

Characterisation of Natural Colloids with Field-Flow-Fractionation (FFF) Techniques for the Assessment of Colloid Assisted Transport of Heavy Metals

Frank v. d. Kammer

Department of Environmental Science & Technology (1-03)
Technical University Hamburg-Harburg; Eissendorfer Strasse 40
21073 Hamburg (Germany)
e-mail: f.kammer@tu-harburg.de

SUMMARY

Colloids may play a significant role in contaminant transport. The objective of this paper is to summarise briefly the impact of colloids on contaminant transport and the potentials that arise with the use of Field-Flow Fractionation on the characterisation of natural colloids in laboratory experiments.

INTRODUCTION

In most cases the migration of heavy metals in the subsurface is attenuated by sorption to the immobile soil matrix. In the 1980s the unexpected transport of radionuclides in the subsurface started the discussion how far mobile colloidal particles (humic acids, mineral particles and bio-colloids) may contribute significantly to transport processes. This led to an extension of the two-phase (solid-solution) model to a three-phase (solid-colloid-solution) model (Ryan & Elimelech 1996). Figure 1 depicts four different situations of contaminant transport through porous or fractured media with regard to the presence of colloidal particles.

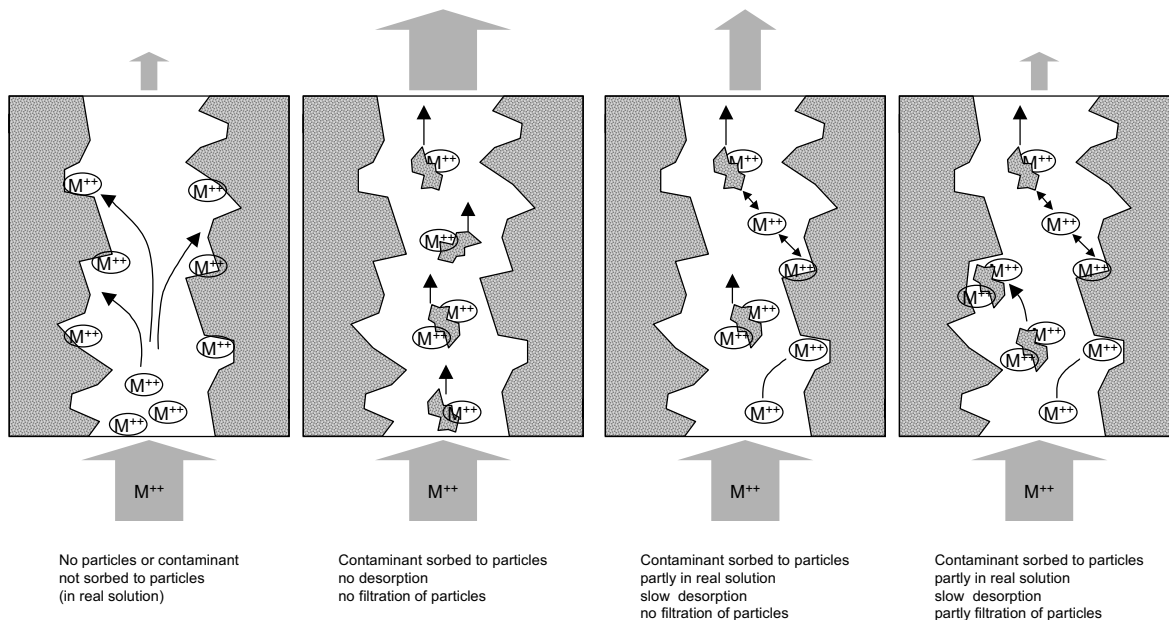


Fig. 1: Simplified plots of colloidal enhanced trace metal transport in porous media

Mobile colloids are often generated by hydro-chemical perturbations and to a less extent by increasing hydraulic shear forces. The focus of several of our studies was therefore on the release of colloids from

soils that are or will be subject to hydro-chemical variations, e.g. near waste disposals or in redox-labile aquifers receiving biodegradable organic carbon. A sample of silty till (10% $< 7\mu\text{m}$) from a core obtained close to an operating, uncontained landfill was used for batch and column experiments. The impact of low pH (4.7) conditions and ionic strength was investigated in batch and column experiments.

To investigate the role of environmental colloidal particles in heavy metal transport we need to detect and characterise those particles and their heavy metal loads in the field and in laboratory experiments. In the case of environmental particles, applied methods have to overcome difficulties arising from complex colloid composition, broad size distributions and varying particle densities/shapes over size. Additionally, the concentration of colloids in natural waters is usually in the $\mu\text{g/L}$ -range and samples lack colloidal stability (McCarthy & Degueldre 1993).

It was shown that Field-Flow-Fractionation (FFF), a rapid and high resolution fractionation technique, can be used for the high resolution fractionation and characterisation of natural colloids (Beckett & Hart 1993). FFF is a family of hydrodynamic fractionation techniques based on colloid interaction with an external field force in a thin, ribbon-like flow channel (Fig. 2). Based on the type of field force colloids are fractionated according to their apparent diffusion coefficient (cross-flow field, FlowFFF), particle volume and density (centrifugal field, SedimentationFFF) or surface charge/mass ratio (electrical field, ElectricFFF).

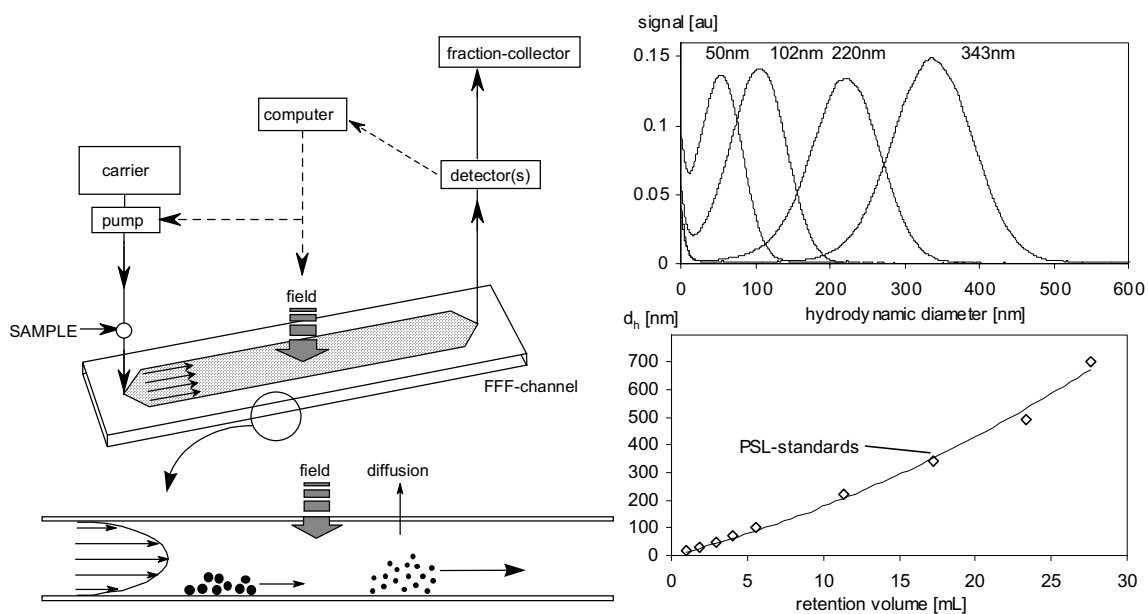


Fig. 2: Schematic layout of an FFF-system and fractionation principles (left), fractogram of four monodisperse latex bead (PSL) standards (r.u.) and a typical calibration curve for the transformation of retention volume to hydrodynamic diameter using PSL-standards (r.l.).

In general a relative mass based size distribution (dm/dd) is derived from the transient signal. For the analysis of natural colloids a multi-detection-analysis was established (v.d.Kammer & Förstner 1998). In relation to the used detectors, size dependent characteristics of the sample can be collected (fluorescence spectra, UV-spectra, independent and absolute hydrodynamic radius, radius of gyration and molecular weight from dynamic and static light scattering, element concentrations from ICP-MS). Since samples are diluted during FFF the method is restricted to laboratory experiments with colloid concentrations above 1mg/L or a sample enrichment is needed.

RESULTS & DISCUSSION

In batch experiments the colloid release potential (water extractable colloids) of the silty till sample was tested. The test was performed by shaking the sample for several minutes and by ultrasonication for 30min at a S/L-ratio of 0.1 in 50mL centrifuge tubes. Afterwards the sample is centrifuged to remove particles $>1\mu\text{m}$ quantitatively. The supernatant was immediately analysed with FFF.

Results for the extracted soil sample are given in figure 3. The sample was analysed before and after calcite (CaCO_3) content was removed with acetic acid/sodium acetate buffer at pH 4.7. The original sample shows a remarkable, extractable colloidal content (270mg/L retained by a 20nm filter) with predominant particle size at about 80nm. The removal of calcite as a cementing agent for small particles increases the extractable colloidal content predominantly in the $<100\text{nm}$ region.

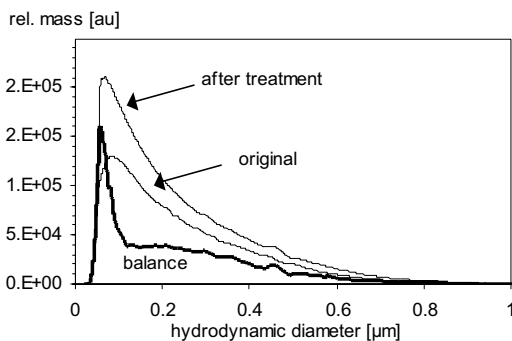


Fig. 3: SedimentationFFF-analysis of a till sample before and after removal of carbonates.

A column experiment was conducted to investigate the effect of calcite removal without the interference of increased calcium concentrations in the batch during calcite dissolution (exp. parameters are given in fig. 4). During the “low-pH phase” approx. 25% of the calcium was removed from the column. No significant release of colloids from the column was detected in that period due to the increased ionic strength (sodium acetate buffer) and the release of calcium (up to 22mmol Ca^{2+} in the column eluate).

FFF-analysis of water extractable colloids in the column material before and after the experiment showed the same behaviour as observed in the batch experiments regarding the shift in size distribution to smaller particles, but no increase in extracted total colloidal mass.

By coupling FFF to a sensitive multi-element detector (HR-ICP-MS) we can gather additional information

FFF-analysis of water extractable colloids in the column material before and after the experiment showed the

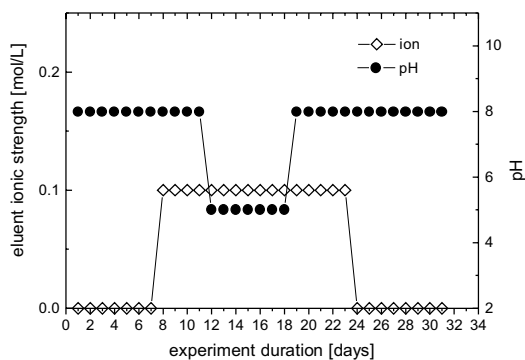


Fig. 4: Input parameters (ionic strength & pH) for the column experiment.

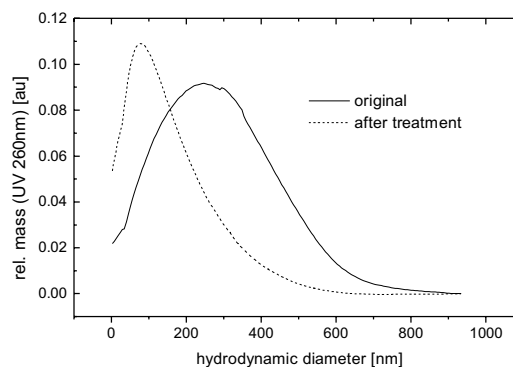


Fig. 5: FlowFFF-analysis of the till sample before and after the column experiment (water extractable colloids)

about the properties of the extracted soil colloids for the transport of heavy metals. Experiments were performed with the original sample and with a sub-sample that was artificially contaminated with heavy metals to simulate the contamination by landfill leachate. Figures 6 and 7 show the results for Pb and Cd. Both metals show a completely different behaviour. While cadmium is associated only with very small particles, lead has no particle size preference. While the overall lead concentration is slightly decreased in

the artificial contamination step, cadmium concentrations are increasing drastically and are associated only with very small particles. In relation to the apparent particle mass and size, Cadmium reached up to 35 g/kg in the 40nm-region. The same selectivity regarding particle size is observed for zinc and copper. The

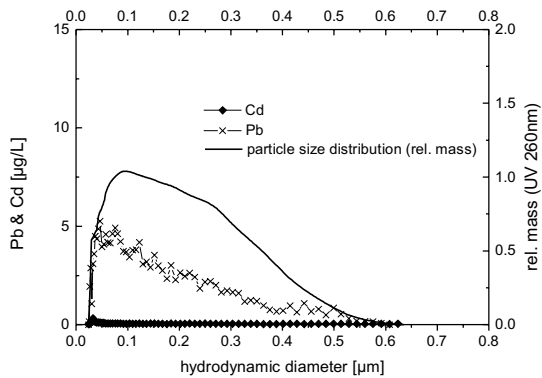


Fig. 6: FFF-ICPMS-analysis of the original till sample (water extract). Bulk sample contained 13ppm Pb and 0.1ppm Cd

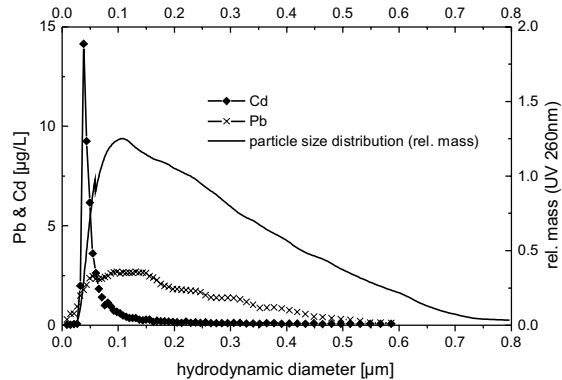


Fig.7: FFF-ICPMS of the artificially contaminated till sample (water extract). Bulk sample contained 961ppm Pb and 347ppm Cd

distribution of major elements (Si, Al, Mn) gives no indication that mineral composition of the <100nm particles is different compared to the larger ones.

CONCLUSIONS

Besides the presence and extractability of colloidal particles, information about size-distributions and contaminant interactions are needed since the retention of colloids during their translocation in porous media is in most cases size specific (Ryan & Elimelech 1996). High resolution information about the distribution of heavy metals over the size distribution of potentially mobile colloids is essential in predicting the contribution of colloids to the migration of heavy metals in the subsurface. FFF-methods are a versatile tool in characterising colloidal samples as long as concentrations are sufficiently high.

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