RMBL Research Application 2024
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Research Title: Diurnal Dissolved Oxygen & Iron Concentration Fluxes in Beaver Floodplains

Introduction:

Gravel-bed river floodplains are fundamental environmental contributors within glaciated mountain landscapes as they have disproportionately concentrated biogeochemical, hydrologic, and ecological processes within their converging terrestrial and aquatic systems.[1,2] They perform critical groundwater recharge, promote riparian habitat, optimize geodiversity, and support hydrologic, sediment, nutrient, and organic matter (OM) exchanges integral to ecosystem productivity and biodiversity.[3] In terms of anthropogenic benefits, floodplains deposit fertile soils rich in minerals and OM to surrounding farms, while dampening peak flows, reducing flood risks, and decreasing flood depths downstream via slowing runoff and storing excess water.[4–6] Floodplain systems are also especially adept to combat ongoing impacts of climate change.[7] By increasing hydraulic gradients and biogeochemical cycles, it not only allows them to eclipse climate impacts like aridification and hydrologic extremes, but also to store and remobilize heavy metals, cool stream temperatures, and serve as crucial carbon sinks.[8,9]

As one of Colorado's most sensitive living resources, floodplain ecosystems, their functions, and downstream capabilities are reliant on the hydrologic engineering of the North American beaver (*Castor canadensis*).[10] Beavers promote hydraulic connectivity between floodplains and interdependent rivers and streams, generating key alluvial zones and placing the extant Castorimorpha as central agents of climate change resilience.[11] Historically, beaver-assisted natural accumulation of OM cultivated anaerobic riverine waters. These waters were extensive and universally prevalent in North American streams.[12] With the introduction of the European fur trade in the 16th century, over-trapping, widespread wood removal from streams, and extensive land use alterations led to the virtual eradication of the Colorado (and much of North America's) beaver populations.[13,14] As a result of the biological invasions, the natural geomorphic, biogeochemical, hydrological, and ecological homeostasis of floodplain ecosystems were substantially compromised.

Beaver dam analogs (BDAs) are man-made structures that offer a low-tech process-based (LTPB) technique designed to leverage crucial environmental processes and benefits of natural beaver dam's.[15] Re-instigating these natural processes enlivens endangered floodplains, returns channel stability, and raises historically-depleted hydraulic connectivity.[16] BDAs are able to emulate natural beaver dam's maintenance of heightened flows later into the summer months, enhance surface and groundwater storage, level flooding events' peak flows, and amplify biogeochemical cycling of nutrients– a vital tool in mitigating stream-floodplain degradation.[11,17] Both restorative LTPB techniques and natural beaver dams are fundamental for conservation efforts in glaciated mountain ecosystems. However, these systems require an in-depth analysis of their biogeochemical significance.[2] Specifically, diurnal cycles and their fluctuations may drive a number of the capabilities of these systems.

Floodplain's ability to vary surface water flows, increase water temperature variations, and thus, enrich their microbial community diversity. This enrichment expands the riverine waters' redox potential. Oxidation-Reduction potential (ORP) measures the reducing or oxidizing capacity of a system, which determines a river or floodplain's ability to break down waste products or contaminants and to recycle available carbon and nutrients into soluble, mobile forms. That capacity is typically measured at the sediment-water interface.[18] ORP can be used to quantify the redox role of floodplains, and that role dictates the efficiency at which they cycle nutrients or store excess carbon dioxide.[19] Beaver ponds are especially rich in dissolved organic carbon (DOC), which is an important electron source for riverine redox reactions.[20] Microbes catalyze those redox reactions.[21] Utilizing the system's use of microbial pathways to generate resistance to acidity changes, the redox chemistry of that system can be evaluated.[19,22] This signifier is the alkalinity, or the buffering capacity, of the floodplain systems. Alkalinity measurements are therefore indicative of the aggregate amount of microbial activity.[23]

Dissolved oxygen (DO) is also an insightful barometer of microbial activity. Increased water temperatures, elevated nutrient levels, or heightened biotic activity reduces the solubility of oxygen in water, resulting in lower recordings of DO. Inversely, cooler water temperature, lessened nutrients, or decreased biotic activity increases the solubility of oxygen, producing higher DO measurements.[24] These indicators place DO as the master variable in controlling microbe operations, determining solubility and mobility of heavy metals, and mediating the redox dynamics of riverine waters. Elements and nutrients occurring in natural waters– like iron (Fe), manganese (Mn), carbon (C), oxygen, (O), and nitrogen (N)– have greater sorption capacity in plants when they are soluble and easily transported. This cycling is aided by the North American Beaver's hydrologic engineering. In the case of iron, the less frequently bioavailable ferrous (Fe II), is more soluble, and therefore more easily absorbed into the system, than the more stable ferric (Fe III).[25] Fe III is rarely free in a riverine system and will always fall out in solid form, typically ferrihydrite (Fe_3O_2).[26] Fe II, conversely, is always present and free in a riverine solution.[27,28] If the nutrients are insoluble or a system is too dry, nutrients present are unable to be transported into or remediated by the system. Beaver assisted environments ensure that those soluble nutrients are readily present, including Fe II.[29] Given that iron is highly redox-sensitive, speciation of this river corridor metal is therefore highly indicative of the redox conditions within a system.

Beaver dam systems are critical in the face of changing climate. They mitigate hydrologic extremes like extreme precipitation events, counteract warming riverine temperatures while maintaining water quality, and dictate indispensable biogeochemical cycles which keep essential elements available to plants and other organisms. [7,29] However, evolving climate extremes threaten reduced specific conductivity, depleted summer baseflow, and lessened capacities to store carbon, nutrients, and heavy metals in the floodplain. This lessened capacity is illustrated by decreased DO levels, signifying more insoluble nutrients that cannot be transported amongst the system. The role of floodplains is therefore reconditioned from serving as carbon sinks and disproportionately concentrated architects of biogeochemical cycling to becoming carbon sources, emitters of ammonia gas, and generators of an overabundance of insoluble nutrients which contributes to eutrophication.[30] These impacts will be worsened by proliferating aridification and depleted baseflows.[31]

As such, the redox dynamics within a floodplain system's surface waters– be it BDA, natural, or untreated– may serve as the foundation of riverine biogeochemical performance. Yet, much of this keystone redox fluctuation in BDA, natural, and untreated systems is predominantly documented during daylight hours, where DO is at an all time high. The diurnal fluctuations in DO measurements demonstrate daytime super saturation of DO levels, while nighttime measurements show a swing to near anoxic conditions. Thus, a substantial portion of aerobic respiration and redox dynamics is underrepresented.[29] Previous studies have examined redox dynamics within river-floodplain systems, but few have explored the complete 24-hour cycle of redox flux across natural beaver dams, artificial beaver dams, and untreated floodplain waters.

I propose an investigation into the factors of 1) how do BDAs, natural, and untreated systems compare with diurnal redox variations in floodplain waters, 2) how do redox dynamics compare between ponds, seeps, and channel waters, 3) how do they compare between pond types, and 4) are the redox fluctuations microbially mediated?

I aim to explore these questions by examining quantitative changes that test:

H1) BDA and natural damned floodplain segments exhibit greater DO levels at night,
H2) heightened Fe II concentrations,
H3) increased alkalinity measurements, and
H4) elevated redox activity.

<u>Specific Methodologies:</u>

1.1 Site Description & Sample Collection

Here, we distinguish pond type to be three categories: return seep, in-stream or channel, and pond; and floodplain systems consist of three designations: Beaver Dam Analogs (BDAs), natural, and untreated. Surface water samples will be collected at the bottom of each water body of interest as our analysis is focussed on the soil-water interface. Samples will be collected along three separate site locations: the Land Trust Confluence Parcel (Crested Butte, CO; 38°52'41.64"N,106°58'45.07"W), the East River "Pump House" (Mount Crested Butte, CO; 38°55'39.49"N, 106°57'30.19"W), and Trail Creek Floodplains (Almont, CO; 38°54'3.55"N, 106°37'8.08"W) in July- August of 2024. Discrete samples will be extracted using 60 mL plastic syringes and filtered through single-use hydrophilic 0.45-μm filters. Collective data from the selected sites will create a comprehensive picture of the hydrological and redox conditions across the study area.

Aqueous phase chemistry measurements including alkalinity, dissolved oxygen (DO), Fe(II), pH, and specific conductivity will be performed in situ immediately after extraction. Triplicate samples for Fe(II) measurement by the ferrozine method will also be immediately placed into hydrochloric acid washed vials, shaded from sun exposure, and kept on ice to preserve redox conditions. For the Land Trust Confluence Parcel (CP), sampling will be taken from 2 pond locations, 3 return seep locations, and 2 in-stream locations. The East River, "Pump House," site sampling will also extract from 2 pond locations, 3 return seep locations, and 2 in-stream locations. The Trail Creek location exclusively focuses on pond locations as those are the largest bodies of water being monitored or manipulated, and therefore the greatest indicators of the success of BDA system emulation. Sampling includes 3 BDA ponds, 2 locations along a degraded flood plain (to utilize as controls for redox conditions), and 3 natural beaver dam ponds (2 in-stream, and 1 hillslope).

1.2 Sample characterization

The following parameters will be measured at each sampling locations: dissolved oxygen, pH, specific conductivity at 25 °C, temperature, Fe(II) concentrations, and alkalinity at each sampling site. Additional qualitative data of the systems, including algae presence and vegetation types, will also be recorded.

1.3 Dissolved Oxygen Calorimetry & Optode Oxygen Monitoring

Dissolved Oxygen is to be spot measured utilizing two methods: a V-2000 Multi-Analyte Photometer, and DO miniDOT Loggers (for 24-hour continuous monitoring).

The CHEMetrics V-2000 Multi-Analyte Photometer is a portable microprocessor-based LED colorimeter calibrated using a 13 mm zeroing vial containing distilled water prior to each series of measurements.[32] CHEMetrics self-filling, premeasured 13 mm ampoules uptake the water sample out of

25 mL within a sample cup, are placed into the photometer, and then the photometer will dictate the DO concentration of the spot measurement in parts per million (ppm). The photometer employs the Indigo Carmine method in which the sample turns blue in proportion to the presence of ppm oxygen.

Calibration of the miniDOT Logger is completed by Precision Measurement Engineering (PME) annually, and no adjustment is necessary by the user. To investigate diurnal DO fluctuations, the miniDOT will be left in the system over a series of days as it is a fully submersible logger which records DO and temperature measurements. Its oxygen sensor is an optode that utilizes a fluorescence method to measure DO concentration in water, and records the data on an internal SD card to be collected and analyzed after retrieval.

1.4 pH & Specific Conductivity Multi Parameterization

Specific conductivity at 25 °C and pH will be measured using a Thermo Scientific Orion Star A pH/ Conductivity Multiparameter Meter and accompanying field probes for pH and specific conductivity. The Multiparameter Meter is calibrated by rinsing the pH and conductivity probes with distilled water, blotting off excess water, and placing into set pH and conductivity solutions. For pH, calibration measurements are taken for pH values of 4.01, 7.00, and 10.01. For conductivity, calibration measurements are taken for values of 84 μS/cm, 447 μS/cm, and 1413 μS/cm. Temperature corrections are made during calibration as necessary.

For in field measurements, aliquots are extracted using 60 mL plastic syringes and filtered through single-use hydrophilic 0.45-μm filters into a 15 mL Falcon conical tube and a 50 mL Falcon conical tube, where the pH and conductivity probes are placed, respectively. The Multiparameter Meter results are then manually recorded.

1.5 Colorimetric Measurements of Fe (II) Concentration

Fe (II) concentrations will be taken by applying two methods: the ferrozine method and in situ colorimetry Fe(II) measurements with (insert name of CHEMetrics kit) using the V-2000 Multi-Analyte Photometer).

Utilizing an ISCO sampler and intake tubing staked in a water body of interest at the select depth at the sediment-water interface in order to minimize sediment disturbances during measurements. The sampler automatically collects at the pre-set timed intervals (eg. every hour on the hour), with the sample volume of 100mL to capture the diurnal fluctuations in Iron (II). Sampling also undergoes purge cycles to clear the intake tubing before each collection period in order to avoid contamination of the sample. The samples are collected into hydrochloric acid washed bottles, collected after a complete sampling cycle, shaded from sun exposure, and kept on ice to preserve redox conditions of Iron (II) concentrations until imminent lab analysis using the ferrozine method.[33]

Truthing for this 24-hour ferrozine sampling method will be executed with the colorimetric CHEMetrics Fe (II) test kit. For the colorimetric method using the photometer, Iron (II) will be measured by PDTS where resulting ferrous iron reacts with PDTS [3-(2-pyridyl)-5,6- bis(4-phenylsulfonic acid)-1,2,4,-triazine disodium salt] to form a pink colored complex with results expressed as ppm (mg/L).[34]

1.7 24-hour Sampling

During the first ISCO deployment for the 24-hour sampling, simultaneous in-person 24-hour verification of Fe (II) concentrations will occur. Tentative sampling times for the in-person diurnal cycles are 11:00 am, 2:00 pm, 5:00 pm, 8:00 pm, 11:00 pm, 2:00 am, 5:00 am, 8:00 am, and 11:00 am. Following the 24-hour sampling, ISCO samples and sampler will be retrieved the following day.

Surface water samples are to be taken from the 24-hour bottles within the sampler, placed into 15 mL Falcon conical tubes, and returned to the lab for processing and analysis utilizing the ferrozine method. Once in the lab, bottles will be cleaned using hydrochloric acidified soap and distilled water. After the initial verification to ensure accurate Fe (II) values, in situ ISCO sampling will continue on its own, as truthing of the ferrozine method has been completed in prior research.[35]

1.7 Total Alkalinity Titration

Total Alkalinity is measured utilizing the CHEMetrics Alkalinity (total) Titrets test kit for 10-100 ppm which utilizes sealed, single-use acid titrants and a mixed pH indicator solution. The water extraction to be tested is filtered and filled to the 20 mL mark in the sample cup where 6 drops of the S-9800 activator solution is thoroughly mixed in. The sample will then be green. If it turns pink, the total alkalinity is 0 ppm and no further titration is needed. Next, the valve assembly is fit over the tip of the Titret ampoule up to the white reference line, and the ampoule is snapped. Inserting the Titret assembly into the Titrettor, the control bar on the valve is used accordingly to pull in amounts of the sample until a color change from pink to green. Once the color within the ampoule is green, the ampoule and Titrettor are separated, the ampoule is placed into the photometer, and then the spot measurement's total alkalinity is expressed in parts per million calcium Carbonate (ppm $CaCO_3$).[36,37]

1.8 Statistical Analysis

In order to determine the relationships and variations between DO and Iron(II) concentrations across pond types and floodplain systems, a linear regression analysis will be performed. Box-and-whisker plots will be employed to provide a cleaner representation of the data trend while allowing multiple sets of data and detail to be presented, including the interquartile range, outliers, and medians of DO or Iron(II) concentrations across floodplain systems and pond types.

In terms of data handling, triplicate samples will be collected for all Iron (II) concentration measurements at each sampling location, in order to reduce random error, ensure consistent results, identify outliers, and provide multiple data points for each condition.

To determine the correlation between DO and Iron (II) concentrations, the regression coefficient, p-value, and confidence intervals will be calculated and visualized within the statistical software R or Python. Employing these analyses assists us to determine the statistical significance and strength of that redox relationship.

Timeline (July 8th-August 9th)

Each week, for a 3-week intensive sampling campaign, will consist of surface water sample collection for quantifying the aqueous chemistry and DO levels of each of the three sites; however, the 24-hour sampling will adjust sites weekly. Prior to the sampling campaign, in-lab preparation of ferrozine reagents, 24-hour sampling vials, and all materials for in-field activities will be prepared, labeled, and organized for convenience during sampling weeks. The following schedule will be used:

Week	Weekday	Tasks
Week 1 (July 8th- 12th)– Confluence Parcel Focussed	Monday	Deploy DO loggers for pond, return seep, and channel locations at Confluence Parcel. Afternoon at East river, "Pump House," location where we'll complete full sampling of colorimetric DO, multi parameterization of pH and Specific Conductivity, sampling for later Fe (II) colorimetric testing, and alkalinity titrations. (Note: Iron (II) CHEMetrics test kits will not have arrived yet) Proposal peer review due.
	Tuesday	At Trail Creek, we will stake necessary sample tubing in ponds to minimize soil-water interface disturbances during measurements, plot GPS at Trail Creek pond, return seep, and channel locations, and complete full sampling (ie. colorimetric DO, multi parameterization of pH and Specific Conductivity, Fe (II) colorimetric testing, and alkalinity titrations. (Note: Iron (II) CHEMetrics test kits will have arrived)
	Wednesday	Full sampling at Confluence Parcel, and set up ISCO for 24-hour sampling on Thursday.
	Thursday	ISCO sampling running. Simultaneous spot measurements for in-person 24-hour verification sampling of Fe (II) will occur. Tentative sampling times: 11am, 2pm, 5pm, 8pm, 11pm, 2am, 5am, 8am, 11am.
	Friday	Nap. In-field at Confluence Parcel, retrieve ISCO, pull samples from the 24-hour bottles, and pull DO loggers. In-lab, plot DO data, process ISCO samples, clean ISCO bottles, and prepare materials for next week.
Week 2 (July 15th- 19th)– Trail Creek Focussed	Monday	At Trail Creek, full sampling, set up ISCO for 24-hour sampling, and deploy DO loggers for Natural pond, hillslope pond, BDA pond, and degraded pond.
	Tuesday	At Confluence Parcel, full sampling. GIS training.
	Wednesday	At East River, "Pump House," full sampling. ISCO running at Trail Creek.
	Thursday	At Trail Creek in-field, retrieve ISCO, pull samples from the 24-hour bottles, and pull DO loggers. In-lab, plot DO data, process ISCO samples, clean ISCO bottles, and prepare materials for next week.
	Friday	Run ferrozine method Fe (II) tests on collected surface water samples at Western Colorado University lab, using microplate readers.
Week 3 (July 22nd- 26th)– Confluence Parcel Focussed	Monday	At East River, "Pump House," deploy DO loggers in pond, return seep, and channel locations. At Confluence Parcel, full sampling, set up ISCO for 24-hour sampling, and deploy DO logger in BeavPond1-1.
	Tuesday	At Trail Creek, full sampling. ISCO running at Confluence Parcel.
	Wednesday	At Confluence Parcel in-field, retrieve ISCO, pull samples from the 24-hour bottles, and pull DO loggers. In-lab, plot DO data, process ISCO samples, clean ISCO bottles, and prepare materials for next week.
	Thursday	Contingency day in case weather or sampling necessitates. Final Paper draft Introduction and Methods due.
	Friday	At East River, "Pump House," full sampling and pull DO loggers. In-lab, plot DO logger data.
Week 4 (July 29th- August 2nd)– Data Analysis and Writing Week	Monday	Run ferrozine method Fe (II) tests on collected surface water samples at Western Colorado University lab, using microplate readers.
	Tuesday-Thursday	Reserved for data analysis (working in R, processing, visualizing, and interpreting results).
	Friday	Final Paper results and discussion due.
Week 5 (August 5th- 9th)– Data Analysis, Writing, and Presentation	Monday	Note: Final paper draft due Wednesday to Sam for feedback. Final presentation either Tuesday or Thursday.
	Tuesday	
	Wednesday	
	Thursday	
	Friday	
Week 6 (August 12th- 16th)– Final Week	Monday	Final Paper due.
	Tuesday	Hike and pack :)
	Wednesday	Depart RMBL, roadtrip!!!

Major Professional Objectives:

Some objectives of my research program here at RMBL are to augment my scientific writing, cross-lab collaboration, navigation of field work tasks, experiences, and data collection & management, and to develop my own independent research project. I aim to collect preliminary data for potential longer term studies into the climate sensitive redox dynamics of Beaver floodplains, and ultimately, I hope to utilize my own research and the research of those around me there at RMBL to better my understanding of overall environmental system functions and shape how I will engage with those systems in the future.

Projected Outcomes:

I plan to complete independent research this summer that I will present orally and as a final paper to add to the RMBL publications database. This project will also be a part of my Interdisciplinary Honors Program's Experiential Learning Research Project in which I will actively complete reflections on my research and process while at RMBL and will present orally in the fall at University of Washington. I will also be examining data from this project further for a presentation in my Undergraduate Research Symposium at University of Washington.

Data Archiving, Curation, & Vouchers:

As part of the RMBL Data Archiving, Curation, and Vouchers, I will participate in workshops and training for spatial and non-spatial metadata and archiving. My Data Management Plan includes a description of the datasets being archived, the dissemination methods, and the timeline for data sharing. I will use the RMBL template metadata form. I will use the default data repository Environmental Data Initiative (EDI), https://environmentaldatainitiative.org/ unless my mentors request a different repository.

Environmental Impacts:

My research involves acidification, titration, colorimetry kits, and iron preservation. As such, it will include chemical waste. However, we have endeavored to calculate the minimum possible test kit, acid, and reagent use in order to minimize this impact. Additionally, our work involves entering wetlands and wildlife areas. With this in mind, we access sites in a manner that avoids trampling of vegetation and new trail creation. All infrastructure from this project (reusable flags which mark sites, metal stakes and tubing for undisturbed sampling, and all other 24-hour sampling materials) will be completely removed at the conclusion of the project, unless being further utilized by my mentor or other researchers. In that case, custodianship will be transferred to the new responsible party.

Relationship to Existing Research:

My independent project is in collaboration with my PI, Sam Pierce's, work which is currently funded by the Department of Energy's Watershed Function Science Focus Area (WFSFA) lead by Eoin Brodie, Ken Williams, Michelle Newcomer (Lawrence Berkeley National Lab) and Kristin Boye (SLAC National Lab). Much of this work is building off of the findings of these collaborators, as well as Marty Briggs, Richard Hauer, and Christian Dewey. Our BDAs are also managed by the US Forest Service and High Country Conservation Advocates (HCCA), a relationship managed by my mentor.

Importance of RMBL to Research:

Executing research at RMBL is critical for research continuity with my mentor and our collaborators, as well as for system access to BDA and beaver dammed sites at Trail Creek, Confluence, and East River.

Outcomes from Previous Research at RMBL:

Previous research conducted by Marty Briggs investigated the seasonality of biogeochemical impacts from beaver-floodplain metal exchange in the East River, discovering beaver floodplains exhibit strong advective flux and large swings from daytime DO supersaturation to near anoxic conditions overnight.[29] These finding suggest strong, continual, and underrepresented aerobic respiration in beaver ponds. Christian Dewey's research found that the beaver-induced increased hydraulic gradient had significant impacts on water residence time, and oxygen and nitrogen fluxes in riverine systems, overshadowing seasonal hydrologic extremes impacts by 10.7-13.3 times greater. Both of these results demonstrate the extensive impact beavers have on floodplain biogeochemistry.

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