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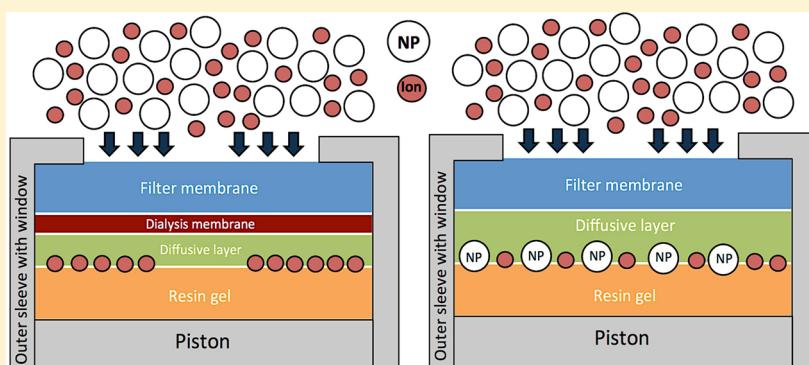
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Measurement of ZnO Nanoparticles Using Diffusive Gradients in Thin Films: Binding and Diffusional Characteristics

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ABSTRACT: Rapid growth in finding new applications for manufactured nanomaterials (MNM) has recently been accompanied by awareness about their related adverse toxicological and environmental impacts. Due to their intrinsic nature, measuring available concentrations of MNMs in the environment is a major challenge. This research is a launching point toward filling this gap, as it presents the potential of the well-established diffusive gradients in thin films (DGT) technique to determine MNMs concentrations *in situ*. Two binding layers commonly used in DGT devices were shown to be able to bind ZnO nanoparticles (ZnO NPs). The use of different types of diffusive layers demonstrated the critical role of their pore size for selective function of the DGT devices. The ZnO NPs can pass through the open pore diffusive layer used in standard DGT devices and be retained by the binding resin layer. However, the diffusion of ZnO NPs can be prevented when a 1000 MWCO (molecular weight cut off) dialysis membrane is placed in the front of the diffusive gel layer. A combination of two or more DGT devices with known diffusive layer properties should enable deduction of concentrations of available ZnO NPs in the environment. Unlike metal ions, determining diffusion coefficient values for ZnO NPs is challenging and greatly affected by shape, morphology, and solution-induced changes of the particles. Attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) demonstrated that retention of ZnO NPs by Chelex and Metisorb binding layers occurs through chemisorption. The superior uptake kinetic for Chelex indicates that it is a better candidate for further development of DGT devices to measure ZnO NPs. These initial results are promising and important for further developing the DGT technique to measure available concentrations of manufactured nanomaterials in the different environmental media (waters, soils, and sediments). Further experiments investigating the effects of pH, ionic strength, and solution chemistry on the performance of DGT for measuring MNM concentrations are needed.

In developed societies, ZnO nanoparticles (ZnO NPs) are commonly encountered¹ because they are a constituent of a wide range of commercially available products, including semiconductors and sun tan lotions.² As these manufactured materials are consumable and their use is increasing, the concentration of ZnO NPs in the environment is likely to rise. Modeling scenarios and field studies, albeit scarce, have shown that ZnO NPs can easily enter soil and water resources.³

Toxicology studies show that ZnO is one of the most toxic nanoparticles.⁴ Effects include inhibition of the root growth of plants and of embryonic development of some fish species.^{5,6} An underlying reason for the toxic effects of ZnO NPs is their increased dissolution in the presence of proteins and organic substances, which could facilitate release of toxic Zn²⁺ in the intracellular environment.⁷

Currently, our understanding of environmental effects and pathways of nanoparticles is hampered by a lack of appropriate measuring techniques.^{1,8} A major challenge in addressing analytical requirements for NPs measurement is sampling and handling. Due to their high ratio of surface area to size, they are highly reactive and their concentrations are prone to change. Ideally, then, their concentrations should be measured using an *in situ* technique.⁸ DGT (diffusive gradients in thin films) is a well-tested, *in situ* method for measuring a wide range of metals and metalloids in terrestrial and aquatic systems.^{9,10} The DGT device has a binding layer, which is covered by a diffusive hydrogel layer and a protective filter membrane that contacts

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the medium. The target chemicals diffuse through the filter membrane and gel layer and then react with the binding material.

As the hydrogels typically used in DGT have an open pored structure, there is the possibility that NPs can diffuse through them and be measured by DGT.¹⁰ It is also possible to equip the diffusive layer of DGT with a molecular cutoff membrane so that it measures only simple inorganic species in solution. By combining these measurements, there is the possibility of using DGT as an *in situ* tool for determining the concentration of nanoparticles in natural waters. Currently, there is a lack of data and agreement regarding the size of nanoparticles that can pass through typically used hydrogels sufficiently rapidly to make measurement by DGT feasible. Van der Veeken et al.¹¹ examined how Pb bound to latex nanospheres bound to hydrogels and measured them by DGT. They concluded that nanospheres of 81 and possibly a 259 nm diameter could diffuse within typical open pored polyacrylamide hydrogels. Davison and Zhang¹⁰ questioned these findings and pointed to an array of less direct evidence which suggested only NPs with diameters <2 nm would diffuse sufficiently rapidly to be measured sensitively, while NPs up to a 5–6 nm diameter might be measured with much reduced sensitivity.

ATR-FTIR (attenuated total reflection Fourier-transform infrared) spectroscopy has been recently used to show that NPs of ZnO bind by chemisorption to both a chelating resin, Chelex, and a commercially available form of titanium dioxide, known as Metsorb.¹² These binding agents are therefore good candidates for use in DGT for the measurement of ZnO NPs. However, no information is available on their performance when they are exposed to ZnO NPs as a binding layer for a DGT device.

This research reports the development of a simple technique, based on DGT, for the *in situ* determination of the concentration of ZnO NPs in the environment. It systematically investigates the extent and rate of binding of ZnO NPs to both Chelex and Metsorb and establishes their elution efficiency. It uses a diaphragm diffusion cell to measure their diffusion coefficients through hydrogels with and without associated molecular cutoff membranes and uses these results to design a DGT system for measuring ZnO NPs. Deployments of DGT are made in a known mixture of Zn²⁺ and ZnO NPs to test its capability and potential as an *in situ* measuring tool for these particles in the environment.

MATERIALS AND METHODS

Nanoparticle Solution Preparation and DGT Devices.

ZnO nanoparticles were obtained from Nanosun (30 nm of ZnO powder without surfactant).¹³ Their primary particle size range is approximately 30–50 nm,¹³ although they have a strong tendency to form aggregates. The pH at which their overall surface charge is neutral, namely, their point of zero charge (ZPC), is 6.5. Prior to each test, a fresh stock of ZnO dispersion was prepared by adding 200 mg of powdered ZnO NPs to 1 L of high purity water (Milli-Q, Millipore, USA), known here as MQ, followed by sonicating for at least 15 min. This stock dispersion was further diluted when needed. Initially, two different types of binding layers were prepared for the experiments: a chelating resin (Chelex-100, Bio-Rad¹⁴) and titanium dioxide (Metsorb, Graver Technologies¹⁵). The diffusive layers, including open pore (thickness ≈0.78 mm), agarose (thickness ≈0.78 mm), and restricted gels (thickness ≈0.76 mm), were prepared in the lab, and 3500 and 1000

MWCO (molecular weight cut off) dialysis membranes (thickness ≈0.05 mm) were obtained from Spectrum Biotech. The binding and diffusive layers were prepared using established methods.^{16,17} The plastic moldings for the DGT devices were obtained from DGT Research Limited (Lancaster, UK).

Analytical Method and DGT Concentration Calculations. After deployments, binding layers were retrieved using acid cleaned tweezers and immersed in 1 mL of ultrapure nitric acid for approximately 24 h. Eluted samples were diluted 10-fold prior to Zn being measured using inductively coupled plasma mass spectrometry (ICPMS, Thermo X7 series).

The mass of Zn in the binding layer, M , was calculated using eq 1.

$$M = C_e(V_{\text{acid}} + V_{\text{gel}})/f_e \quad (1)$$

The concentration of metals in 1 mL of concentrated elution solution is denoted by C_e ; V_{acid} is the volume of elution reagent added to the resin. V_{gel} represents the volume of the binding gel, typically 0.15 mL, and f_e is the elution factor. Time averaged concentrations, C_{DGT} , were quantified using eq 2.^{9,17}

$$C_{\text{DGT}} = M\Delta g/DTA \quad (2)$$

The combined thickness of the filter membrane and the diffusive layer is denoted by Δg (cm), and D is the diffusion coefficient of the analyte (cm²/s); T is the duration of deployment in seconds, and A is the area (cm²) of the sampling window of the DGT device.

Diffusion Coefficients Measurement. A diaphragm diffusion cell, comprising two compartments, which are connected through a 1.5 cm circular opening housing a diffusion membrane, was used to measure diffusion coefficients, as described by Zhang and Davison.¹⁸ Each compartment was filled with 100 mL of 0.01 M NaNO₃. The solution of one of the compartments, labeled C_H , contained known concentrations of ZnO NPs. The other compartment was labeled C_L . For at least 3 h, samples for measuring ZnO NPs were taken at short time intervals, typically 5 min, from the compartment initially free from them. Each sample was immediately acidified using concentrated ultra pure nitric acid to a concentration of 0.1 M HNO₃. Samples were stored at 4 °C and rigorously mixed before analysis.

For diffusion coefficient measurements, three types of diffusive layers were used: Spectrum Biotech 3500 and 1000 MWCO cellulose ester dialysis membrane and polyacrylamide cross-linked with an agarose derivative, known as open pore (OP) diffusive gel. Two other common types of DGT diffusive layer materials, agarose gel and a bis cross-linked acrylamide gel, known as a restricted gel,¹⁶ were used for ZnO NP retention evaluation, uptake kinetics, and DGT deployment experiments.

Elution Efficiency. An elution factor, f_e , was determined for each binding gel by immersing gels in 10 mL of ZnO NPs suspensions (500 µg/L) while shaking for at least 24 h. Retrieved gels were carefully washed with MQ water. To obtain elution factors of the binding gels, concentrations of ZnO NP suspensions in the tubes were measured prior to and after immersion. The elution factor is given by the amount of Zn eluted from the immersed gels divided by the total bound amount on the gel obtained from the change in suspension concentrations.

Binding of ZnO NP to Gels and Uptake Kinetics. To evaluate ZnO NP retention by the binding materials and

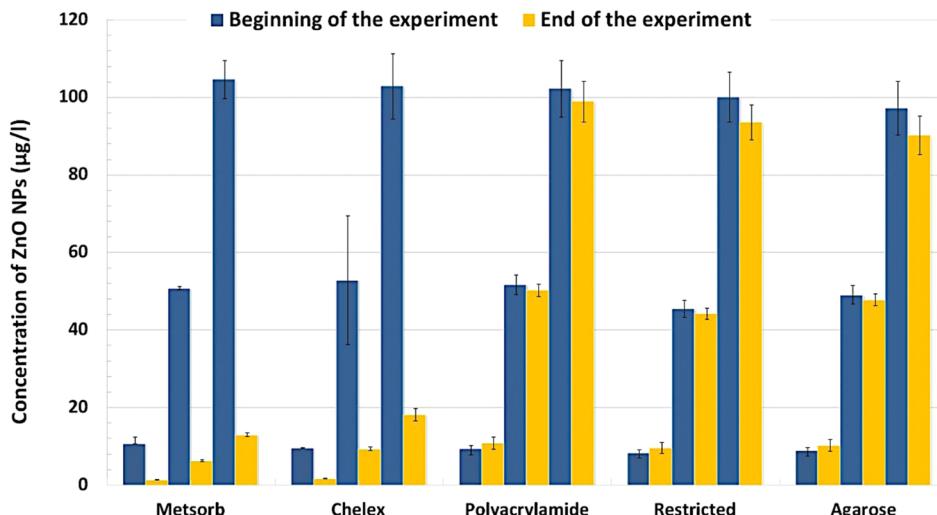


Figure 1. Concentrations of ZnO NPs in 10 mL suspensions before and after a 4 h exposure to diffusive gel and binding gel layers.

diffusive layers, a disc of each of these materials, as used in a DGT device, was exposed to 50 mL of 10, 50, and 100 µg/L of ZnO NPs for a duration of 4 h, while they were shaken on a rotary shaker at 120 rpm. At the end of this test, 100 µL of the suspension was taken to determine the remaining concentration of ZnO NPs. The binding and diffusive layer discs were gently removed, washed with MQ water, and eluted in 1.0 M HNO₃.

In experiments to investigate uptake kinetics of ZnO NPs and Zn²⁺ to the binding layers, discs of the binding gels were immersed in 50 mL of known concentrations (1000, 500, and 200 µg/L) of ZnO NPs or a mixture of ZnO NP and Zn²⁺ in 0.01 M NaNO₃. For the mixtures, approximately equal concentrations of ZnO NP and Zn²⁺ were added to the solution. Then, 100 µL of each solution was sampled at known time intervals, and the differences between the measured and initial concentration of ZnO NPs or Zn²⁺ were determined. The total duration of this experiment was approximately 400 min. The kinetic experiments were run in static (without any agitation) and agitation modes and also using blank samples without the binding layers, to rule out the possibility of precipitation with time due to aggregate formation or partitioning to the vessel walls. Equation 1 was used to calculate the ZnO mass retained by the binding materials. Experiments were replicated at pH 4.5 and 6.5. The low pH was adjusted by adding a few microliters of concentrated ultrapure nitric acid, while pH ≈ 6.5 represents the pH of the suspension of ZnO NPs in 10 mM NaNO₃. The pH was measured at the beginning and end of each experiment.

DGT Deployments. DGT measurements were performed by immersing devices in approximately 2 L of known concentrations of suspensions of ZnO NPs while stirring well using a magnetic follower. C_{DGT} was calculated using eq 2. For the DGT deployment tests where a dialysis membrane was used in a DGT device, it was placed between the OP diffusive gel and the filter membrane. Using a dialysis membrane by itself (thickness ≈ 0.05 mm) does not create a diffusive layer of sufficient thickness to minimize the effect of the diffusive boundary layer (DBL).^{18,19}

Investigation of the Mechanism of Binding. Triplicate samples for each experimental treatment toward attenuated total reflection Fourier-transform (ATR-FTIR) spectrochemical

analysis were prepared. For this, 0.5 g of pure Chelex or Metsorb (binding materials) was exposed to 20.0 mL of 1000.0 µg/L ZnO NPs. The reason for this high concentration is to enable detection by the ATR-FTIR spectroscopy. The samples were shaken for about 4 h on a rotary shaker at 120 rpm and centrifuged for 15 min at 3500 rpm, and then, the supernatant was discarded. To wash the samples, 50 mL of Milli-Q water was added to each of the test tubes, shaken for 10 min, and centrifuged as before. The washing stage was repeated three times to remove residuals of nonchemically retained ZnO NPs. Because water will make significant contributions to infrared (IR) spectra, all of the samples, those exposed to ZnO NPs, the blank binding agents, ZnO NPs, and open pore hydrogel, were dried under pressurized nitrogen gas, 0.4 bar. A Bruker Tensor 27 FT-IR with Helios attachment containing diamond ATR Internal Reflection Element (IRE) was used for data acquisitions (Bruker Optics Ltd, Coventry, UK).

RESULTS AND DISCUSSION

Elution Efficiency. There was no significant difference in Zn concentrations before and after exposure of solutions of ZnO NPs to the diffusive gels (Figure 1). This indicates that there was no binding of ZnO NPs to the diffusive gel layers. Differences in concentrations in solution enabled calculation of mass taken up by the binding gels of Metsorb and Chelex (Figure 1). Elution of the binding layers enabled calculation of elution factors, f_e, for Metsorb and Chelex as 0.90 ± 0.04 and 0.78 ± 0.02, respectively. These values are similar to those reported for Zn²⁺ in solution.⁹

Diffusion Coefficients. Figure 2 shows the time dependence of the measured concentrations of Zn in each compartment of a diffusion cell equipped with an OP polyacrylamide hydrogel, where one compartment, C_H, contained ZnO NPs. Concentrations of Zn in C_H initially declined with time and then reached apparently stable values. These changes could be because of aggregation due to colliding nanoparticles, which would invalidate the measurement of the diffusion coefficient, D. This initial loss of Zn was minimized by sonication of the NPs suspension just before the diffusion test, selecting optimum concentrations of the NPs suspension and optimizing the rate of stirring. The concentrations in the receiving compartment, C_L, increased linearly with time when the Zn

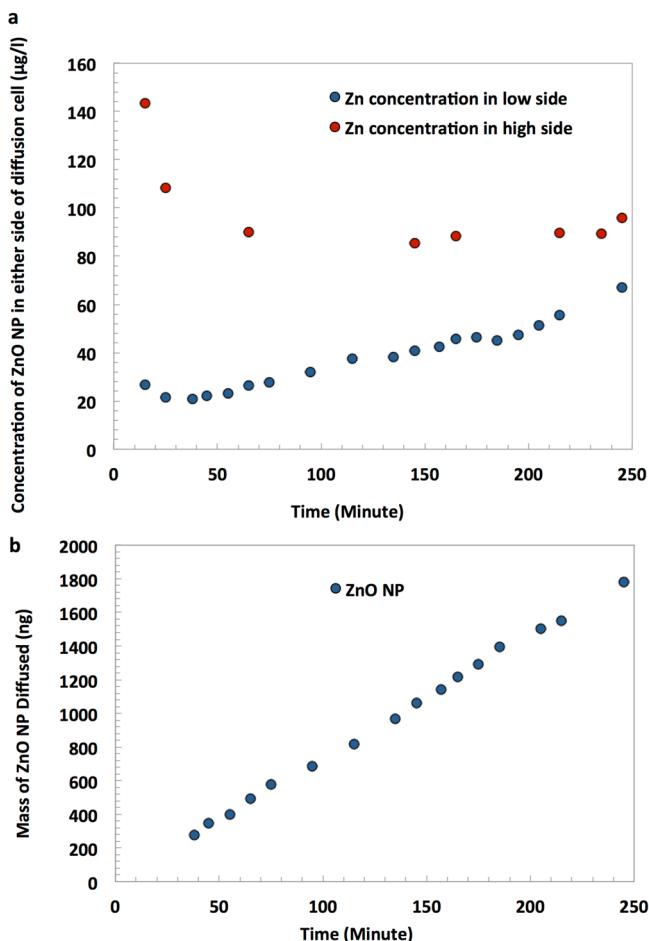


Figure 2. (a) Temporal dependence of the concentration of Zn measured in the two compartments of a diffusion cell separated by a 0.8 mm thick OP gel where the high side compartment, C_H , initially contained an unstable suspension of ZnO NPs. (b) Mass of Zn measured in the receiving compartment, C_L , when the concentration in the high side compartment, C_H , was stable.

concentrations in compartment C_H were effectively constant. Figure 2b shows the change in the mass of Zn in compartment C_L with time. The slope of a plot of mass in compartment C_L with time (Figure 2b) allowed one to calculate D at 22 °C for this preparation of ZnO NPs. The obtained value is $4.07 \times 10^{-6} \pm 9.32 \times 10^{-7} \text{ cm}^2 \text{s}^{-1}$. This value is surprisingly large. In fact, it is close to the Zn^{2+} value of $5.6 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ at 22 °C in this gel. A particle with a molecular weight of 30 000 Da (Da) would be expected to have a diameter of approximately 4.6 nm and a diffusion coefficient in water of $1.1 \times 10^{-6} \text{ cm}^{-2} \text{s}^{-1}$.¹⁰ There are two possibilities: either the molecular weight of this suspension of nanoparticles is very much smaller than expected or nanoparticle diffusion in this polyacrylamide hydrogel is facilitated by the structure, as suggested by van der Veeken et al.¹¹

When 1000 and 3500 MWCO dialysis membranes were used in the connecting window of the diffusion cell, there was no measurable increase, within the experiment time of 250 min, in the concentration of Zn in C_L , showing that ZnO NPs are unable to pass through these membranes. The results of diffusion coefficient measurements have also demonstrated that the process of stirring (or shaking) was unlikely affecting the particle sizes of ZnO NP. Particle size change would lead to a nonlinear relationship of mass versus time.

Uptake Kinetics. The changes with time in the mass of Zn accumulated in binding gel discs exposed to solutions of ZnO NPs or Zn^{2+} are shown in Figure 3a,b. The mass of Zn in the

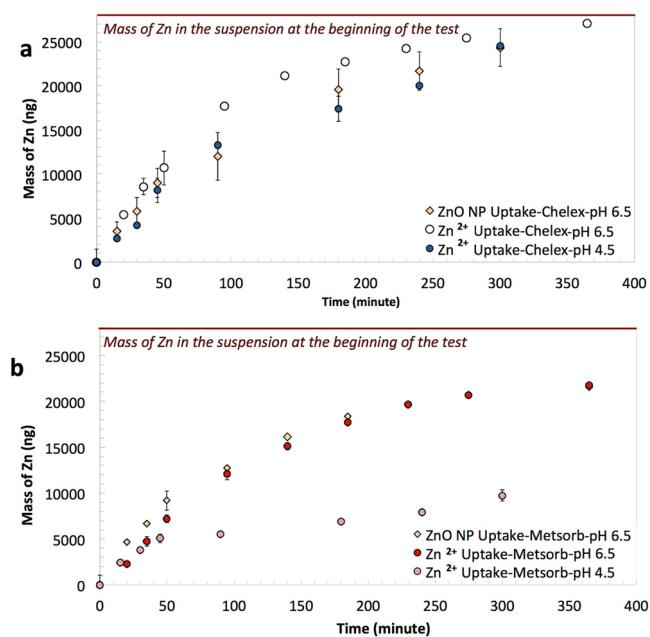


Figure 3. Mass of Zn accumulated by (a) Chelex and (b) Metsorb binding layers exposed for different times to suspensions of ZnO NPs and Zn^{2+} solutions.

suspension at the beginning of the experiment is represented by a horizontal line. The initial slopes for ZnO NPs, Zn^{2+} ($\text{pH} \approx 6.5$) and Zn^{2+} ($\text{pH} \approx 4.5$), binding to Chelex were similar (Figure 3a). There was slightly more uptake between ~100 and ~200 min of Zn^{2+} at pH 6.5 than uptake of either Zn^{2+} at pH 4.5 or Zn from the NPs solution. However, after 300 min, approximately 90% of total NP Zn and Zn^{2+} irrespective of pH was bound to the Chelex. The change with time in the amount of ZnO NPs bound to Metsorb was similar to the relationship observed for Chelex (Figure 3b). However, at any given time, less Zn^{2+} at pH 6.5 is bound to Metsorb than to Chelex. The uptake characteristics of Zn^{2+} by Metsorb at low pH were different. Initially, the uptake slope was similar to that observed for Zn^{2+} at pH 6.5, but after 50 min, the slope was notably reduced. This different behavior might be associated with the higher pzc of Metsorb compared to Chelex. For the low pH test, the surface charge of Metsorb is positive, and therefore, electrostatic binding of positive Zn^{2+} ions is precluded. The implication is that at low pH ZnO NPs do not bind electrostatically.

DGT Measurements. DGT devices with different binding and diffusive layer combinations were deployed in suspensions of ZnO NPs for 4 h at 21 °C at a concentration of approximately 500 $\mu\text{g/L}$ ZnO NP. There were 3 replicates for each combination. In the separate solutions used for the experiments with different binding layers, the analyzed concentrations in solution were slightly different. To enable assessment of the effect of the diffusion layers on the accumulated mass, we have calculated the mass of Zn, M (ng), accumulated by the DGT binding layer (Figure 4). DGT devices with agarose accumulated the highest amount of NPs. The mass was slightly less for OP gel and noticeably less for the restricted diffusive layer. These results are consistent with

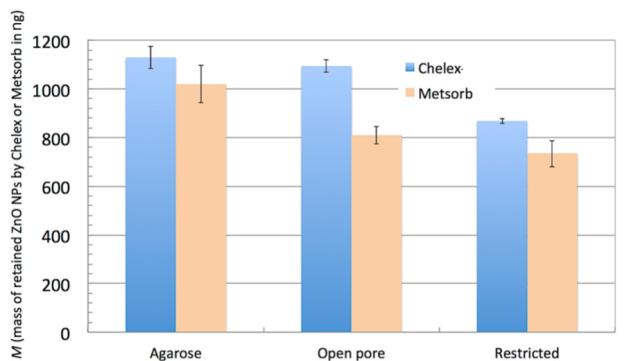


Figure 4. Accumulated mass (ng) of Zn in DGT devices (with 3 different hydrogels as diffusion layers and 2 types of binding materials) deployed in ZnO NPs in suspension for 4 h at 21 °C.

agarose having the largest and the restricted gel having the smallest pore size. Although the trend was the same, irrespective of whether Chelex or Metsorb was used as the binding agent, the results for the OP gel were close to those of agarose when the Chelex binding layer was used. Examination of the error bars suggests that this perceived difference may not be significant.

An experiment was conducted to examine whether it is possible to use DGT devices to measure the concentration of Zn in solution present as ZnO NPs. A mixture of known amounts of ZnO NPs and Zn²⁺, with the aim of having approximately equal amounts, was prepared by first adding Zn(NO₃)₂ to a concentration of \approx 900 μ g/L to a solution of 0.01 M NaNO₃ at a pH of 6.5. The analyzed concentration of Zn was then taken to be the concentration of Zn²⁺. A 2.00 mL aliquot of 1000 mg/L sonicated stock solution of ZnO NPs was then added to make the total suspension volume 2000 mL. It was analyzed for Zn. This total Zn concentration was used to calculate the concentration of ZnO NPs by subtracting the concentration of Zn²⁺ as shown in Figure 5. DGT deployments were then made for 4 h at 19 °C in triplicate using Chelex and Metsorb DGT devices with either open pore hydrogels or open pore hydrogels with 1000 MWCO dialysis membranes. The mass of Zn accumulated using only OP gels reflects the concentrations of ZnO NPs and Zn²⁺, while the accumulated

mass in devices with dialysis membranes provides an estimate of the concentration of Zn²⁺. Knowing the concentration of Zn²⁺ and the diffusion coefficient of ZnO NPs, it is possible to calculate the concentration of ZnO NPs. The concentrations of Zn²⁺ measured using devices with Chelex and Metsorb binding layers were similar, but they were about 18% higher than the initial concentration of Zn²⁺. When these values were used along with the accumulated masses in devices without the dialysis membrane, the calculated concentrations of ZnO NPs were 78% (Chelex) and 56% (Metsorb) of the initial concentration of ZnO NPs. For each type of binding layer, the concentrations of Zn²⁺ and of Zn as ZnO NPs were summed. These DGT estimates of total concentrations were 102% and 90% of the initial measured values for Chelex and Metsorb respectively, suggesting that the measurements made using a Chelex binding layer provide more reliable results. The deviation of DGT measurements of concentrations of Zn²⁺ and ZnO NP from the initial values could be due to changes occurring in the suspensions, particularly dissolution of ZnO NPs.

The precision of the DGT measurements is generally good, with RSD of less than 7%. The limit of detection is 13.46 ng per DGT device, which can be expressed as a concentration of 1.09 μ g/L when a standard DGT device is deployed for 24 h at 20 °C.

Binding Mechanism. Metsorb is a commercially available material provided by Graver Technologies. Not all of the details about its chemical structure are disclosed, but it is known that titanium oxides, TiO₂ and Ti(OH)₄, are Metsorb's main constituents (Figure 6), with the former dominating. As the points of zero charge for titanium dioxide and titanium hydroxide are approximately 6.0²⁰ and 4.5,^{21,22} it is expected that the pH-dependent surface charge of Metsorb will be negative at pH 6.5.

Although extensive information is available about adsorption on titanium oxide (hydroxide) surfaces, the focus is on chemisorption of different ligands on titanium,^{23–26} which differs from this work concerning NPs. Protonated, deprotonated, and neutral hydroxyl groups of ZnO NPs could create attractive forces (mainly through intermolecular hydrogen bond) with deprotonated, protonated, and neutral hydroxyl groups on the Metsorb surface. Attractive forces are also likely

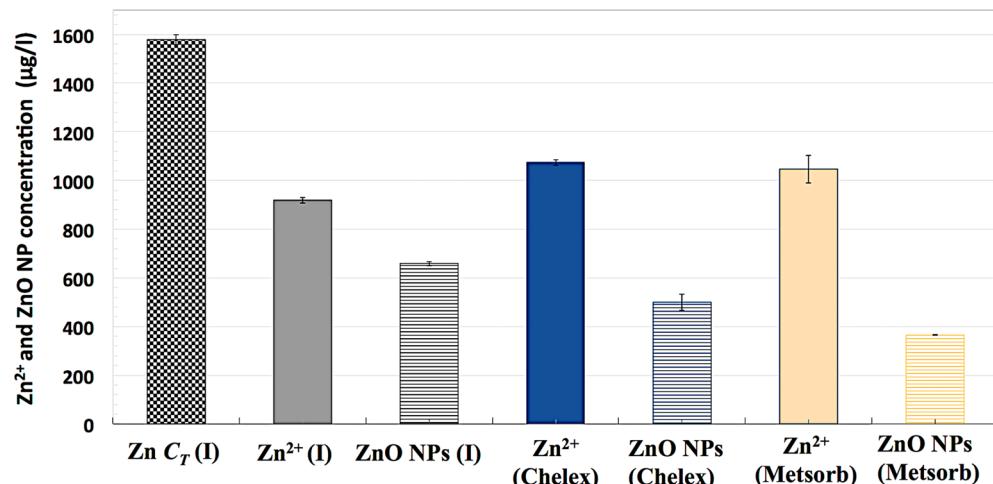


Figure 5. Total concentrations of Zn (C_T) and concentrations of Zn²⁺ and of Zn as ZnO NPs measured directly in solution initially (represented by symbol I) and obtained by DGT devices with Chelex and Metsorb as binding layers.

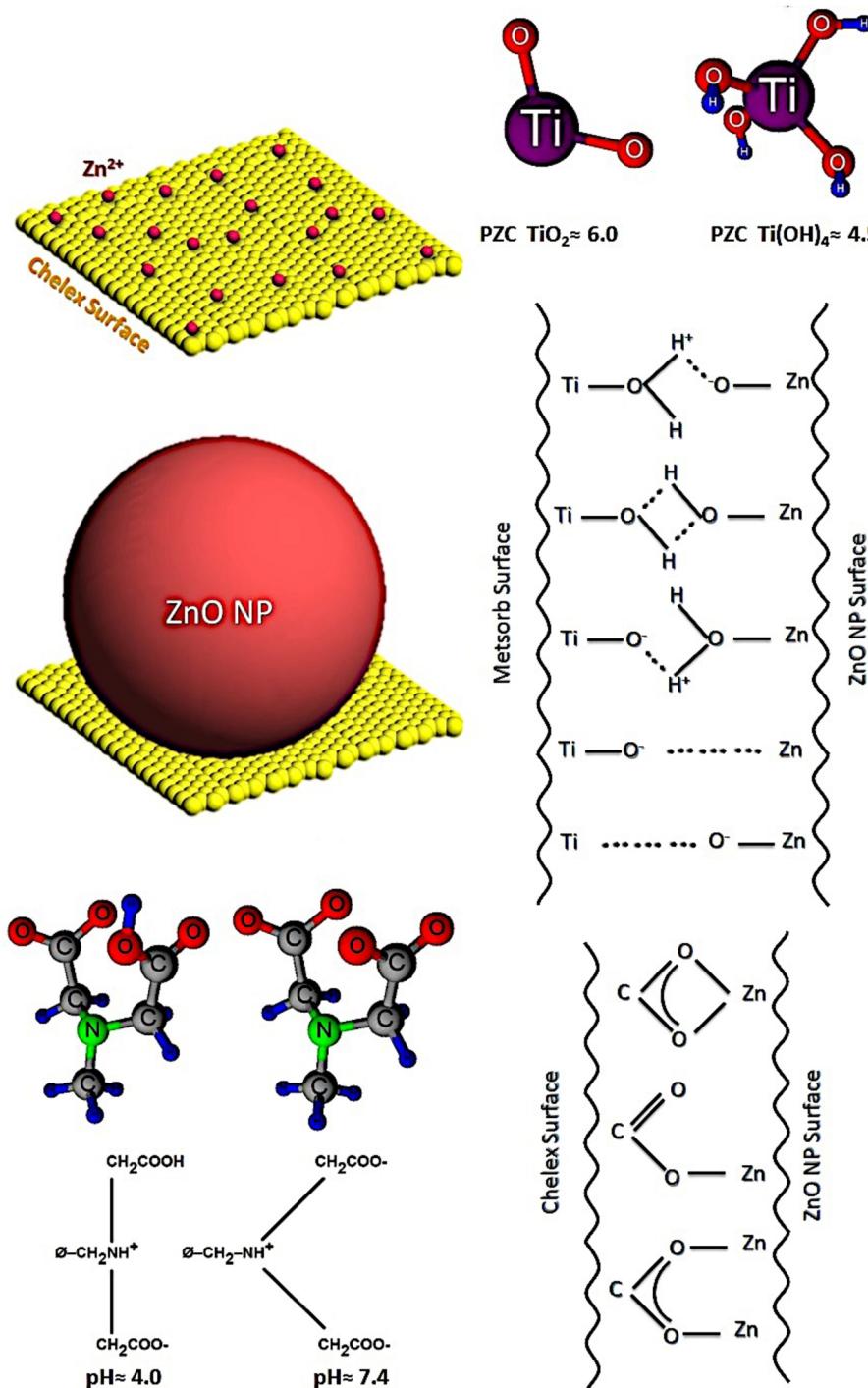


Figure 6. Schematic presentation of Zn²⁺ and ZnO NP binding on Chelex surface, functional groups of Chelex and Metsorb and possibilities of chemical bond formation between Chelex/Metsorb and a ZnO NP.

to exist between the zinc of the ZnO NPs surface and the deprotonated hydroxyl groups of Metsorb and *vice versa*, as schematically depicted in Figure 6. In addition, the presence of van der Waals forces between the two surfaces²⁷ is expected to contribute to the binding of ZnO NPs to Metsorb.

In case of Chelex, especially with regard to its function as a DGT binding layer, notably more studies are available.^{10,17} It is well established that deprotonated carboxyl groups are responsible for binding trace elements in their ionic forms.¹⁷ Deprotonation of carboxyl groups occurs at pH ≈ 4.¹⁴ Similar

to Metsorb, when Chelex is exposed to ZnO NPs, interaction occurs between two surfaces, rather than a functional group and an ion. As well as attraction by van der Waals force, there will be electrostatic attraction between the Zn of the nanoparticle surface and the carboxylate groups of Chelex (Figure 6).

If chemisorption occurs between the adjacent surfaces, Metsorb/Chelex and ZnO NP, the vibrational spectroscopy of the involved functional groups will be affected. Figure 7 shows IR spectra for ZnO NPs, blank Metsorb and Chelex, and Metsorb and Chelex exposed to ZnO NPs. Also, for the open

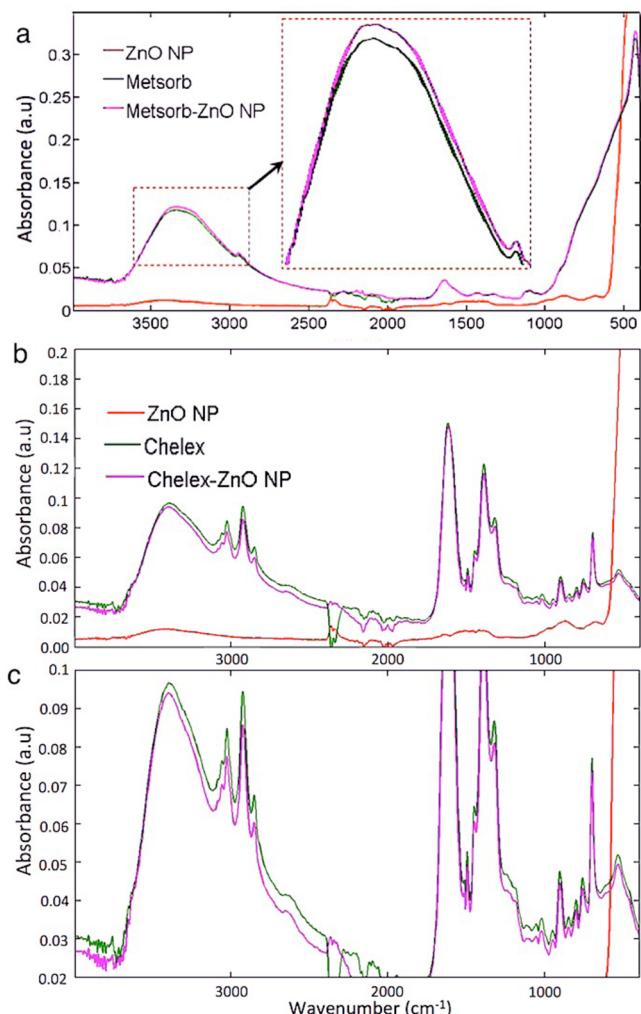


Figure 7. ATR-FTIR spectra of blank Metsorb and Chelex and those exposed to ZnO NPs. Spectra in (a) are Metsorb's spectra and (b,c), respectively, show complete Chelex spectra and when it is magnified.

pore hydrogel, IR spectra were obtained that displayed a featureless flat line, consistent with its polymeric structure, which shows a lack of active functional groups and the inert characteristics appropriate for the diffusive layer of DGT devices.¹⁹ The ZnO NP spectrum shows a major peak at $\approx 460\text{ cm}^{-1}$, that is characteristic of a metal–oxygen vibrational band, in this case ZnO.^{28,29} The blank Metsorb spectrum differs considerably from the spectrum of Metsorb exposed to ZnO NPs. Skewed broad peaks seen between ≈ 400 and $\approx 700\text{ cm}^{-1}$ are due to Ti–O vibration.³⁰ The bands at ≈ 1100 , 1346 , and $\approx 1440\text{ cm}^{-1}$ are most likely due to C–O, C–H, and O–H vibrations of ethenol ($\text{C}_2\text{H}_4\text{O}$),³¹ which, in combination with a homopolymer, constitutes less than 10% of Metsorb.¹⁵ The peak at about 1650 cm^{-1} is possibly due to the presence of Ti(OH)_4 , which leads to formation and bending of HOH on the surface.³² Bending and stretching of the OH of adsorbed water also could create a band at about this wavenumber.³³ Broad peaks appearing at about 3100 – 3600 cm^{-1} could be assigned to stretching/vibration of O–H hydroxyl groups, while the shoulder at $\approx 2960\text{ cm}^{-1}$ is likely due to bending of Ti–OH.³⁰ All aforementioned peaks are present in both blank Metsorb and Metsorb exposed to ZnO NPs. Nevertheless, these two spectra have noticeable differences in their recorded intensities. The intensity of peaks at $\approx 3360\text{ cm}^{-1}$ is a prime

example, suggesting chemisorption of ZnO NP. These spectra support the earlier suggestion that chemical bonds could possibly form between surface hydroxyl groups of Metsorb and ZnO NPs as depicted in Figure 6.

Spectra for Chelex, both blank and exposed to ZnO NPs, are shown in Figure 7. Bands at about 1030 , 1326 , and 1396 cm^{-1} could be, respectively, assigned to C–O stretching, C–H bending, and O–H bending.^{31,34,35} Carboxyl groups of Chelex create a broad peak for O–H stretching, which spans from 2400 to 3400 cm^{-1} . N–H stretching vibrations are also seen between ≈ 3180 and $\approx 3500\text{ cm}^{-1}$ and most likely contribute to the hydroxyl peak. Bands observed at ≈ 2858 and 2924 cm^{-1} are possibly because of symmetric and asymmetric C–H stretching, while the peak at $\approx 3410\text{ cm}^{-1}$ could be assigned to =C–H stretching.³¹ In Figure 7, a clear decrease in intensity of stretching hydroxyl peak is observed when Chelex and Chelex exposed to ZnO NP are compared. In addition, there are noticeable shifts between band wavenumbers of the samples.

CONCLUSIONS

This initial investigation of the feasibility of modifying the DGT technique to quantify available nanoparticles in the environment is promising. It has shown that manufactured NPs of ZnO diffuse through the diffusive gel and filter layers without reacting with them. The measured diffusion coefficients of the ZnO NPs are appreciably less than that of free Zn cations. Their quantitative estimation using DGT requires a mean value of D , but the susceptibility of the size and conformation of the NPs to solution conditions prevents the establishment of universal reference diffusion coefficients within the diffusive gel layer of DGT. The relationship of measured diffusion coefficients to the shape and size of NPs, for particular gel compositions, could probably be best explored using inert latex particles of known size. ATR-FTIR analysis of the blank binding materials and those exposed to ZnO NPs showed that both Metsorb and Chelex are able to retain ZnO NPs through chemisorption. Measurements of uptake kinetics and elution factors demonstrated that ZnO NPs bind more effectively to Chelex than to Metsorb. Although both of these binding materials show potential to be used for determining ZnO NPs using DGT, Chelex offers potentially better performance. These initial experiments indicate that, by using combinations of DGT devices with known diffusive and binding layer properties, available concentrations of targeted chemicals within a certain size range could be measured.

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Notes

The authors declare no competing financial interest.

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