

## ***In situ* Measurement of Trace Metals in Estuarine Waters of Patos Lagoon using Diffusive Gradients in Thin Films (DGT)**

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A técnica de gradiente difusivo de membrana (DGT) foi utilizada para determinar metais lábeis *in situ* durante diferentes condições hidrológicas no estuário da Lagoa dos Patos. As amostras de água foram também analisadas para a fração lábil-Chelex para Cd, Co, Cu, Mn, Ni e Zn usando resina Chelex-100. As concentrações lábeis-DGT de Cd, Cu, Ni e Zn foram mais baixas que a lábil-Chelex, possivelmente devido à ligação do metal coloidal na coluna de resina Chelex. Os resultados do DGT indicaram um decréscimo nas concentrações de todos os elementos, refletindo trocas na especiação dos metais em solução causada pela diminuição da salinidade e associado a mudanças de pH no estuário. Os resultados demonstraram a sensibilidade do DGT para a especiação dos metais e a capacidade do uso da técnica DGT em águas estuarinas altamente dinâmicas para a obtenção de concentrações de metais lábeis integradas ao longo do tempo.

The diffusive gradients in thin-films (DGT) technique was used to determine labile metals *in situ* during different hydrological conditions in the Patos Lagoon estuary. Water samples were also analyzed for Chelex-labile fractions of Cd, Co, Cu, Mn, Ni and Zn using Chelex-100 resin. DGT-labile concentrations of Cd, Cu, Ni and Zn were lower than Chelex-labile concentrations, possibly because colloids were trapped in the Chelex resin column. There was a decrease with increasing deployment time in the concentrations of all elements measured by DGT, reflecting changes in metal speciation in solution caused by the decrease in the salinity and associated with change in pH in the estuary. The results demonstrated the sensitivity of DGT to metal speciation and the feasibility of using the DGT technique in highly dynamic estuarine waters to obtain a time-integrated record of labile trace metals.

**Keywords:** DGT, labile metal, estuary

### **Introduction**

Trace metals are one of the major contaminants of estuarine and coastal areas, as a result of coastal development and, consequently, inputs from many anthropogenic sources.<sup>1</sup> Elements such as Cu, Ni, Mn and Zn play an important role as essential elements in aquatic systems. However, elevated concentrations of these elements, and of non-essential elements such as Cd, may cause toxicity for aquatic organisms. The investigation of metal bioavailability in water is as important as metal concentration when considering the impact of metals on an environment.

The free metal ion ( $M^{2+}$ ) and labile metal species in solution are the forms of dissolved metal often accumulated by aquatic organisms.<sup>2</sup> Uptake may occur directly into phytoplankton cells<sup>3</sup> or across gill membranes in fish.<sup>4</sup> So, speciation studies of trace metals have become important, as it enables evaluation of trace metal bioavailability and mobility. Available techniques include anodic stripping voltammetry,<sup>5</sup> cathodic stripping voltammetry<sup>6</sup> and ion-exchange columns.<sup>7</sup> However, with standard equipment, all these methods require analyses to be done on a sample brought to the laboratory and metal speciation may change in this time from that pertaining to *in situ* conditions.

The technique of diffusive gradients in thin films (DGT) is a tool to determine, *in situ*, labile metal ions in aquatic

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environment. Metal ions are transported by molecular diffusion through a protective 0.45  $\mu\text{m}$  cellulose nitrate filter and a polyacrylamide hydrogel (diffusive gel), and are then finally accumulated on an ion-exchange resin. During the deployment of the DGT devices, metal ions are continuously accumulated, providing *in situ* pre-concentration of multi-elements, in proportion to their bulk concentration.<sup>8</sup> The accumulated metal is measured later in the laboratory and used to calculate the *in situ* concentration in solution using Fick's law of diffusion.<sup>9</sup>

The DGT technique discriminates metal species kinetically, measuring only labile species (free metal cations, inorganic and some small organic metal complexes), which are likely to be readily bioavailable. DGT gives time-integrated concentrations,<sup>8</sup> which can be an advantage in monitoring studies, as variability is automatically averaged. Because trace metal concentrations can be highly variable in estuaries, many conventional grab samples are required to adequately describe the chemical conditions, demanding considerable effort and cost.

Although the DGT method has been demonstrated to be very effective for freshwater systems,<sup>10-13</sup> very few studies have been carried out in estuarine areas.<sup>14,15</sup> Estuarine areas of lagoon systems are known to support high primary productivity and valuable fisheries, but they may also receive inputs from anthropogenic sources. Labile or available fractions of metal ions in the water column may then be accumulated by organisms. Speciation studies are necessary to account for significant effects of metals toxicity to the biota.

The Patos Lagoon is the largest in South America and its estuary is hydrodynamically active, due to winds and freshwater inflow.<sup>16</sup> The estuary is also characterized by a high salinity variation, causing daily variations of chemical constituents and making the estuary highly unstable from a chemical perspective.<sup>17</sup> Extreme variations in salinity are observed during El Niño and La Niña events, when freshwater and seawater are respectively dominant during many months in the estuary.<sup>16</sup> These conditions of extreme salinity cause the disappearance of many benthic organisms used as potential bio-indicators, making it difficult to evaluate bioavailable fractions of trace metals in the water column. Bio-indicators respond to metals from water and food, whereas DGT estimates the labile component of metals in the dissolved fraction of the water. However, DGT devices have been shown to be more sensitive than mussels (*Mytilus edulis*) in detecting differences in metal concentrations between sites, indicating an advantage of DGT in studying the geographic distribution of contamination.<sup>18</sup>

Previous studies have identified some inputs of trace metals to the Patos Lagoon estuary<sup>17,19</sup> from untreated urban

and industrial waste water discharges present around the city of Rio Grande. The increase of the industrialization in the estuary area, together with the dynamic nature of the environment, makes it necessary to evaluate trace metals contaminations in some areas around the city. Total or dissolved metal concentrations are usually determined, however, are unlikely to provide a realistic assessment of exposure of aquatic organisms and other pollutant effects. Therefore, speciation studies are important to enable evaluation of the available labile metal fraction in relation to the total dissolved concentration.

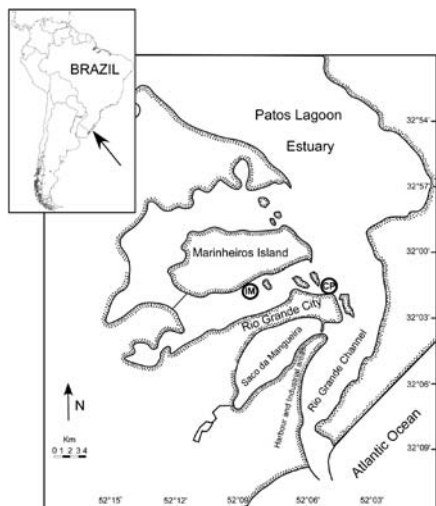
Several DGT devices were deployed in two locations of the Patos Lagoon estuary receiving different anthropogenic contribution. The purpose of this preliminary study was to evaluate the feasibility of making DGT measurements *in situ* in this hostile environment with unstable hydrological conditions. Chelex labile concentrations and total dissolved metal concentrations were also measured for comparison.

## Experimental

### Study sites

The Patos Lagoon is located in the south of Brazil and covers an area of 10,360 km<sup>2</sup>. It is considered the largest choked coastal lagoon in the world<sup>20</sup> and similar to most choked coastal lagoon systems, the Patos Lagoon is wind forced rather than tidal driven.<sup>21</sup> The predominant NE-SW wind regime is the principal forcing factor and it decisively controls circulation, salinity distribution and water levels.<sup>22</sup> The only contact of the lagoon with the sea is through a relatively small inlet at its southern end, near the city of Rio Grande (Figure 1). The lagoon is shallow, having an average depth of about 6 m. The residence time of fresh water is relatively long *ca.* 5 months during winter (June-August), while during the periods of low runoff (January-March) seawater penetrates 200 km into the lagoon. Because of its shallow depth and low tidal range (0.47 m), the water of the Patos Lagoon is vertically well mixed.<sup>23</sup>

Rio Grande city has an industrial park, where the main activity is chemical processes associated with fertilizer, oil and petrochemical industries, which have a high potential for pollution. Untreated sewage is another source of contamination. These main sources are responsible for the presence of high level of nutrients and metals in waters in the vicinity of the city.<sup>19,24</sup> Additional contamination comes from three ports located near the city, one of which is the most important port of Brazil, in terms of the number of containers shipped.



**Figure 1.** Sampling stations in the Patos Lagoon estuary at Rio Grande City (RG) and at Marinheiros Island (MI).

### Procedures

DGT devices were obtained from DGT Research Ltd (Lancaster, UK). The deployment of the DGT devices was carried out during September 2003. Two experimental sites were selected in the estuary, one close to Rio Grande City (RG), with influences of urban and industrial waste, and another located near Marinheiros Island (MI), 4 km from the downtown, where there are solely agricultural activities (Figure 1).

In both experimental sites, DGT devices were deployed back to back attached to a length of 4 mm polypropylene rope at a depth of about 0.5 m. Triplicate DGT devices were collected after 2, 6 and 10 days of deployment period. One DGT probe were randomly chosen as control, and was not deployed in the water column, but maintained in an acid-clean polyethylene bag during the duration of the field deployment. This control was used to correct the concentrations extracted from the probes deployed in the field. Results of the control were 0.003 ng cm<sup>-2</sup> for Cd, 0.001 ng cm<sup>-2</sup> for Co, 0.124 ng cm<sup>-2</sup> for Cu, 0.118 ng cm<sup>-2</sup> for Mn, 0.068 ng cm<sup>-2</sup> for Ni and 1.812 ng cm<sup>-2</sup> for Zn.

The parameter temperature, salinity and pH were measured *in situ* using respectively a thermosalinometer (YSI 30, Yellow Springs) and a pH meter (Mettler Toledo MP120). All measurements and water sampling were conducted daily during the experiments at site RG, but only during the deploying and retrieval time of DGT devices this procedure was adopted at site MI.

Water samples were collected using a Niskin bottle at the same depth as the DGT devices, and analyzed for labile and total dissolved forms of metals. Samples were filtered through a 0.45 µm pore-size membrane filter (Millipore), to obtain the dissolved form. All water samples were preserved

by acidification with 1 mL of 65% v/v Suprapur® nitric acid (Merk) *per* sample liter reaching a final concentration of 20 mmol L<sup>-1</sup>. Water samples were maintained refrigerated (< 4°C) until analysis.

All plastic ware was previously acid-washed in a 20% v/v solution of nitric acid followed by rinsing with Milli-Q water. DGT devices and water samples were handling in a laminar flow bench, wearing disposable and powder-free gloves.

Estimation of trace metals in water samples followed different procedures for high and low salinity waters. Trace metal in water samples (salinity < 5) at the beginning of the DGT deployment (day 0 for the location MI and days 0 and 1 for the location RG) and the end (day 10 for the location MI and days 9 and 10 for the location RG) of the DGT deployment experiment were analyzed as total dissolved concentrations. The remaining samples with salinity above 5 (days 2 and 6 for location MI and day 2 to 8 for location RG) were passed through a Chelex 100 (Bio-Rad) resin column (3 g-sodium form, pH 8; 200-400 Mesh) at a flow rate of 2 mL min<sup>-1</sup> to obtain the dissolved labile fraction and moderately labile metal species, here designated as Chelex-labile fraction. The column was rinsed with 10 mL of Milli-Q water and the metals back-extracted into 20 mL of 2 mol L<sup>-1</sup> Suprapure® nitric acid. In the laboratory, the resin gel of each DGT unit was immersed in 1 mol L<sup>-1</sup> HNO<sub>3</sub> solution prior the analysis (Figure 2). Each resin gel (DGT-labile) and water sample were measured for cadmium, cobalt, copper, manganese, nickel and zinc by ICP-MS (Thermo-Elemental X7) at the University of Lancaster/UK. Quality control of all analyses was ensured by analyzing a SLRS-4 certified reference material. Recovery expressed as percentages of their certified reference values were 100% for Cd, 91% for Co, 103% for Cu, 104% for Mn, 108% for Ni and 123% for Zn.

The results were expressed in terms of mass (ng) and concentration (µg L<sup>-1</sup>) of metal in the resin gel.<sup>8</sup> The mass of metal in the resin gel (M) was obtained using equation 1:

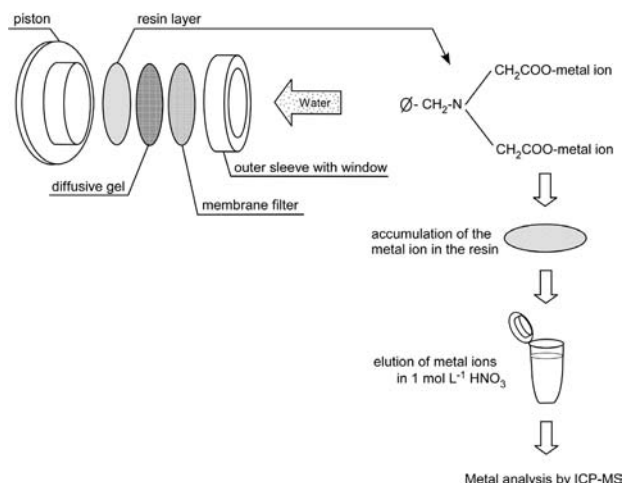
$$M = C_e (V_{\text{acid}} + V_{\text{gel}}) / f_e \quad (1)$$

Where, C<sub>e</sub> is the metal concentration in the 1 mol L<sup>-1</sup> HNO<sub>3</sub> elution solution (µg L<sup>-1</sup>); V<sub>acid</sub> is the volume of HNO<sub>3</sub> added to the resin gel (mL); V<sub>gel</sub> is the volume of the resin gel (mL); f<sub>e</sub> is the elution factor for each metal (0.8).

The concentration of metal measured by DGT (C<sub>DGT</sub>) was calculated using equation 2:

$$C_{\text{DGT}} = M \Delta g / (D t A) \quad (2)$$

Where, Δg is the thickness of the diffusive gel plus the thickness of the filter membrane (cm); D is the diffusion



**Figure 2.** Representation of the DGT components, accumulation and elution of trace metals ions from Chelex-100 resin.

coefficient of metal in the gel ( $\text{cm}^2 \text{ s}^{-1}$ );  $t$  is deployment time (s);  $A$  is exposure area ( $\text{cm}^2$ ).

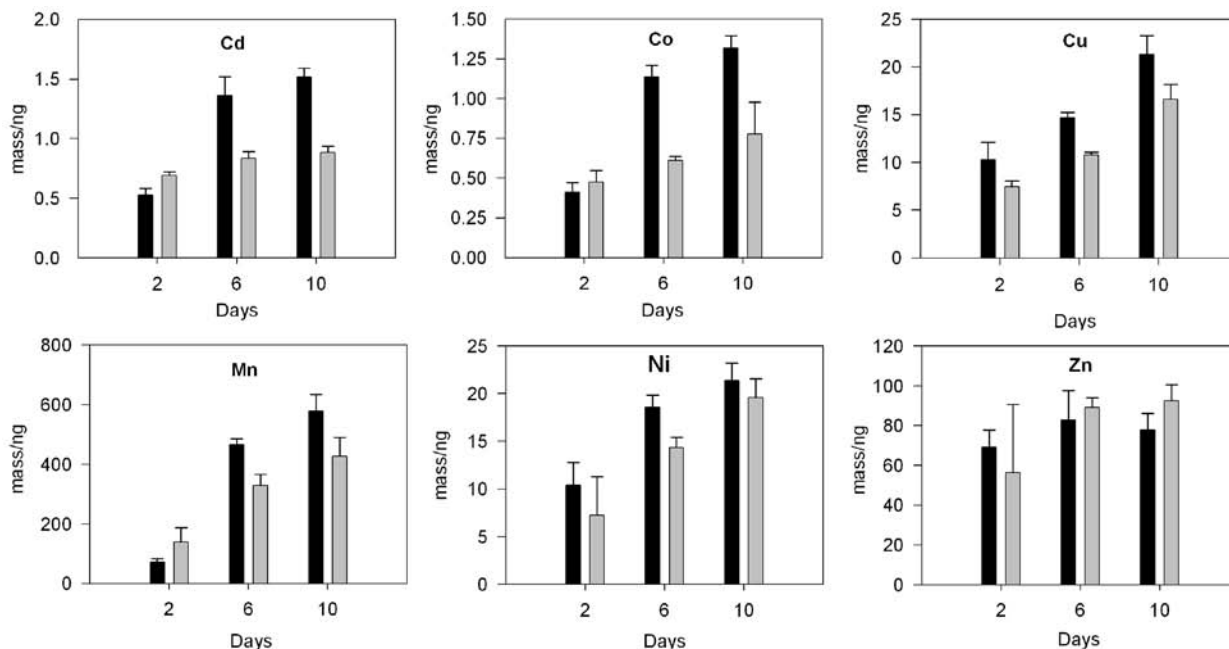
The difference between the DGT-measured trace metal concentrations, from the sites RG and MI, and between the three deployment times were tested by Two-factor Analysis of Variance at a significance level of 5%, after data normalization using  $\log(1+x)$ .

## Results and Discussion

Differences in the mass accumulation of the DGT-labile metals were observed during the ten days deployment

period of the DGT devices. The mass of the diffusive ions (ng) accumulated in the resin gel increased significantly ( $p < 0.05$ ) between 2 and 6 days deployment period for all metals, and for Cu, Mn and Ni between 6 and 10 days. Although there was some visual increase, statistically the mass of Cd, Co and Zn stayed constant between 6 and 10 days deployment period ( $p > 0.05$ ) for both sites (Rio Grande and Marinheiros Island) (Figure 3).

The mean DGT labile concentrations of Co, Cu, Ni and Zn for both experimental sites decreased significantly ( $p < 0.05$ ) after 2 days until the end of 10 days deployment period (Figures 4 and 5). The dissolved Chelex-labile fraction of metals generally increased at day 6, and then decreased (Figures 4 and 5). These measurements are consistent with the DGT results, which are integrated from day 0. The lower DGT measurement at day 6 reflects the lower Chelex-labile measurement prior to day 6. At day 10 the DGT measurement included the increase in the Chelex-labile measurement at day 6 and the subsequent decline. The net result was the slight further decline in the DGT measured concentration. The changes in concentrations can be appreciated in terms of the reduction of the salinity and consequently increase of the pH in the water after six days deployment time (Figures 4 and 5), when strong winds (mean velocity of  $10 \text{ m s}^{-1}$  at day 6 and  $9.8 \text{ m s}^{-1}$  at day 7) from the NE quarter and ebb tide in the estuary occurred. Strong winds from the NE quarter normally cause freshwater to flow out into the estuary, while strong winds from the S quarter favor seawater penetrating to the



**Figure 3.** Mean mass (ng)  $\pm$  SD of Cd, Zn, Co, Cu, Mn and Ni in the resin layer during 2, 6 and 10 days deployment at the Marinheiros Island-MI (■) and at Rio Grande-RG (▒).

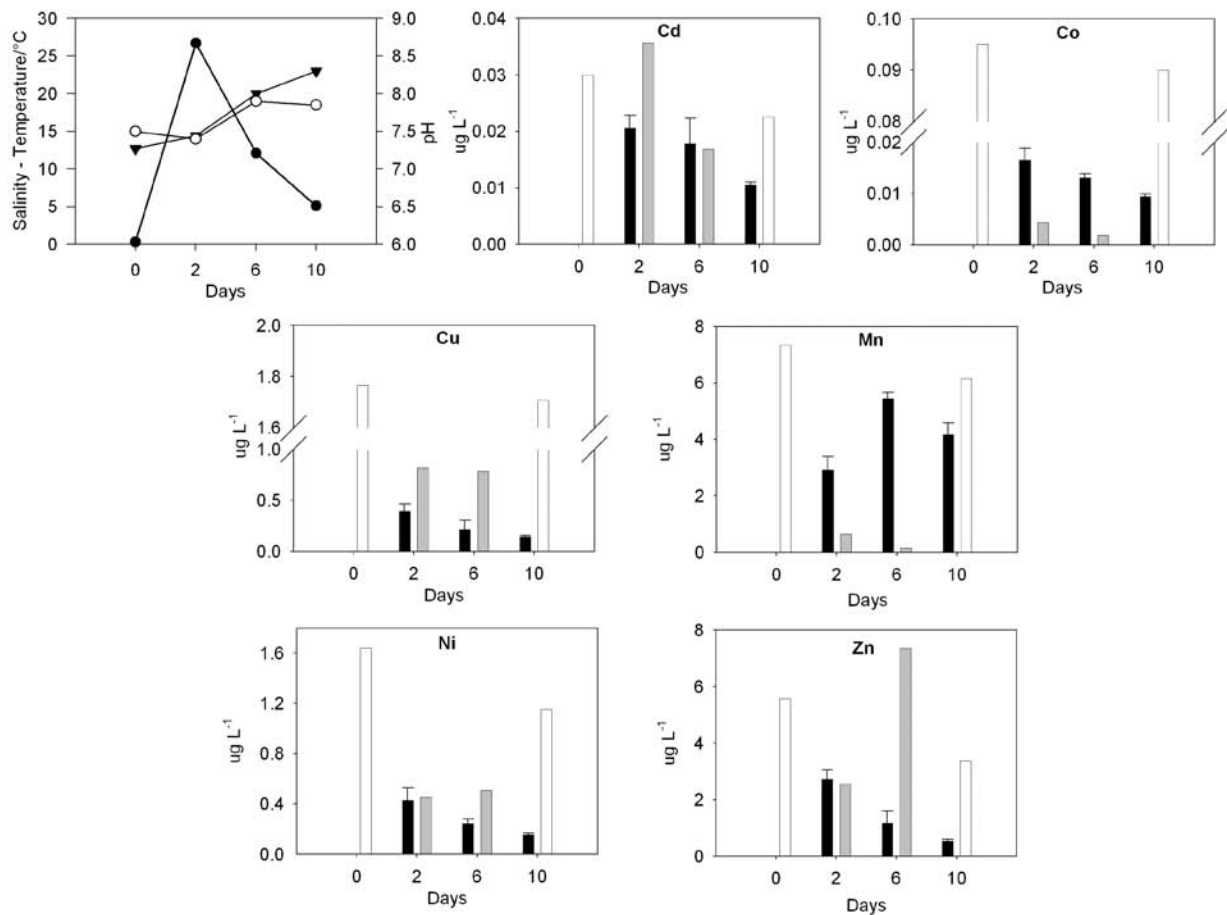
estuary.<sup>22</sup> Previous studies have also shown that dissolved concentrations of Cd, Co and Ni decrease with decreasing salinity in the estuary.<sup>17</sup> The associated rise in pH can remove metals from solution by sorption to particles or colloids not measured by DGT.

The concurrence of the highest salinity and concentrations of DGT-labile metals during the second day of deployment in the estuary, agree with the findings of Dunn *et al.*<sup>14</sup> They demonstrated that DGT-labile metals (Cu, Zn and Ni) were higher during flood tidal phases at Ephraim Island (Broadwater Lagoon, south-east Queensland, Australia), where tidal cycles are well defined. Both results are contrary to normal expectations within estuarine systems, where generally the entrance of marine waters in estuaries normally causes a decrease of trace metal concentrations due to flocculation occurring. This may be associated with the high pH of the freshwater and the wind driven, rather than tidal, mixing of the water types.

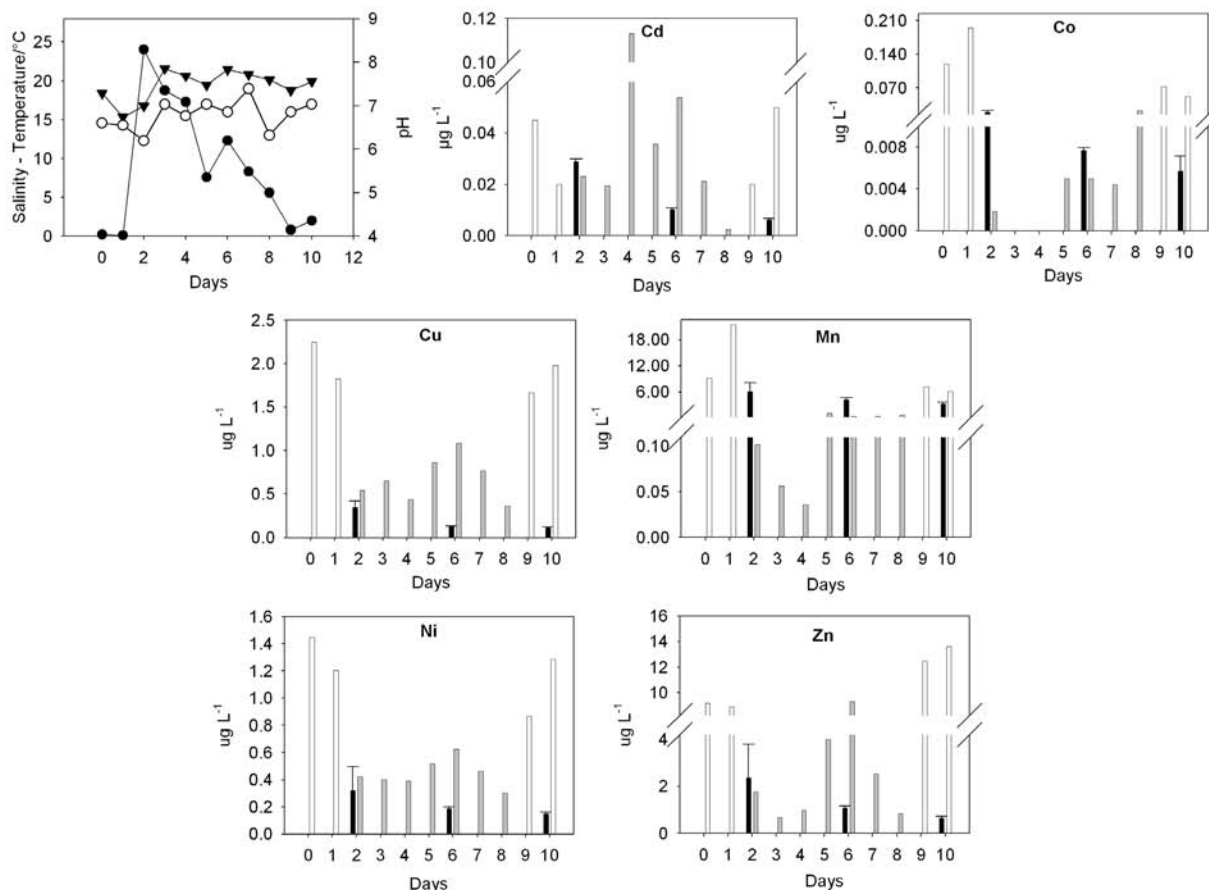
The trend for the DGT-labile concentration of Mn at Marinheiros Island was different from the other metals, as it decreased after six days deployment. Mn is not so sensitive

as other metals to changes in pH.<sup>11</sup> The same ranges of Cu, Ni and Zn concentrations estimated from DGT ( $p > 0.05$ ) were found for both experimental sites during all deployment periods. However, DGT-labile concentrations of Cd and Co were higher at Marinheiros Island ( $p < 0.05$ ) (Figure 4). As concentrations of both elements are very low, they are sensitive to local differences in inputs and processes. Temperature presented some fluctuations and pH was related to salinity changes in the estuary (Figures 4 and 5). Changes in water temperature are considered in the calculation of the DGT-labile metals and changes in the salinity or pH do not affect the performance of DGT.<sup>25</sup>

As wind patterns also changed during the present study, it is likely that the bottom sediments of the estuary were also mobilized. Concentrations of some dissolved components in the water column may then be altered, as observed in previous studies,<sup>24</sup> in which case DGT-labile concentrations will be affected. These effects of sediment remobilization were probably different at the two experimental sites, due to differences in their morphology and currents.



**Figure 4.** Trace metal concentrations ( $\mu\text{g L}^{-1}$ ) in the water and DGT devices of Marinheiros Island site. The total dissolved fraction ( $\square$  0 and 10 days), Chelex-labile fraction ( $\square$  2 and 6 days) and DGT devices ( $\blacksquare$  after 2, 6 and 10 days of deployment). DGT data are represented by mean  $\pm$  SD,  $n=2-3$ . Variations of salinity ( $\bullet$ ), temperature ( $\circ$ ) and pH ( $\blacktriangledown$ ) are given during DGT deployment period.



**Figure 5.** Trace metal concentrations ( $\mu\text{g L}^{-1}$ ) in the water and DGT devices of the Rio Grande site. The total dissolved fraction ( $\square$  0, 1, 9 and 10 days), Chelex-labile fraction ( $\blacksquare$  2 and 6 days) and DGT devices ( $\blacksquare$  after 2, 6 and 10 days of deployment). DGT data are represented by mean  $\pm$  SD,  $n=2-3$ . Variations of salinity ( $\bullet$ ) and temperature ( $\circ$ ) and pH ( $\blacktriangledown$ ) are given during DGT deployment period.

As expected, the concentrations of total dissolved trace metals tended to be generally higher than the Chelex-labile concentrations (Figures 4 and 5), although some exceptions were observed. These included the Cd concentrations on day 2 at the Marinheiros Island (Figure 4) and day 4 at the Rio Grande locations, which may indicate analytical or contamination problems at these very low concentrations.

The DGT-labile concentrations of Cd, Cu, Ni and Zn were in general lower for both sites than the Chelex-labile concentrations, possibly because colloids were trapped in the Chelex resin column and measured. They would not be measured by DGT. Exceptions were found for Co and Mn. Total dissolved concentrations of Co and Mn showed a similar pattern at both sites and there was a high correlation ( $r = 0.94$ ) between the elements. This may be due to sorption of Co by Mn hydrous oxides.<sup>26</sup> However, the lower Chelex-labile concentration, compared to the DGT labile fraction of Co and Mn, for MI measurements suggests that the Mn had been removed from solution by oxidation or aggregation after it had been sampled. This shows the importance of using an in situ measurement like DGT. The

DGT labile and the Chelex-labile trace metals measure different species, and differences have been reported in field studies on freshwaters,<sup>12</sup> estuarine waters<sup>14,27,28</sup> and oceanic waters.<sup>8,27</sup>

The total dissolved trace metal concentrations in estuarine water were generally higher at the Rio Grande site, consistent with the presence of anthropogenic discharges around the city. Marinheiros Island has less urban occupation and the main economic activities are agriculture and fish farming.

Studies with DGT in estuaries are scarce, and the selective ranges of trace metals analyzed as well as the use of distinct deposition times of DGT devices, limited the data comparison. Mean DGT concentrations measured in this study for Cu and Zn at 48 h were compared to measurements from other estuarine areas for comparable deployment times (Table 1). Copper concentrations were similar to those found at Horseshoe Bay and Marine Stadium<sup>28</sup> in Australia. The smaller zinc concentrations are consistent with distinct anthropogenic sources for the Australian sites. Cu measured by DGT at impacted (Pier Four 24) and none impacted (Vineyard Sound) areas<sup>27</sup> sites

**Table 1.** Mean concentrations ( $\mu\text{g L}^{-1}$ ) of trace metal in DGT from different locations

Locations and deployment periods	Cu / ( $\mu\text{g L}^{-1}$ )	Zn / ( $\mu\text{g L}^{-1}$ )	Reference
Marinheiros Island site 48 h (n=2-3)	0.36	2.43	Present study
Rio Grande site 48 h (n=2-3)	0.28	2.09	Present study
Pier Four 24-96 h (n=2-4)	2.45	-	27
Vineyard Sound, MA 24-96 h (n=2-4)	0.85	-	27
Horseshoe Bay 24 h (n=5)	0.31	38.40	28
Marine Stadium 24 h (n=3)	0.45	7.30	28

in the USA also sensibly compared with the measurements (Table 1), given the differences in anthropogenic sources and the water hydrodynamic of each studied location.

These results demonstrated that DGT provides a valid average measure of labile trace metals in highly dynamic estuaries. Besides all the natural changes in estuary environments some important factors that might affect the measurements need to be considered. Some variation in the diffusion coefficients is expected, *ca.* 8%, during changes between fresh and seawater.<sup>8</sup> There is a possibility that biofouling of the filter membrane of the DGT unit can occur during the summer period at the Patos Lagoon estuary. In the present study during the winter it has assumed that there was no influence of biofouling on the filter membrane of the DGT devices, since no visible alteration of the filter was observed. Studies of biofouling effects on filters of the DGT devices in estuaries are limited. Recent studies during a summer season at the Patos Lagoon indicated the presence of algae growing over the filter membrane of the DGT devices after 10 days deployment (unpublished data), when salinity was high. Such films may remove metal ions from solution, making them unavailable for the DGT or effectively increase the diffusion layer thickness.<sup>15</sup> To overcome possibly biofouling problems on the DGT devices, the deployment period could be shorter in the estuarine water of the Patos Lagoon or consecutive deployments for a long period could be used as well, as applied by Dunn *et al.*<sup>14</sup>

## Conclusions

The DGT labile concentrations of Cu, Ni and Zn in the estuary were similar for the different sites studied and lower than Chelex-labile metal. The two measurements, DGT labile and Chelex-labile, were generally consistent with Chelex-labile measurements for Cd, Cu, Ni and Zn being generally higher, due most likely to the inclusion of colloidal metal in this measurement. However, results for Mn and Co showed that the Chelex-labile measurement may underestimate the true *in situ* concentrations. Compared with other estuarine studies, concentrations of DGT-labile metals were low in the Patos Lagoon.

The DGT technique was shown to be a robust procedure for the quantification of trace metals in the water column in distinct sites of the Patos Lagoon, indicating the potential of the DGT devices to be used for deployments of several days in estuaries, to obtain an integrated record of trace metal concentrations. The study demonstrated the feasibility of using DGT in the highly dynamic estuarine areas.

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## References

1. Kennish, M. J.; *Practical Handbook of Estuarine and Marine Pollution*, CRC Press: Boca Raton, Florida, 1997.
2. Morel, F. M. M.; Hering, J. G.; *Principles and Applications of Aquatic Chemistry*, Wiley-Interscience: New York, 1993.
3. Sunda, W. G.; *Biol. Oceanogr.* **1991**, *6*, 471.
4. Richards, J. G.; Curtis, P. J.; Burnison, B. K.; Playle, C.; *Environ. Toxicol. Chem.* **2001**, *20*, 1159.
5. Mota, A. M.; Coreia dos Santos, M. M. In *Metal Speciation and Bioavailability in Aquatic Systems*; Tessier, A.; Turner, D. R., eds.; John Wiley: New York, 1995, ch. 3.
6. Donat, J.; Lao, K.; Bruland, K. W.; *Anal. Chim. Acta* **1994**, *284*, 547.
7. Marshall, W. D.; Momplaisir, G. M. In *Metal Speciation and Bioavailability in Aquatic Systems*; Tessier, A.; Turner, D. R., eds.; John Wiley: New York, 1995, ch. 5.
8. Zhang, H.; Davison, W.; *Anal. Chem.* **1995**, *67*, 3391.
9. Davison, W.; Zhang, H.; *Nature* **1994**, 546.
10. Denney, S.; Sherwood, J.; Leyden, J.; *Sci. Total Environ.* **1999**, *239*, 71.
11. Gimpel, J.; Zhang, H.; Davison, W.; Edwards, A. C.; *Environ. Sci. Technol.* **2003**, *37*, 138.
12. Odzak, H.; Kistles, D.; Xue, H.; Sigg, L.; *Aquat. Sci.* **2002**, *64*, 292.

13. Torre, M. C. A.-D. I.; Beaulieu, P.-Y.; Tessier, A.; *Anal. Chim. Acta* **2000**, *418*, 53.
14. Dunn, R. J. K.; Teasdale, P. R.; Warnken, J.; Schleich, R. R.; *Environ. Sci. Technol.* **2003**, *37*, 2794.
15. Webb, J. A.; Keough, M. J.; *Sci. Total Environ.* **2002**, *298*, 207.
16. Garcia, C. A. E. In *Os Ecossistemas Costeiro e Marinho do Extremo Sul do Brasil*; Seeliger, U.; Odebrecht, C.; Castello, J. P., eds.; Editora Ecoscientia: Rio Grande, RS, 1998, ch. 2.
17. Windom, H. L.; Niencheski, L. F.; Smith, Jr., R. G.; *Estuar. Coast. Shelf Sci.* **1999**, *48*, 113.
18. Shintu, M.; Durante, L.; Maccioni, A.; Meloni, P.; Degetto, S.; Contu, A.; *Mar. Pollut. Bull.* **2008**, *57*, 832.
19. Niencheski, L. F.; Baumgarten, M. G. Z.; *Aquat. Ecosyst. Health Manage.* **2000**, *3*, 515.
20. Kjerfve, B. In *Estuarine Variability*; Academic Press: Orlando, FL, 1986, ch. 4.
21. Fernandes, E. H. L.; Dyer, K. R.; Moller, O. O.; Niencheski, L. F. H.; *Cont. Shelf Res.* **2002**, *22*, 1699.
22. Garcia, C. A. E. In *Subtropical Convergence Environments*; Seeliger, U.; Odebrecht, C.; Castello, J. P., eds.; Springer-Verlag: Berlin Heidelberg, 1997, ch. 6.
23. Niencheski, L. F.; Windom, H. L.; *Sci. Total Environ.* **1994**, *149*, 53.
24. Niencheski, L. F.; Windom, H. L.; Smith, R.; *Mar. Pollut. Bull.* **1994**, *28*, 96.
25. Gimpel, J.; Zhang, H.; Hutchinson, W.; Davison, W.; *Anal. Chim. Acta* **2001**, *448*, 93.
26. Lienemann, C.-P.; Taillefert, M.; Perret, D.; Gaillard, J.-F.; *Geochim. Cosmochim. Acta* **1997**, *61*, 1437.
27. Twiss, M. R.; Moffet, J. W.; *Environ. Sci. Technol.* **2002**, *36*, 1061.
28. Warnken, J.; Dunn, R. J. K.; Teasdale, P. R.; *Mar. Pollut. Bull.* **2004**, *49*, 833.

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