Hydrochemistry of a variably snow-covered catchment

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Streamwater chemistry is useful for measuring contemporary weathering in a catchment. However, streamwater composition can vary seasonally, modulated by evapotranspiration, flow rate, flow paths, and biogeochemical processes within the watershed. We explore the seasonal dynamics of streamwater chemistry in a variably snow-covered catchment in the Boulder Creek Critical Zone Observatory as a foundation for understanding both hydrologic flowpaths and weathering in the catchment.

Gordon Gulch watershed

Gordon Gulch is a 2.7 km^2 forested catchment at ~2600 m a.s.l. in the Colorado Front Range, underlain by Precambrian gneiss and granodiorite. Mobile regolith depths are typically less than 1m, but bedrock tors dot the slopes; depth to fresh rock is ~8-10 m [1, 2]. Snowpack on N-facing slopes melts in spring, pushing groundwater levels up and fueling the annual discharge peak. Snow melts intermittently on S-facing slopes throughout fall, winter, and spring. Solute concentrations in streamwater vary by factors as high as 4 (Cl) to as little as 1.3 (Si), in seasonal patterns.

Cl concentrations shed light on the source of water discharging at different times in the year. Early fall and spring snowmelt produces high Cl concentrations in runoff, which appear to reflect throughfall traveling shallow paths to the stream. Cl peaks are accompanied by high dissolved organic matter (DOM) concentrations [3]. For more than a month after spring snowmelt, water sources are in transition. Cl dips to an annual minimum, approaching the low concentrations seen in precipitation, and lower than groundwater values. Only in very late summer (August) is Cl in streamwater the same as in groundwater. This suggests that late summer is the best time to analyze bedrock weathering from streamwater in this catchment. Perhaps not surprisingly, alkalinity, Ca and Na all rise to steady high concentrations during this time of groundwater fed baseflow.

Watershed dynamics

Streamflow, water-table heights, and water chemistry yield a picture of the watershed "breathing" on an annual basis. A "breath" begins with fall snow, which melts on S-facing slopes. This induces a small rise in water-table height and a dramatic streamwater flush of Cl and DOM. Early spring produces a more sustained rise in Cl, DOM, and the water table. Discharge and the water-table height rise to a dramatic peak during the sustained snowmelt from the N-facing slope. By the time of this crescendo, however, Cl and DOM are in precipitous decline. In midsummer minimally altered precipitation water is expelled during the long summer decline in discharge. The bottom of the breath is late summer, when only groundwater emerges. We will assess solute fluxes and mineral weathering variations during each stage of the annual watershed breath cycle.

[1] Befus (2011) *Vadose Zone Journal* **10**, 915-927. [2] Dethier (2006) *Geomorphology* **75**, 384-399. [3] Gabor (2009) *Eos, Trans. AGU* **90**, Abstract EP53C-0631.

Spectroscopic study of aluminum and gallium complexation by aquatic organic matter

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The fate and behavior of aluminum (Al) in aquatic systems is largely influenced by pH and interactions with natural organic matter (NOM). However, knowledge on the molecular structure and hydrolysis of Al species in presence of aquatic NOM is still limited. In this study Extended X-ray Absorption Fine Structure (EXAFS) and Infrared (IR) spectroscopy was used to characterize Al and gallium (Ga) interactions with organic matter from the Suwannee River at varying metal concentrations and pH. There are relatively few studies of Al interactions with NOM using these techniques [e.g. 1], one reason being the difficulty of analyzing Al in aqueous samples using EXAFS due to its low K-edge energy (1.5596 keV). Ga (K-edge at 10.367 keV), on the other hand, is readily accessible to EXAFS, and could serve as a model for Al because of the similar coordination chemistries of Al(III) and Ga(III). Indeed, previous studies of Al(III)- and Ga(III)-carboxylates have shown that these complexes can be considered analogous with respect to thermodynamic and spectroscopic properties [2, 3].

Our IR spectroscopic results showed that Al(III)- and Ga(III)-NOM interactions occur mainly via carboxylic functional groups, as indicated by characteristic shifts of the carboxyl stretching frequencies in presence of the metal ions. Overall, the behavior of the two systems was very similar, thus supporting our idea that Ga can be used as a model to study the complexation of Al by aquatic NOM.

The EXAFS results indicated that Ga formed chelate complexes in association with aquatic NOM. At low Ga concentrations ($\leq$16 000 μg g^{-1}; pH 5) mononuclear Ga(III)-NOM complexes dominated the speciation while at higher pH values and high Ga concentrations (60 000 μg g^{-1}; pH 5-7) there was a mixture of mononuclear Ga(III)-NOM complexes and a polymeric Ga(III) (hydr)oxide phase. Thus, the organic Ga complexes formed were sufficiently strong to suppress hydrolytic polymerization even at pH 7.0 and high Ga concentrations. An additional finding was that the local structure of the Ga(III)-NOM complexes formed at the lowest concentration (100 μg Ga g^{-1}) clearly differed from those at higher Ga concentrations, which might indicate involvement from different functional groups.

Our combined EXAFS and IR results highlight the significant effects on metal ion speciation induced by the Al(III) and Ga(III)-NOM interactions. Accordingly, these interactions may exert a substantial control over the geochemistry of Al in aquatic systems, and the distribution between mononuclear complexes and polymeric species is likely to influence the toxicity and mobility of Al. Furthermore, the interactions with NOM may play a key role in determining the properties of the solid Al phases e.g. particle size.

[1] K. Elkins, D. Nelson (2002) *Coord. Chem. Rev*. **228**, 205-225.
[2] M. Clausén et al. (2005) *J. Inorg. Biochem.* **99**, 716-726.
[3] M. Clausén et al. (2003) *J. Mol. Struct.* **648**, 225-235.