

## Aquatic colloids: Concepts, definitions, and current challenges

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### Abstract

Colloidal phases in natural waters may be important to various environmental questions, especially those concerning the cycling of vital and toxic trace chemicals. Current treatments of the role of colloids in chemical speciation largely rely on operational definitions of phases such as 1,000-Da ultrafilter and 0.45- $\mu\text{m}$  filter cut-offs. Defining chemical phases exclusively by a physical parameter such as size is contributing to a situation where the observed filterable vs. unfilterable distribution coefficients,  $D$ , are not well predicted from thermodynamically derived sorbed vs. solute equilibrium constants,  $K$ . Achieving the goal of relating the natural distributions of chemicals to theoretical expectations is contingent upon progress in development of a functionally meaningful colloid definition and interpretation of observed distributions of trace substances in terms of the relevant physicochemical properties of the system.

We assess the phase status of typical components in natural waters from a “chemcentric” point of view (i.e. one whose motivation is to understand the cycling of trace chemicals in the environment). As a result, we define colloids so as to provide a thermodynamic grounding for evaluating chemical speciation and a hydrodynamic framework distinguishing phases that are transported with the solution from those that are not. These constraints lead one to define an aquatic colloid as any constituent that provides a molecular milieu into and onto which chemicals can escape from the aqueous solution, and whose movement is not significantly affected by gravitational settling. Such a definition allows development of mass balance equations, suited to assessing chemical fates, that reflect processes uniquely acting on dissolved, colloidal, or settling particle phases.

For aquatic scientists concerned with the behavior and effects of trace chemicals, one important process is the partitioning of those trace constituents between the dissolved and bound pools. The resulting speciation affects the extent to which the chemical participates in various transport and transformation processes. For example, one may anticipate that the truly dissolved trace molecules may participate in homogeneous solution phase reactions, while this is not true for their counterparts sorbed to colloids (particles “immune to gravity”; Graham 1861) or settling particles (henceforth referred to as gravitoids). Such sorbed species may be less bioavailable and may exhibit different photoreactivity than their solution-phase counterparts. Likewise, for transport processes, one may anticipate that dissolved and colloid-bound molecules are carried with the moving fluid (e.g. in sediment porewater irrigation), while the gravitoid fraction may fall out of a mixed water body to loci below. Distinguishing among these functionally distinct forms is essential if we are to elucidate the cycling and effects of trace chemicals in natural waters.

Recently, efforts to quantify the roles of colloids in the cycling of trace compounds have been confounded by the realization that results obtained by the most common sampling technique, cross-flow ultrafiltration (CFF), are operator and equipment dependent (Buesseler et al. 1996). CFF also appears to cause undesired fractionation of colloidal com-

ponents (Gustafsson et al. 1996). Nevertheless, continuing efforts to elucidate the applicability of CFF to collecting natural water colloids, along with development of new approaches for investigating these elusive components, guarantee that the current momentum of colloid studies will be maintained in the near future.

In this paper, we focus on how colloids may influence the cycling of trace compounds in natural waters (i.e. a chemcentric view). In particular, we attempt to constrain how colloidal entities may affect trace chemical speciation. We especially highlight the difference between operational distribution coefficients, hereafter designated with the symbol  $D$ , derived from the ratio of filterable-to-nonfilterable concentrations, from thermodynamically based equilibrium constants, hereafter designated by  $K$ , which quantify the relation between a single, truly dissolved species and a single, bound counterpart. Thus, after we briefly review the history of colloid-related studies, especially those pertinent to partitioning and scavenging processes in natural waters, we offer a definition of colloids based on our chemcentric point of view. This definition is then used to discuss whether various constituents of natural waters should be considered colloidal from the chemcentric point of view and to illustrate how colloid associations might influence chemical cycling.

### Historical perspective

The current picture of speciation and physical states of chemicals in natural waters is a result of a series of historical developments and conceptual formulations involving measures of the abundance of various suspended phases and inferences regarding the modes whereby trace chemicals interact with these phases. By the 1930s, aquatic scientists already worked to separate particulate, colloidal, and dis-

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solved organic carbon phases (POC, COC, DOC). For example, Krogh and Lange (1931) size-fractionated lakewater with "plankton-filters" and "ultrafilters." These ultrafilters were reportedly manufactured by impregnating paper filters with certain "colloidal suspensions under varying conditions" (Zsigmondy and Bachman 1918; Zsigmondy 1926) and were calibrated with macromolecular dyes, colloidal gold of increasing size, and egg albumin (45 kDa). Using a home-built "archea-HTCO" organic carbon analyzer based on catalytic oxidation with cupric oxide at "red-glowing" high temperature, Krogh (1930) determined that POC made up 20% and COC ~15% of the total organic carbon in lake waters—values within the range of recent observations for natural waters using modern CFF and HTCO methods!

Today's distinction between dissolved and particulate phases in geochemistry can be traced back to the application of 0.5- $\mu\text{m}$  cellulose acetate membrane filters to ocean waters by Goldberg et al. (1952). Goldberg (1954) also introduced the concept of "marine distribution coefficient,"  $D$ , as the ratio of an element in such filter-collected solid phases to that in the filter-passing media. In the first natural water application of stirred-cell ultrafiltration techniques (reported 0.003- $\mu\text{m}$  cutoff), Sharp (1973) demonstrated for seawater that most filter-passing organic matter actually could be colloidal. Nearly a quarter-century ago, Sharp called for relinquishing the misleading delineation of particulate and dissolved phases at about 0.5  $\mu\text{m}$ , which by then had become firmly established.

Reports that colloids influence the speciation of low-solubility chemicals in fresh and marine waters appeared in the mid-1970s. For example, Boehm and Quinn (1973) observed that the apparent seawater solubilities of  $n$ -alkane and isoprenoid hydrocarbons decreased when colloidal fulvic acid was removed. Likewise, Sholkovitz (1976) demonstrated the association of inorganic constituents such as Fe, Mn, Al, and P with colloid-sized humic substances, resulting in their co-flocculation during simulated estuarine mixing. Eventually, field studies also supported the idea that colloids could have an important impact on the speciation and fate of trace chemicals, such as when colloids were shown to affect polychlorinated biphenyl (PCB) cycling in the Laurentian Great Lakes (Baker et al. 1986) and in sediment porewaters of New Bedford Harbor (Brownawell and Farrington 1986).

On the theoretical side, Sillén (1961) proposed a thermodynamically based framework using chemical solubilities for interpreting partitioning and scavenging observations. This idea triggered the development of surface complexation models (SCMs) to interpret aqueous-solid partitioning phenomena for charged constituents (Schindler and Kamber 1968; Stumm et al. 1970; Schindler and Gamsjager 1972; Dzombak and Morel 1990). SCMs consider the free energy of solid-water adsorption to be a combination of both the intrinsic strength of the actual sorbate-sorbent bond and the electrostatic energy involved in moving the charged sorbate to the charged surface. Taking the saturated sorbed concentration to reflect unit activity in the solid phase and 1 M to be unit activity in the solution phase, we find

$$K_{\text{SCM}} = \frac{\sigma A}{1M} \exp[-(\Delta G_{\text{chem}} + zF\Psi)/RT], \quad (1)$$

where  $K_{\text{SCM}}$  ( $\text{mol kg}^{-1} [\text{mol liter}^{-1}]^{-1}$ ) is the solid-water adsorption constant,  $\sigma$  is the concentration of one type of reactive site per solid surface area ( $\text{mol sites m}^{-2}$ ),  $A$  is the area of particle surface per mass of solid ( $\text{m}^2 \text{kg}^{-1}$ ),  $\Delta G_{\text{chem}}$  reflects the intrinsic contribution of the energy of bond formation for a chemical distributing itself between a liter of solution and a specific charged site on a kilogram of solids,  $z$  is the charge of the chemical,  $F$  is the Faraday constant,  $\Psi$  is the surface potential relative to the bulk solution,  $R$  the molar gas constant, and  $T$  the absolute temperature.

A hydrophobic partition model (HPM) was also developed for predicting the equilibrium phase distributions of nonionic and hydrophobic organic compounds, HOCs (Karickhoff et al. 1979; Chiou et al. 1979). The natural organic matter in particles offers a relatively nonpolar environment into which HOCs may dissolve. Hence, association of HOCs with the organic matter content of natural particles reflects the difference in excess free energies of HOCs dissolving in natural organic matter vs. dissolving in aqueous solutions (Chiou et al. 1979; Schwarzenbach et al. 1993). As a result, the HPM allows prediction of nonionic compound sorption on the basis of the organic matter content of the particles and the relative solvophilicity of the chemical. Taking unit activity in the solid phase as the (liquid) compound's solubility in the organic matrix ( $C_{\text{om}}^{\text{sat}}$ ; units:  $\text{mol kg}^{-1}$  organic matter [ $\text{om}$ ]) and in the solution as the (liquid) compound's aqueous solubility ( $C_w^{\text{sat}}$ ; units:  $\text{mol liter}^{-1}$  water [ $w$ ]), one may derive a thermodynamic expression:

$$K_{\text{HPM}} = \frac{f_{\text{om}} C_{\text{om}}^{\text{sat}}}{C_w^{\text{sat}}} \exp(-\Delta G_{\text{om}}/RT), \quad (2)$$

where  $K_{\text{HPM}}$  ( $\text{mol kg}^{-1} [\text{mol liter}^{-1}]^{-1}$ ) is the solid-water adsorption constant,  $f_{\text{om}}$  is the organic matter fraction of the sorbent particles ( $\text{kg}_{\text{om}} \text{kg}^{-1} \text{solid}$ ), and  $\Delta G_{\text{om}}$  reflects the free energy of sorbate exchange between a kilogram of natural organic matter and a liter of water.

A major geochemical inconsistency with these sorption models was reported and widely discussed in the 1980s. Distribution coefficients,  $D$  values, for numerous trace chemicals (e.g. Co, DDT) were observed to change as a function of the concentration of the solids in the suspensions studied (e.g. O'Connor and Connolly 1980). Observations of the distribution of  $^{234}\text{Th}$  between filterable and unfilterable phases are typical (Fig. 1). At low solids concentrations ( $\leq 3 \text{ mg liter}^{-1}$ ), the  $D(^{234}\text{Th})$  is seen to be nearly constant at a relatively high value (i.e.  $\sim 10^6$ ). However, at increasing solids concentrations, the observed distribution coefficient decreases steadily. Such data are not consistent with expectations for  $K$ (trace chemicals) put forth by SCM and HPM models (and assuming other properties of the solution like pH do not change.) A unifying quality of these thermodynamic models is that they predict constant  $K$  values for trace chemicals, no matter what the sorbent:solution ratio.

These discrepancies between  $D$  and  $K$  values are due to a combination of factors. First, conventionally nonfilterable media are now recognized to include colloidal sorbent phases in the apparently dissolved phase (Gschwend and Wu 1985). Additionally, situations with high solids concentrations, resulting in rapid removal of colloids and gravitoids

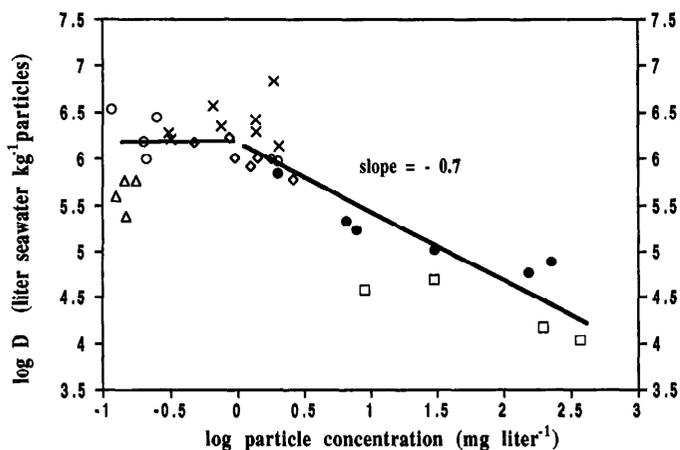


Fig. 1. Observed distributions ( $D$ ) between filter-retained and filter-passing  $^{234}\text{Th}$  in marine surface waters of varying filter-collected solids concentrations. A trend of decreasing  $D$  at solids concentrations greater than approximately  $D^{-1}$  is indicative of the presence of  $^{234}\text{Th}$  adsorbed to particles passing through the filters (the particle-concentration effect). ( $\Delta$ , Baskaran et al. 1992;  $\circ$ , Coale and Bruland 1985;  $=$ , Wei and Murray 1992;  $\diamond$ , Moran and Bueseler 1993;  $\bullet$ , McKee et al. 1984;  $\square$ , McKee et al. 1986)

(e.g. rapid coagulation and settling or rapid phytoplankton growth and grazing), may not allow sufficient solid-water contact for sorptive equilibrium to be achieved. Hence, observations of solid-water partitioning in these cases may not reflect chemical equilibria (Wu and Gschwend 1988; Honeyman et al. 1988; Swackhammer and Skoglund 1993).

In addition to sorption, the other group of processes central to scavenging trace constituents from natural waters involves the removal of sorbent phases from the water column. Both physically and biologically coupled models have been developed to describe colloid coagulation and gravitoid sedimentation. Physical treatment of particle dynamics normally involves Smoluchowski's coagulation theory (1917) coupled with particle removal mechanisms. Good treatments are available of the fundamental factors that govern coagulation: the encounter rate of particles,  $\eta$ , and the fraction of the collisions that result in aggregation,  $\alpha$  (e.g. Friedlander 1977; O'Melia 1987; Israelachvili 1992). Several studies have also observed that colloids are both produced and taken up by microbial and planktonic food webs (e.g., Johnson and Kepkay 1992; Tranvik 1993; Amon and Benner 1994). Biologically coupled aggregation models are hybrids of the thermodynamically based coagulation theory and empirical descriptions of, for example, bloom dynamics. In recent versions, the smallest, primary particles in such models are  $1\ \mu\text{m}$  (Jackson 1990; Hill 1992), which obviously means that the colloids are largely ignored.

Stoke's law for gravity-driven settling, ranging from  $0.1$  to  $100\ \text{m d}^{-1}$  for  $1$ – $100\text{-}\mu\text{m}$  spherical particles, is commonly used to yield a kinetic expression of particulate matter removal (e.g. Lerman 1979). However, porous aggregates, like marine snow, exhibit low specific density and nonspherical geometries (e.g. Alldredge and Silver, 1988; Lick et al. 1993), requiring development of formulations for collision functions and settling rates that considers their hydrodynam-

ic effects (e.g. Stolzenbach 1993; Johnson et al. 1996). A complementary scavenging mechanism to gravitational settling in shallow systems may involve vertical mixing coupled with collection of both gravitoids and colloids at the bed surface (Stolzenbach et al. 1992).

An important feature of both physical and biological models of particle dynamics is that colloids and gravitoids are all part of the same dynamic aggregation-breakup continuum. Net coagulation rates are expected to be a function of the total solids concentration. No matter if coagulation is taken to be physical or biological, particle aggregation can better compete with vertical particle removal in situations of higher solids concentration, and hence a greater fraction of the total particles can be sustained in larger size classes at steady state at higher total solids concentrations (shown schematically in Fig. 2A). Particle size classes, which are lower in mass concentration than smaller particle classes from which they are being formed, may be interpreted as the critical sizes where a net responsiveness to gravitational removal becomes important. Particle size distribution data down through the submicrometer range, required to verify the concepts illustrated in Fig. 2A, are scarce. However, recently Buffle and Leppard (1995) have demonstrated that the predicted particle size distribution curves are seen down to particle sizes of 10s of nanometers in groundwater, lake water, and seawater despite neglecting many solid properties in model calculations (e.g. density, shape).

A ramification of the hypothetical size distributions depicted in Fig. 2A is that it is not straightforward to estimate colloid concentrations from filterable solid loads. One should expect a nonlinear relation between colloid and gravitoid concentrations (shown schematically in Fig. 2B). In suspensions with higher solids concentrations, where the rate of coagulative formation of large particles should be enhanced, greater contamination of the gravitoid fraction by the colloidal particles in conventionally filtered samples may be expected (Fig. 2). Thus, colloid-gravitoid relationships based on ratios of solids retained by and passing through filters (Gschwend and Wu 1985; Moran and Moore 1989; Honeyman and Santschi 1989) seem doomed to inaccuracy because they do not try to account for the critical particle size in the water mass under study.

### Functional definition of aquatic colloids

To characterize better the chemcentric roles of colloids, a definition of what qualifies as a colloid would be useful. In much current work, nonfilterable versus filterable particulate phases is still used to distinguish colloids and gravitoids; this practical approach does not allow us to anticipate accurately many trace chemical behaviors in environmental systems. We suggest that it would be beneficial to adopt a distinction between dissolved versus colloid-associated species based on the nature of trace chemicals' specific molecular interactions and their corresponding thermodynamics descriptors,  $K_s$ . And then, because we are also interested in trace chemical transport, we should distinguish between nonaqueous media whose own cycles are dominated by coagulative versus settling removal mechanisms. Motivated by the need to

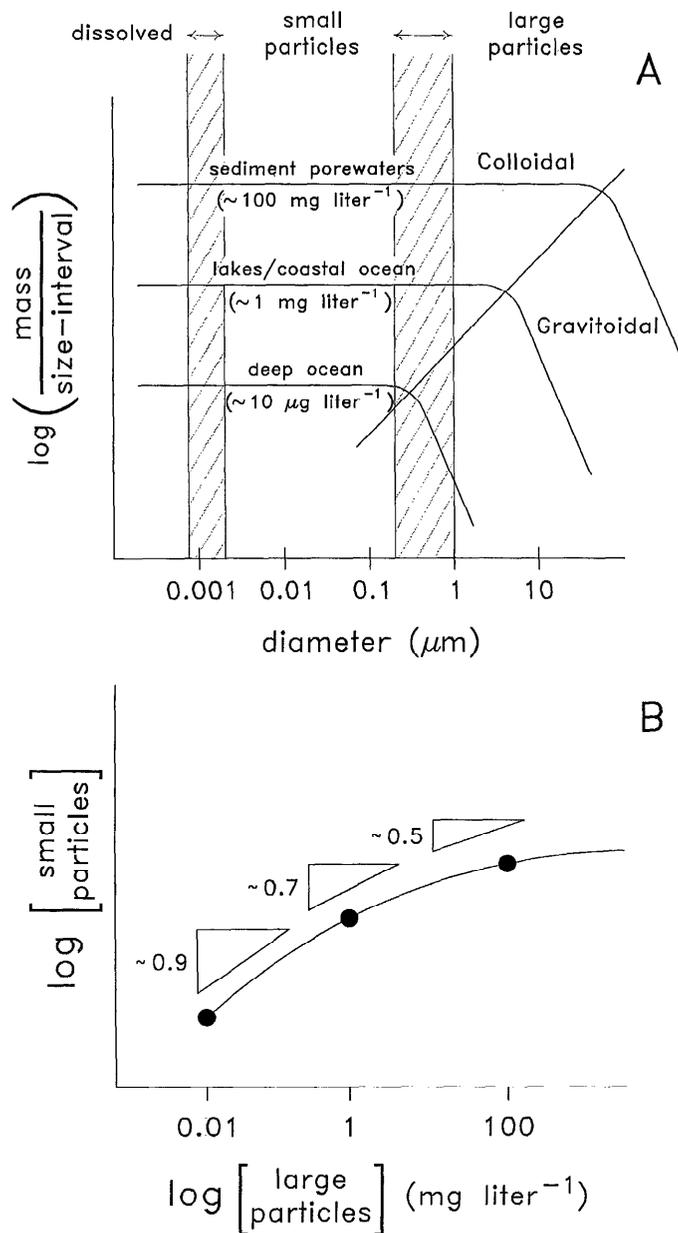


Fig. 2. Hypothetical curves reflecting particle size distributions based on models such as that of Farley and Morel (1986). Concentrations refer to filterable solids concentrations. A. Steady-state particle-size distributions (mass-based) for three aquatic regimes with widely different total solids concentrations. The points where the curves are changing slopes may be interpreted as the functional, chemcentric distinctions between colloids and gravitoids that are seen to be a function of the total solids levels. The hatched regions indicate the traditional, operational distinctions between dissolved-small (colloidal) particles (left) and small-large particles (right). B. Schematic representation (deduced from panel A) of the effect of total solids concentrations on the relative distribution of mass between small and large particle sizes, indicating a nonlinear relationship.

anticipate the behavior of trace chemicals in natural waters, we attempt a chemcentric definition of freshwater and marine colloidal sorbents below.

*Delimiting the dissolved-colloidal boundary*—Because our ultimate goal is to understand better the cycling of chemical compounds in natural waters, the first critical question is: when is some entity large enough to provide an opportunity for trace compounds to move out of the aqueous solution phase and into (absorption) or onto (adsorption) this new medium? The answer yields the chemcentrically relevant distinction between solution species and colloidal ones.

The chemcentric view requires us to consider materials of at least nanometer dimensions. For example, phenanthrene is a polycyclic aromatic hydrocarbon (PAH) of molecular mass 178 Da and extending about 0.7 nm across its longest dimension. Thus, a colloidal medium relevant to phenanthrene must be at least this size. Consequently, if one assumes a lower limit size for colloids consistent with 1–2-nm-diameter spherical particles, then molecular masses of organic macromolecules would have to be larger than  $\sim 300$ – $2,000$  Da. This size is in the range reported for riverine fulvic acids (Aiken and Malcolm 1987) and lacustrine and marine sediment porewater organic macromolecules (Chin and Gschwend 1991).

Next, the chemcentric view suggests that a new phase must also offer trace constituents some volumetric or interfacial microenvironment in which the spatially and temporally averaged bulk properties of the medium are distinguished from those of the aqueous solution. For example, because intermolecular forces are electrostatic in nature, one important bulk property is a medium's dielectric constant (a measure of the medium's ability to transmit polar interactions). One example of a microvolume with clearly different dielectric property from water is a micelle built from about 60 dodecyl sulfate molecules (micellar weight of  $\sim 18,000$  Da and about 4 nm in diameter). The interior of such molecular aggregates provides a nonpolar microenvironment into which HOC molecules like phenanthrene can partition. That this microvolume exhibits a different dielectric nature than the surrounding aqueous solution can be seen in the changed light absorption by incorporated chromophores; for example, vibronic bands of PAHs shift to longer wavelengths when these compounds exist in nonpolar media like micelles rather than water (Chandar et al. 1987). Given the common perception of humic substances as natural micelle-like macromolecules (e.g. Wershaw 1986), one may reasonably imagine that these complex organic constituents provide microenvironments within their interior where there are substantially different bulk properties (like dielectric constants) than exist in the exterior solution phase.

A second necessary trait for an entity to be large enough to be a colloid is the presence of an interfacial region with properties varying from those of the aqueous phase to those of the colloidal phase. For example, if the exterior of the medium includes ionized moieties spaced close enough to influence one another so as not to be well represented by isolated point charges, then a surface potential will exist. A diffuse double layer of counterions will accumulate in a region between the solution and such a colloidal phase. Said

another way, to qualify chemcentrally as colloids, oligo-electrolyte macromolecules or inorganic precipitates need to be large enough and structured so that one should consider the presence of an electrostatic field around them. As discussed by Bartschat et al. (1992), by considering humic substances of molecular mass near 1,000 Da to have such particle-like charging, one may greatly improve our ability to predict the ionic interactions of charged species like  $\text{Cu}^{2+}$  with these organic macromolecules.

In sum, macromolecular entities should be colloidal when they require property descriptions that average bond-scale effects to yield medium properties important to the trace constituents of concern. In general, this criterion translates into nanometer or larger scales, but such a requirement does not necessarily mean that all entities larger than a nanometer are colloids. For example polyelectrolytes, which assume an extended conformation in water and whose charged moieties do not substantially influence one another, would not be colloidal with the chemcentric view espoused above.

*Delimiting colloidal from gravitoidal phases*—There is no upper size limitation to sorbents affecting chemicals on the molecular level. Consequently, a characteristic other than the ability to contribute to phase-partitioning of chemicals must be chosen to distinguish colloidal and larger particulate phases. Because our concern lies with the overall behavior of trace chemicals, we suggest that the delimiter for colloid-bound species vs. gravitoid-bound forms be based on distinguishing environmental transport mechanisms. Thus, colloids should be distinguished from larger sorbents based on their predominant transport with the water, without substantial removal by settling.

Therefore, to distinguish colloids functionally from gravitoids one must consider the conditions and the timescales relevant to natural waters. Particle size distributions (Fig. 2A) result from the kinetic competition between coagulation (of colloids) and sedimentation (of gravitoids). Conceptually, these distinct fates of sorbent mass are reflected by the breakpoint in the solid distribution curves (Fig. 2A, diagonal line). Although the time it takes for a given particle to sink out from the surface layer is independent of overall solid concentrations, the coagulative conversion rate of the same particle is proportional to the abundance of aggregating solids.

The implication is that the distinction between gravitoids and colloids is a function of total solids concentration. The effect of any filterability-based separation is apparent in the idealized size distribution curves (Fig. 2A, hatched regions). For example, at modest concentrations of particles as in the coastal ocean, the typical size-based distinction between gravitoids (particulate) and colloids may no longer coincide with the critical solid size at which settling starts to outcompete coagulation. The current upper-end colloid definition (Fig. 2A, right hatched region), set around  $0.5 \mu\text{m}$ , is wanting because the functional distinction between particles dominated by either coagulation or settling is not constant (Fig. 2A, diagonal line). In this context it is of less significance that some biological and physical formulations of coagulation and settling yield slightly different absolute values of the critical coagulation-to-settling breakpoint at a given site.

Instead, the important concept is that the sorbent-transport-based colloid-gravitoid distinction will vary between sites (Fig. 2A, diagonal line), dependent on the regime-specific coagulation vs. settling rates.

The breakpoint defining particles that predominantly settle is not only a function of total solid levels but a function of the hydrodynamics and particle surfaces of the water body of interest. The depth of the well-mixed layer sets the environmental timescale over which settling must compete with coagulative removal of solid mass from a given size bin. Hence deeper, well-mixed, water systems should exhibit reduced settling importance and consequently comprise even larger colloidal sizes. It is also known that the process of coagulation is a function of particle and aqueous solution properties. For instance, because of differences in solution charge-shielding, particle coagulation in seawater should be more efficient than in freshwater. Hence, all other things equal, seawater colloids should be larger than their freshwater counterparts.

In light of this discussion, it is informative to assess some observations attempting to distinguish between suspended and settling particles. Weilenmann et al. (1989) studied particle transport in two Swiss lakes throughout an annual cycle. Lake Zürich had an enhanced coagulation rate, due to relatively lower levels of colloid-stabilizing humic substances (giving a higher sticking coefficient,  $\alpha$ ). Particles suspended in the epilimnion of this lake were dominated by a narrow size-distribution centered around  $8 \mu\text{m}$ . A bimodal size distribution was observed in the Lake Sempach surface waters. A  $20\text{--}30\text{-}\mu\text{m}$  size fraction was due to bacterial colonies, whereas a  $5\text{-}\mu\text{m}$  centered pool of largely nonliving particles was consistent with the higher levels of stabilizing organic macromolecules in this lake. Based on estimated settling velocities from settling fluxes and solids concentrations, Baker et al. (1991) predicted that settling particles in oligotrophic Lake Superior are roughly  $12 \mu\text{m}$  in size. From these natural water observations, we conclude that colloidal sorbents corresponding to a particle size near  $10 \mu\text{m}$  (to be contrasted with old  $0.5 \mu\text{m}$  definition) may be retained at steady state in surface water suspension of large lakes through an apparent neutral buoyancy arising from coagulative formation outcompeting settling removal.

Thus, from a chemcentric point of view, we propose that an aquatic colloid is any constituent that provides a molecular milieu into and onto which chemicals can escape from the aqueous solution and whose environmental fate is predominantly affected by coagulation-breakup mechanisms, as opposed to removal by settling.

### Illustrations of chemcentric phase speciation

To illustrate how a chemcentric colloid definition differentiates between phases, we consider the speciation of two trace chemicals—copper and phenanthrene (Fig. 3). Although both dissolved and colloidal constituents may associate with these trace substances, we distinguish colloidal phases as those that exhibit medium properties (e.g. nonpolar medium, surface potential). Further, we separate gravitoidal phases based on their propensity to settle (i.e. large, favor-

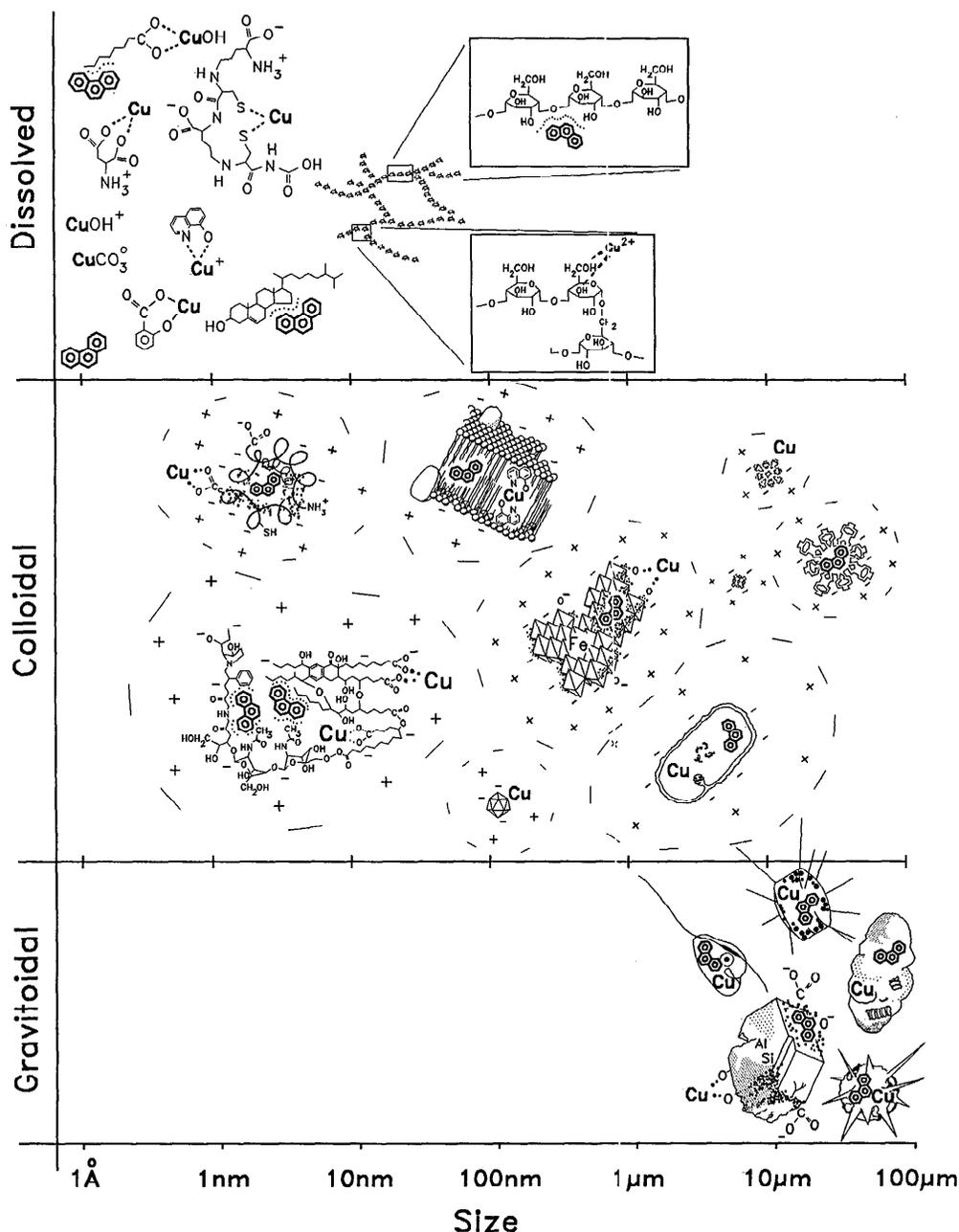


Fig. 3. A chemcentric speciation diagram. Two trace substances, phenanthrene and copper, are used to illustrate how such chemicals' interactions with various constituents may affect their functional speciation.

able shape, and dense enough). It is apparent that dissolved, colloidal, and gravitoidal phases overlap one another on a size axis. One sees that traditional dissolved species include complexes (e.g.  $\text{CuCO}_3$ ), and that the relevant ligands (i.e.  $\text{CO}_3^{2-}$ ) do not exhibit bulk properties (e.g. surface potential) differentiating them from the aqueous phase. Notably, this implies that elongate organic macromolecules that are well mixed with the water solvent do not constitute colloidal phases from our chemcentric point of view. Although very high in molecular weight, extended, long-chain carbohydrates and nonglobular proteins may be considered to be in

the dissolved phase, from the functional perspective of the forces acting on the trace chemical. This view is supported by the finding of Garbarini and Lion (1986) that cellulose (mol. wt.  $\sim 1,000,000$  Da), despite its large size, is unable to sorb hydrophobic compounds to an appreciable extent.

Another implication of a functional chemcentric definition of a colloid is that its state is not limited to solids but may equally well include liquid sorbents. Examples include micelles and other aggregates of amphiphiles such as phospholipids of fragmented membranes (Fig. 3). A chemcentric colloid definition would also include in the colloidal pool such

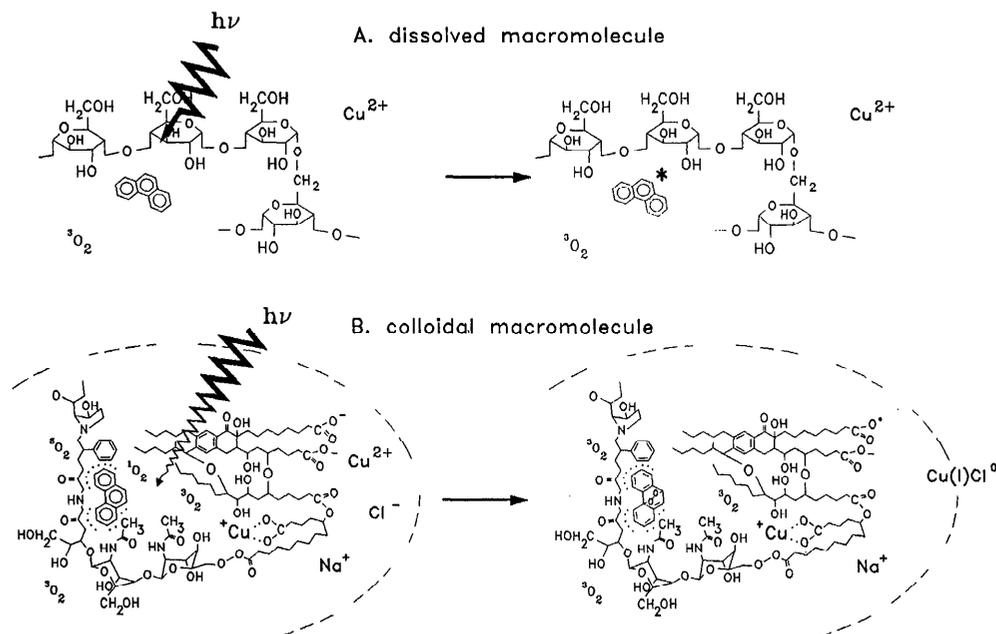


Fig. 4. Effects of the chemcentric speciation on transformations of chemicals. The interaction of trace chemicals with dissolved macromolecules (A), respectively, in/on colloidal macromolecules (B) are providing significantly different surrounding media. Such differences in molecular-scale environment are likely to have implications for the fate of trace chemicals in general as illustrated here by the speciation-dependent processing of the hypothetical probes copper and phenanthrene.

entities as coiled proteins and humic substances if they include hydrophobic interiors or interacting exterior charges best treated with double layer theories. Biological particles such as viruses and nonmotile bacteria should be considered colloids. Also, sufficiently small (i.e. coagulation more important than settling) aggregates such as organically coated, mineral particles (e.g. iron oxyhydroxides or aluminosilicates) would fall in the chemcentrically defined colloid class. Supermicrometer-sized aggregates of marine snow might be considered predominantly colloidal because their near-neutral buoyancies cause coagulation-disaggregation to be more frequent than settling removal.

Finally, gravitoids are those materials that, like colloids, provide substances such as copper and phenanthrene alternative media to aqueous solution. But unlike colloids, gravitoids are separated from the aqueous suspension primarily through gravitational settling due to their own traits (including size and particle density) and environmental situation (e.g. solids concentration, fluid density, solution ionic strength, mixed depth). Hence, larger minerals with associated finer materials or biologically produced aggregates such as 100- $\mu\text{m}$  fecal pellets may not qualify as colloids (Fig. 3). Plankton including diatoms, foraminifera, and radiolaria, to name a few, would not be included as colloids unless one believes their water column fates are predominantly set by predation-driven coagulation.

The merit of the proposed conceptual framework is that it is consistent with the needs of chemical cycling studies. In describing the fates of substances such as copper or phenanthrene, one must recognize the influence of the environmental milieu in the immediate vicinity of the substance of

interest on the rates of various transformations. For example, phenanthrene in an aqueous carbohydrate suspension will be as available to incident light as would a completely aqueous phenanthrene solution (Fig. 4A). However, phenanthrene molecules contained within humic media would likely not experience the same photointensity. Photons may be absorbed by humic chromophores, and the light reaching any phenanthrene molecules in the interior may thus be altered. Further, the phenanthrene absorption within humic media may shift to longer wavelengths due to the more nonpolar local environment. Because natural light is more abundant at longer wavelengths, this may contribute to an enhanced rate of light absorption for the humic-associated species relative to the same molecule absorbing light when it is surrounded by water. Thus, compensating factors may cause the direct photolysis of phenanthrene to be either more or less significant for the molecules located in the interior volume of the colloidal humic macromolecule.

In contrast, one may expect that the relative concentrations of reactive transients (e.g. singlet oxygen ( $^1\text{O}_2$ ), triplet DOM,  $\text{ROO}\cdot$ ,  $\text{HO}\cdot$ ) are elevated in the colloidal organic phase. For example, because molecular oxygen has a higher solubility in organic phases than in water (e.g. Lee and Rodgers 1983), and because organic chromophores have been implicated as sensitizers forming  $^1\text{O}_2$  (Haag and Hoigné 1986), one might expect more  $^1\text{O}_2$  to be formed in suspended organic phases. As a result, indirect photochemical transformations (Fig. 4B), such as the phenanthrene endoperoxide formation after reaction with  $^1\text{O}_2$  and the reduction of copper(II) to copper(I) resulting from reactions within the humic

microenvironment, may require explicit consideration of the relevant colloiddally bound species.

The transport fate of chemicals such as phenanthrene and copper is also dependent on their propensity to be transferred into settling phases. Santschi and others (e.g. Santschi et al. 1986; Honeyman and Santschi 1991) have shown that metals such as copper are first sorbed to colloidal phases, before coagulation of these small sorbents results in the accumulation of the sorbate (e.g. copper) with larger (and therefore potentially settling) solids. Thus, the relative tendency of the chemicals to be transported up the particle-size spectrum via piggy-backing is a function of the colloids with which they associate (McCarthy et al. 1993; Gu et al. 1995).

Another significant practical implication of the conceptual chemcentric colloid framework is that a traditional, filtration-based definition will never succeed in distinguishing species that, in large part, behave independently of size. Hence, to make practical progress toward anticipating the environmental behavior of trace chemicals, analytical approaches that recognize their speciation, such as studies of the light-processing abilities of chemicals of interest, are required to probe the physicochemical distribution and behavior of the colloids and sorbing chemicals of interest.

### Conclusions and current challenges

Studies of aquatic colloids, and in particular those addressing their role in affecting chemical speciation, have accelerated over the past 10 yr. However, only limited progress has been made in relating empirical distribution data to thermodynamically based surface complexation and hydrophobic partitioning models. Enough is now frequently known about the physicochemical system parameters that govern colloid partitioning in natural waters to attempt rationalization of the observed chemical distributions in terms of these well-established theoretical frameworks.

One current challenge complicating the successful application of such an approach is selective assessment of only the organic macromolecules that are able to interact with, and thus change the speciation of, trace chemicals in natural waters. This challenge is especially difficult because, by our definition, not all macromolecules are colloids (i.e. offering an alternative phase to chemicals of interest). Currently used filter-size-based colloidal sorbent definitions constitute a severe limitation to such progress. Ultrafilters do not distinguish between colloidal and noncolloidal macromolecules. Also, filters with approximately micrometer-sized pores are not comprehensively applicable to distinguish between particles that experience significant settling removal from those that do not (e.g. marine snow), especially when applied statically with the same cutoff to environments of different particle dynamics (i.e. Fig. 2A).

Generation of yet more chemical distribution ratios between filter-based gravitoidal, colloidal, and dissolved fractions will do little to further our understanding of chemical speciation and cycling in lake and ocean waters. Real progress is more likely to come from investigations selectively probing the functional colloid-dissolved partitioning through relatively noninvasive techniques such as time-resolving

fluorescence quenching spectroscopy and competitive-ligand titrations coupled with ion-selective electrodes. Such colloid partitioning results need to be accompanied by an increased effort to obtain necessary ancillary system parameters to enable interpretation of these observed *D* values in terms of the corresponding theoretical *K* values. Further, efforts to assess the fraction of sorbing media participating in settling transport are needed. Separation techniques based on specific density should prove useful in this regard, such as analytical ultracentrifugation (e.g. Sipos et al. 1972) and split-flow thin (SPLITT) cells (e.g. Giddings 1988; Fuh et al. 1992).

An aquatic colloid definition is suggested, based on whether the molecular-level interactions of a chemical with a particular entity result in that compound's involvement in colloidal processes (i.e. presence in a nonaqueous environment; participation in coagulation but not settling). Thus, an aquatic colloid is any constituent that provides a molecular milieu into and onto which chemicals can escape from the bulk aqueous solution, while its vertical movement is not significantly affected by gravitational settling.

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