Seasonality of diel cycles of dissolved trace-metal concentrations in a Rocky Mountain stream

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Substantial diel (24-hour) cycles in dissolved (0.1-µm filtration) metal concentrations were observed during summer low flow, winter low flow, and snowmelt runoff in Prickly Pear Creek in southwestern Montana. The stream was alkaline (pH of 7.65-9.06), and dissolved metal concentrations were relatively low (1.8-7.1 µg/L for As, 18-57 µg/L for Mn, and 12-123 µg/L for Zn). The metals are derived from abandoned mine lands in the stream's headwaters; As also is derived from geothermal sources. During seven diel sampling episodes, each lasting 34-61.5 hours, concentrations of dissolved Mn and Zn increased from minimum values in the afternoon to maximum values shortly after sunrise. The timing of diel cycles of dissolved As concentrations exhibited the inverse pattern. The magnitude of concentration increases during individual 24-hour periods ranged from 17-152% for Mn and 70-500% for Zn, and correlated positively with the magnitude of diel increases of pH and temperature, indicating that geochemical processes involving reactive inorganic and organic surfaces on and in the streambed probably control these diel metal cycles. Diel increases of As concentrations (17-55%) were proportionally smaller and less variable among the seasonal sampling episodes than for Mn and Zn, and they correlated poorly with diel increases of pH and temperature. Streamflow among the seven sampling episodes ranged from 0.35-3.3 m^3/s. The timing of minimum and maximum values of diel streamflow cycles was inconsistent among sampling episodes and had little relation to the timing of metal concentration cycles, indicating that hydrological processes are not a primary control of diel metal cycles. Diel cycles of dissolved metal concentrations may occur at any time of year and during various hydrologic conditions in all streams with dissolved metals and neutral to alkaline pH.

Causes of diel cycling of Zn in streams with near-neutral pH draining abandoned mine lands

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Many mining-impacted streams in western Montana with pH near or above neutrality display large (up to 500%) diel cycles in dissolved Zn concentrations (Nimick et al, 2003). The streams in question typically contain boulders coated with a thin biofilm, as well as black mineral crusts composed of hydrous Mn-Zn oxides (HMZO), some of which have the approximate stoichiometry of hetaerolite ($Mn_2ZnO_4 \cdot xH_2O$). Laboratory experiments simulating diel behavior in High Ore Creek (one of the Montana streams with particularly high Zn concentration) show that the Zn cycles are not caused by 24-h changes in streamflow or hyporheic exchange, but rather to reversible in-stream processes that are driven by the solar cycle. Photosynthetic consumption of CO_2 causes pH to rise during the day, at the same time that water temperature (T) increases. This process reverses at night, as pH and temperature drop. The dissolved Zn concentration of water equilibrated with HMZO is highly sensitive to small changes in both pH and T, increasing an order of magnitude for each unit decrease in pH, and decreasing 2.4-fold for an increase in T from 5 to 20ºC. The response of dissolved Zn concentration to changes in either pH or T is rapid and reversible.

The field and laboratory observations are best explained by sorption of Zn^{2+} onto HMZO surfaces. From the T-dependence of residual Zn concentrations in solution, an approximate adsorption enthalpy of -51 kJ/mol was obtained, which is within the range of enthalpy values reported in the literature for sorption of divalent metal cations onto hydrous metal oxides (Trividi and Axe, 2001). Using the derived pH- and T-dependencies from the experiments, good agreement is shown between predicted and observed diel Zn concentration cycles for several historical data sets collected from High Ore Creek. As well, an empirical distribution coefficient has been derived that relates the dissolved Zn/Mn ratio of creek water to the Zn/Mn ratio of mineral crusts forming in several streams – including High Ore Creek – near the Basin Superfund area of Montana.

References

Nimick D.A. et al. (2003) *Water Resources Res*. **39**, 1247.
Trividi P. and Axe L. (2001) *Env. Sci. Tech.* **35**, 1779-1784.