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The determination of free copper in freshwater using the MnO₂- adsorption method

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Abstract

The MnO₂-adsorption method was used to monitor the concentration of free copper in freshwater during one year. Two types of Langmuir linearisations as well as a linear model were applied to process the data. The concentration of free copper was in the order of 10⁻¹¹ M. No correlation was observed with the concentration of dissolved organic carbon or the optical density at 250 or 365 nm.

Keywords: Copper, speciation, freshwater

Introduction

In the nineteen sixties the Limnological Institute in the Netherlands started a long-term research project in Lake Tjeukemeer. Until now physical, chemical and biological parameters have been determined. In the nineteen eighties trace metals were included in the chemical monitoring program. Investigations were focused on a selected group of 'essential' metals. Some of these metals may be toxic, however, if present in too high concentrations. Copper is such a metal which may be limiting and toxic.

Total copper concentration in Lake Tjeukemeer was found to be high enough to be toxic for algae, according to the literature (Anderson and Morel, 1978; Morel *et al.*, 1978; Rueter *et al.*, 1978; Sunda and Guillard, 1976; Sunda and Gillespie, 1979; Petersen, 1982; Sunda *et al.*, 1982). On the other hand, literature reports point at the fact that organic material is able to reduce algal copper toxicity by forming organic copper complexes, involving both synthetic organic ligands (Morel *et al.*, 1978; Allen *et al.*, 1980) and natural organic ligands (Baccini and Suter, 1979; Toledo *et al.*, 1981). Lake Tjeukemeer contains high concentrations of organic material, and the possibility that it may complex copper reducing its availability to the extent of only limiting algal growth cannot be ruled out. This apparent contradiction between high copper concentrations and non algal toxicity was the reason that prompted the start of a research project focused on the bioavailability of copper for algae in Lake Tjeukemeer in relation to copper speciation, described by Verweij (1991). Since copper predominantly exists in the divalent form under

environmental conditions (Huntsman and Sunda, 1980), no attention was paid to monovalent copper. A literature review led to the conclusion that Cu²⁺_{aq} (so-called 'free' copper) controls copper availability (Anderson and Morel, 1978; Sunda and Guillard, 1976; Sunda and Gillespie, 1979; Petersen, 1982; Sunda *et al.*, 1982; Baccini and Suter, 1979; Sunda and Ferguson, 1983; Anderson *et al.*, 1984), although lipid-soluble copper complexes may also be available and toxic too (Florence *et al.*, 1983). It was therefore considered necessary to measure the free copper concentration.

Although no techniques are available that measure Cu²⁺_{aq} directly at concentration levels as low as in Lake Tjeukemeer, a group of techniques uses a combination of measurements and equilibrium calculations to assay Cu²⁺_{aq} indirectly, *i.e.* the ligand competition techniques. The MnO₂ method has been developed by Van den Berg and Kramer (1979a, 1979b, 1982a, 1982b, 1983). The competing ligand, MnO₂, is a solid onto which metals can adsorb. The MnO₂ is prepared synthetically by a redox reaction of Mn(II) and Mn(VII). Calibration is performed in standards resembling the sample as closely as possible, or in UV-radiated samples (to destroy organic matter). Using the Langmuir equation

$$\Gamma = \frac{\Gamma_{\max} * [Cu^{2+}] * K}{1 + [Cu^{2+}] * K} \quad (1)$$

(where Γ is the amount of copper adsorbed (mole copper/mole MnO₂), Γ_{\max} is the maximum value of Γ , $[Cu^{2+}]$ is the concentration of free copper in equilibrium with MnO₂ and K is the conditional stability constant for the adsorption equilibrium),

Γ_{\max} and K can be calculated. In the original version, a copper addition series of the sample is used to determine the conditional stability constant and concentration of the ligands. These data can be used to calculate free copper in the samples. Note that this is an indirect assessment of the free copper concentration, based on an extrapolation to a situation with no copper added. Here we describe a method to calculate the free copper concentration from the decrease in total copper concentration in an unspiked sample equilibrated with MnO_2 .

Methodology

MnO_2 was prepared as described by Van den Berg (1982b). Mn(VII) and Mn(II) were mixed in a ratio 1:1.5, Mn(IV)O_2 formed and subsequently purified. The MnO_2 -‘concentration’ in this stock was 0.05 M. Up to 0.01 M of NaCl was added. The same batch of MnO_2 was used for all experiments. For calibration a standard solution was used with concentrations of Na^+ , Mg^{2+} , K^+ , Ca^{2+} , CO_3^{2-} , SO_4^{2-} and Cl^- resembling lake water as closely as possible. A portion of 50 mL of it was buffered with HEPES (2-[4-(2-hydroxyethyl)-1-piperazinyl]-ethanesulfonic acid) (4 mM; $\text{pK}_a = 7.55$); seven copper additions were made up to 15.7 μM ; 50 μL of the MnO_2 stock was added, resulting in a MnO_2 -‘concentration’ of 50 μM . Samples were also buffered with HEPES, but no copper was added. Standards and samples were shaken for one hour on a shaking bath, set aside for a week and shaken again for half an hour. When shorter equilibration times were used, no useful calibration data could be obtained. Teflon bottles were used for these operations to prevent adsorption onto the wall of bottles. Suspensions were then transferred to centrifugation tubes and centrifugated for half an hour. The efficiency of the centrifugation turned out to be good; no increase in $[\text{Mn}]$ could be observed using graphite furnace AAS. The supernatant was decanted and acidified to a pH of about 2, as recommended by the manufacturer of the AAS. Dissolved copper was measured on an AAS, either by graphite furnace or by flame depending on the concentration. After acidification, we had to allow several hours equilibration, since measuring too soon caused inexplicable problems with the graphite furnace. We suspect that HEPES was responsible for some matrix effect. This possibility was not investigated further, as after a few hours no problems were observed any longer. To be on the safe side, after acidification samples were equilibrated at least overnight. Γ was calculated by subtraction. The equilibrium program GECHEQ (Verweij, 1990a and 1990b) was used to calculate free copper in equilibrium with MnO_2 in the standards (Table 1). The percentage of free copper was independent of the total copper, as the ligands were present in excess. Thus Γ and free copper were known for all standards.

Table 1 Speciation of copper in standards as calculated by the speciation program GECHEQ (Verweij, 1990a and 1990b).

Species	Percentage
[Free Cu(II)^{2+}]	4.62%
$[\text{Cu(II)(OH)}^+]$	4.11%
$[\text{Cu(II)(OH)}_2]$	0.27%
$[\text{Cu(II)(CO}_3)]$	78.96%
$[\text{Cu(II)H(CO}_3)^+]$	0.55%
$[\text{Cu(II)(CO}_3)_2^{2-}]$	1.17%
$[\text{Cu(II)(CO}_3)(\text{OH})^-]$	10.12%
$[\text{Cu(II)(SO}_4)]$	0.19%

It is not obvious that the Langmuir equation is the most appropriate mathematical description of the adsorption process, since it assumes that the adsorbent forms a monomolecular layer on the adsorption surface, and that the desorption rate is proportional to the extent of adsorption (Barrow, 1979). Changes in the surface charge often spoil this last assumption (Barrow, 1979) and may be the reason that this equation cannot always be used satisfactorily to describe the adsorption of metals onto solids (Verweij, 1986).

Van den Berg (1982a) argued that the Langmuir equation could be applied to his results, since only a small amount of MnO_2 was used; he explicitly did not state that adsorption actually occurs in a monomolecular layer. Stroes-Gascoyne *et al.* (1986) concluded that a normal Langmuir equation cannot be used to describe adsorption of copper onto MnO_2 , and proposed an ‘implicit Langmuir model’. Their derivation of that model however contains a few disputable assumptions.

In this paper, data were processed in three ways. The first and second use the Langmuir equation, but differ in its linearisation. The first linearisation, which can be derived easily from equation (1), is recommended by Van den Berg (1982a):

$$\frac{[\text{Cu}^{2+}]}{\Gamma} = \frac{[\text{Cu}^{2+}]}{\Gamma_{\max}} + \frac{1}{K * \Gamma_{\max}} \quad (2)$$

This equation should be used with care however, since at low metal concentrations Γ is proportional to $[\text{Cu}^{2+}]$ (which can easily be seen from equation (1)) resulting in a constant term for the left part of equation (2), making it unsuitable as a dependent variable for linear regression. A second linearisation, which can also be derived easily from equation (1), is suggested here:

$$\frac{1}{\Gamma} = \frac{1}{K * \Gamma_{\max} * [\text{Cu}^{2+}]} + \frac{1}{\Gamma_{\max}} \quad (3)$$

This linearisation can be used at low metal concentrations, but not at high: in that case Γ is

Table 2 Calibration results for the Langmuir linearisations.

parameter	Type of linearisation					
	Verweij			Van den Berg		
	Γ_{\max}	$\log(K)$	r	Γ_{\max}	$\log(K)$	r
average	0.131	7.923	0.9312	1.41	6.781	0.4650
standard deviation	0.187	0.425	0.1471	1.38	0.561	0.2466

nearly constant (Γ_{\max}) because of saturation and is therefore no longer suitable for regression calculations.

It is not clear in advance which linearisation should be used, since the combination of metal concentration and adsorption maximum determines if a concentration must be considered 'low' or 'high'.

If $[Cu^{2+}]$ is relatively low, Γ will be proportional to $[Cu^{2+}]$. So adsorption data are processed in a third way, by supposing adsorption is linearly dependent on free metal concentration:

$$\Gamma = \text{constant} * [Cu^{2+}] \quad (4)$$

It is obvious that Γ is zero when the [free metal] is zero, so regression lines were forced to have a zero intercept.

The Langmuir linearisation methods yield values for Γ_{\max} and K , which can be used to calculate free copper in the samples. The linear model gives a value for free copper by simply dividing Γ by the constant mentioned in equation 4.

The thus obtained values for free copper are in fact not representative for lake water samples, because all calculations refer to suspensions containing MnO_2 . By adding MnO_2 an extra ligand is introduced in the samples, so the free copper concentration is artificially lowered, and

Γ as a function of [free copper]

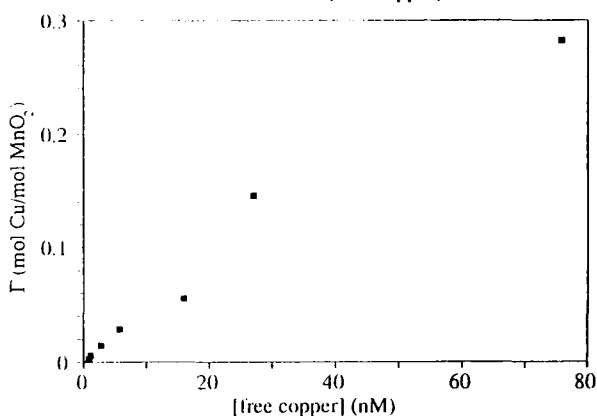


Figure 1 Typical example of a calibration curve, showing Γ as a function of [free copper].

consequently the calculated values are lower than natural values. It is possible, however, to convert [free copper] in the *presence* of MnO_2 to [free copper] in the *absence* of MnO_2 , as shown by Verweij (1991). However, it was calculated that such a conversion increased the free copper concentration by only a few tens of percents, so not the order of magnitude. For this reason and to avoid the simplifications made in the derivation of the conversion, the uncorrected data are displayed in Figure 5.

A complication of the MnO_2 method is the possible competition of organics in natural water samples with copper for the same adsorption sites, because this competition does not occur in the standards. If this phenomenon occurs, Γ will be lowered, resulting in a too low value for free copper. Although Van den Berg stated that neither organic ligands nor copper complexes adsorb onto MnO_2 (1982b), Dempsey and O'Melia (1983) showed that fulvic acids may interact with MnO_x . Van den Berg (1984) later demonstrated that organic copper complexes are not kinetically inert. The implications of this finding for the MnO_2 method are not clear. Weber (1988) stated that both humic acids and their complexes may adsorb onto MnO_2 , but unfortunately he did not give any evidence for this statement.

Total carbonate was determined by titrating 0.05 M HCl and turned out to be constant for both the calibration standards and lake water samples.

Dissolved Organic Carbon (DOC) was analysed with a Phase SEP TOCsinII carbon analyser. Optical density (OD) at 250 and 365 nm was measured on a Zeiss PMQII spectrophotometer.

Results and Discussion

Calibration

A typical example of a calibration curve is shown in Figure 1. Its good linearity already suggests that equation (2) is not a suitable description for our data. Figure 2A confirms that by using the Langmuir linearisation as recommended by Van den Berg (1982a) an average correlation coefficient of only 0.1484 (standard deviation = 0.3903) is achieved. For the other type of linearisation the average is much higher (0.9401; standard deviation = 0.1265),

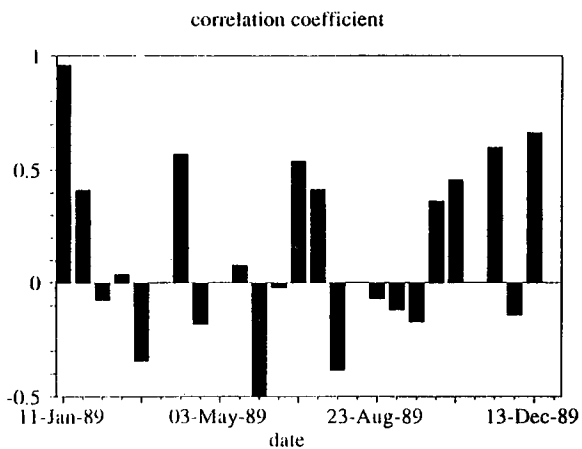


Figure 2A Correlation coefficients Langmuir linearisation of Van den Berg (1982a).

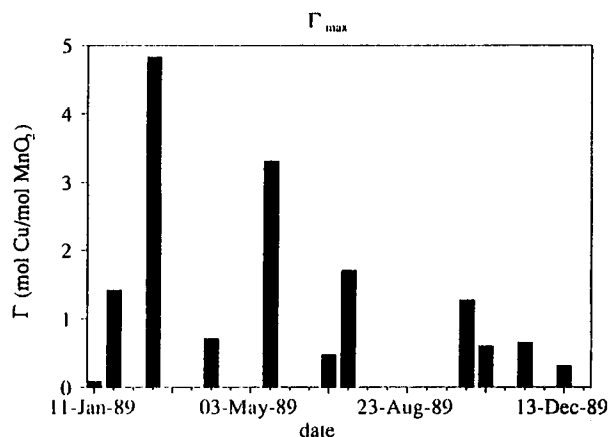


Figure 3A Γ_{\max} Langmuir linearisation of Van den Berg (1982a).

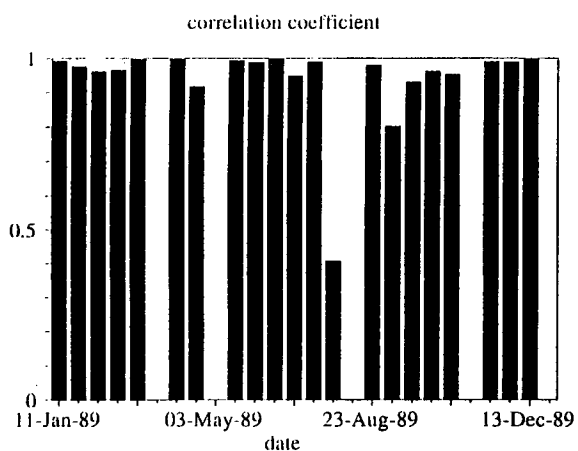


Figure 2B Correlation coefficients Langmuir linearisation suggested in this paper.

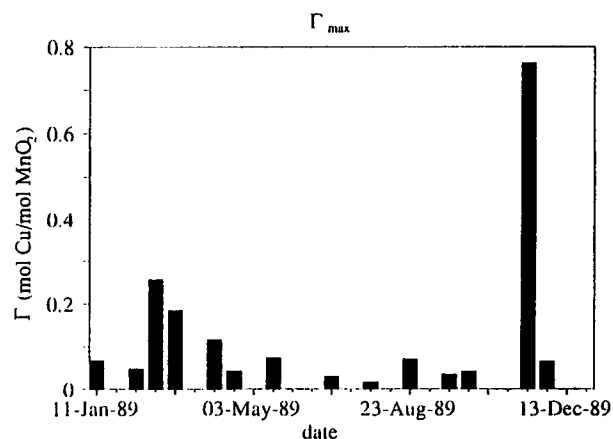


Figure 3B Γ_{\max} Langmuir linearisation suggested in this paper.

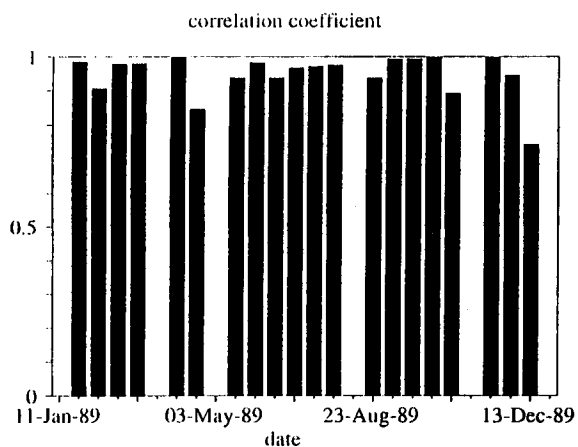


Figure 2C Correlation coefficients linear model.

as can be seen in Figure 2B, and even increases, if calibration obtained on 26th of July ($r = 0.4080$) is omitted, to 0.9667 (standard deviation = 0.0441). Results of the linear model are similar (Figure 2C):

0.9487 (standard deviation = 0.0608). One calibration line is not included in this average because the square of the correlation coefficient was smaller than zero, making it impossible to calculate the square root.

Both equation (2) and (3) (the Langmuir linearisations) sometimes give negative intercepts (equation (2) – ten cases, equation (3) – seven), resulting in (negative) values for Γ_{\max} and K without physical meaning. Results for good calibration lines are shown in Figures 3 (Γ_{\max}) and 4 ($\log(K)$), and Table 2. Remarkable are the values for Γ_{\max} in Figure 3A (linearisation Van den Berg), *i.e.* sometimes they are higher than 1 mole Cu/mole MnO_2 ! For the other linearisation no values higher than one were obtained. $\log(K)$ values were much lower than those reported by Van den Berg (1982b) ($\log(K) = 9$ to 9.5) and Gerringa (1990) ($\log(K) = 9.1$), while their Γ_{\max} values were much lower (0.08 and 0.07, respectively). The reason for this is not clear, but the range of copper concentrations used here was different from the range the cited authors used. Besides, the high standard deviations may

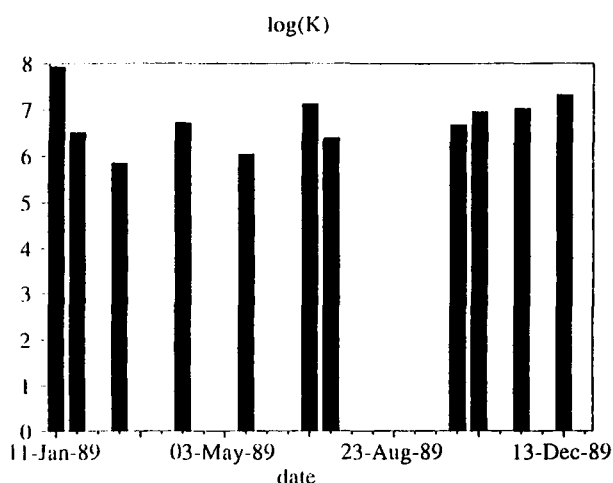


Figure 4A *Log(K) Langmuir linearisation of Van den Berg (1982a).*

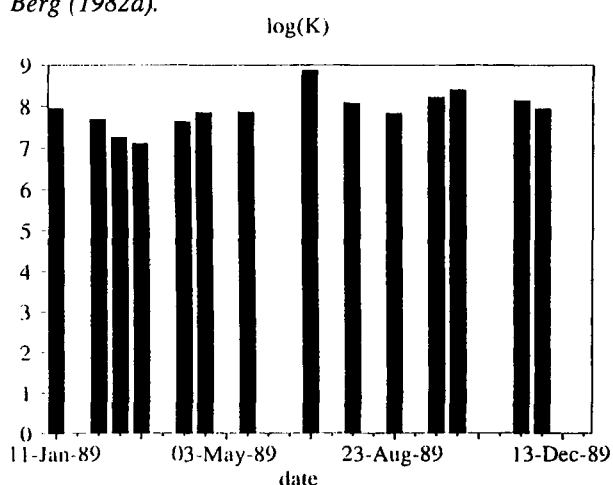


Figure 4B *Log(K) Langmuir linearisation suggested in this paper.*

indicate that the reproducibility of copper adsorption onto MnO_2 was not too good. Another explanation could be the variation of adsorption characteristics of different batches of MnO_2 .

Samples

In several cases, copper was not measurably adsorbed or even had increased in concentration during equilibration due to contamination. This is definitely a disadvantage of our approach to calculate the free copper concentration without adding copper to samples. The other cases are shown in Figure 5. The correction as referred to in the experimental section (to convert values in the presence of MnO_2 to values in the absence of it) has not been applied to these data.

Calculated free copper is around 10^{-11} M. This order of magnitude was fairly insensitive for changes in the amount of copper adsorbed in the samples, as long as a detectable amount adsorbed. It is interesting to compare these results with electrochemical measurements using DPASV (Verweij, 1991). Since ASV covers more than only free copper, MnO_2 -results for free copper concentrations therefore must be lower than the concentration of ASV-labile copper. This is indeed

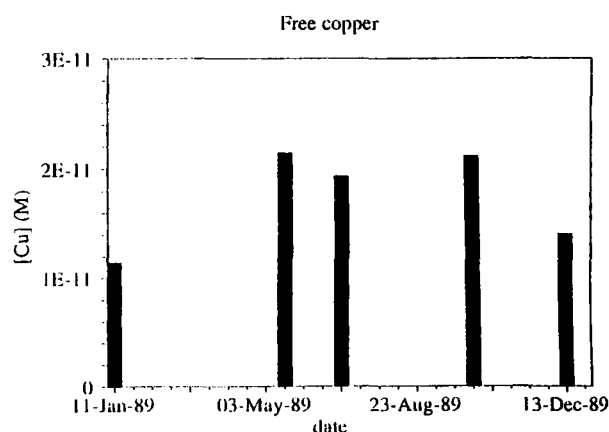


Figure 5A *Free copper Langmuir linearisation of Van den Berg (1982a). Average is 1.75×10^{-11} M; standard deviation 0.40×10^{-11} M.*

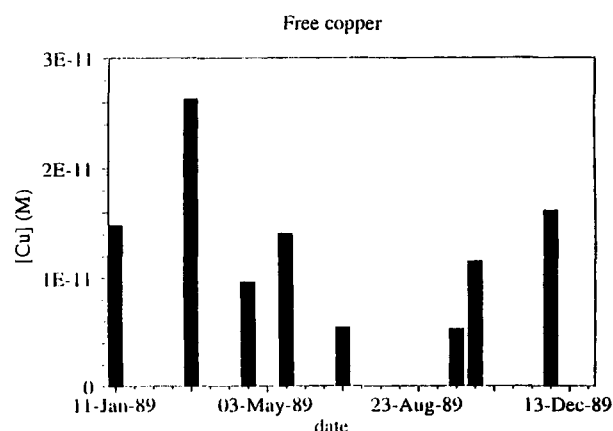


Figure 5B *Free copper Langmuir linearisation suggested in this paper. Average is 1.29×10^{-11} M; standard deviation 0.64×10^{-11} M.*

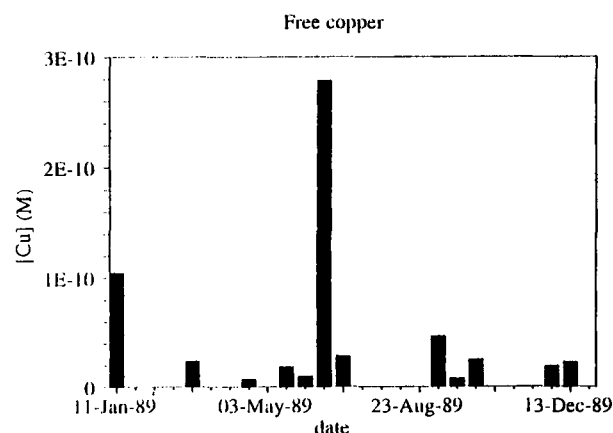


Figure 5C *Free copper linear model. Average is 4.98×10^{-11} M; standard deviation 7.35×10^{-11} M. Note the different scale compared to Figures 5A and 5B.*

Table 3 Correlations of free copper with [Cu]/OD 250, [Cu]/OD 365 and [Cu]/DOC (between brackets: n); * denotes $p < 0.1$.

	Langmuir linearisation		Linear model
	Verweij	Van den Berg	
[Cu]/OD 250	-0.2916 (8)	0.8172* (5)	-0.1414 (12)
[Cu]/OD 365	-0.3042 (8)	0.7102 (5)	-0.1831 (12)
[Cu]/DOC	0.6753* (8)	-0.1579 (5)	0.0964 (12)

the case. MnO_2 -results for free copper concentration are two orders of magnitude lower than ASV- labile copper.

For seawater, Van den Berg also found values of around 10^{-11} M (1982b). From the data of Gerringa (1990) values ranging from 9×10^{-13} to 2×10^{-11} M may be calculated for marine sediment slurries.

Taking into account the results of voltammetric measurements, which point to a high degree of organic copper complexation (Verweij, 1991), it is interesting to investigate possible correlations of organics with free copper as determined using the MnO_2 -method. If free copper concentration is primarily controlled by organic ligands, as from the equilibrium reaction



(where L represents organic ligands) the following relationships can be obtained:

$$a) \quad [CuL] = K * [Cu] * [L] \quad (6)$$

or:

$$b) \quad \frac{[CuL]}{[L]} = K * [Cu] \quad (7)$$

These imply that the concentration of free copper is proportional to $[CuL]/[L]$. However, neither $[CuL]$ nor $[L]$ is known, but since there are high concentrations of dissolved organic material in the lake, it can be assumed that virtually all copper is present as $[CuL]$, while organics are hardly present as copper complexes. So the term $[CuL]/[L]$ simplifies to $[\text{total copper}]/[\text{total organics}]$. Correlations of [free copper] with $[\text{total copper}]/[\text{total organics}]$ are shown in Table 3, where 'organics' are represented by dissolved organic carbon and optical density at 250 and 365 nm. Two correlations are significant at a $p < 0.1$ level, indeed indicating copper complexation is controlled by organics. However, seven of the correlations are not significant (five are even negative), suggesting that

measuring dissolved organic carbon or the optical density at 250 or 365 nm is not specific enough to investigate organic copper complexation. It indicates that at these extremely low copper concentrations only a few functional groups whose concentrations are not proportional to DOC, OD 250 or 365 are responsible for copper complexation. The two significant correlations are therefore probably coincidence.

The average concentrations as obtained by the three calculation methods, were used to calculate inorganic copper in the samples under laboratory conditions and to compare those values with dissolved ($< 0.2 \mu\text{m}$) copper. It appeared that for the Langmuir calculations inorganic copper was slightly more than 1%, while for the linear model a percentage of nearly 5 was found. A large percentage of copper (95 to 99) was therefore organically complexed. Using the data of Van den Berg (1982b) a percentage of 97 organically complexed copper can be calculated for his Irish Sea sample. If the values for $\log(K)$ and Γ_{max} of Van den Berg (1982b) and Gerringa (1990) are used, comparable values for free copper are found.

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