The Mobilization and Release of Mercury, Copper, Iron, Manganese and Selenium from Contaminated Sediment as a Result of Dredging: Laboratory Simulation Studies

Interim Report to the National Rivers Authority
Anglian Region
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1. SUMMARY

This report summarises the results of the dredging simulation experiments undertaken by Imperial College to assess the likely release of mercury and other metallic contaminants from bottom sediments of Rockland Broad if dredging operations using a bucket dredge were to be carried out.

Concentrations of total mercury in the bulk sediment from cores of up to 1 m depth ranged between 8.79-9.81 mg kg^{-1}, indicating considerable contamination of the sediments is still prevalent in the Broad. Simulation of a dredging operation using the modified elutriate test (MET) has indicated that total mercury concentrations will initially increase 3-5 fold over levels present in the column water, to concentrations of 1.5-2 µg l^{-1} total mercury. Within 48 h of sediment disturbance total mercury concentrations in the water column are predicted to be < 1 µg l^{-1} which is within the E.C. regulations of 1 µg l^{-1} total mercury as an annual average. Mercury release from the sediments to the overlying water will thus be a short term effect of dredging. Copper concentrations in the sediment and water were low and disturbance by dredging was shown to be unlikely to cause contamination of the water above the E.C. limit of 28 µg l^{-1} total copper as an annual average.

The oxides and hydroxides of iron and manganese are known to be important sorbing agents for metals such as mercury and thus their release during MET experiments was also monitored. Iron concentrations in the water column were found to be highest immediately after sediment disturbance (1200-1500 µg l^{-1}) with most of the iron being particulate associated. Manganese concentrations peaked at 700 µg l^{-1}, 40-50 fold higher than background water levels. In contrast to iron, approximately 90% of the manganese was in the soluble phase. Concentrations of iron and manganese decreased with time from sediment disturbance, approaching background levels after 48 h.

Selenium forms very insoluble and stable complexes with mercury and copper. Monitoring of selenium release from sediments showed that negligible concentrations were present. Selenium is thus unlikely to play a major role in precipitation of metal contaminants in the overlying water in the Rockland Broad.

Total organic carbon (TOC) concentrations in the overlying water decreased from 120 mg l^{-1} immediately after sediment disturbance to 20 mg l^{-1} after 24 hours. Complexation of soluble mercury by humic and fulvic acids present in the organic matter is thus likely to have occurred, decreasing concentrations of soluble mercury present in the overlying water and promoting settling out of mercury released from the sediments. Total suspended solids concentrations decreased from 100 mg l^{-1} initially to 2 mg l^{-1} after 24 hours, indicating re-suspension of bottom sediments will not persist 1-2 days after dredging.

Several physicochemical parameters, including redox potential, pH, free sulphide ion, free chloride ion and free sulphate ion concentrations were monitored during MET experiments. The redox potential of the sediments decreased from slightly reducing conditions after sediment disturbance to strongly reducing conditions after 24 h, similar to redox potentials for the bulk sediment. The change in redox potential of the sediment caused by sediment disturbance is, thus, a short term effect which will

initially promote contaminant release, but will quickly revert to background conditions under which no additional contaminant release would be expected. The change in sediment pH was small (approximately 0.1 pH units) and did not play a significant role in promoting contaminant release as acidic conditions were not observed. Chloride ion concentrations (230-250 mg l^{-1}) in the overlying water did not vary significantly during MET experiments. Increased concentrations of chloride might be expected to increase the solubility of mercury and thus enhance its release from bottom sediments, but this was not observed. Free sulphide concentrations were below detection limits as sulphur forms very strong and stable precipitates with mercury and copper and would thus not be expected to be free in solution. Sulphate concentrations increased upon aeration of the sediment-water system, but the effect that this has on contaminant release is linked with the sulphide-sulphate redox cycle which has yet to be fully elucidated.

Mercury within the sediment compartment of Rockland Broad is thus still of environmental concern. A dredging operation will cause short-term contamination of the overlying water with mercury. Subsequent disposal of the contaminated dredge spoil at an upland site may, however, increase the availability of mercury to the surrounding environment due to the penetration of oxygen, creating acidic conditions conducive to leaching of metal contaminants. The use of a clay-lined disposal site in this regard will help prevent the re-introduction of mercury to the river. This aspect requires investigation before the full impact of a dredging operation can be assessed.

CONTENTS

2. INTRODUCTION

Previous research by Imperial College investigating the River Yare and its associated Broads has revealed the presence of a point source contamination plume of heavy metals, especially copper and mercury emanating from Whitlingham STW (Imperial College, 1988). A large amount of the contaminated sediment has also accumulated in the Rockland, Wheatfen and Surlingham Broads. In view of the high concentrations of mercury (in some cases approaching 30 mg kg^{-1} total mercury) known to be associated with the Broads' sediment (Imperial College, 1990a,b) and consequent potential for production of lipophilic methylmercury, it has become necessary to assess the environmental impact and consequences of dredging operations in terms of metal release, mobilisation and possible bio-availability.

Dredging is routinely undertaken on the Yare system to maintain navigation channels; it is inherent to the operation that disturbance and redistribution of bottom sediment occurs. In doing so particulate bound contaminants are resuspended to the overlying water. Soluble metal species may be released from the sediment interstitial water or following desorption from the sediment particles themselves. Desorption of metals is greatly influenced by changes in physicochemical conditions and the degree of resuspension and contaminant release varies according to sediment type, hydrological conditions, type of dredging equipment and the operational procedures employed.

The appearance of mercury within sediments is of prime concern since aquatic organisms may bioconcentrate organic mercury within living tissue with the possibility of bioaccumulation further up the food chain, eventually to man. Inorganic mercury may be converted to methyl- or dimethylmercury by anaerobic and aerobic bacteria found within the sediment of streams and rivers (Beijer and Jernelov, 1979). Methylmercury is far more toxic to organisms than inorganic mercury and is thus the species of most concern. Methylmercury is soluble in water although dimethylmercury is thought to be lost to the atmosphere.

Copper is an essential trace element found in aquatic sediments. Continued ingestion of copper may lead to accumulation in animal tissues, especially in the liver (Underwood, 1971). Copper is the most common heavy metal to which aquatic organisms are exposed because of its use as an algaecide and its occurrence as an ubiquitous anthropogenic pollutant. It is a component of sewage effluent, derived from domestic and industrial sources. The availability of this copper depends on the carbonate chemistry of the system. The most important of these reactions is the formation of insoluble malachite ($CuCO_3.Cu(OH)_2$) which occurs above pH 6, but which may be hindered by the presence of organic ligands which compete for the copper (Sylva, 1976).

Selenium is toxic to all animals, although the biochemical mechanism is not known (Ewan, 1978). In small quantities, however, it is an essential nutrient, being an integral part of the enzyme glutathione peroxidase (Harr, 1978). Ferric selenite and combinations of ferric oxides with selenites are quite insoluble and largely unavailable to biological systems (Geering *et al.*, 1968). Selenides of mercury, copper and cadmium are very insoluble. Their insolubility may be the basis for the reported detoxification of methylmercury by dietary selenide and for decreased heavy metal toxicity associated with selenide. Metallic selenides thus form a biologically

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2ʒJune 1993

Dear Geoff,

    Please find enclosed a copy of the interim report entitled "The Mobilisation and Release of Mercury, Copper, Iron, Manganese and Selenium from Contaminated Sediment as a Result of Dredging: Laboratory Simulation Studies" and a current invoice report covering the period 1st April - 31st May.

Yours sincerely,

J.N. Lester
Professor of Water Technology
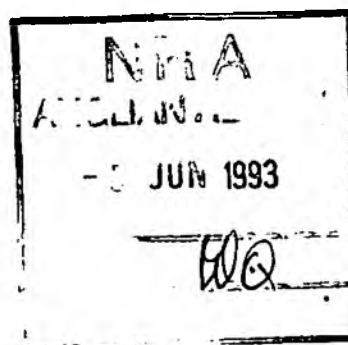
Removal of Mercury Contaminated Sediments in the River Yare.

Project Reference 420

Contract Reference 01/420

Invoice Report 1st April - 31st May.

In accordance with the above contract the first interim report has been compiled. The report details the findings of work carried out on contaminated Rockland Broad sediment collected in January 1993.
In particular, the fate of the metals; mercury, selenium, copper, manganese and iron have been elucidated as a consequence of simulated dredging and sediment disturbance. The results of this investigation, as well as the characterisation of the sediment and overlying water (pH, TOC, redox, salinity, etc.) are presented fully.

Work is now continuing on the effect of saline intrusions and increased organic content on the availability of metals, in particular mercury and methylmercury.
Method development for the determination of sediment buffering capacity is also being carried out as metal mobilisation, as a consequence of a change in sediment pH, requires further investigation.

Experimental protocols for bacteriological studies are presently being prepared. The experiments will elucidate the role of bacteria and factors that affect mercury methylation and demethylation processes such as; temperature , pH, availability of nutrients, etc.

The boat for the annual River Yare survey has been booked for the first week in July (to maintain continuity with previous year's surveys) and preparations for the survey are currently underway.

important sequestering mechanism for both selenium and heavy metals in a largely unavailable form. It is for these reasons that it was considered important to include selenium in the monitoring protocol during the dredging simulation experiments, although there has been no historical contamination of the River Yare with selenium.

2.1   DREDGING

There are three major types of dredge generally used - mechanical, hydraulic pipeline and hopper dredges. A general overview of the use of each type of dredge and its impact on sediment associated contaminants is presented.

Mechanical dredges

Mechanical dredges, commonly called grab, bucket or clamshell dredges, consist of a bucket operated from a crane or derrick mounted on a barge. They are used for dredging up to hundreds of thousands of cubic metres of sediment. Most sediment dispersion by this method occurs by impaction of the bucket on the bottom material and continues as the bucket is lifted. When the bucket breaks the water surface turbid water spills out of the bucket or leaks through openings between the jaws, contaminating the overlying water. Once loaded on the barge, turbid water is often intentionally allowed to overflow to encourage stability and increase the barge's effective load. This practice significantly contributes to the resuspension sediments and associated contaminants during bucket dredging. Bucket dredging causes the greatest suspension of sediment to the overlying water of the methods described here.

Hydraulic pipeline dredges

Hydraulic pipeline dredges use a rotating cutter to excavate the bottom sediment and guide it to a suction pipe for removal. Excavated material is pumped to the designated disposal site through a pipeline as a slurry with a solids content of 10-20% by weight.

Most sediment resuspension is found in the vicinity of the cutter and the level of turbidity produced is related to the type and quantity of material cut which is not removed by suction. This form of dredging is the most commonly used in the USA because of its relatively low disturbance of sediment at dredge sites. Capital expenditure and the availability of suitable disposal sites have limited its widespread use in the U.K.

Hopper dredges

Hopper dredges are used in areas of high shipping traffic or rough water. The dredge is part of a self-propelled ship and as the dredge moves forward the bottom sediment is hydraulically lifted from the channel bottom through a draghead, up the dragarm (suction pipe) and temporarily stored in hopper bins in the ship's hull before permanent disposal at an appropriate site (Peddicord, 1987). This is the largest scale dredging method and can be used to move millions of cubic metres of silt. Resuspension of sediment is in the same order as that of hydraulic pipeline dredges, but initial capital outlay is far greater, making this method suitable for continuous dredging operations only.

2.2 MOBILISATION OF SEDIMENTARY CONTAMINANTS

In order to better understand the potential for contaminant release from sediments caused by dredging operations the various parameters of the undisturbed sediment and the factors most likely to affect these parameters must be considered. The contaminants of major interest are those from anthropogenic inputs and include mercury and copper which are known to contaminate the River Yare, originating from their release in significant quantities from Whitlingham STW until 1976. Controlled amounts according to a consent set by the NRA of no more than 10 μg l^{-1} total mercury in fully treated sewage effluent may still be released (personal communication, NRA, 1993).

Contaminants in sediments have a wide range of availability which depends on lotic (running water), lentic (standing water), estuarine or marine conditions; physical properties of the sediment; nature and form of the contaminants, and the chemical and biological parameters of the water involved. The potential impact of heavy metals from sediments to the surrounding environments is evaluated here strictly with respect to conditions typical of freshwater systems. The generalised behaviour of trace elements and heavy metals in an aquatic ecosystem is determined by:

1. contaminant loading
2. movement of the materials to the sediment
3. behaviour of contaminants within the sedimentary system and interaction with benthic organisms
4. temporal and spatial movement from the original deposition location
5. interactions between non-benthic organisms.

Heavy metals within sediments

Heavy metals commonly find their way into sediments because of the relatively low solubilities of most of their chemical forms and their tendency to enter into complexation and sorption reactions with naturally occurring organic compounds and metal hydroxides (Leland et al., 1978). Oxides and hydroxides of iron and manganese are among the most important sorbing agents for metals and may be generally present in fairly high concentrations (Grieve and Fletcher, 1977). Heavy metals also associate with organic suspended solids from decaying vegetation containing humics and fulvic functional groups. These reactions depend not only on the availability of the interacting solids, but also on the various chemical conditions within an ecosystem, most notably the pH and the degree of oxidation or reduction (Silva, 1976) and the residence time of heavy metals in the water column. In flowing systems the magnitude of water movement will also play a key role.

Investigations of the species present and behaviour of trace elements within the sedimentary compartment will yield insight into the circumstances by which these materials are released back into the overlying water. Heavy metals are often found to be preferentially associated with smaller particle sizes (Helmke et al., 1977) and organic fractions (Benes et al., 1976). These fractions are characteristically associated with the deep water portions of lentic systems and the active sediments of lotic systems. In the case of mercury it is known that sorption occurs more readily to

6

the smaller size fractions (Luoma, 1976). These phenomena are highly pH and oxidation-reduction state dependent and can thus be expected to be strongly affected by dredging activity.

Mobilisation of heavy metals from sediments

Physical, biological and chemical factors contribute to the natural mobilisation of heavy metals. These factors are all inter-related and make up a complex network of interactions which cannot be considered in isolation. Any influences that dredging may exert on these factors could rapidly alter contaminant release from the sediment to the surrounding environment.

The hydrodynamics of a fluvial system is often the rate-controlling step in sediment-water exchange reactions. Currents in the overlying water tend to transport leached material away from the sediment, allowing concentration dependent reactions to proceed. Mixing in the overlying water promotes sedimentary particle suspension which in turn enhances exchange reactions between the particle and soluble phases. Mixing within the surface sediment carries unleached particles and interstitial water to the sediment-water interface, further encouraging exchange. Resuspension by dredging will greatly accelerate all these processes.

The mixing in rivers and streams arises from the flow of water due to differences in elevation of the land through which they flow. Even in the lower reaches of rivers the flow above the sediment and relative mixing within the surface sediment are far greater than for lentic systems. This not only accelerates the relative rate of two-phase interaction, but it also results in substantial transport of sediment. In the case of mercury, which is mainly associated with the particulate phase, this is an important factor and has already been shown to be the major reason for contamination of the Broads where large amounts of sediment have accumulated (Imperial College, 1992). The form in which most of the mass of metals is transported varies, however. Cadmium is almost completely solubilised, lead is generally associated with particulates and zinc behaves in a manner somewhere between these extremes (Jennett and Foil, 1979).

Thus fluvial systems such as the Broads may be remote from direct trace element contamination, but receive contaminated sediments and can be expected to represent a long-term sink for these materials. Dredging can be expected to have differing effects on the remobilisation of heavy metals, depending on the nature of the relationship between the metal and the sediment compartment.

Temperature influences are particularly critical to the rate kinetics for many of the chemical and biochemical transformations which occur in sediments. Few investigations have been carried out into the effect of temperature on the mobilisation of mercury, but it is known that methylmercury production is enhanced after periods of warm weather (Callister and Winfrey, 1986). The actual timing of dredging may be an important consideration if attempts are made to limit the degree of contaminant release. Also, several bacteria common to aquatic ecosystems are capable of transforming fairly immobile species of lead and tin to highly labile ones by alkylation. Mercury alkylation within the River Yare has been discussed thoroughly (Imperial College, 1992). Based on the highly insoluble nature of many metal

7

sulphides, the reduction of sulphate to sulphide by certain bacteria is significant in some systems as it will precipitate most metals, making them largely unavailable.

Closely related and interlinked with the biological factors are chemical factors. The most important chemical factors that will influence the sediment environment are acid-base reactions, oxidation-reduction reactions, complexation, desorption-sorption and precipitation-dissolution reactions.

Acid-base reactions can affect exchange reactions in a number of ways since many chemical reactions are pH dependent. Natural aquatic sediments normally do not show large pH changes because they are usually well buffered due to the presence of large amounts of clay materials and organic matter which can absorb significant quantities of hydrogen ions and, in calcerous systems, precipitated calcium carbonate (Jennett et al., 1980). Changes in pH will affect the nature of sorption sites, the occurrence of precipitation and complexation reactions and the distribution of ionic species. These changes not only affect the position of equilibria, but in many cases the kinetics of exchange reactions too. The critical role of pH in affecting complexation and the rate of adsorption of copper was demonstrated by Sylva (1976). In general, elevated heavy metals levels in receiving waters typically coincide with elevated hydrogen ion concentrations, presumably partly due to increased mobilisation from sedimentary sources.

Desorption-sorption reactions are probably some of the most important types of reactions controlling the exchange of materials between sediments and water. Clays and inorganic crystalline compounds (particularly iron and manganese hydrous oxides) are solids with large surface areas that have sorptive properties. In general, sorption is a fast process that is pH, redox and temperature dependent and somewhat reversible. Several studies have shown that sorbed metals can be released to the water, particularly under low pH and high ionic strength conditions (such as would occur during a saline intrusion). If dredging operations reduced the localised pH, then desorption would be facilitated.

Precipitation reactions contribute to the deposition of trace elements in the sediment, but due to the complexity of fresh water systems and kinetic considerations it is difficult to predict actual precipitation rates. Dissolution of trace elements that are incorporated in amorphous or crystalline precipitates would not be readily expected under constant surrounding conditions as they are tightly bound. However, under drastically altered ionic strength and pH conditions such as might be expected from a major dredging operation, substantial dissolution might be expected.

Complexation reactions are important in sediment-water exchange processes, particularly if various organic compounds such as fulvic and humic acids derived from decomposed vegetation and planktonic organisms are present. The levels of these organic acids are ecosystem and season dependent. Laboratory experiments have indicated that both fulvic and humic acids are highly potent in the mobilisation of sedimentary trace elements (Benes et al., 1976). The formation of a complex in solution acts to enhance the partitioning from the sediment because the complex tends to drive the reaction toward the solution phase. Once sediment disturbance has occurred, mobilisation of heavy metals into the aqueous phase by complexation is facilitated and may act as a significant route for metal release.

8

The overall redox state of the sediment has been shown to play an important role in the mobilisation of trace elements (Farrah and Pickering, 1977). Generally, as the redox potential drops, the mobility of the sedimentary trace metals increases. Although considerable efforts have been made to quantify overall oxidation-reduction characteristics of water and sediment systems by measurements of E_h (the redox potential) using platinum electrodes, these measurements are crude and cannot be used to predict the ratios of oxidised to reduced species. Aerobic environments are normally oxidative while anaerobic environments are reducing. Subsurface sedimentary layers are reducing in most cases while surface sediments and water are typically oxidative. This is the case for the River Yare and Broads sediment and water, but dredging will mix both oxidising and reducing environments, leading to possible changes in the rate of contaminant release.

Kinetics play an important role in redox transformation as the reaction rates are typically slow under most environmental conditions. Redox potential is particularly important in the mobilisation of iron which is significant in light of the extensive adsorption to iron compounds that other trace metals undergo.

2.4 PREDICTION OF POLLUTANT RELEASE AS A CONSEQUENCE OF DREDGING

Having elucidated the main factors affecting bottom sediment dynamics, it is necessary to consider the consequences of dredging in terms of pollutant release and what methods are available for predicting the release of these potentially harmful contaminants from such sediment.

Typical dredging operations involve the use of a bucket dredge which will produce a highly visible plume of suspended sediment with a suspended solids concentration range of 10-100's mg l^{-1} which will extend for 1-2 km from the dredging activity and disappear shortly after disturbance (Peddicord, 1987). The majority of the suspended solids will be redeposited whilst 1-3% remains suspended for a longer period of time. The major chemical change that occurs is as a result of the input of oxygen by stirring and aeration. High concentrations of relatively soluble reduced forms of iron and manganese (FeS and MnS) are oxidised when suspended which then form insoluble oxides and hydroxides that precipitate out and are deposited in bottom mud. Other metals are co-precipitated with iron and manganese so net release of soluble metals from suspended dredged material is low or possibly even absent. The pH is not significantly affected by oxygen input during resuspension, but will be after a few months if disposed of in upland disposal sites where drying out of sediments causes large changes in buffering capacity. Factors such as salinity and redox potential can be expected to show marked changes over a short period of time before returning to background levels. Typically, sediment requiring dredging for navigation can have an *in situ* water content of up to 50%. Fine grained sediments make up 90-98% of the mineral solids with 2-10% and occasionally up to 20% organic solids being present (Peddicord, 1987).

Considering such a scenario, Palermo and Thackson (1988a) developed an elutriate test to simulate physicochemical conditions that will be brought about during a dredging operation and which will affect the release of contaminants. Elutriate is

defined as the centrifuged or filtered clear liquid containing the soluble fraction of a sediment sample. In designing the elutriate test Palermo and Thackson (1988a) considered all of the factors discussed in Section 2.2 which may cause changes in contaminant mobility. In brief, pH; oxidation-reduction potential; chemical composition of overlying water; physical properties of the sediment, including grain size and organic material; and salinity were considered.

A number of factorial experiments (where one experimental parameter was varied whilst keeping all others constant) were performed in an attempt to best simulate the agitation and oxidation; sediment concentration; and retention time of particles in the water column which occur as a result of a dredging operation. These parameters were in addition to the most important factors affecting contaminant release which are the character of the sediment and overlying water being dredged and the type of dredging operation employed. The character of the sediment and water is unique for each location and can only be accounted for by taking representative samples at the intended dredge site. In all cases the modified elutriate test was developed to predict the contaminant release from the 'worst case scenario' using bucket dredging.

By varying the initial concentration of slurry, aerating the sample for different periods of time, and allowing settling for up to 24 hours, a number of optimal conditions for simulation of a dredging operation were obtained. Results were compiled from the analysis of 27 parameters, including dissolved and total nutrients and trace metals. The most suitable vessel for conducting these experiments was found to be a 4 l measuring cylinder. Using analysis of variance procedures at 95% confidence limits the optimal initial concentration of the sediment slurry was found to be 150 g l^{-1} on a dry sediment weight basis. Aeration time was optimised at 1 hour of low level bubbling to give consistency to the handling of material for each site. Dissolved oxygen concentrations in the supernatant were found to be the same regardless of the length of aeration. A maximum settling time of 24 hours was used as no appreciable changes occurred after that time.

Comparison of the results obtained for both dissolved and particulate bound concentrations with actual observations made during dredging operations showed that predictions were within a factor of 2 or 3 of field data. All predictions were higher than observed in the field, especially the contaminant fractions of the total suspended solids. This was likely due to wind resuspension in the field which cannot be accounted for in the laboratory experiments.

The predictive abilities of the modified elutriate test have been investigated by Palermo and Thackson (1988b) and Ludwig et al. (1989). Grimwood and McGhee (1979) reviewed the initially developed elutriate test. Results varied, depending on the sediment type and contaminants considered. The authors found that the elutriate test was successful in predicting concentrations of chromium, cadmium, arsenic, nickel and zinc, but was less successful for lead, mercury and copper because of differing absorptive capabilities of sediments. The modified elutriate test, used in this work, has removed most of these discrepancies and has been officially sanctioned by the United States Environmental Protection Agency (Palermo, 1992).

3.   OBJECTIVES

1. To use the modified elutriate test to simulate the effects that dredging will have on contaminant release from the Rockland Broad bottom sediments.

2. To assess the potential release of mercury and copper to the overlying water at levels considered to be an environmental hazard from sediment known to be contaminated. To also monitor the levels of iron and manganese in the overlying water, known to be important in sorption and precipitation reactions involving other metals, and to attempt to elucidate their role in the availability of mercury and copper.

3. To assess the likely partitioning between dissolved and suspended solid phases for copper, mercury, iron and manganese in the overlying water as a result of dredging operations

4. To assess the availability of and possible roles that sulphur (as sulphide and sulphate) and selenium may play in the oxidation-reduction cycle of sediment disturbed by dredging. The presence of soluble sulphide or selenium would also be expected to play a major role in the complexation of copper and mercury, removing them from the soluble phase.

5. To monitor gross changes in pH, redox potential, temperature and free chloride levels in the sediment and overlying water during simulation of dredging and to assess any affects changes in these parameters may have on contaminant release.

6. To provide an initial evaluation of the appropriate actions to be taken when dredging is carried out on the Broads.

4. MATERIALS AND METHODS

For the methods described in this section all glass- and plasticware was cleaned by soaking in a solution of 5% Decon 90 detergent for 24 hours followed by rinsing three times in reverse osmosis (RO) water (Elgastat, High Wycombe, U.K.), soaking in 10% nitric acid for 24 hours and a final rinsing three times in Milli Q water (Millipore, Watford, U.K.) before air drying. Milli Q water was used for making up all solutions.

4.1 SAMPLING STRATEGY

Sediment and overlying water were collected at low tide on 20th January 1993 from 3 sites on Rockland Broad (Figure 1). Rockland Broad was selected as the initial site for investigation as it is known to have high levels of mercury contamination, sediment deposition by siltation is fairly rapid and it carries most of the boating traffic as it is the biggest of the 3 Broads in the area. Sediment was collected using a drain-pipe corer according to procedures previously described (Imperial college, 1992). Three sites were sampled in a transect across the Broad, corresponding to sites C2, C4 and C5 (Imperial College, 1990). Cores of up to 1 m depth were taken, the sediment being transferred to polythene bags immediately on collection. Excess water was decanted off and the bags sealed to exclude air. Overlying water was collected in 25 l plastic canisters with the exclusion of air. On return to the laboratory the sediment was homogenised by mixing with a plastic rod. Sub-samples were taken for total organic carbon (TOC), total solids content (TS) and total metals analyses. Initial redox potential, pH and temperature readings were also recorded at this stage. The bulk of the sediment to be used for the modified elutriate tests was stored at 13 °C until it was required. The water samples were stored at 5 °C and allowed to return to room temperature before use.

4.2 MODIFIED ELUTRIATE TESTS

The dredging simulation experiments carried out in accordance with the procedures described by the US Army Engineer Waterways Experiment Station, Vicksburg Technical Note EEDP-04-2 (1985). Appropriate volumes of sediment and overlying water were thoroughly mixed to give a final sediment/water concentration of 150 g l^{-1} on a dry sediment weight basis and placed in a 4 l Pyrex glass cylinder (Radleys, Saffron Walden, U.K.; 45 cm x 4.4 cm i.d.). The density of the sediment was predetermined by oven drying a known volume at 105 °C and weighing the dried sediment.

The slurry was aerated for 1 h to ensure oxidising conditions were present in the supernatant water during the subsequent settling phase and to simulate sediment disturbance during a dredging operation. This was done by bubbling air vigorously through a glass tube inserted to the bottom of the cylinder which ensured good agitation of the mixture.

The glass tube was removed and quiescent settling was allowed to occur. After a short time an interface becomes apparent between the supernatant water with low concentration of total solids and the more concentrated settled material. At various
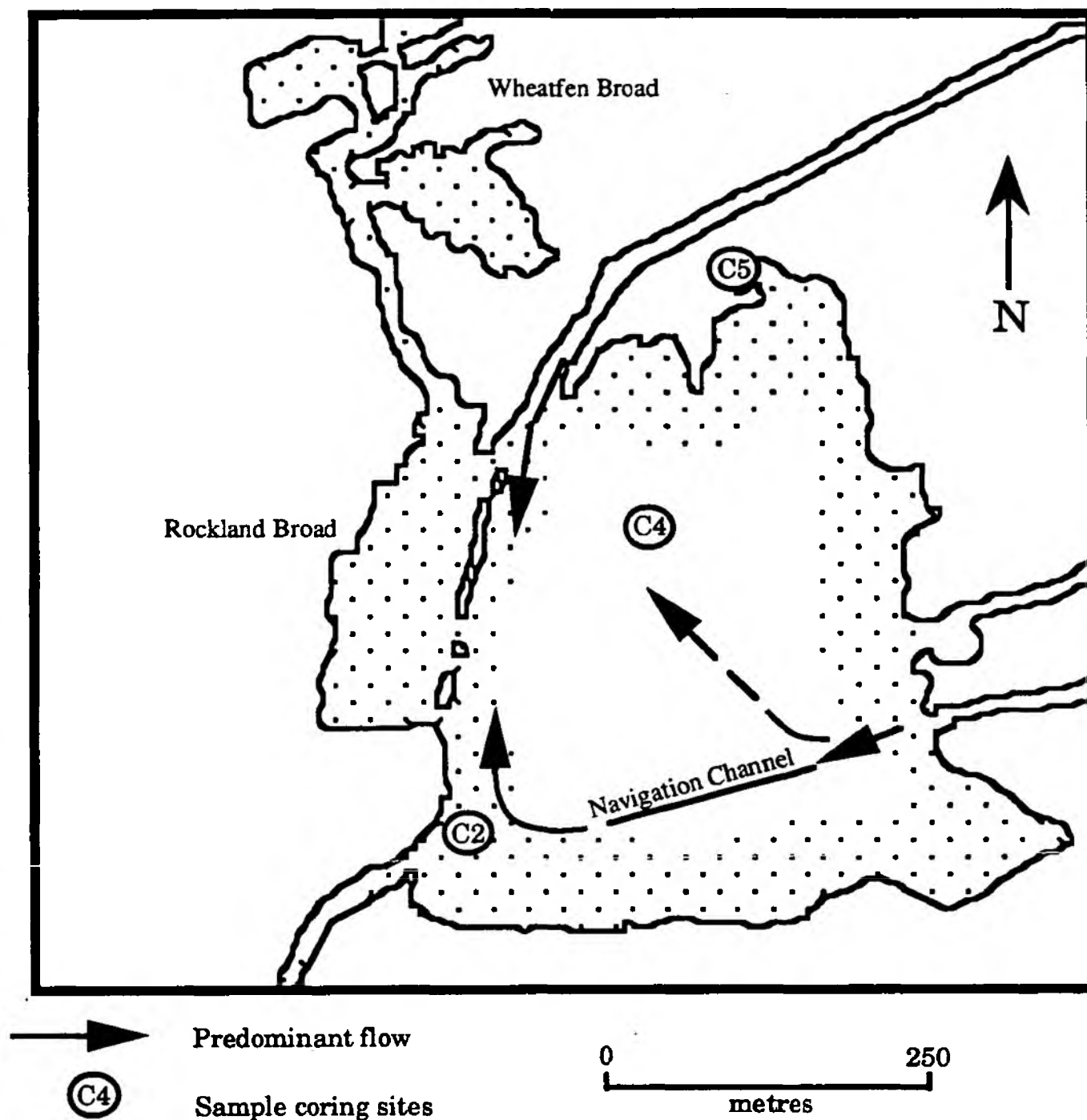
12

Predominant flow

Sample coring sites

0   250
metres

Figure 1 Rockland Broad showing the location of the core sites surveyed.

time intervals up to a maximum of 48 hours after settling had started, samples of the supernatant water were extracted from the cylinder at a point midway between the water surface and the interface using plastic tubing attached to a 60 ml syringe. Care was taken not to resuspend settled matter. The pH, redox potential, temperature, free chloride ion concentration, free sulphide ion concentration and total suspended solids of the supernatant water were monitored *in situ* for each time period by methods described below. The filtrate was preserved with aqua regia to determine the concentrations of dissolved metals. A further subsample was preserved without filtering for determination of total metal concentrations. Subsamples for the determination of TOC and sulphate were also taken.

A further set of experiments was carried out using the same experimental procedure, but the pH, redox potential, temperature and free sulphide ion concentration of the sediment associated with the interstitial water instead of the overlying water were monitored. A diagrammatic summary of the modified elutriate test is shown in Figure 2.

4.3   DETERMINATION OF TOTAL SUSPENDED SOLIDS

Total suspended solids for the modified elutriate experiments was determined by a standard method (Standing Committee of Analysts, 1985) recommended for up to 10 mg l⁻¹ suspended matter. Filter papers (0.45 μm) were pre-washed with water, oven dried at 105 °C for 4 hours, weighed and returned to the oven for a further 30 minutes. This was repeated until the filters attained a constant mass. A 100 ml sample of supernatant water from a modified elutriate experiment was then filtered. The drying and weighing procedure was then repeated. Suspended solids concentrations were calculated as mg l⁻¹.

4.4   DETERMINATION OF TOTAL METAL CONCENTRATIONS

Five metals; copper, iron, manganese, mercury and selenium, were analysed by atomic absorption spectrophotometry (AAS). Approximately 2 g (wet weight) of sediment sample was weighed accurately to four decimal places and digested using aqua regia and a Milestone MLS1200 Mega microwave oven system according to manufacturer's recommendations (Roth Scientific, Farnborough, U.K.). The digestates were transferred to 50 ml volumetric flasks and made up with water. Blank samples consisting of aqua regia were also digested and handled in an identical manner to the sample digestates.

Total concentrations of copper, iron and manganese were determined by flame atomic absorption spectrophotometry using a Perkin-Elmer 5100PC AAS (Perkin-Elmer, Beaconsfield, U.K.) fitted with a Perkin-Elmer AS90 auto sampler. Water samples collected from the modified elutriate tests were analysed for copper concentrations by graphite furnace AAS using a Perkin-Elmer HGA-600 graphite furnace and Perkin-Elmer Zeeman 5100 magnet attached to an AS60 auto sampler. Standard conditions as specified by Perkin-Elmer were used throughout. Blank samples were run and standard sediment samples of known metal ion concentration were analysed. All samples were analysed in duplicate.
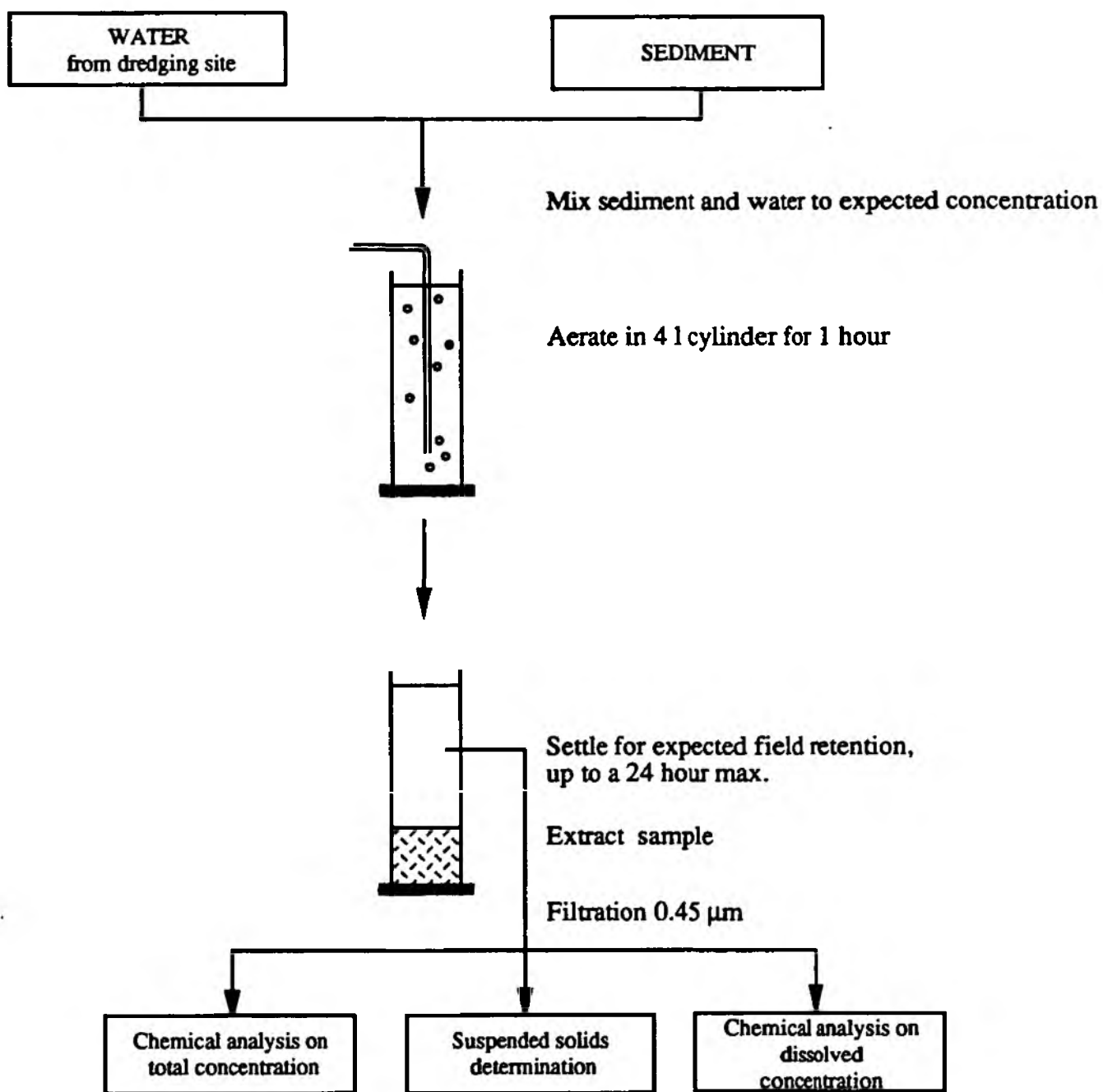
14

WATER
from dredging site

SEDIMENT

Mix sediment and water to expected concentration

Aerate in 4 l cylinder for 1 hour

Settle for expected field retention,
up to a 24 hour max.

Extract sample

Filtration 0.45 μm

Chemical analysis on
total concentration

Suspended solids
determination

Chemical analysis on
dissolved
concentration

Figure 2 The Modified Elutriate Test

15

Total mercury and selenium concentrations in the sediment samples were determined by flow injection metal hydride atomic absorption spectrophotometry using a Perkin-Elmer FIAS200 flow injection system and AS90 auto sampler coupled to a Perkin-Elmer 5100PC AAS. The standard method as supplied by Perkin-Elmer was used. In the case of selenium this included pretreatment of the samples by heating to 90 °C for 20 minutes to convert all selenium to Se(IV) for reduction to Se(0) by hydride. All samples were analysed in duplicate.

4.5   DETERMINATION OF TOTAL ORGANIC CARBON (TOC)

Two different methods for the determination of total organic carbon (TOC) were employed as a single suitable method was not available for analysis of both sediment and water samples.

The method used for the sediment samples was an adaptation of the titration method developed by Quaghebeur *et al.* (1991). Aqueous sodium hydroxide was used to absorb any carbon dioxide produced from the organic compounds in the sediment as a result of an oxidation step using potassium peroxodisulphate. The analytical procedure involves weighing sufficient dry, homogenised sediment to contain ≤ 5 mg C per sample. Above this mass a gradual loss in sensitivity of the method is observed. From previous analysis of samples approximately 20 mg of sample for each analysis was found to be optimal. Each sample was weighed accurately to ± 0.1 mg into a glass vial approximately 7 cm high with an i.d. of 2.5 cm. The sample was dissolved in 8 ml of water and 5 drops of 6 M sulphuric acid and connected to a vacuum line for 20 s to remove any inorganic carbon and dissolved carbon dioxide that may have been produced. 1 g of potassium peroxodisulphate ($K_2S_2O_8$) and 1 ml of 4% $AgNO_3$ were then added to initiate the oxidation process.

To a second vial (4.5 cm high, i.d. 1.4 cm) exactly 1.00 ml of ~2 M standard NaOH solution was added. This smaller vial was placed inside the sample vial which was then sealed with a septum using a crimp top. A needle was inserted through the septum to evacuate the sample vial for a further 10 s. The sample vial was then placed in a sonic bath until the potassium peroxodisulphate was dissolved and subsequently placed in an oven overnight at 70 °C.

The reaction was terminated when the dark brown colour disappeared and the solution cleared. The vials were cooled and the contents of the smaller vials were transferred quantitatively with freshly boiled water into Erlenmeyer flasks. The flask solutions were heated to 70 °C and 1% barium chloride was added until all the carbonate was precipitated as barium carbonate. The remaining NaOH was titrated with standard 0.1 M HCl, using phenolphthalein as the equivalence-point indicator. Analysis time per sample was 5-7 min and the g C kg^{-1} sediment (dry weight) was calculated using equation 1:

$$TOC = 6000(V_A - V_A')C_A/m \qquad (1)$$

where V_A =   volume of standard 0.1 M HCl solution required to neutralise the
volume of NaOH used before exposure to CO_2,

$V_A' =$ volume of standard 0.1 M HCl solution required to neutralise the volume of NaOH after exposure to CO_2,

$C_A =$ concentration of ~0.1 M HCl, and

$m =$ mass of dry sediment weighed (mg).

A Dohrmann DC80 Carbon Analyser (Pollution and Process Monitoring, Sevenoaks, U.K.) was used for determination of TOC in water samples taken during the modified elutriate experiments. In this method potassium peroxodisulphate was used as the oxidant with an additional UV light source to assist in breakdown of any organic carbon to carbon dioxide. The carbon dioxide produced in the oxidation step is pumped into an infra-red detection cell from which the concentration of organic carbon present in the sample was automatically calculated.

A standard 10 µg ml^{-1} potassium hydrogen phthalate solution was utilised as an organic carbon source in order to calibrate the system. A 1 ml sample loop was used and a maximum of seven minutes was allowed for detection of any carbon dioxide produced during the oxidation step. Samples with high chloride ion and/or heavy metal ion concentrations can cause interferences to the analytical system. Any samples likely to interfere were diluted up to 100 times to overcome this problem. Before analysis one drop of orthophosphoric acid was added to each sample which was then purged with oxygen gas to remove any dissolved carbon dioxide or inorganic carbon present in the sample.

4.6 DETERMINATION OF PHYSICO-CHEMICAL PARAMETERS

Sulphate ion concentration was determined by ion-exchange high performance liquid chromatography. The pump (Waters, Lambda-Max model 480LC , Millipore, Harrow, U.K.) was attached to a conductivity meter (Waters model 430). Analyte separation was achieved using an IC-Pak A anion exchange column and a borate/gluconate eluent, according to the manufacturer's standard method.

A chloride ion selective electrode (Orion Research Inc., Cambridge, U.S.A.) in conjunction with a reference electrode (Orion) was used to measure the *in situ* free chloride ion concentration. The electrode was calibrated with 10, 100 and 1000 µg ml^{-1} chloride ion standard solutions and a calibration curve was constructed. The calibration was repeated at the end of each day to check for any drift in response.

A silver sulphide ion selective electrode (EDT Instruments, EDT Analytical Ltd., London, U.K.) was used in conjunction with a double junction reference electrode (Orion Research) to determine sulphide ion concentrations in the supernatant water and sediment during modified elutriate experiments, using a method developed by Midgeley *et al.* (1978). Standard sulphide solutions were prepared from $Na_2S \cdot 9H_2O$ which was standardised potentiometrically using a cadmium solution of known concentration. The cadmium solution was standardised with EDTA using xylenol orange as the equivalence-point indicator and hexamine to buffer the titrate at pH 5. Drift in the electrode response was observed in the unbuffered water samples below 1 µg ml^{-1} free aqueous sulphide and this was considered to be the limit of detection for this method.

The pH of water and sediment samples was measured using a combined pH electrode attached to an ELE portable meter (ELE, Hemel Hempstead, U.K.). The electrode was calibrated using pH 7.0 and 9.2 buffer solutions. In instances when it was not possible to check any drift in response over a long period of time, such as during the modified elutriate tests in which the pH of the sediment was being monitored, a check was made as soon as possible after completion of the experiment to determine what, if any, drift had occurred. It was found in most instances that it was not necessary to adjust results as the drift observed was negligible.

The redox potential of the sediment and water samples was determined using a platinum redox probe attached to an ELE portable meter. The temperature of the sediment and overlying water was measured using an ELE temperature probe attached to an ELE portable meter.

5. RESULTS

5.1 BULK SEDIMENT AND WATER

The metal concentrations and physico-chemical characteristics of the bulk Rockland Broad sediment are presented in Table 1. Metal concentrations for each site were similar. Mercury and copper continue to persist at contaminating levels compared to average shale standards of 0.18 mg kg^{-1} and 45 mg kg^{-1} respectively (Salomons and Forstner, 1984). Site C4 has a slightly higher iron concentration and site C5 a lower manganese concentration than the other sites. These differences would not be expected to have any significant affect on the results obtained from the modified elutriate tests. Selenium concentrations were also higher than the shale standard of 0.06 mg kg^{-1} (Salomons and Forstner, 1984).

The redox potential and pH of the sediment for each site were similar and indicate reducing and slightly acidic conditions respectively. TOC levels for site C5 were higher than for the remaining sites. This was probably due to the location of site C5 near a reed bed which would have contributed large amounts of decaying plant matter. The site was also isolated and away from flowing water.

Table 1 Metal concentrations and physico-chemical characteristics of sediments for the three sites surveyed.

parameter	site C2	site C4	site C5
[Hg] mg kg^{-1}	9.59	8.79	9.81
[Cu] mg kg^{-1}	84.9	117.1	86.2
[Mn] mg kg^{-1}	606.1	678.2	516.7
[Fe] mg kg^{-1}	24730	33093	27847
[Se] mg kg^{-1}	1.52	2.28	3.17
pH	6.40	6.47	6.42
redox mV	-226	-225	-223
%TS	24.2	21.6	15.0
TOC g kg^{-1}	93.07	101.1	111.9

Metal concentrations and physico-chemical characteristics of the overlying water for the three sites surveyed are presented in Table 2. Mercury concentrations were highest at site C5 with levels similar to those previously reported (Imperial College, 1988). Copper concentrations were low in all cases. Site C4 exhibited elevated iron concentrations, in keeping with the higher sediment concentration recorded for this site. Selenium has not previously been determined in the waters of Rockland Broad, but concentrations were found to be similar to background levels.

The redox potentials in the overlying water were positive, suggesting oxidising conditions as might be expected for water exposed to the atmosphere. Slightly alkaline pH values were recorded which is in agreement with previous surveys (Imperial College, 1992). Free sulphide ion levels were below the limit of detection in all cases. Chloride ion concentrations were elevated compared to a previous survey (Imperial College, 1988). TOC concentrations have not previously been reported, but are consistent with background concentrations.

Table 2 Metal concentrations and physico-chemical characteristics of the overlying water for the three sites surveyed.

parameter	site C2	site C4	site C5
[Hg] mg kg^{-1}	0.24	0.45	0.65
[Cu] mg kg^{-1}	3	<1	2
[Mn] mg kg^{-1}	15	15	27
[Fe] mg kg^{-1}	290	520	220
[Se] mg kg^{-1}	-	0.07	0.06
pH	7.52	7.55	7.66
redox mV	+230	+225	+208
[S^{2-}] mg l^{-1}	<1	<1	<1
[Cl$^-$] mg l^{-1}	232	234	253
TOC mg l^{-1}	12	10	14

5.2 MODIFIED ELUTRIATE TEST RESULTS

5.2.1 Metal concentrations

Dissolved and total concentrations of mercury as a function of time during the modified elutriate tests for the three sites surveyed are shown in Figure 3. The background concentrations of mercury are shown for comparison. The concentration of total mercury increased 3-5 fold compared to the background concentation upon sediment disturbance, indicating active release from the sediment compartment. Highest concentrations of total mercury observed were 1.5-2 μg l^{-1}. No clear trend appeared when the three sites were compared. For sites C2 and C5 dissolved mercury levels were consistently close to total mercury concentrations. In the case of site C4 dissolved mercury levels were only 50% of total mercury concentrations. The soluble fraction of mercury reached a peak between 2 and 4 hours after settling began for all the sites, but was more persistent for site C2. Total mercury levels were highest initially, but exhibited an increase between 4 and 8 hours for sites C2 and C4 before beginning to tail off. Site C5 exhibited a continual downward trend from initial high concentrations.

Dissolved and total copper concentrations were approaching detection limits. Results demonstrated no trends (Table 3).
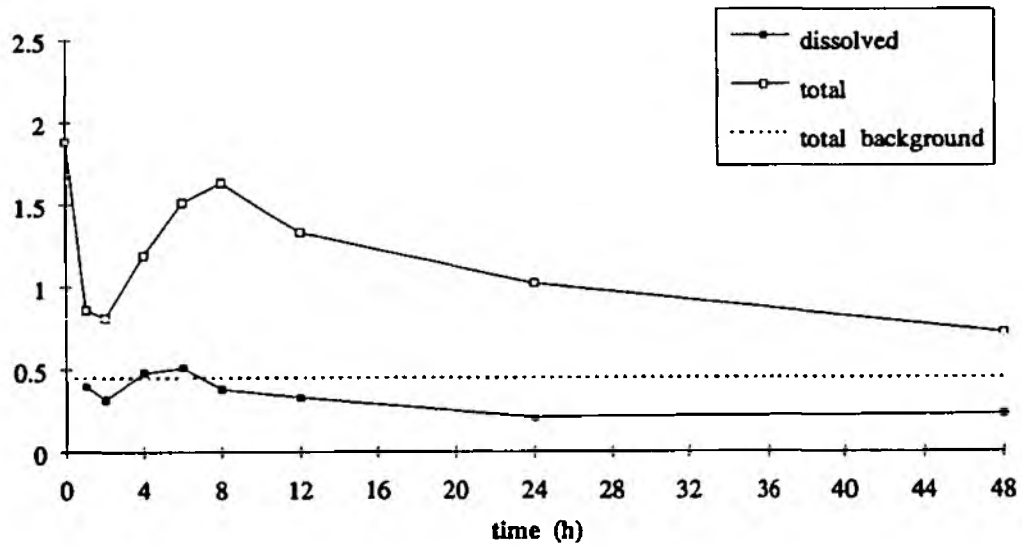
Dissolved and total iron concentrations as a function of time for the three sites surveyed are shown in Figure 4. The background concentrations of iron are shown for comparison. Iron concentrations in the overlying water initially increased 4-5 fold compared to background. Site C4 showed the highest initial concentration of 2500 μg l^{-1}. This is in keeping with the elevated concentrations reported for the sediment and overlying water. The levels of total iron decreased by at least 50% within 48 h of beginning settling in all cases. Dissolved iron levels made up a relatively low fraction (10-20%) of the total iron determined. This proportion rose to 50% after 48 h. Total iron concentrations approached background concentrations after 48 h, except for site C5.

MERCURY

Site C2
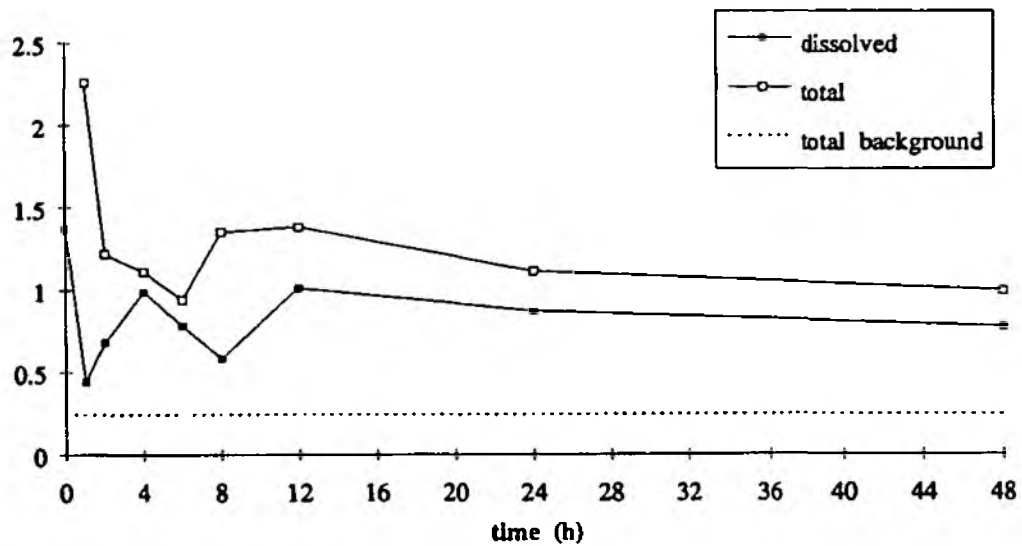
Site C4

Site C5

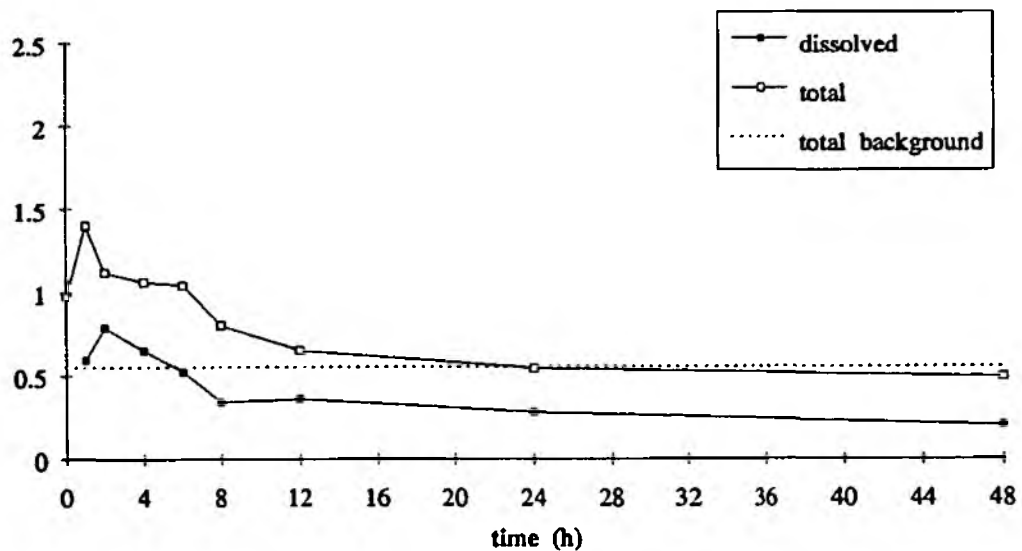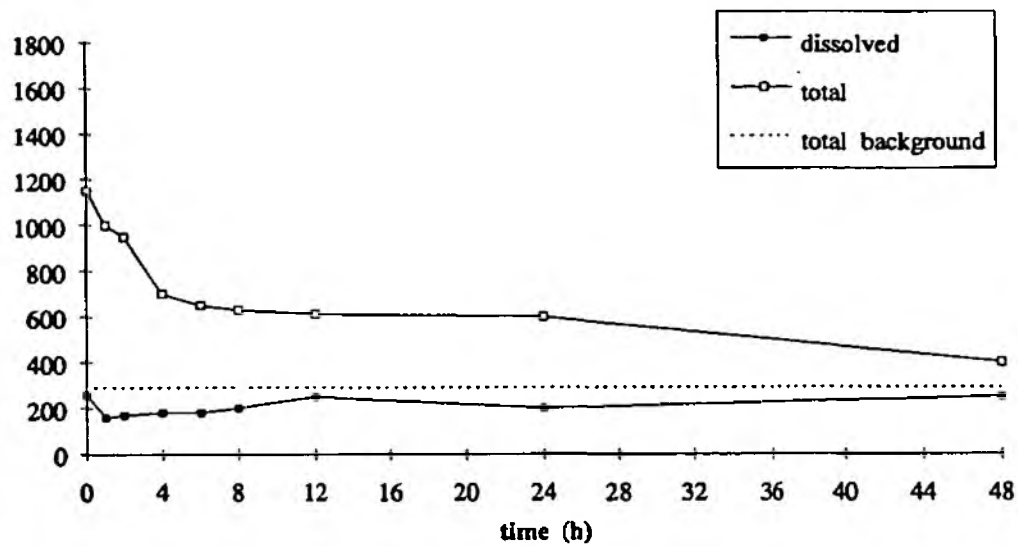**Figure 3** Concentrations of dissolved and total mercury as a function of time during modified elutriate tests for the three sites surveyed
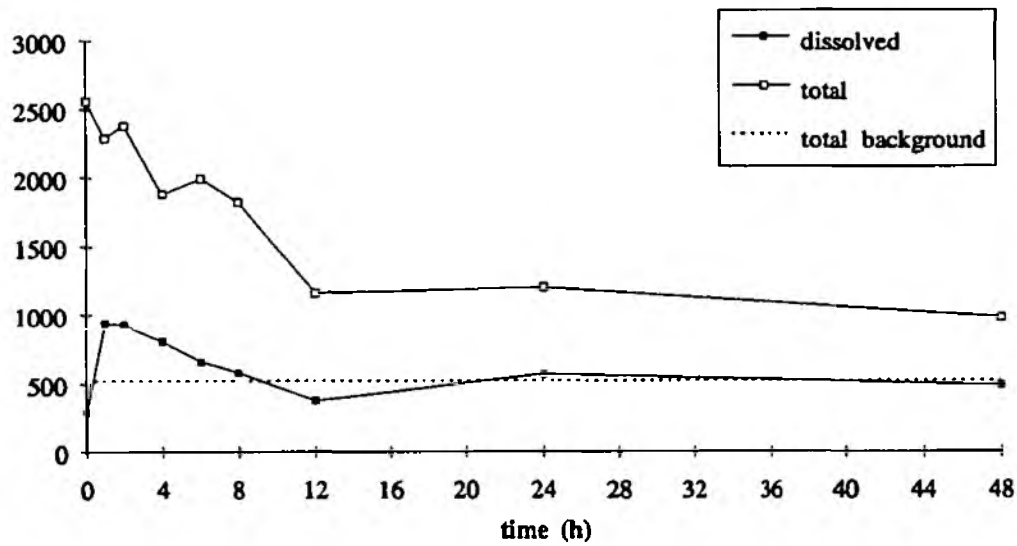
21

IRON

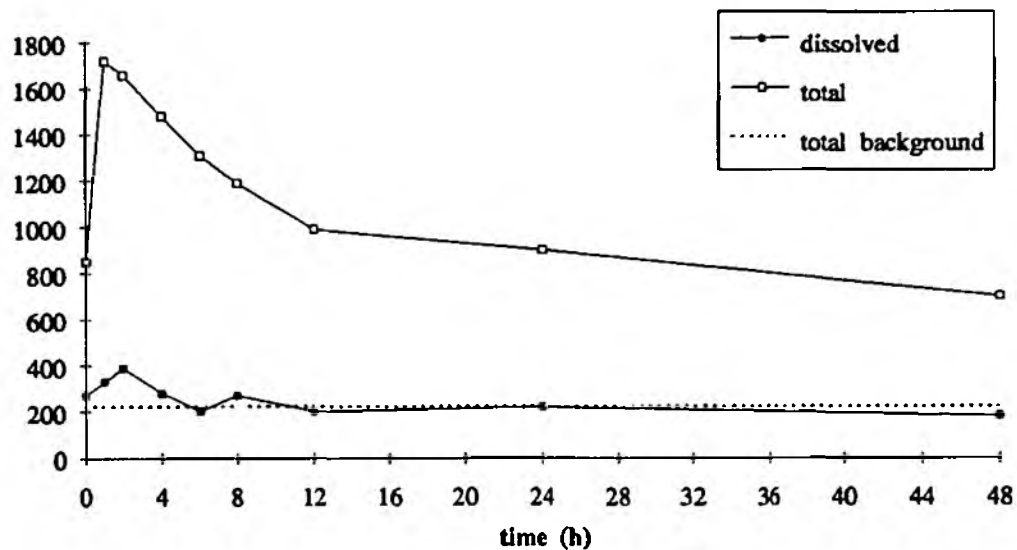## Site C2

Site C4

Site C5

Figure 4   Concentrations of dissolved and total iron as a function of time
during modified elutriate tests for the three sites surveyed

Table 3 Dissolved and total concentrations of copper determined in the overlying water during modified elutriate tests.

time (h)	[Cu] μg l⁻¹					
	site C2		site C4		site C5	
	dissolved	total	dissolved	total	dissolved	total
0	12.6	25.3	14.2	9.6	2.7	14.8
1	21.3	18.1	6.6	7.4	1.6	9.4
2	16.0	30.4	11.8	18.5	7.4	7.8
4	24.6	19.1	12.5	20.6	1.1	9.5
6	20.3	22.8	19.4	14.7	7.6	9.0
8	9.4	42.6	6.8	12.2	4.3	7.1
12	5.2	6.5	-	45.5	9.7	4.2
24	4.0	17.0	16.3	14.8	3.2	6.4
48	7.7	20.4	9.1	12.0	3.2	8.1

Dissolved and total manganese concentrations for the three sites surveyed are shown in Figure 5. The background concentrations are shown for comparison. Elevated concentrations over background levels were observed in all cases. An initial drop in concentration from approximately 700 μg l⁻¹ total manganese was observed for each site. A trend of slight increase to approximately 12 h was then observed before a decline to less than half this concentration after 48 h. This trend was mirrored by the dissolved manganese concentrations with nearly all the manganese appearing to be in the soluble fraction after 8 h. Increases in manganese concentration over background levels were in the order of 30 times initially, dropping to 15 times after 2 days.

All dissolved and total selenium concentrations were very low and in most cases were below detection limits and are included in Table 4 only.

Table 4 Dissolved and total concentrations of selenium determined in the overlying water during modified elutriate tests.

time (h)	[Se] μg l⁻¹					
	site C2		site C4		site C5	
	dissolved	total	dissolved	total	dissolved	total
0	<0.05	0.09	<0.05	0.35	<0.05	0.06
1	<0.05	0.08	<0.05	0.07	<0.05	0.10
2	<0.05	0.13	<0.05	0.08	<0.05	0.11
4	<0.05	0.10	<0.05	0.39	<0.05	0.15
6	<0.05	0.07	<0.05	<0.05	<0.05	0.14
8	<0.05	0.14	<0.05	0.08	<0.05	0.38
12	<0.05	0.14	<0.05	0.11	<0.05	0.12
24	<0.05	0.37	<0.05	<0.05	<0.05	<0.05
48	<0.05	<0.05	<0.05	0.10	<0.05	<0.05

5.2.2 Physico-chemical parameters

The change in the redox potential of the sediment as a function of time is shown in Figure 6. The bulk sediment redox potentials are included for comparison. The trend
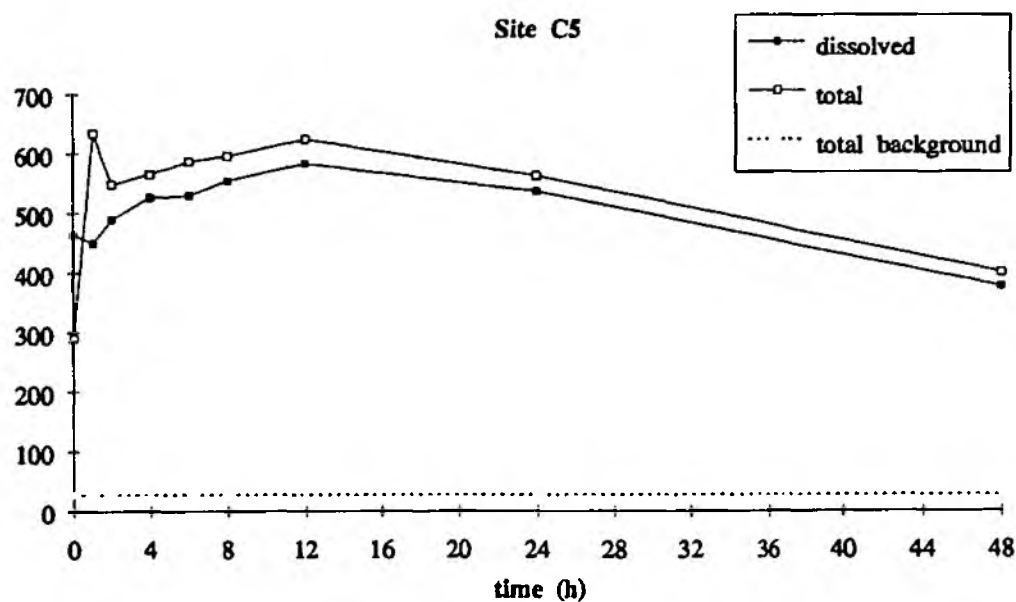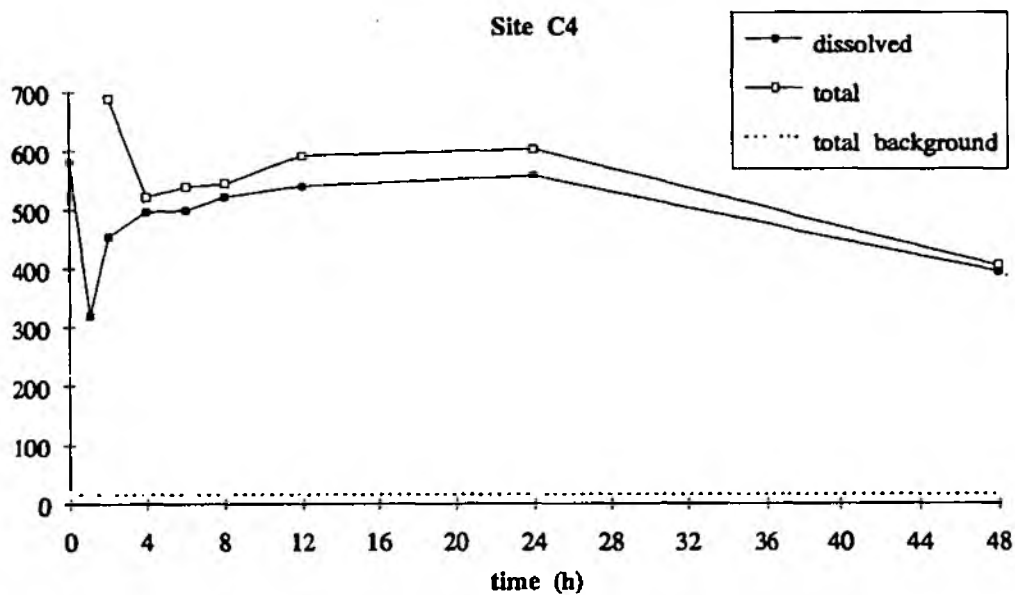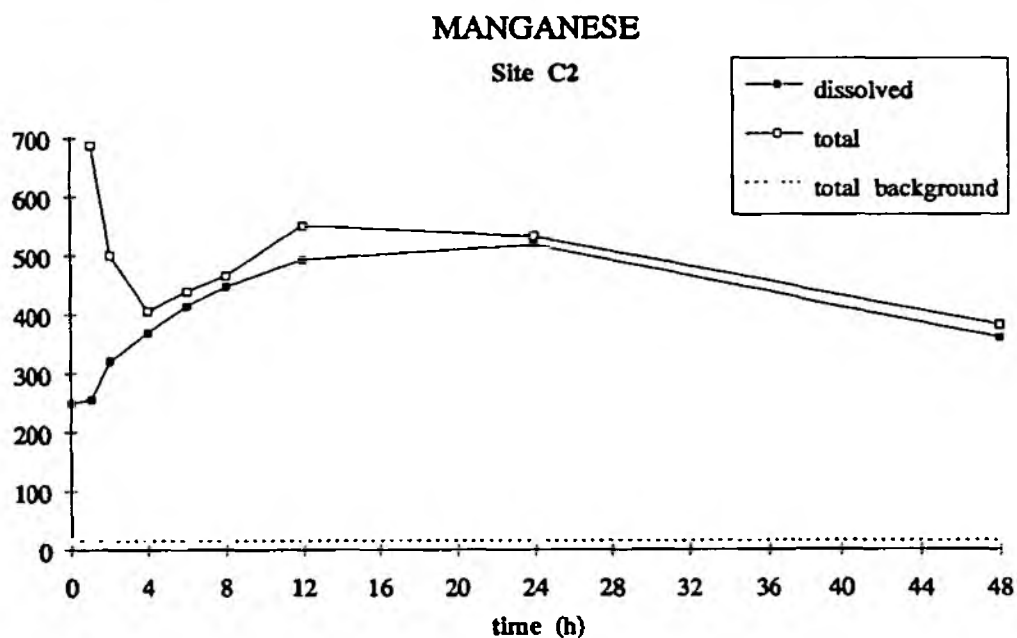
23

MANGANESE

Figure 5 Concentrations of dissolved and total manganese as a function of time
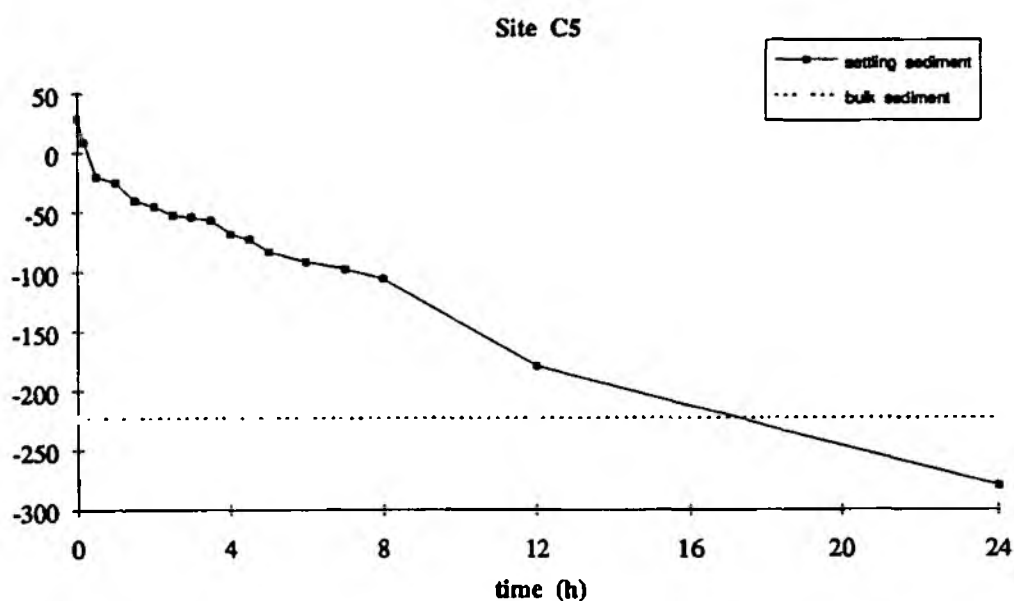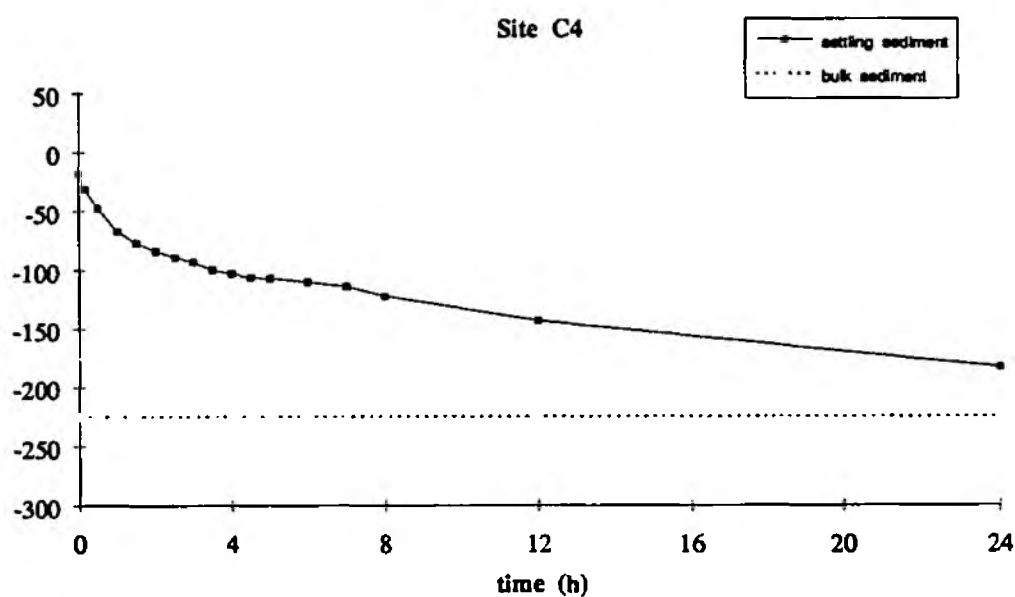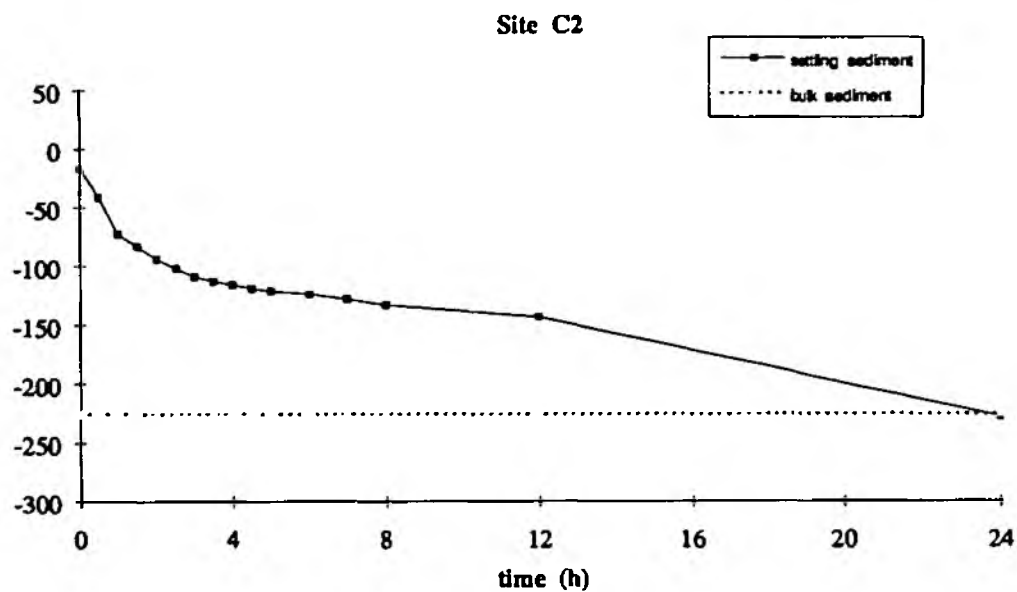during modified elutriate tests for the three sites surveyed

Figure 6   Redox potential of the settling sediment as a function of time during modified elutriate tests for the three sites surveyed

for sites C2 and C4 was a steady decrease in redox potential from an initially slightly reducing potential to a reducing potential approximately equivalent to the bulk sediment redox potential after 24 h. A similar trend was observed for site C5, but a slightly oxidising potential was observed initially. In all cases the sediment was significantly oxidised relative to the initial bulk condition.

The change in sediment pH with time for each site is presented in Figure 7. Sites C2 and C4 showed a decrease in pH of < 0.1 pH units over 24 h whilst at site C5 an increase in pH of approximately 0.1 unit occurred.

TOC concentrations measured in the overlying water as a function of time are shown in Figure 8. Background concentrations are included for comparison. In all cases after 12 h of settling TOC levels had reached a minimum of 20 mg l^{-1} after occurring at levels approximately 3 times higher than that after 1 h of settling. Elevated concentrations of TOC in the water may have been expected for site C5 which had higher TOC concentrations in the sediment, but this was not observed, although levels did not drop off as rapidly in the case of this site. A slight increase in TOC concentration was observed between 12 and 24 h in all cases. There is no obvious reason for this trend, but the increases are small and are within experimental error for the method.

Total suspended solids concentrations were found to range from approximately 120 mg l^{-1} after an hour of settling to 2-5 mg l^{-1} after 24 h. Background concentrations were 1-2 mg l^{-1}. A typical plot for site C5 is shown in Figure 9. Sediment disturbance had no affect on chloride ion concentrations which remained at approximately background levels throughout the experiments. Sulphate concentrations increased initially and then plateaued at these elevated concentrations. A typical plot is shown in Figure 10.

pH
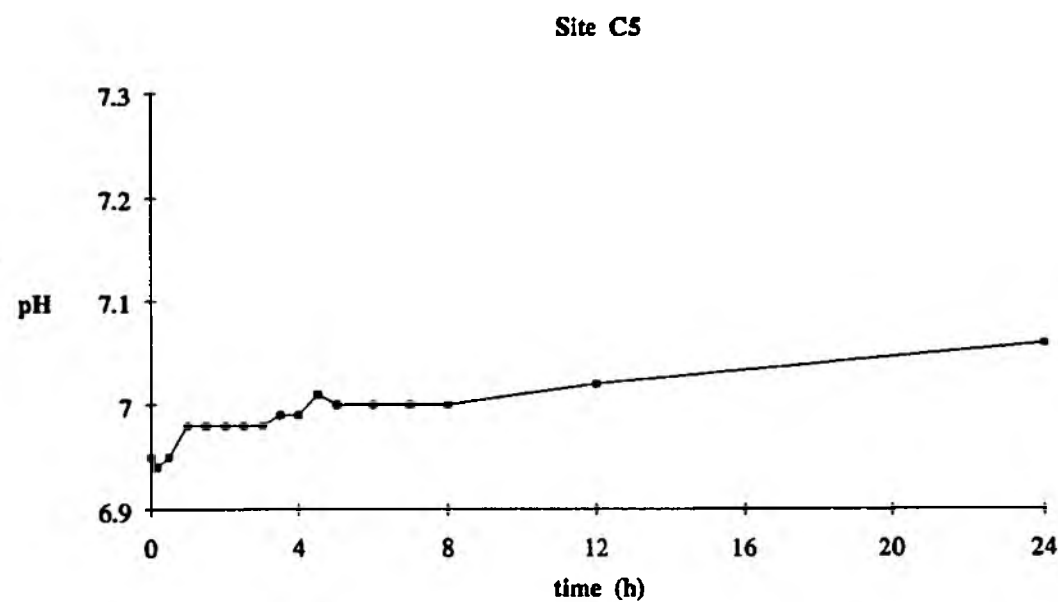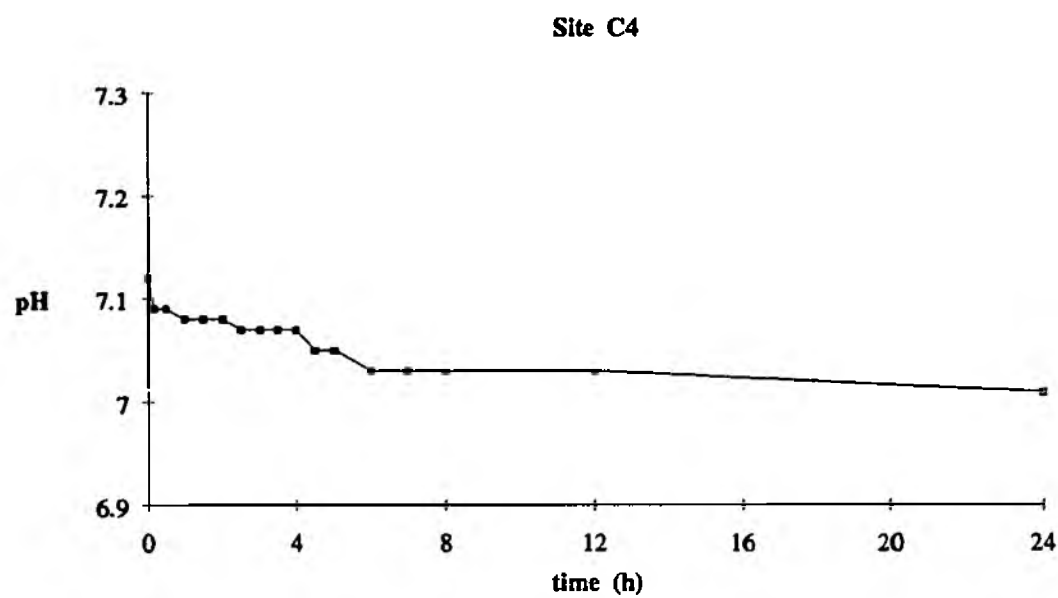
Site C2

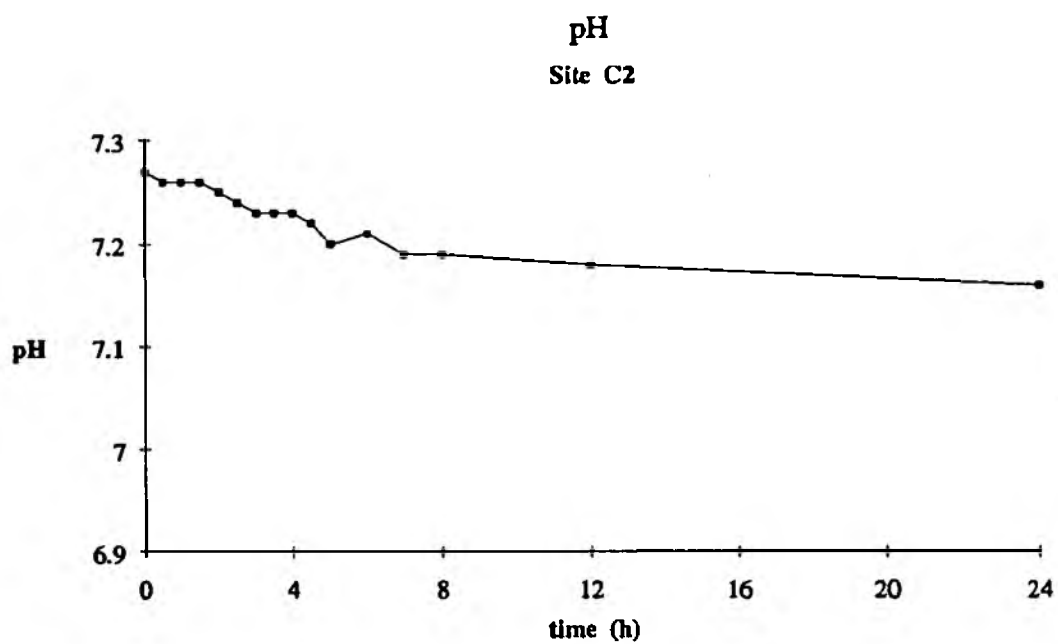## Site C4

Site C5

Figure 7   pH of the settling sediment as a function of time during modified elutriate
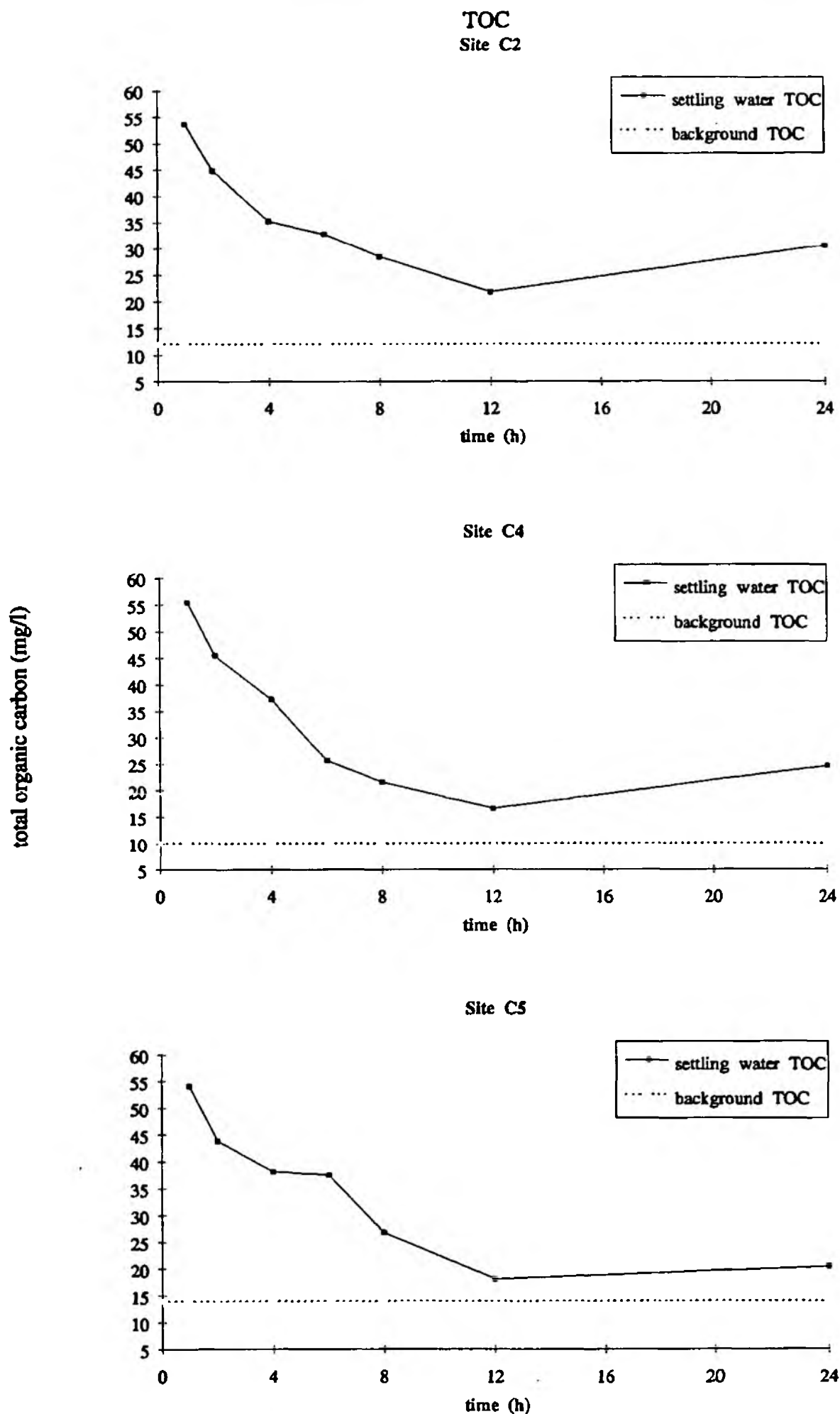tests for the three sites surveyed

Figure 8   Total organic carbon content of the overlying water as a function of time
during modified elutriate tests for the three sites surveyed

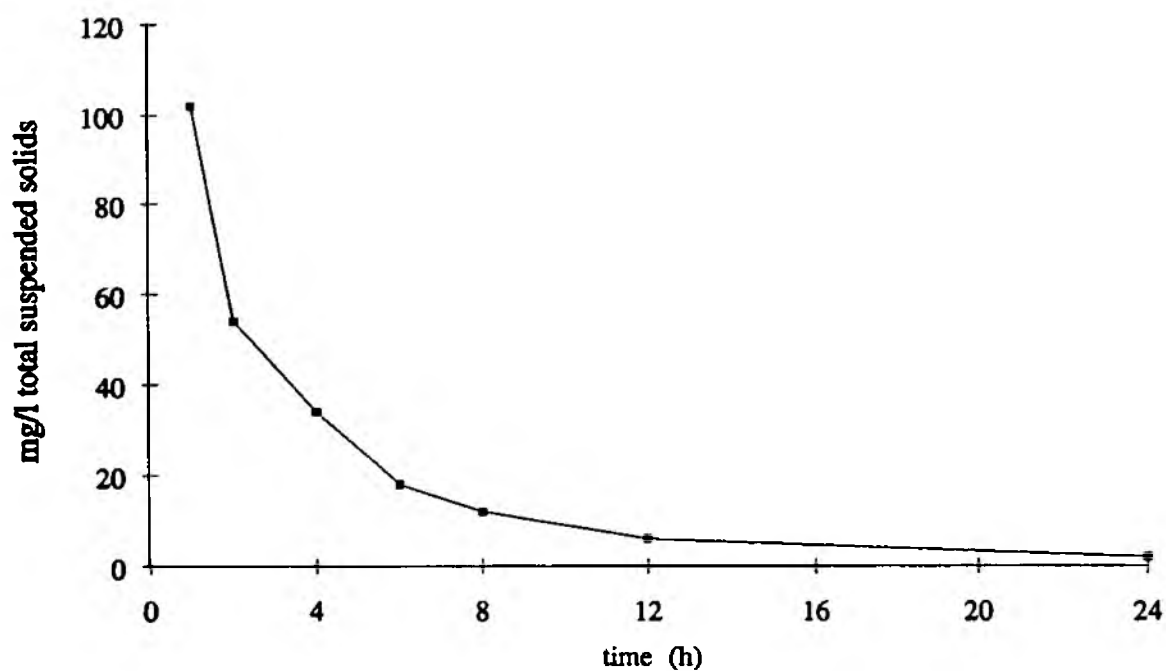## TOTAL SUSPENDED SOLIDS

Figure 9 Total suspended solids concentration of the overlying water as a function
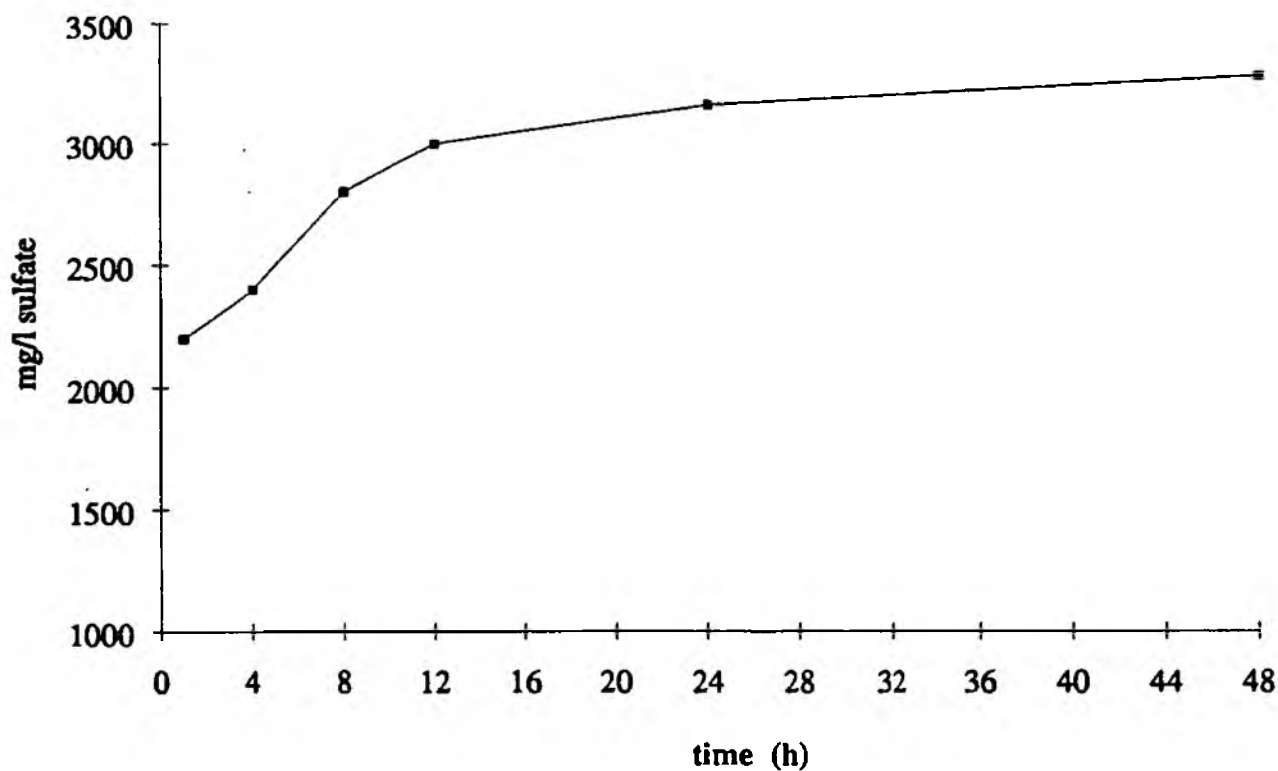of time during a modified elutriate test

SULFATE

Figure 10 Concentration of sulfate in the overlying water as a function of time during
a modified elutriate test

6. DISCUSSION

The MET results have shown that mercury is likely to be released into the overlying water at concentrations in the order of 1.5-2 $\mu g \, l^{-1}$ initially. These levels are 3-5 fold higher than is present in the water normally, but drop to below 1 $\mu g \, l^{-1}$ within 48 hours for site C5 and approach this concentration for the remaining sites. The acceptable E.C. limit for total mercury in river water is 1 $\mu g \, l^{-1}$ as a yearly average (Environmental Quality Standards for List I Substances, 1985). It therefore appears that a dredging operation on Rockland Broad would cause short-term breaches of the E.C. limit, but that there will be no long-term accumulation of mercury in the overlying water. However, if a saline intrusion were to occur the acceptable E.C. limit becomes 0.5 $\mu g \, l^{-1}$ soluble mercury as a yearly average. This may be less acceptable as site C5 has total background concentrations higher than this limit.

Previous monitoring of mercury levels during MET experiments has generally been hampered by the areas under investigation not having contaminating levels of mercury and thus mercury was below detection limits in the overlying water in most cases (Palermo and Thackston, 1988). It is therefore not possible to compare the results obtained for Rockland Broad with similar contaminated sediments.

Concentrations of copper were found to be low in the overlying water, but no clear trend was observed with respect to time. Acceptable concentrations of copper are 28 $\mu g \, l^{-1}$ total copper as a yearly average (Environmental Quality Standards for List II substances, 1985). This limit is not likely to be exceeded in the Rockland Broad.

If released into the overlying water the contaminants (mercury and copper) and manganese and iron will interact with one another and the organic carbon and oxy-species to form new salts and complexes which may precipitate out of the overlying water with time. It was found that most of the manganese released into the overlying water was associated with the soluble phase, whilst the iron tended to be largely particulate associated. This follows trends previously reported (Palermo and Thackson, 1988). The success of prediction of iron release by the MET was found to vary widely with location (Palermo and Thackston, 1988). For 5 sites surveyed for dissolved iron the ratio of mean MET results and field measurements was 0.5-0.8. The corresponding ratio for particulate associated iron concentrations varied from 0.3 to 1.3. This indicates the variation likely to be observed in the success of prediction of results using the MET which, in turn, is a reflection on the difficulty of assessing effects in such complex systems as are generated by dredging. In the case of manganese, ratios of 0.9 and 1.2 have been reported for dissolved and total manganese respectively. These ratios were for one site only, but indicate a good predictive ability for manganese using the MET.

The affects that physicochemical factors such as the change in redox potential and pH are likely to have on the release of mercury and other metals is difficult to determine from the results obtained for Rockland Broad as results are similar for the three sites surveyed. At the same time this gives confidence to the reproducibility of the MET experiments and indicates that the results obtained are likely to have simulated a dredging operation closely. No attempts to correlate factors such as those monitored in this survey have been reported as attempts have rather concentrated on predicting

30

the levels of release of contaminants for environmental quality standards in real dredging operations. The interactions are not likely to be simple and, thus, any correlations obtained may be on the macro scale rather than at the individual parameter level.

The gradual decrease in redox potential with time from slightly reducing to approximately equivalent to bulk sediment levels after 24 hours can be explained in terms of the mixing of bulk sediment with overlying water which had a redox potential of approximately +220 mV and the fact that the slurry had been thoroughly aerated for 1 h before monitoring commenced. As the sediment settled the overlying water settled out from the slurry, returning the sediment to a redox condition similar to that before it was disturbed by slurrying and aeration. These results suggest that the length of time the sediment is likely to be disturbed for during a dredging operation is not sufficient to cause any long-term change in redox potential. Long term change in redox potential caused by dumping dredge spoil at upland disposal sites may have more serious effects. Reproducibility of the results for the sites surveyed suggest that the results are precise, but their accuracy will have to be verified by field monitoring.

The pH was found to vary only very slightly with time and was probably due to the high buffering capacity of the clay particles in the sediments. Under conditions of aeration and metal release by disturbance a larger change in the pH might have been expected, but this was not observed. Metal release was thus little affected by change in pH for the Broad surveyed. Correlations between MET results and field observations during dredging for pH have been reported for 4 different sites (Palermo and Thackston, 1988). For 3 of the sites the correlation was 1.0, indicating that the MET is an accurate way of predicting changes in pH of sediment during a dredging operation.

The low concentrations of free sulphide recorded were not unexpected as metal sulphides are very stable and insoluble. A reduction in pH would have encouraged solubilisation, but this was not observed. Mercury sulphide is the most stable of the metal sulphides of interest in this work and likely acts as an efficient barrier against solubilisation of mercury during sediment disturbance. The reduction-oxidation cycle involving sulphate and sulphide is difficult to monitor in such a dynamic system as one simulating dredging. It is clear that aeration of the sediment-water slurry increases concentrations of sulphate (Figure 10) which will release metals less strongly bound as sulphides (FeS and MnS) to the aqueous phase. However, the effect that this has on the sediment-water system is not easily determined in isolation and will be investigated further in the future.

TOC levels in the overlying water were shown to decrease rapidly within 24 hours of sediment disturbance from approximately 120 mg l^{-1} to 20 mg l^{-1}. It is likely that substantial amounts of metal ions are complexed by the fulvic and humic acids that occur in any organic material present in the overlying water. The complexes will be more colloidal in nature than those of metal oxide precipitants and will settle out of the overlying water more slowly, possibly prolonging the time that metal ions remain in suspension after sediment disturbance. Further investigations are required in this regard.

31

On the basis of previous studies to predict release of metals and other sediment constituents into overlying water (Palermo and Thackston, 1988b), the MET results obtained here can be considered to have predicted the effect of a dredging operation on Rockland Broad with a high level of confidence. Confirmation of this will only be obtained once *in situ* monitoring of a dredging operation has been carried out. It has been assumed that the dredging operation will involve the use of a bucket dredge and the results obtained reflect this assumption. If a dredging method which releases less sediment into the overlying water, such as suction dredging, is used it is anticipated that the contaminant release would be reduced.

There appears at this stage of the investigation that dredging operations will not introduce contaminants at elevated levels into the water column for any significant length of time. The disturbed sediment which is, however, not removed during dredging will eventually settle downstream from the dredging site. This sediment will potentially contain mercury previously unavailable to the biota because of its burial at depth. The mercury will be particularly available to bottom feeders such as eels and to mercury methylating bacteria residing at the water-sediment interface. The affects of dredging in this respect have already been observed in the annual surveys of 1991 and 1992 in which elevated concentrations of mercury over earlier surveys were observed in the region of the construction of a bridge for which dredging had been carried out (Imperial College, 1992b). The affect of this and other more subtle factors is difficult to determine.

The related issue of dredge spoil disposal must also be of major concern in the overall consideration of a dredging operation. At this stage no studies of the disposal site have been carried out, but the potential for release of mercury due to changes in pH and redox potential brought about by penetration of atmospheric oxygen and drying out of the sediment at such a site is considerable. Subsequent leaching of mercury away from the disposal site by seepage and run-off could lead to contamination of a large area around such a disposal site and possible re-introduction of mercury to the river if the disposal site is located close to the river system. Only once these factors have been thoroughly investigated can a coherent dredging strategy be proposed.

7. CONCLUSIONS

1. Dredging simulation by use of the modified elutriate test has shown that mercury release from the Rockland Broad sediments will increase mercury concentrations in the overlying water 3-5 fold over the levels present in the bulk water. Concentrations have been predicted to be 1.5-2 $\mu g\ l^{-1}$ total mercury initially, but will drop to below 1 $\mu g\ l^{-1}$ after 48 hours of settling. The mercury was largely associated with the particulate phase, although this varied from site to site. Standards of 1 $\mu g\ l^{-1}$ total mercury as an annual average are not likely to be breached.

2. Concentrations of copper released from the sediments during MET experiments were low and unlikely to pose any contamination threat during a dredging operation.

3. Manganese and iron, implicated in the removal of soluble metal ions such as mercury and copper from the overlying water by co-precipitation with iron and manganese oxides and hydroxides, were released from the sediments in high concentration. Iron was found to be mostly particulate associated and reached concentrations of 1200-2500 $\mu g\ l^{-1}$, depending on the site. Manganese was mostly soluble with maximum concentrations of 700 $\mu g\ l^{-1}$ measured. Selenium was released in very low concentrations from the sediments and although it can play an important role in removal of soluble mercury and copper ions, was not present in sufficient concentrations to have a measurable effect.

4. Monitoring of physicochemical parameters demonstrated that significant short-term changes in redox potential of bottom sediments may be expected, but that in the longer term a dredging operation is unlikely to affect the reducing conditions prevalent in the sediment. The short-term change in redox potential to less reducing conditions, and in one case oxidising conditions, can be expected to play a major role in the release of metals from bottom sediments for up to 24 h after which sediment redox values will have returned to background values.

5. Changes in pH during MET experiments were small, most likely due to the high buffering capacity of the sediments because of the presence of large amounts of clay and organic materials such as fulvic and humic acids. Organic carbon release into the overlying water was found to be highest initially (approximately 120 mg l^{-1}), decreasing to within twice background concentrations (10-15 mg l^{-1}) after 24 h.

6. Free chloride concentrations were found to remain fairly constant at background concentrations (230-250 mg l^{-1}) throughout the MET experiments, indicating little or no release from the sediments and low interaction with any metals released. Free sulphide concentrations were below limits of detection whilst free sulphate concentrations were shown to increase initially and then to level off within 48 h as a result of the initial 1 h aeration. The reduction-oxidation cycle involving sulphide and sulphate is complex and its role in the release of contaminants from sediments has not yet been elucidated.

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