RELATIONSHIP BETWEEN WATER QUALITY AND ANTHROPOGENIC LANDSCAPE STRESSORS IN THE ST. LOUIS RIVER WATERSHED AND ESTUARY

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Dedication

This thesis is dedicated to my wife Stephanie. Without her support and understanding this would not have been possible.

Abstract

The St. Louis River drains an area of 9,412 km^2 (3,634 mi^2) and empties into the western arm of Lake Superior. Shortly downstream from the Fond du Lac Reservoir, the river opens up into a 48.5 km^2 freshwater estuary that separates Minnesota and Wisconsin. A GIS-based anthropogenic stressor gradient was developed to characterize the anthropogenic stressors within the watershed. The components of the stressor gradient were: road density, point-source pollution permit density, population density, percent agricultural land and percent developed land. Water quality sampling was conducted at 26 sites in the estuary in both nearshore areas and above the mouths of the associated tributaries during multiple flow regimes in 2010-2011. Additional data were analyzed from 34 upper watershed sites sampled in 2009-2010. The stressor gradient was shown to be significantly, positively correlated ($p<0.1$) with TSS, turbidity, TP, NO_2^-/NO_3^--N, DIN, dissolved oxygen saturation, pH, specific electrical conductivity, chloride , sulfate, *E. coli,* and hardness in the upper watershed. In the estuary it was significantly, positively correlated with NO_2^-/NO_3^--N, NH_4^+-N, DIN, and chloride at multiple flow regime and location combinations. The strength of the correlations of the stressor gradient and water quality was generally improved by the removal of the less relevant agricultural component. Sediment-related parameters were either not correlated with the stressor gradient in the estuary or anomalously were negatively correlated. This was found to be due to the non-uniform distribution of more erodible soils. Soil K factor (an erosivity index from SSURGO) was significantly, positively correlated with the sediment-related parameters. Although it was originally designed to help stratify sampling programs across

a gradient of stress and identify reference areas for restoration projects, the stressor gradient was shown to have some predictive power for multiple water quality parameters.

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Introduction

Landscapes and water quality

When studying aquatic issues it is important to consider the landscape's impact on the aquatic system (King et al. 2005, Johnson & Host 2010). Urbanization has been shown to negatively impact water quality, stream habitat, water chemistry and hydrology (Boothe et al. 1997, Galster et al. 2006, Brown et al. 2009, Miserendino et al. 2010, Tu 2011). Perhaps its most obvious consequence is an increase in impervious surfaces that results in decreased infiltration and increased surface runoff (Brabec et al. 2002). When impervious surface levels rise to between 10 to 20% percent of a catchment area the surface water runoff volume is doubled (Arnold and Gibbons 1996). The increased surface water can wash contaminants from roofs, lawns, streets and other surfaces within the urban environment into streams and other waterways. As a result, it has been found that urbanization is positively correlated with many contaminants, including: nutrients, sediments, metals, petroleum products, organic contaminants and many others (Paul et al. 2001). Although some of the inputs are incidental byproducts of our modern lifestyle, such as oil drippings, soil particles and litter, others are more deliberate. Salt and sand are spread in large quantities over our roads and streets in an effort to keep them drivable and safe in winter months. The combination of these two additives entering streams raises both conductivity and total suspended solids (TSS). The latter fills the interstitial spaces of the stream bed; they can also produce acute and chronic stress in aquatic organisms. From 2000-2008 the average annual salt use in the U.S. for de-icing was 16.0 million metric tons per year (Corsi et al. 2010). Additionally, urbanization has been found to increase the average temperatures of streams (Nelson and Palmer 2008).

Urbanization is not the only threat to water quality. It has been found that increasing levels of both agriculture and urbanization in sub-watersheds of a river in France were associated with increased levels of phosphate (PO_4^{3-}) and conductivity (Montuelle et al. 2010). Allan and others (1997) found that runoff volume and sediment and nutrient levels increased not only in streams with higher levels of urban development, but also those with more agriculture. In fact, urbanization is recognized to be second to agriculture for its overall negative impacts on streams (Paul and Meyer 2001). High levels of agriculture have been found to be associated with poor water quality, including increased levels of nutrients and suspended sediment (Johnson et al. 1997, Crosbie and Chow-Fraser 1999, Trebitz et al. 2007, Morrice et al. 2008). In an agriculturally dominated region of Oregon, the percent of land in agricultural use was positively correlated with chloride and nutrients during the wet season (Pan et al. 2004). However, only total phosphorus (TP) had the same relationship during the dry season.

These detrimental impacts on water quality, whether they come from urban, agricultural or other sources, ultimately stress the biotic communities that live in or depend on the waterways (Roy et al. 2007, Uzarski et al. 2007, Brown et al. 2009, Trebitz et al. 2009). Macrophyte diversity and abundance, as well as water quality, were found to be negatively affected by urban development (Akasaka et al. 2010). Additionally, invasive macrophyte species are more likely to be found in agriculturally intensive areas (Quinn et al. 2011). Wang et al. (1997 and 2003) found that increases in the proportion of land used for agriculture or urban purposes was negatively correlated with cold-water fish index of biotic integrity (IBI) scores in Wisconsin and Minnesota. There was an apparent threshold, corresponding with lower fish IBI scores, when agriculture accounted for more than 50% of the landscape or urban uses accounted for more than 10% or 20%. These changes in biota can have negative effects on how we use and enjoy outdoor areas.

Stressor Gradients

Approaches to studying the effects of land use on water quality have been aided by the development and ever-increasing capacity of geographic information systems (GIS). Spatial data can be organized and analyzed more effectively and efficiently than before. One way to utilize GIS to investigate how land cover/land use impacts water quality is through the development of stressor gradients (Danz et al. 2005, Host et al. 2005, King et al. 2005, Danz et al. 2007, Host et al. 2011). Stressor gradients can be as simple as using a single component, such as percent impervious surface, or may include hundreds of components (Brabec et al. 2002, Danz et al. 2005). Spatial data from components that are believed to impact water quality are compiled and organized with a GIS. Then all study units in a specific study area are ranked relative to each other based on the level/intensity of the individual components or a combination of multiple components (Host et al. 2005, Host et al. 2011).

A common approach researchers use to study aquatic systems is to investigate the relationship of water quality to multiple, individual component stressor gradients (Ahearn et al. 2005, Montuelle et al. 2010, Shiels 2010). Ahearn et al. (2005) took this approach in a free-flowing river basin in the western Sierra Nevada Mountains. They worked with a set of five landscape metrics: percent agriculture, percent urban, percent forest, percent grassland and population density. They found that during years of average precipitation, nitrate-N (NO_3^--N) levels were most strongly correlated with gradients of population density, percent grassland and percent forest. They also found that TSS was most strongly related to percent urban and percent agriculture. Stressor gradients are not always successful in producing predictive relationships with water quality variables, though. Shiels (2010) found no statistically significant relationship between TP, *E. coli*, NO_3^--N and a macroinvertebrate metric against 6 stressor gradients, each composed of an individual factor relevant to agriculture. Shiels concluded that using a single grab sample from one date to represent each site, as they did, was insufficient to characterize average water quality at a site and develop significant correlations.

Danz et al. (2005) developed stressor gradients for the U.S. side of the Laurentian Great Lakes using 207 individual components for the Great Lakes Environmental Initiative study (GLEI). These components were grouped into 7 categories: agricultural/agricultural chemical, atmospheric deposition, land cover, human population/development, point and non-point pollution, shoreline protection and soils. Principal component analysis was conducted to summarize each category. The primary principal component from each category was then used as a stressor gradient. Peterson et al. (2007) used stable nitrogen isotope analysis to investigate the relationship between coastal wetland water quality and four of the GLEI stressor gradients: agricultural, land cover, human population and point source pollution. It was found that ^{15}N levels in nearshore biota had positive correlations with the agricultural principal component gradient. Furthermore, ^{15}N levels in plankton and benthos were highly, significantly correlated with the agricultural, land cover and human population principal components. They also found evidence to suggest these relationships were stronger in sheltered bays. They concluded that ^{15}N levels in Great Lakes coastal biota can be used as an indicator of the impact of land use and anthropogenic activity on coastal wetlands.

Danz and others (2007) produced a different set of stressor gradients, again for the U.S. side of the Laurentian Great Lakes, based on 86 variables in 5 categories: agriculture, atmospheric deposition, human population, land cover and point source pollution. The purpose for developing these stressor gradients (as opposed to the ones for the 2005 paper) was to combine them into one cumulative stressor gradient that was based on an equally weighted sum of all the individual categories. This, as well as the individual category stressor gradients, could then be compared to existing Great Lakes coastal water quality and biological data collected for the GLEI project. They found that in Great Lakes coastal wetlands total nitrogen (TN), TSS and chloride (Cl^-) concentrations were higher in wetlands with higher cumulative stress scores. They also found that generally poorer water quality was most strongly correlated with the agricultural component of the stressor gradient. Morrice and colleagues (2008) examined the 2007 stressor gradient in regard to water quality in Great Lakes coastal wetlands. They found that TP, TN, dissolved inorganic nitrogen (DIN), chlorophyll-a, TSS and chloride were strongly correlated with various stressor metrics.

The GLEI stressor gradients were found to correlate well with many measures of water quality and biological integrity (Reavie et al. 2006, Danz et al. 2007, Peterson et al.

2007, Trebitz et al. 2007, Morrice et al. 2008). This raised the question of whether a stressor gradient could be successfully applied to a smaller geographic area. However, the GLEI stressor gradient took considerable time and resources to compile and calculate, making it impractical to update or replicate. Using only five variables to represent anthropogenic stressors, Host et al. (2005) calculated the stressor gradient metric *MaxRel* for the purpose of identifying reference sites throughout the U.S. side of the Great Lakes. Host et al. (2011), building on their previous efforts with *MaxRel*, developed the *SumRel* stressor gradient for the Lake Superior watershed. *SumRel* is cumulative and was designed to represent the sum of relativized stress. It was developed using a high-resolution delineation of the watershed that included over 130,000 sub-catchments that averaged 84 hectares in size and can be grouped into sub-watersheds and watersheds based on flow direction (Hollenhorst et.al 2007). *SumRel* was based on five components: percent agriculture, percent developed, road density, point source pollution discharge permit density and population density. In order to ensure that it could be economically updated in the future or easily developed for a different study area, this stressor gradient was based on publically available spatial data that is of similar scales, is regularly updated and is readily available in both the U.S. and Canada. This study uses the *SumRel* stressor gradient.

St. Louis River Area of Concern

The watershed of the Laurentian Great Lakes has significant areas that are both heavily industrialized and highly populated. As a result, some areas of the Great Lakes have suffered from substantial pollution and habitat degradation. The International Joint

Commission (IJC), formed in 1909, has both U.S. and Canadian representatives. One of their duties is to address water quality problems in the Great Lakes. In 1972 and 1978 Canada and the U.S. signed agreements to limit pollution and clean up existing waste in the lakes (SLRAC 1992). In 1987 the IJC signed a Proclamation that identified 43 Areas of Concern (AOC) in the Great Lakes basin that suffered from water quality degradation severe enough to impair the beneficial uses of those water resources (SLRAC 1992). Twenty six of the AOCs are in the U.S., 12 are in Canada and 5 are shared between the two nations. The Proclamation required that Remedial Action Plans (RAP) be developed for each of the 43 AOCs. The RAPs would outline the specific problems facing each AOC and develop a plan to remediate the area. The lower St. Louis River is one of the 43 AOCs.

The St. Louis River flows into the western arm of Lake Superior. It is located primarily in northeastern Minnesota, but a portion of its lower watershed is located in northwestern Wisconsin. The lower section of the river opens up into a 48.5 km^2 freshwater estuary and is separated from Lake Superior by a 16 km sand spit. The Port of Duluth-Superior was established in the estuary in the 1850’s and benefited greatly from the opening of the Soo Canal in 1854 (SLRAC 1992). The city of Duluth was established on the Minnesota side of the port and the city of Superior was established on the Wisconsin side. Railroads were developed in the early 1870’s and industry proliferated throughout the estuary. Petroleum refineries, tar product manufactures, saw mills, paper mills, paint factories and meat packing plants were among the many industries that lined the estuary and are suspected of discharging waste directly into the water (SLRAC 1992).

As a result of the industrial build-up, more than 16 km^2 (~1/3 of the estuary area) of wetlands have been lost in the estuary since the 1860's (DeVore 1978).

In the early 1970's the water in the St. Louis River was extremely degraded (SLRAC 1992). In response to the high levels of nutrients and organic matter that were being discharged into the river and degrading water quality and habitat, the Western Lake Superior Sanitation District (WLSSD) was formed. The WLSSD wastewater treatment plant began operation in 1978 (SLRAC 1992). It treats wastewater for Duluth, as well as most of the other small cities, towns and industrial customers in the area. Although this dramatically improved the water quality almost immediately, the lower 63 km of the river, including the estuary, were listed as an AOC in 1987 (SLRAC 1992).

In response to the listing, the non-profit St. Louis River Citizen Action Committee (currently call the St. Louis River Alliance (SLRA)) was formed and released Stage One of the RAP for the St. Louis River in 1992. Of the 14 beneficial use impairments (BUI) that the IJC recognizes, 9 were found to occur in the St. Louis River AOC. They include: restrictions on fish and wildlife consumption, fish tumors and other deformities, degradation of fish and wildlife populations, loss of fish and wildlife habitat, degradation of benthos, excessive loading of sediment and nutrients, beach closings, degradation of aesthetics and restrictions on dredging activities. In 2002 the St. Louis River AOC Habitat Plan was released as a summary of needed restoration actions that could be used to develop prioritized projects for which grant funding would be sought. In 2008 Great Lakes Restoration Initiative (GLRI) funding was approved for the use of remediation and restoration activities in AOCs. BUI delisting targets developed by bi-state stakeholder committees were approved in 2009.

In October 2010, portions of the estuary were designated a National Estuarine Research Reserve (NERR) by the National Oceanic and Atmospheric Administration (NOAA)(NOAA 2010) as a result of a 12 year process initiated by the state of Wisconsin, but with significant collaboration from many Minnesota organizations and agencies. Currently, a framework is being developed and implemented to address the BUIs and delisting process. It is funded by the GLRI and is making use of the many decades of technical expertise that has been developed among stakeholders in the region since the development of the Stage One RAP (*http://www.pca.state.mn.us/index.php/water/water-monitoring-and-reporting/contaminated-sediments/sediment-studies-st.-louis-river-area-of-concern.html?menuid=&redirect=1*).

Objectives

In this study we assessed the relationship between anthropogenic stressors and water quality in the St. Louis River Estuary and in the upper St. Louis River watershed. The specific objectives of the project were to:

1. summarize anthropogenic stressors within the St. Louis River watershed and investigate their relationship to water quality in the estuary, its tributaries, and the upper watershed,

2. determine if hydrologic flow regime (i.e. summer baseflow, spring runoff, and storm events) or location (i.e. tributaries versus nearshore) affects the relationship between the stressor gradient and water quality,
3. determine if the stressor gradient's relationship with water quality can be improved by making locally relevant modifications to the stressor index.

Hypotheses

1. Important water quality parameters (i.e. sediment-related parameters, nutrients and perhaps others) will display a predictable and statistically significant relationship with GIS-based metrics along a gradient of stress, with higher stressor values being associated with degraded water quality in the St. Louis River watershed tributaries and in the estuary itself,

2a. the relationship of water quality to the stressor gradient will be stronger during higher flow periods, particularly storm events, than during baseflow events in the estuary and its tributaries,

2b. this relationship will be stronger in the tributaries and weaker in the nearshore areas,

3. adjusting the stressor gradient with locally relevant changes will improve its relationship with the water quality data.

Methods

Study Area

The study was conducted in the St. Louis River watershed on the western end of Lake Superior in Minnesota and Wisconsin, USA (Figure 1). Draining 9,412 km^2 (3635 mi^2), the river is the largest U.S. tributary to Lake Superior. Land use varies widely throughout the watershed and includes: taconite/iron ore mining, urban/industrial centers, forests, wetlands and limited agriculture. The lower section of the river opens up into a 48.5 km^2 freshwater estuary that separates Minnesota and Wisconsin. The lower portion of the estuary is occupied by the Port of Duluth-Superior. It provides shipping access to the Atlantic Ocean through the St. Lawrence Seaway and is the largest dry bulk port in the United States (DSPA 2010).

Stressor Gradient and Landscape Analysis

The stressor gradient was developed by researchers at the Natural Resources Research Institute (NRRI) using ArcMap 9.3 (Environmental Systems Research Institute, Redlands, CA, USA) and Arc Hydro tools (Maidment 2002, Host et al. 2005, Hollenhorst et al 2007, and documented fully in Host et al. 2011). It was based upon five measures of human disturbance: population density, road density, National Pollution Discharge Elimination System (NPDES) point source pollution permit density, percent of land used for agriculture and percent of land developed. Land use data were derived from the 2001 USGS National Land Cover Data Set (Homer et al. 2004); population data were from the 2000 US Census (U.S. Census Bureau 2002); road density data were from USGS TIGER data (U.S. Census Bureau 2002); and point source pollution information was from the NPDES database (EPA 2012). All of the components were equally weighted in the stressor gradient and it was scaled to the entire St. Louis River watershed, which included over 10,000 sub-catchments that were grouped into sub-watersheds based on flow direction. In the upper watershed the sub-watersheds either drain into larger tributaries or the main stem of the St. Louis River. In the estuary study area the sub-watersheds drain directly into the estuary. The data were standardized and normalized as follows: First, non-zero values (x) were log10 transformed and the minimum non-zero value of x was used for all zero values. Next, the transformed values (x') were standardized by subtracting the mean (μ) of all the data from each transformed datum and dividing it by the standard deviation (σ) of all data ((x'-μ)/σ). Following that, the standardized values (x") were normalized by subtracting the minimum value of all the standardized data from each standardized datum and dividing that by the difference between the maximum and minimum of all the standardized values (x"-min)/(max-min). Finally, the sum of the normalized data for each sub-catchment was calculated and then normalized again, resulting in a value from 0-1. This value is called *SumRel*. A *SumRel* of 1.0 is taken to represent maximum aggregate stress for all sub-catchments within the St. Louis River watershed and the estuary. A *SumRel* of 0.0 would be associated with the least stressed sub-catchment in the study area. This is a relative score and is not directly comparable with scores calculated for other watersheds.

SumRel was originally developed for the entire Lake Superior watershed. At that scale it was determined that all 5 components were important. However, compared with other regions, there is not much agriculture in the St. Louis River watershed. Additionally, NPDES permits are concentrated in only a small proportion of the sub-watersheds. To address this, alternative versions of *SumRel* were also calculated for the study area without the percent agriculture component, without the NPDES permit density component, and without both.

Additional landscape analyses were also conducted in the study area. These included: percent impervious surface from the 2001 NLCD; mean stream slope calculated from the stream segment slopes of the sub-catchment units; standard deviation of elevation; and mean soil K factor. An average value for each of these 4 variables was calculated for each sub-watershed that was sampled. The standard deviation of elevation was used to assess the topographical relief (i.e. steepness or flatness) of the area. The K factor represents the inherent susceptibility of a soil type to erosion and is readily used in the Revised Universal Soil Loss Equation (RUSLE; Renard et al. 1991). The K factor values were taken from the 2011-2012 Natural Resources Conservation Services (NRCS) Soil Survey Geographic Database (SSURGO; Soil Survey Staff, NRCS 2012). In the study area slightly less than 10 percent of the land area was represented by polygons that had null K factor values. A weighted average, based on the length of the border each null value polygon shared with non-null polygons, was used to estimate a K factor value in the absence of a reported value. Only the sub-watersheds in the estuary were analyzed for K factor. SSURGO data had not been released for large portions of the upper St. Louis River watershed as of May 2012, making K factor analysis of the entire watershed impractical.

Sub-Watershed selection

In order to investigate the effects of anthropogenic stressors on water quality, 27 sub-watersheds (each comprised of one or more sub-catchments) that drain directly into the estuary and represent a broad range of anthropogenic stressor levels were chosen to be sampled in the St. Louis River Estuary (SLRE; Figure 2, Figure 3). These sub-watersheds range in size from 1 km^2 to 81 km^2. In addition, data from the recent 2009-2010 St. Louis River Surface Water Assessment (SWASLR; Figure 4, Figure 5) were analyzed with respect to the stressor gradient. SWASLR was funded by the Minnesota Pollution Control Agency (MPCA) as part of their state-wide assessment process for identifying impaired waters (*www.pca.state.mn.us*). The study was conducted in the upper watershed above the estuary with no spatial overlap between the two studies. NRRI staff assisted with data collection and analysis (Axler et al. 2011). The 34 sites have watersheds ranging in size from 11 km^2 to 9,184 km^2. Some of the upper watershed sites represent individual sub-watersheds while others are progressively larger and include the sub-watersheds of other sites. The largest sub-watershed includes all 33 other sub-watersheds.

Parameters and Sampling Programs

Estuary samples were collected once during late summer and fall baseflow conditions in both 2010 and 2011 and once during the end of spring runoff in 2011. When physically possible, one sample was taken from the tributary above the estuary water and three nearshore samples were taken in front of the mouth of the tributary, each progressively farther from shore. Equal volumes from each of the three nearshore samples were combined into a single composite sample. In addition, the tributaries of the 16 sites that were accessible by road were sampled during 5 different storm events when precipitation was >0.5” in a 24 hour period (Figure 6).

Water quality parameters follow GLEI guidelines (Reavie et al. 2006) and include a *core suite* (temperature (T), dissolved oxygen (DO), specific electrical conductivity (EC25), pH, turbidity, and clarity) of field measurements using a HydroLab multi-parameter sonde (model MS5) and a 120 cm transparency tube. An *advanced suite* (turbidity, color, TP, TN, ammonium-N (NH_4^+-N), nitrite/nitrate-N (NO_2^-/NO_3^--N), chloride, sulfate (SO_4^{2-}), chlorophyll-a, and phaeophytin) (Table 1) was analyzed in the lab at NRRI for the tributary and composite samples. Storm event tributary samples were analyzed for TSS, but not chlorophyll-a. All data was quality assured and quality controlled (QA/QC) as per NOAA/NERR/SWMP guidelines (NERR 2007) which are consistent with the EPA approved GLEI-QAPP, USGS field methods for *core suite* parameters (USGS 2004), standard methods used by the Minnesota Pollution Control Agency and EPA, and by the Minnesota State Certified NRRI Central Analytical Laboratory (Ameel et al. 2008, MPCA 2009).

The upper watershed samples were collected 10 times each in 2009 and nine times each in 2010 at 34 locations. Sampling dates were evenly spaced throughout the summer with no regard for flow regime (MPCA design). All of the samples were taken from stream/river channels and consisted of single, mid-channel grab samples. In 2009 a *core suite* (T, DO, EC25, pH, turbidity, and clarity) of field measurements using a HydroLab multi-parameter sonde (model MS5) and a 120 cm transparency tube and an *advanced suite* (turbidity, color, TP, TN, NH_4^+-N, NO_2^-/NO_3^--N, Cl^-, SO_4^{2-}, TSS, total volatile solids (TVS), hardness, and *E. coli* were completed. In 2010 only T, DO, EC25, pH, and *E. coli* analyses were conducted. All water quality data were submitted to MPCA and are available via their Electronic Data Access (EDA) system (www.pca.state.mn.us/index.php/topics/environmental-data/eda-environmental-data-access/eda-surface-water-searches/eda-surface-water-data-home.html).

Data Analysis

Estuary data was classified into five different flow regime and location combinations:

1. tributaries-baseflow (n=24),
2. tributaries-spring runoff (n=23),
3. tributaries-storm event (n=16),
4. nearshore-baseflow (n=27),
5. nearshore-spring runoff (n=26).

For baseflow and storm event sites, the mean value for each parameter at each site was used in the statistical analysis. Because the upper watershed sampling was conducted without regard for flow regime (as per MPCA protocol), the mean value of each parameter at each site was used for the analysis of the upper watershed data (n=34). The relationships between the water quality data and the stressor gradient were analyzed using bivariate plots and Pearson correlations (JMP 1989-2011). In addition, the individual components of the stressor gradient, alternative stressor indices based on subsets of the 5 components, percent impervious surface area, and the soil K factor were analyzed for relationships with water quality parameters. Most of the sub-watersheds in Wisconsin and one in Minnesota have soil that is dominated by highly erodible lacustrine clay. Because of this, sub-watersheds were placed into clay-influenced and non-clay influenced groups for additional analysis of the *SumRel* relationship with sediment-related parameters (i.e. TSS, turbidity, clarity and TP; Appendix 7). TP was included in the sediment-related group because of the typical adsorption of phosphate to organic and most inorganic particles (Horne and Goldman 1994, *Wetzel* 2001). The groups were based on the aquatic habitat type map developed by the Habitat Technical Sub-Committee of the St. Louis River Citizens Action Committee for the Lower St. Louis River Habitat Plan (SLRAC 2002; Figure 7). The sub-watersheds associated with clay-influenced bays and clay influenced river mouths were grouped into a “clay-influenced” class. Additionally, based on field observations and soil maps, the sheltered bays up river from the Gary-New Duluth area were included in the clay-influenced class. The remaining sub-watersheds, all of which were associated with either industrial-influenced bays, industrial slips, lower estuary flats or the sheltered bays down river of Gary-New Duluth, were combined into the non-clay-influenced class. Stepwise regression was done to determine which of the individual components of *SumRel* were most relevant. All analyses done on the transparency tube data were conducted on the inverse of the values (1/T-tube) to normalize the data. This also ensured that positive correlations with the stressor gradient represented a decrease in clarity. Outliers more than 2.7 standard deviations from the mean were removed prior to analysis. All analysis was done in JMP (Version 9, SAS Institute Inc., Cary, NC).

Results

Estuary: Tributaries – Spring Runoff

TN ($p=0.085$), NO_2^-/NO_3^--N ($p=0.0060$), NH_4^+-N ($p=0.0096$), DIN ($p=0.0091$) chlorophyll-a ($p=0.0096$) and chloride ($p<0.0001$) were all positively correlated with *SumRel* (Table 2, Figure 8). Turbidity ($p=0.054$) and 1/T-Tube ($p=0.092$) had negative correlations with *SumRel* (Figure 9). Of the individual components TN was best correlated with road density; NH_4^+-N with population density; and NO_2^-/NO_3^--N, chlorophyll-a and chloride with percent land developed. All three of the alternative *SumRel*s had slightly stronger correlations with chloride. Turbidity ($p=0.0098$), 1/T-tube ($p=0.050$) and, to a lesser extent, total phosphorus ($p=0.11$) were all positively correlated with soil K factor (Figure 10).

Estuary: Nearshore – Spring Runoff

Chloride ($p<0.0001$), pH ($p=0.098$) and, to a lesser extent, NO_2^-/NO_3^--N ($p=0.11$) were all positively correlated with *SumRel* (Table 3, Figure 8). NO_2^-/NO_3^--N and pH were most strongly correlated with the point source pollution permit density *SumRel* component. Chloride was most strongly correlated with percent land developed. There was little difference in between the correlations of the water quality parameters to either the *SumRel* or the alternative *SumRel*s. Turbidity ($p=0.001$) was positively correlated with soil K factor (Figure 10).

Estuary: Tributaries – Baseflow

EC25 ($p=0.033$), chloride ($p<0.0001$) and DIN ($p=0.010$) were positively correlated with *SumRel* (Table 4, Figure 8). None of the sediment-related parameters were correlated with *SumRel* (Figure 9). Population density and road density were the individual components of *SumRel* that had the highest correlations with specific conductivity and chloride, respectively. The correlations between *SumRel* and NO_2^-/NO_3^--N ($p=0.011$), NH_4^+-N ($p=0.048$) and DIN ($p=0.002$) improved if the agricultural component was removed. The tributaries during baseflow showed the weakest relationship with *SumRel* compared to the other flow regime and location combinations. Turbidity was marginally, positively correlated with the soil K factor ($p=0.093$; Figure 10).

Estuary: Nearshore –Baseflow

OP ($p=0.015$), NO_2^-/NO_3^--N ($p=0.030$), NH_4^+-N ($p=0.0007$), DIN ($p=0.0024$) and chloride ($p=0.0002$) all had significant, positive correlations with *SumRel* (Table 5, Figure 8). Of the *SumRel* components OP was most strongly correlated with percent agriculture, chloride was most strongly correlated with percent development and NO_2^-/NO_3^--N and NH_4^+-N were most closely correlated with population density. There was little difference between the correlations of the water quality parameters to either the *SumRel* or the alternative *SumRel*s other than slightly stronger correlations with chloride for the alternatives. Turbidity ($p=0.007$) and 1/T-Tube ($p=0.010$) were positively correlated with soil K factor (Figure 10).

Estuary: Tributaries – Storm Event

NO_2^-/NO_3^--N (p=0.049), DIN (p=0.019) and chloride (p=0.036) had significant, positive correlations with *SumRel* (Table 6, Figure 8). Color had a significant negative correlation with *SumRel*. Of the sediment-related parameters, turbidity (p=0.079) and 1/T-Tube (p=0.099) were negatively correlated with *SumRel* (Figure 9). All three alternative *SumRel*s had stronger correlations with chloride and EC25 than the original *SumRel*. The two alternative *SumRel*s without percent agriculture had stronger relationships with NO_2^-/NO_3^--N. Of the individual components of *SumRel*, population density was most significantly correlated with NO_2^-/NO_3^- -N and color, while road density was most strongly correlated with chloride concentrations. Separating the storm events into groups of <1" or >1" of precipitation resulted in slight improvements to the strength of correlations (based on p-value) of NO_2^-/NO_3^--N and NH_4^+-N with *SumRel*, but had negligible effect on the *SumRel* correlations with other parameters. Mean soil K factor of the sub-watersheds positively correlated with TSS (p=0.0013), turbidity (p=0.0034), 1/T-Tube (p=0.0037) and TP (p=0.016) (Figure 10).

Estuary: Clay/Non-clay influenced groupings.

The streams were separated into two groups with respect to soil clay content to further analyze the sediment-related parameters and TP for their relationship with *SumRel* (Appendix 7). Without separation, there were negative correlations or a lack of significant correlation for most location and flow regime combinations. Splitting the sub-watersheds into groups had the general effect of making negative correlations less negative or slightly positive and making slightly positive correlations more positive.

However, a few significantly positive correlations with *SumRel* emerged from the analysis. Turbidity ($p=0.093$) in the nearshore area during baseflow in the non-clay group was positively correlated with *SumRel*. TP in clay groups in the nearshore area during both baseflow and spring runoff was also positively correlated at $p<0.050$.

Upper Watershed: Tributaries

TSS ($p=0.003$), turbidity ($p=0.025$), TP ($p=0.026$), NO_2^-/NO_3^--N ($p=0.022$), DO percent saturation ($p=0.011$), pH ($p=0.0002$), EC25 ($p<0.0001$), chloride ($p<0.0001$), sulfate ($p=0.017$), *E. coli* ($p=0.015$) and hardness ($p=0.002$) were all strongly correlated with *SumRel* (Table 7, Figure 11). Of the individual components, TP had the highest correlation with percent agriculture; sulfate, *E. coli* and TSS were most correlated with percent developed land; DO, EC25 and chloride had the strongest correlations with population density; pH and hardness were most correlated with road density; and turbidity and NO_2^-/NO_3^--N were most strongly correlated with NPDES density. There was no clear trend for the alternative *SumRel*s. Whether they were more or less correlated with water quality than the original *SumRel* varied.

Impervious Surface

Because they were derived from the same original data source, impervious surface (calculated as mean sub-watershed imperviousness from 2001 NLCD data) was correlated with NLCDs percent developed classification at $r=0.99$.

Discussion

SumRel was shown to be significantly, positively correlated with TSS, turbidity, TP, NO_2^-/NO_3^--N, DO percent saturation, pH, EC25, chloride, sulfate, *E. coli* and hardness in the upper watershed. In the estuary it was significantly, positively correlated with NO_2^-/NO_3^--N, NH_4^+-N, DIN and chloride at multiple flow regime and location combinations. Also in the estuary, *SumRel* either lacked correlation or was negatively correlated with sediment-related parameters. The lack of further correlation in both the upper watershed and the estuary may be explained by a number of potential factors, which are discussed in the ensuing sections.

Stressor Gradients and Landscape Variables

One of the problems with using land cover/land use data in stressor gradients is that the components are represented by percentages of total cover and are not independent (VanSickle 2003). An increase in one component, such as agriculture, requires a necessary decrease in the sum of the other components. Another problem with using stressor gradients occurs if the components are not common in the study area. For example, only 4 of the 27 sub-watersheds had NPDES permit discharges within their boundaries. Additionally, 11 of the 27 watersheds had no agriculture and the average agriculture land coverage in the study area was less than 1 percent. This differs from the results found when *SumRel* was calculated over the extent of the Lake Superior basin (Host et al. 2011). In an attempt to address these issues, the three alternative *SumRel*s were calculated and all of the individual components of *SumRel* were analyzed against the water quality data. In general, the percent agriculture land use in a sub-watershed was not correlated with NO_2^-/NO_3^--N, NH_4^+-N, DIN and chloride. Its removal from *SumRel* served to improve *SumRel's* relationship with those parameters in the estuary but had little effect in the upper watershed. Attempts to strengthen the relationship between water quality and *SumRel* through the removal of the NPDES permit density and both the NPDES permit density and the percent agricultural had mixed results with no clear pattern to the resulting changes in correlations. It should be noted though, that there were some significant correlations between various forms of nitrogen and the NPDES component of the stressor gradient in the estuary.

The types and volumes of discharges that NPDES permits represented varied widely in the study area. They included iron ore tailings ponds, wastewater treatment plants, and shopping mall parking lots among others. We initially considered weighting the NPDES permits to account for this variability; a regional waste water treatment plant will likely have different impacts on water quality than runoff from a shopping mall parking lot. However, there were two major problems with attempting to weight the permits: 1) the permits were for a wide variety of contaminants (including many not included in our parameter list) and 2) the contaminants and quantities listed on permits do not necessarily reflect what (if anything) was being discharged. Additionally, the lack of a current, comprehensive monitoring database made it extremely difficult, and beyond the scope of this study, to compile all of the data to reflect potential pollutant loading rates for each permit, which would have been the most appropriate index to calculate. Because of the wide variety of contaminants it also would be difficult to weight the permits for a general stressor gradient. One option would be to weight them for specific parameters and develop an NPDES stressor gradient component that was specifically tailored for each parameter. For example, waste water treatment plants could be heavily weighted and iron ore tailings ponds could be lightly weighted for a phosphorus specific stressor gradient and vice versa for a sulfate specific stressor gradient. Due to the many uncertainties and a lack of resources, we decided not to weight the NPDES permits.

Stepwise regression was used to determine which *SumRel* components were most relevant to the water quality relationships. Overall, population density was shown to be the most highly relevant component of *SumRel*. Comparisons of the strength of the relationships that *SumRel* and population density had with the water quality variables revealed no clear trend for many parameters. However, in nearly all scenarios, NO_2^-/NO_3^--N, NH_4^+-N, DIN, EC25 and chloride had stronger correlations with population density than with *SumRel*. A significant relationship between NO_3^--N and a gradient of population density was also found by Ahearn et al. (2005).

Initially, we were interested in replacing the percent developed component of *SumRel* with percent impervious surfaces. However, our results showed that water quality was related to percent impervious land cover in a very similar manner as percent developed. Additionally, like Angradi et al. (2009), we found percent developed and percent impervious surface are correlated at $r > 0.97$. This was expected because percent impervious is derived from percent developed in the NLCD land cover data. Because of this tight relationship, we decided that replacing percent developed with percent impervious in *SumRel* would have a negligible effect. Other estimates of impervious surface (e.g. photo interpretation, more resolved satellite imagery, LiDAR, etc.) would likely result in more divergent results that may show stronger relationships with water quality.

A potentially informative variable that was not included in *SumRel* is historical land use. Brown et al. (2009), and Allan (2004), suggested that understanding and accounting for legacy land use is crucial to being able to successfully link landscape characteristics to aquatic condition. In this regard, the St. Louis River watershed has gone through dramatic changes. Chemical waste from the companies that lined the estuary, and to a lesser extent up river, was discharged directly or indirectly into the water, ultimately leading to its designation as an AOC (SLRAC 1992). There has been extensive logging, conversion of forest to agriculture, mining and heavy industry in the watershed. It is also important to consider that because groundwater can move on the scale of centimeters per day, it can take decades for soluble chemicals that were deposited away from the channel to reach streams (Wayland et al. 2002). The legacy land use is difficult to quantify, but could improve our understanding of the factors that are driving surface water quality.

An ongoing argument in the study of landscape influence on aquatic systems concerns the appropriate scale to study (Allan and Johnson 1997, Johnson and Host 2010). Johnson et al. (1997), when analyzing the effect of scale in a Michigan catchment, found that for TN, NO_2^-/NO_3^--N, OP and alkalinity there was little difference in the predictive ability between within-riparian land use and land use at the whole catchment scale. However, they found within-riparian land use to be a better predictor of TP and TSS. Additionally, Richards et al. (1996) found that conditions within a 100m buffer of streams were more important than whole catchment conditions for the prediction of sediment-related habitat variables. These studies suggest that certain characteristics of the riparian zone are particularly important in regard to sediment-related water quality parameters. We chose to use whole catchment scale and our stressor gradient failed to provide predictive power for TP, TSS, turbidity and transparency tube clarity. A *SumRel* calculated at the riparian scale might offer more insight into TP and sediment-related parameters.

Location and Flow Regime - Estuary

The sampling was stratified from late April through September with spring runoff sampling occurring in late April and early May, baseflow sampling occurring in July, August, and September and storm sampling occurring from May through August. Johnson et al. (1997) studied how land use, season and other variables affected stream chemistry in the Saginaw Bay drainage of Michigan. They studied 6 major catchments that were composed of 62 sub catchments and found significant seasonal differences in stream TN, NO_2^-/NO_3^--N, NH_4^+-N and PO_4^{3-}-P levels in the major catchments. If seasonal differences exist in the estuary, that would help explain the difference in the general strength of the relationship between spring and baseflow in both the tributaries and nearshore area.

Two basic locations were sampled in the Estuary: nearshore areas and the tributaries associated with them. While the water in the tributaries comes from their respective watersheds, this is not necessarily true in the nearshore areas. The hydrology of the estuary is complex and there are several variables that affect the source of the water in a particular nearshore area. The Lake Superior seiche, which pushes lake water into the estuary on an approximately 8 hour cycle, with higher frequency oscillations as well, can strongly influence the transport of contaminants, nutrients and suspended solids into and out of nearshore areas as far upstream as the Fond du Lac reservoir (Stortz and Sydor 1980, Trebitz et al. 2002, Sorenson et al. 2004, Trebitz 2006; see also *http://www.lakesuperiorstreams.org/streams/data/Java/stLoRvr.html*). Magnesium and dissolved organic carbon have been used as conservative tracers to estimate relative concentrations of river and lake water in the estuary (Trebitz et al. 2002, Hoffman et al. 2010). Based on a conservative tracer mixing method, Hoffman (2011) estimated that at the US Route 53 John A. Blatnik Bridge the water was, on average, 76% river water and 24% lake water from April through July. This mixing and variability has the potential to dilute the relationship estuary water has with the adjacent watershed and could have diminished the strength of the correlations with *SumRel* in those areas. The correlations between *SumRel* and chloride in tributaries and nearshore during both spring runoff and baseflow are all strongly, positively significant ($p < 0.01$). However, the slopes of the least-squares regressions line for the tributaries are more than twice the slopes of the nearshore areas during each of the respective flow regimes indicating that tributary water quality was much more sensitive to landscape stressors than was nearshore water (Figure 8).

Sediment-related Parameters - Estuary

Although the stressor gradient for many of the flow regime and location combinations had statistically significant positive relationships with the various forms of nitrogen and chloride, its negative correlation or lack thereof, with sediment-related parameters (TSS, clarity, turbidity, and total phosphorus) was opposite to what was hypothesized. In effect, it suggested that increased levels of development and agriculture and large populations were associated with clearer waters. To better understand this relationship the data were analyzed with regard to the soils in the region. One of the unique features of this study area is a relatively clear separation between sub-watersheds dominated by lacustrine clay soils and those that are not. All of the streams flowing into the estuary from Wisconsin have watersheds heavily influenced or dominated by the lacustrine deposits of clay and very fine silt associated with Glacial Lake Duluth (Andrews et al. 1980). Compounding the issue, some of the streams in this region are even more susceptible to erosion due to historical changes in land use that continue to affect hydrology and bank stability, and therefore overall rates of erosion (Riedel et al. 2005, Magner and Brooks 2008).

With the exception of Mission Creek, sub-watersheds on the Minnesota side of the estuary are largely composed of loamy/sandy soils and bedrock (Fitzpatrick et al. 2006) and which are less susceptible to erosion than those on the Wisconsin side. An attempt was made to address this disparity by separating the sub-watersheds into two groups based on the aquatic habitat map developed for their Lower St. Louis River Habitat Plan (Figure 7; SLRAC 2002). This map was developed based on the physical characteristics that are considered important to fish, other aquatic organisms and birds. It was done in combination with vegetation mapping to help identify which areas in the estuary were least and most natural. A separation based solely on the presence or absence of the clay soils was not done because several of the streams in the urban and industrial areas on the Wisconsin side have channels that have been heavily modified, armored and/or covered, limiting their potential erosion of the clay soils. The results of these analyses, although mostly statistically insignificant, suggested that differences in soil type and characteristics were an important factor in the relationship between land use/land cover and sediment-related parameters.

The relationship was further explored by investigating components of the RUSLE. The RUSLE proposes that the 6 most important factors in soil erosion are: rainfall erosivity, soil erodibility (K factor), slope length, slope steepness, cover management and support practice (Renard et al. 1991). Using plots and simulated rainfall, Moltz et al. (2011) found actual erosion to be highly correlated with a version of the RUSLE that excluded cover management and support practices. Because a relatively small percentage of our study area is in agricultural production, cover management and support practices are much less relevant. Additionally, because it is a small study area, it is assumed that rainfall erosivity, i.e. from geospatial variations in rainfall intensity, is similar throughout the estuary. Study area slopes were approximated by calculating the mean stream slope and the standard deviation of elevation for each sub-watershed. Neither showed a meaningful relationship with the sediment-related parameters. However, we found a strong relationship between soil K factor and the sediment-related parameters, especially turbidity (Figure 10), and suggest that it could be used as a predictive variable for those parameters.

Estuary vs Upper Watershed

SumRel was more closely correlated with water quality in the upper watershed. The first possible explanation involves scale. Perhaps the generally larger sub-watersheds and larger study area in the upper watershed are at a more appropriate scale for the land use variables and water quality parameters we investigated. There is much evidence, via the GLEI project, that the stressor gradient approach works well on the larger scale of the Great Lakes basin (e.g. Reavie et al. 2006, Danz et al. 2007, Niemi et al. 2007, Peterson et al. 2007, Trebitz et al. 2007, Morrice et al. 2008). Another explanation would involve the sampling program. By spreading the estuary sampling out over three different flow regimes, we had less, and sometimes no replication for particular sites during a given hydrologic regime. Shiels (2010) suggested a single grab sample is not adequate to determine relationships between landscape variables and water quality parameters. The upper watershed, where most sites were sampled 19 times over the course of two summers for the core suite of parameters and 10 times over one summer for the advanced suite, had the advantage of replication. It was sampled with the MPCA goal of relatively even spacing throughout the summer. There was an attempt to classify the data by distinct hydrologic regime through precipitation records. However, because there were so few samples that would have qualified as storm events, they were all pooled together for this study and likely represent baseflow. By including more sample sites and more replications at each site, the data in the upper watershed benefited from the fact that sample populations trend towards normality and better representation of the entire population as the number of individuals included increases (Montgomery et al.

2006). An outlier may not have much impact when there are 18 replications, but if there is only one or no replication an outlier could have dramatic effects. The minimal replication, or lack thereof, may have weakened the potential relationship of *SumRel* to water quality for the estuary sub-watersheds.

Conclusion

Natural resource managers and researchers need fast, reliable and economical methods to predict or assess water and habitat quality. They need to be able to establish effective monitoring programs and determine which areas are the best candidates for remediation and restoration projects, as well as identify potential reference locations for those restoration projects. Analyzing human related stressors within watersheds and developing relevant stressor gradients are a way to assess an aquatic system. However, the accuracy of the stressor gradient should be verified with water quality, habitat, and/or other relevant biological data before it is used as a predictive tool.

By verifying *SumRel* with a water quality assessment, we now know that it can be used as potential predictor of NO_2^-/NO_3^--N, NH_4^+-N, DIN, and chloride in the estuary, and for TSS, turbidity, TP, NO_2^-/NO_3^--N, % DO saturation, pH, EC25, chloride, sulfate, *E. coli* and hardness in the upper watershed with demonstrated precision. We also found that water quality in estuary tributaries had its strongest relationship with *SumRel* during spring runoff while nearshore water quality was most strongly related to *SumRel* during baseflow.

It does appear that *SumRel* can be adjusted for specific study areas to more closely correlate with various water quality parameters. When applying *SumRel* to a new area or at a new scale, it is important to question the validity of its five existing components and to investigate if there are other components that are relevant and should be included. In the St. Louis River Estuary, a sediment specific *SumRel* may include a K factor component. Alternatively, the K factor is so strongly related by itself, that it could serve as a stand-alone stressor gradient for sediment-related parameters. For the estuary, removing the less relevant agricultural component helped to improve *SumRel*'s ability to predict NO_2^-/NO_3^--N, NH_4^+-N, DIN, and chloride levels. Adjustments to address legacy land use may also help to further improve the relationship.

It is important to remember that this, and many other stressor gradients, was not designed to be necessarily predictive of water quality (Danz et al. 2005, Host et al. 2005, Danz et al. 2007, Host et al. 2011). *SumRel* was intended to perform three functions:

1) quantify anthropogenic stressors across the study area,
2) ensure that our sampling sites stratified areas from relatively pristine to relatively disturbed for the purpose of characterizing water quality in the study area,
3) provide a tool to investigate the relationship between landscapes and aquatic systems.

It performed these functions quite well and was also shown to have value as a predictive tool for certain water quality parameters.

Table 1. Water quality methodology and references.

Parameter	Methodology	Additional References
Chloride	FIA colorimetry (Lachat auto analyzer)	Ameel et al. 1998[2008]
Temperature, EC25, pH, Dissolved Oxygen (mg/L and % saturation)	Field sensors (HydroLab multi-sensor)	USGS 2004; Baker et al. 1997
Turbidity	Nephelometry (Turner Designs *Aquafluor;* HydroLab multi-sensor)	APHA 2005; USGS 2004; Baker et al. 1997
Transparency tube (1/T-Tube)	120 cm visual clarity (field)	MPCA. 2007.
Total Phosphorus	Persulfate digestion + FIA (Lachat auto analyzer)	Ameel et al. 1993, 1998[2008]; Patton and Kryskalla 2003; APHA 2005
Orthophosphate	Lab spectrometry	APHA 2005; Ameel et al. 1998[2008]
Total Nitrogen	Persulfate digestion + FIA (Lachat auto analyzer)	Ameel et al. 1993, 1998[2008]; APHA 2005; USGS 2003
[Nitrate+Nitrite]-N	FIA colorimetry (Cd reduction)	APHA 2005; Ameel et al. 1998[2008]
Ammonium-N	FIA colorimetry (Salicylate)	APHA 2005; Ameel et al. 1998[2008]
Sulfate	FIA colorimetry (Methylthymol Blue) (Lachat auto analyzer)	APHA 2005
Phaeophytin	Acetone extraction and spectrophotometry	APHA 2005; Ameel et al.1998[2008]; Axler and Owen 1994
Chlorophyll-*a*	Acetone (90%) extraction and spectrophotometry	APHA2005; Ameel et al.1998[2008]; Axler and Owen 1994
Color	Lab spectrophotometry vs Pt-Co standards	Ameel et al. 1998[2008]; APHA 2005

Table 2. Pearson product-moment correlation coefficients relating water quality parameters in the St. Louis River Estuary to landscape variables and stressor gradients in tributaries during the end of spring runoff in 2011. All correlations shown are significant at $p<0.10$ ($n=23$).

Tributaries – Spring Runoff	**K Factor**	**% Ag**	**% Dvlp**	**Popul-ation Density**	**Road Density**	**NPDES Density**	***SumRel* no NPDES and Ag**	***SumRel* no Ag**	***SumRel* no NPDES**	***SumRel***
Log10 Turbidity (NTU)	0.53		-0.45	-0.70			-0.51	-0.52	-0.38	**-0.41**
Log10 1/T-Tube (cm^{-1})	0.42		-0.48	-0.68			-0.53	-0.52		**-0.37**
Log10 TP (µg/L)				-0.36						
Log10 OP (µg/L)										
Log10 TN (µg/L)					0.39					**0.37**
Log10 NH4-N (µg/L)	-0.40		0.48	0.58	0.42		0.52	0.53	0.53	**0.54**
Log10 NO2/NO3-N (µg/L)			0.59	0.55	0.54	0.36	0.60	0.63	0.53	**0.57**
Log10 DIN (µg/L)			0.65	0.51	0.64		0.64	0.67	0.53	**0.55**
Log10 Chlorophyll-a (µg/L)			0.53	0.43	0.44	0.44	0.50	0.58	0.46	**0.53**
Log10 Phaeophytin (µg/L)										
Log10 Color (pt-co)	0.36			-0.37						
Log10 EC25 (µS/cm)	-0.40			0.64			0.40	0.39		
Log10 Cl (mg/L)	-0.44		0.88	0.83	0.83		0.90	0.84	0.80	**0.77**
Log10 SO4 (mg/L)										
Log10 DO (mg/L)										
DO (% Saturation)										
pH				0.36						
Temperature (˚C)										

Table 3. Pearson product-moment correlation coefficients relating water quality parameters in the St. Louis River Estuary to landscape variables and stressor gradients in the nearshore area during the end of spring runoff. All correlations shown are significant at p<0.10 (n=26).

Open Water Nearshore – Spring Runoff	**K Factor**	**% Ag**	**% Dvlp**	**Popul-ation Density**	**Road Density**	**NPDES Density**	***SumRel* no NPDES and Ag**	***SumRel* no Ag**	***SumRel* no NPDES**	***SumRel***
Log10 Turbidity (NTU)	0.59			-0.67			-0.38	-0.40		
Log10 1/T-Tube (cm^{-1})	0.60			-0.62						
Log10 TP (µg/L)	0.43									
Log10 OP (µg/L)	0.37	0.40								
TN (µg/L)										
Log10 NH4-N (µg/L)										
Log10 NO2/NO3-N (µg/L)						0.38				
Log10 DIN (µg/L)						0.39				
Log10 Chlorophyll-a (µg/L)		-0.44							-0.34	**-0.36**
Log10 Phaeophytin (µg/L)		-0.63								
Color (pt-co)										
Log10 EC25 (µS/cm)										
Log10 Cl (mg/L)	-0.51		0.66	0.63	0.56	0.37	0.68	0.71	0.67	**0.69**
Log10 SO4 (mg/L)			0.34	0.47			0.37	0.38		
DO (mg/L)	0.37					-0.48		-0.43		
DO (% Saturation)				0.52			0.43	0.39	0.38	
pH				0.34		0.36				**0.33**
Temperature (˚C)				0.37						

Table 4. Pearson product-moment correlation coefficients relating water quality parameters in the St. Louis River Estuary to landscape variables and stressor gradients in tributaries during baseflow in 2010 and 2011. All correlations shown are significant at $p<0.10$ (n=24).

Tributaries – Baseflow	**K Factor**	**% Ag**	**% Dvlp**	**Population Density**	**Road Density**	**NPDES Density**	***SumRel* no NPDES and Ag**	***SumRel* no Ag**	***SumRel* no NPDES**	***SumRel***
Log10 TSS (mg/L)										
Log10 Turbidity (NTU)	0.35			-0.47			-0.35	-0.37		
1/T-Tube (cm^{-1})	0.40		-0.35	-0.46			-0.36	-0.35		
Log10 TP (µg/L)										
Log10 OP (µg/L)										
TN (µg/L)						0.46				
Log10 NH4-N (µg/L)				0.42			0.36	0.41		
Log10 NO2/NO3-N (µg/L)			0.38	0.54		0.44	0.43	0.51		
Log10 DIN (µg/L)	-0.34		0.48	0.61	0.36	0.47	0.52	0.60		**0.34**
Log10 Chlorophyll-a (µg/L)										
Log10 Phaeophytin (µg/L)										
Log10 Color (pt-co)	0.39			-0.63			-0.40			
EC25 (µS/cm)	-0.50		0.47	0.64			0.52	0.52	0.43	**0.44**
Log10 Cl (mg/L)	-0.41		0.74	0.69	0.79		0.79	0.75	0.74	**0.71**
SO4 (mg/L)										
Log10 DO (mg/L)				0.50			0.37	0.39		
DO (% Saturation)				0.45						
pH	-0.47			0.44						
Temperature (˚C)	0.47						-0.35	-0.38		

Table 5. Pearson product-moment correlation coefficients relating water quality parameters in the St. Louis River Estuary to landscape variables and stressor gradients in the nearshore area during baseflow in 2010 and 2011. All correlations shown are significant at $p<0.10$ (n=27).

Open Water Nearshore – Baseflow	**K Factor**	**% Ag**	**% Dvlp**	**Popul-ation Density**	**Road Density**	**NPDES Density**	***SumRel* no NPDES and Ag**	***SumRel* no Ag**	***SumRel* no NPDES**	***SumRel***
Log10 Turbidity (NTU)	0.50	0.40		-0.50						
Log10 1/T-Tube (cm^{-1})	0.49	0.41		-0.48						
TP (µg/L)		0.38								
Log10 OP (µg/L)		0.44						0.35	0.44	**0.46**
TN (µg/L)										
Log10 NH4-N (µg/L)			0.49	0.65	0.45	0.40	0.57	0.62	0.57	**0.61**
Log10 NO2/NO3-N (µg/L)			0.43	0.62			0.47	0.49	0.39	**0.42**
Log10 DIN (µg/L)			0.48	0.59	0.40	0.34	0.53	0.57	0.52	**0.55**
Log10 Chlorophyll-a (µg/L)										
Log10 Phaeophytin (µg/L)										
Log10 Color (pt-co)										
Log10 EC25 (µS/cm)										
Log10 Cl (mg/L)	-0.37		0.77	0.74	0.69		0.81	0.75	0.67	**0.64**
Log10 SO4 (mg/L)	-0.34			0.54			0.33			
DO (mg/L)										
DO (% Saturation)		-0.45								
pH		-0.37								
Temperature (˚C)		-0.41	-0.69	-0.45	-0.65	-0.33	-0.67	-0.69	-0.70	**-0.72**

Table 6. Pearson product-moment correlation coefficients relating water quality parameters in the St. Louis River Estuary to landscape variables and stressor gradients in tributaries during storm events in 2011. All correlations shown are significant at $p<0.10$ (n=16).

Tributaries – Storm Events	**K Factor**	**% Ag**	**% Dvlp**	**Popul-ation Density**	**Road Density**	**NPDES Density**	***SumRel* no NPDES and Ag**	***SumRel* no Ag**	***SumRel* no NPDES**	***SumRel***
Log10 TSS (mg/L)	0.73		-0.49	-0.59	-0.50		-0.57	-0.52		
Turbidity (NTU)	0.69		-0.66	-0.78	-0.71		-0.77	-0.66	-0.51	**-0.45**
1/T-Tube (cm^{-1})	0.68		-0.61	-0.72	-0.70		-0.72	-0.60	-0.49	**-0.43**
TP (µg/L)	0.59									
Log10 OP (µg/L)										
TN (µg/L)			0.45	-0.50	-0.48		-0.51			
Log10 NH4-N (µg/L)						0.56				
Log10 NO2/NO3-N (µg/L)	-0.44		0.65	0.88	0.85		0.82	0.76	0.52	**0.52**
Log10 DIN (µg/L)			0.51	0.76	0.60		0.67	0.71	0.53	**0.58**
Log10 Color (pt-co)	0.47		-0.61	-0.80	-0.68		-0.75	-0.64	-0.54	**-0.47**
EC25 (µS/cm)			0.50	0.45	0.77		0.56	0.47		
Log10 Cl (mg/L)			0.57	0.61	0.81		0.67	0.59	0.59	**0.53**
SO4 (mg/L)	0.62		-0.55	-0.74	-0.64		-0.69	-0.57	-0.58	**-0.50**
Log10 DO (mg/L)			0.39	0.46	0.41		0.45	0.40	0.51	**0.45**
DO (%Saturation)										
pH				0.56				0.49		
Temperature (˚C)					-0.50					

Table 7. Pearson product-moment correlation coefficients relating water quality parameters in the upper St. Louis River watershed from the St. Louis River-Surface Water Assessment (SWASLR) project to landscape variables and stressor gradients. All correlations shown are significant at p<0.10 (n=34).

Upper St. Louis River Tributaries – May-Sep	**% Ag**	**% Dvlp**	**Popul-ation Density**	**Road Density**	**NPDES Density**	***SumRel* no NPDES and Ag**	***SumRel* no Ag**	***SumRel* no NPDES**	***SumRel***
Log10 TSS (mg/L)	0.47	0.44	0.48	0.39		0.49	0.55	0.53	**0.58**
Log10 TVS (mg/L)					0.49				
Log10 Turbidity (NTU)			0.37			0.33	0.39	0.34	**0.39**
Log10 1/T-Tube (cm^{-1})									
Log10 TP (µg/L)	0.41	0.31	0.31		0.77	0.32	0.34	0.38	**0.38**
Log10 TN (µg/L)				-0.31	0.57				
Log10 NH4-N (µg/L)					0.78				
Log10 NO2/NO3-N (µg/L)			0.45			0.33	0.42	0.33	**0.41**
Log10 DIN (µg/L)			0.37				0.31		
Log10 EC25 (µS/cm)	0.32	0.82	0.88	0.80	0.74	0.89	0.86	0.83	**0.82**
Log10 Cl (mg/L)	0.42	0.88	0.89	0.85	0.91	0.94	0.88	0.92	**0.88**
Log10 SO4 (mg/L)		0.65	0.62	0.63		0.67	0.68	0.45	**0.50**
DO (mg/L)									
Log10 DO (% saturation)		0.32	0.37	0.34		0.36		0.41	**0.34**
pH	0.33	0.55	0.56	0.62		0.59	0.59	0.60	**0.60**
Temperature (˚C)	-0.36		-0.40	-0.31	-0.88	-0.35	-0.44	-0.36	**-0.43**
Log10 *E. coli* (MPN 100mL)	0.33	0.42	0.37	0.39	0.73	0.42	0.41	0.42	**0.42**
Log10 Hardness (mg/L)		0.72	0.77	0.77	0.80	0.80	0.75	0.62	**0.62**

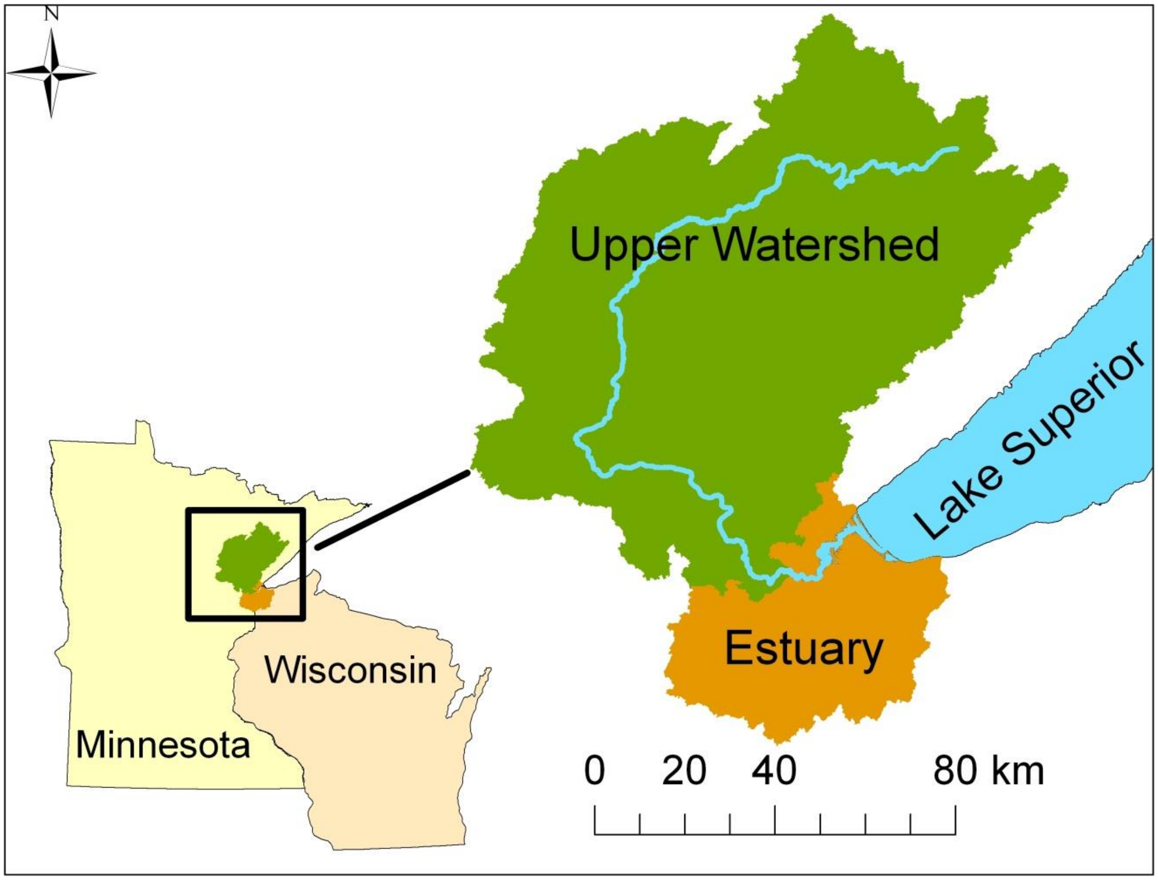

Figure 1. St. Louis River watershed study area in Wisconsin and Minnesota, USA.

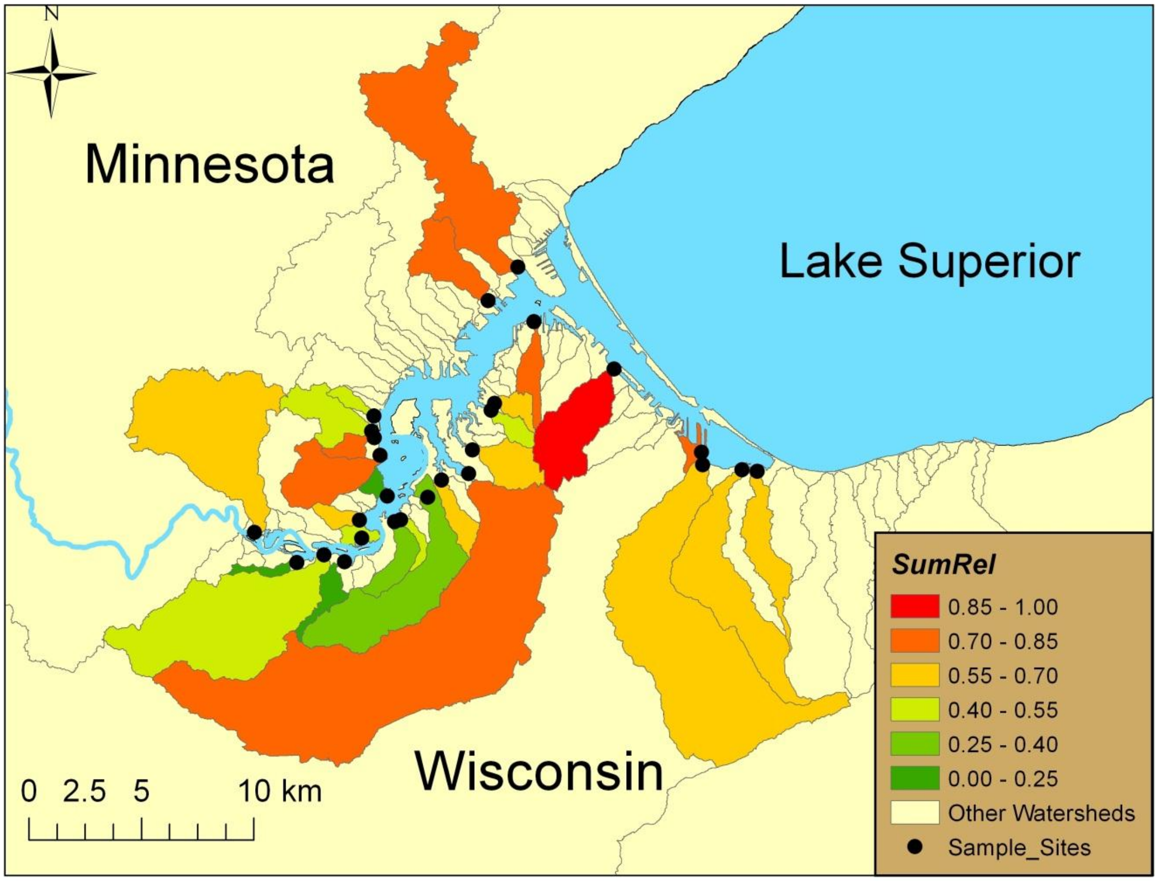

Figure 2. *SumRel* stressor gradient map of the watersheds sampled in the St. Louis River Estuary. A high *SumRel* value represents a relatively disturbed watershed and a low *SumRel* represents a relatively pristine watershed.

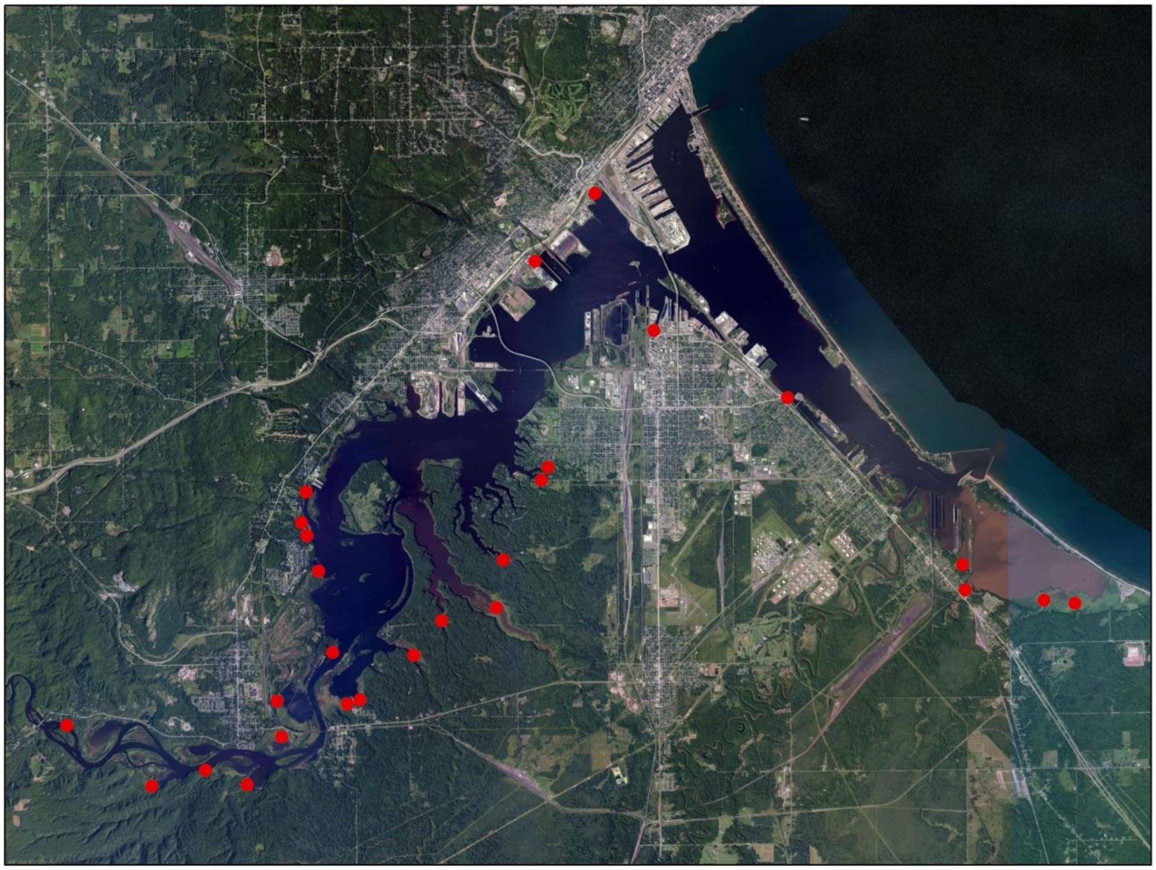

Figure 3. Aerial view of St. Louis River Estuary with baseflow and spring runoff sample site locations.

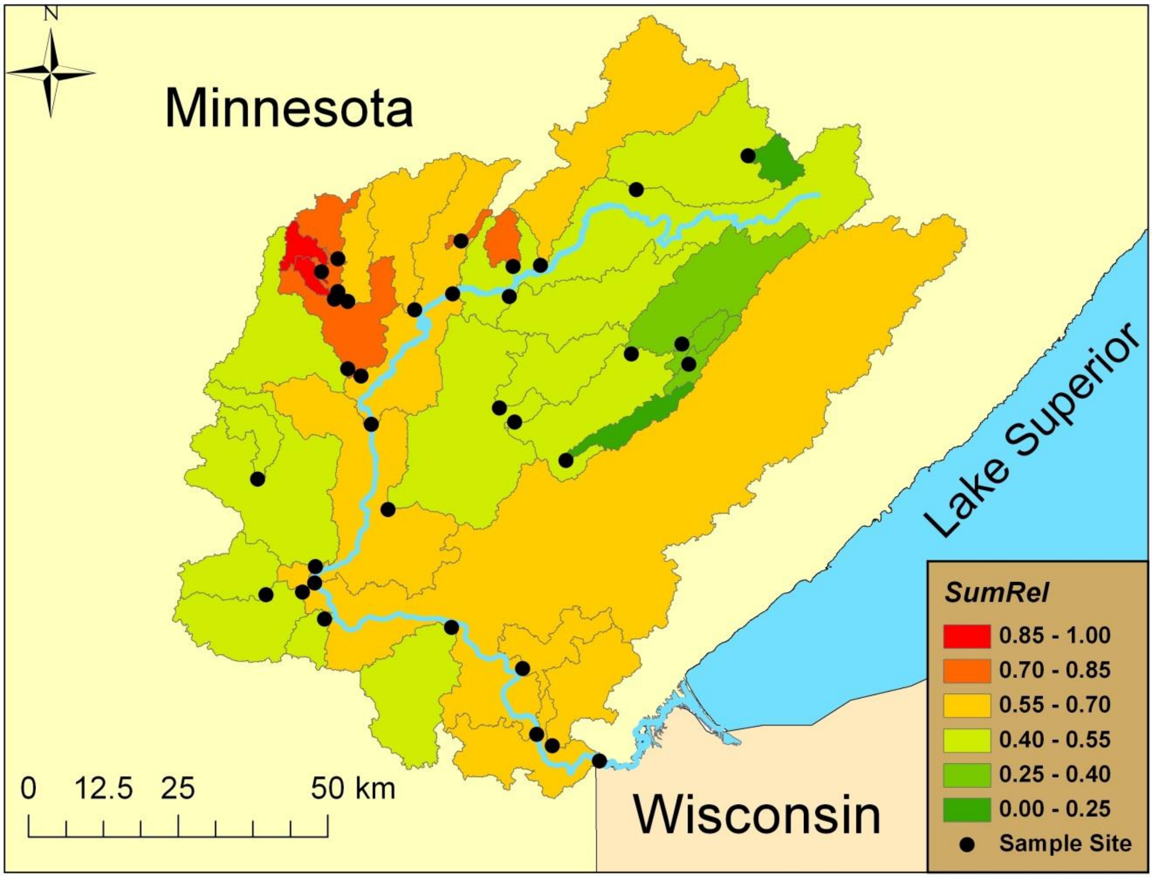

Figure 4. *SumRel* stressor gradient map of the upper St. Louis River watershed for the St. Louis River-Surface Water Assessment (SWASLR) project. A high *SumRel* value represents a relatively disturbed watershed and a low *SumRel* represents a relatively pristine watershed.

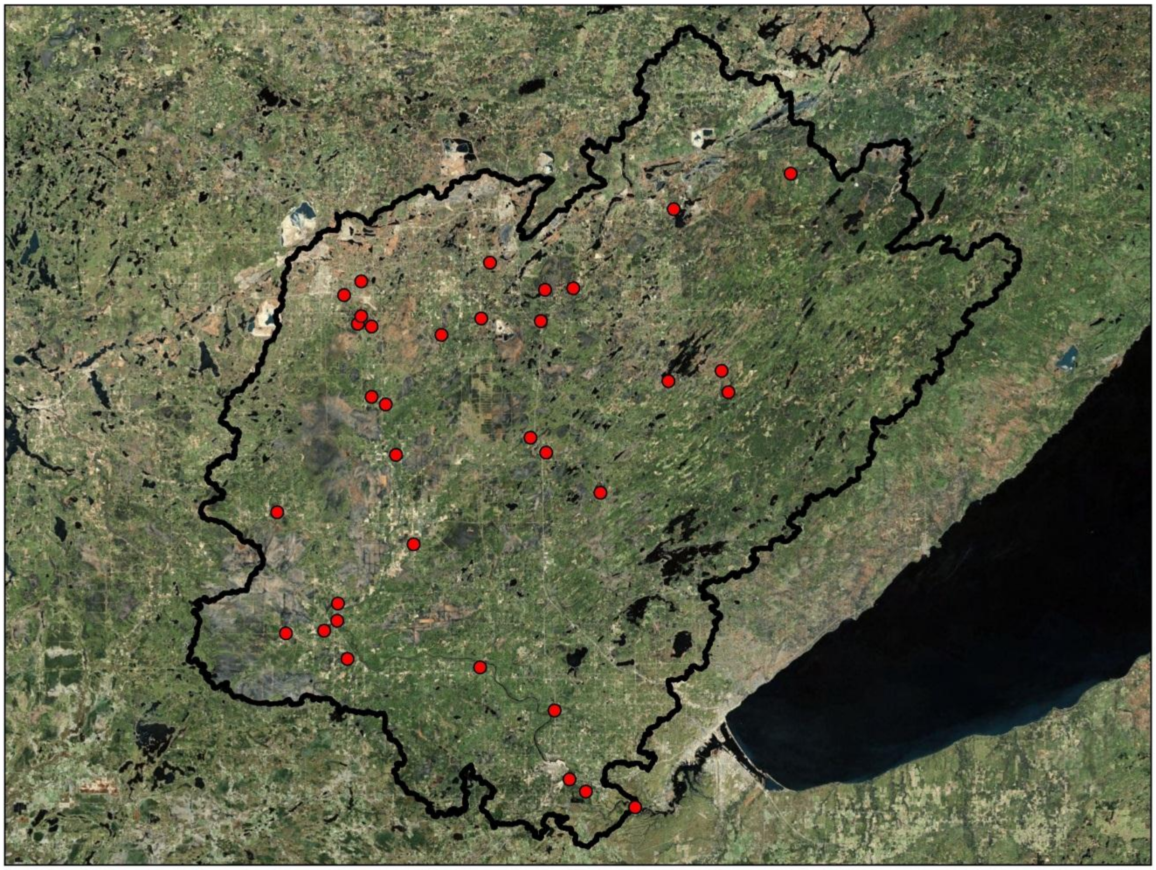

Figure 5. Aerial view of the upper St. Louis River watershed with sample site locations.

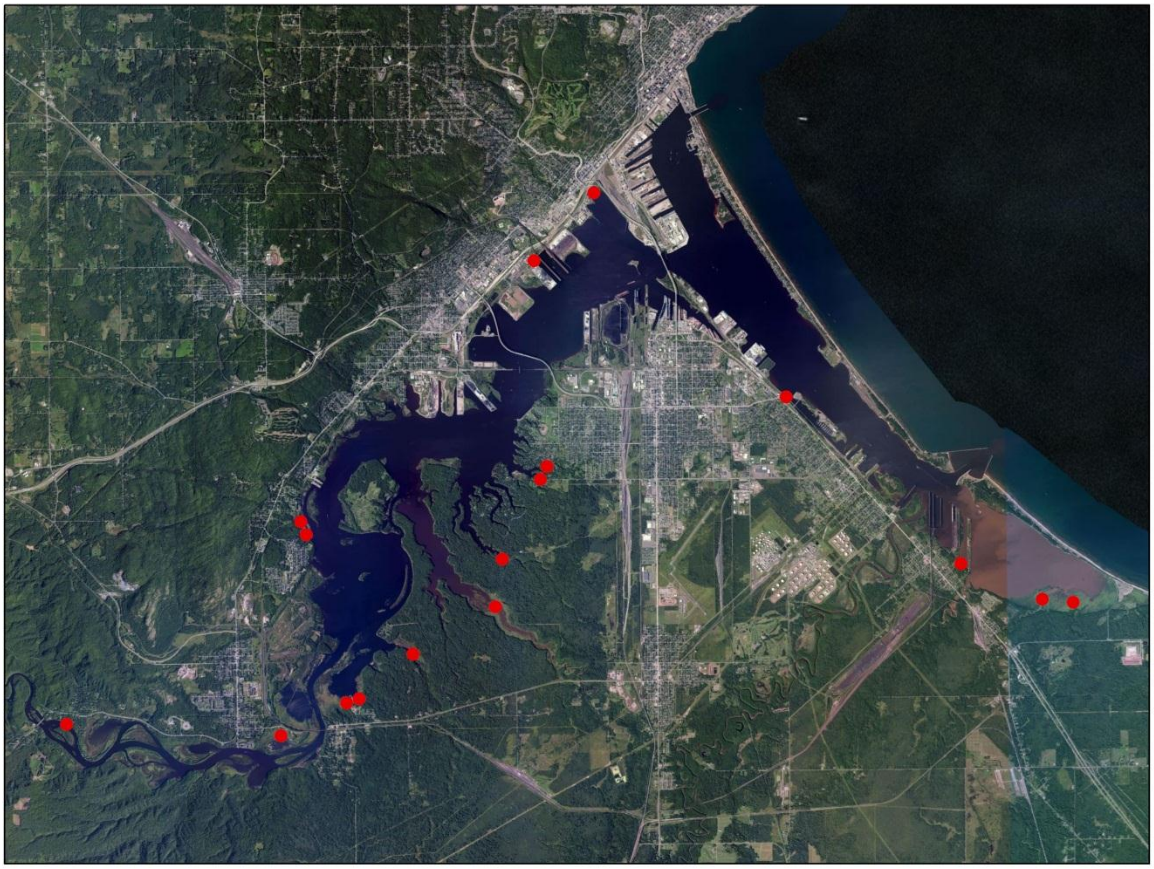

Figure 6. Aerial view of the St. Louis River Estuary with storm event sample site locations.

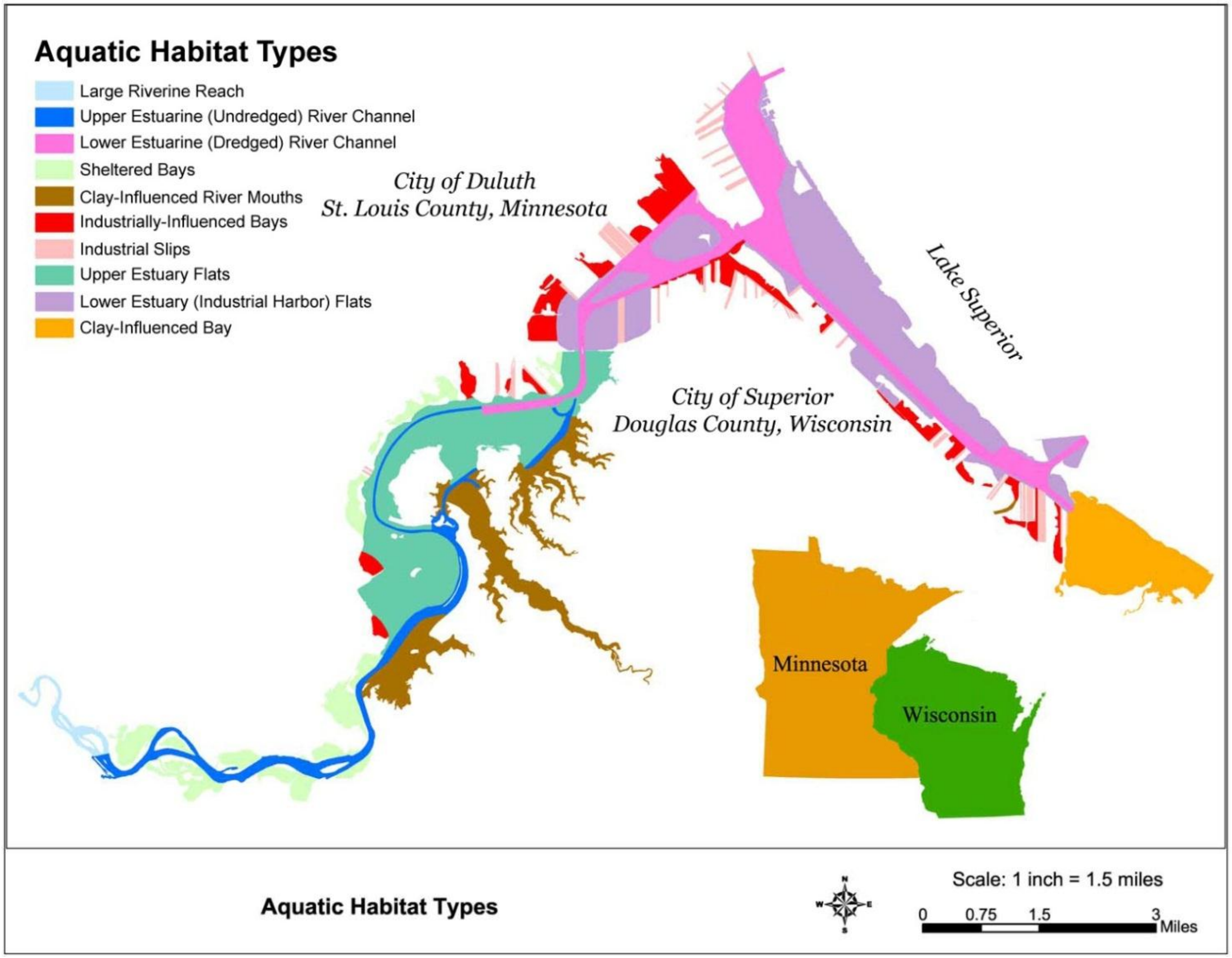

Figure 7. St. Louis River Alliance Aquatic Habitat Types Map (SLRAC 2002).

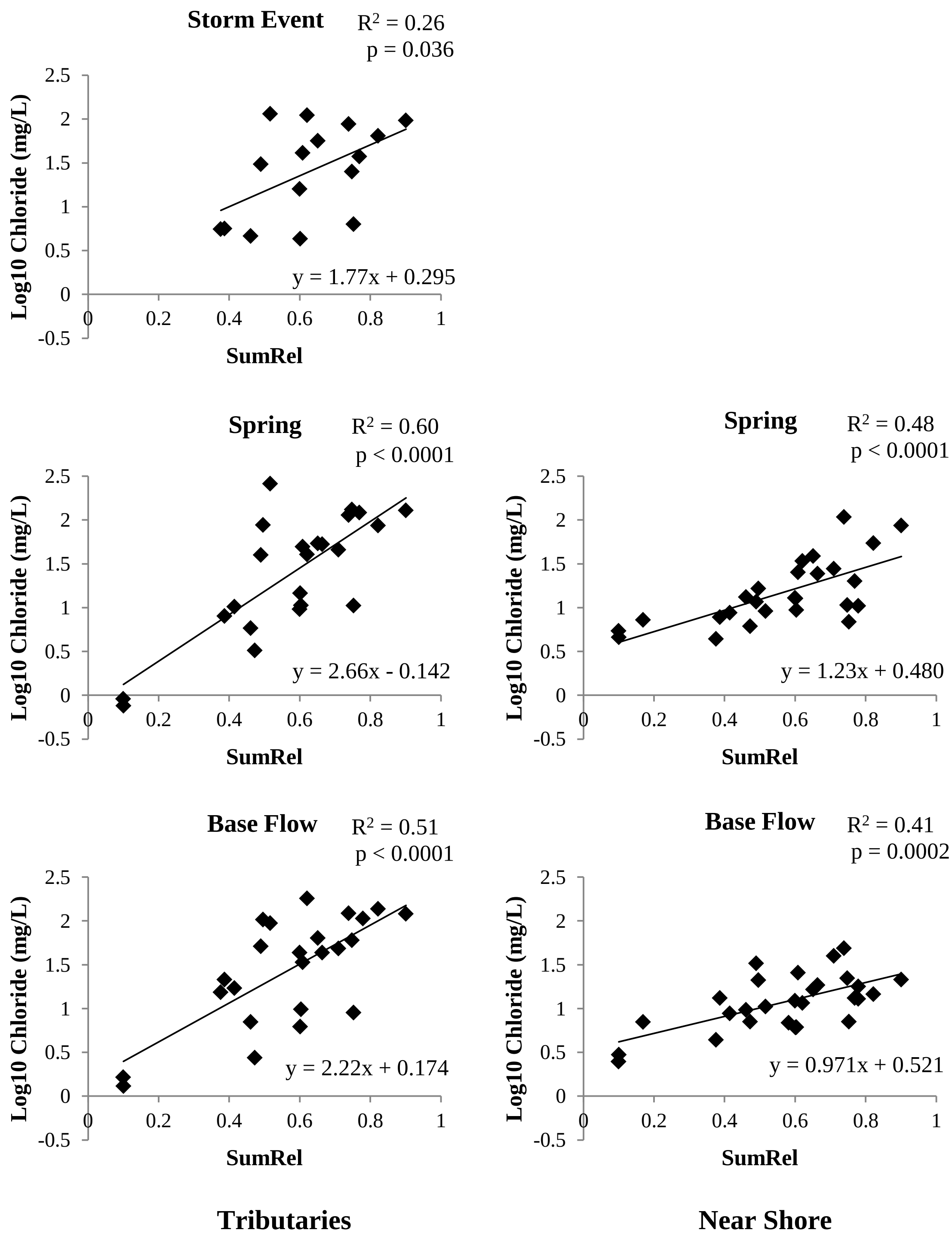

Figure 8. Relationship between SumRel and chloride at different flow regimes and locations in the St. Louis River Estuary.

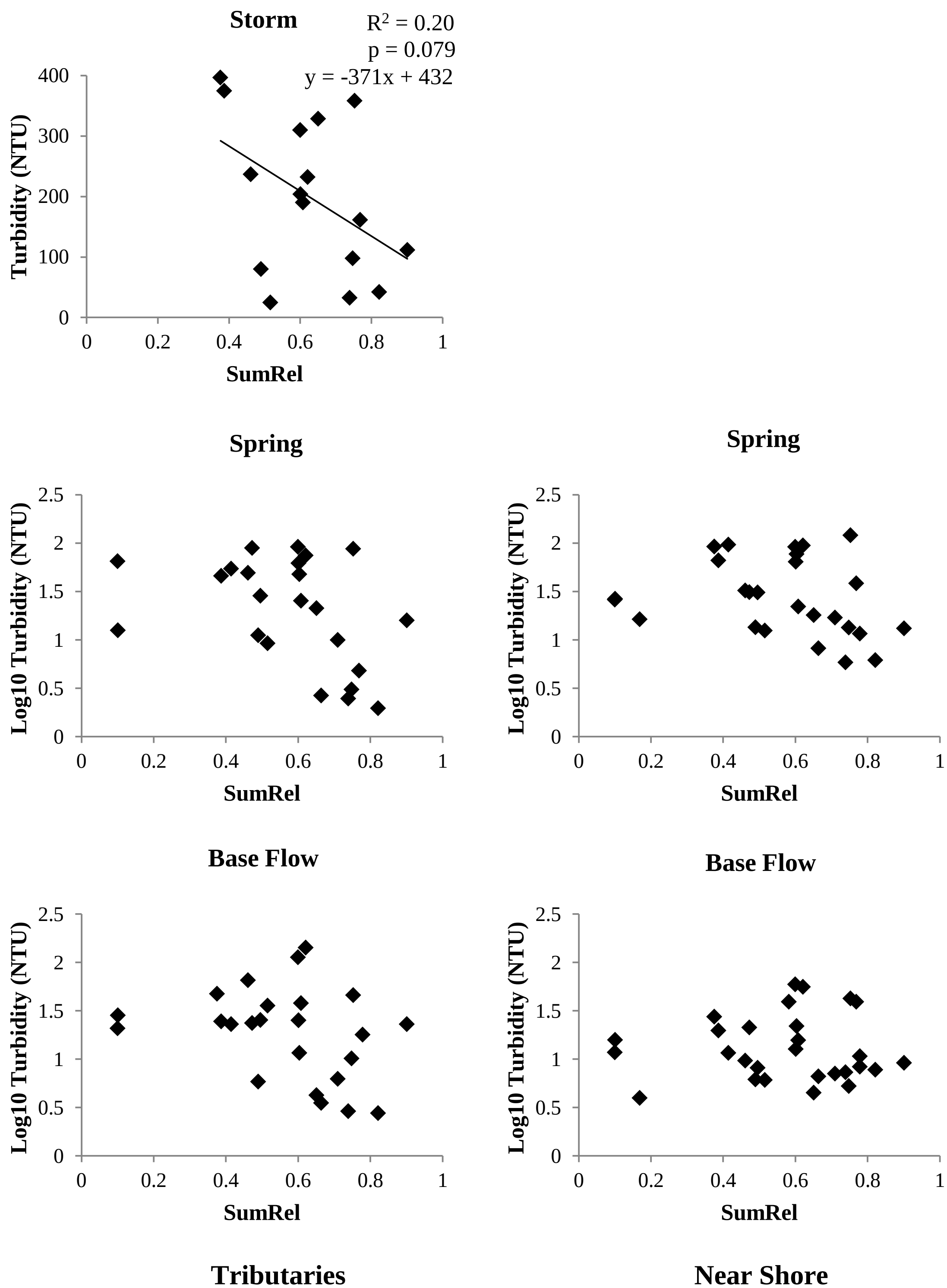

Figure 9. Relationship between SumRel and Turbidity at different flow regimes and locations in the St. Louis River Estuary. Negative correlations prompted further analyses.

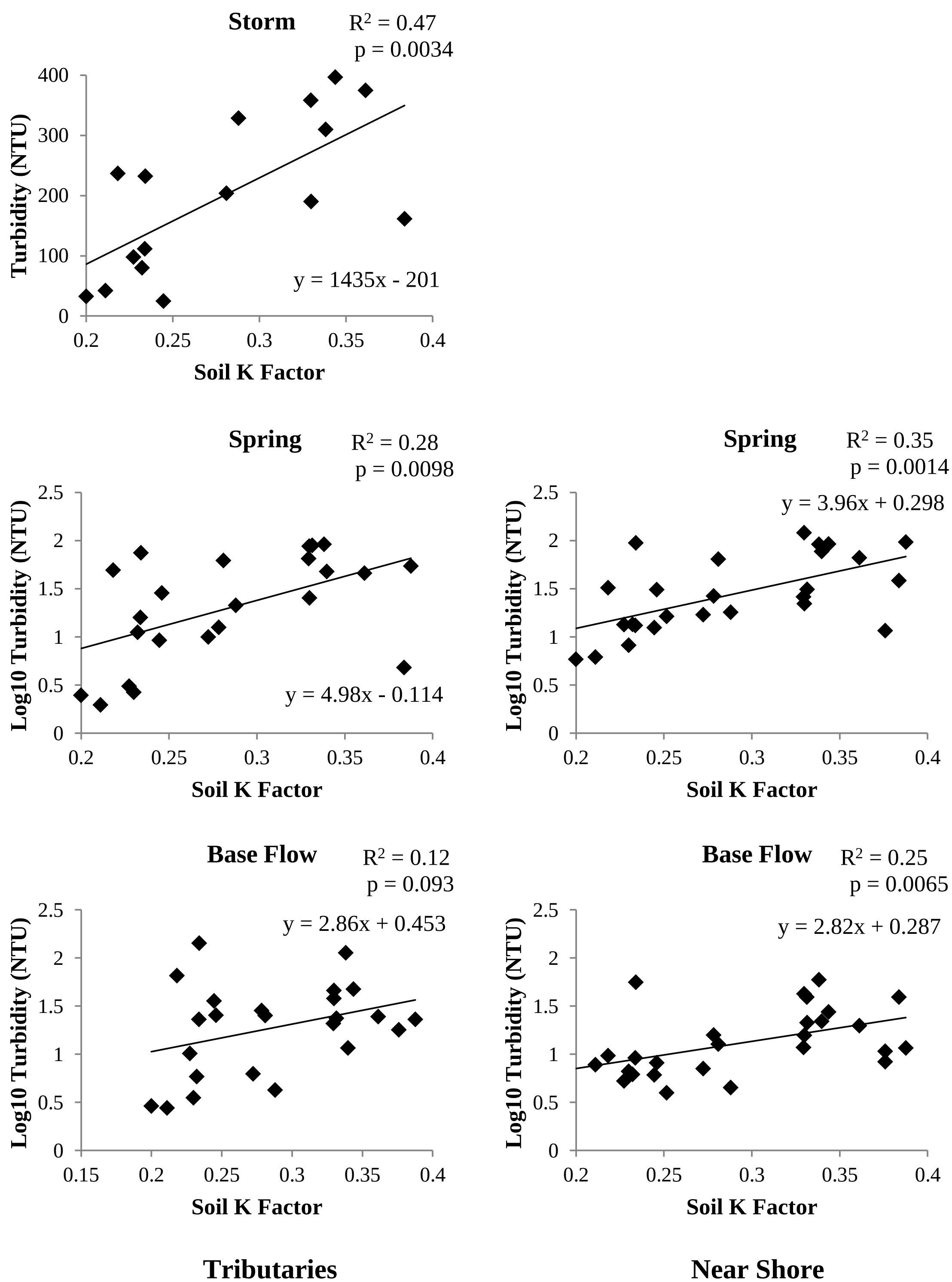

Figure 10. Relationship between soil K factor and turbidity at different flow regimes and locations in the St. Louis River Estuary.

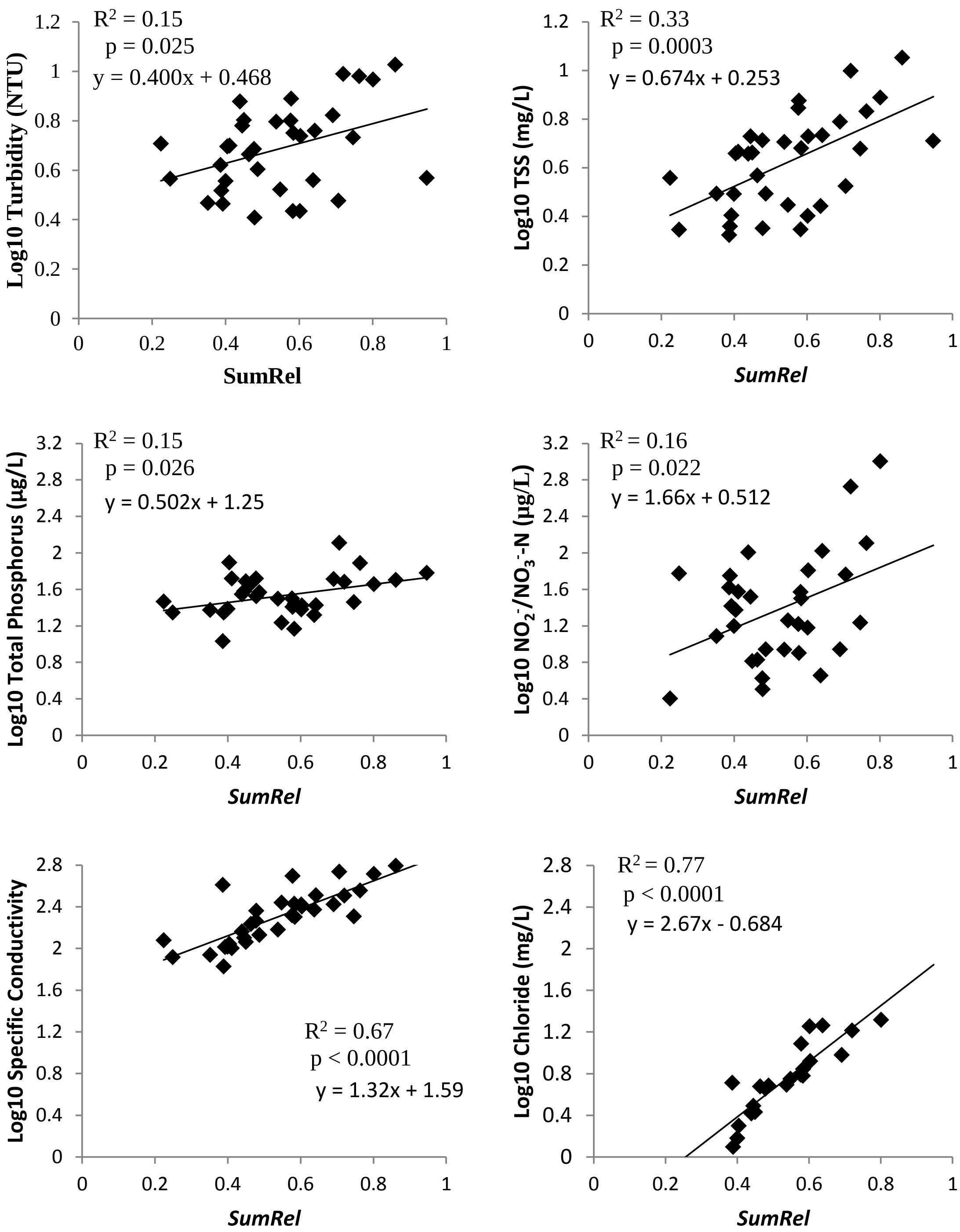

Figure 11. Relationship between *SumRel* and various water quality parameters in the upper St. Louis River watershed.

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Appendices

Appendix A. Pearson product-moment correlation coefficients relating water quality parameters in the St. Louis River Estuary to landscape variables and stressor gradients in tributaries during the end of spring runoff in 2011. Bold values represent correlations significant at $p<0.1$ ($n=23$).

Tributaries – Spring Runoff	K Factor	% Ag	% Dvlp	Popul-lation Density	Road Density	NPDES Density	*SumRel* no NPDES and Ag	*SumRel* no Ag	*SumRel* no NPDES	*SumRel*
Log10 Turbidity (NTU)	**0.53**	0.01	**-0.45**	**-0.70**	-0.31	-0.24	**-0.51**	**-0.52**	**-0.38**	**-0.41**
Log10 1/T-Tube (cm^{-1})	**0.42**	0.08	**-0.48**	**-0.68**	-0.35	-0.14	**-0.53**	**-0.52**	-0.36	**-0.37**
Log10 TP (µg/L)	0.34	0.09	-0.10	**-0.36**	-0.01	0.01	-0.16	-0.13	-0.08	-0.07
Log10 OP (µg/L)	0.14	0.15	0.23	-0.01	0.26	0.26	0.18	0.24	0.21	0.25
Log10 TN (µg/L)	0.10	0.23	0.34	0.04	**0.39**	0.28	0.29	0.34	0.33	**0.37**
Log10 NH4-N (µg/L)	**-0.40**	0.28	**0.48**	**0.58**	**0.42**	0.25	**0.52**	**0.53**	**0.53**	**0.54**
Log10 NO2/NO3-N (µg/L)	-0.31	0.16	**0.59**	**0.55**	**0.54**	**0.36**	**0.60**	**0.63**	**0.53**	**0.57**
Log10 DIN (µg/L)	-0.25	0.11	**0.65**	**0.51**	**0.64**	0.34	**0.64**	**0.67**	**0.53**	**0.55**
Log10 Chlorophyll-a (µg/L)	-0.09	0.17	**0.53**	**0.43**	**0.44**	**0.44**	**0.50**	**0.58**	**0.46**	**0.53**
Log10 Phaeophytin (µg/L)	0.22	-0.33	0.33	0.31	0.34	0.05	0.34	0.28	-0.01	0.01
Log10 Color (pt-co)	**0.36**	0.18	-0.02	**-0.37**	0.10	-0.06	-0.09	-0.10	0.03	0.00
Log10 EC25 (µS/cm)	**-0.40**	-0.07	0.32	**0.64**	0.20	0.15	**0.40**	**0.39**	0.27	0.28
Log10 Cl (mg/L)	**-0.44**	0.24	**0.88**	**0.83**	**0.83**	0.21	**0.90**	**0.84**	**0.80**	**0.77**
Log10 SO4 (mg/L)	0.19	0.07	0.21	0.02	0.23	0.17	0.17	0.20	0.17	0.19
Log10 DO (mg/L)	0.38	0.13	0.05	-0.15	0.29	-0.01	-0.01	-0.01	0.09	0.07
Log10 DO (% Saturation)	-0.31	-0.22	-0.15	0.00	-0.07	-0.30	-0.07	-0.21	-0.23	-0.31
pH	-0.07	0.02	0.04	**0.36**	-0.06	0.05	0.11	0.11	0.09	0.10
Temperature (˚C)	-0.34	-0.05	-0.01	0.29	-0.12	0.04	0.05	0.05	0.01	0.02

Appendix B. Pearson product-moment correlation coefficients relating water quality parameters in the St. Louis River Estuary to landscape variables and stressor gradients in the nearshore area during the end of spring runoff. Bold values represent correlations significant at p<0.1 (n=26).

Open Water Nearshore – Spring Runoff	**K Factor**	**% Ag**	**% Dvlp**	**Popul-ation Density**	**Road Density**	**NPDES Density**	***SumRel* no NPDES and Ag**	***SumRel* no Ag**	***SumRel* no NPDES**	***SumRel***
Log10 Turbidity (NTU)	**0.59**	0.17	-0.32	**-0.67**	-0.11	-0.21	**-0.38**	**-0.40**	-0.22	-0.25
Log10 1/T-Tube (cm^{-1})	**0.60**	0.22	-0.25	**-0.62**	-0.06	-0.11	-0.32	-0.32	-0.14	-0.15
Log10 TP (µg/L)	**0.43**	0.17	0.04	-0.28	0.16	-0.02	-0.01	-0.01	0.07	0.06
Log10 OP (µg/L)	**0.37**	**0.40**	0.07	-0.27	0.25	0.15	0.04	0.08	0.21	0.22
TN (µg/L)	0.32	0.11	-0.06	-0.21	0.09	0.08	-0.06	-0.03	0.01	0.02
Log10 NH4-N (µg/L)	-0.16	0.01	0.08	0.18	-0.02	0.20	0.08	0.13	0.07	0.11
Log10 NO2/NO3-N (µg/L)	-0.01	0.25	0.14	0.12	0.24	**0.38**	0.18	0.27	0.25	0.32
Log10 DIN (µg/L)	-0.07	0.20	0.14	0.15	0.19	**0.39**	0.17	0.26	0.22	0.29
Log10 Chlorophyll-a (µg/L)	-0.02	**-0.44**	0.25	0.29	0.20	-0.05	0.27	0.22	0.00	-0.01
Log10 Phaeophytin (µg/L)	0.25	**-0.63**	-0.02	-0.13	-0.09	-0.20	-0.07	-0.12	**-0.34**	**-0.36**
Color(pt-co)	0.29	0.11	0.16	-0.09	0.18	-0.04	0.11	0.09	0.14	0.12
Log10 EC25 (µS/cm)	**-0.42**	-0.08	0.24	0.34	0.03	0.14	0.22	0.24	0.14	0.16
Log10 Cl (mg/L)	**-0.51**	0.31	**0.66**	**0.63**	**0.56**	**0.37**	**0.68**	**0.71**	**0.67**	**0.69**
Log10 SO4 (mg/L)	-0.22	-0.15	**0.34**	**0.47**	0.22	0.19	**0.37**	**0.38**	0.21	0.24
DO (mg/L)	**0.37**	-0.05	-0.32	-0.32	-0.05	**-0.48**	-0.29	**-0.43**	-0.25	-0.36
DO (% Saturation)	-0.11	0.09	0.34	**0.52**	0.27	0.01	**0.43**	**0.39**	**0.38**	0.35
pH	-0.13	0.17	0.24	**0.34**	0.11	**0.36**	0.25	0.33	0.27	**0.33**
Temperature (˚C)	-0.30	0.01	0.18	**0.37**	-0.01	0.26	0.19	0.25	0.15	0.20

Appendix C. Pearson product-moment correlation coefficients relating water quality parameters in the St. Louis River Estuary to landscape variables and stressor gradients in tributaries during baseflow in 2010 and 2011. Bold values represent correlations significant at $p<0.1$ (n=24).

Tributaries – Baseflow	**K Factor**	**% Ag**	**% Dvlp**	**Popul-ation Density**	**Road Density**	**NPDES Density**	***SumRel* no NPDES and Ag**	***SumRel* no Ag**	***SumRel* no NPDES**	***SumRel***
Log10 TSS (mg/L)	0.26	-0.08	-0.25	-0.26	-0.15	-0.24	-0.26	-0.31	-0.25	-0.30
Log10 Turbidity (NTU)	**0.35**	-0.02	-0.32	**-0.47**	-0.17	-0.22	**-0.35**	**-0.37**	-0.28	-0.31
Log10 1/T-Tube (cm^{-1})	**0.40**	0.13	**-0.35**	**-0.46**	-0.18	-0.13	**-0.36**	**-0.35**	-0.22	-0.23
Log10 TP (µg/L)	0.18	-0.05	0.11	-0.03	0.14	0.09	0.08	0.10	0.04	0.06
Log10 OP (µg/L)	0.24	-0.07	0.29	0.23	0.22	0.32	0.27	0.33	0.18	0.24
TN (µg/L)	0.00	0.07	0.22	0.03	0.34	**0.46**	0.21	0.33	0.20	0.30
Log10 NH4-N (µg/L)	-0.32	-0.10	0.32	**0.42**	0.25	0.31	**0.36**	**0.41**	0.23	0.28
Log10 NO2/NO3-N (µg/L)	-0.26	-0.30	**0.38**	**0.54**	0.28	**0.44**	**0.43**	**0.51**	0.19	0.28
Log10 DIN (µg/L)	-0.34	-0.32	**0.48**	**0.61**	**0.36**	**0.47**	**0.52**	**0.60**	0.25	**0.34**
Log10 Chlorophyll-a (µg/L)	0.02	0.23	-0.11	-0.26	0.02	-0.11	-0.13	-0.14	0.01	-0.02
Log10 Phaeophytin (µg/L)	0.07	0.28	-0.14	-0.21	-0.04	-0.11	-0.14	-0.16	0.03	-0.01
Log10 Color (pt-co)	**0.39**	0.10	-0.34	**-0.63**	-0.15	0.09	**-0.40**	-0.33	-0.27	-0.22
EC25 (µS/cm)	**-0.50**	0.04	**0.47**	**0.64**	0.34	0.21	**0.52**	**0.52**	**0.43**	**0.44**
Log10 Cl (mg/L)	**-0.41**	0.24	**0.74**	**0.69**	**0.79**	0.20	**0.79**	**0.75**	**0.74**	**0.71**
SO4 (mg/L)	0.12	0.07	0.24	0.25	0.19	0.22	0.24	0.28	0.22	0.26
Log10 DO (mg/L)	-0.35	-0.17	0.35	**0.50**	0.17	0.22	**0.37**	**0.39**	0.21	0.24
Log10 (DO % Saturation)	-0.20	-0.01	0.24	**0.45**	0.11	0.13	0.28	0.28	0.22	0.23
pH	**-0.47**	-0.04	0.15	**0.44**	0.03	0.06	0.21	0.20	0.15	0.14
Temperature (˚C)	**0.47**	0.31	-0.39	-0.29	-0.24	-0.25	**-0.35**	**-0.38**	-0.12	-0.17

Appendix D. Pearson product-moment correlation coefficients relating water quality parameters in the St. Louis River Estuary to landscape variables and stressor gradients in the nearshore area during baseflow in 2010 and 2011. Bold values represent correlations significant at p<0.1 (n=27).

Open Water Nearshore – Baseflow	**K Factor**	**% Ag**	**% Dvlp**	**Popul-ation Density**	**Road Density**	**NPDES Density**	***SumRel* no NPDES and Ag**	***SumRel* no Ag**	***SumRel* no NPDES**	***SumRel***
Log10 Turbidity (NTU)	**0.50**	**0.40**	-0.15	**-0.50**	0.03	-0.03	-0.21	-0.20	0.03	0.02
Log10 1/T-Tube (cm^{-1})	**0.49**	**0.41**	-0.12	**-0.48**	0.03	0.08	-0.18	-0.15	0.05	0.06
TP (µg/L)	0.25	**0.38**	-0.03	-0.30	0.13	0.05	-0.06	-0.04	0.13	0.13
Log10 OP (µg/L)	0.21	**0.44**	0.26	0.31	0.28	0.27	0.31	**0.35**	**0.44**	**0.46**
TN (µg/L)	-0.01	0.09	-0.11	0.03	0.01	0.28	-0.04	0.04	0.01	0.07
Log10 NH4-N (µg/L)	-0.02	0.28	**0.49**	**0.65**	**0.45**	**0.40**	**0.57**	**0.62**	**0.57**	**0.61**
Log10 NO2/NO3-N (µg/L)	-0.16	0.07	**0.43**	**0.62**	0.26	0.26	**0.47**	**0.49**	**0.39**	**0.42**
Log10 DIN (µg/L)	-0.16	0.24	**0.48**	**0.59**	**0.40**	**0.34**	**0.53**	**0.57**	**0.52**	**0.55**
Log10 Chlorophyll-a (µg/L)	-0.09	0.13	0.04	-0.10	0.10	0.08	0.02	0.04	0.08	0.09
Log10 Phaeophytin (µg/L)	-0.18	0.10	0.13	0.07	0.14	0.17	0.13	0.16	0.14	0.17
Log10 Color (pt-co)	0.31	0.07	-0.23	-0.14	-0.11	0.00	-0.19	-0.17	-0.11	-0.10
Log10 EC25 (µS/cm)	-0.30	-0.25	0.25	0.32	0.04	-0.07	0.18	0.15	0.01	0.00
Log10 Cl (mg/L)	**-0.37**	0.11	**0.77**	**0.74**	**0.69**	0.11	**0.81**	**0.75**	**0.67**	**0.64**
Log10 SO4 (mg/L)	**-0.34**	-0.04	0.24	**0.54**	0.17	0.07	**0.33**	0.31	0.23	0.23
DO (mg/L)	-0.03	-0.32	0.26	0.29	0.10	-0.08	0.26	0.22	0.07	0.04
DO (% Saturation)	0.01	**-0.45**	-0.01	0.08	-0.16	-0.18	0.00	-0.05	-0.19	-0.22
pH	0.02	**-0.37**	-0.04	0.08	-0.18	-0.28	-0.05	-0.13	-0.21	-0.25
Temperature (˚C)	0.14	**-0.41**	**-0.69**	**-0.45**	**-0.65**	**-0.33**	**-0.67**	**-0.69**	**-0.70**	**-0.72**

Appendix E. Pearson product-moment correlation coefficients relating water quality parameters in the St. Louis River Estuary to landscape variables and stressor gradients in tributaries during storm events in 2011. Bold values represent correlations significant at p<0.1 (n=16).

Tributaries – Storm Events	**K Factor**	**% Ag**	**% Dvlp**	**Population Density**	**Road Density**	**NPDES Density**	***SumRel* no NPDES and Ag**	***SumRel* no Ag**	***SumRel* no NPDES**	***SumRel***
Log10 TSS (mg/L)	**0.73**	0.25	**-0.49**	**-0.59**	**-0.50**	-0.14	**-0.57**	**-0.52**	-0.28	-0.28
Turbidity (NTU)	**0.69**	0.15	**-0.66**	**-0.78**	**-0.71**	-0.10	**-0.77**	**-0.66**	**-0.51**	**-0.45**
1/T-Tube (cm^{-1})	**0.68**	0.11	**-0.61**	**-0.72**	**-0.70**	-0.07	**-0.72**	**-0.60**	**-0.49**	**-0.43**
TP (µg/L)	**0.59**	-0.05	-0.20	-0.42	-0.22	0.00	-0.31	-0.25	-0.28	-0.23
Log10 OP (µg/L)	0.35	-0.02	0.23	0.26	0.24	0.29	0.26	0.34	0.19	0.26
TN (µg/L)	0.36	0.16	**-0.45**	**-0.50**	**-0.48**	0.08	**-0.51**	-0.37	-0.29	-0.21
Log10 NH4-N (µg/L)	-0.19	-0.07	0.14	0.25	0.24	**0.56**	0.21	0.42	0.12	0.30
Log10 NO2/NO3-N (µg/L)	**-0.44**	-0.21	**0.65**	**0.88**	**0.85**	0.24	**0.82**	**0.76**	**0.52**	**0.52**
Log10 DIN (µg/L)	-0.33	0.01	**0.51**	**0.76**	**0.60**	0.40	**0.67**	**0.71**	**0.53**	**0.58**
Log10 Color (pt-co)	**0.47**	0.08	**-0.61**	**-0.80**	**-0.68**	-0.09	**-0.75**	**-0.64**	**-0.54**	**-0.47**
EC25 (µS/cm)	-0.30	-0.08	**0.50**	**0.45**	**0.77**	0.06	**0.56**	**0.47**	0.39	0.34
Log10 Cl (mg/L)	-0.41	0.09	**0.57**	**0.61**	**0.81**	0.13	**0.67**	**0.59**	**0.59**	**0.53**
SO4 (mg/L)	**0.62**	-0.06	**-0.55**	**-0.74**	**-0.64**	-0.05	**-0.69**	**-0.57**	**-0.58**	**-0.50**
DO (mg/L)	0.02	0.00	0.20	0.23	0.41	-0.14	0.25	0.14	0.21	0.12
DO (% Saturation)	-0.02	0.12	0.12	0.13	0.25	-0.04	0.15	0.10	0.20	0.15
pH	-0.08	-0.07	0.21	**0.56**	0.40	0.40	0.40	**0.49**	0.27	0.36
Temperature (˚C)	-0.11	0.33	-0.24	-0.33	**-0.50**	0.33	-0.34	-0.12	-0.04	0.08

Appendix F. Pearson product-moment correlation coefficients relating water quality parameters in the upper St. Louis River watershed from the St. Louis River-Surface Water Assessment (SWASLR) project to landscape variables and stressor gradients. Bold values represent correlations significant at $p<0.1$ ($n=34$).

Upper St. Louis River Tributaries – May-Sep	**% Ag**	**% Dvlp**	**Population Density**	**Road Density**	**NPDES Density**	***SumRel* no NPDES and Ag**	***SumRel* no Ag**	***SumRel* no NPDES**	***SumRel***
Log10 TSS (mg/L)	**0.47**	**0.44**	**0.48**	**0.39**	0.47	**0.49**	**0.55**	**0.53**	**0.58**
Log10 TVS (mg/L)	0.19	0.04	0.14	0.04	**0.49**	0.13	0.19	0.14	0.18
Log10 Turbidity (NTU)	0.27	0.26	**0.37**	0.25	0.30	**0.33**	**0.39**	**0.34**	**0.39**
Log10 1/T-Tube (cm^{-1})	0.14	-0.19	-0.02	-0.21	0.09	-0.09	-0.04	-0.04	0.00
Log10 TP (µg/L)	**0.41**	**0.31**	**0.31**	0.21	**0.77**	**0.32**	**0.34**	**0.38**	**0.38**
Log10 TN (µg/L)	0.08	-0.16	-0.09	**-0.31**	**0.57**	-0.18	-0.11	-0.13	-0.08
Log10 NH4-N (µg/L)	0.12	0.10	0.16	-0.13	**0.78**	0.04	0.15	0.06	0.15
Log10 NO2/NO3-N (µg/L)	-0.02	**0.36**	**0.45**	0.23	0.44	**0.33**	**0.42**	**0.33**	**0.41**
Log10 DIN (µg/L)	0.01	0.29	**0.37**	0.07	0.42	0.24	**0.31**	0.24	0.30
Log10 EC25 (µS/cm)	**0.32**	**0.87**	**0.88**	**0.80**	**0.74**	**0.89**	**0.86**	**0.83**	**0.82**
Log10 Cl (mg/L)	**0.42**	**0.88**	**0.89**	**0.85**	**0.91**	**0.94**	**0.88**	**0.92**	**0.88**
Log10 SO4 (mg/L)	-0.17	**0.65**	**0.62**	**0.63**	0.15	**0.67**	**0.68**	**0.45**	**0.50**
Log10 DO (mg/L)	0.29	**0.39**	**0.46**	**0.41**	-0.01	**0.45**	**0.40**	**0.51**	**0.45**
Log10 DO (% Saturation)	0.19	0.29	**0.37**	**0.34**	-0.29	**0.36**	0.29	**0.41**	**0.34**
pH	**0.33**	**0.56**	**0.56**	**0.62**	0.03	**0.59**	**0.59**	**0.60**	**0.60**
Log10 Temperature (˚C)	**-0.36**	**-0.37**	**-0.40**	**-0.31**	**-0.88**	**-0.35**	**-0.44**	**-0.36**	**-0.43**
Log10 *E. coli* (MPN 100mL)	**0.33**	**0.40**	**0.37**	**0.39**	**0.73**	**0.42**	**0.41**	**0.42**	**0.42**
Log10 Hardness (mg/L)	-0.01	**0.72**	**0.77**	**0.77**	**0.80**	**0.80**	**0.75**	**0.62**	**0.62**

Appendix G. Estuary sample site locations and clay-influenced/non clay-influenced groupings.

Site ID	Latitude	Longitude	Clay-Influenced	Non Clay-Influenced
1	46.65825	-92.27600	X	
3	46.64936	-92.23535	X	
6	46.67298	-92.17765	X	
7	46.68904	-92.20270		X
8	46.69850	-92.20729		X
9	46.67936	-92.16709	X	
10	46.68232	-92.15534	X	
11	46.69112	-92.14939	X	
17	46.68404	-92.01464	X	
18	46.76295	-92.12050		X
19	46.75012	-92.13882		X
23	46.64635	-92.25073	X	
24	46.65541	-92.21403		X
25	46.64629	-92.22368	X	
27	46.66282	-92.21426		X
30	46.66262	-92.19496	X	
31	46.66302	-92.19123	X	
32	46.67233	-92.19867		X
33	46.70440	-92.20583		X
34	46.69621	-92.20510		X
50	46.70893	-92.13705	X	
51	46.70694	-92.13803	X	
53	46.74161	-92.11224		X
57	46.72234	-92.06611		X
61	46.68198	-91.99200	X	
63	46.68131	-91.98418	X	
117	46.68871	-92.01587		X

Appendix H. Upper watershed sample site locations.

Site ID	Latitude	Longitude
S000-021	46.65925	-92.28322
S003-611	46.68241	-92.38569
S005-758	46.87432	-92.88278
S005-759	46.79895	-92.44965
S004-594	46.86151	-92.60509
S005-761	47.08495	-93.03015
S005-762	47.16698	-92.77977
S005-763	47.03885	-92.74345
S005-764	47.19085	-92.49702
S005-765	47.16933	-92.46357
S005-766	47.11098	-92.35062
S005-768	47.27040	-92.20483
S005-769	47.25375	-92.07838
S005-770	47.23967	-92.80175
S000-589	47.35528	-92.86033
S000-597	47.35161	-92.83111
S000-592	47.39639	-92.88861
S005-748	47.41610	-92.85268
S004-601	47.33885	-92.68302
S005-767	47.56592	-91.94100
S000-119	47.36269	-92.59875
S001-065	47.44231	-92.57983
S005-749	47.40313	-92.46425
S005-750	47.35808	-92.47338
S005-751	47.40482	-92.40388
S005-752	47.51707	-92.18979
S005-753	46.91100	-93.01138
S000-596	47.36650	-92.85233
S005-754	47.28427	-92.09275
S005-755	46.95375	-92.90288
S005-303	46.92900	-92.90446
S000-046	46.69992	-92.41956
S005-756	46.91502	-92.93160
S005-757	47.25063	-92.83117