

NRAA 627.152.15 (310.134)

WRc

NRA, ANGLIAN REGION

ENVIRONMENT AGENCY

ANGLIAN REGION CATALOGUE

ACCESSION CODE ADOL

CLASS No. _____

SURVEY OF COPPER SPECIATION IN THE
GREAT OUSE ESTUARY

REPORT NO CO 2725-M

MARCH 1991



COMMERCIAL IN CONFIDENCE

SURVEY OF COPPER SPECIATION IN THE GREAT OUSE ESTUARY

Report No: CO 2725-M

March 1991

Author: M J Gardner and J E Ravenscroft

Contract Manager: M J Gardner

Contract No: 8190

RESTRICTION: This report has the following limited distribution:

External: NRA, Anglian Region

Internal: Contract Manager and Authors

Any enquiries relating to this report should be referred to the authors at the following address:

WRc plc, Henley Road, Medmenham, PO Box 16, Marlow, Buckinghamshire
SL7 2HD. Telephone: Henley (0491) 571531

ENVIRONMENT AGENCY



124662

SUMMARY

The aim of this work is to determine the importance of organic complexing in copper speciation in the Great Ouse estuary.

Information concerning copper speciation in the estuary is needed in order to assess the potential toxic effects of the metal and to indicate whether or not action is required to control copper contamination.

The profiles of dissolved copper and the concentration of complexing ligands versus salinity suggests conservative behaviour in the estuary. The river appears to be the source of both dissolved copper and complexing organic substances. Dissolved copper is shown to be present almost totally (over 98%) in the form of organic complexes. The important role of organic complexation in copper transport has been demonstrated; the impact on copper toxicity is less clear, though it is likely to be significant. The concentrations of ligands in the Estuary are such that the level of free copper ion, at measured levels of total dissolved copper, is held at a concentration of less than $0.1 \mu\text{g l}^{-1}$, across the whole salinity range.

CONTENTS

	Page
SUMMARY	(i)
SECTION 1 - INTRODUCTION	1
SECTION 2 - EXPERIMENTAL	2
SECTION 3 - RESULTS	2
SECTION 4 - DISCUSSION	4
SECTION 5 - CONCLUSION	6
REFERENCES	7

SECTION 1 - INTRODUCTION

Of the range of trace metal contaminants in rivers and estuaries, copper combines widespread use with relatively high toxicity to aquatic life. Consequently, the fate and behaviour of copper has attracted much attention. The form in which copper is present in water is important in determining the likely impact on aquatic life (eg Sunda and Ferguson (1983)).

The way in which the Environmental Quality Standard (EQS) for copper is defined allows for the fact that copper bound by naturally-occurring complexing materials is substantially less toxic to aquatic life than free inorganic copper species (Gardiner and Mance, 1984). Annual average dissolved copper concentrations higher than the EQS value of 5 µg/l (for estuaries) are thus allowed, where complexation can be shown to reduce toxicity. The substances responsible for complexation are referred to as "ligands".

It is acknowledged that natural complexation reduces copper toxicity by several orders of magnitude (Ahnsanullah and Florence 1984; Hunt 1987; Allen *et al* 1980; Borgmann 1983). In any aquatic system it is effectively only the free, uncomplexed copper which exerts a toxic effect. In order to set quality standards on the basis of likely environmental effects, it is necessary to determine the extent and strength of complexation. In practice, the issue of complexation is usually only of interest in a particular location if the dissolved copper concentration is elevated. In such cases, it is important (i) to know the copper complexing capacity (the quantity of copper which could be complexed by natural ligands) of the water concerned and (ii) to be sure that the complexes formed with copper are sufficiently strong that free copper is not likely to be released.

The analytical approach to determining complexing capacity and complex strength has been described in detail in the references by Ravenscroft

and Gardner (1990), Apte *et al* (1990, 1989); Jones and Hart (1989). In principle, the complexing power of any natural ligands in a water sample is assessed by adding an artificial competitor ligand (of known strength and concentration) and determining the extent to which natural complexes are broken down. A series of measurements, made at different copper concentrations and with different amounts of competitor ligand, can be interpreted to give a picture of copper speciation in the sample. More importantly, the measurements can also be used to predict the proportions of free and complexed copper for a range of possible copper concentrations. This provides a way of evaluating the likely environmental impact of both existing and future copper discharges.

NRA, Anglia Region have contracted WRC to examine copper complexation in the estuary of the river Great Ouse. This work has been carried out in conjunction with other NRA research into metal speciation in rivers and estuaries (Contract NRD003, Project leader Dr P Bird).

SECTION 2 - EXPERIMENTAL

A series of five samples covering the full range of salinities was collected on each of two routine NRA sampling runs - December 1990 and February 1991. Samples were filtered and examined for copper complexing capacity. Portions were also analysed for total dissolved metal. Blank samples, to check that sample contamination had been controlled adequately during sample filtration and storage, were also analysed.

SECTION 3 - RESULTS

Analytical data are shown in Tables 1 and 2. Results for blanks were all less than limit of detection for each metal (Cu, $0.1 \mu\text{g l}^{-1}$; Cd, $0.01 \mu\text{g l}^{-1}$; Ni, $0.1 \mu\text{g l}^{-1}$; Pb, $0.02 \mu\text{g l}^{-1}$). Copper complexing capacity is plotted against salinity in Figure 1.

Table 1 - Metal Concentrations

18/12/90 Survey	Samples				
Salinity (‰)	0	4.3	20.5	22.6	33.0
Total Dissolved Metals ($\mu\text{g l}^{-1}$)					
Cu	1.4	1.3	0.64	0.54	0.67
Ni	4.3	4.2	2.4	2.3	0.73
Cd	<0.01	<0.01	0.01	0.03	0.05
Pb	<0.02	<0.02	<0.02	<0.02	<0.02
31/1/91 Survey					
Salinity (‰)	1.5	4.3	23.3	28.3	33.9
pH value	7.96	7.84	7.83	7.85	7.91
Total Dissolved Metals ($\mu\text{g l}^{-1}$)					
Cu	1.2	1.0	0.8	1.0	0.8
Ni	2.75	3.20	1.78	1.67	<0.3
Cd	0.10	0.02	0.08	1.0	0.25
Pb	<0.02	<0.02	<0.02	<0.02	<0.02

Table 2 - Copper Complexing Capacities

Copper Complexing Capacities ($\mu\text{g Cu l}^{-1}$)					
18/12/90 Survey	Samples				
Salinity (‰)	0	4.3	20.5	22.6	33.0
Total ligands*	31.4	33.3	20.1	13.5	9.1
Strongest Ligands*	31.4	29.8	12.6	6.5	3.7
31/1/91 Survey					
Salinity (‰)	1.5	4.3	23.3	28.3	33.9
Total ligands*	32.7	21.0	16.9	11.2	6.8
Strongest Ligands*	32.5	15.3	9.2	3.6	1.3

* Total ligands comprise the sum of ligands for copper complexes of $K' > 10^9$. Strongest Ligands comprise the sum of ligands for copper complexes of $K' > 10^{12}$.

SECTION 4 - DISCUSSION

Copper complexation capacity decreases with salinity (Figure 1) in a way that suggests simple dilution by seawater of lower ligand concentration. The levels of total dissolved metals are all low in relation to EQS values.

In monitoring and controlling metal contamination in the environment, the advantage of determining total dissolved metal is that the basis of measured concentrations is easy to understand. Interpretation with respect to the EQS is also relatively straightforward, after allowing for uncertainties in sampling and analysis. The serious drawback of this approach is that total dissolved metal is not the parameter which relates directly to environmental effects.

Determination of free metal concentrations, or assessment of other environmentally significant metal species, is a more logical approach. Since only a small fraction of the total amount of metal present may be biologically active, effort should be directed towards measuring and controlling this fraction. However, as with any refinement of a more simple approach, the drawbacks are increased complexity in making measurements and difficulty in explaining what has been measured. The former has been overcome, from a technical point of view; some guidance may be helpful with the latter. The questions below are answered in an attempt to provide background information to support the measured values.

What are the complexing agents measured?

These comprise a variety of natural compounds produced as waste by animal life or by decay of vegetable matter. Their precise nature is unknown, but they are likely to consist of a complicated mixture of high molecular weight "humic" materials and simpler protein or sugar-derived molecules (Serritti *et al* 1986; Sholkovitz and Copeland 1983).

How strong are the copper complexes?

This question has a bearing on the possibility of complexed copper being released from weak complexes to exert a toxic effect on aquatic life. As a guide, it may be assumed that all complexing matter detected forms strong complexes. Copper is not likely to be released from such complexes, provided there is no major change in water quality (eg decrease in pH or oxidation of organics).

The distinction between "stronger" and "weaker" categories of ligands, as given in Table 2, is under investigation. It probably indicates different types of ligands. Knowledge of these will assist in understanding the sources and behaviour of complexing matter.

What are the free or inorganic levels of copper in the Great Ouse estuary?

Inorganic copper concentrations have been calculated on the basis of total dissolved copper = $5 \mu\text{g l}^{-1}$ (ie equal to the EQS value). These are shown in relation to salinity in Figure 2. Inorganic copper, given the lower dissolved copper levels which have been observed, will obviously be less than those shown in Figure 2. In all cases, the inorganic copper concentration is less than $1 \mu\text{g l}^{-1}$. In fact, the complexing capacity is sufficient to reduce inorganic copper to $<0.3 \mu\text{g l}^{-1}$ at all salinities below 30 parts per thousand. Above this value the volume of water (and hence dilution) is so large as to make it most unlikely that a concentration of $5 \mu\text{g l}^{-1}$ could ever be reached.

How does the Great Ouse compare with other estuaries?

There appears to be a complexing capacity of over $20 \mu\text{g Cu l}^{-1}$ at the freshwater end of the estuary. This is (in our experience) relatively high compared with other estuaries we have studied. Comparative figures for some other large rivers are as follows: Yorkshire Ouse, $11 \mu\text{g l}^{-1}$; Trent, $14 \mu\text{g l}^{-1}$; Don, $20 \mu\text{g l}^{-1}$; Tweed, $24 \mu\text{g l}^{-1}$; Wharfe, $18 \mu\text{g l}^{-1}$; Severn, $13 \mu\text{g l}^{-1}$. At present, we have insufficient information to comment on the reasons for these differences.

SECTION 5 - CONCLUSIONS

1. Concentrations of total dissolved (0.45 μm filterable) copper in the estuary were found to range between 1.4 and 0.5 $\mu\text{g l}^{-1}$.
2. Organic complexing substances appear to be derived primarily from the river and behave in an conservative manner. The concentration of complexing ligands ranges from a copper complexing capacity of over 20 $\mu\text{g Cu l}^{-1}$ at the riverine end member to around 5 $\mu\text{g Cu l}^{-1}$ at the saline end member. The relatively strong affinity of the ligands for copper is reflected in the measured complex stability constant of 10^9 . This level of complexing ligands is comparable with those found in other major esturaries.
3. The concentrations of copper complexing ligands in the estuary are such that the level of free copper ion, at measured levels of total dissolved copper, is held at a concentration of less than 0.1 $\mu\text{g l}^{-1}$, across the whole salinity range. An increase in copper concentration to levels near to the 5 $\mu\text{g l}^{-1}$ EQS value is unlikely to exceed the complexing capacity in any but the most saline waters. Such an increase in coastal waters is difficult to envisage owing to the large volume of water involved.

REFERENCES

- AHNSANULLAH M and FLORENCE TM (1984) Toxicity of copper to the marine amphipod *allorchestes compressa* in the presence of water and lipid soluble ligands. *Marine Biology* **84**, 41-45.
- APTE S C, GARDNER M J, RAVENSCROFT, J E and TURRELL J A (1990) examination of copper complexation in natural waters using a combination of cathodic stripping voltammetry and computer simulation. *Anal Chim Acta* **235**, 287-297.
- ALLEN H E, HALL R H and BRISBIN T D (1980) Metal speciation Effects on aquatic toxicity. *Env Sci Technol* **14**, 441-443.
- BORGMANN U (1983) Metal speciation and toxicity of free metal ions to aquatic biota In: *Aquatic toxicology*, edited by J O Nriagu, Wiley, New York, 47 - 72.
- GARDINER J and MANCE G (1984) Water quality standards arising from European Community Directives. Water Research Centre Report TR 247.
- HUNT D T E (1987) Trace metal speciation and toxicity to aquatic organisms - a review. WRC Technical Report TR247, Water Research Centre.
- JONES M J and HART B T (1989) Copper complexing capacity in freshwaters using cathodic stripping voltammetric method. *Chemical Speciation and Bioavailability* **1**, 59-63.
- RAVENSCROFT J E and GARDNER M J (1990) Analytical implications of environmental legislation. *Anal Proc* **27**, 265-266.
- SERRITTI A, PELLEGRINI D, MORRELLI E, BARGHIGIANI C and FERRARA R (1986) Copper complexing capacity of phytoplanktonic cell exudates. *Mar Chem* **18**, 351-357.

SHOLKOVITZ E R and COPELAND D (1983) The coagulation, solubility and adsorption properties of Fe, Mn, Cu, Ni, Cd, Co and humic acids in river water. *Geochim Cosmochim Acta* 45, 181-189.

SUNDA W G and FERGUSON R L (1983) Sensitivity of natural bacterial communities to additions of copper and to cupric ion activity. A bioassay of copper complexation in seawater. In: *Trace Metals in Seawater, NATO Conf Series 4, Mar Sci Vol. 4*. Plenum, 871-891.

Figure 1 - *Copper Complexing Capacity versus Salinity*

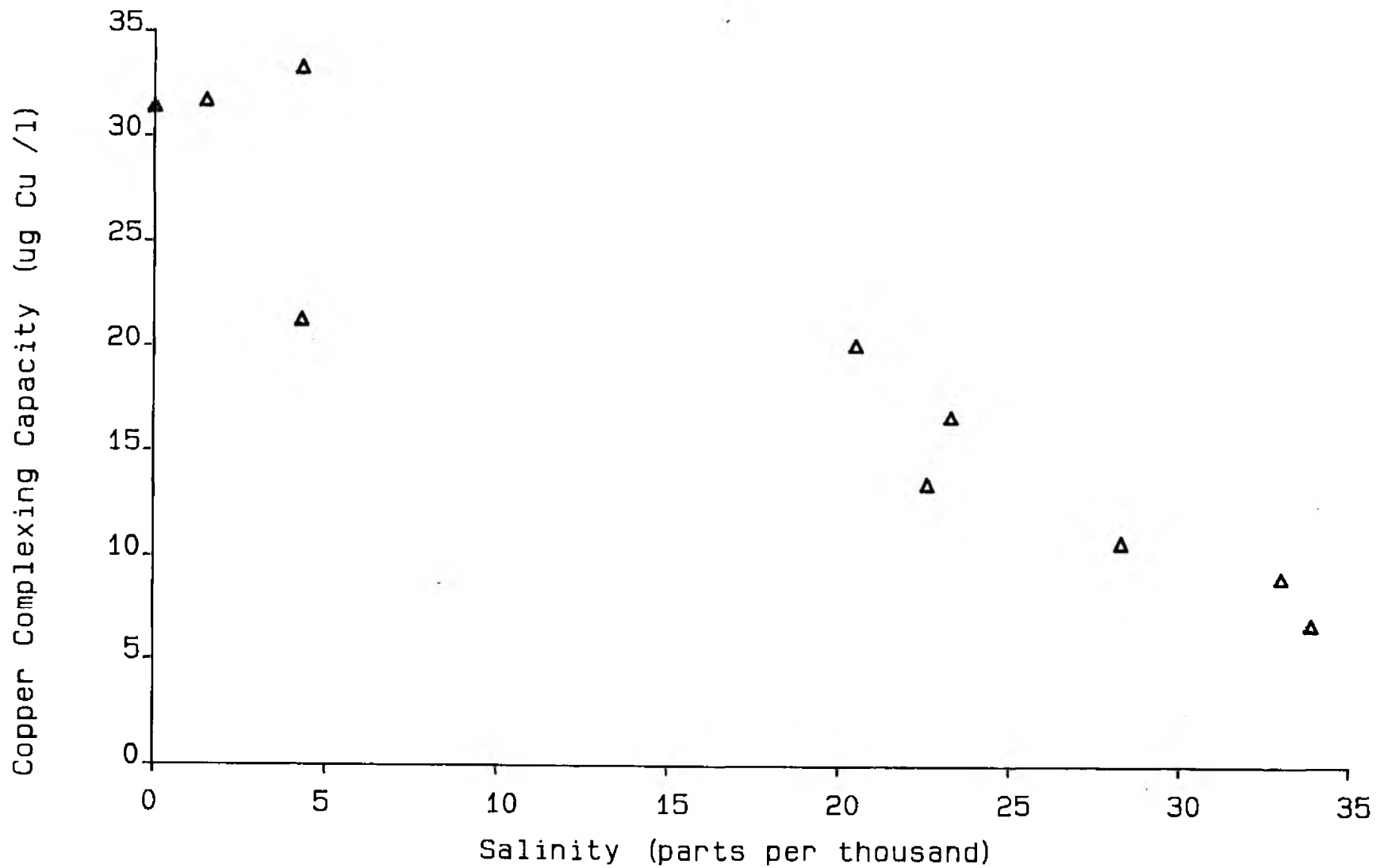


Figure 2.- Modelled Inorganic Copper (given Total Dissolved = 5 μ g/l)

