ESTIMATING SEDIMENT, NUTRIENT, AND MERCURY LOADS FROM FOUR WESTERN LAKE SUPERIOR WATERSHEDS USING CONTINUOUS IN-STREAM TURBIDITY MONITORING

A THESIS
SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL
OF THE UNIVERSITY OF MINNESOTA
BY

Elaine M. Ruzycki

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER OF SCIENCE

Richard P. Axler and George E. Host

December 2010

ACKNOWLEDGEMENTS

This project would not have been possible without Dr. Richard Axler who somehow managed to coax me into finishing my degree. I thank him for all his efforts, guidance, and understanding. I would also like to thank Dr. George Host and Dr. Karen Gran for their comments and suggestions through the document preparation phase.

I'd like to thank Minnesota Sea Grant for providing primary funding for this project; Western Lake Superior Sanitary District for funding the mercury analyses; and additional support provided under the Coastal Zone Management Act, by NOAA's Office of Ocean and Coastal Resource Management in cooperation with Minnesota's Lake Superior Coastal Program (Project No. 306-09-10), the Natural Resources Research Institute (NRRI), and the Duluth, Minnesota stormwater utility. Jesse Anderson of the Minnesota Pollution Control Agency, Tim Tuominen of the Western Lake Superior Sanitary District, and Todd Carlson of the Duluth Public Works and Utilities Department provided valuable technical assistance and advice.

I am also grateful to Jerry Henneck who helped me collect samples and kept the stream sensors working, Norm Will for keeping the data flowing, and Jane Reed for help with databases and field work.

Finally, I would like to thank my husband, Wyat and our daughter, Helen, for their support and my father, who instilled in me a love of the outdoors.

ABSTRACT

Many streams along the Minnesota coast of Lake Superior have been listed as impaired from high turbidity, suspended sediment, or high fish mercury concentrations. Both total suspended sediment (TSS) and total mercury have been shown to be strongly correlated to turbidity in many disturbed watersheds. Total suspended sediments, phosphorus, and total mercury loads were estimated in four western Lake Superior watersheds from 2005-2006 using automated in-stream turbidity measurements. Regression models were developed relating this near-continuous turbidity data to grab sample measures of mercury, suspended sediments and nutrients during differing flow regimes. Suspended sediment and phosphorus loads estimated using the turbidity surrogate were compared to those made using FLUX software, a standard assessment technique based on discharge and grab sampling for TSS. Stream specific turbidity vs. TSS measures were strongly correlated ($r^2 = 0.6$ to 0.95; $p < 0.05$) and total mercury also showed a close relationship with TSS ($r^2 = 0.82$, $n = 23$; $p < 0.05$) for all four streams. Continuous turbidity monitoring appears to be a reasonable surrogate for both suspended sediment and total mercury concentration, providing information when manual sample collection is cost-prohibitive or logistically difficult, and across a wide range of flows.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure 3.3. Measured total mercury concentrations for the four streams grouped by flow regime. Samples were collected during base flows, spring snow melt, and rainfall storm events, during 2004-2006. 1.3 THg ng L^{-1} is the MPCA Lake Superior basin standard to protect wildlife health.

Figure 3.4. Regression plots of total mercury (THg) and particulate mercury (PHg) vs. total suspended sediments (TSS) in the four Duluth, MN trout streams from samples collected during varying flow regimes in 2004-2006 with 95% confidence intervals.

Figure 3.5. In-stream turbidity vs. total mercury concentrations with 95% confidence intervals for all four Duluth area trout streams combined.

Figure 3.6. Total mercury deposited (wet deposition) and rainfall totals during 2005 and 2006 at Stations W108 and MN16 of the Mercury Deposition Network (MDN).

CHAPTER 1 INTRODUCTION

Project Background

Urbanization and rural development with attendant increases in stormwater runoff are impacting streams in Duluth, Minneosta, and in particular, its 16 designated trout streams. Stormwater issues have become increasingly important to resource and regulatory agencies and to the public. In 1998, the city of Duluth established a stormwater utility to address the quality and quantity of surface water moving through the city.In 2003 Duluth was issued a Stormwater Permit under Phase II of the federal Clean Water Act's National Pollution Discharge Elimination System as a municipal separate storm water sewer system (MS4). Beginning in January 2002, with funding through the EPA Environmental Monitoring for Public Access and Community Tracking program (EMPACT) in combination with in-kind effort from project partners, the Natural Resources Research Institute (NRRI) and Minnesota Sea Grant formed a partnership with the city of Duluth, the Minnesota Pollution Control Agency (MPCA), the Great Lakes Aquarium, and the Western Lake Superior Sanitary District (WLSSD) with a goal of enhancing public understanding of aquatic ecosystems and their connections to watershed land use by illustrating the nature and consequences of degraded stormwater and its real costs to society. The project initiated automated water quality monitoring and a website linking the data to GIS, land use, and current and historical water quality and biological databases and a comprehensive "understanding section" to help users interpret the data. Four designated trout streams, Amity, Chester, Tischer, and Kingsbury Creeks, were selected as sites for in-stream monitoring based on usage, geographic coverage of the city, and varieties of watershed land-use and land cover. Since 2002, this project has been collecting in-stream measures of discharge (Q, via stage height), specific electrical conductivity (EC@ 25), turbidity, and temperature every 15 minutes for the four streams almost continuously through the open-water season and in some years, throughout the entire winter when ice conditions permit, and during the spring snowmelt period. The data are transmitted to a website daily for display via a unique data visualization and animation tool. Interactive data visualization tools and interpretive text were developed to visually engage citizens and students via the Internet. These data, supplemented with manual sampling for total suspended solids (TSS), nutrients, and mercury have allowed us to develop regression equations relating these parameters to sensor-determined in-stream turbidity. We then estimated sediment, phosphorus, and mercury concentrations and loads over time scales from < 1 hour to annually.

The consequences of increasing urbanization; deforestation, soil disturbance, loss of wetlands, and increasing imperviousness, include increases in storm water flows that are higher in volume and peak flows, sediment, nutrients, contaminant loads and temperature, reduced aquifer recharge and lower base flows. These stressors can affect stream hydrology, ecology and morphology, potentially causing habitat degradation in the streams and significant impacts in their receiving waters. More specifically these impacts often include (Novotny and Olem, 1994):

- Increased storm runoff volume and declining storm water retention times resulting in larger volumes of water entering the stream channel over shorter periods of time;
- Increase in hydrologic connectivity between watershed and stream due to stormwater drainage structures (storm sewers, roads, sidewalks, curbs) and in some cases, increase in watershed area when these drainage structures cross watershed boundaries;
- Decreased base flows from decreasing groundwater replenishment caused by increases in effective runoff due to loss of wetlands and other retention basins; decreased soil retention due to increases in the percent of the watershed covered by impervious surfaces; decreased aquifer recharge;
- Increased pollutant loads –i. e. sediments, nutrients, salts, heavy metals, pesticides;

- Increased stream temperatures due to runoff gaining heat as it moves over summer heated pavement, lots, roofs, and roads and by reduced shading from riparian canopy.

Non-point source pollution has been recognized as a significant cause of surface water quality problems since the early 1980s (Novotny and Olem, 1994) with eroded sediment having the greatest impact. Sediment concentration in streams is generally a function of soil type, slope and land use within the watershed. Sediment load is a function of both the sediment concentration and volume of water through the stream, with volume being a function of precipitation and resulting runoff. Conversion of previously forested regions into urban landscapes generally increases erosion rates during the construction period. Lands undergoing development (Kellog, 1997; Nietch et al., 2005) undergo increased suspended solids delivery to streams five times per unit area compared to other land uses within the watershed. Other land use changes, primarily increases in imperviousness, often result in increasing stream channel erosion by increasing the frequency and volume of storm flows. In addition, urban structures; streets, gutters, and storm water conveyance structures, often accumulate sediment and other particles between rain events. Subsequently, precipitation flushes these particles quickly into the streams resulting in a peak in sediment and pollutant concentrations prior to a peak in flow (**Figure 1.1**).

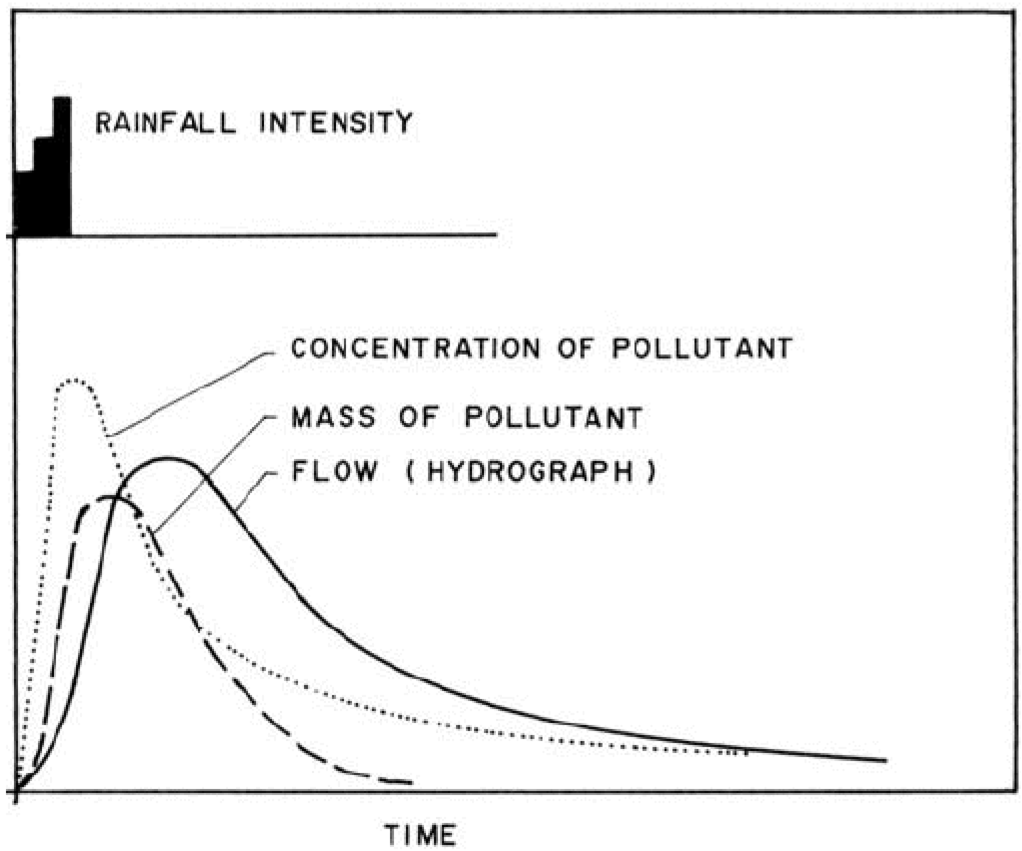

Figure 1.1. Generalized hydrograph for an urban watershed from Novotny and Gordon (1981).

Often, almost 100% of these pollutants are conveyed directly to the streams (Novotny and Gordon, 1981; US Geological Survey [USGS], 2002; CWP, 2003; Bedan and Clausen, 2009).

Land use-land cover (LULC) changes in Great Lakes basin between 1992 and 2001 have included a 33% increase by area in low-intensity development. Twenty-one percent of this new development occurred within 10 km of the shoreline and the majority of those changes taking place within 1 km of the shoreline (Wolter et al., 2006). This increase in hardened surfaces is a major concern because the concomitant increase in storm-water runoff often delivers more sediment, nutrients and other chemicals to the near-shore zone.

Duluth Stream Sediment Study

Duluth, Minnesota (pop 88,000; 2000) is located at the far southwestern corner of Lake Superior (**Figure 1.2**). The 43 streams contained within the city limits are a unique, valued natural resource. Of these 42 streams, 14 are designated brook trout streams. In addition, Duluth area streams, including the St Louis River, form the headwaters of Lake Superior.

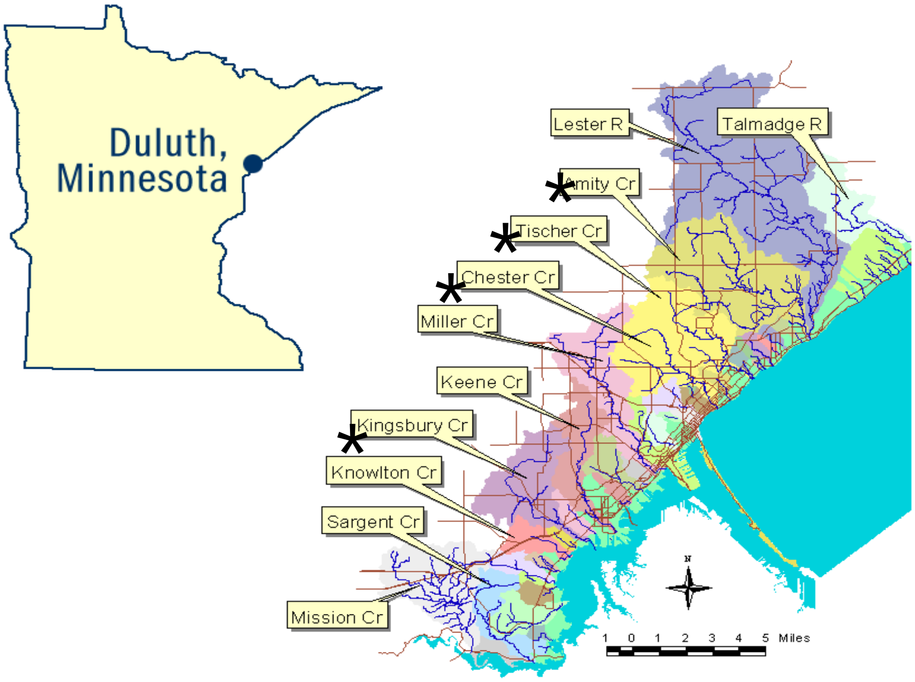

Figure 1.2. Map of Duluth, MN and the major watersheds within the city limits. (*indicates the streams monitored for this project)

Several of these streams are on the Minnesota List of Impaired Waters (305 (d) 2008), and several have been targeted for total maximum daily load (TMDL) development (http://www.pca.state.mn.us/). Streams have been listed as impaired for sediment, turbidity (sediment-associated), temperature, dissolved oxygen, pH, and mercury in fish. All of these streams discharge either directly into ultra-oligotrophic Lake Superior or indirectly via the St. Louis River Estuary-Duluth Superior Harbor. This is particularly important because Lake Superior has been designated as a zero-discharge demonstration project by the International Joint Commission for eliminating inputs of persistent toxic chemicals to the Great Lakes system

(LAMP, 2008; http://www.epa.gov/glnpo/lamp/ls_2008/ls_2008.pdf). Second, the lake's nearshore zone, the source of much of its biological productivity, is extremely nutrient deficient and sensitive to increased inputs of nutrients, suspended solids, turbidity, and organic matter (Rose and Axler, 1998; SOLEC, 2009)

Characteristics of Duluth Area Watersheds

Land cover in the Duluth area is a mix of mainly urban land and forest and shrub with urban areas being concentrated in the city center and along transportation corridors. Population density ranges from 250 people mi^{-2} in the more rural areas to greater than 5000 people mi^{-2} near the downtown area (Fitzpatrick et al., 2006).

The stream flow patterns in this area are driven primarily by the bedrock that exists at or near the land surface. Streams generally flow perpendicular to Lake Superior flowing from headwater altitudes of 550 m, over the escarpment of the Duluth Gabbro Complex, a large sill that extends 240 km northeast from Duluth (Taylor, 1964) then down to the lake at 235 m. Slopes range from 3 to 17% with most streams flowing though glacial till at their headwaters then through bedrock and outcrops in mid to lower reaches (Fitzpatrick et al., 2006).

Duluth is known for its generally cold, snowy winters and moderate to cool summers with Lake Superior driving many climate variables. Annual precipitation averages 29-30 inches (1941-70) with approximately 35% lost as stream runoff and 65% lost as evapotranspiration (Detenbeck et al., 2003), and mean daily temperatures average -5°C in February to 26° C in July (Minnesota Climatology Working Group; http://climate.umn.edu/doc/historical.htm).

Historically, logging and agriculture have been the primary cause of geomorphic disturbance in this region. More recently, deforestation and urban development with resulting increase in imperviousness and watershed connectivity have also become important disturbances (Anderson et al., 2003).

Literature Review

Suspended Sediments

The US EPA (http://iaspub.epa.gov/waters10/attains_nation_cy.control, accessed 26 Oct 10) has listed sediments as the second leading (behind pathogens) cause of impairment in the nation's streams and rivers. The effects of suspended sediment on aquatic biota are well documented (Lloyd, 1987; Sweka and Hartman, 2000, 2003; Newcombe, 2003; Prestigiacomo, 2007;) and include reductions in primary production due to abrasion and decreased light penetration; loss of density and diversity in the macroinvertebrate community through the loss of interstitial space and increased drift; and physiological, behavioral and habitat impacts on fish populations. Water quality is often also reduced due to the suspended sediment related non-point source pollutants including nutrients and heavy metals that complex with fine sediment particles (Nelson and Booth, 2002).

Concentrations of suspended particles found in urban stormwater range from 3-11,000 mg L^{-1} and consist of both organic and inorganic particles from a variety of watershed sources and from within the stream channel. Sediment sources and supply from outside the stream channel include (Novotny and Olem, 1994):

- Street application of sand and salts;
- Construction projects and other soil disturbing activities;
- Forest and other unpaved roads;
- Motor vehicle emissions, tire and road wear;
- Dry deposition (atmospheric);
- Organic matter; leaves, grass clippings, pet waste.

In-stream sources generally result from changes in channel morphology, due to increased discharge. Increased peak flows, frequency and volume often result in channel agradation (erosion from within the stream channel) accompanied by changes in channel morphology such as widening, deepening, and sometimes incising many meters below the original stream bed (Booth and Henshaw, 2000). The higher energy discharge is also able to carry more suspended particles and coarse material held in suspension as discharge (Q) increases. This further exacerbates in-stream channel erosion.

Estimation of Sediment Discharge

Sediment transport in streams can be separated into three components; the dissolved load, the bed-material load, and the wash load. The dissolved component consists of materials in solution. Bed-material loads are made up of the materials present in the stream bed that are generally > 0.062 mm. Wash load is made up of fine particles (< 0.062 mm) that come into the stream from the watershed and are moved readily in suspension and do not interact with the stream bed (Knighton, 1998). In this discussion the term sediment, refers to wash load and suspended load.

Estimating fluvial transport of suspended sediments and associated constituents is necessary to calculate total maximum daily loads (TMDLs), the main tool used to assess and mitigate impairments. The amount of sediment carried by a stream depends on two factors (Gordon et al., 2004):

1. Sediment eroded from upland sources that are transported into the stream.
2. The ability of the stream to carry the washed-in sediments and to erode and transport in-stream bed and bank materials.

Sediment yield is the total amount of material carried by a stream over a specified period of time and requires measures of both flow and concentration from the entire range of flows experienced during that time. However, while continuous flow measurements are common, continuous constituent concentrations are more difficult to obtain. Several methods for load calculations have been developed to overcome data discontinuity and include:

- Sediment Rating Curves

- GIS based models; including Better Assessment Science Integrating point & Non-point Sources (BASINS) and Graphical Constituent Loading Analysis System (GCLAS)
- Turbidity surrogate - Continuous high frequency, in-situ turbidity as a surrogate for other particulate associated water quality parameters
- FLUX Stream Load Computations Model

Sediment rating curves relating sediment concentration to discharge have been shown to generate reasonably accurate estimates of sediment load. They are more useful in larger systems having data records of 20 years or longer and can over predict low and under predict high suspended sediment concentrations (Horowitz, 2008). GIS models generate load estimates based on watershed characteristics including land use and land cover (LULC), watershed area and slope but often require precipitation amount and intensity and soils data. Although useful for scenarios of landscape change, their accuracy depends on how well they are calibrated to actual stream concentrations and loads. The use of turbidity which can be measured near-continuously with in-stream optical sensors as a surrogate for suspended sediment has shown promise recently and is discussed in more detail below.

FLUX Stream Load Computation (V 5.1) is used to estimate annual and event loads using average daily flow data and discrete water quality samples. The FLUX model was developed by William Walker (http://www.wwwalker.net/, accessed 14 Dec 10), and is available from the US Army Corps of Engineers (http://el.erdc.usace.army.mil/elmodels/emiinfo.html, accessed 14 Dec 10). The model uses the flow-concentration relationship developed from the sample record to estimate total mass discharge. FLUX, based on six models, three ratio methods and three regression methods, is used by the Minnesota Pollution Agency (Anderson et al., 2003) and the Metropolitan Council in the Minneapolis-St Paul (Hedlin, et al., 2006) urbanized region to generate load estimates for a number of streams across the state.

Sediments and Particulate-Bound Pollutants

Many pollutants are known to associate with particulates (Christensen, 2001; Davis-Colley and Smith, 2001) by absorption to sediment particles. There is a close link to particulate-P, absorbable-P and other adsorbed pollutants (most priority pollutant heavy metals) and hydrophilic organic contaminants and pathogens (Christensen, 2001; Jastrum et al., 2007). Phosphorus has long been known to be associated with particulates (Novotny and Olem, 1994) and concentrations have been shown to increase during runoff and erosion events (Grayson et al., 1996; Christensen et al., 2000; Hatch et al., 2001). Phosphorus concentration analyses are even more difficult and costly than TSS determinations so the use of turbidity as a surrogate could also prove cost-effective.

Turbidity

Turbidity has been suggested as a surrogate for nutrients (Christensen et al., 2000; Jastrum et al., 2009), fecal coliforms (Christensen et al., 2000), mercury (Anderson et al., 2003; Balough, 2005, 1997), and suspended sediments (Gippel, 1989; Lewis, 1996; Packman, 1999; Prestigiacomo et al., 2007). Turbidity is defined as the optical property of water that causes light to be scattered or absorbed and subsequently not transmitted through the water. Light is scattered by suspended particles and absorbed mostly by dissolved substances (Gippel, 1989), particularly those that add "color" to the water (e.g. black or brown water streams, lakes and wetlands). Particle size greatly affects scattering, with smaller particles being much more effective.

The advantages of continuous in-stream turbidity as a surrogate for other particulate pollutants in waters (Ankorn, 2003) include:

- Low cost relative to intensive water sampling and chemical analyses;
- Safety – ability to estimate in-stream concentrations during high flow events as well as during the weekends and other times when manual sampling is unlikely;

- Allows for an almost instantaneous measurement whereas laboratory analyses may require several days or more before results are available;
- Allows for a better assessment of variability during runoff events over the entire event hydrograph.

Turbidity provides a more “direct view” of changing conditions that are often difficult to observe using manual sample collection.

Disadvantages to the use of turbidity as a surrogate include (Ankorn, 2003):

- Measurement methods differ and the instrumentation is not standardized;
- Suspended sediment particle size and color affect readings;
- Deployment methods must consider where to place the instrumentation to get the most accurate assessment of in-stream conditions. This often involves a compromise between safety, instrument protection, and a representative location that reflects the entire stream cross-section.
- Sample size is small and turbidity may not necessarily track pollutants in terms of depth and cross-sectional distribution within the stream.

Gippel (1989) suggested the main limitation in using NTU to estimate suspended sediments (SS) is that the relationship may not always be linear and may often have a high unexplained variance. Ideally, the turbidimeter should be calibrated with a series of natural sediment concentrations of known total suspended solids (TSS) or suspended sediment concentration (SSC). TSS and SSC are both gravimetric determinations that involve filtering a known sample volume through a glass fiber filter and drying the material collected on the filter to a constant weight. The TSS method allows for use of a sub-sample while SSC involves filtering the entire volume. Direct comparisons between the two methods have determined that TSS can underestimate sediment concentrations if composed of coarser particles (e.g. sand) but tend to be similar for finer suspended sediments (Gray et al., 2000).

Recent advances in multi-sensor technology have allowed cost-effective methods to measure several in-stream constituents including turbidity concurrently and continuously. Several manufacturers have developed self-cleaning sensors with low power requirements that are purported to allow for relatively long-term *in situ* deployments. Instrument designs have been developed to account for the effects of water properties such as sediment particle size, color, and density. Other design considerations include the various *in-situ* interferences such as stray light, bubbles, fouling and scratching. Although at least eight different sensor designs have been developed, only two, the nephelometric (white light) and ratiometric (white light), meet the current standards of EPA Method 180.1, the only regulatory approved method for low-level monitoring (USGS, 2004) in the US. Nephelometric turbidity units (NTU) are most commonly used and reported often regardless of the type of instrumentation used. Both USGS (2004) and Gippel (1989) have suggested the need for traceability to the type of instrument used by using turbidity units described by the USGS (**Table 1.1**).

Field measurements may vary considerably depending on the type of sensor and calibration methods used. Nephelometric turbidimeters measure light scattered at a 90° angle. Ratio turbidimeters (NTRU**;** nephelometric turbidity ratio units) instruments use a white-broadband (400-680 nm) light source, 90° detection angle, and multiple detectors with ratio compensation (USGS, 2004). The development of stream-specific, relative-based criteria, measuring relative increases above background levels using standardized sensors may adequately address these issues.

Table 1.1. USGS turbidity parameter and method codes (USGS, 2004).

NTU (nephelometric turbidity units)	White or broadband (400-680 nm) light source, 90° degree detection angle, one detector.
NTRU (nephelometric turbidity ratio units)	White or broadband (400-680 nm) light source, 90° detection angle, multiple detectors with ratio compensation. (Hach sensor model 2100)
BU (backscatter units)	White or broadband (400-680 nm) light source, 30- (plus or minus 15) degree detection angle (backscatter).
AU (attenuation units)	White or broadband (400-680 nm) light source, 180° detection angle (attenuation).
NTMU (nephelometric turbidity multibeam units)	White or broadband (400-680 nm) light source, multiple light sources. Detectors at 90 ° and possibly other angles to each beam.
FNU (formazin nephelometric units)	Near infra-red (780-900 nm) or monochrome light source. 90° detection angle, one detector. (Hydrolab, sensor model Data Sonde 4;YSI environmental sensor model 6136)
FNRU (formazin nephelometric ratio units)	Near infra-red (780-900 nm) or monochrome light source. 90° detection angle, multiple detectors, ratio compensation.
FBU (formazin backscatter units)	Near infra-red (780-900 nm) or monochrome light source. 30- (plus or minus 15) degree detection angle (backscatter).
FAU (formazin attenuation units)	Near infra-red or monochrome light source, 180° detection angle (attenuation).
FNMU (formazin nephelometric multibeam units)	Near infra-red (780-900 nm) or monochrome light source, multiple light sources. Detectors at 90° and possibly other angles to each beam.

Many studies have assessed the use of continuous, in-stream turbidity as a surrogate for TSS and/or SSC (Lewis, 1996; Packman et al., 1999; Christensen, 2001; Ulrich and Bragg, 2003; Dana et al., 2004; Prestigiacomo, 2007). The majority of studies suggest that the development of a predictive turbidity/suspended sediment model is possible and can be highly reliable. Most authors suggest that the model be site specific and that a sufficient numbers of SS samples be collected to calibrate the model.

Sediment and Mercury

Mercury, a neurotoxin, is toxic to fish, mammals, and humans. Though typically present at very low concentrations in the environment, mercury can accumulate in the tissue of those organisms that consume fish from contaminated waters. About 70% of the mercury in the atmosphere is released from anthropogenic or human sources. Most of that mercury comes from combustion sources such as coal-fired electricity generators and industrial boilers. Mercury has natural sources as well such as volcanoes, geothermal springs, geologic deposits and the ocean (e.g. Grigal, 2002). Though always present at some level before human activity, the levels have increased dramatically, with atmospheric concentrations doubling over the last 150 years (Weiner et al., 2006; Engstrom et al., 2007).

The chemistry of mercury in the environment is complex. Mercury comes to the Lake Superior watershed in three principle forms, elemental Hg (0), ionic Hg (II), and methylmercury. The first two, Hg (0) and Hg (II) are inorganic and are the most mobile forms of this element. Hg (0) also called elemental and gaseous mercury, has a long residence time in the atmosphere traveling globally with the prevailing winds. Hg (0) can be oxidized into the ionic form of Hg (II) by ozone. The ionic form has a much shorter residence time, no longer than ten days and therefore, is usually deposited close to the source. Most of the mercury in the environment is in this inorganic form and is generally not a health concern since it is poorly absorbed by the digestive tract of animals. The third, methylmercury, is an organic form that is highly toxic to nervous systems of higher organisms. Methylmercury is produced from the mercuric ion by sulfate-reducing bacteria in low-oxygenated zones of wetlands and aquatic sediments. This organic mercury is readily accumulated in aquatic biota and biomagnifies to concentrations that are high enough to affect health in higher trophic levels such as game fish, fish-eating birds, mammals, and humans (e g. Grigal, 2002). Known sites of mercury methylation include:

- Low-alkalinity and low-pH lakes

▪ Vegetated lowland areas subjected to prolonged inundation, including new reservoirs

▪ Wetlands and wetland-influenced waters (high dissolved organic carbon [DOC] dark-water lakes and streams)

Statewide, mercury is the major pollutant in about two-thirds of Minnesota's impaired waters. A number of streams along Minnesota's north shore have been listed as impaired by mercury. These streams are the Brule, Poplar, Beaver, Knife, Lester, and St Louis Rivers (**Figure 1.3**).

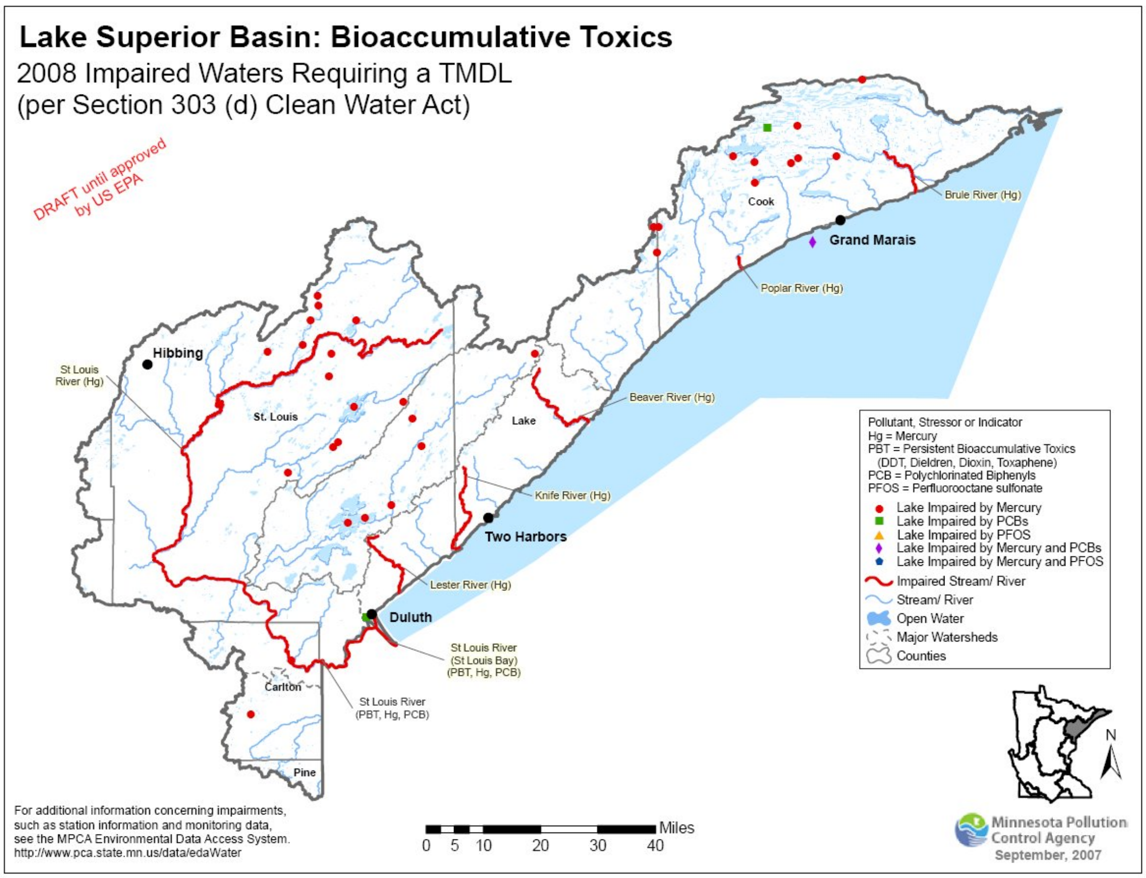

Figure 1.3. The draft 2008 list of Lake Superior basin waters requiring a TMDL for bioaccumualtive toxins.

Atmospheric deposition occurs as dry and wet deposition. Dry deposition of mercury is much more important in forested than open areas because of the large surface area presented by foliage (Grigal, 2002) and has been estimated to be twice wet deposition (St Louis et al., 2001).

The USGS has initiated a number of studies aimed at determining how mercury cycles within stream watersheds and food webs (http://pubs.usgs.gov/fs/fs-016-03, accessed 15 Dec 10). Once it is deposited onto a watershed, mercury cycling and bioaccumulation rates within that watershed are controlled by a number of factors including hydrology, water quality, structure of the aquatic food web and temperature. Hg (II) deposited onto forested ecosystems resides primarily in soils and foliage. Soils form a major pool for mercury that is closely bound to organic matter. Recent work has shown that the release of mercury from this pool is controlled by the decomposition of soil organic matter and erosion (Grigal, 2003; Munthie et al., 2007). There is evidence that "old mercury" is processed differently than newly deposited mercury though again, the processes are not fully understood.

Land cover and land use affect the movement of particulate-bound mercury in the soils to the sites of methylation, low-oxygenated zones in wetlands and aquatic sediments. Activities that cause erosion such as road building, construction, and some forestry practices can increase the movement of this soil-bound mercury pool into lakes, wetlands, and streams where the potential for converting this inorganic form into the toxic organic form exists. Five to 25% of the atmospheric mercury deposited on the terrestrial portion of watersheds has been shown to reach associated receiving waters (e.g. Grigal, 2002). A number of studies, some in Minnesota (Balogh et al., 1997, 2005; Anderson et al., 2003) have found that total mercury concentrations in streams are closely related to the concentration of particulates, particularly during high flow events. Similar results have been observed for urban streams and stormwater. Both Fulkerson et al. (2007) and Mason and Sullivan (1998) concluded that stormwater particulates were the main form of mercury in runoff from Orlando, FL and in an urban Washington, D.C. river, respectively. Whyte and Kirchner (2000) used the strong correlation between SSC and particulate THg to estimate Hg flux in runoff from an abandoned mine in northern California using continuous in-stream turbidity as a surrogate for SSC. Bushey et al. (2008), while targeting Hg species flux during rainfall events in the Adirondack Mountains, New York, did not find a significant correlation with TSS. However, their two study watersheds were essentially pristine, and they did not analyze spring snow melt runoff events.

Objectives

Evaluate the use of continuous, in-stream turbidity sensors in estimating the concentration and loads of several non-point source pollutants in Minnesota north shore streams. More specifically to:

1. Determine the relationship between total suspended solids (TSS), total phosphorus (TP) and continuous in-stream turbidity;
2. Compare loading rates based on continuous turbidity and flow measurements, measured TSS and TP values to those generated by the FLUX model currently used by the Minnesota Pollution Control Agency to estimate loads from north shore streams; and
3. Estimate mercury loading from the Duluth watersheds into Lake Superior based on the relationship between turbidity, TSS and mercury.

Hypotheses

1. Continuous in-stream turbidity measurements can be used as a surrogate measure of total suspended solids (TSS) and total phosphorus (TP) to generate accurate estimates of both these constituents.
2. Continuous in-stream turbidity and discharge monitoring (Q) can be used to compute accurate daily and annual yields of TSS and TP from these watersheds.
3. Continuous turbidity is not different from event-based spot sampling and continuous Q and FLUX modeling.

4. Mercury loads to Lake Superior from these watersheds can be estimated using the continuous turbidity data through the relationship between sediment yields and mercury and an empirical relationship between turbidity and Hg.

CHAPTER 2 - ESTIMATING SEDIMENT AND NUTRIENT CONCENTRATIONS AND LOADS IN THREE WESTERN LAKE SUPERIOR STREAMS: CONTINUOUS TURBIDITY MONITORING VERSUS SPOT SAMPLING AND MODELING.

Introduction

Nationwide, sediments are listed among the top ten leading impairments in assessed rivers and streams (Water Quality Report to Congress EPA 2004; www.epa.gov/owow/305b/) and turbidity is the leading cause of impairment of Minnesota's rivers and streams (EPA, 2008). Turbidity measurements are based on the optical properties of water and these are directly influenced by suspended particles and generally to a lesser extent by dissolved color (Gippel, 1989). Methods relating sediment and turbidity in streams may provide rapid and cost-effective ways to assess sediment concentrations and loads to receiving waters. Sediment concentrations (TSS) are often poorly related to discharge (Q) but the use of streamflow data to estimate TSS is still commonly practiced because Q is more easily and accurately measured than suspended sediment. In many systems, concentrations are different at the same Q on the rising and falling limbs of the hydrograph, an effect called hysteresis. Measurements of in-stream turbidity can account for any hysteresis during runoff events because it is often closely associated with suspended particle concentrations and particularly useful during high flow events when manual sampling is difficult, or during non-Q triggered events like bank slumps and illegal sediment discharges (Gordon et al., 2004).

A number of researchers have assessed the use of continuous, in-stream turbidity as a surrogate for total suspended solids (TSS) and/or suspended sediment concentration (SSC) (Gippel, 1989; Packman et al., 1989; Lewis, 1996; Christensen et al., 2001; Dana et al., 2004; Jastrum et al., 2007). Lewis (1996) found the turbidity/SSC relationship has a number of shortcomings but suggested that the high frequency data from turbidity sensors can overcome the imperfections that exist in the surrogate/constituent relationship. Due to the many factors that can compound the errors in turbidity vs. SSC, or TSS, (e.g. discharge, color, particle size, sediment concentrations, and organic matter) the relationship is site specific and must be calibrated for each site. Turbidity is highly sensitive to the variability in particle size distribution and composition, but once calibrated with a sufficient number of SSC measurements is a useful tool to assess both sediment concentrations and loads. Christensen et al. (2001) used in-stream measures of specific conductivity (EC@25), pH, temperature, turbidity, and dissolved oxygen to estimate total dissolved solids (TDS), sodium, chloride, fecal coliforms as well as sediment. Dana et al. (2004) estimated suspended sediments in the Truckee River, California, using multiple linear regressions of four in-stream parameters including turbidity, Q, temperature and EC@25. However, using a number of variables is problematic because it leaves one open to a loss of predictive capability if one or more of the sensors malfunctions (Lewis, 1996).

Sediment transport in streams can be separated into three components; the dissolved load, the bed-material load, and the wash load. The dissolved component consists of materials in solution. Bed-material loads are made up of the materials present in the stream bed that are generally > 0.062 mm. Wash load is made up of fine particles (< 0.062 mm) that come into the stream from the watershed and are moved readily in suspension and do not interact with the stream bed (Knighton, 1998). In this discussion the term sediment, refers to wash load and suspended load.

The amount of sediment carried by a stream depends on two factors (Gordon et al., 2004):

1. Sediment eroded from upland sources that are transported into the stream.
2. The ability of the stream to carry the washed-in sediments and to erode and transport in-stream bed and bank materials.

Sediment yield is the total amount of material carried by a stream over a specified period of time and requires measures of both flow and concentration presumably from the entire range of flows experienced during that time. However, while continuous flow measurements are more common, hydrograph data for small flashy, relatively undeveloped (unimpacted) streams are uncommon and continuous water quality concentrations are even more difficult to obtain. To overcome this lack of data several methods for load calculations have been developed and include:

- Sediment rating curves
- Geographical information systems (GIS) based models; including BASINS and GCLAS
- FLUX stream load computations model
- Turbidity surrogate - continuous high frequency, *in-situ* turbidity as a surrogate for other particulate associated water quality parameters

Sediment rating curves are empirical models based on the relationship between discharge and sediment concentration. The relationships are better defined in large, stable rivers with long-term datasets (Gordon et al., 2004). GIS models typically relate sediment loads to watershed land use, land cover, and watershed characteristics.

FLUX Stream Load Computations (V 5.1, current version FLUX32; Software for Load Estimation) is used to estimate annual and event loads using average daily flow data and discrete water quality samples. The FLUX model developed by William Walker (www.wwwalker.net/) is available from the US Army Corps of Engineers (http://el.erdc.usace.army.mil/elmodels/emiinfo.html). The model maps the flow-concentration relationship developed from the sample record to estimate total mass discharge. FLUX, based on six models - three ratio methods and three regression methods, is used by the Minnesota Pollution Control Agency (MPCA, 2003) and the Metropolitan Council (Hedlin et al., 2006) to generate load estimates for a number of streams across the state.

Phosphorus has long been known to be associated with particulates (e.g. Novotny and Olem, 1994) and concentrations have been shown to increase during runoff and erosion events

(Leonard et al., 1979; Grayson et al., 1996; Christensen et al., 2000; Hatch, et al., 2001). Phosphorus analyses are even more expensive and more limited than suspended sediment measurements and so the use of turbidity as a surrogate could be cost-effective.

The goal of this study was first to determine if continuous in-stream turbidity data when used as a surrogate measure of total suspended solids (TSS) and total phosphorus (TP) can generate accurate estimates of both these constituents. The second goal was to evaluate potential differences between the sediment and phosphorus load estimates generated by the turbidity-TSS model to those obtained from the FLUX model.

Study Area

Four Minnesota DNR designated trout streams, Amity, Chester, Tischer and Kingsbury Creeks, were selected as sites for in-stream monitoring based on usage, geographic coverage of the city, and varieties of watershed land-uses. Further details regarding the LakeSuperiorStreams.org project that provided the basis for the analyses presented in this paper can be found in Axler et al. (2004, 2006), Lonsdale et al. (2004, 2006) and at http://www.lakesuperiorstreams.org/, accessed 14 Dec 10.

Methods

Automated Sensors

We deployed water quality sensors or stream monitoring units (SMUs) in four streams within the Duluth, MN city limits. The SMUs were located at representative measurement points in the stream cross-section with allowances made for protecting the units from vandalism, debris and sedimentation (**Figure 2.1**). Automated sensors, measuring temperature, specific conductivity (EC@25), turbidity, depth (for flow estimation) were checked approximately at one to three week intervals for cleaning and/or re-calibration by comparison to a YSI 85 or 556 multi-probe water quality analyzer, calibrated daily as per USGS (2004). Probes (**Table 2.1**) were inspected, calibrated, and maintained following the manufacturers recommendations in addition to following USGS (2004, 2006) procedures (see also www.lakesuperiorstreams.org/streams/QA_QC.html).

Table 2.1. Types of sondes and turbidity sensors deployed in each of the streams. Units as per USGS (2004).

Stream	Sonde	Turbidity probes	Turbidity units
Amity	Hydrolab MS5	Hydrolab	FNU
Chester	YSI 6900	YSI 6136	FNU
Kingsbury	YSI 6820	YSI 6136	FNU
Tischer	YSI 6900	YSI 6136	FNU

Figure 2.1. A stream monitoring unit (SMU) as deployed in Chester Creek. Sondes were placed parallel to stream flow with the sensors pointed downstream always in a pool with sufficient depth during base flow.

The SMU control modules (Campbell Scientific Co. CR10X and sensors) were programmed to collect data at 15-minute intervals, which is relevant to the time-scale of storms. Stream discharge in Amity Creek was measured by the Minnesota Pollution Control Agency (MPCA) via an ultrasonic distance sensor and flow calculated from USGS-derived rating curve.

Data Importing (initial data screening)

Each SMU was called daily and data collected since the last call was downloaded. These new data files were stored on the base station computer as comma-delimited ASCII text files. A data importing program rejects specific data if it is outside a pre-defined range for the given parameter. Stage height data were automatically rejected if negative readings were reported. For turbidity, data < - 5 or > 2000 FNU were rejected, and values from - 5 to 0 FNU were set equal to zero. If the data importer encountered a value outside of the range, it generated an appropriate error message in the log file, and disregarded the value. This helped eliminate invalid readings that could be caused by sensor drift or SMU hardware problems. After all of the new data files had been imported the data importer triggered the appropriate programs to create and send updated reports and data-visualization files to the website.

Stream Discharge

Stream discharge (Q) was determined from stage-height per Anderson et al. (2000, 2003) and USGS (2006) with rating curves developed and subsequently used to calibrate Q. Stream depth in Tischer, Chester and Kingsbury was measured remotely using vented pressure transducers with ± 3 mm accuracy. Discharge was determined using rating curves based upon a set of cross-sectional in-stream velocity measurements made with a Marsh-McBirney stream velocity meter over a wide range of discharge conditions. Due to equipment limitations, the greatest depth at which velocity was measured was 1.0 m, which approximates bankfull depth in these streams. Possible implications from this limitation include inaccurate discharge estimates at higher flows. To minimize the potential errors we generated flow estimates made using stream morphometric measures including, slope, roughness, cross-sectional area, and bankfull depth measured at each

SMU location using techniques from Harrelson et al. (1994) with discharge calculations made using Manning's equation. These model derived discharge estimates provided a means to verify those generated by the depth sensors (http://www.lakesuperiorstreams.org/streams/QA_QC.html). Stream depth at Amity was measured by an MPCA owned/operated/maintained ultrasonic distance sensor, and discharge calculated from USGS derived flow rating curves determined by Minnesota USGS and MPCA staff (J. Maygar, MPCA, Duluth, MN 55802).

The Richards-Baker flashiness index (R-B Index) was calculated for each stream using the equation (Baker et al., 2004):

#

$$R - B\ Flashiness\ Index = \frac{\sum_i^n |\Delta qhr|}{\sum_i^n q_i}$$

where q_{hr} is average hourly discharge and q_i is average daily discharge.

Field and water chemistry

Ancillary water quality analyses were collected as per Anderson et al. (2003) in order to directly compare our methods to those used by the MPCA to estimate nutrient and sediment loads from Minnesota's north shore streams into Lake Superior. We collected at least 20 discrete water samples per year during base-flow, spring snowmelt runoff and rainstorm events, as per MPCA protocols, attempting to balance the number of high and low flow observations. Typically, 1.2 cm of rain during a < 24 hr period was used to define an event. Grab samples were collected near the SMU, mid-stream or centroid during low to medium flows, but ~ 1.5 m from the stream bank using a sampling pole with attached 1L bottle during high flows due to safety issues. Samples were collected using bottles that had been pre-rinsed 3X with ambient water before sample collection. Discrete water samples were initially collected at Kingsbury Creek at various points along the hydrograph using an ISCO 6712 slaved to the YSI 6820 stream elevation sensor.

Water samples were analyzed for total phosphorus (TP), total nitrogen (TN), ammoniumnitrogen (NH_4-N), nitrate/nitrite-nitrogen (NO_3/NO_2-N) by FIA/colorimetry using a Lachat autoanalyzer; the anions Cl^-, and SO_4^- by ion chromatography; True color was determined spectrophotometrically (440 nm wavelength) calibrated against Pt-Co standards. Nephelometric turbidity was measured using a HACH 2100P calibrated with Formazin standards (nephelometric turbidity units or NTRU) (APHA, 199;, Ameel et al., 1998; USGS, 2005).

The TSS method was used instead of the USGS suspended sediment concentration (SSC) method (Gray et al., 2000). TSS and SSC are both gravimetric determinations that involve filtering a known sample volume through a glass fiber filter and drying the material collected on the filter to a constant weight. Experience has shown that filter type is important. APHA Standard Methods (1995) specifically lists both Whatman 934-AH and Gelman A/E as acceptable glass fiber filters. The NRRI Central Analytical Laboratory has traditionally used Whatman GF/C filters and has passed performance evaluation testing using those filters. However, from these data, it is important that filter type be recorded during any extended study and that the type not be changed during the study.

The TSS method uses a sub-sample while SSC involves filtering the entire volume. Direct comparisons between the two methods have determined that TSS can underestimate sediment concentrations if composed of coarser particles (e.g. sand) but tend to be comparable for finer suspended sediments (Gray et al., 2000). In this study we chose the TSS method for several reasons. First, TSS data are more easily integrated into the long-term data already collected in this region by the Western Lake Superior Sanitary District (WLSSD), MPCA, the US Environmental Protection Agency Mid-Continent Ecology Laboratory, and several University of Minnesota-Duluth researchers. Second, the high clay content in this region often results in prohibitively long processing times for SSC measures (i.e. multiple filters), that can be logistically prohibitive unless resorting to small sample size that in turn magnifies sampling errors. Lastly, the majority of particles causing increased turbidity in these streams are due to smaller, clay-sized particles, and therefore, our best professional judgment was to use TSS, with careful attention paid to sample mixing during the filtration process, as the best way to estimate the suspended sediment concentration.

Data Summaries

Continuous turbidity sensor data were processed to exclude anomalous readings due to sensor bio-fouling, probe malfunctions, and sediment deposition within the SMU housing (details at http://www.lakesuperiorstreams.org/streams/QA_QC.html). Use of the data visualization tool (DVT) available on the website allowed data assessment in context with the other measured parameters. Once anomalous readings were excluded, the data were summarized as hourly and daily means, minimum, maximum, median, and standard deviations. A standard deviation of ± 3 NTRUs prompted a review of the measured values. Data were generally not excluded unless a known problem existed and in most instances the high variability reflected the flashy nature of these streams with turbidity and Q responding quickly to rain events. Average hourly rather than instantaneous sensor turbidity data were used in the comparison between in-stream and laboratory turbidity. Hourly averages help overcome the variability inherent in instantaneous measures of this parameter.

Load determinations

Linear regression analyses were performed on the manually collected data using STATISTICA (V. 7.1, StatSoft, Inc., 2005). to generate the predictive model for turbidity versus TSS. Stream specific regressions were based on TSS and turbidity samples collected from 2002-2006 (n = 80 to 116). Both natural log (Ln) and Log_{10} transformations were used to normalize the data. A transformation-bias correction procedure (Helsel and Hirsch, 2002; Jastrum et al., 2009) was applied to the re-transformed estimates of TSS. This procedure uses the mean of the re-transformed residuals and essentially "smears" the average error estimate over all estimates.

Suspended sediment loads were determined by summing the products of average daily flow and turbidity-derived TSS concentration according to each stream turbidity vs. TSS relationship:

$$TSS = \Sigma\ [a + b \times \text{turbidity}\ (t)] \times \Delta t \times \Delta\ \text{volume};$$

where a + b x turbidity is the concentration regression line to transform turbidity into TSS and t = time.

The lower and higher predicated values based on the 95% confidence interval were plotted, and the line equations derived for both the upper and lower limits. The predicted TSS values were then back-transformed into mg L^{-1} to provide both and lower and upper 95% confidence intervals for predicted values.

FLUX Stream Load Computations (V 5.1) was used to estimate annual and event loads using average daily flow data and discrete water quality samples using the models and coefficient of variance criteria used by the MPCA (J. Anderson pers. comm.; Anderson et al., 2003).

Results

The exact location of each SMU within a watershed was chosen based upon considerations of security, stability regarding anticipated road and bridge construction activities, and on upstream land use characteristics, resulting in the Chester and Tischer units being placed higher up within the watershed above the escarpment. Streams generally flow perpendicular to Lake Superior flowing from headwater altitudes of 550 m, over the escarpment of the Duluth Gabbro Complex, a large sill that extends 240 km northeast from Duluth (Taylor, 1964) then down to the lake at 235 m. The Amity and Kingsbury stations were located below the escarpment. Because of this, summary interpretations as to water quality differences between streams must be done with caution although in all cases the watershed area above each SMU was > 90% of the total watershed area (**Table 2.2**). Although located within the Duluth city limits these watersheds range from only 2% to 29% urban land cover. Amity Creek, the largest watershed, is 71% forested and even the most urbanized, Tischer Creek, is 53% forested.

Table 2.2. Percent land cover characteristics for the Duluth-area watersheds (Fitzpatrick et al., 2006; Anderson et al., 2003) and watershed area above the stream monitoring units (Minnesota DNR, 1999).

Stream	Forest	Grass	Urban	Shrub	Open water	Developed rural	Wet land	Total area (km^2)	% imper-vious 2003	Area above sensors (km^2)	Area above sensors as % total watershed area
Amity	71	19	2	2	1.0	2	3	43.3	6	42.5	98
Chester	49	10	22	12	0.3	2	5	17.4	7	15.6	90
Kingsbury	36	18	18	19	0.4	2	7	23.3	16	22.6	98
Tischer	53	6	29	3	0.5	5	4	18.9	13	18.4	98

Annual hydrographs for the two study years (**Figure 2.3**) show similar average daily flows for all but Chester Creek, the smallest watershed. Total annual precipitation was 89 cm in 2005 and 72 cm in 2006. Snowmelt runoff occurred during late March through early April in both 2005 and 2006 with about 0.6 m and 0.3 m of snow pack at the beginning of the spring thaw in each year respectively. Significant events included a very wet June 2005 (14 cm) and a 10 cm rainfall over a three-day period in early October 2005.

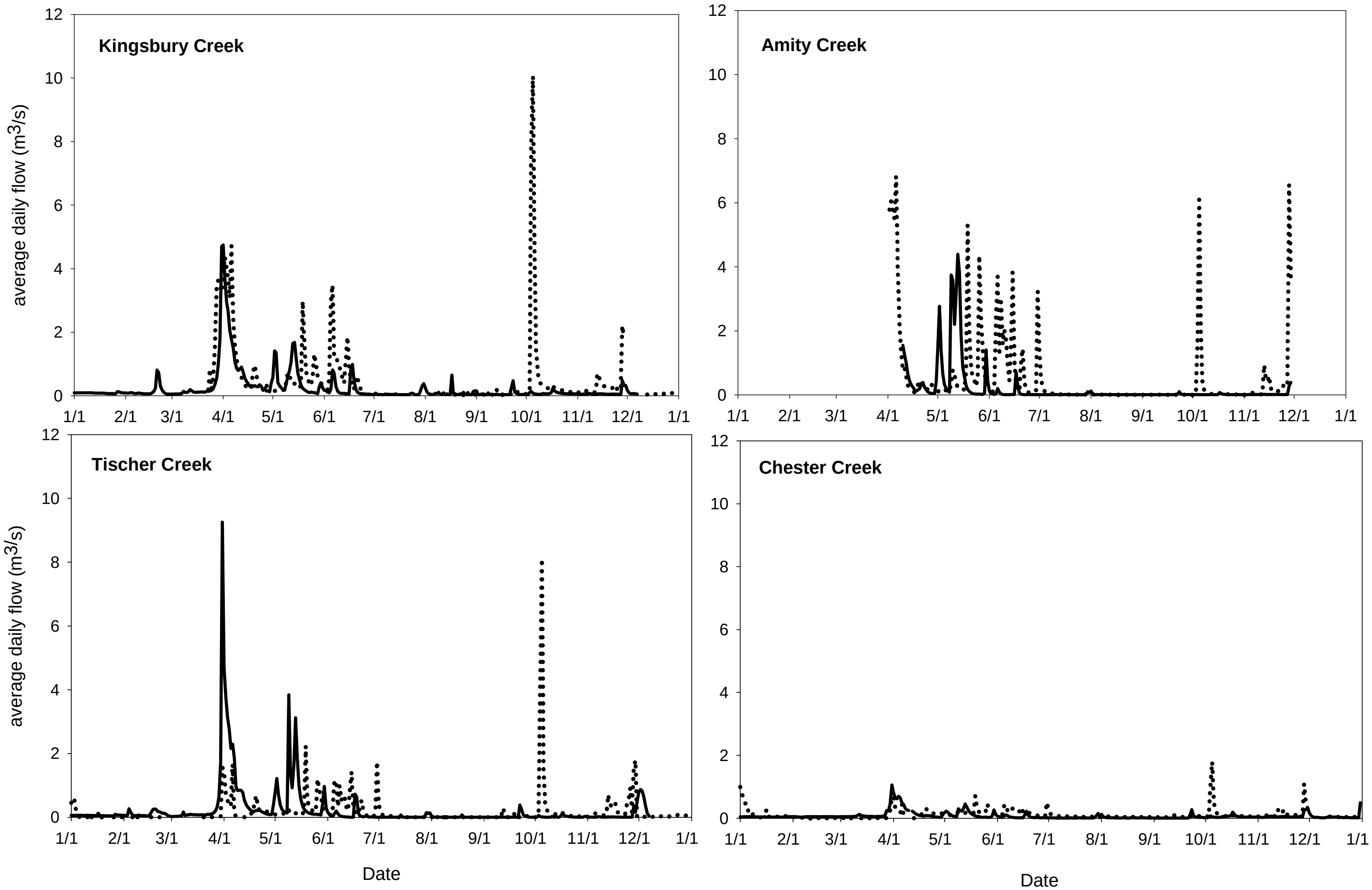

Figure 2.3 Average daily flows ($m^3\ s^{-1}$) for the four Duluth streams during 2005 (dotted line) and 2006 (solid line).

Stream flashiness describes how quickly flow changes from one condition to another. The R-B Flashiness index was calculated for each stream during the 2005 season. This unitless index is based on the total path length of flow divided by the sum of the average daily flow and provides a way to compare flow patterns between streams. Tischer Creek had an index of 2.2, Kingsbury 1.2, Chester 1.0, and Amity 0.9 in 2005. Baker et al. (2004) reported values ranging from 0.54 to 1.2 in Midwestern US streams.

Total Suspended Sediment (TSS) Estimation

Manually collected data from mid-2002 through 2006 were used to establish the turbidity/TSS model. We assumed no major watershed changes occurred during this period. Data gaps resulted from various equipment failures and sometimes loss. The Amity Creek sensor was lost during snow runoff in March-April 2006 and the Kingsbury station was struck by lightning in 2005 resulting in loss of the landline and modem. The Tischer and Chester stations were moved short distances one to three times respectively, for bridge removal and channel modifications. Some turbidity data were lost early in the project because the YSI self-cleaning probes malfunctioned. Sensor data were most complete for all streams (except Amity which was not installed until late 2006) during 2005 and 2006 and these data were used for load calculations.

Another important element of the study involved establishing that the in-stream sensor data were comparable to the manually-collected grab sample data. **Figure 2.4** shows relatively good agreement for all streams, particularly when turbidity is <40 units. This comparison confirmed that measurements made along the stream bottom where the sensors were located, were very similar to vertically integrated grab samples collected from the water column near mid-channel.

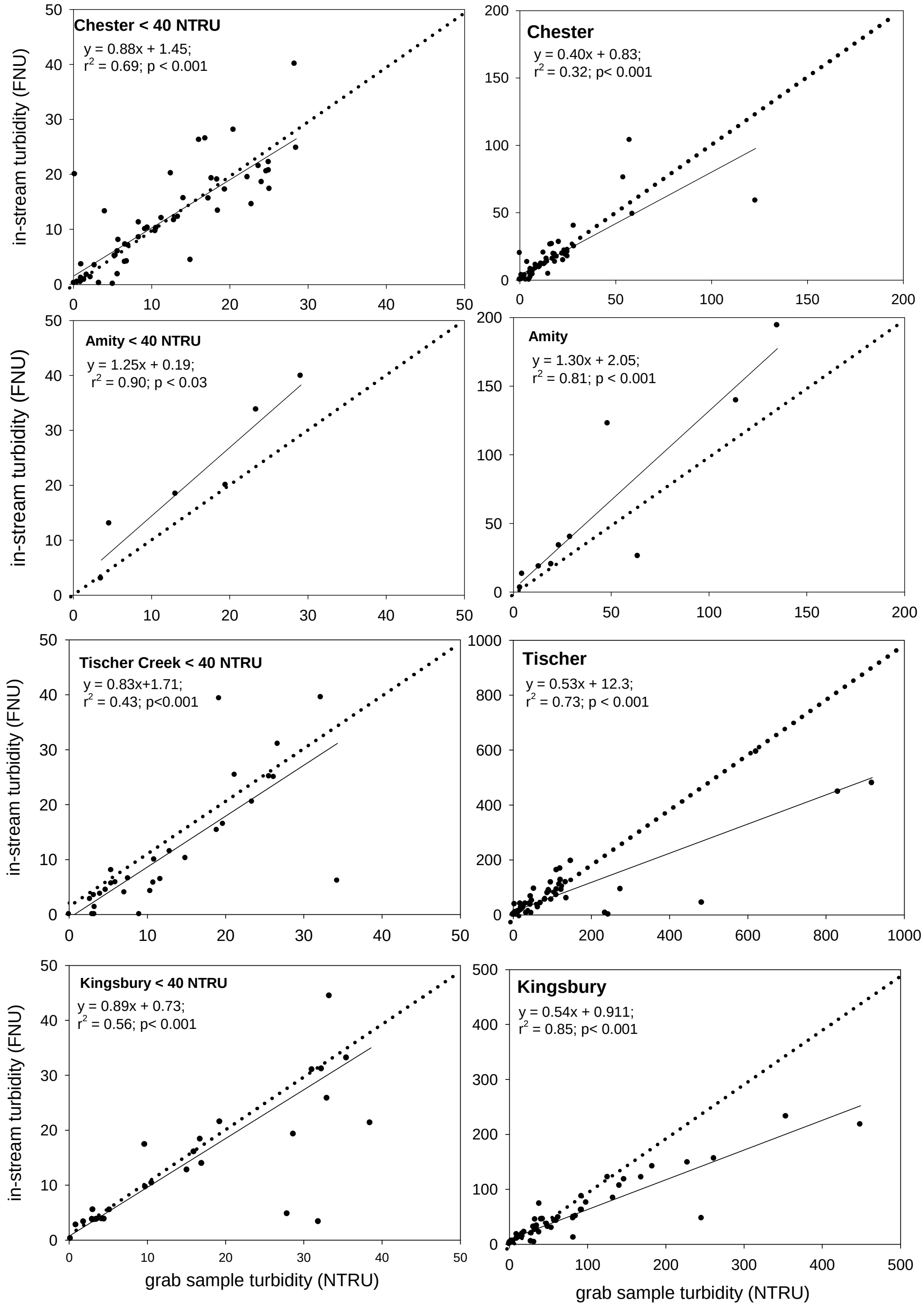

Figure 2.4. Grab sample vs. in-stream turbidity for four streams. The left panels are plots of < 40 NTRU data and the right panels include the full range of turbidity values. The dotted line represents the 1:1 ratio. Note that scales differ between streams to better illustrate the individual data points.

Summary statistics for measures of turbidity, TSS, and total phosphorus (TP) in the four streams from 2002-2006 are shown in **Table 2.3**. Though the data are highly variable there are some apparent differences between the streams. Amity Creek suspended sediments appear to consist of more inorganic than organic particles. Also, Chester Creek turbidity and TSS concentrations were generally lower that the other three streams. The high variability of these data illustrates the importance of collecting data during a wide range of flow conditions.

Table 2.3. Mean ± standard deviation and median results from grab samples collected from 2002 to 2006 in four Duluth, MN trout streams. NTRU turbidity refers to laboratory measures.

Parameter	Amity	Chester	Kingsbury	Tischer
Total suspended solids ($mg\ L^{-1}$)	38 ± 82 13.2 n = 91	15 ±18 9 n = 76	85±134 34 n = 116	67 ±99 35 n =80
Total phosphorus ($\mu g\ L^{-1}$)	68 ± 67 45 n = 87	66 ± 69 50 n = 78	120 ± 134 81 n = 86	154 ±152 90 n = 76
Turbidity (NTRU)	35 ± 69 13 n = 98	17 ± 25 10 n = 82	83 ±100 42 n = 118	83 ±162 28 n = 80

Continuous flow and sonde turbidity plots from the Tischer site during a spring rainfall event (**Figure 2.5**) illustrate how turbidity and flow are often asynchronous with turbidity peaks often occurring before peaks in discharge.

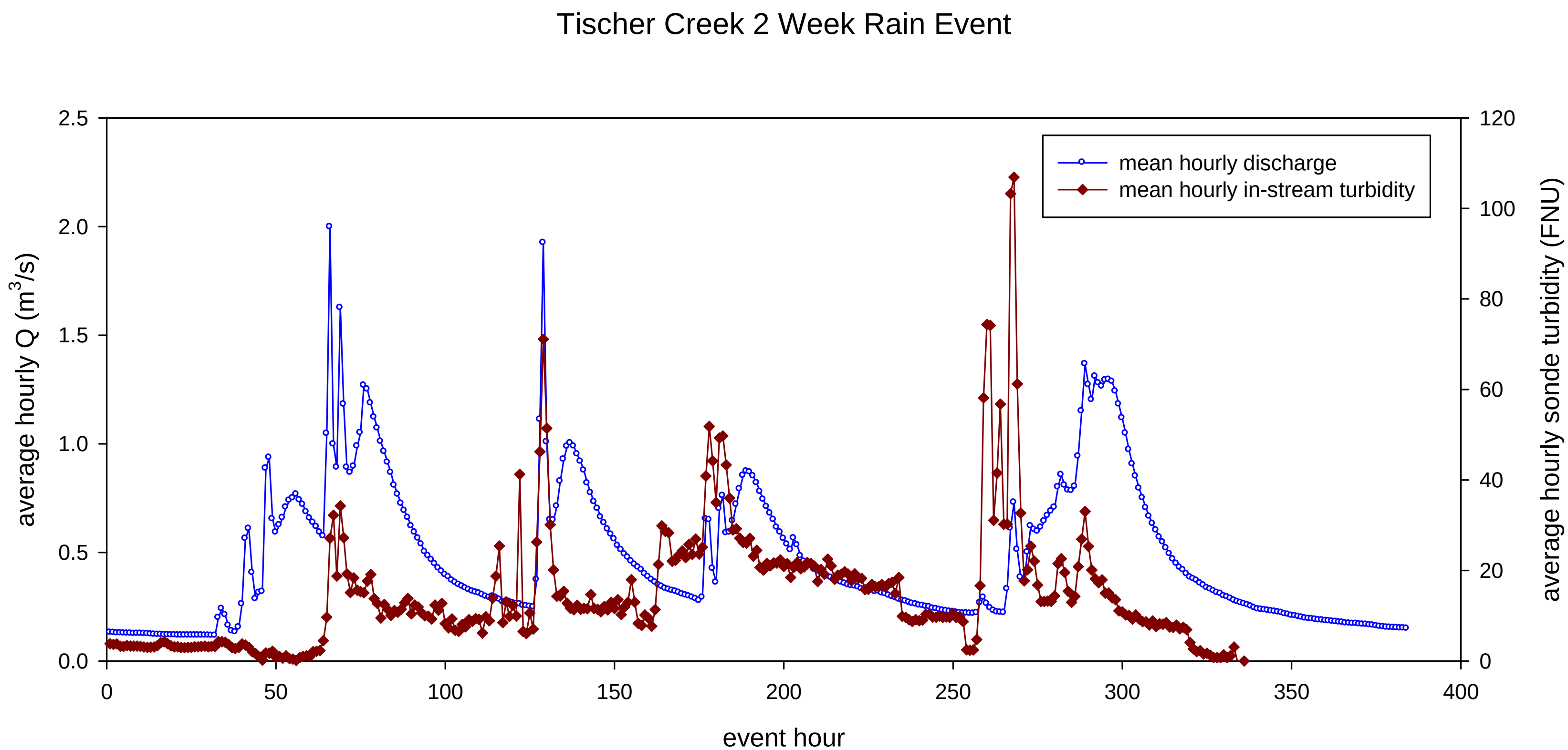

Figure 2.5. Average hourly flow and sonde turbidity data in Tischer Creek during a spring 2005 rain event that illustrates the often asynchronous relationship between the two variables.

Typically, many small streams show an early pulse of sediment on the rising limb before the flow peak reflecting fine-particle resuspension that may differ from the falling hydrograph for the same flow (hysteresis). In this situation, the turbidity may not track suspended sediment as well (i.e. the turbidity:SS ratio has changed from one side of peak flow to the other) thus discharge is often not a good predictor of sediment concentrations. Ideally, a comparison of samples taken both on the rising and falling limb of the hydrograph would illustrate any differences in the relationship that exists over a wide range of flows. Due to the flashy nature of these streams, it was very difficult to collect water samples for TSS during the rising limb. The ISCO sampler on Kingsbury did provide data for a few events collecting discrete samples every two hours once the trigger point, stage height, was reached. TSS mirrored the in-stream turbidity during a rainfall event in May 2005 and both measures tracked flow closely (**Figure 2.6**). This lack of hysteresis was not uncommon, but overall there was an asynchrony between discharge and suspended sediment measures. Antecedent conditions as well as precipitation intensity and duration appear to influence flow and sediment hysteresis in these streams. Unfortunately, the loss of the Kingsbury communications line during an electrical storm prevented further event-based sampling.

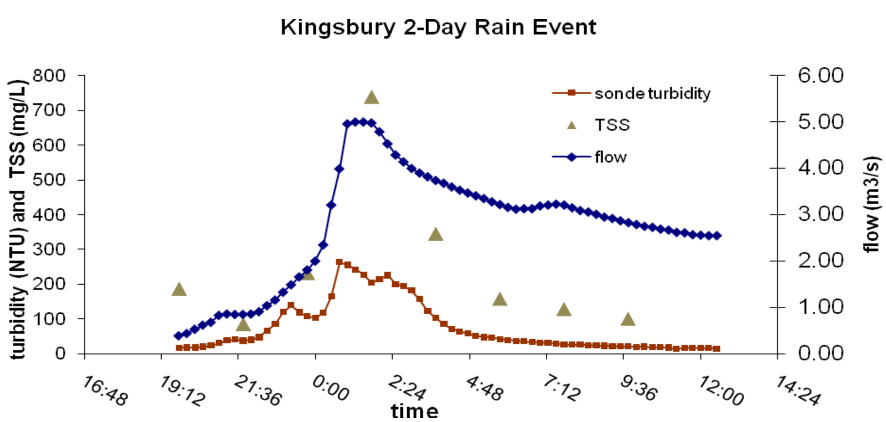

Figure 2.6. Continuous flow and turbidity and grab sample total suspended solids collected using an ISCO sampler during a spring rain event in Kingsbury Creek.

Grab sample data from 2002-2006 were used in regressions of the turbidity-TSS relationships with the assumption that no major changes occurred in the watershed over this time. Multiple linear regression analyses using other continuous data (flow, temperature, and specific electrical conductivity) did not improve the fit of the models. The regression plots for all four streams showed similar slopes of close to 1:1 except for Chester, which was 0.63 (**Figure 2.7**). This underscored the importance of developing stream-specific models.

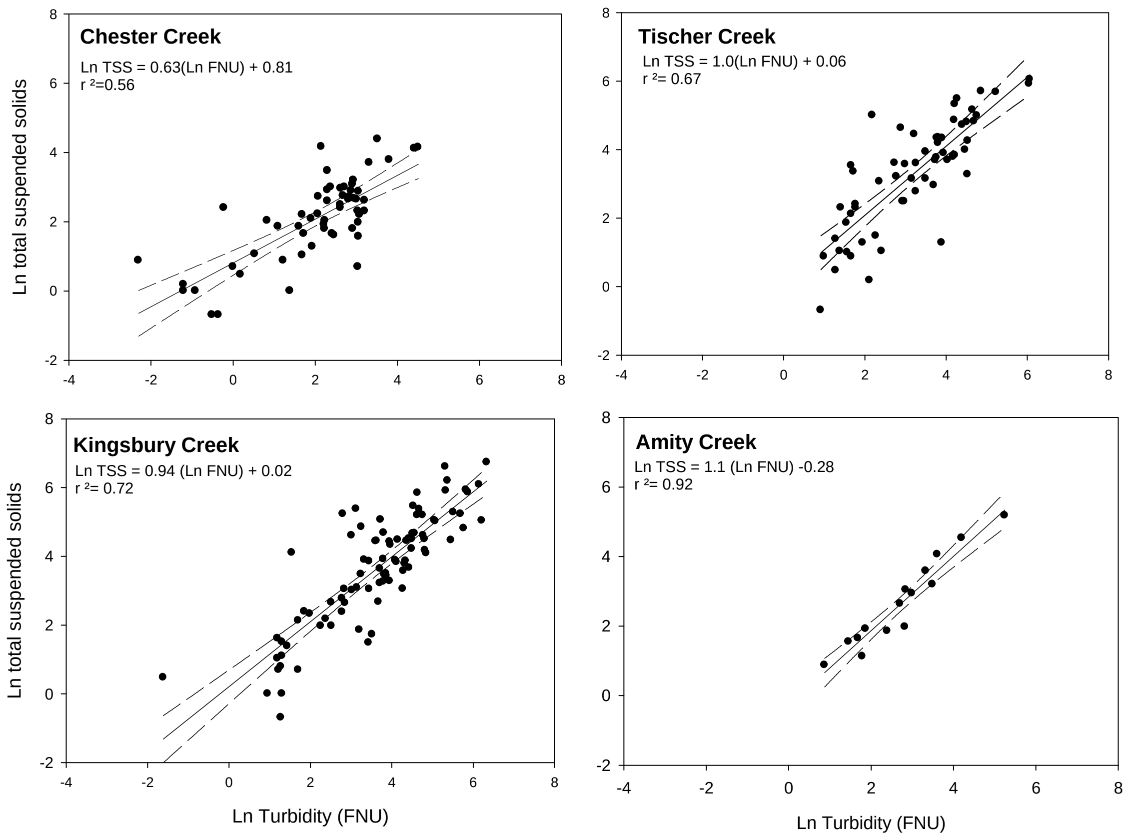

Figure 2.7. Regression plots of continuous in-stream turbidity versus total suspended solid concentrations in the four streams with 95% confidence intervals (dashed lines).

All data, regardless of season or flow regime, were included in each stream model. Natural log transformations provided the best fit for these data.

Phosphorus

Total suspended solids and phosphorus plots showed an approximately 1:2 slope with relatively good correlations with r^2 from 0.49 to 0.76 ($p<0.001$; **Figure 2.8**) indicating a strong relationship between these two variables. Stepwise multiple linear regressions that included the continuously measured variables of Q, EC@25, temperature, and turbidity did not improve the model significantly, so a simple regression model was used. Chester Creek was again most different from the other three streams in terms of TP/TSS (slope) being about 20% lower i.e. less TP per unit TSS and higher variability.

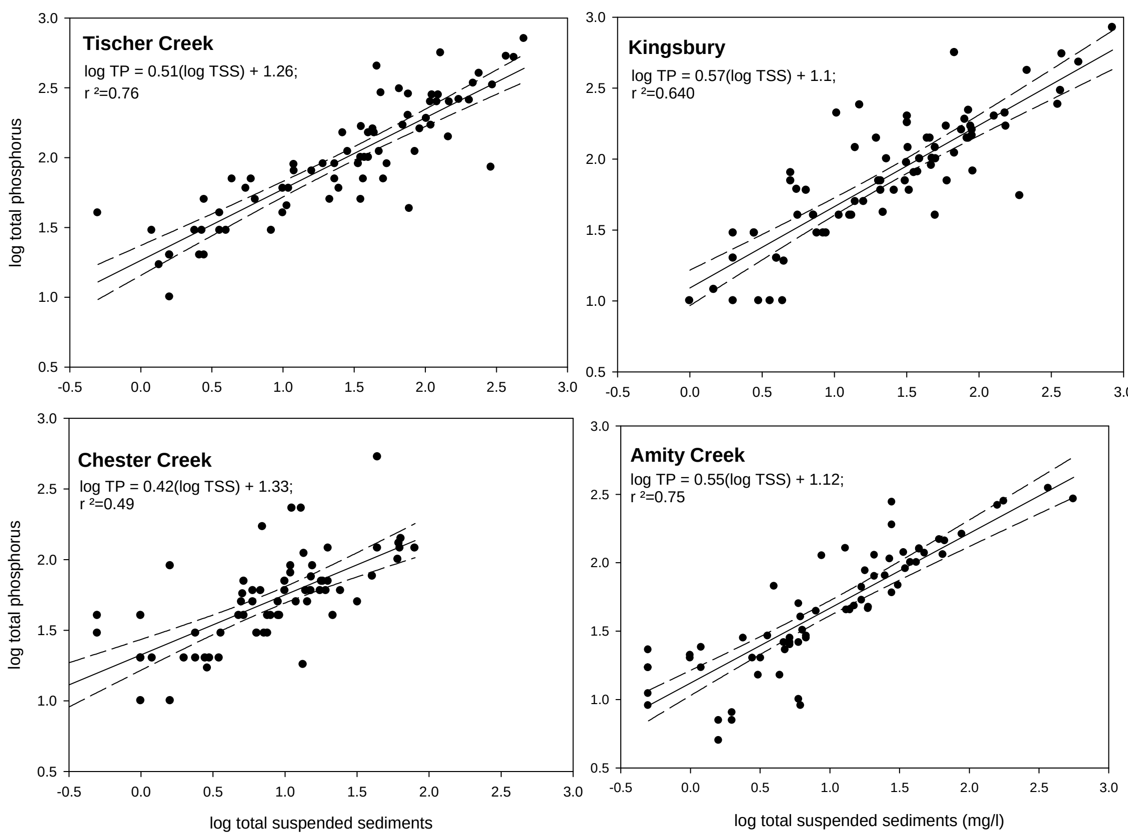

Figure 2.8. Total suspended sediments vs. total phosphorus for each of the streams with 95% confidence intervals (dashed lines).

The log transformed TP versus turbidity relationships were less robust but still significant ($p < 0.001$; **Figure 2.9**). These models were used to estimate TP concentrations and loads. As with TP/TSS, Chester Creek had the lowest slope for TP/turbidity suggesting lower TP per unit turbidity. In addition Chester Creek TSS concentrations were much lower (15 ± 18 mg L^{-1}) than the other streams. Chester TSS ranged from 0 to 80 mg L^{-1} while the other streams often experienced concentrations > 100 mg $L^{-1.}$

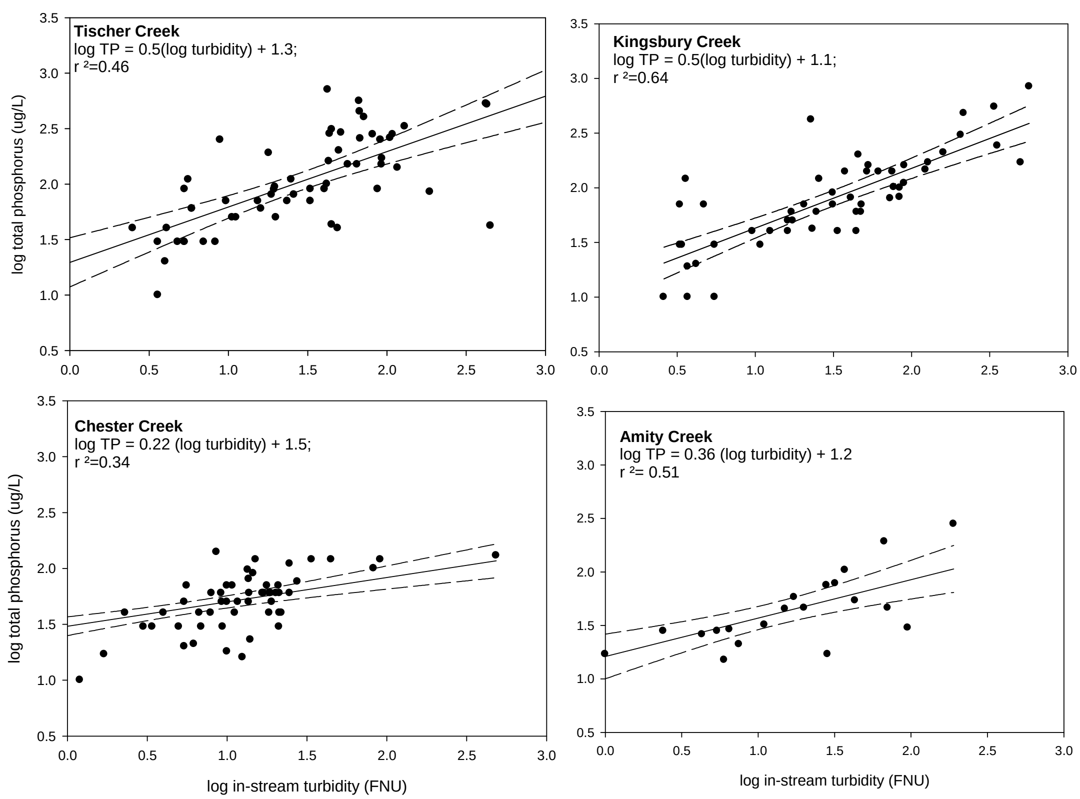

Figure 2.9. Log turbidity versus log total phosphorus plots from Tischer, Kingsbury and Chester Creeks with 95% confidence intervals (dashed lines).

Load Calculations

To correct for the underestimation of the predicted values following back-transformation, we used a smearing estimator as described in Helsel and Hirsch (2002). The smearing estimator “smears” the magnitude of the residuals across the range of x. The result is a slightly higher predicted value across the range of values (**Figure 2.10**).

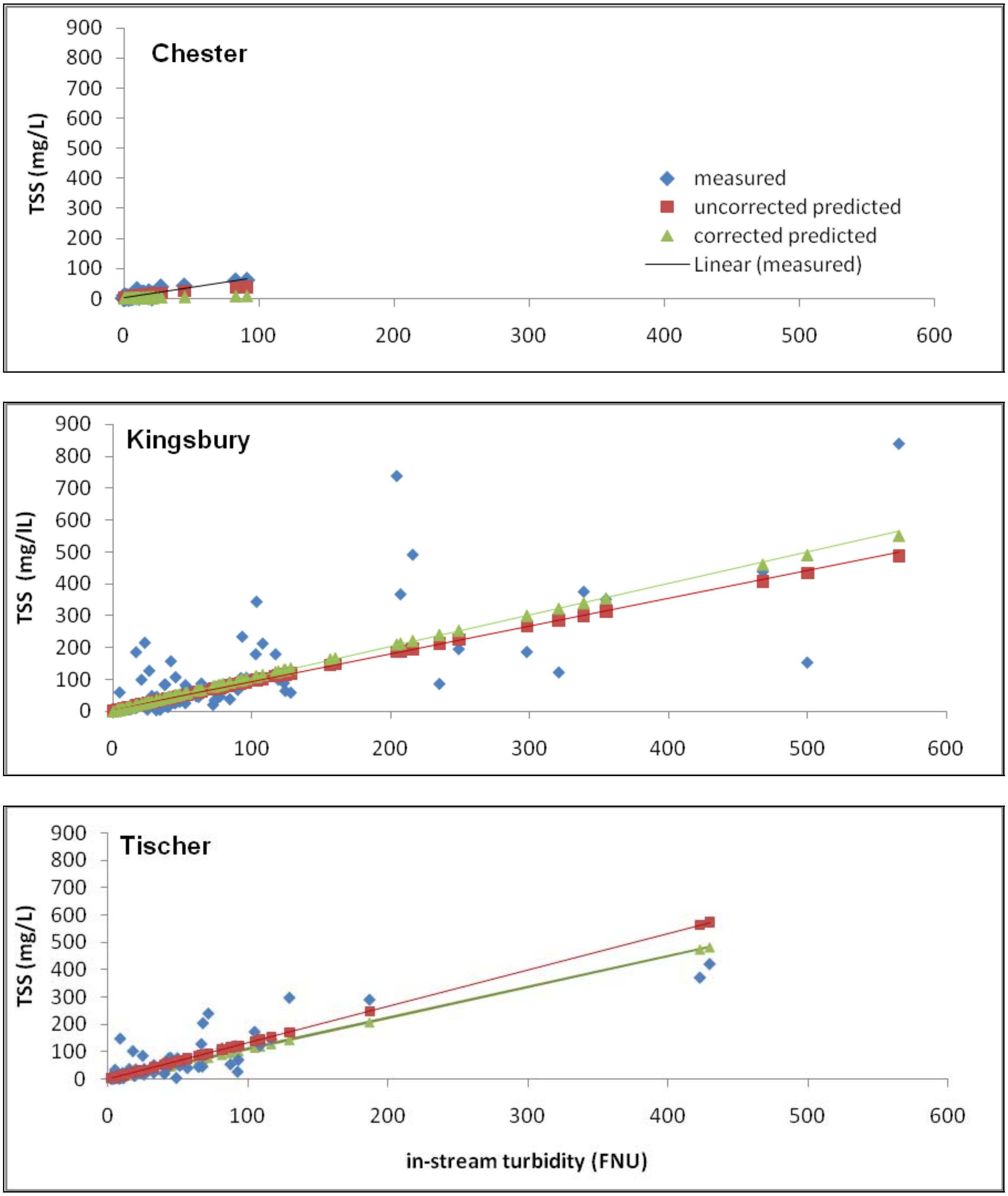

Figure 2.10. Graph plotting in-stream turbidity against TSS from Kingsbury Creek with the regression plots for both the corrected and uncorrected back transformed data.

A correction factor for each regression model was applied to the calculated TSS and resulting load estimates for both Kingsbury (correction factor = 1.13) and Tischer (correction factor = 1.01). The correction factor for Chester (0.22) was much lower than Kingsbury and Tischer most likely because of the low range of TSS and turbidity values. Amity also had too few data to apply this technique. Therefore, corrected sediment load estimates were only made for Kingsbury Creek and Tischer Creek.

Table 2.4 compares the results from the surrogate-derived loads to those derived using the FLUX model for 2005 and 2006. In all cases FLUX estimates exceeded those derived using the turbidity surrogate with relative percent differences from + 53 to + 354. FLUX results for the Duluth Streams data were made using models 2 and 3, the ratio estimator models. While FLUX is a good tool for using a limited amount of grab sample data to estimate constituent loads for an entire year, it appears to overestimate loads in these small, flashy streams. One reason may be the lack of data collected from the rising and falling limbs of hydrographs. FLUX, if not provided enough TSS data, assumes a linear correlation between Q and sediment concentration. However, due to hysteresis and/or lack of data, FLUX cannot account for potentially higher sediment concentrations prior to the occurrence of peak flow. This is not a problem *per se* with the models but rather a problem due to lack of measured sediment concentrations across a wide range of flows. Sampling often occurs past peak flows in these flashy streams due to their short duration, with some peak flows only lasting about four hours. FLUX results might be improved by including samples from both the rising and falling limbs of event hydrographs. FLUX provides a measure of model precision, the coefficient of variance (CV). An acceptable CV for a specific model run is <0.1 (though values 0.1 to 0.2 are acceptable) and our FLUX result CVs ranged from 0.06 to 0.21.

Table 2.4. Estimated basin yields and annual loadings of suspended sediments from continuous in-stream turbidity data (hourly means) and FLUX model. Load RPD = [(FLUX- surrogate)/surrogate] x 100. The low to high TSS loads are based on the lower and upper 95% confidence intervals. Note that Amity sensor data was not available for 2005 and 2006 surrogate estimates are based on 52% of annual data and that the Kingsbury surrogate predicted estimates for 2005 are based on just 60% of the year due to loss of data. FLUX derived loads for Amity Creek were made by J. Anderson (MPCA, pers. comm.). The flow weighted mean concentration (FWMC) is calculated by dividing the total load of a pollutant by the total flow, for the entire year.

				Turbidity-derived			FLUX-derived			
Stream		% year	Total Volume (HM^3)	TSS load (low – high) ($kg\ yr^{-1}$)	TSS yield ($10^5 kg\ km^{-2}\ yr^{-1}$)	FWMC ($mg\ L^{-1}$)	TSS load ($kg\ yr^{-1}$)	TSS Yield ($10^5 kg\ km^{-2} yr^{-1}$)	FWMC ($mg\ L^{-1}$)	TSS Load RPD (%)
Amity	2005	-	-	-	-	-	251,492	0.060	25	-
	2006	52	4.0	162,437 (95,468 – 253,260)	0.040	41	167,844	0.040	26	+3
Chester	2005	94	3.4	20,283 (15,528-27,012)	0.010	6.0	92,026	0.060	26	+354
	2006	100	2.3	14,670 (11,221-19,535)	0.010	6.0	23,130	0.010	10	+58
Kingsbury	2005	60	13.0	323,831 (322,224 - 610,006)	0.14	25	671,367	0.30	51	+107
	2006	93	7.9	110,238 (107,181-201,774)	0.050	14	174,389	0.080	22	+58
Tischer	2005	96	5.1	73,209 (49,453-105,000)	0.040	14	263,830	0.14	52	+260
	2006	93	6.2	109,561 (82,432-174,740)	0.060	18	377,749	0.21	61	+245

Phosphorus loads were also compared using the two methods and the surrogate-derived loads were again much lower than those from FLUX. All FLUX model runs for TP loads had adequate CVs (i.e. < 0.1). Compared to the TSS results, the surrogate-derived TP loads (**Table 2.5**) showed better agreement with the FLUX estimates though in all but one case (Kingsbury 2006) the FLUX results were higher. Watershed yields of TP ranged from 8 to 39 kg km^{-2} yr^{-1} in 2005 and 6 to 25 kg km^{-2} yr^{-1} yr in 2006.

Table 2.5. A comparison of total phosphorus (TP) loads estimated using the turbidity surrogate and the FLUX model. The Amity FLUX loads were provided by J. Anderson (MPCA, pers. comm.). No surrogate-derived TP were made for Amity 2005 due to the lack of sensor data. RPD = [(FLUX-surrogate)/surrogate] x 100.

		Turbidity –derived TP (kg yr^{-1}	FLUX TP (kg yr^{-1})	TP Load RPD (%)
Chester	2005	135	226	+67
	2006	94	102	+9.0
Kingsbury	2005	882	960	+9.0
	2006	375	306	-18
Tischer	2005	310	580	+87
	2006	467	686	+47
Amity	2005	-	652	-
	2006	310	423	+36

Table 2.6 shows several examples of the importance of acquiring high frequency turbidity data during very short term storm events and during spring snow melt runoff. In June 2005 the Duluth area received cumulatively over 13 cm of rain during five events. During October of that year a three-day rain event totaled 11 cm. The 2006 snow melt was particularly short but intense with approximately 30 cm of snow melting over a nine-day period. The in-stream sensors are extremely useful during runoff events when collecting frequent grab samples is potentially dangerous, as well as expensive in terms of labor.

Table 2.6. Event based estimates of discharge, sediment and phosphorus loads with percent of annual for selected events in 2005 and 2006. The percent of annual loading per event were not determined for Amity because turbidity data were not available for much of 2005 and 2006.

	Total volume (HM^3)	% annual discharge	TSS load (kg/event)	% annual TSS load	TP load (kg/event)	% annual TP load
2006 snowmelt						
Kingsbury	3.4	43	64,475	58	179	48
Tischer	2.3	37	63,474	58	215	46
Chester	0.80	35	5,396	37	33	35
June 2005 rain event						
Kingsbury	1.8	14	62,505	19	136	15
Tischer	0.90	18	15,339	21	71	23
Chester	0.50	14	3,541	17	21	16
Oct 2005 rain event						
Kingsbury	2.9	22	175,755	54	297	34
Tischer	1.0	20	22,097	30	76	25
Chester	0.50	14	3,947	19	21	16
Amity	0.90	9.0	106,917	-	151	-

Spring snow melt discharge accounted for 37 to 58% of the TSS loads and 35 - 48% of the TP loads from these streams. The 2006 snow melt period lasted approximately 30 days or 8% of the year. These results support an old adage "90% of the transport takes place during 10% of the time (Horowitz, 2008)".

We did not assess particle size distribution during this study and there is the possibility that the relationship of turbidity to TSS, and turbidity to TP changes with particle size. Particle size can affect scattering, with smaller particles being much more effective (Gippel, 1989). Larger particles scatter less light than an equivalent (by weight) amount of smaller particles. Certainly, a broader range and frequency of TSS and TP data to calibrate the turbidity surrogate model would improve the accuracy of the estimated concentrations and loads across the year.

Conclusions

Turbidity in these four streams is highly dynamic and using in-stream sensors provides a means to assess these fluctuations over a wide range of flows. When coupled with gauged Q the turbidity surrogate yielded a more accurate estimate of FWMC and annual loads of TSS and TP than FLUX. Also, individual streams have different TSS/turbidity, TP/turbidity, and TP/TSS ratios in grab samples of water. These ratios may also vary for a particular stream for different hydrologic regimes, and even a particular event. To adequately assess sediment and related nutrient concentrations and determine loads, data from a wide range of flows are required. The turbidity regression model is based on a relatively small number of grab samples but the load estimate is "refined" by 10,000s of turbidity measurements. We were able to determine relationships between in-stream measurements and subsequently estimate sediment and phosphorus loads for major portions of 2003-2006 including all of 2006 for Tischer, Chester, and Kingsbury Creeks. Surrogate-derived suspended sediment load estimates for all streams except one were 1.5 – 4.5 times lower than those derived using the FLUX Model. Much better agreement was seen between the surrogate and the FLUX estimated TP.

Determining accurate annual loads fundamentally requires an annual hydrograph. Measuring stage height in these northern climates is difficult if not impossible at times due to ice cover. One of the biggest challenges was deploying the sensors during the important spring runoff period in these higher gradient streams. Very little discharge and water quality data exist for spring runoff periods in Minnesota streams. Winter sonde use is risky but provides data during the period of highest loads. We were relatively successful in these efforts, particularly during those years when flow and ice conditions allowed us to continue sensor deployment under the ice. In 2006 for example, we were able to collect an entire year's worth of data for Chester, Tischer and Kingsbury Creeks. Unfortunately, the Amity Creek sensors were washed out and severely damaged by debris and ice after an ice dam broke suddenly during the late March 2006 snowmelt, although the sonde was repaired and replaced by summer. In 2003 and 2007, thick ice conditions and resulting lack of flow required us to remove the sensors during the winter prior to ice-out to prevent damage to the sensors.

There is a need for accurate and representative suspended sediment and nutrient data for Minnesota north shore streams. Particular data types and needs include:

- Annual and high flow, suspended sediments and nutrient loading and flow weighted concentration data,
- Frequency distributions and ranges of suspended sediment and nutrient concentrations,
- Relationships between electronic sensor parameters and other water quality parameters e.g. total phosphorus and nitrogen, dissolved nutrients, salts, metals (mercury), and pathogens.

Collection of these data will provide baseline condition status and subsequently enable trend analyses to guide management decisions. They could also help refine regulatory assessments by providing a sound scientific basis for setting suspended sediment related criteria and standards for sensitive trout streams. These data could also fill gaps in the suspended sediment, nutrient, carbon, and particle-associated heavy metal budgets of Lake Superior and in the long term help us to better understand the relationships between watershed characteristics, water quality and climate variables.

CHAPTER 3 - ESTIMATING MERCURY CONCENTRATIONS AND LOADS FROM FOUR WESTERN LAKE SUPERIOR WATERSHEDS USING CONTINUOUS IN-STREAM TURBIDITY MONITORING

Introduction

Two-thirds of the surface waters on Minnesota's 2008 impaired waters list are listed for high mercury levels in fish and water (Minnesota Pollution Control Agency [MPCA] statewide mercury TMDL, March 2007 found at http://www.pca.state.mn.us/water/tmdl/tmdl-mercuryplan.html, accessed 26 Oct 10). Mercury in fish was the leading cause of impairment in Minnesota's surface waters while mercury in the water also ranked among the leading causes of impairment (http://iaspub.epa.gov/tmdl/w305b_report_v6.state?p_state=MN&p_cycle=2006, accessed 26 Oct 10). Ninety-nine percent of the mercury load to Minnesota's lakes and streams is from atmospheric deposition, with 70% originating from anthropogenic sources and the remaining 30% from natural sources. Minnesota's goal is a 93% reduction in overall anthropogenic mercury emissions from 1990 levels (MPCA, 2009).

Although mercury emissions in the US have declined in recent years, background levels in soils and sediments have remained well above natural levels even in remote regions of the Upper Midwest (Weiner et al., 2006; Engstrom et al., 2007). There is increasing evidence that this legacy ("old mercury") mercury is transported to lakes, reservoirs and wetlands by streams and groundwater flows (Krabbenhoft and Babiarz, 1992; Swain et al., 1992; Balogh et al., 1997; Mason and Sullivan, 1998; Brigham et al., 2009). Harris et al. (2007) suggested that hysteresis could affect how contaminated lakes will respond to decreased emissions of mercury (Hg) with recovery slowed by the release of legacy Hg. Conversion of the inorganic mercury from atmospheric deposition to the more toxic and bioaccumulative methyl-mercury occurs within aquatic ecosystems and understanding how much terrestrial mercury is being delivered to these systems is critical to determining how watersheds will respond to reduced mercury emissions (Mason and Sullivan, 1998; Munthe et al., 2007).

Atmospheric deposition of Hg is the primary mode of input to northern Minnesota watersheds and occurs as dry and wet deposition. Dry deposition of mercury is much more important in forested than open areas because of the large surface area presented by foliage (Grigal, 2002). Wet deposition is monitored nationally through the Mercury Deposition Network but measuring dry deposition is difficult (St. Louis et al., 2001) and estimates are primarily made using models (Brigham et al., 2009). Forests, in particular, appear to facilitate the delivery of atmospheric mercury to watersheds by both scavenging mercury from the atmosphere from dry deposition and stomatal uptake of gaseous Hg. Delivery of Hg to the soils occurs via direct precipitation, throughfall and litterfall. Once deposited, onto watershed Hg enters aquatic systems in two major ways: 1) interflow (infiltrated precipitation flowing above the ground water table); and 2) in overland flow (runoff). Direct precipitation into waterbodies plays a relatively small role because much less of a watershed's area is usually surface water. Interflow contributes Hg enriched hydrophobic organic matter from the soil. Runoff may be enriched with mercury from both atmospheric deposition and from particulate matter washed off surfaces. Terrestrial systems have been estimated to contribute from 62 to 80% of all Hg that enters fluvial systems (Swain et al., 1992; Kolka et. al., 1999).

Forest soils have been shown to be a significant sink for atmospherically deposited mercury (St. Louis et al., 2001; Grigal, 2002). Soils form a major pool for Hg that is closely bound to its organic matter and the release of Hg from this pool is controlled both by the decomposition of the soil organic matter and erosion since Hg readily binds to organic particulates. Wiener et al. (2006) found that concentrations of total mercury in A-horizon soils were highly correlated with organic carbon content in heavily forested Voyageurs National Park in northern Minnesota. Total mercury (THg) concentrations in mineral soils along the Minnesota north shore of Lake Superior has previously been reported as 42.8 ng g^{-1} and 363 ng g^{-1} in mineral and organic forest floor material, respectively (Nater and Grigal, 2002) while 20 - 50 ng g^{-1} have been observed in agricultural soils in southern Minnesota (Engstrom et al., 2007).

Mercury mass balance studies in forested areas have shown that most atmospherically deposited mercury is retained within the watershed with estimates from 10-30% of this mercury being exported in runoff (Hurley et al., 1995; Grigal, 2002). Brigham et al. (2009) found that annual fluvial THg export was less than 50% of the annual atmospheric input in watersheds across the US. In pristine watersheds <20% export has been reported (Swain, 1992; Engstrom, 2007). Major factors affecting the transport of mercury to rivers and streams include watershed characteristics such as watershed size, slope, land use and cover, soil types and erosion rates. Kolka et al. (1999) found that watershed geometry, including the amount of upland and peatland present and water sources had the greatest effect on organic carbon and associated Hg transport. Watershed size plays a role in the amount of THg transported into surface waters (Grigal, 2002; Balogh et al., 2005; Engstrom et al., 2007). Areal THg yields generally decrease as watershed size increases and variances in water yield do not account for the difference suggesting that the THg transport processes were less efficient and loss mechanisms such as sedimentation and volatilization are larger in larger watersheds (Grigal, 2002). There is also evidence that legacy mercury is processed differently than newly deposited mercury though the processes are not fully understood (Hintelmann, et al., 2002; Munthie et al., 2007).

Land use practices that disturb soils, including forest harvest (Sorensen et al., 2009) and agriculture (Balogh et al., 2005), have the potential to deliver more Hg bound to sediments to receiving waters while more natural or pristine watersheds that slow water velocity (including wetlands) may deliver more methyl mercury (MeHg). Urban development may increase THg yields because of increased hydrologic connectivity between urban streams and their watersheds. Brigham et al. (2009) measured export of atmospherically deposited Hg exported from the basin as fluvial Hg from two forested and one urban watershed in Wisconsin at 3-8% and 12-22%, respectively.

Seasonal dynamics such as major runoff events from spring snow melt and intense rainfall events are also important. Hurley et al. (1998) estimated that rivers and streams within the Lake Superior basin contributed approximately 33% of the annual load of mercury to Lake Superior with the most occurring during spring snowmelt. Many other studies have found elevated concentrations of THg during periods of high flow (e.g., Iverfeldt and Johansson, 1988; Scherbatskay et al., 1998; Anderson et al., 2003; Mast et al., 2005; Balogh et al., 2003; Bushey et al., 2008; Schuster et al., 2008; Shanley et al., 2008; Dittman et al., 2010). Sampling during high flow events is crucial primarily because of the high inorganic and organic particulate loads during these periods and the mercury associated with those particles (Balogh, 1997; Mason and Sullivan, 1998; Grigal, 2002; Wall et al., 2005; Dittman et al., 2010). Balogh et al. (2003, 2005) Balogh (1997), and Anderson et al. (2003) showed a strong relationship between THg and total suspended sediments (TSS) in several Minnesota streams, particularly during high flow events. Similar results have been observed for urban streams and stormwater. For example, Fulkerson et al. (2007) and Mason and Sullivan (1998) concluded that stormwater particulates were the main form of MeHg in runoff in both Orlando, Florida and an urban Washington, DC river, respectively. Whyte and Kirchner (2000) used the strong correlation between suspended sediment concentration (SSC) and particulate Hg to estimate Hg flux in runoff from an abandoned mine in northern California using continuous in-stream turbidity as a surrogate for SSC.

The Brule, Poplar, Beaver, Knife, Lester, and St. Louis Rivers in the north shore region of western Lake Superior have been listed as impaired due to Hg in fish tissue, presumably derived mostly from watershed sources of anthropogenic mercury. Knowing current conditions to use as a base-line benchmark as well as understanding when mercury flux is greatest would aid in TMDL development for these watersheds. In addition, very little mercury loading data exist for

Lake Superior basin tributaries (Jeremiason et al., 2009). Because THg is closely associated with particulates, turbidity, measured via *in situ* data-logging sensors, could potentially be used to predict THg concentrations during events when manually sampling for mercury is cost-prohibitive, or logistically not feasible.

Therefore, the objectives for this study were: 1) accurately and precisely determine if *in situ*, near-continuous turbidity data could be used to predict particulate-bound mercury concentrations; and 2) if (1) was possible, to use these predicted mercury concentrations to estimate watershed export into Lake Superior. Of primary interest was to quantify how urban and rural development, with associated increased imperviousness and soil disturbance, facilitates the export of mercury into receiving waters.

METHODS

Site Selection

Four Minnesota Department of Natural Resources designated trout streams (Amity, Chester, Tischer, and Kingsbury Creeks) were selected as sites for in-stream monitoring based on usage, geographic coverage of the city, and varieties of watershed land-uses. Further details regarding the LakeSuperiorStreams.org project that provided the basis for the analyses presented in this paper can be found in Axler et al. (2004, 2006) and at http://www.lakesuperiorstreams.org/, accessed 14 Dec 10. We deployed flow and water quality sensors or stream monitoring units in each of the four streams within the Duluth city limits. The stream monitoring unites were located at representative measurement points in the stream cross-section with allowances made for protecting the units from debris, sedimentation (**Figure 3.1**), and vandalism.

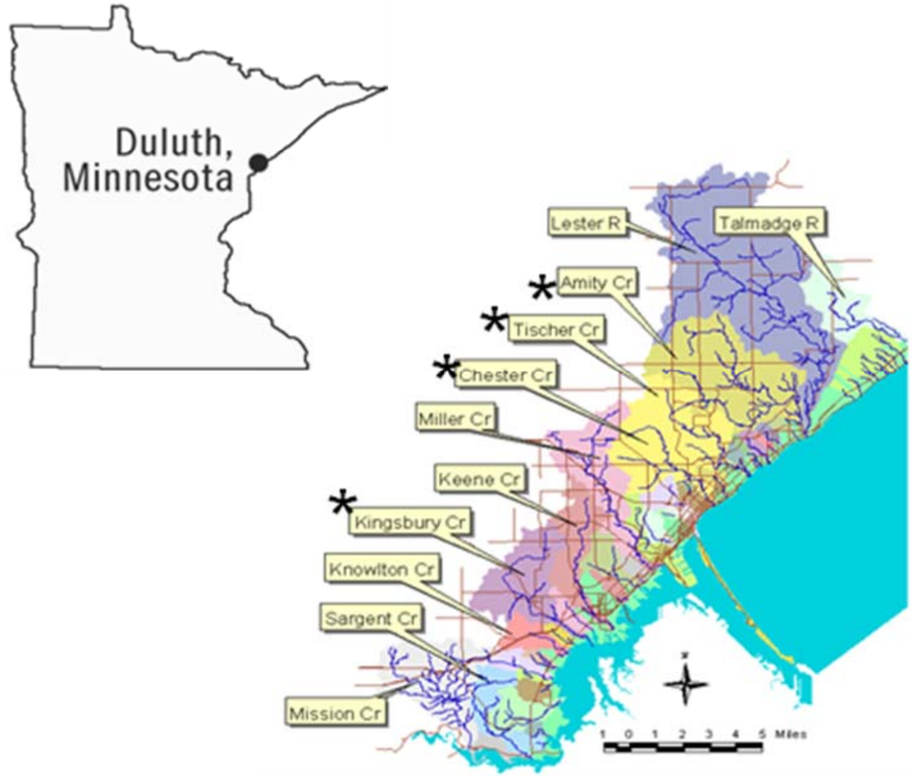

Figure 3.1. Map of Duluth, Minnesota and the major watersheds within the city limits. *indicates the streams monitored for this project.

Automated sensors, YSI (Model 6800 series) and Hydrolab (MS5) measuring temperature, EC25, turbidity (FNU as per USGS, 2005), depth (for flow estimation) were checked approximately weekly for cleaning and/or re-calibration by comparison to an YSI 85 or 556 multi-probe water quality analyzer and bench-measured turbidity with a Hach 2100P. Sensors were inspected, calibrated, and maintained following the manufacturers' recommendations and following USGS (2006) procedures.

Field and water chemistry

Samples for ancillary water quality analyses were collected near the SMU, mid-stream at the point of greatest flow. Samples were collected using a sampling pole with attached 1L bottle that was pre-rinsed with ambient water before collection. Water chemistry analyses followed

American Public Health Association (APHA) (1995) and Ameel et al. (1998) and were performed in the Minnesota Department of Health certified NRRI-UMD laboratory. Water samples were analyzed for the anions Cl^-, and SO_4^- by ion chromatography; true color was determined spectrophotometrically (440 nm wavelength) calibrated against Pt-Co standards; particulate organic matter was measured as loss upon ignition at 550° C (AFDW; dissolved organic carbon was analyzed using the persulfate-ultraviolet oxidation method (Dohrman Carbon Analyzer); total suspended sediment was filtered onto GF/C filters and dried to a constant weight at 103-105°C; and laboratory nephelometric turbidity using a HACH 2100P calibrated with Formazin standards (NTRU) as per USGS (2006).

Ultra-clean mercury sampling and analytical techniques (clean hands/dirty hands into acid-leached glass bottles) were used to collect total (THg), filtered (FHg), and methyl-mercury (MeHg) from four Duluth area streams during both runoff and base flow from 2004 - 2006. Samples from 2004 were collected by personnel from the Western Lake Superior Sanitary District (WLSSD) using similar techniques. Manual samples for total suspended sediment, sulfate, dissolved and particulate organic carbon, chloride, and pH were collected concurrently. Analytical methods for mercury followed Methods 1630 and 1631 (US Environmental Protection Agency [US EPA, 2002; US EPA, 2001]). The sample bottles were transported to and from the sampling locations in double, sealed bags. Samples were analyzed for total mercury (THg) and filtered mercury (FHg) using the cold vapor atomic fluorescence technique by North Shore Analytical, Inc. (Duluth, MN). Methylmercury was determined in the distilled samples using aqueous phase ethylation/gas chromatography with atomic fluorescence detection by the Metropolitan Council Environmental Services Laboratory in Minneapolis, Minnesota (Balogh et al., 2005).

Data Analyses

Continuous turbidity sensor data were screened to exclude anomalous readings from sensor bio-fouling, malfunctions, and sediment deposition. Use of the data visualization tools to view sonde data at http://www.lakesuperiorstreams.org/streams/data/Java/index.html allowed data assessment in the context of other measured parameters including precipitation. Once anomalous readings were excluded, the data were summarized into hourly and daily means, minimum, maximum, median, and standard deviations. Linear and multiple regression analyses were performed on the manually collected data using Microsoft Excel and STATISICA to generate the predictive model for THg. Log $_{10}$ transformations were necessary to normalize some of the data. Predicted daily loads of THg were summed over the entire year to provide estimated annual loads (g yr^{-1}). Estimated annual yields were calculated by dividing the annual loads (g yr^{-1}) by the watershed area (km^2). Flow-weighted mean concentrations (FWMC) were calculated by dividing the annual loads by the total annual discharge volumes (g m^{-1}). Distribution coefficients (K_d) for THg in the water column used to determine the distribution of Hg between filtered (FTHg) and particulate (PTHg) forms were calculated as: $\text{Log}_{10} Kd = \frac{[PTHg]/[TSS]}{[FTHg]}$, in L kg $^{-1}$

Where PTHg (ng L^{-1}) = THg (ng L^{-1}) – FTHg (ng L^{-1}) and TSS in kg L^{-1}.

RESULTS AND DISCUSSION

Watershed characteristics for the four streams are shown in Table 3.1.

Table 3.1. Percent land cover characteristics for the Duluth-area watersheds (Fitzpatrick et al., 2006, Anderson et al., 2003) and watershed area above the stream monitoring units (Minnesota DNR, 1999).

Stream	Forest	Grass	Urban	Shrub	Open water	Developed rural	Wet land	Total area (km^2)	% imper-vious 2003	Area above sensors (km^2)	Area above sensors as % total watershed area
Amity	71	19	2	2	1.0	2	3	43.3	6	42.5	98
Chester	49	10	22	12	0.3	2	5	17.4	7	15.6	90
Kingsbury	36	18	18	19	0.4	2	7	23.3	16	22.6	98
Tischer	53	6	29	3	0.5	5	4	18.9	13	18.4	98

Though located within the Duluth city limits, the streams are all primarily forested. The watershed area above the sensor location represented >90% of the total area.

Measured mercury and ancillary water quality parameters did not vary greatly between these four watersheds. **Figure 3.2** shows the mean and median values for all mercury and ancillary water chemistry measured in each of the four Duluth area trout streams during late 2004 through spring of 2006. All THg values (9-10 samples from each stream in 2004-2006) exceeded the Minnesota Pollution Control Agency mercury standard of 1.3 ng L^{-1} to protect aquatic wildlife health. Average MeHg concentrations were 1% of THg.

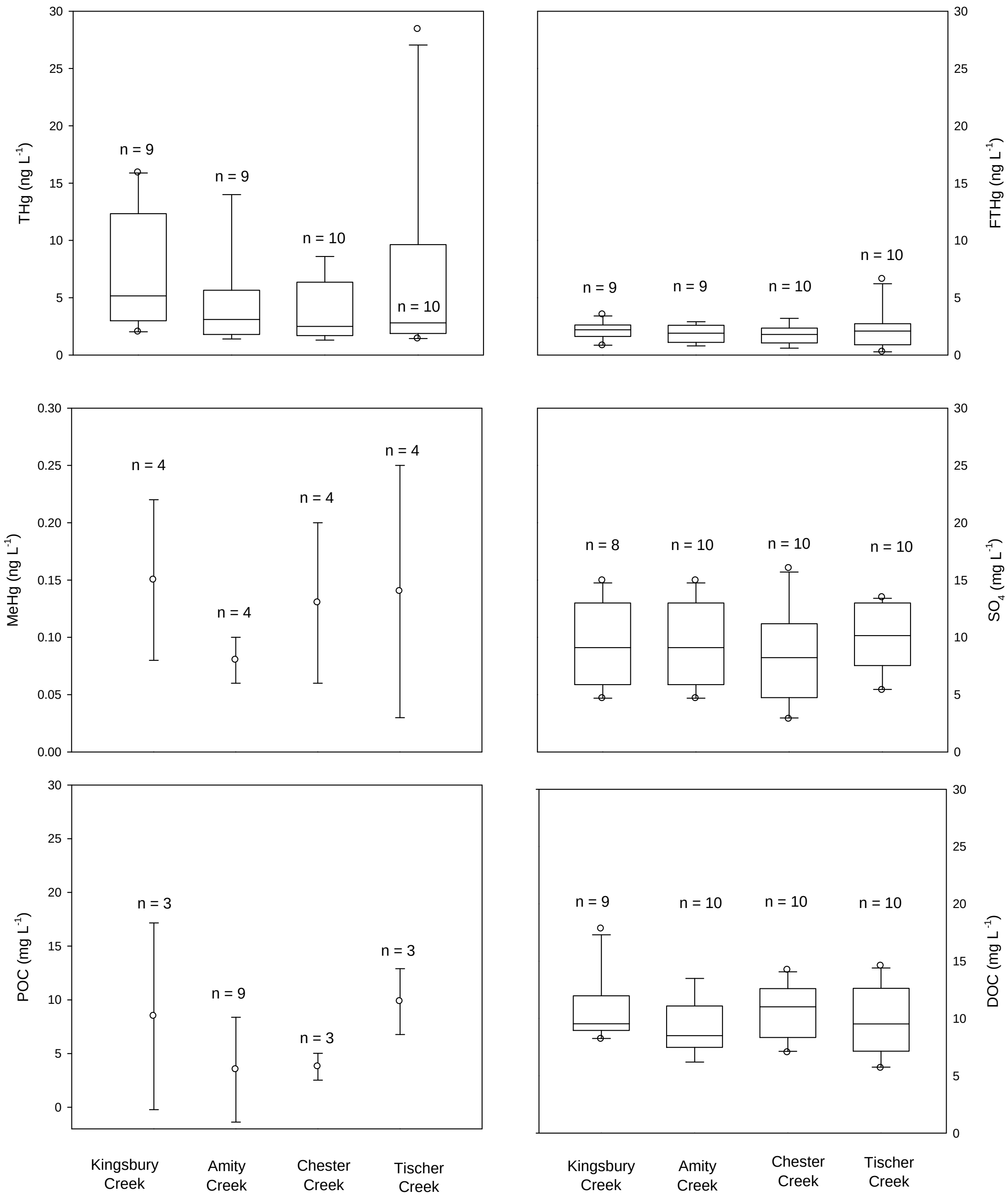

Figure 3.2. Plots showing ranges for total mercury (THg), filtered THg (FHg), total methyl mercury (MeHg), sulfate (SO_4), particulate organic carbon (POC), and dissolved organic carbon (DOC). The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers (error bars) above and below the box indicate the 90th and 10th percentiles. Both MeHg and POC are shown as means ±sd rather than box plots because of low sample numbers. Note that the y-axis scale for the MeHg plot is 100 times less than the other plots.

Mercury concentrations varied throughout 2004 to 2006 in response to climatological and hydrological conditions. The lowest total mercury (THg) values were observed during summer base flow and the highest occurred during an intense June rain in 2005. **Figure 3.3** shows measured THg concentrations grouped by flow regime: base flow, rain event or spring snowmelt for samples collected in 2004-2006.

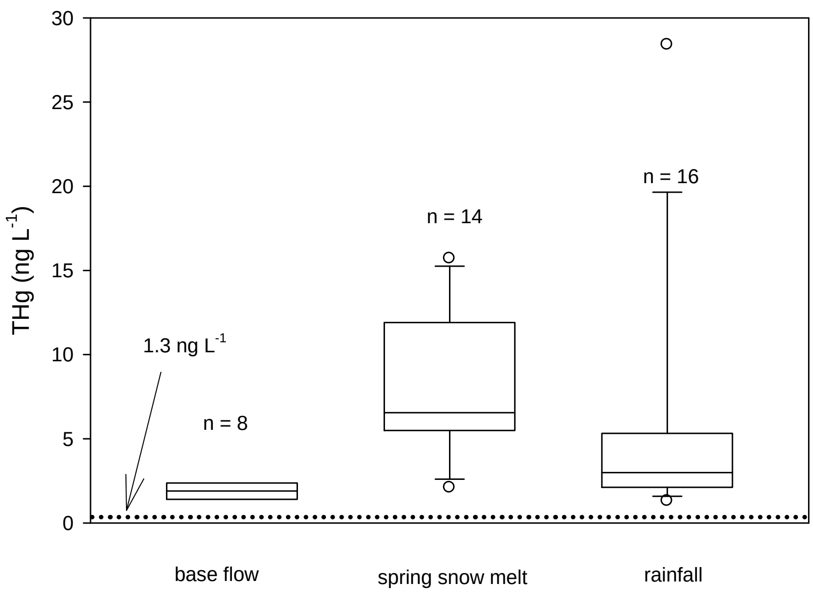

Figure 3.3. Measured total mercury concentrations for the four streams grouped by flow regime. Samples were collected during base flows, spring snow melt, and rainfall storm events, during 2004-2006. 1.3 THg ng L-1 is the MPCA Lake Superior basin standard to protect wildlife health.

Total Hg concentrations found in the Duluth streams were generally similar to those reported for predominately forested watersheds (**Table 3.2**).

Table 3.2. Total mercury (THg) concentrations measured in northern, forested watersheds.

Region	Flow regime	THg (ng L^{-1})	Source
Rocky Mountains	spring snow melt	0.8 – 13.5	Mast et al., 2005
Allequash Creek, Northern Wisconsin	summer	0.5 – 5.5	Krabbenhoft et al., 1995
Sweden	varied seasonally	3.5 to 6.5	Iverfeldt and Johansson, 1988
Boreal forests, Sweden	pre and post timber harvest	4.26 – 4.80	Sorensen et al., 2009
Ontario Precambrian Shield	snow melt	4.6 – 14.6	Allan et al., 2001
	rain –rising limb	6.1 – 13.2	
	rain – falling limb	7.5 – 16.3	
Poplar River, NE MN		2.8 – 3.5	Anderson et al., 2003
St Louis River, NE Minnesota (at Scanlon)	base flow	0.6 – 6.1	Lindgren et al., 2006
Duluth, MN area streams	spring snow melt		
	rain	2.1 – 15.7	This study
	base flow	1.3 – 28.4	
		1.3 – 3.8	

In the Duluth streams both THg and PHg (THg less filtered Hg) concentrations were strongly correlated with TSS (**Figure 3.4**).

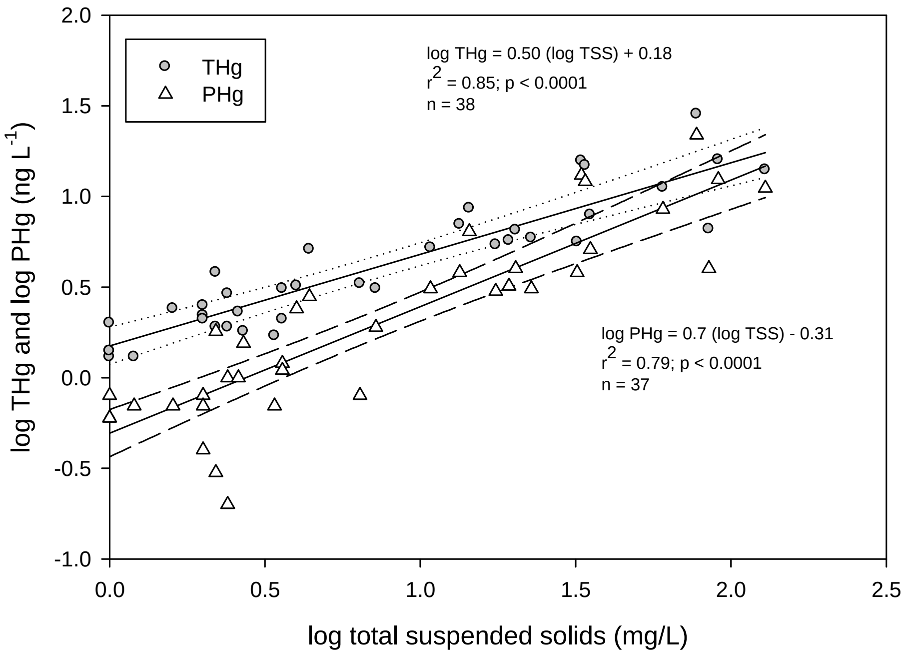

Figure 3.4. Regression plots of total mercury (THg) and particulate mercury (PHg) vs. total suspended sediments (TSS) in the four Duluth, MN trout streams from samples collected during varying flow regimes in 2004-2006 with 95% confidence intervals.

Distribution coefficients, Log K_ds, were calculated for each sample (**Table 3.3**). Higher K_ds suggest a higher affinity of Hg to the particulate phase (Babiarz et al., 1998) and the values observed in the Duluth area streams supported our hypothesis that most of the THg is associated with particles.

Table 3.3. Log_{10} K_d coefficient for several northern US watersheds and this study. Higher log_{10} K_d values indicate that the mercury concentrations associated with particulates are high. Units are L kg^{-1}.

Watershed		Log_{10} Kd	Source
Minnesota 1st order streams		4.7	Fleck, 1999
Wisconsin rivers	spring	4.8	Hurley et al., 2001
	fall	4.9	
Lake Michigan tributaries		5.5	Hurley et al., 1998
Seven Wisconsin Rivers		2.8 to 5.5	Babiarz et al., 1998
Northeastern US streams		4.97 to 5.59	Dittman et al., 2010
Western Lake Superior tributaries		5.2 to 6.6 (mean = 5.8)	This study

Bushey et al. (2008) while targeting Hg species flux during rainfall events in the Adirondack Mountains, New York, did not find a significant correlation between THg and TSS. However, their two study watersheds were very pristine with TSS values less than 10.5 mg $L^{-1}$and they did not analyze spring snow melt runoff events.

Based on previous work relating in-stream turbidity to TSS we developed a model predicting THg concentrations from continuous in-stream turbidity (**Figure 3.5**). A single model was developed that combined data from all streams because the individual stream regression coefficients were not significantly different from each other. Stepwise multiple linear regressions that included the continuously measured variables of flow, EC@25, temperature, and turbidity did not improve the model significantly, so a simple natural log regression model was used:

Log THg = 0.256 (Log turbidity) + 0.469

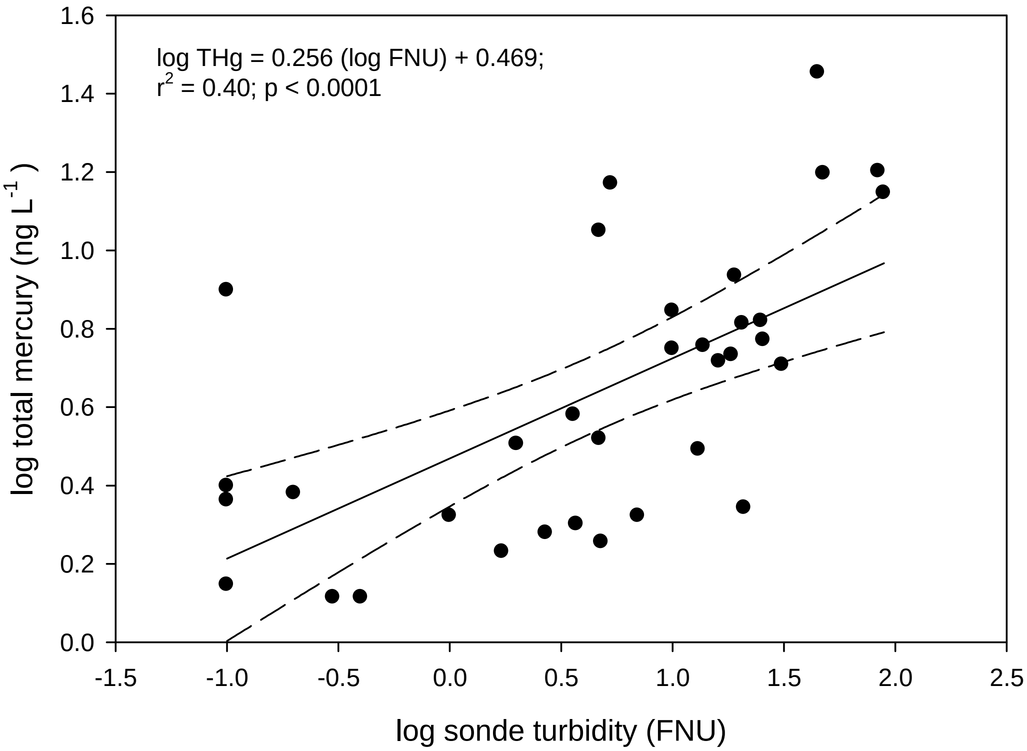

Figure 3.5. In-stream turbidity vs. total mercury concentrations with 95% confidence intervals for all four Duluth area trout streams combined.

A “smearing” bias-correction (Helsel and Hirsch, 2002) factor of 0.99 was applied to the retransformed regression equation to account for the bias introduced when back transforming from natural log to original concentration units. The poorer relationship between THg and turbidity relative to TSS when data from the streams were pooled is due to the variance in the slopes of the TSS vs. turbidity relationship between streams.

THg load calculations (**Table 3.4**) were made by summing estimated daily loads (g L^{-1} day^{-1}) for each period of interest and flow weighted mean concentrations (FWMC) were calculated by dividing average annual concentrations by total annual volume. The annual fluxes estimated for these watersheds, 0.6 to 3.8 µg m^{-2} $year^{-1}$, fall within the range of fluxes summarized by Grigal (2002) where 75% of literature reported fluxes ranged from 1 to 3 µg m^{-2}

yr^{-1}. Brigham et al. (2009) measured fluxes of 0.90 and 0.87 μg m^{-2} y^{-1} in two forested northern Wisconsin streams, while Dittman et al. (2010) measured annual fluxes in four northeastern US watersheds ranging from 1.6 to 6.5 μg m^{-2} y^{-1}.

Table 3.4. Estimated basin yields, annual loadings and flow weighted mean concentrations (FWMC) of THg from continuous in-stream turbidity data. * denotes data representing less than 90% of the water year based on 365 days including ice-covered periods.

Stream		% year reported	Total volume (HM^3)	THg load (g y^{-1})	THg yield (μg m^{-2} y^{-1})	THg FWMC (ng L^{-1})
Amity	2005	--	--	--	--	--
	2006	66	4.0*	23*	0.5*	5.8*
Chester	2005	94	3.5	14	0.9	2.9
	2006	100	2.3	10	0.6	3.5
Kingsbury	2005	60	13.0*	85*	3.8*	10.2*
	2006	93	7.9	43	1.9	6.6
Tischer	2005	96	5.1	23	1.3	5.1
	2006	93	6.2	34	1.8	6.3

Turbidity data were available for >90% of the year for all streams except Kingsbury in 2005 and Amity Creek for both 2005 and 2006. Kingsbury sensor data was lost due to a lightning strike in July 2005 so the Kingsbury load estimates for 2005 are based on 60% of that year. The Amity Creek sensors were not in place until September 2005 and in the spring of 2006 they were washed out and severely damaged by debris and ice. Annual THg loads from the four streams ranged from 10 to 85 g y^{-1}. Annual total mercury surrogate-derived FWMCs all exceed the MPCA standard of 1.3 ng L^{-1} for the Lake Superior basin.

The continuous turbidity and Q data also were used to estimate concentration and load data for major precipitation and runoff events. **Table 3.5** shows several examples of the importance of acquiring high frequency turbidity data during very short term storm events and during spring snow melt runoff.

Table 3.5. Percent of annual TSS and THg loads and total volume for selected events based on turbidity predicted TSS and THg loads and measured discharge.

Event	Stream	% annual TSS	% annual THg	% Total volume
Snow melt 2006	Kingsbury	48	46	43
(~ 8 days late March)	Tischer	55	41	37
	Chester	37	36	33
August 2006 rain	Amity Creek	<1	1	1
(2 days; 2 cm)	Kingsbury	4	3	3
	Tischer	2	2	2
	Chester	3	3	3
June 2005 rain	Kingsbury	15	14	14
(27 days; 14 cm)	Tischer	24	22	18
	Chester	17	16	14
October 2005 rain	Kingsbury	45	26	22
(3 days; 11 cm)	Tischer	31	23	20
	Chester	20	16	14

In June 2005 the Duluth area received over 13 cm of rain during five events. During October of that year a three-day rain event totaled 11 cm. The 2006 snow melt was particularly short but intense with approximately 30 cm of snow melting over a nine-day period. The in-stream sensors are extremely useful during runoff events when collecting frequent grab samples is difficult. The 2006 spring snow melt period contributed 37 to 48% and 36 to 46% of the estimated annual TSS and THg loads respectively and the October 2005 rain event also delivered a large percentage of the total annual loads estimated for that year.

Estimates of five to 25% of atmospheric Hg deposited on the terrestrial portion of the watershed have been shown to reach associated lakes (Grigal, 2002) and less than 50% in all cases in eight streams across the US (Brigham et al., 2009). To our knowledge there are no good estimates of stream THg loads into Lake Superior from its tributaries. For this study we estimated how much of the total mercury deposited onto these watersheds is potentially removed from these watersheds annually. This comparison assumes that there is an unknown release rate of legacy

THg from prior years of deposition. Mercury Deposition Network (http://nadp.sws.uiuc.edu/mdn/ accessed 14 Dec 10) concentrations during the period of 2004-2006 were reported from a station 120 km northeast of Duluth (MN16) and one 72 km to the west (W108). Monthly concentrations were averaged for both stations for the period 2005 to 2006. Concentrations ranged from a minimum of 2.2 ng L^{-1} to a maximum of 110 ng L^{-1} with an overall mean of 12.6 ng L^{-1} (sd = 15.7 ng L^{-1}). These stations record wet deposition in open areas so dry deposition and mercury scavenged by forests is not accounted for. We averaged data from the two stations to derive annual areal loading for each of the watersheds. Total mercury deposited (ng m^{-2}) with precipitation during 2005 and 2006 is shown in **Figure 3.6**.

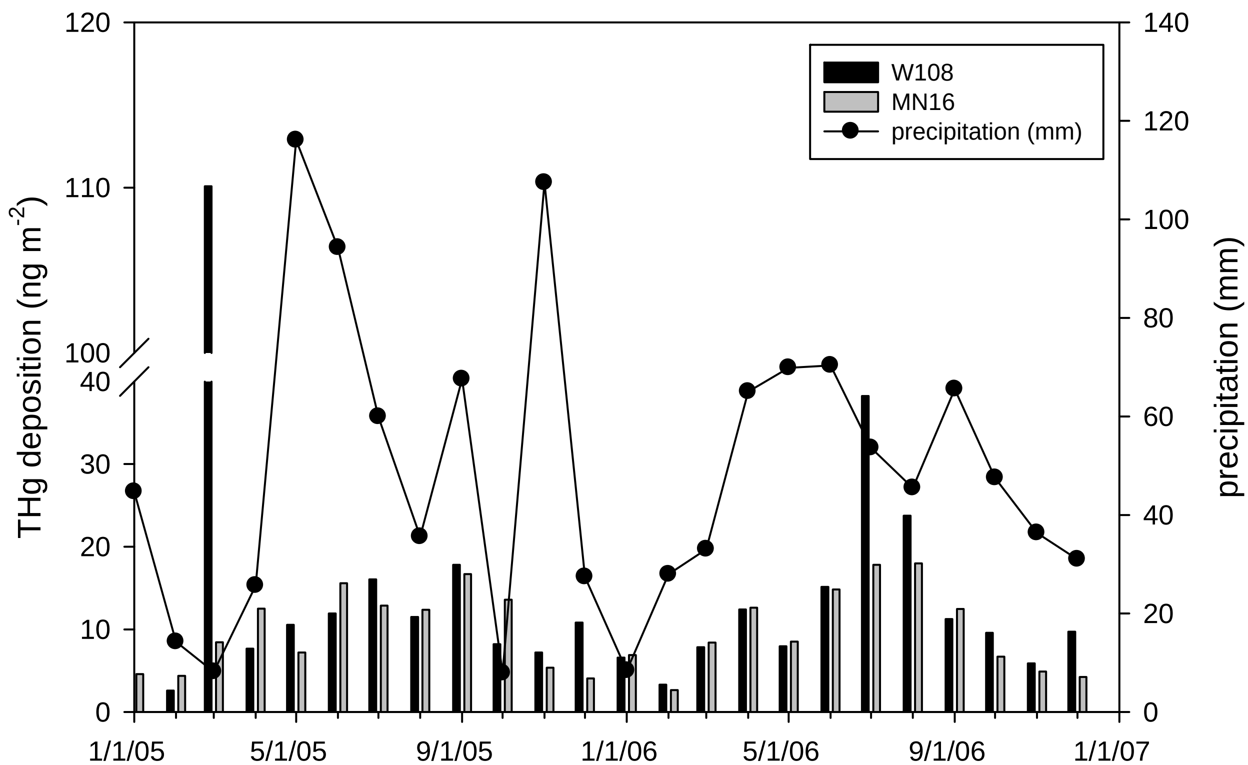

Figure 3.6. Total mercury deposited (wet deposition) and rainfall totals during 2005 and 2006 at Stations W108 and MN16 of the Mercury Deposition Network (MDN).

From these Mercury Deposition Network data assuming dry deposition to be 50% of wet, we estimated atmospheric deposition of THg to be approximately 8.8 µg m^{-2} yr^{-1} for both 2005 and 2006. Dividing areal THg annual loads (μg $m^{-2}yr^{-1}$) by areal loading results in percentage of THg deposition removed though runoff to these streams (**Table 3.6**). This of course does not account for mercury removal through other cycling processes or the movement of legacy mercury from the watershed into the streams. Total yield for all four streams in 2006 was 4.8 μg m^{-2} for a total yield (total of ~ 99 km^2) of 0.5 kg yr^{-1}. Annual loads to Lake Superior were estimated in 2000 to be 280 kg yr^{-1} (Rolfus et al., 2003).

Table 3.6. Surrogate-derived total mercury yields from streams relative to measured THg deposition on an areal basis. Atmospherically deposited THg (dry plus wet) was estimated to be 8.8 μg m^{-2} yr^{-1} for both 2005 and 2006 based on Mercury Deposition Network data.

Stream		Stream yield (μg THg m^{-2} y^{-1})	% of atmospheric THg exported from basin as fluvial Hg
Amity	2005	--	--
	2006	0.5	6.0
Chester	2005	0.9	10
	2006	0.6	7.0
Kingsbury	2005	3.8	43
	2006	1.9	22
Tischer	2005	1.3	15
	2006	1.8	20

Most Duluth streams fall within the 5-25% THg (Grigal, 2002) being delivered annually from terrestrial watersheds to receiving waters during runoff events. Even with legacy mercury in these watersheds these results suggest that most of the Hg deposited annually does not end up in Lake Superior. The 2005 Kingsbury THg yield exceeded that range; possibly because this estimate is based on only 60% of the year and/or that the Kingsbury watershed contains other sources of Hg. In fact, this watershed is in a historically more industrialized area. This estimate also does not account for dry deposition of inorganic mercury that accumulates on surfaces within the watershed and can be delivered via litterfall and throughfall or legacy mercury within soils. In addition, watershed Hg burdens have been presumably been increasing over the past 150 years. It is conceivable that if soils are disturbed by inadequately mitigated development, this legacy mercury may be delivered to the streams during runoff events.

CONCLUSIONS

If a tight relationship exists between total Hg and suspended sediments and turbidity, then continuous, in-stream turbidity can be used as a low cost surrogate for detecting seasonal and annual Hg loads. Near-continuous surrogate data (i.e. ~ 15-minute periods) can lead to a better understanding of the episodic nature of Hg export from these watersheds and combined with concurrent measures of DOC, TSS, and discharge data can help identify streams likely to have high Hg concentrations and define periods of high Hg transport. However, this conclusion is based upon a relatively small number of measured THg values and accuracy would improve if samples from both the rising and falling limb of the hydrograph were collected and analyzed for THg. As with the TSS/turbidity relationships, the THg/turbidity model may be stream specific and these results should be cautiously extrapolated to other northeastern Minnesota and Lake Superior basin streams.

These results provide the first attempt to estimate the delivery of mercury from these small watersheds to Lake Superior. The data presented here do not allow us to directly determine the source of particle bound mercury; whether it is primarily, bank derived and/or bedload (within stream sources) or delivered via runoff from the watershed (washload). They also do not allow us to determine if transported Hg is from recent deposition as opposed to geologic or legacy Hg. However, the mercury-suspended sediment relationship emphasizes the importance of establishing effective watershed management techniques to prevent erosion that will release mercury. Delivery of inorganic mercury from upland areas to riparian zones increases the potential for it to be converted to the more toxic and bioaccumulative methyl-mercury though much is still unknown about the details of these processes in streams, wetlands and groundwater. Climate change, with predicted increases in rainfall intensities (e.g. Novotny and Stefan, 2007) and potential increased erosion rates, therefore, has the potential to increase Hg loads from these sensitive watersheds, even if mercury emissions to the atmosphere and subsequent wet and dry deposition rates are reduced. This highlights the multiple benefits derived from improvements in land use and land cover management in the Lake Superior basin, without which the reduced atmospheric loads of mercury will likely take much longer to be realized in streams and lakes.

BIBLIOGRAPHY

Allan, C.J., A. Heyes, N.T. Roulet, V.L. St. Louis, J.W.M. Rudd. 2001. Spatial and temporal dynamics of mercury in Precambrium Shield upland runoff. Biogeochemistry 53: 13-40.

Ameel, J.J., E.M. Ruzycki, C.J. Owen, R.P. Axler. 1998 (revised 2008). Analytical chemistry and quality assurance procedures for natural water, wastewater, and sediment samples. NRRI/TR-98/28.

APHA. 1995. Standard methods for the examination of water and wastewater, 2120- B. 19th Ed. 1995. American Public Health Association, Washington DC.

Anderson, J., T. Estabrooks, and J. McDonnell. 2000. Duluth metropolitan area streams snowmelt runoff study. Stream Water Quality Assessment Technical Report, March 2000.

Anderson, J. M. Evenson, T. Estabrooks, and B. Wilson. 2003. An assessment of representative Lake Superior basin tributaries 2002. Stream Water Quality Assessment Technical Report, August 2003

Ankcorn, P.D. 2003. Clarifying Turbidity: The potential and limitations of turbidity as a surrogate for water quality monitoring. Proceedings of the 2003 Georgia Water Resources Conference, April 23-24, 2003.

Axler, R., M. Lonsdale, J. Reed, C. Hagley, J. Schomberg, J. Henneck, G. Host, N. Will, E. Ruzycki, G. Sjerven, C. Richards and B. Munson. 2004. DuluthStreams.org: Community partnerships for understanding urban stormwater and water quality issues at the head of the Great Lakes. NRRI Technical Report NRRI/TR-2004/34, December 2004. Natural Resources Research Institute, University of Minnesota Duluth.

Axler, R., C. Hagley, G. Host and J. Schomberg. 2006. LakeSuperiorStreams.org: Making stormwater and stream data come alive for citizens, students, teachers, contractors, resource agencies, decision-makers and scientists. Proceedings US Department of the Interior, US Geological Survey 5th National Water Quality Monitoring Conference, San Jose, CA May 7-11, 2006.

Babiarz, C.L., J.P. Hurley, J.M. Benoit, M.M. Shafer, A.W. Andren, D.A. Webb. 1998. Seasonal influences on partitioning and transport of total and methylmercury in rivers from contrasting watersheds. Biogeochemistry 41: 237-257.

Baker, D.B., P. Richards, T.T. Loftus, and J.W. Kramer. 2004. A new flashiness index: Characteristics and applications to Midwestern rivers and streams. J Am Water Resources Assoc. 40(2):503-522.

Balogh, S.J. 1997. Mercury and suspended sediment loadings in the Lower Minnesota River. Environ. Sci. Technol 31:198-202.

Balogh, S.J., Y. Huang, H.J. Hofferman, M.L. Meyer, and D.K. Johnson. 2003. Methylmercury in rivers draining cultivated watersheds. Sci. Total Environ. 304: 305-313.

Balogh, S.J., Y.H. Nollet, and H.J. Offerman. 2005. A comparison of total and methylmercury export from various Minnesota watersheds. Sci. Total Environment 340(2005): 261-270.

Bedan, E.S. and J.C. Clausen. 2009. Stormwater runoff quality and quantity from traditional and low impact development watersheds. J. Am. Water Resources Assoc. 45(4): 998-1008.

Booth, D.B. and P.C. Henshaw. 2000. Rates of channel erosion in small urban streams. In M. Wigmosta, ed., Stream Channels in Disturbed Environments: AGU Monograph Series, 9/2000.

Brigham, M.E., D.A. Wentz, G.R. Aiken, D.P. Krabbenhoft. 2009. Mercury cycling in stream ecosystems. 1. Water column chemistry and transport. Environ. Sci. Technol. 43: 2720-2725.

Bushey, J.T., C.T. Driscoll, M.J. Mitchell, P. Selvendiran, and M.R. Montesdeoca. 2008. Mercury transport in response to storm events from a northern landscape. Hydrol. Process. 22:4813-4826.

Center for Watershed Protection (CWP). 2003. Impacts of impervious cover on aquatic systems. Watershed Protection Research Monograph No. 1 March 2003, Center for Watershed Protection, MD. (http://www.cwp.org/, accessed 14 Dec 10)

Christensen, V.G., J. Xiaodong, and A.C. Ziegler. 2000. Regression analysis and real-time water quality monitoring to estimate constituent concentrations, loads, and yields in the Little Arkansas River, South-Central Kansas, 1995-99. USGS Water Resources Investigations Report 00-4126.

Christensen, V.G. 2001. Characterization of surface-water quality based on real-time monitoring and regression analysis, Quivira National Wildlife Refuge, South-Central Kansas, December 1998 Through June 2001: US Geological Survey Water-Resources Investigations Report 01-4248, 28 p.

Dana, G.L., A.K. Panorska, R.B. Susfalk, D. McGraw, W.A. McKay, and M. Dornoo. 2004. Suspended sediments and turbidity patterns in the Middle Truckee River, California for the period 2002-2003. Publication No. 41196. Division of Hydrologic sciences, Desert Research Institute, Reno, NV (hhttp://www.truckee.dri.edu/tmdl/SedimentPatternsMiddleTruckeeDRI2004.pdf, accessed 14 Dec 10)

Davies-Colley, R.J. and D.G. Smith. 2001. Turbidity, suspended sediment, and water clarity: A review. J Am Water Res Assoc 37(5): 1085-1101.

Detenbeck, N.E., C.M. Elonen, D.L. Taylor, L.E. Anderson, T.M. Jicha, and S.L Batterman. 2003. Effects of hydrogeomorphic region, catchment storage and mature forest on baseflow and snowmelt water quality in second-order Lake Superior basin tributaries. Freshwater Biol. 48:912-927.

Dittman, J.A., Shanley, J.B., Driscoll, C.T., Aiken, G.R., Chalmers, A.T., Towse, J.E., Selvendiran, P. 2010. Mercury dynamics in relation to dissolved organic carbon concentration and quality during high flow events in three northeastern US streams. Water Resour. Res. 46, W07522, doi:10.1029/2009WR008351.

Engstrom, D. R., S.J. Balough, and E.B. Swain. 2007. History of mercury inputs to Minnesota lakes: Influences of watershed disturbance and localized atmospheric deposition. Limnol. Oceanogr. 52(6): 2467-2483.

Fitzpatrick, F.A., M.C. Peppler, M.M. DePhilip, and K.E. Lee. 2006. Geomorphic characteristics and classification of Duluth-Area streams, Minnesota. USGS SIR 2006-5029.

Fleck, J.A., 1999. Mercury transport through northern forested watersheds: Dissolved and particulate pathways. M.S. Thesis, University of Minnesota.

Fulkerson, M., F.N. Nadia, and L.S. Chasar. 2007. Characterizing dry deposition of mercury in urban runoff. Water Air and Soil Pollution 185:21-32.

Gippel, C.J. 1989. The use of turbidimeters in suspended sediment research. Hydrobiologia, 176/177: 465-480.

Gordon, N.D., T.A. McMahon, B.L. Finlayson, C.J. Gippel, and R.J. Nathan. 2004. Stream Hydrology: An Introduction for Ecologists. John Wiley and Sons Hoboken, NJ, 429 pp.

Gray, J.R., Glysson, G.D., Turcios, and G.E. Schwartz. 2000. Comparability of suspended-sediment concentration and total suspended solids data. US Geological Survey Water-Resources Investigations Report 00-4191, Reston, VA.

Grayson, R.B., B.L. Finlayson, C.J. Gippel, and B.T. Hart. 1996. The potential of field turbidity measurements for the computation of total phosphorus and suspended solids loads. J Environmental Management 47: 257-267.

Grigal, D.F. 2002. Inputs and outputs of mercury from terrestrial watersheds: A review. Environ. Rev. 10:1-39.

Grigal, D. F. 2003. Mercury sequestration in forests and peatlands: A review. J. Environ. Qual. 32:393-405.

Harrelson, C.R., C.L. Rawlins, and J.P. Potyondy, 1994. Stream channel reference sites: an illustrated guide to field technique. Gen. Tech. Rep. RM-245. Fort Collins, CO. US Forest Service, Rocky Mountain Forest and Range Experiment Station, 61 p.

Harris, R.C., J.W.M. Rudd, M. Amyot, C.L. Babiarz, K.G. Beaty, P.J. Blanchfield, R.A. Bodaly, B.A. Branfireun, C.C. Gilmour, J.A. Graydon, A. Heyes, H. Hintelmann, J.P. Hurley, C.A. Kelly, D.P. Krabbenhoft, S.E. Lindberg, R.P. Mason, M.J. Paterson, C.L. Podemski, A. Robinson, K.A. Sandlilands, G.R. Southworth, V.L. St. Louis, M.T. Tate. 2007. Whole-ecosystem study shows rapid fish-mercury response to changes in mercury deposition. Proc. Natl. Acad. Sci. USA 104(16): 16586-16591.

Hatch, L.K., J.E. Reuter and C.R. Goldman. 2001. Stream phosphorus transport in the Lake Tahoe Basin, 1989-1996. Environ. Monitoring and Assessment. 69:63-83.

Hedlin, H., J. Reiners, P. Schulte, Trapp II, A., Tuerk, M., and S. Wood. 2006. Estimating non-point source load and measuring uncertainty. (http://www.metrocouncil.org/environment/RiversLakes/documents/StOlafAbstract.pdf ; accessed 12/6/2010).

Helsel, D.R. R.M. Hirsch. 1992. Statistical Methods in Water Resources. 522p. Elsevier Science Publishing Company, New York, New York, USA.

Hintelmann, H., R. Harris, A. Heyes, J.P. Hurley, C.A. Kelly, D.P. Krabbenhoft, S. Lindberg, J.W.M. Rudd, K.J. Scott, V.L. St. Louis. 2002. Reactivity and mobility of new and old mercury deposited in a boreal forest ecosystem during the first year of the METAALICUS study. Environ. Sci. Tech. 36(23): 5034-5040.

Horowitz, Arthur J. 2008. Determining annual suspended sediment and sediment-associated trace element and nutrient fluxes. Sci. Total Environ 400:315-343.

Hurley, J.P., J.M. Benoit, C.L. Babiarz, M.M. Shafer, A.W. Andren, J.R. Sullivan, R. Hammond, D.A. Webb. 1995. Influences of watershed characteristics on mercury levels in Wisconsin rivers. Environ. Sci. Technol. 29: 1867-1875.

Hurley, J.P., S.E.Cowell, M.M. Shafer, P.E. Hughes, P.E. 1998. Tributary loading of mercury to Lake Michigan: Importance of seasonal events and phase partitioning. Sci. Total Environ. 213: 129-137.

Iverfeldt, A. and K. Johansson. 1988. Mercury in run-off water from small watersheds. Verh. Internat. Verein. Limnol. 23:1626-1632.

Jastrum, J.D., D.L. Moyer, and K.E. Hyer, 2007. A comparison of turbidity-based and streamflow estimates of suspended sediment concentrations in three Chesapeake Bay Tributaries. US Dept Interior and US Geological Service. SIR 2009-5165.

Jeremiason, J.D., L.A. Kanne T.A. Lacoe, M. Hulting, M.F. Simick. 2009. A comparison of mercury cycling in Lakes Michigan and Superior. J. Great Lakes Res. 35:329-336.

Kellogg, W. A. 1997. Metropolitan growth and the local role in surface water resource protection in the Lake Erie Basin. J. Great Lakes Res. 23(3):270-285.

Knighton, D. 1998. Fluvial Forms and Processes: A New Perspective. Oxford University Press, New York, NY.

Kolka, R.K., D.F. Grigal, E.S. Verry, E.A. Nater. 1999. Mercury and organic carbon relationships in streams draining forested upland/peatland watersheds. J. Environ. Qual. 28: 766-775.

Krabbenhoft, D.P., J.M. Benoit, C.L. Babiarz, J.P. Hurley, A.W. Andren. 1995. Mercury cycling in the Allequash Creek watershed, northern Wisconsin. Water Air Soil Pollut. 80: 425-433.

Lake Superior Binational Program. 2008. Lake Superior Lakewide Management Plan (http://www.epa.gov/glnpo/lamp/ls_2008/ls_2008.pdf).

Leonard, R.L., L.A. Kaplan, J.F. Elder, R.N. Coates and C.R. Goldman, 1979. Nutrient Transport in Surface Runoff from a Subalpine Watershed, Lake Tahoe Basin, California. Ecol. Monographs 49(3): 281-310.

Lewis, Jack. 1996. Turbidity-controlled suspended sediment sampling for runoff-event sampling. Water Resources Research, 32(7):2299-2310.

Lindgren, J., N. Schuldt, B. Borkholder, T. Howes, A. Levar, C. Olson, J. Tillman, D. Vogt. 2006. A study of the St. Louis River. Minnesota F-29-R (P)-25, (http://files.dnr.state.mn.us/areas/fisheries/duluth/st_louis_river_study.pdf), accessed 26 Oct 10.

Lloyd, D. S. 1987. Turbidity as a water quality standard for salmonid habitats in Alaska. N Am. J Fish. Manag. 7:34-45.

Lonsdale, M., T.Carlson, R.Axler, J.Walker, C.Hagley, J.Schomberg, M.Granley, and G.Host. 2006. Linking data, public outreach and education: The City of Duluth Stream Outreach Program - www.lakesuperiorstreams.org. Water Environment Federation Proceedings of Annual Meeting: WEFTEC.06 - The Water Quality Event, 79th Annual Conference and Exhibition, Oct 21-25, 2006, Dallas, Texas USA (http://www.lakesuperiorstreams.org/general/articles/Data_Outreach_Education_2006.pdf).

Mason, R.P. and K.A. Sullivan. 1998. Mercury and methylmercury transport through an urban watershed. Water Res. 32(2):321-330.

Mast, M.A., D.H. Campbell, D.P. Krabbenoft, H.E. Taylor. 2005. Mercury transport in a high elevation watershed in Rocky Mountain National Park, Colorado. Water Air Soil Pollut. 164: 21-42.

Minnesota Department of Natural Resources. 1999. Minnesota Watersheds. (http://jmaps.dnr.state.mn.us/mdreporter/dp_full_record.jsp?mpid=26000022&ptid=02&fcid=01&dsid=48; accessed 12/8/2010).

Minnesota Pollution Control Agency (MPCA). 2009. Implementation plan for Minnesota's statewide mercury total maximum daily load. MPCA publication wq-iw4-01p.

Munthe, J., R.A. Bodaly, B.A. Branfireun, C.T. Driscoll, C.C. Gilmour, R. Harris, M. Horvat, M. Lucotte, and O. Malm. 2007. Recovery of mercury-contaminated fisheries. Ambio 36(1): 33-44.

Nater, E.A. and D.F. Grigal. 1992. Regional trends in mercury distribution across the Great Lakes states, north central USA. Nature (London) 358: 139–141.

Nelson, E.J. and D.B. Booth. 2002. Sediment source in an urbanizing, mixed land-use watershed. J. Hydrology 264:51-68.

Newcombe, Charles P. 2003. Impact assessment model for clear water fishes exposed to excessively cloudy water. J. of the American Water Resources Association 39(3):529-544.

Nietch, C.T., M. Borst, J.P. Schubauer-Berigan. 2005. A framework for sediment risk management research. Environmental Management 36(2): 175-94.

Novotny, E.V. and H.G. Stefan, 2007. Stream flow in Minnesota: Indicator of climate change. J. Hydrology 334:319-333.

Novotny, V. and H. Olem. 1994. Water Quality: Prevention, Identification. and Management of Diffuse Pollution. Van Nostrand Reinhold, New York, NY.

Novotny, V. and C. Gordon, 1981. Handbook of Nonpoint Pollution Sources and Management. New York, NY: Van Nostrand Reinhold Company.

Packman, J.J., K.J. Comings, D.K. Booth. 1999. Using turbidity to determine total suspended solids in urbanizing streams in the Puget Lowlands. College Forest Resources, U Washington, Seattle, WA 206/543-5506. (http://depts.washington.edu/cuwrm/research/tssturb.pdf, accessed 14 Dec 10).

Prestigiacomo, A. R., S.W. Effler, D.M. O'Donnell, J.M. Hassett, E.M. Michelanko, Z. Lee, and A.D. Weidemann. 2007. Turbidity and suspended solids levels and loads in a sediment enriched stream: implications for impacted lotic and lentic systems. Lake and Reservoir Manage. 23: 231-244.

Rolfhus, K.R., H.E. Sakamoto, L.B. Cleckner, R.W. Stoor, C.L. Babiarz, R.C. Back, H. Manolopoulos, J.P. Hurley. 2003. Distribution and fluxes of total and methylmercury in Lake Superior. Environ. Sci. Technol. 37: 865-872.

Rose, C. and R.P. Axler. 1998. Uses of alkaline phosphatase activity in evaluating phytoplankton community phosphorus deficiency. Hydrobiologia 361:145-156.

St. Louis, V.L., J.W.M. Rudd, C.A. Kelly, B.D. Hall, K.R. Rolfus, K.J. Scott, S.E. Lindberg, and W. Dong. 2001. Importance of the forest canopy to fluxes of methyl mercury and total mercury to boreal ecosystems. Environ. Sci. Tech. 35(15):3089-3098.

Scherbatskoy, T., J.B. Shanley, G.J. Keeler. 1998. Factors controlling mercury transport in an upland forested catchment. Water Air Soil Pollut. 105: 427-438.

Schuster, P.F., J.B. Shanley, M. Marvin-Dipasquale, M.M. Reddy, G.R. Aiken, D.A. Roth, H.E. Taylor, D.P. Krabbenhoft, and J.F.DeWild. 2008. Mercury and organic carbon dynamics during runoff episodes from a northeastern USA watershed. Water Air Soil Pollut. 187: 89-108.

Shanley, J.B., M. Alisa Mast, D.H. Campbell, G.R. Aiken, D.P. Krabbenhoft, R.J. Hunt, J.F. Walker, P.F. Schuster, A. Chalmers, B.T. Aulenbach, N.E. Peters, M.M. DiPasquale, D.W. Clow, M.M. Shafer. 2008. Comparison of total mercury and methylmercury cycling at five sites using the small watershed approach. Environ. Pollut. 154: 143-154.

Sørensen, R., M. Meili, L. Lambertsson, C. von Brømssen, K. Bishop. 2009. The effects of forest harvest operations on mercury and methylmercury in two boreal streams: Relatively small changes in the first two years prior to site preparation. Ambio 38(7): 364-372.

State of the Lakes Ecosystem Conference (SOLEC). 2009. Nearshore areas of the Great Lakes 2009. Environ. Canada and US Environmental Protection Agency, 905-R-09-013.

Swain, E.B., D.R. Engstrom, M.E. Brigham, T.A. Henning, and P.L. Brezonik, 1992. Increasing rates of atmospheric mercury deposition in midcontinental North America. Science 257: 784-787.

Sweka, J.A. and K. J. Hartman. 2001. Influence of turbidity on brook trout reactive distance and foraging success. Trans. Am. Fish. Soc. 130: 138-146.

Sweka, J.A. and K.J. Hartman. 2003. Reduction of reactive distance and foraging success in smallmouth bass, *Micropterus dolomieu*, exposed to elevated turbidity levels. Environ. Biol. Fishes 67: 341-347.

StatSoft, Inc. (2005). STATISTICA (data analysis software system), version 7.1. www.statsoft.com.

Taylor, Richard B. 1964. Geology of the Duluth Gabbro Complex near Duluth, MN. Minnesota Geological Survey Bulletin No. 44 (http://purl.umn.edu/57070, accessed 29 Nov 10).

Uhrich, M.A. and H.M Bragg. 2003. Monitoring in-stream turbidity to estimate continuous suspended-sediment sediment loads and clay-water volumes in the upper North Santiam River Basin, Oregon, 1998–2000: US Geological Survey Water-Resources Investigations Report 03-4098, 43 p.

U.S. Environmental Protection Agency (US EPA). 2008. Minnesota 2008 Water Quality Assessment Report: Assessed Waters of Minnesota by Watershed (http://iaspub.epa.gov/waters10/attains_index.control?p_area=MN, accessed 14 Dec 10).

U.S. Environmental Protection Agency (US EPA). 2001. Methylmercury in water by distillation, aqueous ethylation, purge and trap, and CVAFS. EPA-821-R-01-020.

U.S. Environmental Protection Agency (US EPA). 2002. Method 1631, Revision E: Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry. EPA-821-R-02-019.

U.S. Geological Survey (USGS). 2002. Hydrologic trends associated with urban development for selected streams in the Puget Sound Basin, Western Washington. US Geological Survey WRI Report 02-4040.

U.S. Geological Survey (USGS). 2004. Turbidity (version 2): US Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6, section 6.7. (http://water.usgs.gov/owq/FieldManual/Chapter6/6.7_contents.html, accessed 15 Decd 10).

U.S. Geological Survey (USGS). 2006. Guidelines and standard procedures for continuous water-quality monitors: Station operation, record computation, and data reporting. Techniques and Methods 1-D3.

Wall, G.R., H.H. Ingleston, and S. Litten, 2005. Calculating mercury loading to the tidal Hudson River, New York, using rating curves and surrogate methodologies. Water, Air, and Soil Pollution 165: 233-248.

Weiner, J. G., B.C. Knights, M.B. Sandheinrich, J.D. Jeremiason, M.E. Brigham, D.R. Engstrom, L.G. Woodruff, W.F. Cannon, and S.J. Balogh. 2006. Mercury in soils, lakes and fish in Voyageurs National Park (Minnesota): Importance of atmospheric deposition and ecosystem factors. Environ. Sci. Technol. 40(20): 6261-6268.

Whyte, D.C. and J. W. Kirchner. 2000. Assessing water quality impacts and cleanup effectiveness in streams dominated by episodic mercury discharges. Sci. Total. Environ. 260:1-9.

Wolter, P.T., C.A. Johnston, and G.J. Niemi. 2006. Land use land cover change in the US Great Lakes basin 1992 to 2001. J. Great Lakes Res. 32: 607-628.