Many potentially toxic trace metals and radionuclides are strongly adsorbed onto surfaces of mineral and organic compounds in soils and sediments, limiting their mobility in the environment. However, recent studies have shown that trace metals in soils, groundwater, rivers, and lakes can be carried by mobile colloidal particles. Understanding the release, transport, aggregation, and deposition of natural colloidal particles is therefore of utmost importance for developing quantitative models of contaminant transport and the biogeochemical cycling of trace metals.

**KEYWORDS:** colloids, groundwater, radionuclide, soil, trace metal, transport, vadose zone

**INTRODUCTION**

Colloidal particles are ubiquitous in environmental systems and can consist of inorganic mineral phases, organic biopolymers or microorganisms (i.e. biocolloids). In general, the importance of colloidal transport in natural systems depends on the presence, stability, and mobility of colloids and their interaction (sorption and reversibility) with the pollutant of interest (McCarty and Zachara 1989). Colloidal particles are usually smaller than about 1 µm in at least one dimension and have a high specific surface area (10–800 m² g⁻¹). They can have a significant impact on the transport of trace metals, which are strongly sorbed to solid phases and therefore rather immobile in the absence of mobile particles (Kersting et al. 1999). Biocolloid transport is relevant both as a pathogen risk and in remediation strategies to degrade or immobilize redox-sensitive contaminants. Also synthetic colloids (e.g. zero-valent iron) have been used in a remediation strategy to clean up aquifer systems contaminated by redox-sensitive pollutants (Kaplan et al. 1996). In this paper, we provide an overview of recent developments in the understanding of colloid-facilitated transport of metals, and we identify some research challenges to be addressed.

**COLLOIDS IN THE ENVIRONMENT**

Colloidal particles are found in virtually all natural waters, including surface waters (i.e. rivers and lakes), soil porewaters, and shallow and deep groundwater systems. In soils and aquifers, mobile colloidal particles originate mostly from in situ generation of submicron-sized mineral and organic matter particles, which are naturally present. Such particles can be composed of clay minerals, mineral precipitates (e.g., Fe, Al, Mn, or Si oxides and hydroxides, carbonates, phosphates), organic biopolymers (e.g. humic and fulvic acids, polysaccharides, and exocellular biopolymeric material), and biocolloids (including viruses, bacteria, and protozoans). Frequently, the close association of mineral and organic components leads to a different colloidal behavior (i.e. hetero-aggregation between different colloid types) compared to the behavior of pure mineral and organic particles (homo-aggregation within a colloid type).

Colloidal particles originating in soils are also found in rivers and lakes. Especially during strong rainfall events, surface runoff and resulting soil erosion can transport large amounts of colloidal particles into adjacent water bodies. Soil colloids can also be transported into rivers and lakes by water rapidly infiltrating through soil drainage systems. Organic colloids in rivers and lakes contain typically 40–80% fulvic compounds of primarily soil origin and a significant proportion (varying seasonally between 10 and 30%) of structural, fibrillar polysaccharides (rigid biopolymers) released from plankton (exudates) or cell wall remnants (Buffe et al. 1998). The stability of inorganic colloids in these systems strongly depends on the relative proportions of stabilizing small, fulvic compounds and destabilizing rigid, fibrillar biopolymers (Buffe et al. 1998).

The release of colloidal particles in soils and aquifers can be strongly enhanced by fluctuations in water saturation, flow velocity, and aqueous solution composition (i.e. pH, ionic strength, redox potential). Such variations are insignificant or at least gradual in most porous or fractured aquifer systems, but can be very pronounced and frequent in the vadose zone (the unsaturated zone, including soils) and fast-flow karst systems. For example, an intense rainfall event typically results in rapid infiltration of water with low ionic strength through soil macropores, causing flow-induced mobilization and chemical conditions favoring colloid release and transport. Chemical and physical perturbations in aquifers can also be related to other factors such as land use, artificial groundwater recharge, anoxic and oxic groundwater mixing, or contaminant plumes leaching from waste-disposal facilities. Such plumes can lead to strong gradients in ionic strength, ionic composition, contaminant concentrations, and redox potential.

Colloids in chemically disturbed systems are commonly formed by precipitation of small particles from aqueous solutions. For example, Mavrocordatos et al. (2000) found 100–200 nm wide globular colloids, rich in Fe, Ca, and organic C, in waters from a karst system in Switzerland. The colloids presumably formed when Fe²⁺-rich water from an acidic, anoxic peat drained into the neutral and oxic karst system, leading to oxidation of Fe²⁺ to Fe³⁺ and precipitation of iron hydroxide colloids. Also, in acid mine drainage,
colloids can be formed by precipitation. Zänker et al. (2002) found that colloids containing Fe, Al, and trace metals formed by the natural mixing of acidic, sulfate-rich acid mine drainage water with near-neutral shaft or surface waters. Mobile colloids can also form in highly alkaline environments. Wan et al. (2004) reported the formation of high concentrations of colloidal calcite in columns packed with sediment from the US Department of Energy’s Hanford site (Washington State, USA), after they were leached with a highly saline and highly alkaline (pH 14) solution. This experiment simulates on-site leakage of high-level nuclear waste from underground storage tanks. These examples show that mobile colloids can form from solution, depending on the local geochemical conditions. Frequently, trace metals or pollutants are associated with these colloids via sorption or coprecipitation.

CHARACTERIZING NATURAL COLLOIDS

Major advances in sampling and characterizing natural colloidal particles have been made during the past decade. Some sampling procedures, especially at high pumping rates, can introduce artifacts, including mobilization of colloids attached at sediment surfaces and creation of colloids by changes in O₂ and CO₂ contents, temperature, pH, and redox potential. New sampling protocols at low purging and pumping rates while monitoring water quality parameters (especially turbidity) have been established to address these concerns (e.g. Backhus et al. 1993). Important colloid properties include (1) concentration (mass concentration, number concentration); (2) size and shape (size distribution, particle morphology); (3) composition (mineralogy, elemental composition, organic components); and (4) surface characteristics (specific surface area, surface charge, sorption capacity). In this paper, we highlight a few selected techniques. For further information, the reader is referred to papers by McCarthy and Deguel dre (1993), Buffle and Leppard (1995), and Kretzschmar et al. (1999).

The mass concentration and elemental composition of colloids in water samples is routinely determined by inductively coupled plasma–atomic emission spectroscopy (ICP–AES) or mass spectrometry (ICP–MS) using direct suspension nebulization. Typically, the water samples are analyzed with and without ultrafiltration or ultracentrifugation in order to operationally differentiate among truly dissolved species, colloids, and suspended particles. Recent developments include the coupling of size fractionation techniques (e.g. asymmetrical flow field flow fractionation, AsymFFFF) with ICP–MS to determine the size-dependent colloid composition and trace metal–colloid association (Plaschke et al. 2001). Size fractionation in AsymFFFF is achieved in a thin ribbon-like channel in a laminar carrier flow, applying a cross-flow perpendicular to the channel flow. The sequence by which colloidal species are eluted is determined by their diffusion coefficient and consequently by their size.

The composition of colloids can be further characterized by a variety of established techniques such as X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier-transform infrared spectroscopy (FTIR), and total organic carbon analysis (TOC). Compared to the mass concentration, which can be obtained from elemental or gravimetric analysis, it is much more difficult to determine in situ the number and concentration of colloidal particles. A very sensitive analytical approach is the laser-induced breakdown detection (LIBD), which is based on the formation of plasma due to a dielectric breakdown in a focused pulsed laser beam when a colloidal particle is present (Kitamori et al. 1988). The plasma is observed either by its light emission or by detection of the acoustic shock wave generated by its rapid expansion.
The shape of colloidal particles is studied mostly by transmission electron microscopy (TEM), high-resolution scanning electron microscopy (HR-SEM), or atomic force microscopy (AFM). Perret et al. (1994) developed specialized ultracentrifugation and staining methods for visualizing the morphology of aquatic colloidal particles by TEM. More recently, synchrotron-based scanning transmission X-ray microscopy (STXM) combined with near-edge X-ray absorption fine-structure (NEXAFS) microspectroscopy was used to characterize the size, shape, composition, and heterogeneity of mineral and organic colloids in soils, groundwater, and surface-water samples. Figure 2 shows STXM images of smectite colloids associated with humic substances (Schäfer et al. 2003) and a water-dispersible colloidal aggregate isolated from a forested surface soil. Further characterization of the chemical heterogeneity of the particles can be achieved by cluster analysis (Lerotic et al. 2004), in which pixels with spectral similarity are grouped. Figure 2 demonstrates that STXM is a very powerful tool to resolve organic/inorganic colloid association and chemical differences under nanoscale resolution.

Perhaps the most important properties of colloids are their surface area and surface charge. The specific surface area determines, together with the surface reactivity, the adsorption capacity of the colloids for trace metals and other environmental pollutants. While the smallest particles do not contribute significantly to the total mass of colloids in a water sample, they usually contribute most of the surface area. Therefore, they are of greatest importance for colloid-facilitated transport of adsorbed metals. The surface charge of colloids is extremely important because colloidal stability and transport are generally described in terms of colloid and aquifer surface charge. Most natural colloidal particles have net negative surface charge. Most clay mineral colloids have pH-independent negative surface charge, due to the crystal structure of clay minerals. The charge of natural organic matter (NOM) is usually dominated by carboxylic and phenolic functional groups, creating pH-dependent negative charge. Only the hydroxides and oxides of iron and aluminum have positive surface charge at pH values below the pH at which the surface charge is zero (pH\text{PZC}), which is near pH 8–9. However, in natural waters, adsorbed NOM renders the surface more negatively charged. Specific adsorption of phosphate and other anions can also add negative charge to the surfaces of Fe- and Al-oxide colloids, which is very important in fertilized soils and nutrient-rich rivers and lakes (Stumm and Morgan 1996).

**PROCESSES CONTROLLING COLLOID MOBILITY**

Understanding the key processes controlling the mobility of colloids in soils, groundwater aquifers, and aquatic systems is a major challenge. The mobility of colloids is governed by a combination of physical, chemical, and in many cases biological factors. Physical factors include the transport of water and gases, the mobilization of colloids by shear and hydration forces, and the filtration of particles in porous media with heterogeneous pore systems. Chemical factors comprise the influence of solution composition on colloid surface charge, the role of natural organic matter in stabilizing colloidal particles in suspension, and the formation of colloids in supersaturated solutions. Biological factors include the growth of biocolloids and the release of surfactants and polysaccharides by microorganisms, which strongly alter mineral surface properties and colloid aggregation. In this article, we address only selected topics of current research. Recent detailed reviews are provided by Ryan and Elimelech (1996), Kretzschmar et al. (1999), and McCarthy and McKay (2004).
The transport of colloidal particles in the environment is dramatically influenced by the tendency of the colloids to form larger flocks (aggregation) or to attach to stationary solid–liquid or gas–liquid interfaces (deposition). The influence of aggregation and deposition on colloid transport in porous media is schematically depicted in Figure 3, along with other important processes influencing colloid transport.

Under certain conditions, colloid-facilitated transport can become the major transport mechanism of strongly sorbing trace metals in soils and aquifers. This was demonstrated for Pb transport in water-saturated soil columns (Grolimund et al. 1996). The soil was first leached with a Pb-containing NaCl solution of high ionic strength to simulate a contaminated plume. Subsequently, the soil porewater was exchanged with low ionic strength CaCl₂ solution to simulate fresh water infiltration. This leaching sequence resulted in two transport fronts, first, an unretarded front in which the salt concentration decreased, and second, a retarded Ca²⁺–Na⁺ exchange front. Between these two fronts, the low ionic strength and high Na⁺ saturation of the soil led to colloid release and colloid-facilitated transport of Pb. Kretzschmar and Sticher (1997) showed in column experiments that Fe-oxide colloids that were stabilized by adsorbed humic substances can also act as carriers for Pb. Denaix et al. (2001) studied mobile colloids in a soil heavily contaminated by former emissions from Zn and Pb smelters in France. They found that 50% of the total Pb was bound to colloids (mostly biocolloids), while 95% of the total Zn was present as dissolved species. The remaining Zn was also associated with biocolloids or smectites.

Colloid-facilitated transport can also play a very important role in the radionuclide mobility in geological formations. It has therefore to be considered in safety assessments of geological nuclear waste disposal sites and risk assessments of highly contaminated sites. For example, at the US Department of Energy’s former plutonium-production Hanford site (Washington State, USA), high-salinity, highly alkaline radioactive waste containing 137Cs and 90Sr has leaked from underground storage tanks into the underlying sediments. Laboratory experiments on columns of Hanford sediment showed that leaching with 1 M NaNO₃ solution and a subsequent decrease in ionic strength causes the mobilization of colloids and illite-associated cesium (Flury et al. 2002). Both findings suggest that colloid-facilitated transport of 137Cs in these extreme environments is an important transport mechanism. Numerous studies furthermore demonstrated that organic and inorganic colloids can increase the mobility of Am, Np, Pu, and U on a laboratory scale. Column experiments by, for example, Artinger et al. (2003) on the influence of radionuclide–humic substances contact time and Dardenne et al. (2002) on the effect of metastable ferrihydrite mineral transformation showed changes in metal sorption reversibility and therefore colloid-enhanced radionuclide migration. Molecular understanding of surface complexation and structural incorporation of radionuclides is therefore a prerequisite for interpreting and reliably predicting the long-term influence of colloids on radionuclide mobility. Another aspect is the upscaling of colloid migration from laboratory to field scale. A few field investigations (i.e., Vilk et al. 1997; Kersting et al. 1999; Geckes et al. 2004) have demonstrated colloid-associated radionuclide mobility on a larger scale. For example, the international Colloid and Radionuclide Retention (CRR) project at the Grimsel Test Site (Switzerland) demonstrated that smectite colloids and colloid-associated 234Pu can be mobile in a natural rock fracture under certain hydrodynamic conditions (flow velocity v_a = 39 m/d). The alkaline (pH 9.6), low ionic strength (I = 2.2 mM) groundwater at the Grimsel Test Site generally favors colloid stability and transport (Fig. 4).

Mobile colloids affect the transport, bio-availability, and natural cycling of trace metals in lakes, rivers, and estuaries. Colloid-bound transport of trace metals is of great importance in contaminated rivers, for example in the Vistula River in Poland, which has been polluted in Pb and Cd by zinc and lead mines in Upper Silesia (Guéguen and Dominik 2003). In the Sacramento River in California, USA, Hg was transported mainly by organic colloids and in a “residual fraction” consisting of Hg mineral phases (Roth et al. 2001). In a study of leachates from tailings at the New Idria and Sulpur Bank mercury mines, in California, Lowry et al. (2004) found that up to 95% of the total Hg was present as organic colloidal phases. As a prerequisite for interpreting the long-term effect of colloids on radionuclide mobility, another aspect is the upscaling of colloid migration from laboratory to field scale. A few field investigations (i.e., Vilk et al. 1997; Kersting et al. 1999; Geckes et al. 2004) have demonstrated colloid-associated radionuclide mobility on a larger scale. For example, the international Colloid and Radionuclide Retention (CRR) project at the Grimsel Test Site (Switzerland) demonstrated that smectite colloids and colloid-associated 234Pu can be mobile in a natural rock fracture under certain hydrodynamic conditions (flow velocity v_a = 39 m/d). The alkaline (pH 9.6), low ionic strength (I = 2.2 mM) groundwater at the Grimsel Test Site generally favors colloid stability and transport (Fig. 4).

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in the Pineland area of New Jersey, USA, an area characterized by sandy soils, peats, and acidic, organic-rich surface waters, trace metals are bound largely to organic colloidal materials (Ross and Sherrel 2004). The studies cited above, along with many others, document the major role of colloidal particles in the transport and cycling of trace metals in the environment.

**RESEARCH CHALLENGES**

Future studies need to address key challenges concerning colloidal transport in saturated and unsaturated (vadose zone) systems. First, representative colloid sampling in seasonally variable environments and the use of appropriate techniques for sampling the vadose zone or weakly permeable formations remain critical challenges. Second, a quantitative understanding of colloid formation, release, stability, transport, and deposition in heterogeneous porous media remains to be developed. While a theoretical framework exists for describing colloid transport and deposition in defined model systems, important effects of charge heterogeneity, variable water saturation, preferential flow, surface roughness, and variable redox conditions are still poorly understood. Third, the molecular mechanisms, thermodynamics, and kinetics of sorption–desorption reactions of trace metals, metalloids, and radionuclides on colloid surfaces must be further investigated because colloid-facilitated transport critically depends on these processes. With the rapid development of computational methods and new analytical techniques, including synchrotron-based spectroscopy and microscopy, there will be exciting new opportunities for addressing these issues.

**Figure 3** (A) Processes controlling the mobility of colloidal particles in water-saturated porous media: (1) release of colloids, (2) aggregation of colloids, (3) immobilization by gravitational settling of flocks, (4) immobilization by straining of flocks or single particles, (5) immobilization by colloid deposition on solid–water interfaces, (6) transport of dispersed colloidal particles over long distances by flowing water.

(B) In unsaturated porous media, additional mechanisms of colloid retardation may occur: (7) immobilization by film straining and (8) immobilization by deposition on air–water interfaces.

**Figure 4** Colloid migration experiment in a 2.23 m natural fracture (dipole)—part of the international joint Colloid and Radionuclide Retention (CRR) project at the Grimsel Test Site, Switzerland. The colloid injection concentration of smectite colloid with a size of 109 ± 10 nm, which was determined by laser-induced break-down detection (LIBD), was adjusted to 20 mg/L. Breakthrough curves are shown for the conservative tracer $^{131}$I (blue solid line), tetravalent $^{244}$Pu (red stars), and smectite colloids (black balls; detected in-line by a mobile LIBD system). Radionuclide and colloid concentrations are normalized to the injected mass or activity $m_0$. A vertical line marks the peak arrival time of colloids and colloid-associated $^{244}$Pu, which typically appear ahead of the conservative tracer (second vertical line) due to size or charge exclusion effects. Background of graph gives a schematic overview of the Grimsel Test Site tunnel and boreholes. Green, filled circles mark the injection (10 mL/min) and extraction boreholes (150 mL/min) of the asymmetrical dipole used for this study. For details see Geckeis et al. (2004). Data of Figure 4 have been published in Geckeis et al. (2004). COPYRIGHT 2004, OLDENBOURG WISSENSCHAFTSVERLAG.