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Combined effects of water temperature and chemistry on the environmental fate and behavior of nanosized zinc oxide

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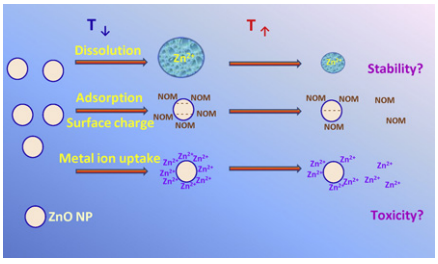
HIGHLIGHTS

- Effects of temperature on ZnO NP behavior were investigated in synthetic freshwaters.
- Water chemistry had more pronounced effects than temperature on the NP aggregation.
- NP dissolution and surface adsorption increased by lowering the temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

Information on the effects of water temperature, among several environmental factors, on predicting the behavior, fate, and exposure risks of engineered nanoparticles (NPs), is scarce. In the present work, the behavior and fate of commercial zinc oxide (ZnO) NPs with an average diameter of 52 nm were extensively investigated in U.S. Environmental Protection Agency standard, synthetic freshwater media with varying pH and hardness containing 2 mg C/L of humic acid as a natural organic matter (NOM) surrogate, in the temperature range from 4 °C to 45 °C, representing very cold to warm waters. While a constant increase of ZnO hydrodynamic diameter was observed with increasing the temperature, results of analysis of variance showed that the temperature effect was insignificant in the samples with enhanced ionic strength, and water chemistry had more pronounced effects than the temperature on the rate of ZnO NP aggregation. With increase of the water temperature, the NP surface charge was partially reduced. ZnO NP dissolution and surface adsorption of NOM and zinc ions were found to be exothermic processes, and the latter was significantly decreased when temperature was increased in all test matrices. This study provides useful information for assessing environmental risks of ZnO NPs in aqueous matrices with various water chemistries and temperatures.

1. Introduction

Engineered nanoparticles (ENPs) are being manufactured and utilized extensively. They are introduced to receiving water bodies through waste streams and/or accidental releases (Nowack et al., 2012). A majority of them have been recognized as toxic contaminants to aquatic organisms due to their high surface reactivity and release of ionic species (Farré and Barceló, 2012; Love et al., 2012). While a number of studies have been conducted to predict the transport and fate of ENPs in various environmental compartments (Auffan et al., 2013), there still remain several uncertainties to link the toxicity of ENPs to their physicochemical interactions and transformation in different media (Lowry et al., 2012; Petosa et al., 2010).

Some researchers have focused on the behavior of metal oxide NPs in both natural and synthetic water samples under well-controlled

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water chemistry conditions (Blinova et al., 2010; K. Li et al., 2011; Li et al., 2013; Miao et al., 2010; Ottofuelling et al., 2011). Among various environmental factors mainly originated from water chemistry such as pH, type and content of electrolyte, and type and content of natural organic matter (NOM), studies on ambient conditions like light and temperature are scarce (Y. Chen et al., 2012; Zhou et al., 2012). So far, the effects of thermal conditions and annealing on the synthesis (Richardson and Lange, 2009; Zhang et al., 2011), crystal structure (J. Yang et al., 2009), catalytic (F. Liu et al., 2013), optical (Koushki et al., 2011; Sikora et al., 2012; J. Yang et al., 2009), and antimicrobial activities of e.g., zinc oxide (ZnO) NPs (Ling et al., 2012) have been reported.

Surface water temperature may vary substantially, and in turn influences physicochemical properties of water body and discharged contaminants. Hence, ENPs will possibly undergo changes in original properties and potentially also toxicity with varying temperature of the receiving water. Since several processes in colloidal chemistry are thermodynamically controlled or thermally induced (Leite and Ribeiro, 2012), any changes in the water temperature may affect the physicochemical interactions and reactivity of NPs in natural waters. While the water chemistry such as pH and ionic strength can significantly affect the NP behavior in aqueous media, the current knowledge suggests that the water temperature is also influential in the aggregation behavior of copper(II) oxide (CuO) (Misra et al., 2012a), cerium (IV) oxide (CeO_2) (K. Li et al., 2011; Zhang et al., 2012; Zhou et al., 2012), and ZnO NPs (Majedi et al., 2014; Zhou et al., 2012). The water temperature has also been reported to exert an effect on the solubility of silver (Ag) (Liu and Hurt, 2010; Kittler et al., 2010), titanium(IV) oxide (TiO_2) (Schmidt and Vogelsberger, 2006), and ZnO NPs (Li et al., 2011b; Majedi et al., 2014; Reed et al., 2012). The majority of these studies did not focus on the role of water temperature, since few incubation temperature conditions were investigated and the significance of this factor among other environmental factors was not evaluated. Furthermore, the temperature effects on the environmental behavior of NPs were not broadly examined in a systematic study. In these studies, with increase of the temperature, either temperature-induced aggregation or disaggregation were observed for various NPs, and the solubility of e.g., Ag NPs, increased while it declined for ZnO NPs.

We previously reported the role of water temperature in the kinetics of aggregation and dissolution of ZnO NPs in some laboratory-prepared samples (Majedi et al., 2013). In that short communication, a limited temperature range was studied, and no standard protocols were used for the preparation of the water samples. Furthermore, important surface properties of the NPs such as surface charge and adsorption were not investigated. The methodological details and some other environmental behavior and implications of ZnO NPs due to temperature variation were not discussed. In another work, we applied a multivariate approach to investigate the effects of combinatorial environmental factors including water temperature on the aggregation and dissolution of ZnO NPs (Majedi et al., 2014). In that study, the concentration of organic acid and electrolyte type were found to be the most influential factors on the NP aggregation, and the aggregation process was promoted with increase of temperature in some selected samples. The temperature effect was also investigated at three levels of (15, 25, and 35) °C among other factors for the dissolution study, and the results showed that, in the combinatorial systems, this factor was less significant compared to other factors such as pH and electrolyte type. Very recently, the effects of temperature change on the long-term stability and metal (dissolved nickel) leaching of single wall carbon nanotubes (SWCNTs) were investigated in different aqueous samples (deionized, fresh, storm, and wastewater) (Adeleye and Keller, 2014). The study showed that the stability of SWCNTs was reduced at an elevated incubation temperature (ca. 40 °C) due to nanotube surface charge reduction which favored aggregation. On the other hand, no significant difference was observed between the long-term metal leaching (over 3 months) at 4 °C and 40 °C in all test matrices.

The current study focuses on the effects of water temperature on the behavior and fate of ZnO NPs in standard, synthetic freshwater samples with varying pH and hardness. Although experiments in natural waters could produce more realistic results, they may not provide direct and necessary information on the processes involved owing to the complexity of these systems. So far, synthetic (artificial) waters that could mimic the conditions of natural waters with reduced complexity, have been widely used for the anticipation of the behavior, fate and toxicity of NPs in aquatic environments (Adegboyega et al., 2012; Lee and Ranville, 2012; Li et al., 2011a; Ma et al., 2013; Miao et al., 2010; Odzak et al., 2014; Oliver et al., 2014; Reed et al., 2012; Wong et al., 2010). The aggregation of these NPs as well as surface charge, solubility, and surface adsorption of NOM and zinc ions (Zn^{2+}) is studied at various temperature levels (4 °C–45 °C), and differences among observations are evaluated by one-way analysis of variance (ANOVA). The occurrence, solubility, bioavailability, and toxicity of ZnO NP are high (Ma et al., 2013), and the NP has been listed as a priority nanomaterial for exposure and effects assessment (OECD, 2010). As such, it is necessary to predict ZnO NP behavior, fate and toxicity in aquatic environments through a systematic study of NP aggregation, dissolution, and adsorption.

2. Materials and methods

2.1. Chemicals

ZnO nanopowder (average particle diameter = 52 nm; see Table 1 for properties), analytical-reagent grade sodium bicarbonate, calcium sulfate, magnesium sulfate, potassium chloride, and humic acid (sodium salt, dissolved organic carbon (DOC) ~54% (w/w)), were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ultrapure nitric acid (65% v/v) and zinc standard solution (1000 mg/L) were obtained from Merck (Darmstadt, Germany). Ultrapure water (18.2 MΩ) was generated by a PURELAB Option-Q water purification system (ELGA LabWater, Marlow, UK).

2.2. Sample preparation

Three types of water samples, very soft water (VSW), moderately hard water (MHW), and very hard water (VHW), were prepared according to U.S. Environmental Protection Agency (EPA) protocol, EPA-821-R-02-013 (EPA, 2002), as standard, synthetic freshwater samples with various pH and hardness levels. The water chemistry (Table S1) and the method of the preparation of these samples are provided as Supplementary Material. Humic acid solution (500 mg/L) was stirred at pH 9.0 overnight to ensure dissolution, and filtered through a 0.1-μm cellulose membrane filter. It was then added to the samples as an NOM surrogate (2 mg C/L). The addition of humic acid did not change the sample pH significantly (<0.1). The pH and ionic strength values of these samples are shown in Table 2. All solutions were passed through 0.1-μm syringe filters (Whatman, Sanford, ME, USA) before use. The temperature of the water samples was adjusted by incubation in a

Table 1
Summary of ZnO nanoparticle properties.

Parameter	Value
Density (g/mL)	5.61
Vendor-reported size (nm)	50–70
Average particle size — TEM-measured (nm)	52 ± 9
HDD — DLS-measured (nm)	330 ± 25
Specific surface area — calculated (m^2/g)	16 ± 2
BET specific surface area — measured (m^2/g)	19 ± 3
Isoelectric point (IEP)	9.0
Zeta potential (mV) in ultrapure water (pH = 6.4)	+23
Purity by TGA (wt.%)	97.13
Moisture content by TGA (wt.%)	1.68