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Assessing colloid-bound metal export in response to short term changes in runoff from a forested catchment

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Soils can act as a source of metals and natural organic matter (NOM) in runoff from catchments. Amounts and intensity of rainfall may influence NOM export from catchments. The presence of NOM and other colloids in water may not only enhance metal export, but also significantly change metal speciation.

In this study, we investigated the response of metal-colloid associations to short-term discharge variations in the runoff from a small forested catchment (Lehstenbach, Bavaria, Germany). Here, the discharge from the catchment outlet responds within hours to rain events. Near-surface flow in organic-rich layers and peat soils has been identified to increase dissolved organic carbon (DOC) concentrations during stormwater runoff.

Flow Field-Flow Fractionation coupled to ICP-MS (FlowFFF-ICPMS) is a high-resolution size separation technique which was used for the detection and quantification of colloids and associated metals. Colloid-associated metals, dissolved metals and metals associated with low-molecular weight organic ligands were also separated by filtration (0.2 μm) and ultrafiltration (1000 g/mol MWCO).

During baseflow DOC concentration was <6 mg/L and the pH ranged between 4.6 and 5.0. The DOC concentration exported at a given discharge was subject to strong seasonal variation and depended on the water level before the discharge event. DOC concentrations were up to 8 fold higher during stormwater runoff compared to baseflow. The export of aluminum, arsenic, rare earth elements (REE) and uranium from the catchment increased during stormwater runoff showing a strong correlation with NOM concentrations. This result was supported by FlowFFF-ICPMS data revealing that NOM was the only colloid type available for metal complexation during all hydrological conditions.

A clear temporal pattern in the association with the NOM was observed for most of the metals under study: During baseflow, 70-100% (Fe), 90% (Al), 60-100% (REE) and 80-85% (U) were associated with the NOM. During stormwater runoff, the dissolved species concentration and those associated with small organic ligands (<1000 g/mol) increased. The pH drop during the stormwater runoff (pH <4) is most likely the main factor for weaker metal-NOM binding. However, only 25 to 50% of the arsenic was associated with NOM, but no relation to discharge, or pH was exhibited.
The results show that fluxes of most trace metals from the catchment are governed by NOM-colloids, even though substantial concentrations are dissolved or associated to low-molecular weight organic substances during stormwater runoff.