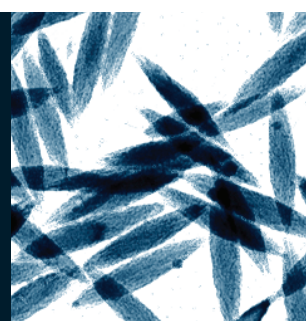# Iron Oxides as Geochemical Nanovectors for Metal Transport in Soil–River Systems

## Martin Hassellöv[1] and Frank von der Kammer[2]

Synthetic phosphate-modified hematite nanoparticles (~300 nm by ~50 nm)

**T**opsoils are often contaminated by trace metals, and it is important to understand how different processes govern the transport of such metals to fresh and marine waters. This paper presents measurements of natural nanoparticles and colloidal organic matter in soil and river samples from Germany and Sweden. In our analytical approach, a nanoparticle separation technique is combined with multielement detection and applied to soil and river samples to link the macroscale field observations with detailed molecular studies in the laboratory. It was determined that lead is associated with iron oxide colloids, which are ubiquitous nanoparticles that can be efficiently transported. Eventually both iron oxides and lead are removed by flocculation under conditions of estuarine mixing. Iron-rich nanoparticles compete efficiently with natural organic matter (NOM) complexation for lead binding in both the soil and river systems studied.

J DXV NQCR9 colloids, nanoparticles, iron oxides, metals, sorption, rivers, porous media

## INTRODUCTION

Due to anthropogenic activity and atmospheric transport and deposition, many trace elements are significantly enriched in topsoil layers over vast areas of the continents. Lead (Pb), for example, is transported from soils through rivers to estuaries, and natural iron (Fe) oxide nanoparticles play an important role in facilitating this transport. Although Pb emissions have decreased substantially since the ban of leaded gasoline, atmospheric deposition from other anthropogenic sources is still significant (Callender 2003). In Europe, Pb levels have decreased about 90% since 1975, and today, Ukraine and Russia account for about 50% of total Pb emissions (von Storch et al. 2003). Lead is an element with a high solid–water partition coefficient, so one would predict it to be bound to and immobilized in the solid matrix of soils. However, according to a study on the fate and geochemistry of Pb in forest topsoils at remote sites in the northeastern United States over a two-decade period following the regulation of Pb in gasoline, there has been a significant decreasing trend in Pb concentration in the topsoil, with a strong correlation between Pb and Fe particulates in the soil matrix. Lead remobilization has been attributed to cotransport on iron oxide particles (Kaste et al. 2006).

Generally, topsoil is enriched in Pb compared to the average composition of the Earth's crust. On average, world soils show an enrichment of about 200%, and soils in densely populated and industrialized areas are still more enriched.

Even stronger Pb enrichment can be found in river particulates (on average ~450%), and marine-clay sediments appear to be the final sink, since these are further enriched; in addition, the fluvial input of Pb to the oceans is ~6 times larger than direct atmospheric input (Callender 2003). Fe oxides and oxyhydroxides have high adsorption capacities for many metals, especially Pb (Benjamin and Leckie 1981), and Pb, Zn, and other metals are associated with the easily reducible fraction in river sediments and soils. This fraction has been operationally defined as poorly crystalline or amorphous Fe and manganese (Mn) oxyhydroxides. The riverine transport of Pb and other metals thus occurs on particles, and the suspended particulate matter (SPM) is the dominant carrier phase. However, due to settling and deposition, cotransport on large suspended particles is not as efficient as on small particles, which are referred to as colloids or nanoparticles (Ross and Sherrell 1999). A better understanding of soil partitioning and soil–river transport is very important for understanding contaminant redistribution at continental scales.

## COLLOID-FACILITATED TRANSPORT OF METALS IN RIVER SYSTEMS

Natural colloids are particles not subject to sedimentation. They are operationally defined as having at least one dimension in the size range of 1–1000 nanometers (nm). Due to their small size, colloids have a much larger specific surface area than larger particulates, and the surfaces of many types of colloids contain a high proportion of functional binding groups for metals. These colloids are at least as reactive as suspended particulates and can appear to be as mobile as dissolved solutes. This colloidal continuum can therefore constitute an important carrier phase for metal transport in aquatic systems, and the term "nano-vector" has been used to describe this phenomenon (Hamon et al. 2005).

The efficiency of colloidal transport is dependent on metal chemistry, on metal–colloid interaction, and on the concentration, nature, and mobility of the colloids. At the macroscale, the relative importance of colloids in the transport of metals may be different from one drainage basin to another. However, colloids are responsible for a significant proportion of the fraction consisting of entities smaller than 0.45 µm (450 nm), which are usually defined as being

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"dissolved" (Ross and Sherrell 1999; Pokrovsky and Schott 2002; Eyrolle and Charmasson 2004). Natural colloids consist of several important organic phases (e.g. humic substances and polysaccharides, but also microbes) and inorganic phases (e.g. Fe and Mn oxides and aluminosilicates); of the latter, Fe oxides are among the most ubiquitous (Filella 2007).

Iron is the fourth most abundant element in the Earth's crust, where it occurs predominantly as Fe oxides. More than a dozen Fe oxides, oxyhydroxides, and hydroxides exist in various environments on Earth (Cornell and Schwertmann 2003). In this paper the collective term FeOx is used to include all of these.

## FORMATION, TRANSPORT, AND TRANSFORMATION OF IRON OXIDE PHASES

Natural FeOx phases are formed and cycled as a result of various redox reactions that take place in soil or groundwater/freshwater redox gradients or in the photochemical redox cycling of Fe. Bacterial mediation is important for Fe redox cycling, and bacterial processes are also known to be responsible for the formation of Fe-bearing nanoparticles. However, such oxides are often associated with the bacterial cells and are not mobile (Banfield and Navrotsky 2001; Kappler et al. 2005). For the formation of the most mobile form of FeOx colloids, e.g. at the scale of a few nanometers, hydrochemical precipitation reactions are likely more important. However, important even for these abiotic processes, microbial activity drives the establishment of the necessary redox gradients for Fe(III) reductive dissolution and subsequent oxidative precipitation as nanoparticles (Canfield et al. 2005).

After oxidation to Fe(III), the next reaction step is formation of various inorganic hydrolysis species. The nucleation of such species is very rapidly initiated, forming, for example, $Fe(OH)_3$ clusters, which start to grow into nanoparticles. These small clusters or nanoparticles grow by continuous supply of Fe(III), by Ostwald ripening (dissolution of small particles in favor of larger ones), or by particle and cluster aggregation (Cornell and Schwertmann 2003; Waychunas et al. 2005). In pure inorganic solutions the FeOx often grows rapidly into large flocs, while in aquatic environments natural organic matter (NOM) plays an important role in hindering the growth. NOM adsorption can passivate (i.e. make unreactive) the surface against further crystal growth and can either induce aggregation by charge neutralization or provide colloidal stability against aggregation, depending on the particle surface area to NOM ratio (Vilgé-Ritter et al. 1999; Sander et al. 2004). Charge-stabilized nanoparticles without organic coatings would otherwise flocculate with only small increases in ionic strength (Cornell and Schwertmann 2003). The water chemistry and presence of NOM therefore influence the growth of FeOx particles, as well as the structure and morphology of the precipitates (Vilgé-Ritter et al. 1999; Wolthoorn et al. 2004).

All FeOx go through a nanophase stage during their formation, and ferrihydrite exists only as a nanomineral. The transition time for other FeOx minerals in the nanoparticulate stage depends on nucleation and growth rates, passivation of the surface (hindered growth), and aggregation rates (Banfield and Navrotsky 2001; Cornell and Schwertmann 2003; Hochella et al. 2008). In the Fe redox cycling processes in soils, sediments, and the photic-pelagic zone, contaminant metals can be incorporated in the FeOx colloids by coprecipitation or surface complexation (Lyvén et al. 2003).

Most early studies of the structures of FeOx minerals were carried out by X-ray diffraction on large single crystals. Nanoparticles of the same mineral may, however, have important differences compared to their larger counterparts (Hochella et al. 2008). The basic unit structures that build up FeOx minerals are octahedral $Fe(O)_6$, octahedral $FeO_3(OH)_3$, or, more rarely, tetrahedral $Fe(O)_4$. Different structural combinations of these in corner-to-corner, edge-to-edge, or face-to-face arrangements give rise to FeOx minerals with different crystal structures, physicochemical characteristics, and metal-binding properties. In the natural environment, only rarely do perfect, continuous crystals form; more common are poorly crystalline phases with defects, unoccupied sites, and impurities.

Detailed mechanistic understanding of Fe and Mn oxide structures and sorption mechanisms has been obtained by the advancement and development of synchrotron-source X-ray spectroscopy. For example, insight into the structure of ferrihydrite is now becoming available (Manceau and Gates 1997; Jambor and Dutrizac 1998; Michel et al. 2007). Ferrihydrite is believed to be a poorly crystalline nanomineral built up of about 20% $FeO_4$ and 80% $FeO_6$ polyhedra. Ferrihydrite is formed by rapid oxidation and hydrolysis. It exists in varying degrees of structure disorder; the two extremes are the so-called 2-line and 6-line ferrihydrites, which are distinguished by their X-ray diffraction patterns. Ferrihydrite is a metastable nanomineral precursor to other minerals, e.g. hematite. In the pioneering studies of FeOx phases as vectors for metals, poorly crystalline phases were termed amorphous Fe oxyhydroxides, or hydrous ferric oxide (HFO). However, the development of more sophisticated instrumentation to study crystal structures at the nanoscale has provided considerable evidence that the previously considered amorphous phases most likely contain a significant contribution of ferrihydrite (Jambor and Dutrizac 1998). Ferrihydrite has a very small primary nanoparticle size and very high specific surface area, and consequently may be the most important FeOx binding and transport phase for trace metals in most aquatic systems.

Lyvén et al. (2003) found that iron oxide colloids in river waters are present as small nanoparticles (smaller than a few tens of nanometers) intimately associated with humic-type natural organic matter. The well-known colloidal stabilizing effect of humic acids (Sander et al. 2004) can be counteracted by the destabilizing effect of fibrillar exudates that can bridge or flocculate Fe colloids (Taillefert et al. 2000). The quality of NOM, which often varies seasonally due to biological activity, can therefore influence considerably the fate and behavior of Fe oxide colloids and associated elements.

## SIGNIFICANCE OF IRON OXIDE NANOVECTORS FOR LEAD TRANSPORT

According to data in the river-monitoring databases of Scandinavia and continental Europe, total Pb concentrations in unfiltered samples generally show a correlation with total Fe. Furthermore, several studies on metal transport in river systems using cross-flow ultrafiltration to isolate colloids from river samples also show a correlation between Pb and Fe concentrations (Ross and Sherrell 1999; Pokrovsky and Schott 2002). Additionally, an attempt to model the solid/solution partitioning of five metals in the Humber catchment rivers, UK, could describe the experimental partitioning of Pb correctly only if an Fe oxide particulate phase was included (Lofts and Tipping 2000). These findings could be interpreted as Pb transport mediated by Fe-rich colloids, although the correlations neither implicate causality nor provide further mechanistic under-

standing. On the other hand, detailed electron microscopy studies on redox-cycling processes in lakes have shown that Pb is associated with FeOx colloids at the single-particle level (Taillefert et al. 2000).

Colloidal transport of metals on FeOx is known to be very important in rivers receiving acid mine drainage (Hochella et al. 2005 and references therein), but the conditions in these waters are site specific, and we do not discuss such processes further in this paper.

In most pristine environmental samples, the contents of sorbed trace metals are too low to be detectable using X-ray spectroscopic techniques or analytical electron microscopy, and therefore macroscopic analyses, as mentioned above, are mainly used.

Due to the difficulties of working with mixed mineral structures and low metal concentrations, the majority of structure and surface speciation studies have been carried out on simple systems or on products synthesized in the laboratory. The binding mechanisms for Pb onto ferrihydrite are mainly monodentate, bidentate edge-sharing, and bidentate corner-sharing coordinations (the relative proportions are to some extent pH dependent) (Fig. 1). Similar binding coordinations (with edge-sharing bidentate complexes dominating) were found for HFO, ferrihydrite, hematite, and goethite (Bargar et al. 1997; Trivedi et al. 2003; Xu et al. 2006 and references therein).

The data presented below originate from the application of a methodology that links macroscale studies and molecular spectroscopic studies. By combining a low-invasive particle-size selective fractionation technique (field-flow fractionation, or FFF) with a sensitive multi-element detection method (inductively coupled plasma–mass spectrometry, or ICPMS), both major- and trace-element distributions can be tracked across the continuous particle-size spectrum. Further, transmission electron microscopy (TEM) can be used with FFF–ICPMS to obtain morphological information on nanoparticles and an understanding of transport mechanisms.

The elemental size distributions of soil colloids and freshwater colloids were studied with these techniques. The soil sample in this study originated from an organic-rich $A_h$ horizon of a gleyic podzol sampled under spruce forest near Neumunster, northern Germany. The colloids were extracted using a mild alkaline extraction routine (constant pH 9), precipitated with HCl at pH 2, washed several times with milli-Q water, redissolved at pH 7, and carefully filtered over 0.2 µm in a 120 mm ø stirred filtration cell at 0.8 bar overpressure and a constant flow rate of 2 mL min$^{-1}$. The obtained size distributions of the organic-rich soil isolates are shown in Figure 2A. The freshwater sample was taken from a small forest watercourse near Gothenburg, Sweden. Apart from the original size distributions, the reactions occurring during mixing with seawater in the transition from freshwater to marine conditions were studied by mixing the freshwater sample with synthetic seawater to obtain salinities of 0, 10, and 25‰ (Fig. 2B).

Two distinct colloidal phases were observed in both the soil isolate and the river water. One was organic (~0.5–3 nm in diameter), as determined by the strong UV absorbance of NOM, humic/fulvic-like fluorescence, and high carbon content. The other was rich in Fe and greater than 3 nm in diameter (Lyvén et al. 2003; Stolpe and Hassellöv 2007). From their size, chemical composition, and morphology, determined by FFF–ICPMS and TEM, these Fe-rich nanophases are interpreted to most likely be ferrihydrite, but further studies on single particles with high-resolution TEM and selected-area electron diffraction are needed for
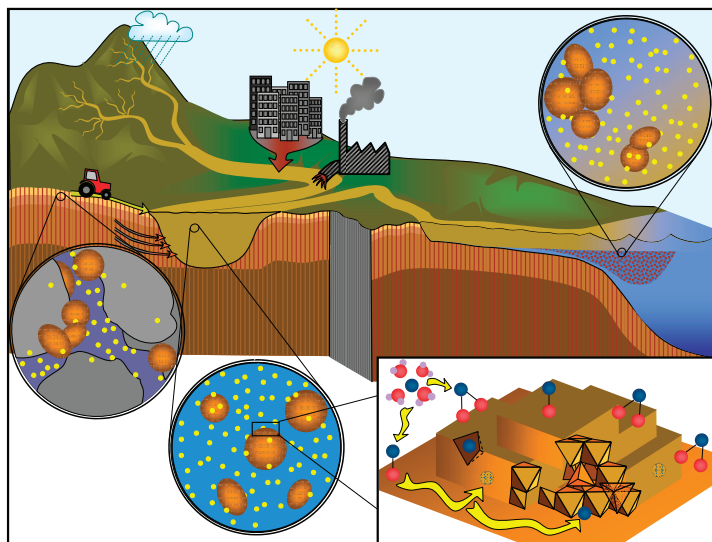


**Figure 1** Schematic view of colloidal transport of Pb on nanoparticulate FeOx (brownish particles) from the upper soil layers via rivers to estuaries. The importance of natural organic matter on colloidal stability is indicated by the yellow particles. In the estuary, the accumulation of mono- and divalent ions in the electrical double layer reduces the electrostatic repulsion provided by the NOM, which results in flocculation and sedimentation of iron oxides and associated elements to the estuarine sediments. The enlarged crystal schematic illustrates the recently suggested crystal structure of ferrihydrite (Michel et al. 2007). In the center position of each octahedron and tetrahedron is positioned an Fe atom, and in each corner an oxygen (here illustrated as red atoms only when binding to Pb, blue). In addition, the established binding coordinations of Pb to ferrihydrite are illustrated (Trivedi et al. 2003). Outer sphere complexes are not important for Pb, which lose its hydration shells upon forming inner sphere complexes. Surface diffusion of Pb is illustrated by yellow arrows.

structure confirmation. Many trace elements are specifically associated with these two phases. For example, Cu is associated with the organic colloids, while Pb associates predominantly with the FeOx particles (in river water, but to some extent also to NOM in the soil). Further, isotope-exchange studies showed a rapid transfer of added Cu and Pb to the organic and iron oxide phases, respectively (Lyvén et al. 2003).

Occurrence of Fe-rich colloids differing in size from the humic-bound Fe and trace metals has been observed in several contrasting environmental compartments in this soil–river system (varying NOM, pH, redox, iron concentration, and drainage basins). This may be partly related to the oxidative formation of FeOx being favorable when pH is higher (above 4), since the Fe-oxidation rate is strongly pH dependent. Furthermore, the competitive Pb binding to Fe oxides compared to NOM (humic substances) is favorable at pH values above ~6 (Lyvén et al. 2003).

Figure 2B shows the colloidal size distributions during a simulated estuarine mixing of forest-creek freshwater with synthetic seawater (Stolpe and Hassellöv 2007). With increasing salinity, the FeOx phases with associated Pb are selectively removed while the NOM and associated metals are conserved (i.e. they are not affected by the increase in ionic strength). As mentioned above, FeOx nanoparticles are electrostatically stabilized in freshwater by coatings of NOM, providing a net negative charge (Sander et al. 2004). As ionic strength increases, e.g. in estuarine environments, the diffuse double layers of the NOM-coated FeOx nanoparticles are compressed enough to allow van der Waals forces to pull particles together, causing flocculation. In
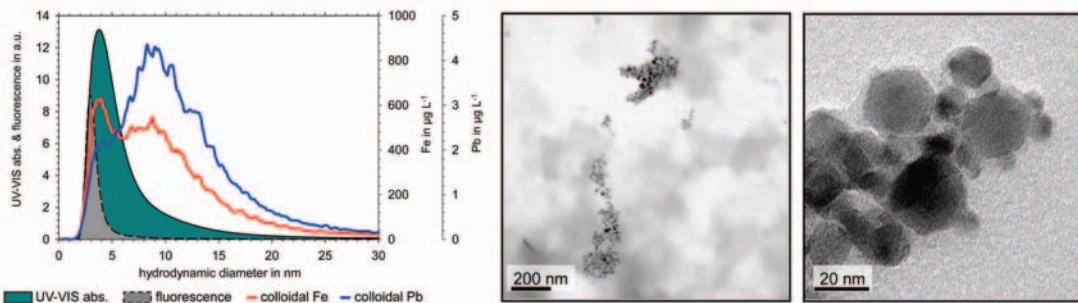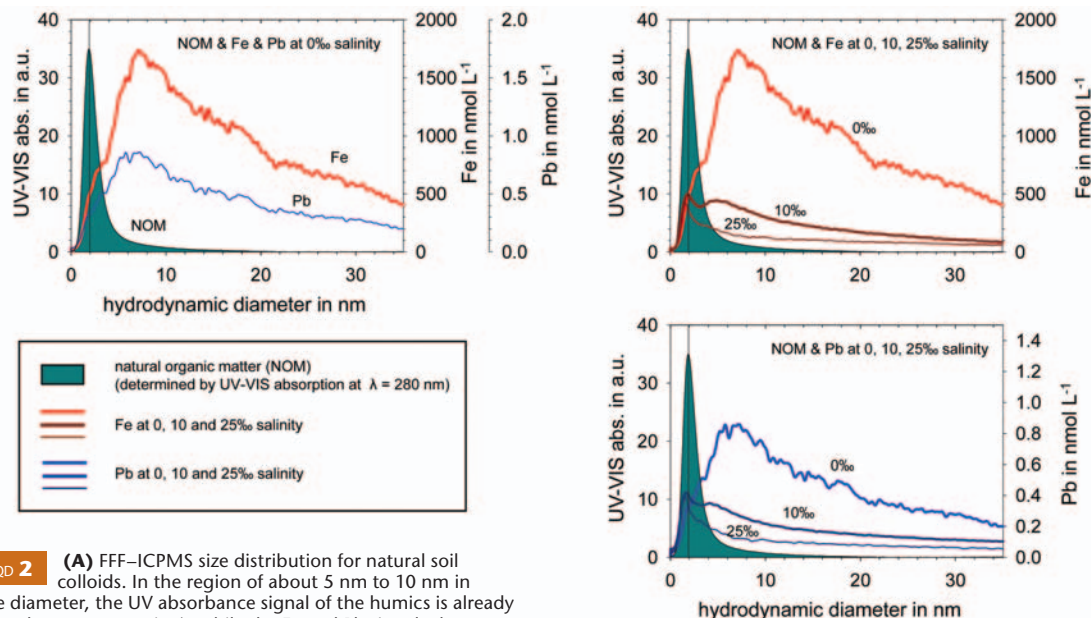
FIGURE 2 **(A)** FFF–ICPMS size distribution for natural soil colloids. In the region of about 5 nm to 10 nm in particle diameter, the UV absorbance signal of the humics is already small (i.e. low concentration), while the Fe and Pb signals show second peaks. The second Fe peak can be interpreted as a second solid, Fe-rich phase present in the sample. On the right, TEM micrographs of the obtained extract are shown. *The colloids were purified by FFF without ultrafiltration.* **(B)** Colloid flocculation study on freshwater undergoing mixing with seawater. Fe and Pb are shown together with the UV absorbance size distributions. The flocculation induced a selective removal of FeOx which results in the residual size distributions as shown. *Reproduced from Stolpe and Hassellöv 2007*

the studied freshwater, the NOM macromolecules not associated with FeOx nanoparticles still have enough negative charge to remain dispersed. This is consistent with classical macroscale studies of estuarine removal of Fe and associated elements (FIG. 1).

Both synthetic and natural Mn oxides show higher sorption efficiency (i.e. the amount sorbed per specific surface area) for Pb than FeOx (O'Reilly and Hochella 2003 and references therein). This can be attributed to Pb diffusing into and being retained within the interlayer of some Mn oxides, especially birnessite (O'Reilly and Hochella 2003). For amorphous hydrous ferric oxides and hydrous Mn oxides, fast surface binding and slow diffusion into internal sites have been observed (Xu et al. 2006). The binding mechanism is the same for external and internal sites. Similar surface diffusion and kinetic control of the sorption of Pb has also been observed for ferrihydrite (Scheinost et al. 2001).

Mn(II) oxidation to $MnO_2$ is known to be either autocatalytic or microbially mediated (Canfield et al. 2005), and, regardless of the process, this oxidation results in rather immobile microparticles that are believed to be important metal scavengers in aquatic systems rather than transport vectors. However, there are indications that, at least in

certain systems, oxidation and coprecipitation of $Mn^{2+}$ on ferrihydrite surfaces may be an even more important metal vector than pure ferrihydrite (Hochella et al. 2005). We want to emphasize that, in the FFF–ICPMS observations in FIGURE 2, Mn is predominantly located in the second, larger fraction, but at a much lower concentration than Fe. It remains to be seen to what extent the vernadite-like Mn-rich mineral discovered by Hochella and coworkers is specific to acid mine drainage systems or a generally important metal vector (Hochella et al. 2005).

## THE NANOGEOCHEMISTRY OF IRON OXIDES (REACTIVITY AS A FUNCTION OF SIZE)

Colloids and nanoparticles gain a larger and larger specific surface area (surface to volume ratio) as the particle size decreases. This is purely a geometrical effect. Since sorption and catalysis are taking place at the surface, mass-based reactivity of the material often increases for smaller particle sizes (Banfield and Navrotsky 2001). In addition, at the nanoscale, other phenomena that can affect the reactivity of the particles also come into play. The understanding of these processes is at the core of nanogeoscience.

For example, from the perspective of a molecule, the surface of a micron-sized particle appears flat, while the surface of a small nanoparticle appears round, but with a roughness. The roughness comes from edges, corners, ridges, and holes in the crystal structure of the nanoparticle (FIG. 1). The relative proportion of these topographic surface features increases as particle size decreases (Chernyshova et al. 2007), and the edges, corners, and crystal defects represent attractive binding sites for metals (sorption) or reactants (catalysis) (Madden and Hochella 2005; Madden et al. 2006). Lead sorption to ferrihydrite takes place
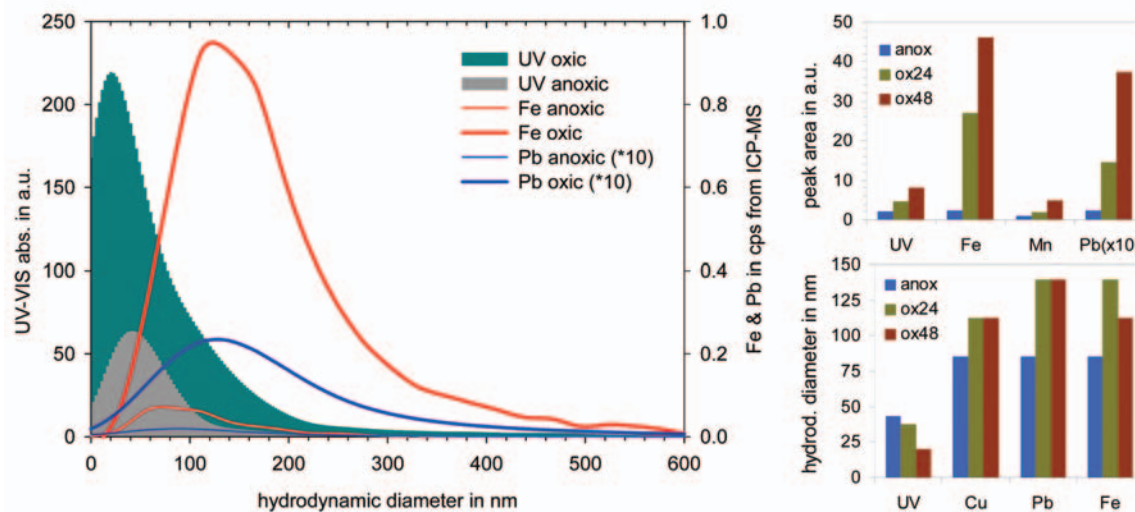
mainly at the edges and corners, with either monodentate (bonded to one oxygen) or bidentate (bonded to two oxygens) attachment (FIG. 1) (Trivedi et al. 2003; Xu et al. 2006). Madden et al. (2006) showed that $Cu^{2+}$ sorbed more strongly to hematite nanoparticles when the particle size was below 10 nm. This could be explained mainly by a higher proportion of high-affinity $Cu^{2+}$ binding sites on smaller nanoparticles.

Particle surface charge is an important property that governs not just aggregation rates but also the accumulation of solutes in the electric double layer and adsorption (FIG. 1). Aggregation rates have been shown to be size dependent (He et al. 2008), which can be due to increased diffusion and collision rates, but also to differences in the charge profiles around smaller particles. Smaller hematite nanoparticles (12 nm) were found to have lower electrostatic repulsion than larger nanoparticles (65 nm). However, the aggregation rate was higher and the critical coagulation concentration (for NaCl as flocculant) was lower for smaller nanoparticles (He et al. 2008).

The piggyback transport of trace metals on colloidal/nanoparticulate carrier phases is largely dependent on the concentration and transport behavior of the carrier phase (e.g. FeOx nanoparticles) and the character of the carrier–contaminant association (Kretzschmar et al. 1999). It is of great importance whether the contaminant (i.e. Pb) is only sorbed to the surface of the carrier particles or if it is enclosed in the particle structure. In the latter case, the contaminant can be released only by the dissolution of the particle itself. There are indications that redox-cycling processes (e.g. in sediments) can lead to contaminant entrapment in the FeOx structure. An anoxic porewater sample was obtained from a sediment core from the Elbe River (Germany). The sample was collected and then stored under a nitrogen atmosphere. After the analysis of the anoxic sample in an FFF channel kept under oxygen-free conditions, the sample was allowed to oxidize under the ambient atmosphere for 48 hours and then was re-analyzed. During oxidation of the porewater, FeOx colloids that bound Pb were formed. This Pb was formerly "dissolved" or bound to humic substances. The fact that the Pb follows a mass-based distribution compared to the FeOx (not shifted to the left; FIG. 3) indicates incorporation into the FeOx particles.

The transport of FeOx nanoparticles is largely dependent on the size of the particles, the presence and chemistry of surrounding mobile or immobile particles (from small polysaccharides to stationary grains and rocks in the aquifer), and the local water chemistry. Pure FeOx minerals will have a positive surface charge under normal environmental pH conditions and hence be quickly deposited on the generally negatively charged stationary grains of the sediments and aquifer materials. In the aquatic environment, FeOx minerals are, however, often coated with NOM. Consequently, and depending on the degree of surface coverage, the surface charge can be neutralized (resulting in flocculation) or even reversed. In the latter situation, the particles become more mobile and resistant to aggregation and deposition (Karathanasis 1999). Particle-filtration theory describes the transport of particles as a function of particle size, water flow rate, and grain size of the porous medium (soil) quite well for simple conditions (fully attractive, nonrepulsive), but still fails when applied to the "real world" where the particles are electrostatically or sterically stabilized against aggregation (Christian et al. 2008 and references therein).

Förstner et al. (2001) showed that goethite nanoparticles coated with NOM cotransport Pb completely through a sand column, while clay and NOM alone are much less effective vectors. Uncoated goethite, however, can quickly deposit on sand and act as a Pb scavenger, reducing Pb transport totally. This underlines the complex interrelation of particle size, pH, redox conditions, and particle–contaminant and particle–NOM interactions for the colloidal transport of contaminants (Karathanasis 1999; Kretzschmar et al. 1999). Therefore, one of the most active research fields in nanogeoscience concerns the identification and description of the processes involved in colloidal or nanoparticulate transport and the determination of their relevance to the local, regional, and global cycling of elements.

## ACKNOWLEDGMENTS

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