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Influence of Sulfide Nanoparticles on Dissolved Mercury and Zinc Quantification by Diffusive Gradient in Thin-Film Passive Samplers

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Abstract

Diffusive gradient in thin-film (DGT) passive samplers are frequently used to monitor the concentrations of metals such as mercury and zinc in sediments and other aquatic environments. The application of these samplers generally presumes that they quantify only the dissolved fraction and not particle-bound metal species that are too large to migrate into the sampler. However, metals associated with very small nanoparticles (smaller than the pore size of DGT samplers) can be abundant in certain environments, yet the implications of these nanoparticles for DGT measurements are unclear. The objective of this study was to determine how the performance of the DGT sampler is affected by the presence of nanoparticulate species of Hg and Zn. DGT samplers were exposed to solutions containing known amounts of dissolved Hg(II) and nanoparticulate HgS (or dissolved Zn(II) and nanoparticulate ZnS). The amounts of Hg and Zn accumulated onto the DGT samplers were quantified over hours to days, and the rates of diffusion of the dissolved metal (i.e., the effective diffusion coefficient D) into the sampler's diffusion layer were calculated and compared for solutions containing varying concentrations of nanoparticles. The results suggested that the nanoparticles deposited on the surface of the samplers might have acted as sorbents, slowing the migration of the dissolved species into the samplers. The consequence was that the DGT sampler data underestimated the dissolved metal concentration in the solution. In addition, X-ray absorption spectroscopy was employed to determine the speciation of the Hg accumulated on the sampler binding layer, and the results indicated that HgS nanoparticles did not appear to directly contribute to the DGT measurement. Overall, our findings suggest that the deployment of DGT samplers in settings where nanoparticles are relevant (e.g.,

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ASSOCIATED CONTENT

Supporting Information

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Tables showing stability constants employed to calculate speciation in uptake experiments. Additional details on the synthesis of 3-mercaptopropyl-functionalized silica gel, preparation of the DGT sampler, metal uptake tests for examining the performance of the binding layer, elution of metals from the filter and agarose layers, and calculation of the diffusion coefficient. Figures showing TEM images of HgS and ZnS nanoparticles, the removal efficiency of dissolved Zn(II) and Hg(II), the uptake of dissolved Zn(II) by DGT samplers, and the structure of a normal and a modified DGT sampler. (PDF)

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sediments) may result in DGT data that incorrectly estimated the dissolved metal concentrations. Models for metal uptake into the sampler may need to be reconsidered.

Graphical Abstract

INTRODUCTION

Diffusive gradient in thin-film (DGT) passive samplers are being increasingly used to monitor for dissolved metals concentrations in aqueous environments and predict their bioavailability to aquatic biota.^{1–3} DGT sampling devices are composed of a diffusion gel layered over a metal-binding resin that strongly binds the metal of interest and drives the uptake of the metal into the sampler.^{1,2} Because of the small pores of the diffusion gel layer (e.g., the commonly used agarose diffusion gels have $d_{\text{pore}} = 77 \pm 11 \text{ nm}$),⁴ it is often assumed that only dissolved metal species can pass through the diffusion layer and accumulate on the binding layer. As such, the mass of metal accumulated m on the binding layer is assumed to be related to the time-weighted average concentration C_b of dissolved metal in bulk solution, as described by the following equation:

$$C_b = \frac{m \times \Delta g}{D \times A \times t} \quad (1)$$

where g is the thickness of the diffusion layer, D is the effective diffusion coefficient of the metal in the diffusion layer, A is the sampling area, and t is the deployment time.^{1,2} Thus, by using eq 1, the concentration of dissolved metal in bulk solution C_b can be deduced by the mass of metal accumulated on the sampler after a known deployment time in the field. In the application of the DGT sampler, researchers often interpreted the resulting C_b value to signify the “truly dissolved” concentration of metal in water and sediment, and this value would then indicate or correlate to the bioavailable metal concentration.^{5–7}

In two recent studies, however, findings have pointed to the possibility of small nanoparticles passing through the diffusion layer and contributing to the DGT measurement. Van der Veecken et al.⁸ reported that latex particles ($d = 260 \text{ nm}$) absorbed with Pb were able to pass through a polyacrylamide gel because of the wide pore-size distribution of this gel. However, this observation was questioned by Davison and Zhang, who argued that such large nanoparticles would undergo trapped diffusion and would not be able to penetrate the gel.² In another study, Pouran et al.⁹ reported that ZnO nanoparticles with $d = 30\text{--}50 \text{ nm}$ could diffuse through both polyacrylamide and agarose gels at rates that were nearly as fast

as those of dissolved Zn species. This result is rather surprising because particles of this size are expected to diffuse at rates that are orders of magnitude slower than those of dissolved species.² However, we note that ZnO dissolution was not independently monitored in this study⁹ despite the fact that ZnO nanoparticles are relatively soluble ($K_{sp} = \sim 10^{-17}$)^{10,11} and are known to dissolve quickly in aqueous solutions.¹² As such, the high diffusion coefficient for ZnO obtained by Pouran et al.⁹ likely derived from the release of dissolved Zn from ZnO nanoparticles.

While there is currently no consensus on the maximum size of the nanoparticles that can pass through the diffusion layer, the possible contribution of nanoparticles to the DGT measurement could be important for the application of the samplers. For example, if nanoparticles are taken up by DGTs, these samplers could be used to quantify nanoparticles in situ, as suggested by Pouran et al.⁹ Moreover, in scenarios where both dissolved and nanoparticulate metal species are taken up by the sampler, eq 1 would not be relevant because m would represent the total accumulated mass of dissolved and nanoparticulate species, which should differ in their effective diffusion coefficient D . Additionally, data provided by DGT samplers would not necessarily indicate metal bioavailability because dissolved metal and nanoparticulate species generally do not exhibit similar bioavailabilities (e.g., in our previous studies, bacterial cultures amended with HgS nanoparticles produced significantly less methyl mercury than those amended with dissolved Hg(II)).^{13,14} For the above reasons, a better understanding of the effect of nanoparticles on the DGT measurement is critical for the application of these samplers, especially in settings where the metal of interest coexists as dissolved and nanoparticulate species.

The objective of our study was to further investigate the effect of nanoparticles on the performance of DGT samplers as a method to quantify dissolved metal concentrations. For this purpose, DGT samplers were exposed to solutions containing mixtures of dissolved Hg(II) and nanoparticulate HgS or dissolved Zn(II) and nanoparticulate ZnS. These mixtures were chosen because (1) Hg and Zn are present in many contaminated sediments, and the speciation of these metals are relevant for metal bioavailability and sediment remediation;^{15–17} (2) in sediments and other anoxic settings, Hg and Zn can persist as a mixture of dissolved and particulate species, including very small metal sulfide nanoparticles ($d < 30$ nm);^{17–21} and (3) DGT samplers are being increasingly proposed as a means to monitor these metals in sediments.^{22–26} Thus, our research is directly relevant to both understanding the effect of nanoparticles on the performance of DGT samplers in general and to the application of the samplers for monitoring Hg and Zn in sediments. To assess the reliability of the DGT measurement, we compared the concentrations of dissolved Hg(II) and Zn(II) measured by DGT samplers with the values obtained by independent measurement methods (i.e., filtration and anodic stripping voltammetry). The speciation of Hg accumulated on the binding layer of the sampler was also examined by X-ray absorption spectroscopy to look for the presence of HgS nanoparticles.

MATERIALS AND METHODS

Materials

Unless noted otherwise, all chemicals used were obtained at the highest available purity. HgS and ZnS nanoparticle stock solutions (nano-HgS and nano-ZnS, respectively) were synthesized by reacting dissolved Hg(II) and Zn(II) with equimolar amounts of S(−II) in solutions containing an excess amount of Suwannee River humic acid (SRHA) following the procedures reported in our previous studies.^{14,20} The nanoparticles were characterized by transmission electron microscopy (JEOL 2100, operated at 200 kV), which revealed that the average primary particle sizes of nano-HgS and nano-ZnS were approximately 6 (± 2.3) and 3.7 (± 1.5) nm, respectively (Figures S1 and S2). The hydrodynamic diameter in the nano-HgS and nano-ZnS stock solutions ranged from $d_h = 30$ –60 nm, as determined by dynamic light scattering (Zetasizer Nano NS, Malvern).

The DGT samplers were constructed with a nitrocellulose membrane filter (average pore size of 0.45 μm), a 0.75 mm thick agarose diffusion layer ($d_{\text{pore}} = 77 \pm 11 \text{ nm}^4$), and a thiol-functionalized silica binding layer. Detailed information on the preparation of the samplers can be found in the Supporting Information and Figures S3 and S4.

DGT Uptake Experiments with Hg and Zn

All uptake experiments were conducted at room temperature ($20 \pm 1 \text{ }^\circ\text{C}$) using hydrochloric acid washed Erlenmeyer flasks that contained 200 mL of test solution. All solutions contained 10 mM NaNO_3 (background electrolyte) and were buffered to pH 7.5–7.7 with 0.5 mM NaHCO_3 (in the experiments with Hg) or 2 mM sodium 4-(2-hydroxyethyl)piperazine-1-ethanesulfonate (HEPES) (in the experiments with Zn). All solutions were prepared using 18.2 $\text{M}\Omega\cdot\text{cm}$ water (Milli-Q reference, EMD Millipore).

In the experiments with Hg, 5 nM of Hg was added to the solution in the form of either $\text{Hg}(\text{NO}_3)_2$ (for the dissolved Hg(II) only experiment) or nano-HgS (for the dissolved Hg(II) and HgS nanoparticles experiment). Note that the source of dissolved Hg(II) in this experiment came from the dissolution of the added HgS nanoparticles. In the experiments with Zn, each solution contained 1000 nM $\text{Zn}(\text{NO}_3)_2$ and 0–5000 nM nano-ZnS. After the addition of the metals, the solutions were kept for ca. 24 h to equilibrate the dissolved and nanoparticulate species. The reactors then were capped with a DGT sampler, inverted, and swirled continuously on an orbital shaker table.

Because the HgS and ZnS nanoparticles were synthesized in the presence of SRHA, the addition of different aliquots of nanoparticle stocks into the DGT reactors introduced different amount of SRHA into the experimental solutions. To maintain a similar solution composition in all experiments, we supplemented different amounts of SRHA to each reactor so that the final concentration of SRHA was 1 mg of C per liter. This was also the concentration of SRHA in the dissolved Hg(II) only and Zn(II) only experiments. Speciation calculations indicated that under our experimental conditions, 100% of the dissolved Hg was in the form of Hg–SRHA complexes, while ca. 31% of the total dissolved Zn was in the form of Zn–SRHA complexes, with the remaining 69% was in the form of Zn^{2+} , ZnOH^+ ,

and ZnNO_3^+ . (Dissolved sulfide was assumed to be absent; see the Supporting Information for further information).

At predetermined time intervals, two reactors were sacrificed and subsampled for measurements of total and dissolved metal concentration in the aqueous phase. In addition, the DGT samplers were disassembled, and the amounts of metal accumulated on the filter, the agarose diffusion layer, and the binding layer were quantified by acid digestion, followed by analysis of the metal in the digestate (see the Supporting Information for information on the acid digestion procedures).

Chemical Analysis

For total Hg analysis, the samples were first preserved with 2.5% (v/v) bromine monochloride for 24 h and analyzed using stannous chloride reduction, amalgamation, cold-vapor atomic-fluorescence spectrometry (CV-AFS) following method 1631 (Environmental Protection Agency).²⁷ Dissolved Hg(II) was analyzed by filtering the sample through a 0.02 μm aluminum oxide syringe filter (Anotop, Whatman) and quantifying for Hg in the filtrate by CV-AFS. Our previous work¹³ indicated that more than 95% of the Hg from a suspension of HgS nanoparticles was captured by this filter.

Samples for total Zn analysis were first acidified with a solution of 0.19 wt % HCl and 1.4 wt % HNO_3 and analyzed by inductively coupled plasma–mass spectrometry (ICP–MS). Total dissolved Zn(II) (i.e., free Zn^{2+} and dissolved Zn(II) complexes) was analyzed by anodic stripping voltammetry (ASV) with a hanging mercury-drop electrode according to methods described in Jiang and Hsu-Kim.¹² This previous work demonstrated that ASV can be used to determine dissolved Zn concentration in a nanoparticle suspension and was consistent with separate measurements using ultracentrifugation and ICP–MS. While the ASV peak height or peak area at the Zn reduction potential (-1.0 V versus Ag/AgCl reference electrode) is linear with dissolved Zn concentration in solution, the slope of this relationship can decrease in the presence of NOM. Therefore, calibrations for the ASV method were constructed with matrix-matched standards (i.e., the same pH, ionic strength, and SRHA concentration as the test mixtures).

Analysis of Hg Speciation by Extended X-Ray Absorption Fine-Structure Spectroscopy

Hg L_{III}-edge X-ray absorption fine-structure spectroscopy (EXAFS; 12 284 eV) was used to investigate the speciation of Hg accumulated on the binding layer. The DGT samplers were first exposed to solutions of 5000 nM nano-HgS for 7 days, after which the binding layers were retrieved, dried, and homogenized using a mortar and a pestle, loaded on an aluminum sample holder, and sealed with Kapton tape.

Hg L_{III}-edge EXAFS spectra were collected on beamline 11–2 at the Stanford Synchrotron Radiation Lightsource following the procedure described previously.¹⁴ The speciation of Hg in the samples were determined by linear combination fitting of the k^3 -weighted EXAFS spectra over a k range of 2.5–9.5 $\text{\AA}^{-1}$, using the spectra of the $\text{Hg}(\text{cysteine})_2$ complex and HgS nanoparticles as references. The $\text{Hg}(\text{cysteine})_2$ and HgS nanoparticle references were prepared according to the procedure reported in Nagy et al.²⁸ and Pham et al.,¹⁴

respectively. Data alignment, deglitching, merging, normalization, background subtraction, k^3 -weighting, and linear combination fitting were performed using the data analysis program Athena.

RESULTS AND DISCUSSION

Impact of Metal Sulfide Nanoparticles on the Uptake of Metal into DGT Samplers

In both of the experiments in which Hg was added as dissolved Hg(II) and as nano-HgS (which will be denoted as the “Hg(II)” and the “nano-HgS” experiments from this point forward), the mass of Hg accumulated onto the binding layer of the DGT sampler increased linearly with exposure time (Figure 1A), as would be expected if the uptake of metal into the sampler was driven by the dissolved Hg(II) concentration gradient in the agarose diffusion layer (i.e., eq 1). The rate of Hg uptake in the nano-HgS experiment was over 4 times slower than that in the Hg(II) experiment (i.e., the slope of 0.0418 ng h^{-1} for the nano-HgS experiment versus 0.178 ng h^{-1} for the Hg(II) experiment; see Figure 1A). According to eq 1, the slower Hg uptake in the nano-HgS experiment could be attributable to the lower concentration of Hg species (C_b) or the slower diffusion coefficient (D) of these species in the agarose layer.

To gain further insight, we quantified the concentration of dissolved Hg in these experiments, employing a $0.02 \text{ }\mu\text{m}$ aluminum oxide filter for the separation from the particulate fraction (Figure 1B). The dissolved Hg was operationally defined as the Hg that passed through the filter. Our previous work indicated that HgS nanoparticles are captured by these filters¹³ even though a fraction of the HgS nanoparticle aggregates could be smaller than 20 nm (i.e., the filter size cutoff) and theoretically can pass through the filter. In the Hg(II) experiment, over 90% of the total Hg passed through the filter, suggesting that most of the added Hg remained in the dissolved form (Figure 1B). In the nano-HgS experiment, between 53 and 67% of the total Hg passed through the filter, suggesting that some of the added nano-HgS underwent a dissolution process that released dissolved Hg(II) into the solution (Figure 1B). Also measured in these experiments was the total concentration of Hg in the solutions, the results of which showed a gradual decrease in the total concentration of Hg over time. The Hg losses were approximately 20% and 30% in the Hg(II) and nano-HgS experiments, respectively, and these unaccounted fractions were presumed to be lost to the sorption of Hg to the container walls and to the part of the DGT plastic housing that was exposed to the solution. Only a small fraction of the Hg loss (i.e., less than 5% of the total loss) was due to the accumulation of Hg on the DGT's filter, the diffusion gel, and the binding layer. The Hg loss to the container walls is not surprising because Hg is relatively hydrophobic, and its tendency to stick to the surface of containers has long been recognized.²⁹

To determine the effective diffusion coefficient D of the dissolved Hg(II) in the agarose diffusion layer, we first normalized the mass of Hg accumulated by the measured concentration of dissolved Hg in each reactor (i.e., the filtered Hg), and the normalized data were plotted versus the experiment duration (Figure 1C). Linear least-squares regressions of these plots yielded slope values of $0.046 \text{ ng nM}^{-1}\text{h}^{-1}$ and $0.022 \text{ ng nM}^{-1}\text{h}^{-1}$. When these values were applied to eq 1, the diffusion coefficient D was found to be $D_1 = 2.92 \times 10^{-6}$

($\text{cm}^2\cdot\text{s}^{-1}$) and $D_2 = 1.39 \times 10^{-6}$ ($\text{cm}^2\cdot\text{s}^{-1}$) for the Hg(II) and nano-HgS experiments, respectively (see the Supporting Information and Figure S5 for detailed explanation on the calculation of D). These results suggest that in the nano-HgS experiment, the dissolved Hg(II) species diffused through the agarose layer at a rate that was twice as slow than that in the Hg(II) experiment. However, it is possible that by defining the filtered Hg as the dissolved Hg(II), we may have underestimated D_2 if some of the filtered Hg were in fact HgS nanoparticles.

Recognizing the limitation associated with quantifying dissolved Hg by the filtration method, we performed similar DGT uptake experiments with Zn and employed anodic stripping voltammetry (ASV) to reliably quantify the dissolved Zn(II) in a mixture of dissolved and nanoparticulate species (refer to Jiang and Hsu-Kim¹² for further information about the ASV method). The Zn experiments were conducted with solutions containing an initial dissolved Zn(II) concentration of 1000 nM and an initial nanoparticulate ZnS (nano-ZnS) concentration range of 0–5000 nM. The ASV measurements throughout the course of these experiments showed that the concentrations of dissolved Zn(II) were relatively constant between 800 and 1000 nM and did not vary appreciably with the nano-ZnS concentration (Figure 2A). Similar to what was observed in the nano-HgS experiment, the presence of nano-ZnS also decreased the rate of Zn uptake into the DGT samplers, with the uptake rate being inversely proportional to the concentration of nano-ZnS in the solution (Figure 2B). Using the dissolved Zn(II) concentration-normalized data (Figure 2C) and the slope values of the lines obtained by least-squares regression of these data (for the purpose of clarity, the regression lines are not shown in Figure 2C), the effective diffusion coefficients for Zn in the agarose layer were calculated to be $D = 3.20 \times 10^{-6}$, 3.24×10^{-6} , 2.93×10^{-6} , 2.19×10^{-6} , and 1.56×10^{-6} ($\text{cm}^2\cdot\text{s}^{-1}$) in the presence of 0, 500, 1000, 2000, and 5000 nM nano-ZnS, respectively. While the presence of 500 and 1000 nM nano-ZnS did not appreciably affect the diffusion coefficient of Zn in the agarose layer, the presence of higher nano-ZnS concentrations (2000 and 5000 nM) decreased the value of D by approximately 1.5 and 2 times, respectively.

Both the Hg and Zn experiments indicate that the presence of nanoparticles slows the uptake of dissolved metal into the DGT sampler. In the Zn experiments, the amounts of Zn accumulated on the filter and agarose layers in the 1 μM Zn(II) + 5 μM nano-ZnS experiment were 2–20 times greater than those in the 1 μM Zn(II) only experiment (Figure 3A). Thus, a possible explanation for the slower metal uptake into the sampler could be that the nanoparticles deposited on the filter and the agarose layers and might have acted as sorbents for metal ions, which decreased the rate at which the dissolved metal species diffused through these layers. In the Hg experiments, in contrast, no clear difference in the amounts of Hg accumulated on the filter and agarose layers was observed between the Hg(II) and the nano-HgS experiments (Figure 3B). However, if a fraction of the accumulated Hg was nanoparticles, the migration of the dissolved Hg(II) species through these layers could also have been retarded due to sorption on the nanoparticles. Attempts were made to identify the nature of Hg accumulated on these two layers (e.g., by using electron microscopy coupled with energy dispersive X-ray spectroscopy and by measurements of acid-volatile sulfide). However, our attempts were unsuccessful for both

Hg and Zn experiments because the amounts the metals and sulfide accumulated were below the detection capability of these methods.

Possibility for the Uptake of Nanoparticles into DGT Samplers

In the previous section, we showed that nanoparticles could decrease the uptake rate of dissolved metal into the DGT sampler. One question that remained to be answered in our research is whether the ZnS and HgS nanoparticles were directly taken up by the DGT samplers. In other words, did the nanoparticles go all the way through the agarose diffusion layer and deposit on the binding layer?

To answer this question, we employed X-ray absorption spectroscopy to examine the speciation of Hg on the binding layer from DGT uptake experiments. For DGT samplers exposed for 7 days to a mixture of dissolved Hg(II) and HgS nanoparticles, the k^3 -weighted Hg-L_{III} EXAFS spectra of the binding layer was best fit to a combination of Hg(cysteine)₂ reference spectra ($84 \pm 2\%$) and the HgS nanoparticles ($16 \pm 2\%$) (Figure 4). In contrast, for a binding layer that was directly reacted with dissolved Hg (also for 7 days), the spectral features were fit to 100% with the Hg(cysteine)₂ reference. We note that these experiments were performed with a relatively large total Hg concentration (5000 nM, i.e., 1000 times greater than in experiments shown in Figure 1), which was necessary to accumulate enough Hg on the binding layer for the EXAFS analysis. Nevertheless, these results indicate the uptake of nanoparticulate HgS into the sampler or the formation of HgS at the surface of the binding layer (i.e., via the precipitation reaction between dissolved Hg(II) and S(II) that had diffused into the sampler; dissolved S(II) was from the dissolution of the HgS nanoparticles).

We believe, however, that the HgS nanoparticles were not penetrating all the way into the DGT sampler, a conclusion made on the basis of a separate experiment with modified DGT samplers (m-DGT) constructed with multiple diffusion layers. In this experiment, the m-DGT contained three agarose layers beneath the filter, but unlike a normal DGT sampler, it did not have a binding layer (Figure S5). The binding layer acts as an infinite sink for metal ions that accumulate in the sampler. Thus, the absence of this binding layer means that there would be no driving force for the continuous uptake of metal into the sampler, and the concentration of metal should be equal across all layers once equilibrium is reached. This was indeed the case when the m-DGT samplers were exposed for 8–49 h to solutions containing only dissolved Hg(II); the mass of Hg on the three diffusion layers were equal to each other (Figure 5A). In contrast, when these samplers were exposed to a mixture of dissolved and nanoparticulate HgS, an increased amount of Hg was observed to accumulate on the outer agarose layer relative to the underlying agarose layers (Figure 5B). This result suggests that, unlike the dissolved Hg(II) species, the HgS nanoparticles were not able to penetrate through the first agarose layer. (The Hg accumulated on the second and third layers is likely the dissolved Hg(II) species that passed through the first layer). Alternatively, the fact that the amounts of Hg accumulated on the agarose layers in the nano-HgS experiment (Figure 5B) were lower than those in the dissolved Hg(II) experiment (Figure 5A) suggests that the HgS nanoparticles were diffusing at a much slower rate than the dissolved Hg(II) species. Therefore, even if the HgS nanoparticles were capable of

penetrating through the agarose diffusion layer, they would not have contributed significantly to the DGT measurement within the two-day experimental time frame. For this reason, the HgS nanoparticles detected on the binding layer in the EXAFS experiment (i.e., $16 \pm 2\%$ of the total Hg on the binding layer) were most likely formed in situ at the surface of the binding layer.

Implication for Interpreting DGT Data

Our research demonstrates the complexity of interpreting DGT data for Hg and Zn, as well as for other metals, if the samplers are deployed in settings where dissolved metal and their corresponding nanoparticles coexist (e.g., in anoxic sediments, surface waters impacted by wastewater discharge and sediment resuspension).^{30–32} In particular, we showed that the dissolved metal species diffused through the DGT diffusion layer at slower rates in the presence of nanoparticles and that their effective diffusion coefficients were not equal to a single value but varied with the concentration of the nanoparticles. Therefore, an erroneous C_b value could be obtained if one utilizes eq 1 without considering the influence of nanoparticles on the effective diffusion coefficient D . For example, in the experiments with Zn, if we were to use a D value of $3.20 \times 10^{-6} \text{ (cm}^2\cdot\text{s}^{-1}\text{)}$ (i.e., the value obtained from the nanoparticle-free experiment), we would have underestimated the concentration of dissolved Zn in the 1000 nM Zn(II) + 5000 nM nano-ZnS experiment by at least 50%. Under conditions with higher nanoparticle-to-dissolved metal ratio, a more pronounced effect could be expected. We also note that other small particles, such as colloidal organic matter, could yield the same outcome of accumulating on the DGT and sorbing metal ion species. DGT measurements in such conditions could significantly underestimate the actual concentrations of dissolved metal in the solution. Research investigating the importance of parameters such as the nanoparticle-to-dissolved metal ratio, concentration and type of dissolved organic carbon, and solution chemistry on the rates of metal uptake by DGT samplers in the presence of nanoparticles is currently underway.

Given that the diffusion coefficient of dissolved metal species could be dependent on the concentration of nanoparticles, it would be challenging, if not impossible, to obtain the true C_b value from DGT measurements in settings where an unknown amount of nanoparticles exists. However, this does not necessarily mean that the use of DGT samplers should be discouraged in such settings. While our experiments indicated that nanoparticles slowed the uptake of dissolved metal species into the DGT samplers, nanoparticles might perform a similar function for dissolved-metal uptake to certain organisms that do not actively take up nanoparticles (e.g., bacteria). Therefore, DGT samplers may still be utilized as a useful means of predicting metal bioavailability for some circumstances. Previous studies have shown that metal bioavailability and toxicity correlated with metal uptake rates into DGT samplers.^{22,23,26,33} Thus, future research investigating the potential use of DGT samplers as a metal bioavailability indicator in the presence of nanoparticles should explore the relationship between the rate of metal uptake into DGT samplers and the rate of uptake by microorganisms.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

Time-course DGT experiments with solutions containing dissolved Hg(II) (red) and mixture of dissolved Hg(II) and nano-HgS (blue). (A) Amounts of Hg accumulated on the DGT binding layer; (B) concentrations of total (open symbols) and filtered (filled symbols) Hg. Filtered Hg was defined as the Hg that passed through a 0.02 μm aluminum oxide filter. (C) Amounts of Hg accumulated on the DGT binding layer normalized by the concentration of filtered Hg (i.e., data in (A) divided by the filtered Hg data in (B)). Experimental conditions: all solutions contained 10 mM NaNO₃ and 1 mg C/L Suwannee River humic acid and had a

pH of 7.5–7.7. Hg was added to a total concentration of 5 nM as dissolved Hg (red) or nano-HgS (blue). The addition of nano-HgS to the solutions resulted in the partial dissolution of nanoparticles, resulting in a mixture of dissolved Hg(II) and nano-HgS. Experiments were conducted in duplicate, and the average values along with the range are presented.

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Figure 2.

Time-course DGT experiments with solutions containing dissolved Zn(II) and mixtures of dissolved Zn(II) and nano-ZnS. (A) concentrations of dissolved Zn(II) measured by anodic stripping voltammetry (ASV); (B) amounts of Zn accumulated on the DGT binding layer; (C) amounts of Zn accumulated on the DGT binding layer normalized by the concentration of dissolved Zn measured by ASV (i.e., data in figure (B) divided by filtered Hg data in figure (A)). Experimental conditions: all solutions contained 10 mM NaNO₃, 1000 nM dissolved Zn, ZnS nanoparticles (0–5000 nM), and 1 mg C/L Suwannee River humic acid

and had a pH of 7.5–7.7. Experiments were conducted in duplicate, and the average values along with the range are presented.

Figure 3.

(A) Mass of Zn accumulated on the filter and agarose layers in the DGT experiments with 1000 nM dissolved Zn(II) (black) and 1000 nM dissolved Zn(II) with 5000 nM nano-ZnS (blue). (B) Mass of Hg accumulated on the filter and agarose layers in the DGT experiments with 5 nM dissolved Hg(II) (red) and 5 nM nano-HgS (blue).

Figure 4.

k^3 -weighted Hg L_{III} -EXAFS spectra of HgS nanoparticles (blue), dissolved Hg-(cysteine)₂ complex (red), dissolved Hg sorbed to thiolated silica beads (green), and Hg on the binding layer of the DGT sampler that was in contact for 7 d with a solution containing 5000 nM nano-HgS (nanoHgS-DGT). Dashed lines: the fits obtained by linear combination fitting, employing the spectra of Hg(cysteine)₂ and nano-HgS as fitting end-members.

Figure 5.

Experiments with DGT samplers that have three agarose diffusion layers and no binding layer. The samplers were exposed for 8 to 49 h to solutions containing 5 nM dissolved Hg(II) (A) or 5 nM nano-HgS (B). All solutions contained 10 mM NaNO₃, 0.5 mM NaHCO₃ (pH of 7.5–7.7), and 1 mg C/L Suwannee River humic acid. (Due to the limited availability of the m-DGT, replicate experiments were not conducted. Therefore, the bars in this figure represent a single sample).