Trace Metal Transport Alteration in a Riverine System Modified by a Dam: A Study of the Inflow and Outflow of the Wynoochee Reservoir

by

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A Thesis
Submitted in partial fulfillment
Of the requirements for the degree
Master of Environmental Studies
The Evergreen State College
June 2022

This Thesis for the Master of Environmental Studies Degree

by

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The Evergreen State College

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June 10th, 2022

Date

ABSTRACT

Alteration of Trace Metal Transport Forms in a Riverine System Modified by a Dam: A Study of the Inflow and Outflow of the Wynoochee Reservoir

Kyle Hontz

The purpose of this study was to determine effects that the Wynoochee Dam and Reservoir in Washington State, USA has on the form and amount of arsenic, cadmium, copper, lead, and zinc trace metals being transported downstream of the dam. Dam reservoirs are effective at sequestering trace metal-laden sediments from a change to lower river velocity. Scholarly research into trace metals within reservoirs and attached to sediments has raised the prospect of multiple biogeochemical processes influencing chemical parameters within a dam reservoir that may mobilize sequestered trace metals for subsequent transport downstream. This prospect formed the basis for thesis research into whether there is a shift occurring in trace metal fractions, dissolved and suspended? Secondly, if there was enrichment of trace metals in the dissolved and suspended fractions occurring between the inflow and outflow of the dam and reservoir. 6 Samples were taken between December 2021 and February 2022 above the dam reservoir and below the dam. Samples were filtered to determine dissolved metals and unfiltered to determine total metals for each site, for a total of 12 samples. Filtered and unfiltered samples were concentrated and analyzed for trace metal concentrations by Graphite Furnace Atomic Absorption Spectrophotometry and Inductively Coupled Plasma-Mass Spectrometry. Upstream and downstream samples were compared for enrichment of trace metals from the dam reservoir. Statistical analysis revealed dissolved copper was significantly enriched over the sampling timeline with a p-value of 0.03. No other metals reached statistical significance over all sampling dates. Sample variation likely obscured some results and 15 calculated zero values indicated methods for analysis was not precise enough for this application. Suspended sediment concentration varied widely over sampling timeline, indicating additional seasonal sampling could reveal seasonal patterns in suspended sediment and metals transport.

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Acknowledgements

I would like to extend my sincere gratitude to my thesis advisor, John Kirkpatrick. John supported me throughout the thesis process, offering valuable feedback on my writing, methodology, and analysis. I appreciate that in the uncertain times of the Covid-19 pandemic, John was flexible in ways to support me and my thesis work.

I would also like to thank the members of the MES Thesis Fund Board for providing me the funds to complete my sample analysis. The MES Thesis Fund expanded the potential breadth of thesis projects by helping to eliminate financial constraints on students.

Thanks to Averi Azar and the MES faculty for always having time to help me and answer my questions. I think that they work above and beyond to ensure every student has the tools at hand to succeed at The Evergreen State College.

1. INTRODUCTION

A dam and the reservoirs they create have temporal and spatial effects on chemical and sediment transport regimes within a riverine system. They can increase residence times in the watershed and the potential for trace metal transport alterations. These alterations in trace metal transport may contribute to trace metal persistence in the water column and bioaccumulation within the reservoir as well as downstream (J. Dong et al., 2018). In an unaltered river, sediment transports the bulk of trace metals attached to sediment surfaces or contained within the sediment with a small fraction being transported in dissolved form (Şener et al., 2014). Altering a riverine system with a large water impoundment like a dam reservoir decreases the velocity of water and can cause settling of even fine sediment that would otherwise pass downstream in periods of decreased flow (Horowitz, 2002; Stanley & Doyle, 2003). In this thesis, the term “dam reservoir” or “reservoir” is used to describe an artificial impoundment of water created by damming a river and not to refer to a naturally created water impoundment.

Dams are often located opposite of the inflow of the reservoir. Sediment settling in reservoirs is stratified vertically and horizontally with finer sediments travelling further than coarse sediments, closer to the discharge of the reservoir. Finer sediments near the dam have a greater potential for disturbance and greater surficial interphase to the water column most sensitive to changing parameters from managed water release (Duan et al., 2019). This differential between fine and coarse sediment is significant because trace metals tend to be more concentrated in fine sediments with increased surface area for adsorption (Bednarek, 2001). Fine sediments can contain trace metals orders of magnitude higher than that of dissolved concentrations in the water column (Horowitz, 2002; Matys Grygar et al., 2018). Disturbance and resuspension of fine sediments can diffuse formerly sequestered trace metals into the water column (Charriau et al., 2011) and can exceed the dissolved riverine flux of trace metals downstream (Duan et al., 2019).

Physiochemical parameter changes in a managed reservoir can be more extreme than that of a previously unimpeded river water and can cause more advantageous conditions for trace metal release from sediments (Brandenberger et al., 2004). Temperature, pH, oxidation-reduction potential, and dissolved oxygen can change the oxidation state of trace metal ions in sediments. Sediment sinks for trace metals can turn into sources of dissolved trace metals (Frémion et al., 2017; Horowitz, 2002; Zhu et al., 2017).

Nutrient enrichment and bioproduction within a managed reservoir can have a dramatic impact on the physiochemical parameters that influence trace metal mobility and toxicity. Photosynthesis and eventual degradation of organic matter produced by excess nutrients can seasonally affect dissolved oxygen and pH in the water column, drastically changing redox conditions that affect precipitation and dissolution of trace metal complexes. In addition to changing physiochemical parameters, primary production in the water column consumes nutrients like phosphorus often complexed with trace metals, dissolving trace metals in the water column and increasing mobility (C. Giles et al., 2016). Microbial reduction of organic matter in the deposited sediment can also dissolve organometal bonds and add to trace metal mobility in the sediment/water column interphase (Masson & Tercier-Waeber, 2014).

Trace metals like copper can be required for biological functions in low concentrations but toxic in higher concentrations. Trace metals like arsenic and mercury have virtually no ecological benefit but can be toxic to many organisms in even the most minute quantities (Has-Schön et al., 2015; White et al., 1995). Naturally occurring levels of trace metals can be increased by atmospheric deposition and the larger surface area of a reservoir further acts to collect anthropogenic pollution directly (Shotbolt et al., 2006). In a watershed, rivers act as conduits for the flux of trace metals through the watershed, but a reservoir increases their residence time and potentially create harmful levels for humans and the riverine ecology.

Suspended sediment trace metals are a potential source of water quality pollution that is not commonly assessed in water quality testing as it is usually filtered out to measure only the dissolved load of trace metals (EPA Method 200.8). Physiochemical parameters of river water often change with transport through a dam reservoir. Bioprocesses and trace metal cycling within the reservoir can increase the potential for enrichment of trace metals present on suspended sediment and colloids. This can represent a portion of trace metals reactive to changes in physiochemical water parameters (Martin et al., 1995).

There are many trace metal pathways from reservoirs that can impact humans. For example, irrigating public spaces with reservoir water instead of rainwater increases the level of trace metals on vegetation and soils Irrigation of food crops with enriched water increases the likelihood of humans ingesting trace metals (Welde Amanuel & Kassegne, 2022). Increased trace metal levels in fish and other food sources collected in dam reservoirs put humans in greater risk of negative health effects from trace metals (Has-Schön et al., 2015). Aquatic organisms can absorb trace metals directly from enriched water and from the local food web through bioaccumulation (Doshi et al., 2008).

Most dams in the U.S. have reached or exceeded their expected life expectancy (Doyle et al., 2003). This realization outlines a greater urgency for the most complete information for the evaluation of dams and their impact to ecology for decisions on dam renewal, removal, or replacement projects. Examining the potential of water pollution by trace metals in any scenario must be a priority before any action is taken. In the case of the European Union, sediments are not taken into account by the water framework directive when evaluating the quality of a water body (Charriau et al., 2011). International approaches for assessment of sediment impact on water quality predominantly rely on direct physical data and not on assessing the potential of sediment trace metal release (Batley & Warne, 2017). Baseline processes must be understood along with specific site conditions, taking into account seasonal and managed conditions to assess the potential for trace metal interactions. Furthermore, general relationships between bioaccumulation of metals and trace metal toxicity are not well understood (Zhang et al., 2014), limiting our understanding of potential negative effects to human and environmental health. Specific sediment studies must be carried out to assess the effect of microbial activities on this potentiality. The interactions between microbes and metals have been studied and well understood for soils, but there have been very few studies have been carried out for freshwater sediments, especially in strictly anaerobic conditions (Gounou et al., 2010) like those in persistently eutrophic reservoirs or deep sediment layers.

Many physical, biological, and chemical processes interact in determining the partitioning of trace metal transport forms. Though all processes can be found within most dam reservoirs, the order of dominance of these processes is unique to each site. In this study, data was collected specifically for the Wynoochee Reservoir to determine what difference these processes had on trace metal concentrations in suspended and dissolved sediment fractions being transported downstream. It assessed whether there was an enrichment of trace metals transported by sediment or dissolved in water. An enrichment of water could pose immediate increased health risks downstream. An enrichment of metals in suspended sediment may have resulted in increased persistence of metal pollution in areas of sediment flux and sequestration further downstream, reactive to changing physiochemical parameters. It was also essential to examine literature on the processes that affected the results of sediment and water data. Site observations also can provide an indication of predominant transformation processes. Results of sediment and water analysis help reveal possible changes in riverine metals flux and form through the Wynoochee Reservoir that may affect downstream ecology and stakeholders.

2. LITERATURE REVIEW

2.1 Introduction

The study of trace metal transport in riverine systems can be broken down into three spatial areas of concern: The sediment column, the overlying water column, and the sediment-water interphase (SWI). Complexation and dissolution from changing oxidation/reduction (redox) conditions can take place in all three areas of concern with oxidation or reduction generally being favored in one area more than others.

To understand the chemical nature of trace metals it is important to consider that trace metals are positively charged ions that tend to favor binding with negatively charged anions for stability in the chemical parameter range of most natural waters (Drever, 1997). In the event of changes in the redox state of the aqueous or sediment matrix that trace metals are in, temporary dissolution may occur (Caetano et al., 2003; Frémion et al., 2017). In reducing conditions like deep in the sediment column, trace metals tend to complex with sulfides, while in oxidizing conditions trace metals favor complexing with oxides (Charriau et al., 2011; Duan et al., 2019). The ever-changing gradient boundary between reduction and oxidation is dependent on dynamic water column conditions. The density of the SWI and the redox state of the overlying water column are the major factors in determining how deep oxidizing conditions penetrate into sediment. Conversely, microbial processes and the decomposition of organic matter at the SWI is a major factor in how far reducing conditions may extend into the water column (Gao et al., 2018). This is an interplay largely affected by water column residence time, nutrient availability, and its accompanying dynamic physical parameters.

2.2 Physical Trace Metal Parameters

The alteration of a river by a dam decreases the velocity of flow, inducing sediment settling and retaining greater concentrations of trace metals in dam reservoirs. Decreased velocity of river flow occurs with a widened cross section of a dam reservoir. This can cause even fine sediment to settle out of the water column. Finer sediments can contain magnitudes higher surface area than coarse sediments, exponentially increasing the potential binding sights with an affinity towards positively charged trace metal ions. An increase of finer sediment in dam reservoirs increases the potential for a larger proportion of trace metals when compared to natural sediment load (Eggleton & Thomas, 2004; Matys Grygar et al., 2018; Ouattara et al., 2018).

No matter if a dams primary use is for flood control, hydroelectricity, or water storage, all dams with large storage reservoirs have diminished seasonal flow regimes which alters sediment transport and physical water column parameters (Zhu et al., 2017). In areas that have prominent dry and wet seasons, natural river flow regimes can vary drastically between seasons. In these areas, it is not uncommon for the majority of sediment transport in unaltered river morphology to occur during pulsed precipitation events (Millares et al., 2020). Not only do dam reservoirs store sediment from seasonal pulses, during periods of low seasonal flow, residence time of the water column increases. This can have a profound impact on the temperature from solar radiation, dissolved oxygen from increased bioproduction, and pH increase from increased atmospheric carbon dioxide influence and decreased water/rock interaction that can buffer pH. All of these parameters can have an impact on chemical interactions with trace metals (Şener et al., 2014; Zhu et al., 2017).

Selective release of water from dam reservoirs can lead to pulses of formerly sequestered trace metals in sediment being released in the water column. Sediments are generally under more reducing conditions than the upper layers of the water column. An increase of flow can dislodge sediments from the SWI and suspend dissolved and complexed trace metals under more oxic conditions (Frémion et al., 2017). This can lead to a significant increase in the water columns previous dissolved trace metal concentration (Monnin et al., 2018). In (Caetano et al., 2003), this effect was studied and determined to be short-lived for most trace metals, but it mobilized the trace metals spatially, increased persistence, and potential for repartitioning.

Managed dam release can create greater variance in redox conditions when compared to a natural river regime and cause changing conditions that cycle trace metals in the water column. Generally, trace metals that are deposited with terrigenous sediment in the sediment layer are under more reducing conditions than the overlying water column. As trace metals are buried, they mineralize as with sulfide complexes and if these reducing conditions are maintained, the trace metals are sequestered if no other factors are present. Disturbances of reducing conditions by managed dam release can reoxidize shallower sediments and cause dissolution of sulfides, releasing trace metals back into the water column to complex with iron and manganese hydroxides that are less stable. This can aid in cycling of trace metals throughout the water column (Audry et al., 2010; Boehrer & Schultze, 2008).

2.3 Sediment-Water Column Interphase (SWI)

Sediments contain the majority of trace metals being transported in a river (Şener et al., 2014). The water column has the most dynamic physiochemical conditions resulting in the SWI in dam reservoirs having the most potential for changes in trace metal mobility (Lehto et al., 2017). This is exacerbated by stratification of sediment settling in a reservoir leaving finer particles often at the furthest from entry in greater contact with the water column. In most dam reservoirs, the furthest area from entry is often close to a dam by reservoirs following the original contours of the riverine morphology. Dam release regime has the greatest effect on sediment resuspension nearest the dam by the narrowing of river cross section and through release, increasing velocity of flow.

The SWI is the least consolidated area of the sediment column and most subject to reoxidation from changes in the overlying water column. For this reason, the SWI is often incorporated in trace metal studies of contaminated sediments and often assumed to be the sediment columns most important aspect concerning potential toxicity to the water column (Duan et al., 2019; Lehto et al., 2017). The SWI nearest the dam is generally fine sediment with higher concentrations of trace metals than more coarse sediments (Horowitz, 1986) that incorporate the majority of trace metal in layers not in direct contact with the water column. Porewater within the SWI layer can have dramatically higher concentrations of trace metals in solution than the overlying water column also contributing to pulses in water column concentration during resuspension events. Organic matter has a high affinity for trace metal complexation and sequestration of organic matter in the SWI can contribute to trace metal concentrations. Decomposition of organic matter can provide dissolved trace metals to the water column or additional trace metals to complex within the SWI. This can add to reactive trace metal concentration in the SWI (Pokrovsky et al., 2012). From the partitioning of trace metals in complexes and the oxidative state, porewater could serve as a sensitive indicator for their transformation compared to other sediment column layers (Duan et al., 2019).

2.4 Sediment Trace Metal Processes

Sediment layers can be a key source of trace metals to the overlying water column, depending on physiochemical conditions. Deep layers of sediment have diminishing concentrations of free oxygen available for oxidative reactions. Under strictly reducing conditions, after oxygen has been completely consumed, sulfide minerals are created and are known to complex with trace metals. Eventually, under enough pressure from top layers of sediment, minerals formed under reduction is lithified into rock. Early lithification of sedimentary rock can release trace metals from their transforming sediment structures, migrating to the upper, more oxic sediment layers. Organic matter is often deposited with sediments and has a high affinity for trace metals forming organic ligands. Decomposition of organic matter in the sediment layers can also contribute to trace metal concentration for sulfidic mineral complexation or migration of trace metals to the (SWI) for either contribution to porewater dissolved concentration, or complexation with oxyhydroxides, a less stable form than sulfide minerals (Duan et al., 2019; Pokrovsky et al., 2012).

2.5 Water Column Trace Metal Processes

The water columns in dam reservoirs are generally less mixed and uniform in their physical parameters than a constantly mixing and flowing river. This leads to increased gradients and bioproduction affecting trace metal mobility. In a water column that is stratified, or semi-stratified, dissolved oxygen is more abundant at the top of the water column and eventually decreases toward the bottom. Iron and manganese Oxyhydroxide complexation takes place under oxic conditions. With a high affinity to most trace metals, oxyhydroxides typically sink through the water column approaching more reducing conditions (Crowe et al., 2007). Eventually, whether in the water column or in the sediment, these complexes will dissolve. Oxyhydroxides that dissolve in contact with the water column release trace metals back into the water column (Crowe et al., 2007). If the redox gradient in the water column is great enough, trace metals can be cycled many times (Boehrer & Schultze, 2008). This is common in temperate lakes and reservoirs despite seasonal water column turnover. Meromictic lakes that are permanently stratified have a temperature and chemical gradient boundary that prevents mixing of the top and bottom layers resulting in oxic trace metal complexes often reduced at the gradient boundary and released back into the top layer of more oxic water to be recomplexed with oxyhydroxides (Boehrer & Schultze, 2008). This same process can occur with nutrient complexes like phosphorus that are complexed with trace metals and released by more anoxic conditions (Giles et al., 2016). Trace metals preference is towards complexation in oxic water layers to particulates. Whether the trace metals complex with nutrients, oxyhydroxides, or terrigenous sediment, trace metals have varying affinity to particulates (Biati et al., 2010) and results in complex speciation that cannot be precisely calculated or modelled in all in situ circumstances (Schröder et al., 2008). This fact might account for the volume of water quality and sediment studies around the world.

Concentration of trace metals can have a significant impact on the cycling of trace metals. During complexation of nutrient particulates in the water column, oxic phosphorus complexes have a high affinity to complex with trace metals. Iron is a common element in natural oxic waters in the form of oxyhydroxides that are known for scavenging trace metals (Crowe et al., 2007). When complexes formed under oxic conditions typical in the upper water column are dense enough they will eventually fall through the water column to be deposited at the SWI or be dissolved under more reducing conditions. Under reducing and semi-reducing conditions, trace metals contained in oxide and nutrient complexes can be dissolved, freeing trace metals to be scavenged in more oxic waters again (Audry et al., 2010). This can lead to cycling of trace metals many times under dynamic water column conditions (Boehrer & Schultze, 2008).

2.6 Microbiological Trace Metal Processes

Microbial processes in contact with the water and sediment column add a layer of complexity that can drastically alter the mobility of trace metals and in some studies, accounts for a majority of trace metal cycling and toxicity (D. Dong et al., 2000; Kara et al., 2017). Photosynthetic bioproduction in the water column is supported by nutrients like phosphorus that is often in complex with trace metals. Even under oxic water conditions that favor trace metal complexation with particulates, this consumption of nutrients can mobilize trace metals to the dissolved phase for partitioning. Under strictly oxic conditions, trace metals are often complexed with oxyhydroxides (Audry et al., 2010).

The complexation of trace metals with oxyhydroxides under oxic conditions creates a potential for greater toxicity to microbial processes that can be a catalyst for trace metal cycling or bioavailability in bioproduction (Louriño-Cabana et al., 2011). The active binding sites in biofilms common in reservoirs have a high affinity to adsorb oxyhydroxides, leaving complexed trace metals in a state of temporary sequestration (Dong et al., 2000). Green algae common in reservoirs as a biofilm and can not only adsorb trace metal complexes but also have a mechanism for active transport of trace metal complexes to many internal layers also containing active binding sites. This supports the researchers assertion that active growth of green algae can support much more intake of trace metals than simple surface adsorbtion (Doshi et al., 2008). This claim supports other researchers claims that trace metal toxicity is closely related to bioproduction cycles within a reservoir (Masson & Tercier-Waeber, 2014; White et al., 1995).

Changes in trace metal regime, particularly from microbial processes in dam reservoirs offers a greater potential for trace metal bioavailability within a dam reservoir (Dong et al., 2018; Gounou et al., 2010) and can present a greater danger to higher trophic levels that depend on bioproduction within the reservoir for food . Bioaccumulation and biomagnification of certain trace metals like arsenic are subject of a great many studies and widely accepted (Has-Schön et al., 2015) but often start in lower trophic levels and are most evident in higher levels trophic levels that are more visible. The varying pathways and mechanisms for bioavailability to higher trophic bioaccumulation are not well understood (Zhang et al., 2014). There are many studies measuring levels of trace metals in ecology but the connective pathway cannot always be accurately predicted (Burger et al., 2018; Has-Schön et al., 2015).

It has been stated in multiple studies that the majority of source for trace metals within the water column of a reservoir can be from the sediment column, with reductive microbial processes accounting for much of this source (Gounou et al., 2010; Majithiya et al., 2018). Trace metals have several paths of chemical transformation in sediments. Trace metal complexes that deposit on the bottom of a reservoir can either be reduced and trace metals transformed into a solid phase for sulfidic complexation or dissolved and released to the water column. Reductive microbial dissolution of trace metal complexes with oxyhydroxides release trace metals, particularly iron, who’s oxidative state in reducing conditions lends to dissolution oxyhydroxides (Boehrer & Schultze, 2008; Crowe et al., 2007). Microbial processes are largely responsible for this dissolution because even top layers of sediment are generally not strictly reducing in chemical nature (Crowe et al., 2007; Gounou et al., 2010).

2.7 Sediment and Water Column Studies and Methodology

A review of literature suggests while not all methods of analysis or in situ sampling utilized are the same, the majority of studies concerning trace metal toxicity and persistence do recognize the important connection between trace metals in the water column and the potential for source from the sediment column (Botsou et al., 2019; Duan et al., 2019; Eggleton & Thomas, 2004; Majithiya et al., 2018). There are very few studies of trace metal toxicity potential sampling only the water column. Suspended sediment is usually filtered out of water samples but can be the most reactive source of trace metals in contact with the water column.

In regards to understanding the changing redox potentials effect on toxicity, most studies methods can be separated into two categories: in situ testing of trace metal mobility and recreating conditions in the lab often supplemented by modelling, both having drawbacks (Monnin et al., 2018).

Earlier studies of trace metal toxicity often relied on in situ physiochemical parameter testing and sequential extraction of trace metals in sediment samples to guide either redox modelling for speciation or physical recreation. Results of the testing and analysis of trace metal partitioning and modelling of toxicity are often unverifiable in accuracy or mismatched results are explained by inferences of other related factors not in that specific field like microbial processes (Birch, 2017; Lehto et al., 2017).

Some later studies reviewed have utilized probed in situ analysis of trace metal speciation and physiochemical parameters (Lehto et al., 2017), likely an acknowledgement of the shortcomings of simplified laboratory analysis and modelling. Given the dynamic nature of water column parameters in managed reservoirs, these methods would best be employed through long-term monitoring and greater area to determine changing circumstances in toxicity and bioavailability (Lehto et al., 2017; Pokrovsky et al., 2012). These methods under the guise of long-term modelling would be best suited to accompanying monitoring of water quality and bioaccumulation of trace metals in organisms common for contaminated aquatic systems. Interdisciplinary studies may advance the lack of understanding in some of the mechanisms between potential trace metal toxicity and bioaccumulation that some researchers have posited (Roosa et al., 2016).

3. METHODS

3.1 Site Selection

The site chosen for this study is the Wynoochee dam and reservoir (Figure 1). It is located in the southwest corner of the Olympic National Forest in Washington State, United States. The watershed of the Wynoochee Reservoir encompasses 42 square miles of mostly selected harvest forest with the headwaters running into the protected and heavily forested Olympic National Park.

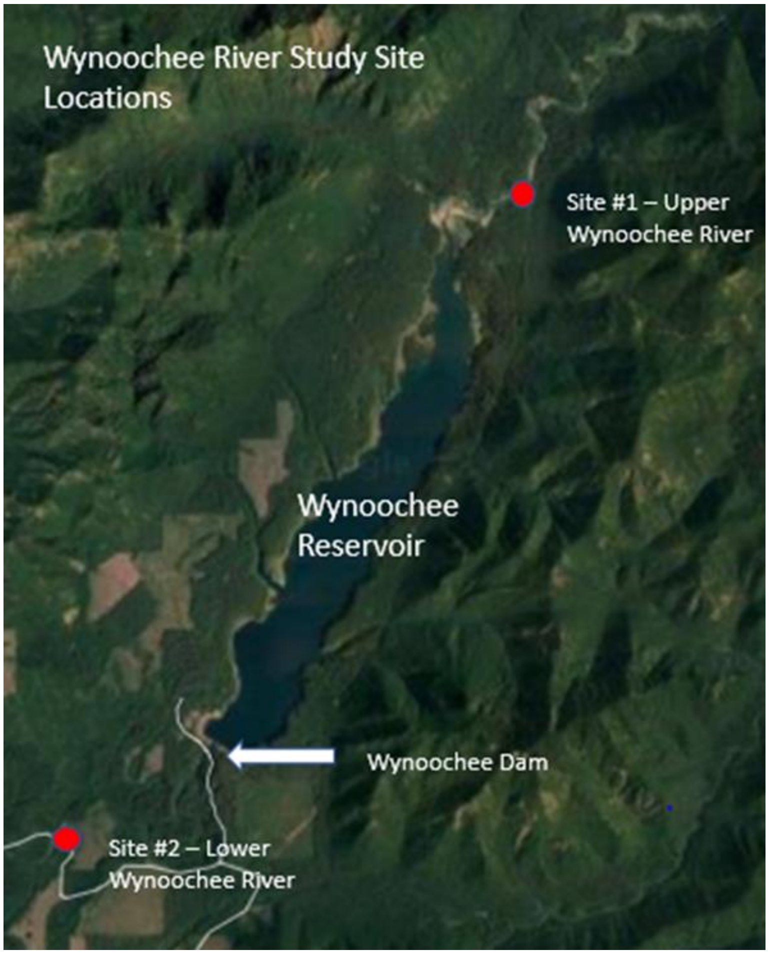

Figure 1. Map of Wynoochee study site area and sampling sites. Sampling locations (2021-2022) added by author, in red circles and labeling text. Image courtesy of Google Maps.

The ideal scenario for this study would be to have a closed riverine system with a dam and reservoir and no additional anthropogenic inputs to determine the effect that the reservoir has on trace metal flux. There was no site that fits that ideal scenario, as there are no closed river systems in existence that experience no anthropogenic chemical inputs. The two factors in determining an appropriate site for this study were to: 1) Minimize anthropogenic trace metal inputs from within watershed infrastructure development that could affect the proportion of trace metal transport fractions being transported downriver. 2) Select a site where direct anthropogenic nutrient inputs were minimal from shoreline development and on-water activity. Additional nutrient cycling within the reservoir could increase trace metal mobility through bioproduction and influence distribution of trace metal concentrations. The goal of this study was to provide as close to a background baseline of transformative trace metal processes from the alteration of a riverine system by a dam reservoir. The extent of permanent development within the watershed of the Wynoochee dam and reservoir as of January 2022 was a small campground, the dam itself and a few forest service roads. The Wynoochee reservoir at this time was considered relatively clean and not known for eutrophic conditions.

Two sample collection sites were chosen. One was upstream the Wynoochee river inlet to the reservoir, the other was approximately 1.2 miles downstream of the dam outlet (Figure 1). The study design required samples from the inlet and outlet of the dam reservoir, but the deciding factors of these particular sampling locations was reasonable walking access, close proximity to the reservoir, and safe access conditions.

3.2 Sample Collection

Water sample collection was performed at the two selected sample collection sites (Table 1) . Samples were collected on three different occasions spanning December 2021 – February 2022. Samples were collected from the bank just under the surface of the water to limit floating debris and in strong current to limit disturbed bank sediment from contaminating samples. The samples were collected in acid-washed polypropylene sample bottles. 1 gallon of water sample was collected each day from each sampling site to be processed into separate sub-samples back in the lab. Steps were taken to limit contamination of sample containers and contamination of samples once collected and during processing (Appendix A).

Table 1 *Sample location, sample type, sample timing, pH, and sample temperature on sampling days.*

Wynoochee River Sample Site Collection

Sample	Location Collected	Date collected	Time collected	Type	pH	Temperature (°C)
1	Upper Wynoochee	12/21/2021	1600	Dissolved Metals	7.56	5.9
2	Upper Wynoochee	12/21/2021	1600	Total Metals	7.56	5.9
3	Lower Wynoochee	12/21/2021	1630	Dissolved Metals	7.51	6.1
4	Lower Wynoochee	12/21/2021	1630	Total Metals	7.51	6.1
5	Upper Wynoochee	1/23/2022	1400	Dissolved Metals	7.54	5.8
6	Upper Wynoochee	1/23/2022	1400	Total Metals	7.54	5.8
7	Lower Wynoochee	1/23/2022	1430	Dissolved Metals	7.48	6.0
8a	Lower Wynoochee	1/23/2022	1430	Total Metals	7.48	6.0
8b	Lower Wynoochee	1/23/2022	1430	Total Metals	7.48	6.0
8c	Lower Wynoochee	1/23/2022	1430	Total Metals	7.48	6.0
9	Upper Wynoochee	2/11/2022	1530	Dissolved Metals	7.52	5.4
10	Upper Wynoochee	2/11/2022	1530	Total Metals	7.52	5.4
11	Lower Wynoochee	2/11/2022	1600	Total Metals	7.44	5.6
12a	Lower Wynoochee	2/11/2022	1600	Dissolved Metals	7.44	5.6
12b	Lower Wynoochee	2/11/2022	1600	Dissolved Metals	7.44	5.6
12c	Lower Wynoochee	2/11/2022	1600	Dissolved Metals	7.44	5.6

Upper Wynoochee - N47° 26.292' W123° 33.652'
Lower Wynoochee - N47° 22.342' W123° 37.394'

3.3 River Flow

Data on river discharge was collected to compare discharge on sample collection dates and to gain additional insight into seasonal discharge magnitude and variation over the sampling timeframe (Figure 2). Though reliable statistical comparison of the river discharge between the upper and lower sites was impossible due to unpredictable variation from managed water release, discharge was measured from an USGS stream gage# 12035400 near the lower site to compare discharge versus aqueous solids and metal concentrations of the reservoir discharge, the end product. Precipitation data was obtained for Quinault, Washington, approximately 13 miles from the Wynoochee Dam during the sampling period to gain insight into precipitation events preceeding sampling (Figure 3).

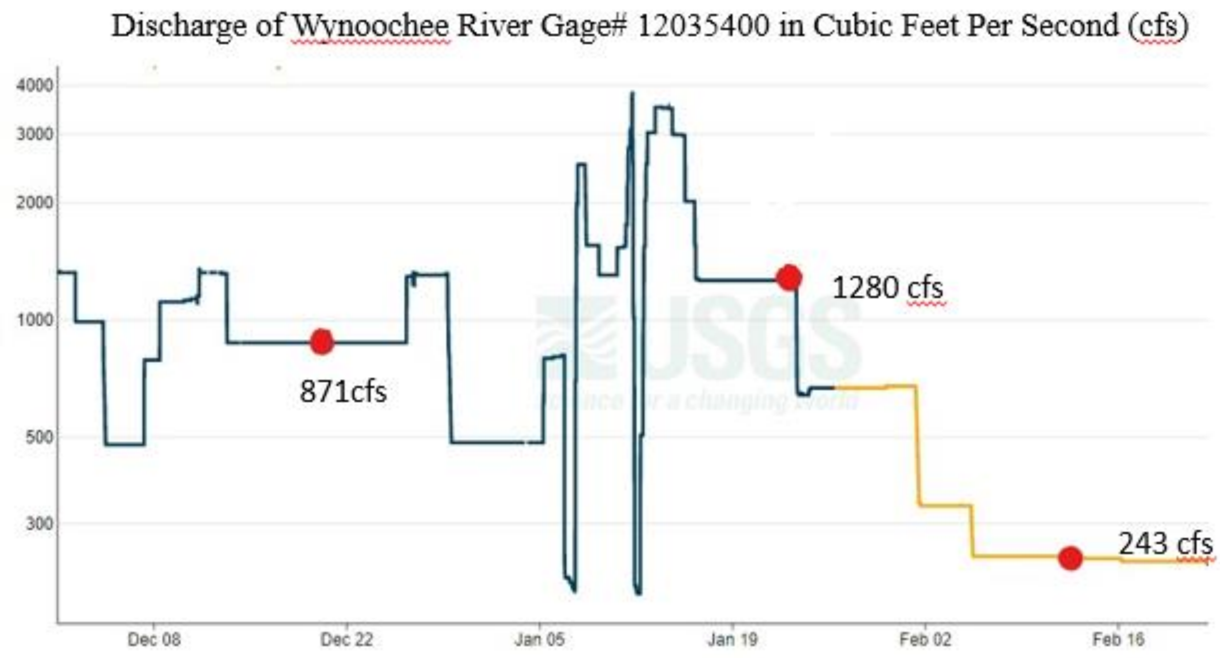

Figure 2 *Hydrograph of Wynoocheee River discharge below dam near Grisdale, WA(December 2021 – February 2022). Sampling dates added by author, in red circles and discharge amounts in text. Courtesy of waterdata.usgs.gov.*

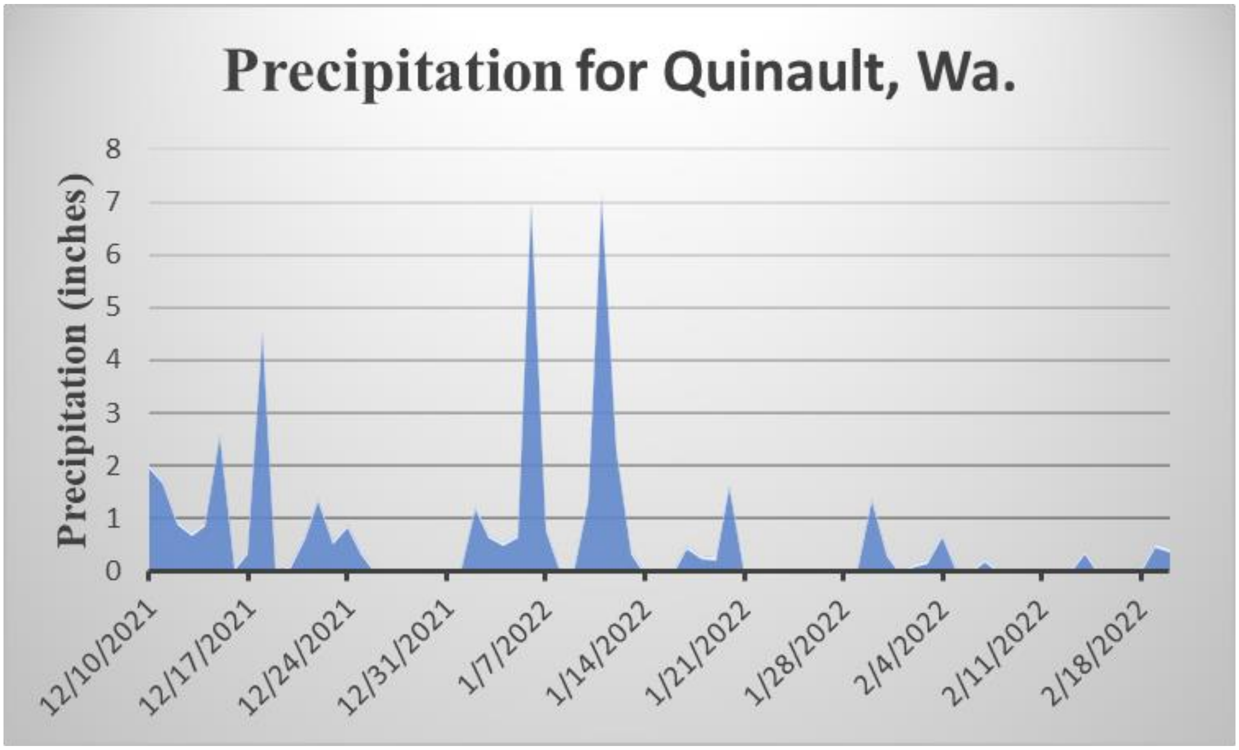

Figure 3 *Chart of daily precipitation totals (December 10, 2021 – February 20, 2022) for Quinault, Washington, approximately 13 miles from the Wynoochee Dam. Chart precipitation data courtesy of wunderground.com.*

3.4 Sample Preparation

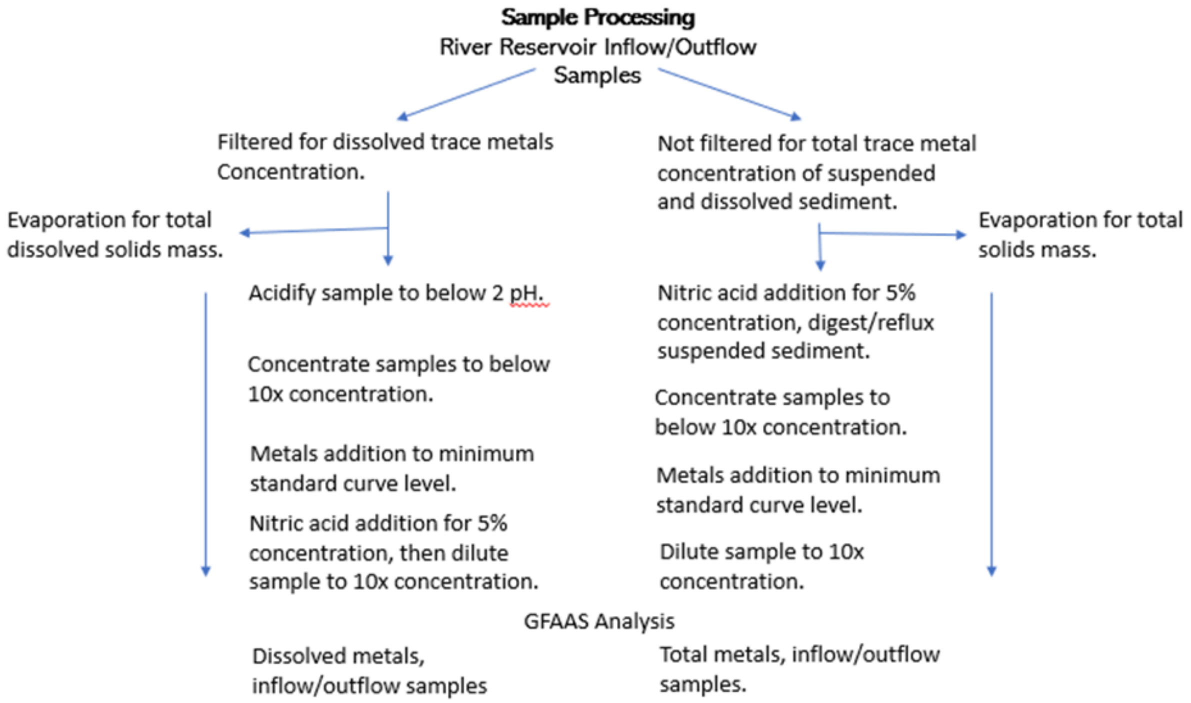

Figure 4 *Flowchart of sample preparation for analysis.*

Portions of water samples from collection sites were processed for arsenic, cadmium, copper, lead, and zinc concentrations in dissolved and suspended sediment fractions. A portion of collected samples was also processed and evaporated for determination of total dissolved solids and total solids concentrations (Figure 4).

Water samples processed for analysis of dissolved metals were filtered within 24 hours of collection by a 0.45 micron mixed-cellulose filter and acidified to below a pH of 2. Water samples processed for determination of total metal concentrations were not filtered. Both sample types were preconcentrated by evaporation to approximately 10 times original concentration based on mass at 100° Celsius by hotplate. Evaporation of samples included an addition of nitric acid during the process to strip trace metals from sediment and inhibit precipitation out of solution. The amount of nitric acid used resulted in the final 100mL samples containing 5% nitric acid, as required by laboratory analysis of the samples. Samples were filtered after preconcentration, a known amount of elements As, Cd, Cu, Pb, and Zn was added before analysis to ensure samples were above the minimum detection level (MDL), then deionized water was added to bring the volume up to 100mL. Lab method blanks were spiked with a known concentration of metals to ensure concentration above MDL and were processed during each sample processing regime to determine whether contamination occurred and to what extent. Sample processing was not done in a clean room environment. To mitigate metals contamination, samples were covered during processing and all equipment in contact with samples was acid-washed and rinsed with deionized water. Lab method blank metal concentrations disparities were subtracted where applicable from sample concentrations to minimize potentially erroneous results from contamination. Elevated levels were detected for 12/21/2021 method blank As 0.2 µg/L, Cu 0.8 µg/L, Zn 0.1 µg/L. Elevated levels for 1/23/2022 method blank Cd 0.3 µg/L, Zn 0.7 µg/L. Elevated level for 2/11/2022 method blank of Zn 0.3 µg/L. A total of 12 samples, 4 sample replicates, 3 lab method blanks were analyzed for arsenic, cadmium, copper, lead, and zinc metal concentrations.

3.5 Laboratory Analysis

Analysis of sample metal concentrations was performed by Libby Environmental, INC (3322 South Bay Road NE Olympia, WA 98506). The method used for analysis of arsenic, cadmium, copper, and lead was Graphite Furnace Atomic Absorption spectrophotometry

(GFAAS) (EPA method 7010). Matrix modifiers were added by the testing laboratory to enhance recovery of lead and arsenic. Samples and blanks were spiked to 4% ammonium phosphate and 10% magnesium nitrate concentration to enhance lead recovery. Samples were also spiked with 6.25% concentration nickel nitrate to enhance arsenic recovery. The samples were analyzed by constructing a calibration curve for As, Cd, Cu, and Pb of known standard concentrations with the MDL representing the minimum concentration of the calibration curve. The MDL for As is 3.0 µg/L, 0.5 for Cd, 5.0 for Cu, and 5.0 for Pb. Quality analysis and quality control included a laboratory control sample, matrix spike, and matrix spike duplicate using a relative percent difference (RPD) to determine recovery. All samples analyzed fell within the acceptable 20% RPD threshold. There were detectable levels of As, Cd, Cu, and Pb in all samples, replicates, and lab method blanks turned over for analysis (Appendix B).

The method of analysis for Zn utilized Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (EPA method 200.8). The samples were analyzed by constructing a calibration curve of known standard concentrations with an MDL of 2.5 µg/L representing the minimum concentration in accuracy of the calibration curve. Quality analysis and quality control included a laboratory control sample and duplicate, method blank, and matrix spike, using a relative percent difference (RPD) to determine recovery. Method blank resulted in nondetectable concentration for Zn. All samples analyzed fell within the acceptable 20% RPD threshold. There were detectable levels of Zn in all samples, replicates, and lab method blanks turned over for analysis (Appendix B).

Sample analysis results were corrected for metals added to all samples and replicates by approximately 5 µg/L for each metal as determined by weight addition calculations and adjusted for contamination if applicable by each corresponding lab method blank results (1). After results are adjusted for added metals and possible contamination, results are adjusted by weight calculation to approximately 10 times dilution to account for sample preconcentration (2). Quality assurance/quality control recovery percentage was applied to sample concentrations to correct for disparity between actual concentrations and analyzed concentrations (3). Filtered samples were subtracted from corresponding unfiltered sample to determine trace metal concentrations of suspended sediment.

(1) **Laboratory Results – Metals Addition (approximately 5 µg/L As, Cd, Cu, Pb, Zn by weight) = Concentrated Sample**

(2) **Concentrated Sample / Concentration factor (approximately 10x based on weight) = Sample Concentration**

(3) **Adjusted Sample Concentration = Sample Concentration / Quality Analysis Recovery %**

(4) **Final Sample Concentration Results = Adjusted Sample Concentration – Laboratory Method Blank Concentration**

Table 2 *Adjusted sample concentration results.*

		Adjusted sample concentration (µg/L)						
	Sample	Arsenic	Cadmium	Copper	Lead	Zinc	Location Collected	Type
12/21/2021	1	0.3	0.2	0.5	1.2	9.1	Upper Wynoochee	Dissolved Metals
12/21/2021	2	0.3	0	0.8	1.4	5	Upper Wynoochee	Total Metals
12/21/2021	3	0.4	0	1.0	3.7	8.4	Lower Wynoochee	Dissolved Metals
12/21/2021	4	0.5	0.2	1.3	1.6	9.8	Lower Wynoochee	Total Metals
1/23/2022	5	7.6	0.2	0.8	1.8	2.2	Upper Wynoochee	Total Metals
1/23/2022	6	0.4	0	0.5	0	1.7	Upper Wynoochee	Dissolved Metals
1/23/2022	7	0.3	0.1	0.9	0.1	4.1	Lower Wynoochee	Dissolved Metals
1/23/2022	8a	0.2	0.1	1.0	0	3.6	Lower Wynoochee	Total Metals
1/23/2022	8b	0.3	0.1	0.8	0.6	4.3	Lower Wynoochee	Total Metals
1/23/2022	8c	0.5	0.1	1.4	0.1	2.4	Lower Wynoochee	Total Metals
2/11/2022	9	0	0	0.2	0.3	1.2	Upper Wynoochee	Dissolved Metals
2/11/2022	10	0	0	2.9	0.2	0.7	Upper Wynoochee	Total Metals
2/11/2022	11	0	0	0.6	0	4.9	Lower Wynoochee	Total Metals
2/11/2022	12a	0	0	0.4	0.1	5.2	Lower Wynoochee	Dissolved Metals
2/11/2022	12b	0	0	0.1	0.1	5.1	Lower Wynoochee	Dissolved Metals
2/11/2022	12c	0	0	0.8	0.1	1.2	Lower Wynoochee	Dissolved Metals

Note. Sample concentrations adjusted for preconcentration, metals addition, and laboratory recovery% prior to subtraction of laboratory method blank concentrations.

3.6 Total Dissolved Solids/Total Solids Analysis

Filtered and unfiltered River water samples were evaporated in a laboratory oven at 90 degrees Celsius in beakers, then weighed to determine the mass of dissolved solids and total solids in micrograms per liter (EPA Method 160.1). Filtered samples were subtracted from corresponding unfiltered sample to determine suspended sediment concentrations (Table 3).

Table 3 *Determination of sample solids by evaporation.*

Aqueous Solids Determination by Evaporation (g/L)

Upper Wynoochee

	12/21/2021	1/23/2022	2/11/2022
Total Solids	0.046	0.036	0.072
Suspended Solids	0.039	0.003	0.001
Dissolved Solids	0.007	0.033	0.071

Lower Wynoochee

	12/21/2021	1/23/2022	2/11/2022
Total Solids	0.024	0.030	0.066
Suspended Solids	0.017	0.001	0
Dissolved Solids	0.007	0.029	0.066

Note. Suspended solids calculated from Total Solids and Dissolved Solids difference in mass.

3.7 Results Analysis

Enrichment from upper to lower site was determined from subtracting upper dissolved and suspended metal concentrations from lower dissolved and suspended metal concentrations. Relative standard deviation of sample replicate metal concentrations was calculated (Table 5) and applied to enrichment values and determined if the range of enrichment was significant, being a range above 0 µg/L. Statistically significant enrichment of dissolved and suspended metal fractions was tested across all sample means to determine if metals were consistently enriched over varying flow regime temporally. A one-tailed, paired t-test of the mean was performed on each metal fraction with an alpha at 90% confidence level (P = 0.1) to appraise statistical significance (Appendix C).

Changes in dissolved and suspended solids proportional mass over sampling dates was compared to changes in dissolved and suspended metal concentrations and determined if any metals had a strong correlation with either the dissolved or suspended solids fraction.

Changes in the proportion of dissolved to suspended metal concentrations between the lower and upper sample sites was compared to determine if any changes occurred in the transport of metal fractions downstream.

4. RESULTS

4.1 Laboratory Method Blanks

A single laboratory method blank was processed for each sample processing batch (Table 4). Batches consisted of samples collected from the same sampling day. Analysis of method blanks determined elevated levels of As, Cu, and Zn from sample processing of samples collected in December. Method blank processing for samples collected in January indicate elevated Cd, and Zinc. Method blank processing for samples collected in February indicate elevated Zn concentration. Laboratory method blank concentrations were adjusted by recovery % of laboratory quality analysis. Results of laboratory method blanks were subtracted from applicable sample concentrations (Table 6-10).

Table 4 *Laboratory method blank concentration results.*

	Laboratory Method Blank (µg/L)		
	12/21/2021	1/23/2022	2/11/2022
Arsenic	0.2*	0.0	0.0
Cadmium	0.0	0.3*	0.0
Copper	0.8*	0.0	0.0
Lead	0.0	0.0	0.0
Zinc	0.1*	0.7*	0.3*

Note: Asterisk denotes concentrations subtracted from calculated sample concentrations.

4.2 Sample Replicates

4 sample replicates, 2 from sample #8 and 2 from sample #12 (Table 2) were analyzed to assess variability in dissolved and suspended metal fraction concentrations in samples. Sample and replicate concentrations were averaged. Relative standard deviation were calculated (Table 5). Standard deviation was applied where applicable to enrichment of metal fractions (Table 6-

10), and as error bars (Figure 5-9) to determine enrichment range. Results were considered significant when enrichment range was above a zero value.

Table 5 *Sample replicate relative standard deviation.*

	Relative Standard Deviation (%)	
	Dissolved Metals	Total Metals
Arsenic	0.00	60.00
Cadmium	0.00	0.00
Copper	92.36	28.13
Lead	0.00	128.57
Zinc	83.48	29.13

Note: RSD calculated from samples 8a-c, 12a-c.

4.3 Sample Enrichment Results

4.3.1 Arsenic

Upper site samples for December and January indicated a positive result for dissolved metal fraction. There was a positive result for suspended metal fraction for upper site in January. Lower site indicates positive results for dissolved fraction of December and January. All sample fractions for each sample date indicated no enrichment with the exception of the dissolved fraction for December.

Table 6 *Arsenic sample concentrations and enrichment.*

Arsenic (µg/L) Sampling Date	Type	Upper River Site	Lower River Site	Enrichment	Enrichment Range
12/21/2021	dissolved	0.1	0.2	0.1	0.1
	suspended	0.0[b]	0.0[b]	0.0	0.0
1/23/2022	dissolved	0.4	0.3	0.0	0.0
	suspended	7.2	0.0	0.0	0.0
2/11/2022	dissolved	0.0	0.0	0.0	0.0
	suspended	0.0	0.0	0.0	0.0

[a] Calculated negative concentration Value.

[b] Calculated negative concentration value after subtracting method blank concentration

Note. Method blank concentrations subtracted from sample concentrations.

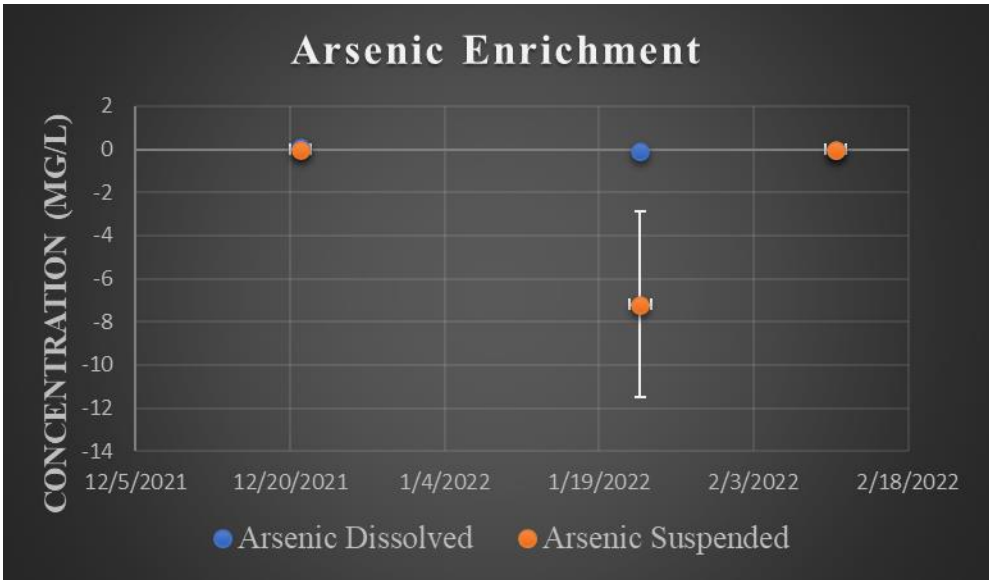

Figure 5 *Arsenic enrichment of dissolved and suspended fractions. Error bars represent relative standard deviation of total metals for samples 8a-c for suspended metal concentration, dissolved metals for samples 12a-c for dissolved metal concentration.*

4.3.2 Cadmium

Upper site samples for December indicated a positive dissolved metal fraction result and a positive result for suspended fraction in January. Lower site sample indicated a positive result for suspended fraction in December. Suspended sediment fraction for December indicated positive enrichment. Remaining fractions and sample dates indicated no positive enrichment results.

Table 7 *Cadmium sample concentrations and enrichment.*

Cadmium (µg/L)

Sampling Date	Type	Upper River Site	Lower River Site	Enrichment	Enrichment Range
12/21/2021	dissolved	0.2	0.0	0.0	0.0
	suspended	0.0[a]	0.2	0.2	0.2
1/23/2022	dissolved	0.0	0.0	0.0	0.0
	suspended	0.2	0.0[b]	0.0	0.0
2/11/2022	dissolved	0.0	0.0	0.0	0.0
	suspended	0.0	0.0	0.0	0.0

[a] Calculated negative concentration Value.

[b] Calculated negative concentration value after subtracting method blank concentration

Note. Method blank concentrations subtracted from sample concentrations.

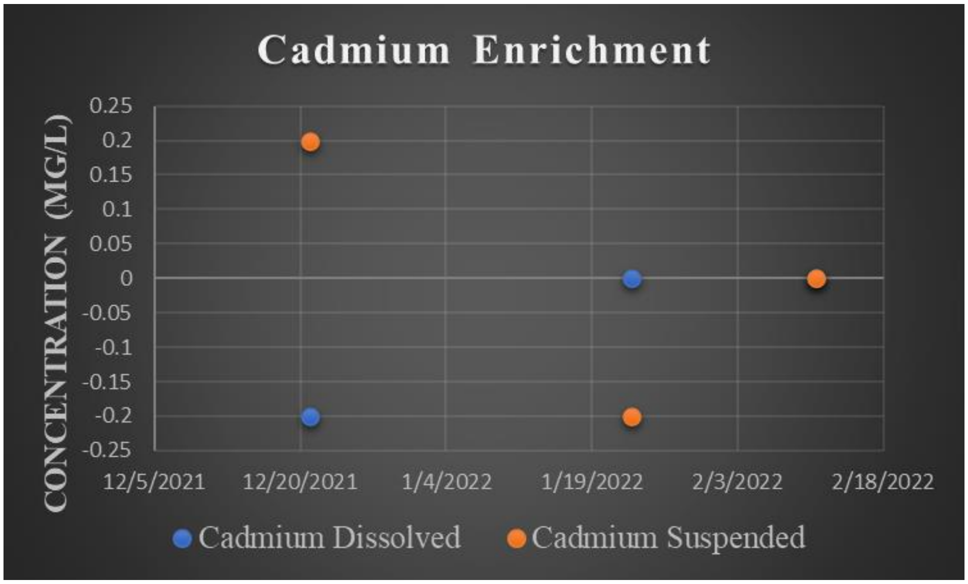

Figure 6 *Cadmium enrichment of dissolved and suspended fractions. Error bars represent relative standard deviation of total metals for samples 8a-c for suspended metal concentration, dissolved metals for samples 12a-c for dissolved metal concentration.*

4.3.3 Copper

Samples from all sample dates indicated positive concentration results for dissolved and suspended metal fractions. Results indicate enrichment of dissolved fraction for all sample dates. No enrichment was indicated for suspended sediment fraction for all sample dates.

Table 8 *Copper sample concentrations and enrichment.*

Copper (µg/L)

Sampling Date	Type	Upper River Site	Lower River Site	Enrichment	Enrichment Range
12/21/2021	dissolved	0.5	1.0	0.5	0.3 - 0.7
	suspended	0.3	0.3	0.0	0.0
1/23/2022	dissolved	0.5	0.9	0.4	0.2 - 0.6
	suspended	0.3	0.2	0.0	0.0
2/11/2022	dissolved	0.2	0.4	0.2	0 - 0.4
	suspended	2.7	0.2	0.0	0.0

[a] Calculated negative concentration Value.

[b] Calculated negative concentration value after subtracting method blank concentration

Note. Method blank concentrations subtracted from sample concentrations.

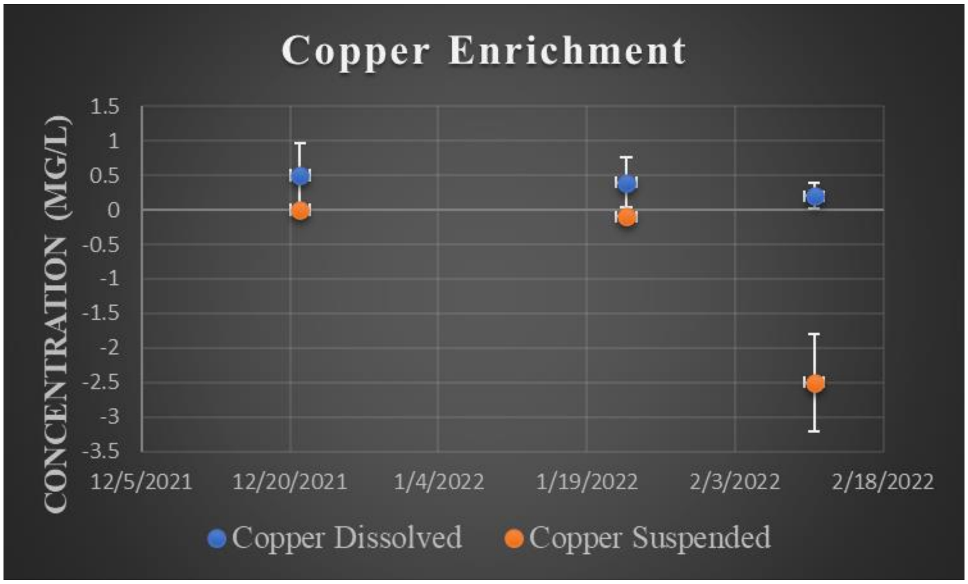

Figure 7 *Copper enrichment of dissolved and suspended fractions. Error bars represent relative standard deviation of total metals for samples 8a-c for suspended metal concentration, dissolved metals for samples 12a-c for dissolved metal concentration.*

4.3.4 Lead

Upper site samples indicated positive dissolved metal fraction concentration results for December and February, and positive suspended fraction results for December and January. Lower site samples indicated positive dissolved fraction results for all three sample dates and positive suspended fraction for January. Results indicated enrichment of dissolved fraction for December and January.

Table 9 *Lead sample concentrations and enrichment.*

Lead (µg/L)

Sampling Date	Type	Upper River Site	Lower River Site	Enrichment	Enrichment Range
12/21/2021	dissolved	1.2	3.7	2.5	2.5
	suspended	0.2	0.0[a]	0.0	0.0
1/23/2022	dissolved	0.0	0.1	0.1	0.1
	suspended	1.8	0.0[a]	0.0	0.0
2/11/2022	dissolved	0.3	0.1	0.0	0.0
	suspended	0.0[a]	0.0[a]	0.0	0.0

[a] Calculated negative concentration Value.

[b] Calculated negative concentration value after subtracting method blank concentration

Note. Method blank concentrations subtracted from sample concentrations.

Figure 8 *Lead enrichment of dissolved and suspended fractions. Error bars represent relative standard deviation of total metals for samples 8a-c for suspended metal concentration, dissolved metals for samples 12a-c for dissolved metal concentration.*

4.3.5 Zinc

Upper site samples indicated positive concentration result for dissolved metal fraction of all sample dates and negative concentration results for suspended fraction for all sample dates. Results indicated positive enrichment of dissolved fraction for January and February, and positive enrichment for suspended metal fraction for December and February.

***Table 10** Zinc sample concentrations and enrichment.*

Zinc (µg/L)

Sampling Date	Type	Upper River Site	Lower River Site	Enrichment	Enrichment Range
12/21/2021	dissolved	9	8.3	0.0	0.0
	suspended	0.0[a]	1.3	1.3	0.8 - 1.8
1/23/2022	dissolved	1	3.4	2.4	0 - 4.0
	suspended	0.5	0.0[a]	0.0	0.0
2/11/2022	dissolved	0.9	3.5	2.6	0.0 - 4.2
	suspended	0.0[a]	1.1	1.1	0.6 - 1.6

[a] Calculated negative concentration Value.

[b] Calculated negative concentration value after subtracting method blank concentration

Note. Method blank concentrations subtracted from sample concentrations.

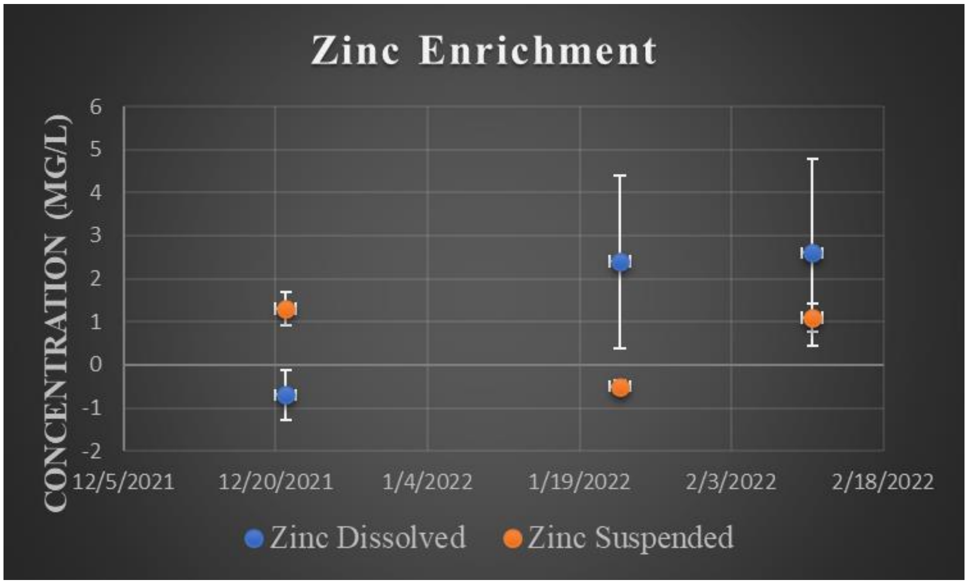

***Figure 9** Zinc enrichment of dissolved and suspended fractions. Error bars represent relative standard deviation of total metals for samples 8a-c for suspended metal concentration, dissolved metals for samples 12a-c for dissolved metal concentration.*

4.4 Dissolved Solids/Suspended Solids

Results of dissolved/suspended solids sample evaporation indicated positive mass of dissolved and suspended solids from upper (Figure 10) and lower (Figure 11) samples with the exception of a negative result for lower site suspended solids for February sample date.

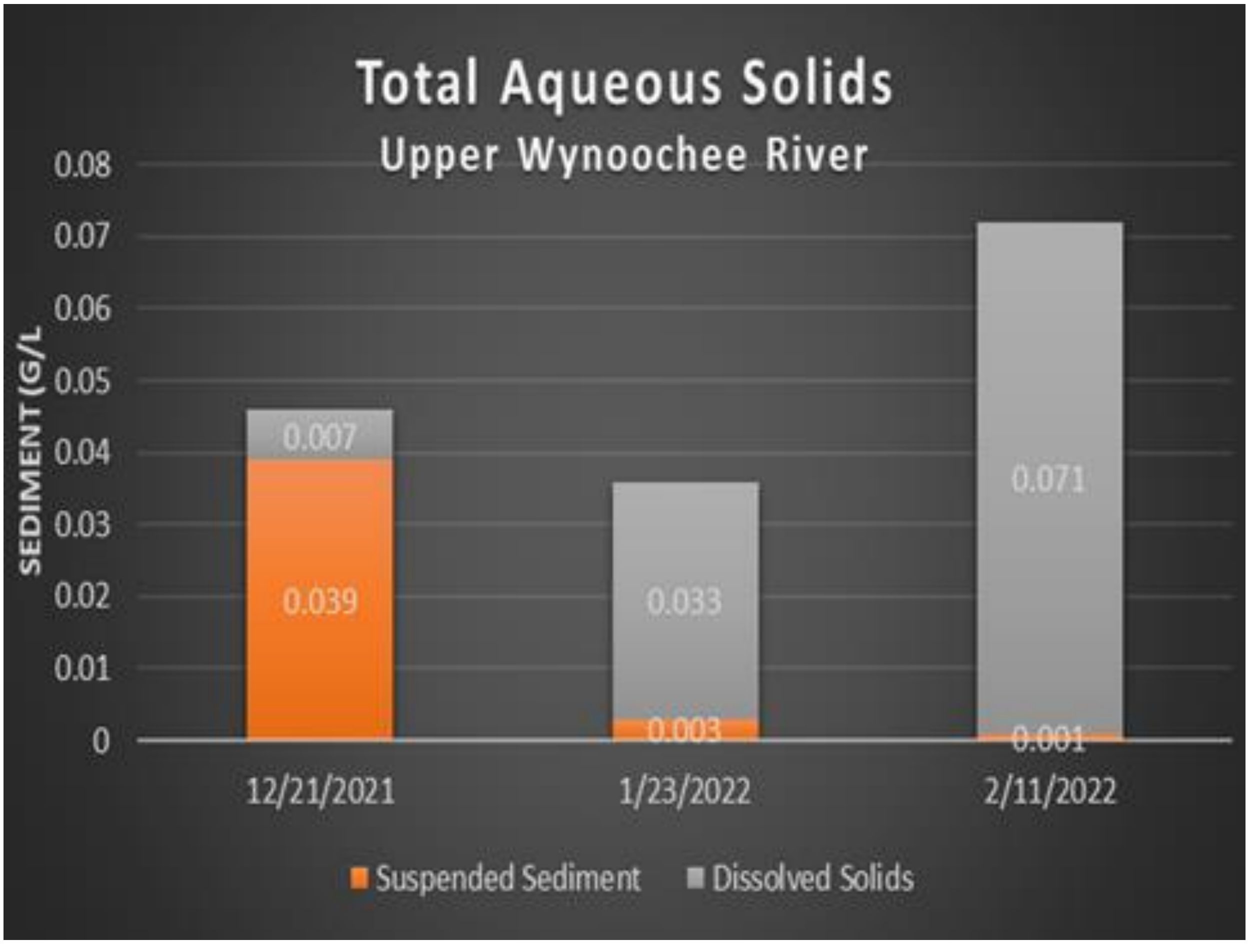

Figure 10 *Upper Wynoochee sample concentrations for dissolved and suspended solids. Suspended solids concentration calculated from dissolved/total solids concentration difference.*

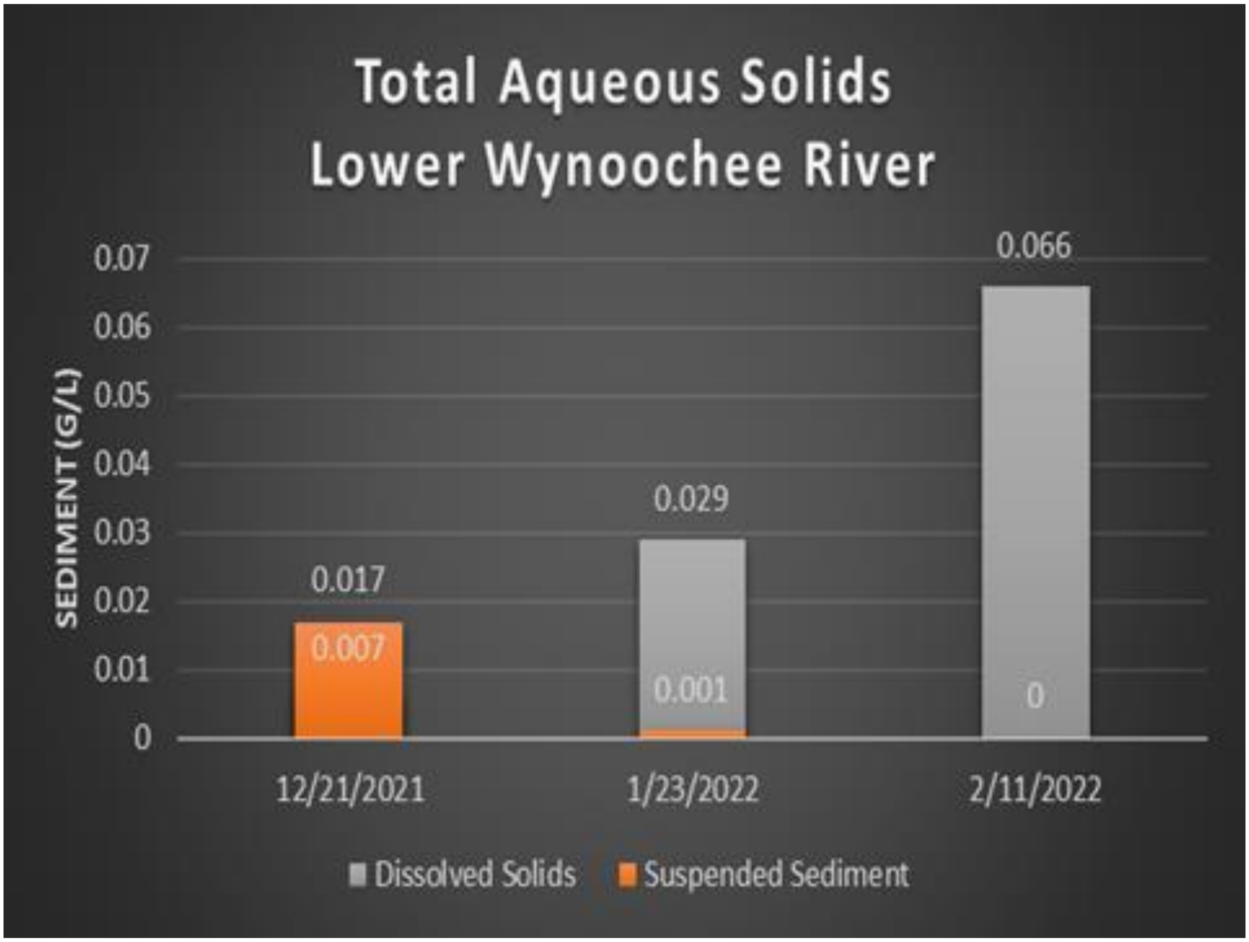

Figure 11 *Lower Wynoochee sample concentrations for dissolved and suspended solids. Suspended solids concentration calculated from dissolved/total solids concentration difference.*

5. DISCUSSION

5.1 Dissolved/Suspended Solids

Both upper and lower sites show similar proportions of dissolved and suspended solids by mass of water samples (Figure 10, 11). Samples for December indicated dominant mass of solids were transported by suspended fraction. Results show a decreasing trend of suspended solids fraction over time. This was despite an increase in river discharge of 1280cfs for January compared to 871 cfs in December (Figure 2).

5.2 Dissolved Metals

Arsenic results indicated no trend of dissolved enrichment across sample dates. Samples for December do indicate an enrichment of As in the dissolved metals fraction of 0.1 µg/L. Cadmium dissolved fraction has one positive result from the upper site in December of 0.2 µg/L but indicates no enrichment in the sample from the lower site. Both As and Cd dissolved fractions were predominantly zero results across sample dates.

Dissolved copper fraction samples indicated positive results across all sample dates ranging from 0.2 – 1.0 µg/L. Results indicate enrichment across all sample dates, enrichment of dissolved fraction for December and January are significant. Dissolved Lead fraction sample results ranged between 0 – 3.7 µg/L with one zero result for January upper site sample. Results indicated significant enrichment of dissolved fraction for December and January samples but not across all sample dates. A paired t-test performed on the dissolved copper fraction yielded a P-value of 0.03 across all sample means, above the threshold of statistical significance of Alpha = 0.1. This indicates there was a statistically significant enrichment of the dissolved copper fraction (Appendix C). Dissolved Zinc fraction samples indicated positive results across all sample dates ranging from 0.9 – 9.0 µg/L. Dissolved fraction samples indicated enrichment for January and February sample dates but neither are significant.

5.3 Suspended Metals

Suspended arsenic fraction has one positive result of 7.2 µg/L for January upper site sample date. With all other samples across the sample dates being negative, this could be considered an outlier data point. Suspended cadmium fraction has one positive result for December lower site with all other suspended Cd fraction results are zero or below. Enrichment of suspended fraction for December was significant.

Suspended copper fraction samples indicated positive results across all sample dates ranging from 0.3 – 2.7 µg/L. Samples indicated no enrichment of suspended copper fraction. Suspended Lead fraction indicate zero results for lower site in December, February and upper site for February. Positive results ranged between 0.1 – 1.8 µg/L enrichment was indicated for December and February sample dates. Zinc suspended fraction samples indicated zero results for upper site for December and February sample dates and for the lower site samples in January. Positive results for suspended Zn ranged from 0.5 – 1.3 µg/l and enrichment was indicated for December and February sample dates and were significant.

Copper dissolved fraction was enriched across all sample dates. Copper suspended fraction decreased between upper site and lower site on January and February sample dates. This was a possible indication of dissolution of complexes containing copper and enrichment of the dissolved fraction. None of the other considered metals exhibited a change in trend from one transport fraction to another between the upper and lower site across more than one sample date. This was despite a temporal trend of solids mass from predominantly suspended to predominantly dissolved. This could indicate none of the considered metals favor one fraction exclusively under oxidizing conditions sampled.

5.4 Sample Replicates and Method Blanks

Sample replicates resulted in relative standard deviation that was above a 20% threshold for dissolved Cu and Zn, and total As, Cu, Pb, Zn. Method blanks indicated inconsistent positives for As, Cd, Cu, with the exception of Zn that indicated consistent positives across method blanks that may indicate persistent laboratory contamination. Despite consistent Zn positive results, sample replicates for Zn show a high variability of 1.0 – 3.2 µg/L for suspended and dissolved fractions equal to or higher than replicate results respectively. This obscures being able to determine whether contamination was an issue in sample processing, or can simply be explained by sample variation. Sample replicate variation for As and Pb were equal to or greater than laboratory method blank results and suggest more sensitive concentration analysis was needed to overcome built in margin of error to sample analysis with GFAAS of +- 20%. For example, the volume of zero results for elements As and Cd suggest that concentration analysis needs to be at least one order of magnitude finer. Sample preconcentration quite possibly magnified sample variation and may have allowed for additional contamination within the processing laboratory. It may have also allowed for additional variation from the margin of error for analyzing a higher concentration from metals addition. Taking this in account, a method of analysis two orders of magnitude finer would be appropriate to eliminate sample variation from metals addition.

6. CONCLUSION

This project compared concentrations of trace metals above and below the Wynoochee Dam and Reservoir. One set of results did identify a statistically significant trend in enrichment of dissolved copper across sampling dates. This project did find a temporal inversion of the dominant proportion of zinc metal transport between dissolved and suspended solids between December and January sample dates. Samples indicated dissolved copper enrichment was statistically significant across all sample dates. Solids sample results indicate a temporal decrease in the proportion of suspended sediment in both lower and upper samples despite a January increase in river discharge over December. This trend may represent a seasonal flushing effect of fine sediments from high river discharge events between sampling days (Vericat et al., 2014). A decrease in suspended sediment mass in samples would likely decrease trace metal concentrations in the suspended sediment fraction. The pH range during sampling was between 7.44 -7.56. There a a multitude of common sediment/chemical complexes that are strongly adsorbing of the considered trace metals in this study and at the pH range observed, such as ferric oxides (Figure 12, 13). Chemical adsorption would suggest that trace metal concentrations would be much higher in the suspended sediment fraction compared to dissolved. This was not observed, even in the first sampling date that was dominated by suspended solid mass over dissolved. This would suggest an alternative process that enabled trace metal mobility to the dissolved fraction. There are multiple processes detailed in the literature review that could account for this but no methods were employed in this study to determine their level of influence on trace metal concentrations in this study. Future work assessing this dissolved trace metal mobility could be fruitful grounds for research.

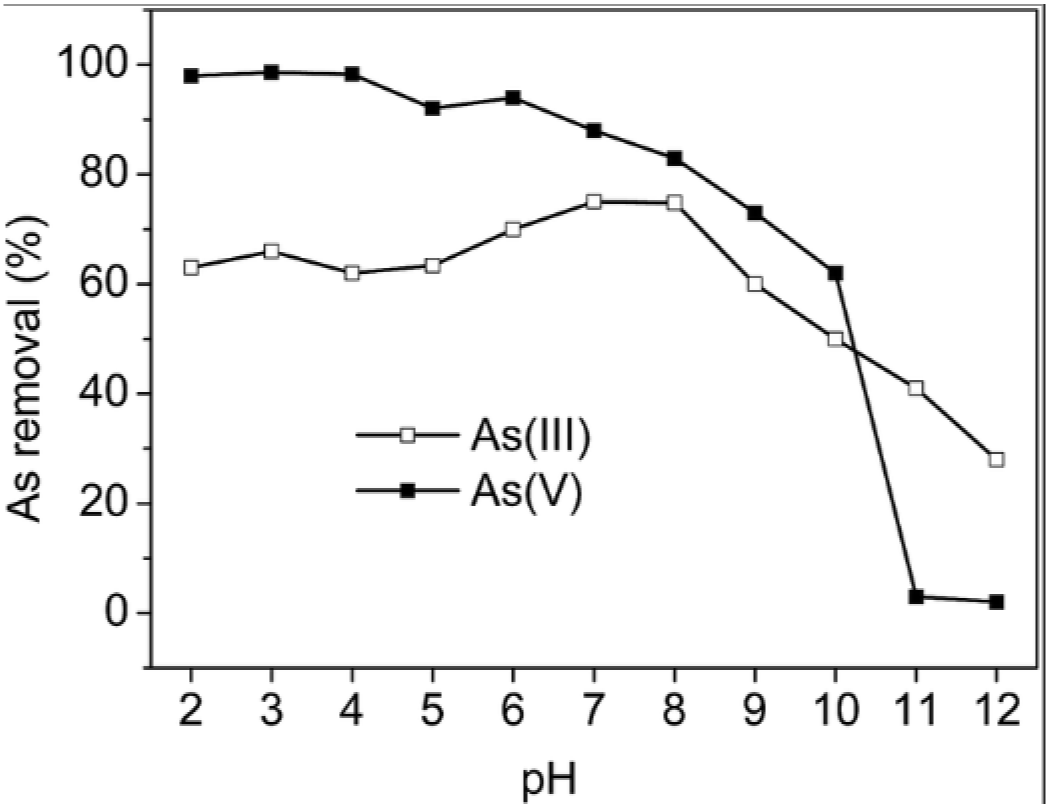

Figure 12 *Arsenic adsorption by hydrous ferric oxide as a function of pH (Cheng et al., 2016).*

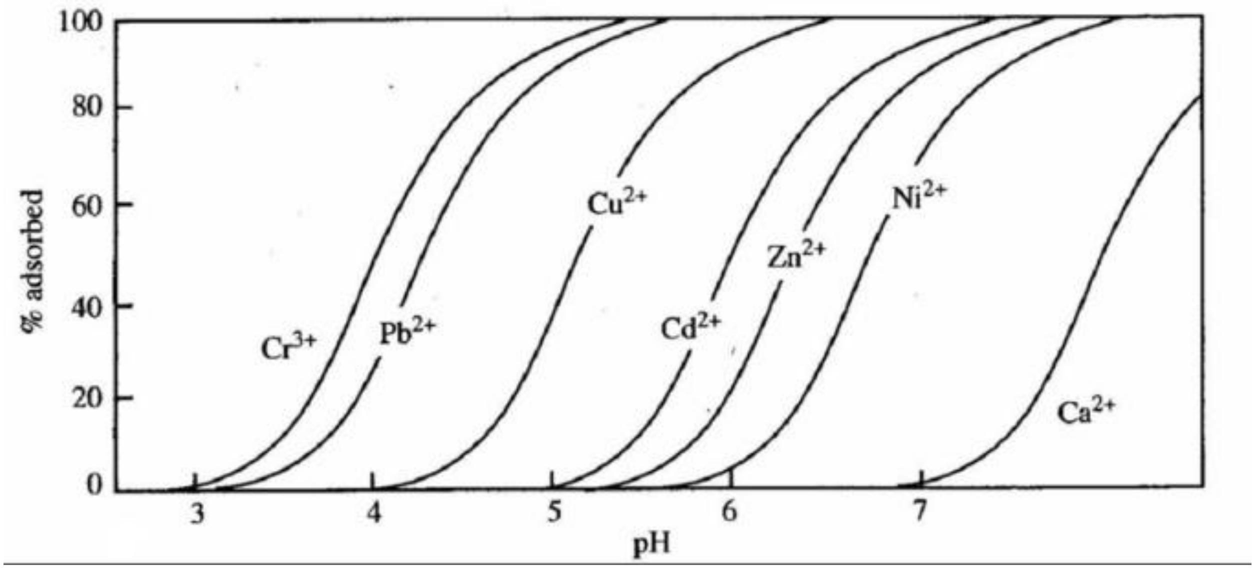

Figure 13 *Trace metal adsorption by hydrous ferric oxide as a function of pH (Jarvis & Mayes, 2012).*

Seasonal precipitation patterns create a reduction in water residence time in Winter, decreasing the potential for in reservoir processes to exhibit an influence on dissolved and suspended trace metal concentrations. Seasonal primary production is increased in warmer months and the timeframe of sampling for this study was in winter, limiting the influence of bioprocesses that have a significant impact on chemical parameters that affect trace metal mobility. Sample collection throughout the seasons could provide insight into whether changes in trace metal concentrations occur seasonally.

Given the sample results and previously mentioned rationale against the methodology employed in sample preparation, obtaining suspended sediment concentrations by difference of dissolved and total concentrations was not ideal with the amount of variation possible in calculated sample results. 8 out of 30 suspended sediment data points were calculated to be a negative value but were reported as a zero value. 3 suspended sediment values were calculated as a negative after subtracting the concentrations of the method blanks. If the dissolved and total metals concentration were accurate, a negative number would not be possible. The amount of calculated zero values indicates that the method of analysis was not sensitive enough for the system studied.

The total potential for downstream water quality degradation was not comprehensively assessed by water quality testing. Water quality testing filters out suspended sediment. Oxyhydroxides commonly attached to suspended biosediments and nutrient complexes are unstable and subject to dissolution from changing physiochemical conditions. Total metal concentrations of dissolved and suspended sediment fractions may be a more appropriate indicator of potentially hazardous water to downstream stakeholders than only the dissolved fraction (Nasrabadi et al., 2018). There was a potential for trace metal release from changing physiochemical conditions within the flow of the river to release suspended sediment and colloidal bound trace metals. There was also the possibility of downstream accretion of metal-bound sediment pockets that may represent a highly reactive source of trace metals under changing river flow. Continuous water quality testing of dissolved metals may detect metal release events from either changes in physiochemical conditions or sediment resuspension events, but intermittent testing for total metal concentrations of dissolved and sediment load may be a less laborous compromise to achieve a more comprehensive picture of hazard potential (Nasrabadi et al., 2018).

In summary, this study showed that statistically significant enrichment of trace metal transport fractions can occur. Suspended sediment concentrations can vary significantly over time, seasonally and with changes in riverflow. Dissolved and suspended sediment concentrations were not directly correlated with trace metal concentrations. Negative calculations and zero concentration values indicated high sample variability and lack of proper resolution in sample analysis. Future studies would need to review sample processing methodology to reduce sample variability and method of sample analysis to obtain more accurate results. Future work would also need to sample seasonally to detect changes from seasonasl influences and at a higher sampling rate for greater reliability of results.

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Appendices

Appendix A Standard Operating Procedure for Collection and Processing of River Water Samples.

Project: Trace Metal Transport Alteration in a Riverine System Modified by a Dam: A Study of the Inflow and Outflow of the Wynoochee Reservoir.

Chemical list:

50% Trace Metal Grade Nitric Acid

Stock Standard Solutions (1000 ppm) for sample additions Cd, Cu, Zn, As, and Pb

Safety and Spill Protocols:

Nitric Acid

Goggles, nitrile gloves, and appropriate protective clothing covering all skin from the neck down will be worn when handling containers containing acid. Care should be taken to be upwind of vapors. In the event of an acid spill in the field, bicarbonate will be used to neutralize the acid. In the event of an acid spill in lab less than approximately 100 mL, spill will be diluted with water and neutralized with bicarbonate. The area will be diluted, neutralized, then cleaned again. Spills over approximately 100 mL, immediate area will be evacuated and lab support staff will be notified.

Metals

Goggles, nitrile gloves, and appropriate protective clothing covering all skin from the neck down will be worn when handling metals in solution. Same care should be taken as when cleaning acid spills as noted above, but spill site will need to be cleaned an additional two times to account for possible metals residue. Spill cleanup materials will be double bagged and disposed of at the direction of lab support staff.

Glassware/plasticware Preparation and use

All glassware and sample bottles in contact with samples will be washed with laboratory soap and triple-rinsed with deionized water. It will then be acid-washed in 4 M HNO_3 bath for a minimum of 24 hours, then triple-rinsed with deionized water before being stored in Ziploc bags.

When transferring sample from one container to another in sample processing, preceding container will be rinsed into new container three times with deionized water to limit analyte loss. Glassware/plasticware will not be reused without being cleaned as mentioned in above paragraph.

Terms:

TDM – Total Dissolved Metals

TM – Total Metals, dissolved and suspended sediment trace metal

TMG – Trace Metal Grade

Field Methods

Water sample collection

Equipment Needed: 1-Liter polypropylene sample bottles, gallon Ziploc bags, GPS meter, field notebook, Watch, pH meter, and storage cooler.

1. Samples will be obtained from area of the river with moderate flow and a depth of at least 2 feet. Sample will be taken below the surface of the water to limit floating debris. Samples will be collected with the polypropylene sample collection bottle by hand in the same river location each time. (6) 1-Liter samples will be collected from each water sample site for each sampling day. Bottles will be rinsed in river water to be collected three times before final sample is removed.
2. GPS readings will be taken for each sample site location, along with date and time.
3. pH readings will be taken from river during collection and corrected for temperature.
4. Sample bottles will be removed from Ziploc storage bags long enough to sample water, then sealed back in bags while wearing nitrile gloves.
5. Water samples will be placed in storage cooler with ice, then transferred to refrigerator immediately after return from the field.

Laboratory Methods

Laboratory Reagent Blank

A reagent blank will be carried through each sample process for TDM and TM. Each blank will contain deionized water as a substitute for the sample. Each blank will receive 10 mL of 50% TMG nitric acid and 100 microliters of metals addition intermediate solution at the same step as the samples. The laboratory reagent blank is used to determine if method contamination or interferences are present in laboratory environment, glassware, and reagents (also serves as a method blank).

Sample Storage and Preservation

Equipment Needed: 47mm Millipore filtration apparatus, 47mm 0.45 micrometer mixed-cellulose filters, Nitrile gloves, 25 mL PP dropper bottle, and pH indicator paper.

1. Water samples will be refrigerated upon return from field sampling.

2. Filtration of samples for TM will be filtered with 0.45 Micrometer mixed-cellulose filter within 24 hours of sampling, then acidified with HNO_3 Trace Metal Grade to a pH of 2 or under. Filtration components in contact with sample will be triple rinsed with filtered sample before final filtrate collection.

Total Dissolved Solids/Total solids by Gravimetric Determination

Equipment Needed: 150 mL beakers, 100 mL volumetric pipette, analytical balance, desiccator.

EPA Method 160.1: Gravimetric Determination of Total Dissolved Solids.

1. Label, then pre-weigh 150 mL beakers with an analytical balance (4 sig.figs.) to be used for Total Dissolved Solids and Total Solids.
2. A 100 mL portion of filtrate from previous procedure will be dispensed before acidification by volumetric pipette into a 150 mL beaker
3. Sample will be evaporated in evaporation oven at 180 degrees Celsius until constant mass is obtained, then cooled in a desiccator and weighed to determine Total Dissolved Solids by mass.
4. A 100 mL portion of unfiltered sample will be measured by volumetric pipette before acidification, then dispensed into a 150 mL beaker and evaporated same as previous sample for determination of Total solids.

Concentration of samples and metals addition for preliminary sample analysis

Equipment Needed: 1000 mL volumetric flask, transfer pipet, 250 mL beaker, watch glass, hotplate, analytical balance, top-loading balance, fume hood.

Cantle, J. E. (1982). Ch. 3. In Atomic absorption spectrometry (p. 51). Elsevier scientific.

J., L. L. H. (1998). Ch. 8. In Spectrochemical analysis by atomic absorption and emission (p. 218). Royal Society of Chemistry.

J., L. L. H., & Perämäki P. (2004). Ch. 8. In Spectrochemical analysis by atomic absorption and emission (p. 313). Royal Society of Chemistry.

1. An approximate 1000 mL portion of filtered and unfiltered sample will be measured by mass on a top-loading balance (3 sig. figs.).
2. A 250 mL beaker will be labeled, weighed, then used for each portion of sample and heated on a hotplate to 85 degrees Celsius covered by a watch glass to prevent contamination. Samples will be evaporated until approximately 20 mL remains. beakers will be cooled, and additional sample will be added for concentration until original 1000 mL sample portions have been reduced to below 100 mL.
3. Weigh sample and beaker.

4. <u>Prepare 2 lab reagent blanks in this procedure comprised of deionized water following the same instructions for sample concentration. Each lab reagent blank will follow separate steps for preparation of TM and TDM samples.</u>

<u>Metals addition intermediate solution preparation</u>

Equipment Needed: 100 microliter – 1 mL micropipette and tips,, 125 mL polypropylene reagent bottle, transfer pipet, analytical balance.

(Analytical balance to be used for 4 sig. figs.)

1. Weigh, then fill one 125 mL PP reagent storage bottle with approximately 80 mL of deionized water.
2. Add 2 mL of 50% TMG nitric acid to PP bottle so final volume will contain 1% nitric acid, Weigh again.
3. Using a micropipette, add 1000ppm stock metal standard solution (500 microliters of Cu, Pb, Zn and 300 microliters As, Cd) to bottleweighing each analyte addition into bottle. Add deionized water to sample storage bottle until approximately 100 mL is obtained, then weigh. This will create an intermediate solution of approximately 5ppm Cu, Pb, Zn and 3ppm As, Cd.
4. Add 100 microliters of intermediate solution with a micropipette to samples to be analyzed after concentration for TDM samples and during digestion procedure for TM samples. Samples will be weighed before and after addition of intermediate solution to obtain sample concentration of added analytes.

<u>Digestion for Analysis of TM</u>

Equipment Needed: micropipette and tips, 250 mL beakers, hotplate, ribbed watch glasses, glass filter funnel, 85mm 0.45 micrometer mixed-cellulose filters, and fume hood.

EPA Method 200.9, Revision 2.2: Determination of Trace Elements by Stabilized Temperature Graphic Furnace Atomic Absorption.

J., L. L. H. (1998). Ch. 8. In Spectrochemical analysis by atomic absorption and emission (p. 218, 228). Royal Society of Chemistry.

1. In this step, the portion of TM sample previously concentrated to below 100 mL will be gently acid refluxed to release trace metals from reactive sediment sorption sites.
2. 10 mL of 50% HNO_3 TMG will be added by micropipette to beaker, then covered with a ribbed watch glass.
3. Sample will be heated to 85 degrees Celsius +- 5 degrees Celsius and will remain at temperature until approximately half of the sample is evaporated.

4. Filtration funnel is rinsed 3x with DI water and filter wetted before gravity filtration.
5. Sample is then quantitatively filtered using a gravity filter rack into a preweighed 125 mL pp sample storage bottle. Filter funnel is triple rinsed into bottle with DI taking care not to exceed 95 mL, then weighed.
6. 100 microliters of metals addition solution will be micropipetted into concentrated and digested TM sample in the sample bottle. Sample bottle is then weighed to determine concentration of added metals.

7. By analytical balance, weight of (125 mL sample bottle + sample portion) – (125 mL sample bottle) will determine sample weight. Calculation is performed to determine amount of deionized water to add to obtain approximate factor of 10 concentration. Deionized water is added until approximate original sample mass is obtained and final concentration is calculated.
8. Sample is then stored in 125 mL polypropylene sample bottles and Ziploc bags in laboratory refrigerator until analysis is done by an outside laboratory.

TDM Sample Metals Addition

100 microliters of metals addition intermediate solution is micro pipetted by mass into TDM sample concentrated to below 100 mL (weighed before and after addition). 10 mL of 50% TMG nitric acid is added by micropipette, then Deionized water is added by mass until approximately 100 mL is obtained (concentration of a factor of 10).

TDM sample is then transferred to a 125 mL polypropylene sample bottle in a Ziploc bag for storage in a laboratory refrigerator until sample analysis is done by an outside laboratory.

Concentration by Difference

1. TDM and TM samples, both acidified to 5% nitric acid will be analyzed by GFAAS for concentration of trace metals.
2. TDM sample concentration will be subtracted from TM sample concentration to determine trace metal concentration of suspended sediment load.

Equipment Needed: 125 mL PP sample bottles

Lab Analysis Methods:

GFAAS and ICP-MS by: Libby Environmental located in Olympia Washington.

Waste Disposal:

Samples without metals addition to be diluted/neutralized and discarded down drain. Standards to be collected in glass waste container(s) and spill cleanup materials containing metals to be stored in double bags and spills containing nitric acid will be neutralized. Disposal of final waste containers and spill cleanup materials to be directed by laboratory staff.

SOP References:

EPA Method 200.9, Revision 2.2: Determination of Trace Elements by Stabilized Temperature Graphic Furnace Atomic Absorption.

J., L. L. H. (1998). In Spectrochemical analysis by atomic absorption and emission (p. 218, 228). Royal Society of Chemistry.

Horowitz, A. J. Comparison of methods for the concentration of suspended sediment in river water for subsequent chemical analysis. *Environmental Science & Technology* **1986**, *20* (2), 155–160.

EPA Method 160.1: Gravimetric Determination of Total Dissolved Solids.

EPA Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry.

Appendix B Initial Sample Laboratory Results.

Laboratory Results, Libby Environmental Inc.					
12/21/2021		Concentration (µg/L)			
Sample	As	Cd	Cu	Pb	Zn
1	8.8	7.0	10.2	16.3	90.0
2	9.0	5.1	14.1	18.1	51.4
3	9.2	4.7	15.8	39.4	82.9
4	10.6	6.5	19.9	20.2	95.8
Recovery (%)	115	82	115	96	93
1/23/2022					
Sample	As	Cd	Cu	Pb	Zn
5	80.7	6.6	13.9	23.0	27.5
6	9.3	5.2	11.2	5.5	22.7
7	8.1	5.8	14.5	5.8	47.8
8a	7.6	5.9	16.2	5.4	42.3
8b	8.7	6.0	14.1	11.8	49.7
8c	10.1	6.2	20.2	6.9	30.1
Recovery (%)	99	93	108	100	104
2/11/2022					
Sample	As	Cd	Cu	Pb	Zn
9	2.4	3.7	6.1	9.2	17.3
10	0.0	3.7	31.0	7.3	13.0
11	4.2	3.1	10.0	4.2	55.9
12a	2.8	3.8	8.4	6.3	58.8
12b	3.2	3.1	5.8	7.8	58.3
12c	0.0	3.1	12.0	6.7	17.9
Recovery (%)	97	95	90	108	103

Appendix C Paired T-Test of Sample Means.

Arsenic (Dissolved)

	Variable 1	*Variable 2*
Mean	0.166667	0.166667
Variance	0.043333	0.023333
Observations	3	3
Pearson Correlation	0.891042	
Hypothesized Mean Difference	0	
df	2	
t Stat	1.6E-16	
P(T<=t) one-tail	0.5	
t Critical one-tail	1.885618	
P(T<=t) two-tail	1	
t Critical two-tail	2.919986	

Arsenic (suspended)

	Variable 1	*Variable 2*
Mean	2.4	0
Variance	17.28	0
Observations	3	3
Pearson Correlation	#DIV/0!	
Hypothesized Mean Difference	0	
df	2	
t Stat	1	
P(T<=t) one-tail	0.211325	
t Critical one-tail	1.885618	
P(T<=t) two-tail	0.42265	
t Critical two-tail	2.919986	

Cadmium (dissolved)

	Variable 1	*Variable 2*
Mean	0.066667	0
Variance	0.013333	0
Observations	3	3
Pearson Correlation	#DIV/0!	
Hypothesized Mean Difference	0	
df	2	
t Stat	1	
P(T<=t) one-tail	0.211325	
t Critical one-tail	1.885618	
P(T<=t) two-tail	0.42265	
t Critical two-tail	2.919986	

Cadmium (Suspended)

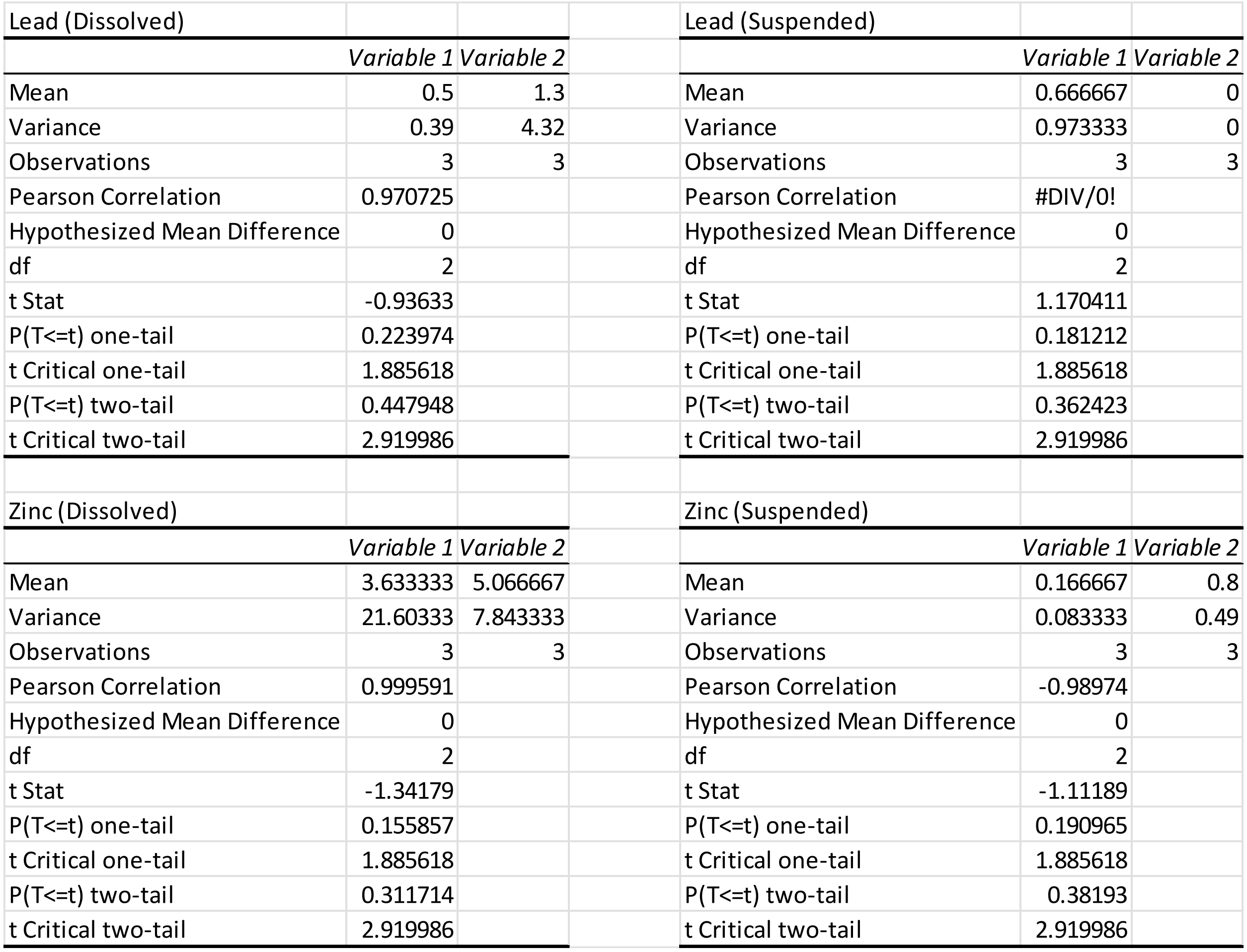
	Variable 1	*Variable 2*
Mean	0.066667	0.066667
Variance	0.013333	0.013333
Observations	3	3
Pearson Correlation	-0.5	
Hypothesized Mean Difference	0	
df	2	
t Stat	0	
P(T<=t) one-tail	0.5	
t Critical one-tail	1.885618	
P(T<=t) two-tail	1	
t Critical two-tail	2.919986	

Copper (Dissolved)

	Variable 1	*Variable 2*
Mean	0.4	0.766667
Variance	0.03	0.103333
Observations	3	3
Pearson Correlation	0.987829	
Hypothesized Mean Difference	0	
df	2	
t Stat	-4.15761	
P(T<=t) one-tail	0.026635	
t Critical one-tail	1.885618	
P(T<=t) two-tail	0.053271	
t Critical two-tail	2.919986	

Copper (Suspended)

	Variable 1	*Variable 2*
Mean	1.1	0.233333
Variance	1.92	0.003333
Observations	3	3
Pearson Correlation	-0.5	
Hypothesized Mean Difference	0	
df	2	
t Stat	1.060562	
P(T<=t) one-tail	0.200018	
t Critical one-tail	1.885618	
P(T<=t) two-tail	0.400035	
t Critical two-tail	2.919986	



Lead (Dissolved)		
	Variable 1	*Variable 2*
Mean	0.5	1.3
Variance	0.39	4.32
Observations	3	3
Pearson Correlation	0.970725	
Hypothesized Mean Difference	0	
df	2	
t Stat	-0.93633	
P(T<=t) one-tail	0.223974	
t Critical one-tail	1.885618	
P(T<=t) two-tail	0.447948	
t Critical two-tail	2.919986	

Lead (Suspended)		
	Variable 1	*Variable 2*
Mean	0.666667	0
Variance	0.973333	0
Observations	3	3
Pearson Correlation	#DIV/0!	
Hypothesized Mean Difference	0	
df	2	
t Stat	1.170411	
P(T<=t) one-tail	0.181212	
t Critical one-tail	1.885618	
P(T<=t) two-tail	0.362423	
t Critical two-tail	2.919986	

Zinc (Dissolved)		
	Variable 1	*Variable 2*
Mean	3.633333	5.066667
Variance	21.60333	7.843333
Observations	3	3
Pearson Correlation	0.999591	
Hypothesized Mean Difference	0	
df	2	
t Stat	-1.34179	
P(T<=t) one-tail	0.155857	
t Critical one-tail	1.885618	
P(T<=t) two-tail	0.311714	
t Critical two-tail	2.919986	

Zinc (Suspended)		
	Variable 1	*Variable 2*
Mean	0.166667	0.8
Variance	0.083333	0.49
Observations	3	3
Pearson Correlation	-0.98974	
Hypothesized Mean Difference	0	
df	2	
t Stat	-1.11189	
P(T<=t) one-tail	0.190965	
t Critical one-tail	1.885618	
P(T<=t) two-tail	0.38193	
t Critical two-tail	2.919986	