Role of water temperature in the fate and transport of zinc oxide nanoparticles in aquatic environment

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Abstract. The influence of water temperature on the aggregation and dissolution kinetics of zinc oxide nanoparticles (ZnO NPs) (mean diameter \textasciitilde40 nm) was investigated. Samples of 100 mg.L\textsuperscript{-1} ZnO NPs were incubated at 15, 25 and 35 °C, similar to the surface temperature of cold freshwater, temperate estuarine, and tropical/sub-tropical coastal marine ecosystems, respectively. The natural organic matter (NOM) content, pH, electrolyte type, and ionic strength (IS), were adjusted on the basis of the water chemistries of typical aqueous systems. Specifically, the time-dependent hydrodynamic diameters (HDDs) and sedimentation plots were obtained over the first 3 h and after 24 h using time-resolved dynamic light scattering (TR-DLS) and UV-visible spectroscopy, respectively. The settling distance was further modeled for the aggregates with various HDDs according to the Stokes’ sedimentation equation. The dissolution kinetics was studied over the first 12 h and after 48 h in term of percentage of released zinc ions. The results showed that the HDD increased at elevated temperatures, termed as temperature-induced aggregation, while dissolution was reduced. The aggregation at higher temperatures further hindered the dissolution due to the decrease in the surface area of the NPs. We express this process as “aggregate-suppressed dissolution”. The maximum aggregation was reached in the tropical coastal marine environment with the HDD \textasciitilde3 \textmu m, and the released zinc ion of 9.2\% was obtained in the cold freshwater. Based on the results, the aggregation rate of 1.57 nm.s\textsuperscript{-1} was estimated for the former, and the dissolution rate of 7.44 \times 10\textsuperscript{-5} mol.L\textsuperscript{-1}.h\textsuperscript{-1} was calculated for the latter, respectively. The predicted values successfully fitted to genuine water samples (<26\% deviation). This study provides useful data for environmental risk assessment of exposure of ZnO NPs to water column and benthic organisms.
1. Introduction
Nanosized materials are extensively used in industry and consumer products. They have been reported to undergo transformation in the environment [1]. Several studies have focused on fate and transport of these materials in the environment. Zinc oxide nanoparticles (ZnO NPs) have found several applications among engineered nanoparticles (ENPs). Since environmental occurrence and bioavailability as well as toxicity of ZnO NPs are very high [2,3], their behavior is worthy of attention. Among a number of environmental factors, temperature plays a key role in all physicochemical processes. It may vary significantly with climate geographies from extremely cold poles to very hot deserts.

In aqueous media, microscopic and macroscopic effects of temperature are of utmost importance. Temperature can change physical, chemical, electrical, hydrological and mechanical properties of fluids such as viscosity, density, dielectric constant, refractive index, diffusion coefficient, hydrolysis, etc with change in intermolecular forces such as van der Waals [4]. It also influences colloidal properties and stability of particles. Temperature has been reported to influence aggregation [5], attachment efficiency [6], dissolution [7], and adsorption of ENPs [8].

The current work reports the role of water temperature in the behavior of ZnO NPs under various simulated conditions that are representative of freshwater, estuarine water, and seawater. Temperature levels are set to indicate cold (15 °C), temperate (25 °C), and tropical (35 °C) surface waters. The settling distance is further calculated to predict the extent of exposure of water column and benthic organisms. Finally, the predicted values of synthetic samples are compared with genuine river and coastal marine samples. This investigation can advance our understanding about fate and transport of ENPs in the nature regarding climate conditions.

2. Experimental

2.1. Chemicals
ZnO nanopowder (zincite, particle size: 24 – 71 nm, specific surface area: 15 – 45 m²/g) was supplied by Alfa Aesar (Ward Hill, MA, U.S.A.). Analytical grade sodium chloride, calcium sulfate, sodium hydroxide, and humic acid (sodium salt), were bought from Sigma-Aldrich (St. Louis, MO, U.S.A.). Nanopure water (18.2 MΩ) was produced with a PURELAB Option-Q water purification system (ELGA LabWater, Marlow, U.K.). All solutions were filtered through 0.2 µm syringe filters (Whatman, Sanford, ME, U.S.A.). The exact humic acid concentration as well as natural organic matter (NOM) concentration were measured with UV–visible spectroscopy at λ = 254 nm using calibration curve of pure humic acid [9]. ZnO nanopowder was dispersed (100 mg.L⁻¹) in solutions containing humic acid and salts, followed by pH adjustment with diluted NaOH. Table 1 shows specifications of synthetic freshwater (SFW), estuarine water (SEW), and seawater (SSW), samples. Samples were incubated in the dark, or in amber glass vessels, for 24 and 48 h. Genuine water samples were collected from river and coastal marine in Singapore.

| Type  | pH | NOM (mg C.L⁻¹) | NaCl (mM) | CaSO₄ (mM) |
|-------|----|----------------|-----------|------------|
| SFW   | 7.5| 30             | 10        | -          |
| SEW   | 8.0| 10             | 50        | 0.5        |
| SSW   | 9.0| 5              | 200       | 1          |

2.2. Methods
Time resolved dynamic light scattering (TR-DLS) was conducted using Model BIC 90Plus DLS analyzer (Brookhaven Instruments, Holtsville, NY, U.S.A.). Sedimentation plots were obtained by measuring the optical absorbance at λ = 368 nm and recording the change in initial absorbance as a
function of time with Model UV-2450 UV–visible spectrophotometer (Shimadzu, Kyoto, Japan). The analyzers were equipped with temperature control accessories for TR analyses. To determine release of zinc ions, samples were first centrifuged at 14000 rpm for 30 min, and filtered through 0.02 µm syringe filters [2,7]. The supernatant was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 7300 DV, Perkin-Elmer, Waltham, MA, U.S.A.). All experiments were performed in triplicate.

3. Results and discussion

3.1. Aggregation and sedimentation

Synthetic water samples were incubated at different temperatures. Figure 1a shows the aggregation rates of these samples, estimated from linear regression analysis of time-dependent hydrodynamic diameter (HDD) curves within the first 60 min (20 min for the SSW sample). As shown, aggregation rate increased with increasing temperature (temperature-induced aggregation). However, this change was not significant for all samples at the 95% confidence level, based on one-way analysis of variance (ANOVA). Since Brownian motion and collision frequency of the NPs increase at elevated temperatures, the interaction energy barrier between NPs would likely be overcome, and the electric double layer (EDL) compressed, thereby attaching NPs to one another [10]. It is worthy to note that viscosity, density, and dielectric constant of water as well as chemical potential, activity and ion mobility of electrolyte also undergo changes with variation of water temperature [4]. The increased van der Waals attractive forces and reduced EDL repulsive forces at higher temperatures as a result of alteration in physical properties of water, electrolytes, and ZnO NPs, can further be estimated using classical/extended Derjaguin–Landau–Verwey–Overbeek (DLVO/EDLVO) theory. It describes the enhanced propensity of NP attachment.

Figure 1b demonstrates influence of temperature on HDD of synthetic samples after 24 h equilibration. ZnO NPs in SSW sample form aggregates with HDD >3 µm, while other samples were effectively stabilized with NOM. The ANOVA results showed that the ZnO NP aggregation was greatly influenced by temperature in the SFW and SEW samples (significant at \( p < 0.025 \) and \( p < 0.01 \), respectively), whereas it did not exhibit significant variation in the SSW sample (\( p > 0.05 \)).

Figure 1c illustrates the aggregation kinetics of these ZnO NP suspensions at 35 °C. ZnO NPs were stabilized in the presence of NOM \( \geq 10 \text{ mg C.L}^{-1} \), and addition of 50 mM NaCl and 0.5 mM CaSO\(_4\) to SEW sample did not markedly enhance the NP aggregation. In contrast, the presence of 200 mM NaCl and 1 mM CaSO\(_4\) significantly increased aggregation kinetics in the SSW sample within the first hour of dispersion of ZnO NPs. Critical coagulation concentration (CCC) should be reached at these levels of electrolytes, thereby exerting the highest aggregation rate [10,11].
Concomitant with the formation of NP aggregates, they would settle in the water column and increase the risk of exposure to benthic organisms in aquatic systems. They may then undergo several transformations in the sediment [1]. Estimation of settling velocity will enable us to predict NPs exposure time to water column organisms. We further conducted sedimentation experiments and modeled settling distance according to Stokes’ sedimentation equation [12]. From aggregation kinetics of synthetic samples (Figure 1c), it was found that the most unstable ZnO NP suspension was in the SSW sample. Hence, the effect of temperature was investigated on this sample.

Figure 2a illustrates sedimentation plots of SSW. While increase in temperature may enhance Brownian motion thereby hindering sedimentation of NPs [6,12], fast formation of large aggregates resulted in efficient removal of the ZnO NPs from the water column, thus decreasing the optical absorbance. Figure 2b shows the calculated Stokes’ settling distance of SSW. As expected, longer distance was observed at higher temperature (e.g. 261 mm at 35 °C). The results were consistent with sharp decrease in absorbance within the initial 20 min due to sedimentation of NPs in the spectrophotometer cuvette (height: 30 mm). The estimated settling distances were 25.6, 31.1, and 33.1 mm, at 15, 25 and 35 °C, respectively. The settling distance was modeled for different synthetic water samples at 35 °C and is illustrated in Figure 2c. Stable ZnO NP suspensions (SFW and SEW) were transported 2.8 and 21.4 mm in the water column after 3 h. This further confirmed that NOM >10 mg.L⁻¹ effectively stabilized ZnO NPs in water.
3.2. Dissolution

The effect of NOM, electrolyte type and concentration as well as incubation temperature were further investigated on dissolution kinetics of ZnO NPs. The high bioavailability and toxicity of ZnO NPs to aquatic organisms have been shown [2,3]. We further simulated real environmental conditions with respect to various temperatures (cold, temperate, and tropical) and water chemistries. Figure 4a depicts the dissolution rate of different synthetic samples within the initial 12 h under various incubation temperature conditions. ZnO has negative enthalpy of dissolution [13]. Hence, increasing temperature would lead to a reduction of its dissolution [7]. The environmental implication is that, if ZnO enters the organism in the form of NPs, body temperature (~37 °C) will induce aggregation and reduce dissolution, and therefore, decrease bioavailability and toxicity of ZnO NPs. However, since ZnO NP is readily hydrolyzed in water [14,15], it would be less likely to accumulate in form of NPs in the organism at low environmental concentration levels.

As can be seen in Figure 3a, a decrease in dissolution rate was observed for SEW samples. The dissolution rates were $6.36 \times 10^{-5}$ and $5.15 \times 10^{-5}$ mol.L$^{-1}$.h$^{-1}$ at 15 °C and 35 °C, respectively. The maximum dissolution rate was given for SFW at 15 °C ($7.44 \times 10^{-5}$ mol.L$^{-1}$.h$^{-1}$). This proved that a high concentration level of NOM (ca. 30 mg C.L$^{-1}$) and low aggregation rate will enhance the dissolution. The enhanced hydrolysis of the NP surface might be attributed to the surface adsorption of humic acid and weakening the surface oxygen bond as well as providing large surface area due to the formation of small aggregates in the SFW medium [14].

Figure 3b demonstrates total percentage of released zinc ions of the synthetic samples under various incubation temperatures after 48 h equilibration. As expected, the lowest dissolution was observed for SSW while the highest was for SFW at 15 °C (9.2%). Electrolytes can enhance dissolution of particles according to the Debye–Hückel law [16]. While it was observed for SEW, very high aggregation kinetics of SSW suppressed dissolution of ZnO NPs in SSW. Figure 3c illustrates the dissolution kinetics of synthetic samples. This suppression is observed when dissolution kinetics of SSW is compared with its aggregation kinetics. We term this process as “aggregate-suppressed dissolution”.

Figure 2. Sedimentation plots (A), and Stokes’ settling distance (B), of ZnO NPs in SSW at different temperatures. Stokes’ settling distance of ZnO NPs in different synthetic waters at 35 °C (C)
Figure 3. Effects of temperature on dissolution rate (A), and released Zn\(^{2+}\) after 48 h (B), of ZnO NPs in synthetic waters. Dissolution kinetics of ZnO NPs in synthetic water samples at 35 °C (C).

3.3. Genuine water samples

To validate anticipation of aggregation and dissolution kinetics of real environmental waters, the results of simulated conditions were compared with those of genuine water samples. ZnO NPs (100 mg.L\(^{-1}\)) were dispersed in genuine samples and incubated at different temperatures. The specifications of these samples are tabulated in Table 2. The characteristics of genuine river water (RW) fitted well with those of the SEW sample. The zinc contents of river and seawater samples were measured prior to dissolution experiments.

Table 2. Characteristics of genuine water samples

| Type             | pH  | NOM (mg C.L\(^{-1}\)) | Salinity (ppt) | Zn\(^{2+}\) (µg.L\(^{-1}\)) |
|------------------|-----|-----------------------|----------------|-----------------------------|
| River            | 7.6 | 10.3                  | 6.3            | 13                          |
| Coastal marine   | 8.1 | 4.2                   | 25.8           | 7                           |

Tables 3 and 4 demonstrate the comparison of the predicted aggregation, and dissolution rates under simulated conditions, respectively. Percentages of deviation were in the range 10.8 – 25.5% and 3.8 – 20.5% for aggregation rate and dissolution rate, respectively. The highest deviation of predicted rates for both the aggregation and dissolution of ZnO NPs were observed for genuine RW, possibly due to the effects of various NOMs and electrolytes. Our results showed that the simulated conditions predicted the fate of ZnO NPs very well in the real aquatic environment.
Table 3. Comparison of aggregation rate (nm.s\(^{-1}\)) of ZnO NPs in simulated synthetic with genuine samples

| Temperature | \(\text{dr/dt (SEW)}\) | \(\text{dr/dt (genuine RW)}\) | deviation (%) | \(\text{dr/dt (SSW)}\) | \(\text{dr/dt (genuine SW)}\) | deviation (%) |
|-------------|----------------|-----------------|--------------|----------------|----------------|--------------|
| 15 °C       | 0.031          | 0.038           | 18.4         | 1.38           | 1.62           | 14.8         |
| 25 °C       | 0.035          | 0.047           | 25.5         | 1.52           | 1.73           | 12.1         |
| 35 °C       | 0.041          | 0.05            | 18.0         | 1.57           | 1.76           | 10.8         |

Table 4. Comparison of dissolution rate \((\times 10^{-5}\) mol.L\(^{-1}\).h\(^{-1}\)) of ZnO NPs in simulated synthetic with genuine samples

| Temperature | \(\text{dC/dt (SEW)}\) | \(\text{dC/dt (genuine RW)}\) | deviation (%) | \(\text{dC/dt (SSW)}\) | \(\text{dC/dt (genuine SW)}\) | deviation (%) |
|-------------|----------------|-----------------|--------------|----------------|----------------|--------------|
| 15 °C       | 6.36           | 7.11            | 10.4         | 1.32           | 1.19           | 10.9         |
| 25 °C       | 5.64           | 6.73            | 16.2         | 1.22           | 1.14           | 7.0          |
| 35 °C       | 5.15           | 6.48            | 20.5         | 1.01           | 1.05           | 3.8          |

4. Conclusion
ZnO NPs are some of the most widely used ENPs and released, when their fate depends on their physicochemical interactions in the environment. These in turn determine the toxicity of these NPs to a variety of organisms exposed to them. Our study provided some insight into the role of water temperature in the behavior of ZnO NPs and could be extended to other ENPs. The influence of temperature was determined in terms of aggregation, sedimentation, and dissolution of ZnO NPs. While it is costly and labor- and instrument-intensive to investigate the fate of ENPs in various aqueous systems and regions (cold, temperate, and tropical), our results clearly showed that the examination of ENP behavior under simulated conditions allows cost- and time-effective anticipation of their behavior in nature to be made.

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