



Comparison of Chemical Speciation of Copper in the Oosterschelde and Westerschelde Estuaries, The Netherlands

L. J. A. Gerringa, T. C. W. Poortvliet and H. Hummel

Netherlands Institute for Ecology, Centre for Estuarine and Coastal Ecology,
Vierstraat 28, 4401 EA Yerseke The Netherlands

Received 29 November 1994 and in revised form 13 February 1995

Keywords: estuaries; copper; speciation; bioavailability; bivalves

The aim of this investigation was to assess the chemical speciation of copper. Although the Cu concentrations in both the dissolved and particulate phases differ strongly between the Oosterschelde (OS) and Westerschelde (WS) estuaries, The Netherlands, the Cu content of the bivalve *Macoma balthica* from both sea arms is comparable. Therefore, chemical speciation of Cu was examined during 1 year at two sites, one in each sea arm.

Two dissolved organic ligand groups could be distinguished. For both sea arms, a relatively weak ligand group with $\log K' = 9.27$ and a mean ligand concentration of $250 \text{ neq Cu l}^{-1}$ was determined. Moreover, a relatively strong group was detected with $\log K' = 13.04$ and a mean ligand concentration of $180 \text{ neq Cu l}^{-1}$ in the WS, and with $\log K' = 13.7$ and a mean ligand concentration of 48 neq Cu l^{-1} in the OS. In both sea arms, the calculated free concentration of Cu^{2+} is extremely low ($< 10^{-14} \text{ M}$).

The strong ligand group is related to salinity and to dissolved organic carbon (DOC) indicating that the river Scheldt and estuarine/marine DOC supply this material. The weak ligand group is related to salinity and marine chlorophyll *a* in the WS, and to DOC in the OS.

The regulating mechanisms of the distribution of Cu over the chemical species are different for the two sea arms. In the WS, there seems to be no equilibrium between dissolved and particulate Cu. Hence the free Cu concentration is determined by complexation with dissolved organic ligands. In the OS, adsorption on particulate organic matter is the key factor. It is even possible to make a good estimate of free Cu in the OS if only dissolved and particulate Cu and POC are known.

It is concluded that *Macoma* does not accumulate Cu from the dissolved phase since the free Cu concentration is too low; food must be the source. Since desorption of Cu from particulate matter in the polluted WS is slow in contrast to desorption in the relatively clean OS, kinetics of particulate Cu seem to be the reason for the relatively high Cu content of *Macoma* in the OS.

© 1996 Academic Press Limited

Introduction

Much research on bioavailability has been done during the last few decades (Sunda & Guillard, 1976; Morel & Morel-Laurens, 1983; Brand *et al.*, 1986; Zhou *et al.*, 1989;

Verwey *et al.*, 1992; Xue & Sigg, 1993) since it was recognized that availability of metals, and especially of copper, is of more importance than its total concentration. Bioavailability is usually studied by determining the speciation. Speciation of Cu in solution in natural waters is dominated by complexation with dissolved organic ligands. These complexes are assumed not to be bioavailable.

The importance of Cu bioavailability is illustrated in the Oosterchelde (OS) and Westerschelde (WS) estuaries (The Netherlands). In contrast to expectation, Hummel and van Urk (1991), and Absil (1993) observed higher or equal concentrations of Cu in the bivalve *Macoma balthica* from the relatively unpolluted OS than in the polluted WS. So, the Cu content of the sediment dwelling *Macoma balthica* is not directly related to total Cu concentrations in water. Also Bordin *et al.* (1992) found a limited external influence at locations with notably higher environmental Cu concentrations. This also seems to hold true for Cu in *Mytilus edulis* (Luten *et al.*, 1986).

Absil (1993) found that the sources of Cu for *Macoma* (from OS and WS) are food and water. In muddy sediments, the sediment also contributed to the Cu content in the animals. An increase of dissolved organic ligands decreased the uptake of Cu by *Macoma*, and at lower salinities the uptake of Cu is more pronounced (Absil *et al.*, 1993). Since the salinity of the WS estuary is lower than in the OS, it is surprising that the Cu content of *Macoma* in both sea arms is comparable. For Cd, however, a relationship was found between pollution grade and metal content of *Mytilus* and *Macoma* (Luten *et al.*, 1986; Bordin *et al.*, 1992). Since, in contrast to Cd, the bioavailability of dissolved Cu is largely dependent on chemical speciation (i.e. organic complexation) (Sunda & Guillard, 1976; Absil *et al.*, 1993), a study of Cu speciation is necessary.

As a result of the construction of a storm surge barrier in 1987, the OS changed from an estuary into a tidal basin with a very low inflow of freshwater and thus barely a salinity gradient ($S=30-32$). Pollution and concentrations of nutrients are low (Smaal & Nienhuis, 1992).

The WS is one of the most polluted estuaries of Western Europe. Large amounts of domestic and industrial wastes are discharged into the river Scheldt and the estuary. The estuary is well mixed with only small vertical salinity gradients. The salinity at the sampling station of the present study varies between 15 and 20, well away from the turbidity maximum. The concentrations of seston can be relatively high due to tidal currents and intensive dredging activities in the estuary (Wollast, 1988). Ninety percent of the non-refractory riverine organic matter is mineralized in the upper part of the estuary. But due to the large supply of nutrients, organic matter produced by photosynthesis in the lower estuary equals almost the amount of terrestrial C removed by respiration (Wollast, 1988).

Due to the chemical and ecological differences between the OS and the WS, it can be expected that the Cu speciation is also different. The variation in Cu speciation for OS and WS are not known. Van den Berg *et al.* (1987) measured relatively high ligand concentrations in the WS, but gave no information about changes with time. It is known that plankton excretes ligands (Moffet *et al.*, 1990; Gerringa *et al.*, 1995a). Also, the particulate phase is not constant with time. Therefore, the Cu speciation and other parameters which possibly influence the Cu speciation have been examined for a year in the OS and WS at a sampling site in each sea arm (Figure 1). To determine the factors influencing Cu speciation, the following parameters have been monitored: salinity, pH, seston, particulate organic carbon (POC), particulate total nitrogen (PTN), chlorophyll *a* and *b* (Chl*a*, Chl*b*), dissolved organic carbon (DOC) and dissolved Zn.

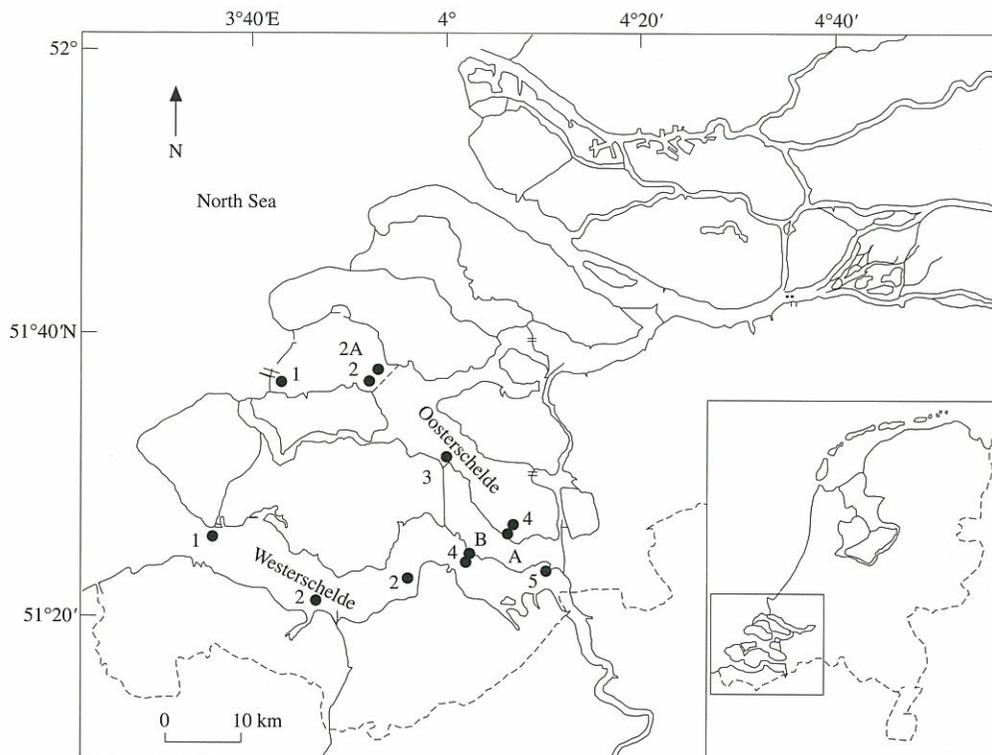


Figure 1. Locations of the sampling sites. A and B are the monitoring stations, 1–5 the sampling sites visited by ship.

Materials and methods

Samples were taken during 1993, fortnightly to monthly at high tide from two sites, one in the Oosterschelde and one in the Westerschelde (A and B in Figure 1). They were taken from the shore with a telescope fishing rod to which a sampling bottle was attached. The idea of sampling at the waterside at high tide is that it is this water that flows over the habitat of *Macoma*. In addition to shore sampling, samples were taken offshore, from RV *Luctor* along the major axis of the two sea arms (Points 1–5 in Figure 1), in autumn (November 1992) and early spring (February 1993). These samples were taken at high tide upstream from the vessel with the sampling bottle just below the water surface. The data from these cruises will not be treated extensively here. They will be dealt with when necessary and discussed elsewhere in detail.

All materials used for metal sampling and metal analysis were acid cleaned (at least 2 weeks in $\text{HNO}_3/\text{milliQ}=1:5$). Sample handling and analysis of metals and speciation measurements were performed in a clean room and MilliQ-water ($\geq 18.2 \Omega^{-1}$) was used, unless otherwise stated. The samples were filtered within 2 h of being obtained. The samples taken from the research vessel were filtered immediately on board. Salinity was measured according to Strickland and Parsons (1972).

Samples for DOC analysis were obtained by filtering through pre-treated glass fibre filters (S&S No. 6) using a glass syringe with filter set. HgCl_2 was added to these samples

to inhibit bacterial activity. Dissolved organic matter was destroyed by UV irradiation and persulphate. CO_2 produced upon oxidation was measured colorimetrically (SE: 0.2 mg l^{-1} or $16.7 \text{ } \mu\text{M}$ DOC; Schreurs, 1978).

Particulate organic carbon (POC) and particulate total nitrogen (PTN) were measured on a Carlo Erba nitrogen/carbon analyser, type NA 1500 (precision 3%; Nieuwenhuize *et al.*, 1994). A division in organic seston and inorganic seston was obtained by subtracting twice the POC content from total seston (determined during the analysis of POC and PTN). Seston originating from algae was calculated by multiplying Chl *a* by 60 (Wetsteyn & Kromkamp, 1994).

Chlorophyll *a* and *b* (Chl *a* and Chl *b*) were measured using high performance liquid chromatography (HPLC) according to Brown *et al.* (1981) (SE: 8%). If Chl *b* was high, marine chlorophyll *a* (Chl *a*_m) was calculated from total Chl *a* minus 5 times Chl *b*. The ratio Chl *a*/Chl *b* fluctuates. The choice of a constant value for this ratio is arbitrary, and '5' was chosen in this study, according to Senger *et al.* (1993).

For the analysis of particulate Cu, the sample was filtered under nitrogen pressure through acid-cleaned $0.45 \text{ } \mu\text{m}$ cellulose nitrate filters. The filters were stored frozen. They were destroyed in a low temperature asher and redissolved in HCl/HNO₃. Particulate Cu was measured with graphite furnace atomic absorption spectrophotometry furnished with a Zeeman background correction using graphite tubes with L'vov platforms (SE: 2 nM).

Part of the sample of the dissolved phase was acidified to pH=2 for the determination of total dissolved Cu and Zn. Dissolved organic ligands were destroyed by UV irradiation in the presence of H₂O₂ for 4 h (Mart, 1979). Cu and Zn were measured by differential pulse anodic stripping voltametry (DPASV), using a hanging drop mercury electrode and a collection potential of -0.6 V for Cu and -1.2 V for Zn (PAR-EEG 303 electrode stand with a 384B analyser) (SE: 3 nM for Cu, 10 nM for Zn).

Speciation of Cu was done by DPASV (collection potential -0.6 V , scan rate 3.33 mV s^{-1}) and differential pulse cathodic stripping voltametry (DPCSV) (collection potential -0.05 V , scan rate 10 mV s^{-1}) and by reversed phase chromatography (Seppak C₁₈, SE, 1.1 nM ; Mills & Quinn, 1984). For DPCSV, salicylaldehyde (SA) was used at a concentration of 10^{-5} M (Campos & Van den Berg, 1994). The alpha factor (α) for the inorganic complexation was assumed to be 50 for both the OS and WS since $\alpha_{\text{inorgorg}} \ll \alpha_{\text{org}}$. The α for the added ligand represents the centre of the detection window of the method and for 10^{-5} M SA (depending on salinity) around 135 000 for OS samples and 180 000 for WS samples. Subsamples were titrated with increasing Cu concentrations and equilibrated for 24 h. A non-linear regression of the titration curve was used to estimate the total natural ligand concentration (Lt) and the conditional stability constant (K') (Gerringa *et al.*, 1991, 1995b). Non-linear regression provides the means to estimate the error boundaries around the values of Lt and K' . Concentrations of ligand groups are expressed in molequivalents of Cu, meaning amount of binding sites for Cu in M.

Adsorption characteristics of POC were determined once (March 1994). Subsamples of 100 ml unfiltered water with additions of 50, 100, 150, 200, 300, 400, 500, 750, 1000, 2000, 3000, 5000, 10 000 and 20 000 nM Cu were equilibrated for 24 h in the dark at $15 \text{ }^\circ\text{C}$, and were shaken continuously. The adsorbed Cu was measured after filtration as particulate Cu described above. The Langmuir equation was used for the calculation of the adsorption characteristics, the conditional binding strength (B'), and the amount of binding sites (Γ_{max}), just as for the complexation characteristics.

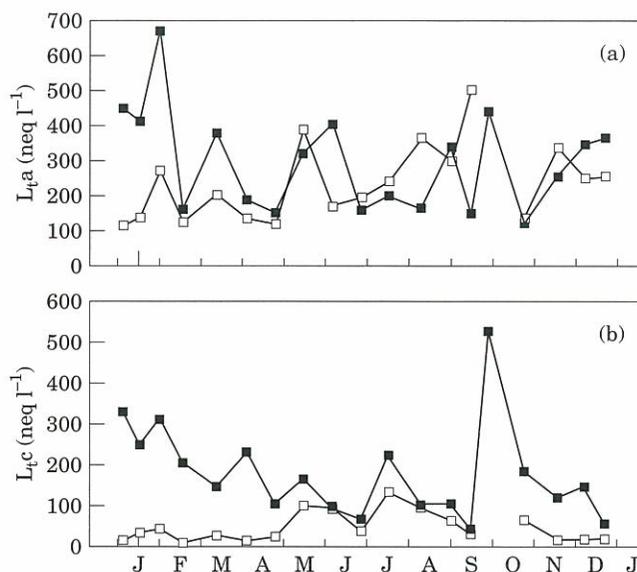


Figure 2. (a) Total concentration of the relatively weak ligand ($L_{t,a}$) as a function of time in the Oosterschelde (OS) and the Westerschelde (WS); (b) total concentration of the relatively strong ligand ($L_{t,c}$) as a function of time in the OS and the WS. \square , OS; \blacksquare , WS.

Automated forward stepwise multiple regression of the data was performed. The minimum tolerance used for entry of parameters into the model was set to 0.01, and alpha to enter and alpha to remove were set to 0.1 (=90% nominal significance level) (Sokal & Rohlf, 1995). Several calculated parameters like organic seston, inorganic seston, seston consisting of algae, Chl a corrected and Q were added to the measured ones. Q is the quotient of particulate Cu and dissolved Cu (both in nM l^{-1}).

Results

The speciation by DPASV and DPCSV resulted in the detection of two ligand groups (Appendix A, Table A1). The relatively weak group was detected by DPASV. It had a conditional stability constant of $10^{9.27}$ ($K' = 10^{8.27} - 10^{10.44}$ for the WS, $K' = 10^{8.4} - 10^{10.22}$ for the OS) and a concentration ($L_{t,a}$) around $250 \text{ neq Cu l}^{-1}$ (between 126 and $673 \text{ neq Cu l}^{-1}$ for the WS and 109 and $506 \text{ neq Cu l}^{-1}$ in the OS). The concentrations are comparable for both sea arms except in the winter when the concentrations are higher in the WS [Figure 2(a)].

The relatively strong ligand group was detected by DPCSV in the WS and OS. It had a conditional stability constant of $10^{13.04}$ ($10^{12.25} - 10^{13.77}$) and $10^{13.7}$ ($10^{12.53} - 10^{15.05}$) respectively, and a mean ligand concentration ($L_{t,c}$) of 180 neq l^{-1} ($43 - 528 \text{ neq l}^{-1}$) and 48 neq l^{-1} ($9 - 131 \text{ neq l}^{-1}$) respectively [Figure 2(b)].

The adsorption characteristics of POC for Cu in the OS showed a conditional binding strength B' of $10^{11.35}$ and a number of sites for Cu, Γ_{max} , of 0.01316 molequivalents of Cu mol^{-1} POC (the 95% confidence intervals are $10^{11.22} - 10^{11.47}$ and $0.01122 - 0.01509$, respectively). This gives, with a mean POC content of $342 \mu\text{M}$ (4.1 mg l^{-1}), $4.5 \mu\text{molequivalents of Cu l}^{-1}$. In the WS, B' was $10^{11.41}$ ($10^{11.30} - 10^{11.51}$) and Γ_{max}

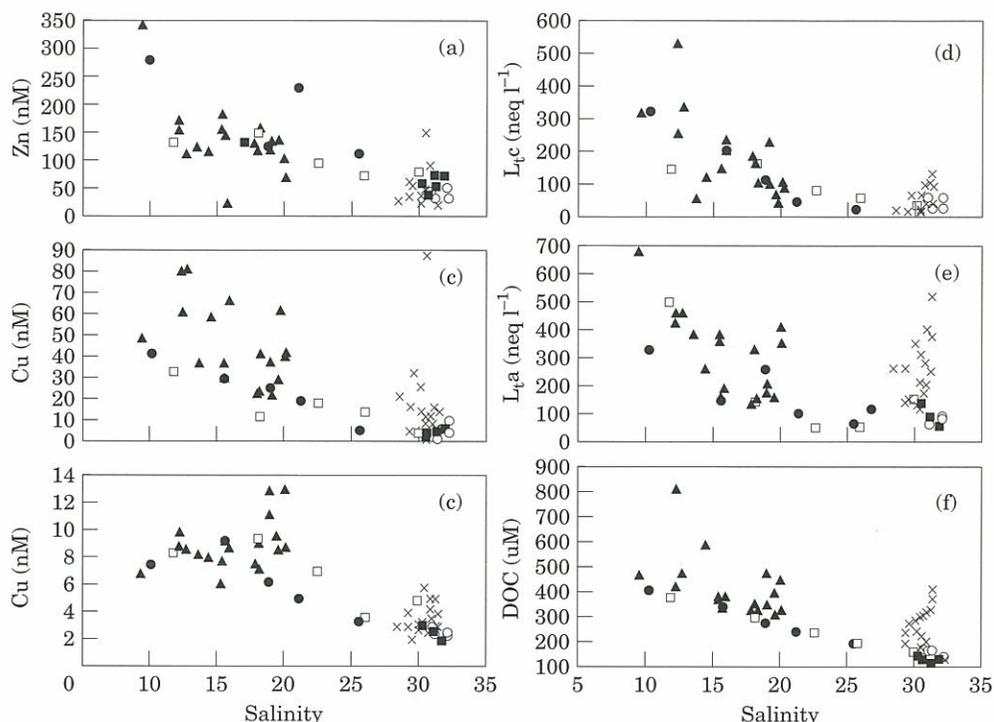


Figure 3. Salinity versus other parameters of monitoring during 1993 in the Oosterschelde (OS) and the Westerschelde (WS) and from samples taken from the ship in November 1992 and February 1993 (see Figure 1). (a) Zinc; (b) Particulate copper; (c) Seppak copper; (d) total concentration of the relatively strong ligand (L_{tc}); (e) total concentration of the relatively weak ligand (L_{ta}); and (f) dissolved organic carbon. ■, OS February 1993; ●, WS February 1993; ○, OS November 1992; □, WS November 1992; X, OS 1993; ▲, WS 1993.

was $0.00841 \text{ moleq Cu mol}^{-1} \text{ POC}$ ($0.00734\text{--}0.00947$), giving, with a mean POC content of $400 \mu\text{M}$ (4.8 mg l^{-1}), $3.4 \mu\text{molequivalents of Cu l}^{-1}$.

The concentrations of total dissolved Zn, total dissolved Cu, particulate Cu, Seppak Cu and the strong ligand in the WS are three times the values found in the OS. Also POC, PTN and seston have higher concentrations in the WS than in the OS (Appendix A, Table A2). Since the OS contains less seston and thus shows deeper light penetration, plankton blooms occur earlier in this sea arm. Yet, the concentrations of chlorophyll *a* during a bloom are higher in the WS. The concentrations of seston at this study's sampling site are relatively high for the OS, which is probably due to sampling from the shore (Appendix A, Table A2).

The salinity at the sampling station in the WS fluctuates with season by the discharge of the river Scheldt. Some parameters vary with salinity, showing a gradient from the freshwater source, the Scheldt river, to the North Sea. Such is the case for total dissolved Zn [Figure 3(a)] and to a lesser degree for particulate Cu, Seppak Cu and DOC [Figure 3(b,c and f)]. The concentrations of dissolved Zn in the OS fit into the dilution line of values of the WS. Particulate Cu and Cu retained by Seppak show a more or less similar behaviour as total dissolved Zn, but variability during 1993 is larger. Other parameters

TABLE 1. Relations found by the multiple regression with $R^2 > 0.5$. For equations (7 and 8), data for both estuaries were used. In equations (3, 5 and 6), the equations in parentheses exclude those parameters for which no straightforward chemical explanation for its contribution could be found

$[Cu_p] = -0.144 + 0.456 POC$	$R^2 = 0.947$	OS	(1)
$Q = 0.101 + 0.0067 POC - 0.0101 PTN$	$R^2 = 0.922$	OS	(2)
$L_a = 583 - 29.2 sal + 12 Chla_c + 0.95 [Zn_d]$	$R^2 = 0.722$	WS	(3)
$(L_a = 883 - 39.4 sal + 10 Chla_c)$	$R^2 = 0.629$	WS)	
$L_a = -52.4 + 1.0944 DOC$	$R^2 = 0.522$	OS	(4)
$L_c = 379 - 24.6 sal + 1.512 PTN + 14.3 CuS$	$R^2 = 0.751$	WS	(5)
$(L_c = 434 - 20.7 sal + 1.694 PTN)$	$R^2 = 0.715$	WS)	
$L_c = -96.2 + 0.4488 DOC + 0.6 [Zn_d]$	$R^2 = 0.586$	OS	(6)
$(L_c = -33.4 + 0.3108 DOC)$	$R^2 = 0.393$	OS)	
$L_c = 117 + 0.4296 DOC - 6.3 sal$	$R^2 = 0.704$	WS+OS	(7)
$[Cu_p] = 58.2 + 0.408 POC - 1.9 sal$	$R^2 = 0.784$	WS+OS	(8)

OS, Oosterschelde; WS, Westerschelde; L_a , total concentration of relatively weak ligand; L_c , total concentration of relatively strong ligand; PTN, particulate total nitrogen; DOC, dissolved organic carbon; POC, particulate organic carbon. Units as in Appendix A. Alpha to enter and alpha to remove were set on 0.1 (90% confidence interval).

The following P values (indicating the significance of the independent contribution of the explanatory variable) were given for the constants and parameters respectively: (1) 0.921 and 0.000; (2) 0.672, 0.000 and 0.015; (3) 0.003, 0.003, 0.005 and 0.034; (4) 0.489 and 0.001; (5) 0.001, 0.000, 0.003 and 0.165; (6) 0.019, 0.001 and 0.041; (7) 0.153, 0.001 and 0.003; and (8) 0.000, 0.000 and 0.000.

which show a relationship with salinity in the WS are the concentrations of both ligands [Figure 3(d and e)]. However, the data from the OS do not fit into the regression with salinity in the WS for these parameters.

The results of multiple regression are shown in Table 1. Only results with R^2 larger than 0.5 are presented. Equations (3, 5 and 6) were repeated without the parameters dissolved Zn [equations (3 and 6)] and Cu retained by Seppak [equation (5)]. The contribution of these parameters to the ligand concentrations could not be explained according to straightforward chemical concepts. Particulate Cu and Q (quotient of particulate and dissolved Cu) in the OS correlate strongly with POC. The ligand concentrations in the WS correlate with salinity as also shown in Figures 3(d and e). The weak ligand group also correlates with $Chla_c$ concentrations and thus with algae, but the strong ligand group correlates with PTN. In the OS, the ligand concentrations correlate with DOC. No relationship was found between L_a and chlorophyll a in the WS when the raw data of chlorophyll a were used. In the OS, an influence of algae by $Chla_c$ on L_a is only found when alpha to enter (and remove) is set on 0.15. No relations are found with Cu retained by Seppak as variable. When the data of the two estuaries are combined, two relationships were found with $R^2 > 0.5$ [equations (7 and 8)]. With particulate Cu, POC and salinity are related; whereas for the strong ligand group, DOC and salinity account for most of the variability.

Discussion

Cu speciation

Van den Berg *et al.* (1987) also found two ligand groups in the WS; a strong ligand with a stability constant 10^{13} – $10^{14.8}$ comparable to the values of the present study ($10^{12.25}$ – $10^{13.77}$), and a weak ligand group with a conditional stability constant $10^{11.5}$ – $10^{12.1}$

higher than the values of the present study ($10^{8.27}$ – $10^{10.44}$). They used catechol as competing ligand with CSV for both (the strong and weak) ligand groups, which is a different method than used in the present study. Using catechol has the drawback that the equilibrium time between catechol, the natural ligands and Cu is fixed to 4 min, whereas equilibrium is seldomly reached within the hour (Donat & Van den Berg, 1992; Van den Berg & Donat, 1992). Moffet *et al.* (1990) also found two ligand groups with conditional stability constants $10^{13.2}$ and $10^{9.7}$ in the Sargasso Sea (using ligand exchange/liquid–liquid partition procedure) which compare favourably with the present results. Coale and Bruland (1988) found two ligand groups with a lower conditional stability constant for the strong ligand and a comparable one for the relatively weak ligand in the North-east Pacific Ocean, as did Coale and Bruland (1990) in the North Pacific Ocean, and Buckley and Van den Berg (1986) in the Atlantic Ocean. Their results were $10^{11.5}$ and $10^{8.5}$ (DPASV), $10^{11.6}$ and $10^{8.6}$ (DPASV) and 10^{11} and $10^{8.5}$ (combination of DPASV, DPCSV with catechol and the MnO_2 method), respectively (see also Xue & Sigg, 1993).

Since the two organic ligand groups in the OS and WS are detected by two methods based on two different principles (DPASV is a physical chemical method, DPCSV a chemical competition method), it is not certain whether the two groups are really two different groups without any overlap. For some samples from the WS, the concentration of the relatively strong ligand is somewhat larger than the relatively weak ligand (Appendix A, Table A1). This is in contradiction with the theory which states that with increasing conditional stability constant the concentration decreases, as postulated by Buckley and Van den Berg (1986), and confirmed by the data of Coale and Bruland (1988, 1990), and Moffet *et al.* (1990). However, it is not likely that the overlap is large since the ligand groups show different relationships with other parameters [equations (3–6) in Table 1].

Using the ligand characteristics, the concentration of free Cu, $[\text{Cu}^{2+}]$, can be calculated. For 1993, the mean $[\text{Cu}^{2+}]$ found in the WS was $14.7 \cdot 10^{-15}$ M, and in the OS was $8.2 \cdot 10^{-15}$ M, which are very low values (Xue & Sigg, 1993). It should be realized that calculation of $[\text{Cu}^{2+}]$ from the characteristics of the determined ligand groups may not be justified because of the above mentioned overlap. Moreover, it is known from very recent experiments (1993, 1994) that during certain periods, another stronger ligand group exists in the WS (Gerringa, unpubl. data). The concentration of this ligand, however, is small and the concentration of sites not filled with Cu is near the detection limit of the method (DPCSV with oxine, Van den Berg, 1986). Since the strongest ligand group, not yet saturated with Cu, largely determines the $[\text{Cu}^{2+}]$ concentration, the mean value for the WS given above may well be an overestimation.

Relation between Cu speciation and environmental variables

The source of the ligand groups in the WS seems to be partly the river Scheldt, since a (negative) relationship exists with salinity. A linear decrease by salinity alone would give a y-axis intercept at salinities of 16–22 [Table 1, equations (3, 5 and 7)]. This reflects that ligand groups from the river Scheldt are degraded or lost in the WS during transport to the North Sea. Besides salinity, ligand concentrations are also related to DOC, which becomes evident when all data from the WS and the OS on the strong ligand are combined [equation (7), Table 1]. Moreover, L_a vs. salinity [Figure 3(e)] shows such a large variability in the OS samples that it is clear that salinity is not the only factor determining its concentration. The variation in the ligand data of the OS is mainly

related to DOC [equations (4 and 6), Table 1]. Thus, although the conditional stability constants are comparable, the ligands, at least the relatively weak ones, seem to have different origins in both estuaries. In the OS, the origin of the weak ligands is not clear but related to DOC. In the WS, both freshwater from the river Scheldt and (as discussed below) algae are partly responsible for the weak ligand group. For the strong ligands, it might be argued that they have a similar origin in OS and WS since they could be described by one regression [equation (7), Table 1] and that the relation with DOC in the WS is masked by the correlation between DOC and salinity.

From the strong association with organic ligands, Regnier and Wollast (1993) have suggested that Cu is mainly bound to organic matter of riverine origin which is progressively mineralized during its transport to sea. The results of the present study confirm their suggestion, and indicate that part of the ligands are of marine or estuarine nature like the ones found in the OS. The relative importance of these ligands can be quantified by their correlation with DOC and Chla content of the estuarine system.

Moffet *et al.* (1990) also found a relationship between Chla and the ligand concentration in laboratory experiments, although this concerned the relatively strong ligand group. They found that the relatively strong ligand was produced by *Synechococcus* sp., a marine cyanobacterium. None of the eukaryotic phytoplankton examined made this strong ligand. Paulson *et al.* (1994a,b) found that organisms could produce ligands that can be retained by Seppak cartridges. Gerringa *et al.* (1995a) found ligands with a conditional stability constant of 10^{10} (detected both by DPASV and DPCSV) in axenic continuous cultures of the marine diatom *Ditylum brightwellii*. This is comparable to the results reported in this paper. Moreover, they found that ligands which could be retained by Seppak cartridges were produced by leakage from broken *Ditylum* cells.

It is surprising that especially in the WS, the relation of the L_c concentration with the Chla content is so obvious. In the WS, the source of the organic material is more diverse and the total concentrations are higher, compared to the OS, where the influence of an algal bloom is expected to be more conspicuous.

In the eastern part of the OS, the ratio between plankton species is in favour of flagellates with respect to diatoms (Bakker & Vink, 1994). In the WS, marine diatoms are dominant at the sampling location (Rijstenbil *et al.*, 1993). It is possible that different plankton species like flagellates do not excrete organic materials which may act as organic ligands for Cu. Another possibility is that due to the large grazing pressure in the OS, plankton is eaten before it decomposes and releases ligands (Bakker & Vink, 1994).

At the sampling station in the WS, however, a positive net production of phytoplankton and a minimum in zooplankton biomass coincide (Soetaert & van Rijswijk, 1993; Soetaert *et al.*, 1994). Zhou *et al.* (1989) found that during the different stages of the growth cycle of diatoms, the nature of ligands depends on the physiological state of the population. Moreover, since the WS is a true estuary with a salinity gradient, dead or dying freshwater phytoplankton is transported seawards. This may also explain the role of algae for the ligand concentration, which is not the case in the OS.

Cu speciation and the solid phase

It seems that organic seston regulates the partitioning of Cu over the dissolved and particulate species in the OS [equation (2), Table 1], whereas in the WS there appears to be no equilibrium between the solid and dissolved species of Cu. Since particulate and dissolved Cu are in equilibrium in the OS, equilibrium should exist between the free Cu

concentration ($[Cu^{2+}]$) and the dissolved organic ligands on the one hand, and the adsorbed particulate fraction on the other hand. The free Cu concentration can be calculated, assuming that the two ligand groups detected are the main ones determining the free Cu concentration. With the accordingly obtained $[Cu^{2+}]$, POC data and particulate Cu ($[Cu]_p$), one can calculate the product ($\Gamma_{ads}B'$) of the amount of sites for Cu (Γ_{ads}) and the conditional constant related to the energy of adsorption per mol POC (B') for each sample,

$$[Cu]_d / \{Ka' * L_{ta} + Kc' * (L_{tc} - [Cu]_d)\} = [Cu^{2+}] = [Cu]_p / POC(\Gamma_{ads} * B') \quad (9)$$

using mol as unit for all concentrations and assuming that dissolved Cu ($[Cu]_d$) is always smaller than the relatively strong ligand concentration which was always the case during monitoring. $\Gamma_{ads} * B'$ estimated with equation (9) varied throughout the year between $10^{8.71}$ and $10^{10.95}$. On the basis of B' and Γ_{max} obtained from the sorption experiment, and POC in the OS, $\Gamma_{max} * B'$ is $10^{9.47}$. Hence the estimation of $\Gamma_{ads} * B'$ using equation (9) is quite accurate. This means that the free Cu concentration in the OS can be calculated from relatively easy POC and particulate Cu determinations.

In the WS, no equilibrium exists between particulate and dissolved Cu. This was also observed by Van Alsenoy (1993). She found that equilibration was very slow between particles in the WS and Cu, and that Cu only showed a detectable desorption at higher salinities and no desorption at <25. This was not influenced at all by an imposed temporary decrease in pH. However, the adsorption characteristics of POC for Cu in the WS could be measured easily, and adsorption was found to occur within 24 h, but, since there is no equilibrium between dissolved and particulate Cu, desorption is slow or not possible, coinciding with the results of Van Alsenoy (1993). Li *et al.* (1984) observed that by coagulation, desorption becomes less than adsorption because metals are locked in.

Ecological significance

Irrespective of the differences in total Cu levels between both sea arms, the Cu concentrations in the bivalve *Macoma balthica* are similar or even higher in the OS in contrast to expectations (Hummel & van Urk, 1991; Absil, 1993). This can now be explained by the observed differences in Cu speciation between both sea arms. *Macoma balthica* accumulates Cu from both food and the dissolved phase, and little from the sediment (Absil, 1993). Although Cu^{2+} is bioavailable, it will play no role in the OS and the WS because of the extreme low concentrations and the high ligand concentrations with high binding strength. Roughly estimated, the maximum Cu^{2+} concentrations are 10^{-14} to 10^{-15} M. These concentrations are extremely low, since concentrations smaller than $10^{-12.5}$ M may cause growth limitation in organisms (Verwey *et al.*, 1992). Considering this, disregarding possible internal regulation by the animals, food must be the main source of Cu for *M. balthica*. Since in the OS, particulate Cu is in equilibrium with Cu^{2+} , it must be reversibly bound to organic particles. This is not the case in the WS. Here desorption of Cu from particles is probably very slow. Although more POC is present in the WS, adsorption sites are less per mol POC than in the OS. Thus POC is carrying potentially less Cu in the WS. Assuming that *M. balthica* in WS and in OS consumes equal amounts of food, ingested particles from the OS are potentially larger sources for Cu uptake than those from the WS. Consequently, Cu levels in *M. balthica* from the OS are relatively high.

Acknowledgements

We wish to express our appreciation to Jan Sinke for the Chla data, Adri Merks for the DOC data, Johan v.d. Zande for salinities, Jaap v. Liere and Yvonne Maas for POC and PTN data, to the crew of the RV *Luctor* and to Bert Sinke for his help whenever necessary. The authors are grateful to Peter Herman and Jacco Kromkamp for their help and the useful discussions, and to Hans van Haren (Netherlands Institute for Sea Research), Christien Absil (School of Animal and Microbial Sciences, University of Reading) and Jack Middelburg for reading and improving the manuscript. Thanks are also due to Rikus Kloosterhuis (Netherlands Institute for Sea Research) who performed the last POC analyses.

References

- Absil, M. C. P. 1993 *Bioavailability of Heavy Metals for the Deposit Feeder Macoma balthica with Special Emphasis on Copper*. Thesis University of Wageningen, The Netherlands, 171 pp.
- Absil, M. C. P., Gerringa, L. J. A. & Wolterbeek, B. Th. 1993 The relation between salinity and copper complexing capacity of natural estuarine waters and the uptake of dissolved ^{64}Cu by *Macoma balthica*. *Chemical Speciation and Bioavailability* 5, 119–128.
- Bakker, C. and Vink, M. 1994 Nutrient concentrations and planktonic diatom-flagellate relations in the Oosterschelde (SW Netherlands) during and after the construction of a storm-surge barrier. *Hydrobiologia* 282/283, 101–116.
- Bordin, G., McCourt, J. & Rodríguez, A. 1992 Trace metals in the marine bivalve *Macoma balthica* in the Westerschelde Estuary (The Netherlands). Part I: Analysis of total copper, cadmium, zinc and iron concentrations—locational and seasonal variations. *Science of Total Environment* 127, 255–280.
- Brand, L. E., Sunda, W. G. & Guillard, R. R. L. 1986 Reduction of marine phytoplankton reproduction rates by copper and cadmium. *Journal of Experimental Marine Biology and Ecology* 96, 225–250.
- Brown, L. M., Hargrave, B. T. & Mackinnon, M. D. 1981 Analysis of chlorophyll-*a* in sediments by high-pressure liquid chromatography. *Canadian Journal of Fisheries and Aquatic Science* 38, 205–214.
- Buckley, P. J. M. & Van den Berg, C. M. G. 1986 Copper complexation profiles in the Atlantic Ocean. A comparative study using electrochemical and ion exchange techniques. *Marine Chemistry* 19, 281–296.
- Campos, M. L. A. M. & Van den Berg, C. M. G. 1994 Determination of copper complexation in sea water by cathodic stripping voltammetry and ligand competition with salicylaldehyde. *Analytica Chimica Acta* 284, 481–496.
- Coale, K. H. & Bruland, K. W. 1988 Copper complexation in the Northeast Pacific. *Limnology and Oceanography* 33, 1084–1101.
- Coale, K. H. & Bruland, K. W. 1990 Spatial and temporal variability in copper complexation in the North Pacific. *Deep-Sea Research* 37, 317–336.
- Donat, J. R. & Van den Berg, C. M. G. 1992 A new cathodic stripping voltammetry method for determining organic copper complexation in seawater. *Marine Chemistry* 38, 69–90.
- Gerringa, L. J. A., van der Meer, J. & Cauwet, G. 1991 Complexation of Cu and Ni in the dissolved phase of marine sediment slurries. *Marine Chemistry* 36, 51–70.
- Gerringa, L. J. A., Poortvliet, T. C. W., Rijstebil, J. W., van Drie, J. & Schot, M. C. 1995a Speciation of copper and responses of the marine diatom *Ditylum brightwellii* upon increasing copper concentrations. *Aquatic Toxicology* 31, 77–90.
- Gerringa, L. J. A., Herman, P. M. J. & Poortvliet, T. C. W. 1995b Comparison of the linear Van den Berg/Ruzić transformation and the non-linear fit of the Langmuir isotherm applied to Cu speciation data in the estuarine environment. *Marine Chemistry* 48, 131–142.
- Hummel, H. & van Urk, G. 1991 Aquatische mollusken chemisch onder druk. In *Flora en Fauna Chemisch Onder Druk* (Hekstra, G. P. & van Linden, F. J. M., eds) Pudoc Wageningen, pp. 103–109.
- Li, Y.-H., Burkhardt, L., Buchholtz, M., O'Hara, P. & Santschi, P. H. 1984 Partition of radiotracers between suspended particles and seawater. *Geochimica Cosmochimica Acta* 48, 2011–2019.
- Luten, J. B., Bouquet, W., Burggraaf, M. M., Rauchbaa, A. B. & Rus, J. 1986 Trace metals in mussels (*Mytilus edulis*) from the Waddenzee, coastal North Sea and the estuaries of Ems, Westerschelden and Eastern Scheldt. *Bulletin of Environmental Contamination and Toxicology* 36, 770–777.
- Mart, L. 1979 *Ermittlung und Vergleich des Pegels Toxischer Spurenmetalle in Nordatlantischen und Mittelmeerischen Küstengewässern*. Ph.D. Thesis, Technische Hochschule, Aachen, Deutschland, 354 pp.
- Mills, G. L. & Quinn, J. G. 1984 Dissolved copper and copper-inorganic complexes in the Narragansett Bay estuary. *Marine Chemistry* 15, 151–172.

- Moffet, J. W., Zika, R. G. & Brand, L. E. 1990 Distribution and potential sources and sinks of copper chelators in the Sargasso Sea. *Deep-Sea Research* **37**, 27–36.
- Morel, F. M. M. & Morel-Laurens, N. M. L. 1983 Trace metals and plankton in the oceans: facts and speculations. In *Trace Metals in Sea Water* (Wong, C. S., Boyle, E., Bruland, K. W., Burton, J. D. & Goldberg, E. D., eds). Plenum Press, New York. Nato Conference Series, Serie IV, Marine Sciences. p. 841–871.
- Nieuwenhuize, J., Maas, Y. E. M. & Middelburg, J. J. 1994 Rapid analysis of organic carbon and nitrogen in particulate materials. *Marine Chemistry* **45**, 217–224.
- Paulson, A. J., Curl, Jr., H. C. & Gendron, J. F. 1994a Partitioning of Cu in estuarine waters, I. Partitioning in a poisoned system. *Marine Chemistry* **45**, 67–80.
- Paulson, A. J., Curl, Jr., H. C. & Gendron, J. F. 1994b Partitioning of Cu in estuarine waters, II. Control of partitioning by the biota. *Marine Chemistry* **45**, 81–93.
- Regnier, P. & Wollast, R. 1993 Distribution of trace metals in suspended matter of the Scheldt estuary. *Marine Chemistry* **43**, 3–19.
- Rijstenbil, J. W., Bakker, C., Jackson, R. H., Merks, A. G. A. & de Visscher, P. R. M. 1993 Spatial and temporal variation in community composition and photosynthetic characteristics of Phytoplankton in the upper Westerschelde estuary (Belgium, SW Netherlands). *Hydrobiologia* **269/270**, 263–273.
- Schreurs, W. 1978 An automated colorimetric method for the determination of dissolved organic carbon in seawater by UV destruction. *Hydrobiological Bulletin* **12**, 137–142.
- Senger, H., Schrader, E. & Bihop, N. I. 1993 Changes in the carotenoid pattern during the synchronous life cycle of *Scenedesmus*. *Botanica Acta* **106**, 72–77.
- Smaal, A. C. and Nienhuis, P. H. 1992 The Eastern Scheldt (The Netherlands), from an estuary to a tidal bay: a review of responses at the ecosystem level. *Netherlands Journal of Sea Research* **30**, 161–173.
- Soetaert, K. & van Rijswijk, P. 1993 Spatial and temporal patterns of the zooplankton in the Westerschelde estuary. *Marine Ecology Progress Series* **97**, 47–59.
- Soetaert, K., Herman, P. M. J. & Kromkamp, J. 1994 Living in the twilight: estimating net phytoplankton growth in the Westerschelde estuary (the Netherlands) by means of an ecosystem model (MOSES). *Journal of Plankton Research* **16**, 1277–1301.
- Sokal, R. R., & Rohlf, F. J. 1995 *Biometry*, 3rd Edition. W. H. Freeman and Company, 887 pp.
- Strickland, J. D. H. & Parsons, T. R. 1972 *A Practical Handbook of Seawater Analysis*. Fisheries Research Board of Canada, Ottawa, 310 pp.
- Sunda, W. G. & Guillard, R. R. L. 1976 The relationship between cupric ion activity and the toxicity of copper to phytoplankton. *Journal of Marine Research* **34**, 511–529.
- Van Alsenoy, V. 1993 *Concentration and Partitioning of Heavy Metals in the Scheldt Estuary*. PhD Thesis, Universiteit van Antwerpen, 290 pp.
- Van den Berg, C. M. G. 1986 Determination of copper, cadmium and lead in seawater by cathodic stripping voltammetry of complexes with 8-hydroxyquinoline. *Journal of Electroanalytical Chemistry* **215**, 111–121.
- Van den Berg, C. M. G., Merks, A. G. A. & Duursma, E. K. 1987 Organic complexation and its control of the dissolved concentrations of copper and zinc in the Scheldt Estuary. *Estuarine, Coastal and Shelf Science* **24**, 785–797.
- Van den Berg, C. M. G. & Donat, J. R. 1992 Determination and data evaluation of copper complexation by organic ligands in sea water using cathodic stripping voltammetry at varying detection windows. *Analytica Chimica Acta* **257**, 281–291.
- Verwey, W., Glazewski, R. & de Haan, H. 1992 Speciation of copper in relation to its bioavailability. *Chemical Speciation and Bioavailability* **4**, 43–51.
- Wetsteyn, L. P. M. J. & Kromkamp, J. C. 1994 Turbidity, nutrients and phytoplankton primary production in the Oosterschelde (The Netherlands) before, during and after a large-scale coastal engineering project (1980–1990). *Hydrobiologia* **282/283**, 61–78.
- Wollast, R. 1988 The Scheldt Estuary. In *Pollution of the North Sea: an Assessment* (Salomons, W., Bayne, B. L., Duursma, E. K. & Förstner, U., eds). Springer Verlag, Berlin, pp. 183–194.
- Xue, H. B. & Sigg, L. 1993 Free cupric ion concentration and Cu (II) speciation in a eutrophic lake. *Limnology and Oceanography* **38**, 1200–1213.
- Zhou, X., Slauenwhite, D. E., Pett, R. J. & Wangersky, P. J. 1989 Production of copper-complexing organic ligands during a diatom bloom: tower tank and batch-culture experiments. *Marine Chemistry* **27**, 19–30.

Appendix

TABLE A1. Ligand characteristics obtained by DPASV and DPCSV. The 95% confidence interval of the estimates are in parentheses. Due to the log-transformation of K' (conditional stability constant), its interval is asymmetric

	OS		WS	
	log K'	Total ligand concentration (neq l ⁻¹)	log K'	Total ligand concentration (neq l ⁻¹)
DPASV				
6/1	9.33 (8.95–9.71)	109 (87–132)		
18/1	9.69 (9.45–9.94)	136 (119–152)	9.59 (8.81–10.39)	413 (321–504)
1/2	9.55 (9.3–9.8)	270 (221–320)	8.83 (8.71–8.95)	673 (634–711)
18/2	9.32 (9.1–9.54)	123 (104–141)	8.77 (8.44–9.1)	158 (112–205)
15/3	8.65 (8.35–8.95)	204 (158–250)	9.98 (9.74–10.22)	380 (349–412)
5/4	8.76 (8.28–9.24)	131 (59–203)	10.44 (8.54–12.35)	188 (139–236)
26/4	–	–	10.17 (9.97–10.38)	150 (143–158)
17/5	8.40 (8.05–8.75)	389 (214–564)	9.01 (8.63–9.38)	322 (243–400)
7/6	8.64 (8.24–9.04)	165 (90–240)	8.27 (7.96–8.59)	403 (252–555)
27/6	9.65 (9.09–10.22)	195 (148–241)	9.16 (8.94–9.39)	158 (135–181)
17/7	9.29 (9.11–9.47)	242 (217–266)	9.04 (8.61–9.47)	199 (155–242)
9/8	9.92 (9.22–10.62)	370 (326–414)	9.25 (9.03–9.47)	165 (146–184)
30/8	9.25 (8.99–9.51)	302 (258–347)	9.13 (8.86–9.39)	346 (281–411)
13/9	9.03 (8.73–9.34)	506 (424–588)	9.28 (8.61–9.95)	150 (106–194)
26/9	–	–	9.15 (8.44–9.87)	446 (316–576)
23/10	9.07 (8.57–9.57)	144 (89–200)	8.91 (8.4–9.43)	126 (79–172)
15/11	10.22 (10.01–10.43)	345 (329–361)	9.17 (8.66–9.68)	258 (186–330)
6/12	9.50 (9.17–9.83)	253 (212–295)	9.50 (9.12–9.88)	354 (311–398)
20/12	9.29 (9.09–9.48)	254 (217–291)	9.10 (8.92–9.29)	373 (325–422)
DPCSV				
6/1	14.55 (13.21–14.88)	15 (11–18)	12.39 (12.21–12.57)	331 (276–387)
18/1	14.52 (14.06–14.99)	35 (32–38)	13.08 (13.03–13.13)	252 (245–258)
1/2	12.86 (12.64–13.08)	44 (37–51)	13.41 (13.26–3.56)	313 (294–333)
18/2	14.57 (13.81–15.34)	9 (8–10)	12.94 (12.74–13.14)	203 (182–225)
15/3	14.07 (13.3–14.85)	28 (23–33)	12.68 (12.58–12.79)	146 (133–159)
5/4	14.53 (13.1–15.96)	15 (11–18)	12.61 (12.51–12.72)	232 (214–251)
26/4	13.31 (12.82–13.79)	23 (18–28)	13.13 (13.03–13.22)	105 (100–110)
17/5	12.91 (12.83–13)	103 (97–110)	13.13 (12.97–13.29)	166 (154–178)
7/6	13.02 (12.82–13.21)	96 (89–104)	13.30 (13.18–13.41)	91 (86–95)
27/6	13.76 (13.38–14.14)	36 (31–41)	13.41 (13.2–13.61)	69 (62–76)
17/7	12.88 (12.64–13.11)	131 (118–145)	12.77 (12.56–12.98)	225 (198–252)
9/8	13.02 (12.71–13.33)	95 (80–109)	13.16 (12.97–13.35)	101 (92–110)
30/8	13.24 (13.05–13.44)	66 (60–72)	13.19 (13.07–13.32)	106 (99–113)
13/9	14.66 (14.12–15.19)	29 (26–32)	13.46 (13.16–13.76)	43 (37–48)
26/9	–	–	12.71 (12.45–12.97)	528 (441–616)
23/10	12.53 (12–13.06)	64 (39–89)	12.25 (11.89–12.61)	182 (108–255)
15/11	–	15	13.11 (12.95–13.26)	121 (108–134)
6/12	14.23 (13.67–14.79)	16 (13–19)	13.34 (13.14–13.54)	143 (129–157)
20/12	15.05 (13.79–16.31)	19 (14–23)	13.77 (13.57–13.97)	56 (51–61)

Day no. 6, 18, 32, 49, 74, 95, 116, 137, 158, 178, 198, 221, 242, 256, 269, 296, 319, 340, 354.

TABLE A2. Data of the monitoring during 1993 at two sampling sites in the OS and WS

Date	Seppak Cu (nM)	Dissolved Cu (nM)	Particulate Cu (nM)	Dissolved Zn (nM)	DOC (μM)	POC (μM)	PTN (μM)	Seston (mg l^{-1})	Chlorophyll <i>a</i> ($\mu\text{g l}^{-1}$)	Chlorophyll <i>b</i> ($\mu\text{g l}^{-1}$)	Salinity
Oosterschelde											
6/1/93	3.1	6.9	8	49	175	153	21	17.8	1.8	0	30.49
18/1/93	5.9	23.8	2	145	167	79	15	19.8	2.4	0	30.49
1/2/93	2.5	7.7	88	86	192	1849	155	382.5	67.8	8.6	30.85
18/2/93	3.2	6.9	2	58	142	38	4	5.2	1.5	0	30.32
15/3/93	2.8	14.5	1	32	217	56	10	23.2	1.2	0	30.53
5/4/93	3.1	11.3	15	32	192	375	31	60.3	8.0	0	29.40
26/4/93	3.0	6.5	13	34	242	337	36	73.4	7.0	0.6	30.22
17/5/93	3.5	6.0	15	30	321	146	21	9.9	3.0	0.3	31.08
7/6/93	5.1	5.7	11	44	308	85	14	4.9	4.3	0.6	30.80
27/6/93	4.3	6.3	7		308	98	0	38.9	2.3	0.7	30.96
17/7/93	4.9	11.0	4	75	325	111	38	37.8	1.5	0.4	31.31
9/8/93	3.9	9.0	5	18	408	160	17	173.6	1.9	0.5	31.49
30/8/93	2.8	4.6	11	42	300	522	57	113.3	17.7	2.4	30.60
13/9/93	3.0	17.5	13	17	375	316	41	60.9	6.9	1.1	31.46
26/9/93											
23/10/93	2.0	14.0	31	51	275	722	277	196.6	35.7	10.3	29.70
15/11/93	2.6	9.0	25	21	287	534	52	128.7	7.9	0.9	30.20
6/12/93	4.0	6.3	5	59	238	118	10	43.9	1.1	0	29.40
20/12/93	3.0	7.2	20	24		404	38	102.7	4.0	1.4	28.60

TABLE A2. *Continued*

Date	Seppak Cu (nM)	Dissolved Cu (nM)	Particulate Cu (nM)	Dissolved Zn (nM)	DOC (μM)	POC (μM)	PTN (μM)	Seston (mg l^{-1})	Chlorophyll <i>a</i> ($\mu\text{g l}^{-1}$)	Chlorophyll <i>b</i> ($\mu\text{g l}^{-1}$)	Salinity
Westerschelde											
6/1/93	8.6	14.0	81	108	475	479	74	135.7	4.6	0	12.67
18/1/93	8.9	31.0	80	170	421	279	41	73.9	2.8	0	12.26
1/2/93	6.9	81.8	47	343	464	404	33	79.6	1.7	0	9.49
18/2/93	9.1	23.0	28	140	342	138	14	41.9	2.4	0	15.70
15/3/93	6.1	5.0	36	178	375	175	21	61.7	2.3	0	15.50
5/4/93	8.7	9.4	65	21	383	408	48	152.1	8.0	0	15.90
26/4/93	7.2	19.8	40	153	333	351	41	104.2	7.3	0.7	18.30
17/5/93	9.1	40.9	22	116	350	313	39	54.9	20.0	0	18.11
7/6/93	12.9	17.3	41	68	333	458	56	70.5	29.4	1.3	20.27
27/6/93	9.6	20.5	28		317	263	4	90.0	13.1	0.8	19.61
17/7/93	12.8	8.2	21	130	350	249	49	81.8	5.5	0	19.08
9/8/93	11.2	17.8	36	115	475	451	44	119.0	7.2	0	19.08
30/8/93	8.8	28.8	39	100	450	367	44	136.8	7.4	0	20.17
13/9/93	8.6	6.8	61	132	400	749	79	156.4	6.2	0.6	19.74
26/9/93	9.9	27.1	59	153	812	1264	176	406.1	24.5	2.8	12.30
23/10/93	7.5	14.6	21	127	333	197	85	76.5	8.2	35.7	17.90
15/11/93	8.0	40.8	57	114	583	497	52	162.6	7.4	1.1	14.50
6/12/93	7.7	16.5	30	151	387	268	21	87.3	2.7	0	15.52
20/12/93	8.3	15.3	36	120		263	29	90.2	2.1	0.5	13.67

DOC, dissolved organic carbon; POC, particulate organic carbon; PTN, particulate total nitrogen.



Erratum

Comparison of Chemical Speciation of Copper in the Oosterschelde and Westerschelde Estuaries, The Netherlands

L. J. A. Gerringa, T. C. W. Poortvliet and H. Hummel

Estuarine, Coastal and Shelf Science (1996) 42, 629–643

It is regretted that two of the relations in Table 1 of the above article were printed incorrectly. The correct table is shown below, with the altered relations printed in bold.

TABLE 1. Relations found by the multiple regression with $R^2 > 0.5$. For equations (7 and 8), data for both estuaries were used. In equations (3, 5 and 6), the equations in parentheses exclude those parameters for which no straightforward chemical explanation for its contribution could be found

$[\text{Cu}_p] = -0.144 + 0.0456 \text{ POC}$	$R^2 = 0.947$	OS	(1)
$Q = 0.101 + 0.0067 \text{ POC} - 0.0101 \text{ PTN}$	$R^2 = 0.922$	OS	(2)
$L_{ta} = 583 - 29.2 \text{ sal} + 12 \text{ Chl}a_c + 0.95 [\text{Zn}_d]$	$R^2 = 0.722$	WS	(3)
($L_{ta} = 883 - 39.4 \text{ sal} + 10 \text{ Chl}a_c$)	$R^2 = 0.629$	WS)	
$L_{ta} = -52.4 + 1.0944 \text{ DOC}$	$R^2 = 0.522$	OS	(4)
$L_{tc} = 379 - 24.6 \text{ sal} + 1.512 \text{ PTN} + 14.3 \text{ CuS}$	$R^2 = 0.751$	WS	(5)
($L_{tc} = 434 - 20.7 \text{ sal} + 1.694 \text{ PTN}$)	$R^2 = 0.715$	WS)	
$L_{tc} = -96.2 + 0.4488 \text{ DOC} + 0.6 [\text{Zn}_d]$	$R^2 = 0.586$	OS	(6)
($L_{tc} = -33.4 + 0.3108 \text{ DOC}$)	$R^2 = 0.393$	OS)	
$L_{tc} = 117 + 0.4296 \text{ DOC} - 6.3 \text{ sal}$	$R^2 = 0.704$	WS+OS	(7)
$[\text{Cu}_p] = 58.2 + 0.0408 \text{ POC} - 1.9 \text{ sal}$	$R^2 = 0.784$	WS+OS	(8)

OS, Oosterschelde; WS, Westerschelde; L_{ta} , total concentration of relatively weak ligand; L_{tc} , total concentration of relatively strong ligand; PTN, particulate total nitrogen; DOC, dissolved organic carbon; POC, particulate organic carbon. Units as in Appendix A. Alpha to enter and alpha to remove were set on 0.1 (90% confidence interval).

The following P values (indicating the significance of the independent contribution of the explanatory variable) were given for the constants and parameters respectively: (1) 0.921 and 0.000; (2) 0.672, 0.000 and 0.015; (3) 0.003, 0.003, 0.005 and 0.034; (4) 0.489 and 0.001; (5) 0.001, 0.000, 0.003 and 0.165; (6) 0.019, 0.001 and 0.041; (7) 0.153, 0.001 and 0.003; and (8) 0.000, 0.000 and 0.000.