

Engineered Nanoparticles in the Environment: Their Fate, Transport and Interaction with Organic Pollutants

E. Sahle-Demessie¹, Amy Zhao¹, Heidi Grecsek²

¹U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Laboratory, Cincinnati, OH 45268

²Perkin Elmer, Inc, 710 Bridgeport Avenue Shelton CT 06484-4794

ABSTRACT

Nanotechnology has emerged as one of the leading fields in science having tremendous application in diverse disciplines. As nanomaterials become increasingly part of everyday consumer products, it is imperative to measure their potential release during production, use, and disposal, and assess their impact on human health and the ecosystem. This compels the research to better understand how the properties of engineered nanomaterials (ENM) lead to their accumulation and redistribution in the environment, whether they could become novel pollutants or if can affect the mobility and bioavailability of other toxins. This study is focused in understanding the adsorption of hydrophobic pollutants to ENM, influence of nanoparticles on the octanol-water partitioning organic pollutants. The suspended particles from the water phase were separated, and the adsorbed substances were analyzed using a combination of thermal-chromatographic- mass spectroscopic techniques. Sorption of hydrophobic organic pollutants to nano-particles increased the concentration of contaminants in the aqueous phase as compared to the "real" partitioning due to the octanol-water partitioning. The effects of nano-materials on the mobility of hydrophobic pollutants such as polyaromatic hydrocarbon compounds with two and three-ring that have relatively small water solubility and pesticides. The study will help to understand the influence of nano-materials on contaminants fate, mobility and bioavailability in the aquatic environment

Keywords: hydrophobic pollutants, nanomaterial facilitated transport, partitioning coefficient.

INTRODUCTION

The fate of an anthropogenic organic compound released into the environment is primarily controlled by a combination of three factors: 1) the prevailing environmental conditions at the point(s) of discharge, transport and subsequent residence, 2) the physicochemical properties of the compound, and 3) patterns of use (that is, locus and timing of introduction). Hydrophobic organic pollutants have a tendency to avoid contact with water and to associate with a nonpolar, nonaqueous environment, such as an organic particle or a particle containing an organic coating or the lipid-containing

biomass of an organism [1]. Natural aquatic systems have many interacting components that could affect the fate of ENM release into the environment (Figure1).

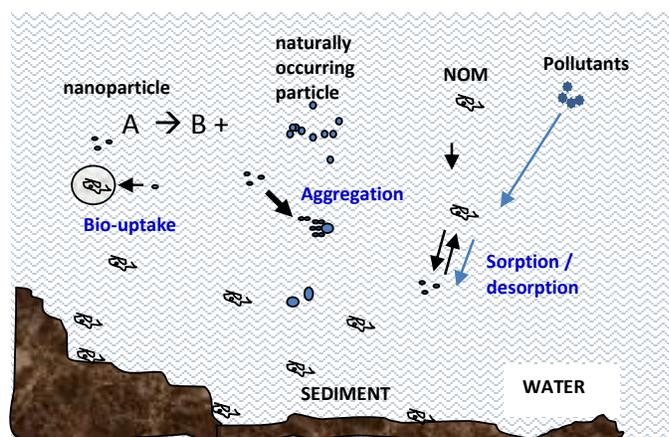


Figure 1 Behavior and fate of hydrophobic pollutants in surface and ground waters

The physico-chemical properties relating to the environmental behavior of hydrophobic organic compounds are mainly affected by the aqueous solubility and octanol-water partition coefficient. Aqueous solubility (S_w) is defined as the equilibrium distribution of a solute between water and solute phases. Because S_w is the maximum solute concentration possible at equilibrium, it can function as a limiting factor in concentration dependent (for example, kinetic) processes. The distribution equilibrium of a compound between water and octanol, K_{ow} , can be determined experimentally, and provides great potential of application. Thus, orders of magnitude predictions are possible for the solid/liquid partitioning of many compounds under many conditions [2].

Hydrophobic pollutants transport adsorbed onto the NP surface and thus may travel a long distance in the environment and increase their bioavailability. This effect has been used to deliver drugs to particular position in animals and plants [3,4].

The octanol-water partition coefficient is the ratio of the concentration of a chemical in octanol and in water at

equilibrium. Octanol is an organic solvent that is used as a surrogate for natural organic matter. This parameter is used in many environmental studies to help determine the fate of chemicals in the environment, such as to predict the extent a contaminant will bioaccumulate in fish. The octanol-water partition coefficient has been correlated to water solubility; therefore, the water solubility of a substance can be used to estimate its octanol-water partition coefficient. The presence of nano-particles influence the octanol-water partitioning of hydrophobic organic water contaminants

EXPERIMENTAL

Materials

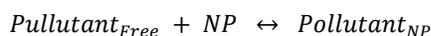
We tested using 2 and 3 ring PAHs for this study including anthracene, naphthalene and phenanthrene and pesticides as probe molecules to study the fate and transport of hydrophobic organic pollutants in water streams nanoparticles. The experimental procedure for this study involves the addition of 0-20 mg/l of PAHs in 200 ml of octanol to 900 ml of DI water containing different concentrations of nanoparticles (ranging from 0-20 mg/l) in Erlenmeyer flask. After stirring the flasks for 5 days the mixture is allowed to settle for 3 hours and then the aqueous and octanol layers will be separated. The aqueous suspensions were divided into three portions. One portion will be extracted with equal volumes of methylene chloride (MC) and hexane. The mixture will be centrifuged and the supernatant organic phase will be collected and injected into GC. The concentrations of PAHs in MC and hexane and water were measured by Gas chromatography analysis. The second portion will be centrifuged at 10,000 rpm for 30 min. The mixture will be decanted and the settled nanoparticles will be put in crucible to dry in oven (105 °C) for 8 hr. The mass fraction of the adsorbed organics on dried particles will be analyzed using thermal gravimetric analyzer (Perken Elmer) and FTIR or TOC

Compound	Mole weight g mole ⁻¹	Boiling point °C	Water solubility mg l ⁻¹	Log K _{ow}
Toluene	92	110	500	2.73
O-xylene	108	144	106	3.12
Naphthelen	128	218	31.7	3.5
Phenanthrane	178	339	1.29	4.45
Anthracene	178	340	0.075	4.46
Heptachlor	373	135	0.056	6.26
Chlordan	409	175	0.1	6.32
Aldrin	364	decomp	0.026	6.5

Table 1 Hyrophobic water pollutants selected for the study

EQUILIBRIUM PARTITIONING

The sorption of polyaromatic hydrocarbons and hydrophobic pesticides on different NMs were investigated Three phase partitioning of POPs are measured by partition Coefficient of pollutant between NP and dissolved phase



Mass balance of pollutant

$$K_{NP} = \frac{[Pollut]_{NP}}{[Pollut]_{Free[NP]}} \dots\dots(1)$$

Rearranging equation 1

$$[pollut]_{total} / [Pollut]_{Free} = 1 + K_{NP}[NP] \dots\dots(2)$$

Where $[Pollut]_{total}$ and $[Pollu]_{total}$ are retentate and permeate concentration. Equation 2 is similar to Stern-Volmer relationship.

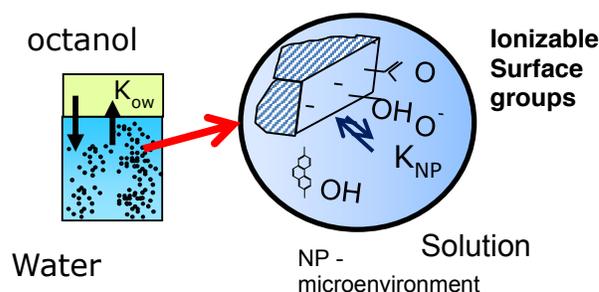


Figure 2. Schematic relationship of the experiment.

A complete phase separation between NP and water is necessary to obtain a valid K_{NP} value. Generally, this cannot be achieved due to the fact that the very fine particles pass through the filter, or do not settle during centrifugation. As a result the concentration of contaminants in the water phase could be overestimated, and the NP-water partition coefficient is underestimated.

In the presence of organic phase the total concentration of the pollutants is related to the concentration in water as;

$$\frac{[Pollut]_T}{[Pollut]_w} = K_{ow} + K_{w-NP}[NP] + 1 \dots(3)$$

RESULTS

Pollutant adsorption on Nanoparticles

The fate of organic compound released into the environment is primarily controlled by factors like the prevailing

environmental conditions at the point(s) of discharge, transport and subsequent residence, the physicochemical properties of the compound, and the patterns of use (that is, locus and timing of introduction). The physico-chemical properties relating to the environmental behavior of hydrophobic organic compounds are mainly affected by the aqueous solubility and octanol-water partition coefficient. Aqueous solubility (S_w) is the equilibrium

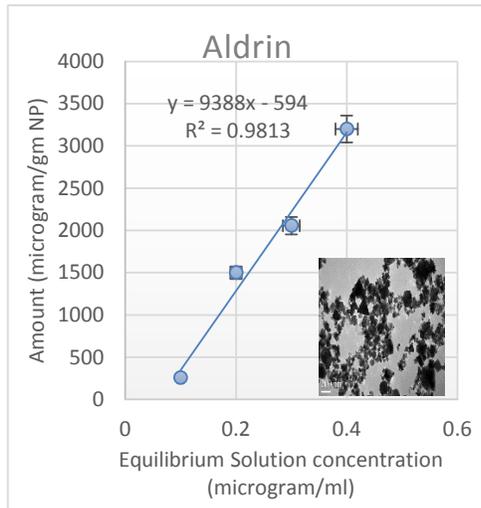


Figure 3 Adsorption capacity of nano-TiO₂ to aldrin as a function of concentration

The results of the solubility enhancement experiments are shown in Figure 3. TiO₂ is effective at binding PAHs and pesticides.

Analyzing Pollutants Adsorbed to NP

TGA Analysis

Thermogravimetric (TGA) analysis was done using Pyrus1 (PerkinElmer). The common feature in the TGA was a dramatic weight loss between approximately 150°C and approximately 350 °C in a N₂ atmosphere, which was not present for bare ENM, and, thus, was assigned to the surface adsorbed organic pollutants. The onset of weight loss and the temperature of maximal weight loss rate (T_{MAX}) showed no dependence on the ENM and were determined by the nature of the chemical group directly attached to the surface. The T_{MAX} values were approximately 350 - 400 °C.

TGA-GC-MS

Nano-TiO₂ separated from the pollutant-water mixture was analyzed using the combination of a TGA with a GC/MS (Figure 4). When samples of NP were heated at linear rate on

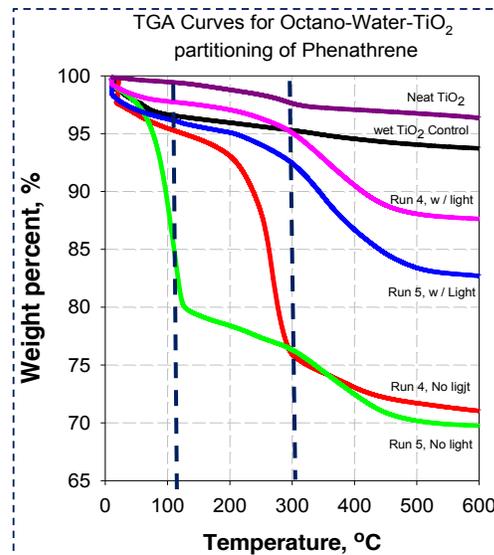


Figure 4 Thermogravimetric analysis of selected samples of PAH adsorbed nano-TiO₂

he TGA furnace moisture, volatile compounds and adsorbed pollutants were released sequentially. These gases were then transferred to the GC where the components were collected. The sample were then run by GC to separate the material and the peaks identified by the MS. Because of its ability to detect very low levels of material in complex mixtures, the TG-GC/MS is a powerful tool for quality control.

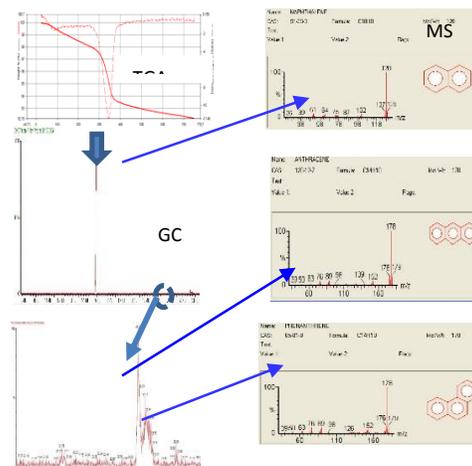


Figure 5 TGA-GC-MS system for the analysis of NP-adsorbed pollutants

Transport of nanomaterials through saturated porous bed

The transport of nanoparticle suspended in water may depend on many factors. A representative breakthrough profile is presented in Figure 6. The breakthrough curves at the presence of various ionic concentrations are shown by the normalized effluent nanoparticle concentration (C/C_0) as a function of cumulative volume normalized to pore volumes. The pH was maintained at 6. The results show that the water chemistry has a great impact on the transport of nanoparticles. In Phase 1, for ionic concentration lower than 10mM, the C/C_0 begins to increase after the first pore volume, and keeps increasing until the feed was switched to the particle free solution. A fast decrease of C/C_0 was observed in Phase 2. During Phase 3, particles which were previously deposited in Phase 2 were partly detached due to a sudden decrease of ionic concentration. Sharp peaks were observed during this phase. The results show that pollutants adsorbed to nanoparticles may be transported through porous media.

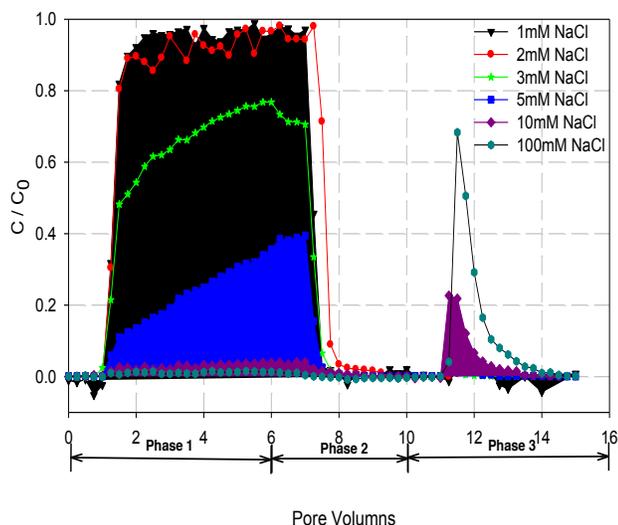


Figure 6 Breakthrough of Ceria nanoparticles through saturated packed column

Nanoparticles in the environment are capable of enhancing the solubility of very hydrophobic PAHs and pesticides. Potentially, this solubility enhancement may contribute to the transport of such PAHs over distances greater than expected.

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