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Measuring ZnO nanoparticles available concentrations in contaminated soils using the diffusive gradient in thin-films (DGT) technique

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ABSTRACT

A major gap in understanding nanomaterials behaviour in the environment is a lack of reliable tools to measure their available concentrations. In this research we use diffusive gradients in thin films (DGT) for measuring concentrations of zinc oxide nanoparticles (ZNO NPs) in soils. Available nanoparticle concentrations were assessed by difference, using paired DGT devices with and without 1000 MWCO dialysis membranes to exclude NPs. We used ZnO because its toxic effects are accelerated through dissolution to Zn^{2+}. Our test soils had different pH and organic matter (OM) contents, which both affect the dissolution rate of ZnO NPs. Woburn (pH≈6.9, OM≈1.8%) and Lufa (pH≈5.9, OM≈4.2%) soils were spiked to a single concentration of 500 mg of ZnO NPs per 1 kg of soil and the available concentrations of ZnO NPs and dissolved zinc were evaluated in 3, 7, 14, 21, 28, 60, 90, 120, 150 and 180 day intervals using DGT. The results showed that the dissolution of ZnO NPs, as well as the available concentrations of both dissolved and nanoparticulate Zn, were much higher in Lufa soil than in Woburn. This work demonstrates that DGT can be used as a simple yet reliable technique for determining concentrations of ZnO NPs in soils and probing its dissolution kinetics.

Keywords : Diffusive gradients in thin-films; DGT; ZnO NPs; Nanoparticles; Zinc oxide dissolution; Chelex; contaminated soils, dialysis membrane

1. Introduction

In situ measurements of chemicals in the environment are crucial for understanding their behaviour and potential environmental impacts. Moreover, beyond the total concentrations of a chemical, speciation and bioavailability are key factors that determine how the chemical can impact biota.[1] Among different commercially available nanoparticles, ZnO is one that has extensive applications in different industries and is incorporated into a range of commercially available products such as semiconductors, tiles and coatings, and skin care products.[2] On the other hand, the limited lifetime of these products means that ZnO NPs may be released into the environment, which raises concerns about their negative environmental impacts.[3] For example, dissolution of ZnO NPs to ionic Zn can increase Zn loading in the environment and associated potential impacts. Some of the reported toxicological effects of ZnO nanoparticles include inhibiting the root growth of plants, toxicity to earthworms[4] and damaging to the embryonic development of fish[5,6]. These important ecotoxicological impacts are mainly attributed to the uptake and subsequent dissolution of ZnO NPs in the presence of organic and biological substances such as proteins, that may accelerate the release of Zn^{2+} in the intracellular environment[6–8] This highlights the importance of reliable assessments of the metal speciation associated with NP inputs to soils and waters, as an essential step to understanding their behavior in the environment.

With respect to understanding the behaviour of ZnO NPs in the environment, particularly in soils, we still face considerable knowledge gaps associated with the selection, development and validation of a soil pre-treatment step that allows the separation of these nanoparticles from the soil without altering their integrity.[9,10] The tendency of these materials to transform from their pristine state via dynamic transformations makes predicting their fate in soil under different environmental conditions even more challenging.[11] Nanoparticles can be characterized, separated, and quantified using several lab instruments including electron microscopy, filtration, chromatography, and plasma (ICP-MS) methods, nevertheless, none of these methods are yet able to give us a reliable estimation of the available concentrations of these materials in the environment. Even determining in what form (nanoscale or aggregate) these nanoparticles remain in the ecosystem involves some degree of uncertainty.

Here we focus on the possibility of using Diffusive Gradients in Thin-films (DGT) for quantifying ZnO NP in soils. The DGT method is a well-established technique that has shown to provide reliable estimates of time-averaged available concentrations of different chemicals, particularly different metal species in soils and waters.[12,13] The DGT device has a binding layer that can irreversibly retain target substances. The binding layer/resin is covered by a diffusive hydrogel layer that allows chemicals to pass through it and be retained by this layer. A filter membrane sits on the top of the diffusive layer, in direct contact with the environment, soil and/or water, and protects the underlying layers.[5,7] These layers sit above a plastic base (known as a piston) and are kept in place by a plastic cap with a sampling window. The structure of the DGT devices and the purpose of each of its component have been previously described in other publications.[12,14]

One of the advantages of the DGT devices is their flexibility for deploying different types of diffusive and binding layers, which allows optimising of these devices for measuring a targeted chemical or group of chemicals.[15] The most common types of diffusive layer are agarose gel, open pore polyacrylamide gel and restricted gels.[5] For the binding layer, Chelex®-100, Metsorb™ and Fe-Oxide are most commonly used.[5] A DGT device can also be equipped with a dialysis membrane (DM) with a known molecular weight cut off (MWCO), between the diffusive gel and the filter membrane, so that it can only sample chemical forms small enough to pass the MWCO cutoff.[6,12]

We have previously shown the potential for DGT to measure ZnO nanoparticles and investigated the retention mechanism of ZnO, Ag and TiO_2 NPs by Chelex®-100 and Metsorb™ using attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy.[1,5,7] In this study we investigate using DGT devices to study the aging and dissolution of ZnO nanoparticles in two different soils: Lufa (pH≈5.9) and Woburn (pH≈6.9) over a period of 180 days. DGT devices with Chelex®-100 and open pore polyacrylamide gel, respectively, as the resin and diffusive layers, were used in this research. Chelex®-100 is a selective cation-exchange resin with a high complexation capacity, that contains dicarboxylic acid amine ($COOHCH_2$-NH-$COOHCH_2$) with carboxyl groups.[5] Chelex®-100 has been proven an effective resin in accumulating trace metals in waters.[7] The DGT is a reliable, robust, and easy to deploy approach, which has shown promising potential for the purposes described above.[7,12,16]

We have previously used DGT devices with and without dialysis membrane (DM) to differentiate between available concentrations of ZnO NPs and ionic zinc in water. We have shown that DGT can take up ZnO NPs as well as its ionic form directly from water and determine the available concentrations of these zinc species with a high accuracy.[5,7] In this paper, we investigated how DGT devices with and without dialysis membrane can help us evaluate the available concentrations of ZnO NPs and its dissolution in contaminated soils. In this study the hypothesis is that by deploying DGTs with and without a dialysis membrane in soils paired measurements can be made of (i) DGT-labile ZnO and ionic Zn; (ii) DGT-labile ionic Zn only, in the same soil.

2 Experimental section

2.1 Chemicals and samples preparations

The ZnO NPs, were obtained from a commercial supplier Nanosun in form of a powder.[17] The nanoparticles point of zero charge (PZC), which is the pH that the surface of charge of a surface is neutral in a non-interacting electrolyte[18], is ≈6.5, which indicates that in the pH range of natural environments these nanoparticles would have approximately neutral to negative surface charge. The particle size is 30-50 nm. The two natural soil samples used were Woburn and Lufa, which were obtained from an agricultural site in the UK and commercially (Lufa 2.2 LUFA Speyer, Germany), respectively. Some basic soil characteristics are given in Table 1.

Table 1., The characteristics of the soils used in this study. Reported pH and %OM values are mean of the three replicates ± standard deviation (OM=organic matter content, WHC=water holding capacity).

Soil	pH	%OM	WHC (g/100g)
Lufa 2.2	5.9±0.07	4.2±0.04	42
Woburn	6.9±0.11	1.8±0.02	32

The water holding capacity (WHC) of the samples was 32 ml in 100 g soil for Woburn, and 41.78 ml if 100 g soil for Lufa. Both soils were air dried, homogenized and sieved through a 2 mm mesh. Prior to the aging experiments high purity water (≥ 18 MΩ.cm, Milli-Q, Millipore, USA), known here as MQ, was added to 1500 g of each soil; to increase the water content of the soils to 50% of their WHC.

The soils samples were kept at 16°C in closed plastic containers, which were previously acid washed and thoroughly rinsed with MQ water, before adding ZnO nanoparticles. For the aging experiments 500 mg/kg of powdered ZnO NPs were added to Woburn and Lufa soils. The dry nanoparticle powder was thoroughly mixed with each soil sample to ensure a homogenous distribution. The samples were incubated at 16°C for 6 months for the aging experiments. Throughout the incubation time, the soil moisture contents were maintained at 50% of WHC. Considering the constant conditions and controlled environment of the incubator the variation of the soil moisture contents were limited and did not exceed 50±3% of WHC at the sampling times. It's worth noting that the soil moistures were set to 50% of WHC at the beginning of the test and they were being evaluated regularly (weekly) during the incubation period. Although it would be possible to prepare stocks of ZnO NPs suspension in MQ water to add to the soil samples instead of dry powdered ZnO NPs, this approach was avoided in order to keep the soil moisture levels constant during the entire experiment.

2.2 Preparing the DGT and Nano-DGT devices

In this study we used two different types of the DGT devices, schematically represented in Figure 1. The DGT binding layer was Chelex-100 ion-exchange resin. and the diffusive layer was an open pore polyacrylamide hydrogel (thickness ≈0.78 mm). The only different between the two types of the DGT devices is presence of a 1000 MWCO (molecular weight cut off) dialysis membranes with thickness ≈0.05 mm in one of them. This type of the DGT device is designed to prevent nanoparticle collection via the use of the low MWCO dialysis membrane, and is referred to as a Nano-DGT[7].

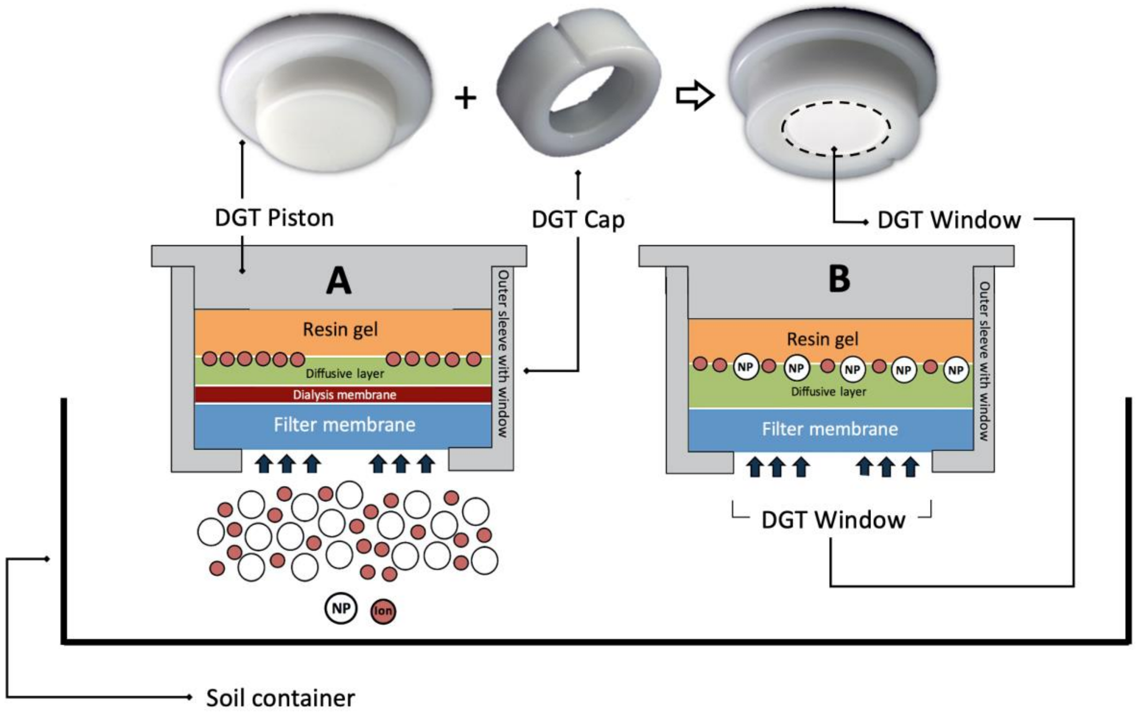

Figure 1., Schematic presentations of the DGT devices deployed in this study. The DGT device, annotated with A, has a dialysis membrane that only allows ionic zinc to reach the binding layer, while the other device, B, allows both ZnO NPs and Zn^{2+} to be retained by the binding layer. In this study the DGT devices were pushed about 3 mm below the soil surface to have good contact with the soil samples.

The chelating resin (Chelex®-100) and the dialysis membrane were purchased from Bio-Rad[19] and Spectrum Biotech[20] respectively. The plastic mouldings for the DGT devices and cross-linker for the hydrogels were obtained from DGT Research Limited (Lancaster, UK, www.dgtresearch.com) and the binding and diffusive gels were prepared using established methods.[12]

2.3 DGT deployments

The incubation period was 180 days from the day that Woburn and Lufa soils were spiked with 500 mg of ZnO NPs per 1 kg of soil and the temperature was kept at 16±1°C. Nano-DGT and DGT devices were deployed at 3, 7, 14, 21, 28, 60, 90, 120 and 180 days after the spiking. For Woburn and Lufa soils at every deployment time, three Nano-DGT and three DGT devices were used for every deployment time. The number of the DGT devices deployed in this study, excluding the control DGTs that were deployed before adding ZnO NPs, was 120; 2 soils×6 DGT devices (3 Nano-DGT and 3 DGT)×10 sampling times.

For each Nano-DGT or DGT device deployment, aliquots of approximately 20 g of soil were used. MQ water was added to the soil samples to increase the water content to approximately 90% WHC, 24 hours prior to each deployment. The deployment time was about five hours (the exact deployment time was recorded for each of the experiments) and the ambient temperature was recorded at the beginning and end of the deployment. For the DGT deployments, the device was gently placed upside down on the surface of the soil, using twist and turn with slight pressure to make sure a good contact between the sampling window and the soil, as can be seen in Figure 2. During the deployments, the soil containers were covered by plastic sheets to prevent water evaporation and to maintain constant soil moisture content.

Figure 2., The DGT deployments for Woburn and Lufa soils. The tests were in triplicates for each time intervals and covered by plastic sheets to prevent water evaporation from soils during the deployment.

After each DGT deployment, soil solutions were extracted by centrifugation at 3000 rpm for at least 30 minutes. Solutions obtained by centrifugation were filtered with 0.2 μm cellulose acetate syringe filters to remove any soil particles. The soil solutions were immediately acidified using ultrapure 0.1 M HNO_3 and stored in a fridge at 4°C.

2.4 Analytical method and DGT concentration calculations

At the end of the deployment, the binding layers of each DGT device was retrieved using acid cleaned tweezers and immersed in 1 ml of ultrapure nitric acid for 24 hours to elute the bound material. The Zn concentrations in the elutriates were measured using inductively coupled plasma mass spectrometry (ICP-MS, Thermo X7 series), following 50× dilution. To determine the time-averaged DGT–labile concentrations of Zn (C_{DGT}), we needed first to calculate the mass of zinc in the binding layer, denoted as *M*. This mass can be obtained using Eq. 1.

$$M = C_e\left(V_{acid} + V_{gel}\right)/f_e \qquad (1)$$

In the above equation, C_e represents the concentration of Zn in acid solution used for elution of Zn, V_{acid} is the volume of acid added to the resin (ml), V_{gel} represents volume of the binding gel, typically 0.15 ml, and f_e is the elution factor, typically 0.8 for trace metals.[21] The DGT measured concentration, C_{DGT}, were quantified using Eq. 2.

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

In equation 2, Δg (cm) is the combined thickness of the filter membrane and the diffusive layer, the thickness of the dialysis membrane in these tests is 0.05 mm[5,7], which is used for the calculations of the DGTs equipped with this layer. The diffusion coefficient of the analyte (cm^2/s) is denoted by *D*, the duration of the DGT deployment in seconds is denoted by *T* and *A* is the area (cm^2) of the sampling window of the DGT device, which in this study was 3.14 cm^2.

2.5 Diffusion coefficient determination

A crucial requirement for determining the DGT measured concentrations, C_{DGT}, is the diffusion coefficient of metals through the diffusive layer. Different diffusive layers used in the DGT devices, based on their pore sizes, have distinctive diffusion coefficients.[22] In this study, as described before, we used open pore hydrogel as the diffusive layer. The diffusion coefficient of Zn^{2+} through open pore hydrogel has been reported in the literature and used in various studies.[12,16,22]

To measure the diffusion coefficient of ZnO NPs in the open pore hydrogel we used a diaphragm diffusion cell (Figure 3). It comprises two compartments (source and receiving), connected through a 1.5 cm circular opening housing a diffusion gel disc. The details of this device, and the process of measuring the diffusion coefficient, have been described and illustrated by Zhang and Davison.[12,22] In this study we added 100 ml of 0.01 M $NaNO_3$ to each compartment of the diaphragm diffusion cell followed by adding a known concentration of ZnO NPs to one of the compartments (source compartment). The device was placed on a magnetic stirrer, and constant stirring was provided to both compartments during the experiment of at least three hours duration. At time intervals, typically five minutes, samples were taken from both compartments. All the samples from both compartments were immediately acidified using concentrated ultra-pure nitric acid. They were stored at 4°C and rigorously mixed before analysis. We repeated the same process with the diffusive gel covered by dialysis membrane, DM 1000 MWCO (molecular weight cut off), but for a longer duration of approximately eight hours, to evaluate whether the zinc oxide nanoparticles could pass through the DM layer during this time.

In this approach the diffusion coefficient through the gel, D, is calculated based on Fick's first law of diffusion[21,22], where F is the flux through the hydrogel/diffusive layer and (dC/dx) is the concentration gradient within the gel, x indicates gel thickness, assuming a linear concentration gradient forms through the gel between the high and low concentrations compartments of the device (Figure 3).

(3)

$$F = D\left(\frac{dC}{dX}\right)$$

The flux is the mass (*M*) per unit area (*S*) per unit time (*t*) as seen in the below equation:

(4)

$$F = \frac{M}{St}$$

When the above equations are combined we have the following equation that allows us to calculate diffusion coefficient, *D*, where ΔC is the concentration difference and effectively constant across the gel thickness, *x*. [16,21,22]

(5)

$$M = \frac{DtS\Delta C}{x}$$

2.6 Elution efficiency

To determine C_{DGT} we need to have the mass of zinc in the binding layer denoted as *M* (equation 1), and an essential component to obtain this mass is the elution factor, f_e. To obtain the ZnO NP elution factor, Chelex binding gel was immersed in 10 ml of zinc oxide nanoparticle suspension (500 µg/l) and shaken for 24 hours. Then, the Chelex binding layer was retrieved and thoroughly washed with MQ water before eluting in 1 ml of 1M HNO_3 solution. The concentrations of ZnO NPs in the suspension both at the beginning and end of the experiment were measured. The elution factor of ZnO NPs was determined by the amount of Zn eluted from the immersed Chelex binding gel, divided by the total bound amount on the gel obtained from the change in the suspension concentrations. This experiment was performed in triplicate.

3. Results and discussion

3.1 Diffusion coefficient and elution efficiency

One of the challenges of using DGT for measuring nanoparticle concentrations in the environment is lack of information on their diffusion coefficients through the diffusion layers[6,7]. This can be attributed to the novelty of using the DGT technique for measuring NP concentrations, and the challenging nature of the experiment. When a diaphragm diffusion cell is used to determine diffusion coefficients of metal ions, the solution remains homogenous through the experiment and the ions diffuse gradually through the hydrogel layer. However, for nanoparticles co-aggregation may affect the homogeneity of the suspension and thus the reliability of the derived diffusion coefficient. This is important as the source compartment of the diaphragm diffusion cell has an initially high concentration of nanoparticles. To keep the ZnO suspension as homogeneous and dispersed as possible, the suspension was sonicated just before placing into the source cell, and constant stirring, using magnet bars, was provided during the experiment.

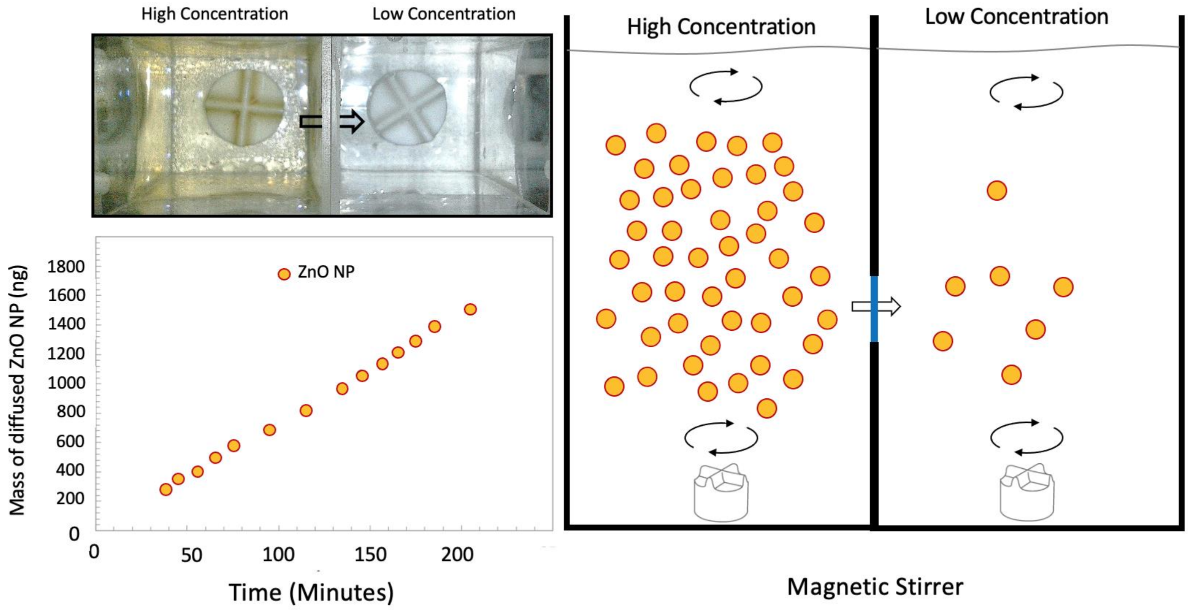

Figure 3., The top left image shows the device that used in this study for determining the diffusion coefficient of our model ZnO NPs through the open pore hydrogel. The bottom left shows the diffusion of ZnO NPs through the hydrogel and their increasing concentrations in the Low Concentration side of the diffusion cell. The right-side image is a schematic presentation of the diffusion cell equipment that was used in this research.

The results showed that the zinc oxide nanoparticles were not able to pass through the dialysis membrane, indicating that the DGT devices equipped with the DM 1000 MWCO are only able to take up ionic zinc. These results were comparable to our previous work.[7] We observed an initial decrease in the concentration of ZnO NPs in the source compartment, but after about 40 minutes it became stable. In the receiving compartment, there was a consistent linear increase in the concentration of the diffused zinc oxide nanoparticles after 40 minutes. Based on the slope of the linear plot of mass in receiving compartment versus diffusion time (Figure 3), the diffusion coefficient, *D*, of ZnO NPs through the open pore hydrogel at 22°C was 4.10×10-6 cm^{2}s^{-1} using the equation 3. This value is surprising large, and close to the diffusion coefficient of Zn^{2+} at 22°C in this hydrogel which is 5.6x10^{-6} cm^{2} s^{-1}.[7] Some studies suggest that the structure of this polyacylamide hydrogel facilitates the diffusion of the nanoparticles, which could be the case in this research and the reason for the obtained diffusion value. [7,23]

It's worth mentioning that at the beginning, and end of the test, samples were taken from the high concentration/ZnO NPs side of the diffusion cell and presence of Zn^{2+} was evaluated in the samples. The results confirmed there was no Zn^{2+} in the source compartment suggesting no dissolution occurred during the experiment and the results could be attributed to ZnO NPs diffusion through the hydrogel layer. In addition, as mentioned earlier the diffusion coefficient test performed with the same concentration of ZnO NPs in the source compartment and DM 1000 MWCO in the diffusion cell showed no zinc in the receiving side indicating that ZnO NPs could not pass through this membrane and there has been no dissolution to Zn^{2+} during the test, which is in agreement with our previous findings.[7] The elution factor, f_e, for Chelex was calculated as 0.78, deduced from elution of the resin layer, which is compatible to the value reported for Zn^{2+} in solution.

3.2 DGT measurements

The DGT devices with and without DM 1000 MWCO were deployed at different time intervals as explained before (Figure 2 shows one of these deployments, there were 3 replicates for each combination). Both pH and organic matter contents are likely the key factors that affect the availability and speciation of ZnO NPs in the soils, which may affect the dissolution and the DGT concentrations of zinc oxide nanoparticles in Woburn (pH≈6.9, OM≈1.8%) and Lufa (pH≈5.9, OM≈4.2%) soils. The results that are shown in Figure 4, belong to the soils spiked with nanoparticles and the measurements represent concentrations obtained by centrifugation (as described before). This figure shows great differences in total zinc (ZnO NPs plus dissolved ZnO NPs to ionic zinc) concentrations between the two soils in the soil solution over the incubation time.

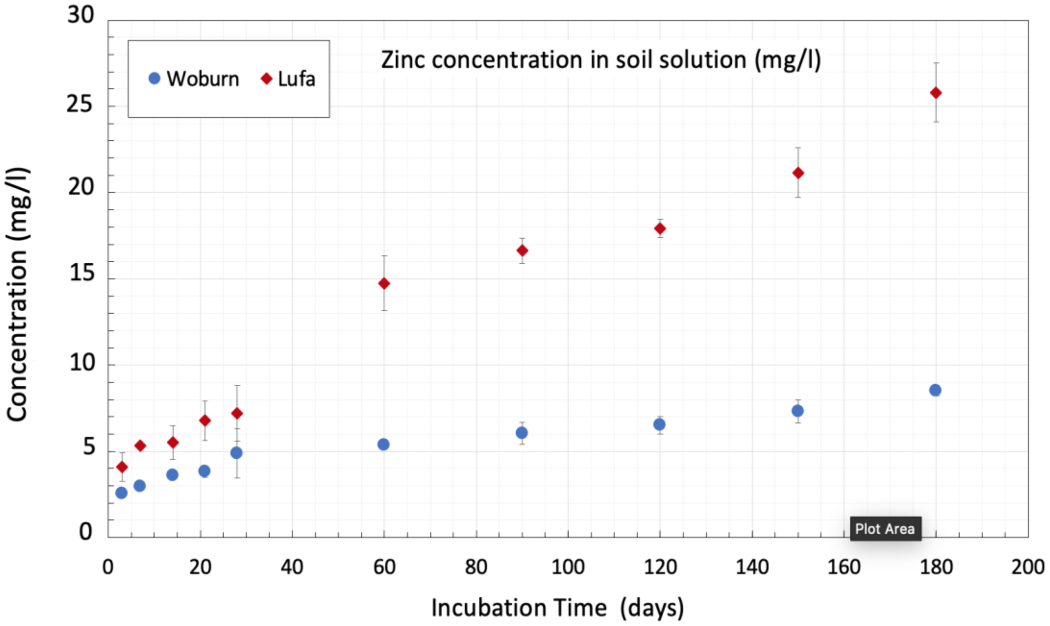

Figure 4., This graph shows the total concentration of zinc in the soil solution for Woburn and Lufa soils at different times.

During the first 28 days of incubation; 3, 7, 14, 21 and 28, a comparable trend can be seen for both soils; a steady linear increase in zinc concentrations. However, the zinc concentrations in Woburn shows a gradual, slow, and limited increase between the 28 and 180 days, while Lufa has a steady steep increase. The concentration of the zinc in the soil solution is nearly doubled in 28 days, from 2.55±0.09 (mg/l) to 4.88±1.42 (mg/l) for Woburn and from 4.09±0.83 (mg/l) to 7.21±1.61 (mg/l) for Lufa. However, from 28 to 180 days Woburn shows only about 1.75× increase in soil solution zinc, 8.52±0.31 (mg/l), while this number is much higher for Lufa, 3.6×, and reaches 25.80±1.72 (mg/l) at the end of the incubation period.

The observed differences in Figure 4 between Woburn and Lufa soils can be attributed to the effect of their pH and organic matter contents. Lufa has an acidic pH, ≈5.9, and previous studies have shown that ZnO NPs exhibit higher dissolution rates at lower pH values and ionic Zn increases with decreasing pH.[4,24,25] On the other hand, Woburn pH is close to neutral, ≈6.9, which is reflected in the behavior of ZnO NPs as can be seen in Figures 4, 5 and 7. As these Figures show the total concentration and availability of the zinc both in NPs and ionic forms are significantly lower in Woburn samples compared to Lufa soil. The differences increase after 28 days of incubation and maintain their trends till end of the incubation period (180 days). The organic matter contents of Lufa is also 2.3× more than Woburn, which facilitates ligand-induced dissolution of ZnO NPs. It has been reported that the higher amounts of organic matter in soils leads to increases in dissolution rates of ZnO NPs.[26] There is a consensus that the presence of natural organic matter in soils facilitate dissolution of ZnO NPs. It has been suggested that the same behaviour can be expected for other metal-based soluble NPs and larger colloidal particles.[26,27]

The ZnO NP point of zero charge (PZC), which is the pH that the overall charge of a surface is neutral[28,29], is ≈6.5, indicating that under the conditions of Lufa soil (pH≈5.9, OM≈4.2%) the surface charge of these nanoparticles would be positive, while under the conditions of Woburn soil (pH≈6.9, OM≈1.8%) would be neutral to negative. It's worth noting that the natural organic matter present in the spiked soils is expected to be adsorbed to the surface of ZnO NPs, which affects the surface charge of these particles. While the soil organic matter surface charge depends on its various components, it is suggested to have a relatively low[28,30] PZC (≤ 5) due to the presence of acidic functional groups on natural organic matter, which indicates that it will carry overall negative surface charge in both Woburn and Lufa soils. Because ZnO NPs have overall positive and negative surface charge in Lufa and Woburn, respectively, we expect to have more favourable electrostatic attachment of OM to ZnO NPs surface in Lufa compared to Woburn. In addition, chemisorption and chemical bond formation could also occur between the hydroxyl groups on the ZnO NPs surface and organic matter that also contribute to the sorption of the organic matters on the nanoparticles surface.

Figure 5 and 6 display the DGT-labile concentrations, $C_{DGT,}$ for Woburn and Lufa soils during the incubation times, obtained by deploying DGT devices with and without DM 1000 MWCO. The concentrations measured by DGT without DM are higher than the concentrations measured by DGT with DM, nearly double at the later stages of incubation for both soils. The DGT device with the DM, referred to as Nano-DGT, allows only dissolved zinc to be retained by the binding layer, while the DGT device without DM can bind any form of zinc that can pass through the diffusive open pore hydrogel. The difference between these two types of DGTs shows the concentration of DGT-labile ZnO NPs (as shown in Figure 7). Figures 5 and 6 also reflect the notable differences between the two soils, primarily the available concentrations of the total and dissolved zinc. At the end of the incubation, the total concentration of zinc (both ionic and NPs) in Lufa is more than 3× higher than Woburn. Also, for the same sampling time the dissolved zinc concentration in Lufa is considerably higher than the total zinc concentration in Woburn soil. This dissolution and available concentrations patterns can be attributed to the soil properties mainly pH and OM content as described earlier.

Information regarding the size of the particles that can pass through the diffusive gels of DGT devices are not consistent. Davison and Zhang[16] have indicated that only very small nanoparticles can pass through the open pore diffusive gels, while Van der Veeken et al.,[23] have examined how Pb bound to latex nanospheres were measured by DGT and concluded that nanospheres of 81 and possibly 259 nm diameter could diffuse through open pore polyacrylamide hydrogels.[7,23] We have previously used the same types of DGT devices that are used in this study for measuring ZnO NPs in water and results showed that they can measure concentrations of zinc oxide nanoparticles in water with a high accuracy.[7]

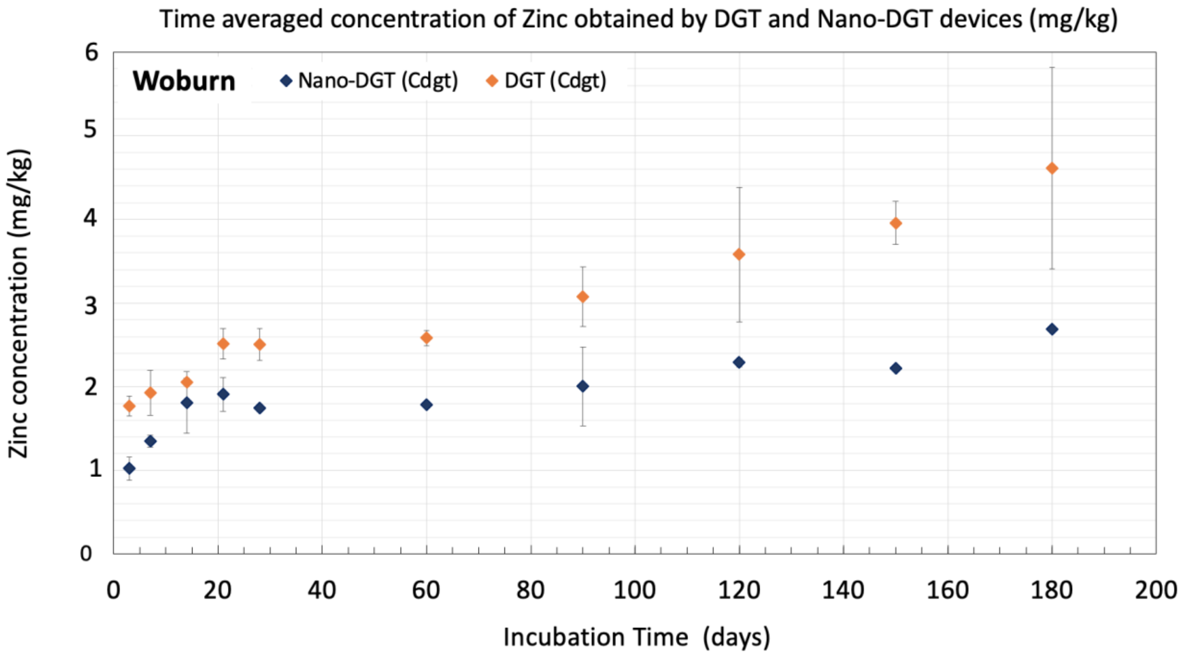

Figure 5., Time averaged concentrations of available zinc measured by the DGT devices in Woburn soil. In this graph Nano-DGT refers to the devices equipped with DM 1000 MW and show the concentration of ionic zinc only while the DGT shows the total concentrations (both ionic and NP) during the aging process.

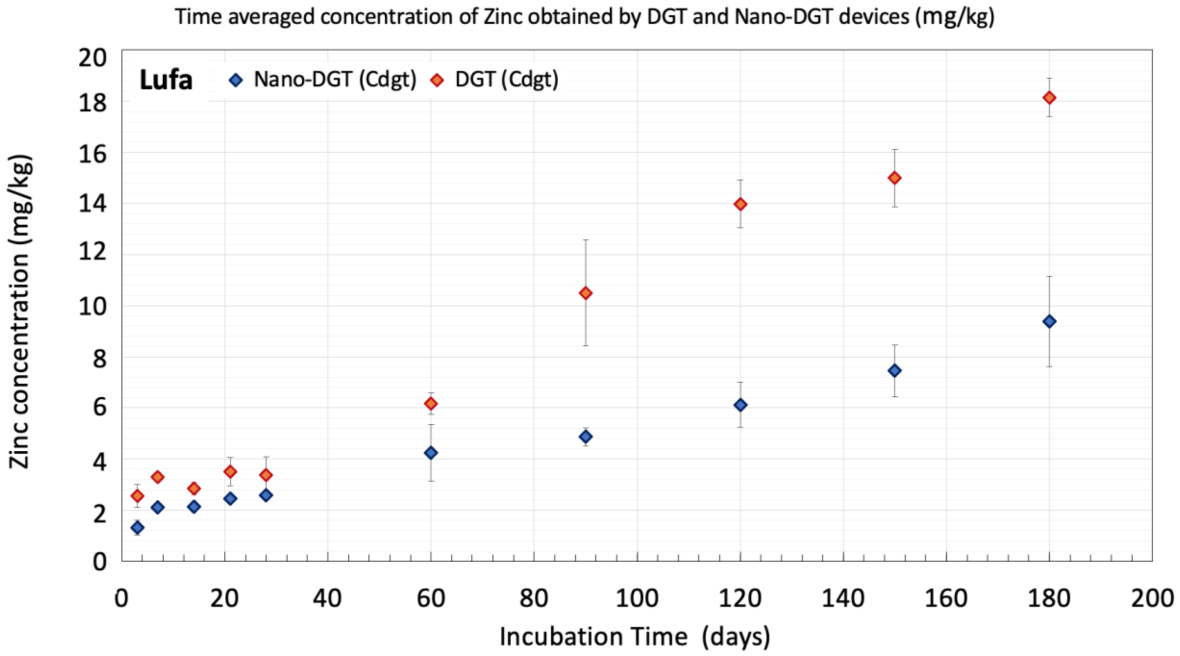

Figure 6., Time averaged concentrations of available zinc measured by the DGT devices in Lufa soil. In this graph Nano-DGT refers to the devices equipped with DM 1000 MW and show the concentration of ionic zinc only while the DGT shows the total concentrations (both ionic and NP) during the aging process.

Figure 7 presents the available concentrations of zinc in both ionic and nanoparticles forms measured by DGT during the incubation times for both Woburn and Lufa soils. As seen in this Figure the available concentrations of ZnO NPs and dissolved zinc in Woburn samples increase with time, nevertheless compared to Lufa soil this increase is, slow, steady and move towards forming a plateau at the end of incubation. On the contrary, Lufa samples maintain their sharp increase for the available concentrations of dissolved and ZnO NPs over time, which indicates potentially more severe ecotoxicological impacts in Lufa soil, or soils with similar properties, compared to Woburn if contaminated with ZnO NPs.

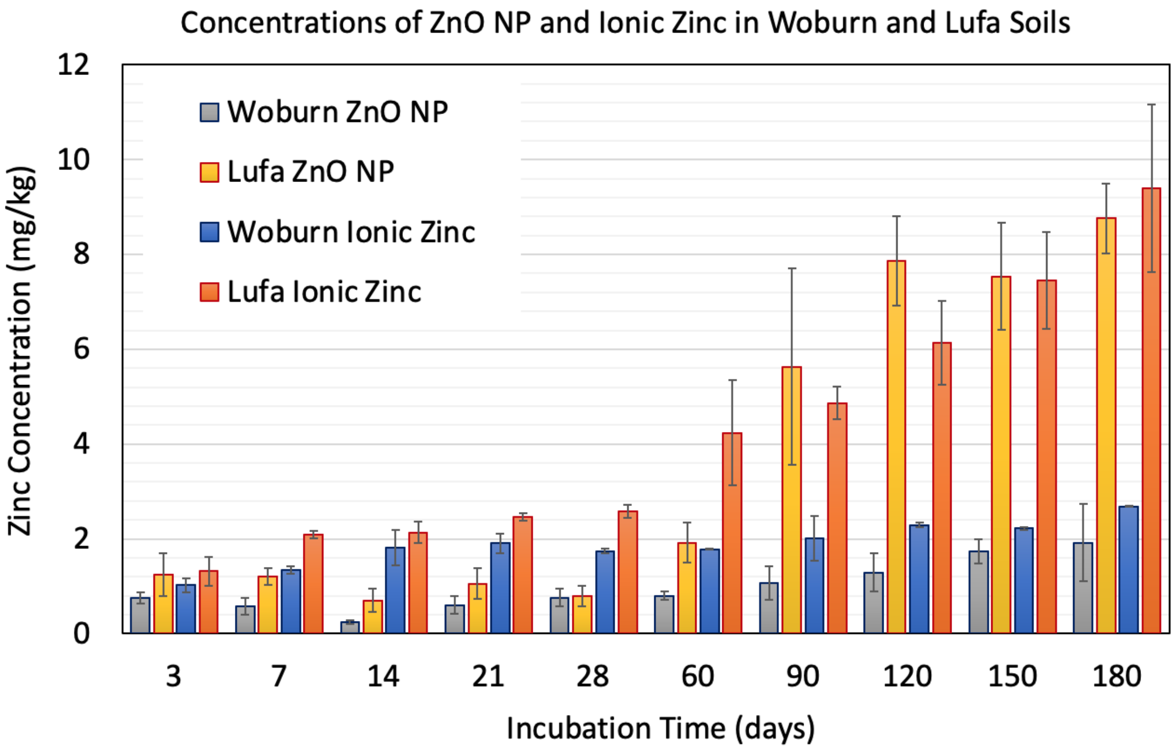

Figure 7., Time averaged concentrations of available Zn^{2+} and ZnO NPs measured by the DGT devices in Woburn and Lufa soils. As shown Lufa (pH≈5.9, OM≈4.2%) has a consistently higher concentration of both species of zinc in soil during the incubation time with an increasing trend for dissolution while Woburn (pH≈6.9, OM≈1.8%) shows considerably slower ZnO NPs dissolution and availability.

These findings are aligned with previous studies that highlight the impacts of pH and organic matter contents on dissolution and toxicity of ZnO NPs. The results also indicate that the living organisms in two soils with the same amount of metal-based NPs contamination may undergo significantly different exposure which could result in differing toxic effects if the soil pH and OM are different [4,31,32] The modified DGT device and the approach used in this study, using paired DGT devices with and without 1000 MWCO dialysis membranes to exclude NPs can be used in situ for field sites to determine concentrations of ZnO NPs and probing its dissolution kinetics. Previous studies have shown promising results for the application of DGT devices to measure metal bioavailability and assess toxicity risk in soils and sediments both in lab and in situ, which indicate the potential for deploying modified DGT devices (with DM) in field tests.[33,34] In this study, as shown in Figure 1 and 2, the DGT devices were pushed about

3 mm below the soil surface to have good contact with the soil samples. If the conditions of the DGT deployment are met e.g., linear concentration gradient can be formed through the gel between the high and low concentrations of the device, the DGT devices could be deployed vertically, as shown in a recent study were the DGT pistons were buried in a way that the upper edge of the DGT pistons were level with the sediment surface.[34]

The successful applications of the DGT technique for determining the concentrations of ZnO NPs in this research reflects the potential of DGT as an in situ and reliable tool for evaluating the available concentrations of different types of engineering nanomaterials in soils. DGT devices with different MWCO dialysis membranes can be used for identifying dissolution kinetics of metal-based NPs in soils which is crucial for understanding their ecotoxicological impacts in the environment. However, deploying the DGT devices for understanding NP behaviour in the environment presents some challenges too. For example, while there are well established diffusion coefficients of ionic elements for DGT deployments, such information rarely exists for nanomaterials, which highlights the need for further research for determining diffusion coefficients of the widely used manufactured nanomaterials in the diffusive hydrogels used in DGT devices.

Conclusions

This initial investigation of the feasibility of deploying modified DGT devices for quantifying available nanoparticles in soils and identifying their dissolution kinetics is promising. We were able to quantify available concentrations of both dissolved and NP zinc during the aging experiments at different time intervals. To the best of our knowledge this is the first in situ method that can differentiate between dissolved and nanoparticulate Zn in soils and provide an assessment of their concentrations in the environment. The findings agreed with other studies and clearly demonstrated the impacts of pH and OM on availability and dissolution of ZnO NPs, which has direct impacts on its toxicity in the environment. For Lufa soil (pH≈5.9, OM≈4.2%) the availability of Zn^{2+} and ZnO NPs were considerably higher than Woburn soil (pH≈6.9, OM≈1.8%), particularly after 28 days incubation. Woburn soil showed a small and slow increase till 180 days and Lufa soil had a steep growing increase in concentrations of available zinc. The results suggest that by deploying DGT devices with and without DM we can further understand NPs behaviour in the environment and investigate on their dissolution, speciation, toxicological impacts and fate. This research shows the potential of DGT as a low-cost, efficient and in situ technique for determining dissolution kinetics and available concentrations of manufactured nanomaterials in the environment. However, further studies are needed for determining the binding mechanisms and the diffusion coefficient of NPs through the DGT diffusive layers as currently very limited information is available.

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