Arsenic, copper, and zinc leaching through preferential flow in mining-impacted soils

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The effect of preferential flow on the spatial distribution and chemical speciation of As, Cu and Zn in a metal(loid) polluted soil was studied within the river bed of a small stream that collects surface runoff from an arsenic-bearing, mainly as scrorodite ($FeAsO4{\cdot}2H2O$), waste pile near an abandoned mine. Water flow domains, either preferential or matrix, were identified by staining techniques, a detailed soil sampling procedure, and statistical analysis. General soil properties were studied in each flow domain. In addition, total metal(loid) content and chemical distribution by means of sequential extraction procedure were done within each flow domain. Lastly, As speciation was studied by X-ray absorption spectroscopic (XAS) methods.

An upper river bed and its underlying subsoil were distinguished, and both were characterized by low pH and high As, Cu, Zn and Fe concentrations as compared to the adjacent soil. Metal(oid) concentrations were higher in the river bed than in the subsoil due to the accumulation of incoming material from the waste pile. In the river bed, higher metal(oid) concentrations were found in the preferential flow domain compared to matrix flow. Instead in the subsoil, preferential flow paths were characterized by a lower ion exchange capacity and lower Cu and Zn concentrations from acidic leaching, and higher concentrations of total organic matter attributed to high root content, compared to the soil matrix. Arsenic was mainly concentrated in the preferential flow paths as As(V). XAS analysis indicated As sorption on iron hydroxide phases as the primary retention mechanism in the subsoil, which may be a reversible process if geochemical conditions change. Preferential flow, acting as a by-pass connecting the highly contaminated river bed layer with deeper soil, has an impact on the distribution of metal(oids) at the study site and may increase the risk for groundwater contamination.

Mechanisms of light-induced flocculation of terrestrial dissolved organic matter and iron

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Dissolved organic matter (DOM) rich water samples from the Great Dismal Swamp (Virginia, USA) were filtered (<0.1 micron) and UV-irradiated (~290 nm lower cutoff) for 30 days. During the irradiation, particulate organic matter (POM) and particulate iron formed. Water samples before and after particle removal, as well as isolated particles, were analyzed by ultraviolet-visible absorption spectroscopy, high temperature combustion (TOC/DOC), solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, and flame atomic absorption spectroscopy (for iron). After 30 days of UV light exposure, 7.1% of the original DOC was converted to particulate organic carbon (POC) while 75% was converted to inorganic photoproducts. Approximately 84% of the absorption in the 250-450 nm region was removed by photobleaching, while 8.3% was removed by photo-flocculation. About 87% of the iron was removed from the dissolved phase after 30 days of irradiation, but iron did not begin to flocculate until a considerable excess of DOM was removed by photodegradation and flocculation between 10 and 20 days of irradiation. These results suggest that, during the initial 10 days, there was still sufficient organic ligands present to keep iron in solution. NMR and FT-IR spectroscopies indicated that the photochemically flocculated POM is significantly more aliphatic than the irradiated DOM. Further, photo-flocculated POM was enriched in amide functional groups, while carbohydrate-like material was resistant to both photochemical degradation and flocculation. When photochemical flocculation is considered, the extent to which photochemistry may remove terrestrial DOM from the upper water column is revised upward by about 10%. Abiotic photochemical flocculation is therefore a heretofore-ignored phenomenon that significantly alters our understanding of sedimentation in humic lakes and the transport of DOM and POM in ocean margin environments such as estuaries.