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Research article

The Diffusive Gradients in Thin Films Technique (DGT) for Trace Metals versus Active Sampling

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Abstract The diffusive gradient in thin films (DGT) technique is an in situ passive sampling method that is designed to accumulate labile metal species in environmental systems. DGTs were applied for the determination of time integrated concentrations of low level dissolved metals in waters in areas of ecological concern. The data revealed heavy metal contamination of waters and tracked the contamination to the source. A comparison of DGT-derived water concentrations with water concentrations measured from grab samples highlighted the effectiveness of passive water samplers for detecting ultra-trace levels of metals. Comparing active and passive sampling techniques showed that both methods produce similar results when used simultaneously at the same sites. The use of DGT technique along with traditional methods offers an extra cost effective method of independent evaluation of environmental sites as well as more sensitive and inexpensive way of obtaining additional information about sites which would be very hard to obtain using active sampling techniques.

Keywords passive sampling, ultra-trace levels, labile metal species, accumulation, time integrated concentrations.

INTRODUCTION

In recent years, passive sampling techniques have been developed to measure dissolved organic and inorganic compounds in waters at sub-nanogram per litre levels. “Passive” samplers are defined as human-made devices where sample collection occurs in a non-active, inert manner.

DGT technique is designed to accumulate labile species in environmental systems (Davison and Zhang, 1994; Davison et al. 2000; Zhang and Davison, 1995; Zhang and Davison, 2000). The currently available DGTs still require further method development and field validation (Warken et al., 2006).

The DGT technique employs an adsorbent (e.g. Chelex-100), usually immobilized in a polyacrylamide gel (the binding or resin gel), to adsorb analyte species from solution. Chelex-based resins can be used for simultaneous collection of many metals in water including silver (Ag), aluminium (Al), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn). The binding gel is separated from the bulk solution by a permeable polyacrylamide gel (the diffusive gel) and a solution diffusive boundary layer.

DGT devices are deployed in an environmental system for a time period ranging from days to months to accumulate analyte species of interest. Following deployment, the binding gel and the diffusive gel are separated and the accumulated analyte is eluted from the binding gel. The concentration of analyte in the eluant is then determined by an appropriate analytical technique, usually inductively-coupled plasma mass spectrometry (ICPMS). The time-averaged concentration of a species in the bulk solution, C, is then calculated using the DGT Equation below, which is derived from Fick's first law of diffusion (Zhang and Davison, 1995); M is the accumulated mass of analyte on the binding gel; Δg is the thickness of the diffusive gel, D is the diffusion coefficient of analyte in the diffusive gel, t is the deployment time, and A is the surface area of the diffusive gel exposed to the bulk solution.

$$C = M\,\Delta g / D\,t\,A \tag{1}$$

The assessment of water quality for the protection of the aquatic ecosystem requires the use of a combination of analytical methods based on the Australian ANZECC/ARMCANZ (2000) decision tree process for assessing metal toxicity in water. An initial step is to calculate site-specific trigger values for metals by using a correction for hardness, calculated from the calcium plus magnesium concentrations expressed as mg/L $CaCO_3$, to the default ANZECC/ARMCANZ (2000) guideline value. The aquatic toxicity decreases with increasing water hardness as soluble metal is precipitated. The next step in the decision tree process uses the measurements of metals in labile or bioavailable forms and metals and metalloids in particulate and insoluble colloidal fractions that can be measured through filtration (<0.45μm) and ultra-filtration (<0.003μm) to determine the bioavailable fractions of metals in waters. DGT samplers offer an alternative to conventional active sampling techniques.

The objective of the present study was to enhance and consolidate DGT applications for monitoring low levels of dissolved metals in water. The study seeks to address the following research questions: (i) how will DGT and active sampling techniques compare in a real world study of a contaminated water body in different environmental conditions; (ii) could the DGT technique be incorporated into the trace metal monitoring programs in waters together with traditional methods and replace them in the future; and (iii) will bioavailability results from DGT analysis add more value to the current analysis by conventional sampling techniques?

MATERIAL AND METHODS

DGT samplers were deployed for 2 days at the Woodcutter mine area in Northern Territory (Fig.1), Australia and in the Tosno river area in St. Petersburg (Fig. 2), Russian Federation.

The major silver-lead-zinc deposits at Woodcutters were mined from 1985 (Noller et al. 2003) to May 2000. Initial deployment of DGTs in Woodcutters Creek at the rehabilitated mine site was undertaken in June 2010 and a further more extensive deployment took place in September 2010 (Noller et al. 2011).

To compare DGT and active sampling techniques in a real world study of contaminated waters in different environmental conditions various experimental designs were established in a major industrial areas of the Russian Federation in January 2011 (Fig.2).

The diffusion coefficient of metals in the diffusive gel D (see Equation above) is dependent on the temperature. Therefore the average temperature of the water at all sites during DGT deployment was estimated. It ranged between 23.4-25.6 °C in the first round and 25.6-27.6 °C in the second round of deployment in the Woodcutter Creek and between 0-1 °C in the Tosno river deployment. At the completion of the deployment period, DGTs were delivered to the QHFSS laboratory where they were kept below 4 °C until prepared for analysis. During the extraction procedure the DGT device was opened, the binding gel and the diffusive gel were separated and the binding gel was submersed in 1 mL nitric acid for over 24 hours to elute the accumulated metals. Then 0.5 mL of extract was made up to 5 mL with nitric acid and water and analysed for metals by ICPMS (ICPMS 7700X, Agilent). At the time of DGT deployment 1L water samples were collected (active sampling) from all sites. Some water samples were filtered through 0.45 and 0.003 μm filters and analysed for metals by ICPMS.

RESULTS AND DISCUSSION

Woodcutter mine site in Australia

Initially 5 sets of DGTs were deployed in Woodcutter Creek in the vicinity of Woodcutters mine site in June 2010 to identify the bioavailable fraction of metals in the creek water (Fig. 1A). The DGTs collect the soluble or labile metal only and enable a comparison to be made with ecotoxicity measurements previously undertaken on creek water.

The measured DGT concentrations were generally higher than some of the filtered fractions. Table 1 shows the data for two major metals: lead and zinc. The grab water samples were collected at the beginning of DGT deployment and therefore represent the concentration of lead and zinc at this particular time. Concentrations of lead and zinc estimated from the DGT data represent their average concentrations over the deployment period (i.e. time integrated concentrations and may differ from spot sampling). Further experimental work performed at this site showed that the concentrations of lead and zinc in water may change significantly within 2-3 days (up to 5-10 times). This can explain the difference between the data.

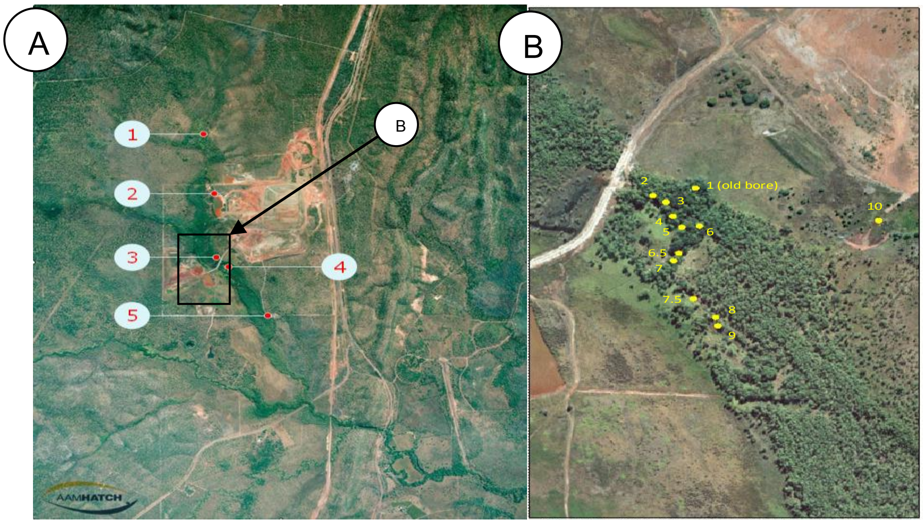

Fig. 1 A Sampling sites at Woodcutter Creek June 2010

1. *upstream site*
2. *new polishing pond outflow*
3. *above Huandot crossing*
4. *seepage below former Tailings Dam 2 at Huandot crossing*
5. *Mine lease boundary*

B. Shallow seepage sampling sites at Woodcutters Creek

September 2010 Site 1 corresponds to June 2010 Site 4

In the second DGT deployment undertaken at Woodcutters Creek in September 2010 (Fig. 1B) grab water samples were collected before and after DGT deployment and the average concentrations of lead and zinc were measured in filtered and unfiltered water. There were insignificant levels of lead present in water at all sites. Good agreement was found between the concentrations of zinc in 0.003 µm filtered grab water fraction and zinc DGT concentrations (Table 2). The minor difference in these values is attributed to the different approach applied with passive and active sampling techniques; that is time integrated water concentration of dissolved metals vs. "single point in time" concentrations. The overall findings from September 2010 were as follows: (i) increased zinc concentration was accompanied by increases in electrical conductivity and sulfate in water; (ii) for an observed hardness range of 800-2200 mg/L $CaCO_3$ the zinc filtered concentration (<0.45µm) marginally exceeded the hardness-adjusted ANZECC/ARMCANZ (2000) trigger value for 95% protection of aquatic species of 72 µg/L; (iii) the zinc DGT concentrations did not exceed the trigger value of 72 µg/L; and (iv) further investigation of actual ecotoxicity is warranted to confirm this finding.

Tosno river in St Petersburg, Russian Federation

DGTs were deployed in Tosno River situated around one of the major industrial areas of St. Petersburg (Fig.2). The deployment of DGTs in this area was aimed at the identification of the contamination source which was suggested to be downstream of site ф N1 (small arrow, Fig. 2). DGTs were deployed at four different sites (фN1, фN2, фN3 and фN4) following the direction of the river flow (large arrow, Fig. 2) for 2 days. At their deployment 5 L water samples were also taken at the corresponding sites (active sampling).

Table 1 Metals in surface water at Woodcutters Creek (16 June 2010)

Site	Metal	Active sampling (µg/L)			Passive sampling (µg/L)
		Total	0.45µm	0.003µm	C from DGT
1	Pb	0.4	0.1	0	0.02
2	Pb	5	0.4	0	0.5
3	Pb	0.4	0.2	0.1	0.06
4	Pb	1	0.1	0.1	0.04
5	Pb	0.3	0.1	0.1	0.5
1	Zn	25	22	20	0.6
2	Zn	31	7	4	29
3	Zn	47	40	25	2
4	Zn	7	5	6	1
5	Zn	33	22	13	22

Table 2 Zinc in shallow seepage entering Woodcutters Creek and nearby groundwater (September 2010)

Site	Sulfate (mg/L)	Zinc (µg/L)			
		Total	<0.45µm	<0.003µm	from DGT
WC1	1200	66	25	9.1	7.5
WC2	701	109	27	16	13.1
WC3	789	850	63	47	16.6
WC4	1490	94	26	23	18.3
WC5	1920	356	73	59	47.6
WC6	1260	271	24	24	15.9
WC7	581	70	32	12	10.5
WC8	628	90	25	12	10.3
WC9	1590	97	47	29	25.1
WC10	509	31	9.6	8.9	3.7

After deployment and recovery the DGTs were delivered to QHFSS by air freight and analysed for the following metals: aluminium, cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead and zinc. Based on the obtained data the concentrations of these metals in water at different sites of the river were estimated using Eq. (1). The results presented in Table 3 showed that a number of metals (aluminium, cadmium, cobalt, chromium and lead) on grab water analysis were not at detectable levels. In contrast DGTs revealed their presence at all sites. Copper, nickel and zinc were only detected in grab water samples collected at Sites фN4 and фN3 though their presence at all sites was proven by the DGT data.

Only two metals, iron and manganese, were found above detectable levels at all sites for both active and passive sampling (Table 3). Despite the difference in the concentrations of these metals found by the two methods, the change of the concentrations from site to site was similar. As the grab water samples were not collected in a time integrated manner, the concentrations of metals differed from the time averaged DGT-derived concentrations.

It is important to note that DGTs accumulate dissolved phase metals and the estimation of the concentrations is based on diffusion through the gel followed by uptake of dissolved phase metals. The DGT results are therefore more appropriate in terms of environmental risk since they represent an immediately available fraction of the chemical or bioavailable fraction. The estimation of metal concentrations by grab or active sampling is based on their total amounts in water including particle associated and colloidal metals. This could also explain the difference in iron and manganese concentrations found by comparing the two methods. The results obtained by two independent methods (active and passive sampling) draw us to the same conclusion - the source of the iron and manganese contamination of Tosno river is most likely situated somewhere between Sites ɸN1 and ɸN2.

Table 3 Metal concentrations in water from grab samples and by DGTs

	Passive sampling (µg/L) (DGT)					Active sampling (µg/L) (grab water)			
	Site ɸN1	Site ɸN2	Site ɸN3	Site ɸN4	95% Confidence interval of mean ± $t_{0.05}$ se[a] Sites ɸN1 - ɸN4	Site ɸN1	Site ɸN2	Site ɸN3	Site ɸN4
Al	16.00	77.00	65.00	63.00	68±19	n/d	n/d	n/d	n/d
Cd	0.26	0.17	0.09	0.09	0.12±0.11	n/d	n/d	n/d	n/d
Co	0.09	0.18	0.17	0.18	0.18±0.01	n/d	n/d	n/d	n/d
Cr	0.62	0.41	0.10	0.10	0.20±0.44[b]	n/d	n/d	n/d	n/d
Cu	9.40	8.70	6.60	5.70	7±3.8[b]	n/d	n/d	n/d	2.7
Fe	51.00	216.00	253.00	245.00	238±48	1300	1900	1500	1800
Mn	1.20	89.00	85.00	84.00	86±6.6	150	290	220	210
Ni	11.00	3.80	0.81	1.40	2.0±3.9	n/d	n/d	3.4	n/d
Pb	0.58	0.52	0.13	0.19	0.28±0.52[b]	n/d	n/d	n/d	n/d
Zn	0.62	65	48.00	45.00	53±27[b]	n/d	n/d	n/d	7.5

Note: a. $t_{0.05}$ = 4.303 from t-distribution table for degrees of freedom (n-1) =2 where n=number of results and standard error (se) = s/√n; b. not significantly different from ɸN1.

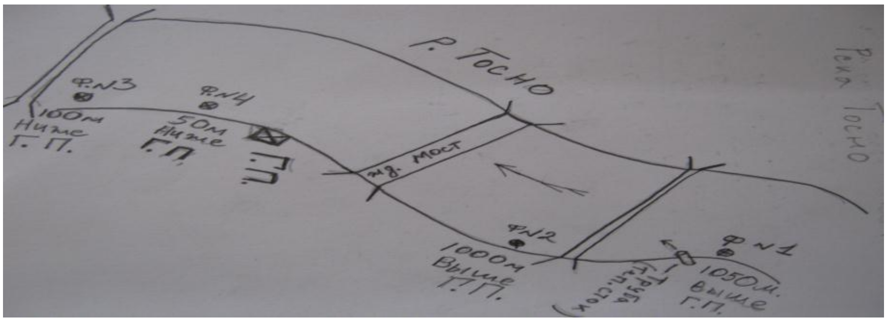

Fig. 2 Deployment sites on Tosno River

The DGT data for the upstream Site ɸN1 was compared with the 95% confidence interval of the mean of the downstream Sites ɸN3 and ɸN4 (Table 3). This comparison showed that, compared with Site ɸN1, there was a significant increase for aluminium, cobalt, iron and manganese going downstream and a significant decrease for chromium, copper, lead and zinc indicating their origin from another source upstream. Thus the DGT data in Table 3 showed that: (i) aluminium, cadmium, cobalt, chromium and lead were present in the water; (ii) aluminium and possibly traces of cobalt were most likely released into the water along with iron and manganese by the same source as their concentrations changed in a similar manner from site to site; and (iii) the source of contamination of water with cadmium, chromium, copper, nickel, lead and zinc was most likely situated upstream of Site ɸN1 as the concentrations of the metals were slowly decreasing from Site ф N1 to Sites ф N3 and ф N4. The use of DGTs in this experimental work provided a more complex picture of contamination of the river with heavy metals than could be achieved by using any conventional active sampling techniques.

CONCLUSIONS

The results obtained in this study show the potential of the DGT technique to measure ultra-trace levels of metals in water reliably at a range of temperature and environmental conditions. Comparison of active and passive sampling techniques showed that both methods produce similar results when used simultaneously. The use of DGT technique along with traditional methods offers an extra cost effective method of independent evaluation of environmental sites as well as more sensitive and inexpensive way of obtaining some further information about sites which would be very difficult to obtain using any conventional active sampling techniques.

This technique allows measurement of time integrated water concentration of dissolved pollutants in contrast to grab sampling techniques which only represent single points in time. DGTs require relatively inexpensive and simple materials for their preparation and there is no power source or active sampling equipment (e.g. pump, flow meter etc) needed during their deployment. The post deployment process of DGT extraction and clean up takes several minutes using minimal consumables and chemicals and can be done in the field if necessary.

The DGT results represent an immediately available fraction of the chemical. DGTs mimic the accumulation that occurs in aquatic biota allowing toxicologists to estimate the actual levels of toxicities of different metals under the specific environmental conditions and their impact on environmental health and health of biological organisms including humans.

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