Hydrobiogeochemical coupling and solute export at the watershed scale

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Abstract: watersheds are the fundamental units that connect terrestrial and aquatic systems and provide ecosystem services including energy, water, nutrients, and habitats [1]. The EPA estimated that more than 40 percent of western watersheds have been contaminated in large part due to abandoned mines [2]. Acidic mine drainage (AMD) that rich in toxic metals are posing serious water risks to public safety [3]. However, metal exports at the watershed scale are difficult to predict because we lack an understanding of interactions between hydrological conditions and biogeochemical reactions.

The Coal Creek, a snow-covered high-elevation watershed, drains an area of approximately 52.8 km² in west-central Colorado. It has three major abandoned mines releasing AMD into the Coal Creek stream [4], which supplies drinking water for the downstream Town of Crested Butte. Field measurements suggest that DOC exhibited enrichment behavior as concentrations (C) increased with increasing discharge (Q). In contrast, the C-Q relationship of Cl and geogenic species (i.e., Na, Ca, and Mg) was one of slight dilution behavior, i.e., decreasing concentrations with increasing discharge. Trace metals including Zn, Mn, and Cd exhibited switch behaviors: concentrations increased in the early stages of snowmelt and then decreased to form a closed hysteretic loop. Spring snowmelt was the dominant hydrologic event that exported ~ 64% and 39% ~ 43% of annual loading of the DOC and metals, respectively. In this study, we aim to develop a bio-reactive transport code to understand watershed biogeochemistry, especially to understand the key ecohydrological control of DOC, nutrients, and metals export at this historic mine site. Specific questions include: 1) how does hydrology (e.g., hydrologic connectivity, tributary mixing) affect CQ relationships of DOC and trace metals? 2) how does biogeochemistry (e.g., carbon decomposition, DOC-metal complexation) regulate trace metal export?

bioRT-Flux-PIHM is a watershed biogeochemistry code coupling between hydrological processes (PIHM), land-surface processes (FLUX-Noah Land Surface Model), and subsurface bioreactive transport (bioRT). The newly added bio module features microbially-mediated reactions, allowing us to solve for spatiotemporal dynamics of DOC, nutrients, and redox-sensitive metals (e.g., Mn). The core bioreactive transport equations includes [5, 6]:

\[ V_i \frac{d(S\theta_i C_m)}{dt} = \sum_{j=N_i}^{N_{j,x}} \left( A_{ij} D_{ij} \frac{C_{m,j} - C_{m,i}}{I_{ij}} - Q_{ij} C_{m,j} \right) + R_{m,i} + R_{b,i} \] (1)

\[ R_m = A_{w,k} k_R \left( 1 - \frac{IAP}{K_{eq}} \right) \] (2)
\[ R_b = \kappa_{\text{max.s}} \cdot X_s \cdot \left( \frac{c_s}{K_{\text{m.s}} + c_s} \cdot \frac{c_{\text{TEA}}}{K_{\text{m,TEA}} + c_{\text{TEA}}} \right) \cdot \left( \prod_{j} \frac{I_j}{I_j + c_j} \right) \cdot f(T) \cdot f(s_w) \] (3)

Where equation (1) is the mass balance governing equation considering advective transport, dispersive/diffusive transport, and geochemical reaction term \( R_m \) and microbially-mediated reaction term \( R_b \). \( V_l \) is total volume of the element \( i \); \( N_{l,x} \) is the index of elements sharing surfaces with element \( i \); the value of \( x \) is 2 for unsaturated zone (infiltration, recharge) and is 4 for saturated zone (recharge plus three lateral flow directions), respectively; \( S_{w,i} \) is the water saturation \( [\text{m}^3 \text{ water/m}^3 \text{ pore space}] \); \( C_{m,i} \) is the aqueous concentration of \( m \) \( [\text{mol/m}^3 \text{ water}] \); \( A_{ij} \) is the grid interface area shared by element \( i \) and its neighbor element \( j \); \( D_{ij} \) is the dispersion/diffusion coefficients \( [\text{m}^2/\text{s}] \); \( I_{ij} \) is the distance between the center of the element \( i \) and its neighbor elements \( j \); \( q_{ij} \) is the flow rate \( [\text{m}^3/\text{s}] \) across shared surface \( A_{ij} ; R_{m,i} \) is the total rate of kinetically controlled geochemical reactions; \( R_{b,i} \) is the total rate of microbially-mediated reactions. The equation (2) is the Transition State Theory (TST) rate law for mineral dissolution and precipitation. \( A_{w,k} \) is the wetted dissolving surface area of mineral \( k \) per volume of porous media \( [\text{m}^2/\text{m}^3] \); \( k_k \) is the intrinsic rate constant \( [\text{mol/m}^3/\text{s}] \); \( IAP \) is the ion activity product; \( K_{eq} \) is the equilibrium constant of the reaction. The equation (3) is the dual Monod rate raw for microbially-mediated reaction. \( \kappa_{\text{max.s}} \) is the maximum utilization rate per biomass on the substrate \( s \) \( [\text{mol/mol biomass/\text{s}}] \); \( X_s \) is the biomass concentration \( [\text{mol biomass/m}^3 \text{ water}] \); \( c_s \) is the substrate electron donor concentration \( [\text{mol/m}^3 \text{ water}] \) and \( c_{\text{TEA}} \) is the terminal electron acceptor (TEA) concentration \( [\text{mol/m}^3 \text{ water}] \); \( K_{\text{m.s}} \) and \( K_{\text{m,TEA}} \) are the half-saturation constant for substrate \( m \) and TEA \( [\text{mol/m}^3 \text{ water}] \), respectively; \( c_j \) is the concentration of inhibitory species \( [\text{mol/m}^3 \text{ water}] \) and \( I_j \) is the inhibition constant \( [\text{mol/m}^3 \text{ water}] \); \( f(T) \) and \( f(s_w) \) are dimensionless environmental factors taking account of the effects of temperature and water saturation on microbial reaction rate.

Preliminary results show that enrichment CQ behaviors of DOC and nutrients are mostly attributed to the spring snowmelt flushing as soil water rose from deeper mineral-rich zones to shallower organic-rich soil horizons and formed lateral flow into the stream, thereby releasing more DOC and nutrients that were previously disconnected from the stream under low discharge conditions. The increased hydrologic connectivity during spring snowmelt period thus connected more nutrient and DOC-rich source areas in the shallow soil zones, keeping higher concentrations at larger discharge conditions. The dilution behavior of base cation and Cl, however, indicates a major chemical source from a constant groundwater influx that is deeper than the soil water and mixing with lower-concentration water in the stream. The mixed CQ behaviors of trace metals are attributed to the aggregated effects of tributary mixing and DOC-metal complexation. Greater hydrologic connectivity during spring snowmelt linking more source areas of DOC and nutrients is likely to enhance DOC and nutrients export and intensify the influence of DOC-metal complexation on trace metal export.

Reference