

**Report as of FY2007 for 2006MT96B: "Student fellowship:
Further investigation of diel cyclic changes of metals in two
Montana rivers."**

Publications

Project 2006MT96B has resulted in no reported publications as of FY2007.

Report Follows

Investigations of diel changes in the concentration of
dissolved Mn and Zn and
sediment-water interactions

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Abstract

Diel concentration changes of metals have been shown to occur in a variety of streams. Photosynthesis and respiration of aquatic plants and microorganisms drive the diel pH cycle in a healthy river. However, temperature-dependent and pH-dependent sorption to surfaces plays a significant role in the concentration cycles of both anions and cations in the river system. Since the transport and fate of chemical species within a river can have a significant impact on the health of the aquatic system and the surrounding environment, an enhanced understanding of the mechanisms affecting diel concentration cycles could lead to a better fundamental understanding of water quality dynamics within natural waters.

In this work, preliminary results are presented for the investigations of diel (24 hour) processes controlling the flux of metals across benthic surfaces across the sediment-water interface.

Previous examinations of the Clark Fork River have demonstrated diel concentration changes in dissolved and particulate forms of Mn, Fe, Zn, Al, and Cu. These concentrations may be affected by daily biogeochemical processes in the benthic biofilm surfaces. It was additionally observed that the concentration of dissolved Mn and Zn cycles were in phase, suggesting that the cycles are linked by a common dependence to temperature, pH, photoperiod, and/or hydrological cycles.

A model has been proposed that links diel concentration changes to the dissolution and precipitation processes in association with biofilm and algal populations through a daily solubility and redox cycle. Initial results of laboratory and in situ experiments are presented providing insight into the role that benthic surfaces have in the diel concentration cycles of metals in streams. Fieldwork included the use of flux-chambers to isolate benthic surfaces from the flowing water column. The concentration changes of Mn and Zn within these isolation chambers are compared to the water column to isolate and identify the origin of the metal diel cycles.

Background

Diel concentration cycling of metals and certain non-metal compounds are well documented.^{1, 2, 3} Daily cycles of temperature, redox, photosynthesis, and respiration predicate cyclic chemical and physical changes in parameters including pH, alkalinity, specific conductivity, dissolved gasses (e.g. oxygen and

1 Parker, S. R., Poulson, S. R., Gammons, C. H., DeGrandpre, M. D., Biogeochemical Controls on Diel Cycling of Stable Isotopes of Dissolved O₂ and Dissolved Inorganic Carbon in the Big Hole River, Montana, *Environ. Sci. & Technol.*, 39(18), 7134-7140, (2005), DOI: 10.1021/es0505595..

2 Nagorski, S.A., Moore, J. N., 1999. Arsenic mobilization in the hyporheic zone of a contaminated stream. *Water Resources. Res.*, 35(11), 3441-3450.

3 Brick C. M. and Moore J. N., 1996. Diel variation of trace metals in the upper Clark Fork River, Montana. *Environ. Sci. Technol.* 30, 1953-1960.

carbon dioxide), redox speciation, and dissolved and particulate element concentrations. The transport and fate of species within a river system can have a significant impact on the health of the aquatic system and the surrounding environment. A better understanding of river system chemistry is necessary, and will lead to improved understanding of the mechanisms affecting diel concentration cycles for a variety of chemical species.

The timing of sampling during the diel cycles can significantly influence the resulting observations of analytes. For example, in the Fisher Creek, Montana, dissolved copper has been observed to undergo a 140% change in concentration during a 24-hour period.⁴ Similarly, dissolved zinc concentration changes of 500% have been observed in the Prickly Pear Creek, Montana.⁵

In a healthy river system, the diel pH cycle is driven by the photosynthesis and respiration cycle of the aquatic plant life and CO₂ consuming micro-organisms⁶, however temperature and pH dependant sorption to substrate, suspended inorganic surfaces, and organic surfaces may also play significant roles in the concentration cycles of both anions and cations in the river system.^{7, 8, 9, 10, 11, 12, 13}

Previous examination of the Clark Fork River, Montana has observed diel concentration changes in dissolved and particulate forms of Mn, Zn, Fe, Al, and Cu.¹⁴ These concentrations may be effected by daily biogeochemical processes in the benthic biofilm surfaces and algal surfaces. It was additionally observed that the concentration of dissolved Mn and Zn cycles were in phase, suggesting that the cycles are linked by a common dependence to temperature, pH, photoperiod, and possibly hydrological cycles.

4 Gammons, C.H., Nimick, D.A., Parker, S.R., Cleasby, T.E., McClesky, R.B., 2005 (2005). Diel behavior of iron and copper in a mountain stream with acidic to neutral pH: Fisher Creek, MT, USA. *Geochim. Cosmochim. Acta*, 69(10), 2505-2516, (2005), DOI:10.1016/j.gca.2004.11.020.

5 Nimick, D. A., Cleasby, T. E., McClesky, R. B., 2005. Seasonality of diel cycles of dissolved trace metal concentrations in a Rocky Mountain Stream. *Env. Geol.* 47, 603-614.

6 Pogue, T.R. , Anderson, C.W., 1994. Processes Controlling Dissolved Oxygen and pH in the Upper Willamette River Basin. *U.S. Geol. Surv. Water-Resources Investigations Report 95-4205*.

7 Fuller, C.C., Davis, J.A., 1989. Influence of coupling of sorption and photosynthetic processes on trace element cycles in natural waters, *Nature*, 340, 52-54.

8 Machesky, M., 1990, Influence of temperature on ion adsorption by hydrous metal oxides. Chemical modeling of aqueous systems I: *American Chemical Symposium Series 416*, edited by R. L. Bassett and D. C. Malchoir, 282-292.

9 Stumm, W, 1992. Chemistry of the Solid-Water Interface. John Wiley & Sons, Inc., NY.

10 Rhodda, D. P., Johnson B. B., Wells, J. D., 1996. Modeling of the effect of temperature on adsorption of lead(II) and zinc(II) onto goethite at constant pH. *J. Colloid Interface Sci.*, 184, 365-377.

11 Nimick, D.A., Moore, J.N., Dalby, C.E., Savka, M.W., 1998. The fate of geothermal arsenic in the Madison and Missouri Rivers, Montana and Wyoming. *Water Resour. Res.*, 34, 3051-3067.

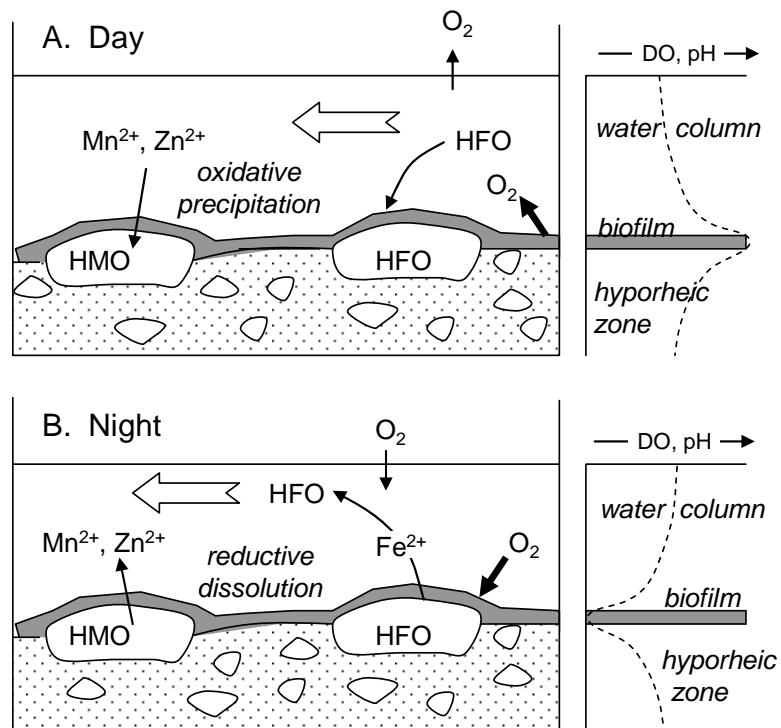
12 Trivedi, P., Axe, L., 2000. Modeling of Cd and Zn sorption to hydrous metal oxides. *Envir. Sci, & Tech.* 34. 2215-2223.

13 Jones, C. A., Nimick, D. A., McCleskey, B., 2004. Relative effect of temperature and pH on diel cycling of dissolved trace elements in Prickly Pear Creek, Montana. *Water, Air, Soil Poll.*, 153, 95-113.

14 Parker, S. R. Ph. D. Thesis, University of Montana, Missoula, MT, 2005.

A proposed model links these diel concentration changes to the dissolution and precipitation in association with biofilm and algal populations through a daily solubility and redox cycle.¹⁴ Other mechanisms that may effect the cycles are:

1. Changes in the influx of dissolved metals from the shallow groundwater.
2. pH and temperature dependant sorption to benthic and suspended surfaces
3. Daytime precipitation of Mn and Zn mineral phases of as impurities incorporated into calcite¹⁴.



The basis of this proposed model is that during the photoactive period photosynthesis creates an oxidative zone. The presence of this oxidative zone promotes the oxidative precipitation of hydrous ferric oxides (HFO) and hydrous manganese oxides (HMO). During the respiration period, the consumption of dissolved oxygen creates a reductive zone. This reductive zone promotes the reductive dissolution of HFO and HMO.

The precipitation of Zn has been linked to the formation of HMO.¹⁵ The half-life of Mn⁺² in well-aerated waters at pH 8 is approximately 100 days, while the half-life of Fe⁺² in a few minutes.¹⁶ This rapid reduction of iron and the slower reduction of manganese to the less soluble Fe⁺³ and Mn⁺⁴ can account for the nighttime buildup of dissolved Mn that is not accompanied with a corresponding increase in dissolved Fe. The kinetics of HFO formation is well established as a first order reaction, however the reduction of Mn⁺² to Mn⁺⁴ and the subsequent formation of HMO is an autocatalytic reaction.¹⁷ The autocatalytic formation of

¹⁵ Shope, C. L.; Ying X.; Gammons, C.H.; The influence of hydrous Mn-Zn oxides on diel cycling of Zn in an alkaline stream draining abandoned mine lands, *Appl. Geochem.* 21, 476-91, (2006).

¹⁶ Davison, W.; Iron and manganese in lakes, *Earth Sci. Rev.*, 34, 119-63, (1993).

¹⁷ Stumm, W.; Morgan, J.; Case Studies: Phosphorus, Iron, and Manganese. *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*; Wiley-Interscience: New York, 1970; 534-5.



HMO may account for the rapid decrease in dissolved Mn during photoactive periods.

Methods

The investigation was performed in three phases. Phase I consisted of

Figure 1: Second-generation flux-chamber, fitted with WTW Multi-340i.

attempting to reproduce the

dynamic cycles observed in nature in a laboratory environment. Phase II focused on the construction and testing of a viable flux-chamber for use insitu. Phase III utilized the flux-chamber to quantify the biota impact on the diel cycle of dissolved Mn and Zn.

Phase I was performed with the use of a commercial available 20 L aquarium with a side-mounted pump. The filtration system was not installed. The tank bottom was lined with bio-encrusted benthic material and filled to capacity with water obtained at the Arrowhead Recreation Park on the Clark Fork River in Deer Lodge, Montana. A control tank was filled with the water from the same sampling, but the benthic lining was not installed.

Each tank was allowed to rest for five weeks under a simulated photo-cycle to reestablish the photosynthesis and respiration cycles of the biomass. The photo-cycle was simulated by a broad-spectrum fluorescent lamp, controlled by an electro-mechanical timer. A light shield was installed to prevent ambient interference.

After the resting period, the tanks were spiked to 100 ppb Mn and 20 ppb Zn in the form $\text{Mn}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$. The photo-cycle was then extended to a 48-hour period (24 hours light, 24 hours dark) to exaggerate the effect of photosynthesis and respiration on the system. The parameters of the system were recorded with a WTW Multi-340i, recording pH, specific conductivity (SC), dissolved oxygen (DO), and temperature.

60 mL water samples were drawn every 24 hours, immediately prior to changing the photo status of the system. Samples were drawn during each sampling event, filtered (using a 20 μm syringe filter), and acidified to 1% with Trace Metal Grade (TMG) Nitric Acid (HNO_3). The experiment was preformed for 2 periods (96 hours). Each sample was analyzed by Graphite Furnace Atomic Absorption Spectroscopy (GF-AAS) for Zn and Mn concentrations.

Phase II focused on the development and construction of a flux chamber for in-situ isolation of biomass. The first design model was seriously flawed and failed to isolate the system from the river column . A redesigned model was developed that strong seal from the environment, and did not show positive

pressure or negative pressure leakage in 12-hour tests. The second-generation flux-chamber was approved by the Principle Investigator and used for Phase III.

Phase III integrated the flux-chamber into a diel sampling event at the USGS flow meter located in the Clark Fork River, approximately 20 meters south of the Milwaukee street bridge, in Deer Lodge, Montana. The stream parameters were monitored for 48 hours using a submersible datasonde, collecting pH, DO, SC, and temperature.

Water samples were taken in duplicate hourly from the river for 27 hours. One sample was acidified to 1% TMG HNO₃ without filtering. The other was filtered using a 0.1 μm cellulose filter, and acidified to 1% TMG HNO₃. Each were analyzed for Mn and Zn by GF-AAS and retained for analysis by Inductive Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

In conjunction to the diel sampling of the Clark Fork River, two flux-chambers were installed into the river and filled approximately half full of indigenous biota from the riverbed. One chamber was fitted with a submersible datasonde, the other fitted with a WTW Multi-340i. The latter chamber was used for sampling, while the former was sealed for the entire sampling event. Both chambers were filled with river water, vented to ensure no trapped gasses, and sealed. The chambers were allowed to rest on the riverbed, completely submerged to ensure temperature equilibration with the surrounding river. Chamber circulation was maintained by battery operated peristaltic pump, piped to each end of the chamber.

The sampling chamber was sampled in duplicate every bi-hourly, in the same method as the river. After each sampling, the sampling chamber seal was broken, the chamber flushed, filled, and submerged. This was conducted in conjunction with the sampling of the river so that the metal concentrations of the chamber could be assumed to be the same as the river at the time the chamber was sealed.

The in-situ was repeated on the Big Hole River, at the USGS river flow gage approximately 2 Km east of Wisdom, Montana.



Figure 2: Placing the sealed chamber onto the riverbed

Results

The tank experiment (Phase I) failed to produce a discernable cycle in the system. The concentration of dissolved Mn and Zn decreased to below detectable levels during the first photoactive period, but failed to increase during the respiration periods. pH and DO levels indicate that a viable photosynthesis

and respiration cycle was present within the tank. Figure 3 shows the sample results from Phase I. The shaded areas represent the dark periods.

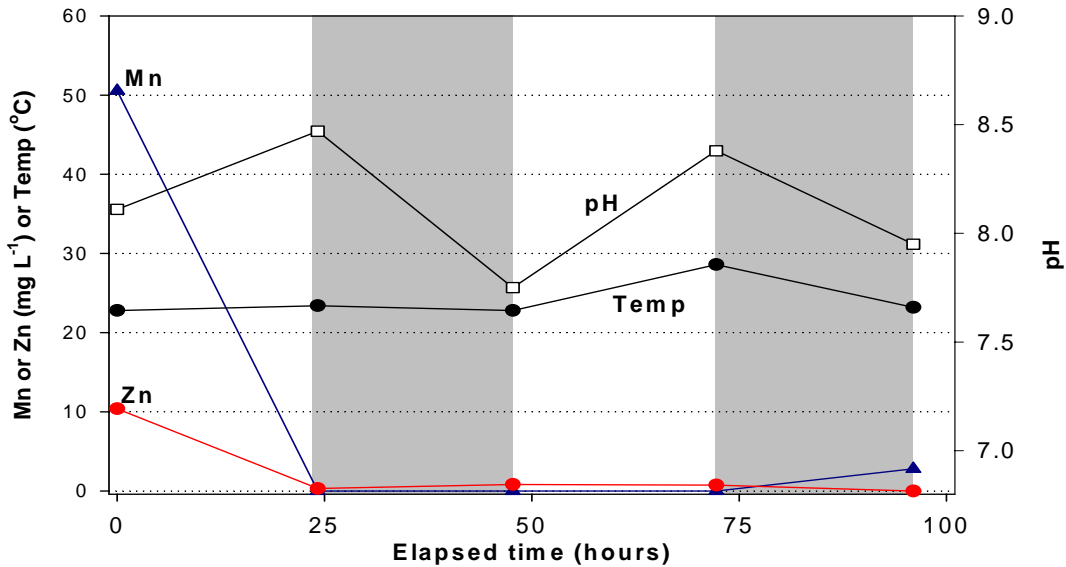


Figure 3: pH, DO, Mn, and Zn results from Phase I.

Preliminary results from Phase III in the Clark Fork River indicate that the chamber photosynthetic cycle increase the amplitude of the diel DO and pH cycles. Figure 4 details the DO and pH cycles in the Clark Fork River and compares the cycles within the chambers.

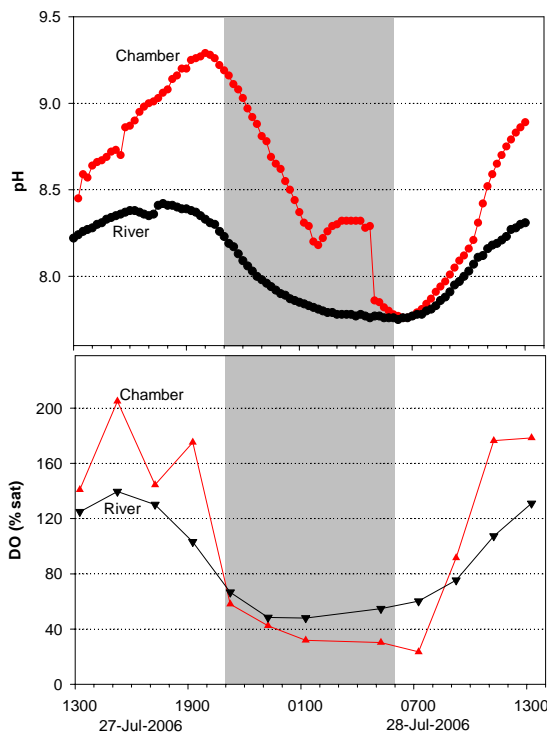


Figure 4: Comparison of pH and DO in the Clark Fork River versus the flux-chambers.

The chamber pH and DO cycles did demonstrate an amplitude increase, however the minimum pH in both the chambers and river were virtually equivalent. The isolation of the chamber from the air column above the river, and diffusion of excess DO to the air column could account for the substantially higher DO in the chamber compared to the river.

Preliminary dissolved metals analysis using a GF-AAS was performed to compare the cycle of dissolved Mn between the Clark Fork River and the chamber.

Figure 5 details the preliminary results. The percent of dissolved Mn change for each two-hour sampling period of the chamber are compared to the river. The chamber appears to increase the rate of dissolved metal sequestration, but does not seem to significantly influence the rate of

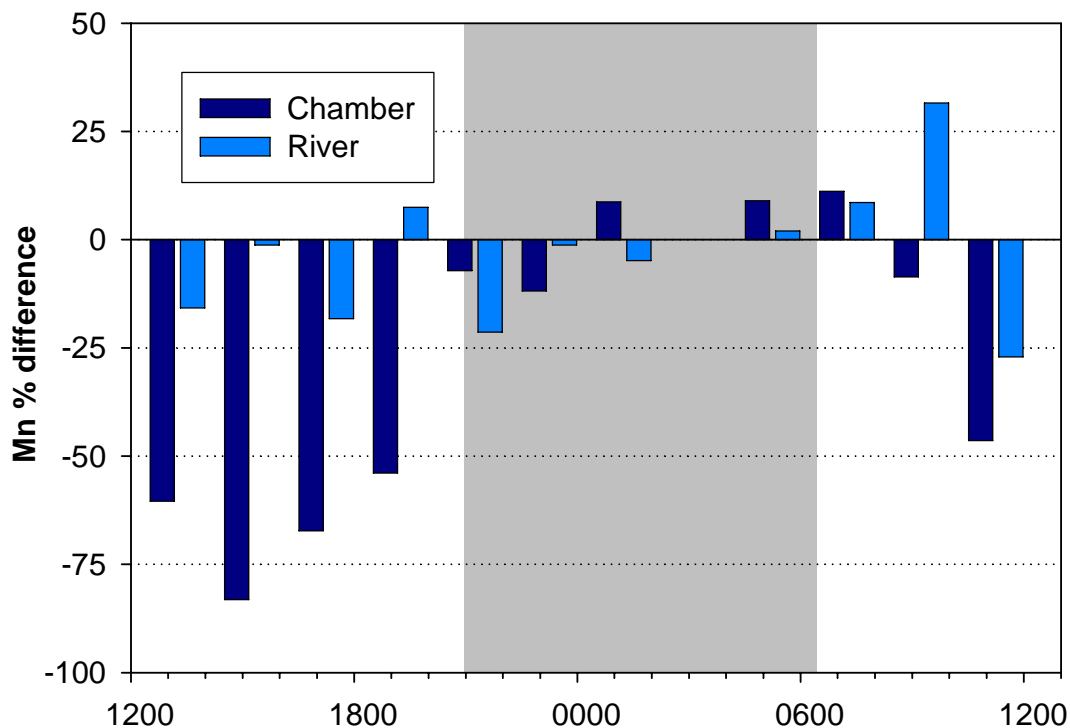


Figure 5: Percentage of dissolved Mn change during a two-hour period in the Clark Fork River and flux-chamber.

nighttime return of the dissolved Mn. A more complete analysis of all samples is currently underway using ICP-AES. Analysis of the replicate sampling of the Big Hole River is planned for early spring 2007, however, the natural dissolved metal concentrations of the Big Hole River may not reveal any further information. Analysis of the Big Hole River samples will be performed by Flame Atomic Absorption Spectroscopy (FAAS) prior to deciding if ICP-AES of the samples is warranted.

Conclusions

Completion of the ICP-AES analysis of the Clark Fork River samples is necessary to make any conclusions on the mechanisms that control the diel cycle of dissolved Mn and Zn. However, the preliminary data does seem to suggest that bioinorganic interactions within the river may have a significant impact on the dissolved Mn concentrations. It is not discernable if the bioinorganic interactions are in any way accountable for the observed increases in the dissolved Mn during the rivers respiration periods.

Additional research into this mechanism is planned, and has been proposed for funding to the United States Environmental Protection Agency and the National Science Foundation. This research will include the development of further flux-chambers, intended to isolate the sediment interactions with the river

and implement microelectrodes to establish the presence of the oxidative and reductive zones that the method suggest are present. If adequate funding is provided, the project will also include Scanning Electron Microscope examination of algal samples taken during a diel sampling event. This data will be used to determine the mineralogical makeup of the HMO and HFO on the algal surface, and analyze the algal samples for absorption and vacuolization of dissolved Mn versus the adsorption to the external cellular wall and associated biofilm colonies on the rivers biota.

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