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Evaluation and Application of the Diffusive Gradients in Thin Films Technique Using a Mixed-Binding Gel Layer for Measuring Inorganic Arsenic and Metals in Mining Impacted Water and Soil

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S *Supporting Information*

ABSTRACT: The diffusive gradients in thin films (DGT) equipped with a Chelex or ferrihydrite binding gel has been designed to enable the measurement of either labile metal species or inorganic arsenic, respectively. In the mine impacted environment, metals and metalloids commonly coexist in a variety of species. This study, for the first time reports the performance of the DGT with a mixed-binding layer (MBL), consisting of Chelex and ferrihydrite for measurements of both metals and arsenic in a single assay. The MBL that consists of a combination of Chelex and ferrihydrite at a ratio of 1:2 has the greatest binding capacity for arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn). The elemental concentrations measured by using MBL-DGT (C_{DGT}) were comparable (92−104%) with the original test solution concentrations (C_{SOL}). The measurement of As by using MBL-DGT was consistent across a wide pH range (3−8) and ionic strength (0.001−0.1 M). At high pH (9), As measurement was slightly affected (~80%). The measurements of Cd, Pb, and Zn were affected at low pH (<3) and high pH (9). Measurements of Cd, Cu, and Pb were affected at low ionic strength (0.001 M). At high ionic strength (0.1 M), measurements of Cd; Cu and Pb were slightly affected. The capacity of MBL-DGT for quantitative measurement in a multielements solution is effectively limited to 15 μg for As and 70 μg for metals per MBL-DGT device. Good correlations ($p < 0.01$) between MBL-DGT measurements and ferrihydrite or Chelex DGT were obtained for As, Cd, Cu, Pb, and Zn in water and soil with exception for Cd and Cu ($p < 0.05$) when deployed in soil.
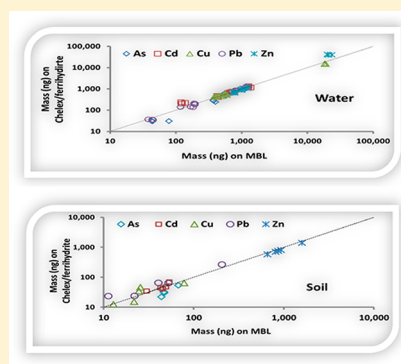
In contaminated environments, especially mining impacted areas and contaminated sites, metals and metalloids (metal/loids) commonly coexist in a variety of inorganic and organic forms ranging from simple hydrated molecules to large organic complexes. The bioavailability of metal/loids to organisms in contaminated water and soil is dependent on the type of metal/loid species present. Free metal/loid species are known to be the most toxic forms to biological organisms.[1] The biological response of organisms to metals in water is proportional to the free-ion activity of the metals, based on the free-ion activity model (FIAM), rather than to their total or dissolved concentrations.[2] Hence, determining the bioavailable fractions of contaminants in water and sediment is recognized as a necessary step for predicting their effect on biota and for assessment of the degree of contamination in water and sediment.[3]

The technique of diffusive gradients in thin-films (DGT) was developed for *in situ* measurement of labile metal species in aquatic systems.[4] Since the first published application of the technique,[5] the DGT has been applied to various aspects of environmental chemistry including metal speciation, metal toxicity and bioavailability, metal−ligand complexation kinetics, and metal complexation-capacity. The DGT technique has been investigated as a surrogate for bioaccumulation of Cu, Cd, Pb, and Zn by mussels[6] and for the accumulation of Cu in the

gills of rainbow trout.[7] Previous study suggested that Cu toxicity on *Daphnia magna* could be predicted from DGT measurements.[8] Gill uptake of aluminum (Al) was more accurately predicted by this technique compared to conventional measurements of Al, as evidenced by strong linear correlations with fish physiological response, increased blood glucose levels, and decreased plasma chloride.[9] It is reported that the better prediction by DGT was attributed to the measurement being *in situ*.[10] The results from a study[11] on assessing heavy metal pollution and ecotoxicological status of rivers showed good correlations between values measured from sediment extracts and DGT measurements at toxic and potentially toxic levels of metals in the sediments. These results support the suitability of using a combination of point and DGT measurements for assessing the chemical and ecotoxicological status of aqueous environments.

To date, the DGT technique has been designed only to be used for separate measurements of either labile metal or inorganic arsenic species. In conventional deployment, a Chelex binding DGT (referred to as Chelex DGT) device is used to

measure labile metal species,[4] whereas inorganic As species,[12−14] inorganic and organic As species,[15] and phosphorus (P)[16,17] are measured using a ferrihydrite binding DGT (referred to as ferrihydrite DGT). A mixed-binding layer (MBL) gel, consisting of Chelex and ferrihydrite adsorbent has been successfully tested for measurement of copper (Cu), manganese (Mn), molybdenum (Mo), and phosphorus (P) in both standard test solution and agricultural soils,[17] but the simultaneous measurements of As, Cd, Cu, Pb, and Zn using an MBL have not yet been evaluated.

This paper reports the first study that investigates the performance characteristics of MBL-DGT (Chelex and ferrihydrite absorbents) for measuring inorganic As and labile metals in a single determination. We focused on As, Cd, Cu, Zn, and Pb as they are commonly found together in soil and water associated with mining impacted environments.

■ MATERIALS AND METHODS

DGT Theory. The principle and application of DGT technology in water and soil have been extensively discussed in other studies.[18,19] Briefly, an ion-exchange resin layer is separated from the bulk solution by an ion-permeable hydrogel membrane (diffusive gel layer) of thickness Δg. Metal ions that diffuse through the diffusive gel layer become rapidly bound by the resin layer. Assuming the concentration gradient of the ions remains constant during deployment time (t), the flux F (mol cm^{-2} s^{-1}) of an ion through the diffusive gel layer is given by Fick's first law of diffusion (eq 1) and the concentration of ions measured by the DGT (C_{DGT}) can be calculated using eq 2[18]

$$F = DC/\Delta g \tag{1}$$

$$C_{DGT} = M\Delta g/(DtA) \tag{2}$$

where D is the diffusion coefficient (cm^2 s^{-1}) for a given metal ion, C is the bulk concentration of an ion, A, the area of hydrogel membrane (cm^2) exposed to the bulk solution, and M, the mass of metals (ng) accumulated in the resin layer over time, t (s). M is determined by eluting the metals from the binding resin layer, followed by analysis using an inductively coupled plasma mass spectrometry (ICPMS) (X7 Thermo Fisher Scientific, Waltham). The MBL-DGT devices used in this study for measurement of both metals and metalloids were equipped with a 0.8 mm thickness diffusion gel layer. Therefore, the diffusion coefficients D of 5.04×10^{-6} cm^2 s^{-1} (at 24 °C) of As reported from a previous study[13] for a 0.8 mm thickness diffusion gel layer plus the thickness of the filter membrane (0.13 mm) were applied in this study.

When DGT devices are deployed in a well-stirred simple standard test solution of large enough volume so that the tested elements are not significantly depleted during the testing period, the concentration (μg L^{-1}) measured by DGT C_{DGT} will theoretically equal the concentration of the test solution (C_{SOL}). In this study, 2 L of a standard test solution containing 50 μg L^{-1} of a mixture of the tested elements, at pH 6 and 0.01 M NaNO$_3$ ionic strength, was used to test the functionality of mixed-binding layer in the DGT device.

The DGT equipped with ferrihydrite binding and open pore diffusive gel were reported for determining successfully total dissolved inorganic As species (As^V and As^{III}).[12,13] In addition, it was suggested that there was no competition effect between As^V and As^{III} in the mixed As^V/As^{III} solution that affect the adsorption of either As species onto the ferrihydrite gel. Therefore, in this study As^V was used in all standard test

solutions for the MBL-DGT. As only inorganic As species was of interest in this study, throughout this paper As^V refers to the inorganic species exclusively.

MBL Gel Preparation. The MBL was prepared by mixing two ion-binding agents, Chelex and ferrihydrite in a gel solution consisting of agarose-derived cross-linker with Milli-Q water and a 40% acrylamide solution.[18] Chelex is commercially available (Bio-Rad Laboratories), and ferrihydrite was prepared as a slurry by titrating 1 M NaOH to 0.1 M Fe(NO$_3$)$_3$ solution until a dark reddish-brown ferrihydrite precipitate was obtained at a pH between 6 and 7. During titration, the solution was vigorously stirred to ensure that the pH did not exceed 7 so that the binding characteristics of the ferrihydrite were not affected.[13,17] The precipitate was washed 3 times with Milli-Q water and stored at 4 °C in the dark. Prior to use, the ferrihydrite slurry was drained of excess water. Three ratios by weight, 1:1; 1:2, and 2:1, of Chelex/ferrihydrite were used in the preparation and testing of the MBL. The MBL was produced by thinly casting mixtures of gel solution and binding agents between two glass plates at setting at 42 °C for 1 h. The MBL gel was observed under a light by the naked eye after it had completely set in order to ensure that an even distribution of the binding agents was achieved. The thickness of the MBL gel produced for this study was 0.6 mm[17] (gel volume was 0.225 mL), which was greater than that of the single binding gel (either Chelex or ferrihydrite) and ensured adequate strength for handling. The MBL and the diffusive hydrogel formed the basis of the DGT which were housed in a plastic molding as detailed by the DGT Research Ltd. (http://www.dgtresearch. com) with an exposure window of 3.14 cm^2 for deployment in test solutions, waters, and soils.

Sample Handling and Detection Limits. The MBL and diffusive gels were prepared, and MBL-DGT was assembled in a laminar flow cabinet in the clean laboratory class-100 at Lancaster Environment Centre, Lancaster University, U.K. Standard test solutions for all experiments detailed below were prepared as mixed elemental (As, Cd, Cu, Pb, and Zn) solutions with elemental concentrations of 50 or 100 μg L^{-1} by dissolving appropriate amounts of analytical grade (Analar) Na$_2$HAsO$_4$·7H$_2$O, Cd(NO$_3$)$_2$·4H$_2$O, Cu (NO$_3$)$_2$·2.5H$_2$O, Pb-(NO$_3$)$_2$, and Zn(NO$_3$)$_2$·6H$_2$O salts in Milli-Q water. Ultrapure HNO$_3$ (SuperPura) was used for eluting the elements from the binding gel by immersion of a binding gel in 1.2 mL of 3 M HNO$_3$ over at least a 24 h period prior to being analyzed by ICPMS.

To minimize contamination, all centrifuge and sample tubes were acid washed (10% HNO$_3$) and rinsed three times with Milli-Q water (18.2 MΩ cm) prior to use. The Certified Reference Material (CRM) TM24.3 (Environment Canada) was selected to validate the analyses made by ICPMS because its chemical properties were approximately similar to natural fresh water and the standard test solutions used in the experiment. Analytical recovery in the ICPMS measurements were checked by including three replicates of the CMR TM24.3 in each batch of the analyzed samples.

Detection limits for each element included in this study were individually determined using blank MBL-DGT units (3 replicates) included from each of individual experiments (5 experiments) of this study (total 3 × 5 = 15). The minimum detection limit (MDL) per MBL-DGT device (ng per device) for each element was obtained as the mean value of the blanks plus 3 times its standard deviation.[20] To enable comparison with experimental data for waters and soils, the MDL values

were converted to solution concentrations (μg L^{-1}) for each element using eq 2 with 24 h deployment and 0.8 mm diffusive gel.

Characterization of MBL-DGT Performance. *Kinetics Binding of MBL Gel.* Experiments were conducted to evaluate the kinetics of ionic binding onto the MBL. MBL discs (3 replicates) were placed in separate vials containing 10 mL of the ~50 μg L^{-1} test solution. Elemental concentration in the test solution was measured at the start and end of deployment. Deployment time intervals were 3, 6, 10, 20, and 40 min and 1 and 2 h. The mass of each tested element that had accumulated onto the MBL discs was determined by using ICPMS.

Elution Efficiencies. The MBL discs were placed in separate vials containing a 10 mL mixed-element test solution, with a concentration of ~50 μg L^{-1}, for 2 h, after which time the binding gels were eluted using four different concentrations of HNO$_3$: 1, 2, 3, and 4 M (1.2 mL of acid per gel). The elemental concentrations in the test solutions before and after deployment and the mass of elements eluted from MBL discs using the different HNO$_3$ concentrations were measured using the ICPMS to obtain elution efficiency.

MBL-DGT Solution Measurement. Three MBL-DGT units were immersed in a 2 L standard test solution containing ~50 μg L^{-1} of mixtures test elements (As, Cd, Cu, Pb, and Zn), with background ionic strength of 0.01 M NaNO$_3$ and pH 6.1. The MBL-DGT units were placed facing the center of the container in such a manner that the plane of the DGT exposure window was vertical and parallel to the wall of the container. The solution was stirred well during the deployment time of 4 h. Aliquots of the solution were sampled prior to immersion, after 2 h of deployment and after 4 h with concurrent solution temperature measurement. The concentrations of As, Cd, Cu, Pb, and Zn in the test solutions and DGTs were measured by ICPMS, and the results were calculated to give C_{DGT} metal concentrations and solution concentrations (C_{SOL}) as described previously for comparison against each other.

Effect of pH and Ionic Strength (IS). To test the effect of pH on MBL-DGT function, MBL-DGT units (with 3 replicates per test) were deployed in the 2 L standard ~50 μg L^{-1} test solution with the pH ranging from approximately 3 to 9. The pH of each solution was adjusted with 0.01 M HCl or 0.01 M NaOH and allowed to stabilize over 24 h prior to adding the stock solution of tested elements to make up ~50 μg L^{-1}.

The effect of ionic strength on MBL-DGT performance was tested at 0.001 and 0.1 M NaNO$_3$ ionic strengths. MBL-DGT units (with 3 replicates per test) were deployed in 2 L of ~50 μg L^{-1} test solutions appropriately adjusted to the required ionic strength with NaNO$_3$. The results were compared against the results obtained from the standard test solution at 0.01 M NaNO$_3$ ionic strength at the same pH and elemental concentrations.

MBL-DGT Capacity. The binding capacity of the MBL-DGT units were determined by deployment in well-stirred solutions with a high (approximately 4 mg L^{-1}) concentration of Cd and Zn, and lower (0.2 to 1.3 mg L^{-1}) concentrations of As, Cu and Pb, for time periods ranging from 1, 2, 4, 6, 8, 12, 16, 24, 48, and 72 h. The accumulated mass of test element after each time period was measured to determine the maximum binding capacity of the MBL of As and metals.

MBL-DGT Deployment in Waters. Water samples were collected from five mining impacted creeks and analyzed for elemental concentrations and the following physicochemical properties [pH, dissolved organic carbon (DOC), water hardness, sulfate (SO$_4$$^{2-}$), nitrate (NO$_3$$^-$), and chloride (Cl$^-$)]. To ensure an adequate concentration range of the test elements, several water samples were spiked with As, Cd, Cu, Zn, and Pb solutions where required corresponding to the required range of concentrations. Three types of binding layer DGT (MBL-DGT, Chelex-DGT, and ferrihydrite-DGT) with 3 replicates for each test were deployed in 2 L of each water sample and stirred well during deployment. The deployment times varied from 4 to 8 h.

MBL-DGT Deployment in Soils. Soil samples from five mining-impacted areas in Queensland, Australia, were collected, air-dried and sieved to give the <2 mm fraction. Total concentrations of test element were analyzed by ICPMS as described. The samples had high total concentrations of As, Cd, and Zn but were low in Cu and Pb, hence Cu and Pb (~500 mg L^{-1} solution) were added to the samples to achieve an adequate range of concentrations (Table S3 in the Supporting Information). The soils were incubated at approximately 50% of water-holding capacity (WHC) for 2 weeks at room temperature and then wetted to 80% WHC with Milli-Q water and allowed to equilibrate for 24 h, prior to DGT deployment to achieve the sufficient moisture level for DGT deployment. The total dissolved metal concentrations (C_{SOL}) in the soil solution were determined from the samples that had been used to determine C_{DGT} after separation of the water phase using a Eppendorf centrifuge 5818 at 1,509g for 5 min and filtered using the 0.45 μm filter. The measured MBL binding capacity and the highest concentrations of As and metal measured in the soil water extracts were used to determine the deployment time to avoid exceeding the MBL capacity. Deployment time was kept to 4 h for soils to avoid exceeding the capacity of the MBL.

Samples of the DGT eluted and the soil solutions (C_{SOL}) were analyzed by ICPMS. The concentration in the soil obtained using DGT (C_{DGT}) was calculated from the eluted concentration as described.[19] DGT devices consisting of the standard Chelex or ferrihydrite single binding agent were deployed in all the water and soil samples in a similar manner to the MBL-DGT experiment described above in order to compare the performance of the mixed binding layer to the DGT with a single binding agent.

RESULTS AND DISCUSSION

Ratio of Mixed Binding Agents. The preliminary results show that the binding efficiency of As was found to be dependent on the amount of ferrihydrite incorporated in the MBL. The mass of arsenic binding into the MBL decreased slightly (~20%) with decreased amounts of ferrihydrite. On the other hand, the uptake of metals (Cd, Cu, Pb, and Zn) was unaffected by the amount of Chelex in the MBL. In addition, increasing the amount of ferrihydrite affected the distribution of both Chelex and ferrihydrite on the gel causing variation of the amount of binding agents on each MBL disk. The 1:2 ratio of Chelex/ferrihydrite produced a more even distribution of the binding agents on the MBL and also resulted in the greatest binding capacity for As and the metals. Therefore, the MBL gel with a 1:2 Chelex/ferrihydrite ratio (1.5 g of Chelex and 3 g of ferrihydrite slurry for 10 mL of gel solution) was chosen for further characterization. The MBL gel in this study contains ~65% ferrihydrite to that of a single ferrihydrite binding gel for As reported by previous studies[12,13] and ~35% Chelex to that of a conventional Chelex DGT for metals.[16]

Table 1. Blanks and Minimum Detection Limits (MDL)[a] of the MBL-DGT and Recovery (%) of CRM TM24.3 on ICPMS for Tested Elements

		As	Cd	Cu	Pb	Zn
Blank (ng/device)		0.9 ± 0.3	0.7 ± 0.1	5.2 ± 1.6	1.3 ± 0.7	8.6 ± 3.0
MDL (ng/device)		0.9	0.3	4.8	2.1	9
MDL ($\mu g\ L^{-1}$) solution[b]		0.06	0.03	0.28	0.1	0.54
TVF[c]		13	0.2	1.4	3.4	8
TVF[d]		13	0.54	3.5	13.6	20
Recovery % of	min	82 ± 5	85 ± 4	85 ± 2	88 ± 1	89 ± 5
CRM TM24.3	max	99 ± 2	104 ± 3	102 ± 2	98 ± 2	109 ± 7

[a]Refer to text for the method used to calculate the MDL. [b]Required solution concentration to obtain MBL-DGT for a 24 h deployment using 0.8 mm diffusive gel at 23 °C. [c]Trigger values to protect 95% freshwater species in soft water[21] (water hardness, 0−60 mg L^{-1} as $CaCO_3$). [d]Trigger values to protect 95% freshwater species in moderate water[21] (water hardness, 60−120 mg L^{-1} as $CaCO_3$).
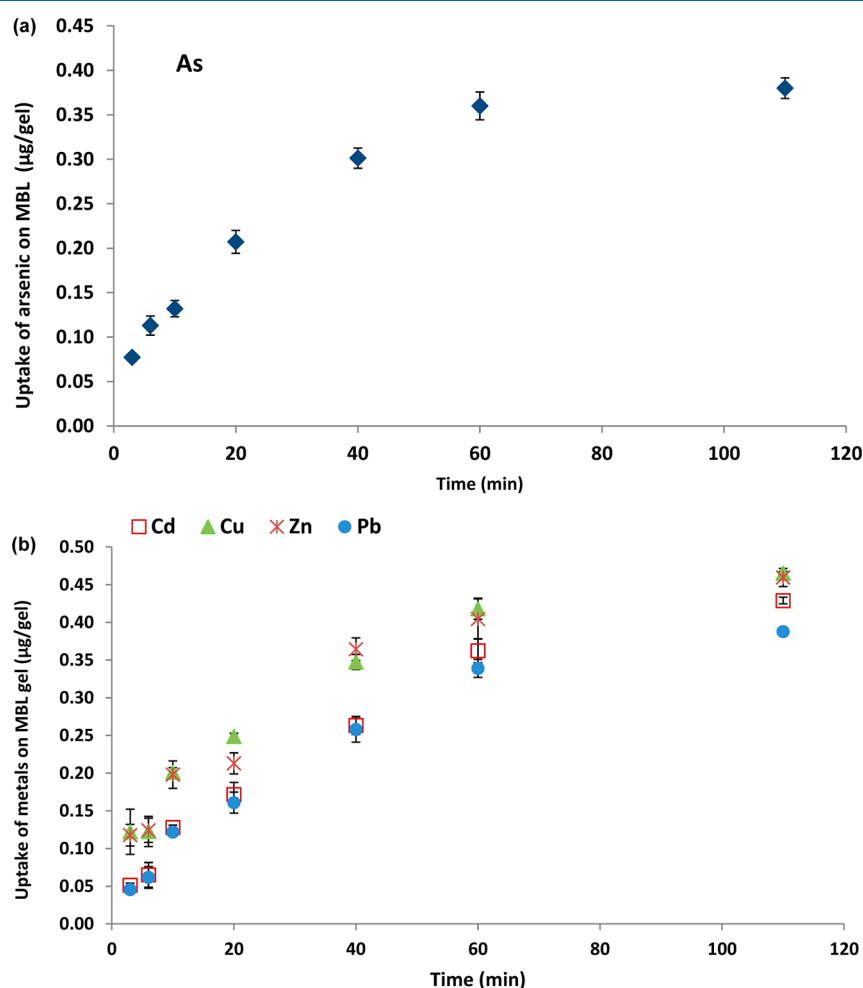

Figure 1. Mass of As (a) and metals (b) accumulated on the MBL gel vs time in test solution (10 mL of ∼50 $\mu g\ L^{-1}$ As, Cd, Cu, Pb, and Zn; pH 6.2, and 0.01 M $NaNO_3$). The measured concentrations of the test solution alone are presented in the Supporting Information (S2).

MBL-DGT Method Detection Limits. The minimum detection limits of the MBL-DGT for As, Cd, Cu, Pb, and Zn ranged from 0.03 $\mu g\ L^{-1}$ for Cd to 0.54 $\mu g\ L^{-1}$ for Zn (Table 1). The trigger values for contaminants in Australian freshwater to protect 95% freshwater species[21] with water hardness ranging from soft to moderate and commonly found in mining-impacted water are shown in Table 1. Comparison of the results shows that the detection limits achieved with MBL-DGT are well below the trigger values of contaminants to protect 95% freshwater species in soft water (lowest trigger values) and average concentrations of contaminants in soil

solution. This suggested that there was unlikely to be a constraint on the use of the MBL-DGT for measurement and assessment of As, Cd, Cu, Pb, and Zn as contaminants in water and soil ecosystems.

Recovery of Certified Reference Material (TM 24.3). The recovery percentage of the test elements using TM 24.3 (Environment Canada Ltd.) varied with time of measurements as indicated by the range of values (Table 1). Nevertheless, recoveries for all elements were within an acceptable range provided by the Environment Canada Ltd. for TM 24.3. The
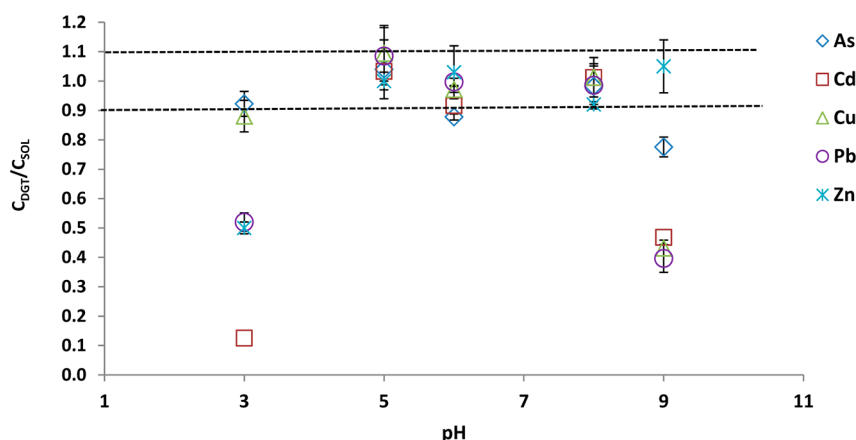
Figure 2. Effects of pH (3−9) on the performance of MBL-DGT in test solution. Dotted lines represent the accepted limits (error bars are standard error). The test solution contained 50 μg L^{-1} mixed tested elements at 0.01 M ionic strength.
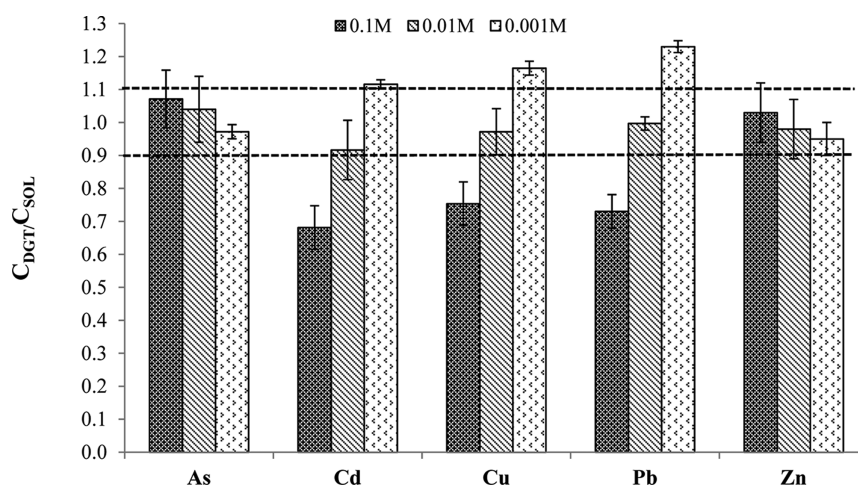

Figure 3. Effects of ionic strength (0.001, 0.01, and 0.1 M NaNO$_3$) on the performance of MBL-DGT. Dotted lines represent the accepted limits. The test solution contained 50 μg L^{-1} mixed tested elements at pH 6.

acceptance recovery range were about 90−110% for As, Cd, Cu, and Pb and 85−115% for Zn.[22]

Kinetics Binding of MBL Gel. All tested elements (As, Cd, Cu, Pb, and Zn) had bound onto the MBL gel with a sharp increase uptake in the initial minutes of exposure (Figure 1). The initially step curve illustrates the fast binding of both metals and As to the MBL. This effective and rapid binding satisfies the basis of the DGT principle, which requires that the elemental concentration at the binding gel surface is effectively zero. As only a small amount of metals or/and As are needed to establish the linear gradient in the diffusion layer, the fact that the binding of As by the MBL was slightly slower than that of metals after 10 min is not a problem.

Elution Efficiencies. The recovery percentages of As and metals increased as the concentration of the acid increased up to 3 M but remained the same with further increase to 4 M HNO$_3$. The highest concentration elution efficiencies were 78 ± 6% (As); 71 ± 1% (Cd); 79 ± 1% (Cu); 68 ± 1% (Pb); and 76 ± 1% (Zn). Therefore, 1.2 mL of 3 M HNO$_3$ per gel was used for all subsequent experiments as an eluent, and the values of elution efficiencies were applied in the C_{DGT} calculations.

MBL-DGT Solution Measurement. The concentrations of As, Cd, Cu, Pb, and Zn measured by DGT (C_{DGT}) deployed in the ~50 μg L^{-1} standard solution (at pH 6 and 0.01 M NaNO$_3$ ionic strength) was in good agreement with the element

concentrations (C_{SOL}) measured directly in the solution. The mean ± se ratios C_{DGT}/C_{SOL} ($n = 3$) for As, Cd, Cu, Pb, and Zn were 1.04 (±0.1), 0.92 (±0.09), 0.97 (±0.07), 1.00 (±0.02), and 0.98 (±0.09), respectively. These results indicate that MBL-DGT used in this study will allow simultaneous quantitative measurement of the tested elements in the test solution.

Effect of pH and Ionic Strength. The concentrations of As and Cu measured by MBL-DGT (C_{DGT}) agreed well with solution concentrations (C_{SOL}) between pH 3 and 8; however, for a pH of 3, C_{DGT} for Cd, Pb, and Zn were smaller than those of the solution concentrations (Figure 2). A possible reason for the smaller values may be competition for binding sites on the Chelex[17] from H$^+$ and Fe^{3+} cations from iron oxide at the low pH. Therefore, MBL-DGT should be used with caution in soil or water at a pH of 3. At a pH of 9, C_{DGT} for all metals except Zn was significantly lower. The effect of pH on MBL-DGT measurement for Zn was in agreement with the results reported by a previous study,[17] which found that Zn uptake by MBL was not affected at pH > 8. Arsenic was affected to a lesser extent than the metals.

At ionic strengths 0.001 and 0.01 M, C_{DGT} for elements (As, Cd, Cu, Pb, and Zn) were close to solution concentration (C_{SOL}) (Figure 3) and in agreement with previous work.[23] At the highest ionic strength (0.1 M) tested in this study, C_{DGT} for

Table 2. Elemental Competition Effects

	C_{DGT}/C_{SOL}				
Tests[a]	As	Cd	Cu	Pb	Zn
As-Cd-Cu-Zn-Pb	0.88 ± 0.09	0.92 ± 0.09	0.97 ± 0.07	1.00 ± 0.02	1.05 ± 0.08
As-Cd-Cu	1.04 ± 0.01	1.05 ± 0.01	0.85 ± 0.01		
As-Cd	1.09 ± 0.03	0.98 ± 0.19			
As-Cu	1.02 ± 0.02		0.86 ± 0.08		
As-Pb	0.93 ± 0.01			0.91 ± 0.09	
As-Zn	1.02 ± 0.03				0.90 ± 0.10

[a]Test solution contained 400 μg L^{-1} mixed tested elements at pH 6 and 0.01 M ionic strength.
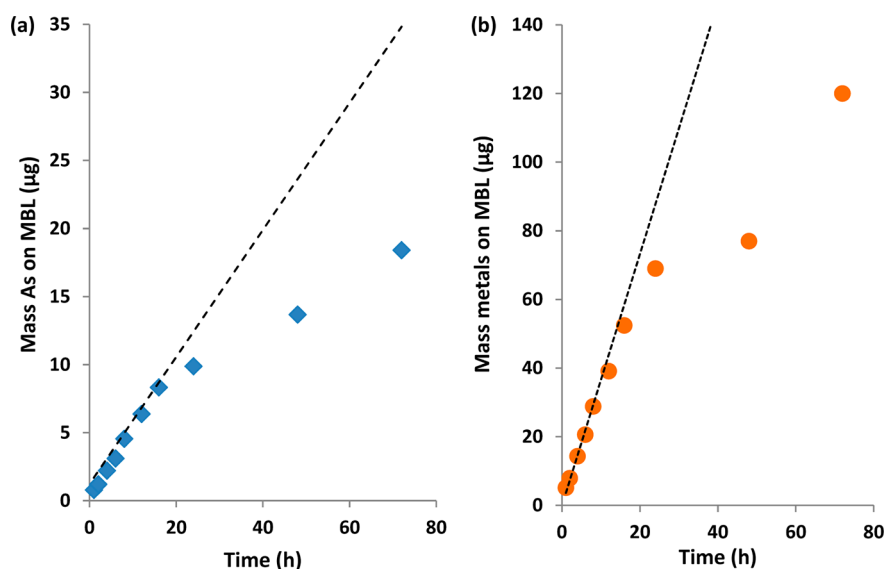

Figure 4. Binding capacity of MBL-DGT (μg) for arsenic (a) and metals (b) in multielements solution. The dotted lines represent the predicted accumulated mass of arsenic and metals by eq 2 from known concentrations.

As and Zn only were not affected, however, for all other elements were lower than solution concentrations.

Elemental Competition. The kinetics of binding based on mass uptake showed that the rate of uptake of As by the MBL gel was slightly slower compared to the uptake of metals (Figure 1). The effect of elemental competition on MBL binding in 6 test solutions of high element concentration (400 μg L^{-1}) showed that the DGT measurement of As (C_{DGT}/C_{SOL}) was unaffected by the presence of one or more metals (Table 2) (values close to 1). The presence of all four metals showed a slightly lowering of mean DGT measured As concentration. Additionally, there was no significant competition between metals for binding sites with C_{DGT}/C_{SOL} values for all being close to 1. The results suggested that possible competition effects between metals with the present of As were likely to be negligible even though the kinetics binding of As into MBL was slower than for the tested metals. This indicates that the fast kinetics of binding of elements to the MBL in the first few minute is crucial for accurate DGT measurement.

Capacity of MBL-DGT. The mass of arsenic and metals taken up by MBL-DGT deployed in the high concentrations multiple elements showed an initial linear increase with deployment time (Figure 4). In the linear region, the uptake of elements was close to the theoretical line calculated (using eq 2) from the known concentrations of the elements in solution, implying that the capacity of the MBL gel was not exceeded at these concentrations. With longer deployment times (beyond 20 h), a linear relationship was not observed and

a significant reduction in mass of metals was observed after 48 h. This indicated that the MBL capacity for metals was exceeded at this point. After 20 h deployment, As uptake maintained a linear increase but at a reduced rate compared to the theoretical predicted line. The results suggest that the uptake capacity per MBL-DGT in a multielement solution of this study was approximately ~15 μg for As and ~70 μg for metals per device. As described above, the mixed binding agents in the MBL was approximately 35% of Chelex for binding metals and 65% of ferrihydrite for As compared to that of single Chelex gel or ferrihydrite gel. The value for As was in good agreement with published studies using single gel binding capacity of ferrihydrite (~30 μg) for arsenic[12,13] pro-rata of binding agent incorporated in the MBL. However, for metal the much lower capacity compared to Chelex gel (~600 μg)[19] may be due to coating of ferrihydrite on the Chelex resin. The effective capacity of the MBL-DGT is limited to 15 μg of As and 70 μg of metals per MBL-DGT (0.6 mm MBL gel thickness, 3.14 cm^2, and 0.225 mL gel volume).

MBL-DGT Deployment in Water and Soil. The test water samples covered wide ranges of water quality and chemical properties and tested elements including pH (4−9); DOC (3−6 mg L^{-1}); water hardness (60−4000 mg L^{-1} as CaCO$_3$); sulfate (12−7000 mg L^{-1}); nitrate (1−11 mg L^{-1}); chloride (30−204 mg L^{-1}); As (100−500 μgL^{-1}); Cd (150−1000 μg L^{-1}); Cu (300−120 000 μg L^{-1}); Pb (30−550 μgL^{-1}), and Zn (100−21 500 μg L^{-1}) (Tables S1 and S3 in the Supporting Information). The soil samples used in this study
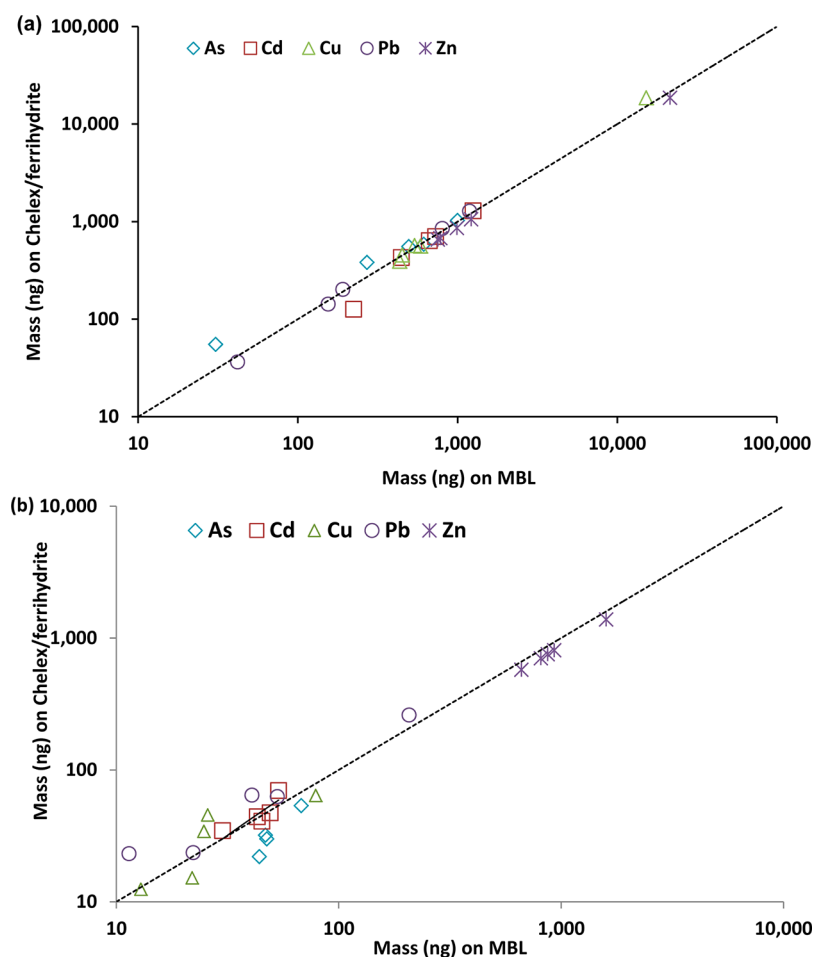
Figure 5. Measured mass (ng) obtained with the MBL-DGT, as compared with mass measured (ng) obtained with the ferrihydrite-DGT for As and with Chelex-DGT for Cd, Pb, and Zn in waters (a) and soils (b). Dotted line represents the 1-to-1.

Table 3. Correlations of Measurements Made by MBL-DGT with Measurements (μg L^{-1}) Using Either Chelex-DGT or Ferrihydrite-DGT

Samples		As	Cd	Cu	Pb	Zn	whole data set
Water	R^2	0.98	0.99	0.99	0.99	1.00	0.99
($n = 5$)	slope	0.96	1.1	1.2	1.1	0.87	0.87
	p^a	0.0006	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Soil	R^2	0.97	0.67	0.73	0.99	0.99	0.96
($n = 5$)	slope	1.1	1.2	0.70	1.2	0.87	0.88
	p^a	0.0011	0.046	0.048	<0.0001	0.0007	<0.0001

^{a}The p values from the tests show the significance of the correlations.

had a wide spectrum of soil solution concentrations of tested elements including As (10−100 μg L^{-1}); Cd (30−65 μg L^{-1}); Cu (20−70 μg L^{-1}); Pb (30−550 μg L^{-1}), and Zn (450−900 μg L^{-1}). The 1:5 soil/water pH of 5 soil samples varied from 5 to 6.5.

Measurements made by MBL-DGT were comparable to those made by Chelex (for metals) or ferrihydrite (for arsenic) in water (Figure 5a) and soils (Figure 5b). The correlation coefficient (R^2) and slope of tested elements measured by MBL-DGT with measurements made by Chelex or ferrihydrite are presented in Table 3. Correlation coefficients (R^2) ranged from 0.98 to 1.00 with all $p < 0.001$ for all test elements in water. Even though, concentrations of sulfate were high in two water samples (W2 and W3) (Table S1 in the Supporting Information), the results indicates that sulfate in water did not affect the measurements of DGT and confirmed results from a previous study.[24] Combining the whole data set for As, Cd, Cu, Pb, and Zn measurements in waters resulted in slopes and correlation coefficients of 0.99 and 0.87, respectively (Table 3).

For soil measurement, the correlation coefficient (R^2) and slopes of As, Pb, and Zn measured by MBL-DGT were comparable with those measurements made by ferrihydrite and Chelex (Table 3). The low values of R^2 for Cd (0.67) and Cu (0.73) with $p < 0.05$ and with a slope of 0.7 (Cu) were observed. The lower slope indicates higher mass accumulated in MBL-DGT. This could be due to possible Cu contamination in ferrihydrite used in MBL. However, combining the whole data set for As, Cd, Cu, Pb, and Zn measurements in soils

resulted in slopes and correlation coefficients of 0.88 and 0.96, respectively. These results are comparable with MBL-DGT measurements for P, Cu, Mn, and Mo (slope of 0.97 and R^2 of 0.95) reported for MBL-DGT deployed in eight agriculture soils.[17] The combination of Chelex and ferrihydrite at the ratio of 1:2 in a MBL binding gel did not appear to prevent the simultaneous accumulation of arsenic and metals from waters and soils.

CONCLUSIONS

The results of this study contribute to a gap in knowledge on the use of MBL-DGT for a single measurement of arsenic and metals which commonly coexist in contaminated environments. Specifically, the DGT equipped with a MBL gel consisting of a combination of Chelex and ferrihydrite in a 1:2 ratio allows simultaneous measurement of As, Cd, Cu, Pb, and Zn tested over a range of solution and deployment conditions. The 3 M HNO_3 (1.2 mL per gel) was found to be the most effective eluent for MBL gel with efficiencies of $78 \pm 6\%$ (As); $71 \pm 1\%$ (Cd); $79 \pm 1\%$ (Cu); $68 \pm 1\%$ (Pb), and $76 \pm 1\%$ (Zn).

The measurements of As by MBL-DGT were consistent across a wide pH range (3–8) and ionic strengths (0.001–0.1 M). However, measurements of Cd, Zn, and Pb were affected at low pH (≤ 3) and of As, Cd, Cu, and Pb at high pH (≥ 9). Low ionic strength (0.001 M) affected measurement of Cd, Cu, and Pb, but at high ionic strength (0.1 M) measurement of Cu and Pb was slightly affected. The capacity of MBL-DGT to enable quantitative measurements in a multielement solution was effectively limited to 15 μg for As and 70 μg for metals (Cd, Cu, Pb, and Zn) per MBL-DGT device.

The performance of MBL-DGT was effective for environmental samples for metals and arsenic when deployed in waters with a wide range of contaminants and physicochemical properties. Good correlations ($p < 0.01$) between MBL-DGT measurements and either DGT devices with Chelex or ferrihydrite gels were obtained for As, Cd, Cu, Pb, and Zn in waters indicating that the MBL-DGT can be deployed in these media with a wide range of concentrations. The MBL-DGT measurements for soils were comparable to those measurements made by ferrihydrite and Chelex except that lower correlations for ($p < 0.05$) Cd and Cu were observed. Caution will be necessary when deploy MBL-DGT for soil to determine Cd and Cu. However, combining the whole data set for all test elements in mining impacted soils resulted in comparable slopes and correlation coefficients with a previous study in agriculture soils. The performance of MBL-DGT tested in this study suggests that MBL-DGT would be a very useful technique for determining labile As and metals (in a single determination) to be applied in the assessment process of water and sediment quality from mining impacted area. Furthermore, the MBL-DGT may be a more cost-effective and robust method for the simultaneous measurement of As and metals in waters and soils compared to existing single binding gel DGT methods.

ASSOCIATED CONTENT

ⓈSupporting Information

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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Notes

The authors declare no competing financial interest.

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