

Using WITCH to quantify landscape and hydrologic controls on solute fluxes in the Critical Zone (Susquehanna Shale Hills Observatory, PA)

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To investigate the hydrologic and landscape controls on shale weathering and their influence on first-order stream solute fluxes, we coupled a numerical chemical weathering model, WITCH, with a physically-based land surface hydrologic model, Flux-PIHM (Penn State Integrated Hydrologic Model). Using this approach, we were able to simulate vertical water and chemical fluxes across two representative landscape features (planar or swale hillslopes). We extrapolate the results from the soil profiles to estimate the chemical loads to the stream over a 32 year period (1980-2012) at the Susquehanna Shale Hills Critical Zone Observatory (SSH-CZO). Observed soil water (10 cm increments) and stream water chemistry collected between 2006-2011 were used to validate the modelling results. The simulation predicted the saturation state of soil water with respect to illite, smectite and kaolinite. Saturation was driven by seasonal drying, with supersaturated conditions persistent around the rooting zone (25-70 cm) during the summer months. As expected, the modelled weathering rates of illite, chlorite and k-feldspar were elevated near the soil surface where fluids were dilute, especially at the onset of fall when solute fluxes (eg. Mg, Na and Si) reached their maximum. Results from Flux-PIHM suggest a more extensive hydrologic connection between the swale hillslopes and the stream as compared with the planar hillslopes. WITCH then documented the role of this hydrologic connection on the stream water chemistry, with swales contributing bigger solute fluxes.

Sediment phosphorus dynamics in a marine coastal lake: Response to seasonal bottom water anoxia

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Low-oxygen conditions are expanding in bottom waters of many coastal systems. Increased availability of the nutrient phosphorus (P) is often important in the development and sustainment of hypoxia. However, the controls on the recycling and burial of P in hypoxic and anoxic marine settings are not well understood. Here, we present results of a detailed study of the sediment biogeochemistry and P dynamics at a site in the seasonally anoxic marine Lake Grevelingen, in the Netherlands. Monthly water column and pore water profiles of oxygen and sulphide for 2012 show a short (1 month) but intense period of bottom water anoxia. Strong seasonality in the pore water profiles of dissolved Fe²⁺ and phosphate is seen. In spring, when bottom waters were oxic, our pore water data indicate dissolution of iron sulfides and calcium carbonate due to activity of electrogenic bacteria [1]. Consequentially there is a strong release of Fe²⁺ to the pore water without an associated release of dissolved phosphate. In this period, most released phosphate remains in the sediment. Upon the onset of anoxia, phosphate release from the sediment to the water column is enhanced, both in absolute terms, when compared to the prior oxic period and relative to dissolved inorganic carbon (DIC) and ammonium. With the return of oxic conditions, Beggiatoa establish at the sediment-water interface and the benthic flux of phosphate is again reduced. Sediment P analyses indicate most P in the sediment is present in the form of organic- and iron-bound P, even at depths where sulphide is present at high concentrations throughout the year. This suggests the presence of a reduced Fe-P phase as found recently in euxinic sediments from the Baltic Sea [2]. Further work will focus on the identification of the sedimentary Fe-bound P forms and a reconstruction of the role of the sediment as a P source and sink over past decades.

[1] Risgaard-Petersen *et al.* (2012) *Geochim Cosmochim Acta* 92: 1-13. [2] Jilbert & Slomp (2013) *Geochim Cosmochim Acta* 107: 155-169