

## A novel DGT-sediment trap device for the in situ measurement of element remobilization from settling particles in water columns and its application to trace metal release from Mn and Fe oxides

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### *Abstract*

A device has been developed for the direct in situ measurement of metal remobilization into solution from settling particles in water columns, based on the technique of diffusion gradients in thin films (DGT). The device comprises a hollow cylinder with a DGT assembly at its base and acts as a traditional sediment trap, except that any remobilization from settling particles is reflected in the mass of metal taken up from solution by the DGT assembly. A control-DGT device (an upside-down trap) was used to measure the metal taken up by the assembly in the absence of remobilization from particles. Deployments of the control device under laboratory conditions and below the well-mixed surface layer of a lake showed that the cylindrical trap design, with a height : diameter ratio of 5 : 1, resulted in negligible turbulence near the base of the trap so that uptake by the control was governed by molecular diffusion. The DGT-trap and -control devices were deployed together within and immediately below the main oxycline of a seasonally anoxic lake in 1996 and 1997. The reproducibility of the metal uptakes measured by the devices in the field was typically better than  $\pm 10\%$  for the controls and  $\pm 20\%$  for the traps. The uptakes of Mn, Co, Al, Ba, and Ni, but not Fe and Cu, were significantly and consistently higher in the trap devices than in the controls. Reductive dissolution of Mn oxide appeared to be the source of the four remobilized trace metals, whereas Fe oxides made no significant contribution. The remobilization of Mn, Co, Al, Ba, and Ni was also reflected in elevated dissolved concentrations in the vicinity of the oxycline. Comparisons of the metal : Mn ratios obtained from the DGT-trap data with those calculated from the water-column concentrations indicated that the elevated concentrations of dissolved Co were derived solely from Mn oxide dissolution, whereas Ba, Al, and Ni also appear to be affected by other processes.

The remobilization of elements from particles into solution is of paramount importance in the biogeochemical cycling of elements and compounds in natural waters. Diverse methods have been used to obtain information about remobilization from particles in the water columns of lakes and oceans. These include laboratory remobilization experiments on recovered samples (Reinfelder et al. 1993), interpretation of vertical profiles of dissolved and particulate element concentrations (Balistrieri et al. 1992; Achterberg et al. 1997), settling rate data obtained from vertical arrays of sediment traps (Davison et al. 1982; Baker et al. 1991), and comparisons between settling rates measured by sediment traps and net sedimentation rates derived from dated sediment cores (Hamilton-Taylor et al. 1984; Sanders et al. 1996). These approaches have the disadvantage of being either indirect or laboratory-based, so that interpretation of the resulting data in terms of remobilization processes operating in the environment is subject to uncertainty. The aim of this study was to measure in situ the remobilization of trace metals from settling particles. The device that was developed is based on

the recently developed technique of diffusive gradients in thin films or DGT (Davison and Zhang 1994). The performance of the device was assessed in the laboratory and in the field, and various field deployments were undertaken to measure remobilization directly. Esthwaite Water (EW) was chosen as the field site because it is a seasonally anoxic lake where water column remobilization of Fe and Mn oxides is known to occur (Davison 1993). One of the features of shallow, productive lakes like EW is that the various geochemical zones in the water column are compressed and overlapping (Hamilton-Taylor and Davison 1995). It is impossible, for example, to differentiate between the remobilization effects of reductively dissolving Mn and Fe oxides based on water-column profiles (e.g., Achterberg et al. 1997) and other traditional approaches. The main aims of the field deployments were therefore to use the DGT-trap device to study the effects of Mn oxide dissolution on trace metal remobilization and to distinguish these from the effects of Fe oxide dissolution.

### Concept and design of device

DGT has previously been used to measure dissolved metal and nutrient concentrations in surface waters (Davison and Zhang 1994; Zhang and Davison 1995; Chang et al. 1998; Zhang et al. 1998a) and sediment pore waters (Zhang et al. 1995; Davison et al. 1997) and remobilization from the solid phase in sediments (Zhang et al. 1995) and soils (Zhang et al. 1998b). The basic DGT assembly is the same as that used for concentration measurements in surface waters (Zhang

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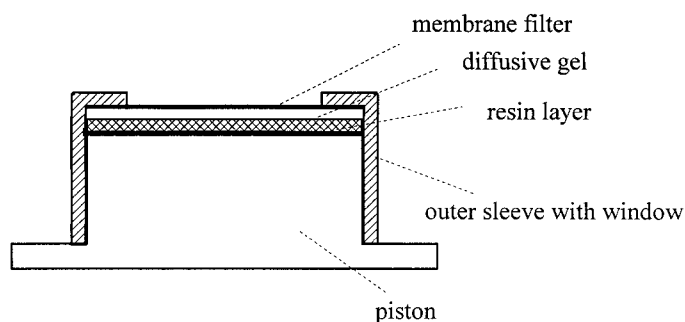


Fig. 1. Schematic cross-section through a DGT assembly.

and Davison 1995) and is shown in Fig. 1. The methods used for preparing the DGT assembly, and extracting and analyzing the metals are described in detail elsewhere (Zhang and Davison 1995). The assembly is circular in plan view and comprises a resin gel layer, a diffusive gel layer, and an outer membrane filter that is in contact with the environmental solution. The resin gel comprises Chelex-100 resin beads dispersed in gel and it acts as a sink for dissolved metals. The diffusive gel layer was 0.4 mm thick in all deployments described in the present study. The diffusive gel and outer membrane allow free passage, by molecular diffusion, of dissolved metal species from the environmental solution to the resin gel and together are referred to as the diffusion layer. Both the binding to Chelex and the diffusive transport are to some extent species dependent. For example large metal–humic complexes may have significantly lower diffusion coefficients than simple inorganic species, thus restricting their transport through the diffusion layer, and inert complexes are unavailable for resin uptake (Zhang and Davison 1999 and additional unpublished data). The mass of metal bound by the resin gel is determined by extraction into a known, small volume of 1 M HNO<sub>3</sub>, followed by analysis using atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectroscopy (ICP-MS), or some other appropriate method.

During deployment, a concentration gradient is established across the diffusion layer between the resin gel and the environmental compartment contacting the membrane surface. The concentration of dissolved labile species is effectively zero at the resin-gel surface due to rapid uptake by the Chelex. The mass uptake ( $M$  in nmol) per unit area ( $A = 3.14 \text{ cm}^2$ ) by the resin represents the mass flux ( $F$  in nmol  $\text{cm}^{-2} \text{ s}^{-1}$ ) integrated over the time ( $t$  in s) of deployment and is a function of the concentration ( $C$  in nmol  $\text{cm}^{-3}$ ) at the membrane surface. With previous water-column deployments of the assembly shown in Fig. 1, concentrations at the membrane surface were maintained at their actual in situ levels (profile 1 in Fig. 2) by efficient turbulent mixing and effectively limitless reservoirs of trace metals (Zhang and Davison 1995). Under these conditions, the actual in situ concentration can be obtained directly from the mass uptake using Fick's first law of diffusion:

$$\frac{M}{At} = F = \frac{DC}{\Delta g} \quad (1)$$

where  $D$  ( $\text{cm}^2 \text{ s}^{-1}$ ) is the diffusion coefficient of a given

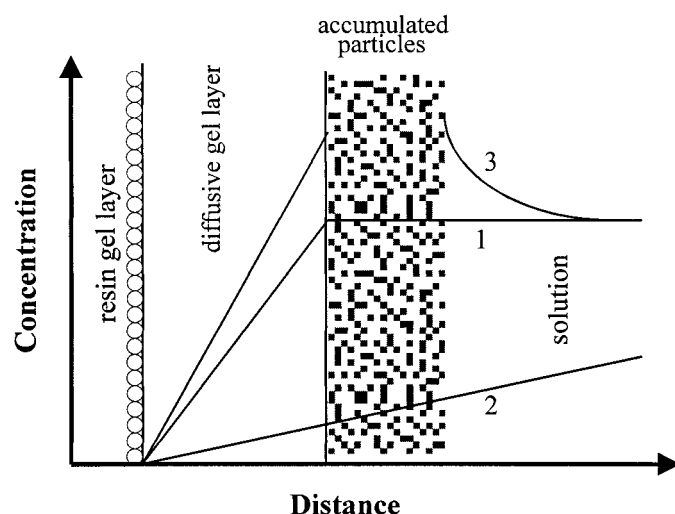


Fig. 2. Schematic representation of concentration gradients. The concentration adjacent to the membrane surface (1) may be maintained at its actual in situ level by efficient mixing in the solution phase; (2) may be determined by resupply through molecular diffusion only; or (3) may be locally elevated relative to the natural in situ concentration due to active remobilization in the DGT-trap device.

metal ion and  $\Delta g$  is the diffusion layer thickness (0.053 cm). In sediments and saturated soils, transport is generally by molecular diffusion and potentially becomes a limiting factor. A second important factor controlling the DGT-measured flux in sediments and soils is resupply from the solid phase so that the concentration calculated using Eq. 1 provides information on resupply properties (capacities and kinetics) of metals from solid phase to solution (Zhang et al. 1998b). Profile 2 in Fig. 2 shows the extreme case where there is no resupply from the solid phase and molecular diffusion is acting alone. It has previously been demonstrated that the diffusion coefficients for inorganic metal species in true solution is the same in the gels used in the DGT assemblies as in water (Zhang and Davison 1999). Subsequent calculations involving Eq. 1 use the temperature-corrected diffusion coefficients for the various metals given by Li and Gregory (1974).

In the present application, the DGT assembly is fitted into a section of PVC tubing with an aspect ratio (length:diameter) of 5:1. When the device is positioned vertically within the water column with the DGT assembly at the bottom (Fig. 3), it has the recommended design characteristics of a sediment trap (Rosa et al. 1991) and henceforth, when deployed in this way, is referred to as the in situ remobilization trap (IRT). The key difference from a normal trap is that when settling solids reach the bottom of the IRT they are in direct contact with the DGT assembly. Therefore any remobilization will create an enhanced supply of metals in the vicinity of the DGT assembly and will be reflected in the DGT uptake. An upside-down IRT was used as a control (see Fig. 3) and henceforth is referred to as the control-IRT. The surface of the DGT assembly within the control-IRT thus comes into contact with the same solution as the assembly surface in the IRT without coming into contact with any

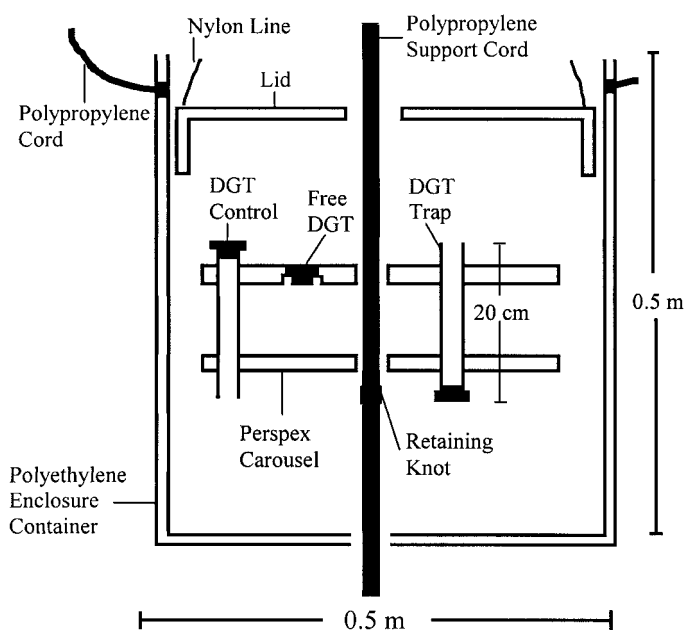


Fig. 3. Schematic cross-section showing the mode of deployment of the DGT-trap and DGT-control devices (i.e., IRT and control-IRT).

settled material. Several IRTs and control-IRTs were routinely mounted in a Perspex carousel (Fig. 3) to enable sampling reproducibility to be calculated. In order that a valid control measurement was achieved, it was necessary that both the IRTs and control-IRTs were in contact with water of the same composition immediately on deployment. This was achieved by initially deploying the trap carousel inside a polyethylene enclosure comprising a removable circular container and lid (Fig. 3).

Two types of remobilization may be detected by the IRT. The first is induced remobilization as previously described for sediments and soils (Zhang et al. 1998b, 1995). Metal uptake by the standard DGT assemblies (Fig. 1) deployed in these environments generally causes a DGT-induced lowering of the dissolved concentration adjacent to the membrane surface relative to the natural in situ concentration. This fall in concentration is counteracted to some degree by resupply from the solid phase and diffusion from surrounding pore waters acting in combination. The resupply from the solid phase may arise, for example, due to the perturbation of an equilibrium sorption or precipitation-dissolution reaction. The key point is that induced remobilization occurs only as a result of the presence of the IRT. The second active-type of remobilization occurs spontaneously in the water column. The microbially driven, reductive dissolution of Mn oxide in suboxic waters is an example of such a process.

Various general conclusions concerning remobilization can be drawn from the comparative metal uptakes obtained with the IRT and control-IRT. The fluxes (or masses) of metal taken up by the IRT ( $T$ ) and control-IRT ( $C$ ) may show the following relationships: (1)  $T/C = 1$ , indicating the absence of remobilization; and (2)  $T/C > 1$ , indicating induced and/or active remobilization. In addition the trap flux ( $T$ ) can usefully be compared with the flux ( $F_{\text{calc}}$ ) calculated from

Eq. 1, assuming that without active remobilization the concentration at the membrane surface would have remained constant at its in situ concentration in the open water column (i.e., under conditions equivalent to profile 1 in Fig. 2). The in situ concentration in the water column is obtained by independent measurement.  $T/F_{\text{calc}} > 1$  implies active remobilization (see profile 3 in Fig. 2). If  $T/C > 1$  but  $T/F_{\text{calc}} \leq 1$ , induced and active remobilization cannot be distinguished by means of these simple comparisons. Information about transport (mixing) processes within the PVC tubing can also be obtained by considering the performance of the control-IRT. For example, minimal metal uptake by the control-IRT can be predicted assuming no remobilization and transport by molecular diffusion (profile 2 in Fig. 2).

### Performance characteristics

*Laboratory experiments*—The performance of the IRT device in the absence of remobilization was examined under constant laboratory conditions using  $\text{Mn}^{2+}$  as a tracer. The aims of the experiments were to determine the extent of metal uptake by the device under simulated field conditions and to compare the results with theoretical predictions and with simultaneous measurements made using the basic DGT assembly without the PVC cylinder. It is in this latter form (shown as the free device in Fig. 3) that the assembly has previously been used to measure water column concentrations.

Three free devices and three IRT devices in control mode were placed in the Perspex carousel and the entire assembly deployed in the dark at  $6^\circ\text{C}$  in 20 L of 0.005 M  $\text{NaNO}_3$  solution, spiked with the equivalent of 5.46 nM (300 ppb)  $\text{Mn}^{2+}$ . Sufficient nitric acid was added to achieve a pH of  $\sim 5$  in order to prevent any significant Mn oxidation. The solution was gently and continuously stirred by a magnetic stirrer. Two experiments were run with deployment times of 24 h and 8 d. In addition to determining the extent of Mn uptake in the DGT devices at the end of the experiments, the final immersion solutions were sampled, filtered through  $0.45\text{-}\mu\text{m}$  membrane filters and analyzed (AAS).

As expected, the directly measured dissolved Mn concentrations (Table 1) at the end of the 24-h and 8-d experiments were effectively unchanged from the initial concentration, indicating no significant loss of Mn. The total amount of Mn taken up by all the DGT devices in the 8-d experiment was equivalent to  $\sim 1\%$  of the total dissolved Mn present. The theoretical uptake was calculated for the well-mixed case where the dissolved Mn concentration at the membrane surface was maintained at 5.46 nM throughout the experiments.

The replicate laboratory deployments of the free devices and control-IRTs showed good reproducibility (Table 1). The measured uptake by the free devices was  $\sim 67\%$  of that calculated for the well-mixed case in both experiments. The uptake was probably  $< 100\%$  due to the likely existence of a significant diffusive boundary layer at the membrane surface under the gentle stirring conditions employed. Speciation effects were unlikely based on the equilibrium speciation code, MINTEQA2, which indicates that the dissolved Mn was present entirely as the free metal ion. The observed

Table 1. Mn uptake by control and free DGT devices under laboratory and field conditions, expressed as mean fluxes.

Experiment	Water depth (m)	Solution [Mn] (nmol l <sup>-1</sup> )	Mn uptake* (pmol cm <sup>-2</sup> h <sup>-1</sup> )			Mean % of calculated uptake	
			Free	Control	Calculated†	Free	Control
24-h laboratory experiment		5.32‡	748±5	116±13	1,129	66	10.3
8-d laboratory experiment		5.48‡	783±2	27.3±1.8	1,165	67	2.3
48-h Esthwaite Water experiment (12–14 Aug 1997)	3.3	0.61	—	21.1±0.5	146	—	15
	4.0	1.82	—	30.0±1.1	406	—	7.4
	5.0	2.11	—	46.1±2.5	459	—	10

\* Mean and standard deviation of two or three devices.

† Calculated Mn uptake by the DGT device, assuming that the concentration in the solution is maintained constant and is unaffected by the device.

‡ The measured concentration at the end of the deployment period in the laboratory incubation.

Mn uptake by the free device, although <100%, indicates that the DGT assemblies performed satisfactorily. Mn uptake by the control-IRT was substantially less than the uptake by the free device and showed a time dependency (Table 1). The minimal expected uptake, assuming transport by molecular diffusion, was estimated using the two-dimensional modelling methodology developed by Harper et al. (1998) taking account of the geometry of the IRT device. The resulting predictions are 18.5% (24 h) and 8.3% (8 d) of the masses that would have accumulated if the solutions were well mixed. The observed values (10.3% and 2.3%) were lower but broadly in line with the predictions suggesting that turbulence was effectively absent from the inner part of the IRT device. The absence of turbulence in the device was perhaps to be expected given that the purpose of a cylindrical design with a 5:1 aspect ratio for sediment traps is to reduce mixing.

*Field conditions*—Control-IRTs were positioned at three depths in EW near the base of the oxycline during a period of summer stratification. Water samples were collected at the start of the 48-h deployment for the measurement of water column concentrations (see below for information on protocols). The results are presented in a similar way to the laboratory experimental data in Table 1. Both the in situ dissolved Mn concentration and the observed Mn uptake by the control-IRT increased with depth as would be expected from the sampling location near the base of the oxycline. The observed uptake varied between 7.4 and 15% (mean 11%) of that calculated for the well-mixed case, where the dissolved Mn concentration at the membrane surface was assumed to be constant at the observed water column concentration. The calculated uptake over 48 h assuming molecular diffusion alone is 14.7% of the well-mixed case. The observed uptakes are therefore in line with the laboratory results in suggesting that the effect of turbulence on metal uptake by the control-IRT was negligible. The results demonstrate the effectiveness of a cylindrical shape and 5:1 aspect ratio in minimizing turbulence within sediment traps under field conditions. The twofold variability in the percentage uptake with water depth may be linked to (1) the locally steep vertical concentration gradients combined with difficulties in maintaining the traps at constant water depths, and (2) the occurrence of nonsteady-state conditions combined with the fact that the control-IRT provides an inte-

grated measurement over time. Obtaining an accurate prediction of metal uptake by the control-IRT under these circumstances, based on the water column concentrations, is clearly difficult.

### Field applications

*Methodology*—Field deployments of IRTs and control-IRTs were undertaken in EW between 14–22 August 1996, 5–9 September 1996, and 12–14 August 1997 at water depths selected on the basis of the redox conditions at the time. The suboxic zone during summer stratification was the focus of attention because previous studies had indicated that the reductive dissolution of Mn oxides was the dominant process in this part of the water column, Fe oxide dissolution being restricted to completely anoxic regions of the lake including the underlying sediments (Davison 1993). Concentrations of total suspended solids in the lake are typically around 1–2 mg liter<sup>-1</sup> but can reach 5–10 mg liter<sup>-1</sup> in surface and deep waters (Sholkovitz and Copland 1982a), while total-mass deposition rates are typically 2–5 g m<sup>-2</sup> d<sup>-1</sup> (Sanders et al. 1996). Mn deposition rates at intermediate depths during August and September, principally as Mn oxides, are typically 30–70 mg m<sup>-2</sup> d<sup>-1</sup> (Davison et al. 1982).

The DGT devices were deoxygenated in the laboratory prior to use. This was achieved by submersion in a container of Milli-Q water that was then bubbled with N<sub>2</sub> gas for 48 h. The deoxygenated box was sealed prior to transport to the field site and placed inside a second box containing deoxygenated sodium sulfite solution. For each deployment two additional DGT assemblies were prepared in the same way to be used as field blanks. All sampling occurred at the deepest point (15 m) in EW. Immediately prior to deployment the container part of the enclosure device (Fig. 3) was filled with lake water, pumped directly from the appropriate deployment depth by means of a peristaltic pump and braided PVC tubing, and an empty carousel then positioned inside the enclosure. The DGT devices were removed from the deoxygenated box and immediately fixed into the submerged carousel by means of nitrile rubber rings. Two or three of the devices were fitted as replicate IRTs and replicate control-IRTs in each carousel. Care was taken to ensure that no air was trapped inside the control-IRTs by rotating the carousel in the enclosure. The lid was placed on top of the

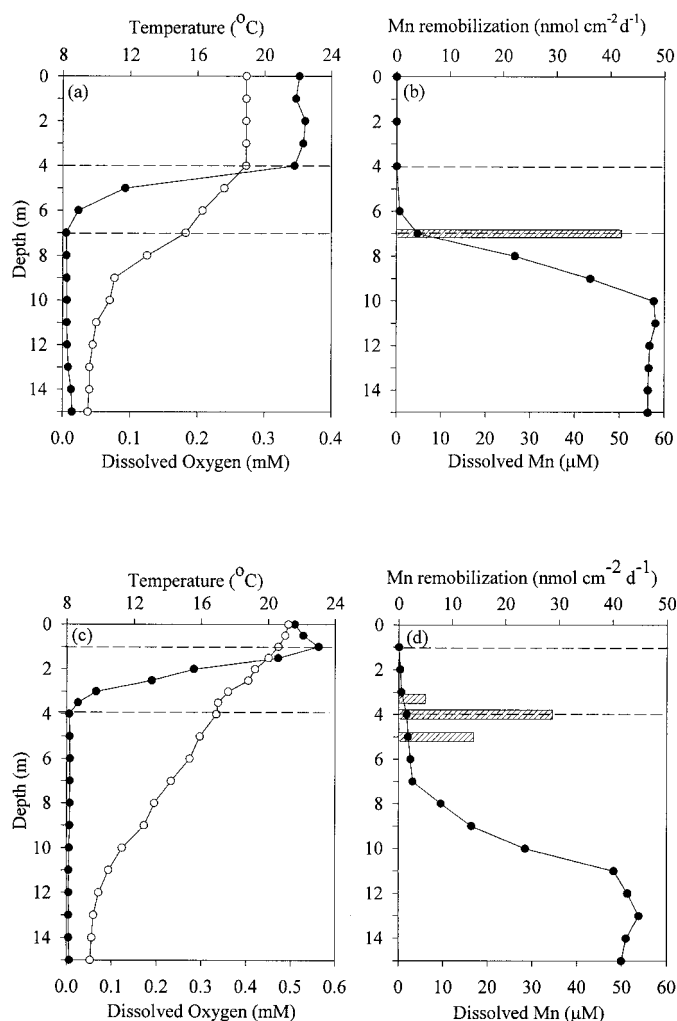


Fig. 4. Vertical profiles of temperature (○), dissolved oxygen (●) and dissolved Mn (●) concentrations, and Mn remobilization rates (hatched bars) in Esthwaite Water. (a,b) Profiles for 22 August 1996 and Mn remobilization rates for the period 14–22 August 1996. (c,d) Profiles for 12 August 1997 and Mn remobilization rates for the period 12–14 August 1997. The upper and lower limits of the oxycline are indicated by dashed lines.

container that was then lowered overboard. At the required depth, the enclosure was removed from the proximity of the carousel exposing the latter to the unrestricted water column. In the simple prototype system, this was achieved by allowing the container to settle under gravity and by raising the lid using polypropylene cords. The carousel and enclosure were fixed to a weighted, polypropylene rope kept taut by a submerged buoy at the top. Following deployment, the DGT assemblies were immediately detached from the PVC tubes and rinsed with Milli-Q water to remove any collected sediment, thus preventing further metal uptake. The assemblies were kept in polyethylene bags until analyzed. The blank assemblies were exposed and then transferred into polyethylene bags on board the boat in a similar way to the sample devices.

Temperature, dissolved oxygen, and dissolved trace metal

Table 2. Metal uptakes by DGT devices deployed at a water depth of 7 m in Esthwaite Water, 14–22 August 1996, expressed as mean fluxes.

Metal	Control* ( $\text{pmol cm}^{-2} \text{d}^{-1}$ )	Trap* ( $\text{pmol cm}^{-2} \text{d}^{-1}$ )	Trap – Control ( $\text{pmol cm}^{-2} \text{d}^{-1}$ )
Mn	$29,000 \pm 600$	$70,900 \pm 1,100$	41,900
Fe	$160 \pm 10$	$9,760 \pm 2,130$	9,600
Co	$3.4 \pm 0.3$	$14.3 \pm 1.4$	10.9
Al	$30.4 \pm 5.9$	$73.4 \pm 12.6$	43.0
Ba	$31.8 \pm 3.1$	$65.7 \pm 5.8$	33.9
Ni	$8.2 \pm 0.7$	$11.6 \pm 1.4$	3.4
Cu	$4.4 \pm 1.1$	$4.2 \pm 2.4$	not detectable

\* Values given as mean and standard deviation of duplicate devices.

concentrations were also determined in the water column. A detailed trace metal profile was obtained for 22 August 1996, corresponding to the final day of one of the DGT deployments. The clean sampling and analytical methods for trace metals are detailed elsewhere (Hamilton-Taylor et al. 1996; Smith 1998). Briefly, water samples were collected by peristaltic pump and braided PVC tubing, filtered on-line through  $0.45\text{-}\mu\text{m}$  membrane filters and stored at pH 2. Trace metal analysis was by electrothermal AAS and ICP-MS. A 15-liter Milli-Q water sample was used to flush the sampling system in the field and then to provide a field blank by taking the Milli-Q water through the entire sampling, handling and analytical protocol. The field-blank concentrations were negligible compared to sample concentrations.

**Results and discussion**—The 8-d trap deployment in August 1996 was at a depth of 7 m that corresponded on 14 August to the middle of the oxycline ( $\sim 50\%$  DO saturation) and on 22 August to the base of the oxycline (DO below detection; see Fig. 4a). These conditions are typical of EW for the time of year. In August 1997, three carousels were deployed simultaneously at depths of 3.3, 4, and 5 m for 48 h. Conditions in 1997 were extremely unusual, linked to exceptionally fine and stable weather before and during the sampling period. The waters were thermally stratified from the surface (i.e., no surface mixed layer) and the oxycline lay between 1 and 4 m (Fig. 4c). The contrasting redox conditions in 1996 and 1997 were also reflected in the profiles of dissolved Mn concentration (Fig. 4b,d). The dissolved Mn profile below 7 m in August 1997 (Fig. 4d) suggests that redox conditions developed in the normal way in the early part of the summer. In contrast, the relatively small increase with depth in dissolved Mn between 2 and 7 m was probably associated with the later upward extension of the anoxic zone that accompanied the period of unusually fine weather.

The reproducibility of metal uptake determined from the replicated IRTs and control-IRTs was good in both years for all metals (Tables 2 and 3). The generally better reproducibility of the controls (typically  $\pm < 10\%$ ) compared to the IRTs (typically  $\pm < 20\%$ ) was to be expected given that uptake by the controls is derived entirely from the solution phase, whereas uptake by the IRTs also includes the effect of remobilization from particles. Mn uptake by the IRTs was invariably much greater than by the corresponding control-IRTs, indicating remobilization in all deployments (Tables 2

Table 3. Mn and Fe uptakes by DGT devices deployed in Esthwaite Water, 12–14 August 1997, expressed as mean fluxes. Uptake values for other metals are included for comparison.

Metal	Water depth (m)	Control* (pmol cm <sup>-2</sup> d <sup>-1</sup> )	Trap* (pmol cm <sup>-2</sup> d <sup>-1</sup> )	Trap – Control (pmol cm <sup>-2</sup> d <sup>-1</sup> )
Mn	3.3	510±10	5,540±720	5,030
	4.0	710±30	29,500±5,000	28,800
	5.0	1,090±60	15,100±1,700	14,000
Fe	3.3	74.1±3.2	84.7±12.9	not detectable
	4.0	46.7±0.9	47.6±2.5	not detectable
	5.0	47.8±6.6	43.9±4.8	not detectable
Co	4.0	0.54±0.05	8.14±0.68	7.60
Al	4.0	100±9	191±39	91
Ba	4.0	55.2±7.1	77.2±3.6	22.0
Ni	4.0	13.3±0.5	105±0	92

\* Values given as mean and standard deviation of three devices, except for the 3.3-m and 4-m controls, which analyze two devices.

and 3). The depths at which Mn remobilization was observed, using the DGT devices, corresponded well with the depths of remobilization inferred by the profiles of dissolved Mn concentration (Fig. 4b,d). Exact correspondence would not be expected in a nonsteady-state system, given that the concentration profiles are a function of the conditions at the time of sampling, whereas the DGT device provides a time-integrated measurement.

Mn uptake by the IRT in August 1997 was highly localized, peaking at 4 m, in contrast to the downward-increasing trend observed for both the in situ dissolved Mn concentration and the uptake by the control-IRT (see Tables 1 and 3, and Fig. 4d). Previous measurements in EW with traditional sediment traps have indicated that once summer stratification is well-established, dissolved Mn is supplied to the hypolimnion predominantly through the reductive dissolution of settling Mn oxides rather than from bottom sediments, and that little or no Mn oxide reaches the sediment surface (Davison et al. 1982). It follows that there must be a midwater maximum in the rate of Mn oxide dissolution, most probably within the suboxic or upper anoxic parts of the water column and coincident with a high rate of supply of Mn oxide. At greater depth, dissolution will decrease as the supply of Mn oxide particles is diminished. The DGT data therefore provide direct evidence for this view of Mn cycling in EW. The deployment between 5 and 9 September 1996 was within the anoxic zone at 9.5 m, and there was no significant difference in Mn uptake between the IRT ( $75.5 \pm 6.7$  nmol cm<sup>-2</sup> d<sup>-1</sup>) and control-IRT ( $82.6 \pm 0.9$  nmol cm<sup>-2</sup> d<sup>-1</sup>). This is attributed to the deployment depth being below the zone of Mn oxide remobilization, i.e., all the settling Mn oxide had dissolved. These data also indicate the value and effectiveness of the control-IRT.

In contrast to Mn, Fe showed evidence of remobilization in 1996 but not in 1997 under similar redox conditions. The occurrence of Fe remobilization in 1996 was surprising because, as stated above, previous evidence has indicated that no reductive dissolution of Fe oxides occurs in the suboxic part of the water column. Although the remobilization of Fe

may have been linked to the increasingly reducing character of the water column with time during the 1996 deployment, as indicated by the upward migration of the anoxic zone, it is thought that a more likely cause was the relatively long deployment period of 8 d.

A long deployment period has the potential advantage of increasing the analytical signal but has important disadvantages. First, in a highly nonsteady-state environment, like EW, the geochemical signal associated with the DGT uptake is likely to reflect several processes as conditions change naturally with time. Probably of even greater significance is the likelihood that conditions change artificially inside the trap device. The DGT-based method attempts to provide a measure of remobilization under in situ conditions. However, conditions inside the trap (i.e., IRT) will almost certainly become more reducing with time because of the build-up of organic matter and microbial activity and the limited resupply of dissolved O<sub>2</sub> due to the lack of turbulence. Microbial activity is the reason why poisons are frequently used with traditional sediment traps (Rosa et al. 1991). The best solution to the problem in the present application is shortening the deployment time as far as possible while avoiding analytical detection problems with the DGT measurements. Shortening the deployment time is also commonly preferred to poisoning with traditional traps. Two weeks has been recommended as an acceptable exposure time when using traditional sediment traps without poisons (see Rosa et al. 1991), although this appears to be too long in the present case. It was for the above reasons that the deployment time was reduced to 48 h in 1997. The absence of any measurable Fe remobilization in 1997, even under anoxic conditions at 5 m, supports the contention that the Fe remobilization observed the previous year was linked to artificially enhanced reducing conditions in the IRTs.

As with Mn, the uptakes of Co, Al, Ba, and Ni were all significantly higher in the IRTs than in the control-IRTs in August 1996 and 1997, indicating remobilization (Tables 2 and 3). By contrast Cu showed no evidence of remobilization. Molar ratios of remobilized metal to remobilized Mn were calculated, based on the difference between the trap and control uptakes after normalizing the uptakes with respect to the appropriate diffusion coefficients. This normalization is necessary because the concentration of each metal at the membrane surface, calculated from the DGT uptake using Eq. 1, is inversely proportional to the diffusion coefficient. Table 4 shows that the DGT-derived ratios of remobilized metal to remobilized Mn in 1997, when no Fe remobilization was detectable, were similar to or higher than the corresponding ratios in 1996. Table 3 shows that the absolute amounts of trace metals remobilized in 1997 were generally large compared to any possible remobilization of Fe that year, which might have occurred but was below detection. The data therefore indicate that the reductive dissolution of Fe oxide makes no significant contribution to the observed remobilization of trace metals, even in 1996 when Fe oxide dissolution was probably artificially induced. Mn oxide dissolution is the most probable source, especially as the remobilization of Co, Al, Ba, and Ni measured by the IRTs was much greater at 4 m than at 3.3 m (the 5-m sample

Table 4. Comparison of metal:Mn molar ratios derived from DGT remobilization measurements with those from regression analysis of water column concentrations in the depth region of Mn redox cycling in Esthwaite Water.

	Aug 1996		Aug 1997 DGT-derived ratio* $\times 10^{-3}$
	DGT-derived ratio* $\times 10^{-3}$	Slope of regression of dissolved [metal] $\dagger \times 10^{-3}$	
Co	0.27	0.29	0.26
Al	1.26	2.42	3.83
Ba	0.66	2.77	0.62
Ni	0.08	0.18	3.20

\* Based on trap minus control uptakes.

$\dagger$  Based on concentrations at the 6–10-m depth.

was lost during analysis). Other sources, such as decomposing algae, cannot be discounted entirely however.

The  $T/F_{\text{calc}}$  ratio provides information about the nature and scale of the remobilization process and about possible speciation effects on limiting metal uptake by the DGT assembly (see *Concept and design of device*). Mn is the only element that is definitely undergoing active remobilization on the basis of the  $T/F_{\text{calc}}$  ratio being  $>1$  (Table 5). The effect of retarded mixing within the IRT device will be the same for all metals, so that the wide range of  $T/F_{\text{calc}}$  ratios (Table 5) reflects differences in the relative scales of remobilization and in possible speciation effects, acting alone or together. For example the high  $T/F_{\text{calc}}$  ratio ( $\sim 0.77$ ) for Co indicates that remobilization is sufficient to maintain the dissolved Co concentration in the IRT at close to its open water-column concentration, while speciation effects on uptake by the IRT must be small or negligible. In contrast the ratio for Ba is actually less than the minimal value shown in Table 5, calculated assuming resupply by molecular diffusion within the IRT device. A ratio less than the calculated minimum can only occur if the Ba measured in the filtered water sample includes species that are not taken up by DGT, such as colloids. A clearer interpretation would be possible with more information on metal speciation. Such subtleties of interpretation highlight the critical nature and benefit of the control-IRT for detecting remobilization.

On 22 August 1996, the concentrations of dissolved Co, Al, Ba, and Ni were elevated around the base of the oxycline. The trace metal concentrations in all cases correlated better with dissolved Mn ( $R \geq 0.97$ ,  $P < 0.01$ ) than with dissolved Fe ( $R \geq 0.83$ ,  $P < 0.05$ ). Table 4 shows the slopes of the linear regressions of dissolved metal against dissolved Mn for these elevated (molar) concentrations. The most striking feature is the more or less constant molar Co:Mn ratio ( $\sim 0.27 \times 10^{-3}$ ) for all the various measurements, suggesting that the dissolved Co accumulating in the mid-part of the water column is derived from Mn oxide alone and is unaffected by any other process. The DGT-derived ratio was the same in 1996 and 1997, suggesting it is a consistent feature in the lake. Another recent study of EW was unable to identify the specific source of the dissolved Co under the same conditions, on the basis of the metal concentrations

Table 5. The ratio of the observed metal uptake by the DGT trap device (T) to the calculated uptake ( $F_{\text{calc}}$ ), assuming that the concentration at the membrane surface remained constant at its water column value.

	T: $F_{\text{calc}}$	
	1996	1997
Mn	2.1	1.33
Co	0.79	0.75
Al	0.27	0.52
Ba	0.06	0.10
Ni	0.13	0.74
Minimum*	0.08	0.15

\* Calculated assuming resupply by molecular diffusion alone.

alone, because of the overlapping nature of the Co, Mn, and Fe profiles (Achterberg et al. 1997). Close relationships between dissolved Co and Mn concentrations and inventories in other lakes have also been attributed to Mn oxide as the common source (Green et al. 1989; Balistrieri et al. 1992).

The pattern with the other metals is more complicated. A consistent DGT-derived Ba:Mn ratio ( $\sim 0.64 \times 10^{-3}$ ) was observed between the 2 yr that was lower than that derived from regression of the dissolved concentrations (Table 4). These results indicate that although release from Mn oxides contributes to the elevated dissolved Ba concentrations, it is not the dominant in-lake source of dissolved Ba. This interpretation is consistent with the evidence provided by the  $T/F_{\text{calc}}$  values (see above) and by previous studies that have suggested that the elevated dissolved Ba concentrations are linked to remobilization from the ciliated protozoa, *Loxodes*, or from algae (McGrath et al. 1989). The suggestion of a link with the redox cycling of Fe (Sholkovitz and Copland 1982b) is not supported by the data. Our results are the first to indicate a Ba–Mn oxide relationship in EW, although Mn redox cycling is reported to be the major control over Ba in Lake Biwa (Sugiyama et al. 1992; Sugiyama and Hori 1994). The Al:Mn and Ni:Mn ratios are even more variable than Ba:Mn (Table 4), suggesting either there is more than one biogeochemical process affecting the distributions of Al and Ni or that the nature of the Al– and Ni–Mn oxide relationships vary during seasonal anoxia in EW.

## General discussion

The possibility that the measured remobilization is affected by modified conditions in the IRT, e.g., through enhanced microbial activity, has been discussed. Minimizing the length of deployment provides a means of avoiding or at least limiting such artifacts. The measured IRT uptake will also be affected by the semiopen nature of the device and the artificially long residence times of settling particles. If there are relatively elevated concentrations of dissolved metals within the trap tubes (only Mn in EW), resulting from active remobilization, in principle some fraction of the remobilized metal could be lost via transport from the tube. The observed control-IRT uptakes have indicated that mixing inside the tubes was predominantly by molecular diffusion both under laboratory and field conditions. Assuming a

typical molecular diffusion coefficient of  $4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , measurably elevated concentrations should only extend about 5–6 cm along the 20-cm tube after a deployment time of 1 week. Therefore in the EW deployments, a negligible amount of Mn was probably lost from the tubes.

The artificially long residence time of the particles in the IRT will lead to an overestimation of local remobilization, even without modification to the chemical and microbial conditions. As settling particles are artificially retained within the trap, they are available for dissolution for a longer period of time than they would be over the same depth interval in the open water column. The scale of the effect is related to the particle settling velocity, the dissolution rate, and the deployment time. It follows that the IRT is providing a remobilization flux integrated over some depth interval greater than that of the tube length (20 cm). The Mn remobilization fluxes ( $T-C$ ) measured by the DGT devices at 7 m in August 1996 and at 4 m in August 1997 were 41.9 and 28.8  $\text{nmol cm}^{-2} \text{ d}^{-1}$  (Tables 2 and 3) or 2.3 and 1.6  $\mu\text{g cm}^{-2} \text{ d}^{-1}$ . These fluxes are similar in magnitude to the measure of remobilization ( $4 \mu\text{g cm}^{-2} \text{ d}^{-1}$ ) obtained from the difference between the Mn settling rates at 8 m and 14.5 m in July 1979, measured using a vertical array of traditional sediment traps (Davison et al. 1982). The  $\text{O}_2\text{-H}_2\text{S}$  interface was then at a more typical depth for EW of  $\sim 9$  m, so that the difference between the 8-m and 14.5-m fluxes approximates to the depth-integrated remobilization of Mn over the suboxic and anoxic parts of the water column at that time.

The metal ratio data derived from the DGT devices provides particularly useful information on remobilization, because the ratios will be unaffected by the semiopen nature of the devices and the long residence times of settling particles within the traps. As demonstrated for Co and Ba, the resulting data can be compared directly with those obtained from other sources, such as water column profiles, to provide valuable and novel insights into element cycling. Furthermore, it is possible to obtain whole-lake budgetary information for all elements if such data exist for one of them. Thus, it is possible to obtain information about the effect of Mn redox cycling on trace metal budgets by combining the trace metal:Mn ratio data, derived from the DGT devices, with the whole-lake budgetary data for Mn in EW collected over many years.

The preliminary deployments in EW have shown that Co, Ba, Al, and Ni undergo water-column remobilization around the base of the oxycline and that this remobilization is not linked to the redox cycling of Fe but most probably to the reductive dissolution of Mn oxide. Interpretation of the DGT-trap data is improved by combining the technique with other measurements. For example, comparisons of metal:Mn ratios obtained from the DGT-trap data with those calculated from water-column concentration profiles indicate that the elevated concentrations of dissolved Co observed in suboxic and anoxic waters are derived solely from Mn oxide dissolution. In contrast the behaviors of Ba, Al, and Ni appear to be affected by at least one additional process. The DGT-trap device derives a number of benefits from its in situ application. The conditions of remobilization, although subject to possible modification, are those that occur naturally in the field. The method avoids problems associated

with storage of particles that are inevitable if remobilization is measured in laboratory incubations. The in situ deployment, together with the fact that the remobilized metals are concentrated into the resin-gel layer, minimizes contamination problems and provides high sensitivity. DGT assemblies suitable for the measurement of other determinants (e.g., P) have also been developed (Zhang et al. 1998a) so that the method has the potential to be extended to other categories of elements requiring different binding agents to Chelex.

In considering the potential for wider application of the method, particularly in the marine environment, the detection limits of the device are probably most critical. Although detection limits were not rigorously considered as part of this study, some useful conclusions can be drawn from the preliminary results. Because the data indicate that the reproducibility of the IRTs is intrinsically poorer than that of the control-IRTs, the ultimate detection limits are likely to be a function of the reproducibilities of both the trap and control devices. Therefore increasing the cross-sectional area of the devices may help to reduce the detection limits, especially in environments with a relatively small number of settling particles per unit area, as in the oceans. A comparison of the standard deviations shown in Tables 2 and 3 suggests that the ultimate detection limits have not been reached as, in the case of every metal, the absolute reproducibilities decreased with decreasing uptake. For example, with the control devices, the lowest relative ( $\pm 2\%$ ) and absolute standard deviations for Mn were obtained with the sample (3.3 m in 1997) having the lowest absolute uptake. These results suggest that the ultimate detection limits are likely to be considerably lower than indicated by the present data, especially where background solution concentrations, and hence control uptakes, are lower, as in the oceans.

It is concluded that the DGT-trap device is capable of producing valuable, direct information on remobilization of metals in the water columns of lakes and possibly the oceans. There is considerable potential for improving the design of the device with respect to both ease of handling and interpretational capabilities. For example the inclusion of a vertical DGT strip inside the tube section of the device would provide information on internal mixing conditions and hence better quantification of absolute remobilization rates.

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