# THE SUCCESS OF ELUTRIATE TESTS IN EXTENDED PREDICTION OF WATER QUALITY AFTER A DREDGING OPERATION UNDER FRESHWATER AND SALINE CONDITIONS

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**Abstract.** Dredging simulation by elutriate tests accurately predicted concentrations of Hg, Cu, Mn and Fe released to the water column from contaminated sediment to within 1 order of magnitude. Hg and Cu concentrations increased by up to 7-fold after dredging, but declined to background concentrations within 48 h. Maximum loadings of Hg and Cu coincided with Fe and total organic carbon (TOC) water column concentrations, suggesting Hg and Cu are adsorbed onto particulates of Fe oxides and organic material. Seasonal changes in redox potential and temperature did not significantly affect metal release from sediments. Saline water did not cause significant increases in contaminant release from sediments to the water column over that observed for freshwater. Water quality standards of 1 $\mu$g l$^{-1}$ Hg and 28 $\mu$g l$^{-1}$ Cu as annual averages were not breached by dredging operations. Long-term effects of dredging on Hg and Cu availability, due to deposition of contaminated material as surficial sediments, is, however, of concern.

## 1. Introduction

The ability to predict the effects of dredging on sediment-bound contaminant availability is of environmental concern and an important consideration for water quality impact assessment. The major zone for the potential release of contaminants is the water column in the vicinity of the dredging operation. High concentrations of relatively soluble reduced forms of Fe and Mn are oxidized following sediment re-suspension and are rapidly re-precipitated and deposited as insoluble oxides and hydroxides. Other metals are co-precipitated alongside the Fe and Mn and thus the net release of soluble metals from suspended dredged material can be low or possibly even absent (Grieve and Fletcher, 1977). Organic matter released from the sediment compartment can also play a role in binding soluble metals and preventing the solubilization of metals already complexed in the sediment (Mierle and Ingram, 1991).

These and other factors have been taken into consideration in the development of elutriate tests for predicting water quality in confined dredge disposal sites (Grimwood and McGhee, 1979; Eichenberger *et al.*, 1980; Palermo and Thackston, 1988a, b). A similar elutriate test was used by Ludwig *et al.* (1989) to predict the extent of contaminant release to the overlying water at dredging sites. In 28 of 38 comparisons the elutriate test predicted the degree of field water contamination

within 1 order of magnitude, the remaining 10 comparisons were more than 1 order of magnitude greater than those observed in the field. The elutriate test thus proved a useful starting point for developing an extended simulation of the concentrations and possible interactions of contaminants with physico-chemical parameters in the water column which control their fate during and after a dredging operation.

Of particular interest was the simulation of the effect of occasional saline intrusions into areas requiring dredging as there would be a greater potential for conversion of contaminants, especially Hg, to their more soluble and bioavailable chloride species. This may have important repercussions for the production of methylmercury which is highly toxic and biomagnifies through the foodchain (Blum and Bartha, 1980; Compeau and Bartha, 1984). Changes in sediment redox potential, water temperature and other physicochemical parameters brought about by the changes in season may also have an effect on metal release from sediments to the water column during dredging. Restriction of dredging operations to certain times of year may thus offer advantages in reducing the potential deleterious effects on water quality.

The simulations and field monitoring were carried out on sediments from the River Yare, Norfolk, U.K. (Figure 1) which were contaminated with Hg and Cu by the discharge of industrial waste waters to the public sewer during the late 1960s and early 1970s. The waste waters underwent conventional two-stage sewage treatment at Whitlingham sewage treatment works (STW) prior to discharge to the river, but significant quantities of Hg and Cu were still released in the final effluent (Goldstone *et al.*, 1990). These metals now reside within the sediments of the river and its associated broads at concentrations of up to 30 mg kg$^{-1}$ Hg and 250 mg kg$^{-1}$ Cu at depths of up to 1 m (Bubb *et al.*, 1991a, b). The results for elutriate studies of sediment disturbance on water column metal concentrations were used to predict field results and their success has been evaluated by comparison with subsequent field monitoring of a dredging operation. The effects of saline intrusion and seasonal changes in physicochemical parameters on water quality after dredging were also simulated.

## 2. Materials and Methods

### 2.1. SURVEY AREA AND SAMPLING

The River Yare and its tributaries drain an area of 1415 km$^2$ of a low-lying plateau in East Anglia, U.K. (National Rivers Authority, 1994), flowing eastwards into the North Sea at Great Yarmouth. The river is tidal downstream of Norwich with variations in height of up to 1 m, but the saline interface generally occurs at Cantley (Figure 1) although it can periodically extend inland as far as Brundall. The water pH is generally slightly alkaline (pH 7.9) whilst dissolved oxygen (DO) concentrations vary seasonally with the occurrence of algal blooms. The geology
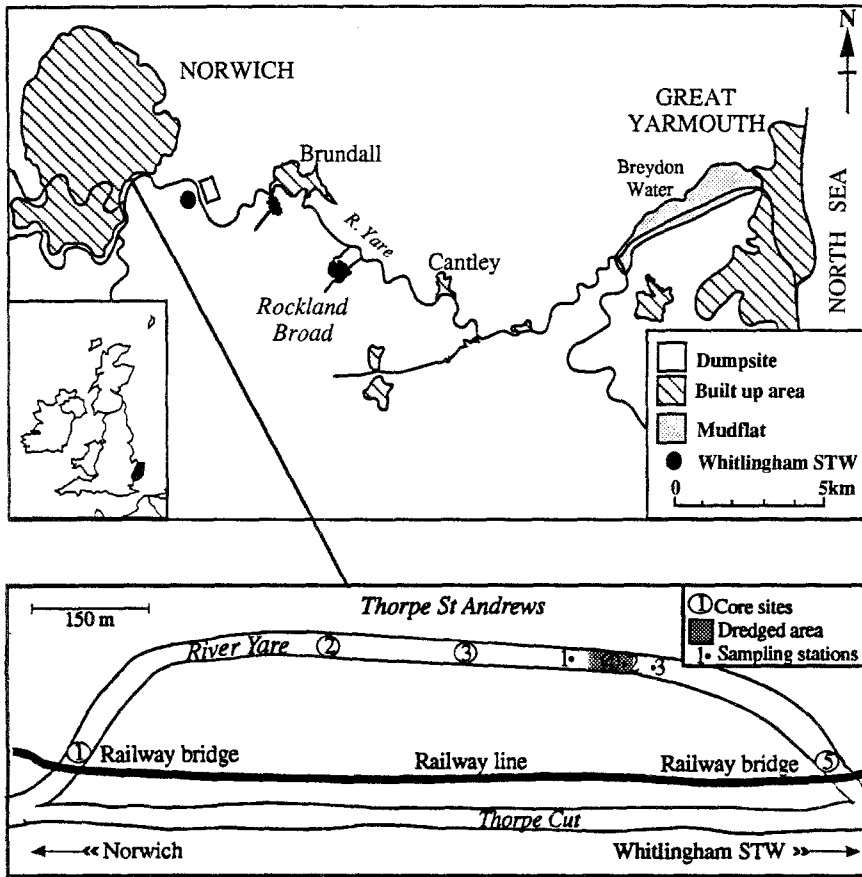
Fig. 1.  Location of cores, the dredging operation and water sampling points on the River Yare, Norfolk.

of the area comprises Cretaceous chalk covered with mixed drift, boulder clays and fluvioglacial sands and gravels.

A stretch of the river at Thorpe St Andrews required navigational dredging (Figure 1) and thus a preliminary survey of the proposed dredge area was undertaken to determine the depth and levels of Hg and Cu contamination. Sediment core samples were taken at 5 locations (Figure 1) using a simple coring device as described by Bubb *et al.* (1993). The cores were subdivided in the field and redox potential, pH and temperature (ELE, Hemel Hempstead, U.K.) were determined *in situ*. Sediment samples for metals and methylmercury analysis were preserved and stored as previously described (Bubb *et al.*, 1991a). A Burke-Ekman grab was used for sampling of surficial sediments 3 months after the dredging operation to assess the long-term effects of dredging on surficial Hg and Cu concentrations.

## 2.2. MONITORING OF THE DREDGING OPERATION

Dredging was carried out for 8 h on 11 November 1993 using a grab dredger. Approximately 120 tonnes of dredged sediment was removed and transferred by barge to an upland disposal site. Monitoring occurred at three sampling stations positioned in mid-channel (Figure 1). Background water samples were collected from each station the day before dredging commenced and then for 50 h from the start of the dredging operation (time 0). The samples were collected 1 m below the water surface in acid-leached sample containers by Casella sampler and immediately sealed with exclusion of air. Samples for total metals analysis were preserved with 1% (v/v) Aristar $HNO_3$ (BDH, Poole, U.K.). Soluble metal samples were syringe filtered through acid-leached 0.45 $\mu$m cellulose acetate filter paper (Whatman, Walkerburn, U.K.) prior to preservation. Filtration and sample blanks were prepared periodically. Total organic carbon (TOC) and methylmercury samples were frozen. Sonde (Grant/YSI 3815) automatic samplers positioned 1 m below the water surface were used to record water temperature, DO concentration, pH, conductivity, salinity and turbidity for each sampling interval.

## 2.3. ELUTRIATE TESTS

Bulk sediment for elutriate tests was collected from Thorpe St Andrews and Rockland Broad (Figure 1) by coring and immediately placed in polythene bags with exclusion of air. Overlying water was collected in plastic canisters approximately 50 cm below the water surface and all samples were stored at the sampling temperature in the dark.

Elutriate tests were carried out, with modifications, according to the method proposed by the Environmental Laboratory of the U.S. Army Engineer Waterways Experiment Station, Vicksburg, U.S.A. (1985). Modifications included mixing appropriate volumes of sediment and overlying water to give a final sediment/water concentration of approximately 50 g $l^{-1}$ on a dry weight basis. For experiments involving salinity effects the water was amended with 30 g $l^{-1}$ of sodium chloride to give a salinity level equivalent to the maximum level monitored at Cantley during a saline intrusion (N.R.A. pers. comm., 1993). The elutriate systems were maintained at the temperature measured during initial sampling. Samples of the supernatant water were extracted at various time intervals up to a maximum of 48 h after setling had started, instead of the single extraction used in the standard method. Samples were treated and physico-chemical parameters monitored as described for the dredging operation.

## 2.4. PHYSICAL AND MINERALOGICAL ANALYSES

Sediments were dry sieved through a series of stacked steel sieves (2500, 1000, 630, 400, 250, 100, 71 and 36 $\mu$m) using a vibrating shaker to determine the size distribution of the sediments. The data are reported as granule (>2500 $\mu$m), very

coarse sand (1000–2500 $\mu$m), medium to coarse sand (250–100 $\mu$m), fine to very fine sand (71–250 $\mu$m) and silt plus clay (>71 $\mu$m).

Mineral identification was performed by X-ray diffraction (XRD) analysis using a fully automated Phillips X-ray diffractometer. Whole rock samples were prepared by grinding dry sediment to a fine powder and mounting on plates for analysis. Clay separates were prepared by soaking 5 g sediment in 150 ml distilled water and 10 ml 6.7% (v/v) ammonia for 48 h. Samples were then centrifuged at 1000 rpm for 4 min and the supernatant vacuum filtered onto ceramic tiles to yield the 2 $\mu$m fraction (Tanner and Jackson, 1947). The clays were further treated by glyconation, and heat treatment to 400 and 550 °C to separate overlying peaks. XRD scans were performed by scanning from 1.6–70 ° 2$\Theta$ using a copper radiation source. Mineral identification was performed by converting the angle of diffraction to d-spacing and matching with mineral powder diffraction files.

## 2.5. CHEMICAL ANALYSES

Sediment samples for total metals analysis were digested using aqua regia in a microwave oven (Milestone MLS 1200) according to manufacturer's recommendations (Milestone, Bergamo, Italy). Total Hg in sediment samples was determined by cold vapour generation using a Perkin-Elmer 5100PC atomic absorption spectrophotometer (AAS) (Perkin-Elmer, Beaconsfield, U.K.). For total Hg in water samples gold amalgamation was used to improve the sensitivity of detection. Total Cu, Fe and Mn concentrations in water and sediment samples were determined by flame-AAS (Perkin-Elmer 5100PC) or graphite furnace AAS (Perkin-Elmer HGA 600). The analytical performance of the systems was assessed by using certified reference materials (BCR 320 river sediment, BCR 277 estuarine sediment), results for which were within acceptable limits.

Sediment methylmercury was extracted according to the method of Longbottom *et al.* (1973). Analysis was performed by flow injection mercury fluorescence spectrophotometry using a Merlin System (P.S.A., Sevenoaks, U.K.) by the method of Edwards *et al.* (1995). TOC in water samples was determined using a Dohrmann DC 80 Carbon Analyser (Pollution and Process Monitoring, Sevenoaks, U.K.) and for sediment samples by the method of Quaghebeur *et al* (1989). Total and volatile solids were determined gravimetrically according to standard methods (Standing Committee of Analysts, 1980).

## 3. Results

### 3.1. PHYSICAL, MINERALOGICAL AND CHEMICAL COMPOSITION OF THORPE ST ANDREWS SEDIMENTS

The sediments contained 70% fine sand, silt and clay (Figure 2) and were composed of calcite, quartz and aragonite. Nearly 25% of the bulk sediment mass was in the
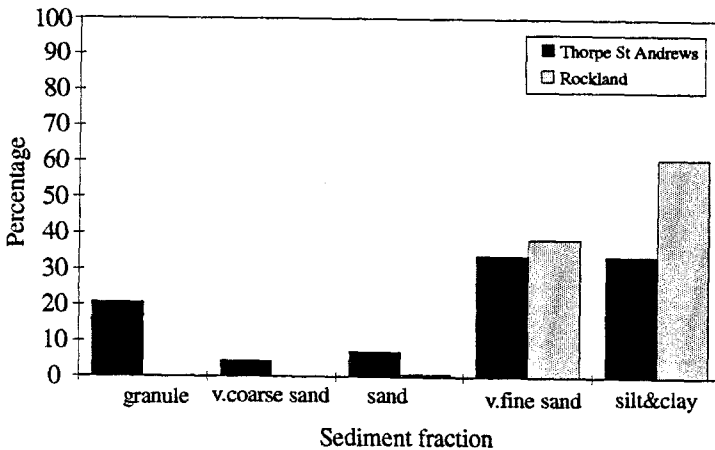
Fig. 2. Size distribution of sediment of Thorpe St Andrews dredge site and for experimental sediment from Rockland Broad.

>2500 $\mu$m fraction and consisted of wood and shell fragments with scattered quartz and calcite grains. Microscopic examination of the remaining fractions indicated primarily calcite with some quartz grains, coated with iron oxides, and shell fragments. Mineral identification of the clay size fraction found no identifiable clays, but rather calcite, quartz and some aragonite.

The preliminary survey of dredge site sediments revealed subsurface enrichment of Hg and Cu with peak loadings of 9.9 mg kg$^{-1}$ and 250 mg kg$^{-1}$ respectively occurring at depths in excess of 50 cm (Figure 3). On the basis of these findings it was recommended to the dredging authority that sediment be dredged to a depth of at least 1 m to ensure that the bulk of the metal contamination was removed. In contrast, Hg and Cu concentrations in the undisturbed overlying water were 5 orders of magnitude lower than in the sediment which acted as the major sink for the contaminant metals (Table I).

### 3.2. COMPARISON OF ELUTRIATE TESTS AND THE DREDGING OPERATION

The dredging operation caused up to 7-fold enrichments of Hg and Cu in the water column (Table II), but for a relatively short period of time compared to Fe and Mn which displayed lower more persistent enrichments. Peak concentrations of metals within the water column occurred within 12 h of dredging and in the case of Mn was observed during the dredging operation, reflecting its relatively high mobility and solubility. These field results are compared with elutriate test data in Figure 4. The fields results presented are for Station 2, but similar results were obtained for the other stations. The elutriate data is an average of 3 settling experiments as results were consistent (Students 't'-tests $p = 0.15$). It should be noted that elutriate test data equates to the first 48 h *after* dredging activities ceased (from time = 8 h) and not the onset of dredging (time = 0 h).

TABLE I

Physico-chemical parameters and concentrations of metals for bulk sediment and water for the elutriate tests and dredge site (Thorpe St Andrews) and elutriate tests on salinity effects (Rockland Broad)

| Parameter | | Thorpe St Andrews | | Rockland Broad | |
|---|---|---|---|---|---|
| Metals | | Sediment (mg kg$^{-1}$) | Water ($\mu$g l$^{-1}$) | Sediment (mg kg$^{-1}$) | Water ($\mu$g l$^{-1}$) |
| Mercury | | 5.24 | 0.05 | 9.81 | 0.05 |
| Copper | | 189.6 | 2.1 | 86.2 | 2.0 |
| Iron | | 24730 | 706 | 27847 | 720 |
| Manganese | | 628.2 | 151 | 606.1 | 115 |
| Temp (°C) | winter | 7.8 | 9.4 | 8.1 | 8.7 |
| | summer | 21.0 | 22.5 | – | – |
| pH | winter | 7.11 | 7.92 | 6.47 | 7.55 |
| | summer | 7.14 | 7.68 | – | – |
| Redox | winter | −209 | +207 | −226 | +225 |
| (mV) | summer | −168 | +292 | – | – |
| % total solids | | 25.1 | – | 21.6 | – |
| TOC (g kg$^{-1}$/mg l$^{-1}$) | | 74.0 | 3 | 101.1 | 10 |
| Chloride (mg l$^{-1}$) | | – | 199 | – | 234 |
| DO | winter | – | 10.6 | – | 10.8 |
| (mg l$^{-1}$) | summer | – | 9.1 | – | – |

TABLE II

Maximum concentrations of metals in the water column and the enrichment over background concentrations in the elutriate (predicted) and field tests (observed) for Thorpe St Andrews

| Metal fraction | Predicted ($\mu$g l$^{-1}$) | Observed ($\mu$g l$^{-1}$) | Enrichment over background | |
|---|---|---|---|---|
| | | | Predicted | Observed |
| Dissolved Hg | nd | nd | – | – |
| Total Hg | 0.57 | 0.34 | 11 | 7 |
| Dissolved Cu | 0.9–2.1[a] | 1.1–2.4[a] | – | – |
| Total Cu | 12.5 | 7.3 | 6 | 4 |
| Dissolved Fe | 983 | 712 | 1.8 | 1.3 |
| Total Fe | 1338 | 1007 | 1.8 | 1.4 |
| Dissolved Mn | 200 | 222 | 1.6 | 1.6 |
| Total Mn | 253 | 292 | 1.6 | 2 |

nd, below detection limit of 0.05 $\mu$g l$^{-1}$.
[a] Contamination by filter papers gave results which varied significantly at the low levels observed, suggesting most Cu was in the particulate phase.
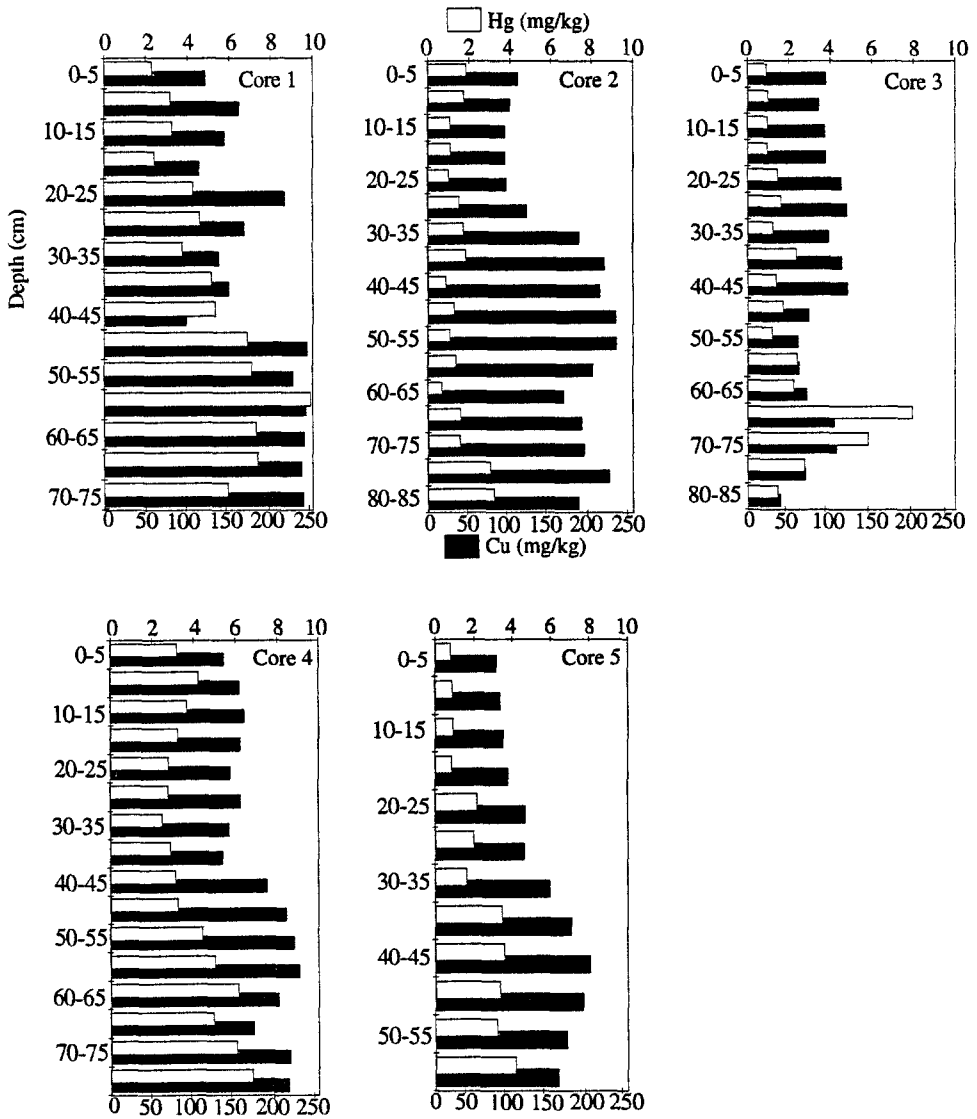
Fig. 3.  Depth profiles of Hg and Cu contamination at the dredge site, Thorpe St Andrews.

The elutriate test simulations successfully predicted the metal concentrations observed in the field monitoring exercise for Hg and Cu to within a maximum factor of 2.2 times the field concentration. In the majority of cases the factor was between 1 and 2, suggesting that even at moderately low Hg and Cu concentrations in the overlying water, the elutriate test provides a sensitive prediction of water quality. Iron and Mn concentrations were accurately predicted by the simulation to within a maximum factor of 1.5 with most predictions lying in the range 0.9–1.2. In
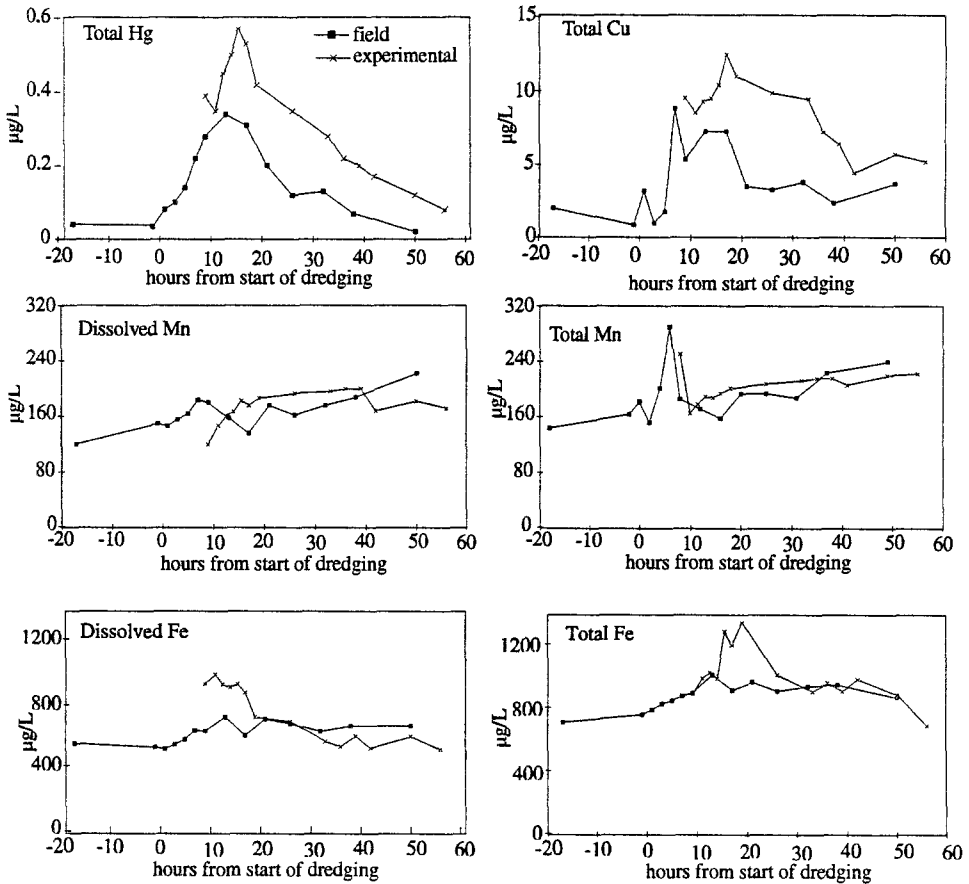
Fig. 4. Field and experimental data for Hg, Cu, Mn and Fe concentrations in the overlying water during and after dredging operation.

all cases, except for Mn, the simulations predicted maximum metal concentrations higher than those observed in the field (Table II).

The elutriate tests predicted that Hg and Cu concentrations in the water column should peak within 7 h of cessation of dredging and approach background concentrations 48 h after dredging. This was observed for the field water samples and suggests that Hg and Cu were at least partially associated with Fe which displayed a similar water column profile. Regression analysis at 95% confidence limits indicated the strongest metal-metal correlation was between Hg and Fe in the overlying water ($R = 0.63$) with Cu and Fe concentrations less strongly but still significantly correlated ($R = 0.52$). The majority of both Fe and Mn was however soluble (<0.45 $\mu$m) rather than particulate associated with 85% dissolved Mn and 70% dissolved Fe in both the elutriate tests and field monitoring. Dredging appeared to have less pronounced effects on water physico-chemistry. An exception was that for TOC concentrations (Figure 5) which displayed a 4-fold increase
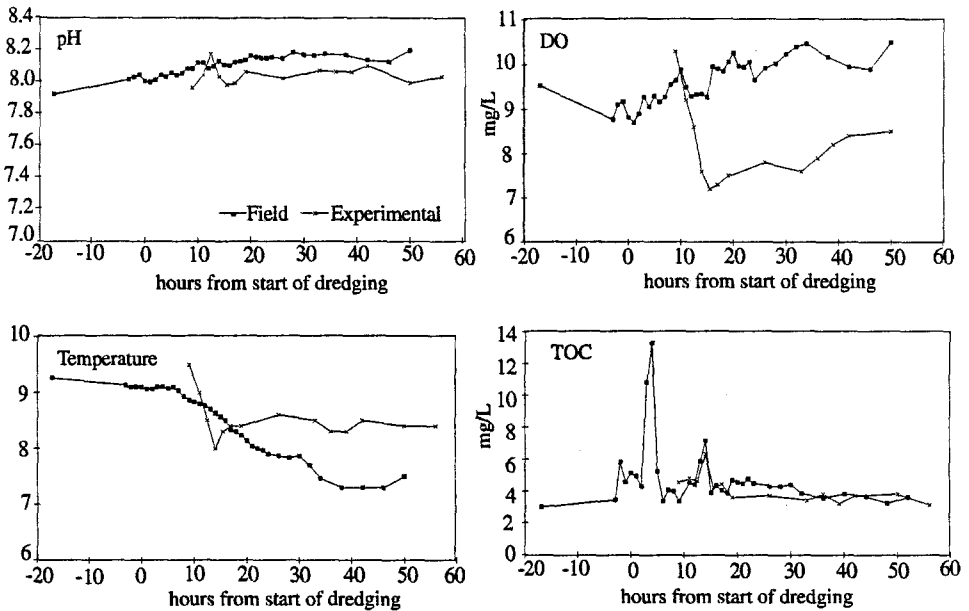
Fig. 5.  Experimental and field values for pH, DO, temperature and TOC.

above the background concentration of 3 mg $l^{-1}$ during the dredging operation before dropping rapidly once dredging had stopped. A second peak was evident at time 12–14 h which coincided with the release of Hg, Cu and Fe to the overlying water, before returning to the background concentration. In the elutriate tests TOC was significantly correlated with Hg ($R = 0.65$), but not with Cu ($R = 0.4$) which indicates the existence of strong organic-Hg complexation in the water column.

The predicted and observed values for pH, DO, temperature and TOC are compared in Figure 5. Although the pH was generally 0.1 pH units lower in the elutriate tests than that observed in the field (pH 8–8.1), the simulation did predict a fairly constant pH which was confirmed during the dredging operation. Dredging therefore had no effect on surface water pH in the River Yare system. Values for DO were predicted to show a steady decline from 10 mg $l^{-1}$ 1 h after settling had begun to 7 mg $l^{-1}$ at 8 h; however, a slight recovery to 8.5 mg $l^{-1}$ was predicted after 48 h. This was not seen in the field. Since DO concentration depends on temperature the continuous drop in temperature observed in the field (from 9.4 to 7.2 °C over 50 h) could have affected the water DO concentration profile observed. The diffusion of oxygen into the elutriate system does not simulate field conditions very closely as there is not a continuous supply of fresh water flowing through the simulation as occurs in the field. Conductivity values were predicted to fluctuate slightly around 0.85 mS $cm^{-2}$ which was observed in the field. Dredging thus had little impact on DO concentrations or conductivity of the River Yare water.
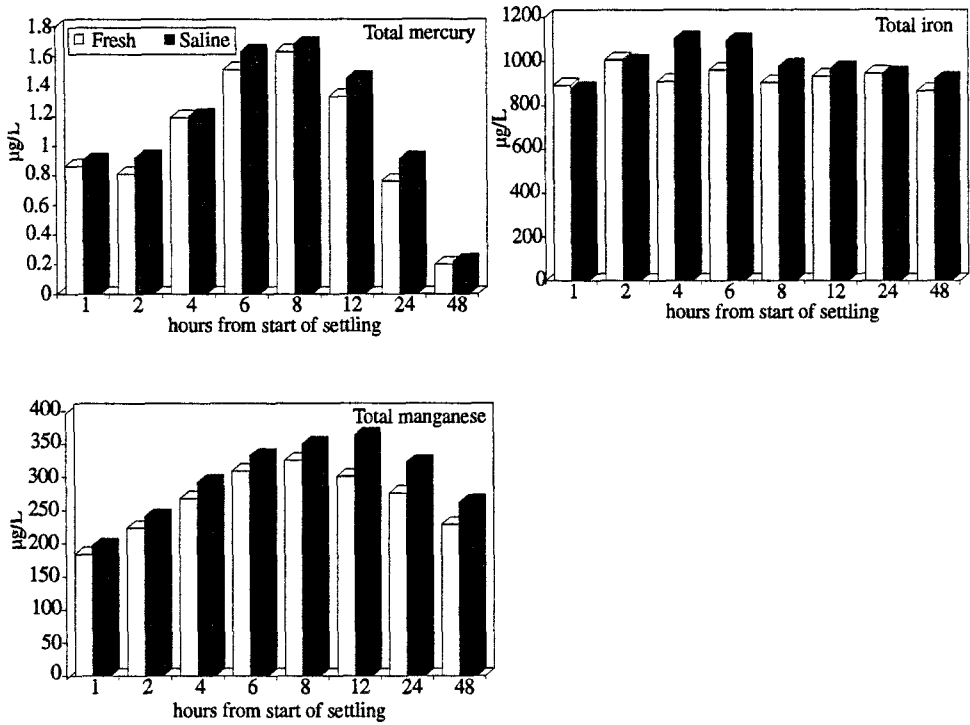
Fig. 6.   Elutriate test results under fresh and saline water conditions.

## 3.3.  EFFECT OF SEASONAL CONDITIONS ON METAL REMOBILIZATION

Elutriate tests on sediment taken from the dredge site during the summer months were used to compare the likely remobilization of metals under two extreme seasonal conditions. Initial metal concentrations within the sediment and water column were similar to those found during the winter months. The most important physicochemical changes were a 40 mV increase in sediment redox potential and 13 °C increase in sediment and water temperature (Table I). Neither of these changes produced significantly different results for the release of metals (all 't'-tests $p>0.05$) from those presented for the elutriate tests conducted under winter conditions (Figure 4).

## 3.4.  EFFECT OF SALINITY ON METAL REMOBILIZATION

Rockland Broad sediment was used to conduct elutriate tests with and without the addition of sodium chloride to determine the effect of a saline water intrusion on metal remobilization during a dredging operation. The sediment is 55% silt and clay with a small amount of medium sand and no sediment larger than 250 $\mu$m (Figure 2). The principal minerals are calcite and quartz with minor aragonite and trace pyrite. The clay size fraction was composed of smectite, kaolinite and
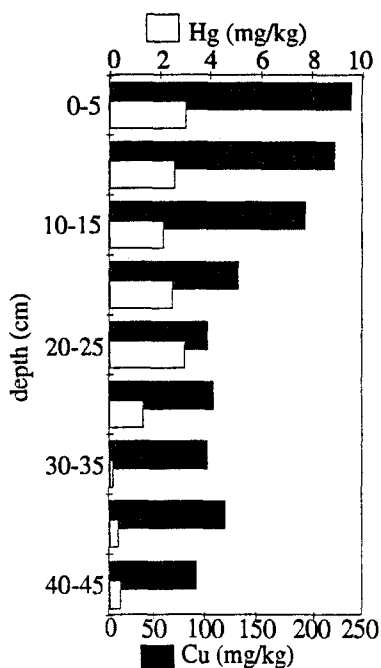
Fig. 7. Depth profile of Hg and Cu in sediment core 4 taken 3 months after dredging.

illite. Bulk sediment and water parameters used in the elutriate tests are given in Table I. Mercury contamination of this sediment was twice as high (9.8 mg kg$^{-1}$) as that observed at the dredge site whilst the Cu concentration was lower (86 mg kg$^{-1}$). Total concentrations of Hg, Fe and Mn obtained in the overlying fresh water and more saline water are presented in Figure 6 and indicate that metal release was not significantly different (students 't'-test $p = 0.09$) in the two experiments, but concentrations always tended to be slightly higher under simulated saline conditions. Copper concentrations in the overlying water did not exceed 5 $\mu$g l$^{-1}$ and changes in concentration observed were not sufficient to provide statistically significant data.

### 3.5. POST-DREDGING EFFECTS ON SEDIMENT CONTAMINANT LOADINGS

Grab samples of surficial sediment taken 3 months after the dredging operation indicated a two-fold increase in Hg and Cu concentrations in the top 2 cm of sediment within a 50 m radius of the dredging area. The average surficial concentration of Hg before dredging was 0.9 mg kg$^{-1}$ which increased to 2.2 mg kg$^{-1}$ while surficial Cu concentrations nearly doubled from an average of 112 mg kg$^{-1}$ to 198 mg kg$^{-1}$. These increases were probably caused by the overlaying of more highly contaminated sediment dredged up from depth. This view is supported by a core taken from the dredged site (Figure 7) which exhibits high concentrations of Hg

in the upper layers, decreasing down the core which is the reverse contamination profile to that obtained during the preliminary survey of the area. This increase in surficial Hg and Cu concentrations may have implications for the long-term effects of dredging operations on metal availability.

## 4. Discussion

Elutriate tests have previously been validated as a method for predicting metal release to the overlying waters following sediment disturbance by dredging (Ludwig *et al.*, 1989). By making minor modifications to the test procedure it has been possible to use the test to accurately predict water quality for Hg, Cu, Mn and Fe in the River Yare over an extended period of time. The simulation predicted water quality for the 4 metals to within a factor of 1–1.5 times that observed in the field in most cases. This factor rose to a maximum of 2.3 for the low concentration contaminants, Hg and Cu, where small differences between predicted and observed values led to relatively large ratios. All predictions were within 1 order of magnitude of field values.

Resuls obtained for metals released in the elutriate tests for the dredge site were generally conservative, i.e. they predicted concentrations higher than those observed in the field, as has been previously reported (Ludwig *et al.*, 1989; Palermo and Thackston, 1988b). Conservative elutriate data for Hg at 2 sites was reported by Ludwig *et al.* where field water concentrations were 0.1 $\mu$g l$^{-1}$ and predicted concentrations varied between 0.5 and 100 $\mu$g l$^{-1}$ (between 1 and 3 orders of magnitude). The variable succes of the simulation for Hg in these cases is not clear, but is possibly due to the low concentrations encountered in the sediment. The River Yare is a more contaminated system, allowing Hg concentrations to be predicted to within a smaller range of error.

Dredging caused a sizeable short-term release of Hg and Cu into surrounding water which declined to background concentrations within 48 h. The strongest correlation of the release of these metals was with the TOC concentration profile. Increases in concentrations of dissolved organic carbon (DOC) have previously been correlated to increases in water Hg concentrations in river systems (Mierle and Ingram, 1991). Comparison of the time at which peak TOC concentrations were observed in the simulations and the field (Figure 5) with the peak Hg and Cu concentrations (Figure 4) suggest that these metals are largely associated with the organic fraction probably comprising humic and fulvic acids. Lindberg *et al.* (1975, 1977) demonstrated similar behaviour for Hg and DOC in a dredging operation in which Hg had a peak concentration of 5 times the background concentration in the water column 3 h after sediment disturbance, decreasing within 4.5 h to a steady state value.

Saline water did not appear to have an important effect on concentrations of Hg or Cu released to the overlying water during sediment disturbance. This is probably

due to the stability of the metal complexes already present in the sediment and the relatively short contact time of the metal contaminants with the saline water before settling out occurs. In the field, effects of saline water intrusions on the concentration of Hg in the water column differ widely and appear to be governed by the amount of suspended matter in the saline water and not by the salinity directly (Lindberg *et al.*, 1975). Increased salinity does, however, cause a decrease in the Hg complexing ability of fulvic acid, but organic-Hg complexes already formed under low salinity conditions in the sediment appear to be little affected by later influxes of seawater (Xu and Allard, 1991). Similar results have been reported for organic-Cu complexes (Förstner *et al.*, 1989). Thus, over the short timespan that Hg and Cu concentrations increase in the water after dredging little mobilization is likely to occur from organic-Hg or organic-Cu complexes due to increases in salinity. The long term effect of increased salinity levels on biotic Cu uptake by *Hediste diversicolor* was also found to be negligible in the range 7.6–30.5‰ Cl (Ozoh, 1991). This implies that no adverse effects to water column total Hg or Cu will occur if dredging of contamianted fresh water sediment occurs during periods of saline water intrusion.

As the water pH remained fairly constant during and after the dredging operation it is assumed that pH in the range of 7.9–8.1 did not play a significant role in the release profiles observed for Hg and the other metals. Hannan and Thompson (1977) concluded from elutriate tests conducted with radio-labelled $^{203}$Hg that water in the pH range 7.5–8.1 was not an important mobilization factor in various sediments and soils. Under the slightly alkaline and oxidized (pH 8.0, 250 mV) water column conditions prevailing at the River Yare dredge site, Hg has been shown by Gambrell *et al.* (1980) to be mostly bound to the high molecular weight organic fraction (humics) and to the reducible fraction containing Fe and Mn oxides with low levels of dissolved Hg (0.05%). Moderately acid reduced (pH 5.0, –150 mV) and weakly alkaline oxidized (pH 8.0, 500 mV) conditions, however, enhanced soluble levels of Hg (Gambrell *et al.*, 1980). Duarte *et al.* (1991) also found a 7-fold decrease in Hg desorption from sediments in the pH range from 5 to 8 while Mosello *et al.* (1989) reported substantial improvements in water quality for trace metal concentrations on elevating the pH of lake water from pH 6 to 6.5. This implies that the slightly alkaline and oxidized conditions in the River Yare water may minimize metal desorption during sediment disturbance. The calcareous nature of the sediments in the River Yare also provide a highly buffered system which is unlikely to suffer from the radical decreases in pH required to induce elevated releases of Hg and Cu from the sediments upon dredging.

Variations in oxygen availability can also stimulate metal desorption from sediments (Wang *et al.*, 1985) but although water DO concentrations did change during dredging this did not correlate with the release of Hg or Cu into the water. This was probably because extreme decreases in DO concentrations are required to produce significant increases in Hg and Cu water concentrations. Increased Hg release from sediment as DO was depleted from 4 to 0 $\mu$g ml$^{-1}$ was reported by Wang *et al.*

(1989). The release of Hg under these conditions can be partially attributed to the dissolution of Fe and Mn oxides and hydroxides with which it is associated. In the River Yare DO concentrations remained comparatively high (9–10 mg $l^{-1}$), suggesting an oxygen-rich environment which would not bring about metal desorption from particulates.

The release of Mn from the sediment compartment, which occurred much more rapidly than for Fe, probably reflects differences in their geo-chemical partitioning (Osaki *et al.*, 1990a, b). Sequential extraction studies on the River Yare (Bubb and Lester, 1994) have shown that Mn in the sediment compartment is associated with exchangeable (20%) and carbonate (40–50%) forms and is therefore relatively receptive to changes in the physicochemical environment. The release of Hg and Cu to the water column coincided with elevated Fe and TOC loadings in the water which are therefore considered to be the major factors controlling Hg and Cu release from contaminated sediment in the River Yare system.

Seasonal changes in redox potential, temperature and DO were not great enough to cause any significant changes in metals released into the water column during the period of 48 h monitored; however, the wider implications of increased bacterial metabolic rates leading to higher Hg methylation rates during the summer months must also be drawn into the equation before a definitive statement can be made about the most appropriate time of year for dredging Hg contaminated sediments. Presently it appears likely that periods of protracted cold weather will prove the most suitable time for dredging to reduce the risks to resident biota of uptake of methylmercury produced by bacteria as a consequence of sediment disturbance.

Mercury and Cu concentrations in the overlying water did not breach designated E.C. limits of 1 $\mu$g $l^{-1}$ total Hg and 28 $\mu$g $l^{-1}$ total Cu as respective annual average (Environental Standards for List I, II Substances, 1992) at the dredge site where maximum bulk sediment concentrations were 5.2 mg $kg^{-1}$ and 190 mg $kg^{-1}$. Using the equation of Ludwig *et al.* (1989) to calculate 90% confidence limits for upper bound concentrations of contaminants from elutriate data results for the dredge site, Hg concentrations can be expected to not exceed 0.8 $\mu$g $l^{-1}$ while Cu will not exceed 18 $\mu$g $l^{-1}$, Fe 3780 $\mu$g $l^{-1}$ and Mn 360 $\mu$g $l^{-1}$ and then only for a short period of time.

Despite the apparent low release to the water column of metals, elevated Hg and Cu loadings were detected in surficial sediments in the vicinity of the dredge site 3 months after sediment removal. The total amout of Hg removed in the 120 tonnes of sediment dredged was 0.63 kg. Considering the approximate volume of water to be affected by dredging as 1350 $m^3$ and the peak Hg concentration observed in the water as 0.34 $\mu$g $l^{-1}$, the maximum amount of Hg present in the water column was 0.46 g. This indicates that at peak loadings, 0.07% of the Hg removed was present in the water column. Similarly for Cu, 22.75 kg was removed with a maximum of 9.8 g (0.04%) suspended in the water column. This data suggests that the two-fold increases in surficial Hg and Cu concentrations observed 3 months after dredging could not be have been caused by the settling out of contaminated suspended solids,

but as data collected for the water column was taken at a depth of 1 m below the surface, no account was taken of suspended sediment movement at the sediment-water interface where suspended solids concentrations will be far higher and where settling will also occur more rapidly. Turbidity monitored at various depths during the dredging indicated that there were higher suspended solids loadings close to the river bed which probably caused the increases in surficial sediment Hg and Cu concentrations observed. Future monitoring studies should consider this aspect when evaluating the impact of dredging activities.

## 5. Conclusions

The dredging of sediment containing 5.2 mg kg$^{-1}$ Hg and 190 mg kg$^{-1}$ Cu did not breach water quality standards for these metals and this was successfully predicted by the elutriate tests. The changes in Hg and Cu concentrations in the water column were strongly linked with trends in Fe and TOC concentrations, suggesting these parameters were implicated in the rapid settling out of the contaminants and a return to background concentrations within 48 h of the cessation of dredging. Changes in redox potential and temperature of sediment brought about by seasonal effects did not significantly alter the release of metals from sediments into overlying water under simulated conditions. Salinity effects on the release of Hg and Cu from sediments to the water column upon sediment disturbance were found to be insignificant for the River Yare system. There are, however, some concerns about the long-term implications of setting out of contaminated material dredged in the downstream environment which is left exposed on the river bed.

## Acknowledgements

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