An overview of factors influencing the colloid/particle favoured relocation of contaminants

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**Abstract** Contaminants partition between the solid and the aqueous phase. Those sorbed to the solid phase are regarded as retarded or immobile. The solid phase—the matrix of the soil or aquifer—can be mobile itself as suspended or colloidal particles. In the unsaturated zone, with fast changing gradients in hydrochemistry and water content, suspended particles can play a major role in contaminant relocation.

**Key words** colloids; contaminants; filter theory; heavy metals; particles; PAH; unsaturated zone

**INTRODUCTION**

The ability to predict contaminant transport is one of the main requirements for sustainable management of site remediation or groundwater protection. The major pathways and transport mechanisms must be defined. Most approaches to describing and predicting transport phenomena treat aqueous systems as a two-phase system: a mobile aqueous phase and an immobile solid phase. Contaminants partition between these two systems and those that have a strong tendency to sorb readily to the solid phase are considered to be virtually immobile or retarded.

However, colloidal and suspended particles also may be mobile in saturated or unsaturated environments. The composition of these colloids/particles is expected to be chemically similar to that of the surface of the aquifer material. Thus, they can also sorb organic and inorganic contaminants (McCarthy & Zachara, 1989). Predictions on the transport of contaminants may fail if micro-particle facilitated transport is not taken into consideration.

Many nonpolar organics, e.g. polycyclic aromatic hydrocarbons (PAH), PCP and dioxin, have a strong tendency to adsorb to the solid phase. Inorganic trace substances, like heavy metals and radionuclides can show the same tendency (Backhus & Geschwend, 1990) forming colloids/particles themselves. Thus long-term risk assessment should take colloid-bound relocation of contaminants into consideration.

**ORIGIN OF PARTICLES**

In this paper we refer to colloids (or particles) as potentially mobile solids including macromolecular (or “dissolved”) components of organic carbon. They can cover a broad size range from a few nm up to 10–20 μm. Thus, common filtration techniques in groundwater quality monitoring, i.e. filtration through 0.45 μm filters, may exaggerate the concentration of dissolved elements and underestimate the total element
content. Particles can be colloidal stable or suspended. The colloidal stability and transport behaviour of a particle is a complex function of the surface charge density, surface chemistry, water chemistry and flow velocity. These conditions change along the flow path in the unsaturated or saturated zone. Thus, for practical reasons colloids and suspended particles are often not differentiated.

Many different particles can be expected in aqueous environments. The soil itself consists of small particles <20 μm. These particles were deposited during sedimentation and genesis of the soil or aquifer, or formed by post-depositional weathering of thermodynamically unstable primary minerals. The composition of these particles depends on the sedimentation conditions, the chemistry of the pore water solution, the mineral content of the original geological material and the climate. The dominating inorganic particles are alumino silicates, oxides and hydroxides of aluminium, iron, manganese, as well as calcium and magnesium carbonates and silica (McCarthy & Zachara, 1989).

A second group of particles is formed by precipitation or mobilization due to a geochemical gradient along the flow path. Particles can form or be mobilized due to changes of parameters like pH, Eh, electrical conductivity or the dissolved gas content. Seepage of water with a high content of organic carbon can lead to anoxic conditions by microbial reduction of O₂, NO₃⁻, NO₂⁻, MnO₂, Fe(III)-oxide, SO₄²⁻ and CO₂. Iron and manganese coatings of the soil material are dissolved during this process and liberate formerly fixed particles and elements in these coatings. Nevertheless, the total content of iron and manganese, released by dissolution of these cements, is limited by the solubility of carbonates and sulphides.

Bio-organic substances are from a third group of micro-particles (Jenkins & Lion, 1993). Organic macromolecules and humic substances can be released or brought in by the infiltrating water. Bacteria attached to the matrix may become unattached or can be infiltrated. They may release extra-cellular matter or cell fragments. Another rare but very important and conceivably dangerous group are spores and viruses. Most of these organic substances and microorganisms have a strong tendency to adsorb to particles.

**TRANSPORT OF PARTICLES**

Suspended or colloidal particles can be mobile if they are not susceptible to filtration and are stable with respect to agglomeration and dissolution. Filtration effects can be either straining filtration or physico-chemical collection. While the maximum size of mobile particles is limited by straining filtration and pore velocity, the concentration and size distribution of particles in the nanometer size range are controlled by physico-chemical filtration. A minimum filtration rate can be observed at a size range close to 1 μm for bacteria and polystyrene beads, and around 0.2 μm for clay minerals. At these size ranges straining filtration is less effective in most porous aquifers and physico-chemical filtration does not reach its maximum (Fig. 1).

The collection of particles on the soil material strongly depends on the surface charge. If the surface charge of the particles and soil matrix are opposite, collection is enhanced. Differently charged particles favour coagulation and consequently sedimentation. This effect is even more complex for clay minerals, because the edges and faces may show opposite charge. A charge reversal of particles can occur due to the adsorption processes of polyelectrolytic substances. The adsorption of humic substances
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Fig. 1 Results of column experiments with polystyrene beads. The column is filled with natural sand and gravel with a mean grain size of 2.4 mm. Squares, triangles and dots are experimental results at different pore velocities. Lines are results calculated following the filter theory of Rajagopalan & Tien (1976) and Yao (1968). The filtration factor is defined by the equation at the right top of the figure ($c/c_0 = \frac{\text{concentration at column outflow}}{\text{inflow}}, x = \text{column length}, \alpha = \text{filtration factor}$).

(HUS) to positively charged particles like ferrihydrite can cause a charge reversal and facilitate transport (Fig. 2). Batch experiments were performed with a Malvern Zetasizer after an equilibration time of 24 h for particle–HUS interaction. Zeta potential was measured allowing an equilibration time of ~5 min after pH adjustment. Ferrihydrite particles show a charge reversal at pH 8. At higher pH values these particles are negatively charged, at lower pH, they are positive. Humic substances are charged negative throughout the whole pH range. If humic substances are added to ferrihydrite particles the surface charge of the positively charged particles is masked by the sorption of the negatively charged polyelectrolyte. Thus, sorption of humic substances can significantly alter the transport behaviour of particles. Besides the surface charge, the chemical stability of the particles themselves is also very important with respect to their mobility.

Major importance should be attributed to fingering and preferential flow. In macro-pore systems flow velocities are high and filtration rates are low. Thus, large amounts of mobile particles could be relocated by this transport mechanism. In addition, in the unsaturated zone the gas phase plays an important role in particle transport (Wan & Wilson, 1994).

Particle bound transport reduces the retardation factor and should be taken into account if:

- particle concentrations are high,
- particles are stable (no dissolution),
- particles are mobile (no filtration),
- particles interact strongly and irreversibly with the contaminant,
- particles are more mobile than the aqueous phase.

If the contaminant interacts irreversibly with the particles but particle mobility is lower than in the aqueous phase, particles lead to an enhanced retardation factor.
CONCLUSIONS

Colloidal and suspended particles are abundant in all natural aquatic environments. The size range of these particles is from a few nm up to several µm. Inorganic particles consist mainly of precipitates, alumino silicates and quartz. To the group of organic particles belong bacteria, spores, viruses and humic substances as well as extra-cellular material.

The mobility of these particles is linked to the chemical and physical boundary conditions. Because these conditions vary over small distances and time periods in the unsaturated zone, it is very difficult to predict particle transport.

Hydrophobic contaminants like PAH can have a strong tendency to sorb to solid phases. Heavy metals and radionuclides can sorb to a solid phase or form particles themselves. If the particles are more mobile than the aqueous phase, then contaminant transport can be enhanced, and conversely, if they are less mobile, interaction with particles will lead to contaminant retardation.

REFERENCES


