Chapter 8

GENERAL ASPECTS OF AQUATIC COLLOIDS IN ENVIRONMENTAL GEOCHEMISTRY

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INTRODUCTION

A recent emphasis in society is on conducting mining activities with the least environmental impact possible. A manifestation of this is the cost monitoring of contaminant levels in surface and ground waters, usually in order to meet specific environmental regulations. However the simple collection of monitoring data may not provide understanding of either the actual impact of mining on the environment or suggest the most appropriate treatment processes for specific mining wastes. More detailed information on the chemical and physical forms of contaminants is needed. One aspect of this is that the occurrence and distribution of natural and anthropogenic chemicals in natural water systems is strongly influenced by their partitioning between solid and aqueous phases (Allan, 1986). Therefore contaminant behavior is generally defined in terms of "two-phase" water-rock interactions where metals, for example, are present either in the stationary solid phases of the country rock, ore pad, waste rock pile, tailings empoundment, or slag heap or they are present as mobile, aqueous phase solutes. For groundwater the solid phase is considered to be the stationary aquifer material. In surface waters the solid phases generally considered are the sediments in the stream, pond, or lake bottom. Accordingly, computer models have been developed that address dissolution, precipitation, adsorption, and desorption between the solid and aqueous phases as well as the formation of various solute species and complexes.

The reality is, however, that most natural water systems are three-phase systems, the third phase being a mobile solid phase in the form of suspended matter. Turbidity is the macroscopic, visual evidence of suspended matter in a water system. A certain portion of suspended matter, the largest particles first, will settle out over time. However, by some estimates (Moran and Moore, 1989), as much as one half of the suspended matter in natural waters is less than 1 μm (10^{-6} meter) in diameter and does not settle out over even long periods of time. By definition these particles are "colloids" and represent a "permanent" phase, which, of all the solid phases, can potentially exert the most significant control over water-borne chemicals. The small size of colloids results in a very high surface area per unit mass that facilitates all surface area-dependent interactions between solution and solid components. Extensive laboratory studies of contaminant sorption to colloidal phases (i.e., metal oxides, clays, etc.) has resulted in a reliable but evolving physicochemical understanding of this process

(Morel and Geschwend, 1987). However sufficient data are currently lacking on the abundance and chemical nature of colloids in natural waters.

The available evidence clearly shows that significant amounts of certain trace elements in surface waters occur in the colloidal component of suspended solid phases. Interest in the environmental importance of colloids has been further heightened over recent years (McCarthy and Zacara, 1989) as a result of evidence which suggests that colloids can be mobile in porous media and may therefore act as transport phases for colloid-associated contaminants in soils and ground waters. Therefore, ground waters must also be considered intrinsically three-phase systems. This complicates the previously-held view of contaminant transport in groundwater as consisting of a two-phase chromatographic process where solutes are partitioned between solution and an immobile aquifer matrix. Numerous two-phase models for contaminant transport have been devised which include equilibrium adsorption and ion exchange with respect to the stationary matrix (e.g., AGU-10, HST-3D, MOC, ONE-D, SUMATRA-1, and SUTRA etc.; see IGWMC, 1992 for descriptions). Where mobile colloids are present, contaminants having an affinity for interaction with solid surfaces may not be retarded as significantly as predicted by current physicochemical models because part of the sorbent solid phase is also mobile.

It is important for the environmental geochemist to have an understanding of what colloids are, what influences their chemical and physical stability, how they are transported in natural waters, and how contaminants associate with colloids. Both the transport of colloids and their interactions with contaminants are dependent on the physical and surface chemical properties of the colloids; these topics will be addressed in varying depth in this chapter. Emphasis will be given to the basic properties of colloidal systems and how these affect colloid transport. Available data on the occurrence and environmental significance of colloidal particles will also be presented. In this paper, the focus will primarily be on metal and radionuclide contaminants. Transport of biocolloids, bacteria and virus, and interactions of organic contaminants with colloids, while extremely important, are considered outside the scope of this paper and discussion will be limited. Adsorption of metals by solid phases is addressed by Smith (1999) and by colloids specifically by Rees (1991). The reader is referred to other reviews for discussion of organic contaminant interaction with colloids (Morel and Geschwend, 1987; Rees, 1991).

DISSOLVED VERSUS COLLOIDAL PROCESSES

Major processes affecting metal transport in surface waters are illustrated on Figure 8.1 (adapted from Forstner and Salomons; 1983). "Dissolved Processes," shown on the right, include metal complexation by inorganic and organic ligands, which are quantitatively described by equilibrium-based thermodynamic constants that are well known for a variety of metals and simple ligands. Also included are metal, metal-ligand and ligand sorption reactions with well defined solid components as described by empirical relationships and various physicochemical models. Among the physicochemical models addressing sorption of ionic contaminants to solid surfaces are those that employ conditional surface sorption constants to account for electrostatic and specific chemical interactions (Smith, 1999). These constants are known for many metals and solid phases such as clays and iron, manganese, and aluminum oxides and hydroxides.

In contrast, "Colloidal Processes," shown on the left side of Figure 8.1, include metal complexation and sorption with less well-defined components, such as complex organic and inorganic colloids. These processes are poorly understood. The limited amount of thermodynamic or even empirical data for such reactions is due mainly to the complexity and heterogeneity of organic colloids and the lack of characterization resulting from the difficulties associated with their collection.

Uncertainty in sorption constants also arises from the practical difficulty in separating colloids from dissolved phases in laboratory experiments. Colloids behave similarly to solutes in that they are not effectively removed by centrifugation or filtration. The

commonly observed apparent decrease in sorption coefficients of organic and inorganic contaminants observed with increasing total solids concentration (Morel and Gschwend, 1987) has been explained by the presence of colloids that were not completely separated from the aqueous phase (Morel and Geschwend, 1987). Contaminants associated with colloids are mistakenly measured as part of the solution phase, therefore reducing the observed sorption coefficient. The amount of colloids present increases with increasing total solids and if colloids are taken into account the partitioning coefficient becomes invariant with suspended solids concentration, as predicted by most sorption models.

DEFINITIONS OF AQUATIC COLLOIDS

Filtration through a 0.45 μm pore-size membrane, although quite arbitrary, has been widely accepted as a means of separating particulate from "dissolved" species. Such an operational definition ignores the issue of colloids entirely. Chemical species present in whole or raw natural waters may be more accurately considered to physically occur in a variety of modes. These modes of physical occurrence define an essentially continuous series which we will refer to as the solute/colloid/suspended sediment continuum. While the pure end member modes are easily conceptualized as: (a) dissolved ions or molecules; and (b) macroscopic particles with or without associated ions or molecules, the intermediate modes require further explanation. The word "colloid" as used here collectively identifies the intermediate continuum of modes. Chemical species that may be referred to as "colloidal" include: (a) discreet chemical species with sufficient size or mass to behave as colloids (macromolecules); (b) amorphous or crystalline chemical compounds that exist in the solid phase as colloid particles; and (c) chemical species associated with (usually by sorption) compositionally distinct, colloid-size particles and whose mobility is controlled by those particles.

A colloidal system is more easily described than a colloid itself as a two-phase system in which one phase is uniformly and permanently distributed or dispersed in the second phase. This is in contrast with both a true solute/solvent system, which comprises a single phase, and a suspended-sediment/solvent system, which is a two phase system but is typically not uniform and never permanent. Although natural colloidal systems exist for every binary combination (except gas-in-gas) of solid, liquid and gas phases (e.g., fog is a liquid-in-gas colloidal system), our sole focus here is on the most geochemically relevant systems, those with an aqueous dispersing medium, and dispersed solid particles, known as sols. Chemically, colloids behave like solids requiring consideration of surface area and charge and other aspects of heterogeneous reaction theory. Physically or hydrodynamically however, colloids behave somewhat like solutes principally because of their small size.

An exceedingly wide variety of natural colloidal material has been identified in surface and ground waters (Table 8.1). Natural colloids can be subdivided into two main groups, including:

1) sparingly soluble, hydrophobic (also termed lyophobic or solvophobic) materials that have an inherent resistance to chemical interactions with water (e.g., insoluble minerals) and;
2) hydrophilic (also termed lyophilic or solvophilic) materials that are polar and hence form direct hydrogen bonds with water (e.g., macromolecular organics, polymeric precipitates).
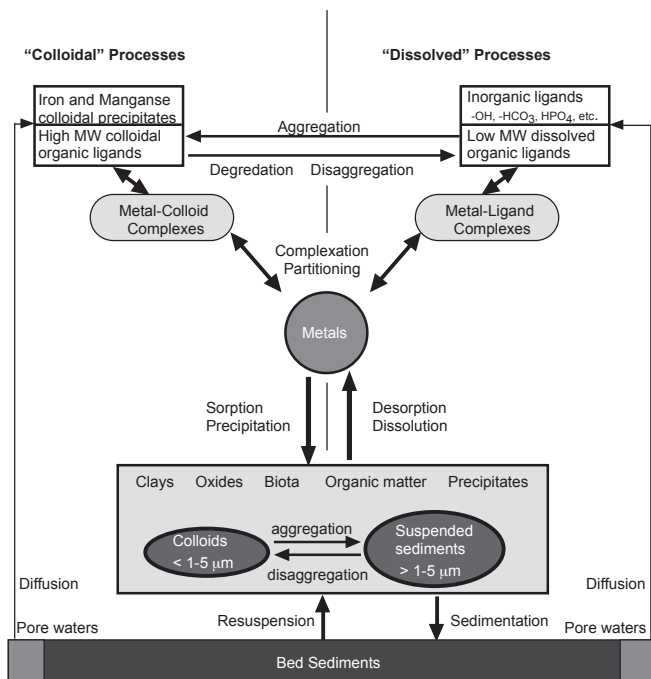
Adapted from Forstner and Salomons (1983)

FIGURE 8.1—Comparison of "dissolved" versus "colloidal" processes which affect the physical and chemical form of pollutants in surface waters.

Long-term kinetic stability as a suspension is a fundamental property a colloid and a colloidal system. For hydrophobic solids, permanent dispersion or suspension is maintained by the random thermal activity of water molecules (Brownian movement). In order for this mechanism to be effective, the particle must be sufficiently small to allow spatially uneven bombardment by water molecules. Evenly distributed bombardment of the surface of a large particle would result in no net displacement and consequently gravity and density differences would ultimately cause the particle to settle (Halliday and Resnick, 1967) or float on the aqueous medium. If not for the presence of ions of like charge on the colloid surface, the hydrophobic nature of these particles would tend to force them together during mutual particle collisions and promote aggregation, which would in turn lead to larger and larger particle sizes and eventual destruction of the colloidal system. These surface ions promote coulombic repulsion between particles and allow interactions with water molecules thus making the particles effectively more hydrophilic. Naturally hydrophilic macromolecules, which more closely approach true solute behavior, maintain their colloidal stability via interactions between charged functional groups and water molecule dipoles. Such large molecules frequently undergo some flexure or folding to best accommodate these interactions. Large molecules that are inherently hydrophobic (e.g., oils and greases) may form stable colloidal systems (an emulsion or liquid-in-liquid colloidal system) through interaction with surfactants, which are large molecules having both hydrophobic and hydrophilic portions. The hydrophobic molecule interacts with the hydrophobic portion of the surfactant while the hydrophilic end of the surfactant interacts with water. A micelle is thus formed and the hydrophobic molecule is stabilized.

matically affect biological productivity, turbidity is an important water quality issue (Greenberg et al., 1992).

Although particle size is not part of the technical definition of a colloid, in order for particles to be dispersed by Brownian motion they must be very small but yet not so small that they are actually ions or individual simple molecules (i.e., not part of the aqueous phase). In order to produce the Tyndall effect they must have sufficient size to scatter light. Generally, "colloid" is only operationally defined by environmental scientists, typically in terms of the ability of a particle to pass a certain filter or molecular sieve size. Similarly, it is conceptually convenient to describe the differences between solutes, colloids and suspended solids in terms of particle diameters or molecular weights. However, numerous operational factors, such as filter efficiency, and particle density and surface charge, influence and generally complicate separations based on size. Colloids clearly lie between solutes and suspended solids in the size continuum of water-dispersed particulate matter (Fig. 8.2) but the size cutoffs are a matter of debate (Table 8.2). Generally the size of colloids is quoted as simply being sub-micron or, more specifically, ranging from 0.001 to 1.0 µm (1 to 1000 nm). A slightly larger lower size limit is used by some while others extend the upper range to 2–5 µm to coincide with the classical clay-silt boundary, while still others further extend this range to 10 µm (Stumm and Morgan, 1981). As is generally the case when describing a continuum, intermediate limits and bounds are necessarily arbitrary.

In this paper we assume that the size distinction between solute (i.e., truly dissolved) and colloidal constituents is best drawn at the upper size limit for thermodynamically well defined species (i.e., simple inorganic and organic aquo-ions). The largest hydrated-ion size parameter in Debye-Huckel equations (cf., Nordstrom and

TABLE 8.1—Some examples of aquatic colloids (colloidal species of greater importance given in bold).

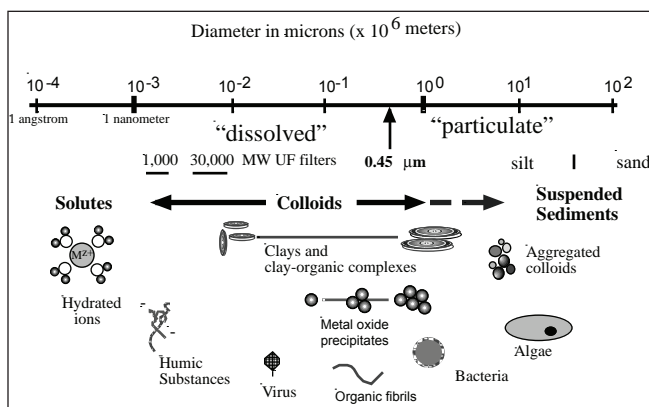| Hydrophobic colloids	Hydrophilic colloids
Minerals	Macromolecular organic matter
- **Phyllosilicates, clays**	- **Humic and fulvic acids**
- **Iron, manganese, and aluminum**	- Polysaccharides
oxides and hydroxides	- Proteins
- Framework silicates	Polymeric precipitates
- Carbonates, sulfides, and phosphates	- Silica gel
Biocolloids (living and non-living)	- Alumina gel
- **Bacteria**	
- Virus	
- **Organic detritus**	

Another fundamental property of colloidal systems, in addition to their physical stability, is their ability to scatter light, known as the Tyndall effect. Interactions between a beam of incident light and colloidal particles include refraction, polarization, reflection and adsorption. The collective effect is that some of the incident light is scattered in all directions and the colloidal suspension appears turbid. The light scattering characteristics of a given suspension are complexly related to concentration, size, shapes and molecular weight of the colloidal particles (Moore, 1972). These relationships have led to the development of important tools for the investigation of colloids such as photon-correlation spectroscopy for colloid size determination and electrophoretic light-scattering for surface charge determination (Rees, 1987). Because the overall decreased light transmittance of turbid water can dra-

FIGURE 8.2—The solute/colloid/particle size continuum and examples of aquatic colloids.

TABLE 8.2—Generally accepted colloid size limits in microns.

Lower diameter	Upper diameter	Reference
0.0005	5	Driscoll, 1986
0.001	1	Domenico and Schwartz, 1990
		Freeze and Cherry, 1979
		Metcalf and Eddy Inc., 1991
0.003	1	Pankow, 1991
0.005	10	Stumm and Morgan, 1981

Munoz, 1986), of 11 Å or 0.0011 µm, corresponds well to the 0.001 µm lower size limit for colloids accepted by many authors. Examples of inorganic species with these large sizes are some fully hydrated, high-valent actinide (Th^{4+}), lanthanide (Ce^{4+}) and transition elements (Zr^{4+}). It should be pointed out that colloid "sizes" are referenced either to their linear dimensions of length, width or diameter (units of microns or nanometers) or their mass (usually in terms of molecular weights or Daltons). Organic molecules must reach molecular weights of several hundred to a few thousand Daltons in order to reach similar hydrated ion sizes. The relationship between mass and size of organic molecules depends on molecular shape in solution and the compound's density.

The colloid-suspended particle boundary can be based on the wide spread use of 0.45 µm filtration, but larger particles do in fact behave like colloids. An upper size limit of approximately 2 to 5 µm better describes the hydrodynamic behavior of larger colloids that make them mobile in surface and ground waters, as will be discussed shortly.

Colloidal particles in natural waters may be composed of an exceedingly wide variety of natural and synthetic materials ranging from macromolecules (molecular weight >1000) to oxides and phyllosilicates, as shown on Figure 8.2. Obviously the relative importance of various colloids will vary with the environment of the water. For example, it is likely that in biologically productive surface waters, living microorganisms and non-living organic materials will dominate the colloid population. In waters affected by mining operations, iron and aluminum oxides and clays may be the most abundant colloids (see Nordstrom and Alpers, 1999). Bacteria may also be important in these types of waters due to their role in the generation of acid-mine drainage (see Mills, 1999).

Colloids originate in at least three ways:

1) They can be acquired from the surrounding environment by disaggregation/dissolution and entrainment. This includes, for example, suspension of primary or authigenic clays, acquisition of atmospheric dust by rain, weathering of framework silicates, suspension of oxides and oxyhydroxides, dissolution of fulvic acids in soil profiles, and washing of mineral and rock fragment fines from tailing piles or soil profiles.

2) They can result from *in-situ* aqueous phase precipitation due to changing chemical or physical conditions. This includes, for example, precipitation of calcite due to pH changes, precipitation of iron oxides and(or) sulfides due to redox changes, formation of complex phosphate mineral suspensions at chemical interfaces in lakes, and polymerization of dissolved silica due to pH changes.

3) They can result from biological activity, for example, the growth and death of microbes, production of fibrils, organic skeletons and protein-rich cell fragments (Leppard, 1992), and biologically mitigated precipitation or dissolution of minerals.

SIGNIFICANCE OF AQUATIC COLLOIDS

The environmental significance of colloids mainly arises from their very large specific surface areas that facilitate reactions between truly dissolved solutes and the particle surfaces. These heterogeneous reactions include simple electrostatic sorption, chemisorption, coadsorption, catalysis of complexation, redox and hydrolysis reactions among solute species and dissolution, precipitation and leaching. Increased surface area is an express or implied factor in increasing either the equilibrium capacity, for example, the solubility or sorption capacity of a solid, and(or) the chemical kinetic rates of these reactions. The significance of small particles like colloids in influencing the available surface area can be illustrated in several ways that will be discussed in the following paragraphs.

As particle size decreases, the total surface area per unit mass of suspended material increases dramatically. Since adsorption is, at least in part, a surface area-extensive process it is logical that the total adsorption capacity of a volume of water with suspended matter will be related to the particle size of that suspended matter. A theoretical number of particles, and hence the associated total surface area, is easily calculated for a known concentration of suspended matter with a particular density assuming a uniform particle size (d, sphere diameter or cube side length) and regular shape. Gregg and Sing (1982) and Parks (1990) provide formulae for calculating particle number and total areas for different shapes and non-uniform size distributions. For example, 1 µm spheres of quartz would have a specific surface area of 2.26 m^2/g. Simple estimates such as these tend to underestimate surface areas of natural materials due to complex shapes, porosity, and surface defects (White and Peterson, 1990; Davis and Kent, 1990). For example, Parks (1990) shows a plot of measured specific surface area as a function of grain size for natural quartz sand and crushed quartz that indicates approximately 10 m^2/g is reasonable for 1 µm diameter particles. Figure 8.3 illustrates the effect of dividing a 1 cm cube of hematite into smaller and smaller cubes. Not only does the number of cubes increase tremendously, the total surface area approaches 1000 m^2/g at the lower size limit for colloids. Taking this one step further, consider the reactivity of the hematite itself. Obviously any reaction must take place with the surficial atoms of iron and oxygen, for example those within 2 angstroms of the surface. As the particle size decreases below 1 µm, the percentage of atoms near the surface rises dramatically and approaches 100% at 1 nm; thus almost the entire mass of hematite is immediately available for reaction.

Experimental adsorption data is typically reported in the form of isotherms that compare the dissolved concentration of some solute (mass/vol) with the sorbed concentration (mass/mass). The
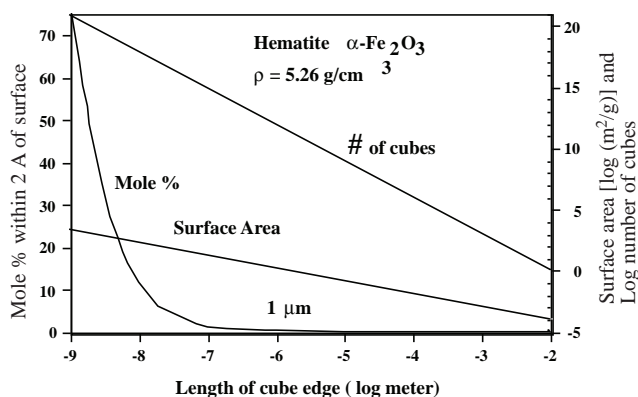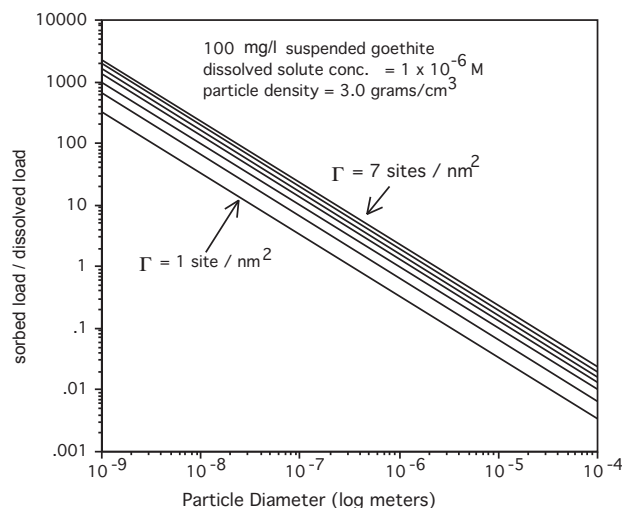

FIGURE 8.3—Plot showing the changes in surface area that would result from progressively dividing a 1 cm cube of hematite into smaller and smaller cubes. For particles of 0.01 µm (1 x 10^{-8}m), the percentage hematite within 2 Å of the particle surface is approaching 100%. Since Fe and O radii are each on the order of 1 Å this means that a significant number of atoms are subject to reactions that occur at the particle surface.
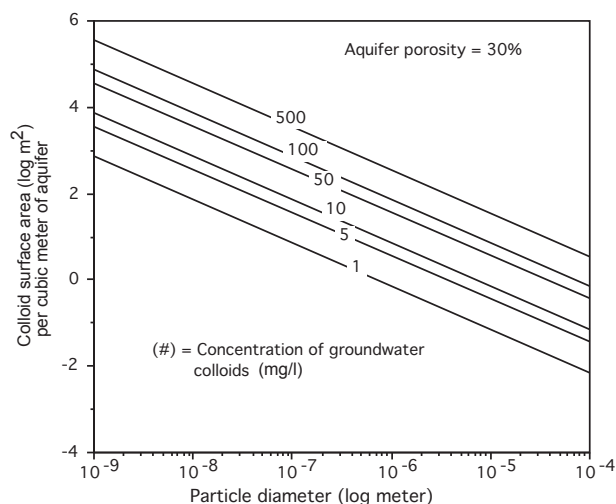
same experimental data may be normalized to the measured surface area of sorbent and reported as sorption site density for an individual sorbed species (Γ, sites/nm^2) or Γ_{max} for conditions of maximum sorption (see Smith, 1999, for a detailed discussion of adsorption densities). Davis and Kent (1990) report sorption site density data derived from numerous sources for various materials, including α-FeOOH, other iron oxides, titanium oxide polymorphs, aluminum oxides and hydroxides, amorphous silica and kaolinite. Sorption site densities are also reported for α-FeOOH as derived from adsorption experiments involving OH$^-$, H$^+$, F$^-$, SeO$_3{}^{2-}$, PO$_4{}^{3-}$, oxalate and Pb^{2+}. For the latter data, Γ values vary from 0.8 to 7.3 sites/nm^2, in part due to intrinsic differences in adsorption mechanisms for different sorbates and in part due to differences in experimental conditions.

Figure 8.4 illustrates the combined effects of particle size and sorption site density on the suspended matter-sorbed versus solute load assuming full saturation of available sorption sites with sorbate ions and 1:1 ratio of sorption sites to sorbed ions. The plot suggests that a water sample with 100 mg/l of some suspended matter (e.g., α-FeOOH having Γ = 2.6 to 7) and 10-6 moles/l truly dissolved solute (e.g., 0.2 mg/l dissolved Pb2+) could contain significantly greater concentrations of the same solute as a suspended matter-sorbed phase. In this extremely simplistic scenario, as the particle size decreases the moles of metal associated with colloids may equal or exceed the moles of metal actually dissolved. The picture is complicated in natural waters by (1) competition of multiple metals species for the available sites, (2) aqueous complexation of the metal, and (3) variable site densities and variable aqueous concentrations.

Figure 8.5 illustrates the importance of colloid surface area relative to the surface area of solid aquifer material in a groundwater. A cubic meter of hypothetical aquifer composed of 1 mm diameter spherical sand grains (ρ = 2.5 g/cm^3), and having 30%

FIGURE 8.5—Particle size dependence of total particulate surface area (m^2) available in the liquid phase of 1 m^3 of a saturated 30% porosity aquifer. Lines represent different concentrations of suspended matter (mg/l).

porosity, has a computed total surface area of 4200 m^2 and a specific surface area of 2.4E-3 m^2/g. An approximately equivalent total surface area would be available in the liquid phase if the pore water contained 580 mg/l of similar-density, spherical, 0.1 μm diameter particles or 5.8 mg/l of 0.001 μm particles. These suspended loads would have calculated specific surface areas of 24 and 2400 m^2/g respectively. Assuming the larger particle size (0.1 μm) and the lower concentration (5.8 mg/l), a groundwater velocity of 1 m/day would result in a surface area equivalent to the aquifer matrix passing through the aquifer volume every 100 days.

These examples, although very simplistic, illustrate the potential importance of colloids to the chemistry of contaminants in groundwater and other natural aqueous systems.

SURFACE CHARGE ASPECTS OF COLLOIDS

A colloid, like any other particle in an aqueous medium, is bounded by an interface that separates the two phases. Such an interface is a region of tremendous complexity, lateral inhomogenity, and extreme microtopography, and is rarely if ever static (Hochella, 1990). Electrical charges are an integral and ubiquitous characteristic of solid-aqueous phase interfaces and strongly influence the thickness and nature of the transition zone between the two bulk phases. The total amount of electrical charge at the interface is a surface area-intensive function. In the case of colloidal particles, or any suspended particle for that matter, this electrified nature of the interface has three very important consequences:

1) Electrical forces of attraction and repulsion control how closely two particles may approach one another and whether or not there will be sufficient tendency for them to remain together if the approach is close enough or forceful enough; this is the basis for coagulation or agglomeration of suspended matter, and controls the stability and transportability of colloids in the aqueous medium. This aspect of surface charge is discussed in following paragraphs.

FIGURE 8.4—Theoretical comparison of dissolved and suspended loads as a function of site density and particle size of goethite. Each line represents a different surface sorption site density ranging from 1 to 7 sites/nm^2. If there is complete occupancy of the surface sites, the suspended load can carry significantly greater amounts of the constituent than the aqueous phase.

2) Electrical charges associated with particle interfaces influences the processes of adsorption that allow metal ions, anions and organic molecules to become associated with particles. So, electrical forces influence the identity and abundance of sorbed ions and molecules associated with colloids. These ions and molecules may be contaminants of environmental interest. This aspect of surface charge is discussed by Smith (1999).

3) By combination of the first two consequences, electrical interfaces influence the physical and chemical transportability of colloid-associated contaminants.

Origin of colloid surface charge

The basic concepts involved in the formation of surface charge are presented in detail by Smith (1999). In the following paragraphs the concepts of surface charge development most relevant to describing the behavior of colloids are reviewed.

"Permanent" (i.e., not affected by the aqueous environment) surface charges have their origin within the bulk solid phase where substitutions of similar-sized but different-charged atoms lead to a net lattice charge imbalance. These charges are typically negative in sign (e.g., substitution of Al^{3+} for Si^{4+} in the tetrahedral layer or Mg^{2+} for Al^{3+} in the octahedral layer of smectite clays). The result of the lattice charge deficiencies is a non point-source electrostatic surface charge which gives rise to such phenomena as cation exchange. Non-stoichiometric substitutions in other minerals such as carbonates can generate similar charges.

Another source of surface charge is located on the actual particle surfaces and occurs due to the amphoteric nature of surface hydroxyl groups. These groups exist as either $X-O^-$, $X-OH^o$, or $X-OH_2^+$, where X represents the surface of the particle. The relative abundance of each of these surface groups and therefore the net surface charge, is a function of the pH of the aqueous medium (positively charged at lower pHs and negatively charged at higher pHs). The pH where the surface is neutral is the ZPC or zero point of charge.

Another mechanism for surface charge development is the sorption of ions to the particle surface. In most aquatic environments the sorption of organic matter on suspended particles has been shown to most greatly influence particle surface charge (Tipping and Cooke, 1982; Beckett, 1990). Hunter and Liss (1979) concluded that adsorption of organic matter is responsible for the observation that particles have a net negative charge in almost all natural waters, regardless of the particle mineralogy. Natural organic material is a complex mixture of polyelectrolytes, whose charge primarily results from carboxylic acid functional groups (-COOH) with pKa values in the range of 3–4. Thus at typical environmental pHs they tend to be negatively charged (-COO⁻). Adsorption of organic matter to mineral surfaces is primarily through a ligand exchange mechanism where -COO⁻ groups bond directly to the metal (i.e., Al, Fe, Mn) and displace the surface OH group. Not all COO⁻ groups of the organic matter are involved in sorption to the particle surfaces and those remaining provide the net negative charge shown to occur on particles in natural waters. The sorption of organic matter in turn effects colloid stability (Tipping and Higgins, 1982; Liang and Morgan, 1990) and chemical removal of organic coating has been shown to reduce colloid stability significantly (Gibbs, 1983).

Surface charge and colloid stability

The interactions of colloids with one another and with macroscopic solid phases are governed by hydrodynamic and chemical forces (O'Melia, 1987). The physical stability of colloids (not to be confused with chemical stability with respect to dissolution) refers to their ability to remain in suspension by avoiding aggregation due to particle interactions. Hydrodynamic forces tend to bring suspended particles into contact with one another. Figure 8.6 illustrates the physical processes contributing to particle collisions in surface waters. Gravitational aggregation is caused when colloids collide with larger, rapidly settling particles. Random collisions between colloids due to Brownian motion occur with greater frequency as colloid size decreases and result in what is called perikinetic aggregation. Colloidal particles in lakes are subject to aggregation, via both these processes and is dependent on both particle surface charge and initial particle size (Ali et al., 1985). Aggregated particles are then subject to sedimentation which may act to transport adsorbed metals from the water column to the sediments (Sigg, 1985). The overall result of these two aggregation mechanisms is that particles of intermediate size, on the order of a few μm, tend to be the most stable in non-flowing water bodies. Collisions also occur when particles are being transported in zones of steep fluid velocity profiles (orthokinetic aggregation) such as occur in turbulent rivers. The bulk chemical properties between settling colloidal aggregates and not-settling colloids can be very different, especially in respect to their organic matter and trace metal content (Ranville et al., 1991).

Collision of two particles can have two outcomes, either the particles adhere to each other or they do not (O'Melia, 1992). As two similar, like-charged hydrophobic particles approach each other they begin to experience electrostatic repulsion as the gap between them closes. As the separation decreases the electrostatic repulsive forces increase and more energy is required to continue the approach. However, if the separation can be made sufficiently small, van der Wall's attractive forces begin to come into play and ultimately overwhelm the repulsive forces and aggregation can take place. The overall surface charge and the thickness of the dif-
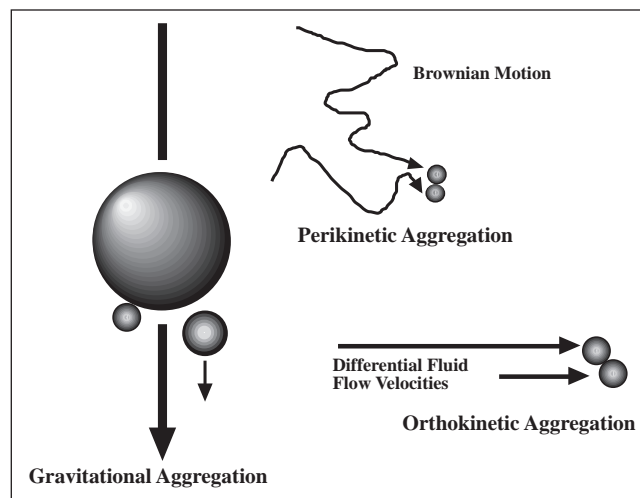

FIGURE 8.6—Physical processes causing particle collisions in surface waters that can lead to particle aggregation.

fuse charge layer surrounding the particle controls the magnitude of the repulsive force. The diffuse layer charge thickness is decreased by the presence of ions, especially multi-valent species, in the aqueous media. Therefore, as ionic strength increases the diffuse charge cloud shrinks and the repulsive force decreases and aggregation is more likely.

An example of this process may be observed in the behavior of iron oxyhydroxide precipitates that form in streams that receive acid-mine drainage. These types of streams often have abundant flocculated iron oxides on the streambed that are easily resuspended. Iron oxides often form as very small colloidal particles with diameters less than about 0.1 μm. These small primary particles have been observed to occur in much larger aggregates that rapidly settle to the streambed, as illustrated on Figure 8.7 (Ranville et al., 1991b). It is likely that the relatively high concentration of sulfate ion that occurs in these streams effectively neutralizes the net positive charge on iron oxyhydroxides that exist at pHs below 7–9 and also reduces the electrical double layer thus promoting particle aggregation.
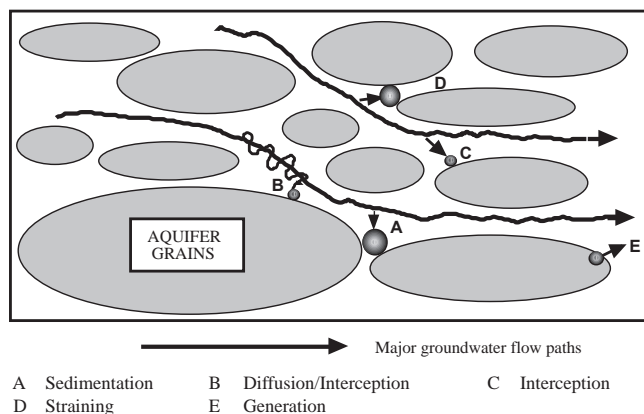
THEORY OF COLLOID MOBILITY IN POROUS MEDIA

The abundance of colloids in groundwater is a function of their source area and(or) *in-situ* processes. Weathering and disaggregation results in the generation or release of colloids from the grain surface. Movement of colloids in a groundwater aquifer involves all the mechanisms of surface water transport with the added complications of finite pore sizes, very complex flow paths and abundant opportunity to interact with the solid aquifer matrix. This is illustrated in Figure 8.8, is described in detail by McDowell-Boyer et al. (1986) and is summarized here. An exhaustive review of colloid mobilization and transport in ground water is given by Ryan and Elimelech (1996).

Colloids may or may not penetrate an aquifer depending on their relative size compared to the pore size of the porous media.
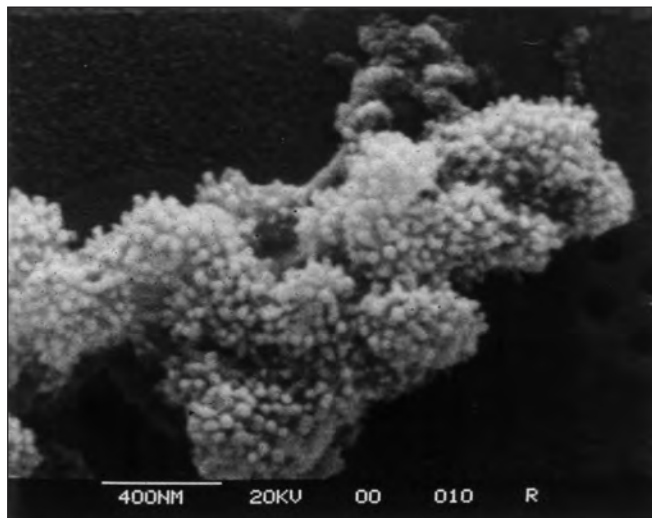
FIGURE 8.7—Scanning electron photomicrograph of a suspended iron oxyhydroxide particle collected from a stream receiving acid-mine drainage. Primary iron oxyhydroxide particles appear as spheres of about 0.05 μm diameter that are aggregated into larger particles with diameters of a few μm.

Major groundwater flow paths

A Sedimentation	B Diffusion/Interception	C Interception
D Straining	E Generation	

FIGURE 8.8—Processes occurring in a porous medium that affect colloid transport in ground water.

The grain size of the porous media is directly related to pore size, is considerably easier to measure, and therefore the more widely-used parameter. When the particle diameter/media diameter (d_p/d_m) is greater than 0.1, particles are normally excluded from a porous media and form an external cake. Somewhat smaller particles entering the porous media are subject to gravitational settling (depending on the flow velocity) and straining. Straining is the process whereby particles become trapped when they reach constrictions in the pores. Straining appears to be most important when d_p/d_m is between 0.1 and 0.05. Significant losses of porosity may occur due to straining, and the mechanism itself may become more important when either d_p increases, due to colloid agglomeration, and(or) when d_m decreases due to changes in lithology. The combination of these mechanisms probably result in the upper size limit for suspended and(or) mobile particles in porous media. According to these parameters, even the largest colloids (1 μm diameter) could easily enter a fine sand aquifer with uniform spherical grain sizes of 0.1 mm. Assuming clay-sized (0.001 mm) aquifer grains, colloids up to 50 nm could potentially move through the available pore spaces. Obviously these are very conservative estimates and do not take into account irregular grain shapes and non-uniform packing, which would reduce the maximum size of transportable particles.

For particles small enough to penetrate a porous media, the probability that they remain suspended or entrained in the prevailing flow depends in large measure on particle-media interactions. McDowell-Boyer et al. (1986) regard the process as physical-chemical filtration comprised of the initial collision and subsequent attachment mechanisms. A larger suspended particle may collide with a matrix surface as a result of gravitational forces "pulling" it from the flow path, or the trajectory of the flow lines may result in direct interception of the particle by the media surface. For smaller particles and perhaps all colloids, Brownian motion-based diffusion is the predominant collision mechanism. Brownian motion allows colloids to diffuse from the principle flow region within pore spaces and closely approach the aquifer grains where attachment may occur. Attachment is determined by the complex nature of the electrified interface and is a balance between attractive and repulsive forces as previously described. Attractive forces are dependent upon the nature of the particles whereas repulsive forces, due to charge on the surface are also

dependent upon water chemistry. Water chemistry parameters of importance include pH (Kita et al., 1987) and ionic strength (Cerda, 1987; McDowell-Boyer, 1992).

The consequence of the processes that remove both large and small particles is an optimum particle size for transport in porous media (Yao et al., 1971). The greatest mobility is shown to occur for particles near 1 μm. This suggests that filtration through 0.45 μm filters may result in under-estimation of colloid-associated contaminant transport. These processes have been most clearly demonstrated by the work of Harvey et al. (1989) with various tracer tests which were conducted between monitoring wells in a glacial aquifer on Cape Cod, MA under conditions of natural and induced flow gradients. Chloride and bromide were used as conservative tracers and fluorescent-labeled bacteria and submicron latex spheres were used to study the mobility of particles. These tests demonstrated that:

1) Micron- and submicron-size particles can easily migrate in porous media.
2) Average velocities of particles may exceed those of conservative solutes.
3) As predicted, submicron-size particles travel more slowly than micron-size particles.
4) The chemical functionality of the spheres (carboxyl, carbonyl, uncharged) affects retention and retardation.

The transport of these spheres was successfully modeled by colloid filtration theory (Harvey and Garabedian, 1991).

Additional research reveals the potential impact of colloids on adsorbed contaminant transport in a porous media. Puls and Powell (1992) compared the mobility of arsenic associated with iron oxide colloidal particles to that of truly dissolved arsenic in laboratory columns of natural aquifer material. Tritium was used as conservative tracer. The following was reported; FeOx colloids moved very easily through the columns (shown by the similarity of the tritium and colloid arrival times), colloid-associated As was transported through the columns 21 times faster than dissolved As, and colloid velocity was a function of colloid size and the ionic environment of the solutions.

METHODS OF ANALYSIS OF AQUATIC COLLOIDS

The study of environmental colloids requires special care in their collection and physical, and chemical characterization. The bulk chemical properties of colloids are less sensitive to post-sampling changes than the surface chemical properties and the physical properties of particle size and degree of aggregation. The ease of alteration of a colloid's properties, combined with their low concentrations in most waters, which generally require sample concentration, make these materials extremely difficult to study unambiguously.

Aspects of sample collection

Full understanding of the distribution of dissolved and particulate components in any natural water requires that special care be taken to obtain representative samples and to avoid the creation of sampling artifacts. Artifacts include any result of the sampling process which causes the sample, as presented for analysis, to be physically or chemically different from the water *in situ*. While considerable attention has been given to the impact of sampling

artifacts on dissolved or presumably dissolved components (Barcelona, 1990; Kent and Payne, 1988; Smith et al., 1988; Herzog et al., 1991; Palmer et al., 1987; Barcelona and Helfrich 1986; U.S. EPA, 1986, and many others), less regard has been focused on particles, and especially colloids. It is now clear that the act of sampling, especially of ground waters, can alter suspended particulate populations *in situ* and therefore bias information, not only about the particulates themselves, but also about dissolved constituents (Ryan and Gschwend, 1990; Backhaus et al., 1986).

The problem of artifacts is especially acute in groundwater sampling because:

1) Physical and chemical conditions in deep or confined aquifers and even some relatively shallow, unconfined aquifers may be significantly different than those at the surface.
2) The act of sampling can impose dramatic changes in the immediate vicinity of the sampling point.

Regarding the first point, differences in total pressure, partial pressures of reactive gases (e.g., CO_2 or H_2S), temperature, and light can affect; composition of dissolved gases and other volatile components, heterogeneous equilibria involving gas phases, and reaction rates. These in turn can alter the redox state, carbonate equilibria, and pH, which can initiate precipitation-dissolution reactions, shifts in aqueous phase speciation, and(or) changes in sorption-desorption equilibria. Many of these potential reactions can affect the identity, quantity, stability, size, and sorbed chemical composition of colloidal phases.

Regarding the second point, well development activities that often induce considerable turbulence, such as purging and sample collection (especially when done with high-volume pumps), can mobilize particles from the aquifer matrix because these actions can impose higher-than-normal piezometric gradients and can result in accelerated flow velocities. This results in the mobilization of particles that might otherwise remain attached to the aquifer media and(or) disturbance of the size distribution of existing suspended matter; either could alter the distribution of analytes in the sample. EPA currently recommends low velocity sampling whenever possible (Puls and Barcelona; 1989).

Only recently have the effects of sampling on groundwater colloids been studied (Backhus et al., 1986; Puls et al., 1990). Puls et al. (1991) found that bailed samples contained significantly higher concentrations of particulate chromium and arsenic than pumped samples. This presumably was due to turbulence in the well that caused re-suspension of particles from either the bottom of the well or from the surrounding aquifer. Furthermore, Puls et al. (1991) found differences between pump types which related primarily to sampling rate. A bladder pump (flow rate = 0.6–1.1 l/min) produced 13 times less particles than a low speed submersible pump (2.8–3.8 l/min) and 20 times less than a high speed submersible pump (12–92 l/min). Light scattering intensity, a measure of particle concentration, has been shown to decrease as pumping rates decreased (Ryan and Geschwend, 1990) indicating unnatural entrainment of particles by pumping. Light-scattering and turbidity measurements have also shown that in some cases, many more well casing volumes must be purged to reach a stable particulate concentration than for stabilization of dissolved groundwater chemical parameters such as pH, dissolved oxygen, temperature, and Eh (Ryan and Geschwend, 1990; Puls et al., 1991). Gschwend et al. (1990) employed a modified gear pump to obtain groundwater samples at very low rates in order to study colloids. These studies collectively suggest that groundwater samples

should be taken at low pumping rates (<100 ml min^{-1}) and that particle-sensitive parameters such as turbidity should be monitored to determine purging volumes.

Water should not be withdrawn from a well bore faster than it recharges under normal hydrostatic conditions, so as to not exceed normal interstitial flow velocities. This pertains to purging as well as sampling. To achieve this there should be no drawdown during purging or sampling where a single aquifer is present. Where multiple aquifers are present the individual water producing intervals should be isolated if possible and the *in-situ* pressure monitored during withdrawal. Such practices raise the issue of practicality, particularly in the case of a slowly-recharging monitoring well. Sampling protocol decisions should not be made on the basis of very short term cost analysis but on the long term benefits of accurate baseline data, reproducible values and understanding.

An additional concern for groundwater sampling where colloid-sensitive parameters are concerned is contact with the atmosphere. Formation of ferric oxyhydroxide precipitates and their subsequent flocculation are common occurrences when reduced waters are exposed to air. A study the colloid-facilitated groundwater transport of radionuclides in the Gorleben aquifer (F.D.R.). avoided this problem by transferring samples directly into resin coated aluminum drums equipped with an N_2 atmosphere (Lieser and Hill, 1992; Deerlove et al., 1991; and Kim et al., 1992).

In sampling surface waters, precautions similar to those used in groundwater sampling to exclude exposure to the atmosphere, must be taken when sampling lakes and reservoirs, especially where anaerobic zones exist. Redox-sensitive species such as iron exist as very different phases in oxic and anoxic waters and have been shown to exist in significant amounts as colloids at the oxic-anoxic boundary (Buffle et al., 1989). For flowing surface waters (rivers, canals, etc.) the non-homogenous distribution of particles vertically and horizontally must be taken into account. Techniques to obtain horizontally and vertically integrated, discharge-weighted samples should be used (Meade and Stevens, 1990). Pressure-compensating, isokinetic bag-samplers allow collection of sample volumes at each point which represent the proportion of flow at that point. From this data the mass flux of colloidal particles can be computed. These methods have recently been used to investigate colloidal size distributions in the Mississippi River (Rees and Ranville, 1990).

Current standard filtration practices

Sample filtration is a critical aspect of natural water sampling, both to the geochemist interested in details of solute speciation, modeling and transport mechanisms, and to those concerned with regulatory compliance and(or) water facilities operations. Filtration is also a point of considerable disagreement revolving around suspended particles and colloids (Nielsen, 1991). For the geochemist, equilibrium-based solute modeling utilizing analytical data from samples which include particulate-associated cations or anions as a significant portion of the "dissolved" solute is an exercise in futility. For owner/operators of water facilities or environmentally regulated facilities, specified sample filtration practices are mandated for regulatory compliance (even though such practices may produce misleading data); however, additional correct and elective filtration practices may be necessary to obtain an accurate understanding of process control.

Standard practice for filtration of those natural waters intend-

ed for "dissolved" (as opposed to "suspended," "total," or "acid-extractable") species analysis is to filter through a submicron, typically 0.45 µm, membrane filter. The selection of the 0.45 µm pore size appears to have its origin in early bacteriology and the smallest dimensions of some bacteria. It is not apparent that such a size was ever intended to address solutes. Greenberg et al. (1992) suggests either vacuum or pressure filtration through a 0.4 or 0.45 µm polycarbonate or cellulose acetate filter for dissolved metals analysis, certain inorganic non-metals like sulfate and phosphate, and waters to be analyzed by ion chromatography, but make no recommendations for other constituents. The U.S. EPA (1986) specifies 0.45 µm filtration for metals analysis on one split of the sample and no filtration of the other split. The U.S. Geological Survey (1982) recommends filtration for all dissolved inorganic constituents through a non-metallic 0.45 µm filter. Barcelona (1990) cautions that dissolved gases and volatile organic constituents are notable exceptions to the above recommendations and should never be determined in filtered samples. "Dissolved" is thus operationally defined as anything passing a 0.45 µm filter but Hem (1985) alludes to the inadequacy of this definition.

Recent studies have revealed the particulate-associated nature of significant portions of ions and molecules in the <0.45 µm fraction of natural waters. These observations obviously compromise the 0.45 µm filter pore size-based operational term "dissolved" which clearly ignores colloids. This is further discussed in the "Colloids in Natural Waters" section. Filtration using 0.45 µm membranes is also inadequate to determine colloid-associated chemical species as colloid sizes spans a range which encompasses this size.

Particle size analysis

Many techniques exist for the size analysis of colloidal particles, however, the discussion of these methods will be limited in this paper. Methods include those based on light-scattering, microscopy, sedimentation, filtration, and dialysis. Coupling of some size analysis methods with a wide variety of chemical analysis gives additional information of the composition of various sized particles. Since the focus of this discussion is contaminant transport only those methods providing chemical information will be presented.

Scanning electron microscopy and transmission electron microscopy are extremely useful techniques for examining colloids (Nomizu et al., 1988). Microscopy provides the most direct way of sizing particles but is very time consuming and care must be taken to avoid creation of artifacts. Limited chemical information is provided by energy-dispersive X-ray analysis (EDAX) commonly available with SEM instruments. Electron microscope techniques for examining colloids in natural waters have been reviewed by Leppard (1992).

Considerable difficulty exists in differentiating between colloids and dissolved species. Filtration through micro-porous membranes, dialysis, and centrifugation at high gravities have been employed for this separation (Batley, 1990). Obviously the distinction between "colloidal" and "dissolved" is operational and furthermore, many factors affect the actual physical size or molecular weight of particles passing a given nominal filter pore size, especially when membrane filtration is employed. Filtration through successively smaller pore sizes has most commonly been used to give size distributions of colloidal-sized particles and to

ultimately obtain the "dissolved" fraction of natural waters (Kennedy et al., 1974; Wagemann and Brunskill, 1975; Danielsson, 1982; Laxen and Chandler, 1982; Hoffman et al., 1981; Tanizaki et al., 1992).

Factors affecting the results of filtration were carefully examined by Buffle et al. (1992), including such variables as filter type, filter loading, and flow rates. Two major types of commercial filters exist and were examined: (1) depth filters, composed of a complex mat of fibers which retain particles within the matrix of the filter; and (2) screen filters, which consist of non-porous materials containing discrete holes that retain particles on the surface of the filter.

The most important physicochemical processes occurring during filtration were (1) concentration polarization (i.e., buildup of particles) at the membrane surface, which promotes coagulation and alteration of the size distribution, and (2) membrane exclusion effects which inhibit the passage of very small particles through pores with similar diameters. Honeyman and Santschi (1991) documented the failure of 0.25 μm ^{59}Fe-hematite particles to pass a 0.40 μm membrane filter, apparently as a result of aggregation at the filter surface. The study of Buffle et al. (1992) illustrated how dependent the results of filtration are on procedural technique and suggests that any interpretation of particle size measurements based on filtration must be carefully examined within the context of how the filtration was performed. Often filtration is routinely performed in the field with little control over the methods used. This has ominous consequences as to how valid our current data base is on the "true" distribution of solutes, colloids, and suspended particles in natural waters.

Cross-flow filtration is a very promising filtration method which may overcome some of the aforementioned problems associated with filtration (Gutman, 1987). In tangential or cross-flow filtration, a high flow rate is maintained parallel to the filter membrane while a much lower flow rate of filtrate passes through the membrane. This method induces large shear forces near the membrane surface and thus reduces both the concentration polarization region and membrane fouling. Filtration membranes are generally stacked in order to provide large areas, on the order of a few square meters, to further limit filter fouling. The method allows processing of large volumes of water to isolate colloids in significant quantities without reduced filtration rates. Cross-flow filtration uses systems based on either hollow-fibers (4–8 l min^{-1} @ 0.2 μm, Kuwabara and Harvey, 1990; Marley et al., 1991) or flat membranes (10–12 l hr^{-1} @ 10000 MW or ≈ 10 nm, Whitehouse et al., 1986, 1990). A number of studies have utilized these techniques with success in producing upwards of gram quantities of material in the colloid size range. Tangential-flow filtration using different sized membranes in series has been used successfully to isolate particles in various colloidal size classes Douglas et al. (1996). The accuracy of the size cutoff for tangential-flow filtration has not as yet been investigated.

Continuous-flow centrifugation is a useful technique for the large scale isolation of suspended particles and larger colloids. In this method a suspension is continuously passed through a spinning centrifuge. Larger particles are retained on the walls of the centrifuge bowl whereas solutes and smaller particles are carried through (Horowitz et al., 1989). Continuous flow centrifugation has been used to separate river water particles down to about 0.3 μm (Leenheer et al., 1989; Rees et al., 1991; Douglas et al., 1996). It has been noted that suspended particles retained by continuous flow filtration, when disaggregated, show similar particle size dis-

tributions to the colloids not retained by the centrifuge (Rees et al., 1991). This suggests either the particles occur as aggregates in the sample or aggregation occurs in the centrifuge.

A new and very powerful method of colloid size analysis is field-flow fractionation (Beckett et al., 1988). This method, analogous to chromatography, provides high resolution and a continuous distribution unlike sequential filtration which has low resolution, which is defined by the number of pore sizes used. Various sub-techniques of field-flow fractionation exist which allow analysis of particles ranging in size from 0.001 to 50 μm. Because this method elutes the fractionated particles, fractions can be further analyzed for their composition. This technique has been shown to be useful to study colloid-pollutant interactions (Beckett et al., 1990), especially with the recent direct coupling of the FFF technique to ICP-MS analysis (Ranville et al., 1998; Taylor et al., 1992; Murphy et al., 1993).

COLLOIDS IN NATURAL WATERS

Colloids occur to varying extents in essentially all aquatic environments. The colloids present in surface waters and ground waters consist of mixtures of generally similar materials. However, the relative abundance of each component can vary from one environment to another. Specific examples of the types and abundances of colloids in various environments are given in the following paragraphs.

Surface water colloids

Most data on the importance of colloids in aquatic systems come from studies of surface waters. Fluvial suspended sediments are generally composed of aggregates and contain variable percentages of particles less than 2 μm. Walling and Moorehead (1989) found the amount of less than 2 μm material ranged from about 10–30%. After disaggregation the amount of less than 2 μm material increased to 40–80%, with 5–30% less than 0.2 μm.

Some researchers have found little or no differences between 0.45 μm filtrates and ultrafiltrates (10–100 K daltons) for most elemental concentrations, suggesting little colloidal material less than 0.45 μm (Taylor et al., 1990; Waber et al., 1990). In contrast, Hoffman et al. (1981) used an ultrafiltration scheme to investigate trace metal concentrations in sizes ranging from less than 10,000 to greater than 100,000 daltons. Their results show significant amounts of trace metal were present as colloidal particles in the upper Mississippi River. Salbu et al. (1985) studied colloidal metals in surface and ground waters using filtration, dialysis, and centrifugation; they found, for example, that the majority of Cd and Cr were present in the 0.1–0.005 μm fraction. Moran and Moore (1989), using cross-flow filtration, found 15% of the <0.45 μm aluminum to be present in the <10,000 dalton fraction of open sea water.

The size distribution and concentrations of 46 elements in eight Japanese river waters was determined by Tanizaki et al. (1992) using filtration and ultrafiltration. They were able to divide elements into groups based on their affinities for various size classes, including: suspended sediments (>0.45 μm); colloid fractions of 0.45 mm–10,000 dalton and 10,000–500 daltons; and solutes <500 dalton. Transition elements were largely present in the >0.45 mm, 10,000–500 dalton, and <500 dalton fractions. The

most dramatic colloidal effects were evident in the trace element determinations, particularly REEs, where typically less than 20% of the <0.45 μm fraction content was present in the <500 dalton fraction (see Table 8.3). These results compare favorably with those of Kim et al. (1992) who studied REE elements in ground waters.

TABLE 8.3—Average percentages of the concentration of 44 chemical species in 0.45 mm filtrate that remain in 500 dalton ultrafiltrate. Data from Tanizaki et. al. (1992).

Species	% remaining	Species	% remaining	Species	% remaining
Cl	98.2	Ca	71.1	Mo	28.0
Na	93.2	Mn	66.9	Ho	20.0
Al	90.2	Ta	65.2	Th	18.0
Rb	89.6	Ni	42.4	Sm	16.0
K	89.5	As	42.0	Ce	13.0
SiO_2	88.7	Cr	40.5	Eu	11.9
Cs	87.7	$SO_4^=$	40.5	Yb	11.7
$CO_3^=$	86.3	Co	37.9	La	10.3
Au	84.0	W	37.8	Tb	10.2
V	74.6	U	34.2	Sc	9.6
Sb	74.0	Zn	32.1	Fe	9.3
Ba	72.8	Se	31.9	Lu	8.6
Sr	72.5	Hf	30.6	Tm	7.8
Br	72.1	$PO_4=$	29.9	Ag	5.2
Mg	71.1	Organic C	28.6		

Table 8.4 contains selected results of an exercise using the data of Tanizaki et al. (1992) as input for chemical modeling using PHREEQE (Parkhurst et al., 1980). The results illustrate the potential differences that can arise from the use of chemical data which include some particulate-associated ions in the solute values. Major ion concentrations and the mineral saturation indices solely based on them (e.g., calcite, halite, etc.) are relatively unaffected by filtration. However, minor and trace element concentrations and the predicted thermodynamic solubility of solid phases containing those elements show greater impacts. For example, ferrihydrite ($Fe(OH)_3$) appears to be slightly supersaturated in the <0.45 μm filtrate (SI = log(IAP/K_{sp}) = 0.84) but is undersaturated (SI = -0.23) in the more truly "dissolved" (<500 dalton) fraction. In the case of zinc, results using <0.45 μm indicate supersaturation with a zinc phosphate mineral, whereas <500 dalton data indicate undersaturation with respect to this mineral. More work should prove fruitful in establishing the true nature of transported loads in natural waters. It should, however, already be evident that thermochemical-based modeling of <0.45 μm filtrates should be limited to those constituents not significantly attenuated by such filters.

Humic substances, which are ubiquitous in surface and ground waters, exist at the boundary between dissolved and colloidal size with molecular weights of about 700 to 2000 daltons, and as such are best considered macromolecules. These materials are excellent complexers of metals and radionuclides in solution (Buffle, 1988). Humic substances sorbed to surfaces generally affect the metal sorption of the particles by increasing sorption at low pH (Davis, 1984; Tipping et al., 1983). Some recent work, however, suggests a lesser role for sorbed organic matter in trace metal partitioning in acid mine drainage (Smith et al., 1992), presumably due to competition from the abundant dissolved iron for binding sites. Humic substances have been demonstrated to influence the transport of organic contaminants in aquatic systems (Enfield and Bengtsson, 1988). The transport of cadmium through soil columns was greatly enhanced by the presence of humic material (Dunnivent et al., 1992).

Higher molecular weight organic colloids have been found to occur in estuarine waters (Sigleo and Helz, 1981) and porewaters at high concentration (Chin and Geschwend, 1992a). These colloids have been shown to affect the partitioning of hydrophobic organic chemicals (Means and Wijayaratne, 1982; Chin and Geschwend, 1992b) and are expected to also bind trace metals. Porewater organic colloids can diffuse into overlying waters and may act to enhance the flux of contaminants from these sediments (Thoma et al., 1991).

Colloidal iron and manganese phases are common in surface waters (Laxen, 1983) and are often present in regions of redox boundaries. These boundaries frequently occur in lakes at the oxycline, where dissolved oxygen disappears due to biological respiration. These particles are generally a few tenths of a micrometer in size and are associated with organic matter and phosphorous (Buffle et al., 1989).

A very important redox-active system is acid-mine drainage. In these systems ferrous iron is oxidized to ferric iron, which then hydrolyzes and subsequently precipitates as colloidal hydrous iron oxides and hydrous iron hydroxysulfates (see Nordstrom and Alpers, 1999; Smith, 1999). Colloidal iron can make up a significant portion of total suspended iron in these systems and can also adsorb and transport trace metals (Smith, 1999). Roughly an order of magnitude difference between 0.45 μm and 0.01 μm filtered iron has been shown to persist in a river for hundreds of kilometers downstream of acid-mine drainage inputs (Kimball et al., 1995). Solubility calculations for iron hydroxides will not only be affected by the enhanced solubility of small particles (Langmuir and Whittemore, 1971) but in a more practical sense by the choice of filter pore size used to determine "dissolved" iron (Kimball et al., 1992). Acid-mine drainage systems are the only environment where positively charges particles have been clearly demonstrated

TABLE 8.4—Selected geochemical modeling (PHREEQE) results of data from Tanizaki et al. (1992) comparing the mineral saturation indices [SI = log(IAP/K_{sp})] obtained by inputting "dissolved" concentrations into the model using either 0.45 μm or 500 dalton filtrate data. IAP is the product of the aqueous ion activities of the species that are formed by dissolution of the mineral and K_{sp} is the minerals solubility product. For a mineral at equilibrium SI = 0, for supersaturation SI > 0, and for under saturation SI < 0.

Mineral	$Al(OH)_3$ amorphous	$KAl(SO4)_2(OH)_6$ alunite	$CaCO_3$ calcite	$Fe(OH)_3$ ferrihydrite	$FePO_4.2H_2O$ strengite	$Zn_3(PO_4)_2$
SI (<0.45 mm)	-0.005	-0.54	-1.5	0.84	-0.55	1.5
SI (<500 Dalton)	-0.20	-2.1	-1.7	-0.23	-2.1	-0.12

to exist in surface water (Newton and Liss, 1987; Ranville et al., 1991b). This occurs primarily as a result of insufficient organic matter to fully coat the extensive iron hydroxides surfaces formed in these systems. This may affect both metal interaction with iron oxyhydroxide colloids and particle stability, and hence transport.

Soil and groundwater colloids

A significant amount of the mineral and organic components of soils are colloidal in size. These components are bound up in aggregates that make up the "texture" of soils. The properties of some soil colloids were studied by Bremner and Genrich (1990). In a study of ten Iowa Mollisols they found that on average, 30% of the soil mass was less than 2 μm in size. Even more importantly, the <2 μm fraction contained 68, 73, and 80% of the total organic matter, iron and cation exchange capacity respectively. Mobilization of soil colloids can thus carry colloid-associated contaminants vertically into the aquifer. Vertical transport of DDT adsorbed on sewage particles and Paraquat adsorbed to montmorillonite was observed in soil columns by Vinten et al. (1983). The addition of calcium chloride significantly reduced the amount of pesticide transported, presumably either by aggregation and straining in the pores or by sorption of the particles to the soil matrix. The physical structure of soils will greatly influence colloid transport. Macropores, consisting of connected fractures and root channels, have been shown to facilitate the transport of organic and mineral colloids in soils (Chittleborough et al., 1992). The presence of these macropores will complicate transport modeling which is based on flow through porous media, particularly for colloids.

Very few studies have investigated the nature and amount of colloids naturally present in groundwater (Reynolds, 1985). Salbu et al. (1985) used centrifugation, filtration, hollow-fiber ultrafiltration and dialysis to determine colloid concentrations in groundwater. The concentrations of 20 elements were determined in four size fractions: >0.45 μm, 0.45–0.1 μm, 0.1–0.005 μm, <0.005 μm. In the groundwater, iron, zinc, and copper were primarily present as particles >0.45 μm, whereas chromium, cadmium, and manganese showed significant amounts in each of the size fractions. Colloidal particles have been found in deep fractures in granite at a concentration of 10^{10} particles/l (Degueldre et al., 1989); these colloids consisted primarily of small alumino-silicates. Waber et al. (1990) studied the relationship between colloid content of the river Glatt and a shallow aquifer which is continuously recharged by the river. Colloid (<0.45 μm) concentrations in the river were computed to be approximately 2.3 mg/l, of which >90% was composed of organic matter. In contrast, the colloid concentration in the groundwater was an order of magnitude less, thus leading the authors to conclude that transport of colloids from the river to the groundwater was insignificant.

Natural and anthropogenic changes to the chemistry of soil and ground waters can result in the formation or liberation of colloids. This is particularly true for changes that may remove cementing agents, which bind together soil and aquifer matrix colloids. Ryan and Geschwend (1990) found that dissolution of iron hydroxides by infiltration waters with naturally low Eh released colloidal kaolinite and other alumino-silicates. Dissolution of iron hydroxides might also be expected to release organic matter that has been shown to strongly adsorb to iron hydroxides (Tipping and Cooke, 1982). This process might mobi-

lize contaminants associated with the released organic matter. Geschwend et al. (1990) found that perturbation of the carbonate equilibrium of a groundwater near a coal ash disposal site resulted in dissolution of calcite and decementation which released colloids into the groundwater. SEM-EDX analysis suggested these colloids were composed of alumino-silicates and residual carbonate cements. Changes in groundwater conductivity or pH can mobilize otherwise immobile colloids. Significant amounts of colloidal particles have been mobilized by artificial recharge of an aquifer by low conductivity surface water (Nightingale and Bianchi, 1977); from turbidity data, these researchers estimated a groundwater particle concentration of 9.93 mg/l and that approximately 148 metric tons of particles were liberated from the overlying sandy soils during one year of recharge. These colloids appeared to be effectively transported since no decrease in recharge rate was observed. Application of gypsum prevented mobilization of colloids by destabilizing the colloids.

Precipitation of colloids resulting from human-caused perturbations in water chemistry can occur in aquifers. Reaction of phosphorous-rich sewage effluent with aquifer iron resulted in the precipitation of ferrous phosphate colloids in a sand and gravel aquifer at Cape Cod (Geschwend and Reynolds, 1987). These particles were approximately 0.1 μm in size and fairly monodisperse. Particle concentration was estimated at 10^6 particles/liter.

Biocolloids

Much of the information on colloid transport in ground waters comes from work with biocolloids. Bacteria and viruses, have been demonstrated to be transported over significant distances in groundwater (Gerba and Bitton, 1984). Laboratory experiments have shown pH to be a major factor in interaction between bacteria and the aquifer matrix (Scholl and Harvey, 1992). The deposition of bacteria in soil columns can be modeled by using electrical double layer theory (see Smith, 1999) to explain bacterial stability and clean-bed filtration theory to describe the physical processes involved (Martin et al., 1992).

Radionuclides

One of the most important areas for concern over colloid-facilitated transport of contaminants is of that of radionuclide transport. Most radionuclides are considered extremely insoluble or highly sorbing, and hence immobile in the aquatic environment. A number of studies have indicated the radionuclides are indeed mobile in groundwater and this may be attributed to colloid transport. Bates et al. (1992) clearly show the formation of colloids containing radionuclides by the interaction of waste glass with water. These colloids form near the surface of the glass and can be released into solution. Colloid associated radionuclides were found at the Nevada test site, where after a nuclear test, colloid concentrations in the cavity formed were on the order of 10 mg/l (Buddemeier and Hunt, 1988). Hollow-fiber ultrafiltration was used by Lowson and Short (1990) to investigate colloids in groundwater down-gradient from a uranium ore body. These researchers found colloids in the size range of 1.0–0.018 μm were composed of iron and silica, and contained uranium and thorium. Although only a minor proportion of the total uranium was associated with the colloids, a significant amount of ^{230}Th was associ-

ated with the colloid. Enhanced transport of americium and plutonium in an aquifer in an arid climate was demonstrated by Penrose et al. (1990). Predicted transport based on measurements of radionuclide sorption to soil materials were on the order of a few meters, whereas observations showed transport of several kilometers.

Kim et al. (1992), using membrane filtration, determined the abundances of a wide variety of elements in >0.4, 0.4–0.1, 0.1–0.002 and 0.002–0.001 μm fractions of deep (150–300m) ground waters from a sedimentary sequence overlying a salt dome intended for disposal of radionuclides. Their results showed that 70–87% of REE, selected transition metals, uranium and thorium, 99% of americium (Am^{3+}) and curium (Cm^{3+}) and 90+% of DOC found in the <0.4 μm filtrates were removed by filtration through 0.001 μm filters. Thus the 0.4 μm filtrate provided a significant overestimate of the dissolved content of these constituents. Acidification, however, allowed effectively all Am and Cm to pass the 0.001 μm filter and time resolved laser fluorescence spectroscopy (TRLFS) indicated these elements were bound to fulvic acid colloids. Puls and Barcelona (1989), working with ground waters from the Globe, Arizona area, observed a steady decrease in major, minor and transition elements using 10, 0.4 and 0.1 μm filters respectively.

MODELING COLLOID TRANSPORT

Modeling of colloid-facilitated transport is in its infancy. Various models exist which describe filtration and coagulation effects but few overall transport models for ground waters are available. These are reviewed and classified by Mills et al. (1991). An early one-dimensional colloid transport model was presented by Travis and Nuttal (1987). Mills et al. (1991) developed a conceptual model (COMET, COlloids-MEtal Transport) to predict colloidally-facilitated transport of metals in porous media and incorporated it into EPA's CML model for multimedia exposure assessment. Their calculations suggest greatly enhanced transport of contaminants when colloids are present, if the colloid-solute partition coefficient is significantly greater than the immobile aquifer-solute partition coefficient. The incorporation of more sophisticated adsorption models, as opposed to partition coefficients, into a similar framework may provide better results.

CONCLUSIONS

Colloids are recognized as a distinct mobile solid phase in the majority of natural water systems. These particles are capable of hosting heterogeneous reactions typically ascribed to immobile solid phases, but exhibit mobilities similar to those of true solutes and the aqueous media itself. An important role for colloidal particles in facilitating transport of contaminants in surface and ground waters is theoretically reasonable and is supported by a relatively small but rapidly growing number of field and laboratory studies. Interest is strong not only in the area of understanding the existing role of colloids in a given situation but also in the area of manipulating colloids to control contaminant migration (McCarthy and Wobber, 1993).

The mobility of particles in the micron size range, as shown by laboratory studies and limited field data, suggests that standard filtration practices (0.45 μm) may overestimate truly dissolved con-

centrations (including contaminant loads). On the other hand, the use of ultrafilters may result in seriously underestimating the total transported contaminant load, which includes that portion carried by colloids. Furthermore, filtration results are greatly affected by factors such as flow rate through the filter, total volumes filtered through a given filter apparatus, concentration of particles, filter type, and sample storage time. Often these variables are not considered during the design of field sampling schemes and(or) filtering practices are not reproducible from one sampling event to the next. Even if considered, these variables are often not closely controlled in the field due to the pressure to obtain samples in a rapid, cost-effective manner. For this reason, the EPA has suggested the collection of both unfiltered and filtered water samples (Puls et al., 1991). If significant differences are found, further examination is recommended to access the possibility of colloidal transport. It should be pointed out that such a comparison yields little direct evidence about colloid-associated loads if a relatively large pore size filter (e.g., 0.45 μm) is employed.

The magnitude of the general importance of colloids and colloid-facilitated transport is yet to be determined, especially in groundwater systems. In the case of ground waters it appears that the most important factor determining the mobility of natural colloids is the groundwater chemistry. In particular, changes to groundwater chemistry (i.e., pH, ionic strength, redox, and chemical composition) due to human activities can influence colloid stability. Colloids may be formed by *in-situ* precipitation reactions or liberated from aquifer material. Similarly, alterations in the ambient chemistry may result in destabilization of existing colloids through flocculation or adhesion to the matrix. In the course of investigations of groundwater contamination sites, determination of the spatial distributions of colloids may give important clues to understanding the migration of contaminants and the most effective means of remediation.

Various aspects of groundwater sampling protocol, such as pump type, purging schedules, sampling rate, and control of redox and dissolved gases can influence colloid populations and hence the results of chemical analyses. This is particularly true of unfiltered or inadequately filtered samples. Improper sampling techniques which disturb the groundwater in the vicinity of the well bore may result in artificially high levels of particulates. Observed temporal variations in dissolved and particulate concentrations may therefore be as much due to differences in sampling and filtration techniques as due to real physicochemical speciation. It cannot be strongly enough stressed that our understanding of the nature of contaminants in surface and groundwater will be incomplete until uniform sampling protocols, which accurately determine the presence of micrometer and sub-micrometer sized particles are developed.

Particle size and density control the movement of colloids and particles in porous media such as porous sedimentary rock. Surface charge and the nature of specific chemical surface sites are factors that control the attenuation of colloids and particles by porous media. The combination of these factors of particle movement and attenuation determine the mobility of these particles in groundwater. Despite the identification of these factors, transport of colloids and particles is currently only poorly modeled by filtration theory in even simple systems. Much work will be required to develop models for particle transport in soils and aquifers which are heterogeneous in nature.

Despite the current lack of a clear understanding of the role of colloids in contaminant transport, interest in colloids will contin-

ue to grow. It is now necessary for careful work to be done to develop the techniques and data bases which will, in time, provide a clearer picture of what, if any, role colloids play in the overall environmental fate and transport of contaminants in surface and ground waters.

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