INFLUENCES OF HYDROLOGY AND BIOGEOCHEMISTRY ON CONSTITUENT LOADS IN THE HELLS CANYON COMPLEX

Virginia Krause

ABSTRACT

The health and stability of reservoir ecosystems have been threatened by an insurgence of methylated mercury that rapidly bioaccumulates through the food chain. The Hells Canyon Complex (HCC), a reservoir system in Idaho, provides the ideal conditions for such methylation processes during its seasonal stratification events. The fluxes for two important constituents (sulfate, nitrate) of mercury methylation within the reservoirs were calculated over a 3-year timeframe using a USGS computation package and assessed in terms of mass balance relationships. It was determined that sulfate loads are hydrologically driven, while nitrate loads deviate from discharge and may be reflective of redox transformations within the reservoir. These results have important implications as to the production, fate, and transport of methyl mercury through the reservoir system.

INTRODUCTION

Mercury methylation has become a prominent concern for many river and reservoir systems due to methyl mercury (MeHg) production in anoxic and stratified waters. The HCC of the Snake River, a series of three hydroelectric reservoirs, exhibits seasonal stratification and high deposition of Hg(II) that stimulate the internal production of MeHg.[1] This production is promoted in the presence of dissolved organic matter (DOM) and terminal electron acceptors (e.g., iron, sulfate), which are commonly observed in anoxic waters of both the Brownlee and Hells Canyon reservoirs within the HCC (Figure 1).[1,2] Terminal electron acceptors and precursory compounds for DOM (e.g., nitrate) are of particular importance

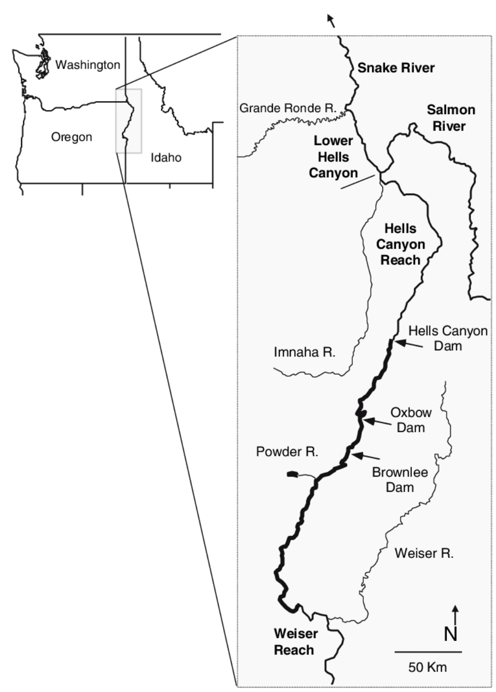

Figure 1. *Map of Hells Canyon Complex reservoir series within the Snake River, ID.*[3]

because of their influences on the bioavailability of anerobic bacteria that aid in the methylation process. Therefore, an understanding of the behaviors of constituents such as nitrate (NO_3^-) and sulfate (SO_4^{2-}) is necessary to further investigate MeHg production. Both NO_3^- and SO_4^{2-} are expected to follow trends of discharge seasonally, with high concentrations in winter and early spring and low concentrations through summer and fall.[4,5] Consequently, changes in flux during anoxic conditions may not be a direct reflection of decreased discharge, but rather of redox transformations that reduce the concentrations of SO_4^{2-} and NO_3^-. During events of stratification, these constituents undergo redox transformations that alter their chemical availability and flux rates through the reservoir system. SO_4^{2-} reduction occurs in the hypolimnion of a stratified system, while nitrogen cycling can occur throughout the metalimnion and epilimnion.[6,7] Chloride (Cl^-) can be used as a reference constituent to measure changes in load, due to its inert properties and propensity to follows source and sink behaviors of discharge.[8] This research investigates the impact of discharge and stratification trends on constituent loads of important compounds (NO_3^-, SO_4^{2-}) to MeHg production in an effort to identify the major controlling factors, hydrologic or redox transformation, of flux rate changes. Understanding the movement and controlling factors of such constituents will help identify locations and controls of MeHg production.

OBJECTIVES

The overarching goal of this study is to contribute to the development of a Total Maximum Daily Load (TDML) for the HCC using principles of mass balance. Transformations of important compounds to MeHg are expected to occur in the anoxic conditions of the reservoirs, which may be reflected in the net gains or losses of the constituent fluxes. Specifically, this goal can be broken down into three main objectives:

1. Investigate mass balance dynamics for discharge in the HCC.
2. Establish baseline net gain or loss parameters for a conservative analyte (Cl^-) to use for comparison of other constituent trends.
3. Evaluate monthly net gains and losses from SO_4^{2-} and NO_3^- compared against the baseline to determine any major deviations in behavior unaccounted for by discharge.

These specific objectives will produce graphic representations of constituent net gains or losses across the entire reservoir series in relation to discharge.

HYPOTHESIS

The flux rates of three main constituents (Cl^-, NO_3^-, SO_4^{2-}) will be assessed in this study, leading to the development of three individual hypotheses.

1. Changes in chloride flux will be directly associated to changes in discharge, allowing chloride to act as an inert tracer of the system.
2. Sulfate reduction will occur in the hypolimnion to decrease sulfate loads through the HCC system at a degree that cannot be reflected through discharge alone.
3. Nitrate loads will vary more dramatically compared to other seasonally dependent analytes and discharge because ubiquitous nature of denitrification throughout the water column.

METHODS

Constituent Loads

The fluxes for Cl^-, NO_3^-, and SO_4^{2-} were calculated over a 3-year (2018-2020) time frame using the U.S. Geological Survey *R* package Loadflex. This package compares three methods of load determinations: interpolation, rloadest, and composite. The interpolation model connects observations through linear fits to establish predicted points and rloadest fits predictions through maximum likelihoods. The composite model, which was selected for this research, creates predicted points through regression to generate residuals fit through interpolations. The interpolated residuals are then corrected via error estimations, allowing the composite model to have the strongest corrections to uncertainty bias.[9] The codes for each constituent were run for four locations: Brownlee Inflow (Weiser), Brownlee Outflow, Oxbow Outflow, Hells Canyon Outflow. The preceding outflow site was assumed to be the inflow of that successive reservoir. Due to the size and degree of stratification, as well as previous studies of the system, the Brownlee Reservoir experiences the most change in discharge and chemical processes, and therefore was investigated in greater detail through this study. Additional data was collected for the Oxbow and Hells Canyon reservoirs but were not assessed in as much detail. Concentrations and total flux rates were established at the daily, monthly, and annual timescale. Corresponding discharge data used in instantaneous load estimates was also provided from daily streamflow gauges monitoring through the U.S. Geological Survey.

Net Gain or Loss

The calculations of net gain or loss for each constituent relied on the principles of mass balance, which state that changes in the reservoir are defined by the change in outflow to inflow (Eq. 1).

$$Net\ Change = Outflow - Inflow \qquad \textit{Equation 1}$$

If the resulting value was positive, the system experienced a net gain and if the resulting value was negative, the system faced a net loss. These gains and losses were then compared to mass balance dynamics of discharge at a monthly scale over the time series. An assessment of the degree of trend matching between constituent load and discharge (i.e., both gain for a given month, both lose for a given month, no match for a given month) allowed for determinations of whether the constituent was hydrologically controlled or if there were other potential processes driving movement.

RESULTS/DISCUSSION

Discharge

In order to understand constituent load dynamics, it is first imperative to assess the general hydrologic schemes of the HCC. A compilation of streamflow gauge data collected from USGS operated sites allowed for the development of hydrographs for each of the three reservoirs including initial inflow to the system (Figure 2).

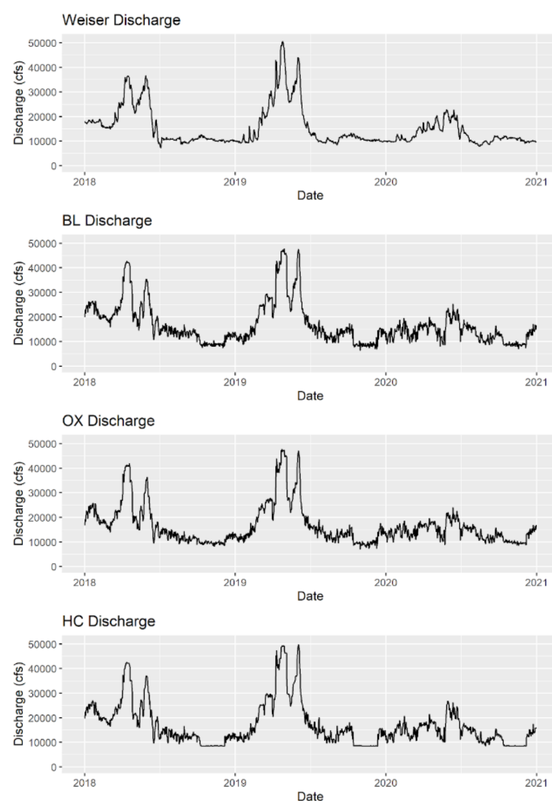

Figure 2. *HCC reservoir hydrographs from where (a) Weiser Discharge= initial inflow of the Brownlee Res. (b) BL Discharge =Brownlee Res. outflow, (c) OX Discharge= outflow of the Oxbow Res. and (d) HC Discharge=Hells Canyon Res. outflow.*

Little variation occurs in terms of magnitude and trend across the three reservoirs, confirming the notion that most of the hydrologic processes occur in the Brownlee Reservoir. Various flow regime components can be identified through these hydrographs, including peak magnitude flow that aligns to snowmelt and dry season baseflow that aligns with the periods of stratification in the Brownlee and Hells Canyon reservoirs.

Chloride

The expectation for Cl^- was that it will act as a conservative analyte through the HCC, where a majority of the changes to Cl^- will be reflected by changes in discharge. The net gains and losses for each should therefore appear very similar between the two processes (Figure 3).

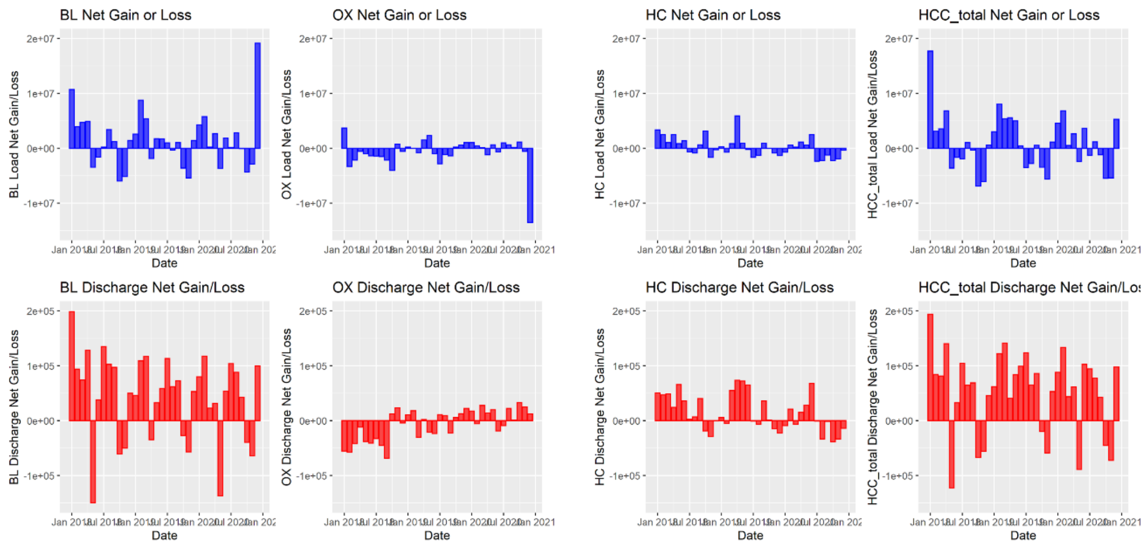

Figure 3. *Monthly net gains and loses calculated for (blue) chloride loads and (red) discharge across the HCC, where BL=Brownlee Reservoir, OX=Oxbow Reservoir, HC=Hells Canyon Reservoir, and HCC_total=total HCC complex.*

Observations of these reservoir trends further confirm the theory that a majority of the hydrologic and chemical processes occur in the Brownlee Reservoir, as most of the net gains and losses of Brownlee dominate the trends of the total complex (Figure 3). Therefore, only the Brownlee reservoir will be considered for the remainder of this study.

In isolating the Brownlee Reservoir, it can be seen that during times of high discharge the reservoir acts as a source of Cl^- and during net discharge losses the reservoir acts as a sink (Figure 4). *The overall trending of gain or loss matches between Cl^- loading and discharge 92% of the time, meaning only 8% of the monthly mass balances deviate*. This 8% deviation may be explained through outliers in Cl^- load that were not properly adjusted, as seen in the large spike in Dec. 2020 (Figure 4). Additionally, minor additions of Cl^- from adjacent tributaries may not have been proportionally reflected in discharge. Despite these minor deviations in trend, it can be said that with a 92% match in trend between discharge and Cl^- that Cl^- is hydrologically driven through the system and acts as a semi- reliable tracer.

Sulfate

During events of stratification and mercury methylation production, SO_4^{2-} may undergo redox transformations that cause reductions of SO_4^{2-} into sulfides. This process occurs via sulfate-reducing bacteria that exist within the hypolimnion of anoxic environments.[6,7] Since the Brownlee Reservoir experiences thermal stratification, it was theorized that the reservoir will act as an overall sink to SO_4^{2-} that does not align with source and sink trends of discharge.

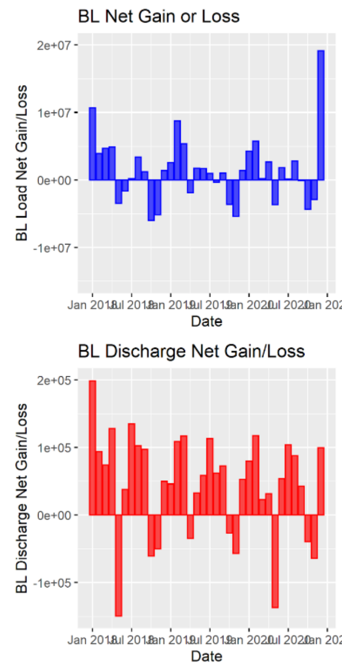

Figure 4*. Monthly net gains and losses for (blue) Cl^- loads and (red) discharge.*

An assessment of the net gains and losses for both SO_4^{2-} and discharge reject this theory, as a majority of the net gains and losses in SO_4^{2-} are matched by the trends of gains and losses in discharge (Figure 5). *The two processes match in terms of both gaining or both losing through 89% of the dataset, with only 11% opposite trend.* This means that SO_4^{2-} is mostly hydrologically driven through the system based on its mass balance comparison to discharge. Due to the nature of stratified systems and lack of underflow, it is possible that SO_4^{2-} reduction still occurs alters the concentrations to a significant degree in this system but does not reach into the thermocline and therefore is not reflected by load calculations. A more detailed analysis stratification trends, specifically in the SO_4^{2-} loads during periods of destratification when the hypolimnion beings to mix back into overflow, would be useful in future determinations.

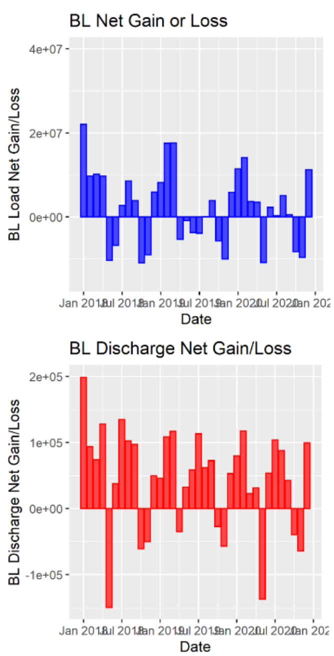

Figure 5*. Monthly net gains and losses for (blue) SO_4^{2-} loads and (red) discharge.*

Nitrate

Unlike SO_4^{2-}, the redox transformations of NO_3^- can occur throughout the entire water column during events of stratification.[4] This creates a higher likelihood of chemical alterations to the constituent load. Using the same principles of mass balance as for Cl^- and SO_4^{2-}, the net gains and losses for NO_3^- were calculated and compared against that of discharge (Figure 6).

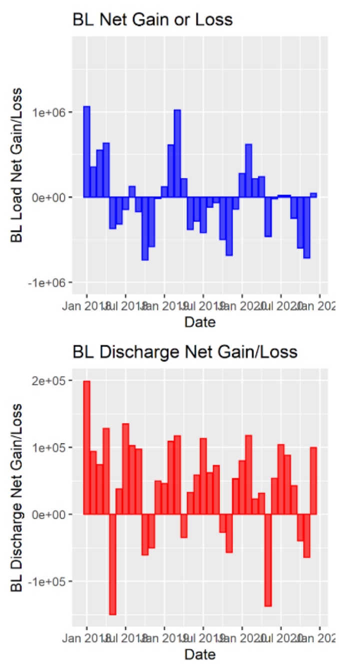

***Figure 6**. Monthly net gains and losses for (blue) NO_3^- loads and (red) discharge.*

There is a much clearer pattern of seasonality in the nitrate gains and losses that aligns with the periods of reservoir stratification, where each stratified period acts as a major sink for NO_3^-. *In comparing the net changes in constituent load to discharge, there is only a 64% match, meaning that 36% of the timeframe NO_3^- loads do not align with discharge net gain or loss.* Therefore, NO_3^- is not conclusively driven by hydrology, and likely have biogeochemical processes like denitrification that cause these larger deviations in monthly trend.

Land management practices may also influence the trends of nitrate, specifically from agricultural water demands. In Idaho, there are no strict regulatory practices for water withdraws in public systems, so upgradient of the HCC in the Snake River large water withdraws are taken and later returned as agricultural return water. This returned water is contaminated with farming products and excess nutrients from fertilizer that can alter the concentrations on NO_3^- that travel into the HCC on a seasonal basis.

CONCLUSIONS

The main objective of this investigation was to assess the dynamics of the HCC using mass balance to identify whether hydrology or biogeochemistry controls constituent loads. Three major hypotheses were defined through this objective: (1) Cl^- will act as a conservative analyte to provide a baseline, (2) SO_4^{2-} reduction will be reflected as a net loss that deviates from discharge, and (3) NO_3^- loads will vary most dramatically due to redox transformations. Through a comprehensive analysis of the net gains and losses for constituents loads and discharge, the first and third hypotheses were supported, and the second hypothesis was rejected. Trends in Cl^- and SO_4^{2-} load matched well to that of discharge, meaning they are likely hydrologically controlled, while NO_3^- loads varied more significantly, which indicates potential reflection of redox transformations. Understanding the drivers of constituent loads through the HCC provides necessary fundamental analysis for locations and trends of MeHg production as well as seasonal trend dependence. Additionally, this research will help to inform the development of a TMDL for the HCC which will be used to define reservoir operations. The scientific methods and results of this study also provide the foundation for work outside the HCC in other mercury-impaired systems, like that of the Santa Clara, CA reservoir systems.

LIMITATIONS

This report was conducted as part of an on-going project within the HCC and therefore reflects preliminary results based on the available data of the system. Further investigations on trends and statistical relationships are necessary for definitive analysis. An additional limitation includes a lack of available data of adjacent tributaries that contribute to the Brownlee Reservoir.

ACKNOWLEDGEMNTS

This work is financially supported through the Idaho Power Company and US Geological Survey. Research pertaining to this report is conduced under advisement of Dr. Brett Poulin at the University of California, Davis. Austin Baldwin of the USGS has provided constituent load codes associated to the open source USGS Loadflex package.

CITATIONS

[1] Baldwin et al. (2020). “Seasonal dynamics and interannual variability in mercury concentrations and loads through a three-reservoir complex.” *Environ. Sci. Technol., 54* (15), 9305-9314

[2] Poulin et al. (2019). “Geochemical factors controlling dissolved elemental mercury and methylmercury formation in Alaskan wetlands of varying tropic status.” *Environ. Sci. Technol., 53* (11), 6203-6213

[3] Braatne et al. (2008). “Analyzing the impacts of dams on riparian ecosystems: A review of research strategies and their relevance to the Snake River through Hells Canyon.” *Environ. Manage., 41* (2), 267-281

[4] Huntington et al. (1994). “Hydrologic processes controlling sulfate mobility in a small forest watershed.” *Water Resour. Res., 30* (2), 283-295

[5] Vanni et al. (2001). “Dissolved and particulate nitrate flux from three adjacent agricultural watersheds: A five-year study.” *Biogeochemistry, 54*, 85-114

[6] Boyko et al. (2021). “Biogeochemical cycling of sulfur, manganese and iron in ferruginous limnic analog of Archean Ocean.” *Geochim Cosmochim. Ac., 296*, 56-74

[7] Rysgaard et al. (1995). “Seasonal variation in nitrification and denitrification in estuarine sediment colonized by benthic microalgae and bioturbating infauna.” *Mar. Ecol. Prog. Ser., 126*, 111-121

[8] Svensson et al. (2012). “Is chloride a conservative ion in forest ecosystems?” *Biogeochemistry, 107*, 125-134

[9] Appling et al. (2015). “Reducing bias and quantifying uncertainty in watershed flux estimates: the R package loadflex.” *Ecosphere, 6* (12), 1-25