

## **INFLUENCE OF COLLOIDS AND SEDIMENTS ON WATER QUALITY**

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### **Summary**

The influence of colloidal material and aquatic sediments on water quality is a very broad topic. This chapter will focus on how particulate material and sediments influence the fate, transport, and cycling of trace organic and inorganic chemicals that impact water quality. Also the manner in which colloidal material can significantly impact contaminant transport in groundwater systems will be discussed.

Colloids are ubiquitous in surface water environments; they are reactive and behave differently from dissolved molecules. Colloids have a significant role in regulating trace elements, major ions, and organic contaminants distribution in surface water systems including lakes, rivers, estuaries and oceans. It has been found that up to 99.9 percent of total heavy metals in riverine or lacustrine systems can be associated with colloidal material. Thus, only 0.1 percent seems to be present in aqueous solution or sorbed to particles larger than about 0.2  $\mu\text{m}$ . Efforts to understand and quantify contaminant fate and transport in these systems need to consider colloidal interactions with other colloids, with contaminants, and with the active sediment bed.

Colloids have been recognized as having the potential to significantly influence the fate and transport of pollutants in groundwater systems. Sorption of contaminants to mobile colloidal material in aquifers has led to the advancement of a new conceptual model for contaminant partitioning and transport that contains three-phases: aqueous (mobile), colloidal (mobile) and solid (fixed). In certain groundwater systems, it has been found

that the aqueous mobile phase is negligible, and that virtually all transport observed was due to contaminants sorbed to colloids.

Due to a strong partitioning of many contaminants to the solid phases present in aqueous systems, sediments remain a significant reservoir of contaminants in lakes, rivers, estuaries, and harbors. Numerous chemicals continue to impact ecosystem health due to their persistent and bioaccumulative properties.

## **1. Overview of Significance**

It has been well established that numerous trace constituents and certain major ions are controlled by the behavior of colloidal material. To a large extent, surface phenomena are responsible for this association, although major ions may also exhibit behavior governed by solubility (e.g. formation or dissolution of particles). Colloidal material and sediments are also closely related, as much of the colloidal material present in lakes, rivers, estuaries and oceans is deposited as sediment. The movement of these particles has a pronounced influence on adsorption of hydrophobic organic contaminants (HOCs) to colloids followed by gravitational settling of the colloids and burial in the sediment. For example, such process has been found to be the most significant removal mechanism for hydrophobic organic contaminants in the Laurentian Great Lakes of North America.

Resuspension of the surface layer of sediment can also be a significant source of pollutants, organic matter, and nutrients to the water column. The sediment surface layer (the top few centimeters) may contain greater masses of organic matter and nutrients than the entire water column. Deep burial in sediments is many times considered a safe repository for contaminants associated with those sediments, although large storms have the capacity to resuspend and redistribute the contamination making it available once again. However, even this mechanism of resuspension/desorption is somewhat controversial, as it has been found that contaminated sediments from four sites within Hamilton Harbor (Ontario, Canada) had excess sorptive capacity for metals and did not appear to act as sources of dissolved metals to the water column. In the case of hydrophobic organic contaminants release from resuspended sediments, it is likely desorption kinetics that control contaminant release to the water column, as numerous studies have demonstrated extremely slow desorption of hydrophobic organic contaminants from aged sediments.

## **2. Sources and Characteristics of Particulate Material**

The characteristics of particulate and colloidal material are largely dependent upon its source and thus the unique environmental system under consideration. In open ocean systems the majority of particulate matter is biotic in origin and is generated in the upper surface layer of the ocean. This is in contrast to riverine systems that are heavily influenced by erosion of material in the watershed. Large lakes may be qualified as a mix of these two extremes. Biogenic colloids (cellular debris, algae, phytoplankton) may contribute significantly to the overall particle concentration in the water, and inputs of abiotic particles from erosion processes may also be significant.

The characteristics of particles that are of interest depend upon the processes that are being considered. For the focus of this chapter, the primary concern is fate and transport of contaminants, which is strongly linked to the fate and transport of the particulate material (see *Multimedia Fate and Transport of Organic Pollutants*). It is useful here to establish some definitions related to particles. Following fairly well established conventions, which will be followed in this chapter, “particle” or “particulate material” are general terms used to describe a molecular entity larger than approximately 1 nm. “Particle” may also be used in a restrictive sense in contrast to “colloid.” A standard differentiation is that a solute or dissolved material is less than 1 nm, colloidal material is greater than 1 nm and less than 0.45  $\mu\text{m}$ , and a particle is larger than 0.45  $\mu\text{m}$ . These size cutoffs are more-or-less arbitrary, and have arisen from the traditional definition of “dissolved” vs. “particulate”, which has been based upon filtration using a 0.45  $\mu\text{m}$  filter. However, these size ranges do continue to have some utility, as it is generally regarded that particles less than 0.45  $\mu\text{m}$  will not settle on their own (i.e. without aggregating with other particles), nor are they susceptible to aggregation due to fluid shear. Larger particles may have sufficient settling velocities to be significant in natural environments. It should be pointed out that others have suggested colloids should be considered to range in size from 1 nm to 1  $\mu\text{m}$ , with solutes being smaller and particles larger. Finally, it has been suggested that absolute size should not form the basis for the definition of colloidal, but rather the behavior of the material. Thus, a definition of a colloid has been proposed as “...any constituent that provides a molecular milieu into and onto which chemicals can escape from the aqueous solution, and whose movement is not significantly affected by gravitational settling”. A visual description of these definitions is shown in Figure 1.

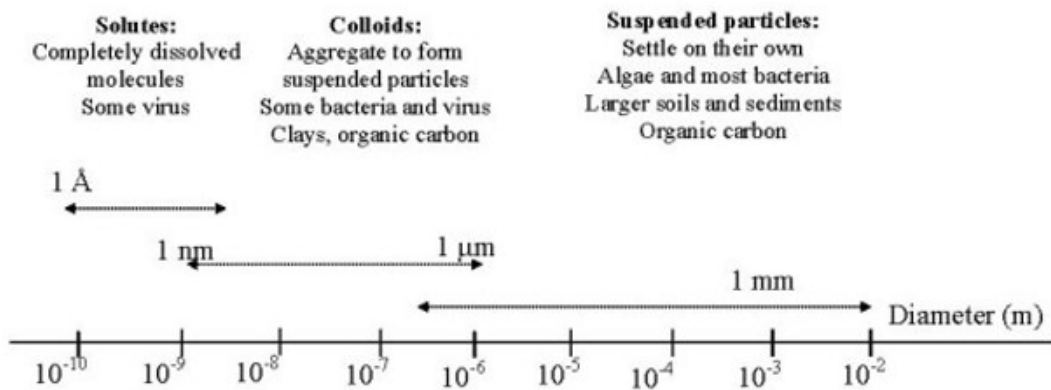


Figure 1: Descriptive sizes for solutes, colloids, and suspended particles

Particle concentration in an environmental system is a second important characterization. As a general statement, riverine systems contain the highest particle concentrations, followed by estuaries and lakes, coastal waters, and finally the open ocean. From a river to the bottom of the ocean, particle concentration may range over six orders of magnitude. Even groundwater systems contain significant concentrations of colloids, and over the last decade it has been recognized that these colloids often play a pivotal role in contaminant transport in groundwater aquifers.

In addition to size distributions and absolute concentrations, the fate of particles and their chemical reactivity are primarily dependent upon the surface characteristics of the particles. Important surface characteristics include surface area, surface site density, surface charge characteristics (charge as a function of pH, point of zero charge), and the chemical reactivity of surface functional groups. As will be discussed below, the fate and transport of colloidal particles is strongly a function of the surface charge.

The relationship between a given contaminant and colloidal material typically depends upon specific interactions between the two. For example, hydrophobic organic contaminants (HOCs) will typically bind strongly to organic matter, so an important characterization of colloidal material would be the extent of surface coverage by organic matter, or perhaps the fraction of colloids that derive from biotic materials. However, there are additional mechanisms by which HOCs may bind with inorganic colloids such as hydrophobic exclusion from the aqueous phase. In consideration of any particular environmental system, it is critical to investigate the specific nature of the colloidal material present, and the interaction of colloids and contaminants of concern. More details on specific binding mechanisms for trace metals and HOCs will be presented below. It is important to note here that colloids in natural surface water systems are, in general, high in organic carbon. It has been estimated that about 50 percent of operationally-defined “dissolved organic carbon” is actually colloidal. Furthermore, abiotic colloids are typically found to have at least some surface coverage of organic material, which may derive from humic material, proteins and other decay byproducts, bacteria, etc.

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### Biographical Sketches

**Dr. Kevin H. Gardner** is an Associate Professor at the University of New Hampshire and Director of the Center for Contaminated Sediments Research. He previously held academic appointments at Case Western Reserve University and Hofstra University. Dr. Gardner's primary areas of expertise and research are related to contaminated sediments and colloid behavior. Recent work includes the development of a method for in-situ remediation of PCB-contaminated sediments using zero-valent metals, development of beneficial use options for contaminated dredged sediments (wetland creation, cement manufacture, lightweight aggregate manufacture), and assessments of leaching behavior from sediments under various management scenarios. His work related to colloidal behavior spans from the use of computer models to describe colloid aggregation to the development of techniques to deposit reactive colloids on aquifer media to accomplish in-situ remediation of contaminant plumes.

**Dr. Defne S. Apul** is an Assistant Professor at the University of Toledo. She has a Bachelor of Science degree in chemical engineering with a specialization in biochemical engineering from Bogazici University, Istanbul, a Master of Science degree in Environmental Engineering from Michigan Technological University, Houghton, MI, and a Ph.D. from the University of New Hampshire. Ms. Apul has worked on nutrient and organic carbon cycling in Lake Superior and analyzed settling and resuspension of particulate matter as well as tributary inputs, primary production and biodegradation in the water column. Ms. Apul's research areas of interest include surface water quality, unsaturated water movement and contaminant transport modeling, risk assessment, and probabilistic techniques.