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In Situ Measurements of Labile Al and Mn in Acid Mine Drainage Using Diffusive Gradients in Thin Films

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The technique of diffusive gradients in thin films (DGT) can be used for in situ measurements of labile metal species in water, but the application for this method on acid mine drainage (AMD) is complicated due to reduced sampler adsorption of metals at low pH. This study evaluates the use of DGT on labile Al and Mn in AMD (pH 3.1−4.2). DGT measurements were performed both in standard solutions in the laboratory and in situ in the field. Laboratory results show that DGT can be used in water with pH as low as 3.0 for Al and 4.0 for Mn without correcting for reduced adsorption. Below pH 4.0, the adsorption of Mn showed a linearly decrease with pH to ∼55% at pH 3.0. Taking this correction into account revealed that 84−100% of the total dissolved Al and Mn measured in the field was DGT-labile. Measurements using DGT agreed well with predictions using the speciation program WHAM VI. This study shows that the use of DGT can be extended below the previously reported pH working range for Al, and for Mn using a simple linear correction with respect to pH, and demonstrates that the technique can be applied for monitoring time-integrated labile metal concentrations at AMD sites.

Metals exist in a variety of inorganic and organic species in aquatic systems, ranging from simple hydrated molecules to large organic complexes. The availability of these metals to living organisms, and thus potential toxicity, depends on the nature of these species and methods to discriminate between them are needed to assess the environmental impact.[1−3]

A promising analytical speciation method is diffusive gradients in thin films (DGT).[4] DGT is based on the principle of diffusion of hydrated metal ions and complexes through a hydrogel layer of known thickness and pore size, followed by an immobilization of the metal ions on a chelating resin. The resin is subsequently removed, and the metals are extracted by acid and detected. Only metal species that are mobile (capable of diffusing sufficiently quickly through the hydrogel layer) and labile (dissociate within the time window of a few minutes) contribute to the measured mass. Different options of hydrogels are available for discriminat-

ing between complexes.[4] Using the conventional APA hydrogel, as in this study, allows free hydrated metal cations, most inorganic complexes, and small organic complexes to be detected.[4] As the resin only adsorbs free and kinetically labile metal ions, this approach therefore provides a better measure of biologically available metals than do dissolved or total metal concentrations.[4] A great advantage of the DGT device is that it can be deployed in situ as sampling and storage have been shown to induce changes in the nature and distribution of metal species in the water.[5] Furthermore, as the sampler provides a time-integrated measure of the labile metal concentrations in the water and can be deployed in time spans ranging from a few hours to several months,[6,7] it may consequently give a better measure in waters with great temporal variability in element composition than conventional water sampling with subsequent laboratory analysis.

A limitation to the DGT technique is the reduced performance of the chelating Chelex-resin at both high and low pH ranges, and for most metals it functions best in the pH range of 5−10.[6] The lower pH limit for the use of DGT is determined by the competition between metals and hydrogen ions for the binding agent. Cd has been found to bind relatively weakly and can only be measured down to pH 5, while Cu binds very strongly and can be measured down to pH 2.[6] Other metals usually lie between these extremes.[6] This pH working range is a challenge for the application of DGT on acid mine drainage (for monitoring metals other than Cu) where the pH is typically between 2 and 5. DGT has previously been used for Al speciation measurements in solutions as low as pH 3.5,[8−10] but DGT performance for Al has only been documented down to pH 4.0.[10] DGT measurements of Mn have previously been reported to work down to pH 3.5.[6]

In this study, the DGT technique was applied on acid mine drainage (AMD) from a coal mine waste rock pile in Svalbard (78°N), where high Al and Mn concentrations have previously been suggested to be the main cause of plant degradation in the

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area.[11] The study may also have broader interest as Al and Mn are reported to be toxic in many ecosystems where low pH levels are observed;[12] Al is known to form strong organometallic complexes that may significantly reduce toxicity,[13] and alternative Al speciation techniques such as equilibrium dialysis, Clarke's quickly reacting Al method, and the Donnan membrane technique are known to be prone to inaccuracy and are time-consuming.[14−16] It has to be noted, however, that these alternative techniques are based on different separation principles and therefore detect other fractions of Al in solution than DGT.

The aim of the study was to (1) investigate the pH-dependence of adsorption of Al and Mn on the resin layer of the DGT in the pH range from 2.5 to 4.5 under controlled conditions in the laboratory; (2) perform in situ measurements with DGT in the acid mine drainage to assess the labile concentrations of Al and Mn, applying possible corrections found in the laboratory experiment; and (3) compare observed labile concentrations with predictions using the speciation program WHAM VI.[17]

EXPERIMENTAL SECTION

DGT. Standard piston-type DGT samplers for metals obtained from DGT Research Ltd. were used throughout this study. The samplers contained a Chelex 100 chelating resin in the Na form, covered with an APA hydrogel,[18] and a 0.45-μm membrane filter as described previously.[4] Using Fick's first law of diffusion and known diffusion coefficients of metal ions within the diffusive hydrogel, concentrations of metal in the water can be determined from the amount of metal captured on the resin according to eq 1.[4] C is the concentration of metal in solution, M is the mass of

$$C = M\Delta g/DAt \qquad (1)$$

metal captured on the resin, Δg is the thickness of hydrogel and membrane filter, D is the diffusion coefficient of the metal ion within the gel, A is the exposure area, and t is the deployment time.

The mass of metal on the resin is calculated from the metal concentration in the elution sample (C_e), the volume of the elution fluid (V_{HNO_3}) and the chelating resin (V_{gel}), and an elution factor (f_e) needed to compensate for incomplete metal removal from the resin according to eq 2.[4] Hydrogel thicknesses in the supplied

$$M = \frac{C_e(V_{HNO_3} + V_{gel})}{f_e} \qquad (2)$$

DGT samplers were 0.80 mm and the membrane thickness and

exposed area for diffusion 0.13 mm and 3.14 cm^2, respectively. The diffusion coefficients provided by DGT Research Ltd. (Al, 4.14 $\times$ 10^{-6} cm^2 s^{-1}; Mn, 5.09 $\times$ 10^{-6} cm^2 s^{-1}; at 20 °C) were used for the average temperatures measured during the deployment period. The volumes of the elution fluid and the resin layer were 2.0 and 0.16 mL, respectively. An elution factor of 0.8 was applied for both Al and Mn using 1 M superpure HNO$_3$.[4]

All equipment was washed in 0.1 M HNO$_3$ and rinsed in MilliQ water prior to use, and disposable gloves were worn during all handling.

Experiments in the Laboratory. To investigate the DGT performance at low pH for Al and Mn in water similar to acid mine drainage, containers with 2.5 L of 0.01 M NaNO$_3$(based on MilliQ water) were prepared and Al(NO$_3$)$_3$ and Mn(NO$_3$)$_2$ added to a concentration of ~100 μg L^{-1} Al and Mn. The pH was adjusted to 2.5, 3.0, 3.5, 4.0, and 4.5 (three replicates) using superpure HNO$_3$ and NaOH, and the pH was checked just prior to and after the experiment (WTW multi 340i meter with SenTix 41 pH gel electrode). An initial weak NaNO$_3$ solution was used to avoid problems with DGT in very dilute solutions.[18] A DGT sampler was then added to each container and suspended vertically halfway down the container. The solutions were stirred continuously throughout the experiment. The DGT devices were deployed for 3 h and then removed and rinsed with MilliQ water, prised open for removal of the resin gels, which were then placed in polyethylene vials, and eluted in 2 mL of 1 M superpure HNO$_3$ for at least 24 h. A sample of the eluents were then taken, diluted 5 times, and analyzed by inductively coupled plasma mass spectroscopy (ICPMS; Agilent 7500CS) at the National Environmental Research Institute (NERI) in Roskilde, Denmark. Three blank DGTs were also measured following the same elution procedure. Water temperatures was measured at the beginning and at the end of the deployment period (<2 °C difference), and samples (3 replicates) of the bulk solutions were taken. Samples were analyzed for Al and Mn using ICPMS (<10% difference between beginning and end). The average temperature and Al and Mn concentration were then used to represent the solution temperature and Al and Mn concentration throughout the deployment period.

Experiments in the Field. DGT measurements were performed in situ in acid mine drainage coming from a coal mine waste rock pile (~200 000 m^3) situated in Bjørndalen on Svalbard, high-arctic Norway (78°N); see Søndergaard et al.[19] for a detailed description. The waste pile is located on a sloping mountain site where water from uphill areas, in addition to the sparse precipitation (41 mm from June to September 2005), passes through the waste rock and transports pollutants generated within the pile. Four different polluted sites were selected downstream the pile in streams and small pools with a flow velocity of more than 2 cm s^{-1} as recommended[6] and with a minimum of turbulence. The sites were chosen to represent the variation in pH observed in runoff within the area most affected by the AMD. One site (site 4) was placed in a small stream just downstream the waste pile, while the other three sites (sites 1−3) were situated in various places along an excavated trench further downstream designed for a previous experiment[19] and with the purpose of collecting all

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runoff from the pile. At these four sites, a total number of 48 DGT measurements were performed from 22 July to 11 August 2006. One DGT unit was deployed at each site during each measurement. The DGT units were left suspended vertically from a rod in the middle of the water column using a piece of fishing line and a weight tied to the end. The deployment period varied from 4 to 6 h, and the temperature and pH were measured just before and just after deployment of the DGT. The DGT unit was then removed from the water, thoroughly rinsed with MilliQ water, and stored in clean plastic Zip-lock bags until dissembled in the laboratory as described above. Three DGT units were also chosen as control blanks following the same procedure but not immersed in the water column.

Water samples were collected in the middle of the deployment period to represent the average water composition. Each sampling included two 20-mL water samples that were filtered through 0.45-μm filters and stored in polyethylene bottles in the dark at 5 °C. One of the subsamples was acidified by superpure 1 M HNO_3 to keep the pH below 2 and later analyzed by ICPMS for Fe, Al, Mn, Zn, Ni, Cu, Cr, Cd, Pb, K, Na, Mg, and Ca as well as for dissolved organic carbon (DOC) using a Shimadzu 5000A total organic carbon analyzer at the Institute of Biology, University of Copenhagen. Untreated samples were analyzed for anions (Cl^-, SO_4^{2-}, and NO_3^-) using ion chromatography (IC; Metrohm 761 Compact IC) at the Institute of Geography and Geology, University of Copenhagen. Blanks and standards were placed between every 10 samples analyzed by IC and ICPMS. In situ measurements of electrical conductivity and redox potential (using a TetraCon 325 conductivity cell and SenTix ORP redox electrode (WTW)) were made as part of the water sampling.

Modeling with WHAM VI. The speciation model WHAM VI[17,20] uses model VI[17,20] for complexation of metals by humic (HA) and fulvic acids (FA). This model is a discrete site/electrostatic model, and the parameters for describing the binding of metals to humic substances used in the model have been optimized by fitting data obtained from a wide range of laboratory studies for metal binding to isolate HA and FA.[17,20]

In this study, only the default model parameters were used and the model inputs included total dissolved concentrations of Fe(II), Fe(III), Al, Mn, Zn, Ni, Cu, Cr, Cd, Pb, K, Na, Mg, Ca, SO_4, NO_3, Cl, FA, and HA, pH, and temperature. As only total dissolved Fe was measured using ICPMS, the separation between Fe(II) and Fe(III) species were estimated by means of another speciation model PHREEQC[21] using the same input parameters as for WHAM VI and the pe values calculated from the redox measurements. While this approach may not be accurate, it was still considered acceptable as model runs assuming all Fe to exist as Fe(II) or Fe(III), respectively, resulted in a less than 7% difference in degree of complexation. As only 60−70% of the DOC is reported to be active with respect to metal binding for a range of freshwater systems,[22] 40% of the measured DOC was excluded as being inert, and the remaining 60% to comprise of 100% FA
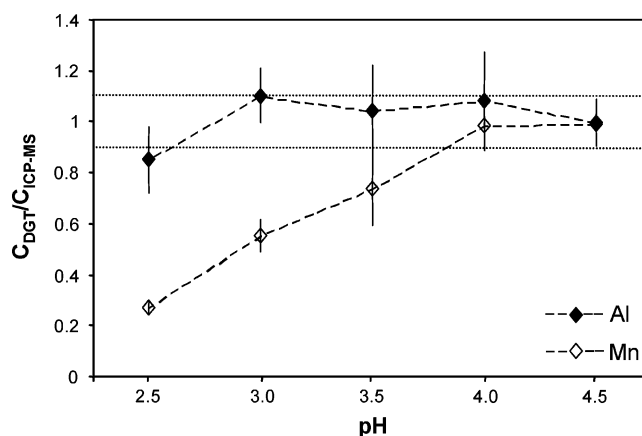
Figure 1. Effect of pH on the measurements of Al (100 μg L^{-1}) and Mn (100 μg L^{-1}) by DGT, determined by the ratio of metal concentrations measured by DGT (C_{DGT}) to the concentrations obtained by direct ICPMS measurements in solution (C_{ICPMS}). Each point represents the average ± one standard deviation of three replicates. Dotted lines show deviations of 10% from a C_{DGT}/C_{ICPMS} ratio of 1.

similarly to other speciation studies.[23] This variable, which was to be given in grams per liter FA, was calculated using the DOC concentrations by assuming 50% of the weight of FA to represent organic carbon.[24] Using 30 or 50% of the DOC as being inert instead of 40% had little effect on the degree of complexation (<6%).

RESULTS

pH Effects on DGT Measurements of Al and Mn Observed in the Laboratory. The DGT measured concentrations of Al and Mn (C_{DGT}) relative to the concentrations measured by ICPMS (C_{ICPMS}) in the pH range 2.5−4.5 are shown in Figure 1. At pH 3.0 and above, DGT measurements of Al agreed well with bulk concentrations of Al and the average values were within the 10% of precision reported for the DGT method.[4] This was also the case for Mn at pH 4.0 and above. For Al, the DGT measurements declined below pH 3.0 and were on average (±SD) 85 ± 13% at pH 2.5. DGT measurements of Mn declined below pH 4.0 to 74 ± 14% at pH 3.5, 55 ± 6% at pH 3.0, and 27 ± 3% at pH 2.5 and showed a linear trend in this pH interval (C_{DGT}/C_{ICPMS} = 0.476pH − 0.908; r^2 = 0.95; p < 0.05). The DGT performance for Mn found here was close to that reported previously[6] but suggests that measurements have to be corrected at pH 3.5. The three blank DGTs were found to contain less than 1% of the mass of Al and Mn accumulated by devices used in the experiment.

Chemical Composition of the Acid Mine Drainage. The composition of runoff coming from the waste rock pile measured at four study sites is shown in Table S-1 (Supporting Information). Total dissolved Al concentrations varied from 0.35 to 13 mg L^{-1} and Mn concentrations from 0.16 to 1.7 mg L^{-1}. DOC concentrations were 1.9−28 mg L^{-1}. The pH ranged from 3.1 to 4.2, and the redox potential varied from 716 to 805 mV relative to the standard hydrogen electrode (corresponding to pe values of 13−15). Separation of the measured total dissolved concentration of

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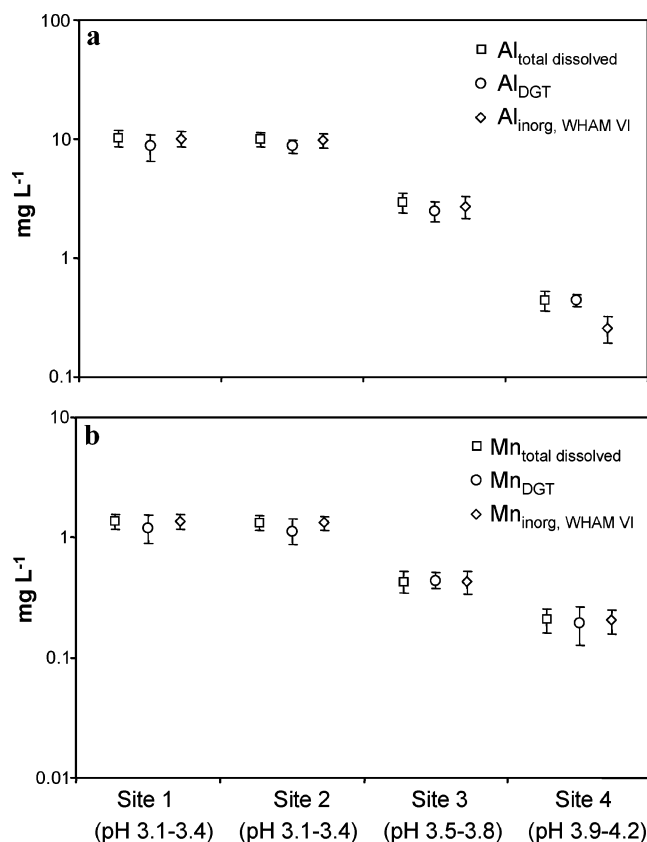
Figure 2. Speciation of Al (a) and Mn (b) in runoff from the coal mine waste rock pile in Bjørndalen during July and August 2006. Points represent mean values + one standard deviation of measured total dissolved concentrations, DGT-labile concentrations and concentrations of inorganic species modeled using WHAM VI at four study sites (n = 12, 14, 12, and 10 at sites 1, 2, 3, and 4, respectively).

Fe into Fe(II) and Fe(III) species using the speciation program PHREEQC predicted the Fe(II) species to account for 0−32% of total Fe. Ionic strengths were calculated to 2.6×10^{-3}−1.4×10^{-2}.

In Situ Measurements of Labile Al and Mn and Predicted Values Using WHAM VI. The measured average DGT-labile concentrations of Al (±SD) ranged from 84 ± 16 to 100 ± 12% of the average total dissolved concentrations of Al as shown in Figure 2a. As the performance of DGT for Al with respect to metal binding was found to be 100% down to pH 3.0, no corrections were made as the lowest pH measured in the runoff was 3.1. DGT-labile Mn concentrations were corrected below pH 4.0 by applying the regression line found previously. The corrected average DGT-labile concentrations of Mn were found to range from 85 ± 21 to 103 ± 16% of the measured total dissolved Mn concentrations (Figure 2b). Control DGTs contained less than 1% of the mass of Al and Mn accumulated by field devices.

The average concentration of total inorganic Al and Mn species as predicted by WHAM VI ranged from 58 to 100% of total dissolved Al (Figure 2a) and 98−100% of total dissolved Mn (Figure 2b), and results were within the average ± one SD from the DGT measurements, except at site 4 (pH 3.9−4.2). Here, predicted values of inorganic Al (58 ± 14% of total) were markedly lower than the DGT measured Al (100 ± 12% of total). Typical input parameters for WHAM VI are listed in Table S-2 (Supporting Information).

DISCUSSION

Application and Perspectives for Using DGT on Acid Mine Drainage. DGT have been used for measuring labile metals (Al, Fe, Cu) in acidic soil solutions with pH as low as 3.5[8−10,25] but has not previously been used on AMD. Performance tests of DGT in the laboratory using standard solutions show that DGT can be used for monitoring labile Al down to pH 3.0 without correcting for reduced adsorption at the chelating resin. For Mn, the adsorption below pH 4.0 decreases and the DGT measurements have to be corrected. A good agreement was found between total inorganic Al and Mn species in the AMD predicted by WHAM VI and in situ DGT measurements performed at field sites with a pH below 4.0. This suggests that the performance tests done in the laboratory are valid and apply to AMD sites. The WHAM VI model has previous been used successfully to describe organic complexation of Al and Mn in acidic solutions with a good agreement between total inorganic and DGT-labile species.[9,26]

The only marked difference between DGT and model results was noted for Al at site 4. There are several possible explanations for the discrepancies between measured and modeled Al at this site, which may also have more general interest: (1) The measured DOC could be more inert with respect to metal binding than assumed in the modeling. (2) Small Al−DOC complexes could contribute to the Al measured by DGT as observed previously.[9] (3) The chemical speciation of the water is not in thermodynamic equilibrium.

As site 4 has the highest pH values (pH 3.9−4.2), the degree of complexation with DOC is predicted to be highest here as DOC concentrations did not vary significantly between sites. The measured DOC was within the range observed in freshwater from other Arctic field studies.[27−30] Furthermore, water sampled at an unpolluted site upstream the waste pile contained similar amounts of DOC (results not shown), suggesting that weathering of coal within the pile did not contribute markedly to DOC measured in the runoff. Consequently, there is no reason to expect that the DOC observed at this site should differ in metal complexation ability from DOC in other freshwater systems. Reid et al.[31] found that slurry from coal contained from 31 to 69% FA and less than 1% HA, so even if all DOC observed here originated from the weathering of coal, it still would not be sufficient to explain the discrepancy.

The detection of small Al−DOC complexes by DGT would contribute to the disagreement, but the magnitude of this effect as observed by Jansen et al.[9] suggests that it is not the whole explanation. A more likely explanation to the disagreement is that the metal ions have not yet reached thermodynamic equilibrium with the DOC constituents as assumed in the modeling. In fact, at the study site, runoff from the pile containing dissolved metals

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generated within the pile is mixed and transported with water from upstream areas flowing through the pile and with additional surface water from outside the pile. The mixed water is subsequently transported downhill to the main river relatively fast (minutes). As complexation kinetics between strong organic ligands and metals in solution is known to be slow, with complete equilibration requiring up to days and weeks,[32–34] which is further reduced by the observed low water temperatures (0−5 °C), it is likely that the thermodynamic equilibrium assumed in the modeling has not yet been reached in the water at this site. As the DGT measurements of labile Al correspond to predicted values at the other sites and since DGT has previously been validated and used successfully in solutions with pH around 4.0,[8–10] it indicates that more Al is labile at this site than predicted by the model and that care should be taken when using chemical equilibrium models to assess the lability of metals in mine waste effluents.

As more than 84% of dissolved Al and more than 85% of dissolved Mn was measured to be labile at this study site and since total inorganic Fe, Zn, Ni, and Cu species are close to 100% as predicted by WHAM VI, the real strength of DGT for monitoring labile metals in AMD, compared to alternative techniques, is to perform time-integrated in situ measurements in environments with significant temporal variations. This is at least the case for AMD with a chemical composition close to that investigated. If pH in the AMD is below the 100% DGT performance limit of the metals of interest, knowledge of the temporal variation in pH as well as the pH-dependent correction factor is necessary for accurate measurements. Consequently, provided other effects such as biofouling do not present a problem, DGT has the potential to become a very valuable tool for long-term monitoring of labile concentrations of metals, including Al, Mn, Cu, Fe, and Zn in acid mine drainage.

CONCLUSIONS

This work has demonstrated for the first time that DGT can be an efficient tool to measure labile metal concentrations in AMD. The focus of this study was Al and Mn due to their suggested environmental impact in the study area. Labile Al and Mn concentrations were measured in runoff with pH as low as 3.1. Concentrations of labile Al and labile Mn, using a simple pH-dependent correction for Mn below pH 4.0, were generally in agreement with model predictions using the WHAM VI speciation program, indicating a fairly accurate estimate. DGT measures the labile metal fraction that is believed to be a better measure of the "bioavailable" metal amount than the total concentration and determines time-integrated metal concentrations during potentially long deployment periods (up to weeks/months). These results show that this technique can be a viable alternative to more conventional techniques for monitoring AMD. More detailed investigation of the pH dependence of adsorption by DGT at low pH for all metals of interest, as well as performance studies of DGT in varying real world matrixes, are needed for further future applications on AMD.

SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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