

METAL-BASED COAGULANT EFFECT ON SEDIMENT SLURRY
FOR THE LAKE COMBIE RESERVOIR SEDIMENT AND
MERCURY REMOVAL PROJECT, GRASS VALLEY CA

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by

Nicholas Graham

Summer 2017

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LIST OF ABBREVIATIONS AND DEFINITIONS

°C	Degree Celsius
λ	Wavelength (nm)
Al	Aluminum
As	Arsenic
AU	Absorbance Units
BAL	Brooks Applied Laboratory
CAWSC	California Water Science Center
CERCLA	Comprehensive Environmental Response Compensation and Liability Act
Cr	Chromium
DBP	Disinfection By-Product
dHg	Dissolved Mercury
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
USEPA	U.S. Environmental Protection Agency
USFS	U.S. Forest Service
Fe	Iron
fHg	Filtered mercury
gal	Gallon
gal/hr	Gallon per Hour

gpm	Gallon per Minute
Hg	Mercury
L	Liter
MDL	Method Detection Limit
MeHg	Methylmercury
mg/L	Milligram per liter
mL/L	Milliliter per liter
Mn	Manganese
Mo	Molybdenum
MRL	Minimum Reporting Limit
ng/L	Nanogram per liter
Ni	Nickel
NID	Nevada Irrigation District
nm	Nanometer
NTU	Nephelometric Turbidity Units
Oz	Ounce
PHg	Particulate Mercury
ppm	Part per million
PSM	Polar Star Mine
RPD	Relative Percent Difference
SUVA₂₅₄	Carbon-normalized specific absorbance

TDS	Total Dissolved Solids
THg	Total Mercury
TMDL	Total Maximum Daily Load
TSS	Total Suspended Solids
USGS	United States Geological Survey
UV	Ultra Violet
QAQC	Quality Assurance, Quality Control
Zn	Zinc

ABSTRACT

METAL-BASED COAGULANT EFFECT ON SEDIMENT SLURRY FOR THE LAKE COMBIE RESERVOIR SEDIMENT AND MERCURY REMOVAL PROJECT, GRASS VALLEY CA

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This study was conducted to assist Nevada Irrigation District (NID) in the analysis of a sediment and mercury removal treatment process at the Lake Combie Reservoir, Grass Valley CA. Part of the removal process consisted of administering metal-based coagulants to promote the sedimentation of fine grain materials. Field-scale tests resulted in process effluent below regulatory criteria for total metal concentrations including mercury (Hg), chromium (Cr), iron (Fe), magnesium (Mg), molybdenum (Mo), nickel (Ni), and zinc (Zn). Additional sediments from future sites (Combie Lake and Greenhorn Creek) and alternative coagulants (LBP-2101 and Clar+Ion 5057) were tested in the sedimentation process. Furthermore, prediction models for continuous real time total mercury (THg) and filtered mercury (fHg) concentrations during the sedimentation treatment process are presented. The models use the parameters; total suspended solids

(TSS), total dissolved solids (TDS), and ultraviolet absorbance (A_{254}) as proxies for THg and fHg concentrations. The multivariate regression models had R^2 values of 0.97 and 0.85 for the prediction of THg and fHg, and p-values <0.0001 . Continuous monitoring of these proxies at pre- and post-treatment locations coupled with the predictive capabilities of the models suggest that full scale implementation of the sediment and mercury removal process at Lake Combie Reservoir can operate within regulatory criteria with the ability to identify an exceedance before effluent is released.

CHAPTER I

BACKGROUND

As a result of the historic gold mining operations in the Sierra Nevada from 1849 to the 1950s (Churchill, 1999), residual mercury (Hg) continues to propagate from hydraulic and hard rock mine sites to downstream ecosystems (Domagalski, 2001; Fleck et al., 2011; Singer et al., 2013). Hg contamination in the aquatic food web presents a potential risk to human health and the environment, creating a need for remediation practices in affected watersheds, such as the Yuba and Bear Rivers where fish are some of the most contaminated in the Sierra Nevada due to extensive mining (May et al., 1999).

Gold (Au) deposits are found in either hard rock (gold-quartz veins, lode) or placer deposits (alluvial, unconsolidated, auriferous gravels) (Alpers et al., 2005a). Hard rock deposits were mined using underground methods. Placer deposits were hydraulically mined or dredged using high-pressured water cannons or monitors to break down gravel deposits rich with gold (Averill, 1946). In both cases, gold extraction involved using a sluice with a series of riffles and troughs where liquid elemental mercury could be added to amalgamate with the fine grain gold, helping it to settle out for recovery (Alpers et al., 2005a).

From the 1850s to the early 1900s, miners used liquid elemental mercury (quicksilver) in all practices of gold recovery. An estimated 26 million pounds of mercury was used to increase the recovery rate of gold in California, primarily in the Sierra Nevada and Klamath-Trinity Mountains (Churchill, 1999; Hunerlach et al., 1999;

Slotton et al., 1997). Liquid elemental mercury fuses with gold creating high-density gold-mercury amalgams, which sink more rapidly allowing less dense sand and gravel slurries to pass over and through the sluice. When high volumes of turbid water flowed through sluices, overloading its ability to recover gold, the finer gold and mercury particles were discharged out of the sluice box before sedimentation could occur resulting in their transport to downstream environments (Hunerlach et al., 1999).

Mercury use for gold recovery ranged from 0.1 to 0.36 lb/ft² or 0.05-0.15 kg/m² of sluice, with a typical sluice having an area of several thousand square feet (Alpers et al., 2005a). During the late 1800s when the best operating efficiencies existed, an estimated ten percent of total added mercury was lost to the environment (Averill, 1946). Under less than ideal operating conditions, an average annual loss rate was estimated around 25 percent of mercury added (Bowie, 1905). Placer mining operations in the Sierra have been estimated to account for 10 million pounds of mercury lost to the environment, while hard rock mines account for about 3 million pounds of mercury lost (Hunerlach et al., 1999). With such vast quantities of mercury lost to the environment, downstream propagation of liquid elemental mercury entrained in the mine tailings was inevitable and continues today (Singer et al., 2013).

Mercury that was not recovered from mining practices was transported and deposited downstream of sluice configurations along with the sediments displaced by mining practices (Miller et al., 1996; Lecce et al., 2008; Singer et al., 2013). According to James (1989), approximately 90% of the mercury and sediment displaced by mining remained within the Bear River basin for more than 100 years. James also hypothesized

that during flood events mercury-laden sediments would suspend with runoff and transport downstream. Once in suspension, sediments can travel downstream and accumulate behind dams within reservoirs (Minear and Kondolf, 2009). Accumulation of sediments in reservoirs can result in economically and ecologically starved habitats, incised riverbeds, and increased bank erosion rates (Williams and Wolman, 1984; Kondolf, 1997).

Present-day reservoir sediment yields have been estimated to be 219 m³/km²/yr in the Sierra Nevada geomorphic region (Minear and Kondolf, 2009). Sediment accumulation in reservoirs is a current and pressing issue for water storage facilities and flood protection, adding to the complication that many sediments of the Sierra Nevada are contaminated by mercury (Snyder et al., 2004).

When trapped mercury-laden sediments are in the presence of sulfate-reducing bacteria in an anoxic environment, inorganic elemental mercury (IHg) can be methylated to organic methylmercury (MeHg) (Slotton et al., 1997). Once mercury has been converted to MeHg, primary producers such as phytoplankton can take up this bioavailable organic form that can bioaccumulate and biomagnify through trophic levels (Slotton et al., 1997; Mason et al., 2006; Benoit et al., 2009; Bergamaschi et al., 2011). The primary mechanism for MeHg exposure in humans is through ingestion of sport fish (California Office of Environmental Health Hazard Assessment, 1999). According to the United States Environmental Protection Agency (USEPA) the water quality criteria for MeHg is 0.3 mg/kg of wet-weight fish tissue, as outlined under the Clean Water Act Section 304(a) (EPA, 2001). MeHg is a neurotoxin (Kurland et al., 1960) and

consumption of Hg-contaminated fish represents a serious human health threat (Shilling et al., 2010). Methods to control and effectively treat Hg-contaminated sediments are pivotal to restoring environments impacted by Hg contamination.

Under the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) multiple federal agencies have undertaken Hg cleanup efforts within the Northern Sierra Nevada. Under the direction of the USEPA, remediation efforts at the Polar Star Mine (PSM) within the Dutch Flat Mining District were made (Hunerlach et al., 1999). Remediation efforts were carried out by removal of wooden sluice boxes remaining from mining practices, cleaning, and return of large boulders and gravel, and the excavation of fine grain sediments (“fines”) that were too small for recovery by a physical Hg separation process. The US Forest Service (USFS) performed Hg removal efforts at the Sailor Flat hydraulic mine (DeGraff, 2007). USFS excavated 40 ft deep to expose the sluice tunnel floor where a concrete mixture was injected to immobilize the Hg-contaminated gravel. Soil was then compacted over the exposed tunnel to prevent potential Hg methylation. At the Boston mine within the Red Dog mining district, the Bureau of Land Management (BLM) excavated 93 cubic yards from a sluice tunnel and 26 feet of a feeder shaft (Tetra Tech, 2004). BLM then ran excavated sediments through a physical separation process, contained contaminants, and cleaned sediments within 6 inches to 2 feet thick concrete lined excavated shafts (Tetra Tech, 2004). Although these sites were successful source-area efforts to remove Hg, Hg-contaminated sediments from hundreds of abandoned mines still continue to propagate to downstream environments (Hunerlach et al., 1999).

At Lake Combie Reservoir, which lies between Rollins and Camp Far West Reservoirs within the Bear River watershed (Figure 1), the Nevada Irrigation District (NID) is developing an innovative sediment and mercury removal project. Removal and treatment of contaminated sediments utilize both mining processes and water treatment technology commonly practiced at wastewater treatment facilities.



Figure 1. Location of Lake Combie, Rollins, Camp Far West Reservoir, and Bear River. Created in ArcGIS under USGS CAWSC license.

CHAPTER II

INTRODUCTION

In the heart of California's hydraulic gold mining region outlined by G.K Gilbert (1917) and approximately 45 miles northeast of Sacramento lies Lake Combie Reservoir within the Bear River watershed (Figure 2).

Lake Combie Reservoir is owned and operated by the Nevada Irrigation District (NID) and holds 5,555 acre-feet of water storage at full capacity. Lake Combie Reservoir and the 10 miles of the Bear River are listed on the State Water Resources Control Board (SWRCB) 2010 Integrated Report under section 303(d) as impaired for mercury. Under the requirements of this report, SWRCB mandated a Total Maximum Daily Load (TMDL) in 2015. In 2003, dredging of accumulated sediment in the reservoir ceased due to mercury being stirred up by the dredging operations (Monohan and Crough, 2012). As a result NID has been unable to maintain the reservoir capacity by dredging of accumulated sediments. The SWRCB is currently developing guidelines for a reservoir Hg TMDL for mercury-impaired reservoirs in one load allocation effort. Reservoir operators will be required to develop management techniques to reduce Hg contamination in fish and to downstream environments (SWRCB, May 2016).

In order to maintain the reservoir, NID is developing a sediment and mercury removal project at Lake Combie. NID has tested innovative techniques and technologies to remove Hg from dredged sediments and process water including the use of coagulants

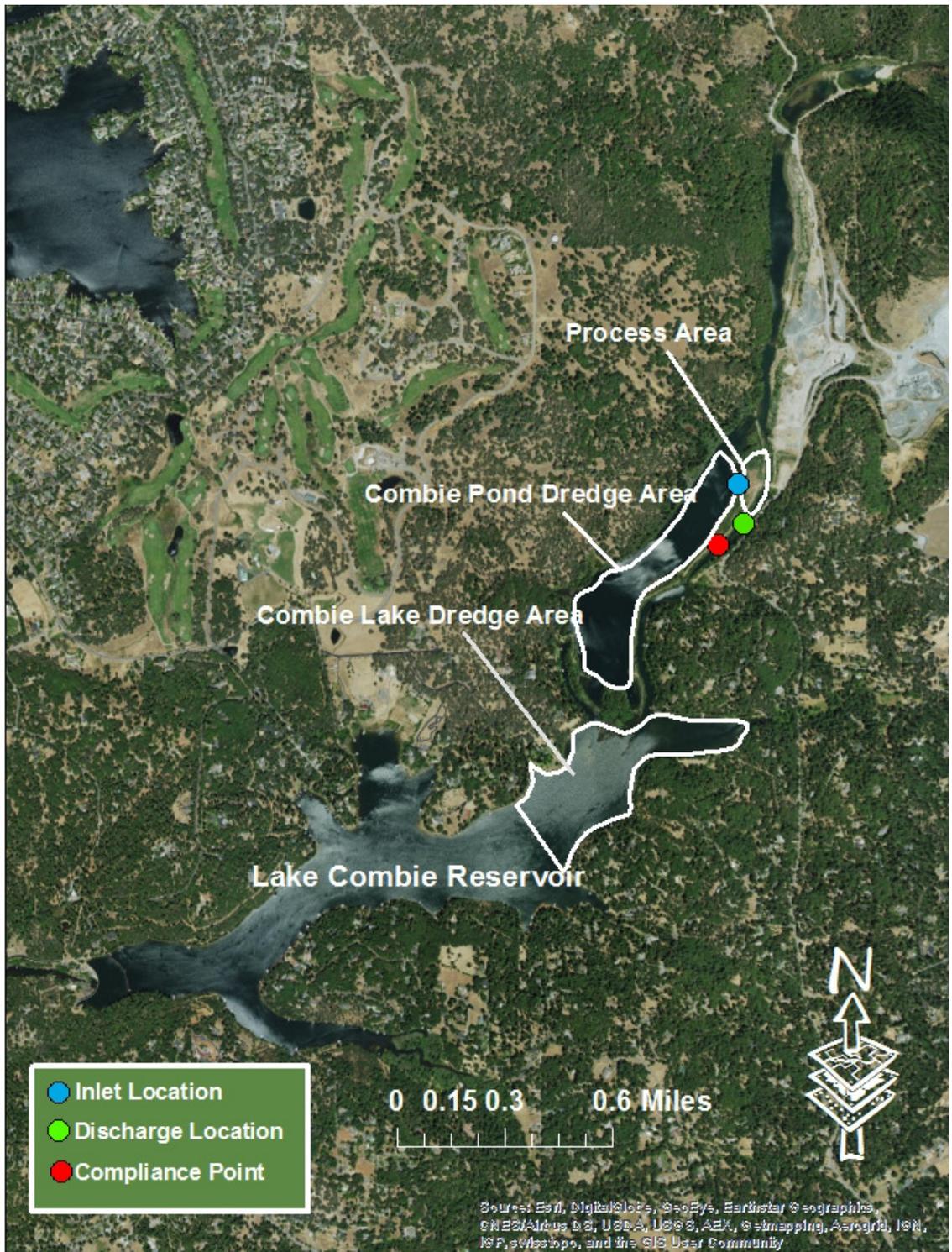


Figure 2. Map of Lake Combie Reservoir sediment and Hg removal project, Nevada City CA. Created in ArcGIS under the USGS CAWSC license.

to return clean water back to the reservoir. The purpose of the sediment and mercury removal project at Lake Combie is to:

- a. Remove accumulated sediment from the reservoir.
- b. Remove mercury from dredged sediments.
- c. Return clean water back to the reservoir.
- d. Inform best management practices for maintaining reservoirs in the Sierra Nevada affected by mercury contamination.
- e. Determine if sediment and mercury removal from the reservoir results in a less contaminated fish population.

Equipment efficiency tests were conducted in replicate closed systems in 2009 at Lake Combie Reservoir by NID. Tests indicated that the treatment process removed an average of 93% of the total Hg (THg) in the free elemental form (Hg(0)) in the sand size greater than 0.63mm in the sediment sources through the use of a modified centrifuge (Monohan and Crough, 2012). However, Hg and other metals associated with fine-grained materials (<0.63mm) were still left in the slurry created by the process. Title 22 metals of the California Code of Regulations (22 CCR) such as Cr, Hg, Fe, Mo, Ni, and Zn were analyzed during these tests as well as a host of other organic compounds as a part of developing an antidegradation analysis for the project (Monohan and Crough, 2012). Additionally, neither methylmercury (MeHg) nor 'reactive' mercury (RHg(II)) was removed in the sediment and water treatment process project (Monohan and Crough, 2012). In an effort to remove the remaining sediment-bound Hg and other metals,

additional treatment steps and tests including the use of settling tanks and coagulants were scheduled to take place.

In December of 2014, NID conducted three tests using different source sediments and coagulants to determine the effluent characteristics of the sediment and water treatment process. One coagulant type was tested against one source material on each test day. For the purpose of monitoring the process efficiency a series of sample locations were established, these locations included: Bear River water entering the treatment facility (Background), the wheelwash mixing tank where the slurry to be treated with coagulants was pumped to, two in-series open-top sedimentation tanks where flocculation of the treated slurry occurred, and finally the regulatory compliance point 300 feet downstream of process effluent within the Bear River (Figure 3).

This thesis reports the results of the most recent tests of NID’s sediment and Hg removal process using Combie Lake sediments and the combination of two

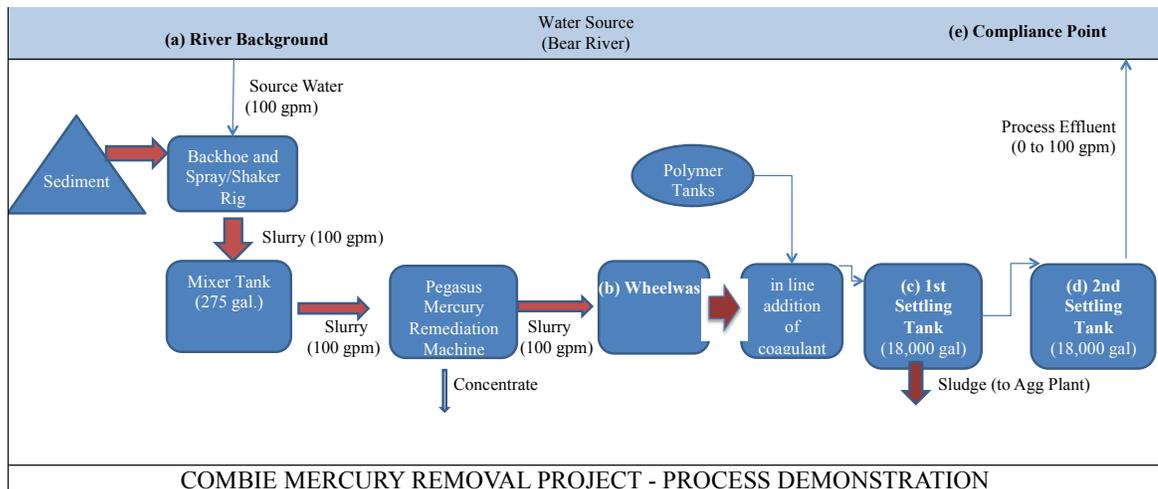


Figure 3. Process diagram with sample locations. Sample locations include River Background (a), Wheelwash (b), Tank 1 (c), Tank 2 (d), and Compliance point located 300 feet downstream of process discharge (e).

coagulants, BHR P-50 and 665-P. Additionally, this thesis analyzes previous mercury removal tests from December 2014 conducted on Combie Pond and Greenhorn Creek materials utilizing the Clar+Ion 5057 and LBP-2101 coagulants. Using all the test data, a low cost monitoring method for continuous measurements of in-situ water quality during operations, a model for these water quality parameters to predict Hg removal efficiency, and to provide instant feedback on process effectiveness is proposed.

CHAPTER III

LITERATURE REVIEW

The following literature review identifies body of works that describe and validate the use of coagulants within NID's Lake Combie Hg and sediment removal process. The structure of the literature review starts with Hg and how it can propagate through the environment and then highlights known associations between Hg and dissolved organic carbons (DOCs). The focus of the literature review then shifts towards coagulants and their use within the water treatment industry followed by research conducted on the use of such coagulants for the reduction of Hg concentrations.

Hg and Sediment Transport

Gibbs' (1977) article, "Transport Phases of Transition Metals in the Amazon and Yukon Rivers," summarized how metals of the transition group are transported by a river. Gibbs states that within aquatic systems trace metal levels are closely related to suspended sediment concentrations. The two key mechanisms of transition metal transport were crystalline formations on particles and hydroxide coatings (Gibbs, 1977). Sediment or particulate matter accounted for greater than 97% of transition metal loading to downstream environments and ultimately the ocean (Gibbs, 1977).

In order to understand and quantify Hg and Methylmercury (MeHg) transport, Bishop et al. (1995) and Scherbatskoy et al. (1998) studied and sampled spring runoff from forested catchments over a two-year (1994-1996) period in northern Vermont. Following the study, Bishop concluded that THg concentrations in stream water

correlated with the organic fraction of suspended sediment. Bishop et al. (1995) and Scherbatskoy et al. (1998) found that a majority of Hg transport occurred during higher flow and turbid periods. However, Bishop et al. (1995) found that during snowmelt fed flows MeHg and Hg concentrations declined. Bishop et al.'s (1995) findings suggest that there are other factors than the amount of flow and sediment concentrations affecting the movement of Hg. This is important because Sierra Nevada is a snowmelt dominated hydrologic system throughout the summer months, but does receive rain-derived inputs during the winter and spring months, implying the changing conditions for possible Hg transport.

In an effort to characterize concentrations of trace elements on suspended material, water-quality samplings were conducted in Camp Far West Reservoir and other tributary arms, CA from 2001-2003 (Alpers et al., 2006). Following THg and suspended sediment concentration determinations, relationships were found to exist between total suspended sediment (TSS) and THg concentrations within the northern California reservoir. The highest concentrations of THg per milligram of suspended sediment were measured during the fall ($0.4 \mu\text{g Hg/g}$ sediment) and winter months ($1.0 \mu\text{g Hg/g}$ sediment). Concentrations then declined during the spring and summer months ($<0.4 \mu\text{g Hg/g}$ sediment). This finding supports that mercury, both particulate (pHg) and filtered (fHg), as well as other metals are moving downstream with high flow events as particulates bound to sediments.

Hg – DOC Association

Haitzer et al. (2002) explored the interactions between Hg and dissolved organic matter (DOM). Both studies found that Hg was associated with DOM concentrations. To identify how mercury and DOM varied at different concentrations Haitzer measured a wide range of Hg-to-DOM concentrations using an equilibrium dialysis ligand exchange method. Using this method Haitzer et al. (2002) identified that at concentrations below 1 μg of Hg per mg of DOM, the interactions between Hg and DOM were strong. While at concentrations greater than 10 μg of Hg per mg of DOM the binding strength determined by carboxyl groups were much lower. Suggesting the binding between Hg and DOM is controlled by the small fraction of DOM containing the stronger organic thiol group binding sites. Ravichandran (2004) also concluded that DOM interacted very strongly with Hg, and documented that DOM can affect Hg speciation, solubility, mobility, and toxicity within aquatic systems. These findings support the Hg-DOM interactions and highlights that in systems with high DOC concentrations bonding between the two may have effects on Hg type and transport rates.

In an approach to parameterize DOM ultraviolet-visible absorption spectra, Helms et al. (2008) used two distinct spectral slope regions to compare DOM from dissimilar water types, wetlands and photobleached oceanic water. Spectral slopes of the 275-295 nm and the ratio between 275-295 nm and 350-400 nm slopes were found to be related to the DOM molecular weight. This study also identified that the property of UV-visible light absorbance fluctuated with chemical composition and concentration and thus could be used as a proxy for DOC composition and concentration (Helms et al., 2008).

Ultraviolet absorbance at 254 nm (A_{254}) and specific ultraviolet absorbance 254 nm ($SUVA_{254}$) were evaluated for use as proxies for filtered mercury (fHg) and chemical composition of DOC (Weishaar et al., 2003; Dittman et al., 2009). $SUVA_{254}$ is a descriptive absorbance parameter that is operationally defined as the absorbance value of A_{254} divided by the DOC concentration in milligrams per liter multiplied by 100, otherwise known as carbon-normalized specific absorbance (Weishaar et al., 2003). $SUVA_{254}$ is strongly correlated with dissolved aromatic content in aquatic systems, and by extension DOC as a whole (Weishaar et al., 2003). In addition A_{254} was documented to have a high association with Hg concentrations ($R^2=0.92$) (Dittman et al., 2009). Similarly, Weishaar et al. (2003) found that $SUVA_{254}$ has a strong correlation with the aromatic content or quality of DOC. These correlations have been used in a multivariate analysis for the in-situ prediction of Hg species. With high analysis costs of trace metal Hg, limited hold times of Hg samples, and difficulty of capturing high flow events, using such proxies provided an effective inexpensive approach to gathering Hg concentrations as demonstrated by Dittman et al. (2009) in three forested watersheds in New Hampshire, Vermont, and New York, U.S.A.

Coagulants in Water Treatment

In a study conducted by Duan and Gregory (2003), the characteristics of widely used forms of aluminum and iron based coagulants in water and wastewater treatments and their effect on inducing sedimentation were studied (Duan and Gregory, 2003). Through a comprehensive review of literature, Duan and Gregory (2003) found that charge neutralization and “sweep flocculation,” the two main mechanisms for

particle removal, depend on pH, DOM content, and coagulant dosages to increase the attraction between metal/pathogen bound particulates to produce a neutral dense flocculation or “floc” that settles out of solution.

To understand the reactions between dissolved organic carbon (DOC) and chlorine as well as its effect on the ability of a coagulant to induce sedimentation, Richardson and others reviewed 30 years of research on the occurrence, genotoxicity, and carcinogenicity of 85 Disinfection By-Products (DBPs) (Richardson et al., 2007). Richardson and others (2007) conferred that within the drinking-water treatment industry DOC has been known to be a potential constituent of concern because of its ability to react with chlorine. Water treatment facilities commonly use chlorine as a disinfection product, and DOC in the presence of chlorine can form carcinogenic DPBs. To prevent the formation of these DBPs, drinking water facilities employ the use of coagulants to settle out DOC by the agglomeration of colloids prior to disinfection with chlorine (Richardson et al., 2007).

Documented within the textbook, *Water Supply and Pollution Control* (“Chemical Treatment Processes,” Chapter 11), Viessman et al. (2009) describes treatment methodologies from the Office of Drinking Water, U.S. Environmental Protection Agency’s “Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual.” In wastewater treatment facilities, coagulants have been used for the removal of harmful particulate-bound pathogens, dissolved organic carbon (DOC), color, and turbidity for the protection of human health and environmental concerns (Viessman et al., 2009). These coagulants increase the sedimentation rate by stripping or cancelling

the repelling charges between particles. Coagulants are introduced in succession of two parts, counter-ions introduced first to neutralize and strip repulsive charges between colloids (Viessman et al., 2009), and long chain polymers that act as “sweeping” mechanisms and sweep bridged colloids into a floc (Viessman et al., 2009). By inducing sedimentation of flocculants, coagulants effectively reduce turbidity, DOC, particulate-bound pathogens, and reduce color impurities. Commonly used coagulant types consist of ferric, aluminum, and organic salts, each having different removal tendencies depending on amounts of dissolved organic matter (DOM) present in the water to be treated and the desired level of removal (Viessman et al., 2009). Different parameters such as temperature, alkalinity, ionic strength, and pH of a solution can all affect the ability of a coagulant to induce sedimentation (Viessman et al., 2009). Laboratory analysis such as bench-tests are often used to find the most efficient concentration and type of coagulant for a given source material prior to large-scale implementation (Viessman et al., 2009)

Coagulant Use for Hg Removal

A laboratory jar test study was conducted (Henneberry et al., 2011) to assess the Hg removal potential of three industrial grade coagulants: ferric chloride, ferric sulfate, and poly aluminum chloride coagulant through particle settling. Using acid rinsed Teflon bottles suitable for trace-metal analysis and magnetic stir bars, filtered Hg laden agricultural drainage water was treated with 0%, 20%, 40%, 60%, 80%, and 100% of an optimal coagulant dose found using a streaming current detector (SCD) commonly used within water utility treatments. Following completion of jar tests a 97% and 80% reduction of inorganic Hg and methylmercury (MeHg) concentrations occurred from pre

to post treatment (Henneberry et al., 2011). These results provided fundamental insights for field application of coagulants for the removal of Hg from agricultural drainage waters within Twitchell Island, Sacramento, California (USA).

Field tests consisted of experimental dosing of Hg-contaminated agricultural waters in nine constructed wetland cells at Twitchell Island within the Sacramento-San Joaquin Delta (Ackerman et al., 2015). Two types of coagulants, polyaluminum chloride and ferric sulfate, were tested and compared to a control. Following treatments with coagulants total mercury (THg), filtered methylmercury (fMeHg), and DOC concentrations in effluent waters from the constructed wetlands were reduced by 59-76%, 40-70%, and 65-86% respectively. Results suggest that the use of such coagulants was an effective management tool to induce sedimentation and effectively reduce mercury concentrations within effluent (Ackerman et al., 2015).

Purpose of the Study

The purpose of this study was to inform NID on the resultant water quality following coagulant water treatment during the sediment and mercury removal project. Bench-scale analyses of coagulants were tested for field-scale application, and the effect of coagulant additions on the trace metal concentrations was measured. This study described the effectiveness of coagulant additions on reduction of effluent turbidity, characterized the distribution of mercury between the particulate and filtered fractions, quantified the relationship between total mercury and total suspended solids, and attempted to identify variables with predictive abilities for filtered mercury (fHg) and

total mercury (THg) concentrations. The primary objectives of this study were to answer the following questions:

1. What concentrations of the 665-P and BHR-P50 coagulants result in a treated solution with turbidity levels below the operational requirement of 5 NTU at bench-scale?
2. Will concentrations of the 665-P and BHR-P50 coagulants from bench test analyses achieve a turbidity level below 5 NTU at field-scale?
3. How will concentrations of total suspended solids (TSS) and filtered and particulate mercury (Hg), arsenic (As), manganese (Mn), nickel (Ni), selenium (Se), aluminum (Al), chromium (Cr), iron (Fe), and zinc (Zn) vary from background locations to the post-treatment compliance point 300 feet downstream of the discharge, and deviate from predicted values?
4. How do fHg and pHg concentrations change after coagulant addition during the sediment and Hg removal process?
5. What are the relationships between total nonfiltered mercury (THg) and total suspended solids (TSS) throughout the sediment and mercury removal process for various sediment source materials?
6. What is the amount and variation of DOC concentrations, UV absorbance, and SUVA₂₅₄ for the Combie Lake, Combie Pond, and Greenhorn Creek sediments throughout the sediment and Hg removal process?
7. What are the predictive capabilities of TSS, TDS, DOC, A₂₅₄, and SUVA₂₅₄ on fHg and THg concentrations using a multivariate analysis?

CHAPTER IV

MATERIALS AND METHODS

Materials

Sediment Sources

Source materials from three locations (Combie Pond, Greenhorn Creek, and Combie Lake) were excavated and stockpiled for use in the remediation process (Figure 4). All three sediment sources came from within the Bear River watershed. Combie Pond and Combie Lake were excavated from Lake Combie itself (Figure 2) while Greenhorn Creek, a Hg impacted waterbody, was excavated from Rollins Reservoir (Figure 1) located upstream of Lake Combie.



Figure 4. Stockpiled source materials from Combie Lake, Combie Pond, and Greenhorn Creek locations. Photo taken by Carrie Monohan (12/02/2014).

Sediment was excavated in the dry, during the summer months of 2014 when the reservoirs were low using a backhoe and transported by truck to the process location. Stockpiles were covered in plastic sheeting and wrapped in straw wattles for preservation. Additional sediment was stockpiled in days prior to each test as needed. NID ran a total of nine experimental tests using different combinations of source material and coagulants. Test 1 was conducted on Combie Lake material, test 2 on the Combie Pond material, test 3 on Greenhorn Creek material, and tests 4-9 were conducted on Combie Pond material (Table 1).

TABLE 1. SEDIMENT AND MERCURY REMOVAL TESTS DESCRIPTION
 Test number, test date, source material, coagulants(s) used, and effluent release on a yes (y) or no (n) basis.

Lake Combie Sediment and Mercury Removal Tests				
Test #	Date	Source Material	Coagulant(s) used	Discharge to Bear River
1	12/2/2014	Combie Lake	LBP-2101	n
2	12/4/2014	Combie Pond	Clar+Ion 5057	n
3	12/8/2015	Greenhorn Creek	BHR-P50	n
4	4/20/2015	Combie Pond	BHR-P50/665-P	n
5	8/26/2015	Combie Pond	BHR-P50/665-P	n
6	8/31/2015	Combie Pond	BHR-P50/665-P	n
7	9/1/2015	Combie Pond	BHR-P50/665-P	n
8	9/2/2015	Combie Pond	BHR-P50/665-P	n
9	9/9/2015	Combie Pond	BHR-P50/665-P	y

Bench tests were conducted on Combie Pond material transported in a five-gallon bucket to CSU Chico. Samples were stored on campus in the Center for Water and the Environment (CWE) laboratory at room temperature and in a dry environment. Sediment was archived until the completion of the sediment and mercury removal process in September 2015.

Coagulants

Four coagulants were tested at the field-scale during the Sediment and Mercury Removal Process: LBP-2101 for test 1, Clar+Ion 5057 for test 2, BHR-P50 for test 3, and a powder form coagulant 665-P that was used in combination with the BHR-P50 for tests 4 through 9 (Table 1). The LBP, Clar+Ion, and BHR coagulants were all in the aqueous form. Two of the coagulants, LBP-2101 and 665-P are considered trade secrets and their chemical compositions are unavailable. BHR-P50 is comprised of 15-20% polyaluminum chloride hydroxide sulfate while the remaining chemical components are non-hazardous or considered at de minimis quantities and therefore not listed on the safety data sheet (SDS) (BHR-P50; HaloKlear: Bothell, WA, Sept 18, 2014). The Clar+Ion 5057 consists of aluminum sulfate, sulfuric acid, and polyquaternary amine (Clar+Ion; MDS No. GC-8084; General Chemical: Parsippany, NJ, Oct 3, 2012). All four coagulants are corrosive and all routes of entry (skin and eyes contact, ingestion, and inhalation) can cause mild to severe irritation or burning (LBP-2101; HaloKlear: Bothell, WA, Sept 27, 2014, DWT 665-P; Dober Research Works: Woodridge, IL, Aug 7, 2009).

For tests 1, 2, and 3 the Clar+Ion, BHR-P50, and LBP-2101 pre-mixed coagulants were kept in 55-gallon plastic drums onsite. For both bench and field-scale tests 4-9 the 665-P coagulant and BHR-P50 were used in combination. In accordance with company specifications the 665-P coagulant was mixed with water to obtain a 0.25% by weight solution, or 47.25 g of coagulant for every five gallons of water. Mixtures were performed onsite using 5-gallon Jeri cans for water volume measurements and an analytical scale (readability: 0.1 mg) for polymer dry weight. Water used for

mixtures was from an onsite well. To ensure product effectiveness, 665-P mixtures were mixed on site in 35 gallon plastic trash cans, slowly over a 10-15 min period using a drill-powered paint mixer, and allowed to sit for 24 hours before use as advised by HaloSource ©. For tests 5 through 9, the BHR P-50 coagulant was diluted to a ten-part water to one part coagulant mixture, 10 gallons of H₂O for every 1-gallon of coagulant. During tests 4 through 9, mixed coagulant solutions and bulk extra were stored on location. Coagulants were covered and locked within a mobile trailer storage unit when not in use to prevent contamination.

Methods

Bench-Scale Tests

Slurry Solution Preparation. In order to best resemble the field-scale applications, sediments were mixed with Bear River water to create a solution with a turbidity \geq 1,000 NTU. Sediment was added in 20 g increments to five gallons of Bear River water until the desired turbidity level was achieved. A Hanna Turbidimeter (HI 98703) was used for turbidity measurements. The unit was calibrated prior to each day of use as described below in the physical water quality measurements section. The turbidimeter has a maximum detection limit of 1,000 NTU, once the slurry turbidity produced a reading greater than this limit the slurry was considered to be field-scale equivalent. A new slurry solution was prepared at the beginning of each day of the bench tests to create a comparable solution between coagulant injections. Water samples were taken by submerging 500 mL beakers into a well-mixed bucket of the slurry mixture to collect a vertically integrated composite of slurry solution prior to coagulant test.

Coagulant Tests. Coagulation tests were conducted on Combie Pond material using both BHR P-50 and 665-P coagulants. Pre-mixed coagulants were brought to CSU Chico from the project site for bench tests. A six-paddle mixer or gang stirrer was used and provided by the Civil Engineering Department of CSU Chico. The slurry solution was mixed at 300 rpm for 45 seconds per coagulant addition to ensure a well-mixed solution. Following the rapid mix, the paddle mixer was reduced to a slow mix rate of 30-40 rpm for 15 minutes to allow for flocculation to occur. Immediately following flocculation, a 60-minute sedimentation period began. The bench-scale mixing method was adopted from HaloSource and the sedimentation period was modified to simulate laminar flow within sedimentation tanks at the field-scale. Turbidity measurements were taken at T0, T30, and T60; 0, 30, and 60 minutes after coagulant additions. Turbidity measurements were taken in 10 mL aliquots and collected from mid-depth of the water column using a 50-mL pipette. This procedure was replicated using a range of coagulant concentrations until the turbidity was reduced to < 5 NTU.

Coagulant tests started at coagulant concentrations of 0.8 mL/L of 665-P and 0.4 mL/L of BHR-P50 using a 0.1-mL syringe. Bench-scale 665-P coagulant dosages were reported by the coagulant dry weight rather than the total 0.25% by weight mixture with water. To achieve more consistent injection rates at the field-scale, coagulants were diluted to a 3:1 ratio for the 665-P and 11:1 for the BHR-P50. A total of 22 bench tests were performed at varying concentrations until the desired clarity (< 5 NTU) was reached following sedimentation. Concentrations that were found to be effective or reduced turbidity to below 5 NTU were duplicated to ensure replicability.

Field-Scale

Sediment and Mercury Removal Process Description. The sediment and mercury removal equipment consists of multiple in-line technologies to achieve specific water quality goals (Figure 3). Stockpiled source materials were mixed using a backhoe and a spray/shaker rig to remove the largest grain sizes of pebble and cobble. The slurry mixture was pumped to the mobile “Pegasus Mercury Remediation Machine” where the slurry was run through a modified Knelson Concentrator, removing liquid elemental mercury and gold. The slurry was then sent to a mobile wheelwash unit for sand removal before the coagulant addition. Sand removed from this unit was transported to an aggregate plant for repurposing or sale.

The slurry was then treated with the BHR-P50 and 665-P coagulants. Coagulants were administered by direct injection at two locations within the feed line separated by 100 feet of piping. An inline static mixer was placed after each injection point to ensure a well-mixed solution. LMI Milton Roy (Model # C771-25HV) electronically-controlled metering pumps were used for coagulant additions. Dose rates were managed by adjusting two control dials, “stroke” or volume of fluid per cycle and “speed” or number of cycles per minute. The coagulant BHR-P50 was applied first followed by the 665-P. The treated slurry was then pumped into the first of two in-succession open-top 20,000-gallon settling tanks, allowing for sedimentation of the agglomerated colloids and particles to occur. Once Tank 1 was full, treated water was decanted into Tank 2. Following the sedimentation period, the effluent from Tank 2 was decanted to the Bear River, provided that water quality of the effluent met the regulatory

criteria. Alternatively, if effluent did not meet criteria, it was discharged to a settling basin constructed onsite.

Coagulant Injections. Using concentrations found to be effective at the bench-scale, the field-scale equivalent concentrations were calculated. For field scale application, the selected bench test concentration in ppm (1,500 ppm in the example below) was multiplied by 100 gpm (flow rate at field-scale) and then multiplied by 60 (min per hour) to calculate an injection rate in gallon per hour (Equation 1).

$$\frac{1500}{10^6} \left(\frac{\text{Parts of coag}}{\text{Parts of H}_2\text{O}} \right) \times 100 \frac{\text{gal}}{\text{min}} \times 60 \frac{\text{min}}{\text{hr}} = 9 \frac{\text{gal}}{\text{hr}} \quad (1)$$

For an injection rate of 9 gal/hr the LMI pump was set to 100% stroke and 90% speed, according to the user's manual calculation (Equation 2).

$$1.0 (100\% \text{ stroke}) \times 0.9 (90\% \text{ speed}) \times 10 = 9 \frac{\text{gal}}{\text{hr}} \quad (2)$$

Pumps were primed prior to start up by running the LMI pumps to purge air from within the feed lines to ensure proper application to the slurry at start up.

Water Quality Sampling. Water samples were collected from the Bear River (ambient conditions), wheelwash (mixing point before polymer injection), Tank 1 following polymer injection (1st of two sedimentation tanks in series), Tank 2 (2nd sedimentation tank), and at a compliance point 300 feet downstream of the effluent discharge within the Bear River (Figure 3).

Samples were collected prior to start up, approximately every two hours of run time, and or from the furthest location of treatment achieved for that day, given that test duration varied. With a flow rate of 100 gpm and a capacity of 20,000-gallon per tank

the two-hour sampling interval was set to occur after approximately every half tank of slurry was treated. All samples were collected using an extension on a PVC pipe as grab samples using EPA Method 1669 “Clean hands dirty hands.” Acid washed sample bottles supplied by the lab, were triple rinsed in native water, double bagged, and stored on ice in a cooler ($< 4.0^{\circ}\text{C}$) for overnight shipment to Brooks Applied Laboratories (BAL) (Bothel, WA) for analysis. DOC sample bottles were 125 mL amber glass pre-combusted at 450°C and supplied by the California Water Science Center (CAWSC). DOC samples were filtered using a pre-combusted $0.3\text{-}\mu\text{m}$ glass fiber filter prior to determination within 24 hours after collection.

Samples were analyzed for total suspended solids (TSS), total and dissolved mercury (THg, dHg), arsenic (TAs, dAs), manganese (TMn, dMn), nickel (TNi, dNi), selenium (TSe, dSe), aluminum (TAI, dAl), chromium (TCr, dCr), iron (TFe, dFe), zinc (TZn, dZn), and molybdenum (TMo, dMo) using methods described in Table 2.

Dissolved (d) fractions shown in Table 2 were filtered using a $0.45\text{-}\mu\text{m}$ capsule filter.

Brooks Applied Laboratory reported values for the total (T) and dissolved (d) fractions; particulate concentrations (pX) were calculated by subtracting the dissolved (dX) concentrations from the total (TX) concentrations. If a particulate concentration was negative, Brooks Applied Lab credited the total metal concentration to the dissolved or filtered fraction. For clarification, the dissolved (d) fraction will be referred to as filtered (f) throughout the rest of this report. For all samples BAL QAQC procedures were followed, including: percent recovery from a known quantity of a certified reference material to gauge the accuracy of the analytical method of recovery, percent recovery of a

TABLE 2. EPA LABORATORY METHODS USED
Method minimum detection limits (MDL) and minimum reporting
limits (MRL) are listed for total (T) and dissolved (d) fractions.

Brooks Applied Laboratory Analysis					
Analite	EPA lab method	Basis	MDL	MRL	Units
TSS	EPA 160.2	T	0.6	1.9	mg/L
Hg	EPA 1631	T	0.26	1.02	ng/L
		d	0.25	1.01	ng/L
As	EPA 1638 DRC	T	0.013	0.032	µg/L
		d	0.012	0.03	µg/L
Mn	EPA 1638	T	0.021	0.063	µg/L
		d	0.02	0.061	µg/L
Ni	EPA 1638	T	0.04	0.21	µg/L
		d	0.04	0.2	µg/L
Se	EPA 1638 DRC	T	0.025	0.074	µg/L
		d	0.024	0.071	µg/L
Al	EPA 1638	T	1.05	3.16	µg/L
		d	1.01	3.03	µg/L
Cr	EPA 1638	T	0.05	0.3	µg/L
		d	0.05	0.15	µg/L
Fe	EPA 1638	T	1.4	5	µg/L
		d	1.4	5	µg/L
Zn	EPA 1638	T	0.06	0.2	µg/L
		d	0.06	0.2	µg/L
Mo	EPA 1638	T	0.01	0.04	µg/L
		d	0.01	0.04	µg/L

known quantity or matrix spike added to a native sample, a relative percent difference of a duplicate matrix spike analysis to evaluate the precision of recovery, and the relative percent difference between native samples and their duplicates (taken in field).

DOC and Optical Measurements

DOC concentrations and optical properties were performed at the U.S. Geological Survey (USGS) Organic Matter Research Laboratory (OMRL) in Sacramento, CA. Concentrations of DOC were measured in mg/L by high-temperature catalytic combustion using a Shimadzu TOC-VCSH total organic carbon analyzer (Shimadzu Scientific Instruments, Columbia, MD), using a modified version of the EPA method 415.3 (USEPA, 2005). The accuracy and precision of the DOC measurements were within 5% of the internal standard (caffeine), laboratory replicates, and matrix spikes (Hansen, 2014). Absorbance spectra were collected within 24 hr of sampling on filtered, non-acidified samples at room temperature (25°C) in 1 cm quartz cuvettes using a spectrophotometer and a CCD detector (Aqualog®; Horiba Instruments Inc., NJ, USA). Absorbance readings were performed on a double-grating monochromator, 150-Watt Xenon lamp with a 5 nm bandpass and a 1-second integration time at wavelengths of 240-600 nm. Absorbance intensities were expressed in absorbance units (AU). Samples with absorbance intensity at 254 nm (A_{254}) greater than 3.0 AU were diluted and reanalyzed to ensure linearity. Absorbance values (A_{254}) were used for specific UV absorbance ($SUVA_{254}$) calculations. $SUVA_{254}$ ($\text{mg L}^{-1} \text{m}^{-1}$) represents an “average” absorptivity for all the molecules that comprise the DOC in a water sample and is calculated by dividing A_{254} (expressed in m^{-1}) by the DOC concentration (mg/L) (Weishaar et al., 2003).

Optical measurements were within quality control limits indicated by laboratory standards potassium dichromate and quinine sulfate, a standard reference

material, Lipton® unsweetened iced tea, as well as laboratory replicates for every 10 samples (Hansen, 2014).

Physical Water Quality Parameters

Turbidity measurements were performed on a Hanna Turbidimeter (HI 98703) during both the bench and field-scale tests. The turbidimeter was calibrated prior to each day of use with a 4-point calibration curve using premade solutions of <0.1 NTU, 15 NTU, 100 NTU, and 750 NTU factory standards purchased from Hanna. Turbidity samples from field-scale tests were collected as grab samples from just below the surface at every location using supplied 10-mL cuvettes. Samples were collected just below the water surface to limit the collection of floating debris that could alter turbidity measurements.

Prediction of Concentrations at Compliance Point

A mass-balance model (Equation 3) was used for the prediction of a particular constituent of concern using the concentration in Tank 2 (the last location before discharge, Figure 3), and low flow summer average flow rates for the Bear River from Monohan and Crough (2012) to predict its concentration in the river 300ft downstream of the discharge at the regulatory compliance point.

$$C_{R2} = \frac{C_{R1} * Q_{R1} + C_{eff} * Q_{eff}}{Q_{R1} + Q_{eff}} \quad (3)$$

Where:

C_{R1} = Constituent concentration in surface water upstream of Combie Reservoir

C_{R2} = Predicted constituent concentration in surface water at compliance point

Q_{R1} = Flow rate of Bear River into Combie Reservoir

Q_{eff} = Flow rate of effluent discharge from the Project

C_{eff} = Constituent concentration in effluent from the Project

Coagulant Mechanisms of Mercury Removal

Plots of pHg (x-axis) and fHg (y-axis) from all nine tests were plotted on a log-log scale. Plots were created using results from all sample locations within the removal process. As effluent water quality did not meet regulatory standards for tests 1 through 8, they were not released to the river and not used for this calculation. The average Hg concentrations from each sample location in the process were plotted and connected to show concentration changes in the Hg fractions from the river background to Tank1, Tank 2, and the compliance point 300ft downstream of discharge.

Filtered-Particulate Hg Distribution

Bar graphs of fHg and pHg concentrations were created for each type of coagulant used to illustrate the fHg and dHg distribution changes throughout the removal process at each sample location.

Total Nonfiltered Mercury and Total Suspended Solids Relationship

A plot was created showing total nonfiltered Hg concentration (y-axis) and total suspended solids (x-axis) from all nine tests. Data were categorized by type of source material used for the tests and oriented on a log-log scale to evaluate slopes. Slopes represent a change in THg concentration (ng/L) relative to changes in TSS concentrations (mg/L) or nanograms of Hg per milligram of total suspended sediment. Analysis provided an apparent Hg concentration on suspended material.

Multiple Regressions in “R”

Using “R Studio” and tests 1, 2, 3 and 9 data, the only tests for which DOC samples were collected, a predictive model was created for two response variables, filtered mercury (fHg) and nonfiltered mercury (THg) concentrations in ng/L. Predictions were made as a function of multiple explanatory variables: TSS (mg/L), TDS (mg/L), DOC (mg/L), A_{254} (AU), and $SUVA_{254}$ ($L\ mg^{-1}\ m^{-1}$). Samples taken from the wheelwash in the sediment and mercury removal process were omitted from the model as the values reflect super-saturated conditions prior to coagulant treatment. Assumptions made for multiple regressions were:

- A linear model was appropriate.
- There was constant variance.
- Errors were independent.
- Errors were normally distributed.

A reduced model was then created using the “stepAIC backward” function in R, as not all of the variables were significant. The StepAIC command is a stepwise reduction of variables and outputs a model that increases the strength of the resultant p value by eliminating non-essential variables and increasing the degrees of freedom for the sample mean (Akaike, 1973). “Backward” refers to starting with an initial model containing all possible explanatory variables and then eliminating the least significant factors. Finally, a residual plot was created to determine if there was either a random scatter or pattern in the residuals. Evenness and no observable trends in this plot represent no violations of the regression assumptions. A line was added to the residual plot at (0, 0)

which represents the line where predictions would fall if the model resulted in values exactly as observed. The variations from this line are where evenness or observable trends were determined.

CHAPTER V

RESULTS

Bench-Scale Coagulant Additions

The most effective dose of coagulants was 1.6 mL/L of the 665-P and 0.2 mL/L the BHR P-50 of slurry to be treated. For informing the field-scale applications of coagulants, bench-tests were run using the same sediment material and coagulants as in the field. Bench-scale coagulant dosages determined to be effective in the reduction of turbidity below 5 NTU were used to increase the efficiency of sediment and mercury removal during field-scale application. Coagulants tested in jar tests were the diluted 665-P (3:1) and BHR-P50 (11:1) solutions respectively. Coagulant concentrations ranging from 0-12.0 mL/L of the 665-P and 0-0.5 mL/L BHR-P50 were tested.

Table 3 displays the bench-scale coagulant dosages and the resulting turbidity changes at 0, 30, and 60 minutes of the sedimentation period. All treatments started with slurries having initial turbidities ≥ 1000 NTU. During jar test number 3 on 04/17/2015 the turbidity was reduced to 99.6% of the initial value after the flocculation period, T (0), and an additional 0.18% and 0.04% reduction at T (30) and T (60) respectively, for an overall reduction of 99.82%. This was the greatest percentage of reduction and at the quickest rate of all dosages while using the diluted coagulants tested.

For all bench-tests conducted, a range of 91.0 % to 99.8 % reduction in turbidity was observed, while bench-tests conducted with diluted coagulants resulted in a 99.5 % to 99.8 % reduction in turbidity. The greatest reduction in turbidity occurred at

TABLE 3. BENCH-SCALE COAGULANT DOSAGES AND RESULTING TURBIDITIES
 Table describing varying ranges of 665-P and BHR-P50 coagulant doses and
 their resulting effect on turbidity.

Jar Test analysis 4/10/15, Combie Pond material						
Jar #	665-P Dosage (ml/L)	BHR-P50 Dosage (ml/L)	Turbidity (NTU)			
			Initial	T(0)	T(30)	T(60)
1	0.8	0.42	>1000	76.2	34.7	10.2
2	0.8	0.42	>1000	52	29.2	10.5
3	0.8	0.5	>1000	53.5	66.7	33.5
4	0.8	0.5	>1000	125	118	89.6
5	0.8	0.28	>1000	106	77.6	61.4
6	1.6	0.42	>1000	58.9	35.9	35.2

Jar Test analysis 4/13/15, Combie Pond material						
Jar #	665-P Dosage (ml/L)	BHR-P50 Dosage (ml/L)	Turbidity (NTU)			
			Initial	T(0)	T(30)	T(60)
1	0.8	0	>1000	210	173	156
2	4	0	>1000	70.5	53.6	53.4
3	8	0	>1000	64.8	49.1	48.2
4	12	0	>1000	65.6	50.3	48.4
5	0.8	0.2	>1000	3.6	1.32	1.89
6	1.6	0.2	>1000	1.81	1.26	0.85
7	1	0.2	>1000	3.09	1.73	1.06
8	1	0.2	>1000	2.17	1.99	1.18

Jar Test analysis 4/17/15, Combie Pond material						
Jar #	665-P Dosage (ml/L)	BHR-P50 Dosage (ml/L)	Turbidity (NTU)			
			Initial	T(0)	T(30)	T(60)
1	0.8	0.2	>1000	9.11	5.78	4.64
2	1.2	0.2	>1000	6.16	3.65	3.2
3	1.6	0.2	>1000	3.55	1.77	1.38
4	2	0.2	>1000	5.06	2.01	1.57
5	2	0.2	>1000	5.98	3.11	2.2

Note: 665-P diluted to 3:1 ratio, BHR-P50 diluted to 11:1 ratio to create more consistent pump rate at field scale.

Jar Test analysis 8/19/15, Combie Pond material						
Jar #	665-P Dosage (ml/L)	BHR-P50 Dosage (ml/L)	Turbidity (NTU)			
			Initial	T(0)	T(30)	T(60)
1	0.8	0.2	>1000	9.72	4.92	4.29
2	1	0.2	>1000	8.16	4.44	3.85
3	1.2	0.2	>1000	8.34	4.86	3.92

Note: 665-P diluted to 3:1 ratio, BHR-P50 diluted to 11:1 ratio to create more consistent pump rate at field scale

the dose rates of 1.6 mL/L and 0.2 mL/L of the 665-P and BHR-P50 coagulants, and was selected to test at the field scale.

Field-Scale Coagulant Tests

Coagulant dose rates of 1.6 mL/L (665-P) and 1.5 mL/L (BHR-P50) were operationally found to be more effective for the reduction of turbidity than bench test results (1.6 and 0.2 mL/L) indicated (Table 4). During test 9 on the Lake Combie pond material, beginning at 8:00 AM on 9/9/2015, the coagulant injection rates were kept constant throughout the test period so that the effect of coagulant dose rates on effluent turbidity could be evaluated (Table 4). Table 4 depicts the field-scale turbidity response to coagulant treatment as a function of run time within Tank 1 and 2. Dose rates calculated from Equation 1 were held throughout the test period at 1.583 mL/L of diluted 665-P (3:1) and 1.5 mL/L of diluted BHR-P50(11:1) solutions, equivalent to 9.5 and 9.0 gallons of coagulant per hour, respectively (Table 4).

TABLE 4. TEST 9 FIELD-SCALE TIME SERIES COAGULANT DOSE AND TURBIDITY RESPONSE AT THE BACKGROUND, TANK 1, AND TANK 2 SAMPLING LOCATIONS OF THE REMOVAL PROCESS

9/9/2015 Combie Lake Material							
Time*	665-P (mg/L)	Field Scale (gal/hr)	BHR- P50 (mg/L)	Field Scale (gal/hr)	Background Turbidity (NTU)	Post Treatment Turbidity (NTU)	
						Tank 1	Tank 2
T1	1.6	9.5	1.5	9	2.31	8.4	
T2	1.6	9.5	1.5	9	2.31	11	14
T3	1.6	9.5	1.5	9	2.31	9.5	16
T4	1.6	9.5	1.5	9	2.31	15	12
T5	1.6	9.5	1.5	9	2.31	7.8	9.9

Note: *T1(8:40am), T2(10:30am), T3(11:00am), T4(12:00pm), T5(1:00pm)

Turbidity values in Tanks 1 and 2 were equal to or lower than 16 NTU at all sampling times (T1-T5) (Figure 5). According to the mass balance model (Equation 3) with a background turbidity of 2.31 NTU and low summer average flow of 10.5 cfs (Monohan, and Crough. 2012) in the river, an effluent with turbidity of 51 NTU in Tank 2 would result in a turbidity level within +/- 1 of background level or <5 as permitted by the operational criteria at the compliance point 300ft downstream. With effluent turbidity values <16 NTU, the downstream compliance point maintained levels below regulatory standards set by the Technically Conditioned Water Quality Certification (CVRWQCB, 2012).

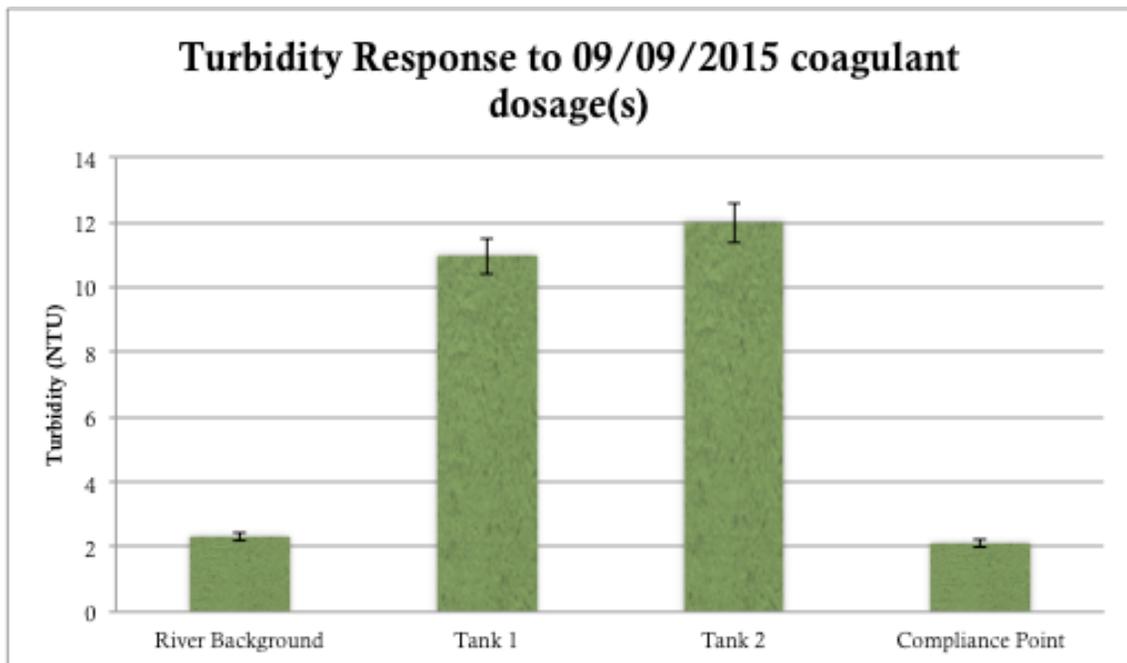


Figure 5. Field-scale coagulant dose-turbidity response. River background, tank 1, tank 2, and compliance point response to 1.583 and 1.5 mL/L of the 665-P and BHR-P50 coagulants (mixed coagulant mass/slurry volume).

Water Quality Treatment Results

Depicted below are the TSS, filtered and particulate concentrations (Table 5) and total metal concentrations (Figure 6) of Al, As, Cr, Hg, Fe, Mo, Ni, and Zn from the Bear River background and post-coagulant treatments in Tank 1, Tank 2, and the compliance point 300ft downstream of the discharge within the receiving water of the Bear River for test 9

Filtered and particulate concentrations including TSS either decreased or had little to no change from pre- to post-treatment. Following treatment, filtered Hg (fHg) increased from 0.81 ng/L to 0.93 ng/L, fFe increased from 47.9 µg/L to 368 µg/L, and pNi increased from 0 µg/L to 0.18 µg/L. Although fHg, fFe, and pNi concentrations increased during treatment their total concentrations were below their respected regulatory criteria as shown in Figure 6. The changes in concentrations from pre to post treatment for Hg and Ni were within the minimum detection limits reported by BRL of 0.51 ng/L and 0.2 µg/L thus classifying observed increases insignificant. Settling tank 2 had the highest concentrations of all sampling locations (Figure 6). All parameters tested had lower concentrations at the downstream compliance point than the reference background point (Figure 6). Concentrations not shown at a few of the sample sites in Figure 6 are a result of the value being below the scale of the graph.

Background, Predicted, and Measured Concentrations at Compliance Point

A mass-balance model (Equation 3) was utilized to calculate concentrations of constituents of concern from the treatment process at the compliance point located 300 feet downstream from the effluent discharge. Using the background concentration of a

TABLE 5. TEST 9 PRE VS. POST FILTERED AND PARTICULATE METAL AND TSS CONCENTRATIONS
 Brooks Applied Labs metal and TSS data analysis of water samples from the Lake Combie Reservoir
 sediment and mercury removal process

Sample Location	Date	Pre/Post Treatment	Total aluminum		Total arsenic		Total chromium		Total mercury		Turbidity (NTU)
			Filtered (µg/L)	Particulate (µg/L)	Filtered (µg/L)	Particulate (µg/L)	Filtered (µg/L)	Particulate (µg/L)	Filtered (ng/L)	Particulate (ng/L)	
River Background	9/9/2015	Pre	32.2	46.1	1.54	0	0.25	0.28	0.81	3.11	2.31
Tank 1	9/9/2015	Post	27	195	2.22	0	0.25	0.46	2.84	18.86	10.93
Tank 2	9/9/2015	Post	1060	0	1.91	0.42	51.4	0	3.68	19.02	11.97
Compliance Point	9/9/2015	Post	5.16	26.04	1.05	0.14	0.25	0	0.93	2.1	2.1

Sample Location	Date	Pre/Post Treatment	Total iron		Total molybdenum		Total nickel		Total zinc		TSS (mg/L)
			Filtered (µg/L)	Particulate (µg/L)	Filtered (µg/L)	Particulate (µg/L)	Filtered (µg/L)	Particulate (µg/L)	Filtered (µg/L)	Particulate (µg/L)	
River Background	9/9/2015	Pre	47.9	1012.1	0.449	0	2.1	0	3.85	0	2.7
Tank 1	9/9/2015	Post	36	266	0.5	0	2.18	0.88	0.8	9.8	12.5
Tank 2	9/9/2015	Post	1060	0	10.6	0	22.3	0.2	116	0	9.4
Compliance Point	9/9/2015	Post	368	622	0.435	0	0.7	0.18	0.45	0	3

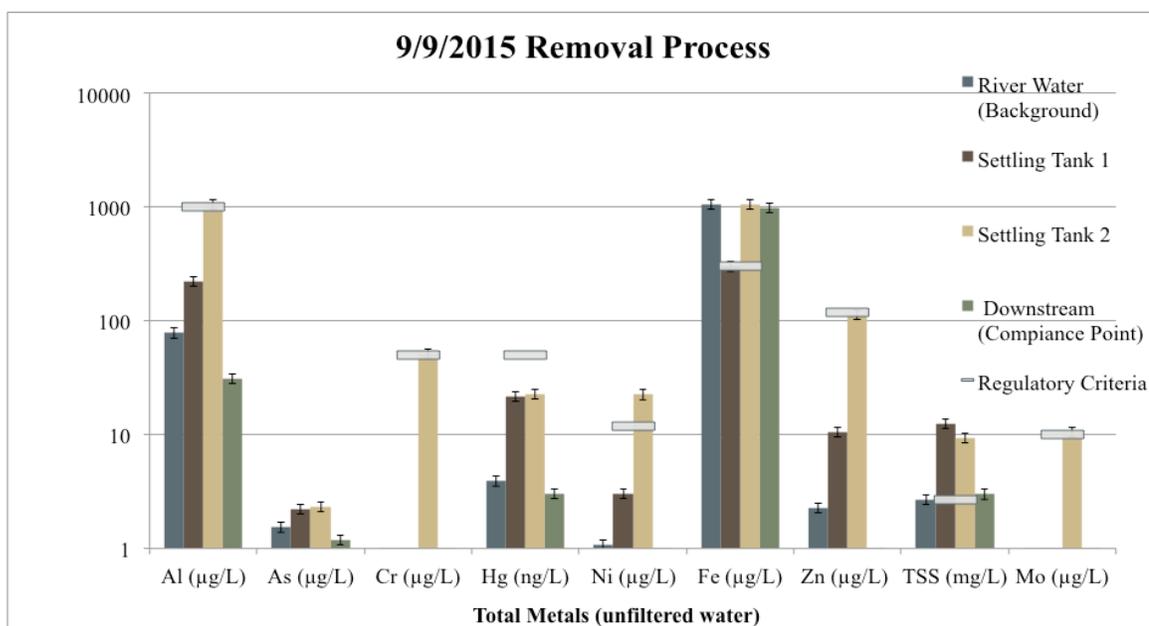


Figure 6. Total metal concentrations from pre to post treatment with associated regulatory criteria for the 09/09/2015 Lake Combie sediment and mercury removal process.

constituent, its concentration in Tank 2, the process pump rate, and an estimated flow rate in Bear River, water quality predictions were made for the compliance point. Samples were collected at the compliance point for comparison between predicted and actual concentrations.

Water quality comparisons were made using the background concentrations in the Bear River, calculated values at the compliance point, and measured water quality values at the compliance point 300ft downstream of the discharge (Table 6).

With the exception of total arsenic and total iron, TSS, and turbidity were below regulatory criteria and within operating permits at the compliance point (Table 6). Although the measured compliance point levels of 1.19 $\mu\text{g/L}$ and 1,060 $\mu\text{g/L}$ for TAs and TFe were in exceedance of their regulatory standards (0.018 and 300 $\mu\text{g/L}$), they were

TABLE 6. BACKGROUND VS. COMPLIANCE POINT PREDICTED AND MEASURED CONCENTRATIONS
 Parameter percent differences and associated regulatory criteria added to show change from pre to post treatment,
 predicted concentrations were calculated from Equation 3.

Bear River Predicted vs. Measured Water Quality at Downstream Monitoring Point 9/9/15									
Parameter	Fraction	Background		Predicted		Measured		*% Difference	**Regulatory Criteria
		Result	Unit	Result	Unit	Result	Unit		
Al	T	78.30	µg/L	98.12	µg/L	31.20	µg/L	-60.15	87µg/L
Al	f	32.20	µg/L	53.38	µg/L	5.16	µg/L	-83.98	
As	T	1.37	µg/L	1.39	µg/L	1.19	µg/L	-13.14	0.018µg/L
As	f	1.54	µg/L	1.55	µg/L	1.05	µg/L	-31.82	
Cr	T	0.53	µg/L	1.57	µg/L	0.25	µg/L	-52.83	50µg/L
Cr	f	0.25	µg/L	1.30	µg/L	0.25	µg/L	0.00	
Fe	T	1060.00	µg/L	1059.59	µg/L	990.00	µg/L	-6.60	300µg/L
Fe	f	47.90	µg/L	68.76	µg/L	622.00	µg/L	1198.54	
Hg	T	3.92	ng/L	4.31	ng/L	3.03	ng/L	-22.70	50ng/L
Hg	f	0.81	ng/L	0.87	ng/L	0.93	ng/L	14.81	
Mo	T	0.45	µg/L	0.66	µg/L	0.43	µg/L	-4.45	10µg/L
Mo	f	0.45	µg/L	0.66	µg/L	0.44	µg/L	-3.12	
Ni	T	1.08	µg/L	1.52	µg/L	0.88	µg/L	-18.52	12µg/L
Ni	f	2.10	µg/L	2.52	µg/L	0.70	µg/L	-66.67	
TSS	T	2.70	mg/L	2.84	mg/L	3.00	mg/L	11.11	125 mg/L
Turbidity	T	2.31	NTU	2.51	NTU	2.10	NTU	-9.09	< 5 NTU
Zn	T	2.27	µg/L	4.55	µg/L	0.44	µg/L	-80.62	120µg/L
Zn	f	3.85	µg/L	6.16	µg/L	0.45	µg/L	-88.31	

Note: *% difference is between river background and measured levels at compliance point 300ft downstream of discharge.

**Regulatory criteria in total form and from California Regional Water Control Board (CRWQCB), 2005

consistent with and no greater than background levels within the Bear River, which exceeded water quality standards (1.37 and 1,060 $\mu\text{g/L}$).

The mass balance model was conservative in predictions relative to observed as values predicted were greater than measured, using the concentrations from Tank 2 in the model represents a protective result to stay within regulatory criteria for a wide range of flows. Based on the low flow in the receiving water (estimated 10 cfs) and a 60 min delay from time of release to time of collection, results at the downstream location (300 feet) are assumed to accurately represent the effects of effluent on Bear River water quality. Samples were collected one hour following discharge to allow for the effluent water to travel the 300 feet and be represented in the sample. However, flows may have been less than 10 cfs and were not measured, with such low flow velocities the process effluent influence on Bear River water quality might not have been detected downstream. It may be that if more time was allowed for the effluent to reach the downstream location, the effects of the effluent on Bear River water quality would have increased.

Hg Phase Distribution Throughout Coagulation/Flocculation

As THg, fHg, and pHg have varied effects on ecosystems, plots of the fHg and pHg concentrations during the water treatment process for each coagulant type were used to evaluate the coagulants effect on the Hg concentration of each fraction. Particulate and filtered Hg concentration changes from pre to post-coagulant treatment were reflective of coagulant dose and type used. Comparisons were made using Tests 1, 2, and 3 with the LBP-2101, Clar+Ion 5057, and P-50 coagulants respectively and Tests

4-9 with the combination of the 665-P and BHR-P50 coagulants. Values from all sample locations of the treatment process were used to show the progression of Hg distribution from pre to post-treatment. To obtain pHg concentrations, fHg were subtracted from THg concentrations. The ratio between pHg and fHg concentrations is important to assess the amount and distribution of Hg within the effluent and what effect these changes may have on the environment, as fHg is known to be more bioavailable (Slotton et al. 1997; Roth et al., 2001; Choe and Gill, 2001; and Choe et al., 2003).

Particulate and Filtered Hg Concentration Changes

LBP-2101

While using the LBP-2101 coagulant, fHg increased from 1.95 ng/L in the Bear River Background to 12.77 ng/L in the wheelwash, then increased to 13.25 ng/L within Tank 1, and finally decreased to 11.9 ng/L inside Tank 2 (Figure 7). Particulate Hg increased from 2.17 ng/L in the Bear River Background to 16,609.23 ng/L in the wheelwash, then decreased by three orders of magnitude to 51.3 ng/L within Tank 1, and finally decreased to 6.3 ng/L inside Tank 2 (Figure 8).

Clar+Ion 5057

While using the Clar+Ion 5057 coagulant fHg decreased from 4.94 ng/L in the Bear River Background to 2.34 ng/L in the wheelwash, then increased to 8.79 ng/L within Tank 1, and finally decreased to 5.36 ng/L inside Tank 2 (Figure 7). Particulate Hg increased from 24.36 ng/L in the Bear River Background to 14,597.67 ng/L in the

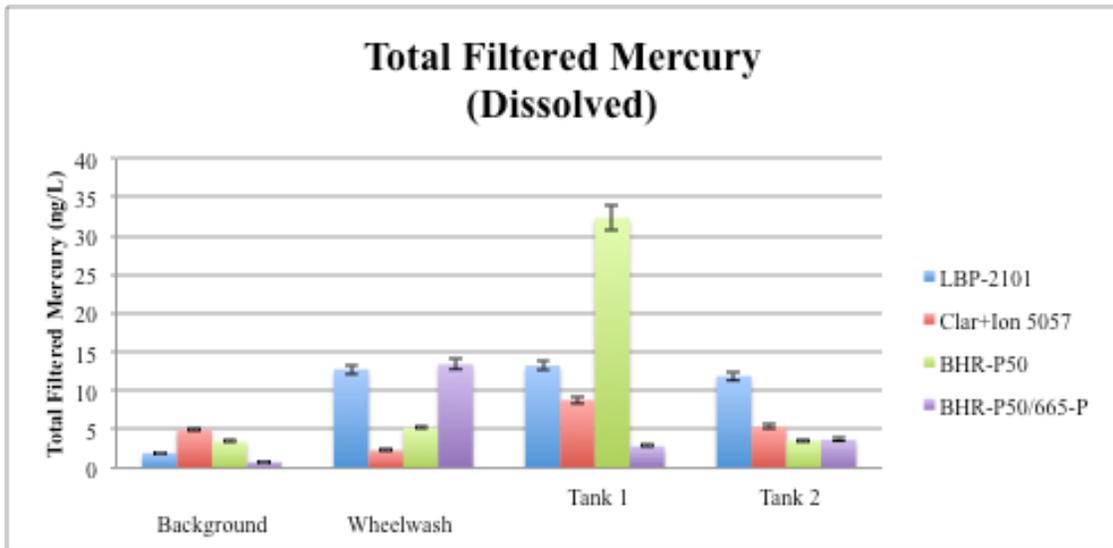


Figure 7. Filtered Hg concentrations during treatments of each of the coagulants tested.

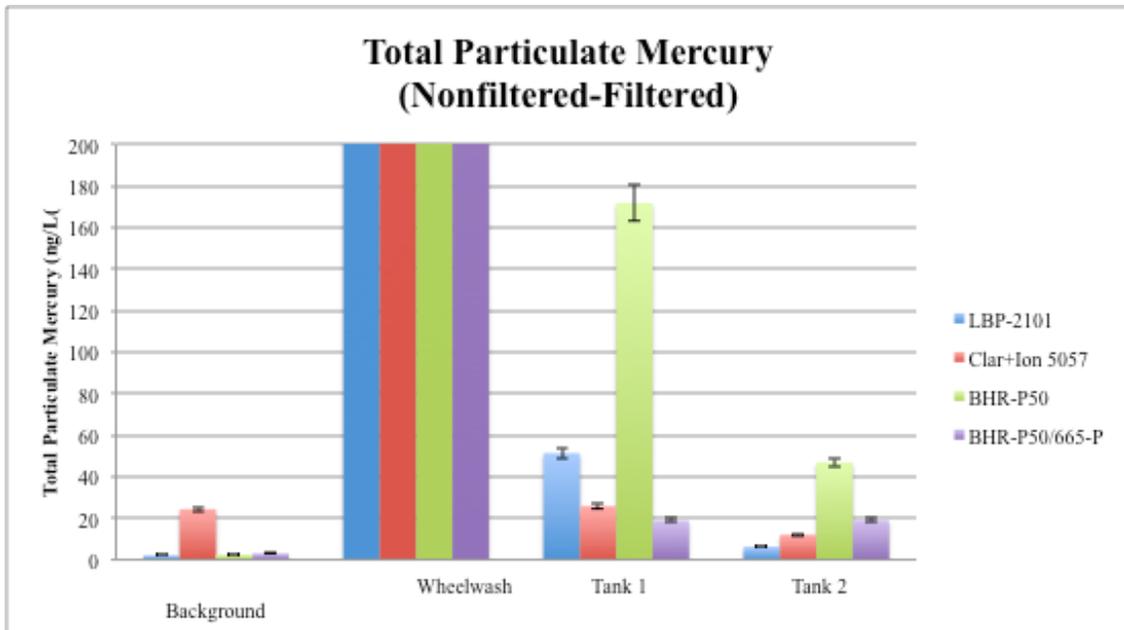


Figure 8. Particulate Hg concentrations during treatments of each of the coagulants tested. Wheel wash concentrations are greater than 200 ng/L, actual values are off the scale of this graph.

wheelwash, then decreased by three orders of magnitude to 25.81 ng/L within Tank 1, and finally to 12.04 ng/L inside Tank 2 (Figure 8).

BHR-P50

While using the BHR-P50 coagulant fHg increased from 3.45 ng/L in the Bear River Background to 5.23 ng/L in the wheelwash, fHg then increased to 32.33 ng/L within Tank 1, and finally decreased to 3.57 ng/L inside Tank 2 (Figure 7). Particulate Hg increased from 2.56 ng/L in the Bear River Background to 6,785 ng/L in the wheelwash, then decreased by one order of magnitude to 171.67 ng/L within Tank 1, and finally to 46.83 ng/L inside Tank 2 (Figure 8).

BHR-P50 and 665-P

As shown below in Figure 7, while using the combination of both the BHR-P50 and 665-P coagulants, average Hg concentrations were compared across all 6 tests (Tests 4-9). Filtered Hg increased from 0.88 ng/L in the Bear River Background to 13.42 ng/L in the wheelwash, then decreased to 2.84 ng/L within Tank 1, and finally increased to 3.68 ng/L inside Tank 2 (Figure 7). Particulate Hg increased from 3.11 ng/L in the Bear River Background to 2,387 ng/L in the wheelwash, decreased by two orders of magnitude to 18.86 ng/L within Tank 1, and finally to 19.02 ng/L inside Tank 2 (Figure 8).

Particulate Hg-Filtered Hg Ratios

LBP-2101

There was an approximate 1:1 ratio of pHg: fHg in the Bear River background on the day of test 1, 12/02/2014 (Figure 9). In the wheelwash where the highest

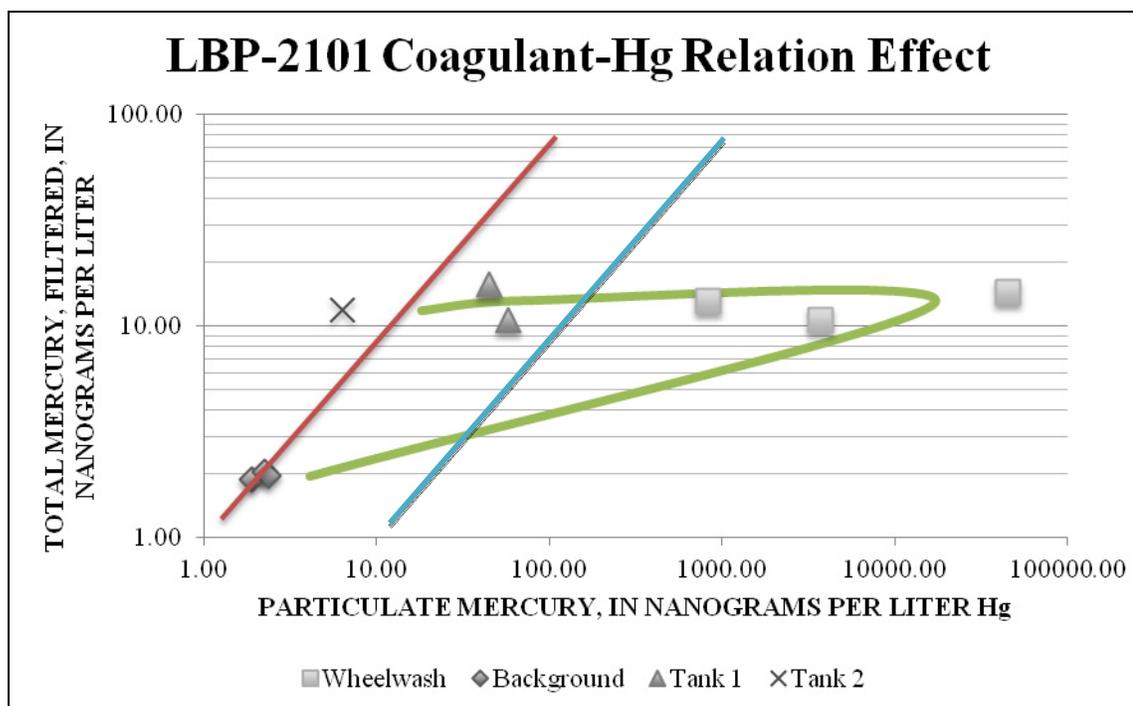


Figure 9. Hg phase distribution using the LBP-2101 coagulant. Diagonal red and blue lines represent 1:1 and 1:10 ratios between fHg and pHg fractions. Green line represents the progression of the average pHg: fHg ratios during the process.

turbidities were observed, there was a 1,300:1 ratio of pHg: fHg. Inside Tank 1 the ratio dropped by three orders of magnitude to a 4:1 ratio of pHg: fHg. Inside Tank 2, the ratio switched from a particulate dominated system to a filtered with a ratio of 1:2 pHg: fHg.

Clar+Ion 5057

There was a 5:1 ratio of pHg: fHg in the Bear River background on the day of Test 2, 12/04/2015 (Figure 10). In the wheelwash where the highest turbidities were observed, there was a 6,000:1 ratio of pHg: fHg. Inside Tank 1 the ratio dropped by three orders of magnitude to a 3:1 ratio of pHg: fHg. The ratio inside Tank 2 decreased to 2:1 pHg: fHg.

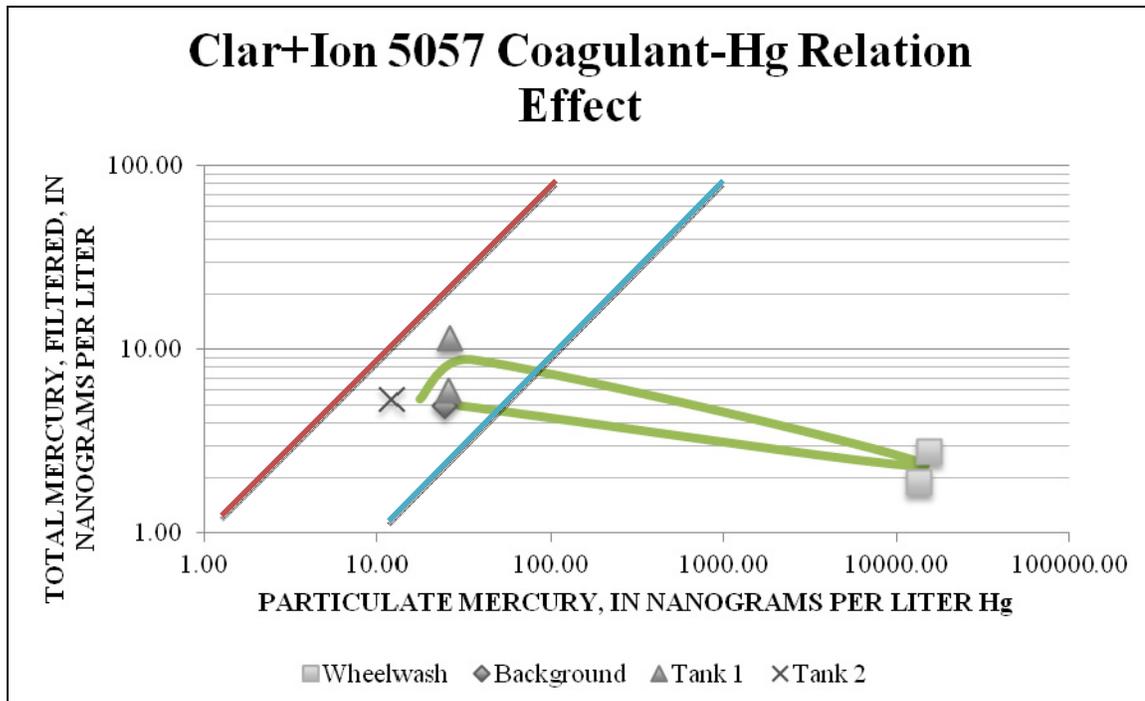


Figure 10. Hg phase distribution using the Clar+Ion 5057 coagulant. Diagonal red and blue lines represent 1:1 and 1:10 ratios between pHg and fHg fractions. Green line represents the progression of the average pHg: fHg ratios during the process.

BHR-P50

There was a measured 3:4 ratio of pHg: fHg within the Bear River background on the day of Test 3, 12/08/2014 (Figure 11). In the wheelwash where the highest turbidities were observed, there was a 1,300:1 ratio of pHg: fHg. Inside Tank 1 the ratio dropped by three orders of magnitude to a 5:1 ratio of pHg: fHg. Inside Tank 2, containing the effluent that would be released back to the Bear River, the ratio increased to 13:1 pHg: fHg.

BHR-P50/665-P

Average fHg and pHg ratios from tests 4 through 9 of the treatment process were compared. There was an average of a 6:5 ratio pHg: fHg in the Bear River

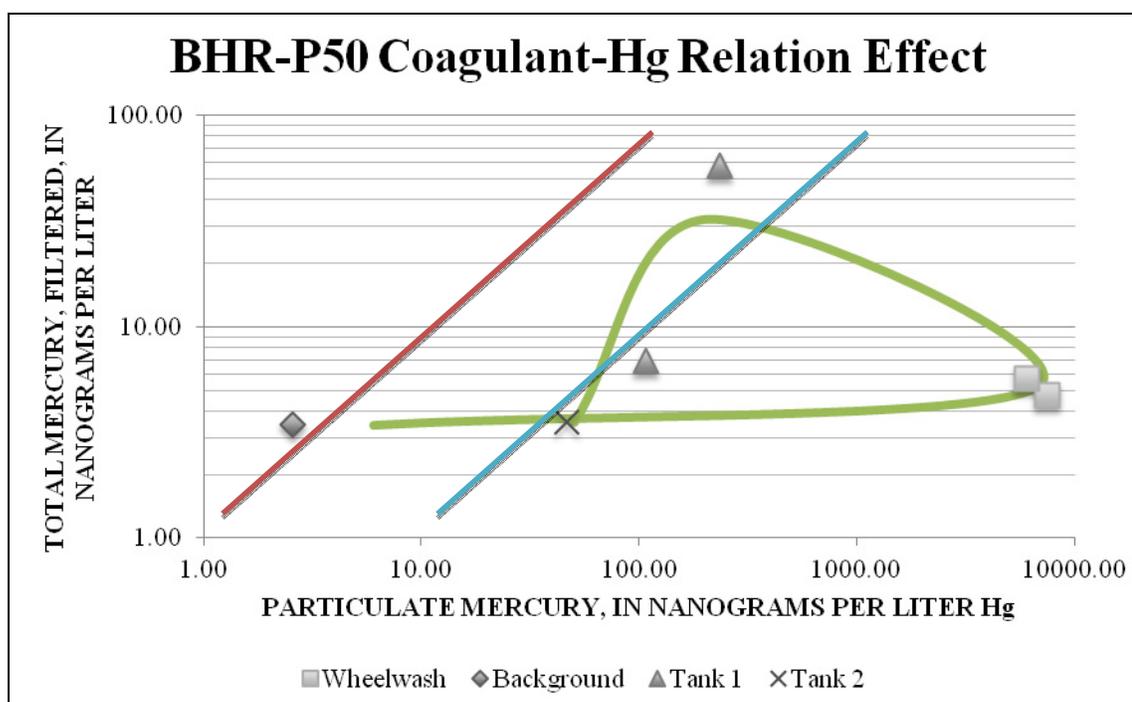


Figure 11. Hg phase distribution using the BHR-P50. Diagonal red and blue lines represent 1:1 and 10:1 ratios between pHg and fHg fractions. Green line represents the progression of the average pHg: fHg ratios during the process.

background across all test days (04/20/2015, 08/26/2015, 08/31/2015, 09/01/2015, 09/02/2015, and 09/09/2015) (Figure 12). In the wheelwash where the highest turbidities were observed, there was an average of 175:1 ratio of pHg: fHg. Inside Tank 1, the ratio dropped by one order of magnitude to an average of 8:1 of pHg: fHg. Tank 2 the pHg: fHg ratio decreased to an average of 3:1.

Relationship of Total Nonfiltered Mercury with TSS

In order to analyze the relationship between THg and TSS concentrations during the sediment and Hg removal process, TSS concentrations for all three sediment sources were compared to their relative THg concentrations at all locations of the

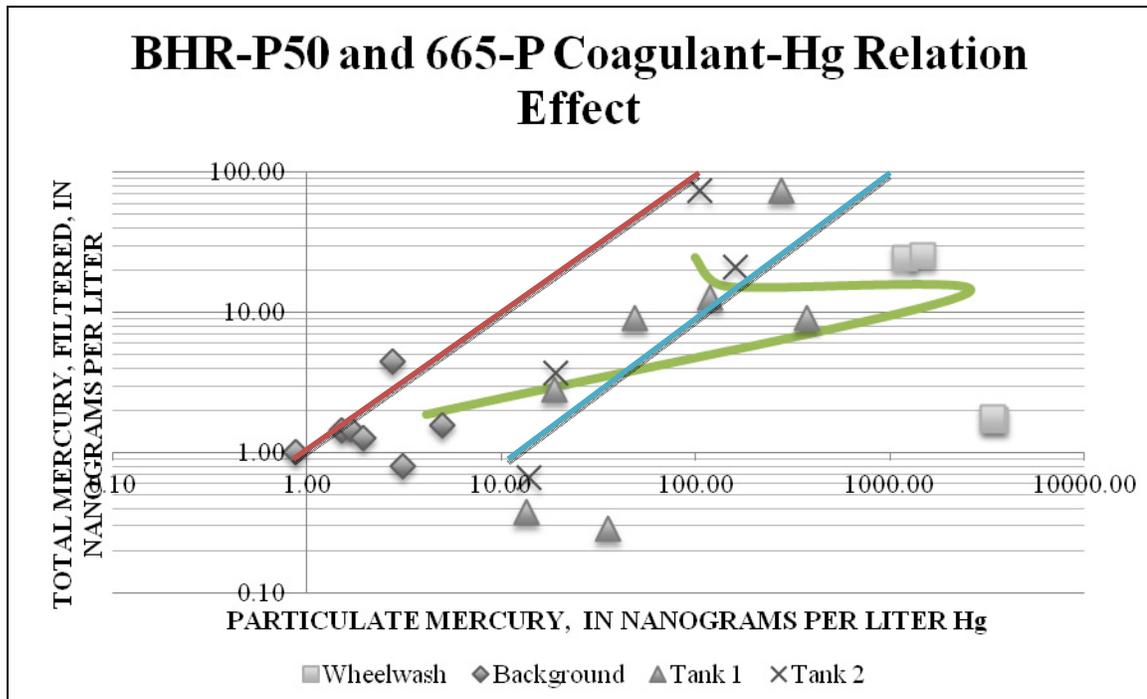


Figure 12. Hg phase distribution using the BHR-P50 and 665-P Coagulants. Diagonal red and blue lines represent 1:1 and 10:1 ratios between particulate and filtered Hg fractions. Green line represents the progression of the average pHg: fHg ratios during the process.

treatment process. Changes in Hg concentrations relative to changes in TSS concentrations are represented by the slope of a linear relationship. Since slope is defined as change in y divided by change in x, the units of slope in this case result in ng of Hg/mg of suspended sediment. Alternatively, ng Hg/mg TSS can be expressed as parts of Hg per million parts of TSS (1ng/1,000,000 mg) or ppm. Trends in THg concentrations per mg of sediment (slope) highlight either an increase or decrease in Hg contamination by site.

Combie Lake Material

Combie Lake material had the greatest range of TSS (5- 50,000 mg/L) and Hg (3- 45,000 ng/L) concentrations throughout the sediment and mercury removal process.

The combined average slope at all sample locations of the Combie Lake material was 1 ng THg/ mg TSS. Samples collected from the wheelwash location had the greatest concentrations of sediment and mercury, but were lower than the combined average of 1 ng THg/mg TSS. (Figure 13).

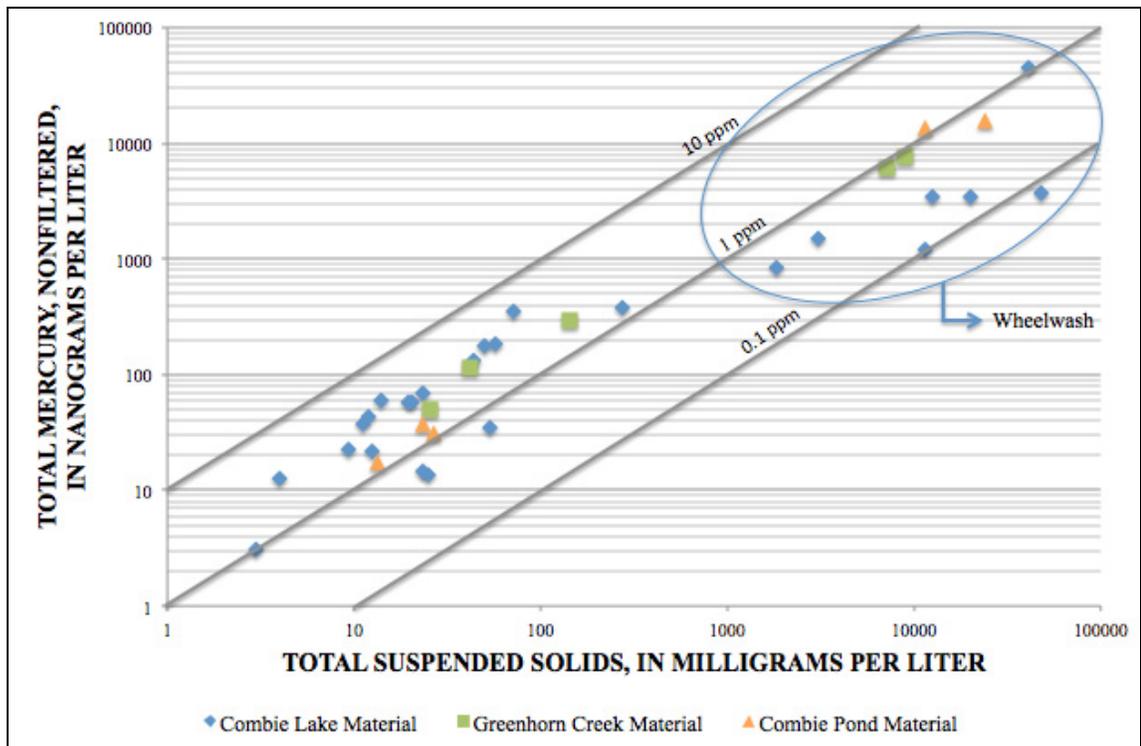


Figure 13. Relationship between nonfiltered total Hg and Total Suspended Solids concentrations for each material processed. Diagonal lines represent ratios of THg in suspended solids, which are equal to the concentration of Hg in suspended solids, in ppm.

Greenhorn Creek Material

Greenhorn Creek material had the lowest range of total suspended solids, 25-9,000 mg/L, and Hg, 50-7,500 ng/L, concentrations throughout the sediment and mercury

removal process. The average slope of Greenhorn Creek material, ng THg/ mg TSS, at all sample locations within the process were 1 (Figure 13).

Combie Pond Material

Combie Pond material ranged from 13-24,000 mg/L of total suspended solids and 17-15,000 ng/L of THg throughout the sediment and Hg removal process. The average slope of the Combie Pond material, ng THg/ mg TSS, at all sample locations within the process were 1 ng of Hg/ mg of suspended sediment (Figure 13).

LBP-2101-Metals Relationship

Concentrations of pHg and fHg were 3 and 6 times greater in Tank 2 than river background levels during the sediment and Hg removal process utilizing the LBP-2101 coagulant (Test 1) on Combie Lake material. With the increased amounts of both fractions of Hg in the treated effluent, release into the Bear River could potentially increase both the amount of biologically available Hg (Alpers, et al., 2006) and Hg that could become methylated within downstream ecosystems (Slotton, et al., 1997). However, the THg concentration that would have been released (30.80 ng/L) was less than the regulatory criteria (50 ng/L) permitted by the California Regional Water Quality Control Board (CRWQCB, 2005). The full-time use of the LBP-2101 coagulant in the sediment and Hg removal project could potentially create a new issue by relocating the Hg contamination of the Combie Lake material to within the water column of the Bear River. Increased concentrations from pre to post treatment, although within regulatory criteria, could potentially increase Hg loads (concentration*discharge) to the Bear River, specifically the filtered Hg loads.

Other metals (Al, As, and Ni) were analyzed to compare filtered and particulate sedimentation rates. The LBP-2101 coagulant was found to effectively return (fAl, fAs, and fNi) concentrations within Tank 2 (34 µg/L, 0.263 µg/L, and 0.94 µg/L) to background levels (29.6 µg/L, 0.291 µg/L, and 0.6 µg/L, Figure 14). Conversely, all three particulate metal concentrations increased from pre to post treatment (Figure 14), indicating that the filtered fraction had no change from pre to post treatment.

Although only select metals were analyzed, it appears that the use of the LBP-2101 coagulant effectively maintained THg concentrations below regulatory criteria, but may also have introduced additional contaminants. Although the effluent created using the LBP-2101 coagulant was within regulatory criteria, the increased concentrations of Al, As, and Ni metals could be a direct result of the coagulant make up and or overdosing of coagulants. Further tests should be conducted on a full suite of metals pre vs. post coagulant treatments to quantify potential effects on water quality associated with the coagulants.

Clar+Ion 5057-Metals Relationship

Using the Clar+Ion 5057 coagulant (Test 2) on the Combie Pond material (Figures 6 and 7), a 50% reduction in pHg: fHg ratio (5:1 to 2.5:1) occurred. Given that fHg maintained background concentrations from pre to post treatment, this observed reduction suggests that the Clar+Ion 5057 coagulant was more effective at reducing pHg concentrations.

Since fHg is considered more bioavailable than pHg (Alpers, et al., 2006) and harmful to ecosystems (Alpers, et al., 2006, Slotton, et al., 1997), the reduction of THg

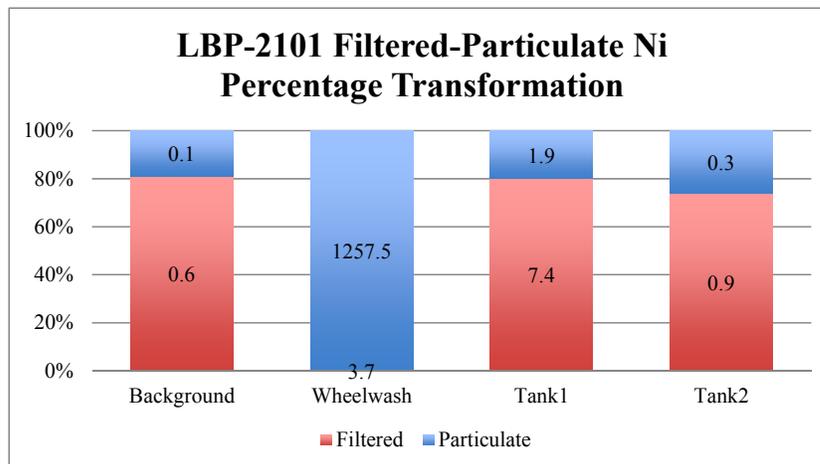
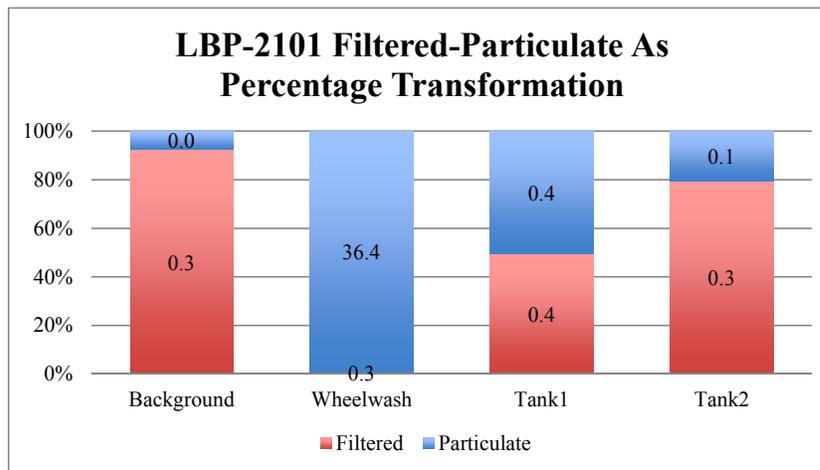
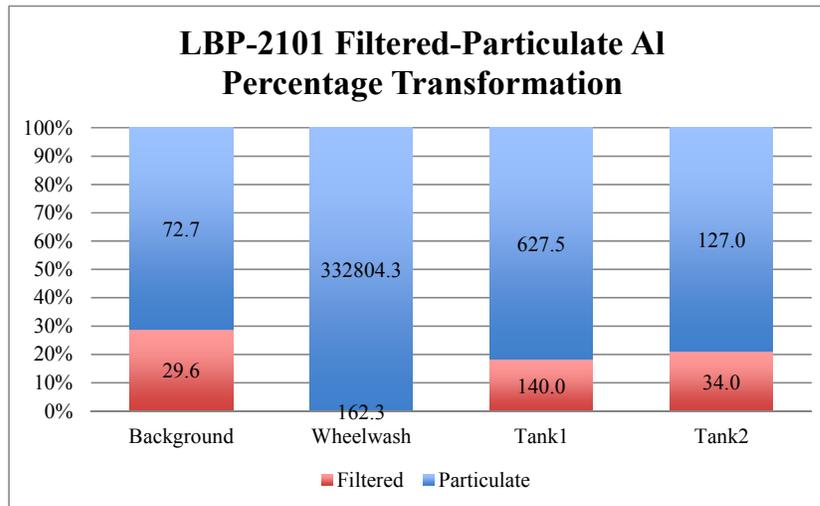


Figure 14. Change in filtered and particulate Al, as, and Ni distribution during treatment with LBP-2101. Data labels are average concentrations in µg/L.

without increasing fHg through the removal process implies that the Clar+Ion 5057 could be effective for full-scale use at the Lake Combie Reservoir sediment and Hg removal project. Use of the Clar+Ion 5057 coagulant in the sediment and Hg removal process would result in Hg removal from sediment sources and could improve water quality pertaining to the fHg fraction with the effluent release. These observed results of maintaining fHg while reducing THg concentration suggest further full-scale testing with the Clar+Ion 5057 should be conducted. Clar+Ion 5057 coagulant appeared to increase fractions of Al, As, and Ni (Figure 15). Clar+Ion 5057 increased fAl concentration by 2, fAs concentration 2.5 times, and fNi concentration 14 times from pre to post treatment. Conversely, particulate concentrations decreased by 57% for Al, 70% for Ni, and returned As to background levels following treatments. As observed with Hg, the Clar+Ion 5057 appears to have a greater removal of the particulate form than the filtered. Even though the Clar+Ion 5057 can remove fHg and pHg contamination in the process effluent, the elevated levels of other metals analyzed are a cause of concern for use in the Lake Combie Reservoir sediment and mercury removal project.

BHR-P50-Metals Relationship

The BHR-P50 coagulant (Test 3) on the Greenhorn Creek material resulted in a THg concentration increase from 6.01 ng/L in river background to 50.4 ng/L in Tank 2. Filtered Hg had a post-treatment concentration in Tank 2 of 3.57 ng/L and was similar to the river background (3.45 ng/L, Figures 7 and 8). This observed increase in pHg: fHg ratio suggests that the BHR-P50 coagulant more effectively removed fHg than pHg.

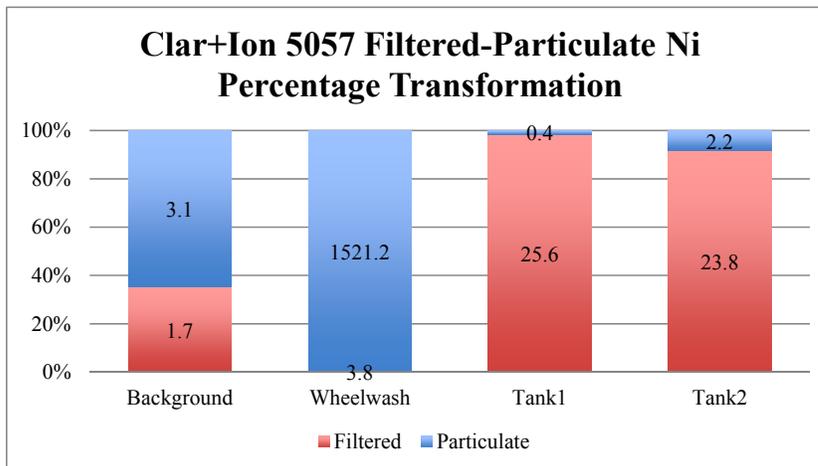
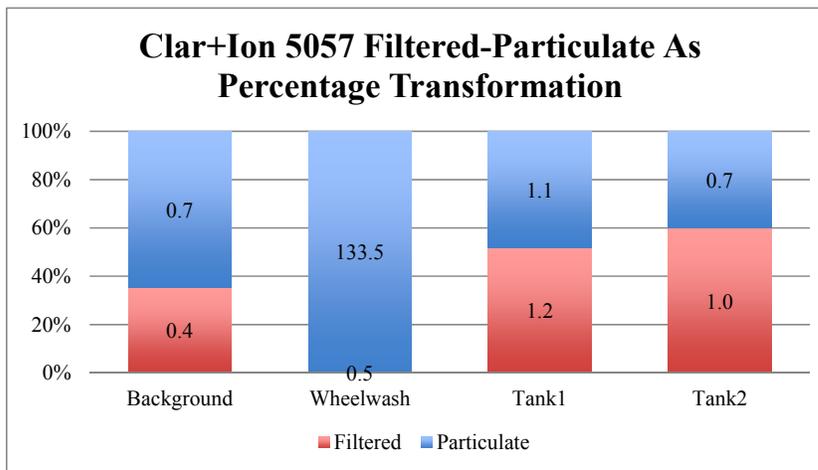
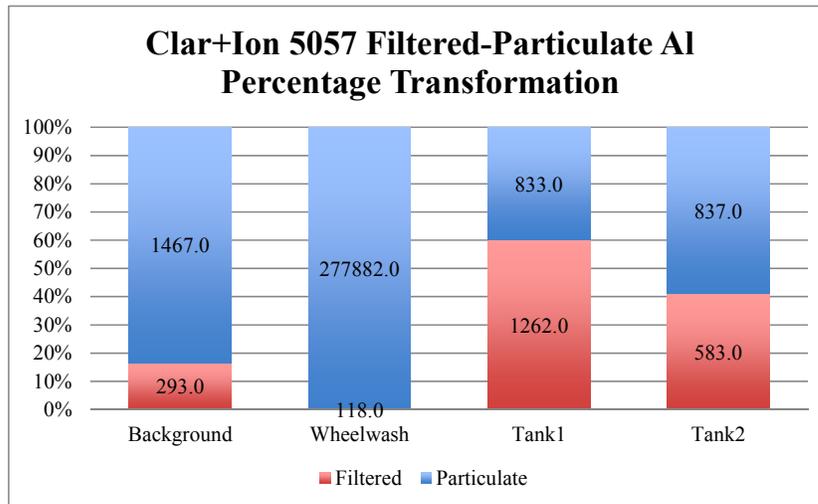


Figure 15. Change in filtered-particulate Al, As, and Ni distribution during treatment with Clar+Ion 5057. Data labels are average concentrations in ng/L.

Although the more bioavailable fHg fraction was not increased by the use of the BHR-P50 coagulant, an increase in the concentration of pHg in the effluent released to the Bear River could potentially increase the amount of Hg available for downstream methylation (Slotton, D.G., et al. 1997).

The BHR-P50 coagulant did not effectively remove filtered or particulate fractions of Al, As, and Ni (Figure 16). Aluminum increased by magnitudes of 8 and 4 in the particulate and filtered forms, arsenic increased by 10 and 1.5 times, and nickel concentrations increased by 2.5 and 9 times. The combination of elevated levels of pHg, filtered and particulate Al, As, and Ni suggests that the use of the BHR-P50 coagulant in the Lake Combie Reservoir sediment and mercury removal project could result in additional metal contamination in the Bear River. With elevated pHg, TAl, TAs, and TNi concentrations during the sediment and Hg removal process, full time use of the BHR-P50 coagulant could result in further degradation of Bear River water quality.

BHR-P50/665-P-Metal Relationship

The combination of BHR-P50 and 665-P coagulants (tests 4-9) on the Combie Pond material resulted in an increase in the ratio of pHg: fHg concentrations from pre (1: 1) to post (3: 1) treatment (Figure 12). Particulate and filtered Hg concentrations increased by a magnitude of 10 and 2 times from Bear River background to Tank 2 of the sediment and Hg removal process (Figures 7 and 8). This suggests that BHR-P50/665-P coagulants were effective at decreasing pHg more than fHg, despite an overall increase in total Hg concentration. However, even with this increase in the resulting effluent to 22.7 ng/L, THg concentration was still below the regulatory criteria of 50 ng/L (CRWQCB),

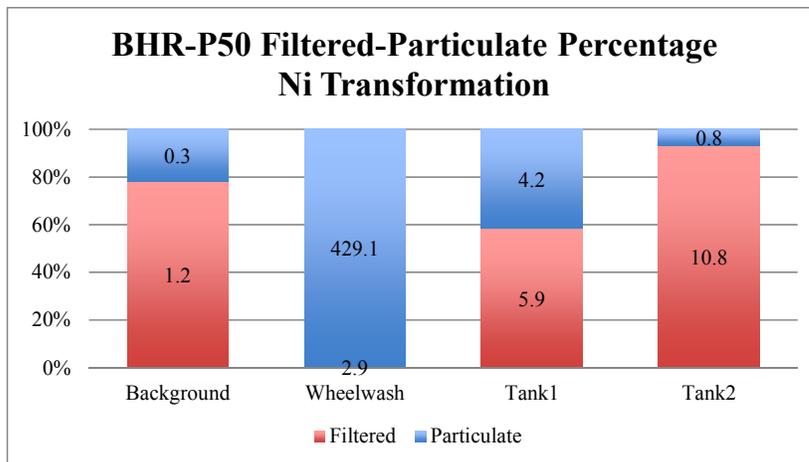
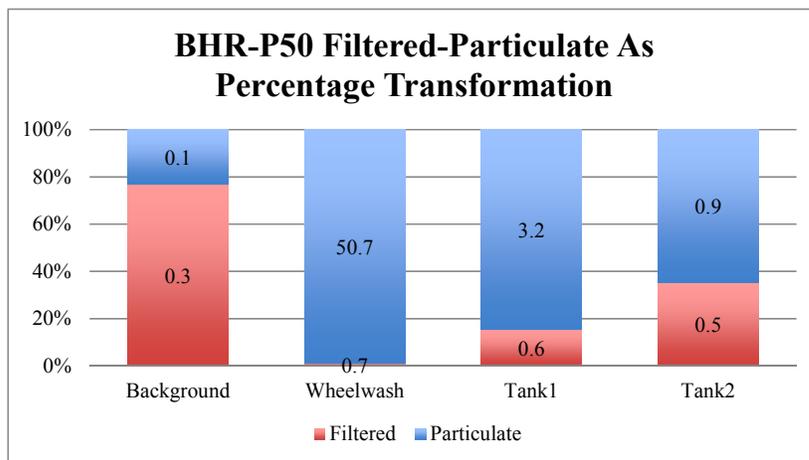
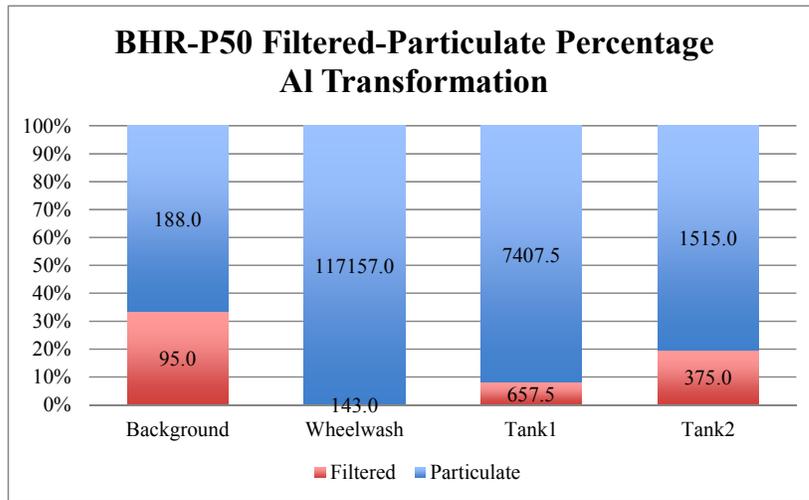


Figure 16. Change in filtered-particulate Al, As, and Ni distribution during treatment with BHR-P50. Data labels are average concentrations in ng/L.

2005. An increased amount of fHg and pHg concentrations in the effluent could potentially increase both the biologically available Hg and the Hg available for methylation to occur.

The BHR-P50 and 665-P coagulants effectively decrease pAl and pNi concentrations to background Bear River levels. However, the use of the BHR-P50 and 665-P coagulants resulted in an increase of fAl (33x), fAs (1.2x), and fNi (10.5x) concentrations from pre to post treatment (Figure 17). This increase of Hg, Al, As, and Ni concentrations suggest that the use of BHR-P50 and 665-P coagulants in treatment purposes can act as an additional source of metals in the effluent created. Even though the BHR-P50 and 665-P coagulants can help to remediate Hg contamination in the sediment process effluent, the elevated levels of filtered Al, As, and Ni concentrations is a cause of concern for use in the Lake Combie Reservoir sediment and mercury removal project.

DOC and Absorbance

To gain a better understanding of how DOC concentrations and optical characteristics varied throughout the removal process, samples were collected from the Bear River as background, within Tank 1 and 2 of the removal process and at a downstream compliance point during Tests 1, 2, 3, and 9 of the Lake Combie sediment and mercury removal project (Table 7). Test 9 was the only test to release to the Bear River therefore; the only day DOC characteristics were determined at the compliance point.

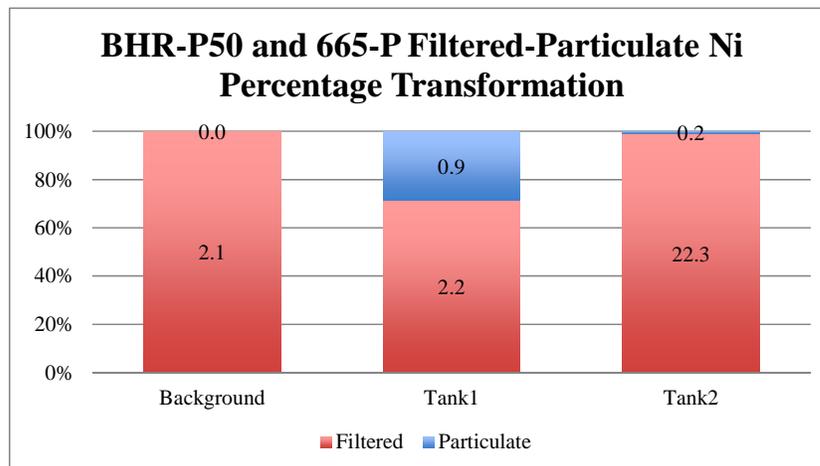
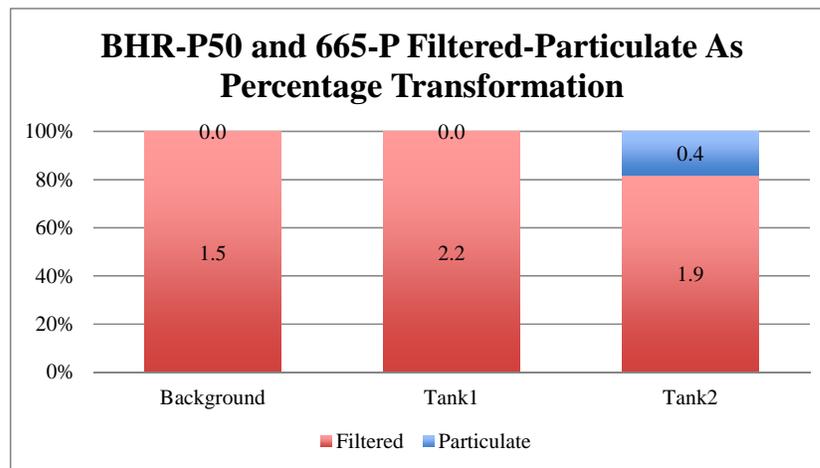
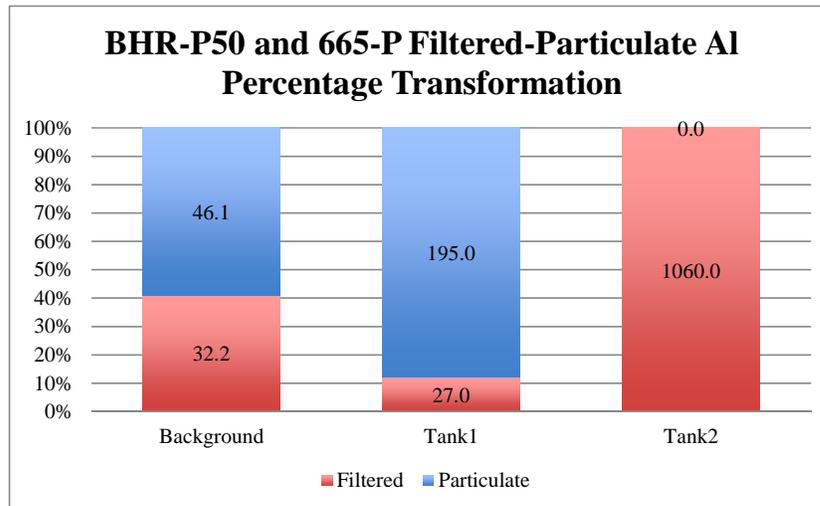


Figure 17. Change in filtered-particulate Al, As, and Ni distribution during treatment with BHR-P50 and 665-P. Data labels are average concentrations in ng/L

TABLE 7. DOC, UV ABSORBANCE (A), AND SUVA₂₅₄ VALUES FROM TESTS 1, 2, 3, AND 9 OF THE LAKE COMBIE SEDIMENT AND MERCURY REMOVAL PROJECT
 Samples separated by test number and source materials: Combie Lake (CL), Combie Pond (CP), and Greenhorn Creek (GH).

DOC and Spectral Parameters															
Test #	Source Material	Location	Date	DOC (mg/L)	A ₂₅₄ (m ⁻¹)	A ₂₈₀ (m ⁻¹)	A ₃₅₀ (m ⁻¹)	A ₃₇₀ (m ⁻¹)	A ₄₁₂ (m ⁻¹)	A ₄₄₀ (m ⁻¹)	A ₄₈₈ (m ⁻¹)	A ₅₁₀ (m ⁻¹)	A ₅₃₂ (m ⁻¹)	A ₅₅₅ (m ⁻¹)	SUVA ₂₅₄ (mg C L ⁻¹ n)
1	CL	River Background	12/2/2014	2.06	0.07	0.05	0.02	0.02	0.01	0.01	0.00	0.00	0.00	0.00	3.4
1	CL	River Background	12/2/2014	2.07	0.07	0.05	0.02	0.02	0.01	0.01	0.00	0.00	0.00	0.00	3.4
1	CL	River Background	12/2/2014	2.12	0.07	0.05	0.02	0.02	0.01	0.01	0.00	0.00	0.00	0.00	3.3
1	CL	Tank 1	12/2/2014	7.63	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.4
1	CL	Tank 1	12/2/2014	10.10	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.3
1	CL	Tank 1	12/2/2014	12.26	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.2
1	CL	Tank 2	12/2/2014	2.48	0.06	0.05	0.02	0.01	0.01	0.01	0.00	0.00	0.00	0.00	2.6
1	CL	Tank 2	12/2/2014	4.84	0.04	0.03	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.8
1	CL	Tank 2	12/2/2014	6.42	0.03	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.5
2	CP	River Background	12/4/2014	4.49	0.27	0.22	0.11	0.09	0.06	0.05	0.03	0.03	0.03	0.02	5.9
2	CP	Tank 1	12/4/2014	6.13	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.4
2	CP	Tank 1	12/4/2014	5.15	0.03	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.6
2	CP	Tank 2	12/4/2014	5.87	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.4
3	GH	River Background	12/8/2014	2.90	0.11	0.09	0.04	0.03	0.02	0.01	0.01	0.01	0.00	0.00	3.9
3	GH	Tank 1	12/8/2014	1.38	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.1
3	GH	Tank 1	12/8/2014	3.25	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.6
3	GH	Tank 2	12/8/2014	3.38	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.6
9	CP	River Background	9/9/2015	1.55	0.10	0.08	0.04	0.03	0.02	0.01	0.01	0.00	0.00	0.00	6.2
9	CP	Tank 1	9/9/2015	1.73	0.04	0.03	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	2.1
9	CP	Tank 2	9/9/2015	1.64	0.05	0.04	0.02	0.02	0.01	0.01	0.01	0.00	0.00	0.00	3.1
9	CP	Compliance Point	9/9/2015	1.46	0.08	0.07	0.03	0.03	0.01	0.01	0.01	0.00	0.00	0.00	5.7

Combie Lake (Test 1)

During Test 1 of the removal process using Combie Lake sediments and the LBP-2101 coagulant, DOC concentrations averaged 2.08 mg/L in the river background, 9.99 mg/L within Tank 1, and 4.58 mg/L in Tank 2. DOC concentrations increased 5 times from the river background to Tank 1 and then decreased by a factor of 2 from Tank 1 to 2. Of all wavelengths of UV light evaluated, the greatest density of absorbance occurred at 254 nm (A_{254}). A_{254} averaged 0.07 m^{-1} at the river background, 0.03 m^{-1} within Tank 1, and 0.04 m^{-1} in Tank 2. Using DOC and A_{254} values, SUVA_{254} was calculated to average $3.3 \text{ mg C L}^{-1} \text{ m}^{-1}$ in the background, $0.3 \text{ mg C L}^{-1} \text{ m}^{-1}$ in Tank 1, and $1.3 \text{ mg C L}^{-1} \text{ m}^{-1}$ within Tank 2.

Combie Pond (Test 2)

During Test 2 of the removal process using Combie Pond sediments and the Clar+Ion 5057 coagulant, the DOC concentration was 4.49 mg/L in the river background, averaged 5.65 mg/L within Tank 1, and 5.87 mg/L in Tank 2. Of all wavelengths of UV light evaluated, the greatest density of absorbance occurred at 254 nm (A_{254}). A_{254} was 0.27 m^{-1} at the river background, 0.03 m^{-1} within Tank 1, and 0.02 m^{-1} in Tank 2. Using DOC and A_{254} values, SUVA_{254} was calculated to be $5.9 \text{ mg C L}^{-1} \text{ m}^{-1}$ in the background, $0.5 \text{ mg C L}^{-1} \text{ m}^{-1}$ in Tank 1, and $0.4 \text{ mg C L}^{-1} \text{ m}^{-1}$ within Tank 2.

Greenhorn Creek (Test 3)

During Test 3 of the removal process using Greenhorn Creek sediments and the BHR-P50 coagulant, the DOC concentration was 2.90 mg/L in the river background, averaged 2.31 mg/L within Tank 1, and 3.38 mg/L in Tank 2. Of all wavelengths of UV

light evaluated, the greatest density of absorbance occurred at 254 nm (A_{254}). A_{254} was 0.11 m^{-1} at the river background, 0.02 m^{-1} within Tank 1, and 0.02 m^{-1} in Tank 2. Using DOC and A_{254} values, SUVA_{254} was calculated to be $3.9 \text{ mg C L}^{-1}\text{m}^{-1}$ in the background, averaged $0.8 \text{ mg C L}^{-1}\text{m}^{-1}$ in Tank 1, and was $0.6 \text{ mg C L}^{-1}\text{m}^{-1}$ within Tank 2.

Combie Pond (Test 9)

During Test 9 of the removal process using Combie Lake sediments and the combination of BHR-P50 and 665-P coagulants, the DOC concentration was 1.55 mg/L in the river background, 1.73 mg/L within Tank 1, 1.64 mg/L in Tank 2, and 1.46 mg/L at the downstream compliance point. Of all wavelengths of UV light evaluated, the greatest density of absorbance occurred at 254 nm (A_{254}). A_{254} was 0.10 m^{-1} at the river background, 0.04 m^{-1} within Tank 1, 0.05 m^{-1} in Tank 2, and 0.08 m^{-1} at the downstream compliance point. Using DOC and A_{254} values, SUVA_{254} was calculated to be $6.2 \text{ mg C L}^{-1}\text{m}^{-1}$ in the background, $2.1 \text{ mg C L}^{-1}\text{m}^{-1}$ in Tank 1, $3.1 \text{ mg C L}^{-1}\text{m}^{-1}$ within Tank 2, and $5.7 \text{ mg C L}^{-1}\text{m}^{-1}$ at the downstream compliance point.

Multiple Regression Analysis for Filtered Mercury (fHg)

Using an ANOVA analysis of variance, a model for the prediction of fHg concentrations was developed using TSS, DOC, A_{254} , TDS, and SUVA_{254} values from Tests 1, 2, 3, and 9 as explanatory variables.

The ANOVA prediction of fHg was the following equation:

$$fHg \left(\frac{ng}{L} \right) = 6.20 + 0.390(X_1) + 0.416(X_2) - 33.766(X_3) - 0.083(X_4) + 0.346(X_5) \quad (3)$$

Where:

X_1 = Total Suspended Solids (mg/L)

X_2 = Dissolved Organic Carbon (mg/L)

X_3 = A_{254} (AU)

X_4 = Total Dissolved Solids (mg/L)

X_5 = $SUVA_{254}$ ($\text{mg C L}^{-1}\text{m}^{-1}$)

According to the ANOVA output, there was a residual standard error of 5.63 on 14 degrees of freedom, a multiple R^2 value of 0.86, and a significant p-value <0.0001 for the model as a whole.

For the ANOVA reduced model prediction of fHg obtained in R, variables of total suspended solids (TSS), A_{254} , and total dissolved solids TDS were selected to have the greatest significance.

The ANOVA prediction of fHg reduced model equation was as follows:

$$fHg \left(\frac{ng}{L} \right) = 9.032 + 0.387(X_1) - 32.563(X_2) - 0.087(X_3) \quad (4)$$

Where:

X_1 = Total Suspended Solids (mg/L)

X_2 = A_{254} (AU)

X_3 = Total Dissolved Solids (mg/L)

The model had a R^2 value of 0.85, meaning 85% of the variation in fHg was explained by TSS, A_{254} , and TDS variables. The model had a residual standard error of 5.4 on 16 degrees of freedom and p-value <0.0001 .

A scatter plot of the residuals against the corresponding fitted value was created to observe any possible trends. Any trend seen in this plot would suggest a violation of regression assumptions (Kornwe-Nievergelt, 2015). The plot created had no visible trends, thus supports the validity of the reduced model (Figure 18).

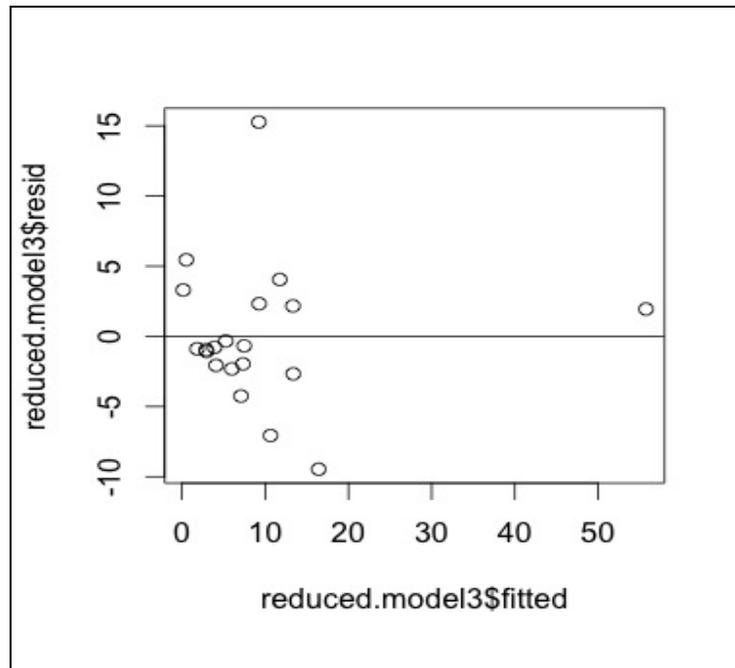


Figure 18. Residual plot for the reduced fHg model. Residuals represent difference between calculated values of fHg concentrations from model equation and actual values observed. A line at (0, 0) was fitted to show variation from the actuals.

Multiple Regression Analysis for Nonfiltered Mercury (THg)

Using an ANOVA analysis of variance, a model for the prediction of THg concentrations was developed using TSS, DOC, A_{254} , TDS, and $SUVA_{254}$ values from tests 1, 2, 3, and 9 as explanatory variables.

The ANOVA prediction of THg equation was as follows:

$$THg \left(\frac{ng}{L} \right) = 29.32 + 2.083(X_1) + 0.332(X_2) - 176.01(X_3) - 0.248(X_4) - 1.068(X_5) \quad (5)$$

Where:

X_1 = Total Suspended Solids (mg/L)

X_2 = Dissolved Organic Carbon (mg/L)

X_3 = A_{254} (AU)

X_4 = Total Dissolved Solids (mg/L)

X_5 = $SUVA_{254}$ ($mg\ C\ L^{-1}m^{-1}$)

According to the ANOVA, there was a residual standard error of 11.11 on 14 degrees of freedom, a Multiple R^2 value of 0.98, and a significant p-value <0.0001 for the model.

According to the ANOVA output for the reduced model prediction of THg calculated in R, variables of total suspended solids (TSS (mg/L)), A_{254} , and total dissolved solids TDS (mg/L) were used.

ANOVA output prediction of THg reduced model equation was as follows:

$$THg \left(\frac{ng}{L} \right) = 30.253 + 2.086(X_1) - 206.81(X_2) - 0.248(X_3) \quad (6)$$

Where:

X_1 = Total Suspended Solids (mg/L)

X_2 = A_{254} (AU)

X_3 = Total Dissolved Solids (mg/L)

The model had a R^2 value of 0.97, which means that 97% of the variation in THg was explained by TSS, A_{254} , and TDS variables. The model has a residual standard error of 10.6 on 16 degrees of freedom and p-value <0.0001 .

A scatter plot of the residuals against the corresponding fitted value (Figure 19) was created to observe any possible trends. The plot created had no visible trends, thus further supporting the validity of the reduced model (Kornwe-Nievergelt, 2015).

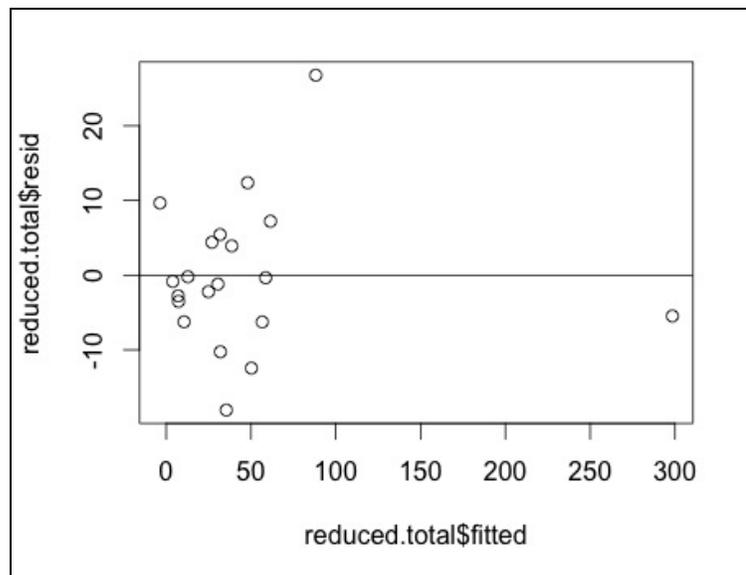


Figure 19. Residual plot for the reduced THg model. Residuals represent difference between calculated values of DHg concentrations from model equation and actual values observed. A line at (0, 0) was fitted to show variation from the actuals.

CHAPTER VI

DISCUSSION AND CONCLUSIONS

Bench-Scale Coagulant Additions

The first objective of this study was to determine the concentrations of coagulants 665-P and BHR-P50 that would result in a treated solution with turbidity levels ≤ 5 NTU at the bench-scale. The bench-scale coagulant dose rates of 1.6 mL/L of 665-P and 0.2 mL/L of BHR-P50 resulted in a solution with less than 5 NTU (Table 3). The bench-scale tests were conducted under ideal conditions where ambient temperature, dosage, mixing rate, suspended sediment concentrations, and laminar flow for sedimentation of floc to occur were maintained. These variables, which are difficult to keep constant at the field-scale, can alter the effectiveness of coagulant dose.

Field-Scale Coagulant Additions

The second objective of this study was to apply the concentrations of coagulants from the bench-scale analysis at the field-scale to determine their effectiveness in improving effluent water quality to values below regulatory criteria. For the Combie Pond sediment source, 9.5 gph of 665-P and 9.0 gph of BHR-P50 were found to be effective in reducing effluent turbidity and trace metal concentrations to below regulatory standards (Table 4). These dose rates were operationally found to be more effective than bench-tests originally suggested.

At the field-scale, the ability to keep a constant feed of sediment within the slurry to be treated by the coagulants was difficult. The manual feed rate of sediment to

the sediment removal process by the use of a backhoe was highly variable as the amount of sediment in the bucket changed from one addition to the next. With the changing concentration of sediment in the slurry, the amount of coagulant needed to effectively reduce effluent turbidity to below the regulatory criteria had to be adjusted frequently. As a result, the experimentally dose rate found from the bench-scale tests was not effective at achieving turbidity below regulatory criteria (5 NTU), subsequently the dose rates were increased. Excess coagulant added to the slurry could have affected effluent water quality with possible release of additional metals that make up the coagulants. To monitor this issue, slurry samples were periodically taken from the feed line into Tank 1 from a pour valve to check for coagulant performance before the slurry entered the tank. Based on a visual determination of settling velocities of the treated slurry within the grab sample, the backhoe operator was notified to either speed up or slow down sediment feed rates accordingly. For future studies using this sediment removal process, a mixing chamber to contain the slurry pre-treatment would help to maintain homogenized sediment densities and reduce the risk of overdosing.

Treatment Results

The third objective of the study was to determine how total suspended solids (TSS), filtered and particulate metals (mercury (Hg), arsenic (As), manganese (Mn), nickel (Ni), selenium (Se), aluminum (Al), chromium (Cr), iron (Fe), and zinc (Zn) varied between river background concentrations and post-treatment concentrations at the compliance point 300 feet downstream of the discharge. A comparison between measured TSS and metal concentrations in the river upstream of the process site, discharge at the

compliance point, and predicted values from Equation 3 was carried out. The comparison allowed for the mass balance model to be evaluated against measured predicted values. Of the constituents monitored at the downstream compliance point, only total As (1.19 µg/L) and total Fe (990 µg/L) were in exceedance of regulatory criteria at 0.018 and 300 µg/L, respectively (Table 6). However, the background concentrations for total As (1.37 µg/L) and total Fe (1,060 µg/L) were also above the regulatory criteria. Total effluent As and Fe concentrations were at or below background levels and therefore within acceptable operating criteria. Constituents monitored in the sediment removal process (TSS, Hg, Mn, Ni, Se, Cr, and Zn), were reduced at the compliance point when compared to background levels. Additionally, concentrations of TSS, Hg, Mn, Ni, Se, Cr, and Zn were below regulatory criteria when measured at the compliance point.

Tank 2 had concentrations of Ni (22.5 µg/L), Mo (10.6 µg/L), and Cr (51.4 µg/L) that were all in exceedance of their respective regulatory criteria (12 µg/L, 10 µg/L, and 50 µg/L) while Hg and Zn were below regulatory standards. However, using the mass balance model which accounts for dilution, on the elevated concentrations of Ni, Mo, and Cr in Tank 2, the predicted concentrations at the compliance point were expected to be lower than regulatory standards (Ni 1.52 µg/L, Mo 0.66 µg/L, and Cr 1.57 µg/L). Based on the measured river background and compliance point water quality data, the sediment and mercury removal process effluent had minimal to no effect on water quality when compared to river background levels.

Test 9 effluent was released to the Bear River, and changes in water quality were measured at the regulatory compliance point 300 ft. downstream. The water quality

data at the compliance point were found to be consistent with background water quality levels in the Bear River, suggesting that the effluent had no detectable influence on Bear River water quality. Water samples collected at the downstream compliance point were collected one hour after the treated effluent was released. Given the summer low flow average of 4,752 gpm (or 10.59 cfs) in the Bear River, a one hour of wait time should have allowed the effluent to travel 300 feet downstream and mix. However, during Test 9 the Bear River had very low flow. Low flow within the river may have led to a delayed response in water quality at the compliance point, and samples collected at this point may not have reflected the impact of the water treatment effluent. Additional tests on the effect of the effluent should be run during times of greater velocities in the river to obtain a more representative, well-mixed sample of effluent and Bear River water downstream of the discharge point. Flow velocities should be monitored during the time of discharge to gain an accurate wait time for mixing to occur.

Filtered and Particulate Hg Relationship During Coagulation/Flocculation Treatment

The fourth objective was to determine the effect of coagulants used at the field scale on fHg and pHg concentrations from pre to post treatment. Hg associated with dissolved and colloidal phases are considered more biologically available than coarser particulate fractions (Alpers et al., 2006). Therefore, evaluations of Hg fractions in the influent and effluent waters are an important component of evaluating the effect of coagulants on Hg. As documented in Alpers et al. (2006), Roth et al. (2001), Choe and Gill (2001), and Choe et al. (2003), portions of water samples containing Hg that pass

through filters may contain colloidal nanoparticles smaller than filter pore size. Hg that passes through filter pores are operationally defined to be part of the dissolved or filtered fraction, resulting in the overestimation of dissolved concentrations as these nanoparticles can be attributed to the dissolved fraction when in fact still in the particle form. Changes in particulate and filtered metal concentrations due to the treatment process could alter downstream environment conditions and should be monitored.

All coagulants tested were capable of returning treated water to the Bear River with concentrations below regulatory criteria for Hg. Although THg concentrations were below regulatory criteria, all tests generated treated water with increased Hg concentrations from pre to post treatment. These elevated Hg levels could compound over time and increase the likelihood of MeHg production within the Bear River watershed. As Hg concentration data from these tests are compared for each coagulant type, it should be noted that other factors such as process engineering, sediment feed rates, polymer injection rates, the source of material, and accumulation of sediment occurring in the tanks may also alter results. For all nine tests, the majority of pHg within the wheelwash was removed through particle sedimentation prior to coagulant treatment. However, the potential addition of other metals (Al, As, and Ni) in both filtered and particulate forms by coagulants needs to be further understood before implementation for full-scale use.

Relationship of Total Nonfiltered Mercury with Total Suspended Solids

The fifth objective was to determine the relationship between THg and TSS for each of three sediment source materials throughout the sediment and mercury removal process to evaluate the level of Hg contamination. The THg and TSS relationship varied from 0.01 to 7 ppm of Hg to TSS (ng Hg/mg TSS) in Combie Lake, Greenhorn Creek, and Combie Pond sediment sources (Figure 13).

Combie Lake Material

Although the Combie Lake material was only processed once, the greatest variation of THg and TSS concentrations was observed during the removal process. At all sample locations, except the wheelwash, the relative concentrations of THg to TSS was 0.5ppm to 5ppm (ng Hg/mg SS). At the wheelwash sampling location, the relationship between THg and TSS was around 0.5ppm (ng Hg/mg SS) +/- 0.5ppm. The purpose of this location was to allow the largest sediment sizes (sand) to be removed from the slurry by sedimentation before polymer treatment, the observed drop of Hg in the ng Hg/mg TSS ratio from the wheelwash to Tank 1 suggests pHg may be settling along with sand prior to coagulation.

Greenhorn Creek Material

Greenhorn Creek material had the least amount of variation of THg and TSS concentrations of the three sources sampled. Conversely to the Combie Lake material, the Greenhorn Creek material that was also process, little variation in ng Hg/mg TSS was observed. At all locations sampled within the sediment and Hg removal process, the relative concentrations of THg to TSS were approximately 1ppm (ng Hg/mg TSS). This

observed 1ppm ratio is consistent with background levels observed in a previous study of the geochemistry of water and sediment within Greenhorn Creek (Alpers et al., 2005b). The Hg to TSS ratios observed in this study and previous studies indicate that sediments from Greenhorn Creek are consistently within the 1ppm (or ng Hg/mg TSS) range.

Combie Pond Material

Combie Pond material had a slightly greater variation of THg and TSS concentrations than Greenhorn Creek material, but it was still less than Combie Lake material. At all locations sampled within the sediment and Hg removal process, the relative concentrations of THg to suspended solids were approximately 1 ppm (ng Hg/mg TSS). The observed 1ppm (ng Hg/mg TSS) ratio is consistent with the geochemical characterization of water and sediment within Greenhorn Creek, (Alpers et al., 2005b), which is upstream of Lake Combie Reservoir and within the Bear River watershed.

The variation in Hg concentrations within the Combie Lake source material will have direct implications for Hg removal rates during treatments. Varying ranges of Hg concentrations within the sediment may have an effect on the coagulants ability to conglomerate both filtered and particulate substances. Combie Lake material was the only sediment source to deviate from the mean of 1ppm (ng Hg/mg TSS) within the wheelwash location of the sediment and mercury removal process. A grain size distribution analysis of all three sources could be conducted to quantify the physical properties of the three sediment sources. Differences in grain size distribution can alter the ability of the coagulant to effectively induce sedimentation (Viessman et al., 2009).

Additionally, fHg and THg concentrations at each grain size scale could be determined to identify potential Hg speciation differences between sediment sources.

DOC and Absorbance

The sixth objective of this study was to evaluate the amount of variation of DOC concentrations, UV absorbance intensities, and $SUVA_{254}$ for each of the sediments sources tested throughout the sediment and Hg removal process.

The absorbance intensities of water samples from tests 1, 2, 3, and 9 ($\lambda = 254\text{-}555\text{ nm}$) were found to increase towards the shorter wavelengths, specifically 254 nm. Water samples with the highest density of absorbance around the lower wavelengths are associated with humic substances (MacCarthy et al., 1985). $SUVA_{254}$ values of background water samples (3.3, 5.9, 3.9, and 6.2 $\text{mg C L}^{-1} \text{m}^{-1}$) from tests 1, 2, 3, and 9 supplement the humic substance source assumption as $SUVA_{254}$ has been documented to be a good indicator of the humic fraction (Weishar et al., 2003). Coagulation practices are known to be effective at removing humic substances when $SUVA_{254} > 2.0 \text{ mg C L}^{-1} \text{m}^{-1}$ (Weishar et al., 2003), therefore using coagulation for DOC removal and in turn Hg removal was feasible for all tests of the sediment and Hg removal project. $SUVA_{254}$ values reduced from pre to post treatment, reinforcing the ability of the coagulants to remove dissolved humic substances from the effluent. Additionally, the observed reduction in absorbance and $SUVA_{254}$ was mirrored by a reduction in Hg concentration. The correlated decreases between these optical characteristics and Hg concentrations suggest the use of $SUVA_{254}$ and A_{254} as possible indicators or proxies for Hg

concentrations. Monitoring $SUVA_{254}$ therefore appears as a useful tool to maintain coagulant efficiency on inducing sedimentation.

Multivariate Analysis

The seventh objective was to determine the predictive capabilities of TSS, TDS, DOC, A_{254} , and $SUVA_{254}$ for fHg and THg concentrations using a multivariate analysis. A stepAIC reduction from the full model to the reduced was run, this reduction eliminated the least significant parameters (DOC and $SUVA_{254}$) to create a more statistically significant model. The final reduced model included the variables: TSS, TDS, and A_{254} for both THg and fHg. These variables can be monitored in-situ in real time to track the effectiveness of the process at decreasing Hg concentrations below regulatory standards. An alternative for evaluating Hg concentrations as mentioned in Haitzer et al. (2002), Alpers et al. (2006), Lamborg et al. (2003), Ravichandran (2004), Dittman et al. (2009), Weishaar et al. (2003), is to use water quality parameters such as TSS, A_{254} , and TDS as potential proxies for Hg concentrations. THg and fHg analyses are costly and time sensitive from the time of collection to the time of analysis, making real-time evaluation difficult to achieve. Where as, TSS, TDS, and A_{254} can all be monitored in-situ, produce real time values, and are generally less expensive than trace level Hg analysis.

With both THg and fHg prediction models having statistically significant R^2 values (0.85 and 0.97 and p-values <0.0001), the use of such models at Lake Combie Reservoir for the sediment and Hg removal project is conceivable. While there are individual correlations between each of the parameters evaluated in the regression model,

the combination of all factors result in a stronger correlated model. Multivariate regression models developed for predicting fHg and THg concentrations at Lake Combie Reservoir could allow for continuous in-situ monitoring. Continuous monitoring of both inlet and outlet waters would help improve treatment effectiveness and maybe mediate risks involved with degrading water quality that may occur from effluent discharge relating to THg and fHg concentrations. Since the models were developed specifically to reflect Lake Combie water quality trends, these models are appropriate for this location only. Models should also be thoroughly tested with supplemental sampling of Hg and optical characteristic determinations to confirm the long-term use. Before the models can be implemented at other treatment locations, baselines and thresholds of constituents of concerns should be established and evaluated with similar methods and confirmation sampling throughout the treatment process.

The main goal of this study was to inform NID and other interested parties on best management practices for reservoir maintenance and sediment removal in northern Sierra Nevada watersheds impacted by Hg contamination. Utilizing coagulant dose rates established from this study coupled with in-situ water quality proxies for Hg concentrations, the sediment and mercury removal project at Lake Combie Reservoir, CA can remove Hg-contaminated sediments, treat, and return water to the Bear River without violating water quality criteria for THg. However, as a by-product of the use of metal-based coagulants, additional metals were released to the Bear River. Although the released metals were below regulatory criteria, the effect of fulltime coagulant application during the process may create a new contamination issue. Though the

sediment and mercury removal Project returned treated water within water quality criteria, the treated effluent contained levels of both THg and fHg, which are the more bioavailable, reactive, and harmful forms of Hg that were above river background. Although effluent was within regulatory standards for THg (50 ng/L), continuous full-scale operation may reintroduce fHg previously attached to previously trapped sediments to the water column of the Bear River. Newly transferred Hg to within the water column could increase the possibility of the methylation of Hg to occur in downstream environments.

The successful removal of treated Hg-contaminated sediments from a reservoir can increase water storage capacity while remediating a historic and widespread contamination of Hg-bound sediments. As many watersheds within the northern Sierra Nevada mountain range have similarly impacted sediments, this study can act as a model for remediation efforts of other reservoirs.

CHAPTER VII

RECOMMENDATIONS

The sediment and water treatment process could have alternate results as sediment sources change from one site to the next. Additional bench-tests of the dredged material and coagulants should be conducted as the physical location of the sediment retrieval moves and the composition of the dredged material changes. Movement into different zones of the reservoir deposits can be associated with changes in sediment composition (Morris and Fan, 1998; Snyder et al., 2004) and could affect the ability of the coagulants to reduce turbidity and trace metal concentrations. Total and filtered Hg concentrations across grain size fractions should be determined for each sediment source tested to identify possible Hg speciation differences between them. Future bench tests should also be conducted in triplicate for more robust results and increased confidence of dosage amounts. Sediment and Hg removal from Greenhorn Creek and Combie Pond would require additional tests for coagulant type and effectiveness on the reduction of turbidity and trace metal concentrations.

To optimize coagulant sedimentation following treatment and to reduce the possibility of over dosing, sediment masses within slurries need to be as consistent as possible. The introduction and use of metal-based coagulants to the Bear River during the treatment process could alter the background metal concentrations from their respective norms. During the field-scale application, maintaining a constant concentration of sediment in the slurry to be treated was difficult and misleading. The over or under

dosing of the slurry may have affected the coagulants ability to reduce turbidity. The use of a mixing tank to create a homogenized slurry may ensure better coagulant application and sediment treatment. Another possible change to increase efficiency of treatment would be to implement an automated injection mechanism that increases or decreases coagulant dose based on turbidity or sediment concentrations within the slurry. Additionally, studies should be conducted on a full suite of metals for both particulate and filtered concentrations for each coagulant type to understand the possible implications of introducing these metal-based coagulants to the natural water regime within the Bear River watershed.

The effect of changing fHg and pHg concentration ratios on downstream ecosystems needs additional research. Although processed effluent may be within regulatory criteria, changes in the fractionation of fHg and pHg can affect the amounts of the bioavailable and reactive forms of Hg, influencing biota to an unknown extent (Slotton et al. 1997; Alpers et al., 2006). Monitoring for both pre and post conditions should be conducted on water quality, sediments, and biota of multiple trophic levels to develop response terms associated with the sediment and mercury removal process. The sediment and mercury removal process might also benefit from running additional tests with the Clar+Ion 5057 coagulant because of its ability to return fHg concentrations to river background levels while maintaining the THg concentrations below the regulatory standard.

Operating under the mandated water quality criteria for the treatment process at the downstream compliance point is pivotal for operation success. Low flow velocities

during Test 9 discharge may have misrepresented the effluent water quality at the regulatory compliance point. Testing during times of greater flow velocities in the receiving waters to better represent the effect of the effluent on Bear River water quality is needed. The flow velocities in the receiving water should be monitored during discharge to develop an accurate wait time for effluent water quality to be detected at the compliance point.

The main recommendation from this study is to develop the prediction model using the highlighted variables TSS, TDS, and A_{254} as proxies for continuous real-time THg and fHg concentrations. The prediction model will require confirmation sampling of all variables during operations. Determination of the highlighted variable including THg and fHg will refine and adjust the initial findings of these relationships. Use of the prediction model would result in real-time process evaluation for THg and fHg removal prior to release, which saves costs on trace metal analysis, and labor associated with sample collection. Confirmation sampling and model refinement for each source material needs to be conducted in order to develop the relationships between variables as sediments sources change.

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APPENDIX A

QAQC For BAL