

Mercury removal in municipal wastewater: The role of TSS and DOM in meeting Great
Lakes discharge limits

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1. Introduction

Mercury (Hg) is a naturally-occurring, metallic element with a complex, biogeochemical cycle. Hg toxicity varies depending on the form, but methylmercury (MeHg), a readily-available organic form of Hg that both bioaccumulates and biomagnifies up the food chain, presents the most risk to humans and ecosystems (Gabriel & Williamson, 2004). Reducing Hg releases to the environment has been a federal priority since 1972, through the implementation of the Clean Water Act (CWA) and National Pollution Discharge Elimination System (NPDES). These federal regulations are enforced at the state level, and in Minnesota, the Pollution Control Agency (MPCA) determines discharge limits for Hg from point sources. For most of the state, total Hg discharge limits for municipal wastewater range between 5 ng/L to 10 ng/L (MPCA, 2007). However, point sources of Hg in the northern regions of Minnesota that discharge into the Lake Superior watershed must comply with a more stringent 1.3 ng/L total Hg limit set by the Great Lakes Initiative. This federally recognized initiative aims to reduce bioaccumulative chemicals in the Great Lakes ecosystem (USEPA, 1995), but is handled differently in each Great Lakes state.

In water, Hg predominately exists in an ionic form, complexed to organic and inorganic ligands (Sterritt & Lester, 1984). As a “soft” metal, both inorganic and MeHg ions have a higher affinity toward binding to “soft” ligands even if they are present at a lower concentration than “hard” ligands. (Haitzer et al, 2002). In aerobic waters, Hg ions form inorganic complexes with sulfur, hydroxide, and chloride, but also have a strong affinity towards reduced sulfur groups on dissolved organic matter (DOM) (Benoit et al,

1999; Haitzer et al, 2002; Hsu & Sedlak, 2003; Hsu & Sedlak 2005; Poulin et al, 2017). The relative concentrations of both Hg and organic matter influence binding affinities toward other ligands. In the Haitzer et al. (2002) study of natural waters, reduced sulfur groups on DOM were found to dominate Hg binding sites at low Hg-DOM ratios (0.01 ug to 1 ug of Hg/mg of DOM) but carboxylic groups dominated at high Hg-DOM ratios (10 ug to 1000 ug of Hg/mg of DOM).

Stability constants have been used to describe the mechanisms and implications of Hg-DOM interactions, but the calculated values are highly variable between studies and environmental conditions (Stasinakis & Thomaidis, 2010). An effective partition coefficient, K_D , describes the net effect of adsorption and desorption to particles in a two-phase (solid and dissolved), as it represents the in-situ ratio of particulate-bound Hg (Hg-PM) to Hg in the dissolved phase (Hg-DOM) (Gerbig et al, 2011). This effective partition coefficient K_D is usually subject to limitations imposed by the operational definition of the dissolved phase and is not able to definitively describe the mechanisms involved in Hg-DOM or Hg-PM partitioning. However, this net ratio of solid to ‘dissolved’ Hg (Hg_D , commonly $< 0.45 \mu\text{m}$) is a useful to describe and analyze the phases relevant for Hg transport and help identify geochemical factors that influence Hg binding (Gerbig et al, 2011, Lee et al. 2001).

Hg in municipal wastewater treatment plants (WWTPs) binds to both particulate and dissolved organic matter (*Figure 1*). The majority of Hg mass is removed with sludge during solid-liquid separation, due to the well-established understanding of metal uptake by biomass and the high binding affinity of Hg to particulate organic matter (Cheng et al,

1975; Gilmour & Bloom, 1995). In the dissolved phase, municipal wastewater exhibits low Hg-DOM ratios and reduced sulfur groups can be assumed to be the dominate Hg binding sites on DOM (Haitzer et al, 2002; Xia et al, 1999). Large changes to suspended solids concentration, as well as operational conditions designed to maximize solid-liquid interactions, influence Hg partitioning and speciation differently at each plant and at different locations within a plant (Crane et al, 2010). In most cases, very low, but relevant Hg concentrations persist in municipal wastewater effluent (Stasinakis & Thomaidis, 2010).

The Hg mass remaining in municipal wastewater effluent, distributed among the operationally-defined dissolved phase (particles smaller than filter pores, typically 0.45 to 1.5 μm) and breakthrough particulate matter (particles larger than 1.5 micron), is frequently enough to push some facilities in the Great Lakes region over the low 1.3 ng/L discharge limit. For context, rainwater in the region contains ~5 to 10 ng/L Hg (NADP, 2019). To further reduce concentrations and comply with stringent limits, many facilities are now evaluating or implementing additional tertiary technologies aimed at Hg removal, such as membrane filters, tertiary clarifiers, and dual media filters; however, little standardized guidance is available to decision makers to determine which of these expensive technologies is best suited for removing Hg to exceedingly low-levels at a specific treatment plant. The lack of guidance is partly due to a limited understanding of how Hg moves and changes binding phases during transport through a wastewater treatment system. The key determinants of whether Hg remains bound to effluent particles or filter-

passing DOM/colloids in municipal wastewater is especially relevant for design of tertiary treatment aimed at very low-level Hg removal.

There are many studies investigating Hg transport in various natural systems (Benoit et al, 2001; Hsu and Sedlak, 2003; Gabriel & Williamson, 2004; Ravichandran, 2004); and, occasionally, a comparison between natural systems and a wastewater treatment system (Muresan et al, 2011). Most studies of Hg in wastewater involve individual wastewater treatment systems (Balogh & Liang, 1995; Hsu-Kim and Sedlak, 2005; Gbondo-Tugbawa et al, 2010; Pernet-Coudrier et al, 2011; Liu et al, 2018), and there is only limited research comparing Hg transport across a variety of wastewater treatment systems (Gardner et al, 2013; Suess et al, 2020).

With the data generated from this research, we hope to determine how dissolved and particulate Hg concentration, K_D values, and DOM and PM quantity and composition

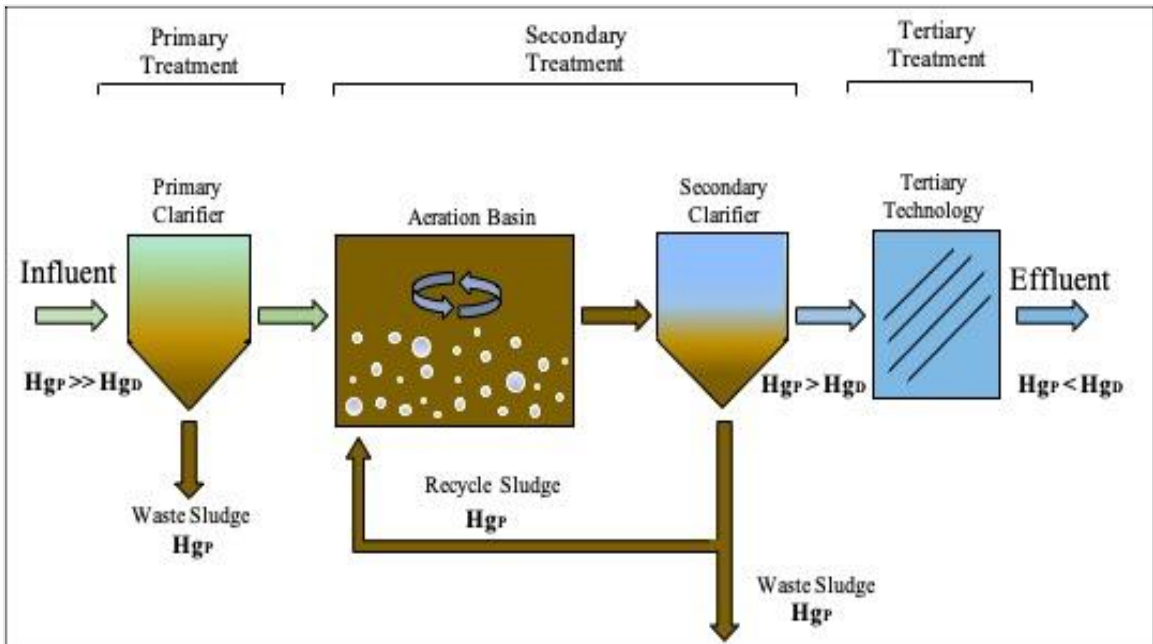


Figure 1. The expected flow of Hg through a traditional activated sludge wastewater treatment system indicating where particulate Hg, H_{gr} , and dissolved Hg, H_{gd} , should be the dominate phase.

are related to the efficacy of tertiary treatment technologies for Hg removal. The goal of this study is to provide insight into the movement of Hg through a wastewater treatment plant by comparing the water chemistry of the influent, post-secondary treatment, and effluent samples with overall Hg removal at 11 municipal wastewater treatment plants. Though the focus is on net partitioning among operationally defined dissolved and particulate phases, we also characterize the elemental composition of DOM and PM - with a focus on sulfur quantities in influent and effluent wastewater at a subset of treatment plants - to identify whether a simple accounting of sulfur in dissolved and particulate phases may help to understand Hg binding.

2. Methods

2.1 Wastewater Treatment Facility Selection

This study characterized Hg in the context of varying water chemistry at 10 different wastewater treatment plants in and around the St. Louis River Watershed in northeastern Minnesota and one facility far outside of this watershed in western Minnesota. The wastewater treatment plants involved in this study (*Table 1*) were selected for their assortment of town source waters, secondary wastewater technology and, where applicable, tertiary wastewater technology. All facilities in the Great Lakes Basin are obligated to meet low-level Hg discharge limits and several facilities have made recent technological investment to reach effluent Hg limits below 1.3 ng/L.

In this study, facilities with activated sludge treatment are referred to as “traditional” wastewater systems. This category includes Aurora, Two Harbors, Babbitt, WLSSD, and WLSSD-Clearas.

Table 1. Municipal WWTPs involved in the study, organized by category, along with each town’s source water and treatment

| WWTP | Source Water | Secondary Treatment | Tertiary Treatment | |
|---------------------------------------|------------------|---------------------|--------------------|--|
| Traditional AS Facilities | | | | |
| Aurora | St. James Pit | AS | Dual media | |
| Babbitt | Wells | AS | None | |
| Two Harbors | Lake Superior | AS | Dual media | |
| Virginia | Missabe Mine Pit | AS | Dual media | |
| WLSSD | Lake Superior | PureOX AS | Dual media | |
| WLSSD-Clearas | Lake Superior | PureOX AS | Algal Unit | |
| Advanced Technology Facilities | | | | |
| CIRSSD | FR Mine Pit | SBR | Membrane | |
| Detroit Lakes | Wells | MBR | End of MBR | |
| Pond Facilities | | | | |
| Beaver Bay | Lake Superior | Pond | Gravel filter | |
| Biwabik | Canton Pit | Pond | Pond | |
| Trickling Filter Facilities | | | | |
| Hoyt Lakes | Colby Lake | Trickling | None | |
| Silver Bay | Lake Superior | Trickling | Clarifier | |

The Aurora and Two Harbors wastewater facilities have a tertiary dual media filter, composed of a large porosity anthracite layer on top and a sand layer on the bottom, following activated sludge treatment. WLSSD also has a dual media filter but utilizes a PureOx activated sludge system. In addition, the wastewater is more industrial than municipal due to large quantities of papermill effluent entering into the wastewater facility. The WLSSD-Clearas facility is a pilot system in which some of the wastewater from the WLSSD PureOx activated sludge system is diverted to a biological nutrient removal (BNR) unit, which uses algae as the tertiary treatment.

The other facilities were placed into three categories for data analysis. The advanced technologies category includes the MBR system at Detroit Lakes, which utilizes a 0.01-micron filter, and the tertiary 10-micron membrane at CIRSSD. The two pond systems in this study, including Biwabik and Beaver Bay, are intermittent discharge ponds that are commonly emptied in two batch discharges during the warm months from May to October. Biwabik has a secondary pond followed by a tertiary pond while Beaver Bay follows the secondary pond with a single pass tertiary gravel filter. The last category is the trickling filters at Silver Bay and Hoyt Lakes. Silver Bay has tertiary sludge blanket clarifiers following the secondary treatment by trickling filters with circular final clarifiers. Hoyt Lakes does not have tertiary technology and the highly colored, DOM-rich, town source water undergoes extensive drinking water treatment before circulating through the town and into the wastewater facility.

A subset of treatment plants was selected for PM and DOM analysis. These plants were chosen for further study due to either their unique wastewater composition or tertiary technology. The CIRSSD WWTP was chosen for its 10-micron rotating tertiary membrane filter, Hoyt Lakes WWTP for its highly colored source water, Two Harbors WWTP for its combination of municipal water and brewery water, WLSSD WWTP for its combination of municipal and paper mill water, and WLSSD-Clearas WWTP for the algal tertiary treatment technology.

2.2 Sample Collection

Synoptic sampling of all of the wastewater treatment facilities involved collecting grab samples of wastewater at the influent, post-secondary treatment, and effluent, prior to chlorination and UV (if present). Samples for Hg analysis were obtained directly out of pipes or by using a dipper, twice rinsed with each sample before collection, and placed in new PETG bottles that had been also double-rinsed with sample. All samples collected for Hg analysis followed the clean hands protocol as described in EPA Method 1669 (USEPA, 1996). Blanks and duplicates were handled identically to the wastewater samples. A field blank was collected once per field sampling day using ultra-filtered water from the laboratory with a Hg concentration below detection limits with a mean of 0.15 ng/L and standard deviation of 0.08 ng/L. A duplicate was collected once per field sampling day.

Sampling for DOM and PM isolation involved collecting grab samples from the influent and effluent at the subset of facilities into new, 5-gallon buckets rinsed three times with the sample. A 3-gallon bucket with a rope cord was used when samples could not be directly collected into the containers.

2.3 Sample Preservation and Storage

Samples for DOC, SUVA, Hg_D, cation, and anion analysis were filtered through 0.45-micron flip-mates (Environmental Express, EW-35202-09) via vacuum pump. DOC samples were preserved with 0.1% HCl (v/v; HCl 37%, Sigma) and stored in acid washed or combusted, amber glass vials. Cation samples were preserved with 0.5% HNO₃ (w/w; Nitric Acid 70%, Fisher) and stored in 15 mL plastic centrifuge tubes. Unfiltered (Hg_T), and filtered, (Hg_D), Hg samples were preserved with 0.5% Trace Metal-HCl (v/v; TM-HCl

34-37%, Fisher) and stored, double bagged, in new PETG bottles. Samples for total suspended solids (TSS), specific UV absorbance (SUVA), and anion analysis were stored, unpreserved, in PETG bottles. Samples were filtered and preserved within 24 hours of collection and kept in the dark at 4°C.

Bulk samples for DOM isolation were filtered through a 0.45-micron capsule filter (Whatman Polycap GW, 6714-6004) using a peristaltic pump and acidified to pH 2 with concentrated HCl (HCl 37%, Sigma). Effluent samples were filtered and preserved within 48 hours from collection and influent samples within 72 hours from collection. Samples were stored in the dark at 4°C until analysis. Solid-phase DOM and PM isolates were not chemically preserved. The samples were stored in combusted glass vials and kept in the dark at -17°C.

2.4 Sample analysis for ions, TSS/TSS, DOC, Hg

SUVA analysis followed EPA Method 415.3 (USEPA, 2009) using a 1 cm quartz cell. Wavelength measurements were made on unpreserved, filtered sample using a Hach DR 5000 Spectrophotometer within 24 hours of sample collection. TSS was measured following Standard Methods 2540D (Standard Methods). Samples were sent through a combusted, 1.5-micron glass-fiber filter (Whatman, 934-AH) to collect particulates. The filter was then dried for overnight at 105°C before weighing. Subsequently, volatile suspended solids (VSS) was obtained by combusting the filters at 550°C for 30 minutes. Volume filtered varied between samples and ranged from 1 mL for some influent samples to 2 L for effluent samples. Anions were measured by ion chromatography (IC) using a

Dionex Integrion HPIC according to EPA Method 300.0 (USEPA, 1991). Cations were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using an iCAP 7600. (Fassel & Kniseley, 1974; Dahlquist & Knoll, 1978). Anions and cations were used to calculate the ionic strength of each sample using the Debye-Huckel equation. DOC was analyzed using the high-temperature combustion method described in Standard Methods 5310B (Standard Methods) using a total organic carbon analyzer instrument (TOC-Shimadzu). Hg analysis was run in accordance with EPA Method 1631 (USEPA, 2002).

2.5 DOM & PM Isolation and Elemental Characterization

Bulk DOM was isolated from the wastewater following the method described in Dittmar et al (2008). Bond Elut PPL cartridges (Agilent, 12255002), made of a styrene-divinylbenzene polymer that retain most polar substances, were used to isolate the DOM in 0.45-micron filtered, acidified samples. Two cartridge volumes of methanol (v/v; Methanol 99.9%, ACS Grade, Fisher) were sent through the cartridge followed by five cartridge volumes of MilliQ[®] water prior to the sample. 0.45-micron filtered wastewater samples were pumped through the cartridge using a peristaltic pump with Teflon tubing at a rate below 40 mL/min and not exceeding 2 mmol per g of sorbent. Typical volumes sent through a single cartridge ranged from 500 mL to 4 L, depending on the sample. A composite of the permeate was collected for DOC analysis to determine recovery. Two cartridge volumes of 0.01M HCl (v/v; HCl 37%, Sigma) were pumped through the cartridge to remove salts and the permeate was discarded. After 5 minutes of air drying the

cartridge, two cartridge volumes of methanol were gravity filtered through the cartridge to extract the DOM off of the sorbent into combusted glass vials. The methanol-DOM slurry was stored at -17⁰C before blowing down the methanol with nitrogen gas. The sticky DOM isolate was then freeze-dried to remove any remaining methanol. Samples were stored at -17⁰C until analysis. Cartridges were not reused and MilliQ[®] water blanks were run to ensure there was no contamination from the cartridges. PM was obtained by filtering wastewater samples through a 1.2-micron, polycarbonate membrane filter (Isopore[™], RTTP04700). The particulates captured on the filter were scraped into a combusted glass vial with a metal spatula and freeze-dried. Both PM and DOM samples were stored at -17⁰C until analysis.

DOM and PM isolated samples were measured for elemental composition (CNS) using a Vario EL Cube. The samples were weighed into tin capsules and dosed with 38mL/min O₂ for 90 s. The CO₂ trap is heated to 240⁰C for 90 s and the SO₂ trap is heated to 260⁰C for 150 s.

2.6 Precision and Accuracy

Precision and accuracy are especially important for this research due to many of the results being close to low-level detection limits. Method precision for Hg was calculated using relative differences between duplicate measurements and detection limit was 0.2 ng/L. Method precision for DOC and elemental analysis was calculated using the standard deviation of analyzed standards. TSS precision was calculated for each volume of water filtered using error propagation (*Equation 1*):

$$1. (\Delta C)^2 = \left(\frac{\partial C}{\partial m_1} * \partial m_1^2 \right) + \left(\frac{\partial C}{\partial m_2} * \partial m_2^2 \right) + \left(\frac{\partial C}{\partial V} * \partial V^2 \right)$$

where $\frac{\partial C}{\partial m} = \frac{-m_2}{V} \frac{\partial C}{\partial m_2} = \frac{m_1}{V'}$ and $\frac{\partial C}{\partial V} = -\frac{m_1 - m_2}{V^2}$, in which V is volume of water filtered, ∂m_1 is equal to the precision of the first weight (0.0001) and ∂m_2 is equal to the precision of the second weight (0.0001) and ∂V is the precision of the volume. A table of the precision for each volume filtered can be found in the appendix (*Table A1*). The detection limit of the scale used for TSS measurements is 0.0005 g.

2.7 Data and Statistical Analysis

Hg_T analysis measured the concentration of all Hg species in an unfiltered water sample. Analysis of Hg_D included all Hg species in the 0.45-micron filtered water sample. Particulate Hg (Hg_P), the sum of all Hg species on particles greater than 0.45-micron per liter of water, was calculated as the difference between the Hg_T concentration and the Hg_D concentration. The concentration of Hg per milligram of TSS (C_P) was calculated by normalizing the Hg_P by TSS. The effective partition coefficient, log K_D, was found by taking the log ratio of C_P to Hg_D.

Percent removal for Hg_T and TSS from influent to effluent was calculated as the difference between the influent and effluent concentrations over the influent concentration and multiplied by 100. The contribution of tertiary technology on percent removal for Hg_T and TSS was calculated as the difference between the post-secondary and effluent concentrations over the influent concentration and multiplied by 100.

Sulfur and carbon content were incorporated into the DOM, Hg, log K_D, and TSS, noted as DOM_S (*Equation 2*), Hg_{D-S} (*Equation 3*), C_{P-S} (*Equation 4*), log K_{D-S} (*Equation 5*),

TSSc (Equation 6), using the following calculations: quantified with the fraction of each element in phase

$$2. DOM_S \left[\frac{mg\ S}{L} \right] = DOC \left[\frac{mg}{L} \right] * \frac{1}{f_{C,DOM}} \left[\frac{mg\ DOM}{mg\ C} \right] * f_{S,DOM} \left[\frac{mg\ S}{mg\ DOM} \right]$$

$$3. Hg_{D-S} \left[\frac{ng\ Hg_D}{mg\ S} \right] = \frac{Hg_D \left[\frac{ng}{L} \right]}{DOM_S \left[\frac{mg\ S}{L} \right]}$$

$$4. C_{P-S} \left[\frac{ng\ Hg_P}{mg\ S} \right] = \frac{C_P \left[\frac{ng\ Hg_P}{mg\ TSS} \right]}{f_{S,PM} \left[\frac{mg\ PM}{mg\ S} \right]}$$

$$5. \log K_{D-S} \left[\frac{ng}{ng} \right] = \log \left(\frac{C_{P-S} \left[\frac{ng\ Hg_P}{mg_S} \right]}{Hg_{D-S} \left[\frac{ng\ Hg_D}{mg_S} \right]} * 10^6 \right)$$

$$6. TSS_C \left[\frac{mg}{L} \right] = TSS * \frac{f_{C,PM}}{100}$$

The significance of differences between the mean concentrations for influent and effluent concentrations were evaluated with ANOVA. The data in this study was not normally distributed. Normal statistical analysis using ANOVA and regression were still run on the limited data set, though future analysis will evaluate lognormal comparisons of the data. Single factor ANOVA analysis with a 0.05 significance level was used to determine differences between Hg and other concentrations at different locations in the plant. Regression analysis with 95% confidence level was used to determine if a significant relationship existed between an independent variable and a dependent variable. Duplicate samples were not included in statistical analysis. Detroit Lakes was not included in statistical analyses involving post-secondary data due to the sample point being a mixed

liquor sample instead of a typical post-secondary sample in which most suspended solids have been removed.

3. Results

3.1 Hg concentrations and removal in dissolved and particulate phases

Hg_T concentration (*Table 2*) in the influent samples ranged from 3.1 ng/L to 126.8 ng/L. Post-secondary Hg_T concentrations were between 0.29 ng/L to 13.2 ng/L and effluent Hg_T concentrations ranged from < 0.2 ng/L to 4.8 ng/L. Single factor ANOVA indicates that, among all the wastewater plants included in the study, the average of post-secondary Hg_T concentrations is significantly lower than the average of effluent Hg_T concentrations ($p = 0.05$). On average, the facilities removed 90% of the Hg_T from influent to effluent.

Detroit Lakes had the highest influent Hg_T concentration, at 126.8 ng/L, and the MBR system was able to remove 98.5% of the Hg_T. However, 1.9 ng Hg_T/L remained in the effluent concentration. CIRSSD had the lowest influent Hg_T concentration at 3.1 ng/L, and more than 70% of the total Hg_T removal occurred in the tertiary membrane filter. During both sampling events at CIRSSD, the facility produced an effluent Hg_T below 1.3 ng/L.

At the “traditional” activated sludge facilities with dual media filters, including Aurora, Two Harbors, Virginia, and WLSSD, the bulk of the Hg_T removal occurred during secondary treatment with, on average, less than 6% of the influent Hg_T concentration removed by the tertiary filters. Two Harbors and Virginia produced effluent Hg_T

Table 2. Measured Hg_T (ng/L) and Hg_D (ng/L) concentrations at the influent, post-secondary, and effluent sample locations for each WWTP. Total % removal, the fraction of influent removed by the effluent, and the tertiary removal, the fraction of influent removed from tertiary treatment, is listed for Hg_T.

| WWTP | Hg _T (ng/L) | | % Removed (total) | % Removed (tertiary) | Hg _D (ng/L) | | | Hg _P (ng/L) | | | |
|---------------------------------------|------------------------|-------------------|-------------------|----------------------|------------------------|----------|----------|------------------------|----------|----------|-----|
| | Influent | Post-Sec Effluent | | | Influent | Post-Sec | Effluent | Influent | Post-Sec | Effluent | |
| Traditional AS Facilities | | | | | | | | | | | |
| Aurora (winter) | 38.2 | 4.0 | 4.8 | 87.5 | -1.9 | 1.2 | 0.4 | 0.4 | 37.0 | 3.6 | 4.4 |
| Aurora (spring) | 13.6 | 2.6 | 2.2 | 83.9 | 3.3 | 3.8 | 0.6 | 0.7 | 9.8 | 2.1 | 1.4 |
| Two Harbors (fall) | 45.0 | 2.7 | 1.2 | 97.4 | 3.3 | 2.0 | 0.6 | 0.6 | 43.1 | 2.1 | 0.6 |
| Two Harbors (fall) | 23.0 | 0.8 | <0.2 | 99.1 | 2.6 | 5.5 | — | 0.2 | 17.6 | — | — |
| Two Harbors (winter) | 59.7 | 1.9 | 0.6 | 99.0 | 2.2 | 6.9 | 0.5 | 0.2 | 52.7 | 1.5 | 0.4 |
| Virginia (fall) | 9.2 | 1.4 | 0.9 | 90.2 | 5.5 | 0.9 | 0.3 | 0.9 | 8.4 | 1.1 | 0.0 |
| Virginia (spring) | 21.2 | 1.3 | 1.0 | 95.5 | 1.7 | 1.4 | 0.6 | 0.6 | 19.8 | 0.7 | 0.4 |
| WLSSD | 61.4 | 1.4 | 2.2 | 96.3 | -1.4 | 3.0 | 1.4 | 1.8 | 58.4 | 0.0 | 0.5 |
| WLSSD-Clearas | — | 11.9 | 1.0 | — | — | — | 0.8 | 0.9 | — | 11.1 | 0.1 |
| Babbitt** | 19.6 | — | 2.6 | 86.7 | — | 1.0 | — | 0.7 | 18.6 | — | 2.0 |
| Advanced Technology Facilities | | | | | | | | | | | |
| CIRSSD (fall) | 3.1 | 2.8 | 0.6 | 81.7 | 70.5 | 1.1 | 0.3 | 0.3 | 2.0 | 2.5 | 0.3 |
| CIRSSD (fall) | 10.6 | — ^a | 0.6 | 94.4 | — | 2.1 | — | 0.6 | 8.4 | — | 0.0 |
| Detroit Lakes | 126.8 | 11.2 | 1.9 | 98.5 | 7.3 | 1.7 | 2.5 | 0.5 | 125.1 | 8.7 | 1.4 |
| Pond Facilities | | | | | | | | | | | |
| Beaver Bay | 14.2 | 0.5 | 2.9 | 79.3 | -16.9 | 3.7 | 0.5 | 2.6 | 10.5 | 0.0 | 0.4 |
| Biwabik* | 83.6 | 0.3 | — | 99.7 | — | 4.8 | 0.3 | — | 78.8 | 0.0 | — |
| Trickling Filter Facilities | | | | | | | | | | | |
| Hoyt Lakes | 16.4 | 6.7 | 4.7 | 71.4 | — | 1.3 | 0.6 | 0.9 | 15.1 | 6.1 | 3.8 |
| Silver Bay | 5.0 | 13.2 | 0.9 | 81.2 | *** | 1.6 | 0.5 | 0.5 | 3.4 | 12.7 | 0.5 |

Hg method precision ± 7%

— No data

* Biwabik was only sampled at the influent and post-secondary treatment locations.

** Babbitt was only sampled at the post-secondary and effluent treatment locations.

*** Silver Bay % removed (tertiary) was not calculated due to the elevated post-secondary concentration.

^a Detroit Lakes “post-secondary” is not a true post-secondary sample due to the nature of MBR systems.

concentrations below the 1.3 ng/L limit during replicate sample events. Aurora had the least Hg_T removal of the dual media/activated sludge facilities and produced an effluent exceeding 1.3 ng Hg_T/L during both sample events. The dual media filter did not contribute to Hg_T removal during the fall sampling event but contributed 3.3% removal during the

spring sampling event. WLSSD experienced a higher Hg_T concentration in the effluent than the post-secondary sample and contained more than 1.3 ng Hg_T/L. An influent Hg sample was not collected for the WLSSD-Clearas facility but the pre and post algal unit Hg data revealed a 92% Hg_T decrease from the algal treatment alone. The activated sludge treatment at Babbitt, which was not followed by any tertiary treatment, was able to remove 87% of the Hg_T, leaving 2.93 ng Hg_T/L in the effluent.

At the secondary pond systems at Beaver Bay and Biwabik, excellent Hg reductions occurred and effluent water contained less than 0.6 ng Hg_T /L in the samples following the ponds. An effluent sample was not collected at Biwabik but the post-secondary sample collected is expected to be equivalent to an effluent sample at this plant. The effluent sample at Beaver Bay contained 2.9 ng Hg_T/L, significantly more Hg_T than in the post-secondary sample. This indicates that the tertiary gravel filter contributed Hg into the water, rather than removing it. However, the sample was collected after discharge was stopped and the gravel filter had likely dried out, possibly causing the biofilm to die and leach out Hg into the water when the filter was temporarily turned on for our sample collection. Gravel filters are typically meant to have a continuous flow, year-round (USEPA, 2000) and so the results from this facility are not in line with theoretical gravel filter models.

The two trickling filter facilities, Hoyt Lakes, with no tertiary treatment, and Silver Bay, with a tertiary clarifier, were on the low end of Hg_T removal. Hoyt Lakes had the lowest total Hg_T removal at 71.4% and contained an effluent concentration of 4.7 ng Hg_T/L. Silver Bay removed 81% of the Hg_T from influent to effluent, but had low Hg_T in the influent. Oddly, the post-secondary sample contained much higher Hg_T compared to the

influent, such that the tertiary clarifier removed over 93% of the Hg_T present after secondary treatment (effluent $Hg_T = 1$ ng/L).

Hg_D concentrations (*Table 2*) ranged between 0.9 ng/L and 6.9 ng/L in the influent samples and between 0.2 ng/L and 2.6 ng/L in the effluent samples. Among all samples for this study, post-secondary and effluent Hg_D concentrations were not significantly different from each other (ANOVA, $p = 0.6$). Net Hg_D removal from influent to effluent was highly variable among facilities. On average, effluent Hg_D was 58% lower than influent Hg_D . WLSSD, Hoyt Lakes, and Beaver Bay contained the highest effluent Hg_D concentrations, contributing greater than half of the Hg_T concentrations. No clear trend was present between Hg_D removal and type of secondary or tertiary technology.

Influent Hg_P concentrations (*Table 2*) ranged between 2 ng/L to 125 ng/L and were reduced by 75% to 100% through the treatment process, resulting in effluent Hg_P concentrations ranging from 0 ng/L to 4.4 ng/L. Post-secondary Hg_P concentrations were significantly lower than effluent Hg_P concentrations (ANOVA, $p = 0.03$). Aurora and Hoyt Lakes had the highest effluent Hg_P concentrations at 4.4 ng/L and 3.8 ng/L, respectively, which contributed to greater than half of their Hg_T concentrations. Despite removing 98.9% of the Hg_P , the MBR at Detroit Lakes produced an effluent with 1.4 ng/L Hg_P , contributing to greater than half of the Hg_T concentration. However, this Hg_P value is questionable considering the effluent water had less than 0.1 ng/L TSS; error likely exists in the Hg_T , TSS, and/or Hg_P to cause this calculated result.

As an entire data set, effluent Hg_P concentrations were not significantly different from effluent Hg_D concentrations (ANOVA, $p = 0.17$). In the influent, Hg_P was typically 2 to 20 times higher than Hg_D.

3.2 TSS and DOC binding phases for Hg

Quantifying the solid and dissolved-phase carbon concentrations through wastewater treatment is important for understanding the movement of Hg. In this study, solids, as TSS, decreased in each WWTP from influent to effluent (*Table 3, Figure 2*). Influent TSS concentrations ranged from 16.2 mg/L to 600 mg/L and were reduced to between 0.4 mg/L to 52 mg/L post-secondary treatment. Effluent TSS concentrations ranged between 0 mg/L to 19 mg/L. On average, facilities removed 95% of the solids from influent to effluent. The Hoyt Lakes facility was the outlier in the data set, removing only 62% of solids throughout the plant.

The tertiary contribution to overall solids removal varied between the plants but ranged from 0.1% to 21.4% of the influent concentration. The facilities with dual media filters, including Aurora, Virginia, Two Harbors, and WLSSD experienced 1.4% to 21.4% of the total TSS removal from tertiary treatment. While the dual media filter at Two Harbors produced relatively consistent removal efficiencies, the Aurora and Virginia filters had significantly different removal efficiencies between replicate sampling events; the winter sampling event at Aurora and fall sampling event at Virginia had 1.4% and 5.2% TSS removal, respectively, contributed by the filters, whereas the spring sampling events had 21.1% and 21.4% TSS removal, respectively, from the filters. The WLSSD-Clearas

algal unit removed 4.8% of the total TSS removal while the dual media filter at WLSSD on the same day removed 3.8% TSS. A replicate sampling event at WLSSD had 2.8% TSS

Table 3. Measured TSS (mg/L) and DOC (mg/L) concentrations at the influent, post-secondary (PS), and effluent sample locations for each WWTP, as well as the calculated removal efficiencies from influent to effluent and the percent removal contribution by tertiary technologies (where applicable).

| WWTP | TSS (mg/L) | | | | | DOC (mg/L) | | | | |
|---------------------------------------|------------------|-------------------|------------------|-----------|-----------------------|------------|--------------------|----------|-----------|-----------------------|
| | Influent | PS | Effluent | % Removed | % Removed by Tertiary | Influent | PS | Effluent | % Removed | % Removed by Tertiary |
| Traditional AS Facilities | | | | | | | | | | |
| Aurora (winter) | 144.0 | 2.0 | 0.0 | 100.0% | 1.4% | 18.16 | 5.08 | 6.35 | 65.0% | -7.0% |
| Aurora (spring) | 57.0 | 17.0 | 5.0 | 91.2% | 21.1% | 39.03 | 10.40 | 6.90 | 82.3% | 9.0% |
| Two Harbors (fall) | 99.0 | 6.8 | 2.5 | 97.5% | 4.3% | 32.53 | 7.82 | 6.97 | 78.6% | 2.6% |
| Two Harbors (summer) | ----- | ----- | ----- | ----- | ----- | 214.49 | ----- | 9.60 | 95.5% | ----- |
| Two Harbors (fall) | ----- | ----- | ----- | ----- | ----- | 15.14 | 6.70 | 6.25 | 58.7% | 3.0% |
| Two Harbors (winter) | 357.0 | 9.0 | 1.0 | 99.7% | 2.2% | 19.74 | 7.64 | 7.86 | 60.2% | -1.1% |
| Virginia (fall) | 93.0 | 5.2 | 0.4 | 99.6% | 5.2% | 11.93 | 8.21 | 7.89 | 33.9% | 2.7% |
| Virginia (spring) | 201.0 | 46.0 | 3.0 | 98.5% | 21.4% | 22.19 | 7.71 | 7.11 | 68.0% | 2.7% |
| WLSSD (winter) | 600.0 | 26.0 | 11.0 | 98.2% | 2.5% | 196.44 | 67.92 | 61.02 | 68.9% | 3.5% |
| WLSSD (summer) | ----- | ----- | ----- | ----- | ----- | 154.68 | ----- | 48.40 | 68.7% | ----- |
| WLSSD (fall) | 524 ⁺ | 26 ⁺ | 6 ⁺ | 98.9% | 3.8% | 135.68 | ----- | 45.90 | 66.2% | ----- |
| WLSSD-Clearas | 524 ⁺ | 26 ⁺ | < 1 ⁺ | 99.8% | 4.8% | 135.68 | 47.26 | 40.25 | 70.3% | 5.2% |
| Babbitt** | 68.0 | ----- | 2.0 | 97.1% | n/a | 11.52 | ----- | 11.08 | 3.8% | n/a |
| Advanced Technology Facilities | | | | | | | | | | |
| CIRSSD (fall) | 16.2 | 2.7 | 0.3 | 98.1% | 14.8% | 16.20 | 7.52 | 7.22 | 55.4% | 1.9% |
| CIRSSD (summer) | ----- | ----- | ----- | ----- | ----- | 12.18 | ----- | 3.50 | 71.3% | ----- |
| CIRSSD (fall) | 19.0 | ----- | ----- | ----- | ----- | 75.36 | ----- | 48.36 | 35.8% | ----- |
| Detroit Lakes | 158.0 | 4500 ^a | 0.0 | 100.0% | n/a | 55.10 | 19.19 ^a | 8.71 | 84.2% | n/a |
| Pond Facilities | | | | | | | | | | |
| Beaver Bay | 214.0 | 0.6 | 0.4 | 99.8% | 0.1% | 62.66 | 11.66 | 10.34 | 83.5% | 2.1% |
| Biwabik* | 86.0 | 0.4 | ----- | 99.5%** | n/a | 27.97 | 8.64 | ----- | 69.1% | n/a |
| Trickling Filter Facilities | | | | | | | | | | |
| Hoyt Lakes | 50.0 | 17.0 | 19.0 | 62.0% | n/a | 16.43 | 14.63 | 16.97 | -3.3% | n/a |
| Silver Bay | 26.0 | 52.0 | 2.5 | 90.4% | *** | 12.94 | 7.09 | 5.96 | 53.9% | 8.7% |

TSS precision varies by volume

DOC method precision ± 0.07

----- No data

* Babbitt was only sampled at the influent and post-secondary treatment locations.

** Biwabik was only sampled at the post-secondary and effluent treatment locations.

*** % removed by tertiary was greater than 100% due to the elevated PS TSS concentration

^a Detroit Lakes “post-secondary” is not a true post-secondary sample due to the nature of MBR systems.

+ TSS values obtained by the WWTP

- Calculated assuming TSS effluent value of 1 mg/L

** Based on removal after post-secondary concentration.

removal from the dual media filter.

The 10- μm membrane filter at CIRSSD contributed to 14.8% of the total TSS removal. The removal contribution from the tertiary, 0.01- μm filter at Detroit Lakes was not comparable to others due to the post-secondary sample not being a true post-secondary sample. The solids removal contribution from Silver Bay's tertiary clarify was also not comparable due to an assumedly uncharacteristic increase the TSS concentration coming out of the trickling filter (secondary technology). The spike skewed the percent removal calculation and resulted in an uncharacteristically high removal contribution from the tertiary filter. The gravel filter at Beaver Bay apparently only contributed 0.1% of solids removal, however, this filter is not continuously run and is only used during the discharge. Sampling at this facility had occurred after the filter had been off for a few weeks and was only turned back on for a few minutes for our sample collection. Thus, results obtained after the gravel filter may not be representative of the technology.

While wastewater technologies are not designed to target DOC removal, DOC generally decreased from influent to effluent (*Figure 2, Figure 4, Table 3*) but appeared to reach a removal limit around 6 mg/L to 10 mg/L DOC. Influent DOC concentrations ranged between 11.5 mg/L to 214.5 mg/L and were reduced to between 5.1 mg/L to 67.9 mg/L following secondary treatment. Effluent DOC concentrations ranged from 3.5 to 11 mg/L (excluding WLSSD which had 61 mg/L DOC in effluent). Among the entire dataset, post-secondary and effluent DOC concentrations were not statistically different ($p = 0.69$). The DOC concentrations remained not statistically different even when the outliers, WLSSD and WLSSD-Clearas, data points were removed ($p = 0.67$). On average, 60.5% of DOC

was removed from influent to effluent, however, keeping in mind the observed inability to remove below 6 to 10 mg/L, many of the facilities with lower percent removal hit that limit prior to the tertiary treatment.

The dual media filter at Two Harbor caused the greatest reduction in DOC, with 95.5% removed from influent to effluent during the summer sampling event; however, this facility removed only 59% - 79% during the other three replicate sampling events. The MBR system at Detroit Lakes had the next greatest reduction in DOC, with 84.2% removed from influent to effluent, followed by the activated sludge/dual media technology at Virginia and pond/gravel filter at Beaver Bay which had 82.3% and 83.5% DOC decreases from influent to effluent, respectively. The lowest DOC removals occurred at the two facilities without tertiary treatment; Babbitt's activated sludge system removed only 3.8%

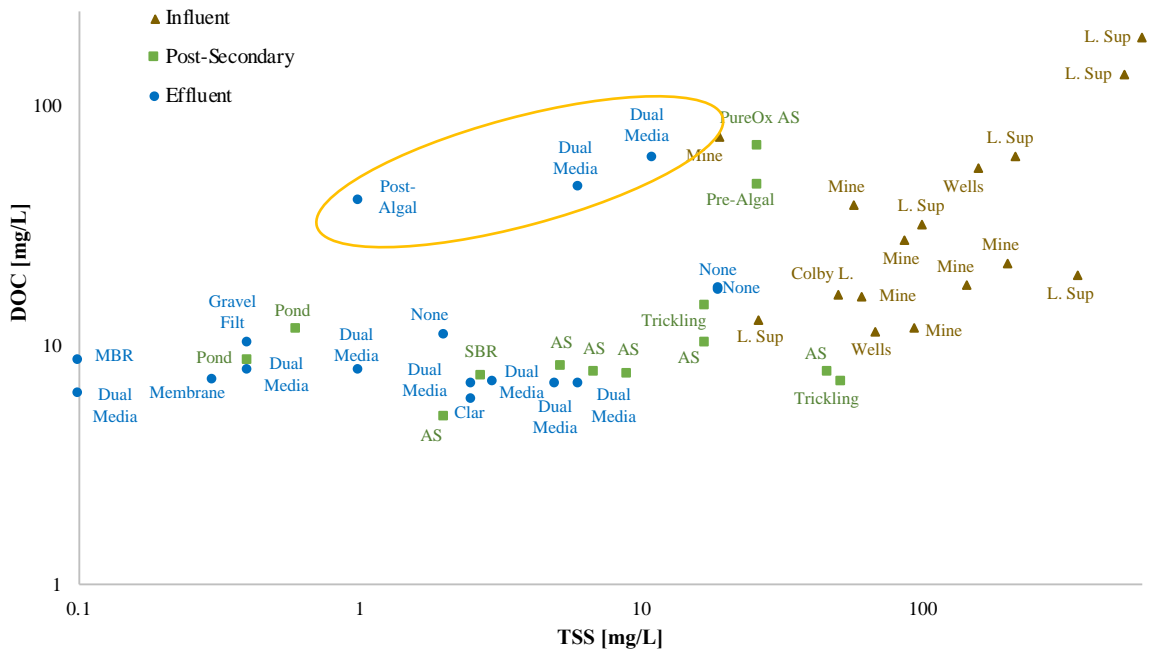


Figure 2. DOC (mg/L) vs. TSS (mg/L) for influent (brown triangles), post-secondary (green squares), and effluent (blue circles) wastewater samples. The overall trend moves from top right to bottom left. TSS values of zero were adjusted to 0.1 to be visible on the plot. WLSSD outlier data points are circled.

of the influent DOC and Hoyt Lakes trickling filter did not remove any DOC. WLSSD had the greatest concentration of DOC in the influent and effluent, and the activated sludge/dual media filter was able to remove 68% of the DOC. Tertiary technologies contributed to an average 2.8% DOC removal with the greatest contribution at 9.0 %.

There is a strong, positive correlation between DOC and TSS (*Figure 2*) among the influent samples ($p = 2.72E-5$, Multiple R = 0.84, $R^2 = 0.70$) but the relationship weakens among the post-secondary and effluent samples. Excluding WLSSD, in which the DOC data is skewed high, 10 mg/L TSS appears to be the concentration below which the correlation between DOC and TSS ceases to be meaningful.

3.3 Relationships between Hg removal, TSS removal, and DOC removal

A positive regression correlation was found between TSS and Hg_T in the overall data set, indicating that as TSS decreases, Hg_T also decreases (Multiple R = 0.61, $p = 1.08E-5$) (*Figure 3*). However, the relationship between TSS and Hg_T appears to vary considerably among the plants and the predictability of the regression model explains less than half of the variability (R^2 value of 0.37). The regression between Hg_T and TSS showed a weak, positive correlation among the influent wastewater ($R^2 = 0.14$, multiple R = 0.38, $p = 0.16$) and a stronger, positive correlation at the effluent wastewater ($R^2 = 0.4$, multiple R = 0.63, $p = 0.009$), indicating the reliability of predicting Hg_T concentration from TSS concentration is greater for effluent samples, relative to influent samples. This trend continued when post-secondary samples were incorporated into the regression; a regression that included influent and post-secondary data yielded an $R^2 = 0.31$, multiple R = 0.55, p

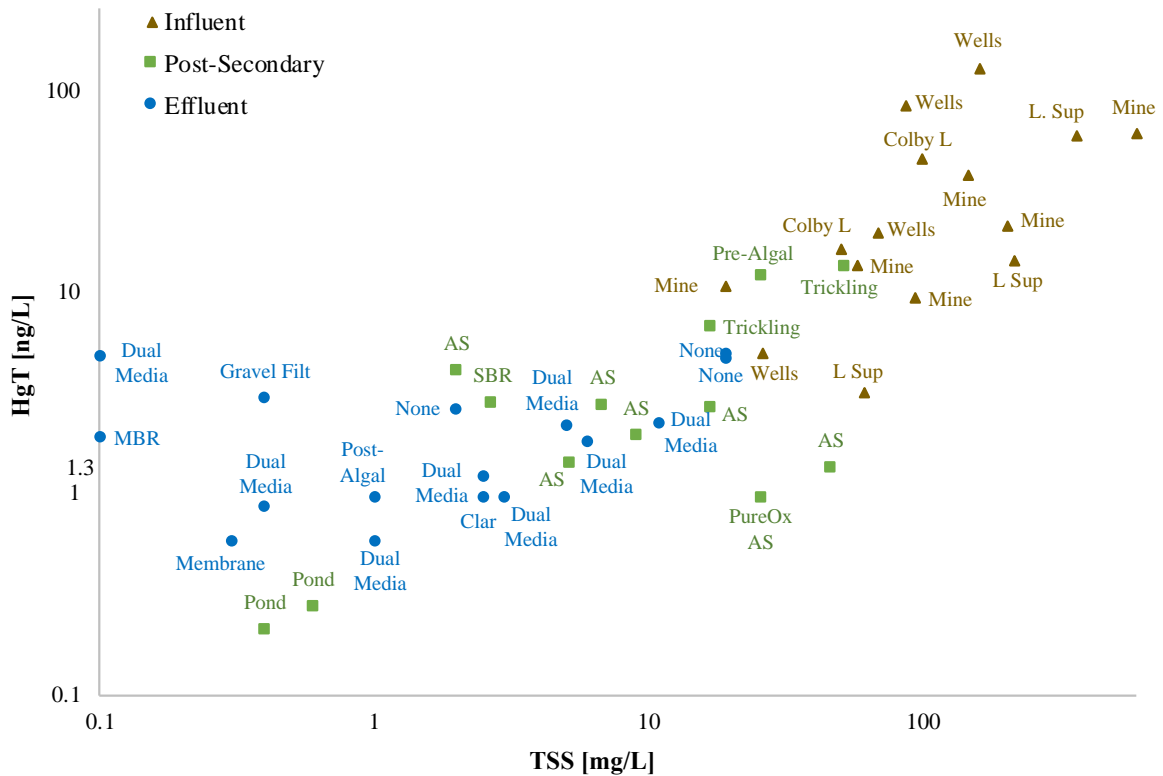


Figure 3. TSS (mg/L) vs. Hg_T (ng/L) for influent (brown triangles), post-secondary (green squares), and effluent (blue circles) wastewater samples. TSS values of zero were adjusted to 0.1 to be visible on the plot.

= 0.002 and a regression using both post-secondary and effluent data yielded $R^2 = 0.38$, multiple R = 0.61, $p = 0.0003$.

When separated by technology type (*Figure 4*), the Hg_T -TSS regression curves appear to vary among plants, even within similar technologies. Due to limited data points, only the “traditional” AS sludge systems (*Figure 4a*) had enough data to for regression analysis; a strong, positive correlation was observed between TSS and Hg_T ($R^2 = 0.76$, multiple R = 0.87, $p = 1.14E-8$). Graphs of the other technologies (*Figure 4b-4d*) have considerable variation in the relationship between TSS and Hg_T , and limited data prevented a rigorous statistical analysis of the Hg_T -TSS relationship.

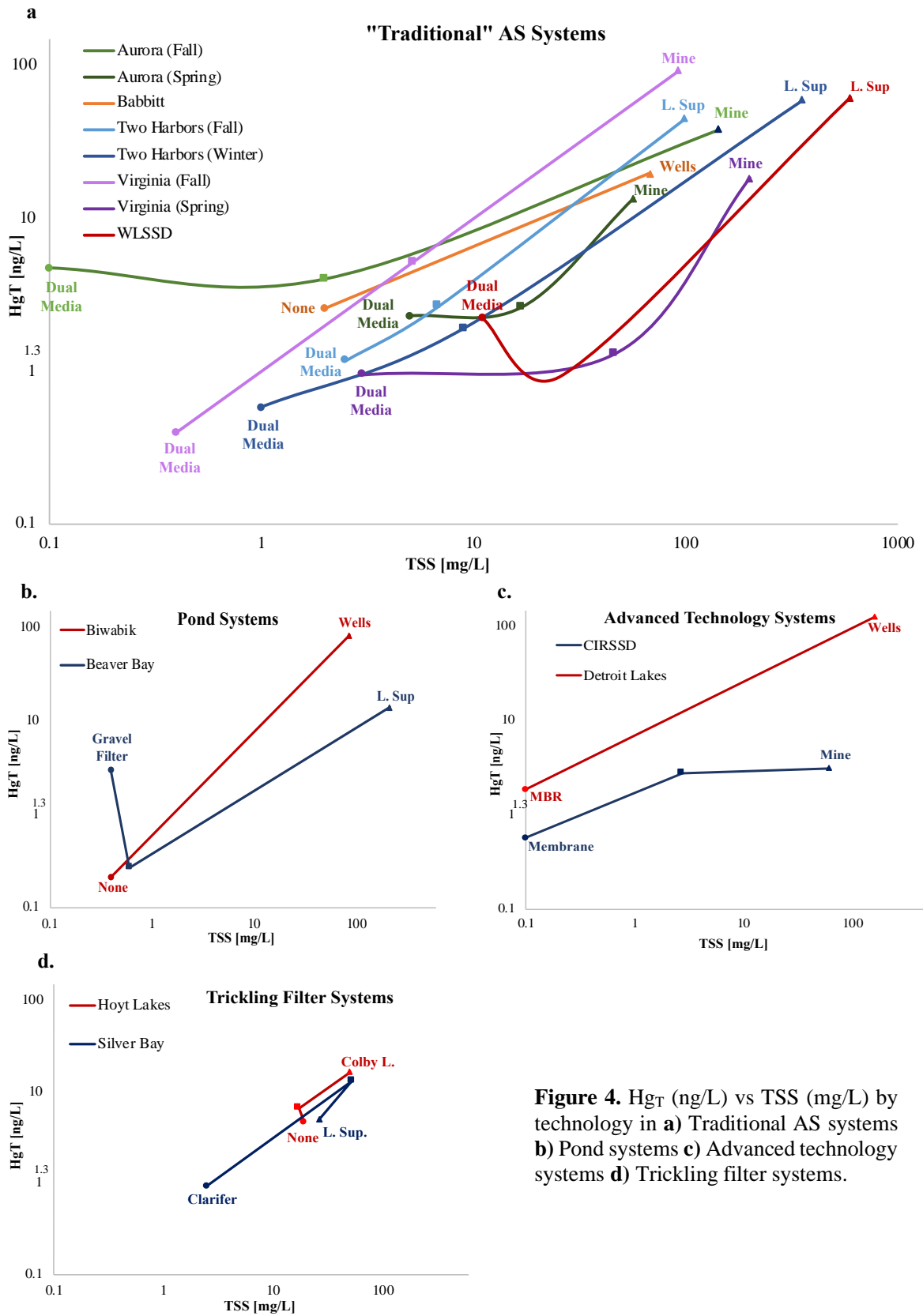


Figure 4. Hg_T (ng/L) vs TSS (mg/L) by technology in **a)** Traditional AS systems **b)** Pond systems **c)** Advanced technology systems **d)** Trickling filter systems.

3.4 Phase Partitioning – particulate Hg and log K_D

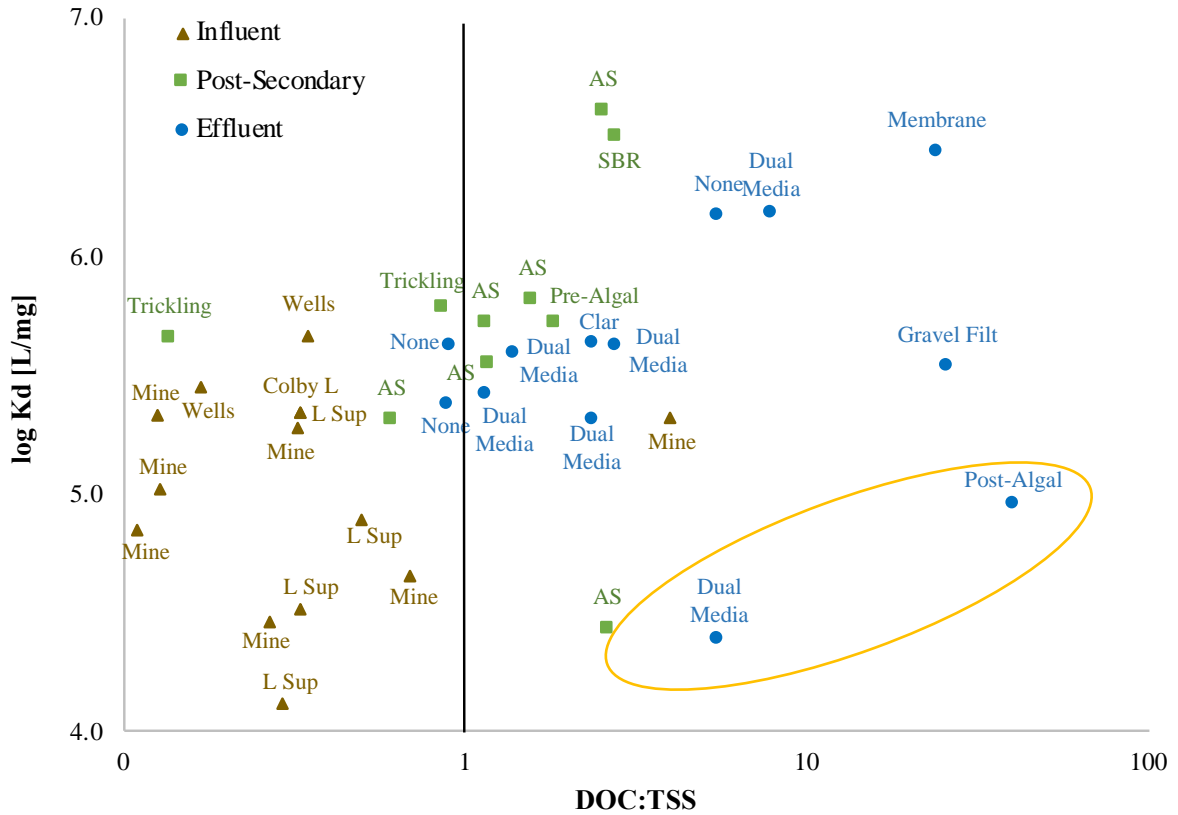


Figure 5. Log K_D (L/mg) vs. DOC:TSS for influent (brown), post-secondary (green), and effluent (blue) wastewater samples. A division has been placed at DOC:TSS = 1 to emphasize DOC is less than TSS on the left of the division and DOC exceeds TSS on the right. WLSSD outlier data is circled.

DOC (mg/L) to TSS (mg/L) ratios were used to compare Hg partitioning with carbon abundance in each phase (dissolved and particulate) among wastewater treatment plant locations. Most of the wastewater facilities contained greater TSS concentrations than DOC concentrations in the influent samples, where the ratio of DOC:TSS is below 1, and greater DOC concentrations than TSS concentrations in the effluent samples, where the ratio of DOC:TSS is greater than 1 (*Figure 5*). Two outliers existed in this data set that did not follow this pattern; an influent sample with a high DOC exceeding TSS and the effluent

at Hoyt Lakes which contained a slightly greater TSS concentration than DOC concentration.

C_P values (Table 4) were variable from < 0.03 to > 1.5 ng/mgTSS, but the average C_P did not vary significantly among sample locations within the plants ($p > 0.1$). Most facilities experienced an increase in C_P value from influent to effluent, suggesting that, on average, Hg concentrations per milligram of TSS

Table 4. C_P and log K_D values calculated for each sample, where applicable.

| WWTP | CP (ng/mg) | | | log KD (L/mg) | | |
|---------------------------------------|------------|----------|----------|---------------|----------|----------|
| | Influent | Post-Sec | Effluent | Influent | Post-Sec | Effluent |
| Traditional AS Facilities | | | | | | |
| Aurora (fall) | 0.26 | 1.8 | — | 5.33 | 6.61 | — |
| Aurora (spring) | 0.17 | 0.12 | 0.29 | 4.66 | 5.32 | 5.59 |
| Two Harbors (fall) | 0.43 | 0.31 | 0.24 | 5.35 | 5.73 | 5.62 |
| Two Harbors (fall) | — | — | — | — | — | — |
| Two Harbors (winter) | 0.15 | 0.16 | 0.35 | 4.33 | 5.55 | 6.18 |
| Virginia (fall) | 0.09 | 0.21 | — | 5.02 | 5.82 | — |
| Virginia (spring) | 0.1 | 0.02 | 0.12 | 4.85 | 4.44 | 5.32 |
| WLSSD | 0.1 | — | 0.04 | 4.52 | — | 4.39 |
| WLSSD-Clearas | — | 0.43 | 0.08 | — | 5.72 | 4.96 |
| Babbitt** | 0.27 | — | 0.98 | 5.45 | — | 6.18 |
| Advanced Technology Facilities | | | | | | |
| CIRSSD (fall) | 0.03 | 0.93 | 0.87 | 4.47 | 6.5 | 6.44 |
| CIRSSD (fall) | 0.44 | — | — | 5.32 | — | — |
| Detroit Lakes | 0.79 | — | — | 5.67 | — | — |
| Pond Facilities | | | | | | |
| Beaver Bay | 0.05 | — | 0.9 | 4.12 | — | 5.54 |
| Biwabik* | 0.92 | — | — | 5.28 | — | — |
| Trickling Filter Facilities | | | | | | |
| Hoyt Lakes | 0.3 | 0.36 | 0.2 | 5.35 | 5.79 | 5.38 |
| Silver Bay | 0.13 | 0.24 | 0.2 | 4.9 | 5.66 | 5.64 |

increase through treatment. WLSSD and WLSSD-Clearas were the only facilities that had lower C_P values in the effluent than the influent. The changes observed in both C_P and Hg_D values from influent to effluent across this data set resulted in varying log K_D values that were not correlated with Hg_T ($p = 0.4$, $R^2 = 0.02$, multiple $R = 0.13$).

Despite greater quantities of DOC in proportion to particulate matter, log K_D values (table 4) typically increased from influent to effluent, indicating greater Hg partitioning to

the few remaining solid particles (per particle mass) rather than the (relatively) more abundant DOC. The WLSSD and WLSSD-Clearas facilities were the outliers in the data set that exhibited a lower log K_D than other plants and a decreased log K_D from influent to effluent, indicating greater Hg partitioning to the DOC than to particulates in the effluent than in the influent.

3.5 DOM SUVA

SUVA was measured as a proxy for DOM aromaticity as a marker for potential changes in the nature of DOM throughout treatment. As a data set, the influent, post-secondary, and effluent SUVA values were not statistically different from each other ($p = 0.36$) (table 5). Influent values ranged from 0.68 to 2.89. Differences were observed among facilities when grouped by town source waters, suggesting that the chemistry of water reaching the wastewater facilities

Table 5. SUVA values measured on the influent, post-secondary, and effluent locations.

| WWTP | Influent | Post-Secondary | Effluent |
|--------------------------|----------|----------------|----------|
| Aurora (fall) | 1.64 | 1.29 | 1.13 |
| Aurora (spring) | 0.73 | 1.43 | 1.98 |
| Two Harbors | 0.83 | 1.58 | 1.74 |
| Virginia (fall) | 2.04 | 2.23 | 2.21 |
| Virginia (spring) | 1.18 | 2.42 | 2.59 |
| WLSSD | 1.68 | ----- | 3.43 |
| WLSSD-Clearas | 1.68 | 4.09 | 3.45 |
| Babbit | 2.89 | ----- | 1.11 |
| CIRSSD | 1.65 | 2.16 | 2.15 |
| Detroit Lakes | 0.68 | ----- | 1.81 |
| Beaver Bay | 0.91 | 1.54 | 1.54 |
| Biwabik | 1.22 | 1.66 | ----- |
| Hoyt Lakes | 2.11 | 2.6 | 1.26 |
| Silver Bay | 1.28 | 1.32 | 1.66 |

depends strongly on the community characteristics. The coefficient of variance in SUVA values between the facilities in towns that utilize Lake Superior water, including Beaver Bay, Silver Bay, Two Harbors, and WLSSD, was 33%, however this value did reduce to 23% when WLSSD, an outlier due to large quantities of paper mill water in the influent,

was removed. Influent SUVA values also changed between replicate visits; both Aurora and Virginia had higher SUVA values in the fall/winter sampling event than in the spring sampling event.

Post-secondary SUVA values ranged between 1.29 and 4.09 and increased from the influent values in all facilities except the Aurora facility during fall sampling. Increased SUVA between the influent and post-secondary locations indicates the DOM in the wastewater becomes more aromatic as the wastewater undergoes biological treatment (Weishaar et al 2003). Effluent SUVA values ranged from 1.11 to 3.45. A consistent trend was not observed between SUVA in post-secondary samples and SUVA in effluent samples; some facilities experienced slightly more aromatic DOM following tertiary treatment while some effluents became more aliphatic. The trend was not consistent among similar secondary nor tertiary technologies. The only two facilities that showed relatively large decrease in SUVA value between post-secondary and effluent locations were CIRSSD (membrane filter) and Beaver Bay (gravel filter).

The greatest changes in SUVA between influent and effluent were observed at WLSSD and WLSSD-Clearas. The effluent SUVA values at WLSSD and WLSSD-Clearas were 105% greater than the influent SUVA values, indicating more aromatic DOM in the effluent. A decrease was observed between the post-secondary and effluent SUVA values at WLSSD-Clearas, indicating the DOM become more aliphatic from the algal unit. A post-secondary SUVA value was not obtained at WLSSD so the impact from the dual media filter cannot be evaluated.

Differences in both SUVA value and direction toward aromatic or aliphatic were observed in replicate sampling events. The influent SUVA values between the spring and fall sampling events at Aurora differed by 55%. In addition, the fall samples became more aromatic through treatment while the spring samples become more aliphatic. The influent SUVA values during the two sampling events at Virginia also differed, however, the values measured at the post-secondary and effluent locations between sampling events only differed by 8% and 15%, respectively.

SUVA values did not correlate to $\log K_D$ values in any of the sample locations ($p > 0.1$) (*Table A2*). Using the absorbance values at 254 instead of SUVA (a proxy for both aromatic abundance and aromatic nature) also did not show any correlations. However, SUVA may have a weak, positive correlation with the effluent Hg_P/Hg_D partition, which differs from $\log K_D$ in that the Hg_P concentration is not normalized by TSS concentration ($R^2 = 0.36$, multiple $R = 0.6$, $p = 0.05$) (*Table A3*). A correlation was not observed using absorbance 254 in the influent or post-secondary locations ($p > 0.1$)

3.6 Sulfur quantities on PM and DOM Composition

Elemental analysis (*Table 6*) shows PM samples are comprised of between 11.5% - 42% carbon, 3% - 6% nitrogen, and 0.4% - 2% sulfur while DOM samples are comprised of between 52% - 57% carbon, 0.8% - 2.7% nitrogen, and 1.3% - 3.4% sulfur.

C:S and C:N ratios of organic matter in wastewater varied by sample location and by sample fraction (PM and DOM). C:S values were higher in the PM than in the DOM for each sample location, except for CIRSSD influent, indicating typically more sulfur in the dissolved phase per milligram of carbon. A trend was not observed between sample

Table 6. Percent elemental composition and elemental ratios of C, S, and N in wastewater DOM and PM at influent, post-secondary, and effluent locations.

| Facility | Sample Location | PM | | | | | DOM | | | | | |
|---------------|-----------------|------|-----|------|-------|------|------|-----|------|------|------|----------------|
| | | % C | % S | % N | C:S | C:N | % C | % S | % N | C:S | C:N | % DOM Recovery |
| CIRSSD | Influent | 29.4 | 1.9 | 3.52 | 15.5 | 8.4 | 54.6 | 1.4 | 2.06 | 39.7 | 26.5 | 61.2 |
| | Effluent | 18.6 | 0.4 | 1.05 | 51.3 | 17.8 | 50.9 | 1.3 | 2.82 | 39.2 | 18.0 | – |
| Hoyt Lakes | Influent | 31.3 | 0.6 | 2.90 | 54.2 | 10.8 | 54.5 | 2.0 | 2.71 | 27.5 | 20.1 | 59.4 |
| | Effluent | 25.7 | 0.5 | 3.76 | 52.0 | 6.5 | 57.7 | 1.3 | 1.84 | 45.3 | 31.4 | 45.7 |
| Two Harbors | Influent | 42.7 | 0.4 | 4.08 | 104.0 | 10.5 | 51.5 | 2.2 | 4.06 | 22.9 | 12.7 | 73.4 |
| | Effluent | 11.5 | 0.1 | 0.56 | 224.6 | 20.4 | 57.1 | 0.9 | 2.38 | 64.5 | 24.0 | – |
| WLSSD | Influent | 39.4 | 0.9 | 5.33 | 45.5 | 7.4 | – | – | – | – | – | – |
| | Post-Sec | – | – | – | – | – | 52.0 | 2.3 | 0.98 | 22.3 | 53.2 | – |
| | Effluent | 41.3 | 1.4 | 5.85 | 30.0 | 7.1 | 54.4 | 3.4 | 0.83 | 15.9 | 65.4 | 23.5 |
| WLSSD-Clearas | Influent | – | – | – | – | – | 54.1 | 2.9 | 0.61 | 19.0 | 89.4 | – |
| | Pre-BNR | – | – | – | – | – | 51.6 | 2.4 | 0.90 | 21.6 | 57.1 | – |
| | Post-BNR | – | – | – | – | – | 50.9 | 2.7 | 1.18 | 18.8 | 43.2 | – |
| | Effluent | – | – | – | – | – | 53.6 | 1.7 | 0.87 | 32.2 | 61.4 | – |

Method precision for % C \pm 0.4
 Method precision for % S \pm 0.2
 Method precision for % N \pm 0.09

locations in the PM or DOM fraction. The C:N values were lower in the PM fraction than the DOM fraction, indicating relatively more nitrogen in the PM than the DOM. The C:N values were fairly consistent in the PM fraction, ranging from 7 to 10, but highly variable in the DOM fraction, ranging from 20 to 65. Within the DOM fraction, effluent samples displayed higher C:N ratios than post-sec and influent samples, indicating reduced nitrogen in the dissolved fraction from influent to effluent.

In addition to the observed differences in elemental composition between influent and effluent samples, the amount of DOM recovered by the PPL cartridge (*Table 6*) also indicated chemistry changes through the treatment process; the influent extraction recoveries were about 10% higher than effluent extraction recovery. These results also

suggest DOM changes in wastewater chemistry occurring through wastewater treatment. The PPL cartridge is able to extract a wide range of polar and non-polar DOM, but previous studies have found high extraction efficiencies for land-based DOM than marine DOM (Dittmar et al, 2008), which may explain why recoveries were observed to decrease through treatment as the wastewater became less anthropogenic and more characteristic of DOM derived from biological activity during the wastewater treatment process rather than the DOM present in the influent.

3.7 Sulfur-normalized TSS, DOM, and Hg Concentrations

Table 7. Sulfur-normalized DOM, TSS, Hg_D, Hg_P, and log K_D values for facilities analyzed for elemental composition.

| | DOMs (mg/L) | | TSSs (mg/L) | | Hg _D (ng Hg _D /mg DOMs) | | Hg _P (ng Hg _P /mg TSSs) | | K _{D-S} (ng Hg _P /mg TSSs/ng Hg _D /mg DOMs) | |
|--------------------|-------------|----------|-------------|----------|--|----------|--|----------|---|----------|
| | Influent | Effluent | Influent | Effluent | Influent | Effluent | Influent | Effluent | Influent | Effluent |
| CIRSSD | 0.41 | 0.18 | 1.196 | 0.001 | 2.7 | 1.7 | 1.7 | 238.8 | 0.62 | 139.63 |
| Hoyt Lakes | 0.59 | 0.37 | 0.290 | 0.093 | 2.3 | 2.3 | 51.9 | 41.2 | 22.92 | 18.11 |
| Two Harbors | 1.42 | 0.11 | 0.406 | 0.001 | 1.4 | 5.4 | 106.1 | 478.4 | 76.80 | 89.11 |
| WLSSD | 10.37 | 2.89 | 5.220 | 0.152 | 0.3 | 0.6 | 11.2 | 3.2 | 39.19 | 5.20 |

Since sulfur is usually an overwhelmingly strong binding phase for Hg in many situations (Xia et al. 1999; Poulin et al. 2017; Rachivadian, 2004; Hsu & Sedlak, 2003), we used the PM and DOM elemental composition data from CIRSSD, Hoyt Lakes, Two Harbors, and WLSSD, to calculate concentration of TSS_S, DOM_S, Hg_{D-S}, Hg_{T-S}, and K_{D-S} (table 7, Figure 6). The quantity of sulfur content in the DOM and TSS per liter of water decreased from influent to effluent. More sulfur was typically present in the DOM than the TSS at both influent and effluent locations, as indicated by lower TSS_S:DOM_S ratios below

1.0 (Figure 7). CIRSSD's influent was the outlier that had very low DOMs in the influent and contained more sulfur in the TSS than the DOM at the influent location.

The Hg_{P-S} concentration at CIRSSD increased while Hg_{D-S} decreased from influent to effluent, despite effluent sulfur concentrations being greater in the dissolved phase than the particulate phase. The ratio of $Hg_{P-S}:Hg_{D-S}$ increased drastically from influent to effluent, resulting in a large increase in $\log K_{D-S}$ between the two locations.

Two Harbors and Hoyt Lakes both had greater sulfur content in the DOM than TSS at both influent and effluent locations. The Hg_{D-S} concentration at Hoyt Lakes did not change from influent to effluent, but the Hg_{P-S} concentration decreased, causing the $\log K_{D-S}$ value to slightly decrease from influent to effluent. Both Hg_{D-S} and Hg_{P-S} increased from influent to effluent at Two Harbors, however, the Hg_{P-S} values were so much larger than the Hg_{D-S} values, that the overall $\log K_{D-S}$ increased.

WLSSD had the greatest influent sulfur concentration, containing roughly five times more sulfur in the TSS and DOM per liter than the other facilities. The Hg_{P-S} value was also five times greater than the Hg_{D-S} value, but the overall $\log K_{D-S}$ decreased in the effluent compared to the influent, indicating Hg partitioned to the dissolved phase more than the particulate phase in the effluent compared to the influent.

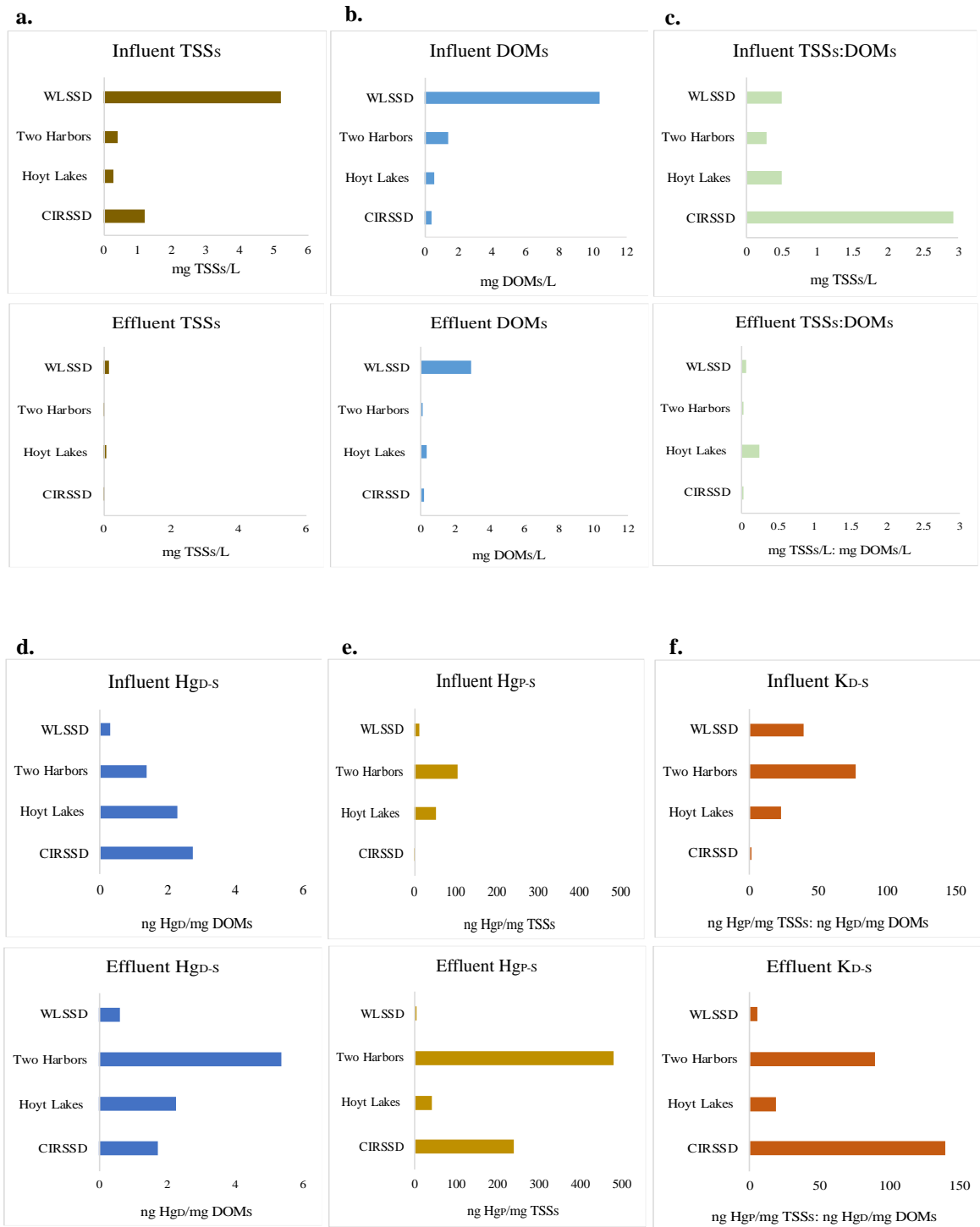
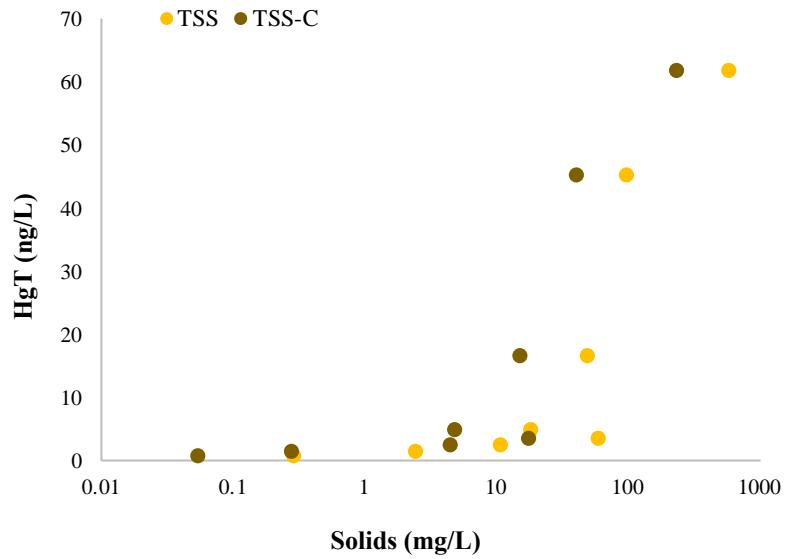


Figure 6. Sulfur content in influent and effluent DOC, TSS, HgD, and HgP concentrations, as well as in calculated K_D and TSS:DOM ratios. **a)** TSS_S **b)** DOM_S **c)** TSS_S:DOM_S **d)** Hg_{D-s} **e)** Hg_{P-s} **f)** K_{D-s}.

3.8 Carbon-normalized TSS

TSS values were normalized to carbon content at the facilities with elemental composition data to investigate if carbon, instead of TSS, improved the predictability of Hg_T



(Figure 7). As a data set,

Figure 7. Solids as TSS (yellow) and as TSS_C (brown) vs Hg_T for the elementally analyzed data set.

the regression of TSS_C and Hg_T ($p = 0.007$, $R^2 = 0.72$, multiple $R = 0.85$) was weaker than the regression of TSS and Hg_T ($p = 0.006$, $R^2 = 0.73$, multiple $R = 0.86$). These results indicate that relationship between Hg_T and solids concentration does not change between using TSS and TSS_C. It is anticipated that continued analysis with the larger State of Minnesota compliance data set will strengthen this analysis.

4. Discussion

This study investigated the correlation of major elements associated with Hg complexation, including carbon, as DOM and TSS, and bulk sulfur in each phase. The relationship between Hg, TSS, and DOC, as well as their effect on $\log K_D$ and C_P values, are discussed in detail below. Elemental composition for PM and DOM, in particular sulfur content, was also measured; however, more data is required for a thorough interpretation.

4.1 Relationship between Hg, TSS, and DOC

Hg binds strongly to suspended particulate matter and TSS is a permitted quantity and a major design variable for wastewater treatment. Across the entire dataset, TSS was typically reduced by > 95 % and in some cases to less than 1 mg/L in effluent wastewater. Most of this reduction in TSS concentration occurred prior to the tertiary treatment processes. A downward trend in Hg_T concentration was also observed from influent to effluent in the WWTPs (*Figure 3*) and was, in many cases, proportional to TSS removal. Most of this reduction in Hg concentration occurred prior to the tertiary treatment processes, but post-secondary wastewater did not typically contain less than 1.3 ng/L Hg_T. On average, facilities experienced over 90% Hg_T removal and the average 6% contributed by dual media filters in the “traditional” AS plants was often enough to reach below 1.3 ng/L Hg_T.

The relationship between Hg_T and TSS became stronger through the treatment process (*Figure 3*). There was significant variance in this relationship, however, and this variance among the wastewater plants and locations within plants is almost certainly introduced by Hg’s propensity to bind to remaining solid phase and dissolved ligands with variable properties. For the subset of data for which elemental composition was available, the relationship did not improve when TSS was normalized by organic carbon content, indicating other ligands on the TSS other than carbon influence relationship to Hg.

DOC also exhibited a downward trend from influent to effluent and was concurrent with solids removal until about 10 mg/L TSS (*Figure 2*). DOC was not able to be removed below ~6 mg/L among the plants visited, however, Hg reductions continued to decrease to

below 1 ng/L, even in the presence of significant remaining DOC (Figure 3). The ratio of DOC to TSS increased from influent to effluent at each facility (Figure 5). TSS concentrations exceeded DOC concentrations in the influent but this reversed after secondary treatment, in which the vast majority of solids were removed and the DOC concentration surpassed the remaining TSS concentration. It appears challenging to lower Hg_D to below ~0.25 to 1.0 ng/L in wastewater effluent, assumedly due to an apparent limit on DOC reductions.

The distinction between Hg_D and Hg_P are important for understanding the propensity of a plant to meet effluent limits and may be contextualized with both TSS and DOC. As a data set, Hg_D concentrations did not differ between post-secondary and effluent sample locations, indicating tertiary treatment does not significantly reduce dissolved Hg concentrations. Most tertiary treatment technologies are not designed to target removal of dissolved (< 0.45 μm) ionic or particle matter. The fact that there was no significant difference between the mean of Hg_P and Hg_D in effluent samples, however, suggests that, on average, these two quantities are not different from one another. This means that, in most cases, additional particulate removal from effluent samples would help to lower Hg_T by lowering Hg_P . However, the persistence of Hg_D quantity due to the presence of DOC, even at low levels (~ 0.5 ng/L Hg_D) is a still considerable fraction of a 1.3 ng/L Hg_T limit; because facilities give little consideration toward removing DOM and concomitant Hg_D , a facility needing to meet 1.3 ng/L will have little margin of error in removing Hg_P .

4.2 Log K_D and C_P

Since K_D is the ratio of C_P and Hg_D , the quantity may be expected to decrease through a treatment system as Hg binding phases on DOC become relatively more abundant compared to Hg binding phases on TSS. Unexpectedly, $\log K_D$ values in this study typically increased from influent to effluent (*Figure 5*), indicating greater relative Hg partitioning to the particulate phase than the dissolved phase as the treatment progressed, despite lower TSS:DOC ratios. WLSSD was the outlier in the data set that experienced a decrease in $\log K_D$ from influent to effluent, indicating increased relative Hg partitioning to the dissolved phase as the treatment progressed. $\log K_D$ among effluent and post-secondary samples is not clearly related to TSS:DOC and actually shows the opposite trend of what may be expected based on relative ratios of dissolved and particulate ligands. For example, in natural aquatic conditions, reactive thiol groups on DOM typically control Hg binding (Haitzer et al, 2002; Ravichandran, 2004) and in soil organic matter, dissolved Hg concentration increases through dissolution out of soil and sediment matter with increased DOM presence (Gerbig 2011).

A clear relationship was not observed between $\log K_D$ values and Hg removal. In a conceptual model where concentration of Hg per particle of TSS (C_P) is constant, greater $\log K_D$ values would be expected to have greater Hg reductions in wastewater that had similar TSS removal. In our dataset, C_P differed among the plants and at different points within plants, and this variation in C_P contributed to varying $\log K_D$ values. In fact, C_P exhibited as large or larger variations compared to Hg_D , even within a single wastewater treatment plant, suggesting that the phases involved in partitioning between solid and dissolved phases in wastewater are not uniform through a treatment process. Additionally,

variations in C_P among wastewater plants suggests that Hg binding to solid phases in effluent wastewater is not overwhelmingly similar, even though most municipal wastewater plants have similar biological processes producing abundant particulate and dissolved organic matter.

This variation in C_P caused a loss of the expected relationship between $\log K_D$ and Hg removal, assuming similar TSS removal (lower K_D , less Hg removal), since within the data set, there are instances of lower $\log K_D$ values being associated with greater Hg_T reductions than those with higher $\log K_D$ values. So constant C_P with constant, equilibrium partitioning between solid-phase and aqueous-phase ligands is not a sufficient basis for explaining Hg partitioning between dissolved and solid phases.

The reason for the observed increase in $\log K_D$ is unclear, but could be due to a change in the composition of the DOM from the influent to the effluent, in which the DOM at the end of the system has less Hg binding capacity/affinity than the influent DOM; in most cases, effluent DOM had less sulfur relative to the influent DOM (*Table 6, Table 7*). In addition, the availability of binding sites on the DOM may be a small fraction of the total DOM concentration (Haitzer et al, 2002; Muresan et al, 2011). Another explanation could be a relative loss of particles with lower C_P . If particulates with less Hg are preferentially settled or degraded during the treatment process, the remaining particulates would skew the C_P results, and thus the $\log K_D$ values, to show elevated particulate phase mercury. Finally, Hg may not be at equilibrium between the two phases, as assumed in this study. Other research has shown Hg equilibrium with DOM can take up to 24 hrs and the

release of bound Hg may be slow even when in contact with strong binding sites (Gerbig 2011).

Investigation of overall changes in DOM composition through wastewater treatment via SUVA analysis also did not correlate to $\log K_D$ in this study. This suggests that this proxy for aromaticity and, thus DOM composition relevant for Hg binding, is not by itself an effective tool for explaining wastewater DOM's propensity for Hg partitioning.

4.3 Elemental Composition, S and C normalized concentrations

Investigation of the elemental composition of wastewater revealed PM carbon content varies widely both among facilities and sample locations, but is consistently less than the DOM, which is comprised of about 50% - 60% carbon. Bulk sulfur quantities were also typically higher in the DOM than the PM, and ranged from 1.3% - 3.4% in the dissolved fraction.

Normalizing the binding phase quantities (DOM and PM) to S fraction allowed for a more detailed evaluation of the mechanisms involved in Hg partitioning to dissolved and particulate phases. Despite the observation that sulfur quantities in DOM exceeded that of sulfur quantities on PM in effluent DOM (Table 7), Hg binding continued to favor PM, as indicated by K_{D-S} values greater than 1.0. As with $\log K_D$, several reasons could be causing K_{D-S} values to increase, such a change in binding capacity and/or binding site availability, or a lack of reaching equilibrium between the two phases. A more detailed investigation of the nature of sulfur binding sites would be needed to interpret the interactions between wastewater S and Hg. Poulin et al. 2017 suggested that DOM with more abundant sulfur

also has a higher fraction of thiol groups with a higher propensity to bind Hg, but the conclusions of that research, which focused on wetland porewater, may not apply to wastewater.

Though sulfur normalization did not significantly change the trend in results, both Hg_{D-S} and Hg_{P-S} appear to increase through treatment, suggesting more Hg is bound to each sulfur atom in the effluent. This could be due to the loss of Hg from phases with lower Hg-S ratios during the treatment process and the sulfur that remains in the effluent DOM and particulate phases has a higher binding affinity for Hg. However, our own dataset is limited and only bulk sulfur was analyzed.

4.4 Other ligands to be investigated

While study focused on bulk sulfur quantity, solids, and total Hg, further investigation analyzing specific sulfur groups and/or methyl mercury (MeHg) may expand our understanding on how Hg partitions in wastewater.

Inorganic reduced sulfur is known to strongly bind to Hg under anoxic conditions and even outcompete DOM (Ravichandran, 2004). While reduced sulfur groups are thought to weaken binding strength in the presence of oxygen, reduced sulfur groups on DOM have been observed in oxic surface waters, suggesting that these ligands may still be important even under oxic conditions (Hsu-Sedlack, 2003; Poulin et al, 2017). In addition, while stability constants for Hg-DOM complexes vary widely between studies, the values are typically high and on the order of compounds with thiol structures (Ravichandran, 2004, Xia et al. 1999). This suggests that analyzing the reduced sulfur binding sites may

explain why Hg continues to partition to the particulate phase, as reduced binding sites are stronger than oxidized binding sites (Gerbig, 2011).

MeHg is another species that was not considered in this study. MeHg tends to have lower log K_D values compared to inorganic Hg, as MeHg complexation with DOM increases the compound's solubility. Increased solubility can make it difficult to remove from the water and in one study, only 30% of MeHg was removed with the sludge (Gilmore & Bloom, 1995). A limited preliminary analysis of MeHg in this study suggests that the influent samples contain more MeHg than the effluent samples, but in both locations, less than 10% of Hg_T was MeHg. Further analysis is needed to make a more complete interpretation of the importance of MeHg on wastewater Hg removal.

4.5 Technology comparison

The “traditional” facilities experienced the majority of Hg removal during secondary treatment, however the removal contribution from the dual media filter enabled facilities during 4 sampling events to reach compliance when secondary treatment alone did not reach the limit. Babbitt did not reach the limit from secondary treatment and did not have tertiary treatment to further remove Hg and solids. Virginia and Two Harbors met the Hg_T limit during both fall and spring sampling events and a majority of the Hg remaining in effluent was Hg_P. Aurora did not meet the Hg limit during either sampling event and a majority of the Hg remaining in effluent was Hg_P; the tertiary filter was not able to remove more. WLSSD also had a large quantity of dissolved Hg in the effluent, contributing to 79% of the Hg_T, and had the greatest quantity of DOC in the inf and eff

relative to other plants in the data set. ...The change in Hg_D concentration between post-secondary and effluent locations varied among the facilities but did not change by more than __ in this study.

The Algal unit had excellent Hg_P removal and did not create a net change in Hg_D conc. This tertiary technology was able to meet the discharge limit while the effluent out of the dual media filter at this plant on the same day was not. The algal unit contains a very small membrane that isolates algal biomass from the wastewater and likely the small filter size resulted in very little Hg_P passing into the algal unit's effluent.

The 10-micron membrane filter at CIRSSD and the 0.01-micron MBR system at Detroit Lakes both removed TSS to below 0.5 mg/L and had high percent Hg_T removal. The membrane filter removed 70% of the Hg_T in the system during the fall sampling event. However, the smaller filter size in the MBR contained more Hg_P than the larger membrane filter. Further evaluation of historic data will conclude if this was an anomaly or if the filter size is only effective to a certain pore size and become ineffective when too small.

The pond systems in this study had excellent TSS, DOC and Hg_T removal and produced effluent Hg_T concentrations below 1.3 ng/L without active tertiary technology. Unlike ponds in warmer climates, outdoor wastewater ponds in northern Minnesota are only discharging twice a year for a couple of weeks in the Spring and a couple of weeks in the Fall. The pond is emptied and then it is ready to be refilled. The long retention time between intermittent discharge periods allows the particulates to sink, producing low concentration effluent waters. The ponds behave as enormous settling basins with very long residence time, creating conditions in which the growth of algae or other DOM-

altering processes may occur which are different from traditional wastewater conditions. A study of the historic data and/or increased sampling events during the summer months would allow further understanding of pond systems during discharge periods when the system has reduced retention time. Historic data will also better analyze the effectiveness of the gravel filter at Beaver Bay as it will have data during the months in which the filter is normally operated.

The trickling filters in this study did not remove as much TSS and Hg_T as some of the other secondary treatments in this study and even contributed TSS and Hg_T to the water during our sampling. In the post-secondary sample at both facilities, more than half of the Hg_T concentration was composed of Hg_P (*Table 2*). The tertiary clarifier at Silver bay was able to compensate for the trickling filter and remove the Hg_P, producing an effluent below 1.3 ng/L. Hoyt Lakes was over the limit due to lack of tertiary to contribute to additional Hg_T removal.

4.6 Study limitations

The results and conclusions from this technology review may be limited by the assumption that facilities with similar technologies are independent replicates of one another and therefore from the same population; as seen in the results of this study, this is not necessarily the case. Every wastewater facility operates differently and parsing out the variability in performance of specific technologies may only be possible in a larger data set. More data points for each technology would allow for ANOVA and regression analysis to occur on additional technology types, other than the “traditional” AS plants as conducted

in this study. Utilizing historic data in future analysis will provide additional data points to not only strengthen statistical analysis, but also identify technological trends and the impact of storm events. Continued sampling may be required as historic data do not typically contain DOC measurements and Hg_D is not analyzed at every plant.

Lastly, all of the statistics in this study were conducted under the assumption that the data were normally distributed, which is not the case for most parameters. Log-normal distribution or non-parametric statistical analyses may be more appropriate for this data set and will be further investigated for future analysis.

5. Conclusion

This study investigated the major ligands involved in Hg complexation, including particulate carbon, dissolved organic carbon, and considered the bulk sulfur concentration of these phases, to gain an understanding of the mechanisms involved in Hg partitioning and removal.

The facilities in this study were able to remove 90% of Hg_T entering the treatment plant, however, this was not always enough removal to produce an effluent containing less than 1.3 ng/L Hg_T . The only facilities able to produce water below the Hg limit from secondary treatment alone were the two pond systems. At the facilities with tertiary technology, the effectiveness of the tertiary treatment to remove Hg varied both between different tertiary technologies as well as among similar tertiary technologies. In addition, their efficacy varied between sampling days for the facilities visited more than once, which

may be attributed to plant operations, such as changes in hydraulic loading or technology performance, or error may have been introduced during sampling analysis.

Both dissolved and particulate Hg contributed to facilities exceeding the Hg limit, indicating that meeting discharge limits at very low Hg levels may be possible through solids removal alone, but that DOC quantity is relevant and may provide a practical limit to Hg removal from municipal wastewater in many cases. Of the plants we sampled, Hg_D was frequently below the stringent Great Lakes limit, but this remaining Hg_D is still a considerable contribution when working at such low Hg_T levels, meaning that complete, or nearly complete, particulate removal would be required to consistently meet a 1.3 ng/L Hg_T effluent limit.

The effective partitioning coefficient, $\log K_D$, showed that most facilities experienced a net increase in Hg binding to the particulate phase compared to the dissolved phase, despite DOC concentrations exceeding TSS concentrations and greater amount of sulfur containing ligands in the dissolved phase.

Continued efforts are needed to further understand how Hg partitions in wastewater and why $\log K_D$ values increase, rather than decrease, through treatment. Future investigation of the number and availability of binding sites on DOM and PM and analysis of reduced sulfur groups on these binding sites may provide future insight. Additionally, MeHg measurement and a study of kinetic equilibrium may reveal what species of Hg is most prominent in wastewater and how quickly Hg is bound and released off of organic matter. Analysis of historic data will also benefit both the mechanistic understanding of Hg partitioning and the evaluation of tertiary technologies, helping to determine whether the

results presented here are representative of the system performance. A synthesis of data from other plants and historical conditions will strengthen the results and may present patterns in the technological performance at each facility.

Having a clearer understanding of Hg partitioning in wastewater should enable a more thorough evaluation of technologies aimed at Hg removal to very low-levels from municipal wastewater. With an understanding of Hg partitioning and water chemistry parameters that most influence this partitioning, engineers, operators, and resource managers can evaluate tertiary technologies and operational conditions that best handle removing Hg_T to exceedingly low levels.

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7. Appendix.

Table A1. TSS precision values by volume.

| Volume (mL) | Precision (mg/L) |
|-------------|------------------|
| 2000 | 0.1 |
| 1000 | 0.2 |
| 750 | 0.2 |
| 500 | 0.4 |
| 250 | 0.7 |
| 150 | 1.2 |
| 100 | 1.8 |
| 75 | 2.3 |
| 50 | 3.5 |
| 30 | 5.8 |
| 1 | 173 |

Table A2. Effluent SUVA vs effluent log K_D

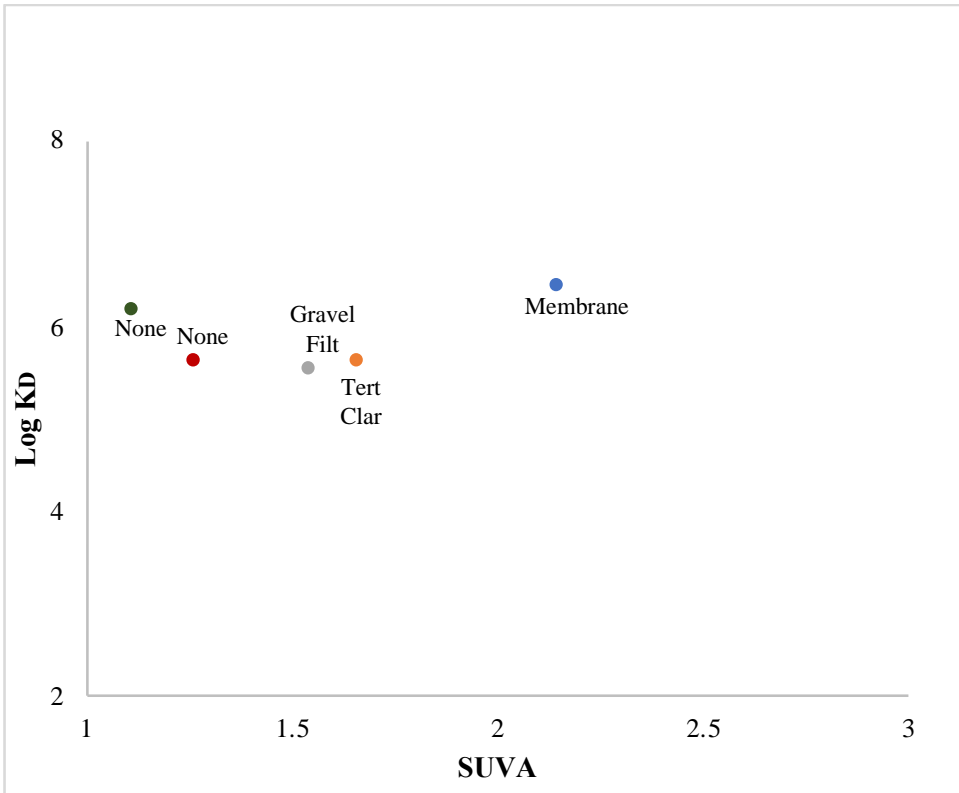


Table A4. Cation and anion data, reported in mg/L.

| WWTP | Location | Fl- | Cl- | SO42-S | NO3-N | PO42-P | Al | B | Ca | Cr | Cu | Fe | K | Mg | Mn | Na | P | Pb | Zn | Ionic Strength |
|--------------------------|--------------|------|-------|--------|-------|--------|--------|-------|--------|-------|-------|-------|--------|--------|-------|--------|--------|-------|--------|----------------|
| Aurora (fall) | Influent | <0.1 | 53.6 | 125.7 | <0.1 | 0.7 | 0.121 | 0.257 | 85.617 | <0.1 | 0 | 0.11 | 15.362 | 92.502 | 0.146 | 74.644 | 1.603 | <0.1 | 0.034 | 1.75E-02 |
| | Post-Sec | <0.1 | 81.7 | 123.1 | 16 | 0.4 | <0.1 | 0.165 | 98.292 | <0.1 | 0 | 0.043 | 14.007 | 102.95 | 0.019 | 76.526 | 0.751 | <0.1 | 0.081 | 1.93E-02 |
| | Effluent | <0.1 | 82.2 | 124.7 | 16.7 | 0.3 | <0.1 | 0.169 | 91.415 | <0.1 | 0 | 0.043 | 12.969 | 96.186 | 0.023 | 71.064 | 0.665 | <0.1 | 0.08 | 1.83E-02 |
| Aurora (spring) | Influent | <0.1 | 51 | 73.5 | 0.6 | 0.7 | 0.091 | 0.104 | 62.955 | <0.1 | 0 | 0.199 | #REF! | 59.505 | 0.078 | 51.162 | 1.577 | <0.1 | 0.002 | 1.17E-02 |
| | Post-Sec | <0.1 | 62.7 | 64.7 | 8.1 | <0.1 | 0.121 | 0.102 | 58.55 | <0.1 | 0 | 0.026 | 8.033 | 49.776 | 0.005 | 45.952 | 0.153 | <0.1 | 0.003 | 1.05E-02 |
| | Effluent | <0.1 | 67 | 69 | 8.8 | <0.1 | 0.1 | 0.109 | 57.941 | <0.1 | 0 | 0.025 | 8.002 | 50.994 | 0.005 | 45.505 | 0.161 | <0.1 | 0.001 | 1.07E-02 |
| | Effluent dup | <0.1 | 65.9 | 68.7 | 8.7 | <0.1 | 0.149 | 0.107 | 58.524 | <0.1 | 0 | 0.038 | 8.092 | 52.078 | 0.004 | 52.078 | 0.166 | <0.1 | 0.002 | 1.10E-02 |
| Babbitt | Influent | <0.1 | 23.4 | 7.2 | <0.1 | 0.7 | 0.975 | 0.08 | 18.863 | <0.1 | 0.068 | 0.089 | 7.076 | 9.285 | 0.062 | 35.08 | 1.1709 | <0.1 | 0.158 | 3.43E-03 |
| | Effluent | 0.3 | 24.8 | 7.7 | 1 | <0.1 | 1.066 | 0.061 | 19.728 | <0.1 | 0.072 | 0.096 | 7.287 | 9.725 | 0.065 | 36.394 | 1.825 | <0.1 | 0.167 | 3.67E-03 |
| Beaver Bay | Influent | <0.1 | 42.3 | 5.8 | <0.1 | 3.1 | 0.33 | 0.353 | 44.89 | 0.006 | 0.03 | 0.793 | 22.06 | 10.754 | 0.205 | 40.504 | 9.532 | 0.061 | 0.105 | 6.70E-03 |
| | Post-Sec | <0.1 | 33.2 | 3.8 | <0.1 | <0.1 | 0.064 | 0.173 | 29.95 | <0.1 | <0.1 | 0.121 | 8.271 | 7.631 | 0.011 | 33.163 | 1.611 | 0.028 | 0.01 | 3.82E-03 |
| | Effluent | <0.1 | 22.3 | 3.3 | <0.1 | <0.1 | <0.1 | 0.313 | 32.078 | <0.1 | 0.014 | 0.09 | 5.667 | 8.132 | <0.1 | 27.49 | 1.074 | 0.055 | 0.008 | 3.61E-03 |
| Biwabik | Influent | <0.1 | 23.9 | 9.8 | <0.1 | 1.1 | 0.102 | 0.251 | 31.78 | <0.1 | <0.1 | 0.167 | 11.456 | 20.881 | 0.057 | 30.634 | 2.857 | 0.033 | 0.025 | 5.23E-03 |
| | Post-Sec | <0.1 | 45.4 | 14.7 | <0.1 | <0.1 | <0.1 | 0.247 | 32.607 | <0.1 | <0.1 | 0.058 | 7.672 | 17.442 | 0.017 | 38.664 | 0.093 | 0.02 | 0.011 | 5.07E-03 |
| CIRSSD | Influent | <0.1 | 52.1 | 7.6 | <0.1 | <0.1 | 0.052 | 0.333 | 54.366 | <0.1 | <0.1 | 0.317 | 7.97 | 19.218 | 0.229 | 40.464 | 1.391 | 0.065 | 0.02 | 6.34E-03 |
| | Post-Sec | <0.1 | 38.6 | 9.4 | 3.7 | <0.1 | 0.073 | 0.158 | 51.554 | <0.1 | <0.1 | 0.03 | 6.991 | 17.896 | 0.012 | 33.342 | <0.1 | 0.026 | 0.029 | 5.71E-03 |
| | Effluent | <0.1 | 37.4 | 9.3 | 3.2 | <0.1 | 0.13 | 0.252 | 49.152 | <0.1 | <0.1 | 0.114 | 6.662 | 16.993 | 0.016 | 31.389 | 0.104 | 0.035 | 0.024 | 5.51E-03 |
| Detroit Lakes | Influent | <0.1 | 323.8 | 6 | 3.4 | <0.1 | <0.1 | 0.273 | 107.6 | <0.1 | 0.012 | 0.102 | 15.152 | 39.807 | 0.09 | 307.54 | <0.1 | <0.1 | 0.073 | 2.04E-02 |
| | Post-Sec | <0.1 | 395.5 | 6 | <0.1 | 6.8 | <0.1 | 0.268 | 107.84 | <0.1 | 0.013 | 1.645 | 23.524 | 42.13 | 0.141 | 306.9 | 10.623 | <0.1 | 0.057 | 2.34E-02 |
| | Effluent | <0.1 | 396.9 | 5.3 | 3.3 | 0.3 | <0.1 | 0.263 | 103.02 | <0.1 | 0.013 | 0.116 | 14.573 | 37.539 | 0.085 | 298.55 | <0.1 | <0.1 | 0.075 | 2.08E-02 |
| Hoyt Lakes | Influent | 0.2 | 41.7 | 13.6 | <0.1 | 1.1 | <0.1 | 0.254 | 24.014 | <0.1 | 0.03 | 0.579 | 8.202 | 13.612 | 0.273 | 35.846 | 2.574 | <0.1 | 0.053 | 4.66E-03 |
| | Post-Sec | <0.1 | 45.4 | 16.9 | 0.5 | <0.1 | 0.305 | 0.206 | 20.121 | <0.1 | 0.011 | 0.156 | 8.46 | 12.034 | 0.342 | 38.294 | 0.349 | <0.1 | 0.077 | 4.14E-03 |
| | Effluent | <0.1 | 46.4 | 20.9 | 0.2 | <0.1 | 0.111 | 0.272 | 20.563 | <0.1 | 0.004 | 0.119 | 8.745 | 12.057 | 0.333 | 39.235 | <0.1 | <0.1 | 0.016 | 4.22E-03 |
| | Effluent dup | <0.1 | 47.2 | 19.7 | 0.2 | <0.1 | <0.1 | 0.235 | 20.562 | <0.1 | 0.007 | 0.109 | 8.645 | 12.067 | 0.34 | 39.191 | <0.1 | <0.1 | 0.017 | 4.17E-03 |
| Silver Bay | Influent | <0.1 | 11.5 | 3.4 | <0.1 | <0.1 | 0.122 | 0.266 | 67.851 | <0.1 | 0.17 | 0.128 | 4.159 | 20.54 | 0.045 | 23.989 | 0.637 | 0.04 | 0.075 | 6.12E-03 |
| | Post-Sec | <0.1 | 16.6 | 8.7 | 1.4 | <0.1 | 1.33 | 0.212 | 62.474 | <0.1 | 0.013 | 0.031 | 3.27 | 20.355 | 0.027 | 23.346 | <0.1 | 0.029 | 0.023 | 6.08E-03 |
| | Effluent | <0.1 | 15.6 | 6.6 | <0.1 | <0.1 | 0.127 | 0.178 | 63.666 | <0.1 | <0.1 | 0.027 | 3.047 | 20.563 | 0.034 | 22.553 | <0.1 | 0.022 | 0.022 | 5.85E-03 |
| Two Harbors | Influent | <0.1 | 32.7 | 4.9 | <0.1 | <0.1 | 0.067 | 0.248 | 52.186 | <0.1 | <0.1 | 0.254 | 8.456 | 19.444 | 0.099 | 33.213 | 1.966 | 0.017 | 0.04 | 6.01E-03 |
| | Post-Sec | <0.1 | 29 | 9.1 | 5.7 | <0.1 | 0.348 | 0.27 | 54.671 | <0.1 | <0.1 | 0.08 | 6.579 | 19.477 | <0.1 | 32.996 | 0.097 | 0.038 | 0.042 | 5.97E-03 |
| | Post-Sec dup | <0.1 | 22.9 | 7.6 | 3.5 | <0.1 | 0.358 | 0.149 | 55.719 | <0.1 | <0.1 | 0.052 | 6.659 | 19.854 | 0.005 | 33.333 | 0.126 | <0.1 | 0.052 | 5.88E-03 |
| | Effluent | <0.1 | 30.4 | 9.2 | 5.4 | <0.1 | 0.315 | 0.204 | 55.513 | <0.1 | <0.1 | 0.058 | 6.638 | 19.538 | <0.1 | 33.227 | 0.111 | 0.028 | 0.041 | 6.01E-03 |
| Virginia (fall) | Influent | <0.1 | 102.4 | 9 | <0.1 | <0.1 | 0.072 | 0.275 | 76.255 | <0.1 | <0.1 | 0.188 | 8.739 | 47.98 | 0.22 | 116.33 | 1.275 | 0.038 | 0.018 | 1.24E-02 |
| | Post-Sec | <0.1 | 111.2 | 15 | 18.6 | <0.1 | 0.063 | 0.248 | 74.991 | <0.1 | <0.1 | 0.101 | 10.42 | 48.027 | 0.009 | 76.104 | 0.281 | 0.035 | 0.03 | 1.17E-02 |
| | Effluent | <0.1 | 107.6 | 14.6 | 19.1 | <0.1 | <0.1 | 0.334 | 74.632 | <0.1 | <0.1 | 0.089 | 10.567 | 47.43 | <0.1 | 75.436 | 0.257 | 0.064 | 0.02 | 1.16E-02 |
| Virginia (spring) | Influent | <0.1 | 137.7 | 19 | 2.4 | 1.2 | 0.0395 | 0.082 | 65.51 | <0.1 | 0.015 | 0.131 | 12.141 | 43.089 | 0.164 | 90.496 | 1.766 | <0.1 | 0.0255 | 1.16E-02 |
| | Post-Sec | <0.1 | 157 | 18.4 | 8.7 | 0.1 | 0.022 | 0.088 | 66.999 | <0.1 | 0.004 | 0.072 | 11.932 | 48.921 | 0.013 | 95.266 | 0.285 | <0.1 | 0.037 | 1.23E-02 |
| | Effluent | <0.1 | 156.3 | 17.9 | 8.3 | 0.1 | 0.03 | 0.079 | 68.8 | <0.1 | <0.1 | 0.06 | 13.485 | 49.105 | 0.003 | 99.667 | 0.303 | <0.1 | 0.046 | 1.25E-02 |