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Trace metal speciation measurements in waters by the liquid binding phase DGT device

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Abstract

The speciation measurements of trace metals by the diffusive gradients in thin-films technique (DGT) using a poly(4-styrenesulfonate) (PSS) aqueous solution as a binding phase and a cellulose dialysis membrane (CDM) as a diffusive layer, CDM-PSS DGT, were investigated and showed good agreement with computer modelling calculations. The diffusion coefficients of ethylenediaminetetraacetic acid (EDTA) complexes with Cd^{2+} and Cu^{2+} were measured and compared with those of the inorganic metal ions. CDM-PSS DGT device was tested for speciation measurement in sample solutions containing EDTA, tannic acid (TA), glucose (GL), dodecylbenzenesulfonic acid (DBS) and humic acid (HA) as complexing ligands forming organic complexes with varying stability constants. Lower percentages of DGT labile copper concentrations over total filterable copper concentrations obtained from the deployments in freshwater sites indicated that copper complexes with organic matter were basically not measured by the devices.

Keywords: CDM-PSS DGT; Speciation; Trace metals; Waters

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1. Introduction

Natural waters contain various ligands that can form complexes with trace metal ions [1,2]. Consequently, free metal ions (or more strictly, the aquo-complexes) are usually a minor component of the total metal species present. Inorganic and organic metal complexes have very different physical properties from each other, such as charge, size, diffusion coefficient and bioavailability. In situ speciation measurements of metal ions are necessary to provide valuable environmental information. The newly developed diffusive gradients in thin films technique (DGT) has been applied for this purpose over the past decade [3]. Conventionally, it employed a polyacrylamide hydrogel diffusion layer with known exposure area (A) and thickness (Δg), to allow analyte to diffuse through it with diffusion coefficient (D), and a binding phase, Chelex 100 resin impregnated polyacrylamide hydrogel, to accumulate the species diffused. The concentration (C) of labile metals in waters, i.e., species that are diffusible through the diffusion layer and reactive to the binding phase, can be calculated using the DGT equation [3,4] by measuring the mass of a metal (M) in the binding phase accumulated for certain deployment time (t):

$$C = \frac{M\Delta g}{DAt} \qquad (1)$$

A new DGT device employing poly(4-styrenesulfonate) (PSS) aqueous solution as a binding phase and a cellulose dialysis membrane (CDM) as a diffusive layer for DGT analysis was reported recently [5]. The homogeneous mobile liquid binding phase provided the excellent contact between the binding phase and the diffusive layer to increase reproducibility [5]. Performance of the device was compared with other DGT devices in our previous publication [6]. This

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paper describes in details the speciation measurements of the CDM-PSS DGT under laboratory conditions and in natural waters. The CDM-PSS DGT measures species whose sizes are small enough (not excluded by the diffusive membrane), and which are selectively bound in PSS solution [5]. Species can also be distinguished on the basis of their diffusion coefficients, which influence the fluxes through the diffusion layer.

The fraction of metal species measured by this DGT device was compared with theoretical calculation of inorganic metal ion fraction using appropriate models, where applicable, for various ligands commonly found in natural waters, including ethylenediaminetetraacetic acid (EDTA), humic acid (HA), tannic acid (TA), glucose (GL) and dodecylbenzenesulfonic acid (DBS). The DGT devices were also deployed in various natural water sites with varying levels of organic contents.

2. Experimental

2.1. Measurement of EDTA-metal complex diffusion coefficients

Diffusion coefficients of metal-EDTA complexes through the CDM membrane (12,000 MWCO, <5 nm pore size [7], Sigma) were measured using the diffusion cell of the same design as described by Zhang and Davison [8]. The membrane was pretreated following the procedures recommended by Sigma [5]. The membrane disc was sealed in between the two compartments to ensure the membrane was the only path for mass transport. One compartment (source) contained 0.40 mM EDTA (Aldrich) and 0.090 mM Cd(II) or 0.16 mM Cu(II) in a 50 ml synthetic lake water matrix (Windermere, UK) [5,9]. The other compartment (receiving) was filled with purified 0.020 M poly(4-styrenesulfonate) (PSS) (Aldrich) [5] in a 50 mL solution of the same matrix. Samples were taken from both compartments and measured by flame atomic absorption spectroscopy (FAAS, SpectrAA-200, Varian) at an hour intervals up to 16 h. The diffusion coefficients were calculated using equation:

$$D = \frac{M\Delta g}{C'At} \tag{2}$$

Average concentration at the sampling intervals (C') was used to correct concentration changes in the source compartment.

2.2. Measurement of DGT-labile fractions

DGT devices were assembled as previously reported [5]. The opening of the polyethylene tube containing purified 0.020 M PSS solution was covered smoothly and sealed tightly with a pretreated CDM membrane of 50 μm thickness. The devices were deployed with membrane side facing down to ensure the contact of membrane and PSS solution. Two solutions of synthetic Windermere Lake water [9] (pH 6.8) containing: (i) 0.70 μM Cu(II) and (ii) 0.40 μM Cd(II) were spiked with ligands of EDTA (Aldrich), tannic acid (TA Aldrich) and dodecylbenzenesulfonic acid (DBS, Sigma) at molar ratios of 1.8:1.0, 1.0:1.0 and 1.0:1.8 with the metal ions, and humic acid (HA, molecular weight 13,000 [10], Aldrich) concentrations of 9.36, 5.2 and 2.9 mg L^{-1} for Cd and 16.4, 9.1 and 5.1 mg L^{-1} for Cu. These solutions were stirred over night at 23 °C room temperature before nine DGT devices were deployed, to allow equilibration of the complexation reactions. Three devices were taken and dismounted for FAAS measurement every 12 h, while the total metal concentrations in the solution were measured at the same time by ICP–MS. The DGT-labile concentrations were calculated according to the DGT equation. The DGT-labile fraction of metal ions (Ψ) was defined as

$$\Psi = \frac{\text{DGT labile metal ion concentration}}{\text{total metal ion concentration}} \tag{3}$$

2.3. Theoretical calculation of inorganic Cu and Cd fractions

The theoretic inorganic metal ion fraction ($\Psi_{\text{theoretical}}$), the fraction not bound by the spiked ligands, was calculated using the speciation function of the IUPAC Stability Constants Database (SC-database model, Academic Software) [11] for ligands of TA, GL and EDTA and using the WHAM (V6) speciation code for HA [12]. These calculations require inputs of known parameters, e.g. stability constants of the metal-ligand complexes, dissociation constants of the ligands, concentrations of the ligands and metal ion, pH of the solution, as shown in Table 1.

2.4. Field deployments of the DGT devices

Each deployment consisted of nine CDM-PSS DGT devices mounted on a foam buoy. The devices were deployed in various natural water sites on the Gold Coast, Australia, by being anchored to a jetty for 48 h. Two seawater sites were chosen: the first was a jetty within Runaway Bay Marina (which had previously been shown to have high trace metal concentrations, particularly Cu [13]); the second was on a canal site in Biggera Waters (with relatively lower boat traffic). Two freshwater sites were also chosen: one with relatively high concentrations of natural organic matter (NOM), Parkwood Pond; and the other with less NOM, Loders Creek. All the DGT devices were rinsed thoroughly with deionised water (Milli-Q) after collection, to minimise contamination.

Grab water samples were also collected at each site, at the beginning, middle and end of the DGT deployment period, in polyethylene sample containers (Nalgene), pre-cleaned with 10% nitric acid solution. The samples were filtered immediately on site through 0.45 μm pore size cellulose nitrate membranes (Whatman) and acidified with 65% suprapur nitric acid (Merck) (2 ml acid per litre of sample) to $pH < 2$.

Temperature, pH and salinity were also measured on site and average values were used for the purpose of estimating diffusion coefficients. The dissolved organic carbon

Table 1
Thermodynamic constants used for theoretical speciation calculation

	$\log \beta_{Cu1}$	$\log \beta_{Cu2}$	$\log \beta_{Cd1}$	pK_{a1}	pK_{a2}	pK_{a3}	pK_{a4}	Molar mass
EDTA [34]	18.9		16.5	1.99	2.67	6.16	10.26	336.2
TA [27]	5.4	9.1		8.68				1701

Note: All constants are for 25 °C and I = 0 M; the solution pH was 6.8; the total concentrations of Cd(II) and Cu(II) were 0.40 and 0.70 μM, respectively. log β: logarithm cumulative stability constant; pK_a: negative logarithm acid dissociation constant. EDTA: ethylenediaminetetraacetic acid; HA: humic acid; TA: tannic acid.

concentrations (DOC) were measured using a Dohrmann DC-190 TOC analyser.

2.5. Measurement of Cu and Cd concentrations

Concentrations of Cu and Cd transported from the source compartment to the receiving compartment in the diffusion cell were measured by FAAS. Standards were matrix-matched with PSS. The detection limits (3σ) of this method were 8.3×10^{-3} μg L^{-1} for Cu and 7.2×10^{-4} μg L^{-1} for Cd.

The concentrations of Cu and Cd accumulated by the PSS in the DGT devices were measured by ICP–MS (Agilent Technologies, 7500 Series, Germany) after a five-fold dilution. Standards were matrix-matched with PSS diluted accordingly. The detection limits of this method were 8.7×10^{-5} μg L^{-1} for Cu and 1.5×10^{-5} μg L^{-1} for Cd.

The 0.45 μm filtered Cu and Cd concentrations of the grab water samples were also analysed by ICP–MS. Standard solutions were matrix-matched with NaCl and $MgCl_2$ diluted accordingly. The detection limits of this method were 6.0×10^{-4} μg L^{-1} for Cu and 6.0×10^{-4} μg L^{-1} for Cd in saline waters; 3.9×10^{-4} μg L^{-1} for Cu and 4.0×10^{-4} μg L^{-1} for Cd in fresh waters.

3. Results and discussion

3.1. Diffusion coefficients of EDTA-Cu and EDTA-Cd complexes

The calculation of DGT labile concentration is dependent on the diffusion coefficients of trace metal species in the diffusive layer (see Eq. (1)). The accumulation of metal ions in the binding phase arises from all labile metal species, including free metal ions, inorganic and organic complexes, which possess different diffusion coefficients. In order to correctly interpret the DGT speciation measurement it is vital to characterize the different diffusion coefficients of the different metal species. One ligand for which the complexing properties have been well established is EDTA. EDTA forms strong complexes with Cu^{2+} and Cd^{2+} primarily in a 1:1 ratio, so will be an ideal surrogate to measure the diffusion coefficient of a metal complex. The experiment can be set up so that there is effectively no free or inorganic metal species present in solution; in other words, the diffusion coefficient of the complex can be measured without interference from other metal species. Being able to measure the diffusion coefficient of this complex will allow a full characterization of the DGT speciation measurement of a known solution containing that complex. General trends may then be made concerning the prediction of other metal complexes, for which diffusion coefficients are less readily characterised.

An excess amount of EDTA was used in the source solution to ensure virtually all metal ions were complexed. The diffusion coefficient of the metal complex can therefore be measured in isolation from free and inorganic metal ion diffusion. The Cd and Cu concentrations measured in the receiving solution were all below the detection limits of this FAAS method (5.3×10^{-7} mol L^{-1} for Cu and 8.1×10^{-8} mol L^{-1} for Cd) within 16 h. The diffusion coefficients of EDTA-metal complexes can thus be estimated to be less than 2.2×10^{-9} cm^2 s^{-1} for Cd and 8.1×10^{-9} cm^2 s^{-1} for Cu, respectively. These diffusion coefficients were over two orders of magnitude lower compared with the free metal ion diffusion coefficients in the membrane under the same conditions (2.5×10^{-6} cm^2 s^{-1} for Cd^{2+} and 1.9×10^{-6} cm^2 s^{-1} for Cu^{2+}) [5], while the diffusion coefficient of Cu–HA complex with more complicated structures was only one order of magnitude lower than that of Cu^{2+} in the polyacrylamide gel (6.18×10^{-6} cm^2 s^{-1} for Cd^{2+} and 6.28×10^{-6} cm^2 s^{-1} for Cu^{2+} [8]), used in traditional DGT device as a diffusive layer. Dramatic decrease of the diffusion coefficient of metal EDTA complexes in the membrane was due to the smaller pore size (<5 nm) [8] and tortuous structure of the membrane [14] and stereochemistry of the complexes. The open pore structure of the gel may be responsible for the relatively free diffusion of the ions in it, as explained by Zhang and Davison [8]. This indicates that, with this CDM-PSS DGT device, the accumulation of free metal ions could be more than 200 times faster than the accumulation of their complexes with organic ligands, assuming that they were present at similar concentrations. Even if the metal-EDTA complex was present at concentrations 10 times higher than the free metal ions, it would be underestimated considerably. However, in natural waters, fractions of metals bound to organic ligands may vary from metal to metal. In seawaters, for example, about 50% of dissolved lead [15,16], 15–35% of dissolved cadmium [17] and >90% of dissolved copper [18,19] and zinc [20,21] are usually found to be complexed to natural organic ligands. According to the equation deducted by Zhang [22], $M = (C_{in}D_{in} + C_{or}D_{or}/\Delta g)At$, mass of a metal measured by DGT (M) was contributed both from inorganic species ($C_{in}D_{in}$) and organic species ($C_{or}D_{or}$). In the case of lower percentage complexation of a metal, or lower concentrations of complexed metal, the complexed metal measured by this CDM-PSS DGT is insignificant.

Diffusion coefficients of metal ions in water are inversely proportional to the cubic root of their molecule weight [23], although other factors such as shape and charge are also important:

$$D = \frac{3.3 \times 10^{-5}}{Mw^{1/3}} \tag{4}$$

A similar relation might be expected for ions in the membrane, although the structure of membrane is more complicated. As EDTA has either a comparable or a smaller molecular mass compared with other likely organic ligands, such as HA, TA, GL, and DBS, the diffusion coefficients of the metal complexes, which will be discussed in detail in a following paper, are likely to be similar to or lower than those of the metal–EDTA complexes. Therefore, it is likely that this CDM-PSS DGT will measure largely inorganic and free metal ions, in preference to even small complexes with organic ligands.

However, in natural waters the speciation of trace metals is very complex, with a great range of inorganic and organic ligands present. The complexes that form from each of these ligands will have their own concentrations and diffusion coefficients, and therefore their own fluxes. The next section discusses experiments that investigated the measurements of metals by this CDM-PSS DGT device in the presence of different complexing reagents at various proportions.

3.2. Measurement of labile metal ions in the presence of ligands

As discussed in our previous publication [6], the mass of a particular metal, measured in the PSS solution of a DGT device, is the sum of all forms of the metal that are able to diffuse through the CDM membrane and are retained by the PSS solution. In other words, the measurable metal species are those with sizes small enough to diffuse through and with reactivity to PSS. This measurement process by the DGT devices can occur via several mechanisms:

(1) Exclusion of species larger than the pore size or molecular weight cut-off (MWCO) of the diffusive medium.

(2) Differentiation of metal species upon diffusion coefficient differences, i.e. collection of low diffusion coefficient species in PSS solution can be insignificant.

(3) Differentiation of metal species upon different interactions of the binding phase functional groups with the diffused metal species. Free metal ions, Cu^{2+}, Cd^{2+}, are efficiently bound to the PSS solution [5]. Metal complexes can react with PSS binding phase through two possible reaction routes [24]:

  (3a) Formation of intermediate ternary metal complexes, L–M–L′ followed by leaving of the original ligand [24], where L is a inorganic or organic ligands in sample water solution, L′ is binding functional group of PSS phase and M the metal ion, Cu^{2+} or Cd^{2+}.

  (3b) Dissociation of the complexes within the time frame required for the species to diffuse across the diffusive layer before they are bound by PSS solution [25].

The effect of various ligands, present at differing ratios with the metal ions, on the DGT-labile measurement was studied. The DGT-labile concentration was compared with a theoretical calculation of inorganic metal species concentration (where possible), as a fraction of the total metal concentration. This comparison was used to indicate which speciation mechanism was dominant. Mechanism (1) was not relevant in these laboratory solutions except for the HA solutions, since the molecular weights of TA, GL, and DBS were far lower than the MWCO of the membrane used. Mechanism (2) was likely to always be occurring to some extent. If the DGT-labile fraction was found to be the same as the theoretical estimation then it was likely that diffusional selectivity was the dominant mechanism. This is because the complexed species would have diffused through the dialysis membrane much slowly and effectively be insignificant to the DGT measurement compared with the inorganic metal species which diffuse through much quickly. In other words only the inorganic fraction is DGT-labile.

Mechanism (3a) will only become important for species which are not selected against significantly by mechanism (2) (i.e. having fluxes greater than 1% of the fluxes of the inorganic metal species) and for which the ligand binds the metal ions more strongly than the PSS solution. The laboratory experiment would not be able to examine this mechanism. It is possible that no such species exist when using the dialysis membrane diffusive layer, for which mechanism (2) becomes more important than for the polyacrylamide diffusive gels. Zhang and Davison [8] have measured the diffusion coefficients of fulvic and humic acids in water and in several types of diffusive gels. In their work the diffusion coefficient was retarded by one order of magnitude at most, whereas the diffusion coefficients of large molecules/complexes through the dialysis membrane are likely to be retarded to a much greater extent, as described earlier.

The final potential mechanism (3b), based on dissociation of complexes at the time scale of diffusion through the dialysis membrane, can be considered to be a modifier to both mechanisms (2) and (3a), with the former being more important. If a significant fraction of metal ions dissociates, this would have the effect of increasing the DGT-labile fraction when compared with the theoretical estimation of the inorganic metal fraction.

Before these predictions are discussed with respect to the experimental results obtained, it is however important to note that other factors could also be responsible for a difference in the DGT-labile fraction and the theoretically estimated inorganic fraction. One major factor is the uncertainty in the stability constant and stoichiometry of the complexes used in the speciation software. The humic substance ligands have a great variety of forms that occur in nature and any particular sample will have binding sites with a range of stability constants present [23,26]. For some ligands stability constants may not have been known while for others such as EDTA there is a high degree of certainty. The precision of the DGT technique will also be a factor in establishing which mechanism is predominant. If the DGT-measured fraction is statistically equivalent to the theoretical inorganic fraction ($\alpha = 0.05$) then mechanism (2) can be considered to dominate.

3.2.1. Labile metals in the presence of EDTA

EDTA was the first ligand investigated. It was found that, as the molar ratio of metal ion/EDTA decreased, the DGT-labile metal fractions dramatically decreased (Table 2). Both Ψ_{Cd} and Ψ_{Cu} became virtually 0 at 1:1 molar ratio and lower. Therefore, as expected, with EDTA as the complexing ligand, the free and inorganic metal ion concentration is effectively equal to the metal ion concentration minus the EDTA concentration. The fact that no Cu and Cd were measured in solutions with metal/EDTA ratios ≤ 1 indicates that the complexes are being selected against due to mechanism (2); i.e. slow diffusion through the dialysis membrane.

The theoretical free and inorganic metal ion fractions at a different molar ratio of metal ions/EDTA were calculated (Table 2). The results revealed that both the DGT labile metal fractions and the theoretical free and inorganic metal ion fractions were very similar and followed the same trend when the molar ratio of metal ion/EDTA varied. The Ψ_{Cd} values of 65.0% and 44.3% and Ψ_{Cu} values of 65.3% and 43.5% were very close to the theoretical values for 3:1 and 1.8:1 molar ratios of Cd/EDTA and Cu/EDTA, respectively (Table 2). The agreements between DGT measurements and theoretical calculations indicate that DGT measured inorganic metal ion concentrations in the EDTA solutions.

3.2.2. Labile metals in the presence of humic acid

The effect of HA concentrations in the sample solution on the DGT-labile fraction for Cd and Cu (Ψ_{Cd} and Ψ_{Cu}) is also shown in Table 2. When the HA concentration in 0.4 μM Cd solution increased from 2.9 to 5.2, to 9.4 mg L^{-1}, the percentages of the DGT labile metal ion measured decreased from 51.0% to 32.8% to 18.7% (Table 2), which were close to the theoretical calculations, indicating that, as the concentration of HA increased, more metal was bound. It was also shown that, in 0.7 μM Cu solution, as HA concentrations increased from 5.1 to 9.1 to 16.4 mg L^{-1}, the percentages of metals measured by this DGT device over the total filterable metal

Table 2
Effect of ligands to metal ion molar ratio on the DGT labile metal ion fraction and fraction unbound by ligand calculated by speciation models

Molar ratio of metal ion/ligand	Ψ_{Cd} (%)[a]	$\Psi_{Cd,theoretical}$ (%)[b]	Ψ_{Cu} (%)[a]	$\Psi_{Cu,theoretical}$ (%)[b]
EDTA				
3.0:1.0	65.0 ± 3	66.8	65.3 ± 2	66.7
1.8:1.0	44.3 ± 2	44.5	43.5 ± 1[c]	44.4
1.0:1.0	0	0	0	0
1.0:1.8	0	0	0	0
TA				
1.8:1.0	64.3 ± 2	–	70.1 ± 1	92.3
1.0:1.0	47.5 ± 3	–	66.7 ± 3	86.7
1.0:1.8	38.8 ± 2	–	58.4 ± 4	78.2
GL				
1.8:1.0	96.3	–	101	–
1.0:1.0	88.3	–	97.9	–
1.0:1.8	80.3	–	90.9	–
DBS				
1.8:1.0	81.5	–	96.0	–
1.0:1.0	64.8	–	84.3	–
1.0:1.8	52.8	–	75.7	–

Molar ratio of metal ion/ligand		Ψ_{Cd} (%)[a]	$\Psi_{Cd,theoretical}$ (%)[b]	Ψ_{Cu} (%)[a]	$\Psi_{Cu,theoretical}$ (%)[b]
$C_{HA/Cd}$ (mg L^{-1})[d]	$C_{HA/Cu}$ (mg L^{-1})[d]				
HA					
2.9	5.1	51.0 ± 2[c]	56.8	15.7 ± 0.2	0.14
5.2	9.1	32.8 ± 4[c]	38.2	12.3 ± 0.4	0.03
9.4	16.4	18.7 ± 3[c]	21.2	0.2 ± 0.2	0

[a] Ψ_{Cd} and Ψ_{Cd} are the DGT labile fraction of Cd and Cu. The values shown here were the averages of seven replicate experiments.

[b] $\Psi_{Cd,theoretical}$ and $\Psi_{Cu,theoretical}$ are the free and inorganic metal ion fraction of Cd and Cu calculated by SC-database model [11] (EDTA, TA, GL and DBS) and WHAM-V6 (HA).

[c] Results were cited from our previous publication [6].

[d] Concentrations of HA (mg L^{-1}) in 0.40 μM Cd solutions or in 0.70 μM Cu solutions.

concentrations kept the decrease trend and were low, from 15.7% to 12.3% to 0.2%, compared with the Cd measurements (Table 2). The DGT labile metal fractions obtained for Cu were much lower than that for Cd. This result can be attributed to the stronger binding of Cu to HA. In addition, the values of Ψ_{Cu} obtained were higher than the theoretical values (Table 2). Further studies are needed to find out what the discrepancy between the DGT measurements and the theoretical calculations was, i.e. whether the theoretical calculations were underestimating the free and inorganic metal species due to the limitation of using currently available stability constants for the calculations, which may vary from different sources of HA, or this DGT device measured not only inorganic copper species, but some fractions of bound copper to HA, which could dissociate in the diffusion layer [25], or react directly with the binding phase through ligand exchange mechanism [6].

3.2.3. Labile metals in the presence of tannic acid

Table 2 also shows the effect of the molar ratio of metal ion/TA on the ratio of DGT-labile concentration to the total concentration for Cd and Cu (Ψ_{Cd} and Ψ_{Cu}). As expected, both Ψ_{Cd} and Ψ_{Cu} decreased as the molar ratio of TA/metal ion increased. When the metal ion/TA molar ratio increased from 1.0:1.8 to 1.0:1.0 to 1.8:1.0, the percentages of the DGT labile metal ion increased from 38.8% to 47.5% to 64.3% for Cd and 58.4% to 66.7% to 70.1% for Cu.

pH effects were not considered in the theoretical calculations for TA shown in Table 2, as the stability constant values used in Table 1 were obtained at pH 5, at which the TA functional groups were dominantly in –OH form, and TA is a polyphenolic substance with high pK_{a} value of 8.68 [27]. As shown in Table 2 the DGT-labile Cu fractions, Ψ_{Cu}, were substantially less than the theoretical values for all molar ratios used. The most likely reason for this was a difference between the stability constant [27] used in the speciation software and that of the sample of tannic acid used. However, these results may also be explained by the complicated interactions between the metal ions and tannic acid. Possible physical and chemical absorptions of the metal ions to tannic acid may keep some metal ions as "bound" ions [27]. It is not possible to conclude a likely mechanism for speciation of the TA complexes based on these data. However, given the results obtained for the HA and EDTA complexes in the previous sections, the most likely mechanism is the retarded diffusion of the complexes compared with the inorganic metal ions.

No $\Psi_{\mathrm{Cd,theoretical}}$ was given for TA-Cd due to the lack of the stability constant. It has been reported previously that no significant complexation occurs between Cd^{2+} and TA [27]. However, our results do not support this, as the Ψ_{Cd} values obtained were even smaller than that of $\Psi_{\mathrm{Cu},}$ for each given molar ratio of TA/metal ion. This suggests that Cd^{2+} was bound more tightly to TA than Cu^{2+} was.

Comparing the results for HA and TA shown in Table 2, it can be seen that the DGT labile metal fractions in the presence of TA were higher than those in the presence of HA, especially for Cu. This indicates that the interactions between TA and metal ions were not as strong as that of HA. This result agrees with Ross's results [28] where it was reported that TA belongs to the category of weaker natural binding ligands compared to the HA ligand, which is rich in both primary amines and carbohydrates.

3.2.4. Labile metals in the presence of glucose

Table 2 shows that the DGT-labile metal fractions for both Cd and Cu (Ψ_{Cd} and Ψ_{Cu}) decreased as the molar ratios of metal ion/glucose decreased. The 1.8:1.0 ratio for both metals and the 1.0:1.0 ratio for Cu gave DGT-labile fractions close to 100%. The strongest binding, 1.0:1.8 for Cd, gave a DGT-labile fraction of only about 80%. These observations demonstrate that glucose weakly binds the metal ions in a way to make them non-DGT-labile. This effect was larger for Cd^{2+} than for Cu^{2+}. For a given molar ratio, the DGT-labile metal fractions, obtained for both Cd and Cu in the presence of glucose, were much higher than that obtained in the presence of HA, TA or EDTA, due to the weaker interactions between the metal ions and the glucose [29,30]. Although there is no theoretical calculation for comparison due to the lack of corresponding stability constants, given that the metal-glucose species are likely to diffuse much slowly through the dialysis membrane than the inorganic species, it is likely that the DGT-labile fractions measured here largely represents the inorganic metal ion fraction [31]. It is also possible that mechanism (3a), dissociation of the complex during diffusion through the dialysis membrane, is important here given the weak complexes formed with glucose.

3.2.5. Labile metals in the presence of dodecylbenzenesulfonic acid

As shown in Table 2, the DGT-labile metal fractions for both Cd (Ψ_{Cd} values are 81.5%, 64.8% and 52.8% for Cd/DBS molar ratios of 1.8:1.0, 1.0:1.0 and 1.0:1.8) and Cu (Ψ_{Cu} values are 96.0%, 84.3% and 75.7% for Cu/DBS molar ratios of 1.8:1.0, 1.0:1.0 and 1.0:1.8) decreased as the molar ratios of metal ion/DBS decreased, particularly for Cd. This indicates mid-strength binding for Cd^{2+} and somewhat weaker binding for Cu^{2+}. The binding strength for both Cd and Cu seemed to be between that for the TA and glucose ligands. Like the TA case, it seems that the most likely mechanism responsible for speciation of the metal–DBS complex is slow diffusion through the dialysis membrane, although there may be some dissociation occurring as well.

Based on the above results, the PSS-DGT device seems to largely measure the inorganic fractions of metal ions in solutions. Metal complexes with EDTA, HA and TA are non-DGT-labile while complexes with glucose and DBS are unlikely to be measured, although the later cannot be confirmed in this study. For ligands with greater stability constants, such as EDTA, the non-complexed fraction was much lower and therefore so was the DGT-labile fraction.

Table 3
Major cation concentrations, dissolved organic carbon, salinity, pH and water temperature on the DGT deployment sites[a]

Test Sites	Measured parameters							
	$[K^+]$ (mM)	$[Na^+]$ (mM)	$[Ca^{2+}]$ (mM)	$[Mg^{2+}]$ (mM)	DOC (mgC L^{-1})	pH	Salinity	Temperature (°C)
Runaway Bay Marina	13.2	530	32.1	43.6	0.93	8.1	34.3	26.2
Biggera Waters	14.7	524	26.3	72.2	1.1	7.9	35.7	25.7
Parkwood Pond	0.56	1.1	0.41	1.9	12	5.2	0.23	28.3
Loder Creek	0.080	0.87	1.4	0.18	7.5	6.5	0.31	25.3

[a] The cation concentrations were measured by FAAS after appropriate dilutions. Other parameters were measured at the beginning, middle and the end of the DGT deployment and averaged.

Table 4
Diffusion coefficient of metal ions in the dialysis membrane at different test sites[a]

Test Sites	Diffusion coefficient ($\times 10^{-6}$ cm^2 s^{-1})	
	D_m (Cd^{2+})	D_m (Cu^{2+})
Runaway Bay Marina	0.30	0.22
Biggera Waters	0.30	0.21
Parkwood Pond	1.0	0.89
Loders Creek	1.4	1.0

[a] Diffusion coefficients of Cd^{2+} and Cu^{2+} in the membrane in the tested sites were determined by the measurements of mass diffused through the membrane in solutions containing NaCl and $MgCl_2$ of concentrations equivalent to the ionic strengths of the sites using the diffusion cell described in Section 2.

The order of increasing DGT-lability of the complexes was EDTA < HA < TA < DBS < glucose for both Cu and Cd. This speciation is influenced largely by retardation of the flux of the complex through the dialysis membrane.

3.3. Field deployments

The complicated mixture of ligands in natural waters can potentially influence the DGT-labile measurements. One previous field study to investigate the speciation of the DGT-measurements using the conventional Chelex 100 gel as the binding phase and polyacrylamide gel as the diffusive layers found that 55.2% of the Cu complexes with organic matter were DGT-labile [22].

The newly developed PSS DGT devices were deployed at several sites for in situ trace metal ion speciation. Both fresh (Parkwood Pond and Loders Creek) and saline water (Runaway Bay Marina and Biggera Waters) sites were chosen.

In order to obtain the diffusion coefficients in the dialysis membrane for inorganic Cu and Cd species, the matrices of each site were first determined. The composition of these matrices is given in Table 3. Synthetic solutions were then prepared matching the major cation composition of the water at each site. The diffusion coefficients of Cd and Cu species for each test site were measured in these synthetic solutions according to the previously described method [5] and are shown in Table 4. The magnitude of diffusion coefficients obtained was dependent on total ionic strength. The values of diffusion coefficients obtained from the salty waters (Runaway Bay Marina and Biggera Waters) were much smaller than those obtained from fresh waters (Parkwood Pond and Loders Creek) due to the high ionic strength of the former.

The results obtained from the field deployment are summarised in Table 5 for both Cd and Cu. For the seawater sites, the 0.45 μm-filterable Cu components determined by ICP–MS were found to be very similar: 1.20 μg L^{-1} for the Biggera Waters site and 1.30 μg L^{-1} for the Runaway Bay Marina site. The DGT-labile Cu concentrations were 0.55 μg L^{-1} for both the Biggera Waters site and the Runaway Bay Marina site. These data represent 46% and 42% of the 0.45 μm-filterable Cu, respectively. These percentages are effectively the same when experimental uncertainties are taken into consideration, probably because the sites are part of the one well-flushed and mixed coastal lagoon (Gold Coast Broad Water).

For the seawater sites, both the 0.45 μm-filterable and DGT-labile Cd concentrations were much lower when compared to Cu. Higher concentrations of copper were because of the release of antifouling paints from boats berthing

Table 5
DGT labile and 0.45 μm-filterable concentrations of Cd and Cu

Test sites	Runaway Bay Marina	Biggera Waters	Parkwood Pond	Loders Creek
Cd				
C_{DGT}[a] (μg L^{-1})	0.039 ± 0.009	0.043 ± 0.01	0.019 ± 0.008	0.014 ± 0.006
C_F[a] (μg L^{-1})	<0.6	<0.6	<0.4	<0.4
Ψ[b] (%)	>6.5	>7.2	>4.8	>3.5
Cu				
C_{DGT}[a] (μg L^{-1})	0.55 ± 0.04	0.55 ± 0.03	0.050 ± 0.007	0.025 ± 0.008
C_F[a] (μg L^{-1})	1.30	1.20	0.61	0.51
Ψ[b] (%)	42	46	8.2	4.9

[a] C_{DGT} and C_F are the DGT labile metal ion concentration and the total filterable metal ion concentration measured by ICPMS respectively. Data presented here are the mean values of three replicates.

[b] Ψ is defined as the DGT labile metal concentration (C_{DGT}) divided by the total filterable metal ion concentration (C_F).

at the sites. The 0.45 μm-filterable Cd components for the Biggera Waters and the Runaway Bay Marina sites were found to be below the detection limits. The DGT labile Cd concentrations were 0.043 μg L^{-1} for the Biggera Waters site and 0.039 μg L^{-1} for the Runaway Bay Marina.

For the freshwater sites, the DGT-labile Cu concentrations obtained from the fresh water sites were 0.050 μg L^{-1} for Parkwood Pond and 0.025 μg L^{-1} for Loders Creek. The DGT-labile Cd concentrations obtained from the freshwater sites were 0.019 μg L^{-1} for Parkwood Pond and 0.014 μg L^{-1} for Loders Creek. Both were much lower than in the seawater sites.

The freshwater sites had higher DOC levels and also had lower DGT-labile concentrations compared with the seawater sites (Tables 3 and 5). DOC has been used as an indicator of the amount of complexation with organic matter that is likely to occur [32,33]. Given the results in the previous sections of this paper, it is likely that the low DGT-labile measurements are due to a higher proportion of the Cu and Cd being complexed to organic matter and therefore becoming non-labile to the CDM-PSS DGT device, or, partly due to the low 0.45 μm-filterable metal concentrations. Of course this should be studied in much more detail as part of future studies.

4. Conclusions

It was demonstrated that the CDM-PSS DGT device was capable of measuring DGT labile fraction of metal ions. The measurement in solutions containing various complexing ligands showed good agreement with SC-database model and WHAM model calculations. The measured DGT labile metal fractions were explained by the three mechanisms proposed. This helped to better understand the definition of DGT labile concentration.

The speciation capability of this CDM-PSS DGT technique was supported by the Cu results from natural water sites. At the tested freshwater sites with higher lever of DOC, lower DGT labile Cu fraction was measured due to the complexation of metals to humic substances. However, further research is required for other elements, such as Cd, whose measurements were limited by the limitation of detection limits in this study.

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