	162	2.3	10	2	51	7

The levels of PTEs found in the dredgings are high compared to those found in agricultural land. Data from the National Soils Resource Institute show that in 1980 average PTE levels in agricultural topsoils for England and Wales were 91 for zinc, 44 for chromium, 45 for lead, 27 for nickel, 20 for copper, 11 for cobalt and 1 for cadmium.

Table 3.4 Concentrations of PTEs (mg kg⁻¹ dry weight) in sediments from industrialized British Estuaries. Data for the Tees are from Davies et al. (1991), for the Tamar from Bryan and Uysal (1978), Mersey, Taylor (1986) and for the Thames from O’Reilly Wiese et al. (1997)

Estuary	Period	Cd	Cr	Cu	Ni	Pb	Zn
Tees	1988	<0.5 - 8.5	10 - 380	10 - 1100	11 - 92	40 - 990	40 - 2900
Tamar	1974	<0.1 - 5.4	39 - 91	111 - 521	33 - 64	112 - 697	195 - 1150
Mersey	1974-83	<0.1 - 5.8	<1 - 155	<1 - 219	1 - 364	1 - 741	7 - 994
Thames (Tilbury)	1916-94	0.31 - 4.68	51 - 136	32 - 145	30 - 70	26 - 207	107 - 507

Comparison with published PTE data where strong acid digests were used shows that Cd concentrations found in the Thames dredgings are the highest ever recorded in an industrialized British estuary (Table 3.4).

With the exception of selenium and boron, PTEs from the experimental site samples were all highly correlated. Inter-elemental correlations are similar to those found in the preliminary samples. There was no significant correlation between manganese and the PTEs (Table 3.5). The lagoons were filled for three months, followed by an 18 month drainage period. As the samples come from across the lagoons and from different depths within the lagoons, this implies that the inter-elemental correlations shown are a common characteristic of dredged material deposited in the lagoons.

Table 3.5 Correlations between element concentrations in the experimental site samples.

Highlighted correlations are significant at $p < 0.0001$, $n = 59$.

	Cu	Ni	Cr	Pb	Cd	Zn	Hg	As	Se	Mn	total B
Cu	1										
Ni	0.91	1									
Cr	0.95	0.96	1								
Pb	0.90	0.83	0.90	1							
Cd	0.92	0.90	0.94	0.89	1						
Zn	0.96	0.91	0.95	0.94	0.94	1					
Hg	0.89	0.82	0.85	0.87	0.84	0.89	1				
As	0.87	0.89	0.90	0.83	0.86	0.88	0.81	1			
Se	0.30	0.34	0.33	0.21	0.26	0.28	0.19	0.4	1		
Mn	0.07	0.28	0.14	0.01	0.13	0.07	-0.08	0.08	0.24	1	
total B	0.20	0.24	0.19	0.14	0.17	0.17	0.23	0.24	0.32	0.1	1

3.3.4. PARTICLE SIZE ANALYSIS

When particle sizes are plotted on a soil triangle a discrete grouping of samples with some high sand outliers is produced (Figure 3.3). This results from the filling method. Though Mertens et al. (2001), consider that pumping dredged material into a confined area will give rise to a strong soil texture gradient, due to different sedimentation velocities, Vervaeke et al. (2001) found that this method of disposal results in a polarisation of soil textural classes between sand and finer material, with only a slight texture gradient in the finer material. Similarly, when this disposal method was used for dredged material from the Scheldt, Vandecasteele et al. (2002) found that sand

built up close to the discharge opening, and that the silt in the rest of the lagoon was relatively homogenous.

An eye witness account of the filling of the Rainham lagoons said that when the dredged material is pumped out under pressure any sand or gravel present falls rapidly out of suspension in the vicinity of the inlet pipe, while the rest of the material forms a viscous liquid which settles out over time. The scattering of high sand samples are caused by coarse material under the inlet pipe becoming unstable and slumping over the lagoon when it reached a certain height, creating discrete layers of coarser material (Mike Hann, Civil Engineer, Cranfield University pers. comm.).

The discrete grouping of the samples shows that little, if any, separation between the clay and silt fractions occurred while the Rainham lagoons were being filled. This led to the hypothesis that the silt and clay fractions were not moving independently, but as aggregates. A literature review of recent studies in sediment transport, the results of which were covered in 1.6.1, showed that this was likely to be the case. Subsequent examination by SEM shows that particles are bound together by organic matter. The first two initial hypotheses, that hydraulic filling of the lagoons would result in horizontal gradation of material based on sedimentation characteristics, and thus result in higher contaminant levels at either end of the lagoons compared to the mid-section discharge point were shown to be false.

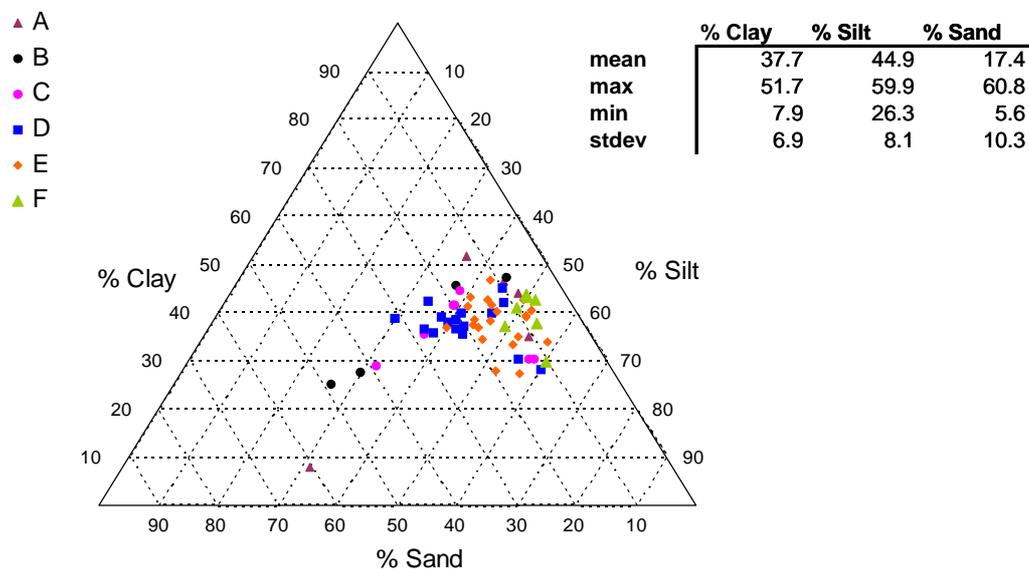
One of the original objectives of the research was to develop sediment quality criteria which could be used to discriminate between samples of material assumed to have a high degree of spatial heterogeneity. It was expected that mineralogy would be a useful determinant of PTE loading, since a close correlation between clay and PTEs has been noted from a range of terrestrial and aquatic systems.

Mermut et al. (1996), for example, found highly significant correlations between clay content and the total amount of PTEs in both soil surface horizons and parent material in thirteen sites in Saskatchewan, where the percentage clay varied from 6 to 75%. A similarly high affinity between PTEs and clay minerals was found by Wang and Chen

(1998) in 200 samples from eleven of China's eastern alluvial plains. No correlation between selenium and clay minerals was found in either study.

In aquatic systems there is an almost ubiquitous high positive correlation between PTEs and that fraction of the sediment where particle sizes are less than 63 μm (the fines). This relationship between the fines and PTEs is generally assumed to be the result of either direct adsorption onto clays or adsorption on clay associated organic coatings (Jones and Franklin, 1997), since clay minerals have both a large natural PTE loading and a greater active surface area for adsorption.

Trace element adsorption on clay is the result of two separate mechanisms. Trace elements may be adsorbed in clay interlayers as a result of cation exchange, or they may be a result of inner-sphere complexation on silanol and aluminol groups at clay particle edges (Abollino, 2003). Elements such as aluminium or lithium, regarded as conservative elements within the clay matrix, are widely used as normalisers to allow PTE loading to be compared in sediments with different grain sizes and mineralogy.



A signifies cumulative PTEs of less than 800 mg kg^{-1} , **B** PTEs between 800 and 1000 mg kg^{-1} , **C** PTEs between 1000 and 1200 mg kg^{-1} , **D** PTEs between 1200 and 1400 mg kg^{-1} , **E** PTEs between 1400 and 1600 mg kg^{-1} , and **F** PTEs between 1600 and 1800 mg kg^{-1} .

Figure 3.3 Relationship between soil texture and PTE loading in the experimental site sample

Mapping figures for cumulative PTEs (the sum of the concentrations in mg kg⁻¹ of Cd, Zn, Cu, Hg, Cr, Pb, Ni and As) against soil texture (Figure 3.3) does not show the expected relationship between clay and PTEs, but instead shows a clear relationship between the silt fraction and high PTE content. The twenty-eight samples with a cumulative PTE concentration greater than 1400 mg kg⁻¹ (Group E) have a silt content between 40% and 60%, and a sand content of less than 20%. The seven samples with a PTE concentration greater than 1600 mg kg⁻¹ all have silt contents of between 50% and 60%, and sand contents of less than 15%. Soil texture is much more variable for those samples with cumulative PTE concentrations of less than 1400 mg kg⁻¹. Figure 3.3 also shows the means, ranges and standard deviations for the particle size fractions measured.

The relationship between individual PTEs and different size fractions of the sediment is shown in Table 3.6. Overall, PTEs tend to be positively associated with the silt fraction, and negatively associated with the sand fraction. There is no discernible association between the clay fraction and PTEs in the experimental site samples, or between the clay fraction and the silt fraction. There is a highly significant negative correlation between both the clay and silt fraction and the sand fraction.

Table 3.6 Correlation between PTEs and particle size in the experimental site samples. Marked correlations are significant at $p < 0.005$, $n = 59$

	Cu	Ni	Cr	Pb	Cd	Zn	Hg	As	Se	% Clay	% Silt
% Clay	-0.06	0.03	0.05	-0.11	0.02	-0.11	-0.16	0.18	0.26	1	
% Silt	0.41	0.51	0.46	0.26	0.33	0.34	0.32	0.43	0.22	-0.04	1
% Sand	-0.33	-0.48	-0.45	-0.17	-0.31	-0.24	-0.19	-0.4	-0.37	-0.63	-0.75

3.3.5. C, N AND S CONTENTS

As mentioned in the previous chapter, sulphate reduction has traditionally been considered to be the most important terminal electron accepting process in marine and estuarine anaerobic sediments. Berner and Raiswell (1983) demonstrated that when a high rate of metabolisable organic matter is available to sulphate reducing bacteria, intense sulphate reduction leads to organic matter accumulation and a high sulphide concentration.

An important reaction which occurs in sulphur-rich anaerobic sediments is the immobilisation of PTEs as insoluble metal sulphide precipitates. The sulphate reducing bacteria produce reduced sulphur species which readily react with metals. Iron is quantitatively most important in these reactions, so the end product is normally iron monosulphide, but transition metals are favoured over iron in this reaction because of their lower solubility (Reuther, 1999).

Disposal of sulphide rich sediments to land may lead to drying and subsequent oxidation of the sulphide to sulphate. Metal sulphide oxidation is highly acidifying, and likely to lead to metal mobilisation. (Lucassen et al. 2002) found that the sediment S(Ca + Mg) ratio could be used empirically to predict whether such mobilization would occur. Metal mobilization is likely when this ratio exceeds 2:3.

Because of these considerations it was decided to quantify C, N and S. The means, ranges and standard deviations for nitrogen, organic carbon, inorganic carbon and sulphur from the experimental site samples are shown in Table 3.7. The last column in the table shows the molar C:N ratio.

Table 3.7 Percent contents of C, N and S in the experimental site samples.

	% N _{tot}	% C _{org}	% C _{inorg}	% S _{tot}	C:N ratio
mean	0.40	5.31	1.13	0.51	15.6
stdev	0.07	0.86	0.27	0.09	2.5
max	0.53	7.44	1.91	0.69	27.4
min	0.24	2.75	0.41	0.34	13.0

The correlation coefficients for particle size fractions and nitrogen, organic carbon, inorganic carbon, total sulphur and the molar C:N ratio are shown in Table 3.8, which shows the highly significant correlation between sand and the C:N ratio ($p > 0.0001$), and the highly significant negative correlation between the silt fraction and the C:N ratio. The correlation between total nitrogen and the silt and sand fractions, and between clay and the C:N ratio is less strong, though still highly significant ($p < 0.005$).

Table 3.8 Correlations between N, C_{org}, C_{inorg}, S, C:N ratio and particle size in the experimental site samples. Marked correlations are significant at p < 0.0001, n = 58.

	% N _{tot}	% C _{org}	% C _{inorg}	% S _{tot}	C:N ratio
% Clay	0.01	-0.24	-0.19	-0.23	-0.43
% Silt	0.44	-0.06	0.38	0.16	-0.68
% Sand	-0.39	0.22	-0.21	0.00	0.89

In most non-tropical surface soils 90% of sulphur is in organic forms (Killham, 1994). Wang et al. (2001) reviewed the range of values for total sulphur concentrations in the top 0.4 m of world soils. These range from 0.014% on a Mongolian chernozem to 0.05% in Minnesota soils. The N:S ratio in soil organic matter tends to be 10: 1.1-1.4 (Kowalenko, 1978). The fact that sulphur contents exceed nitrogen contents in the dredgings shows that most of the sulphur present in the dredgings is in inorganic form, resulting from the fixation of sulphate ions of marine origin by sulphate reducing bacteria (SRBs) during the anaerobic oxidation of organic matter.

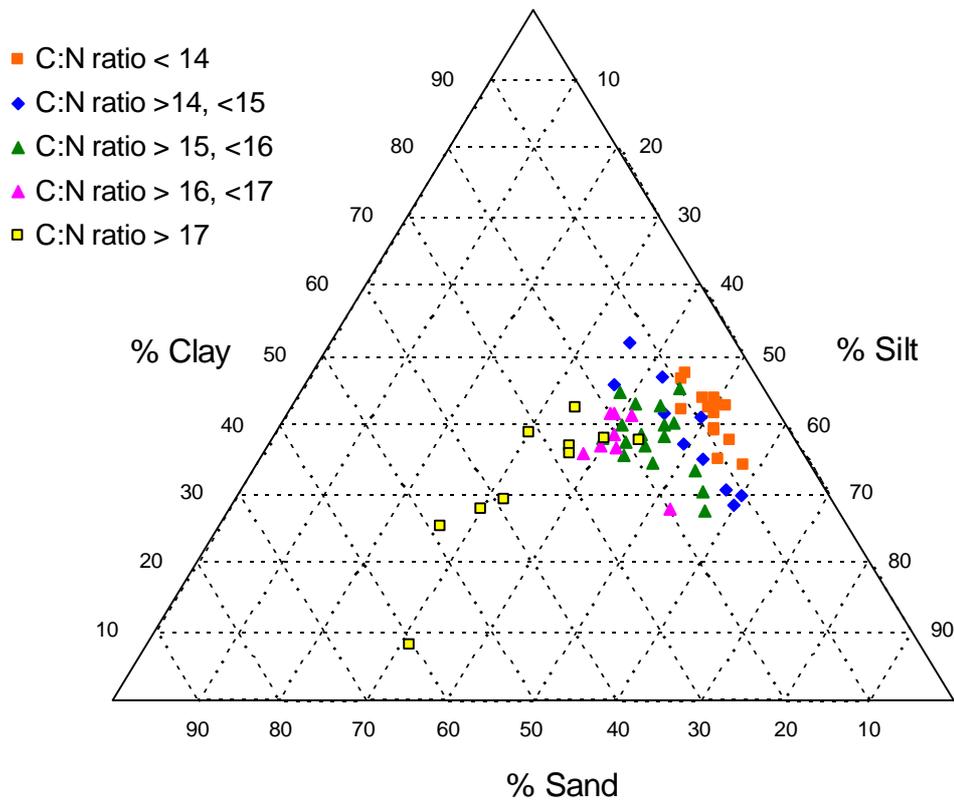


Figure 3.4 Relationship between soil texture and molar C:N ratio.

Figure 3.4 illustrates the form the relationship between soil texture and the C:N ratio takes. Those samples with a C:N ratio of less than 14 are restricted to a discrete band roughly aligned along the 10 % sand line, with a silt content of between 45 % and 58 %. Unitary increases in the C:N ratio produce a banded pattern along the sand axes, where each band is more variable with respect to soil texture than the preceding band.

Table 3.9 Correlations between PTEs and N, C_{org}, C_{inorg}, sulphur and the C:N molar ratio

Marked correlations are significant at $p < 0.0001$, $n = 57$.

	Cu	Ni	Cr	Pb	Cd	Zn	Hg	As	Se	Mn
% N _{tot}	0.90	0.86	0.91	0.86	0.90	0.88	0.78	0.82	0.25	0.02
% C _{org}	0.69	0.56	0.61	0.75	0.69	0.73	0.66	0.59	0.01	-0.35
% C _{inorg}	0.24	0.36	0.33	0.31	0.31	0.31	0.26	0.37	0.23	0.25
% S _{tot}	0.55	0.56	0.55	0.59	0.55	0.59	0.54	0.43	0.10	-0.23
C:N molar	-0.24	-0.38	-0.37	-0.09	-0.23	-0.15	-0.13	-0.29	-0.36	-0.52

Table 3.9 shows the correlations between organic carbon, inorganic carbon, total sulphur and total nitrogen. The strongest correlations are found between nitrogen and the PTEs. The strong linear relationships between individual PTEs and nitrogen are shown in Figure 3.5.

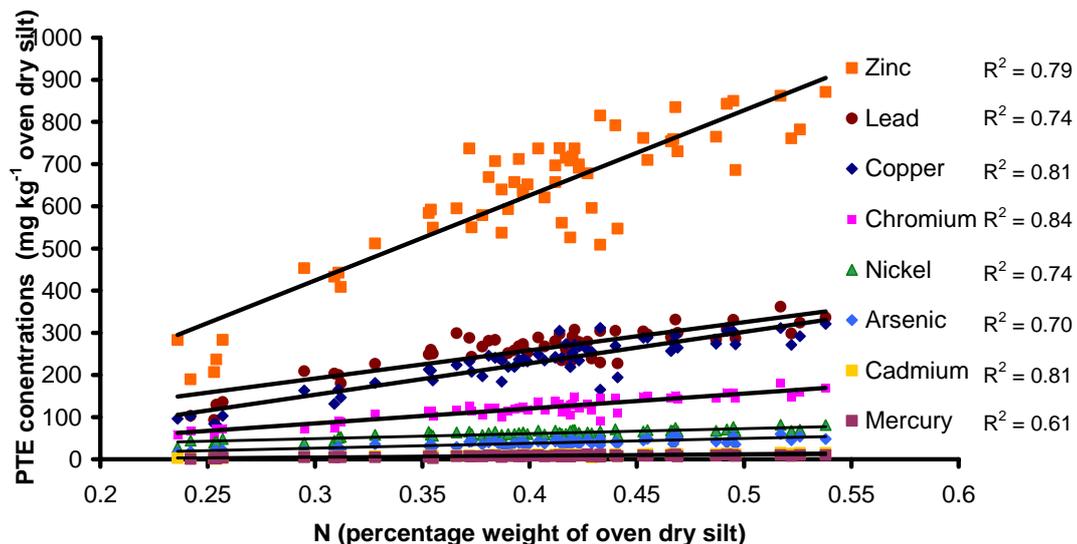


Figure 3.5 Correlations between PTEs and nitrogen in the experimental site samples, $n = 59$.

Given that potentially toxic elements are usually found in a range of different mineral carrier phases and that nitrogen can be used as a proxy for organic carbon, the most

obvious hypothesis for the correlation between nitrogen and trace metals in the core and the experimental site samples is:

- That the potentially toxic elements have been released from mineral carrier phases
- That the PTEs have subsequently been complexed by organic matter

3.3.6. WATER SOLUBLE IONS , ELECTRICAL CONDUCTIVITY AND PH

At the beginning of the research the point in the estuary that the dredgings came from was unknown. It was known that marine disposal was retained for a proportion of material dredged from the navigation channel. Because of the geographic position of the pump at Coldharbour Point, it was assumed that material landward of this point, (i.e. from the mid and upper estuary) would be disposed of there. This stretch of the river covers the zero to 19 PSU isohalines. Salinity and sodicity may play an adverse role in vegetation establishment and soil development, so a range of water soluble ions was quantified.

Table 3.10 Concentrations (mg kg⁻¹ silt dry weight) of water soluble ions in the experimental site samples.

	B	Na	K	PO₄²⁻	Cl	Ca	Mg
Mean	6.1	648	173	3.5	738	1323	331
St dev	1.3	291	34	1.1	398	577	128
Max	9.2	1322	244	6.5	1741	2828	642

Table 3.11 Correlations between measured water soluble ions and EC in the experimental site samples Highlighted correlations are significant at p> 0.0001, n = 60.

	WS B	WS Na	Ws K	WS PO₄²⁻	WS Cl	WS Ca	WS Mg
WS B	1						
WS Na	0.65	1					
Ws K	0.82	0.86	1				
WS PO₄²⁻	-0.1	-0.13	-0.16	1			
WS Cl	0.46	0.89	0.69	-0.14	1		
WS Ca	0.83	0.37	0.6	-0.02	0.19	1	
WS Mg	0.89	0.58	0.76	-0.06	0.43	0.93	1
EC1:5	0.89	0.75	0.83	-0.1	0.63	0.81	0.88

Table 3.10 shows the means, ranges and standard deviations of water soluble ions in the within block samples in mg kg^{-1} oven dry silt, and Table 3.11 the correlations between ions.

Table 3.11

Shaw (1996) demonstrated a theoretically sound model for conversion of $\text{EC}_{1:5}$ to the electrical conductivity of a saturation extract (EC_{SE}) using the general equation;

$$\text{EC}_{\text{SE}} = \text{EC}_{1:5} (500 + 6 \Theta/\text{SP})^b$$

Where Θ is the air dried moisture content, SP is the saturation percentage and the power term b represents the mix of totally soluble and sparingly soluble salts in the solution. This is determined by the proportion of soluble chloride salts in relation to the $\text{EC}_{1:5}$. When this equation is used to convert $\text{EC}_{1:5}$ to EC_{SE} , a mean EC of 6.2 dS m^{-1} is found, with a range of between 19.4 and 0.8 dS m^{-1} , and a standard deviation of 4.3 dS m^{-1} .

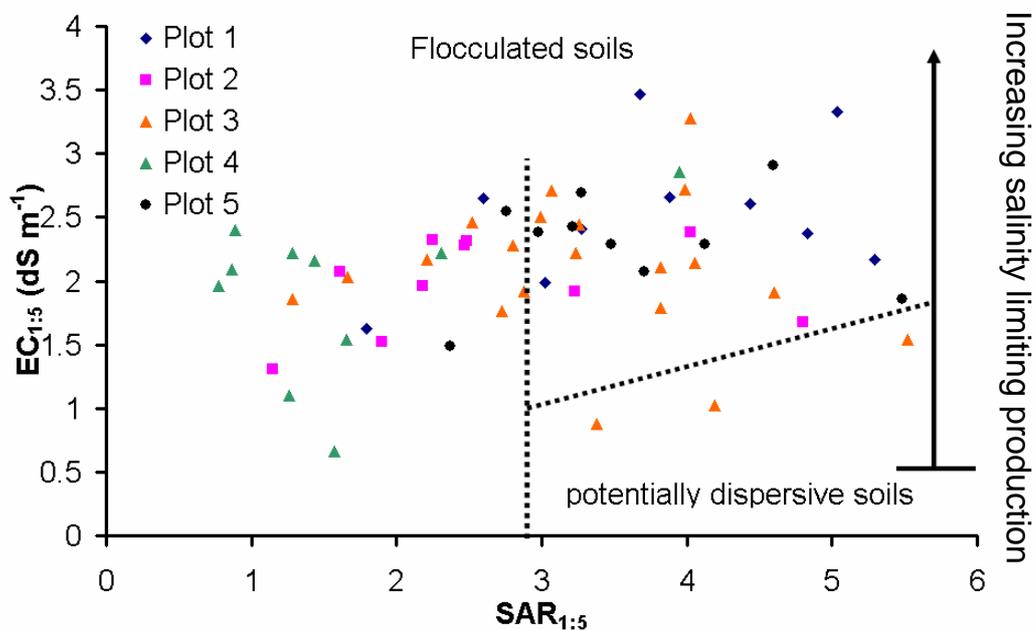


Figure 3.6 Sodium Adsorption Ratio (SAR) versus $\text{EC}_{1:5}$.

The value of the sodium adsorption ratio (SAR) is defined as

$$\text{SAR} = [\text{Na}] / \left(\frac{1}{2} [\text{Ca} + \text{Mg}] \right)^{1/2}$$

Where concentrations are in mmol l^{-1}

This was calculated using the Na, Ca and Mg data from the 1:5 aqueous extract, and so will be referred to in the text as $\text{SAR}_{1:5}$.

With regard to soil structural instability caused by sodicity, Rengasamy (1999) concluded that the major factors influencing clay dispersion are the SAR and EC of the soil solution, and developed a predictive model using these parameters. Figure 3.6 is based on this model. A high electrolyte concentration in the soil solution counteracts the effects of sodicity, but the sensitivity of plants to salinity means that plant growth suffers with increasing salinity.

The parent material of the North Kent Marshes is marine alluvium, and was assumed to be a natural analogue for the Thames dredgings. Widespread under-drainage was introduced in the early 1960s, leading to the development of sodicity over large areas of land within a decade. Drainage allowed the soluble salts to leach out, and this in turn caused soil deflocculation and soil structure deterioration (Hazelden et al. 1986).

In the past soils have been defined as sodic or non-sodic according to some critical value of the exchangeable sodium percentage (ESP) of a soil, where $\text{ESP} = (100 \times \text{Exchangeable Na}) / \text{CEC}$ (cation exchange capacity). American workers have traditionally regarded 15 as the critical value, while Australian and South African workers have used 5 or 6. More recently, workers in the field (e.g. Sumner, 1993) have concluded that sodic soils are better defined by their behaviour than measures of their composition.

The model developed by Rengasamy (Figure 3.6) and the figures derived using Shaw's equation for the conversion of $\text{EC}_{1:5}$ to EC_{SE} are predictive of plant

performance and soil conditions on the experimental site, but to a limited extent. The soil structure is poor in the group of samples with high SAR and low EC which are labeled “potentially dispersive”. Field notes made during the establishment of the field trials ranked germination rate and subsequent plant growth in the Blocks in the order 4 > 2 > 3 > 5 > 1. Modelled values for EC_{SE} are, however, far too high to be a realistic reflection of conditions in the root zone of the plants. Mesophytes are physiologically incapable of tolerating these levels of salinity, and plant growth was good on all Blocks.

Shaw (1999) and Rengasmay (1999) were working with natural soils, where problems with salinity had evolved over time due to vegetation clearance and irrigation for agriculture. Marine alluvium is the result of slow accretion of material over time. The use of methodologies devised for these types of soils to assess salinity and sodicity in material recently removed from a confined disposal facility and in the process of ripening does not, in retrospect, appear appropriate.

3.4. RESULTS B: CORE SAMPLES

The results from the experimental site samples and the concurrent literature search led to several hypotheses.

1. The strong positive relationship found between PTEs in the preliminary and experimental site samples were a result of processes occurring in the river. Similar relationships would be found between these elements in all lagoons and at all lagoon depths.
2. A conventional mineral soil will normally have around 1-6% organic matter (Brady, 1990), in the topsoil, and a much lower figure in the subsoil. The organic matter content of the dredgings is much higher. This led to the hypothesis that the organic matter is in a form where it is protected either physically or chemically from microbial decomposition. A review of the literature shows that though resistant organic matter is associated with anoxia, which mechanism or mechanisms are involved remains controversial.
3. As the lagoons were filled sequentially, lagoon depth can be regarded as a proxy for time. The results of the literature review on historical pollution in

the Thames suggested there would be a pollution gradient from the base of the lagoon to the top of the lagoon, reflecting temporal changes in contaminant loading.

4. The strong correlations between water soluble ions of marine origin Cl^- , K^+ , Na^{2+} led to the assumption that these ions were behaving conservatively. This led to the hypothesis that leaching efficiency of the dredged material was low, that salts were being retained within the profile, and that salt distribution in the material was the result of the depositional mechanism and complex weather mediated factors.

3.4.1. POTENTIALLY TOXIC ELEMENTS

Copper concentration in the core samples varied between 117 and 370 mg kg^{-1} oven dry silt, with a mean of $261 \pm 67 \text{ mg kg}^{-1}$. Zinc concentration varied between 488 and 1365 mg kg^{-1} , with a mean of $931 \pm 203 \text{ mg kg}^{-1}$. Figure 3.7 shows the variation in copper and zinc concentrations with lagoon depth, and is the result of plotting the mean values for copper and zinc for each core section against the mid-point of that core. For example, the mean of the three values for the core section from 0.5 m to 1 m was plotted against 0.75 m.

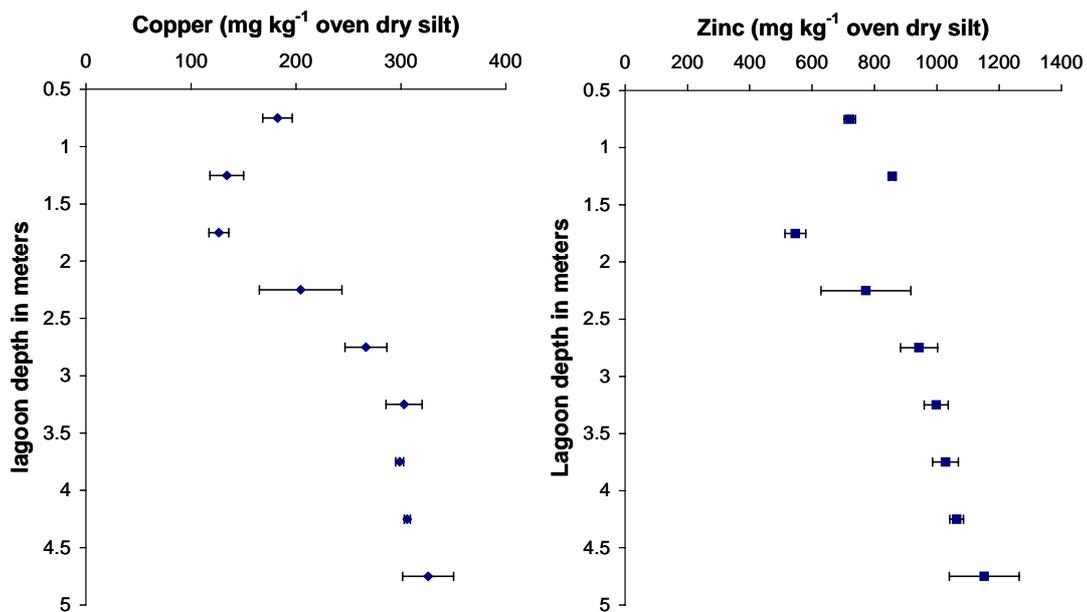


Figure 3.7 The variation of copper and zinc (mg kg^{-1}) with lagoon depth in the core.

Concentrations of both elements show a significant increase with depth. The mean copper concentration in the uppermost core section is $182 \pm 14 \text{ mg kg}^{-1}$. This increases to $326 \pm 24 \text{ mg kg}^{-1}$ in the lowest core section. Comparable values for zinc are $720 \pm 18 \text{ mg kg}^{-1}$ and $1152 \pm 112 \text{ mg kg}^{-1}$. The increase in metal concentration with increasing depth is not uniform. Concentrations show an initial decrease from the surface to the 1.5 to 2 m core section, where the lowest values are found, and increase thereafter. The distribution patterns of the elements show a marked similarity. The length of the error bars show that this similarity extends to within core variability. The only exception to this general pattern is in the 1 to 1.5 m core section, where copper shows a decrease and zinc an increase.

3.4.2. PARTICLE SIZE ANALYSIS

Figure 3.8A and 8B shows the variation in particle size distribution with lagoon depth in the core. Figure 3.8A shows the percentage composition of each particle size fraction on the X-axis, and the relative position of each sample on the Y-axis. B shows the same information on a soil triangle.

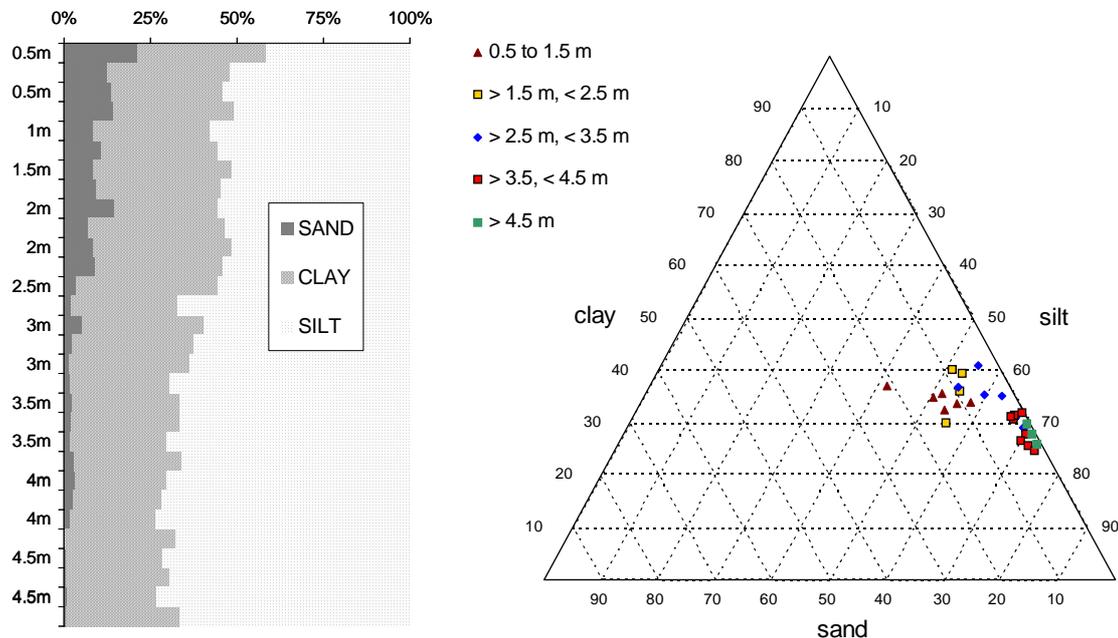


Figure 3.8A and 8B Variation in Particle Size Distribution with depth in the core.

The sand and clay fractions decrease with increasing depth in the lagoon. Mean sand content in the 0.5 to 1 m core section was 15.9 ± 4.8 %, decreasing to 0.7 ± 0.1 in the 4.5 to 5 m core section. Clay decreases from 35 ± 2.4 % to 27.9 ± 2.5 over the same depth. Silt, by contrast, increases with increasing depth, from 49 ± 6.7 % in the uppermost core section to 71.4 ± 1.9 at the base of the lagoon.

The grouping of data points in the soil triangle shown in Figure 3.8B illustrates the decrease in textural variability in core section samples occurring with depth. Samples from below three metres exhibit a much lower degree of variability than those from above three meters.

Copper and zinc in the core had a high negative correlation with the clay and sand fractions, and a high positive correlation with the silt fraction (Table 3.12). The correlation between both elements and clay was less strong than that for the other two size fractions ($p < 0.001$ for clay and copper; $p < 0.002$ for clay and zinc). There is a strong negative correlation between both the clay and sand fractions and the silt fraction.

Table 3.12 Correlations between Particle Size, Cu and Zn in the core.

Marked correlations are significant at $p > 0.0001$, $n = 30$.

	<i>Cu</i>	<i>Zn</i>	<i>Sand</i>	<i>Silt</i>
Cu	1			
Zn	0.96	1		
Sand	-0.83	-0.74	1	
Silt	0.81	0.73	-0.89	1
Clay	-0.55	-0.5	0.5	-0.84

3.4.3. C, N AND S CONTENTS

Sulphur, carbon and nitrogen all tend to increase with increasing depth in the lagoon, though the increase is not uniform, with the lowest percentages of all three elements occurring between 1.5 and 2 m (Figure 3.9). The distribution of these elements with lagoon depth is very similar to the distribution pattern for copper and zinc shown previously (Figure 3.7). Sulphur exhibits a much higher degree of variability within core sections than either carbon or nitrogen.

Table 3.13 shows the correlation coefficients for the relationship between copper, zinc, nitrogen, sulphur and organic carbon. There was no significant correlation between inorganic carbon and any of the measured parameters (data not shown).

Table 3.13 Correlations between Cu, Zn, N_{tot}, S_{tot} and C_{org}. Marked correlations are significant at p > 0.0001, n = 30.

	Cu	Zn	N _{tot}	S _{tot}	C _{org}
Cu	1				
Zn	0.96	1.00			
N _{tot}	0.92	0.89	1.00		
S _{tot}	0.69	0.67	0.71	1.00	
C _{org}	0.88	0.92	0.91	0.68	1.00
C:N ratio	-0.80	-0.69	-0.87	-0.56	-0.62

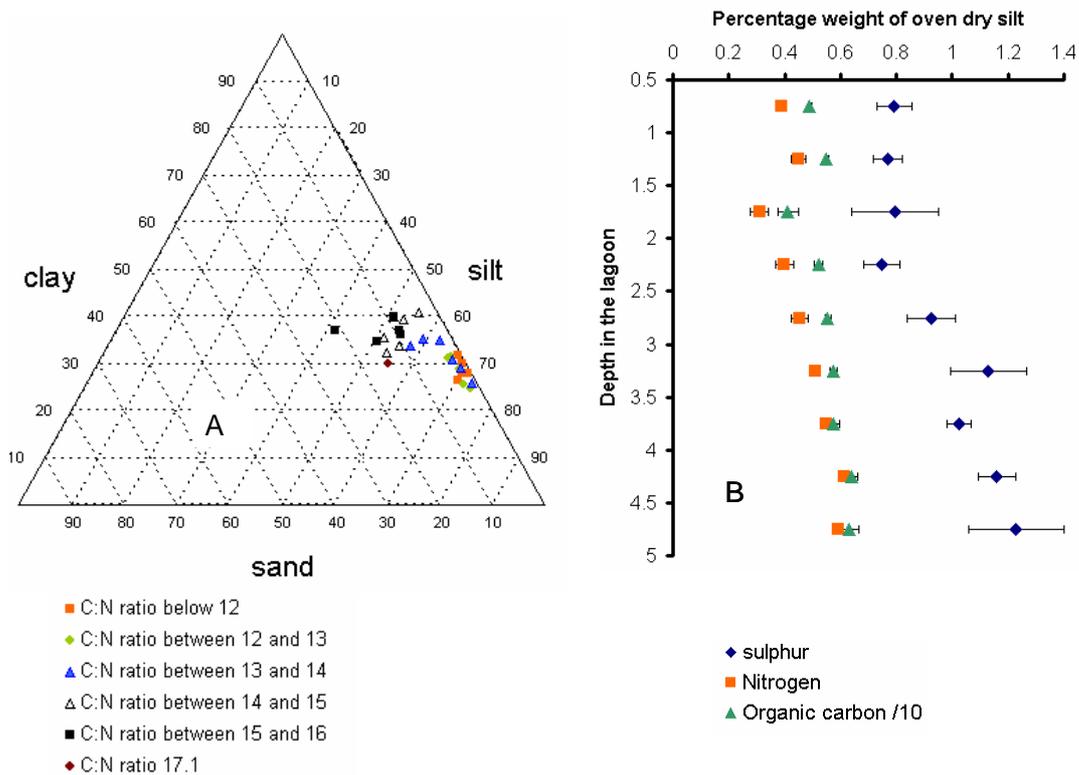


Figure 3.9 Relationship between C:N ratio and particle size and C:N ratio with depth in the core.

Figure 3.9 shows the relationship between C:N ratio and soil texture, the changes in C:N ratio with lagoon depth, and the variation in carbon, nitrogen and sulphur concentrations with lagoon depth. Samples with relatively high C:N ratios come from

the upper layers of the lagoon, and are comparatively heterogeneous with respect to soil texture. By contrast, samples with the lowest C:N ratios form a tight discrete group characterized by high silt and low sand content. The changes seen in organic matter with lagoon depth are not those that would be predicted by ecological theory. One would expect organic matter to decline with lagoon depth, due to progressive mineralization over time by micro-organisms, yet there is more organic matter in the dredged material in older deposits. Though nitrogen is generally preferentially mineralized in sediments, leading to a subsequent increase in the C:N ratio over time (Jørgensen, 1983), the data from the core showed that the lowest C:N ratios were associated with the deepest, and by inference oldest, material deposited. Organic matter fractions differ in their reactivity. The assumption is made in models of early diagenic processes in sediment that organic fractions with lower C:N ratios will decay faster (Wijsman et al. 2002). The oldest Rainham dredgings have low C:N ratios, and so would be expected to be labile.

The lagoons would certainly have been anaerobic, but this should not have precluded organic matter mineralization through fermentation and methanogenesis, which generally prevents the sequestration of large amounts of organic material in anaerobic ecosystems (Stanier et al. 1986). These considerations add weight to the hypothesis the organic matter is either being physically or chemically protected. The change in C:N ratio implies that a change has occurred in the quality of the organic matter with time.

The strength of the correlation coefficients for the relationships between nitrogen, sulphur, organic carbon, sand, silt and clay is given in Table 3.14.

Table 3.14 Relationship between C, N, S and particle size fractions. Marked correlations are significant at $p > 0.0001$, $n = 30$.

	N_{tot}	S_{tot}	C_{org}	Sand	Silt	Clay
N_{tot}	1					
S_{tot}	0.71	1				
C_{org}	0.91	0.68	1			
Sand	-0.82	-0.64	-0.64	1		
Silt	0.89	0.78	0.72	-0.89	1	
Clay	-0.72	-0.71	-0.61	0.50	-0.84	1
C:N ratio	-0.87	-0.56	-0.62	0.82	-0.85	0.64

3.4.4. CHLORIDE AND ELECTRICAL CONDUCTIVITY

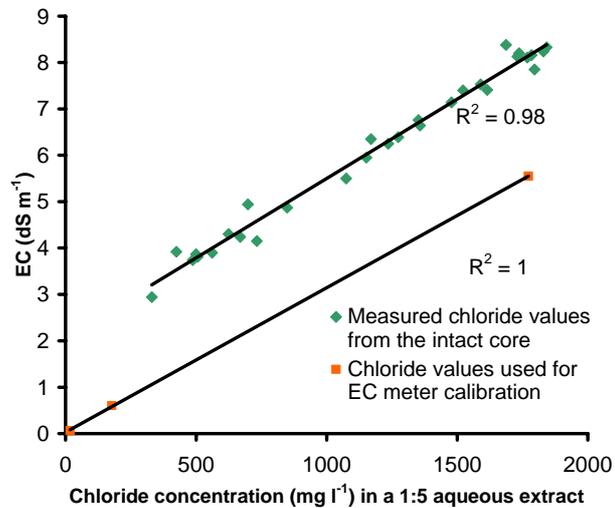


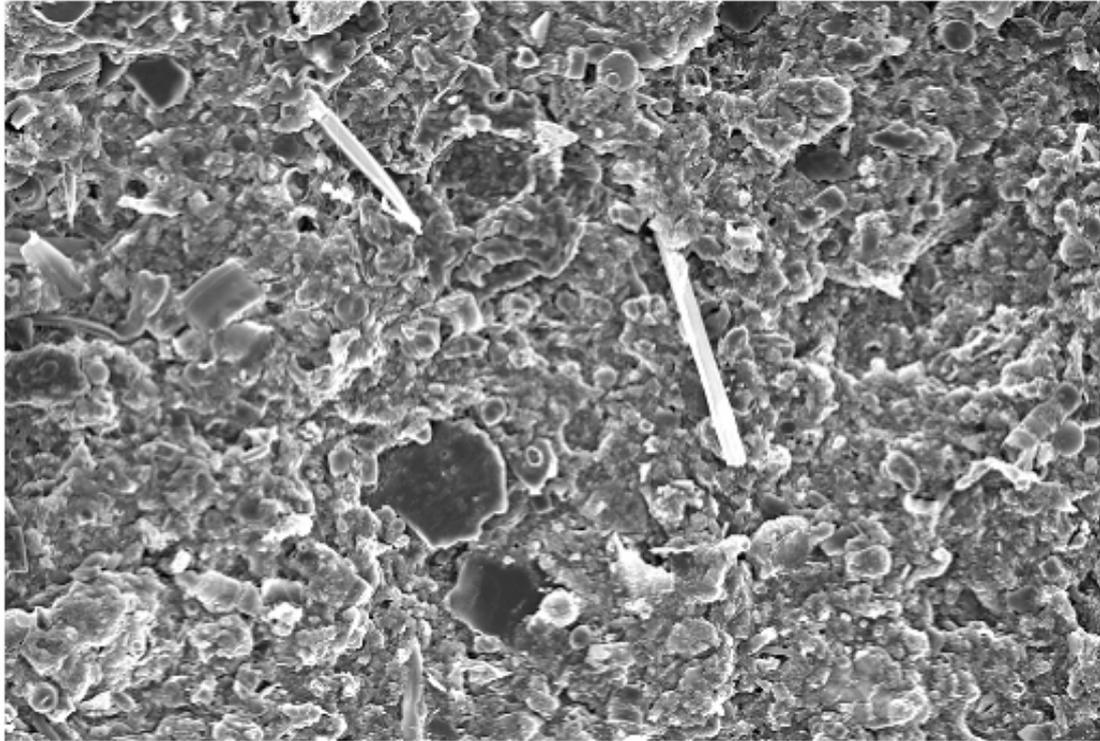
Figure 3.10 Relationship between chloride concentration and EC in the core.

Table 3.14 shows the relationship between chloride concentration and EC in the core, and shows that the resulting linear relationship runs parallel to the line produced when calibrating an EC meter. EC is a measure of all ions in solution, and the proportional contribution of chloride varies between 0.34 and 0.71. This suggests that what is being measured in the aqueous solution is chloride and some species with a constant EC of $\approx 2.1 \text{ dS m}^{-1}$.

3.4.5. SEM AND EDX ELEMENTAL ANALYSIS

SEM and EDX elemental analysis were carried out on core samples to see if the precise location of the PTEs could be determined. It was later established that this technique is unsuitable for that purpose, as the resolution at which EDX is carried out is not sensitive enough to pick up the relatively small quantities of PTEs present.

The SEM electro-micrographs show the extremely fine texture of the material, and the close association between organic and mineral matter. Figures 3.11-3.16 show elemental maps in a representative core sample. Fe is diffuse. Al, Si and Ca have more localized distributions, suggesting they are incorporated in discrete mineral phases. Sodium and chloride are strongly correlated.



200µm

Electron Image 1

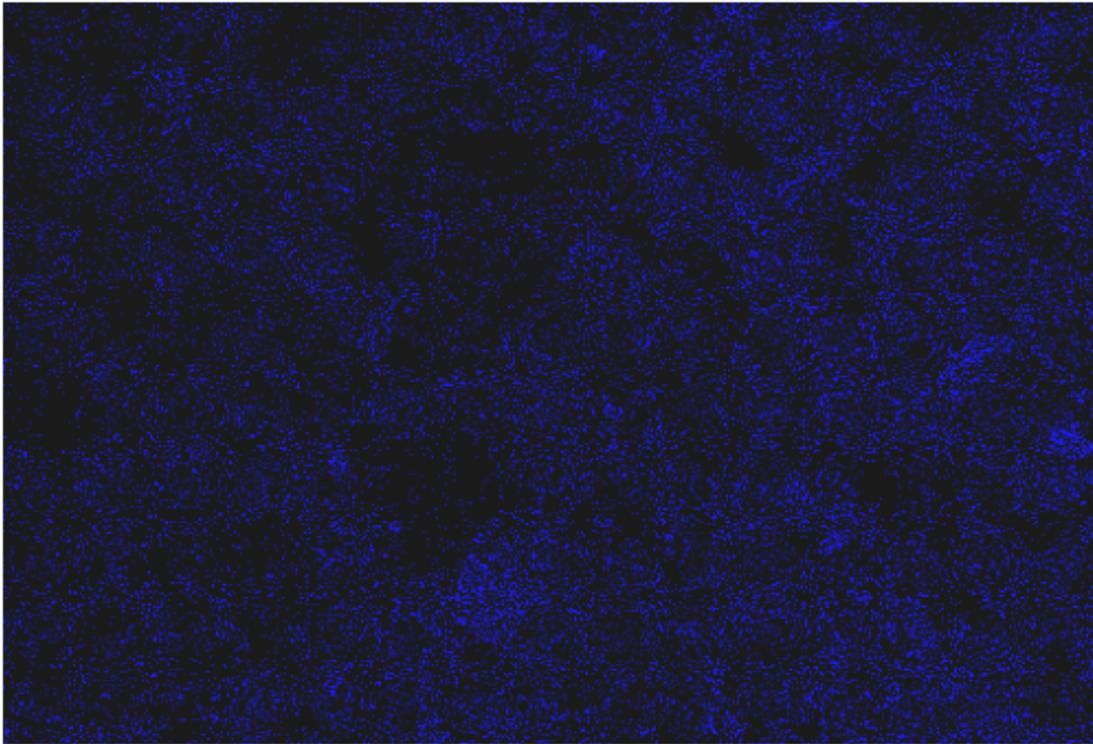


Figure 3.11 SEM-EDX elemental map of aluminium in a core sample.

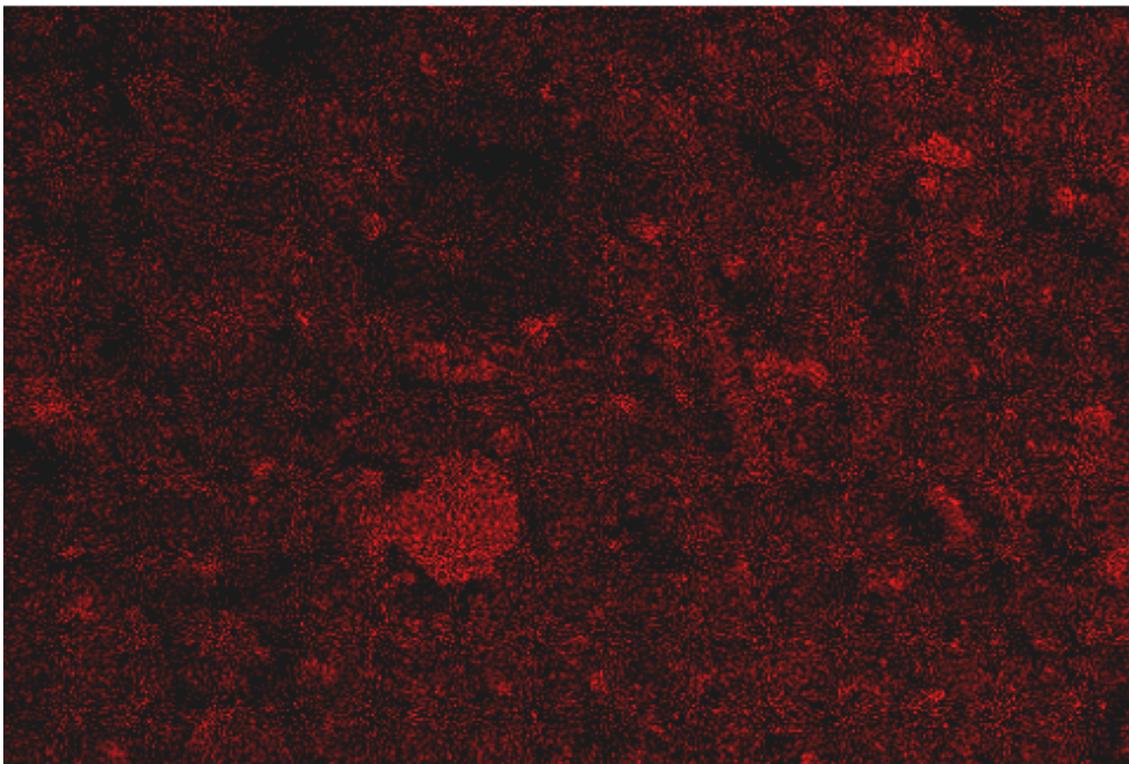
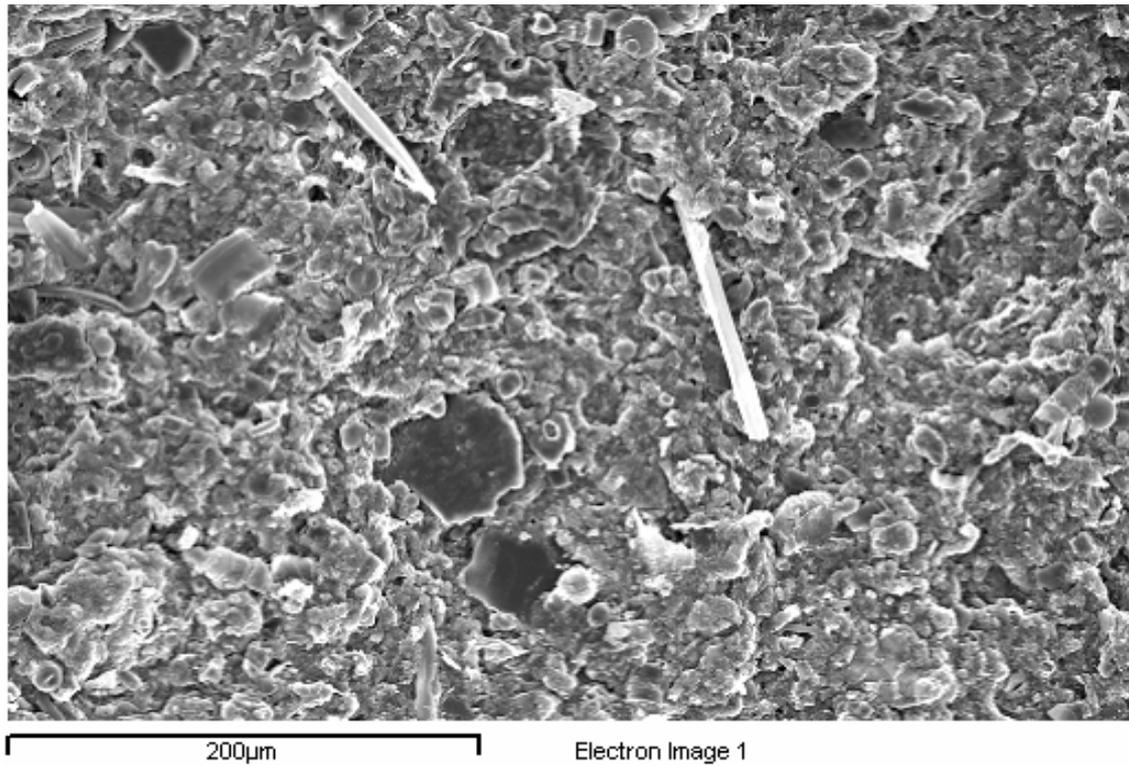
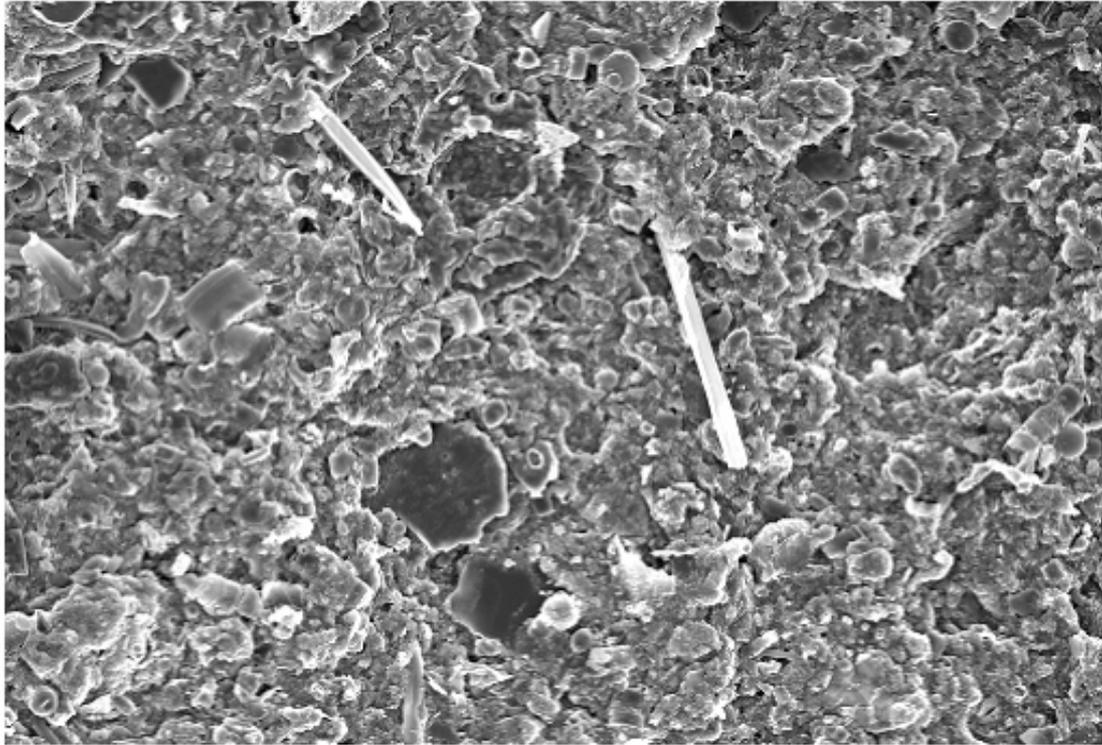


Figure 3.12 SEM-EDX elemental map of silicon in a core sample.



200µm

Electron Image 1

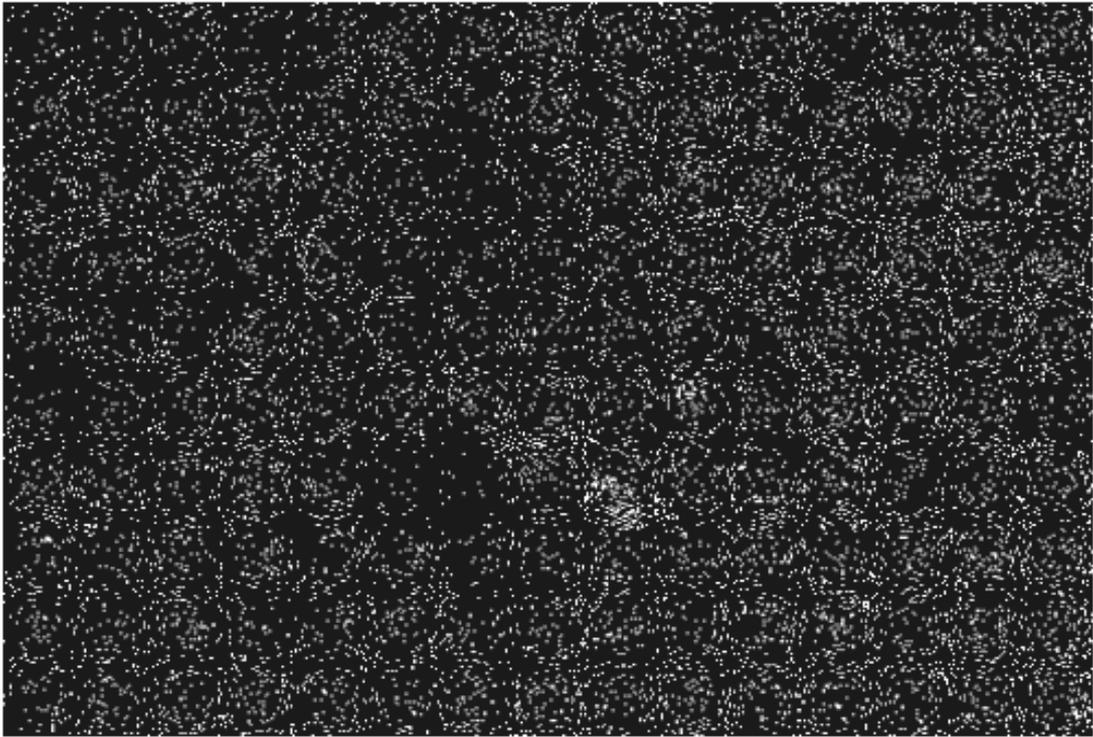
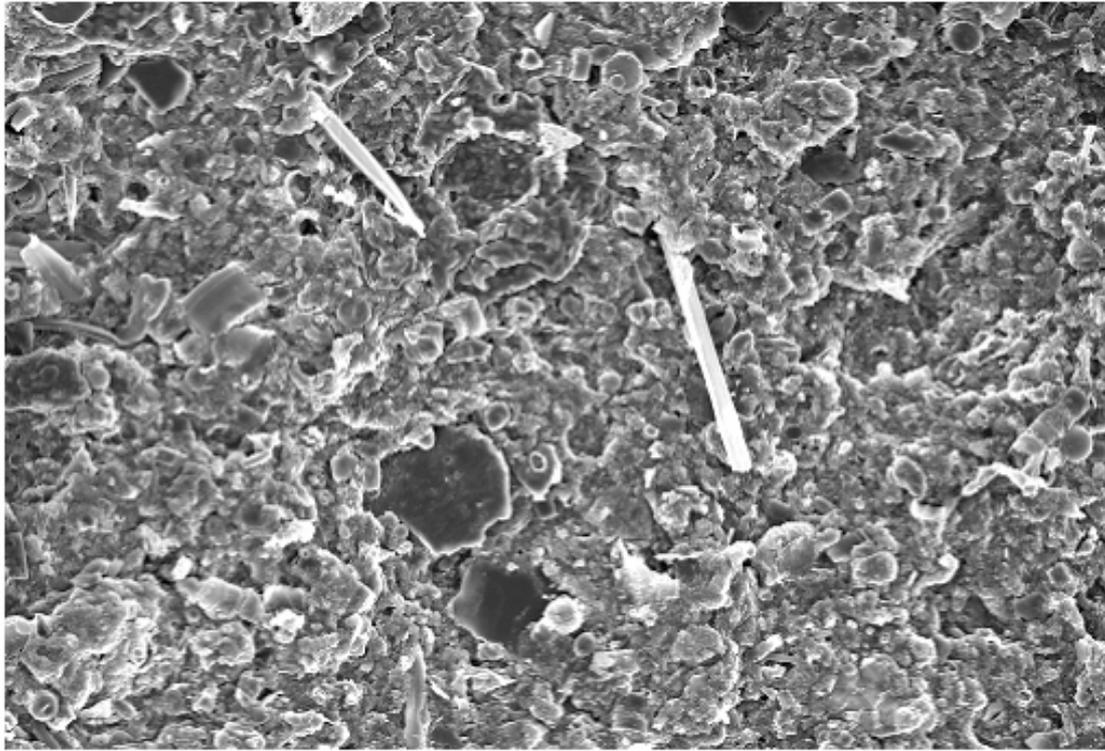


Figure 3.13 SEM-EDX elemental map of iron in a core sample.



200µm

Electron Image 1

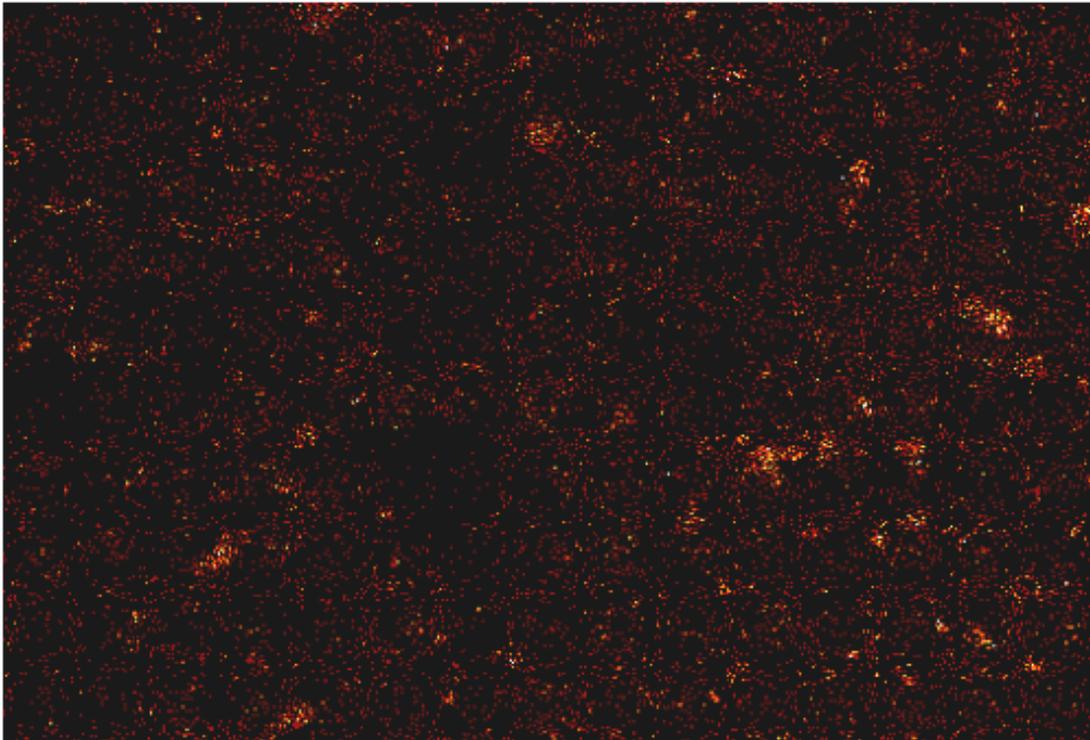
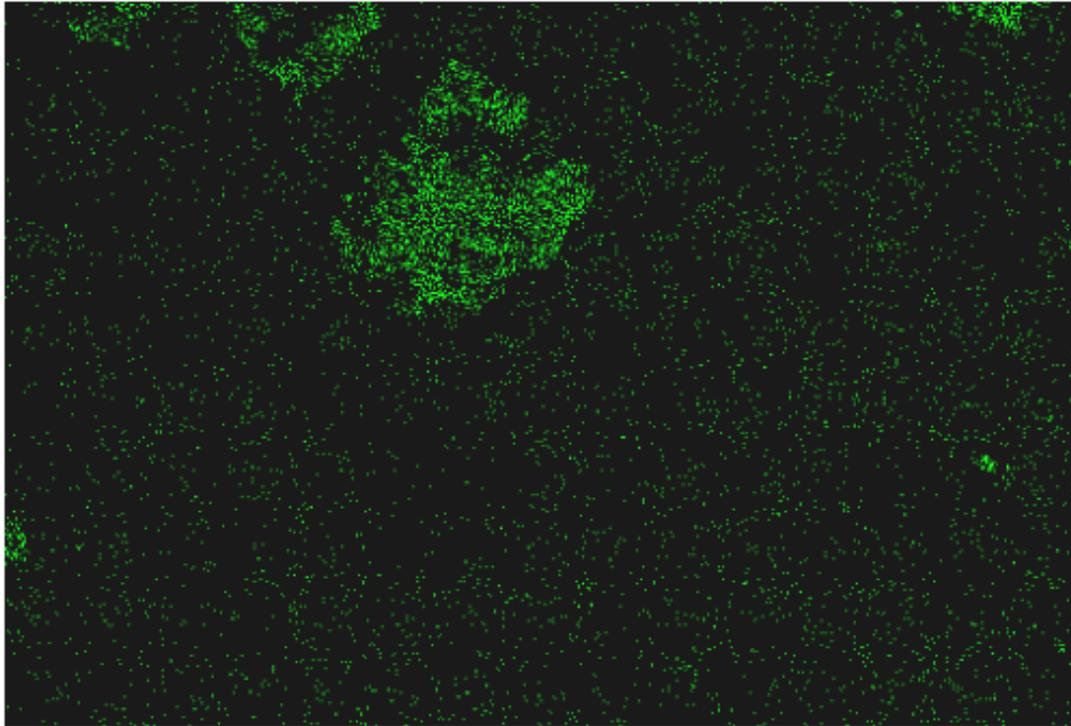
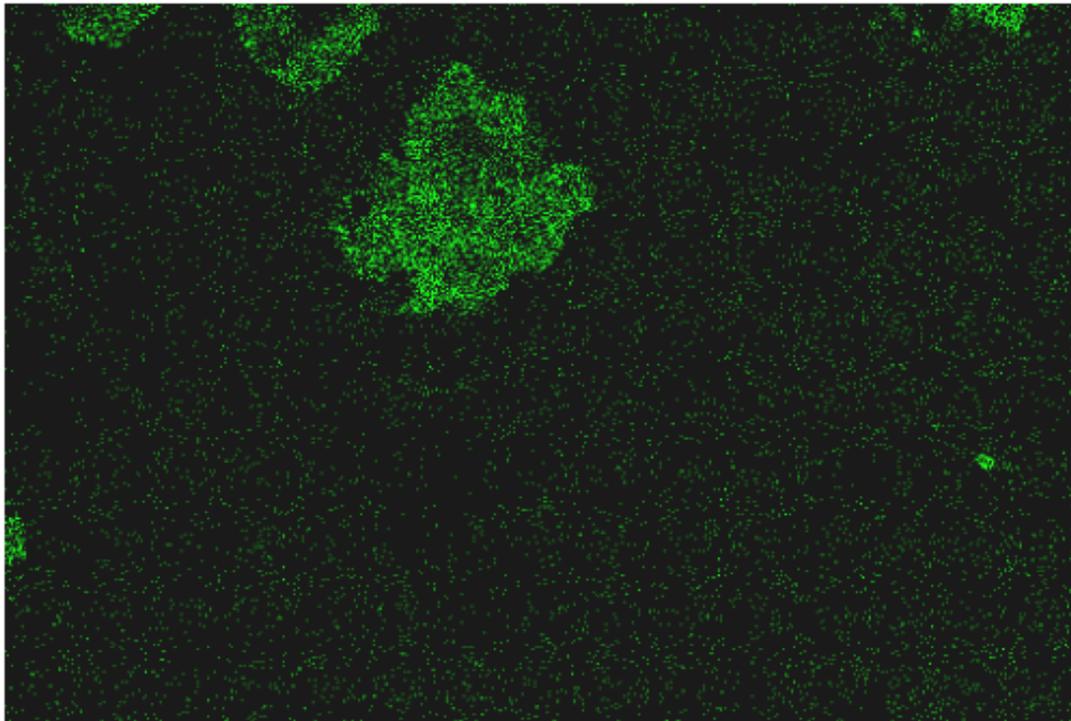


Figure 3.14 SEM-EDX elemental map of calcium in a core sample.



Sodium Ka1_2



Chlorine Ka1

Figure 3.15 SEM-EDX elemental map of sodium (top) and chlorine (bottom) in a core sample.

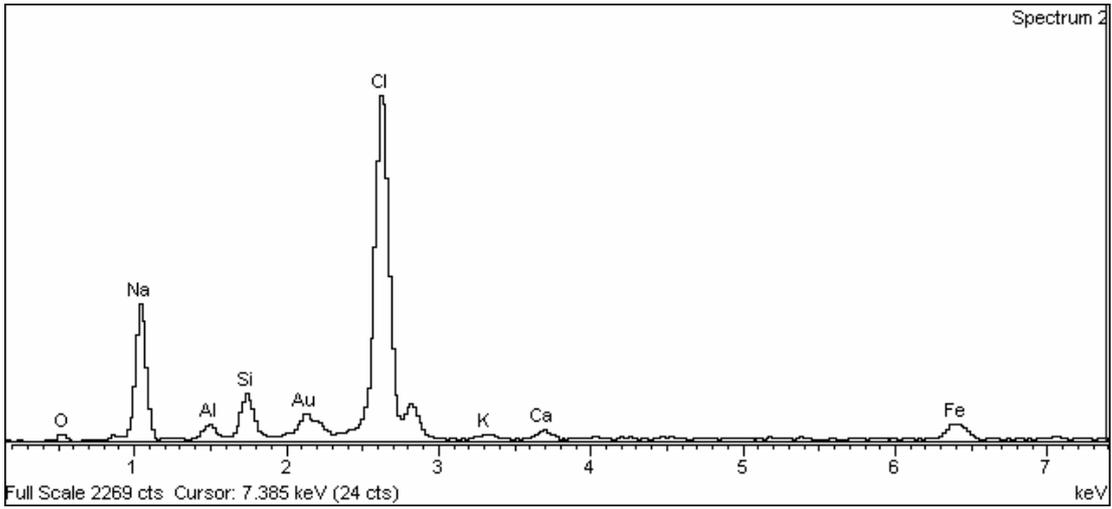
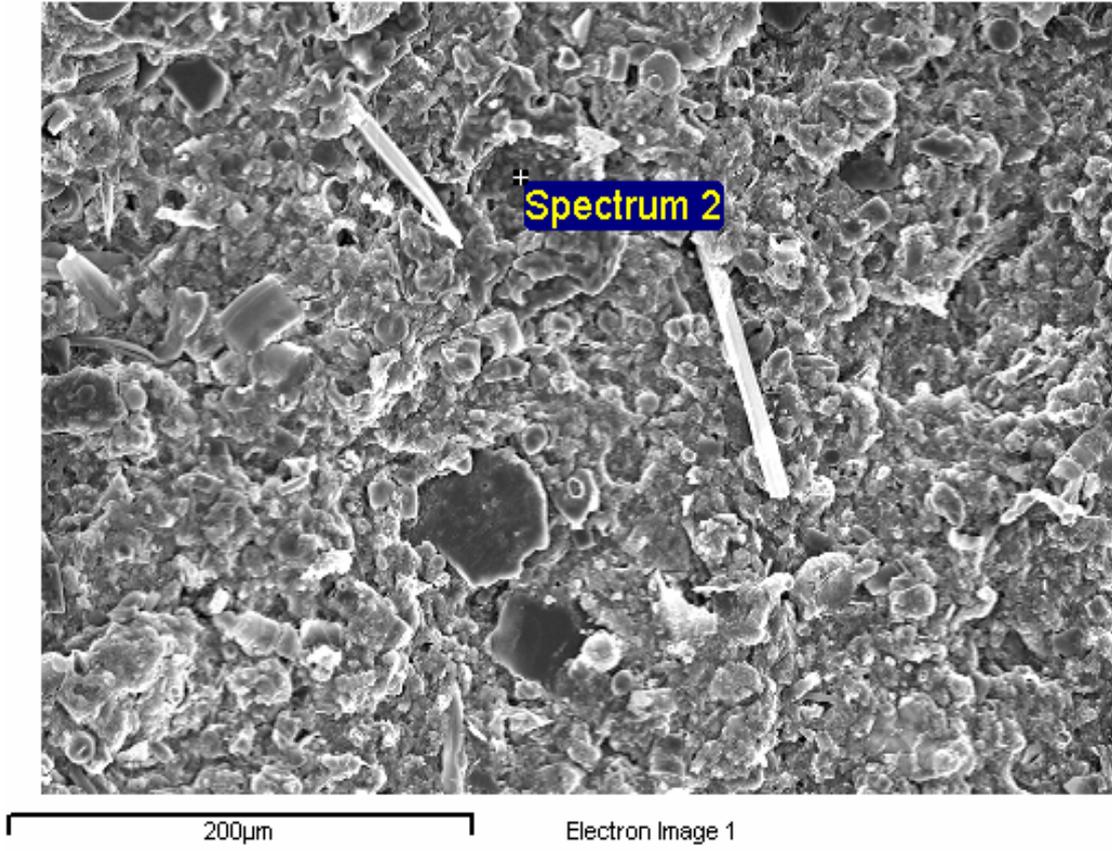


Figure 3.16 SEM-EDX spectrum of a salt crystal in a core sample.

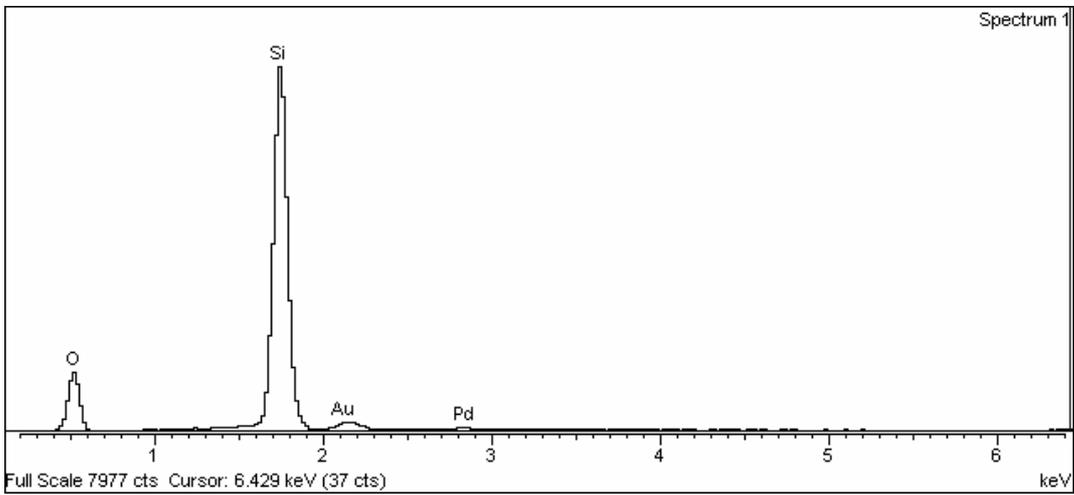
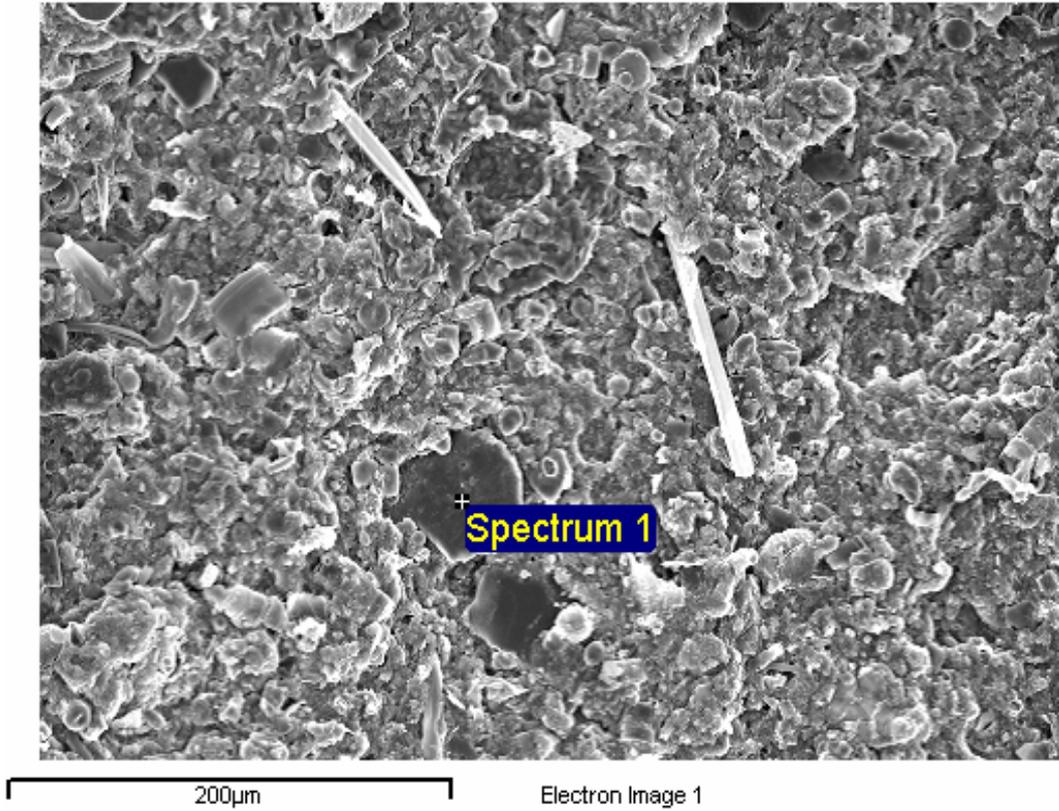


Figure 3.17 SEM-EDX spectrum of a quartz crystal in a core sample.

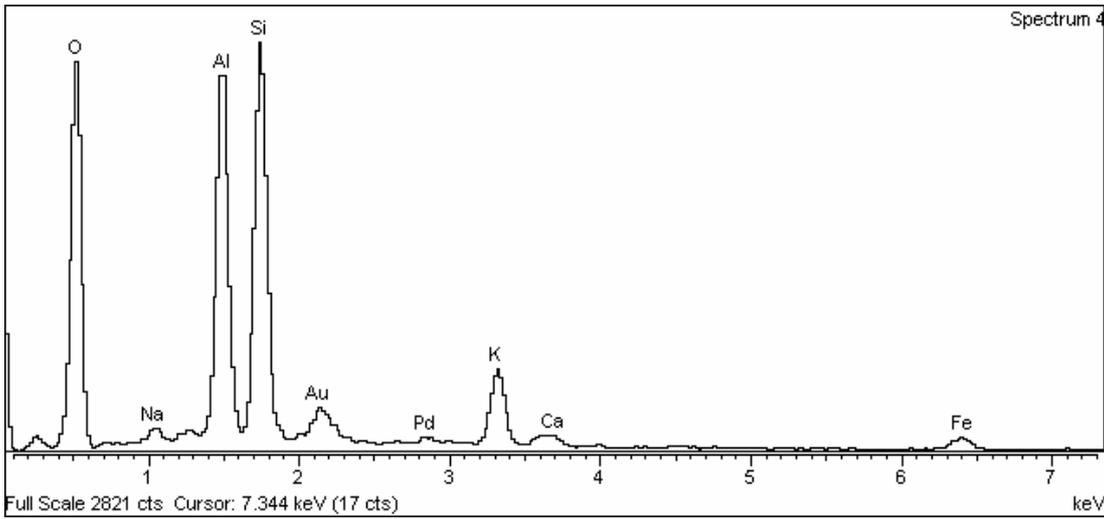
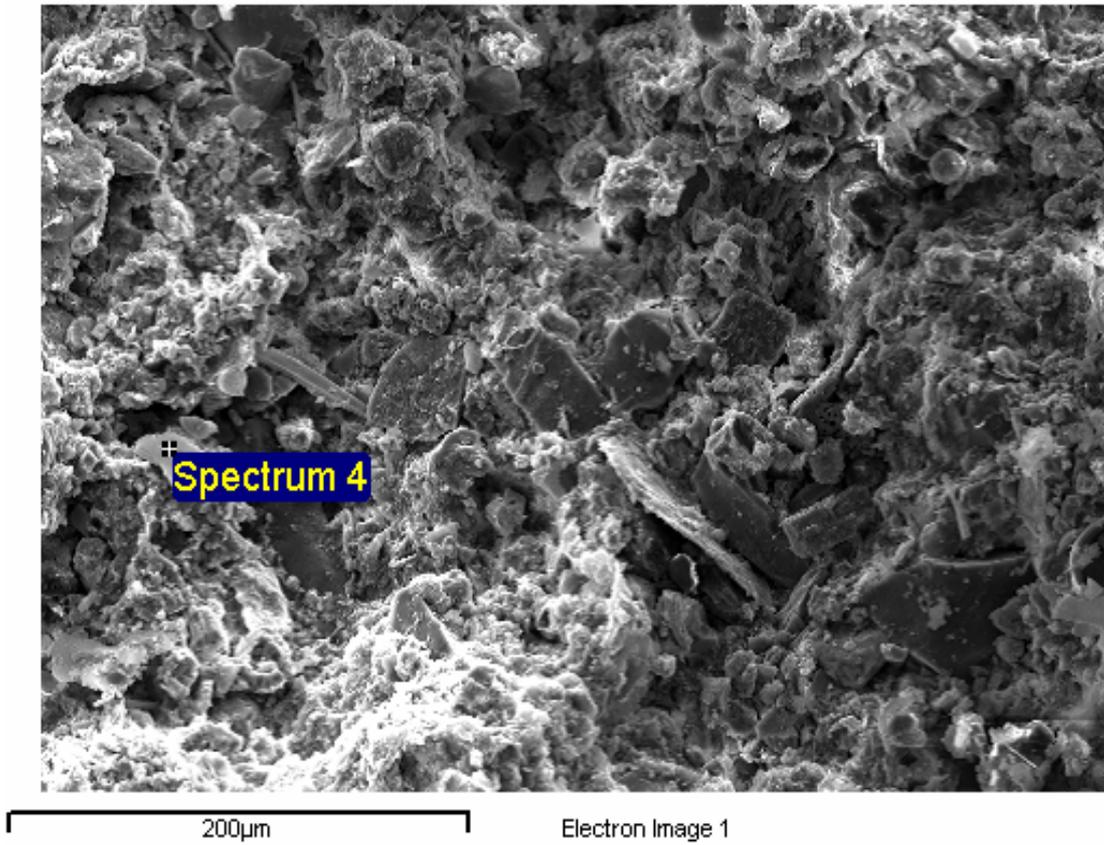


Figure 3.18 SEM-EDX spectrum of a clay particle in a core sample.

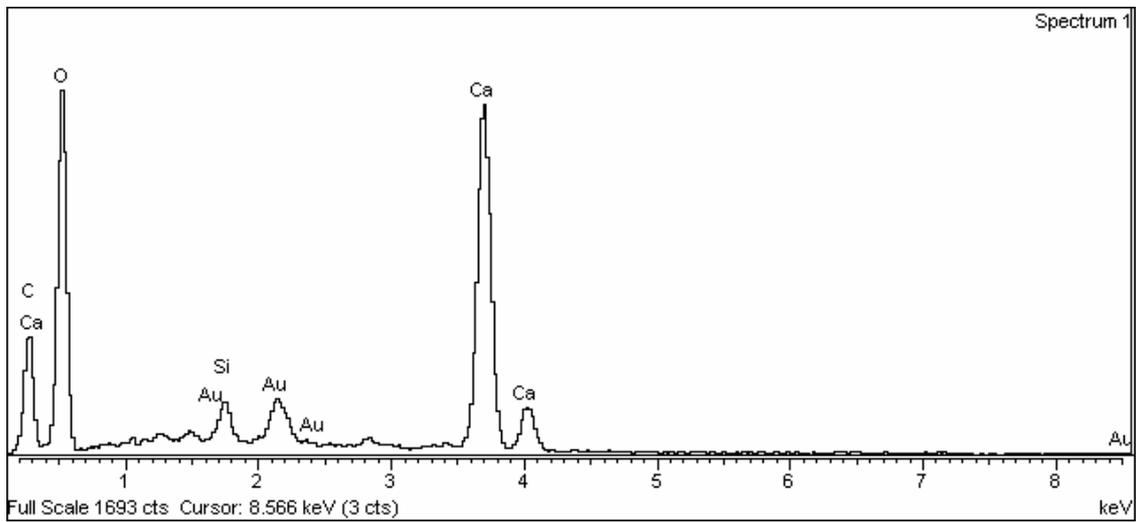
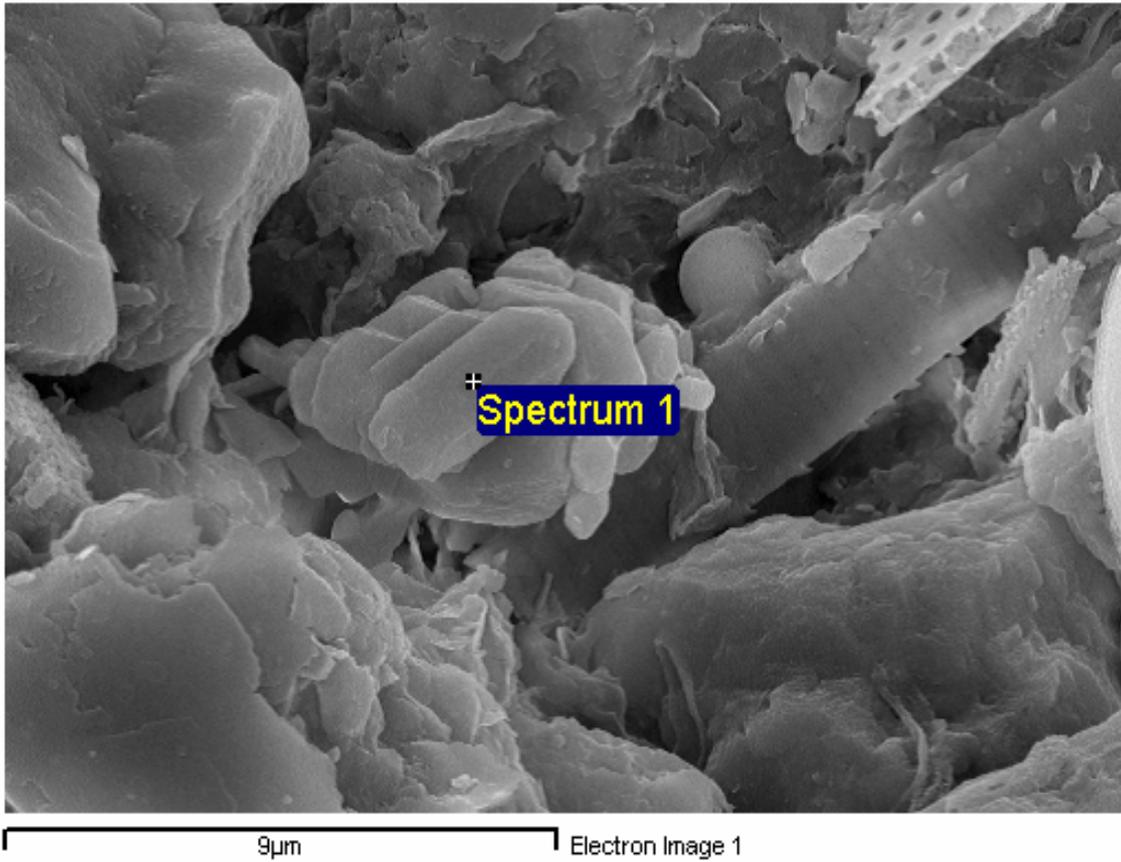


Figure 3.19 SEM-EDX spectrum of a calcite crystal in a core sample.

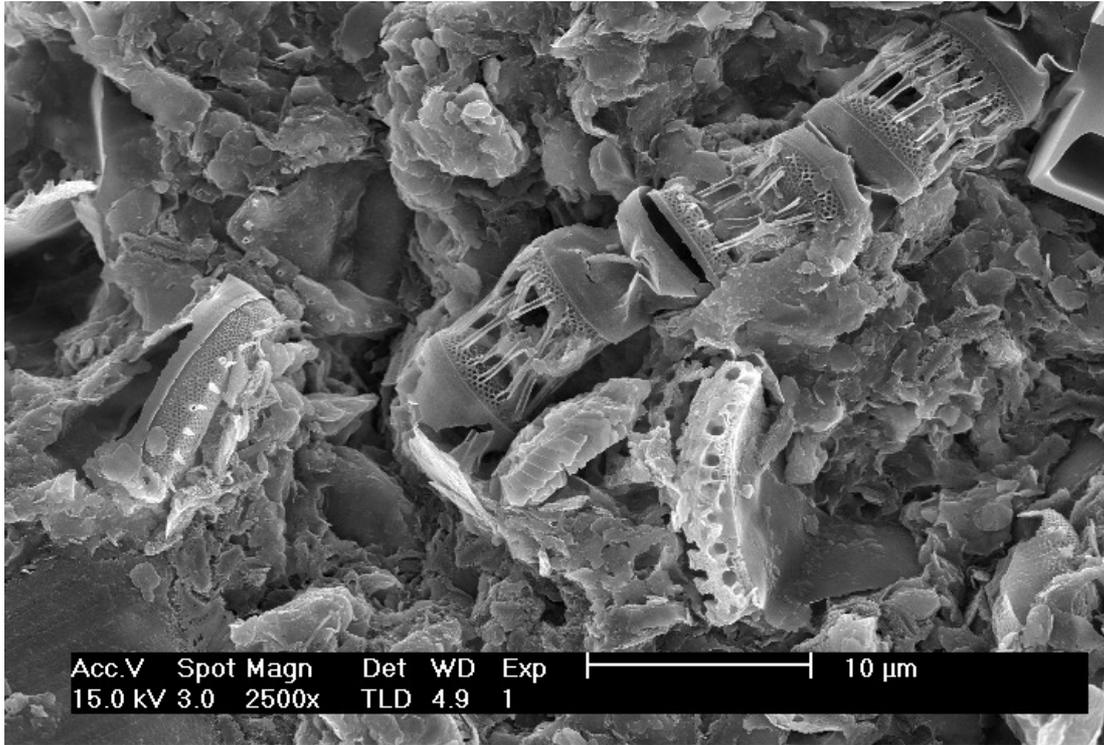


Figure 3.20 SEM electromicrograph of diatoms in a core sample.

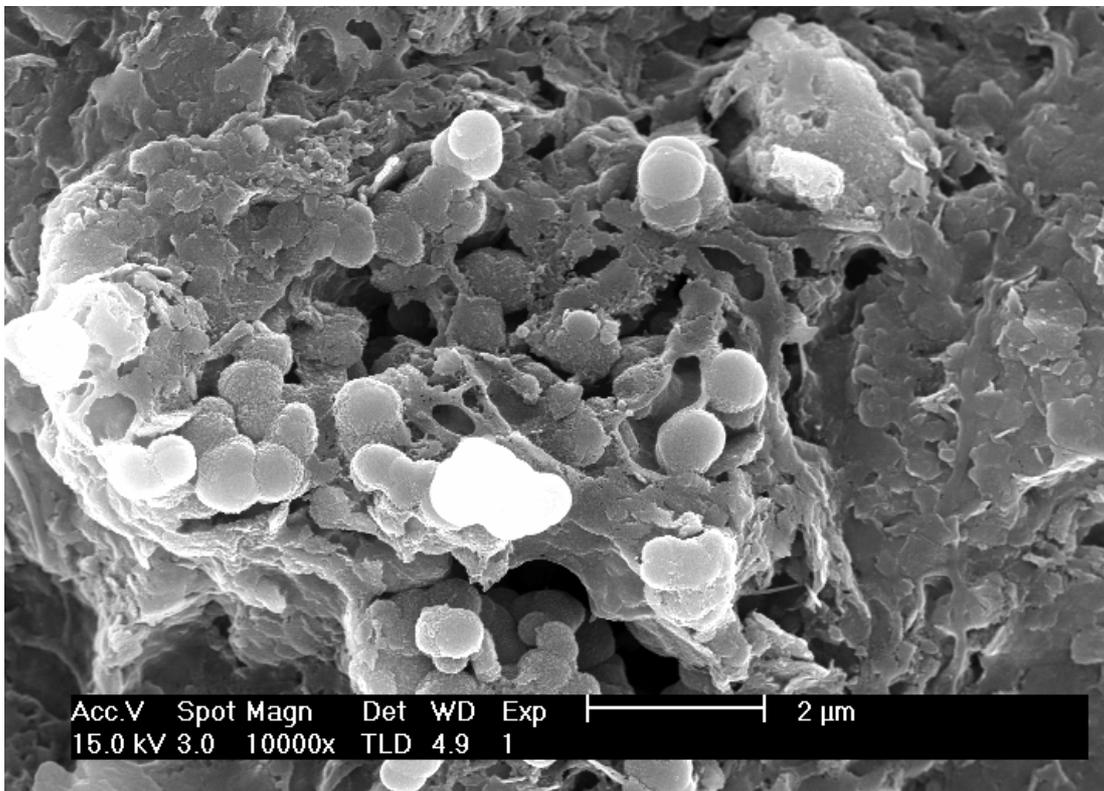


Figure 3.21 SEM electromicrograph of structures resembling mineralised coccoid bacteria from a core sample.

3.5. DISCUSSION

When results from the characterization of the core are compared with those from the experimental site samples, similarities and differences are apparent. Both sets of samples had common origins; their source is material dredged from the Thames and deposited in the Rainham lagoons. The core samples were removed, sealed, and preserved, so subsequent changes are the result of storage. The experimental site samples were removed, mixed, and spread over a porous substrate, on a site which had topographical relief. The main focus of this discussion will be on differences between the samples. The similarities will be described briefly, and dealt with more fully when they are integrated with the historical data and a wider literature review in Chapter 5.

3.5.1. WATER-SOLUBLE IONS, ELECTRICAL CONDUCTIVITY AND pH

The most obvious differences between the two samples are those in the relationship between electrical conductivity and chloride ions. In the core there is an almost perfect correlation between chloride and electrical conductivity. In the experimental site samples electrical conductivity is relatively poorly related to chloride concentrations ($r^2 = 0.39$), and the equations of the lines for the linear regressions are very different. In the core the equation of the line is $EC_{1.5} = 1.51 + 0.0009 [Cl]$, whereas for the experimental site samples it is $EC_{1.5} = 2.07 + 0.0007[Cl]$.

There is also a large difference in chloride concentration in the two sample sets. Concentrations of chloride ions in the core range between 1652 and 9211 $mg\ kg^{-1}$, with a mean of $5896 \pm 2568\ mg\ kg^{-1}$ whereas they are between 72 and 1741 $mg\ kg^{-1}$ with a mean of $738 \pm 398\ mg\ kg^{-1}$ in the experimental site samples.

Sodium, chloride, magnesium, boron, sulphate and potassium are conservative ions in sea-water, with constant ratios. These ions are highly correlated in the experimental site samples, but the ratios between the ions differ radically from the ratios found in sea-water. The source of these ions may not be marine, since sodium pentaphosphate is a common additive in detergents, boron is widely used in cosmetics and potassium

is common in most soils. What is unusual is that extraction by de-ionised water results in close correlations between the ions.

The following discussion suggests a possible reason for these differences in ions, and its implications for salinity and sodicity when the dredgings are used as a substrate. The discussion will begin with a probable explanation for chloride distribution within the lagoon.

Chloride concentrations are relatively high and variable in the 0.5 to 1 m core section. The lowest concentration is found in the 1.5 to 2 m core section, and increases progressively until a plateau is reached of around 8000 mg l⁻¹ in the 3.5 to 4 m core section (Figure 3.22).

3.5.1.1. VARIATION OF CHLORIDE DISTRIBUTION WITH LAGOON DEPTH

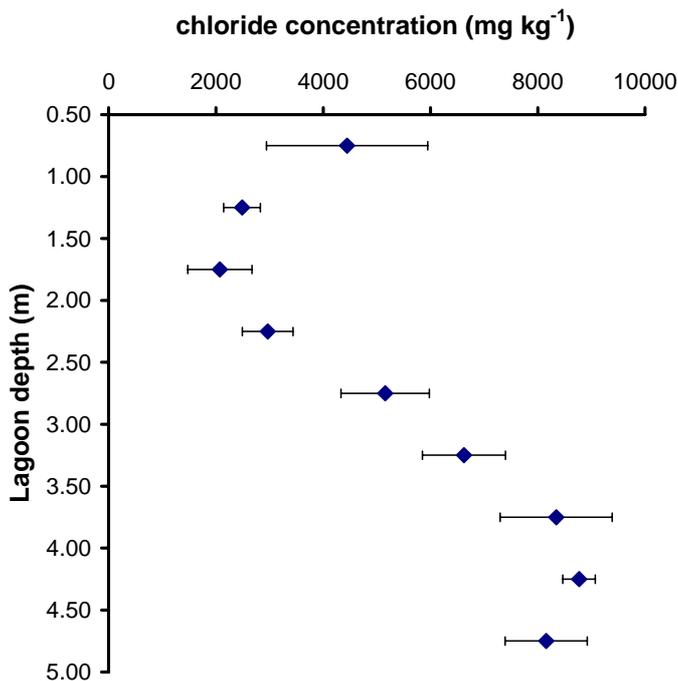


Figure 3.22 Variation in chloride concentration with lagoon depth. Error bars represent the standard deviation.

There was considerable tidal and seasonal salinity variation in the stretches of the river that the dredgings came from. Half-tide salinity was ≈ 500 mg l⁻¹ at low tide in January, and $\approx 9\ 000$ mg l⁻¹ at high tide in July ((Figure 3.23, Juggins, 1992). This

prohibits accurate calculation of the initial mean chloride concentration in the lagoons. Chloride makes up 55.3% of sea-water salinity, and silty clay loams have a total porosity of 45% (Hall et al. 1977), so it is possible to say that initially maximum chloride concentrations would have been around 2000 mg kg⁻¹, and the bulk of the material much lower. The disposal method is likely to have led to salt distribution being fairly homogenous during the period when the lagoons were being filled.

The clay banks are five metres high, presenting a large external surface area for evapotranspiration. The presence of *Phragmites australis* on the lagoons shows that impeded drainage has created a permanent perched water table near the top of the lagoon, so the chloride is present in solution. Typical values of saturated hydraulic

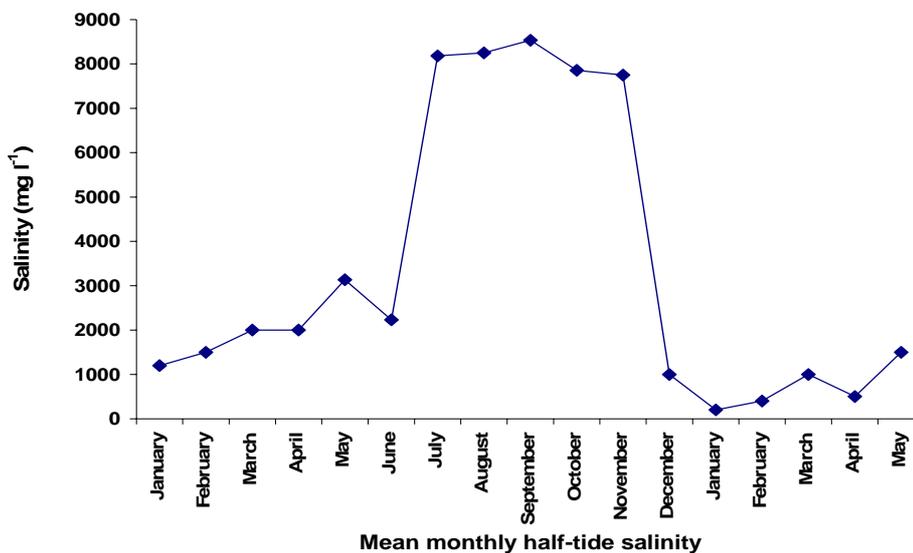


Figure 3.23 Mean monthly half-tide salinity at Coldharbour Point for the period January 1985 to May 1986 (data from Juggins, 1992).

conductivity for clays are 0.06 cm h⁻¹, compared to 0.15 cm h⁻¹ for a silty clay loam. Differences in water potential between the lagoon banks and the atmosphere may lead to higher rates of Ks through the clay walls than those quoted in the literature.

Clay forms an impermeable barrier to dissolved NaCl such that it may be used in reverse osmotic water purification systems (Liangxiong et al. 2003). This would lead

to preferential loss of water and retention of salt. This is likely to be the explanation for the concentration of salt at the base of the lagoon.

Rainwater entering the lagoon during the winter will create a hydraulic head of freshwater. Water movement is predominately horizontal under conditions of saturated flow. Diffusion from the saline body of water into the overlying freshwater body, with the constant seasonal addition of freshwater explains the linear decrease in the lagoon between 2 and 3.5 m.

The chloride pattern in the 0.5 to 2 m strata of the lagoons has a different origin. The establishment of *Phragmites*, which is deep-rooting, will have both increased the depth that water is removed from and water removal rates over those for abiotic capillary rise and evaporation from the sediment surface.

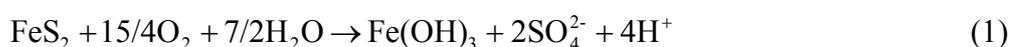
The increase in chloride in the upper strata is likely to be the result of a weather-mediated pattern of precipitation carrying soluble salts down the profile in winter and evapotranspiration drawing them up from the perched water table in the summer. Armstrong et al. (1996) have demonstrated a seasonal pattern of salinity in the marine alluvium of the North Kent marshes caused solely by capillary rise. Increased pumping by vegetation will lead to higher quantities of dissolved salts in the water becoming concentrated in the upper part of the profile.

3.5.2. EC AND WATER SOLUBLE IONS (CORE)

The main components of electrical conductivity in the core are probably due to Cl^- and SO_4^{2-} formed in pyrite oxidation. Sulphide minerals are generally unstable in the presence of oxygen and water (Keith and Vaughan, 2000). They break down and release any PTEs associated with them when they react with water to generate acidity. The acidity generated can break down other minerals present, causing them to release their associated PTEs. The most common metal sulphide present is generally pyrite. Pyrite oxidation occurs very slowly as a purely chemical reaction, but the rate is increased significantly when bacteria are present. *Thiobacillus ferrooxidans* promotes

the oxidation of Fe(II) and other sulphides, *Thiobacillus thiooxidans* oxidises sulphide to sulphuric acid.

In calculations of the acid producing potential of a soil, the assumption is made that all S is present as FeS₂, and is oxidised by reaction (1). When CaCO₃ is present in the soil, acidity is neutralised by reaction (2) and the calcium and sulphate ions form gypsum (CaSO₄·2H₂O). Gypsum is a sparingly soluble solid, and saturated gypsum solutions have an EC of 2.2 dS m⁻¹ irrespective of soil water ratio (Shaw, 1999).



The data in Figure 3.10 are probably affected by sample preparation. Air drying and sieving the soil would have exposed the sulphide to oxygen, and the addition of water would have caused the chemical reaction with carbonates described above. Measures of electrical conductivity in the core samples result from the rapid oxidation of pyrite and the retention and measurement of all chloride held within the soil matrix.

Even though the soil had been air dried and ground, the pH of the 1:5 extracts from both the experimental site and core samples ranged from 6.21 to 7.5, with a mean of 6.8 ± 0.28. It is difficult to imagine any environmentally realistic situation where such extreme oxidation of the dredgings would occur, so this suggests that the neutralizing capacity is sufficient to prevent PTE mobilization caused by pyrite oxidation induced acidity.

3.5.2.1. EC AND WATER SOLUBLE IONS (EXPERIMENTAL SITE SAMPLES)

As discussed above, removing anaerobic dredgings from a poorly permeable lagoon and spreading them over a porous substrate is likely to result in pyrite oxidation. The average sulphur content of core samples is 0.98 ± 0.25% dry weight with a minimum of 0.64%. The average inorganic carbon content is 1.22 ± 0.15% dry weight. Sulphur and inorganic carbon contents of the experimental site samples are smaller, at 0.5 ±

0.08% and $1.13 \pm 0.27\%$ dry weight respectively. The sulphate ion is not strongly retained in soils, and carbon dioxide will be degassed, so these differences suggest that pyrite oxidation has occurred after the dredging were deposited on the experimental site, and that the sulphate and carbon dioxide reaction products have been lost from the system. The comparatively low levels of chloride in the experimental site samples suggest that chloride, another mobile anion, has also been leached.

Since the healthy growth of mesophytes on the experimental site is incompatible with the high level of salinity suggested by the measures of electrical conductivity, EC measurements are probably the result of the concentration and localization of the water soluble electrolytes as ped cutans, and their subsequent solubilisation in the water used to extract the ions. There are visible ped cutans on the experimental site. These are of different thicknesses, occurring as a fine white powder or as a thicker white precipitate. They are likely to be mixed phases of water-soluble ions, with the identity of the ions dependent on the pedogenic processes that the individual sample had gone through.

Leaching of solutes can only occur through pores in which there is moving water, and most of the soil matrix is protected within peds (Leeds-Harrison and Shipway, 1984). Solutes held within the peds are protected until they diffuse to the ped surface (Addiscott, 1984). This implies that more solute leaching will occur on parts of the site where drainage, either by virtue of topography or because the material has been subject to less compaction, is more rapid. In summer, solutes and oxidation products will be partially leached by rapid infiltration during rain events. In winter more prolonged showers lead to a rapid reduction in hydraulic conductivity with ponding and run-off in low-lying areas and areas that have been compacted.

Pyrite is stable under anoxic conditions (Preda and Cox, 2000). The low porosity of the dredged material, coupled with well-developed cutans means that oxygen transport into ped interiors will be a function of ped size, and that those samples where smaller peds have formed will have lower chloride contents and higher

contents of pyrite oxidation products. Weathering of pyrite-bearing acid rock and acid soil is well studied. Common secondary minerals formed when pyrite oxidises under natural environmental conditions are jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) (Preda and Cox, 2000) and natrojarosite ($\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$). It is possible, given the high concentrations of potassium in the water-soluble ions, that jarosite may be present as a secondary mineral phase.

3.5.3. PARTICLE SIZE ANALYSIS (CORE)

There has been a striking change in the relative abundance of different size fractions over time. The fine lamination of the material in the core shows that no post-deposition disturbance has occurred. Changes in the particle size distribution pattern in the lagoons must therefore reflect changes in the relative abundance of different size fractions in dredged sediments during the period the lagoons were being used.

Since the two main sources for the mineral component of sediment in the affected reaches are fine material from terrestrial run-off and coarser material from the sea, a decrease of inputs from the river or an increase in inputs from the sea could have led to these changes. Such a change may have occurred after 1976, when work on the Thames Barrier began, but is unlikely before then. Inglis and Allen (1957) suggested that the navigation channel to the Royal Docks had altered sediment transport in the river by creating a current that carried marine sediment upstream. The Royal Docks remained open until 1982, so the navigation channel would have been in place for the entire period of utilization of the lagoons.

Juggins (1992) studied changes in diatom populations along a transect of the Thames estuary in 1985 and 1986. The peak in allochthonous diatoms from shallow marine environments is roughly coincident with the peak in suspended sediment found by Inglis and Allen (1957). If the assumption is made that diatoms in suspension behave in more or less the same way as sedimentary particles, this can be interpreted as further proof that no great change in sediment transport pattern occurred during the period when the lagoons were being filled. All the evidence that suggests that marine

and terrestrial sediment inputs to the reaches the dredgings came from were more or less constant during the relevant period.

Changes in the silt fraction have been noted elsewhere in the Thames. O'Reilly Weise et al. (1997) characterised cores from Tilbury basin, some twenty kilometres seaward of the sewage outfalls. Since dredging was discontinued in the Tilbury Basin after 1965, they were able to date these cores to pre and post 1966 by using dredging data. They comment that in the lower core sections a positive correlation ($r = 0.55 - 0.88$) was found between Ag, Cd, Cu, Hg, Pb and Zn and between most metals, percentage volatile solids, percentage silt and total organic carbon. They attribute these relationships to an increase in sand in the middle of the lower core sections. They found only weak correlations ($r = 0.11 - 0.26$) between these factors in the upper core.

In their study of disposal sites for dredgings from the Scheldt, Vandecasteele et al. (2002) found highly significant decreases in both the silt fraction and the organic matter content over time. Percentage silt dropped from a mean of 53.7 to 49.7, and percentage organic matter from 8.6 to 7.6 before and after 1965. This was possibly associated with a reduction in organic pollution in the river. The mean annual dissolved oxygen concentrations in the Scheldt were at their lowest at the Dutch/Belgium border between 1970 and 1980, and have since increased (Zwolsman et al. 1996).

The most important change in inputs to the Thames over time was the decrease in organic matter inputs from the sewage outfalls, and the consequent increase in dissolved oxygen. I suggested in Chapter 2 that the precise correlation of the variation in silicate/sesquioxide ratio with the zone of intense microbial activity in the WPRL data and the position of the diatom bloom was evidence for the dissolution of silicate minerals. If this suggestion is correct, the tight grouping of the samples in the bottom three metres of the lagoon can be interpreted as representing the time period when silicate dissolution was most intense. The marked increase in sand and more

variable texture in more recent deposits may show a switch towards seasonal silicate dissolution as the oxygen status of the river improved.

Though the Thames no longer suffers from chronic anoxia, other rivers do. The best studied of these is the Scheldt, which shares many features with the Thames. Decomposition of organic matter in the Scheldt still leads to anoxia in the water column. The affected zone may be as long as 30 km during summer (Zwolsman et al. 1997). The finest sediments in the Scheldt occur in the maximum turbidity zone, between the city of Antwerp and the Dutch border, where dissolved silicate has been shown to have a maximum (Zwolsman et al. 1997).

3.5.4. ORGANIC MATTER AND POTENTIALLY TOXIC ELEMENTS

Though the two sample sets share the same correlation between PTEs and N, they differ in their relationship between PTEs and organic carbon. The correlation between nitrogen and metals is much higher in the experimental site samples than the correlation between carbon and PTEs, whereas there is little difference in the correlation between organic carbon and nitrogen and PTEs in the core samples. The field site is now vegetated, so there will now be two organic matter pools, one historic and one current. Terrestrial plant C:N ratios vary from 20:1 to 30:1 in legumes to 100:1 in strawy residues. It follows that organic residues entering the soil are likely to contain large amounts of carbon and comparatively small amounts of nitrogen, so that soil N will not be altered so much by the addition of current organic matter as carbon. The relationship between N and PTEs on the experimental site would have been lost if a large fraction of the organic matter had been mineralised, so the preservation of the strong relationship between N and PTEs adds weight to the suggestion made in section 3.3.9 that the organic matter may be resistant to oxidation.

I discussed in Section 3.3.2 the rationale for considering the correlation between nitrogen and PTEs and amongst PTEs in the Rainham silts as being a result of a process or processes going on in the Thames when the dredgings were removed. This led to the hypothesis that PTEs were released from mineral carrier phases, and subsequently complexed by organic matter. A literature search showed that similar

correlations are not only found in modern sediments in estuaries, salt marshes and near coastal environments, but have also been noted in the geological record, as follows.

3.5.4.1. PTE/ORGANIC MATTER CORRELATIONS IN COASTAL WETLANDS

Callaway et al. (1998) found high correlations between potentially toxic elements and organic matter in 143 samples taken from five coastal wetlands in England, the Netherlands and Poland. Inter-elemental correlations ranged between 0.69 and 0.93 for Cd, Cr, Cu, Ni, Pb and Zn. The correlation between metals and organic matter was between 0.7 and 0.9. These correlations were all highly significant, with a probability of less than 0.0001.

The purpose of the study was to convert depth profiles to chronological profiles using ^{137}Cs dating to identify changes in potentially toxic element loading from 1890 to 1990. A high marsh and a low marsh core were taken from each site. The high and low sites had very different accretion rates, leading to large differences in depth profiles. When the profiles were adjusted to reflect time of deposition, they showed a high degree of similarity. Callaway et al. concluded from the similarity between high marsh and low marsh cores that there had been no post-depositional mobility of trace metals within the cores, and that they were a true representation of depositional element concentrations.

3.5.4.2. PTE/ORGANIC MATTER CORRELATIONS IN A VERTICALLY STRATIFIED ESTUARY

Yurkovskis (2004), in a study of biogeochemical phase exchange processes along a salinity gradient in the highly eutrophied Dauvaga river in Latvia found that particulate N was highly correlated with Cd, Cu, Pb, Ni, Cr and Zn, and that these elements were highly correlated amongst themselves.

The Dauvaga has a highly stratified circulation with restricted vertical exchange between the near bottom saline current and the upper fresh water layer. The potentially toxic elements and nitrogen increased with increasing salinity, while particulate matter decreased with salinity. Yurkovskis suggests that the trace elements were coupled with phytoplankton. If so, this is no simple relationship, as

particulate nitrogen content increases several fold with salinity while chlorophyll a concentration (used in the study as a proxy for phytoplankton) remains fairly constant.

3.5.4.3. PTE/ORGANIC MATTER CORRELATIONS IN A WELL MIXED MACROTIDAL ESTUARY

Conditions in the Scheldt greatly resemble those in the Thames when deposition at Rainham began. It is a highly modified, well mixed, macrotidal estuary with a long (two to three months) residence time, which receives large discharges of untreated domestic and industrial waste (Baeyens, 1998). The river has a pronounced turbidity maximum, where the water column is anoxic during the spring, autumn and summer (Zwolsman and van Eck, 1999). Sedimentation and seasonal anoxia occur in a narrow stretch of the river in the central brackish zone, in the vicinity of Antwerp (Zwolsman et al. 1996).

Zwolsman et al. (1996) collated the results of eleven studies, covering the period between 1959 and 1990, of the potentially toxic element concentrations in the surficial sediments of the Scheldt. He found strong inter-elemental relationships between As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn throughout the entire Scheldt estuary. All PTEs were highly correlated with organic matter.

In a subsequent study of suspended sediments in the Scheldt, Zwolsman and van Eck (1999) found a strong correlation between metals, and, in stark contrast to the distribution pattern in the Dauvaga, where metal content increased with increasing salinity, an almost exponential reduction in metal loading along the salinity gradient. This pattern of reduction in potentially toxic trace element loading with increasing salinity was also found in the consolidated surficial sediments, and was attributed to the dilution of metal rich particulate matter of fluvial origin with clean particulate matter from the sea. In contrast to the study of consolidated sediments, no correlation was found between particulate nitrogen and trace metals in suspended sediment in the Scheldt (Zwolsman, 1996).

3.5.4.4. PTE/ORGANIC MATTER CORRELATIONS IN THE GEOLOGICAL RECORD

Algeo and Maynard (2004) divided 185 cores from shales deposited during the Middle to Late Devonian (359 - 385 million years ago) into three groups using

potentially toxic element concentrations and total organic carbon. The lower part of the cores consisted of laminated organic matter enriched black shale, while the upper part was a non-laminated organic matter poor grey shale. Lamination in sedimentary rocks occurs when the water oxygen content is too low ($< 0.2 \text{ ml O}_2 \text{ l}^{-1}$) to support the respiration of benthic organism, so there is no bioturbation. The sediment had been deposited over a relatively short ($\approx 10^5 \text{ yr}$) period.

Table 3.15 Correlations between and amongst PTEs, and between PTEs and organic carbon in a Late Devonian black shale. EF indicates the trace element enrichment factor compared to values for the grey shale investigated in the same study (Algeo and Maynard, 2004).

	Zn	Pb	Cu	Ni	Cr	EF
Corg	0.73	0.57	0.69	0.92	0.93	
Zn	1					6.3
Pb	0.61	1				8.8
Cu	0.65	0.61	1			1.5
Ni	0.77	0.43	0.67	1		3.4
Cr	0.78	0.58	0.71	0.93	1	6
Mn	-0.30	-0.40	-0.41	-0.32	-0.40	0.84

Algeo and Maynard found no correlation between potentially toxic element concentration and total organic carbon in 48 grey shale samples, where total organic carbon was always less than 2.5% by weight. Strong positive correlations between Zn, Pb, Cu, Ni and Cr and between the elements and total organic carbon were found in 89 black shale samples where the total organic carbon was between 2.5 and 10% (Table 3.15). The extent to which the elements were enriched compared to their concentrations in the grey shale cores is given in the last column of Table 3.15 as the enrichment factor.

They identified a third group where total organic carbon exceeded 10%. These samples showed a modest increase in the enrichment factor for Cu, Ni and Cr and a much weaker positive correlation with organic carbon. The Pb enrichment factor doubled, and the enrichment factor for Zn increased by an order of magnitude.

A pattern which is common in nature is likely to have a common mechanism behind it. This is by no means an original observation. Callaway (1998) considers that these high correlations show that though the metals are coming from different sources, they are behaving similarly chemically. Yurkovskis (2004) finds “the affinity of all observed trace metals to organic matter regardless of their diverse geochemical nature” to be suggestive of strong biotic interference. The fact that the same pattern occurs in the geological record shows that the same phenomenon is not necessarily the result of anthropogenic trace metal inputs.

The preservation of the relationship in the Rainham dredgings, Callaway et al.’s study of marshes, and Algeo and Maynard’s shale study indicate that, under certain environmental conditions, the relationship between organic matter and PTEs may be stable both in the short (decades) and the long (millions of years) term.

Desorption of potentially toxic elements from mineral carrier phases are commonly attributed to changes in ionic strength (Millward and Liu, 2003), decreases in pH, or decreases in redox potential.

The examples quoted above show that metal/organic matter relationships either increase with increasing salinity (Yurkovskis, 2004) or decrease with increasing salinity (Zwolsman, 1996). This suggests that salinity plays a minor role at most in trace metal enrichment of organic matter. Bulk water in the Thames, Dauvaga and Scheldt all had above neutral pH, too high to cause metal mobilization. The evidence from the Thames itself (O’Reilly Weise et al. 1997), and from the geological record (Algeo and Maynard, 2004) indicate that the most likely cause of metal/organic matter relationships is in some way connected with decreases in redox potential.

3.5.4.5. REDOX REACTIONS

The behaviour of the redox sensitive metals, Fe and Mn, can give important information on the redox status during diagenesis. In the study of PTE distributions in high and low salt marshes carried out by Callaway et al. correlations between Fe and Mn and the six other metals were lower, with values between 0.07 and 0.35. The

pattern of Fe and Mn distribution with depth was typical of submerged sediments, with highest values in the surface oxidized zone, and a decrease with depth.

The Dauvaga samples for PTE analysis were taken during an intensive spring flood in March 2001, when suspended particulate matter was at its highest. Particulate Mn ranged from 1.8 to 2.4 mg g⁻¹ in March 2001, but from 6.7 to 13.9 mg g⁻¹ in June, 1999. This large seasonal difference suggests a redox driven phase change from insoluble Mn(IV), which would be associated with the particulate matter, to soluble Mn(II). Yurkovskis could, however, find no evidence of low bottom water oxygen concentrations.

PCA analysis of suspended sediments in the Scheldt (Zwolman and van Eck, 1999) showed that iron and phosphorus co-varied with trace metals, while Mn was uncorrelated with any measured parameters.

3.6. SUMMARY AND CONCLUSIONS

3.6.1. SALINITY AND SODICITY

Differences in salinity between the intact-core and experimental site samples have emerged within a few years. These are likely to be the result of continuing and relatively rapid pedogenic processes. Changes in soil structure over the experimental period have not been quantified, but it appears that some soil physical features are no longer as marked as they were initially. There has been no recurrence of the ponding, hard-crusting and run-off which occurred in the first winter, and vegetation cover appears to be having a beneficial effect. Methodologies developed for the prediction of the effects of sodicity and salinity in naturally occurring saline soils or marine alluvium are probably inappropriate when used to assess these characteristics in dredged material disposed of to a confined disposal facility, and then applied to land.

3.6.2. PTE/ORGANIC MATTER CORRELATIONS

The physical and chemical characterization of the dredgings revealed relationships which, though unexpected, could not have occurred by chance. The probability of

obtaining the nitrogen-PTE relationship observed in the experimental site samples was shown by regression analysis to be 3.2×10^{56} . Each lagoon was filled sequentially once every three months, and these relationships are found in separate samples of material removed from the river at 18 month intervals. This relationship was clearly the result of processes occurring in the river.

The strong link between Beckton and Crossness sewage outfalls and the “mud reaches” means that the inter-elemental relationships and the relationship of PTEs with nitrogen could be interpreted as demonstrating the effect of single point source of both PTEs and organic matter. Though the greater part of the PTEs is obviously of anthropogenic origin, and the outfalls must certainly have made an important contribution to PTE loading in the estuary, they are unlikely to have been wholly responsible. The relationship remained long after improvements to the sewage works, and occurs in other environments. There are many examples of other such relationships in the literature. A high positive correlation existed historically between these elements and organic matter (correlation coefficient >0.9) (Hirner et al. 1990) in the now almost pristine Rhine.

London was a major manufacturing centre, and many industries in the Metropolitan area, including flour mills, margarine works, sugar refineries, distilleries and paper mills, were discharging directly into either the Thames or its fresh water tributaries, such as the Lee (DSIR,1964). Legislation over industrial effluents was comparatively lax. The water used to scrub flue gases from the Battersea and Bankside Power stations was, for example, discharged to the estuary on a daily basis (DSIR, 1964). Beckton and Crossness are downstream of the Central London built-up area, where, due to the retention of the old sewers as storm overflows, a significant proportion of sewage enters the river untreated and there is a great deal of urban run-off.

There are very few studies of PTE contamination in the Thames, and none from the relevant period. It is known from data supplied by the Environment Agency and its predecessor the National Rivers Authority, that, of total discharges of copper, nickel and zinc to the Thames between 1990 and 1995, the River Thames itself contributed

41% of copper, 37.1% of nickel and 30.3% of zinc (Stevenson and Ng, 1999). Comparative figures for Beckton and Crossness combined were 18.1% for copper, 23.9% for nickel and 13.3% for zinc.

The simplest explanation for the strong relationship between nitrogen and metals is that a high percentage of all PTEs in the dredged material are in the organic phase. This does not appear to be uncommon. When Hirner et al. (1990) extracted organic matter from a range of recent and ancient sediments it was often strongly – up to three orders of magnitude – enriched in PTEs. This, too, implies that PTEs were removed from other carrier phases and complexed by the organic phase. Integration of the historical data from the Thames with the results from the present study and with the published data from other researchers cited above adds weight to this hypothesis. The existence of the same pattern in the geological record shows that the mechanism by which this occurred is not necessarily linked to anthropogenic activity.

3.6.3. REDUCTIVE DISSOLUTION OF PTE CARRIER PHASES

Iron and manganese oxides are important carrier phases for PTEs. The work of the WPRL leaves little doubt that there was wide-scale reductive dissolution of these phases in the river over time. In addition to their role as terminal electron acceptors for microbial respiration, iron and manganese oxides are important carrier phases for potentially toxic elements (Calmano and Förstner, 1983; Jones and Turki, 1997). It has been shown that reductive dissolution of Fe(III) oxides tends to lead to the release of contaminant metals (Lovely, 1991). The dissolution of Mn oxides and release of adsorbed trace metals has also been proposed as an important mechanism (Bratina et al. 1998). Conditions at the beginning of the depositional period were such that re-oxidation of these phases and readsorption of the PTEs could not have occurred.

Material from the stretch of the river the dredgings came from has a unique particle size distribution, with a very much higher concentration of fines and less sand than other parts of the river. This has invariably been attributed to transport and depositional processes. An alternative explanation, given the increase in the sand fraction over time, the strong negative correlation between the sand and silt fraction,

and the evidence from other environments that organic ligands can solubilise silica, is an *in situ* reduction in the size of sand particles as a result of intense microbial activity.

The lack of association between clays and PTEs, and the apparent decline in aluminium suggests that this may also have been solubilised. If this is so, the use of aluminium concentrations as a normaliser may be inappropriate in grossly polluted environments. Any element used in this way must

- covary in proportion to the naturally occurring element of interest;
- be insensitive to inputs from anthropogenic sources;
- be geochemically stable, and not subject to reduction/oxidation, adsorption/desorption or any other diagenic processes (Luoma, 1990).

3.6.4. SULPHUR

Though there are high levels of sulphur in the material, the very strong correlation with nitrogen argues against sulphides as an important metal binding phase. The amount of sulphur in the dredgings is indicative of intense biological sulphate reduction. Many of these elements are chalcophilic, i.e. they have an affinity for sulphur, and readily react with reduced sulphur species to form metal sulphides. The association with organic matter suggests that the formation of organo-metallic complexes preceded sulphate reduction. Despite the high sulphur concentrations, the risk of PTE mobilization through sulphide oxidation appears low, since pH remained circumneutral after intense oxidation in 90 samples.

Though most other studies have found that PTEs and organic matter are most strongly associated with the clay fraction, both were found in this study to be strongly correlated with the silt fraction. This fraction was, moreover, associated with lower C:N ratios.

CHAPTER 4 – FIELD AND GREENHOUSE EXPERIMENTS

4.1. INTRODUCTION

The original aim of this research, the development of techniques for discriminating between “dirty” and “clean” fractions so that the lagoons could be mapped, became obsolete with the realisation that PTE loading is likely to be relatively homogenous across the lagoons, to increase with depth in the lagoon in a predictable manner, and that quantities of elements of regulatory concern are frequently above soil guidance values. Cadmium, copper and zinc concentrations are particularly elevated. The mean cadmium concentration is $9.5 \pm 3.2 \text{ mg kg}^{-1}$, almost five times higher than the soil guidance value.

Clay minerals, iron and manganese oxyhydroxides and organic matter are normally the most important sorbent solids for PTEs in porous media (Langmuir et al. 2004). As a result of estuarine processes, clays and Fe/Mn oxyhydroxides in the Thames dredgings have been subjected to reductive dissolution, and the PTEs are probably concentrated in the oxidisable soil fraction as organo-metallic and organo-metallic-mineral complexes. Most iron is likely to be present as iron sulphide, and, given the large discrepancy between LOI and organic matter, manganese as manganese carbonates. As the sulphide oxidises, acidity will be produced. pH is the most important factor in the mobility of most PTEs (Langmuir et al. 2004; Ross, 1994). Acidity will also dissolve carbonates, increasing the mobility of any associated PTEs.

The conditions in the Thames that created this unusual phase partitioning are relatively uncommon, so it is unclear how transferable information on plant uptake from this study is for the re-use of dredgings *per se*. It may be useful for that subset of dredgings where prolonged water column anoxia has concentrated PTEs in the organic matter fraction, though the suite of metals involved and their ratios will be dependent on inputs particular to the specific river. In a recent series of papers from

the USEPA it was suggested that, given the present poor understanding of those factors controlling metal bioavailability in terrestrial systems, a useful approach may be to look at PTE bioavailability in major soil groups (Kaputcka et al. 2004). The dredgings dealt with here are very similar in origin to the black shales, a fairly common soil parent material. Time and weathering under oxic conditions have, however, almost certainly altered phase partitioning in this substrate, whereas the dredgings were, until recently, stored under anaerobic conditions, where the phase partitioning created in the river would have been preserved.

Re-use of the Thames dredgings in the field experiment involved removal from the lagoons, and application to land. The net effect was to increase the surface area to volume ratio. This is likely to have increased PTE bioavailability on two counts.

- By causing the dredgings to have a much greater exposure to oxygen, thus potentially altering PTE speciation.
- By vastly increasing the surface available for biological interactions.

The data presented here show actual values of PTEs in the above and below ground biomass of relevant native plants grown in the dredgings in a long-term study under realistic exposure conditions where they were subject to natural stressors and biotic interactions.

The important research questions are:

- Does the unusual phase partitioning and multi-elemental contamination present in this material cause phytotoxicity in a range of environmentally relevant plants?
- Is PTE bioaccumulation in these plants high enough to pose a threat to consumer organisms?
- Are changes likely to occur in PTE speciation via normal environmental processes that will increase their bioavailability?

Specific objectives were:

- To grow a range of environmentally relevant perennial plant species under ambient exposure conditions for three seasons.

- To measure PTE contents in above and below ground plant biomass.
- To manipulate those factors likely to increase the concentrations of free ions in the soil solution under controlled greenhouse conditions, in order to determine what changes elicit a response.

4.2. FIELD TRIALS

4.2.1. MATERIALS AND METHODS

4.2.1.1. SITE DESCRIPTION

The experimental site is on a small part of a large landfill site. The area immediately behind the site has ceased to be used for waste disposal, and has been capped and covered, forming a large sloping mound. The site is on the lower part of the mound, and slopes both down towards the Thames, and from the middle to the sides. Its area is 2 ha. The access road for the part of the landfill that is still in use runs along the upper boundary of the site, dividing it from the rest of the mound. The road is in frequent use by HGVs, creating large amounts of dust.

Soil conditions on the experimental site vary seasonally. In summer, a hexagonal cracking pattern develops on the horizontal plane. These cracks are generally greater than 1 cm wide, and are occasionally considerably wider. There is no information on the depth the cracks extend to. Since hydraulic flow is proportional to the cube of the width of the drainage pathway, hydraulic conductivity differs with moisture content (Ringrose-Voase and Bullock, 1984). In summer, water moves down these cracks by

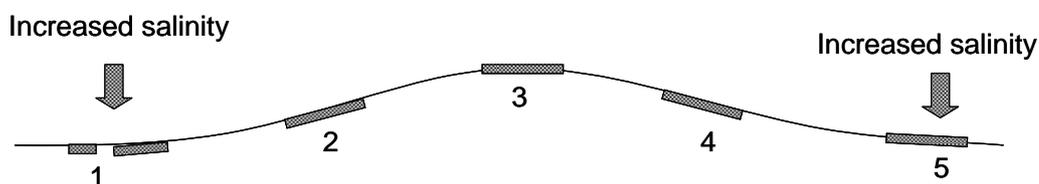


Figure 4.1 Experimental site in cross section showing the location of the individual blocks with respect to topography and salinity.

preferential flow, rather than infiltrating through the soil matrix. In winter, the soil swells, and the cracks shrink or seal. Winter run-off carries salt from higher to lower parts of the site (Figure 4.1).

The native plants that have colonised the site have a distinctly halophytic tendency, and include many salt-marsh species. Some mesophytes are present. At the start of the project there was a clear zonation between halophytes and mesophytes based on topography. Low lying ground was dominated by halophytes, while higher ground had a greater proportion of mesophytes. This pattern has become much less pronounced over time, with the mesophytic tendency in the ascendancy. The commonest species at the top of the slope are *Tripleurospernum maritima*, *Aster tripolium*, *Beta vulgaris*, *Brassica nigra*, *Conium maculatum*, *Daucus carota*, *Chenopodium* spp. and *Atriplex* spp. In higher areas the vegetation has a rather gross appearance, with *Brassica nigra* often exceeding five feet in height. In low lying areas the vegetation is reduced in size, containing species such as *Spergularia maritima*. The species present include some rarities, such as the salt-marsh grasses *Puccinellia rupestris* and *Polypogon monspeliensis*.

4.2.1.2. SELECTION OF SPECIES

The plant community considered most likely to be established on post-industrial sites in the Rainham area, either by natural colonisation or by seeding, was the mesotrophic grassland MG1. The seed for a selection of species from that community was obtained from a nursery specialising in native wild flowers, to ensure a full range of genetic variability.

The experimental plan consisted of five replicates of ten test species. These test species were composed of four dicotyledonous species (*Tarraxacum officinale*, *Leucanthemum vulgare*, *Medicago sativa*, *Centurea nigra*) and four graminaceous species (*Alopecurus pratensis*, *Festuca rubra*, *Arrhenatherum elatior*, *Dactylis glomerata*). The remaining two “species” were self-sown herbs and self-sown grasses.

The physical properties of the dredgings lead to summer drought and winter inundation. Plants were chosen with a range of root architecture so that some idea of which morphotypes best tolerated these conditions could be gained. *Tarraxacum* has a fleshy tap-root, with leaves confined to a basal rosette. *Leucanthemum* has robust woody roots which are fairly close to the surface, whereas *Centaurea* roots extend further into the soil. *Medicago* roots are finer, more branched, and capable of extending to depth. Grasses generally have more finely divided root systems than herbaceous plants. *Festuca* is fine leaved, stoloniferous, and has a shallow dense root system. *Dactylis* is robust and tufted, with a coarser root system. Both *Alopecurus* and *Arrhenatherum* are tall and erect, with deeper roots.

4.2.1.3. SITE PREPARATION

Dredged material had been removed from the lagoons, deposited on the site and subsequently sown with a *Lolium perenne/Trifolium repens* ley in 1998. A site inspection in August, 2001 found patchy cover of grass and clover. The site was thickly covered with coarse large-leaved plants. These were mainly native annuals, most commonly members of the non-mycorrhizal and salt tolerant Chenopodiaceae, *Chenopodium rubra* and *Atriplex* spp.

In September of 2001 contractors sprayed the existing vegetation with glyphosate. They subsequently prepared a seed bed by tilling and harrowing. A site inspection in October showed that the clover had not been killed, but had been buried. The cultivation had been shallow, and the earth in the cultivated areas was in wet, sticky clods. Additionally, the work had been carried out when the ground was wet, causing compaction and further impeding drainage. The original plan had been to place the Blocks centrally. The entire lower part of the site was underwater, so the Blocks were positioned about ten metres from the upper edge of the site. The presence of a large area of standing water meant that Block 1 had to be divided in two, one part with four sections and the other with six sections. Posts were driven in to the corners of each block, and individual 5 m by 5 m sections marked out with canes.

4.2.1.4. VEGETATION ESTABLISHMENT AND MAINTENANCE

Seeds were sown in November and December of 2001. The clover roots were removed manually from each 5 m by 5 m section, using spring tine rakes. A single plant species was sown in each section, and the seeds worked into the soil surface using rakes. Seeds were sown at twice the normal density to ensure adequate germination. The plots were monitored for seed emergence. Germination was high in all plots, and despite localised seedling loss due to surface run-off during the winter of 2001-2002, dense cover by the selected species in all plots was achieved. The plots were weeded regularly to maintain the single species of interest as a monoculture. A two foot strip around each block was kept free of vegetation by spraying with glyphosate, and the native vegetation that colonised the rest of the site was mowed several times a season.

4.2.1.5. VEGETATION SAMPLING

The vegetation was sampled on two occasions. The first of these was in late August, 2003. A 1 m² square from each 5 m x 5 m stand was pre-selected using random coordinates. With the exception of *Leucanthemum vulgare* samples, the above ground biomass from a representative 25 cm² area within the square was cut at 2 cm above the substrate, to avoid substrate contamination. *L. vulgare* had died back post-flowering, and only basal rosettes (circa 4 cm in diameter) were available for sampling.

An additional 10 samples of *Festuca rubra* were taken from a randomly selected section. There were thus 60 samples, five replicates from each of the 10 plant species, plus an additional 10 samples of *Festuca rubra*. Samples were stored in paper bags, folded over to prevent contamination. These were oven-dried for 18 hrs at 102°C. The leaves were removed from the stems and milled, and 2 g of the material acid-digested as described for soils in Chapter 3. The acid digests were analysed for Cu, Pb, Ni, and Zn content using AAS. Cadmium was analysed using AAS with graphite furnace.

The vegetation was sampled for a second time on 10 May, 2004. Samples once again consisted of the above ground biomass from a 25² cm area, selected using random co-ordinates. The original plan was to take five replicates from each *Dactylis glomerata* section, five replicates from each *Medicago sativa* section, a single sample from each of the remaining 30 single species section, and a single sample from each of the self-sown herb and self-sown grass sections. On reaching Block 2, it was found that the 5 m *Dactylis glomerata* square had been very precisely sprayed with weed-killer, so there are only 20 above and below ground samples for this species. Collocated underground plant material was taken from sampling sites using a garden fork. There were thus 85 root samples and 85 corresponding shoot samples, making a total of 170 samples.

Brassica nigra, a very common plant on the experimental site, is known to accumulate and tolerate foliar Se concentrations of several hundred mg kg⁻¹ at lower substrate Se concentrations than those at Rainham (Marschner, 1995). This species was preferentially sampled on the “self-sown” herb sites when it occurred within the 1 m² random co-ordinates (4 out of 5 samples).

Above ground biomass was oven dried, and the leaves removed and milled. 2 g samples were acid digested. Roots were carefully washed, oven-dried and milled and 2 g samples acid-digested. The acid digests were analysed for Cu, Zn, Pb, Cd, Cr, Se and As. AAS was used for Cu, Zn, Pb and Cr. AAS with hydride generation was used for Cd, As and Se.

4.2.2. RESULTS

Table 4.2 shows the means and standard deviations found in plants from the experimental site. Above ground biomass was not washed before acid digestion, as unwashed vegetation was felt to better represent total exposure for consumer organisms. The data presented is therefore inclusive of aerial deposition.

Table 4.1 shows the wide variation in PTE concentrations found in “normal” vegetation in non-polluted environments, the range in “contaminated” plants, and the

maximum levels chronically tolerated by domestic animals. The figures given for Pb and Cd are not reflective of animal tolerance, but are intended to be protective of human consumers of animal liver, kidney and bone (Chaney, 1989). The data for maximum dietary levels were derived from the addition of soluble salts of a single PTE to the diet, and may differ in bioavailability from the same dosage in natural foodstuffs (Chaney, 1989).

The data shown for “normal” and “contaminated” plants in Table 4.1 is somewhat generalised. Different figures are given for “normal” ranges by different authorities. “Normal” concentration ranges cited in the literature for cadmium, for example, vary from 0.2-0.8, 0.1-1 and 0.1 to 2.4 mg kg⁻¹ dry weight (Kabata-Pendias and Pendias, 1992; Chaney, 1989; Alloway, 1990). Alloway’s figure appears more realistic, as the USFDA (United States Food and Drug Administration) Total Diet Study report concentrations of 2.2 ± 1.2 mg kg⁻¹ dry weight for iceberg lettuce (Darmody et al. 2004). Additionally, concentrations appear to refer to shoot concentrations, though only Chaney explicitly states this in the text. The optimal copper supply for the growth of tomato plants, for example, has been experimentally established as 50 µg l⁻¹, resulting in a root copper content of 64 mg kg⁻¹ dry weight, and leaf copper content of 14.6 mg kg⁻¹ (Marschner, 1995).

Table 4.1 Concentration ranges of PTEs in normal and contaminated plants, and the maximum dietary levels chronically tolerated in domestic animals. (a) from Alloway (1990). (b) from Kabata-Pendias and Pendias (1992). (c) from Chaney (1989).

Element	Level in plants (mg kg ⁻¹ dry weight)		Maximum levels chronically tolerated (mg kg ⁻¹ dry diet) ^c			
	Normal ^a	Contaminated	Cattle	Sheep	Swine	Chicken
		Plants ^b				
As	0.02 - 7	5 -20	50	50	50	50
Cd	0.1 - 2.4	5 - 30	0.5	0.5	0.5	0.5
Cr	0.03 - 14	5 - 30	3000	3000	3000	3000
Cu	5 - 20	20 - 100	100	25	250	300
Ni	0.02 - 5	10 - 100	50	50	100	300
Pb	0.2 - 20	30 - 300	30	30	30	30
Se	0.1 - 2	5 - 30	2	2	2	2
Zn	1 - 400	100 - 400	500	500	500	500

If Table 4.1 is taken at face value, three out of five samples from the August 2003 harvest of *Leucanthemum vulgare* would be classed as borderline contaminated with respect to Cu, Pb and Cd. *Taraxacum officinale* falls within the “contaminated” range for Pb due to one very large outlier (92.8 mg kg⁻¹). Self-sown herb was “contaminated” with respect to Cd, due to a single sample containing 11.9 mg kg⁻¹. Foliar cadmium concentrations were above “normal”, but below “contaminated” concentrations in May in *Centaurea nigra*, *Taraxacum officinale* and self-sown herbs. Table 4.2 indicates all plants where “normal” and “contaminated” ranges are exceeded.

Root concentrations of copper were within the “contaminated” range in all plant species. Root concentrations of cadmium were within the “contaminated” range in *Alopecurus pratensis*, *Arrhenatherum elatius*, *Dactylis glomerata*, *Festuca rubra*, the self sown grass and *Centaurea nigra*, and were above normal in the remaining species. *A. pratensis* had accumulated high root concentrations of all elements measured save As. *Alopecurus pratensis* showed evidence of bioconcentration of cadmium and copper in the root zone. Root tissue PTE concentrations were lower than substrate concentrations in all other samples.

August 2003

Element	<i>Alopecurus pratensis</i>	<i>Arrhenatherum elatius</i>	<i>Dactylis glomerata</i>	<i>Festuca rubra</i>	Self-sown grass	<i>Centaurea nigra</i>	<i>Leucanthemum vulgare</i>	<i>Medicago sativa</i>	<i>Taraxacum officinale</i>	Self-sown herb
Foliar concentrations mg kg ⁻¹ dry weight										
Cd	0.7 ± 0.5	0.6 ± 0.4	0.5 ± 0.2	0.9 ± 0.3	0.5 ± 0.4	0.2 ± 0.0	4 ± 2.4**	1.6 ± 0.4	1.5 ± 0.6	3.9 ± 5.2**
Cu	9 ± 1.2	10 ± 3	9 ± 2.9	6 ± 1.8	7 ± 2.3	12 ± 1.1	28 ± 7.5**	11 ± 1.7	15 ± 3.3	18 ± 6.5
Ni	3.2 ± 0.9	2.9 ± 1	3.4 ± 0.3	4 ± 0.9	3 ± 1.2	4 ± 0.4	6 ± 2*	3.8 ± 0.4	2.8 ± 1.2	2.9 ± 0.7
Pb	9 ± 9	8 ± 3.9	10 ± 9.9	4 ± 1.1	7 ± 3.6	23 ± 4.3*	28 ± 12.4**	7 ± 1.5	26 ± 41.3**	11 ± 6.2
Zn	202 ± 98 (n = 5)	68 ± 22 (n = 5)	82 ± 18.3 (n = 5)	52 ± 7.2 (n = 15)	110 ± 46 (n = 5)	76 ± 10.3 (n = 5)	298 ± 12.1 (n = 5)	148 ± 22.6 (n = 5)	137 ± 0.6 (n = 5)	168 ± 65.1 (n = 5)

May 2004

Foliar concentrations mg kg ⁻¹ dry weight										
As	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.1 ± 0.1	0.1 ± 0.0	0.1 ± 0.1	0.1 ± 0.1	0.0 ± 0.0
Cd	0.6 ± 0.5	0.5 ± 0.7	0.6 ± 0.3	0.8 ± 0.3	0.4 ± 0.3	1.2 ± 1.7*	1.7 ± 0.2	0.7 ± 0.2	2.1 ± 0.5*	2.2 ± 1.4*
Cr	1.1 ± 0.5	0.6 ± 0.2	0.9 ± 0.5	1.0 ± 0.4	0.6 ± 0.5	1.5 ± 1.2	0.7 ± 0.5	0.4 ± 0.4	1.4 ± 0.8	0.5 ± 0.3
Cu	16 ± 1.1	9 ± 2.4	16 ± 3	11 ± 4	13 ± 4.4	13 ± 1.7	19 ± 1.5	12 ± 1.5	14 ± 2.7	15 ± 1.9
Pb	5 ± 1.9	5 ± 5.5	3 ± 2.6	5 ± 2.9	3 ± 1.9	11 ± 3.4	17 ± 9.6	5 ± 2.6	9 ± 1.3	13 ± 5.9
Se	0.1 ± 0.0	0.2 ± 0.0	0.3 ± 0.1	0.1 ± 0.1	0.2 ± 0.1	0.1 ± 0.0	0.2 ± 0.0	0.4 ± 0.1	0.1 ± 0.1	0.2 ± 0.0
Zn	124 ± 26.3 (n = 5)	54 ± 12.3 (n = 5)	56 ± 13.4 (n = 20)	45 ± 11.4 (n = 5)	92 ± 34.4 (n = 5)	41 ± 1.3 (n = 5)	158 ± 20 (n = 5)	80.6 ± 15.3 (n = 25)	85 ± 16 (n = 5)	149 ± 35.7 (n = 5)
Root concentrations mg kg ⁻¹ dry weight										
As	0.4 ± 0.1	0.3 ± 0.2	0.2 ± 0.1	0.3 ± 0.2	0.2 ± 0.1	0.4 ± 0.2	0.7 ± 0.2	0.1 ± 0.1	0.2 ± 0.1	0.1 ± 0.1
Cd	18.9 ± 3.9**	4.3 ± 3.7**	5.4 ± 3.9**	9.5 ± 6**	4.8 ± 3.2**	6.6 ± 6.9**	4 ± 0.5*	3.2 ± 1.6*	2.4 ± 0.5*	2 ± 0.9*
Cr	12.3 ± 2	5.8 ± 1.1	7.3 ± 3.9	5.9 ± 3	5.3 ± 2.8	2.9 ± 1.7	2.9 ± 1.3	2.7 ± 2	0.7 ± 0.6	4.4 ± 1.5
Cu	347 ± 60**	78 ± 33**	77 ± 23.4**	167 ± 79.8**	93 ± 70.7**	50 ± 16.3**	37 ± 9.1**	24 ± 5.4**	33 ± 10.1**	20 ± 5.5**
Pb	32 ± 6.3**	10 ± 4.4	10 ± 9.3	24 ± 12.4*	7.4 ± 6.1	2.6 ± 2.4	7 ± 5.1	2.3 ± 2.7	2 ± 2.1	3.8 ± 5.6
Se	1.9 ± 0.4**	0.9 ± 0.3	0.8 ± 0.3	0.9 ± 0.6	0.8 ± 0.9	0.6 ± 0.3	0.6 ± 0.2	0.4 ± 0.1	0.3 ± 0.1	0.1 ± 0.1
Zn	389 ± 38.6** (n = 5)	136 ± 37.6 (n = 5)	128 ± 64.9 (n = 20)	250 ± 83.9 (n = 5)	185 ± 42.9 (n = 5)	97 ± 17.8 (n = 5)	101 ± 32 (n = 5)	102 ± 37.4 (n = 25)	76 ± 52 (n = 5)	128 ± 46 (n = 5)

Table 4.2 PTE concentrations in plant tissues. * indicates that at least one sample exceeded the range of tissue concentrations found in “uncontaminated” plants. ** indicates that at least one sample exceeded the range found in “contaminated” plants.

The plants were harvested at different life stages. The dicots flowered before the August harvest, and the material was (with the exception of *Leucanthemum vulgare*) mature. The second harvest was taken during the active growth period, when plants were in all cases about to flower. T-tests for independent groups showed significant differences in foliar tissue concentrations of elements between the two harvests, though these are species specific (Figures 4.2, 4.3, 4.5 and Table 4.3).

Table 4.3 Statistical significance of changes in foliar tissue concentrations of Cd, Pb, Zn and Cu between August 2003 and May 2004

Element	<i>M. sativa</i>	<i>L. vulgaris</i>	<i>T. officinale</i>	<i>C. nigra</i>	<i>D. glomerata</i>	<i>A. elatius</i>	<i>A. pratensis</i>	<i>F. rubra</i>
Cd	>0.001	ns	>0.05	ns	>0.001	ns	ns	ns
Pb	ns	ns	ns	>0.01	>0.001	ns	ns	ns
Zn	>0.001	>0.001	>0.01	>0.001	>0.001	ns	>0.001	ns
Cu	ns	ns	ns	ns	>0.001	ns	ns	>0.05

The plants sampled were from different positions and genetically variable sources. Substrate PTE loading varies widely over the experimental plots, and sample numbers were small. These trends should therefore be regarded with a degree of caution. Nevertheless, there is some evidence for temporal variation in plant uptake of PTEs. Foliar Zn content was significantly higher in six out of eight species in August than it was in May. High tissue Zn is generally associated with younger tissue, falling from 204 mg kg⁻¹ in the youngest leaves of Zn sufficient rice plants to 18 mg kg⁻¹ in mature leaf blades (Marschner, 1995).

Figures 4.2 – 4.4 illustrate the strong general trend, in the species studied, for grasses to accumulate high concentrations of PTEs, relative to dicotyledonous plants, in the root zone, and for limited translocation of these elements to shoots. These Figures also show the pronounced differences in PTE uptake between species.

Comparison of error bars for the non-essential elements Cd and Pb show that tissue concentrations of these elements are more variable than for those of the essential elements Zn and Cu. Concentrations of Pb and Cd are higher in dicot shoots than they are in grass shoots. Cr and Se are strongly retained in the roots of both grasses and dicots.

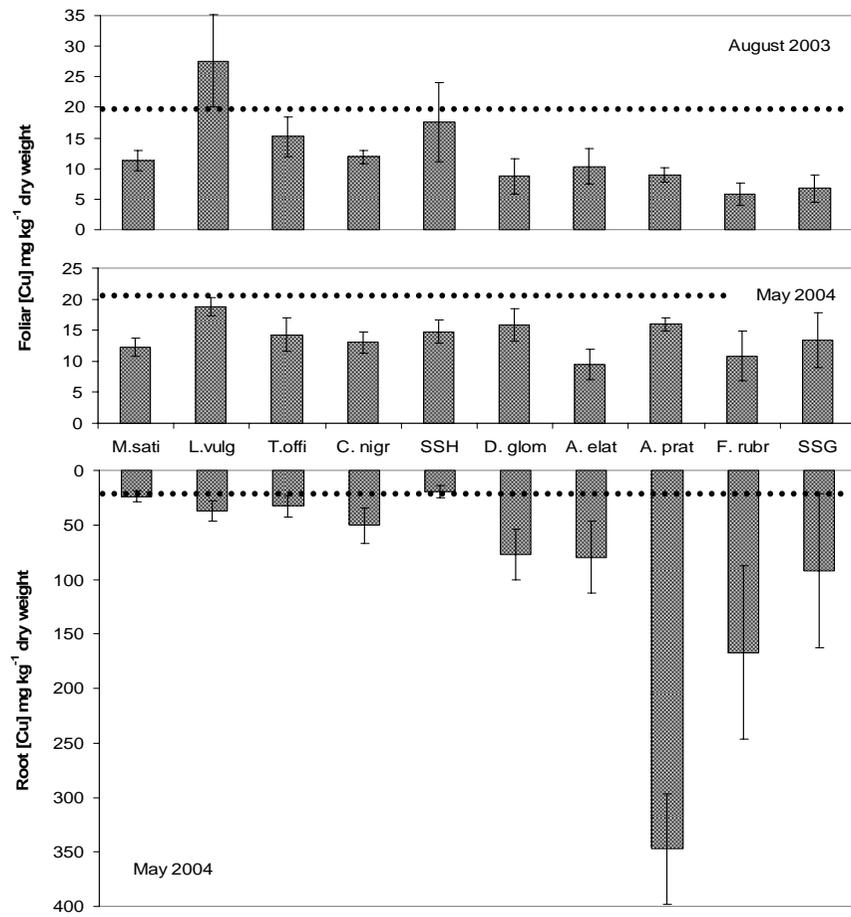
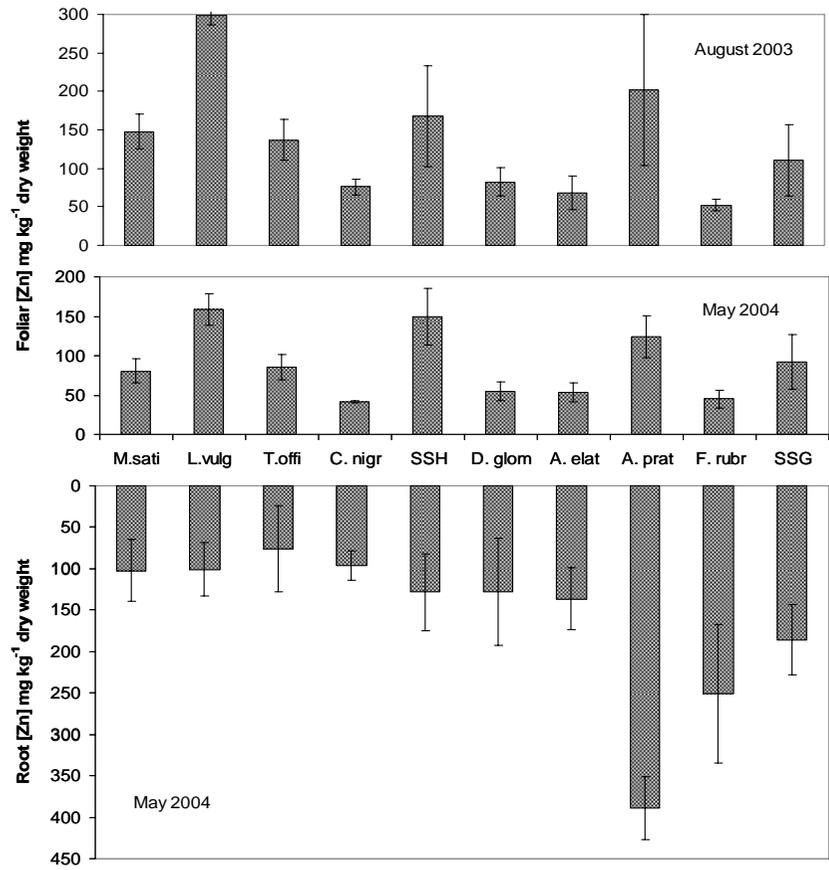


Figure 4.2 Zinc and copper concentrations found in the leaves and shoots of plants from the experimental site. Dotted lines represent the limit of the range found in normal vegetation according to Alloway (1990).

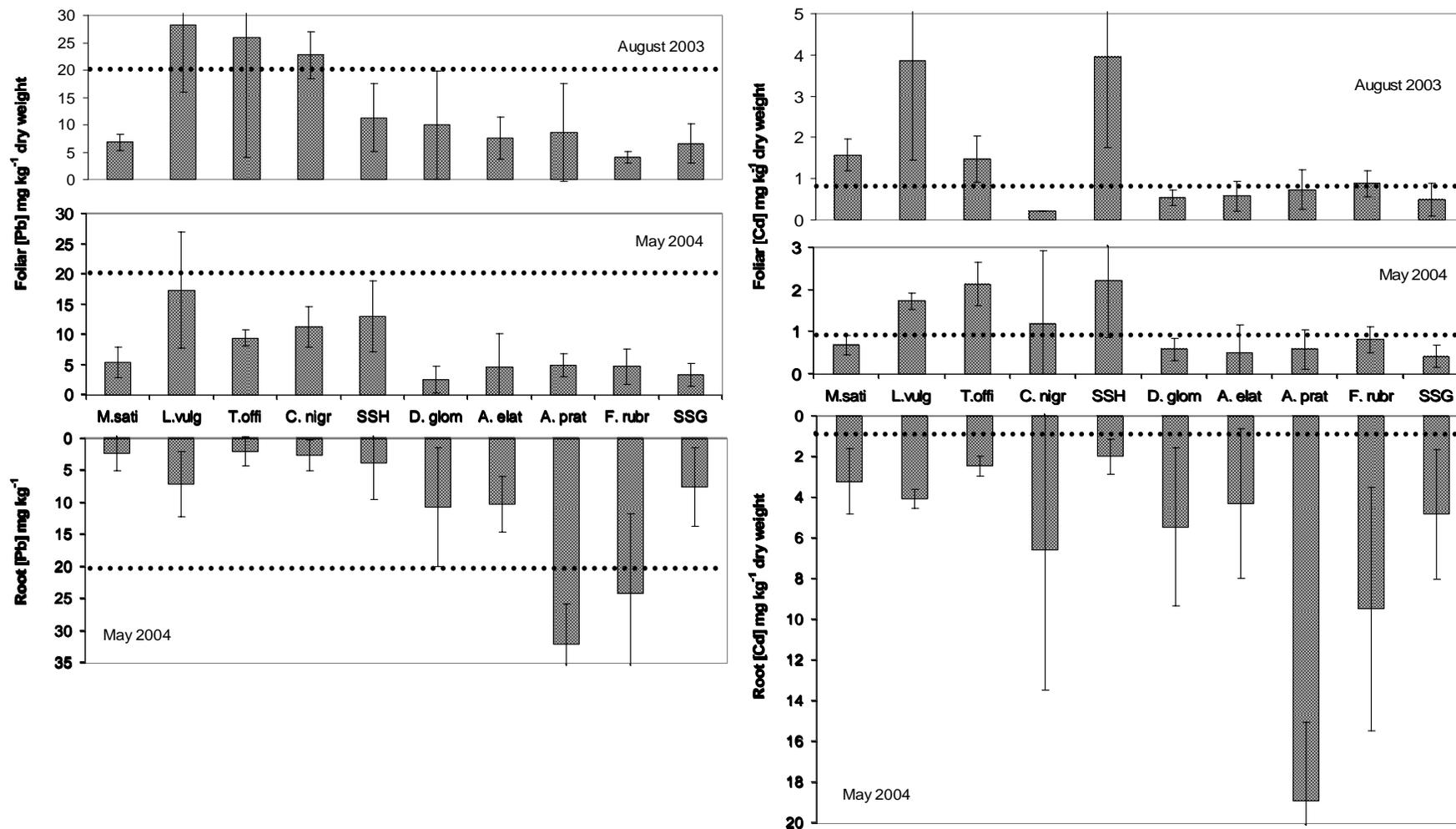


Figure 4.3 Lead and cadmium concentrations in the leaves and shoots of plants from the experimental site. Dotted lines represent the limit of the range found in normal vegetation (Kabata-Pendias and Pendias, 1994).

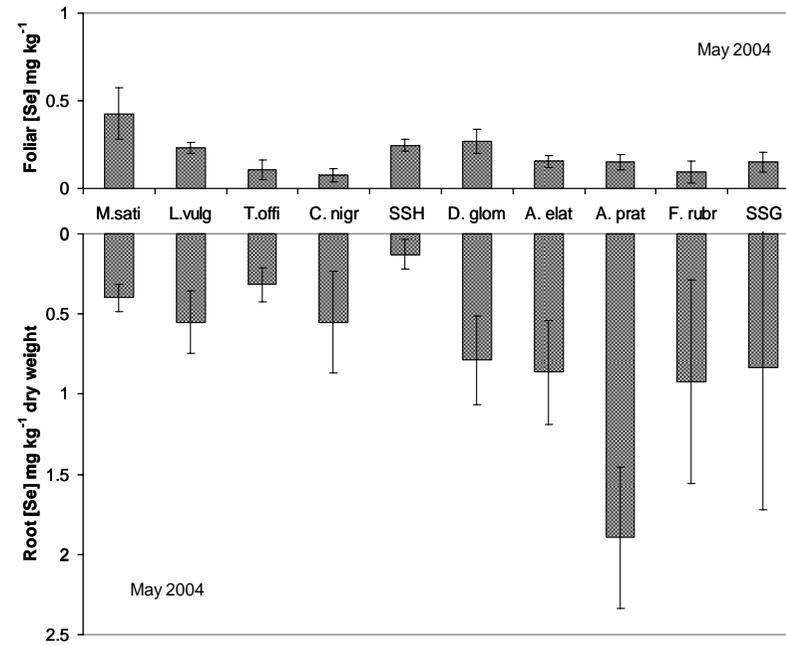
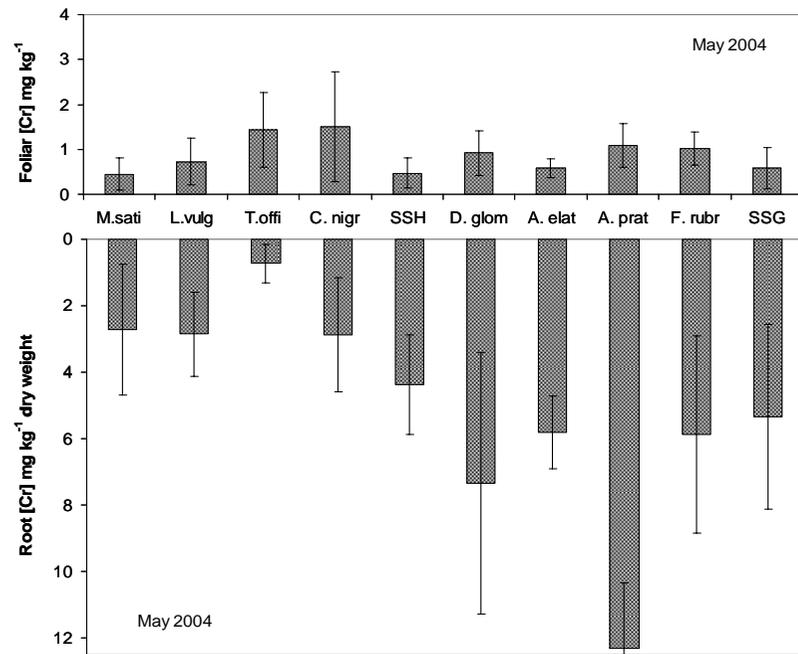


Figure 4.4 Chromium and selenium concentrations in the leaves and shoots of plants from the experimental site.

4.2.3. DISCUSSION

Research on plant uptake of PTEs under field conditions has mainly focused on protecting the food-chain by establishing safe application limits for the disposal of wastes containing PTEs to agricultural land, and on plant uptake in sites that have been heavily impacted by industrial processes such as mining and smelting. The latter often result in foliar concentrations of PTEs in vegetation great enough to be a danger to human and animal health. Foliar concentrations in *Lolium perenne* at the Avonmouth (UK) Pb-Zn smelter, for example, are 225 mg kg⁻¹ Pb, 1600 mg kg⁻¹ Zn and 50 mg kg⁻¹ Cd (Ross, 1994).

PTE concentrations in the Rainham dredgings lie between these two extremes, and are typical of many degraded brown-field sites where human activities have resulted in elevated concentrations of a mixture of PTEs, with poorly understood environmental consequences. There is very limited published information on tissue PTE concentrations in native plants grown under field conditions, and even less on concentrations in plant roots.

4.3. GREENHOUSE EXPERIMENT

The aim of the experiment was to manipulate those factors considered most likely to cause an increase in PTE bioavailability in the dredgings under field conditions over time. The factors investigated were the effects of differences in water-regime, differences in substrate aggregate sizes, and the presence or absence of unripe, green, acidic municipal compost.

The rationale behind the experiment was that growing vegetation on the dredgings would, over time, produce a more open and porous soil structure, allowing water and air access to the ped interiors, with a consequent increase in oxidation and free ions in the soil solution.

The rationale behind using small aggregates was that the action of soil invertebrates and plant roots may cause a reduction in the size of peds and homogenize the substrate. An

orange substance is present in discrete masses ranging from the size of a grain of rice to the size of a walnut in air dried material. This is assumed to be oxidized iron from iron pyrite. The rationale for using larger aggregates was that the oxidization of pyrite may cause local “hot spots” where pH drops dramatically, resulting in microsite metal mobilization and pockets of high metal bioavailability. pH remains circum-neutral when samples with sulphur contents up to 1.7% are air-dried, passed through a 2 mm sieve and then rewetted, so the carbonate content in the bulk soil is likely to neutralize this effect on the large scale.

Wetting and drying cycles were considered likely to mimic seasonal changes in hydraulic conductivity and cause pulses of microbial activity and subsequent increases in organic matter mineralization. The addition of green manure was intended to act as a surrogate for litter input, stimulating microbial decomposition processes and providing organic ligands for metal chelation.

4.3.1. MATERIALS AND METHODS

2 plant species, *Dactylis glomerata* and *Medicago sativa* were grown in silt from the Rainham lagoons in a greenhouse for 120 days between April 5th and August 2nd of 2004. *Phragmites* roots were present in the material used for the greenhouse trials, showing that it came from the upper, vegetated stratum of the lagoon. Pots were arranged in a randomized block design.

An attempt had been made to homogenize the substrate in spring 2003 using a cement mixer. Twenty replicates were subsequently checked for metal content, showing that this had only been partially successful. Correlations between PTEs are shown in Table 4.4. These were smaller than those found on the experimental site, and there were

Table 4.4 Correlation coefficients in dredged material used for greenhouse trials. Significant correlations are marked ** where $p < 0.01$, and * where $p < 0.05$ (n = 20).

	Copper	Zinc	Lead	Nickel	Cadmium
Copper	1				
Zinc	0.72**	1			
Lead	0.65**	0.62**	1		
Nickel	0.74**	0.52*	0.58**	1	
Cadmium	0.12	0.13	0.05	0.37	1

differences in the inter-elemental ratios.

Mean copper, zinc, cadmium and nickel contents were lower than the corresponding means from the experimental site, whereas mean lead content was higher (Table 4.5).

Table 4.5 Means and standard deviations of the copper, zinc, lead, cadmium and nickel contents in the dredged material and municipal compost used in the greenhouse-based experiment.

	Copper	Zinc	Lead	Nickel	Cadmium
mean (dredgings)	155	543	334	35	3.9
stdev (dredgings)	42	93	77	4	0.9
mean (compost)	55	202	99	10	1.2
stdev (compost)	12	45	17	1	0.2

A proportion of the material was stored in the greenhouse in open pots and allowed to air dry. A further proportion was stored under cover in field moist condition. Two aggregate sizes, 2 cm and 4 mm were prepared by sieving. The dredged material sets like concrete when dry, and has an almost wax like quality when field moist, so the smaller aggregate sizes were prepared by pounding the air dry material, and chopping the field moist material in an industrial food-mixer prior to sieving.

The prepared substrates were used to fill pots with a capacity of 10 l. Green municipal compost from the Cleanaway municipal composting site at Pitsea in Essex was evenly incorporated at a 1:8 v/v ratio in pots with a compost treatment. Concentrations of PTEs in the green municipal compost are given in Table 4.5.

A preliminary trial had established that the material could be rewetted by slow infiltration. Water containers attached to tubes ending in dripometers were suspended over each pot, and each pot brought to field capacity. A portion of each prepared substrate was sieved over the top of the pots to ensure good seed/substrate contact, and seeds of the relevant plant sown. After thirty days, when plants were well-established, one of two watering regimes was introduced.

The soil was maintained close to field capacity, or plants were taken to just above permanent wilting point. When plants had wilted, an equal amount of water was slowly

added to each pot to bring the substrate back to field capacity by slow infiltration. There were four wetting and drying cycles in all.

Treatments for the randomized block design were:

Two aggregate sizes, 4 mm and 2 cm

Two watering regimes (no water stress and wetting and drying cycles)

Two plant species

Two compost treatments

This gave sixteen treatments. The trial started with 6 replicates of each.

4.3.2. RESULTS

Roots, shoots and soils of three replicates were processed. 4 *D. glomerata* root systems, 1 *M. sativa* root system and 3 soil samples were found to contain extremely high copper concentrations. These were 3645, 721, 735 and 4947 mg kg⁻¹ dry weight for *D. glomerata*, and 1114 mg kg⁻¹ for *M. sativa*. The soil samples contained 7230, 4857 and 898 mg kg⁻¹. High substrate copper and high root copper only corresponded in one instance, when 898 mg kg⁻¹ was measured in the substrate and 4947 mg kg⁻¹ was measured in the root.

Table 4.6 PTE concentrations in roots and shoots of *D. glomerata* and *M. sativa* (mg kg⁻¹ dry wt.).

<i>D. glomerata</i> root concentrations (mg kg ⁻¹)						<i>D. glomerata</i> foliar concentrations (mg kg ⁻¹)				
Element	Valid N	Mean	Min	Max	Std.Dev.	Valid N	Mean	Min	Max	Std.Dev.
Cu	20	98.0	59.4	143.0	24.3	24	6.7	4.0	12.4	2.5
Zn	20	128.8	77.4	200.5	38.1	24	48.8	27.9	93.4	16.3
Pb	20	27.4	9.0	44.5	8.8	24	1.8	0.0	5.9	1.3
Ni	20	9.6	3.5	18.1	4.2	24	1.5	0.0	5.3	1.3
Cd	20	3.3	0.8	10.4	2.5	24	0.3	0.0	0.7	0.2

<i>M. sativa</i> root concentrations (mg kg ⁻¹)						<i>M. sativa</i> foliar concentrations (mg kg ⁻¹)				
Element	Valid N	Mean	Min	Max	Std.Dev.	Valid N	Mean	Min	Max	Std.Dev.
Cu	21	18.3	8.4	37.8	8.5	24	9.5	6.8	14.0	1.8
Zn	21	45.6	20.3	85.4	18.9	24	75.1	39.0	108.0	17.2
Pb	21	5.0	0.0	13.8	3.6	24	2.2	0.0	6.9	1.7
Ni	21	2.0	0.0	6.6	1.3	24	1.1	0.0	2.8	0.9
Cd	21	1.2	0.2	3.6	0.9	24	0.4	0.0	0.8	0.2

The source of the Cu could not be the municipal compost, as four of the five root samples came from compost-free pots. The contamination appears to be localized, as

quartering pot material and subsampling for substrate analysis did not always pick it up, and its presence did not automatically translate into large root concentrations. After removal from the lagoons the dredgings had been left in the car-park of a landfill site for collection for several weeks. It is possible that the material was contaminated during this period. Samples where there was evidence of Cu contamination were excluded from subsequent analyses.

Metal concentrations in above- and below-ground plant material are shown in Table 4.6. Root concentrations exceed those found in contaminated plants for all elements in *D. glomerata* roots, and for Cd in *M. sativa* roots. All foliar tissue concentrations were within normal range.

No correlations were found between substrate metal levels and either above or below ground plant tissue levels, either when raw data was used, or when the plant uptake factor - the ratio of the element in the plant to that in the soil - was used. Data were analysed using ANOVA. No correlations were found between foliar tissue and any treatment variable, or between herb roots and any treatment variable. Some statistically significant differences were found between grass root concentrations and treatments (Table 4.7).

Table 4.7 Differences between treatments in *Dactylis glomerata* roots

Element	Texture	Watering treatment	plus or minus compost
Cu	0.035	n/s	0.001
Zn	n/s	0.009	n/s
Pb	n/s	n/s	n/s
Ni	0.01	0.001	0.00004
Cd	n/s	0.45	n/s

Where compost had been added mean concentrations generally tended to be smaller. This was significant only for Cu and Ni. Results were, however, very variable (Figure 4.5). *D. glomerata* plants which were subjected to a wetting drying regime showed higher mean root concentrations for all elements quantified, though these were only significant for Zn, Ni and Cd (Figure 4.6).

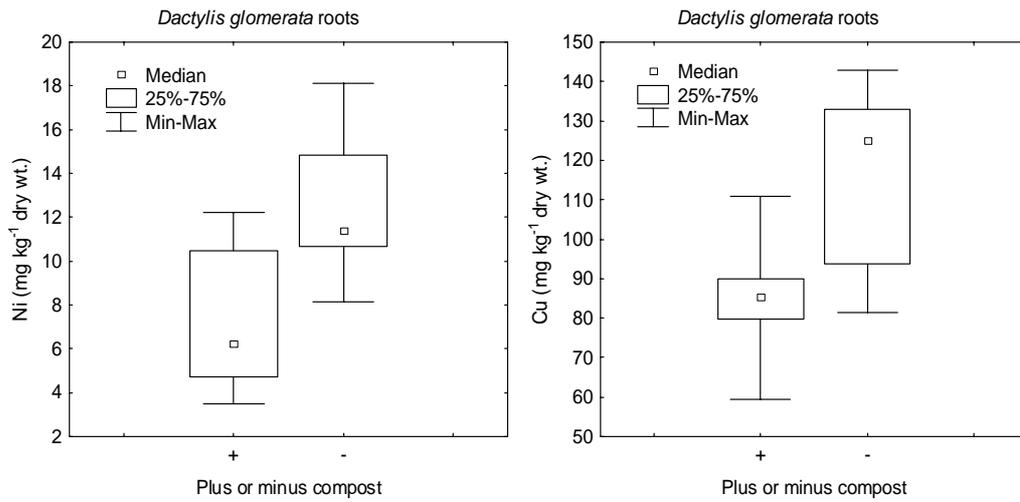


Figure 4.5 Box and whisker plots showing means and ranges of Cu and Ni concentrations in *Dactylis glomerata* roots grown with and without added compost (mg kg⁻¹ dry wt.).

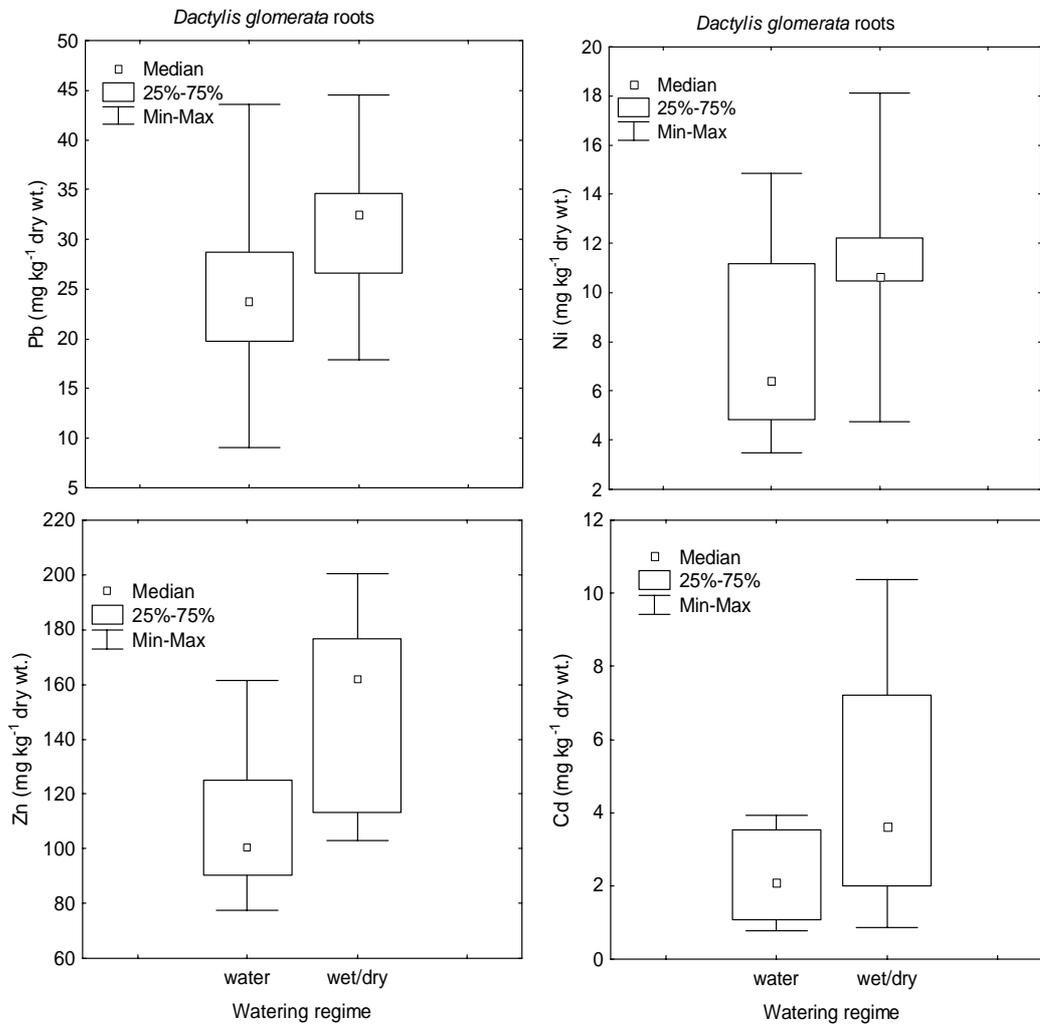


Figure 4.6 Box and whisker plots showing means and ranges of Pb, Zn, Cd and Ni concentrations in *Dactylis glomerata* roots grown with and without a wetting and drying cycle (mg kg⁻¹ dry wt.).

4.3.3. DISCUSSION

A great deal of work on PTE uptake by higher plants has been carried out in sterile and simplified laboratory experiments, using soluble metal salts. The results of these studies are poorly related to complex field situations. In an experiment on multi-elemental contamination in *Medicago sativa* using an artificial soil (70% sand, 25% gravel and 5% bentonite clay), the control, which received metals only as trace quantities of water-soluble metal salts in a plant nutrient solution, had shoot concentrations of 40 mg kg⁻¹ Cu and 160 mg kg⁻¹ Zn (Peralta-Videa et al. 2002). The concentrations of Cu and Zn found in *Medicago sativa* leaves in the present study were 12.3 ± 1.5 mg kg⁻¹ and 80.6 ± 15.3 mg kg⁻¹ (n = 20, field experiment) and 9.5 ± 1.8 and 75.1 ± 17.2 mg kg⁻¹ (n = 24, greenhouse experiment) (i.e. foliar Cu content in plants grown on the multi-elemental contaminated silts was less than a third and foliar Zn content less than a half of the concentrations found in a control supplied with trace amounts of soluble metal salts).

In the same study, soluble metal salts were added to the artificial soil to produce a final concentration of 50 mg kg⁻¹ of Cd, Cu, Ni and Zn. *M. sativa* plants grown in this medium for 15 days had shoot concentrations at pH 7 of 202 mg kg⁻¹ Cd, 105 mg kg⁻¹ Cu, 437 mg kg⁻¹ Ni and 160 mg kg⁻¹ Zn (Peralta-Videa et al. 2002). Live *M. sativa* plants have been shown to be capable of accumulating 26600 mg kg⁻¹ Zn, 8500 mg kg⁻¹ Ni, 1200 mg kg⁻¹ Cu, 6000 mg kg⁻¹ Cr and 10700 mg kg⁻¹ Cd when a single metal salt is supplied (Peralta-Videa et al. 2002). In a database prepared for the US Department of Energy (Section 4.4.1), significant differences were found between data from experiments using salt amendments and datasets from field observations, with the use of soluble salts generally resulting in plants accumulating larger concentrations of PTEs than occurred in the field. This led to the omission of these studies from the final models, and further emphasizes the difficulties in extrapolation from studies using soluble salts.

The greenhouse experiment carried out during the present research attempted to mimic natural processes, so that the results would be environmentally relevant. In retrospect this attempt appears naïve. Time constraints and the labour intensive nature of the

experiment resulted in only three of the replicates being processed, and the presence of Cu contamination in the substrate meant that even these were incomplete.

The experiment was overly complex, and the apparent response of the grass roots to treatments open to alternative interpretations. The response to the wetting/drying cycle in the grass roots may be related to drought stress in the grasses, rather than the effect of this treatment on soil factors governing bioavailability. The lower concentrations of Ni and Cu when compost was added may simply be the effect of roots accessing these elements from compost-rich microsites.

Interpretation is further complicated by the miss-match between the greenhouse substrate and the material on the experimental site, and the failure to homogenize the greenhouse substrate. The material was, however, subjected to extreme oxidation, which is likely to have increased PTE bioavailability in this substrate, and the results therefore add weight to the observations from the field experiment that PTEs in the dredgings are not readily plant available.

4.4. GENERAL DISCUSSION

4.4.1. PLANT UPTAKE OF PTEs

A common approach to risk assessment is the use of “plant uptake” or “bioaccumulation” factors, calculated by dividing the plant metal concentration by the soil metal concentration. A database of bioaccumulation concentrations from a comprehensive range of published studies was prepared for the US Department of Energy’s Office of Environment and Management (Bechtel Jacobs Company LLC, 1998) with the aim of producing and validating empirical models for the uptake of inorganic chemicals from soils by plants. However, plant foliar concentrations versus soil concentrations from the resulting data are highly scattered, even if the data are log-transformed. This underlines the limited power of models using total substrate PTE concentrations to predict plant tissue concentrations.

The database does, however, serve to put the present study in context. “Uptake factors” calculated with the foliar data from the field experiment at Rainham are much smaller than the geometric mean uptake factors derived from the database for all measured PTEs, with the exception of Pb. Depending on season, Cd concentrations are 3.7-5.4 fold smaller, Cu concentrations 2-2.5 fold smaller, and Zn concentrations 1.9-2.8 fold smaller. The Pb value is, however, 20% greater than the geometric mean uptake factor in August, and 40% smaller in May. Lead is not generally taken up by higher plants to any significant extent at any pH, due to its strong sorption by Fe/Mn oxides, and consequent immobility (Langmuir et al. 2004). The relatively high bioavailability of Pb in the Thames dredgings may be linked to the reductive dissolution of the Fe/Mn oxides in the river.

The likely co-distribution of PTEs in the Thames dredgings presents a particular challenge for terrestrial plants. Though all these elements may have species-specific toxic effects at critical concentrations, essential micro-nutrients can have adverse effects both when these are limiting and when they are in excess.

Plants evolved with PTEs present in variable amounts in the environment. Soils developed on parent materials such as ultramafic rocks or black shales are naturally high in these elements. As a consequence, plants can maintain homeostasis, i.e. regulate the activity of essential elements at constant internal and active concentrations so that physiological functions can be preserved, over fairly wide internal and external concentration ranges (Kapustka et al. 2004). The concentration ranges where supply is “sufficient” in the case of essential elements or “tolerable” in the case of non-essential elements varies between species and amongst species depending on their separate evolutionary history.

Most current PTE uptake models are variations of the Free Ion Activity Model (Morel, 1983). This is based on the concept that plant uptake of a particular PTE is related to the activity of the free ion in the soil solution bathing roots. Plant exposure to PTEs is thus constrained by abiotic factors that determine partitioning of the free ion between the soil solids and the soil solution, i.e. metal absorption/desorption and

precipitation/dissolution reactions. Free ions released from soil solids are delivered to root surfaces by diffusion or mass flow with the transpiration stream. A refinement of the Free Ion Activity Model is the Biotic Ligand Model, in which complexation of free ions by organic and inorganic ligands in the soil solution are allowed for, as well as competition effects with other cations at root absorption surfaces (McGeer et al. 2004).

In the models described above plants respond to elevated PTE levels in the root zone by expending metabolic energy to either exclude the element at the point of entry across the internal membrane, or by post-uptake sequestration as inert granules, binding by organic molecules called phytochelatins, or localisation of the element in the vacuole. These detoxification mechanisms may result in large internal concentrations in response to elevated external PTE concentrations even in plants that are not classed as “hyperaccumulators” (McGeer et al. 2004). Bioaccumulation of PTEs may cause adverse effects in organisms feeding on the plants.

The activities of PTEs in the soil solution in contaminated soils may be limited by rate processes controlling release from the soil solids (McGeer et al. 2004). Acute exposure to large PTE concentrations in solution will be lethal to all but the most metal tolerant cultivars, whereas a larger proportion of plants will be able to acclimate to chronic moderate exposure. When influx exceeds regulation or detoxification capacity, sub-lethal toxic effects may occur. These are generally inhibition of root extension growth, distorted leaves and discoloured foliage (Marschner, 1995). This is more likely to occur where land is used for arable cropping, and the plants are grown as a monoculture with a limited gene pool. Symptoms of phytotoxicity are likely to be masked when native plants colonise a contaminated site. Metal tolerance is genetically based (McLaughlin et al. 1999). The alleles for metal tolerance are widely distributed, so in these situations the short-term response will be selection for metal tolerant individuals, and the long-term result will be adapted semi-natural vegetation.

The Thames dredgings contain large percentages of clay and organic matter, which are important sorbents for PTEs. The cation exchange capacity is large. The calcium carbonate content in the dredgings neutralized acid generated in sulphate oxidation so

that pH remained near neutral after sieving, drying and re-wetting. The pH in the root zone under field conditions is likely to exceed the values found after these procedures. In-situ abiotic factors are therefore likely to result in extremely low equilibrium concentrations of PTEs in the soil solution. The evidence from the field experiment at Rainham is that concentrations are too small to have an inhibitory effect on either germination or the establishment of healthy plants, even if seeds are from unexposed populations. Foliar concentrations are generally within “normal” ranges, as seen above, and there is no evidence of toxic effects.

All plants were robust and morphologically normal, showed no symptoms of chlorosis, and flowered and set seed at the normal period. *Medicago sativa* has a known sensitivity to Cu (McGeer, 2004). *Brassica nigra* is known to hyperaccumulate Se (Marschner, 1995). *M. sativa* is growing well, reproducing well and self-seeding, and tissue concentrations of Se in *B. nigra* are very low. *Medicago sativa* and *Trifolium repens* form symbioses with the nitrogen fixing bacteria *Rhizobium*, which is PTE sensitive. Both species had nodulated well, and the nodules had pinkish interiors indicating that leghaemoglobin was being produced. PTE uptake at Rainham appears to be driven by plant demand for essential micronutrients, rather than the supply of free ions in the soil solution, as illustrated in Figure 4.6.

Plant roots are not passive receptors of free ions but actively modify their environment (Marschner, 1995). Their influence can extend far beyond the immediate vicinity of the root. Plants in natural, oxic, environments are almost invariably associated with fungal symbionts and associated microbial populations, and the plant-symbiont-microbe complex is known to exert strong regulatory control on the solubility of substances beyond the root into the rhizo- or mycorrhizosphere. Arbuscular mycorrhizas increase Cu and Zn uptake, root tip mucilage protects the apical meristem by binding metals, low molecular weight exudates mobilize metals (Marschner, 1995). The mechanisms used by plants to access limiting nutrients from solid-phase substances are well characterised only for the macro-nutrient phosphate, and the micro-nutrient iron (Marschner, 1995). The multi-elemental contamination at Rainham means that any stratagem for mobilising

tissue. Higher plants can be divided into two groups according to the stratagem used for accessing Fe.

Strategy 1, used by dicots and non-graminaceous monocots, involves an increase in reducing capacity and an enhanced net excretion of protons. This strategy will tend to access poorly soluble cations from the Fe/Mn oxide and carbonate phases. For reasons already discussed there are not likely to be large pools of Fe/Mn oxides associated with PTEs in the Rainham dredgings.

Grasses are Strategy II plants, responding to Fe deficiency by the release of high concentrations of phytosiderophores. These are non-proteinogenic amino acids that solubilise and mobilise Fe. Plant siderophores can also mobilize Zn (Zhang, 1993). When barley plants were grown in a calcareous soil (7% CaCO₃), root exudates of Fe-deficient barley plants were shown to have a much higher capacity to solubilise Zn, Mn and Cu than were Fe-sufficient plants (Marschner, 1995). The mean CaCO₃ content in the Rainham silts is around 10%.

A secondary feature of Strategy II plants is the presence of a highly specific Fe-phytosiderophore transport system on the plasma membrane of root cells. Grass phytosiderophores are known to form complexes with other PTEs, but the translocator in the membrane has a low affinity for the resulting complexes, so this may lead to enhanced concentrations of PTEs in the root apoplasm (Marschner, 1995).

There is some evidence that this occurs. Crop cultivars are categorised as Fe-efficient and Fe-inefficient on the basis of their capacity to produce phytosiderophores in response to soil Fe deficiency (Marschner, 1995). Uptake of Cd, Cu, Pb, Mn, Ni and Zn has been shown to be greater in Fe-efficient cultivars of *Avena sativa*, when compared to Fe-inefficient cultivars (Mench and Fargues, 1994). This was attributed to increased solubilisation of metals by phytosiderophores.

The data presented here represent the tissue concentrations in higher plants after three growing seasons on a substrate containing a complex multi-elemental mixture of PTEs,

long enough for adverse effects of even low-level chronic toxicity to occur. Despite the large concentrations of PTEs in grass roots, the answer to the first research question is that there is scant evidence of phytotoxicity or of bioaccumulation of abnormal concentrations of PTEs.

Homeostatic regulation in plants exists to maintain tissue concentrations in the range between deficiency and toxicity levels for essential elements and below toxicity for non-essential elements for the particular species or cultivar. Leaving aside the special case of hyperaccumulators - plants adapted to metaliferrous soils that accumulate very large quantities of PTEs - there are striking differences in critical toxicity concentrations between plants and domestic animals. The widest variation in critical deficiency and toxicity concentrations is found for Mo, which has a range of 0.1-1000 mg kg⁻¹ dry weight in plants, whereas toxicity to ruminants is caused by concentrations of 5 – 10 mg kg⁻¹ in forage plants (Marschner, 1995).

4.4.2. RISKS TO CONSUMER ORGANISMS

Bioaccumulated metals can serve as an exposure source through trophic transfer, and so cause toxicity through dietary exposure to consumer organisms. Chaney (1989) introduced the concept of the “soil-plant” barrier. This author classified metals into three groups. The first consists of elements such as Ag, Cr, Sn, Ti, Y and Zr, Hg and Pb that are either characterized by low solubility or low mobility in soils, and consequent low plant uptake, or are strongly bound in roots and not translocated to foliar tissues at concentrations injurious to animal or human health.

A second group B, Cu, Mn, As, Ni and Zn, though readily taken up by plants, are phytotoxic at concentrations below those harmful to consumer organisms. Chaney considers that most environmental risk is associated with a group of elements, Cd, Co, Mo and Se, which are not strongly adsorbed to soils or roots, and are toxic to consumer organisms at concentrations below those at which they are phytotoxic. Significant yield reduction in lettuce and wheat is reported to occur only when foliar Cd concentration reaches 188 and 36 mg kg⁻¹ dry weight respectively (Miller et al. 1995).

Neither Co nor Mo was quantified in the present study, and plant tissue Se concentrations are well within tolerable range. Cadmium concentrations are, however, higher than those cited by Chaney as being chronically tolerated by domestic livestock. Cadmium is highly toxic, and accumulates in the liver and kidneys (Beyer, 2000). It is impossible, given the conflicting opinions in the literature, to form any opinion on the ecological risk associated with the Cd concentrations found at Rainham.

Despite the very high substrate concentrations at Rainham, plant tissue concentrations do not appear to be particularly elevated when compared to published data. Concern over dietary intake of Cd resulted in the German Government setting an advisory limit of 600 ng g⁻¹ for sunflower kernels. This led to a screening programme in the United States, where the concentration range was found to be 310 to 1340 ng g⁻¹. Fewer than 10 of the 200 lines tested were below the advisory limit (McLaughlin et al. 1999). Cadmium in the leaves of durum wheat cultivars was found to range between 280 and 864 ng g⁻¹ at the 4 to 5 leaf stage (McLaughlin et al. 1999). The finding of the Total Diet Study that iceberg lettuce contains 2.2 ± 1.2 mg kg⁻¹ dry weight has already been mentioned. Mean foliar concentrations of cadmium found in the Rainham vegetation were 0.9 ± 0.7 in the May harvest and 1.2 ± 1.8 mg kg⁻¹ in the August harvest. If only grasses are considered, mean foliar concentrations in May were 0.37 ± 0.32 mg kg⁻¹.

Beyer (2000) considers that evidence of serious harm to wild animals, even at grossly contaminated sites, is slight. The World Health Organisation considers that concentrations in the human renal cortex may be as high as 200 mg kg⁻¹ wet weight before there are adverse health effects. As a result of Zn mining, Shipham in Somerset has the highest levels of soil cadmium in the UK. In gardens the range is from 2-360 mg kg⁻¹, with a median of 91 mg kg⁻¹, and in the surrounding agricultural land the range is 30-800 mg kg⁻¹. Dietary Cd intake is high locally. A long term study of human populations found markers of renal dysfunction but could not detect any adverse health effects (Morgan et al. 1988). A similar study of aged residents whose diet included home grown vegetables in Palmerton, USA, where soil Cd concentrations exceed 100 mg kg⁻¹, also failed to find evidence of injury (McLaughlin et al. 1999).

By contrast, consumption of rice and vegetables grown in soil with 7-70 mg kg⁻¹ of Cd in the vicinity of the Jinzu river in Japan has been shown to cause a disease called itai-itai (from the Japanese for ouch-ouch). This disease mainly affects post-menopausal women and is characterised by brittle bones and skeletal deformities.

The difference in health effects between Jinzu and Shipham is caused by complex interactions between soil factors, plant uptake factors and cultural factors. Shipham has a soil content of 6-14% CaCO₃, a pH of 7.4 and high concentrations of Fe/Mn oxides; the Jinzu floodplain has a soil content of 0.4% CaCO₃, a pH of 5.1 and low Fe/Mn oxides, so Cd is much more plant available. The Japanese women were suffering from dietary deficiencies of Ca, Fe, Zn, protein, fat and vitamin D during dietary exposure to Cd, factors thought to exacerbate Cd toxicity (McLaughlin et al. 1999).

The active debate over the effects of chronic low-level Cd exposure to humans is matched by debate over its effects on soil organisms and wildlife. Maximum permissible soil concentrations as low as 0.0019 mg kg⁻¹, based on protection of avian worm predators, have been suggested by some authors, while others consider that the toxicity of Cd has been exaggerated (Beyer, 2000).

Three small mammal species – the wood mouse, the bank vole and the common shrew – were used to monitor Cd bioavailability on three Flemish disposal sites for dredged sediments. These species have habitat ranges smaller than the surface area of the disposal sites. One site had been used for maintenance dredging from canal widening, and was effectively normal soil, while the other two had concentrations of Cd and Zn comparable to those found at Rainham. Cd and Zn were strongly positively correlated with organic carbon, and carbonate concentrations were high. No significant differences in Cd and Zn content in the small mammals were found between the sites, though there was evidence that Cd accumulated in their tissues at all sites, especially for the common shrew, which has a diet of soil invertebrates, insects and molluscs. When the highest concentrations found in small mammals were used as input in the BIOMAG model, predicted concentrations in the kidneys of their likely predators, the Tawny Owl and the weasel, were 3 and 4.3% of the no-effects concentration (Mertens et al. 2001).

It is not possible to answer the second research question, since it is impossible to reach any conclusions on the environmental risk posed by the elevated Cd concentrations found in the vegetation at Rainham.

4.4.3. *ALOPECURUS PRATENSIS AND FESTUCA RUBRA*

Two of the plant species used in the present study, *Alopecurus pratensis* and *Festuca rubra*, were found to accumulate high concentrations of PTEs in the root zone. These plants are used in turf grass and are considered to be metal-tolerant (Best et al. 2004). When they were grown in soils contaminated with Pb and Zn in concentrations roughly comparable with the present study, shoot concentrations of Pb for both species remained <10 mg kg⁻¹, while Zn was 259 mg kg⁻¹ in *A. pratensis* shoots, and 111 mg kg⁻¹ in *F. rubra*. Best et al. found that root concentrations varied with soil concentrations (Table 4.8). These are very much higher, at similar substrate concentrations, than those found in the present study, where *A. pratensis* had 389.1 mg kg⁻¹ Zn and 32.1 mg kg⁻¹ Pb, and *F. rubra* had 250 mg kg⁻¹ Zn and 24.1 mg kg⁻¹ Pb.

Table 4.8 Root and shoot of concentrations Pb and Zn in *A. pratensis* and *F. rubra* (Best et al. 2004)

Soil concentration mg kg ⁻¹		<i>A. pratensis</i> roots mg kg ⁻¹		<i>F. rubra</i> roots mg kg ⁻¹	
Pb	Zn	Pb	Zn	Pb	Zn
50	64	34	123	27	87
233	163	159	288	96	223
256	245	191	473	127	344
331	366	288	744	248	566

The evidence from this study and from the study cited above is that these two species are not metal tolerators but mobilize and accumulate PTEs. Concentrations of Cd and Cu were found in this study to be higher than substrate concentrations in the roots of *A. pratensis*.

4.5. CONCLUSIONS

Despite the large concentrations of PTEs in the Thames dredgings, and with the important reservation that above ground plant material was only harvested on two

occasions, when some evidence of temporal variation was found, PTEs in the above ground foliage of plants grown over three seasons under field conditions were generally within the ranges found in plants from uncontaminated sites.

Some species had Pb and Cd contents indicative of borderline contamination, but there was no evidence of either phytotoxicity or large-scale bioaccumulation. High germination rates and the establishment of healthy plants show that there are low concentrations of free PTE ions in the soil solution. This is attributed to strong sorption of these elements on soil solids. Comparison with a data-base of field studies showed that concentrations of all elements measured, with the exception of Pb, were several fold smaller in plant foliage than would be predicted from substrate concentrations alone.

Though the substrate was variable with respect to PTE loading, and the seed genetically variable, the strongest predictor of plant tissue levels of PTEs on the Rainham experimental site was the identity of the plant species. This is in keeping with previous studies (Hooda et al. 1997, and references cited therein).

Grasses and dicots responded to the presence of PTEs in different ways. These differences in uptake pattern between the grasses and dicots are here hypothesized to be linked to the different strategies used by these groups to access poorly soluble essential elements, and the unusual phase partitioning and co-location of essential and non-essential elements in the dredgings. The grasses were characterized by small foliar and large root PTE concentrations. There is evidence for strong sequestration of PTEs in the roots of *Alopecurus pratensis* and *Festuca rubra*. This has the potential, through organic matter cycling, to concentrate PTEs into the upper strata of the soil profile. Cadmium and Pb show much more variability than the essential elements Zn and Cu, suggesting poorer plant regulatory control over non-essential ions than over essential ions. Lead contents were smaller in dicot roots than shoots. Though Cd content was greater in grass than dicot roots, it was greater in dicot shoots.

Cadmium concentrations in the foliage were in excess of those known to be chronically tolerated in domestic animals when Cd is supplied in the diet as a soluble salt, and the animals are intended for human consumption. It is unclear what the ecological implications of this are.

Concentrations of PTEs in the foliage of plants at the experimental site are generally very much smaller than in the dredgings. This study has not considered direct exposure via dust inhalation or soil ingestion, or poisoning of birds due to ingesting earthworms or soil invertebrates.

CHAPTER 5 – GENERAL DISCUSSION

5.1. INTRODUCTION

The aim of this chapter is to integrate the various elements already introduced into a scientifically credible whole. The data from the characterisation of the Rainham dredgings revealed interesting relationships at the macroscale, in particular

- Large rates of mineral dissolution in the river
- Large accumulation of PTEs in the organic fraction
- Low bioavailability of PTEs

My explanation for these relationships is based on historical, microbiological, hydrological and geological science.

I propose here that microbial consortia within flocs in the water column in the maximum turbidity zone of the Thames Estuary dissolved PTE carrier phases. Mineral dissolution was driven by the requirement of one component of the consortia, dissimulatory iron-reducers, for respiratory Fe(III). Release of PTEs was a bi-product of this. The PTEs subsequently became associated with various components of the organic fraction through processes such as precipitation on living or dead bacterial cell walls; precipitation on bacterially produced extracellular substances; and uptake by bacteria and sequestration within cells. They may also have been incorporated in secondary mineral phases formed from ions released during mineral dissolution.

Since zones of maximum turbidity in estuaries are characterised by cycles of deposition and resuspension and long retention times, extensive organic mineralization occurs there. Mixing is likely to result in the homogenisation of material trapped in the zone. The resulting even distribution of organo-metallic and/or organo-metallic-mineral complexes throughout the mineral matrix would result in strong correlations between element concentrations as found here.

This chapter briefly summarises relevant research from a range of disciplines in support of this hypothesis, and then relates these to the observations made in the Thames. It concludes with a brief discussion of the wider implications.

5.2. SITE OF REDUCTIVE DISSOLUTION – WATER COLUMN VS. BENTHOS

In section 1.6 it was explained how the maximum turbidity zone in an estuary is associated with the convergence at bed level of landward and seaward flows (Figure 5.1). Particles are trapped there despite the presence of strong currents, and go through frequent cycles of sediment settlement and resuspension (Baeyens, 1998). Particle behaviour partially depends on current velocities. Spring tides cause re-suspension and widespread distribution of suspended solids, neap tides lead to the local formation of fluid mud, and high tides are associated with a great increase in turbidity (Baeyens, 1998).

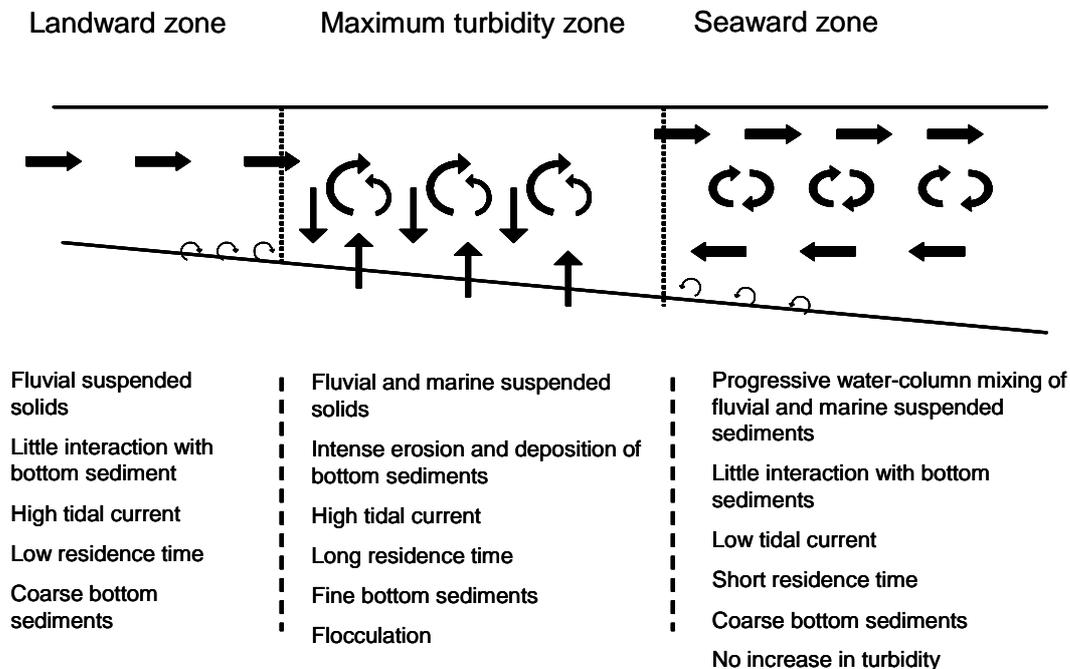


Figure 5.1 Diagram of suspended sediment transport in an estuary (adapted from Baeyens, 1998)

A discrete fraction of the particles are bacteria-rich. In the Colombia River these particles are responsible for 87% of biological activity, though they contain only 38% of the particulate organic carbon (3.7% by weight, with a C/N ratio of 7.6) and 38% of the total particle mass (Crump and Baross, 2000). They cycle in a different way from other particles. They are the first to be mobilised during flood tides and the last to settle. They form large aggregates at slack tide, which are broken up by shear flow at high

velocity, behaviour also seen in the Elbe and Dollard estuaries. Dissaggregation is diminished at neap tides because of reduced water velocity and shear forces (Crump and Baross, 2000).

The frequent erosion and re-suspension of sediments, coupled with the long retention time shifts particulate organic matter mineralization from the benthos to the water-column. Most organic matter in estuaries is mineralised in the turbidity maxima, though the fraction varies between estuaries, from 50% in the relatively unpolluted Gironde, to > 90% in the highly polluted Scheldt (Frankignoulle et al. 1998). This causes a drastic increase in the partial pressure of carbon dioxide ($p\text{CO}_2$) and an oxygen minimum. The equilibrium $p\text{CO}_2$ value is 360 μatm . In November 1994, the $p\text{CO}_2$ for the Scheldt and the Thames were 9425 μatm , and 5200 μatm respectively, associated with dissolved oxygen contents of around 25% saturation in the Scheldt and 50% saturation in the Thames (Frankignoulle et al. 1998).

Though the large amount of suspended solids in turbidity maxima means that most organic carbon in estuaries is concentrated there, percentage particulate organic carbon (%POC) is lower. %POC generally decreases abruptly as suspended particulate matter increases, and then stabilises to a constant value that varies between estuaries. This is 1.5% for the Gironde, 3.5% for the Loire and 4% for the Elbe, three relatively unpolluted estuaries with long residence times and pronounced maximum turbidity zones (MTZ) (Abril et al. 2000; Abril et al. 2002). The decrease in %POC in the MTZ is much more gradual in the polluted Ems. Despite intense mineralization in the MTZ, stabilisation of % POC does not occur in the highly polluted Scheldt, showing that, though heterotrophic mineralization rate increases with increasing organic matter inputs, the system can become saturated (Abril et al. 2002). Long term incubations have demonstrated the refractory nature of the stabilised organic matter, which remains within the turbidity maximum until it is carried to the coast during extreme high river discharge periods (Abril et al. 2000).

Estuarine turbidity maxima are particularly associated with the production of “fluid mud”, an expression first coined by Inglis and Allen (1957) to describe the masses of

cohesive sediment they found moving in high density clouds through relatively clean water above the true bed of the Thames. They noted that these masses either had a well-defined upper boundary or could extend several metres into the overlying water column. Section 1.6.1 showed that fluid mud is formed through the alteration of the hydrodynamic properties of discrete particles through flocculation.

Sylvester and Ware (1976) used an echo sounder to locate “fluid mud” masses in the Bristol Channel, when the overlying water-column was close to oxygen saturation. The mud was anaerobic, resembled “a light, floccular, biological sludge”, settled very slowly, and had a carbon content of 2.5 - 7%. It was brown, rather than black, so it was not sulphidogenic.

Nitrate and metal reduction within fluid mud has recently been demonstrated in the turbidity maximum of the well-oxygenated Gironde estuary (Robert et al. 2004). The suspended particulate matter concentration of the upper part of the fluid mud was around 100 g l⁻¹, increasing to between 250 and 500 g l⁻¹ at depth, and lay over the consolidated sediment, defined as settled solids which cannot be eroded by tidal currents. The fluid mud layer had been deposited several days previously. Though the overlying water column was oxic, denitrification was observed in the upper part of the fluid mud layer, followed by intense manganese dissolution and the concurrent release of Cd, Ni and Pb in the lower layer. No manganese reduction occurred in the consolidated sediment, though it was isolated from the oxic water column by a thick layer of hypoxic mud. The fluid mud layer is, in the Gironde, restricted to the navigation channel of the upper estuary (Abril et al. 2000), and only occurs during low discharge periods and spring and neap tides. Material dredged from the navigation channel will, therefore, preferentially remove fluid mud.

Sections 3.4.3.2 and 3.4.3.5 cover Yurkovskis’ study of the well-oxygenated Dauvaga, where he found a high inter elemental correlations, and a PTE/ particulate N correlation, coupled with very low concentrations of Mn. Yurkovskis commented that he could find no evidence of low bottom water oxygen. The study by Robert et al. shows that Mn reduction can occur within a discrete mass of “fluid mud” in well-oxygenated water.

5.3. FLOCS

Section 1.6.1 described how recent work has shown that estuarine suspended sediment, the origin of “fluid mud”, is made up of flocs. These are complex systems, made up of minerals, non-living organic matter and microbial populations embedded in extracellular polymeric substances (EPS). A floc may be considered a “mini-community” (Hawkes, 1978, cited in Hamer 1997), and is defined by Droppo (2001) as an “individual micro-ecosystem (composed of a matrix of water, inorganic and organic particles) with autonomous and interactive physical, chemical and biological functions of behaviours operating within the floc matrix.”

The biotic and bioorganic component is made up of the EPS, micro-organisms, and non-living macromolecules of organic matter that are trapped by the floc and provide organic substrates for microbial metabolism (Droppo, 2001). EPS is a general term for physically and chemically complex organic matter excreted by micro-organisms, which frequently exceeds cellular production and biomass (Decho and Herndl, 1995). It is made up of variable amounts of proteins, carbohydrates, (phospho)lipids and DNA (Flemming and Wingender, 2001). The proportions of these components are governed both by the microbial populations present (El-Mamouni et al. 1995), and by environmental factors, substrates and nutrient availability (Hamer, 1997).

EPS, by virtue of its complex molecular structure, performs a range of functions. Fine fibrils (4-20 nm) provide a large surface area for nutrient and mineral adsorption (Droppo, 2001); the presence of hydrophilic and hydrophobic regions may serve to protect and localise the extracellular enzymes required for the hydrolysis of organic matter (Decho, 2000); it provides a habitat where micro-organisms can co-exist, allowing the optimisation of the spatial arrangement of different microbial populations (Davey and O’Toole, 2000); and it allows microbial assemblages to develop synergistic relationships which are maintained over time (Flemming and Wingender, 2001).

Until recently flocs were examined using scanning electron microscopy, causing flocs, which are > 99% hydrated, to dehydrate and collapse. Confocal scanning laser microscopy allows hydrated flocs to be studied, revealing their complex and elaborate

three dimensional structure (Davey and O'Toole, 2000). There are pores and channels within the EPS matrix (Costerton et al. 1994). Pores between 10 -100 nm in size make up 20-50% of the floc volume, while another 5-10% consists of pores > 100 nm (Barker et al. 1998). Floc pores act as channels for the transport of respiratory and nutritional substrates into the floc interior, and the removal of excreted products of microbial metabolism to the bulk water (Davey and O'Toole, 2000).

The observation of differential cycling of the most bacterially rich component of the suspended sediments in the Columbia River has parallels with studies of floc behaviour in bioreactors. These show that flocs are structurally polymorphic, altering their shape to fit the prevalent hydrodynamic conditions and nutrient conditions (Davey and O'Toole, 2000). Turbulence leads to the production of elongated EPS streamers which oscillate in the bulk water. Aggregation alters the sedimentation rate. Complex bacterial communities in anaerobic sludge bed reactors form granules when they have no surface to attach themselves to, preventing them from being washed out (Davey and O'Toole, 2000).

In most of the thousands of flocs studied in natural aquatic systems by Droppo (2001) the inorganic component consisted of Fe, Al/Si or Si elements. It's considered likely (Leppard, cited in Droppo, 2001) that these are iron hydroxides, clay minerals and silicates. This concurs well with observations from the Thames, where the inorganic mineral component would have had both marine and terrestrial contributions.

5.4. MICROBIALLY DRIVEN PROCESSES WITHIN FLOCS

In addition to being sites of microbe-microbe and microbial-organic matter interaction, flocs are sites of microbe-mineral interaction. Though little is as yet known regarding the microbial role in the cycling of lithospheric elements and their transfer to the biosphere, there is a growing body of evidence showing that microbes access essential elements by dissolving minerals, a process traditionally assumed to be due to chemical and physical processes. Some examples of microbially enhanced mineral dissolution, such as the solubilisation of poorly soluble phosphate minerals by higher plant fungal

symbionts (Marschner, 1995) or the production of Fe-binding siderophores by marine phytoplankton are well characterised. It is becoming evident that these examples are likely to be the tip of a very large iceberg. The kinetics of even thermodynamically favourable reactions may be very slow in natural environments if they are not microbially mediated.

Living cells are thermodynamically open, constantly absorbing energy and nutrients from the environment for cell biosynthesis and maintenance, growth, replication and nutrient acquisition (Mohr and Schopfer, 1994), and constantly excreting transformed matter and energy to the external environment. The nature of the waste products from microbial metabolic activity is determined by the species involved, the external conditions, and the identities of energy sources and the terminal electron acceptors used. Since microbial metabolic activity can couple the oxidation of almost any organic or mineral energy source to the reduction of a range of electron acceptors (Nealson et al. 2002), the by-products of microbial metabolism, excreted from the cell as metabolic end products or intermediary metabolites, may be gaseous, liquid, solid, alkaline, acid, complexing and reducing compounds (Berthelin et al. 2000).

Mineral dissolution linked to microbial metabolism involves three separate mechanisms. (Berthelin et al. 2000).

- The release of organic acids and complexing compounds
- The oxidation and reduction of mineral elements
- Changes in pH and Eh

Abiotic silicate weathering is generally a very slow process. Reaction kinetics are controlled by temperature, pressure, ionic strength, chelating ligands and the concentrations of H^+ and OH^- (i.e. the pH) (Bennett et al. 2001). pH is the most important factor in abiotic weathering. Increases in either alkalinity or acidity enhance weathering, so this is slowest at circumneutral pH.

Microbes can do little to alter temperature and pressure (Bennett et al. 2001). However, colonies of bacteria as well as individual cells can strongly alter the pH, Eh and ionic strength of their external environment. In aqueous environments bacteria are covered by a thin layer of unstirred water. Nutrients taken in and metabolites excreted by bacteria must all pass through this hydrodynamic boundary layer. If rates of consumption or release of solutes exceed rates of diffusion across the boundary layer then concentration gradients develop across it (Shultze-Lam et al. 1996).

Microbes release large quantities of organic substances that act as ligands (extracellular enzymes, extracellular polymeric substances (EPS), organic acids, specific organic compounds such as siderophores and metabolic by-products) and may also release excess protons and hydroxyls to balance their cationic and anionic intake (Bennett et al. 2001). Resulting complexation and acid-base reactions in the external solution may result in mineral dissolution. The release of organic acids and complexing compounds is particularly associated with fermenting bacteria under anaerobic conditions (Valsami-Jones and McEldowney, 2000).

The reduction of iron was long regarded as a predominately abiotic process, resulting from low redox potentials, but significant abiotic reduction of iron has never been demonstrated. However, bacterial iron reduction, either coupled to H₂ or organic carbon oxidation, is now well established (Brown et al. 1999). In addition to its role as an electron acceptor in anaerobic respiration, iron is needed by organisms in large amounts as a nutrient, since it is a key component of cytochromes and iron-sulphur proteins required for electron transport. In order to meet their iron requirements, microbes may respond to small concentrations of dissolved iron in the external medium by secreting siderophores, organic compounds that form hexadentate complexes with iron, so dissolving iron in minerals.

Pure cultures grown on single carbon substrates in simplified laboratory experiments are unlikely to be very informative of the *in situ* behaviour of organisms living as part of a consortium in a continuously perturbed estuarine environment. They are, however, informative of the bacterial potential for mineral dissolution.

Pure culture studies have shown that both a commercially available siderophore and bacteria can accelerate the release of Fe from hornblende by up to 20 times over abiotic controls that lacked siderophores in six days. Siderophores without bacteria enhance Si, Fe and Al release, while bacteria in flow-through experiments cause an increase in Si and Fe release (Kalinowski, 2000).

Other microbial exudates have also been shown to greatly enhance silicate dissolution. Pure strains of bacteria in batch culture with sand grain sized feldspar and biotite have been shown to increase the release of Al and Si from feldspar, and Si, Fe and Al from biotite by up to two orders of magnitude when compared to abiotic controls (Barker et al. 1998). The same study showed that Si is preferentially released during feldspar dissolution at neutral pH, whereas the release of both Al and Si is enhanced at low pH.

5.5. AUTHIGENIC MINERAL PRECIPITATION

Microbes are implicated in the precipitation as well as the dissolution of minerals. Bacterial cell walls are rich in anionic functional groups such as carbonyls and phosphoryls. This gives bacterial surfaces a net anionic charge and combines with their large surface area to volume ratio to make them very effective at attracting metallic cations from dilute solutions (Schultze-Lam).

Metals bind onto the active sites, and the resulting metallic precipitates are stabilised by the cell wall, which reduces the interfacial tension between the mineral nucleus and the bulk water phase (Southam and Donald, 1999), thus lowering the activation energy required for crystallisation (Sokolov et al. 2001). An individual bacterium is capable of precipitating more than its own weight in metallic cations (Shultze-Lam). Since the cations, in turn, attract negatively charged counter-ions, the bacteria can act as nuclei for the formation of fine-grained minerals. The minerals formed are initially hydrous and poorly crystalline, but the phases re-order and become more crystalline in time.

Konhauser et al. (1994) showed that bacteria from submerged epilithic riverine microbial biofilms were all highly mineralised with an authigenic clay. The authors

presented a series of transmission electron micrographs showing different developmental stages of the mineral. The bacterial capsules initially become iron encrusted. As hydroxyls, aluminium and silicon precipitate, a poorly ordered gel-like phase is formed. The aggregates within the gel become more ordered, progressing first to an amorphous and finally to well-crystallised phase with a composition between glauconite and kaolinite.

The minerals formed as a result of microbial metabolism are partially governed by the counter-ions present, and partially by biological factors. At one end of the continuum, mineralization is under complete biological control. An example of microbially controlled mineralization is the creation of magnetosomes. These are complex precipitates of magnetite produced by magnetotactic bacteria to enable them to align themselves with the Earth's magnetic field and maintain their vertical position.

In other cases the type of mineral formed is altered by bacterial metabolic activity. A small cyanobacterium with an S-layer (a paracrystalline layer external to the cell and formed of protein units) causes the precipitation of calcite in a lake where the water is supersaturated with respect to CaSO_4 (Shultze-Lam). When the cyanobacteria are seasonally metabolically inactive gypsum tends to form. When they are active consumption of HCO_3^- as a carbon source results in the release of OH^- to the surrounding water ($\text{HCO}_3^- \rightarrow \text{CO}_2 + \text{OH}^-$) causing a high pH in the vicinity of the cells. The solubility product of CaCO_3 is thereby exceeded locally and precipitation occurs in the S-layer.

Authigenic minerals may also form abiotically in environments rich in organic matter. The use of organic material as a template for silica-based inorganic material is well established. Volkmer et al. (2003) demonstrated the self-assembly of star shaped titania-silica shells using a totally abiotic system at normal temperatures and neutral pH. They showed that if oil droplets similar in size to silicifying unicellular organisms are shaken in an aqueous solution containing silica and titanium substrates, they will, in a few days, produce shells about 10 to 100 microns in size, which are robust enough to

have their structure completely preserved after air drying and subjection to argon plasma at reduced pressure.

The minerals associated with bacterial metabolism have similar crystal habits and chemical composition as abiotically formed minerals (Brown et al. 1997). It is therefore difficult to distinguish between biologically mediated and abiotic mineral formation. Bacterial involvement in ancient mineral deposits is inferred from the presence of kerogen, low temperatures during formation, and inclusion of micro-fossils in the mineral matrix (Southam and Donald, 1999). Bacteria have been implicated in the production of diverse geological formations such as iron-silica deposits, magnetite, sulphides, phosphorites and carbonates (Southam and Donald, 1999).

Current biomineralisation has been well-studied in environments impacted by acid mine drainage. Metal cations precipitate out of solution onto bacteria, and eventually encrust them. As mineral growth continues, individual bacteria are joined together. This aggregation causes the organo-metallic complexes to settle to the sediments (Southam and Donald, 1999). Microbial population densities are an order of magnitude higher when they are in biofilms, leading to an increase in metal adsorption and immobilisation. PTEs are less likely to be remobilised from the resulting bacteria-metal-clay aggregates because of the low surface area to volume ratio of flocs compared to individual encrusted cells (Southam and Donald, 1999).

Prediction of the minerals formed as a result of microbial metabolism is likely to be difficult. The same micro-organisms can form different minerals in different environments. Brown et al. (1997) have succeeded in culturing a mesophilic biofilm from an underground habitat. This biofilm precipitates ferrihydrite and siderite when *in situ*. Experimental manipulation of the carbon to iron ratio in the culture media has resulted in a range of different minerals including siderite, ferrous hydroxide, vivianite, ferrihydrite and haematite. In pure culture studies the identity and crystallinity of the secondary mineral phases formed by the reduction of hydrous amorphous ferric oxides by *Shewanella putrefaciens* were shown to be influenced by the buffer composition, the

presence of phosphate and the bacterial respiration rate. Phases formed were magnetite (Fe_3O_4), siderite (FeCO_3) and vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) (Zachara et al. 1998).

5.6. IRON REDUCTION

When deposition at Rainham began freshwater flow at Teddington Weir was the major determinant of differences in water column oxygen status. The changes in the zonal pattern of nitrate and sulphide in the water column reflect population changes in the microbial consortia. Figure 2.6 shows that for a large part of the year in extensive zones of the river, iron reduction was the dominant terminal electron accepting process.

Though iron reduction by fermentative bacteria has been known since early in the 20th century, it was only in the late 1980s that it was shown that some micro-organisms could use Fe(III) as a respiratory substrate under anaerobic conditions. Subsequent research has demonstrated that this is a common trait occurring in bacteria with a wide range of physiologies, widely differing phylogenies and in many different environments (Frederickson and Gorby, 1996).

Most research on Fe(III) reduction to date has concentrated on the reduction of Fe (III) oxides, a generic term for a group of diverse iron oxides, hydroxides and oxide hydroxides ranging in crystallinity from amorphous ferrihydrite to well crystallised goethite, biotite and magnetite, with varying energy yields. (Straub et al. 2001). The redox pair ferrihydrite/Fe(II) has a potential of $\approx +100$ to -100 mV, whereas the Fe_3O_4 (magnetite)/Fe(II) pair has a potential of -314 mV (Straub et al. 2001). Environmental samples contain a mixture of different minerals.

Despite Fe(III) reduction being generally more energetically favourable than either sulphate reduction or methanogenesis, the two latter processes are frequently observed in anoxic sediments and subsurface environments which contain substantial quantities of Fe(III) oxides. This is because the reduced Fe(II) produced by iron (III) reduction can physically prevent further Fe(III) oxide reduction in several different ways. It can bind to the active sites of Fe(III) oxides or precipitate on the cell walls and EPS of iron reducing bacteria, or form secondary mineral phases such as vivianite and siderite on

the surface of Fe(III) oxide phases (Roden and Urrutia, 2002). Dissimulatory iron and manganese reducing bacteria in direct contact with iron and manganese oxide use enzymes located in their cell membranes to destabilise the mineral structure. Fe(II) does not inhibit these enzymes (Roden and Urrutia, 2002).

Fe(II) inhibition of Fe(III) reduction can be reduced by the addition of metabolically active cells without Fe(II) coatings, or the addition of organic ligands (Roden and Urrutia, 2002). Advective Fe(II) removal results in an increase in Fe(III) reduction from $13 \pm 2.2\%$ in batch cultures to $95 \pm 3.7\%$ in continuous flow reactors (Roden et al. 2000). This experiment used synthetic goethite, previously shown to be the form of Fe(III) oxide most resistant to microbial dissolution (Roden et al. 2000).

Most iron in aquatic and marine settings is not found as iron hydroxides, but as part of the structure of primary and secondary silicate minerals (Kostka, 2002). Recent work has shown that iron in these minerals can also be used as a respiratory substrate. Enrichment cultures of native microbial consortia can respire structural Fe(III) in smectite clay, with growth equal to that on Fe(III) oxide (Kostka, 2002). When the primary silicate anorthoclase is the sole source of Fe(III) and P for a microbial community, the mineral is rapidly dissolved with the concurrent release of dissolved silica and reduction of iron (Bennett et al. 2001). Brown et al (1997) have shown that a biofilm dominated by iron-reducers from an underground laboratory can leach ferric iron from its granite substrate, and use this as a respiratory substrate.

Reductive dissolution of iron and manganese oxides, clays and primary silicates are likely to cause significant changes in mineralogy. Bioreduction of Fe(III) in smectite by *Shewanella oneidensis* causes the dissolution of smectite, and the simultaneous formation of a different clay, illite, which contains significantly more potassium and significantly less silicon than the smectite parent material (Kim et al. 2004). Reduced iron released as the smectite dissolves leads to the formation of other biogenic minerals. These were siderite (FeCO_3) and vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot (\text{H}_2\text{O})_8$).

Reductive dissolution is also likely to cause significant changes in PTE speciation and availability. As discussed previously, clays are, because of their large surface area to volume ratio and density of negatively charged reaction sites, regarded as very important in PTE adsorption. The dissolution of aluminosilicates leads to the release of Si, Fe and Al (Maurice et al. 2001; Barker et al. 1998). Any process that results in the microbial dissolution of clays will affect the mobility of associated potentially toxic elements. Trace element isomorphic substitution is common in primary minerals, occurring when minerals crystallise from a silicate melt (Sposito, 1989). Dissolution of primary silicates implies that microbial activity is capable of releasing even residual phase trace metal impurities, normally regarded as being non-available.

The fate of the PTEs released during microbially mediated mineral dissolution within natural flocs is to be: bound on bacterial cell walls; bound on floccular ESP; immobilised within mineral precipitates; sequestered intracellularly; biomethylated and transported out of the cell; or released to the external medium

The formation of organo-metallic complexes is likely to have been an important process in the Thames. Transition metals, by virtue of their valences, hydrated radii, hydration energies and electronegativities have a strong affinity both for bacterial cell walls and for extracellular polymeric substances (papers cited in Konhauser, 1998). Metallic cations shown to bind to EPS include Pb, Sr, Zn, Cd, Co, Cu, Mn, Mg, Fe, Ag and Ni (Decho, 1990). Reduced humic acids are known to bind metallic PTEs more strongly than oxidised humic acids do (Kappler et al. 2004).

Different PTEs are likely to behave differently at the micro-scale. The uptake and removal of potentially toxic ions in conventional activated sludge treatment is an accepted feature of waste water treatment, though the mechanisms involved have not been characterised (Hamer, 1997). Leppard et al. (2003) used multi-scale microscopic techniques ranging from conventional microscopy (with a resolution of 0.3 μm), to transition electron microscopy (with a resolution of 0.001 μm), to study activated sludge flocs. Their aim was to relate individual metals spatially to different, selectively stained, floc substructures. The resulting images were used to derive chemical and

biological information about the association between colloidal matrices and given metals. Identification of different colloidal “species” was carried out by examining floc sections, and forming an overview of their relative abundance.

They found evidence of definite preferential localisation of potentially toxic elements within flocs. 98% of silver was associated with sulphur in granular colloids in the EPS matrix. These granules were found at the edges of spatially extended floc material, and were probably in direct contact with the bulk water. No silver was ever found inside a bacterial cell. Lead was, by contrast, always associated with phosphorus in the bacterial cytoplasm. Zinc was mainly extracellular.

The environmental fate of PTEs will also be dependent on the species present. A microbial consortium will be composed of many diverse microbes, each with its own evolutionary history and response to toxic metals in its environment. Species-specific differences in the fate of PTEs have been found in pure culture studies. Ragnardottir and Chavlet (2000) showed that two micro-organisms, *Saccharomyces cerevisiae* and *Pseudomonas aeruginosa* are both capable of accumulating 10-15% of their dry weight in uranium. They found differences in the location of the uranium. *S. cerevisiae* built up 0.2 µm thick layers on the cell wall, while *P. aeruginosa* sequestered it internally.

PTEs can also be immobilised in mineral phases. During microbial reduction of lepidocrocite, an iron oxide, by *Shewanella alga* in long term batch experiments zinc added to the culture medium was strongly bound in an unidentified mineral phase that could not be extracted by 0.5 M HCl. Zinc immobilisation was associated with magnetite formation (Cooper et al. 2000). Parmar et al. (2000) showed that the same bacterium could remove 60% of dissolved Sr^{2+} added to the culture. The Sr^{2+} was both complexed by the bacterial cell wall and incorporated into precipitating siderite.

Carbonate precipitation is often associated with iron-reduction. Where the mineral substrate for iron-reduction is an iron oxide, alkalinity is increased in the immediate environment of the microbial cell by the release of bicarbonate and hydroxyl ions. The increase in alkalinity and saturation with respect to the carbonate ion creates conditions

favourable to carbonate precipitation. This is likely to be enhanced in estuarine environments, where there will be abundant calcium and magnesium ions from seawater.

Carbonate precipitation is known to favour a type of co-precipitation – i.e. the simultaneous precipitation of a chemical element with other elements – called solid solution formation (Sposito, 1989). Solid solution formation occurs where there is a high degree of structural compatibility between the trace element and the host mineral, and may lead to the uniform replacement of a major element with the trace element. The Ca in calcium carbonate may be replaced by Cd (Sposito, 1989). Solid solution formation of secondary aluminosilicates may lead to the incorporation of Ni, Cu and Zn as replacements for structural Al (Sposito, 1989). Pb, Zn, Cu and Ni occur in solid solution in pyrite (Algeo and Maynard, 2004).

5.7. THE THAMES ESTUARY

Anthropogenic activity inadvertently created an analogue of a continuous flow anaerobic bioreactor in the maximum turbidity zone of the Thames Estuary from the 1940s until the beginning of the 1960s. Embankment of the river in Central London, the reduction of the width of the river at its mouth with its consequent increase in the tidal range and the construction of the dredged navigation channel combined to increase energy within the system. The sewage outfalls contributed large amounts of organic material. Thermal pollution had raised the water temperature 5°C above the rest of the river (DSIR, 1964). The final straw was probably when re-oxygenation of the river by wind and tide was impeded by the presence of non-biodegradable detergent residues at the water/atmosphere interface.

By this time all higher trophic levels in the zone had long since gone, leaving only heterotrophic bacteria. Intense microbial activity since the construction of the sewage outfalls had, over decades, produced an enrichment culture from the resident microbial populations. For the adapted microbial consortia in the Thames survival required only discrete seasonal changes in community structure accompanied by shifts in the dominant terminal electron acceptors used. Increases in sulphate reduction and

sedimentation led to human intervention; the WPRL's record of conditions in the Thames being placed in the public record; sediments from the affected zone being deposited in the lagoons at Rainham over the next two decades; and simultaneous changes in organic matter input to the river.

When deposition at Rainham began, dissolved oxygen concentrations in the MTZ were relatively stable. The Thames Survey Committee Report includes quarterly data on temperature, river flow and dissolved oxygen for the years 1920-1962. In the decade between 1952 and 1962 the lowest point of the oxygen sag curve exceeded 10% only during the 4th quarter of 1960. This was associated with an exceptionally high mean flow of 232 m³ s⁻¹ at Teddington Weir, and resulted in a dissolved oxygen content of 12%. During the same decade mean average flow was 119 m³ s⁻¹, 45 m³ s⁻¹, 21 m³ s⁻¹ and 78 m³ s⁻¹ for the 1st, 2nd, 3rd and 4th quarters of the year respectively (DSIR, 1964). Under the Thames Conservancy Act of 1932, the statutory minimum flow is 8.94 m³ s⁻¹. This was not met on an average of 24 days a year between 1933 and 1974 (Gameson and Wheeler, 1977).

Changes in the quantity and quality of sewage discharges to the Thames while the Rainham lagoons were in operation were rapid, continual and substantial. The WPRL developed a formula for calculating the effective oxygen demand that was later used by Gameson and Wheeler (1977) to show how this decreased over time (Table 5.1)

Table 5.1 The effective oxygen demand (tonnes per day) for three major sewage outfalls. (Data from Gameson and Wheeler, 1977)

Period	Mogden	Beckton	Crossness	Total
1950-53	77	504	212	793
1956-58	83	366	222	671
1960-62	75	283	251	609
1966-67	24	263	117	404
1968-70	28	250	60	338
1971	16	203	50	269
1972	15	170	29	214
1973	12	153	34	199

Major improvements to Beckton were completed in 1975, reducing its effective oxygen demand to 35 tonnes a day, and the total from the three sewage outfalls to 80 tonnes a

day, an order of magnitude lower than it had been in 1950. These changes in substrate quality impacted on microbial populations. No sulphide was found in the river after 1966, and anoxia became infrequent. In the sediment from the lagoon core this has resulted in increases in the C:N ratio and decreases in organic matter content.

The marked homogeneity in the texture of the lower part of the core suggests that, despite this, rates of mineral dissolution and re-precipitation remained relatively stable long after organic matter inputs declined and anoxic conditions became rare. Some changes in texture may have occurred. The silt fraction is between 2 -65 μm . A gradual increase in particle size over time in the lower part of the core would not have been revealed by the methods used in this study.

The increasing heterogeneity in the upper part of the core probably represents a threshold at which bulk water oxygen content for much of the year relegated iron reducers, the previously dominant functional guild, to a greatly reduced niche, as an increase in organic matter mineralization by aerobic bacteria occurred. This is likely to have resulted in profound changes in the quantity of suspended sediment in the turbidity maximum.

Aerobic micro-organisms use a diffusible, water soluble terminal electron acceptor. They are often capable of totally respiring a carbon substrate to CO_2 and H_2O , leaving no direct trace in sediments. Iron reducers need the catabolic activity of fermentative bacteria to hydrolyse complex organic macromolecules and produce their carbon substrates. Since aerobes do not have the same dependency on complex consortia as anaerobes, and do not need to produce EPS and “electron shuttles” to access their respiratory substrate, the increase in oxygen is likely to have resulted in less carbon being diverted to floc production and maintenance. There are likely to be strong selection pressures against floc inhabitants producing enzymes that degrade the floc structure (Flemming and Wingender, 2001).

5.8. THE N/PTE RELATIONSHIP

Domination of the microbial consortia by iron reducers has far reaching implications at the macroscale. Fe(III) reducing bacteria are unique in using a component of a solid mineral matrix as a respiratory substrate. Iron reduction requires Fe(III) in mM concentrations (Maurice et al. 2001). Since iron is seldom the major component of minerals, the scale of iron reduction in the Thames represents extensive reductive dissolution of Fe(III) bearing minerals and implies substantial release of associated PTEs and other elemental components of these minerals.

The literature cited above and the strong correlation with nitrogen suggests that the PTEs were subsequently complexed by bacterial material and EPS, or precipitated as authigenic minerals. Processes within the MTZ itself, where a large volume of sediment was trapped and continually mixed, would have been sufficient to effectively homogenize the suspended material, resulting in the distinctive N/PTE signature.

It is also possible that the products of mineral dissolution have different environmental fates, and that this led to the local enrichment and retention of PTEs within the MTZ. The density of surface charges on the iron and manganese oxides mean these contain higher metal loadings than clays, which have greater PTE contents than primary silicates. Iron oxides break down to the hydroxyl ion and Fe(II), both soluble ions.

In addition to being adsorbed or precipitated, some Fe(II) and Mn(II) will be advected from the system. Where active manganese and iron reduction is known to occur in consolidated sediments, accumulation rates of Fe(II) and Mn(II) in pore waters are an order of magnitude lower than gross production by dissimilatory metal reduction due to adsorption and precipitation processes (Thamdrup, 2000). When Fe(III)-smectite was dissolved and re-precipitated as illite by iron reducers under anaerobic conditions, approximately 10% of the Fe(II) produced was detected in the aqueous solution while the rest was in biogenic solids (Kim et al. 2004).

If there is significant retention of PTEs while Fe(II), Al, and Si are advected, PTEs are likely to become enriched in sediments retained in the turbidity maximum. It is perhaps

unwise to extrapolate from different studies, but the large discrepancies in the Al and Fe concentrations between this study and that by Attrill and Thomas, and the much higher concentrations of Al and Fe found at the Tilbury basin by O'Reilly-Weise et al. suggest that this may have occurred in the Thames.

It is worthy of note that the same N/PTE signature appears in all the sediments examined in this study, though it is less striking in the surficial strata of the lagoons. If microbial dissolution of mineral phases causes this relationship, this implies that iron reduction was considerable even after the major improvements to Beckton sewage works in 1975.

5.9. THE SILT FRACTION

Evidence has been presented that the striking changes in sediment texture occurring over time in the Thames turbidity maximum resulted from mineral dissolution and precipitation within microbial flocs. Figure 5.2 is an SEM electro-micrograph of material from a depth of 3.5 m in the lagoon, showing the extremely fine texture and the intimate association between organic matter and individual particles

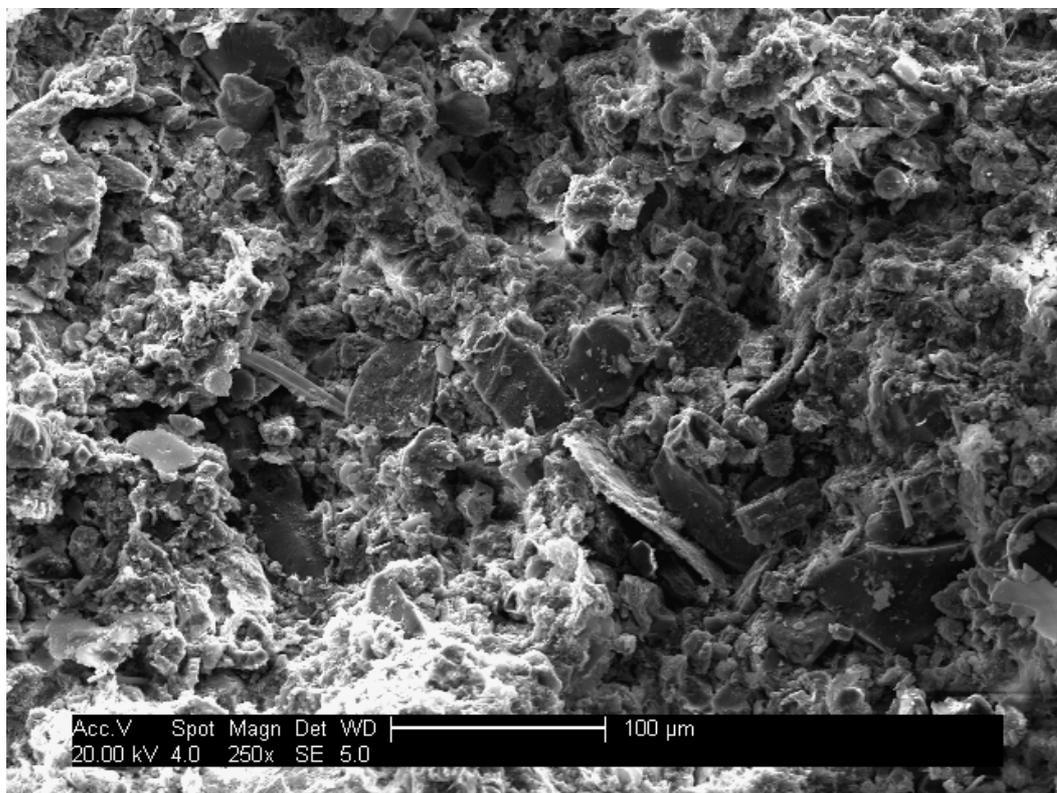


Figure 5.2 Electron micrograph of the dredged material.

Though the dissolution and re-precipitation of silicates and phyllosilicates has never before been suggested as a process operating in modern hypoxic estuaries, studies of organic rich sediments from the geological past show that increases in quartz silt can occur either through a reduction in the size of individual sand grains, or through the authigenic formation of quartz.

The former process was identified in a study of organo-mineral relationships in the organic-rich Oxford Clay Formation. Numerous quartz grains with corroded outlines were found. These were coated with organic matter. SEM/BSE imaging showed that the corroded edges were organo-mineral complexes (Benin and Kenig, 1994).

Quartz silt in mudstones was believed until recently to originate either from the mechanical abrasion of sand during transport processes, or from the deposition of airborne dust from warm deserts. This interpretation is currently being re-appraised following the demonstration that almost all the quartz silt in Late Devonian black shales from the eastern US was formed *in situ* (Scheiber et al. 2000). The evidence for this was three-fold, based on the morphology of the silt-sized quartz, the degree of luminosity revealed by cathodoluminescence and differences in oxygen isotopes. These grains were generally surrounded by a thin amber film of organic matter. Scheiber suggests that the silt is formed by the precipitation of dissolved silica inside algal cysts. Authigenic quartz is known to precipitate when silica concentrations in interstitial water reach 14 ppm (Benin and Kenig, 1994).

The use of the pipette method to determine the silt fraction simply quantifies which percentage of a given sample consists of discrete particles between 2 and 65 μm . It is not informative over mineralogy. Examination of the microfabric of the dredgings using SEM was carried out before the present hypothesis was formulated, in an unsuccessful attempt at showing that the PTEs were in the organic fraction. Individual particles examined by energy-dispersive x-ray spectroscopy were of quartz, clay and calcium carbonate, and the silt particles of quartz and calcium carbonate. Figure 5.3

shows an electron micrograph of a calcium carbonate crystal in close association with organic material, suggesting that it may be of authigenic origin.

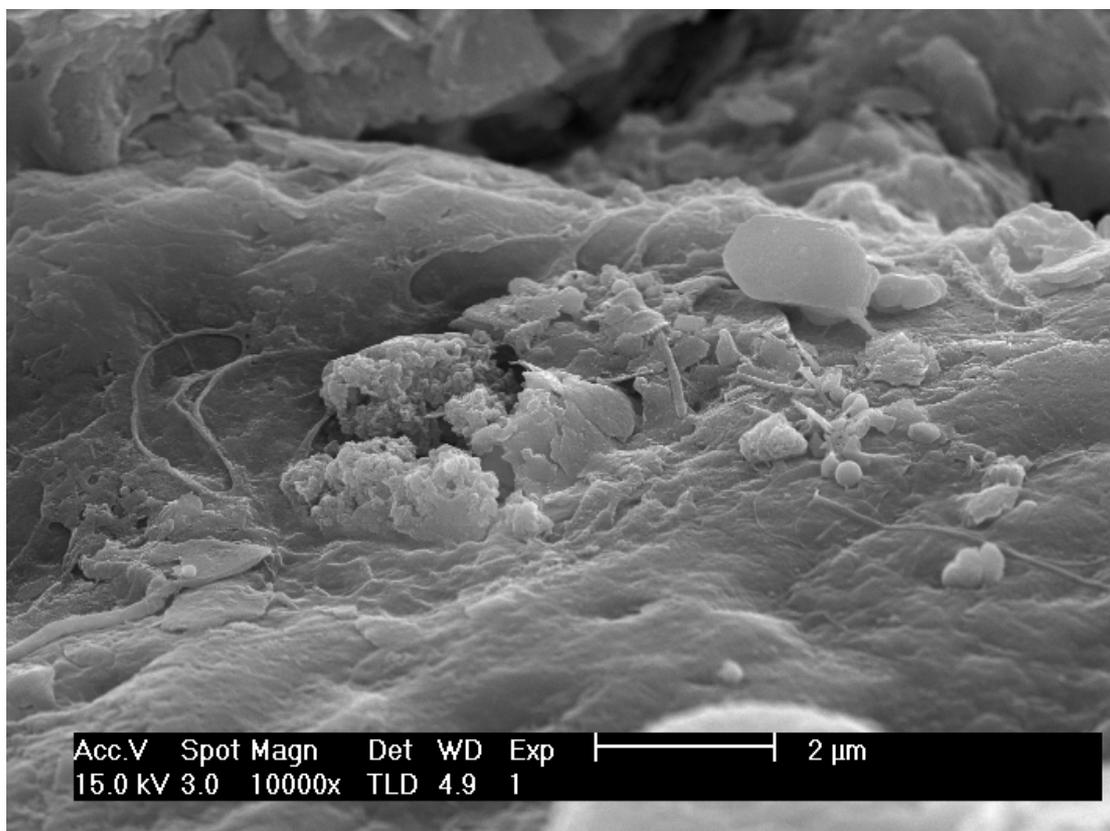


Figure 5.3 Electron micrograph showing calcite crystal associated with organic matter.

The continuation of iron reduction and silicate dissolution implied by the N/PTE association long after oxygen (and fish) had returned to the “mud reaches” suggests that iron reduction within flocs in estuarine turbidity maxima may be widespread.

Environmental studies of iron reduction have so far been restricted to consolidated sediments and terrestrial settings, which are, for a host of reasons, much less favourable to the process than estuarine turbidity maxima. At the macroscale, fluxes of marine and terrestrial suspended sediment through the zone represent the continuous renewal of reduction capacity in the form of fresh iron and manganese oxides, clays and primary silicates; a net throughput of water allows the advection of potentially inhibitory metabolic waste products, such as Fe(II), from the system; while a long retention time traps organic matter, so promoting intensive biogeochemical cycling and the development of the estuarine oxygen minimum.

Insoluble iron oxides cannot diffuse in settled sediments or terrestrial settings. This difficulty doesn't exist in the dynamic environment of a turbidity maximum, where floc EPS acts as a sticky trap for Fe(III) containing minerals. Synergistic relationships with fermenting bacteria, in particular, are likely to greatly increase the efficiency of iron reduction. The large amounts of chelating ability produced as organic matter is degraded will enhance iron reduction in several ways. The presence of organic acids alone is sufficient to accelerate dissolution of mineral respiratory substrates. Organic acid chelation of Fe(II) will prevent its inhibitory effect on iron-reduction. The net energy gain from chelated Fe(III) is higher than it is from either amorphous or crystalline iron oxides. The Fe(III)-NTA/Fe(II)-NTA redox pair has a potential of +385 mV, and the Fe(III)-citrate/Fe(II) citrate pair a potential of +372 mV (Straub et al. 2001). Modification of the Eh in microenvironments within flocs will tend to protect obligate anaerobes from oxygen. Possible additional advantages of a floccular existence for iron-reducers include the localisation of extracellular enzymes and "electron shuttles", reversibly redox-active molecules produced by some iron-reducers to facilitate electron transfer between the microbe and the solid phase ((Hernandez and Newman, 2001). Water abstraction and lower rainfall during the summer months lead to longer sediment retention times, enhancing the conditions likely to promote iron reduction.

It is possible that iron reduction in estuarine MTZs is a widespread process, and has not been detected. Direct detection of a process localised in a moving cloud of mud near the bottom of a highly dynamic and turbid part of an estuary is unlikely to be simple. Most Fe(II) released is likely to be adsorbed, and the proportion released to the water column will not remain detectable for very long in oxic waters. Fe(II) is highly reactive, and the energy required to oxidise it to Fe(III) relatively small (Christensen et al. 2000). The half-life of Fe(II) in oxygenated water is in the order of a few minutes (Davidson and Seed, 1983). Re-oxidation of Fe(II) is not dependent on oxygen, but can be re-oxidised by other species, such as Mn(IV), nitrite or nitrate. Strains of facultative-anaerobic nitrate-reducing bacteria capable of coupling the reduction of nitrate to N₂ with the stoichiometric oxidation of Fe(II) to ferrihydrite, a potential substrate for

Fe(III) reducers, under anoxic conditions have been isolated (Straub et al. 2001). This creates the potential for iron-reduction using recycled iron in a high energy yielding form within a turbidity maximum.

5.10. SUMMARY AND CONCLUSIONS

MTZ in estuaries are zones of intense organic matter mineralization by heterotrophic bacteria, and are generally associated with estuarine oxygen minima. The bacteria responsible live as sessile microbial consortia within a highly structured extracellular organic matrix. Bacteria, EPS and associated minerals are collectively known as flocs. The basic floc unit is a micro-aggregate. Micro-aggregates can coalesce to form larger flocs at certain states of the tide. Larger flocs may also combine to form “fluid mud”.

As a consequence of microbial modification of the micro-environment and aggregation phenomena, anaerobic bacteria can live and function even when the bulk water is oxygenated, so a proportion of organic matter in estuaries may be mineralised using an electron accepting process, the nature of which cannot be predicted from bulk water data.

The proportions of the different functional guilds in the microbial assemblages inhabiting the flocs change in response to changes in the external medium. Though many factors associated with microbial metabolism may result in the dissolution and re-precipitation of solid minerals, the reliance of iron reducing bacteria on a respiratory substrate that is part of the mineral matrix means that this form of metabolism invariably leads to high rates of reductive dissolution of Fe oxides, clays and primary silicates.

Conditions in estuarine MTZ are likely to favour iron-reduction, but the dynamism of this environment creates obvious problems for the study of these processes *in vivo*. It would be difficult to design a laboratory experiment that adequately represented a system where adapted microbial consortia were continuously perturbed by the cycle of the tides and by unpredictable flood events, and existed under non-steady state conditions characterised by gradients in bulk-water environmental parameters such as

temperature, salinity, pH and Eh, and with continuous and fluctuating fluxes of mixed substrates.

Sediment from the Thames turbidity maximum currently stored in lagoons at Rainham in Essex forms a physical and chronological record of the changes occurring in minerals and preserved organic matter during the transition between a period when organic matter mineralization was dominated by iron reduction in an anoxic environment, to one where iron reduction was a localised process in an oxic environment. There is evidence of mineral dissolution throughout the period.

The presence of a localised anaerobic fluid mud layer within oxygenated water allows the regeneration of released Fe(II) to amorphous Fe(III) oxyhydroxides, and hence substrate recycling. Oxidation of the Fe(II) aquo iron to the Fe(III) aquo iron is rapid in oxygenated waters, occurring within a few minutes.

If the mechanism proposed above is correct, it resulted in a distinctive “organic matter/PTE” signature. Published research shows this correlation is not uncommon in eutrophied estuaries, demonstrating that the same process may be occurring elsewhere. This may have consequences for trace metal availability, the marine food chain and organic carbon sequestration.

The eventual fate of all organic matter is to be mineralized, sooner or later. Transferring and concentrating potentially toxic elements from more resistant phases to a potentially labile organic matter phase may increase their bioavailability within estuaries, major sites of primary production. This has major implications for water quality.

If the organic matter is resistant, then sediments from estuarine environments may be operating as a huge carbon sink, for both organic and inorganic carbon. The discussion in section 1.5.3 shows that a major factor in atmospheric oxygen homeostasis is the balance between the oxidation of organic rich sedimentary rocks and the sequestration of reduced organic carbon in current sediments. Identifying which guilds have the

capacity to sequester large amounts of carbon in a relatively inert form, and the circumstances in which they do so opens up the prospect of manipulating the biota so that some mitigation of anthropogenic carbon discharges occurs.

Dissolution of mineral carrier phases implies an alteration in the geochemical cycling of iron, aluminium and silica. Estuaries are conduits for the transfer of dissolved silica and iron, important nutrient ions for the marine phytoplankton, to the seas. Perturbation of these cycles may result in changes in phytoplanktonic communities, the base of the marine food chain.

The process described above would have resulted in most iron, aluminium and silica released re-precipitating as fine-grained minerals closely associated with organic matter, and may be the origin of the frequently observed close association between mineral surface area and recalcitrant organic matter in coastal shelf regions (1.5.3).

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