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MICHIGAN'S WATER CHEMISTRY MONITORING PROGRAM

A REPORT OF STATEWIDE SPATIAL PATTERNS 2005-2014
AND FIXED STATION STATUS AND TRENDS 1998-2014

REPORT BY

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Acronyms

AMV	Aquatic Maximum Value
BTEX	Benzene, Toluene, Ethylbenzene, and Xylene
CaCO3	Calcium Carbonate
CMI	Clean Michigan Initiative
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
ECBP	Eastern Corn Belt Plains
EGLE	Department of Environment, Great Lakes, and Energy
FCV	Final Chronic Value
GIS	Geographic Information System
GLEC	Great Lakes Environmental Center
HELP	Huron Erie Lake Plains
kg/year	Kilograms per Year
km	Kilometers
MDEQ	Michigan Department of Environmental Quality
MDL	Method Detection Limit
MDNR	Michigan Department of Natural Resources
mg/L	Milligrams per Liter
MTBE	Methyl Tertiary Butyl Ether
NCHF	North Central Hardwood Forests
ng/L	Nanograms per Liter
NLAF	Northern Lakes and Forests
NPDES	National Pollutant Discharge Elimination System
NTU	Nephelometric Turbidity Units
%	Percent
PCB	Polychlorinated Biphenyl
QA/QC	Quality Assurance/Quality Control
RL	Reporting Limit
SK	Seasonal Kendall
SM	Standard Methods
SMNIDP	Southern Michigan Northern Indiana Drift Plains
STORET	Storage and Retrieval
TDS	Total Dissolved Solids
TMDL	Total Maximum Daily Load
TOC	Total Organic Carbon
TR	Tobit Regression
TSS	Total Suspended Solids
µg/L	Micrograms per Liter
µmhos/cm	Micromhos per Centimeter

μS/cm	Microsiemens per Centimeter
USDHHS	United States Department of Health and Human Services
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
WCMP	Water Chemistry Monitoring Program
WHO	World Health Organization
WQS	Water Quality Standard
WRD	Water Resources Division
WSLH	Wisconsin State Laboratory of Hygiene

Preface

Comprehensive water quality monitoring programs are essential to the Michigan Department of Environment, Great Lakes, and Energy (EGLE), formerly the Michigan Department of Environmental Quality (MDEQ), to assess water quality throughout the state of Michigan. The Michigan Water Chemistry Monitoring Program (WCMP) is one program that provides EGLE with a solid foundation of knowledge to base management decisions and prioritize efforts as an agency.

The 1997 report, “A Strategic Environmental Quality Monitoring Program for Michigan’s Surface Waters,” (Strategy) (MDEQ, 1997) identified the following 4 major goals of the Water Resources Division (WRD) and listed individual objectives within each of the WRD programs:

1) Assess the current status and condition of waters of the state and determine whether water quality standards (WQS) are being met.
2) Measure spatial and temporal water quality trends.
3) Evaluate the effectiveness of water quality prevention and protection programs.
4) Identify new and emerging water quality problems.

The Strategy was written at a time when resource constraints forced funding and staffing for water quality programs to decrease considerably. A Strategy Update was written (MDEQ, 2005) after those resource constraints were alleviated with annual appropriations of Clean Michigan Initiative (CMI) funds, allowing the Strategy to be fully implemented. The latest update was written in 2017 (MDEQ, 2017a). While programs have grown and evolved through the years, the same fundamental goals continue to drive monitoring efforts.

Previously published WCMP reports are available at https://www.michigan.gov/egle/about/Organization/Water-Resources/GLWARM/water-chemistry. Quality assured data used in these reports are available upon request. These data are also available online in the federal Storage and Retrieval (STORET) system at https://www.epa.gov/waterdata/storage-and-retrieval-and-water-quality-exchange or via the Water Quality Portal at https://www.waterqualitydata.us/. Older water chemistry data (i.e., pre-1998) can be found in Michigan Department of Natural Resources (MDNR) (1993) or at the STORET Legacy Data Center at https://www3.epa.gov/storet/legacy/gateway.htm.

The WRD would like to acknowledge and thank the partners who support the WCMP. These include: the United States Environmental Protection Agency (USEPA); United States Geological Survey (USGS); EGLE, Remediation and Redevelopment Division, Laboratory Services Section; Wisconsin State Laboratory of Hygiene (WSLH); LimnoTech; White Water Associates; and Great Lakes Environmental Center (GLEC).

Several figures in this report were created using ArcGIS® software by Esri. ArcGIS® and ArcMap™ are the intellectual property of Esri and are used herein under license. Copyright © Esri. All rights reserved. For more information about Esri software, please visit www.esri.com. Several graphs and tables in this report were created using the statistical software R Version 3.2.2 (R Core Team, 2015).

Introduction

Sampling for the EGLE WCMP began in 1998 using part of a $500,000 appropriation by the State Legislature. The program was a first step towards improving water quality monitoring in Michigan since funding reductions in the mid-1990s, which severely restricted monitoring capabilities (Aiello, 2008). In 1998, monitoring stations were located in Michigan's Great Lakes connecting channels and tributaries to Lake Huron and Lake Erie. The following year monitoring stations were located in the connecting channels, tributaries to Lake Michigan and Lake Superior, and Grand Traverse and Saginaw Bays. In 2000, monitoring stations in the connecting channels, bays, and major tributaries of all of Michigan's Great Lakes were sampled. In 2001, with the assistance of the CMI, the WRD was able to establish a consistent sampling program, including monitoring in major tributaries, the Great Lakes connecting channels, and Grand Traverse and Saginaw Bays.

A probabilistic sampling design was added to the WCMP in 2005 to establish a water chemistry statewide status and trends program. The addition of a probabilistic component to the WCMP gave the WRD the ability to extrapolate results and make stronger conclusions at the statewide and other regional levels. For example, the tributary data show spatial patterns in parameters (e.g., chloride, mercury); however, tributary conclusions are truly limited to comparing specific sites, not regions. The probabilistic sampling design includes 250 (initially) randomly chosen sites sampled at a rate of 50 sites each year over a 5-year period. The random design allows for regional comparisons in water quality. The third cycle for sampling began in 2015 and at the end of the third cycle the probabilistic data will be used to investigate temporal trends.

Where appropriate, contaminant concentrations are also compared with water quality criteria such as Michigan's R 323.1057 (Rule 57) of the Part 4 WQS (Part 4 Rules), promulgated pursuant to Part 31, Water Resources Protection, of the Natural Resources and Environmental Protection Act, 1994 PA 451, as Amended (MDEQ, 2006 and 2018).

Analytes, Sampling Methods, and Analytical Methods

Samples generally were collected as grab samples from a single point in surface water (e.g., in the flow of the stream) at an approximate 0.3- to 1.0-meter depth. Field measurements of dissolved oxygen (DO), temperature, pH, and conductivity (as specific conductance) were taken at the sample location during each sampling event using a calibrated multi-parameter water quality monitoring instrument.

Conventional and nutrient water chemistry samples were collected and handled using EGLE-approved procedures (MDNR, 1994), and were analyzed by EGLE Environmental Laboratory. For total mercury and trace metals, sample collection and handling were carried out in accordance with USEPA Method 1669 (USEPA, 1996). Mercury samples from probabilistic sites were analyzed at the EGLE Environmental Laboratory. The EGLE Environmental Laboratory did not develop the capability to analyze for mercury until 2005; therefore, to maintain laboratory consistency in the WCMP dataset, mercury samples from the major tributaries, bays, and connecting channels were (and continue to be) analyzed by the WSLH, which has analyzed these mercury samples since 1998. The EGLE Environmental Laboratory does not have the capability to analyze non-mercury trace metals at levels necessary for trend analysis. Therefore, all non-mercury trace metals samples were analyzed by the WSLH.

Analytical methods and quantification levels are shown in Appendix A-1. Additional samples (e.g., field blanks, field replicates) were collected in the field for data quality assurance/quality control (QA/QC) purposes (MDEQ and USGS, 2001; MDEQ, 2003a, 2007b, and 2017b; and Roush, 2013). Generally, as noted in a previous WCMP report (Roush, 2013), replicates were collected at a rate of 10 percent (%) and field blanks were collected at a rate of 5%; for total mercury sampling, one-half of the field blanks were substituted with trip blanks[1]. Participating analytical laboratories have QA/QC programs and use peer-reviewed analytical methods. Analytical methods employed by the WCMP have remained the same since the project was initiated in 1998, unless otherwise noted in Appendix A-1.

Data that did not meet certain criteria (e.g., particular laboratory codes [WSLH and EGLE]) were excluded from analyses. Data that were flagged as outliers compared to historical data were retained for analyses. This is because it is unknown if these high values are due to natural variation at the site or sampling, handling, or analysis error. For details about laboratory codes that resulted in the exclusion of some data from spatial and temporal analyses for all the types of water bodies examined in this report (probabilistic sites, Great Lakes tributaries, bays, and connecting channels), plus additional QA/QC review information, please refer to Section 1, particularly Table 1-2 and associated text.

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[1] MDNR (1994) recommends that for all parameters other than volatile organics, as a minimum, 1 blank should be collected for every 20 investigative samples (i.e., 5%), but for some programs a frequency of 1 blank for every 10 investigative samples may be more appropriate (i.e., 10%). The MDEQ and USGS (2001) state that the purpose of trip blanks is to monitor possible contamination introduced via vapor phase into unopened (sealed) sample containers as they are transported from place to place, and that in the context of this program, only parameters considered subject to vapor phase contamination (e.g., mercury) had trip blanks collected for them. Trip blanks were provided by the WSLH for mercury.

Statistics

All summary statistics and boxplots were generated using the software R Version 3.2.2 (R Core Team, 2015) via the RStudio interface (version 0.98.976). Data were analyzed using the following R packages: NADA (Lopaka, 2013), survival (Therneau, 2015), ggplot2 (Wickham, 2009), pgirmess (Giraudoux, 2016), multcompView (Graves et al., 2015), wq (Jassby, 2016), interval (Fay and Shaw, 2010), EnvStats (Millard, 2013), restrend (Lorenz, 2015), and Icens (Gentleman and Vandal, 2019). Some additional calculations (e.g., in Appendices C-3 and C-5) were made using Microsoft Excel 2013.

Historically, data below analytical quantitation or detection levels, including negative values, were used directly in analyses based on the recommendations of Porter et al. (1988) and Gilliom et al. (1984) or were replaced with one-half the Method Detection Limit (MDL).

Improvements in the capability of statistical programing have allowed for more complex analyses that more accurately account for the uncertainty of values below detection levels. Throughout this report, analyses follow the recommendations of Helsel (2012) using interval censored data unless otherwise noted. Medians and quartiles were calculated using non-parametric Turnbull interval-censored survival functions (Helsel, 2012). Summary statistics for probabilistic data from 2005-2009 may vary slightly from Roush (2013) because of this change in treatment of data below detection limits; however, overall spatial trends are expected to be similar due to the relatively small amount of data below detection limits for most parameters at probabilistic sites.

For parameters that did not have any values below the laboratory's reporting limits (RL), summary statistics (e.g., minimum, quartile 1, median, quartile 3, and maximum) and boxplots were generated using the base (standard) R environment.

In Roush (2013), 2002-2008 loading estimates were provided for the WCMP major tributaries and the Great Lakes connecting channels. For the present report, loading estimates for the WCMP major tributaries are presented through 2013, in addition to the historical estimates mentioned above. The USGS (Michigan) staff generated loading rate estimates for the Great Lakes tributaries (for all years through 2013) (Appendix A-3) and the connecting channels (through 2008) (Appendix A-4) for total phosphorus, total chloride, total suspended solids (TSS), total mercury, and total trace metals using the Stratified Beale Ratio Estimator described by Richards (1994) (see also Richards et al. [1996]). WCMP staff explored generating load estimates for the Great Lakes connecting channels past 2008; however, since 2009-2013 flow data appear to be mostly provisional or perhaps not directly comparable[2], the decision was made to not attempt to generate estimates at this time.

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[2] In late 2008, the USGS established gaging stations near the upper ends of the St. Clair and Detroit Rivers (see "St. Clair River at Port Huron, MI" [gauge #04159130] and "Detroit River at Fort Wayne, Detroit" [gauge #04165710] at https://waterdata.usgs.gov/nwis); however, those flows may not be directly comparable to historical flow estimates for the whole rivers (which were based upon multiple National Oceanic and Atmospheric Administration water level gauges along each river; see Fay and Noorbakhsh [2010]). For historical Great Lakes connecting channel flow data, one source is a file named, "GL Connecting Channel Flows, 1900-present.xlsx," available at the Great Lakes Dashboard data download page managed by the National Oceanic and Atmospheric Administration's Great Lakes Environmental Research Laboratory *(The link provided was broken and has been removed)* [under "sourceSpreadsheets"] or *(The link provided was broken and has been removed).* Note that circa 2010, flows for the St. Clair River and Detroit River for years 1987-2008 were revised due to an apparent

Mean values are more affected by extreme values (likely observed during very high or very low flow conditions) than median values. In terms of relating concentrations to loadings, using a mean value makes sense. According to Richards (1998), it is not uncommon for 80-90% or more of the annual pollutant load to be delivered during the 10% of the time with the highest fluxes. On the other hand, when looking at concentrations that are *typically* found in a stream, or change over time, a median provides a better measurement, thus median values were computed for most other summary statistics.

Spatial/Seasonal

In the absence of sub-detection limit data, between group (e.g., STORET, ecoregion, stream order, etc.) comparisons were made using Kruskal-Wallis tests with a significance level of p = 0.05 (Helsel, 2012). Where Kruskal-Wallis tests were significant, multiple comparisons were made using Dunn's test (Siegel and Castellan, 1988). An underlying assumption of this test is that distributions between groups are similar with the only difference being shifts in medians. There were some instances where this assumption could not be validated, and thus, statistical comparisons were not made. These comparisons were used to determine if there was any statistically significant variability among sampling stations or sampling months.

In the presence of sub-RL data, summary statistics were generated using Turnbull methods as described in Helsel (2012). Comparisons among groups (STORET, ecoregion, month, etc.) were conducted using the interval-censored form of the generalized Wilcoxon test. Post-hoc multiple comparisons were not performed due to software limitations; however, groups were semi-quantitatively ranked by their distributions within the bays and connecting channels. Support for these censored data analyses is provided by Helsel (2012).

Temporal

Temporal trend analyses were performed using Seasonal Kendall trend analysis for uncensored data. This test measures the strength of monotonic trends and is appropriate for continuous variables with non-normal distributions (Helsel, 1993 and 2012; Helsel and Hirsch, 2002). Each month (April-November) was used as a "season" and the test was conducted, by station, for each parameter. The goal of defining seasons is to remove temporal variation to have a better ability to find changes over time (Helsel et al., 2006; Helsel and Hirsch, 2002). Seasonal Kendall trend analysis assumes a single pattern (either upward or downward) of trend across all seasons, otherwise the results may be misleading (Helsel and Hirsch, 2002; Schertz et al., 1991; Gilbert, 1987; van Belle and Hughes, 1984; Matzke et al., 2014). A detailed description of uncensored Seasonal Kendall tests can be found in Hoard et al. (2009).

Trends in parameters with censored data were measured using Tobit linear regression techniques (Helsel and Hirsch, 2002). The Tobit trend test is a parametric regression. When using Tobit trend tests, water quality values were log transformed. A minimum of 20% of the data was required to be above the detection limit for Tobit trend analysis. For the Great Lakes tributaries, analyses performed by the USGS (Hoard et al., 2018) used Tobit analyses on individual Great Lakes tributaries that had more than 5%, but less than 50%, of their data censored. For the Great Lakes bays and connecting channels, Tobit linear regression was used to identify trends in parameters with at least 1 censored data point, but not more than 50% censored.

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change in conveyance capacity of the channels, possibly due to major dredging projects (see the above-mentioned spreadsheet and Fay and Noorbakhsh [2010]).

Table 2-3 shows the calendar dates associated with each seasonal breakdown.

Box Plots

Box plots are frequently used in this report. Refer to Figure 1 (below) for a diagram of box plot features.

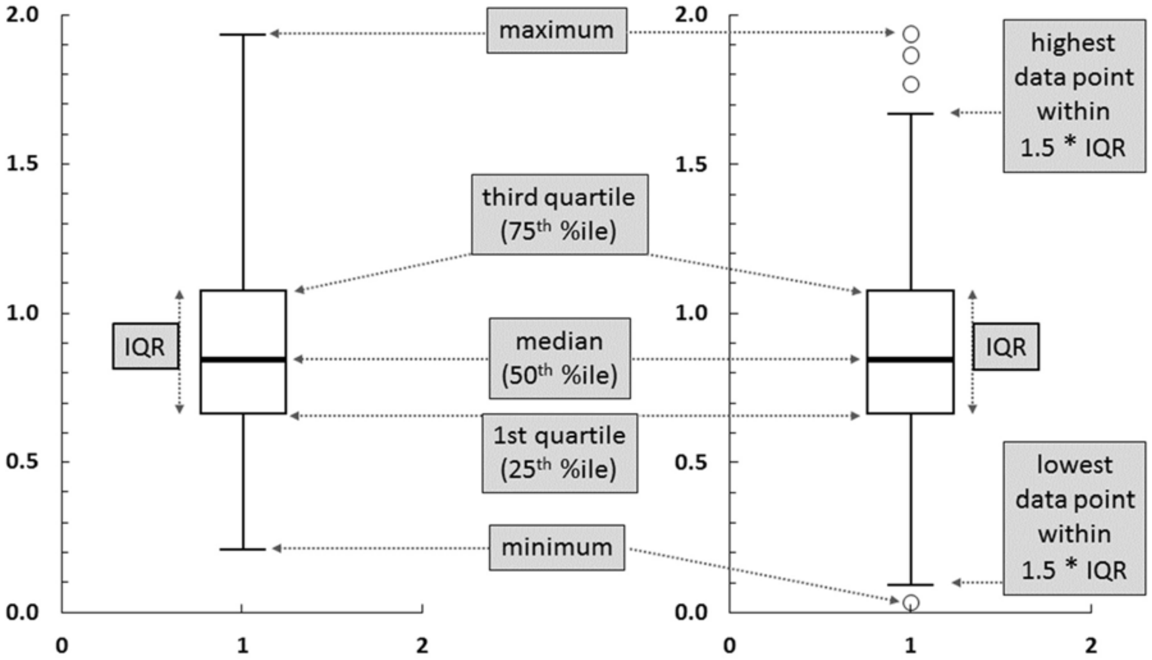

Figure 1. Diagram of boxplot features for datasets with censored data (left, “Spear style”) and for datasets that do not have censored data (right, “Tukey style”) as described in Krzywinski and Altman (2014a) and R Core Team (2015). IQR = Inter Quartile Range.

Summary of Parameters and Background on Select Michigan WQS

Alkalinity – A measure of acid-neutralizing capacity (Harrison, 2000; Williamson and Carter, 2001). Alkalinity is largely dependent on local geology and the concentration of bicarbonate compounds present in the water column (Kaushal et al., 2013). Areas with granite typically have low alkalinity, whereas areas with limestone have high alkalinity. Carbonates frequently contain magnesium and calcium, so alkalinity is often related to hardness.

Calcium – Measured as total calcium (Ca) in water. Common sources of calcium include weathering of local geological features as well as cement factories, fertilizers, and runoff from fields treated with lime (Harrison, 2000). Calcium is a component of total dissolved solids (TDS) and is 1 of the 2 cations used to calculate water hardness.

Chloride – Measure of total chlorides in water. Typically formed as a salt with a cation bound to chloride (e.g., sodium chloride, or NaCl, is table salt). Sources of chlorides include natural weathering of rock and sediment, as well as wastewater treatment, road salting, agricultural runoff, and water from oil and gas wells (World Health Organization [WHO], 2011). Chlorides are regulated in R 323.1051 of the Part 4 rules. This rule states that waters of the state designated as a public water supply source shall not exceed 125 milligrams per liter (mg/L) of chlorides as a monthly average, except for the Great Lakes and connecting waters, where chlorides shall not exceed 50 mg/L as a monthly average.

Chlorophyll a – A measure of the concentration of chlorophyll a in the water column. Chlorophyll a is used in photosynthesis; therefore, chlorophyll a is an indirect measure of the amount of algal biomass and productivity (USEPA Office of Water, 2007b). Chlorophyll a measurements are typically limited to limnologic surveys.

Conductivity – A measure of water's capability to conduct electrical flow. Conductivity is directly related to the concentration of cations and anions in water. Ions come from salts, chlorides, sulfides and carbonates (USEPA, 2011). These compounds, which dissolve in water, are known as electrolytes. Specific conductance (provided in this report) is conductivity corrected for the influence of temperature and is expressed as conductivity at a standard temperature of 25°C (USEPA, 2011; Williamson and Carter, 2001).

Dissolved Organic Carbon (DOC) – DOC is a measure of the dissolved component of total organic carbon (TOC). The bioavailability and toxicity of trace metals is linked to the concentration of DOC in water (Smith et al., 2015). As DOC accumulates in the water column, metals coalesce and become less soluble. Similar to TOC, DOC concentrations are positively correlated to biochemical oxygen demand and chemical oxygen demand (Brezonik and Arnold, 2011).

DO – DO is a measure of the mg/L of oxygen in water. It is necessary for aquatic life. DO is affected by temperature, photosynthesis, and respiration (Michaud, 1994; Allan and Castillo, 2007). Sources of pollution affecting DO include organic runoff from sources such as wastewater treatment plants, eutrophication, septic system leaks, paper mills, and animal manure/feed lots (Michaud, 1994). DO levels are regulated in R 323.1064 of the Part 4 rules. WQS for DO are generally, with some exceptions, 7 mg/L for all Great Lakes, connecting waterways, and inland surface waters designated to be protected for coldwater fish and 5 mg/L for all other inland stream and lake waters (MDEQ, 2006).

Hardness – The measure of dissolved minerals in water. Hardness may cause deposition of scale in pipes, water heaters, and boilers (Williamson and Carter, 2001). Here, hardness is estimated using calcium and magnesium concentrations and expressed as mg/L calcium carbonate ($CaCO_3$). Primary sources of calcium and magnesium include natural weathering of rocks such as limestone ($CaCO_3$) (Brezonik and Arnold, 2011).

Magnesium – A measure of total magnesium (Mg) in water. Magnesium is an essential nutrient, which can also be toxic at exceptionally high levels, although its toxicity is dependent upon the hardness of water (WHO, 2011). Common sources include weathering of local geological features as well as fertilizers, liming, pyrotechnics, and airplane/missile construction (Salminen et al., 2005). Magnesium is a major component of hardness (Brezonik and Arnold, 2011).

Mercury – A measure of total mercury (Hg). Mercury is a toxic, bioaccumulative chemical of concern. Bioaccumulation is the process by which organisms accumulate contaminants in their tissues at concentrations several times greater than they are present in the water column (Salminen et al., 2005). Natural sources of mercury include volcanoes and geological mercury deposits; however, the more common source is anthropogenic and includes coal combustion and metal processing (Salminen et al., 2005; ATSDR, 1999). Michigan’s WQS for water column mercury concentration are 0.0013 micrograms per liter (µg/L) (or 1.3 nanograms per liter [ng/L]) for the protection of wildlife and 0.0018 µg/L (or 1.8 ng/L) for the protection of human health (e.g., fish consumption) (MDEQ, 2006).

Nitrogen – Nitrogen is an essential nutrient for plants and animals. Total nitrogen is the sum of all organic and inorganic species of nitrogen (Brezonik and Arnold, 2011). Sources include runoff, wastewater treatment plants, and all sources of organic and inorganic matter. Like phosphorus, Michigan’s WQS for nitrogen is determined by R 323.1060, Plant Nutrients, of the Part 4 rules. Part 2 of this rule states that “nutrients shall be limited to the extent necessary to prevent stimulation of growths of aquatic rooted, attached, suspended, and floating plants, fungi or bacteria, which are or may become injurious to the designated uses of the surface waters of the state.”

Ammonia – An inorganic form of nitrogen. Total ammonia is the sum of NH_4^+ (ammonium ion) and NH_3 (unionized ammonia) concentrations (USEPA, 2013). Unionized (NH_3) ammonia readily converts to less toxic ammonium (NH_4^+) in the presence of water, which is assimilated by plants (Brezonik and Arnold, 2011). (Note: in situations where values of pH and temperature increase, the concentration of unionized ammonia increases and the concentration of ammonium ion decreases [USEPA, 2013].) Natural sources of ammonia include decomposition of organic waste, forest fires, and nitrogen fixation, while anthropogenic sources include livestock, agricultural fertilizer, and municipal runoff (USEPA, 2013). When ammonia reaches elevated levels in the water, fish and aquatic macroinvertebrates have difficulty excreting ammonia, leading to toxic buildup within tissues (USEPA, 2013).

Nitrate – Nitrate is an inorganic form of nitrogen that dissolves in water and is biologically available for primary production (WHO, 2011). Elevated nitrate can result in algae blooms and subsequent depletion of oxygen when the blooms decompose. A major source of nitrate is inorganic fertilizer runoff, wastewater treatment, and oxidation of nitrogenous compounds (WHO, 2011). High levels of nitrate in drinking water can lead to methemoglobinemia (blue-baby syndrome) in infants (WHO, 2011).

Nitrite – Nitrite is an inorganic form of nitrogen that can be taken up by aquatic plants. Its concentrations are typically low in ambient water because it is readily converted to nitrate by bacteria (WHO, 2011).

Total Kjeldahl Nitrogen – The sum of organic nitrogen and total ammonia (Brezonik and Arnold, 2011). If concentrations of ammonia and Kjeldahl nitrogen are known, the concentration of organic nitrogen can be calculated.

pH – A measure of hydrogen ions in water, also known as the acidity of water (Michaud, 1994). pH is on a scale from 0 to 14; solutions below 7 are acidic and solutions above 7 are basic. pH is strongly affected by alkalinity, which is water's ability to neutralize acid (Michaud, 1994).

Phosphorus – Michigan's WQS for phosphorus is determined by R 323.1060. This is a two-part rule, with the first part relating to point source discharges of total phosphorus in regards to Great Lakes protection, and the second part states, "nutrients shall be limited to the extent necessary to prevent stimulation of growths of aquatic rooted, attached, suspended, and floating plants, fungi, or bacteria, which are, or may become, injurious to the designated uses of the surface waters of the state."

Orthophosphate – Phosphorus exists in water as dissolved or particulate phase. Orthophosphate includes the dissolved inorganic form of phosphate required by plants for growth (Michaud, 1994). As opposed to particulate phosphorus, orthophosphate is readily available to be taken up by plants (Michaud, 1994). Natural sources of phosphate include erosion of sediment and parent rock, whereas anthropogenic sources include sewage and fertilizer runoff.

Total Phosphorus – Phosphorus is an essential nutrient for plants and animals. It is often the limiting nutrient in freshwater because it is not as abundant as carbon and nitrogen (Brezonik and Arnold, 2011). Total phosphorus includes dissolved phosphorus plus the phosphorus found in particles or bound to sediment (Domagalski and Johnson, 2012). More detailed information about the different forms of phosphorus can be found in Jarvie et al. (2002) and Allan and Castillo (2007). Sources include soils, rocks, fertilizer runoff, manure runoff, water treatment plants, and decomposition of organic matter (Brezonik and Arnold, 2011). Water samples analyzed for total phosphorus are not filtered.

Potassium – Potassium is an essential nutrient (WHO, 2011). Potassium can be leached naturally from geologic formations. A common anthropogenic source of potassium is agricultural fertilizer (WHO, 2011; Salminen et al., 2005).

Secchi Disk Depth – A measure of water transparency. The depth of water at which a secchi disk, attached to a rope, can no longer be seen. Secchi disk measurements are limited to lake and pond (limnologic) assessments and are not applicable to stream surveys.

Sodium – Sodium is an essential nutrient. Common sources of sodium include road salt and animal wastes (Salminen et al., 2005). Similar to potassium, sodium binds to clay particles and is not considered highly mobile in surface waters with high clay content (Salminen et al., 2005).

Sulfate – Measure of total sulfates in water. Sulfate can be formed as a salt with a cation bound to SO_4^{2-} such as $FeSO_4$ (Salminen et al., 2005). Sulfate is an anion constituent of TDS. Sources include the natural weathering of rocks and the combustion of fossil fuels (major source) and the production of cement, steel, and crushed limestone for roads (WHO, 2011; Salminen et al., 2005).

TOC – TOC includes all natural organic matter as well as synthetic compounds in a body of water such as detergents, pesticides, plastics, and herbicides (Brezonik and Arnold, 2011; Nelson and Sommers, 1996).

TDS – TDS measures the combination of cations, anions, minerals, and silts dissolved in water (WHO, 2011). Major components include calcium, magnesium, potassium, sodium, bicarbonates, chlorides, and sulfates as well as organic matter dissolved in water (Brezonik and Arnold, 2011; WHO, 2011; Salminen et al., 2005). Common sources of TDS include sewage, urban runoff, industrial waste, and drinking water treatment as well as natural sources such as mineral springs and weathering of rock.

TSS – TSS measures particles larger than two micrometers, which are left after filtering for TDS. TSS includes solids such as plants, animals, algae, silt, sand, and other sediments (Michaud, 1994). The more solids there are in the water the less clear the water will be. Michigan's WQS for TSS is determined by R 323.1050, which states, "surface waters of the state shall not have any of the following physical properties in unnatural quantities which are or may become injurious to any designated use: turbidity, color, oil films, floating solids, foam, settleable solids, suspended solids, and deposits" (MDEQ, 2006). TSS concentrations less than 20-25 mg/L in water typically do not change the appearance of water and may be considered "clear" flow (MDEQ, 2016a; Singleton, 2001). Water with TSS levels between 40-80 mg/L may appear cloudy, while concentrations over 150 mg/L may look dirty (MDEQ, 2016a).

Trace Metals – EGLE regulates many toxic substances in surface waters with numeric criteria derived using R 323.1057. These numeric criteria are one measure used to determine if Michigan's WQS are met. While not all pollutants have numeric criteria, trace metals monitored for the WCMP do and were evaluated to ensure WQS were met. EGLE uses a hardness-based approach to calculate numeric criteria for many trace metals, including total chromium, total copper, total lead, total cadmium, total nickel, and total zinc. The hardness value collected at the time of sampling was used to calculate an individual WQS at each site.

Cadmium – A measure of total cadmium (Cd) in water. Cadmium is a metal that is found naturally in the earth's crust and can be released by weathering (WHO, 2011). Various forms of cadmium are soluble in water, depending on the conditions of the body of water. Cadmium is also emitted in the production of phosphate fertilizers (WHO, 2011) and is a byproduct of zinc, lead, and copper extraction. It is found in batteries, pigments, and steel plating and is a stabilizer in the manufacturing of plastics (USEPA - Office of Water, 2016). It is also used in solar cells and color displays (USEPA - Office of Water, 2016). Cadmium is toxic at unnaturally high concentrations, although its toxicity is dependent upon the hardness of water.

Chromium – Measure of total chromium (Cr) in water. Chromium is a micronutrient that can become toxic at unnaturally high concentrations. Various forms of chromium are slightly water soluble, depending on pH and DO and each form has different toxicity (WHO, 1996). Chromium originates from leather tanning, audio and video production, lasers, dyes, and paints (WHO, 1996). Trivalent chromium (chromium-3) and hexavalent chromium (chromium-6) are the most common forms of chromium that occur in natural waters in the environment[3]. Hexavalent chromium has a fixed WQS, while trivalent chromium toxicity is hardness-dependent (Roush, 2013; MDEQ, 2018).

Copper – Measure of total copper (Cu) in water. Copper is a micronutrient that is toxic at exceptionally high concentrations, although its toxicity is largely dependent upon hardness. Copper naturally occurs in the earth's crust; however, it can also be released from anthropogenic activity such as mining, agriculture, leather manufacturing, lake management, and municipal runoff (USEPA - Office of Water, 2007a).

Lead - A measure of total lead (Pb) in water. Lead is toxic at exceptionally high concentrations, although its toxicity is dependent upon the hardness of water. Various forms of lead are soluble in water, depending on the conditions of the water (WHO, 2011). Lead can be found naturally in the Earth's crust; however, anthropogenic sources of lead include lead-based paint, pipes, fossil fuels, ceramics, and various other metal-containing products (WHO, 2011; Salminen et al., 2005).

Nickel – A measure to total nickel (Ni) in the water column. Nickel is a micronutrient for plants; its toxicity to organisms is largely dependent upon hardness. Nickel is found naturally in the Earth's crust; however, it is also released from power plants, batteries, waste incinerators, oil refineries, ceramics, textiles, fertilizers, and metal industries (WHO, 2011; Salminen et al., 2005).

Zinc - Zn is a micronutrient that can become harmful if it reaches unnaturally high levels. The toxicity of zinc is dependent upon water hardness. Zinc is found naturally in the Earth's crust and can be released by weathering; however, anthropogenic sources of zinc also include batteries, paints, coal plants, fungicides, insecticides, landfills, and various other metal manufacturing processes (Salminen et al., 2005).

Trophic State Index – Trophic State Index is a classification system designed to classify lakes, ponds, and reservoirs based upon biological productivity. Indicators of trophic state include total phosphorus, chlorophyll a, and secchi disk depth. Trophic State Index classifications include eutrophic, mesotrophic, and oligotrophic, in order of most-to-least productive. Typically, eutrophic lakes are characterized by high nutrients, high algal biomass, and low water clarity whereas oligotrophic lakes are characterized by nutrient limitation, low algal biomass, and high water clarity (Carlson, 1977).

Turbidity – Turbidity is an optical measure of water clarity and measures the amount of light scattered by particles in the water (Brezonik and Arnold, 2011; Michaud, 1994). Turbidity and TSS are related; however, turbidity does not quantify the mass of suspended material in a unit of water. Also, turbidity can be affected by dissolved organic matter, which is not accounted for by TSS.

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[3] See https://www.epa.gov/dwstandardsregulations/chromium-drinking-water. See also USEPA (1980).

SECTION 1. PROBABILISTIC MONITORING 2005-2014: STATEWIDE SPATIAL PATTERNS

1.1 INTRODUCTION

Statewide monitoring of 250 randomly selected sites (referred to as probabilistic) began in 2005 with the goal of evaluating statewide spatial and temporal trends for select water chemistry parameters (Figure 1-1, Appendix B-1). Fifty sites are sampled each year with 1 complete cycle occurring every 5 years. Following this design, 2014 marked the end of 2 complete cycles. Beginning in 2015, the third cycle of sampling began, and statewide temporal trend analysis will be possible once results are obtained; however, this report is limited to spatial analyses of the data collected from 2005 to 2014.

1.2 MAJOR CONCLUSIONS

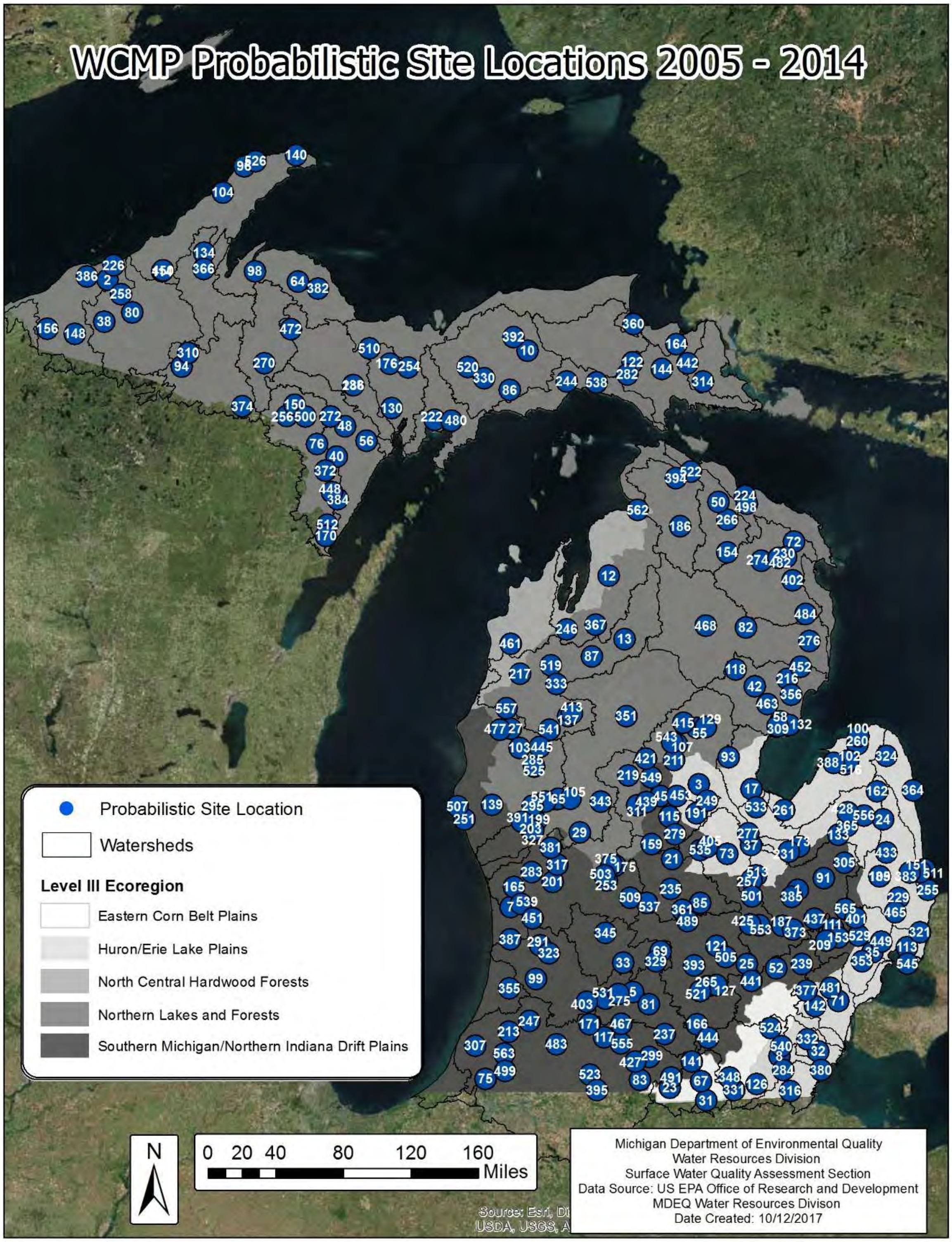
Mercury and copper were the only trace metals found at levels that exceeded the Other Indigenous Aquatic Life and Wildlife Designated Use Criteria from 2005 to 2014 at probabilistic sites. Mercury exceedances were widespread throughout the state, while copper exceedances were limited to the Western Upper Peninsula/Keweenaw Peninsula.

Fifty-four ± 7% of the perennial river miles in Michigan met the mercury WQS of 1.3 ng/L using probabilistic data collected from 2005 to 2009, and 46 ± 7% of the perennial river miles in Michigan met the mercury WQS using probabilistic data collected from 2010 to 2014.

Ninety-eight ± 2% of the perennial river miles in Michigan met hardness-based copper WQS using probabilistic data collected from 2005 to 2009, and 98 ± 2% of the perennial river miles in Michigan met the hardness-based copper WQS using probabilistic data collected from 2010 to 2014.

Cadmium, chromium, lead, nickel, and zinc did not exceed WQS at any sites from 2005 to 2014.

Cadmium, chromium, lead, and zinc concentrations varied throughout the state. Chloride, TSS, hardness, specific conductance, and nickel concentrations were greatest in southeast Michigan. Sulfate and phosphorus concentrations were greatest in the Saginaw Bay region. DOC, mercury, and copper concentrations were greatest in the Upper Peninsula. Surface water chemistry varied by ecoregion, stream order, geology, and land cover.



Michigan Department of Environmental Quality
Water Resources Division
Surface Water Quality Assessment Section
Data Source: US EPA Office of Research and Development
MDEQ Water Resources Divison
Date Created: 10/12/2017

Figure 1-1. Probabilistic water chemistry monitoring sites visited from 2005-2014. Sites are shown within ecoregion.

1.3 METHODS

1.3.1 Site Selection and Study Design

Sites were provided by the USEPA, including additional “backup” locations, using a multi-panel stream survey design with a target population of all perennial rivers and streams within Michigan. The sample frame was Reach File Version 3-Alpha based on the 1:100,000-scale dataset (USEPA, 1998). Strahler Order was added as a Multi Density Category of first, second, third, and fourth + groups (stream orders higher than 4 were placed in the fourth order category; Strahler, 1957). Sample size within Strahler Order was weighted to achieve equal sample size across Strahler Order classes for the 250 sites. Site locations within their respective ecoregions are displayed in Figure 1-1.

Due to changes in WRD priorities and objectives throughout the initial years of the project, some design modifications have occurred. In 2005, 50 sites were sampled. From 2006 to 2009, 50 new, randomly chosen sites were selected to be monitored each year along with 5 sites from the previous year of sampling for a total of 55 sites per year. At the start of the second cycle of monitoring (i.e., 2010), 25 of the sites sampled in 2005 were resampled to monitor temporal trends, while 25 new sites were randomly chosen to monitor statewide spatial trends and have a truly random sample design. However, this design was not repeated in 2011. Instead, it was decided that the original sites that were randomly chosen from 2005 to 2009 would become fixed (i.e., would be resampled every 5 years) with the emphasis in monitoring placed on temporal trends and analysis of spatial trends being limited to those sites that were randomly chosen from 2005 to 2009. Additional changes in site locations for logistical reasons are listed in Appendix B-2.

Each site was visited 4 times during its monitoring year, with samples collected in May, July, September, and November. Sites that were dry during their first sampling event were replaced with alternate sites. Sites that were successfully sampled during their first sampling event but dry during subsequent visits were not replaced. A site list of all probabilistic sites, including STORET numbers, can be found in Appendix B-1.

Further details on probabilistic site selection can be found in the Michigan Multi-Panel Stream Survey Design memo (Appendix B-3).

1.3.2 Data Analyses

1.3.2.1 Spatial Analyses

Many factors, both natural and anthropogenic, may influence the chemical composition of waters across the state. These factors may include features such as geology, vegetative cover, atmospheric deposition/air currents, and land cover. Several of these were evaluated to determine if they could explain variation in concentrations across the state including: ecoregion, stream order, surficial geology, and land cover. There are likely interactions among many of these factors; however, at this time, interactions could not be statistically evaluated because methods have not been developed to test complex models with interval-censored data (see Introduction: Statistics for more information).

Ecoregional Analyses

An ecoregional analysis is included to determine if water chemistry parameters are consistent throughout the state or variable dependent on ecoregion. Omernik Level III Ecoregions of the Continental United States System was chosen because it delineates zones using geologic, physiographic, vegetative, climate, soil, land use, wildlife, water quality, and hydrologic patterns (Figure 1-1; Omernik and Gallant, 1988). Five distinct ecoregions are present within Michigan: Northern Lakes and Forests (NLAF), North Central Hardwood Forests (NCHF), Huron Erie Lake Plains (HELP), Southern Michigan Northern Indiana Drift Plains (SMNIDP), and Eastern Corn Belt Plains (ECBP). Descriptions of ecoregions and corresponding hydrology can be found in Appendix A-2 or Michigan's WCMP (Roush, 2013).

To examine differences in concentrations among ecoregions, the watershed upstream of each probabilistic site was first delineated using the Watershed Tool in ArcGIS. The dominant ecoregion, or the ecoregion making up the greatest percentage of area within each watershed, was then determined using Level III Ecoregions of Michigan (USEPA, available at https://edg.epa.gov/metadata/catalog/main/home.page). The dominant ecoregion was then used in all statistical analyses.

Stream Order Analyses

A stream order analysis is included to determine if water chemistry parameters are consistent throughout the state or variable dependent on stream order. Stream order was chosen because parameter concentrations are likely a function of geologic, physiographic, vegetative, climatic, and hydrologic processes, as well as a number of other processes, which differentially influence streams dependent on their size and location within the watershed. Stream order was determined using Strahler Order (Figure 1-2; Strahler, 1957; USEPA, 1998) with streams grouped into first order, second order, third order, and fourth + order streams (i.e., streams fourth order or greater).

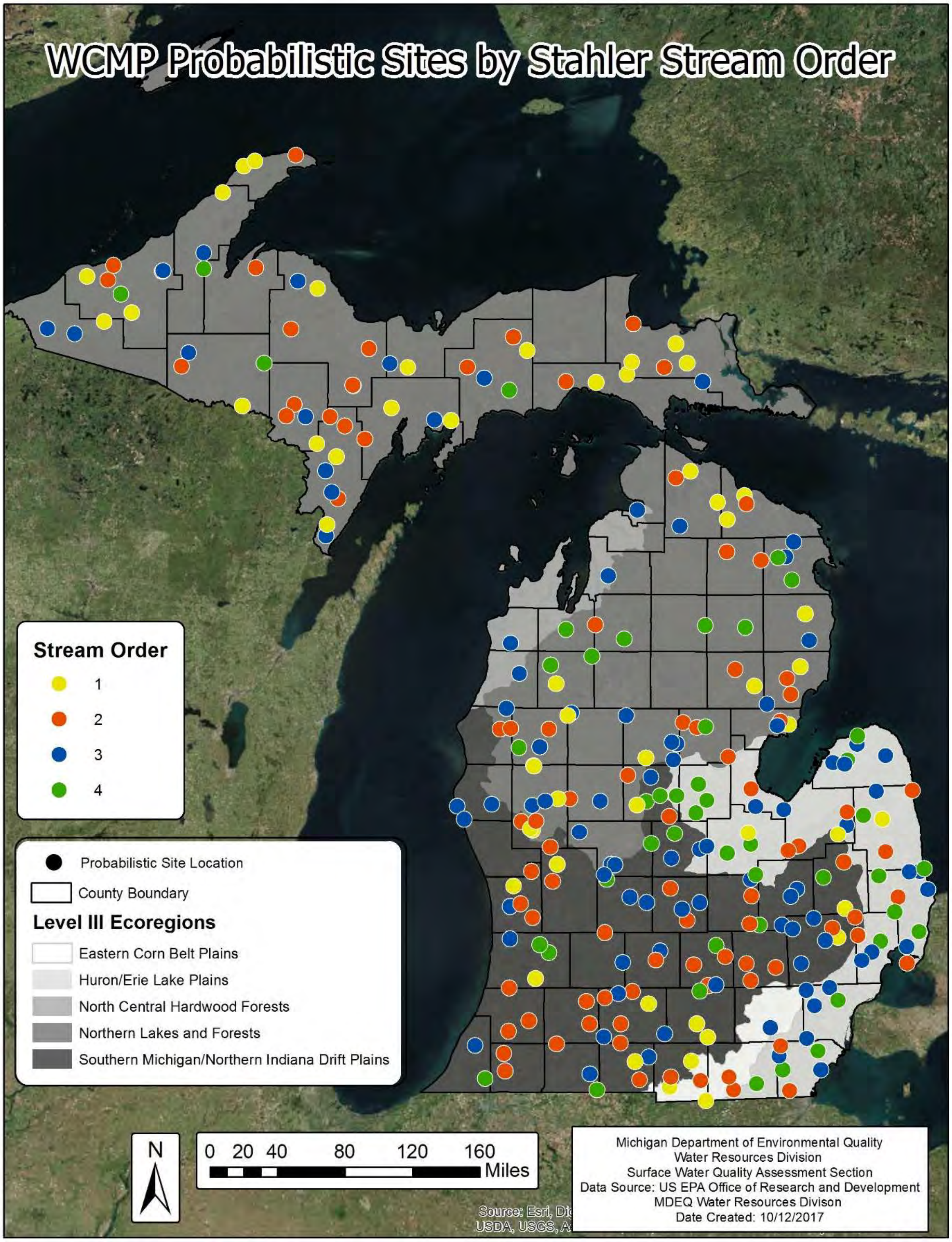
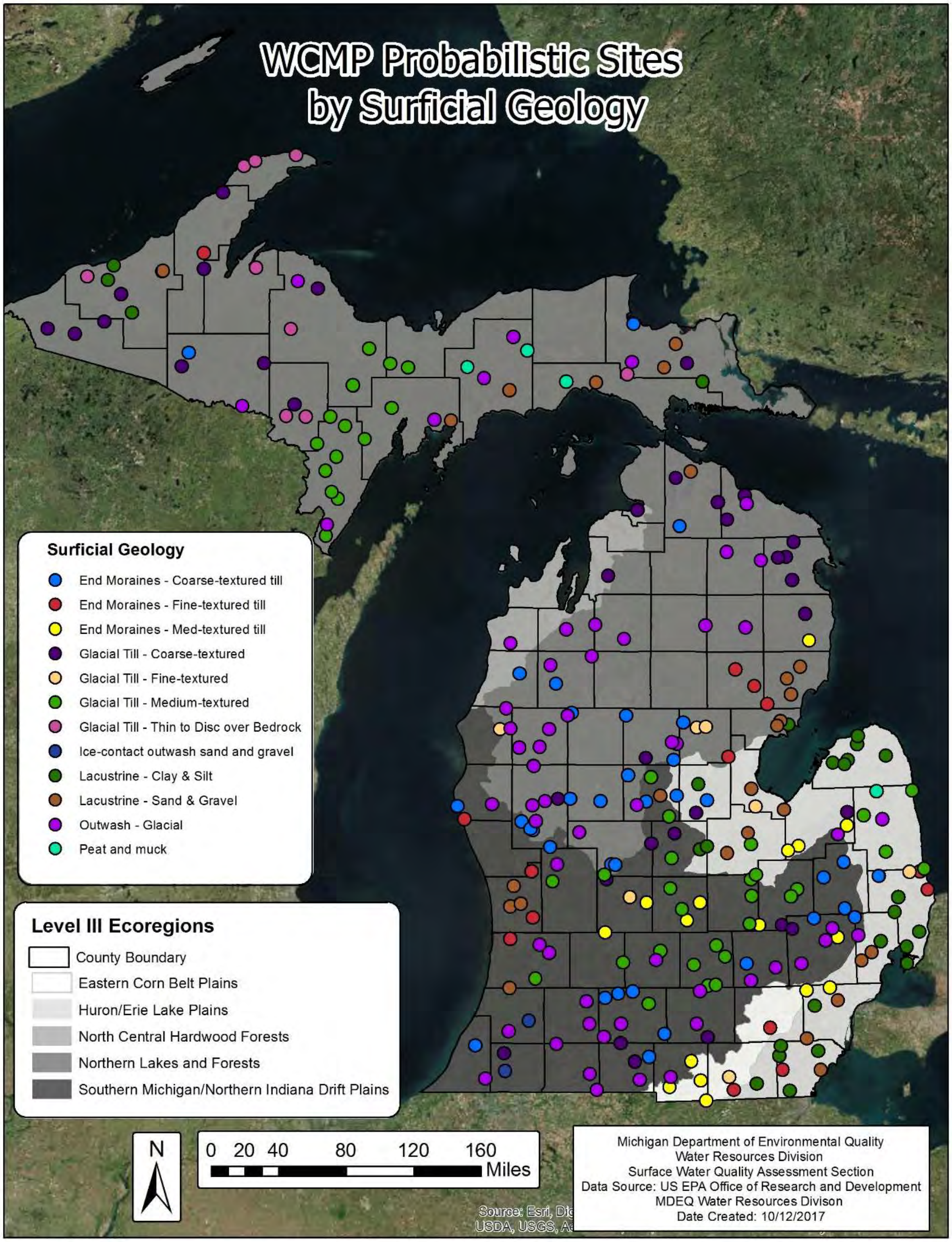


Figure 1-2. Probabilistic water chemistry monitoring sites visited from 2005-2014 by Strahler Stream Order.

Geology Analyses

Many trace metals and conventional pollutants have been shown to be strongly correlated with geology as a result of weathering of rock or erosion of soils (Allan and Castillo, 2007). Geology also hierarchically influences many environmental variables such as hydrology that directly influence chemical concentrations and their availability to biota (Allan and Castillo, 2007). Therefore, geology was also examined to determine if water chemistry parameters could be explained by geologic features. Because of the geologic complexity of Michigan, this analysis included both a qualitative review of bedrock geology throughout Michigan and a quantitative analysis of surficial geology.

To examine the influence of surficial geology on concentrations, the watershed upstream of each probabilistic site was first delineated using the Watershed Tool in ArcGIS. The dominant surficial geology type, or the surficial geology type making up the greatest percentage of area within each watershed, was then determined using the Michigan Quarternary Geology shapefile available from the Michigan Geographic Data Library (Figure 1-3; *(The link provided was broken and has been removed)*; Farrand and Bell, 1982). The dominant surficial geology type for each site was then compared for each parameter.



Source: Esri, Di
USDA, USGS, A

Michigan Department of Environmental Quality
Water Resources Division
Surface Water Quality Assessment Section
Data Source: US EPA Office of Research and Development
MDEQ Water Resources Divison
Date Created: 10/12/2017

Figure 1-3. Probabilistic water chemistry monitoring sites visited from 2005-2014 within surficial geology type.

Land Cover Analyses

Chemical concentrations in surface water are often influenced by anthropogenic activities and alterations in the surrounding watershed (Allan and Castillo, 2007). Land cover is a good surrogate measure for potential human-induced disturbances. Therefore, the potential impacts of different land cover types were examined to determine if they may explain parameter concentrations, as well as to pinpoint potential sources of impairment.

To examine the influence of land cover type on concentrations, the watershed upstream of each probabilistic site was first delineated using the Watershed Tool in ArcGIS. The dominant land cover type, or the land cover type making up the greatest percentage of area within each watershed, was then determined using the National Land Cover Database (NLCD) (2011) from the Multi-Resolution Land Characteristics Consortium (Homer et al., 2015, NLCD, 2011; Figure 1-4; Table 1-1). The dominant land cover type was then used in statistical analyses.

One limitation of this analysis is that certain land cover types (Table 1-1) may have a disproportionate influence on chemical concentrations relative to their areal coverage. The presence of development, in particular, may have an influence on concentrations even when it is not the dominant land cover type within the watershed. To explore this idea, the influence of presence of development, regardless of areal coverage in the watershed, was also evaluated. A minimum of 1% areal coverage was used to determine if development was present or absent (i.e., if development did not make up at least 1% of the watershed, development was considered absent).

Within the NLCD 2011 Land Cover categories, development is broken down into 4 categories partially defined by how much impervious surface is present: open space (< 20% impervious surface), low intensity (20-49% impervious surface), medium intensity (50-79% impervious surface), and high intensity (80-100% impervious surface; Table 1-1). Low, medium, and high intensity were used for this analysis and were compared to sites without development (i.e., less than 1% development). Sites with more than 1 type of development present (i.e., high, medium, low) were placed into the highest intensity type present in the watershed for this analysis. Therefore, this analysis compared 4 groups of sites: those with the presence (defined as > 1% areal coverage) of high intensity development, presence of medium intensity development, presence of low intensity development, and absence of development (defined as < 1% areal coverage).

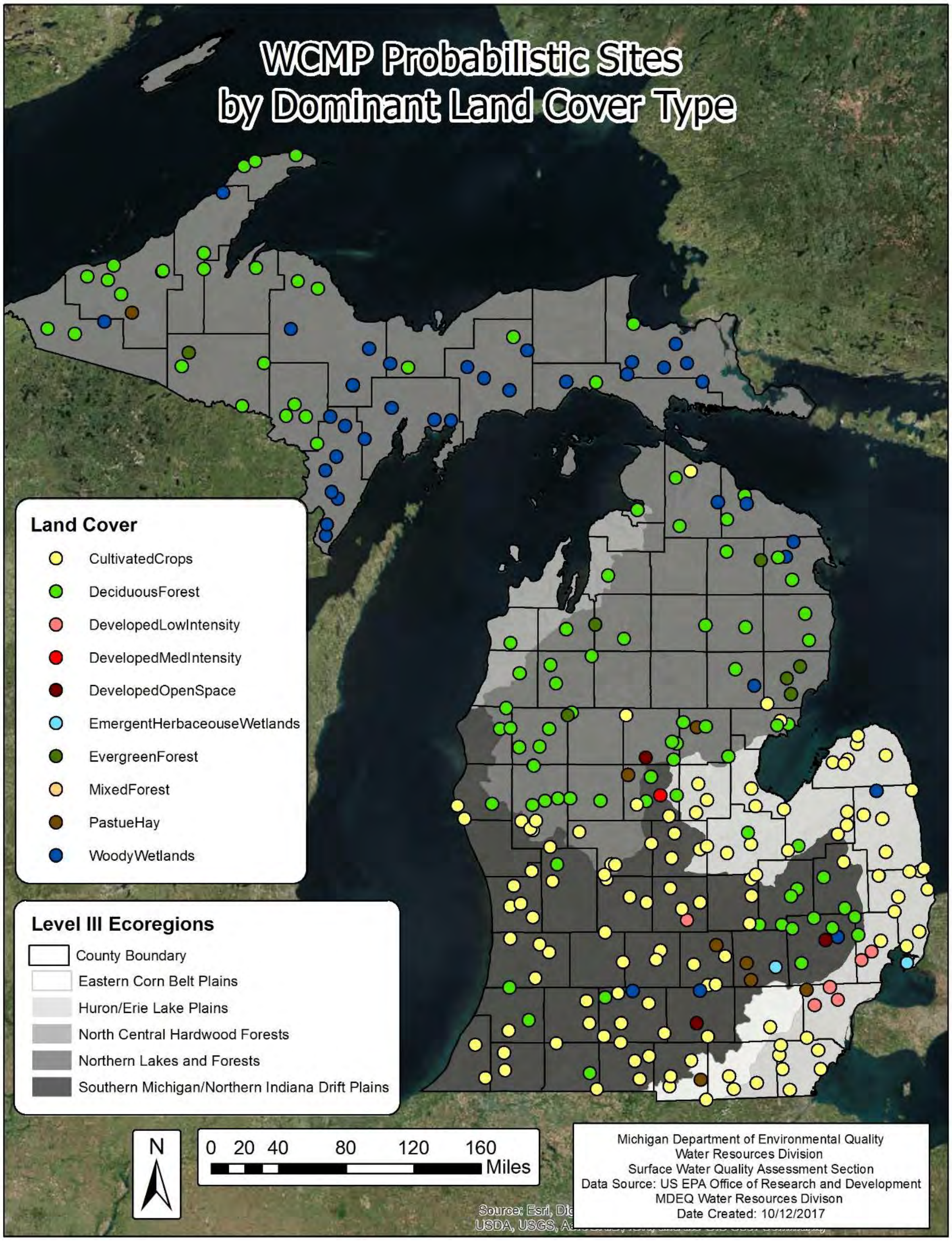


Figure 1-4. Probabilistic water chemistry monitoring sites visited from 2005-2014 by dominant land cover type.

1.4 RESULTS AND DISCUSSION

1.4.1 Nutrients & Conventional Parameters

Eight nutrients and conventional parameters have been consistently sampled or calculated every year at probabilistic sites: calcium, chloride, DOC, hardness-calculated, magnesium, sulfate, total phosphorus, and TSS. Statewide spatial patterns for these parameters are detailed below.

DO, temperature, pH, and specific conductance are also measured at each site and likely influence the concentrations and bioavailability of other parameters. However, spatial patterns are not evaluated because these parameters can have strong diel fluctuations and were not measured at consistent times within or across sites.

1.4.1.1 Chloride

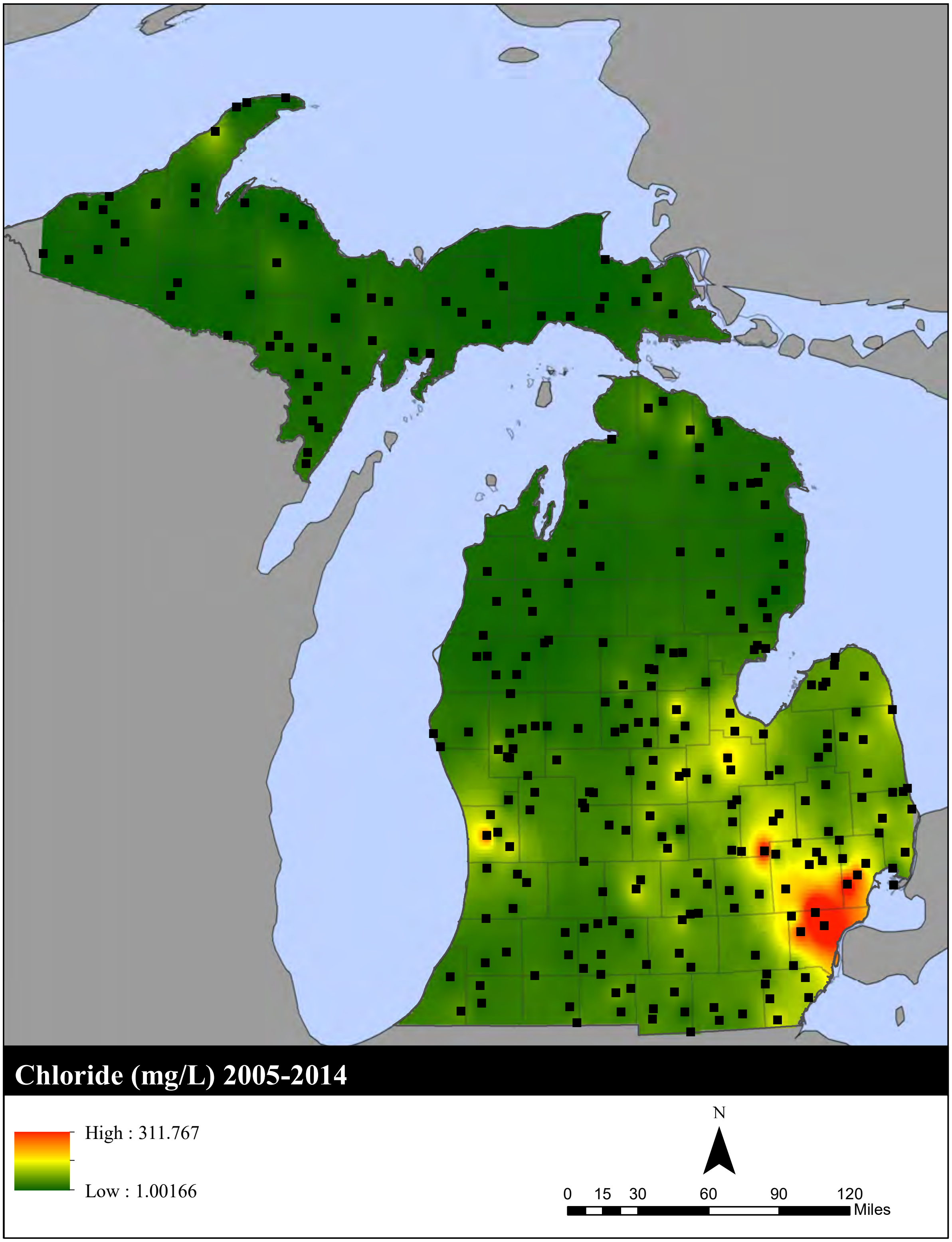


Figure 1-5. Inverse distance weighting interpolation image of median chloride concentrations (mg/L) from 2005-2014.

Chloride is a major anion that can enter surface water via natural or anthropogenic pathways (e.g., road salt or fertilizer application, water conditioning salts, and sewage) and can be toxic to aquatic life at high concentrations (Kelly et al., 2012; USEPA, 1988). The USEPA derived ambient water quality criteria for chloride in 1988 setting an acute aquatic life value of 860 mg/L and a chronic aquatic life value of 230 mg/L (USEPA, 1988). However, EGLE does not currently have aquatic life criteria for chloride.

From 2005 to 2014, chloride concentrations were detectable (i.e., above the MDL of 0.05 mg/L) in 98.4% of samples and quantifiable (i.e., above RL of 1.0 mg/L) in 97.9% of samples collected at probabilistic sites (n = 2,114 samples). Chloride sample concentrations ranged from nondetect to 987 mg/L (STORET #700605), and site median concentrations ranged from 1 to 312 mg/L. The majority of samples collected were below levels of concern and only 1.8% of all chloride samples collected from 2005 to 2014 were greater than the USEPA chronic criteria of 230 mg/L.

Chloride median site concentrations were greatest in southeast Michigan (Figure 1-5), in particular, within the Clinton River and Detroit River sites. In addition to anthropogenic sources of chloride, there are large expanses of natural salt deposits in southeast Michigan, which may explain the greater chloride concentrations in this area. Median concentrations were greatest in the HELP, ECBP, and SMNIDP ecoregions, and lowest in the NLAF ecoregion, although the NCHF ecoregion did not differ from the ECBP, SMNIDP, or NLAF ecoregions (Figure 1-6A; $X^2 = 158.21$, $df = 4$, $p = <0.001$). Median concentrations also increased slightly with increased stream order at a statewide scale (Figure 1-6B; $X^2 = 14.23$, $df = 3$, $p = 0.003$).

Median chloride concentrations were greater at sites where the upstream watershed was dominated by lacustrine clay and silt surficial geology compared to sites where the upstream watershed was dominated by thin to discontinuous glacial till over bedrock and glacial outwash sand and gravel/postglacial alluvium, but did not differ among other surficial geology types (Figure 1-6C; $X^2 = 38.15$, $df = 11$, $p = <0.001$). The ability of runoff or streamflow to erode soils or keep sediments suspended is largely dependent on particle size and water velocity (Allan and Castillo, 2007). Lacustrine clay and silt surficial geology is characterized by finer sediments than glacial outwash sand and gravel/postglacial alluvium suggesting the finer particle size of lacustrine clay and silt may be more easily transported or stay suspended longer in rivers surrounded by these geologies.

Median chloride concentrations varied by dominant land cover type and were greater at sites where the upstream watershed was dominated by low intensity development and cultivated crops compared to sites where the upstream watershed was dominated by deciduous forest, evergreen forest, and woody wetlands (Figure 1-6D; $X^2 = 114.1$, $df = 9$, $p = <0.001$; Table 1). This suggests that anthropogenic sources of chloride and/or alterations to the landscape may contribute to increased concentrations in surface water (*e.g.,* application of road salts and brines, decreased permeability of soils, increased runoff rates, and irrigation practices).

Additionally, when chloride concentrations were compared solely to the presence of varying levels of development (none, low, medium, and high) in the upstream watershed, median chloride concentrations were greater when development was present relative to when development was absent. Moreover, chloride concentrations were greater when high and medium intensity development were present than when low intensity development was present in the watershed ($X^2 = 132.8$, $df = 3$, $p = < 0.001$). This suggests that the presence of development alone may influence chloride concentrations irrespective of the percentage of development in the watershed. Coupled with the results from the first analysis, the influence of development on chloride concentrations may be exacerbated with increased areal coverage of this land cover type.

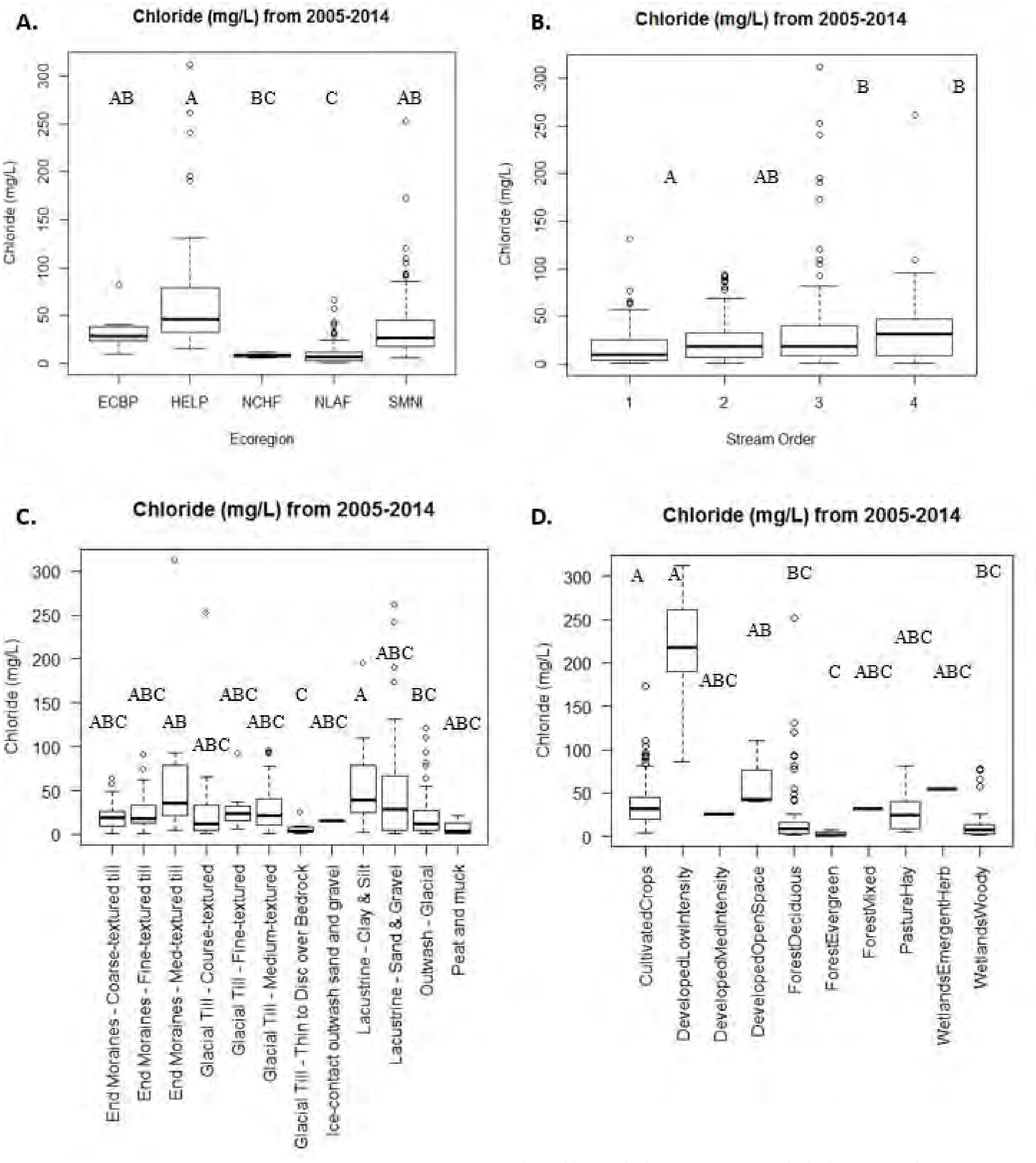


Figure 1-6. Median site chloride concentrations (mg/l) by (A) Ecoregion, (B) Stream Order, (C) Surficial Geology, and (D) Land Use from 2005-2014 (different letters denote significant difference in Kruskal Wallis post hoc Dunn tests at α = 0.05; sample sizes shown in Table 3).

1.4.1.2 DOC

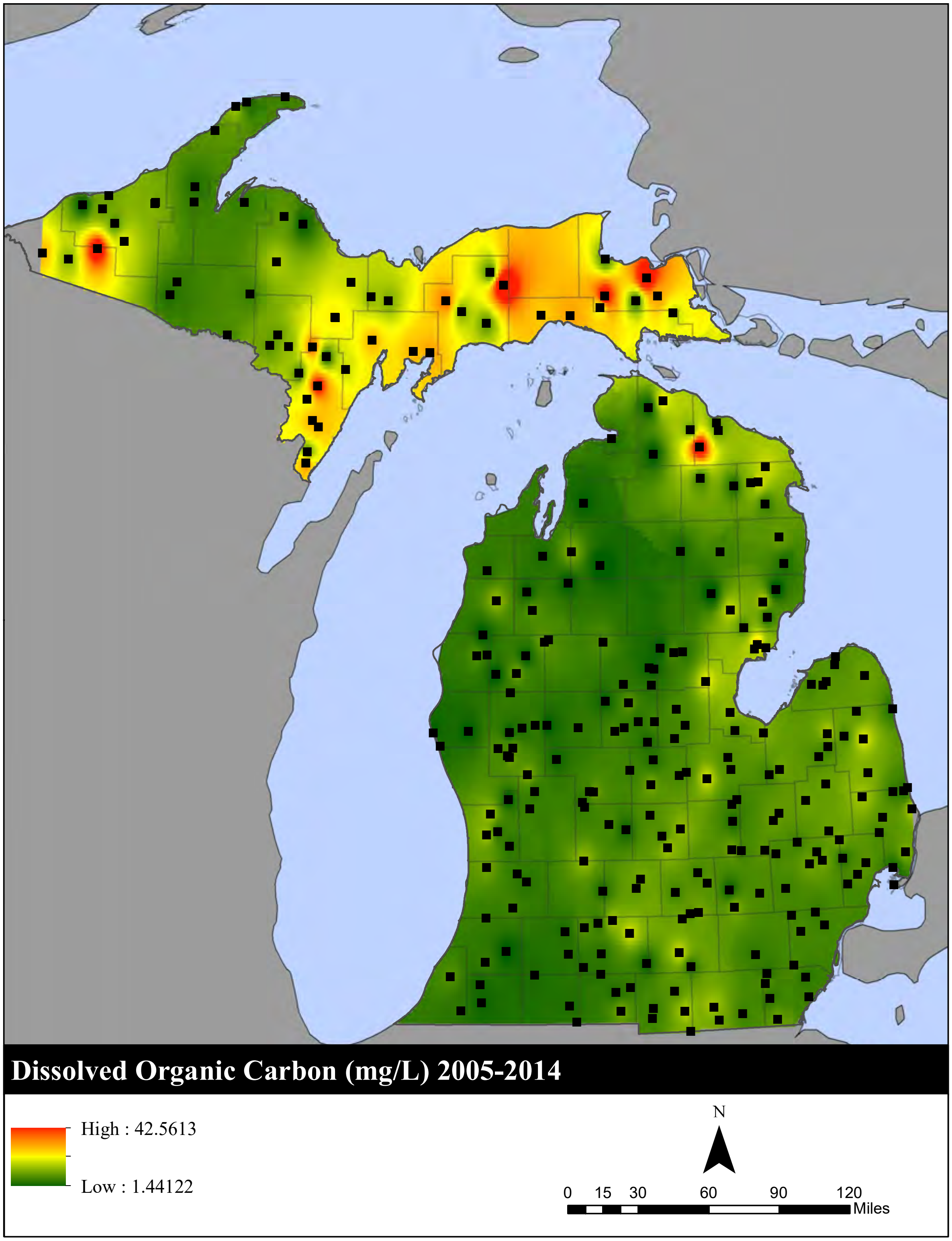


Figure 1-7. Inverse distance weighting interpolation image of Median DOC concentrations (mg/L) from 2005-2014.

DOC is a measure of the dissolved component of TOC (Brezonik and Arnold, 2011). DOC generally makes up the majority of organic carbon in lotic waters (Allan and Castillo, 2007) and is biologically important because it provides an energy source for microbial processes (Allan and Castillo, 2007) and is thought to regulate the toxicity of some metals (MDEQ, 2007a). For example, copper toxicity decreased as DOC increased in Upper Peninsula water bodies (MDEQ, 2007a).

From 2005 to 2014, DOC concentrations were quantifiable (i.e., above MDL and RL of 0.5 mg/L) in 99.9% of samples collected at probabilistic sites (n = 2,033 samples). DOC sample concentrations ranged from nondetect to 82 mg/L (STORET #770118), while site median concentrations ranged from 1.4 to 43 mg/L.

DOC median concentrations were greatest in the Upper Peninsula and lowest in southern Michigan (Figure 1-7). Median site DOC concentrations did not differ by ecoregion (Figure 1-8A; $X^2 = 7.88$, $df = 4$, $p = 0.10$) although the greatest concentrations of DOC were found in the NLAF ecoregion. Median concentrations were also slightly higher in first order streams and decreased with increased stream order at a statewide scale (Figure 1-8B; $X^2 = 16.36$, $df = 3$, $p = < 0.001$). DOC can enter river systems through a variety of avenues including groundwater, subsurface or interflow, surface flow, leachate from detritus or terrestrial origin, throughfall, or extracellular release and leachate from algae or macrophytes (Allan and Castillo, 2007). Greater DOC concentrations in first order streams, especially in heavily forested ecoregions like NLAF, may be explained by the disproportionally high contribution of DOC allocthonous inputs, and surface and subsurface flow in first order streams relative to higher order streams in these areas.

Median DOC concentrations were greatest at sites where the upstream watershed was dominated by peat and muck and medium-textured glacial till compared to sites where the upstream watershed was dominated by glacial outwash sand and gravel/postglacial alluvium, but did not differ among other surficial geology types (Figure 1-8C; $X^2 = 34.46$, $df = 11$, $p = < 0.001$). Peat and muck are, by definition, decomposing organic matter so greater DOC in sites where the upstream watershed is dominated by peat and muck in not unexpected.

Median DOC concentrations varied by land cover type and were greater at sites where the upstream watershed was dominated by woody wetlands compared to sites where the upstream watershed was dominated by deciduous forest, evergreen forest, and cultivated crops (Figure1-8D; $X^2 = 67.52$, $df = 9$, $p = < 0.001$). It is important to note the majority of WCMP probabilistic sites where the upstream watershed was dominated by woody wetlands are located in the Upper Peninsula (Figure 4). However, when excluding all Upper Peninsula sites, DOC median concentrations were still greater at sites where the upstream watershed was dominated by woody wetlands compared to sites where the upstream watershed was dominated by cultivated crops or deciduous forest ($X^2 = 25.15$, $df = 8$, $p = 0.001$) suggesting that dominant land cover type may be more important than spatial location on the landscape (i.e., Upper Peninsula) in predicting DOC concentrations.

Additionally, when DOC concentrations were compared to the presence of varying levels of development (none, low, medium, and high) in the upstream watershed, median DOC concentrations did not differ between sites where high intensity development, medium intensity development, low intensity development, or no development was present in the upstream watershed ($X^2 = 7.016$, $df = 3$, $p = 0.071$).

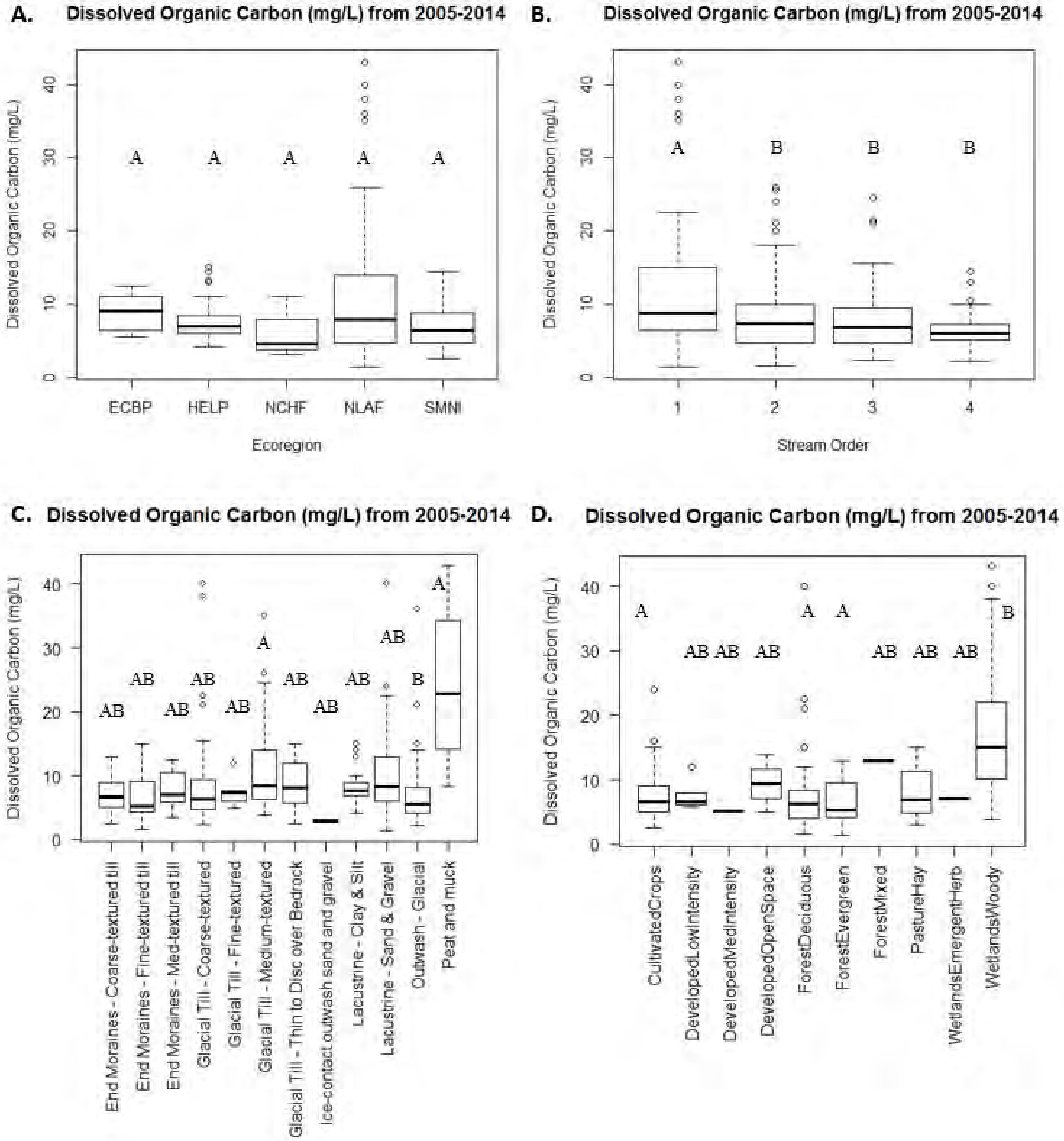


Figure 1-8. Median site DOC concentrations (mg/L) by (A) Ecoregion, (B) Stream Order, (C) Surficial Geology, and (D) Land Use from 2005-2014 (different letters denote significant difference in Kruskal Wallis post hoc Dunn tests at α = 0.05; sample sizes shown in Table 3).

1.4.1.3 Sulfate

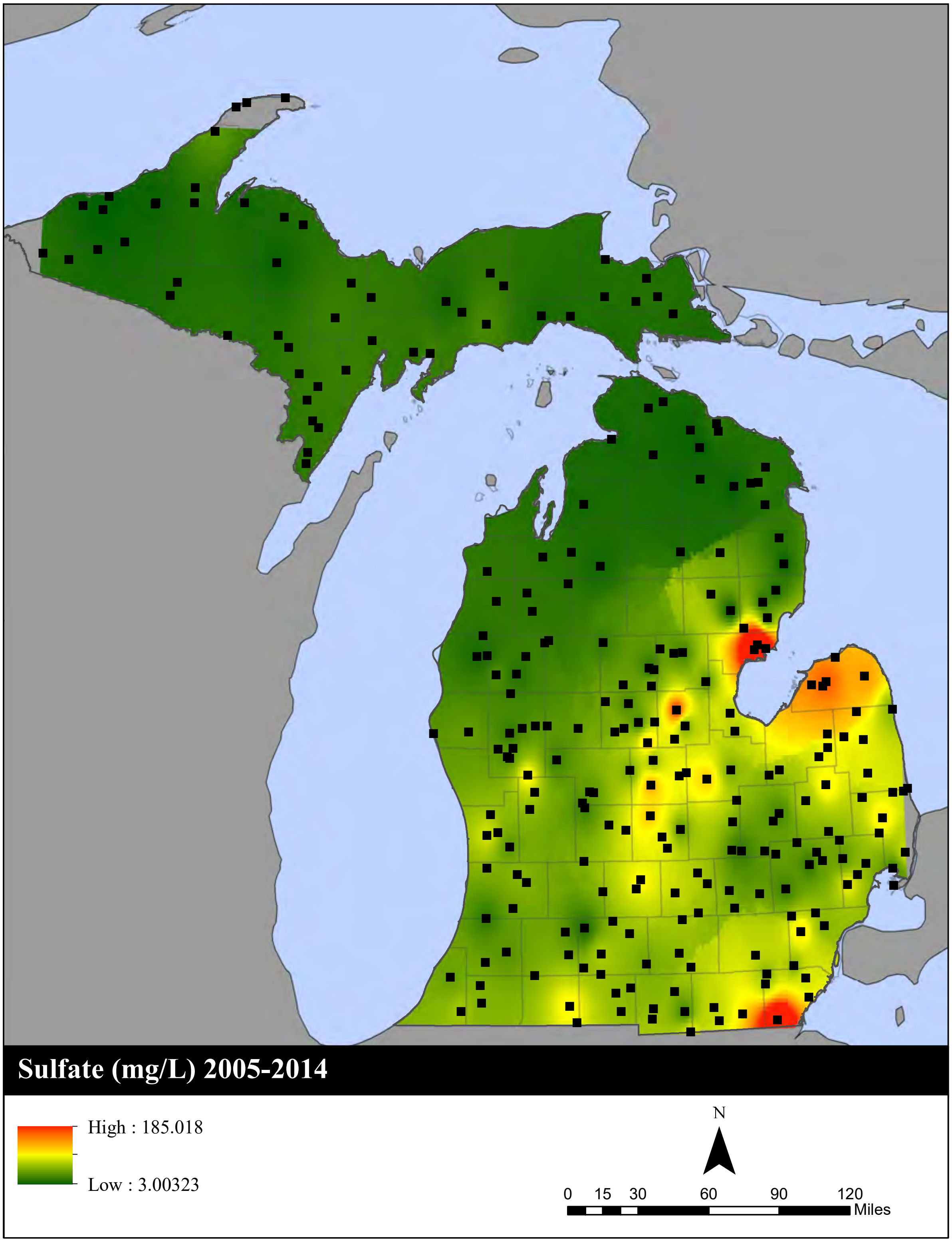


Figure 1-9. Inverse distance weighting interpolation image of median sulfate concentrations (mg/L) from 2005-2014.

Sulfate is a major anion that can enter surface water via natural or anthropogenic pathways (Allan and Castillo, 2007). Sulfate, like chloride, can be toxic to aquatic life at high concentrations (e.g., Soucek and Kennedy, 2005); however, neither EGLE nor the USEPA currently have numeric surface water criteria for sulfate.

From 2005 to 2014, sulfate concentrations were detectable (i.e., above MDL of 0.6 mg/L) in 96.9% of samples and quantifiable (i.e., above RL of 2.0 mg/L) in 96.8% of samples collected at probabilistic sites (*n* = 1,735 samples). Sulfate sample concentrations ranged from nondetect to 843 mg/L (STORET #580557), and site median concentrations ranged from nondetect to 228.5 mg/L.

Sulfate median concentrations were greatest near the Saginaw Bay, and in general, increased from northwest to southeast Michigan (Figure 1-9). The area near Saginaw Bay with greatest sulfate concentrations is known to have natural deposits of $CaSO_4$, which likely influences surface water concentrations to some extent. Sulfate median concentrations were also greatest in the ECBP, HELP, and SMNIDP ecoregions, and lowest in the NLAF and NCHF ecoregions (Figure 1-10A; X^2 = 138.85, *df* = 4, *p* = < 0.001). Concentrations increased slightly with stream order and were significantly greater in second, third, and fourth order streams compared to first order streams at a statewide scale (Figure 1-10B; X^2 =21.36, *df* = 3, *p* = < 0.001).

Sulfate concentrations generally varied across surficial geology types with the exception of greater sulfate concentrations at sites where the upstream watershed was dominated by lacustrine clay and silt and medium-textured glacial till compared to sites where the upstream watershed was dominated by coarse-textured glacial till and thin to discontinuous glacial till over bedrock (Figure 1-10C; X^2 =48.043, *df* = 11, *p*= < 0.001).

Median sulfate concentrations varied by dominant land cover type but were greater at sites where the upstream watershed was dominated by low intensity development and cultivated crops compared to sites where the upstream watershed was dominated by deciduous forest, evergreen forest, or woody wetlands (Figure 1-10D; X^2 = 128.36, *df* = 9, *p* = < 0.001).

Additionally, when sulfate concentrations were compared to the presence of varying levels of development (none, low, medium, and high) in the upstream watershed, median sulfate concentrations were greater when development was present relative to when development was absent, but did not differ between high, medium, and low intensity development (X^2 = 41.986, *df* = 3, *p* = < 0.001). This suggests that presence of development alone may influence sulfate concentrations irrespective of the percentage of the watershed in development, and that coupled with the results from the first analysis, the influence of development on sulfate concentrations may be exacerbated with increased areal coverage of this land cover type.

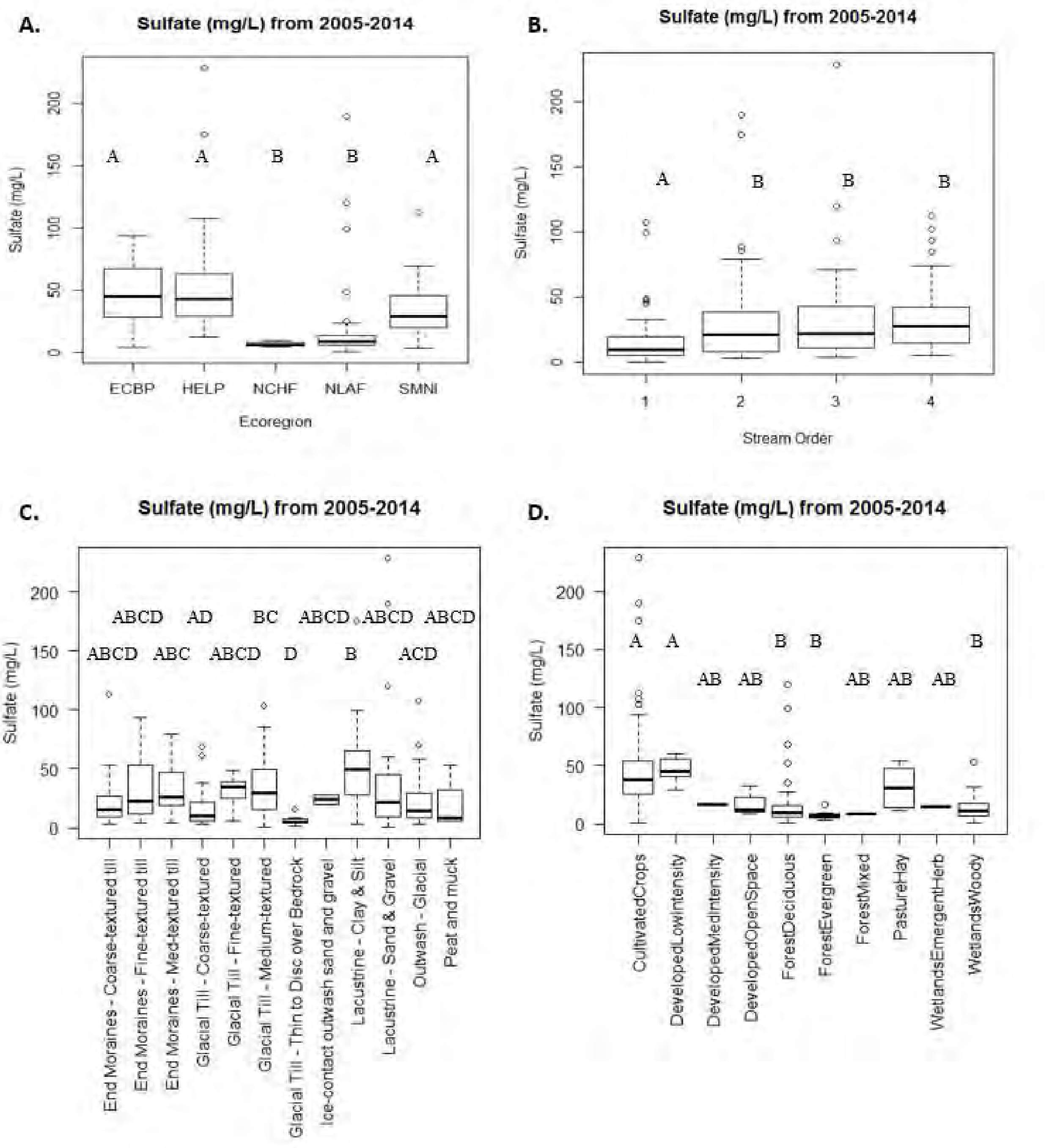


Figure 1-10. Median site sulfate concentrations (mg/l) by (A) Ecoregion, (B) Stream order, (C) Surficial Geology, and (D) Land Use from 2005-2014 (different letters denote significant difference in Kruskal Wallis post hoc Dunn tests at α = 0.05; sample sizes shown in Table 3).

1.4.1.4 Total phosphorus

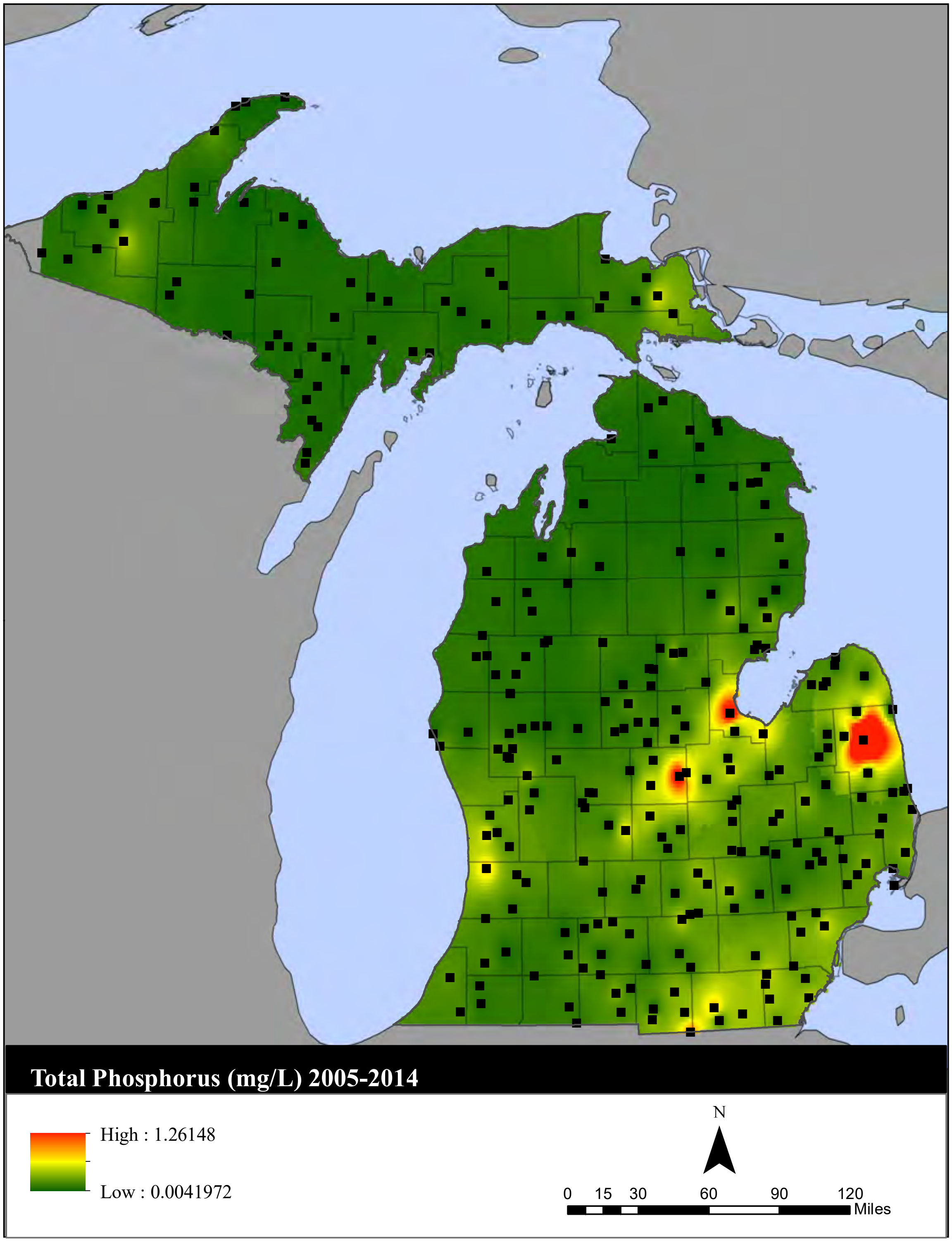


Figure 1-11. Inverse distance weighting interpolation image of median total phosphorus concentrations (mg/L) from 2005-2014.

Phosphorus is an essential nutrient for living organisms and can enter surface water via natural processes or as a result of anthropogenic activities (APHA et al., 1995). Phosphorus is often, but not always, the limiting nutrient in rivers and streams that controls plant and algae growth (APHA et al., 1995). Because of this, artificial increases in phosphorus can lead to excessive plant and algae growth, which can further lead to water quality degradation (e.g., seasonal declines in DO; Allan and Castillo, 2007). Michigan has nutrient water quality criteria that protects against excessive growth of plants, fungi, or bacteria, which are, or may become, injurious to the designated uses of the state; however, EGLE does not have numeric criteria for phosphorus (MDEQ, 2006).

From 2005 to 2014, total phosphorus concentrations were detectable (i.e., above MDL of 0.003 mg/L) in 99.1% of samples and quantifiable (i.e., above RL of 0.005 mg/L) in 98.4% of samples collected at probabilistic sites (n = 2,130 samples). Total phosphorus sample concentrations ranged from nondetect to 5.5 mg/L (STORET #760249), and site median concentrations ranged from $0.003 < x < 0.005$ mg/L (between the MDL and RL) to 1.275 mg/L.

Total phosphorus median concentrations were greatest in the Saginaw River watershed, eastern thumb region, and southeast Michigan; however, high concentrations of total phosphorus were also found in the Macatawa watershed and a few sites in the Upper Peninsula (Figure 1-11). Total phosphorus median concentrations were greatest in the ECBP and HELP ecoregions, and lowest in the NLAF and NCHF ecoregions (Figure 1-12A; X^2 =105.55, df = 4, p = < 0.001), and did not differ across stream order at a statewide scale (Figure 1-12B; X^2 = 4.78, df = 3, p = 0.19).

In 2000, the USEPA published recommendations for developing nutrient criteria for rivers and streams (USEPA, 2000). These recommendations included identifying reference conditions of several parameters, including total phosphorus, which could be used to develop water quality criteria. The USEPA used the lower 25th percentile of all data (datasets from Legacy STORET, National Stream Quality Accounting Network, National Water Quality Assessment, and USEPA Regions 5 and 7 from 1990 to 1999) to roughly approximate reference conditions, or conditions of surface waters that have minimal impacts caused by humans, for each Level III ecoregion and each aggregate ecoregion (combinations of Level III ecoregions). For total phosphorus, these reference conditions (across all seasons) were greatest in the ECBP (0.07 mg/L) and HELP ecoregions (0.0625 mg/L) and lowest in the SMNIDP (0.03125 mg/L), NCHF (0.02875 mg/L), and NLAF (0.012 mg/L) ecoregions, closely following the same overall ecoregional pattern observed from 2005 to 2014 for probabilistic site medians (Figure 1-12A).

Median total phosphorus concentrations were greater at sites where the upstream watershed was dominated by end moraines of medium-textured till or lacustrine clay and silt compared to sites where the upstream watershed was dominated by coarse-textured glacial till, thin to discontinuous glacial till over bedrock, and glacial outwash sand and gravel/postglacial alluvium, but did not differ among other surficial geology types (Figure 1-12C; X^2 = 69.64, df = 11, p = < 0.001).

Median total phosphorus concentrations varied by dominant land cover type but were greater at sites where the upstream watershed was dominated by pasture/hay or cultivated crops compared to sites where the upstream watershed was dominated by deciduous forest and woody wetlands (Figure 1-12D; X^2 = 108.35, df = 9, p = < 0.001). Additionally, the 10 greatest site medians were found at sites where the upstream watershed was dominated by cultivated crops indicating some farming practices (e.g., fertilizer application, tilling) may influence total phosphorus concentrations in surface water. Total phosphorus was also greater at sites where the upstream watershed was dominated by low intensity development compared to sites where the upstream watershed was dominated by deciduous forest, but sites where the upstream watershed was dominated by low intensity development did not differ from those where the upstream watershed was dominated by cultivated crops, pasture/hay, or woody wetlands (Figure 1-12D; $X^2 = 108.35$, $df = 9$, $p = < 0.001$).

Additionally, when total phosphorus concentrations were compared to the presence of varying levels of development (none, low, medium, and high) in the upstream watershed, median total phosphorus concentrations were greater when development was present relative to when development was absent ($X^2 = 49.224$, $df = 3$, $p = < 0.001$). Moreover, total phosphorus concentrations were greater when high and medium intensity development were present than when low intensity development was present in the watershed. This suggests that presence of development alone may influence total phosphorus concentrations irrespective of the percentage of the watershed in development, and that coupled with the results from the first analysis, the influence of development on total phosphorus concentrations may be exacerbated with increased areal coverage of this land cover type.

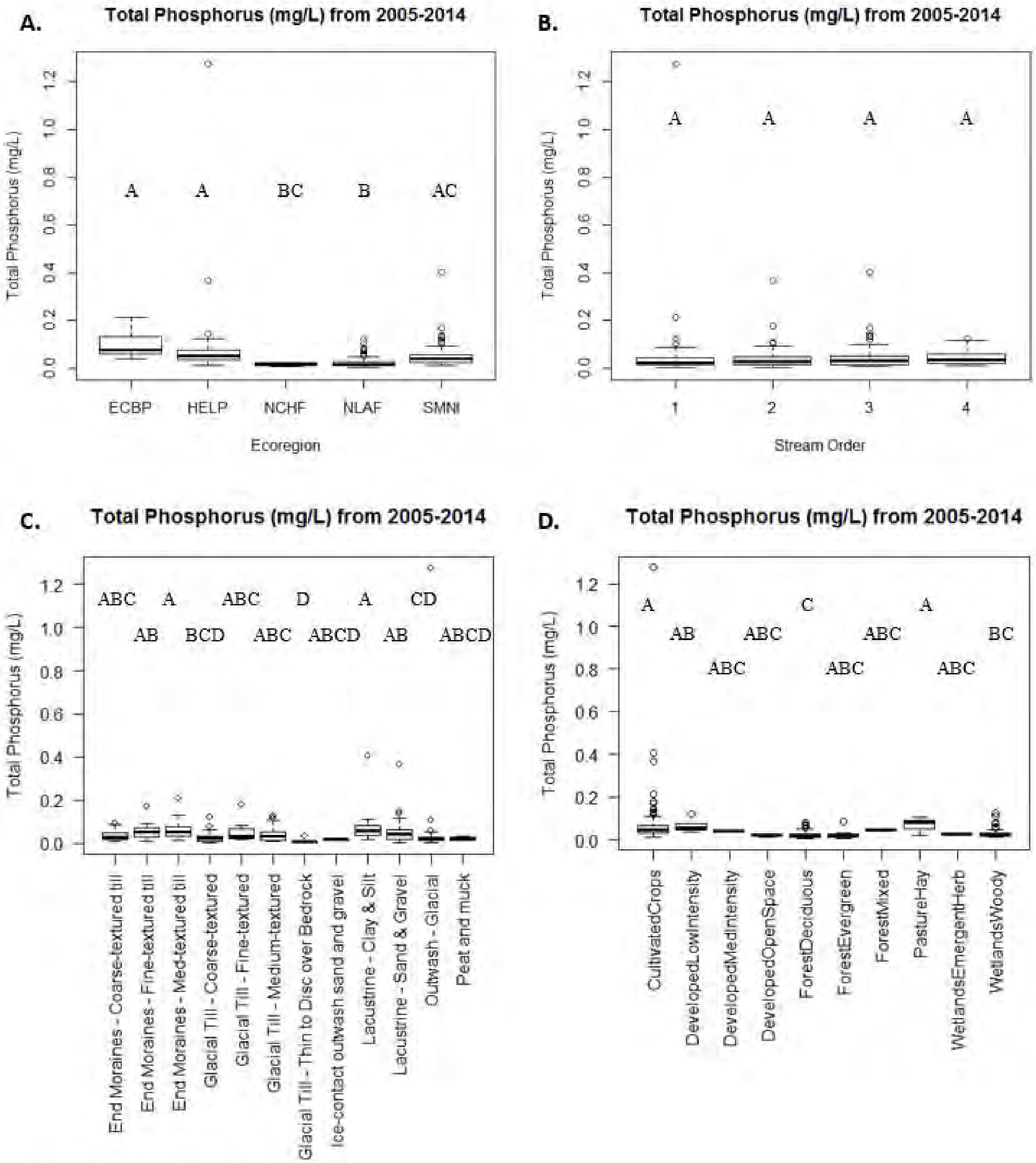


Figure 1-12. Median site total phosphorus concentrations (mg/l) by (A) Ecoregion, (B) Stream Order, (C) Surficial Geology, and (D) Land Use from 2005-2014 (different letters denote significant difference in Kruskal Wallis post hoc Dunn tests at α = 0.05; sample sizes shown in Table 3).

1.4.1.5 Total suspended solids

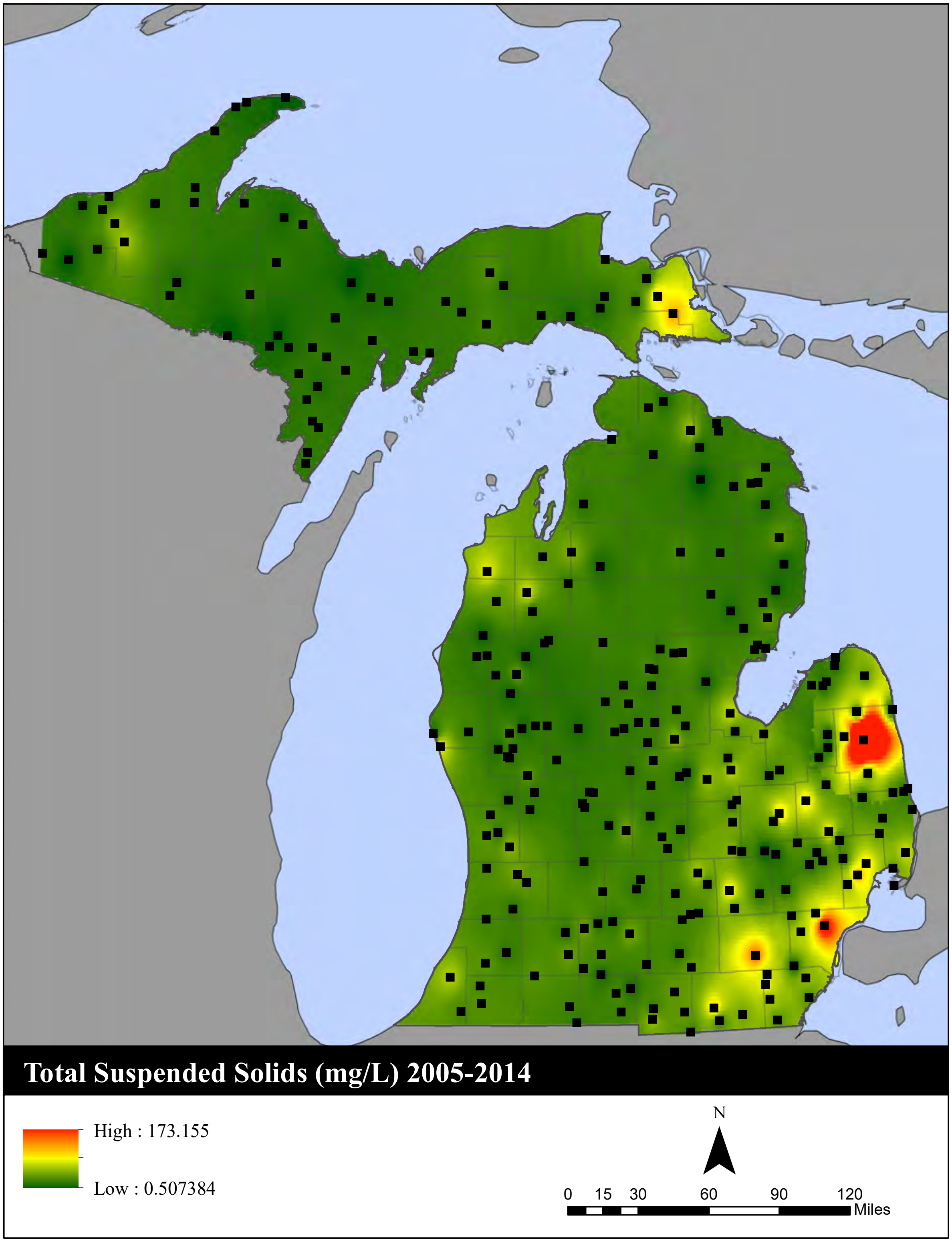


Figure 1-13. Inverse distance weighting interpolation image of median TSS concentrations (mg/L) from 2005-2014.

TSS is a measure of all organic and inorganic particles suspended in water (MDEQ, 2016a). TSS is biologically important because the amount of suspended material in the water column can influence water temperature, light penetration, plant growth, DO concentrations, and physical habitat availability (MDEQ 2016a). Michigan has narrative water quality criteria for TSS under Rule 323.1050., which states that waters of the state shall not have suspended solids, among other physical properties, in "unnatural quantities which are or may become injurious to any designated use".

Total suspended solid concentrations were detectable (*i.e.,* above MDL of 1 mg/L) in 83.6% of samples and quantifiable (*i.e.,* above RL of 4 mg/L) in 58.5% of samples collected at probabilistic sites from 2005 to 2014 (n = 2,128 samples). TSS sample concentrations ranged from nondetect to 7100 mg/L (STORET #760249), and site median concentrations ranged from nondetect to 175 mg/L.

TSS median concentrations were greatest at one site in the Thumb region (Custer County Drain, STORET #760249) and the Rouge River (STORET #821522; Figure 1-13). TSS median concentrations were similar across the ECBP, HELP, NCHF, and SMNIDP ecoregions and lower in the NLAF ecoregion although concentrations did not differ between the NCHF and NLAF ecoregions (Figure 1-14A; $X^2 = 53.718$, $df = 4$, $p = < 0.001$). TSS median concentrations were greater in fourth order streams at a statewide scale than first to third order streams (Figure 1-14B; $X^2 = 18.10$, $df = 3$, $p = < 0.001$).

Median TSS concentrations were greater at sites where the upstream watershed was dominated by end moraines of medium-textured till, lacustrine clay and silt, and lacustrine sand and gravel compared to sites where the upstream watershed was dominated by thin to discontinuous glacial till over bedrock, but did not differ among other surficial geology types (Figure 1-14C; $X^2 = 30.30$, $df = 11$, $p = 0.001$). This suggests smaller sediment size of surficial geology in the surrounding landscape may result in greater TSS concentrations.

Median TSS concentrations differed by land cover type and were greater at sites where the upstream watershed was dominated by low intensity development, pasture/hay, and cultivated crops compared to sites where the upstream watershed was dominated by deciduous forest or woody wetlands (Figure 1-14D; $X^2 = 48.687$, $df = 9$, $p = < 0.001$).

Additionally, when TSS concentrations were compared to the presence of varying levels of development (none, low, medium, and high) in the upstream watershed, median TSS concentrations were greater when development was present relative to when development was absent, but did not differ among low, medium, or high intensity development ($X^2 = 26.513$, $df = 3$, $p = < 0.001$). This suggests that the presence of development may influence TSS concentrations irrespective of the percentage of the watershed in development, and that coupled with the results from the first analysis, the influence of development on TSS concentrations may be exacerbated with increased areal coverage of this land cover type.

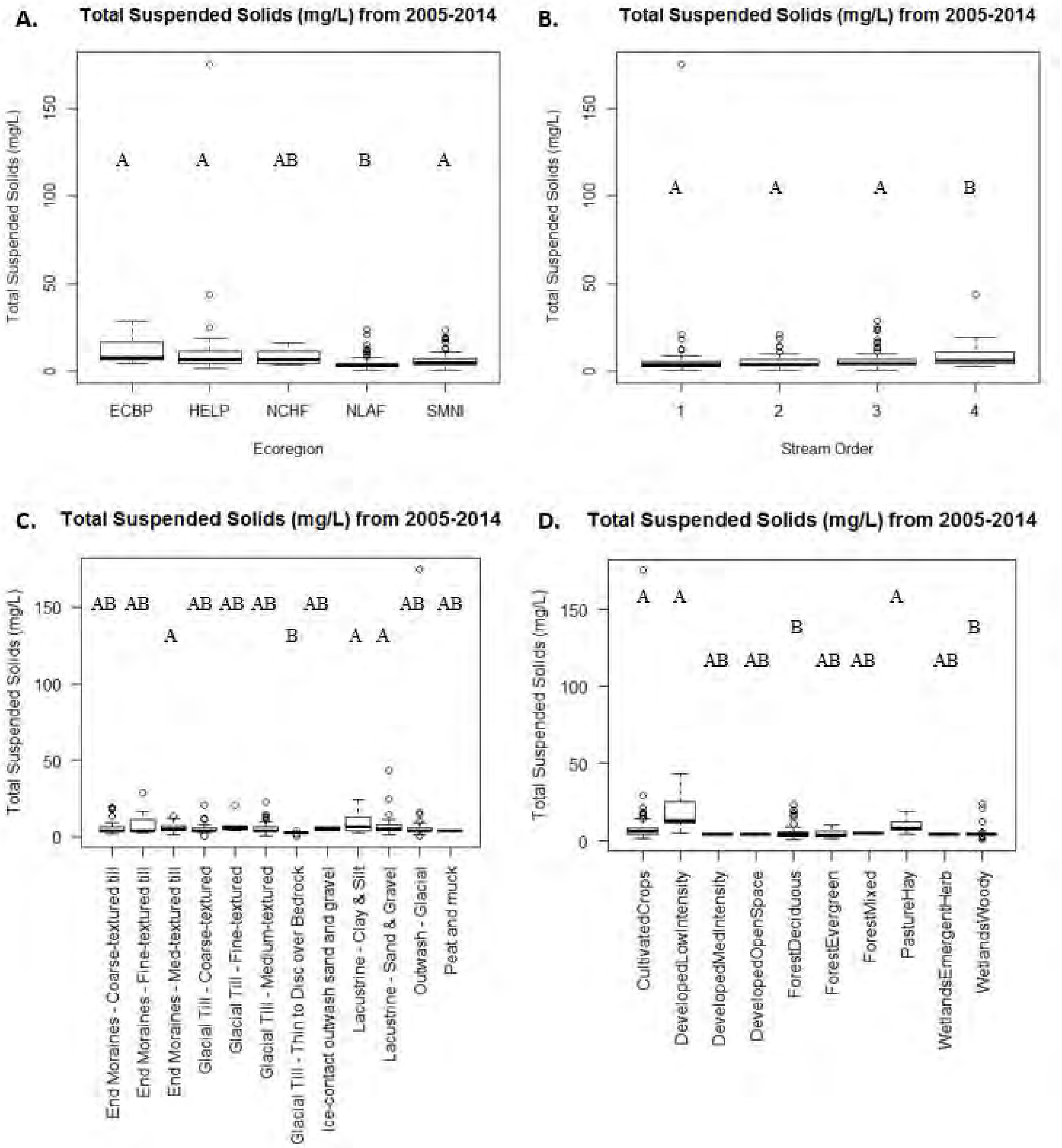


Figure 1-14. Median site TSS concentrations (mg/L) by (A) Ecoregion, (B) Stream Order, (C) Surficial Geology, and (D) Land Use from 2005-2014 (different letters denote significant difference in Kruskal Wallis post hoc Dunn tests at α = 0.05; sample sizes shown in Table 3).

1.4.1.6 Calcium, magnesium, hardness-calculated

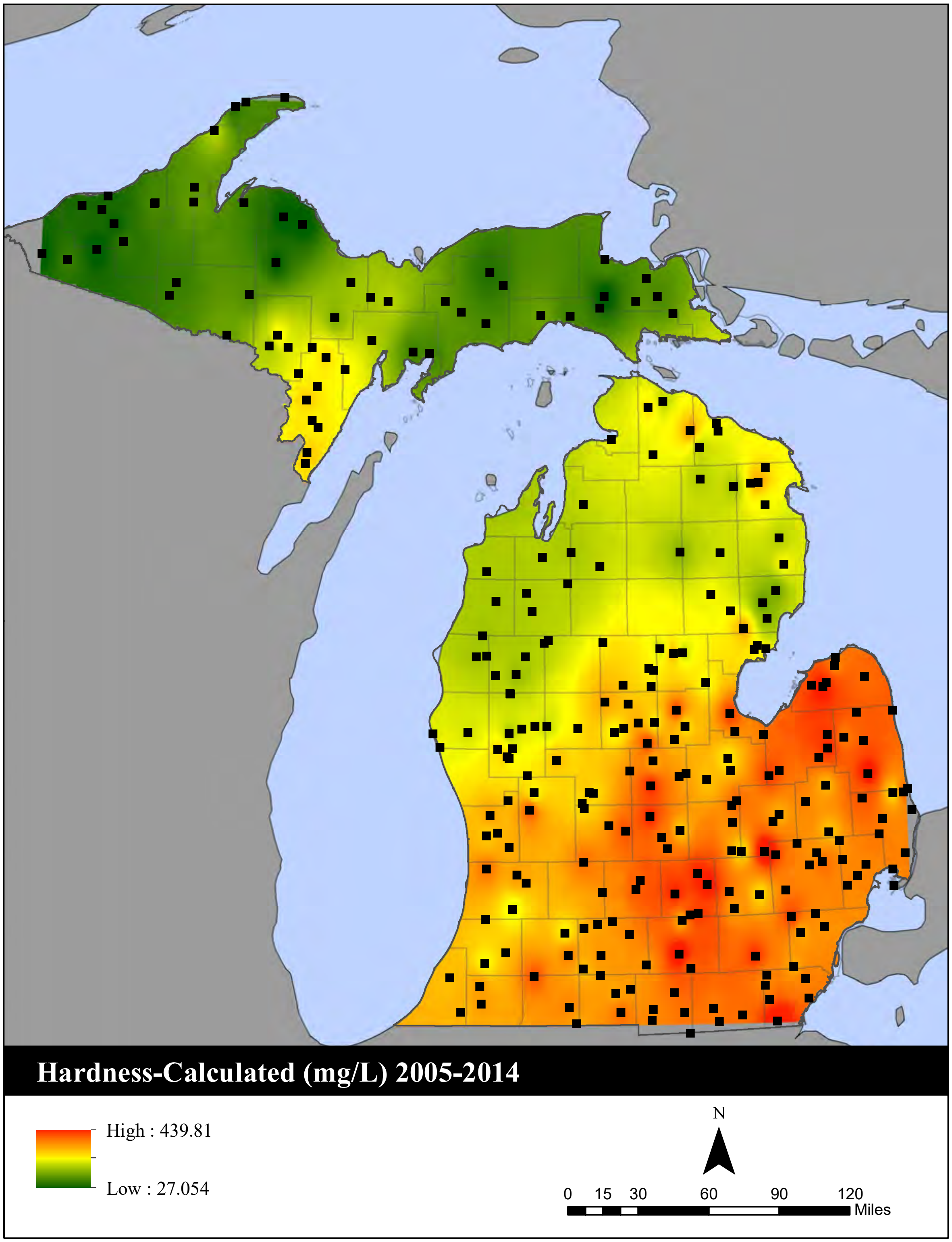


Figure 1-15. Inverse distance weighting interpolation image of median hardness-calculated concentrations (mg/L) from 2005-2014.

Hardness is a measure of the calcium and magnesium ions in water (Allan and Castillo, 2007) expressed as CaCO3. Hardness is biologically important, in part, due to its ability to regulate the toxicity of many metals and pollutants (e.g., MDEQ, 2013).

Calcium concentrations were quantifiable (i.e., above RL of 1 mg/L) in 100% of samples (*n* = 2,137 samples), and magnesium concentrations were quantifiable (i.e., above RL of 1 mg/L) in 99.9% of samples collected at probabilistic sites from 2005 to 2014 (*n* = 2,136). Calcium concentrations ranged from 2.243 to 273 mg/L (STORET #580557), while magnesium concentrations ranged from nondetect to 66 mg/L (STORET #580557). Calculated hardness ranged from 8.6 mg/L to 954 mg/L (STORET #580557) across all samples, and site median calculated hardness ranged from 16.5 to 479.5 mg/L.

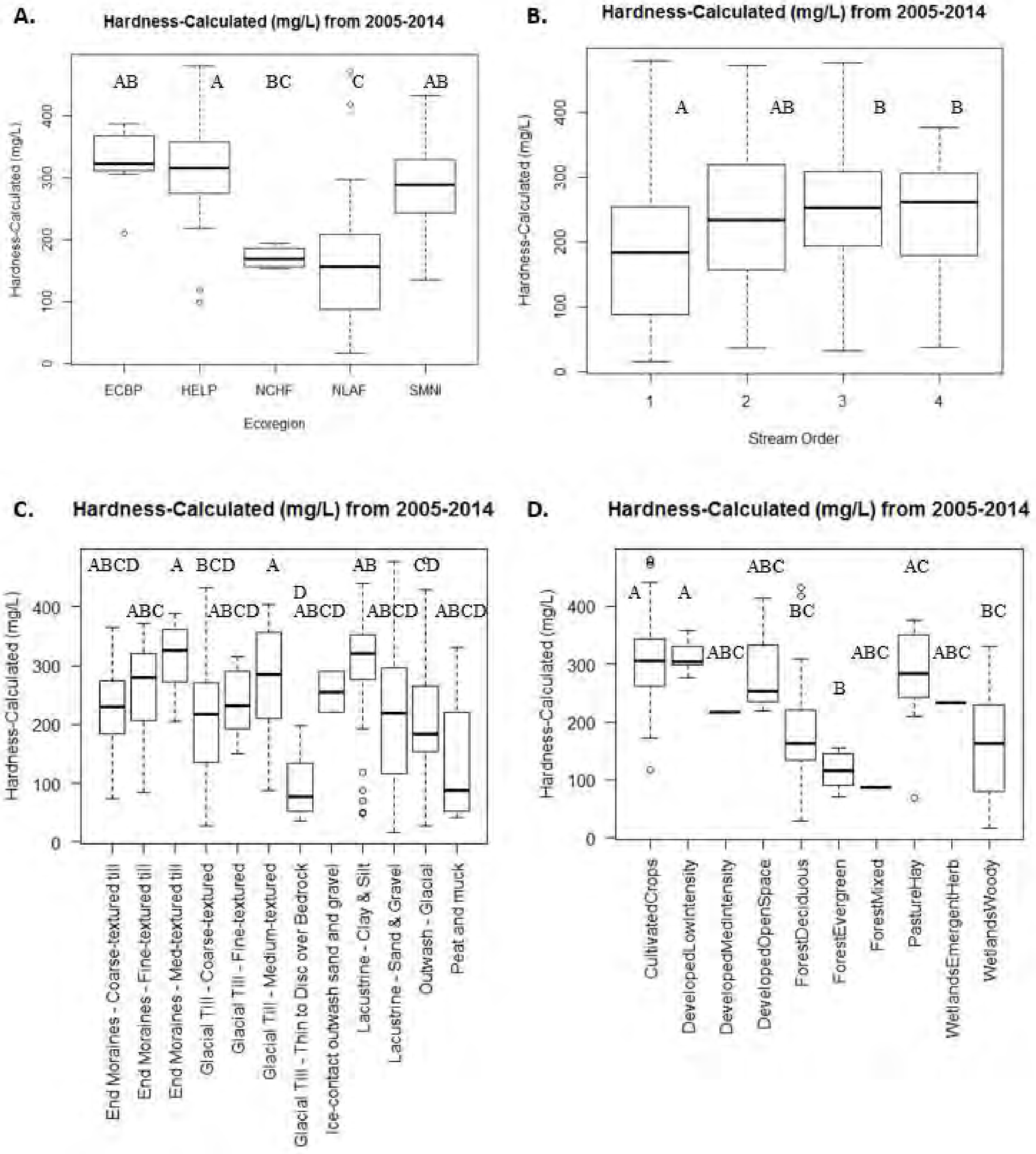
Hardness median concentrations increased from northwest to southeast Michigan (Figure 1-15). Median concentrations were greatest in the ECBP, HELP, and SMNIDP ecoregions and lowest in the NLAF ecoregions (Figure 1-16A; $X^2 = 145.45$, $df = 4$, $p = < 0.001$). Hardness median concentrations were greater in third and fourth order streams compared to first order streams at statewide scale (Figure 1-16B; $X^2 = 11.51$, $df = 3$, $p = 0.01$).

Geologically, the Lower Peninsula and eastern parts of the Upper Peninsula are composed of sedimentary rocks consisting of shales, limestones, and sandstones, while the western end of the Upper Peninsula is composed of mostly igneous and metamorphic rocks, which are characteristically more resistant to erosion. Limestone, a sedimentary rock, which covers much of the Lower Peninsula is made up of largely $CaCO_3$, which in conjunction with weathering leads to greater water hardness in these areas.

Surficial geology results also indicate erodibility and makeup of geologic features may influence hardness. Median hardness concentrations were greater at sites where the upstream watershed was dominated by end moraines of medium-textured till, medium-textured glacial till, or lacustrine clay and silt compared to sites where the upstream watershed was dominated by thin to continuous glacial till over bedrock (i.e., less erosive and igneous rock), or glacial outwash sand and gravel/postglacial alluvium (Figure 1-16C; $X^2 = 58.97$, $df = 11$, $p = < 0.001$).

Median hardness concentrations differed by land cover type and were greater at sites where the upstream watershed was dominated by low intensity development and cultivated crops compared to sites where the upstream watershed was dominated by deciduous forest, evergreen forest, and woody wetlands (Figure 1-16D; $X^2 = 136.15$, $df = 9$, $p = < 0.001$).

Additionally, when hardness concentrations were compared to the presence of varying levels of development (none, low, medium, and high) in the upstream watershed, median hardness concentrations were greater when development was present relative to when development was absent ($\chi^2 = 66.162$, $df = 3$, $p = < 0.001$) but did not differ among low, medium, and high intensity development. This suggests that presence of development may influence hardness concentrations irrespective of the percentage of the watershed in development, and that coupled with the results from the first analysis, the influence of development on hardness concentrations may be exacerbated with increased areal coverage of this land cover type. As with many parameters, both geology and anthropogenic disturbance likely influence hardness concentrations in surface water.



A. Hardness-Calculated (mg/L) from 2005-2014

B. Hardness-Calculated (mg/L) from 2005-2014

C. Hardness-Calculated (mg/L) from 2005-2014

D. Hardness-Calculated (mg/L) from 2005-2014

Figure 1-16. Median site hardness-calculated concentrations (mg/L) by (A) Ecoregion, (B) Stream Order, (C) Surficial Geology, and (D) Land Use from 2005-2014 (different letters denote significant difference in Kruskal Wallis post hoc Dunn tests at α = 0.05; sample sizes shown in Table 3).

1.4.2 Trace Metals and Mercury

Trace metals are metals typically found at low concentrations in the environment. Six trace metals have been consistently sampled at probabilistic sites: cadmium, chromium, copper, lead, nickel, and zinc. Cadmium, nickel, and zinc were sampled from 2006 to 2014, while chromium, copper, and lead were sampled from 2005 to 2014. Low-level mercury was also sampled at probabilistic sites from 2005 to 2014. Statewide spatial patterns for trace metals and mercury are detailed below.

1.4.2.1 Cadmium

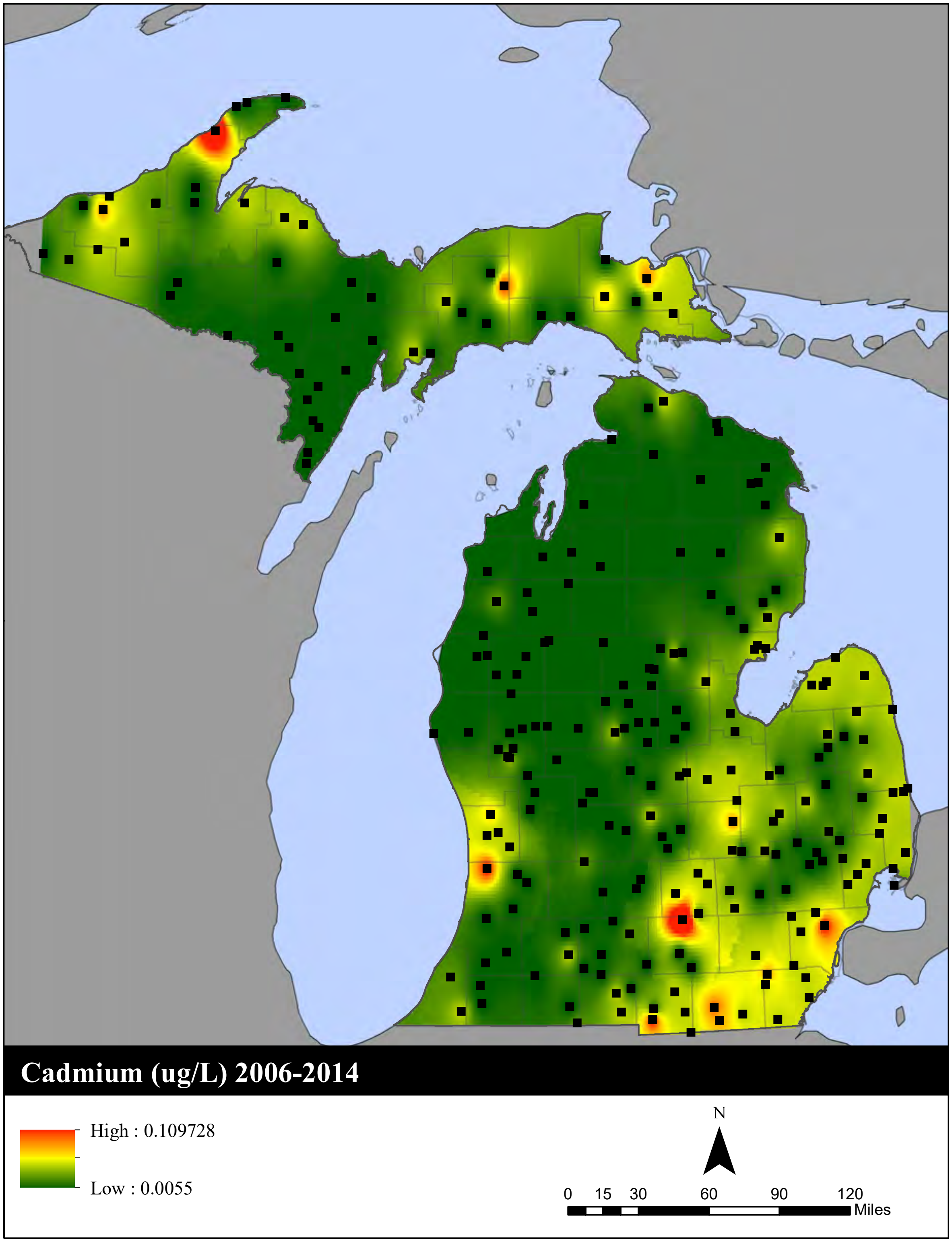


Figure 1-17. Inverse distance weighting interpolation image of median cadmium concentrations (µg/L) from 2006-2014.

Cadmium is a heavy metal normally found in low concentrations in freshwater environments (USEPA, 2016). Cadmium may enter aquatic systems through weathering of bedrock or erosion of soils, atmospheric deposition, or through direct discharge from industrial operations, agricultural fields, or contaminated sites (e.g., USEPA, 2016; United States Department of Health and Human Services [USDHHS], 2012a). Typical concentrations of cadmium in freshwater of the United States range from 0.002 to 0.08 µg/L, and rarely reach more than 15 µg/L (Mebane, 2006).

Although typically rare, cadmium can be highly toxic to some aquatic life. In a study of acute toxicity of 63 metals on a freshwater amphipod *Hyalella azteca*, cadmium was the most toxic metal on a molar basis (Borgmann et al., 2005). The toxicity of cadmium is also thought to vary with water hardness; therefore, EGLE uses a hardness-based approach to calculate numeric water quality criteria for cadmium.

From 2006 to 2014, cadmium concentrations were detectable (i.e., above MDL of 0.011 µg/L) in 40% of samples and quantifiable in 8% of samples (i.e., above RL of 0.037 µg/L) collected at probabilistic sites (n = 1,942 samples). Cadmium sample concentrations ranged from nondetect to 0.56 µg/L, and site median concentrations ranged from nondetect to 0.11 µg/L. Site-to-site variability in cadmium concentrations was evident across the state (Figure 1-17). Differences in cadmium concentrations between ecoregions, stream order, surficial geology, and land cover were not examined due to the low sample size of detected values. In general, cadmium does not appear to be a water quality concern for aquatic life, and from 2006 to 2014, cadmium did not exceed water quality criteria at any probabilistic sites.

1.4.2.2 Chromium

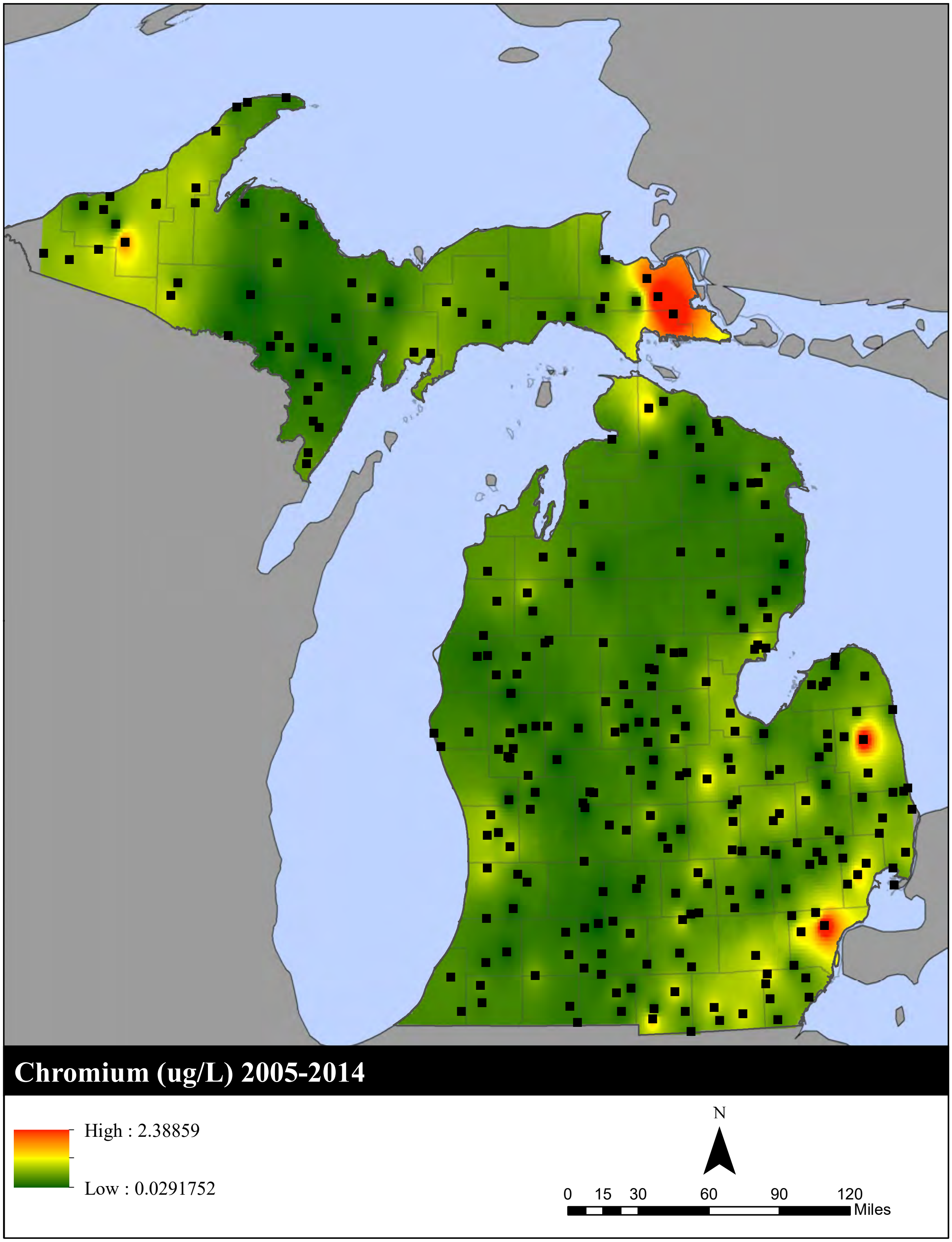


Figure 1-18. Inverse distance weighting interpolation image of Median Chromium concentrations (µg/L) from 2005-2014.

Chromium, like cadmium and other trace metals, can enter aquatic systems through a variety of avenues including geologic weathering, erosion of soils, and direct discharge from point sources, agricultural fields, or contaminated sites (USDHHS, 2012b). Industrial and manufacturing discharges can also contribute large amounts of chromium to surface waters (USDHHS, 2012b).

From 2005 to 2014, chromium concentrations were detectable (i.e., above MDL of 0.057 µg/L) in 94% of samples and quantifiable (i.e., above RL of 0.19 µg/L) in 72% of samples collected at probabilistic sites (n = 2,088 samples). Chromium sample concentrations ranged from nondetect to 101 µg/L, and site median concentrations ranged from nondetect to 2.48 µg/L.

Median chromium concentrations were slightly greater in the HELP ecoregion than the NLAF and SMNIDP ecoregions, but NLAF and SMNIDP concentrations did not differ from the ECBP and NCHF ecoregions (Figure 1-19A; $X^2 = 24.584$, df = 4, p = < 0.001). Median chromium concentrations did not differ by stream order at a statewide scale (Figure 1-19B; $X^2 = 2.55$, df = 3, p = 0.47).

Median chromium concentrations were also slightly higher at sites where the upstream watershed was dominated by lacustrine clay and silt than sites where the upstream watershed was dominated by end moraines of coarse-textured till, medium-textured glacial outwash, thin to discontinuous glacial till over bedrock, and glacial outwash sand and gravel/postglacial alluvium, but were similar across all other geologies (Figure 1-19C; $X^2 = 37.51$, *df* = 11, *p* = < 0.001).

Median chromium concentrations differed by land cover type and were greater at sites where the upstream watershed was dominated by low intensity development compared to sites where the upstream watershed was dominated by deciduous forests, but did not differ among other land cover types (Figure 1-19D, $X^2 = 31.04$, *df* = 9, *p* = < 0.001).

Additionally, when chromium concentrations were compared to the presence of varying levels of development (none, low, medium, and high) in the upstream watershed, median chromium concentrations were greater when high intensity or medium intensity development land cover was present within the watershed compared to when development was absent within the watershed ($X^2 = 8.19$, *df* = 3, *p* = 0.042). However, chromium concentrations did not differ between sites where low intensity development land cover was present in the watershed and sites where development was absent within the watershed. This suggests that the presence of medium to high intensity development may influence chromium concentrations irrespective of the percentage of the watershed they make up, whereas the presence of low intensity development alone does not appear to explain high chromium concentrations unless it is the dominant land cover type in the watershed.

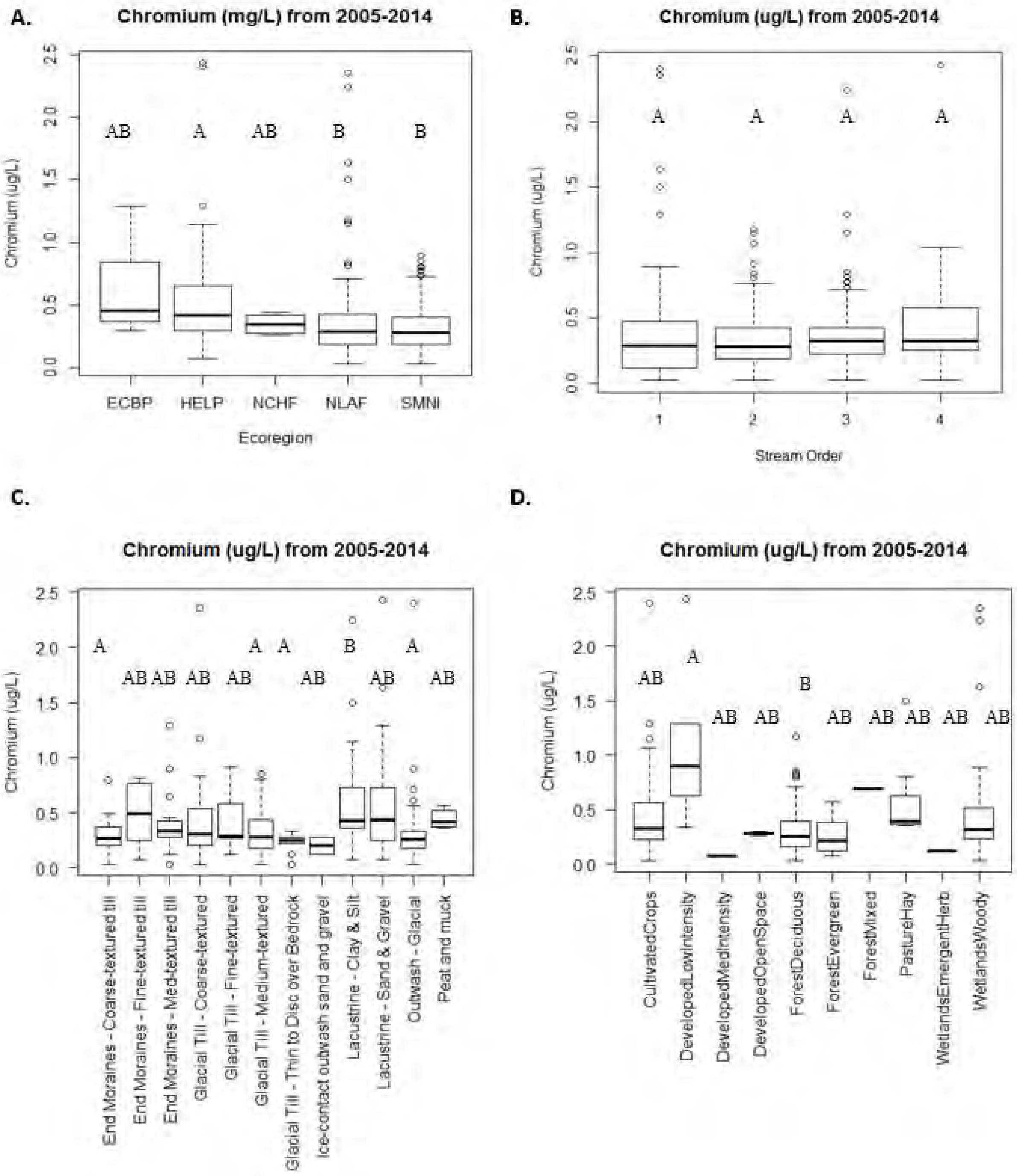


Figure 1-19. Median site Chromium concentrations (µg/L) by (A) Ecoregion, (B) Stream Order, (C) Surficial Geology, (D) Land Use from 2005-2014 (different letters denote significant difference in Kruskal Wallis post hoc Dunn tests at α = 0.05; sample sizes shown in Table 3).

The highest median concentrations of chromium were found in Custer County Drain (STORET #760249) in the thumb region of Michigan's Lower Peninsula, the Munuscong River in the eastern Upper Peninsula (STORET #490149 and 170291), and the Rouge River in Southeast Michigan (STORET #821522; Figure 1-18). The high median chromium concentration in Custer County Drain was largely driven by samples taken in 2005, which ranged from 0.294 µg/L in May to 101 µg/L in September (Figure 1-20). Additionally, in September and November 2005, Custer County Drain had some of the greatest concentrations of total phosphorus, TSS, hardness, copper, lead, and mercury in the state. Concentrations were much lower and less variable in 2010 and 2015 (Figure 1-20; preliminary data for 2015) and follow-up surveys have noted the stream dries up on occasion. Custer County Drain also had the maximum chromium concentration recorded from 2006 to 2014 at 101 µg/L; however, the concentration was far below its corresponding hardness-based water quality criteria (Final Chronic Value [FCV] = 411.29 µg/L and Aquatic Maximum Value [AMV] = 3,161.9 µg/L).

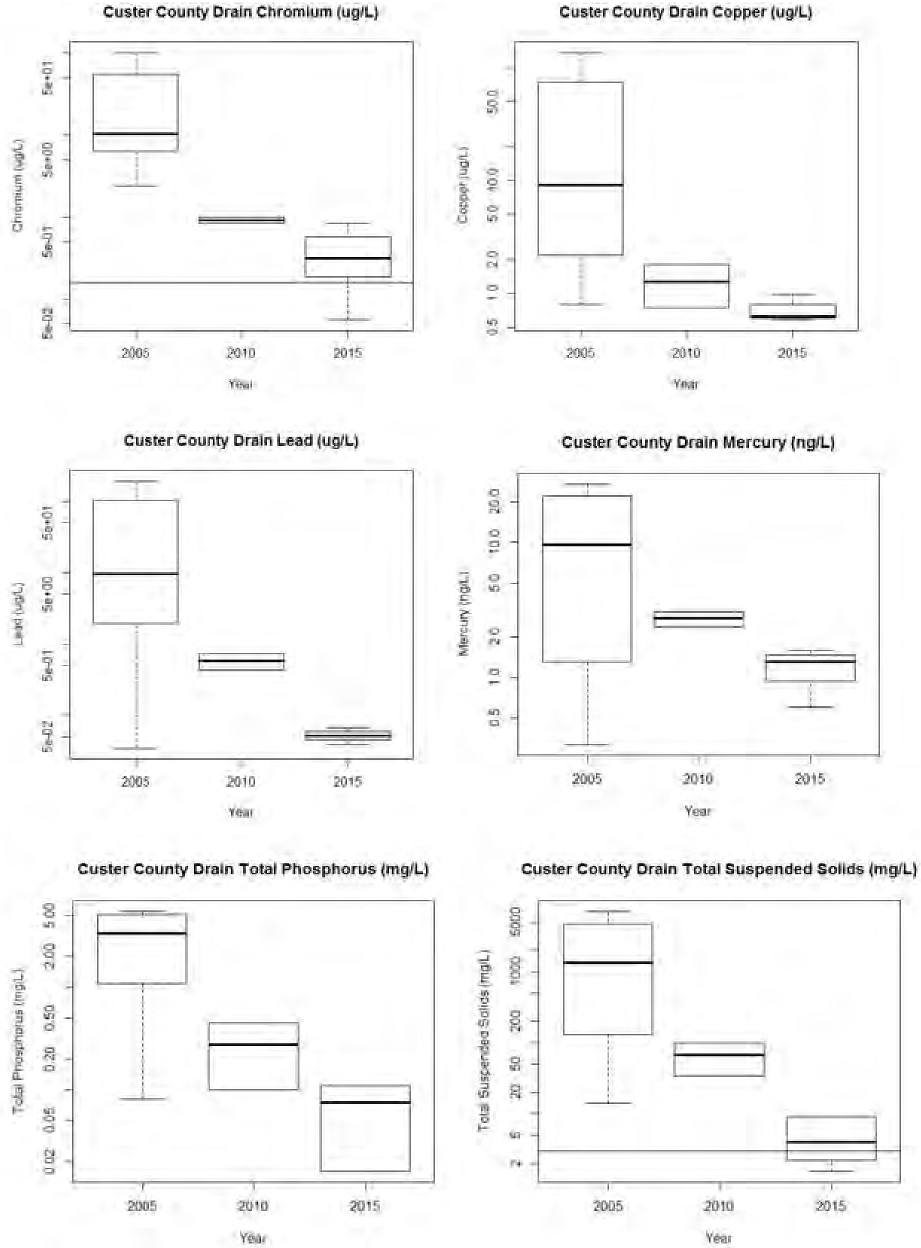


Figure 1-20. Select trace metal and conventional pollutant results at Custer County Drain site (STORET #760249) from 2005 to 2015 (2015 data is preliminary).

In contrast to the Custer County Drain site, the Munuscong River and Rouge River sites have had consistently higher chromium concentrations when compared to the rest of the state with approximately 92% of samples at the Munuscong River and Rouge River sites having concentrations > 1 µg/L (max = 3.3 µg/L). Statewide chromium concentrations were > 1 µg/L in 11% of all samples taken from 2006 to 2014 (*n* = 2,088). Although the Munuscong River and Rouge River sites had higher median concentrations relative to other sites, chromium in general does not appear to be a concern for aquatic life. Hardness-based water uality criteria ranged from 46.10 to 90.72 µg/L at the Munuscong River site at Kallio Road (STORET 170291), 63.63 to 159.02 µg/L at the Munuscong River site at Rutledge Road (STORET 490149), and 153.36 to 216.88 µg/L at the Rouge River site at Warren Road (STORET #821522). The maximum chromium concentrations recorded at these sites were 3.33 µg/L, 3.33 µg/L, and 3.2 µg/L, respectively. Chromium also did not exceed WQS at any other probabilistic sites from 2005 to 2014.

1.4.2.3 Copper

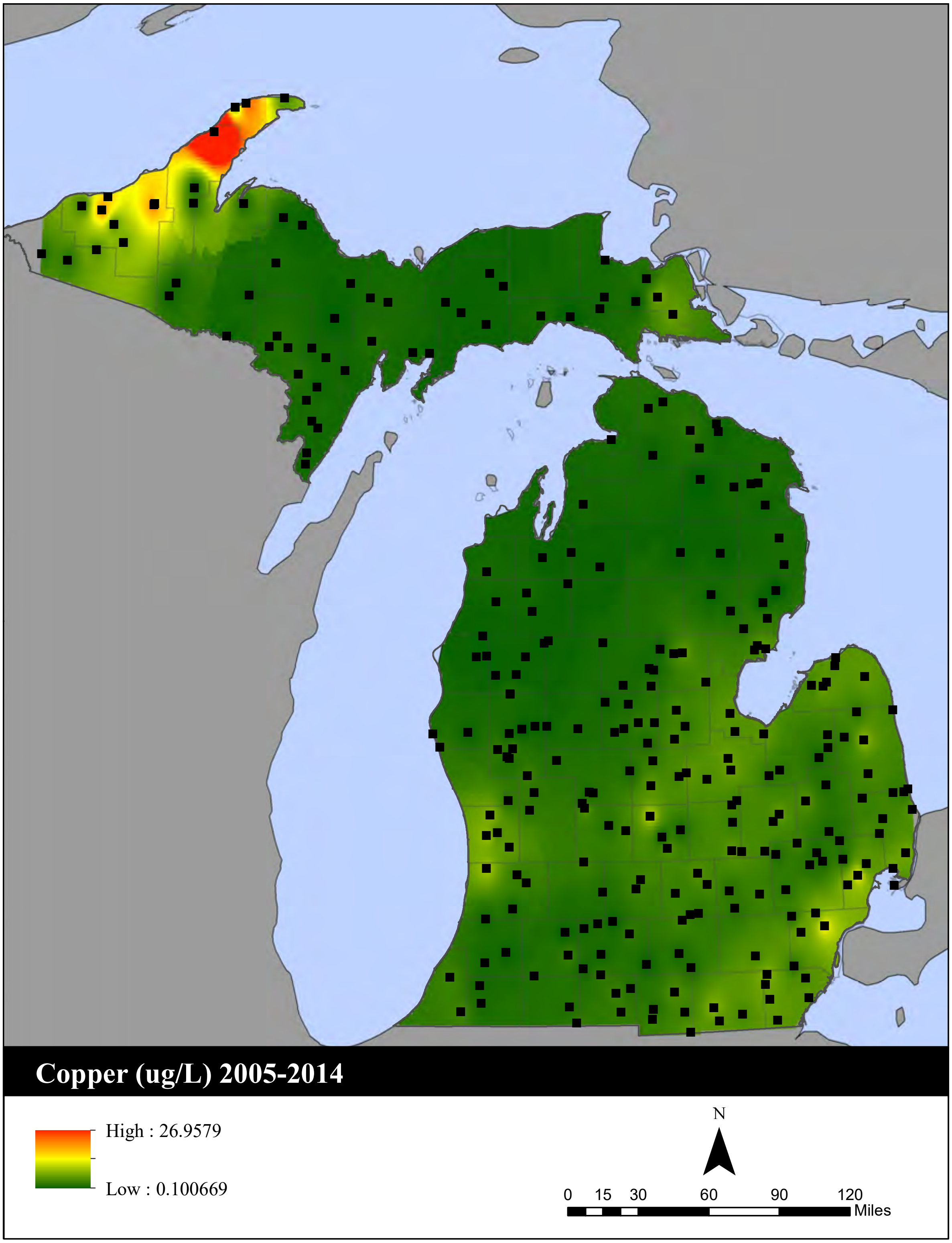


Figure 1-21. Inverse distance weighting interpolation image of median copper concentrations (µg/L) from 2005-2014.

Like other trace metals, copper toxicity has historically been thought to vary with water hardness due to cationic competition with calcium and magnesium (e.g., Naddy et al., 2003). However, there is also evidence that copper toxicity may vary with DOC because when bound to dissolved matter or other particulate organic matter, the availability of copper to aquatic life is greatly reduced (e.g., McGerr et al., 2002; Hyne et al., 2005). EGLE has evaluated the relationship between copper toxicity, water hardness, and DOC in several Upper Peninsula waters and found that copper toxicity in Upper Peninsula waters is highly dependent on DOC concentrations and poorly correlated with water hardness (MDEQ, 2007a). As a result, site-specific copper water quality criteria, taking DOC into account, were developed for some streams with high copper and DOC concentrations (MDEQ, 2013); however, sites throughout the rest of the state continue to be evaluated using hardness-based water quality criteria.

From 2005 to 2014, copper concentrations were detectable (i.e., above MDL of 0.03 µg/L) in 99.9% of samples and quantifiable (i.e., above RL of 0.10 µg/L) in 99.2% of samples collected at probabilistic sites (n = 2,101 samples). Copper sample concentrations ranged from nondetect to 136 µg/L, and median site concentrations ranged from 0.03 < x < 0.10 (between MDL and RL) to 27.1 µg/L. Not surprisingly, copper concentrations were greatest in the western Upper Peninsula and Keweenaw Peninsula (Figure 1-21). These areas have expansive deposits of native copper and were mined heavily from the mid 1800s to early 1900s (Bornhorst and Barron, 2011). Remnant stamp sands in these areas are thought to be major sources of copper to groundwater and subsequently surface water in some areas (Kotke, 2011).

Median copper concentrations within ecoregions were greatest in the HELP and ECBP ecoregions, and lowest in the NLAF and NCHF ecoregions; however, variability was greatest in the NLAF ecoregion with concentrations ranging from nondetect to 47.1 µg/L, and median site concentrations ranging from $0.03 < x < 0.10$ (between MDL and RL) to 27.1 µg/L (Figure 1-22A; $X^2 = 90.93$, $df = 4$, $p = < 0.001$). The NLAF also contained the 5 highest median site concentrations in the state. Copper concentrations did not differ between stream orders at a statewide scale (Figure 1-22B; $X^2 = 7.22$, $df = 3$, $p = 0.07$).

Median copper concentrations were greater at sites where the upstream watershed was dominated by lacustrine clay and silt compared to sites where the upstream watershed was dominated by lacustrine sand and gravel and glacial outwash sand and gravel/postglacial alluvium, but were similar across other geology types (Figure 1-22C; $X^2 = 82.15$, $df = 11$, $p = <0.001$), even when excluding sites within the Keweenaw Peninsula ($X^2 = 81.19$, $df = 11$, $p = <0.001$).

Median copper concentrations differed by land cover type and were greater for sites where the upstream watershed was dominated by low intensity development and cultivated crops compared to sites where the upstream watershed was dominated by deciduous forests, evergreen forests, or woody wetlands, but did not differ among other dominant land cover types (Figure 1-22D; $X^2 = 85.208$, $df = 9$, $p = < 0.001$).

Additionally, when copper concentrations were compared to the presence of varying levels of development (none, low, medium, and high) in the upstream watershed, median copper concentrations were greater when high intensity development and medium intensity development land cover were present in the upstream watershed than when development was absent in the upstream watershed ($X^2 = 41.719$, $df = 3$, $p = < 0.001$). Median copper concentrations were also greater in sites where low intensity development was present in the upstream watershed compared to sites where development was absent in the upstream watershed; however, median concentrations did not differ between sites where low intensity development was present and sites where medium intensity development was present. This suggests that presence of development alone may influence copper concentrations irrespective of the percentage of the watershed in development.

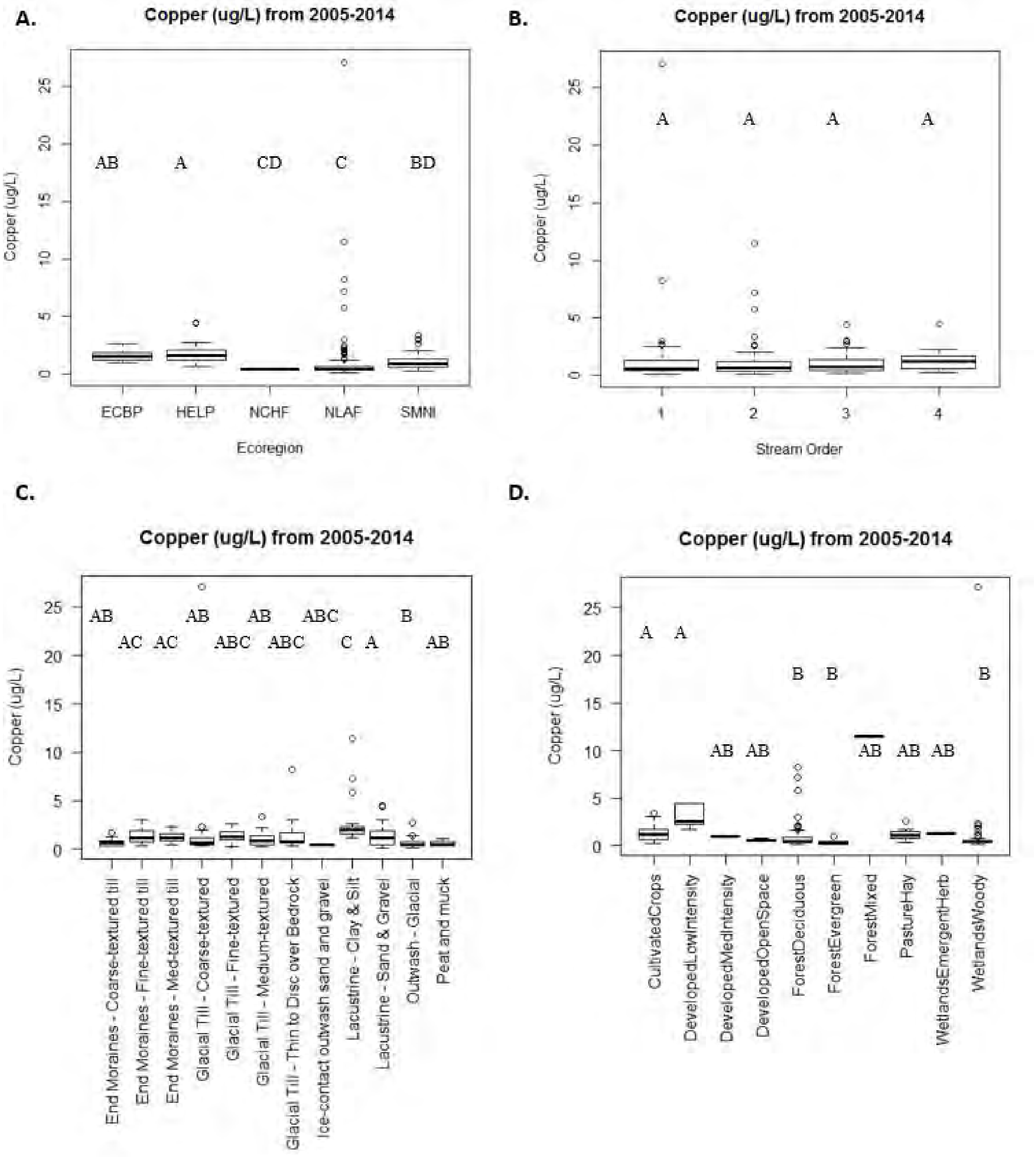


Figure 1-22. Median site copper concentrations (µg/L) by (A) Ecoregion, (B) Stream Order, (C) Surficial Geology, and (D) Land Use from 2005-2014 (different letters denote significant difference in Kruskal Wallis post hoc Dunn tests at α = 0.05; sample sizes shown in Table 3).

Copper exceeded its hardness-based FCV water quality criteria 30 times, its AMV 14 times, and its Final Acute Value once at 8 different probabilistic sites, which resulted in nonattainment of the Other Indigenous Aquatic Life and Wildlife designated use at 3 sites (Figure 1-23). Three additional sites would have been listed in 2005 (STORET #760249), 2006 (STORET #660140), and 2008 (STORET #030699) following new listing methodology (*i.e.*, only 1 AMV or FCV exceedance in a given year needed, as opposed to 2 AMV exceedances previously needed); however, they were considered attaining in the statewide attainment calculation below because following the Integrated Report assessment methodology at the time they were sampled, they would have been attaining (MDEQ, 2016b). Those sites not attaining were: Begunn Creek (STORET #310508), which exceeded criteria in 2007 and 2012; Tributary to West Branch Firesteel River (STORET #660090), which exceeded criteria in 2007 and 2012; and West Branch Duck Creek (STORET #660138), which exceeded criteria in 2005 and 2010. All 3 of these sites are in or near the Keweenaw Peninsula (Figure 1-23). Although many sites within the Keweenaw Peninsula have site-specific aquatic life values for total copper (R323.1057(2)(R)(ii)), no probabilistic sites have site-specific criteria.

It was determined that 98 ± 2% of the perennial river miles in Michigan met the hardness-based copper WQS using the probabilistic data collected from 2005 to 2009, and 98 ± 2% of the perennial river miles in Michigan met the hardness-based copper WQS using probabilistic data collected from 2010 to 2014.

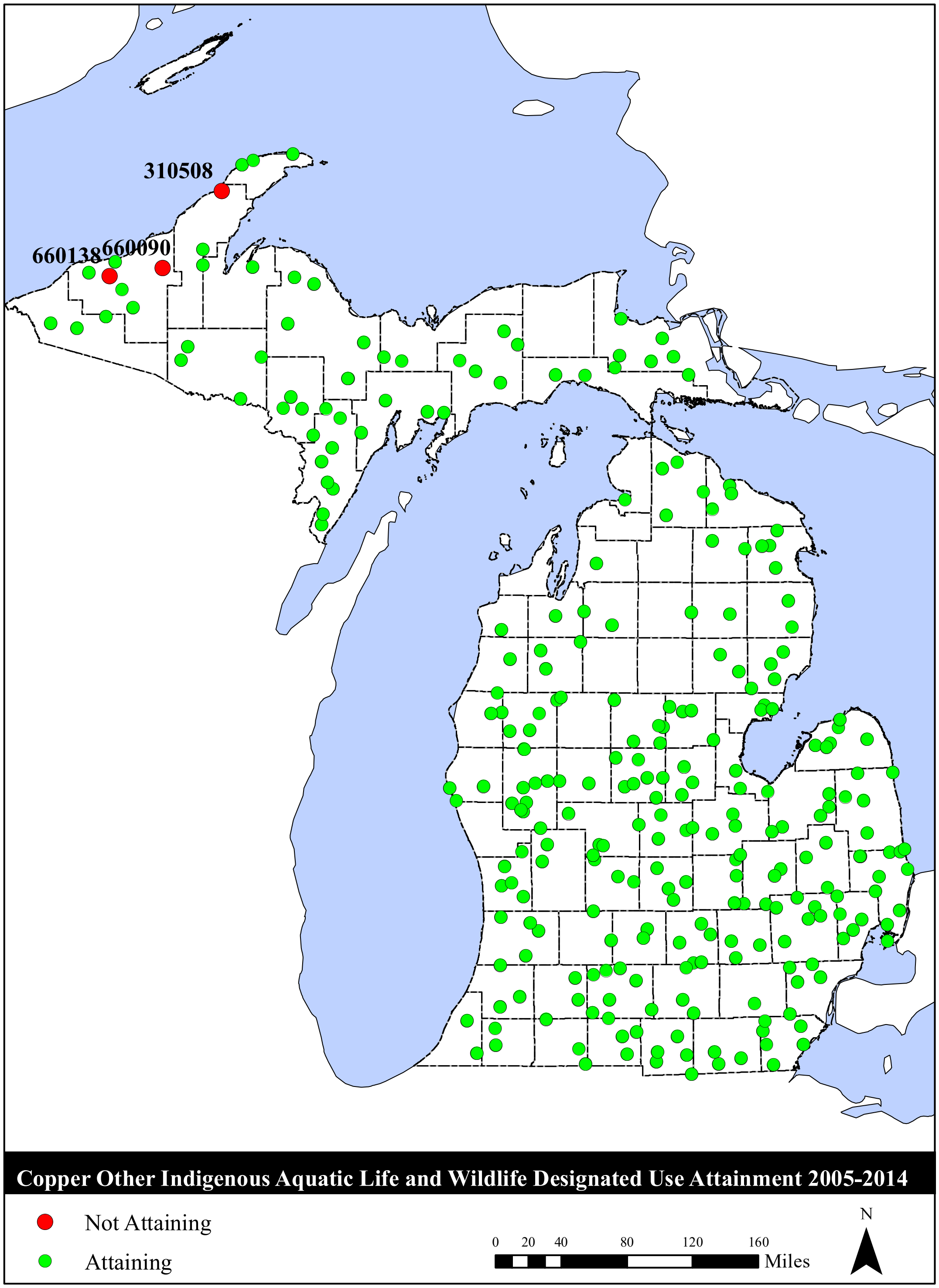


Figure 1-23. Probabilistic sites that were not attaining the Other Indigenous Aquatic Life and Wildlife designated use due to copper exceedances for at least 1 year between 2005 and 2014.

1.4.2.4 Lead

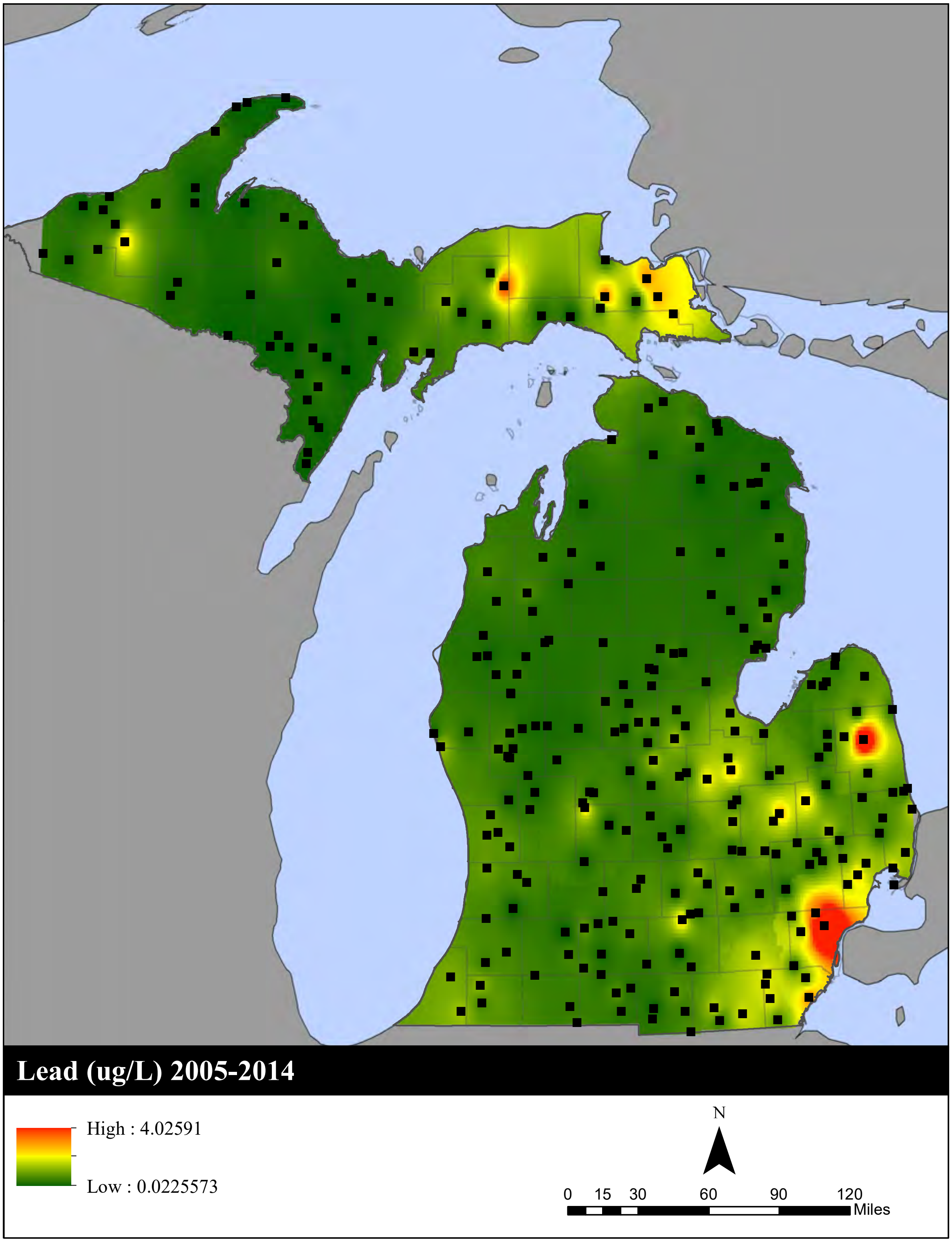


Figure 1-24. Inverse distance weighting interpolation image of median lead concentrations (µg/L) from 2005-2014.

Lead, like other trace metals, is a naturally occurring element typically found in low concentrations in the environment (USDHHS, 2007). However, lead can also be introduced to aquatic systems through anthropogenic activities such as manufacturing, mining, industrial practices, and a variety of domestic uses (USDHHS, 2007). Toxicity of lead, as with other trace metals, is thought to vary with water hardness; therefore, EGLE uses a hardness-based calculation to determine water quality criteria.

From 2005 to 2014, lead concentrations were detectable (i.e., above MDL of 0.0041 µg/L) in 99.8% of samples and quantifiable (i.e., above RL of 0.041 µg/L) in 86.9% of samples collected at probabilistic sites (n = 2,080 samples). Lead sample concentrations ranged from nondetect to 188 µg/L (STORET #760249), and site median concentrations ranged from 0.0041 < x <0.041 (between MDL and RL) to 4.105 µg/L.

Site-to-site variability in lead concentrations was present across the state with slightly greater concentrations in the eastern Upper Peninsula and southeast Lower Peninsula (Figure 1-24). Median concentrations also varied by ecoregion (Figure 1-25A; $X^2 = 74.72$, $df = 4$, $p = < 0.001$) and stream order (Figure 1-25B; $X^2 = 13.555$, $df = 3$, $p = 0.004$) at a statewide scale. Median concentrations were greatest in the HELP ecoregion although all ecoregions had median lead concentrations < 1 µg/L in the majority of samples (Figure 1-25A). Median lead concentrations were greatest in third and fourth order streams at a statewide scale (Figure 1-25B).

Median lead concentrations were greater at sites where the upstream watershed was dominated by lacustrine clay and silt or lacustrine sand and gravel compared to sites where the upstream watershed was dominated by thin to discontinuous glacial till over bedrock and glacial outwash sand and gravel/post glacial alluvium surficial geology, but did not differ among other surficial geology types (Figure 1-25C; $X^2 = 38.727$, $df = 11$, $p = < 0.001$).

Median lead concentrations differed by land cover type and were greater at sites where the upstream watershed was dominated by low intensity development compared to sites where the upstream watershed was dominated by deciduous forests, evergreen forests, and woody wetlands, but did not differ from other land cover types (Figure 1-25D; $X^2 = 56.325$, $df = 9$, $p = <0.001$).

Additionally, when chloride concentrations were compared to the presence of varying levels of development (none, low, medium, and high) in the upstream watershed, median lead concentrations were greater when high intensity development and medium intensity development land cover were present in the upstream watershed compared to when low intensity development was present in the upstream watershed or development was absent in the upstream watershed ($X^2 = 56.356$, $df = 3$, $p = < 0.001$). Additionally, median lead concentrations were also greater in sites where low intensity development was present in the upstream watershed compared to sites where development was absent in the upstream watershed. This suggests that presence of development alone may influence lead concentrations irrespective of the percentage of the watershed in development.

Lead did not exceed WQS at any probabilistic site from 2005 to 2014.

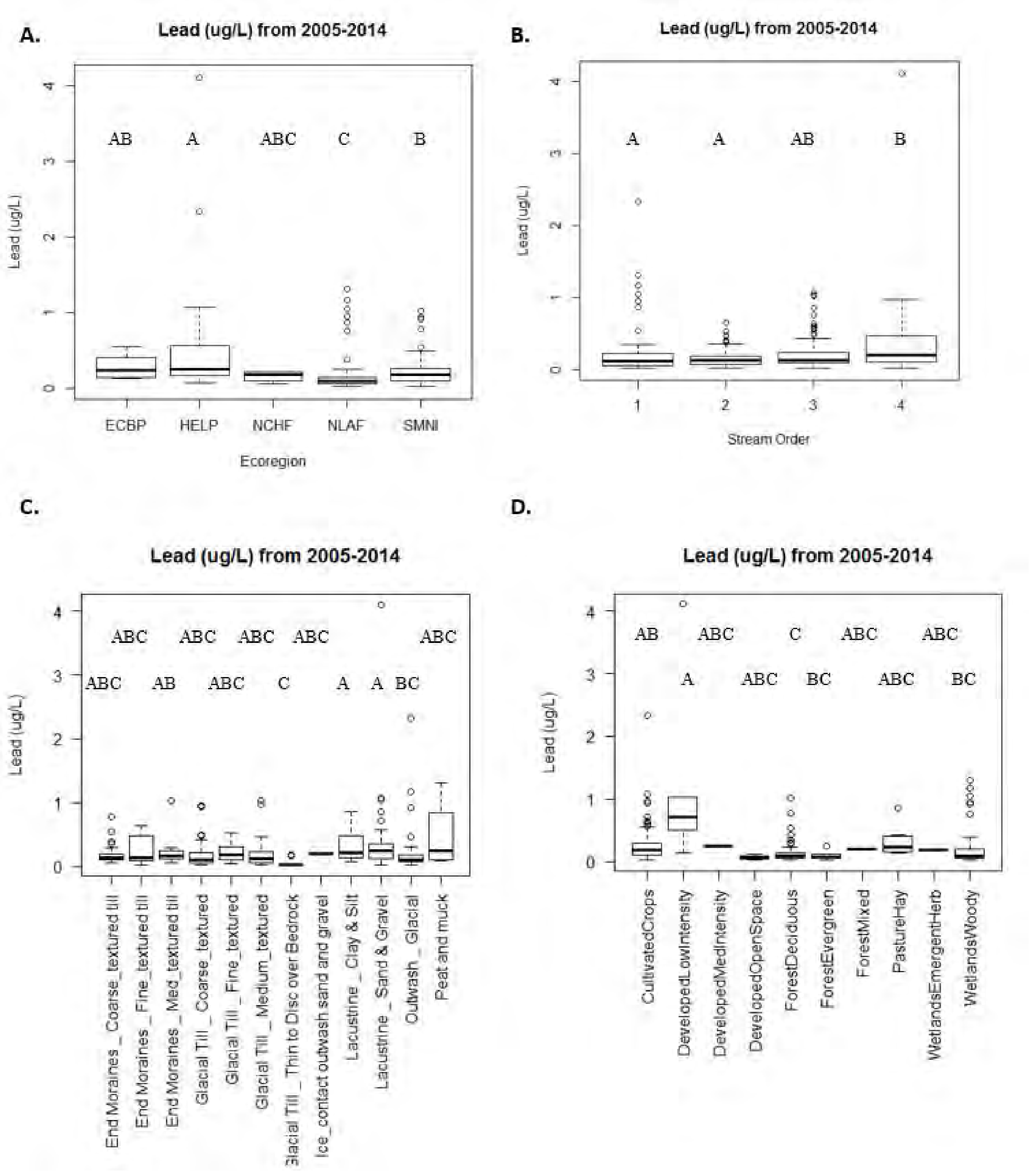


Figure 1-25. Median site lead concentrations (µg/L) by (A) Ecoregion, (B) Stream Order, (C) Surficial Geology, and (D) Land Use from 2005-2014 (different letters denote significant difference in Kruskal Wallis post hoc Dunn tests at α = 0.05; sample sizes shown in Table 3).

1.4.2.5 Nickel

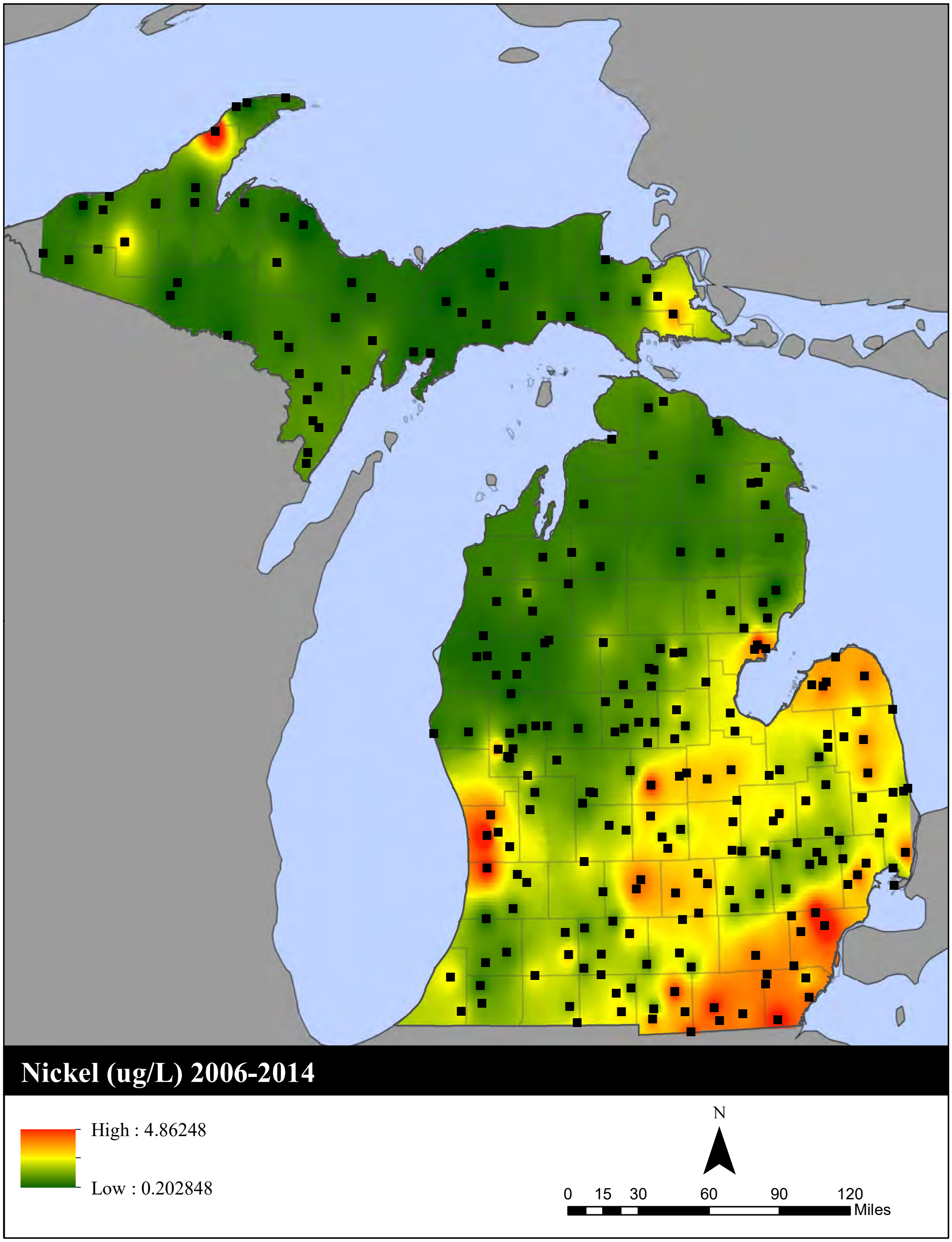


Figure 1-26. Inverse distance weighting interpolation image of median nickel concentrations (µg/L) from 2006-2014.

Nickel is naturally occurring at low concentrations and is a natural constituent of soil (USDHHS, 2005a). It is also a product of many anthropogenic activities (manufacturing, automotive, industry, wastewater treatment) (USDHHS, 2005a). Nickel can enter surface water via runoff, weathering, soil erosion, point sources, or atmospheric deposition (USDHHS, 2005a).

From 2006 to 2014, nickel concentrations were detectable (i.e., above MDL of 0.093 µg/L) in 99.9% of samples and quantifiable (i.e., above RL of 0.31 µg/L) in 94.9% of samples collected at probabilistic sites (n = 1,853 samples). Nickel sample concentrations ranged from nondetect to 26 µg/L (STORET #030699) and site median concentrations ranged from $0.093 < x < 0.31$ (between MDL and RL) to 4.89 µg/L.

In general, nickel median concentrations increased from northwest to southeast Michigan (Figure 1-26). The ECBP and HELP ecoregions had the greatest median nickel concentrations from 2006 to 2014 (Figure 1-27A; $X^2 = 124.05$, $df = 4$, $p = <0.001$). Concentrations did not differ among stream order at a statewide scale (Figure 1-27B; $X^2 = 5.65$, $df = 3$, $p = 0.13$).

Median nickel concentrations were greater in sites where the upstream watershed was dominated by end moraines of medium-textured till and lacustrine clay and silt compared to sites where the upstream watershed was dominated by end moraines of coarse-textured till, coarse-textured glacial till, thin to discontinuous glacial till over bedrock, and glacial outwash sand and gravel/postglacial alluvium (Figure 1-27C; $X^2 = 68.46$, $df = 11$, $p = <0.001$).

Median nickel concentrations varied by land cover type but were greater in sites where the upstream watershed was dominated by low intensity development, pasture/hay, and cultivated crops compared to sites where the upstream watershed was dominated by deciduous forest, evergreen forest, and woody wetlands (Figure 1-27D; $X^2 = 126.83$, $df = 9$, $p = <0.001$).

Additionally, when chloride concentrations were compared to the presence of varying levels of development (none, low, medium, and high) in the upstream watershed, median nickel concentrations were greater when development was present relative to when development was absent, but did not differ among low, medium, and high intensity development ($X^2 = 63.079$, $df = 3$, $p = <0.001$). This suggests that presence of development alone may influence nickel concentrations irrespective of the percentage of the watershed in development.

Nickel did not exceed WQS at any site from 2006 to 2014.

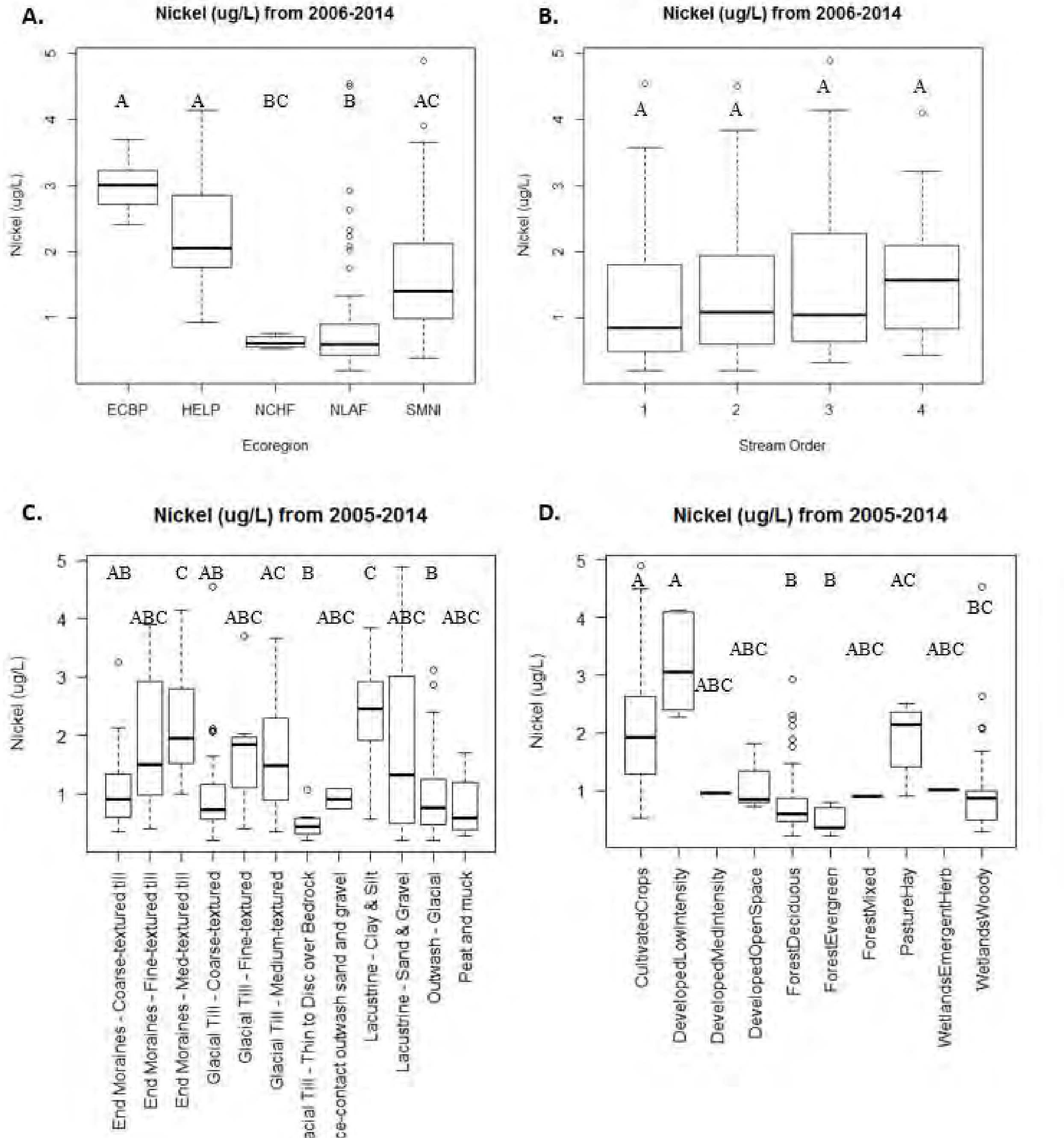


Figure 1-27. Median site nickel concentrations (μg/L) by (A) Ecoregion, (B) Stream Order, (C) Surficial Geology, and (D) Land Use from 2006-2014 (different letters denote significant difference in Kruskal Wallis post hoc Dunn tests at α = 0.05; sample sizes shown in Table 3).

1.4.2.6 Zinc

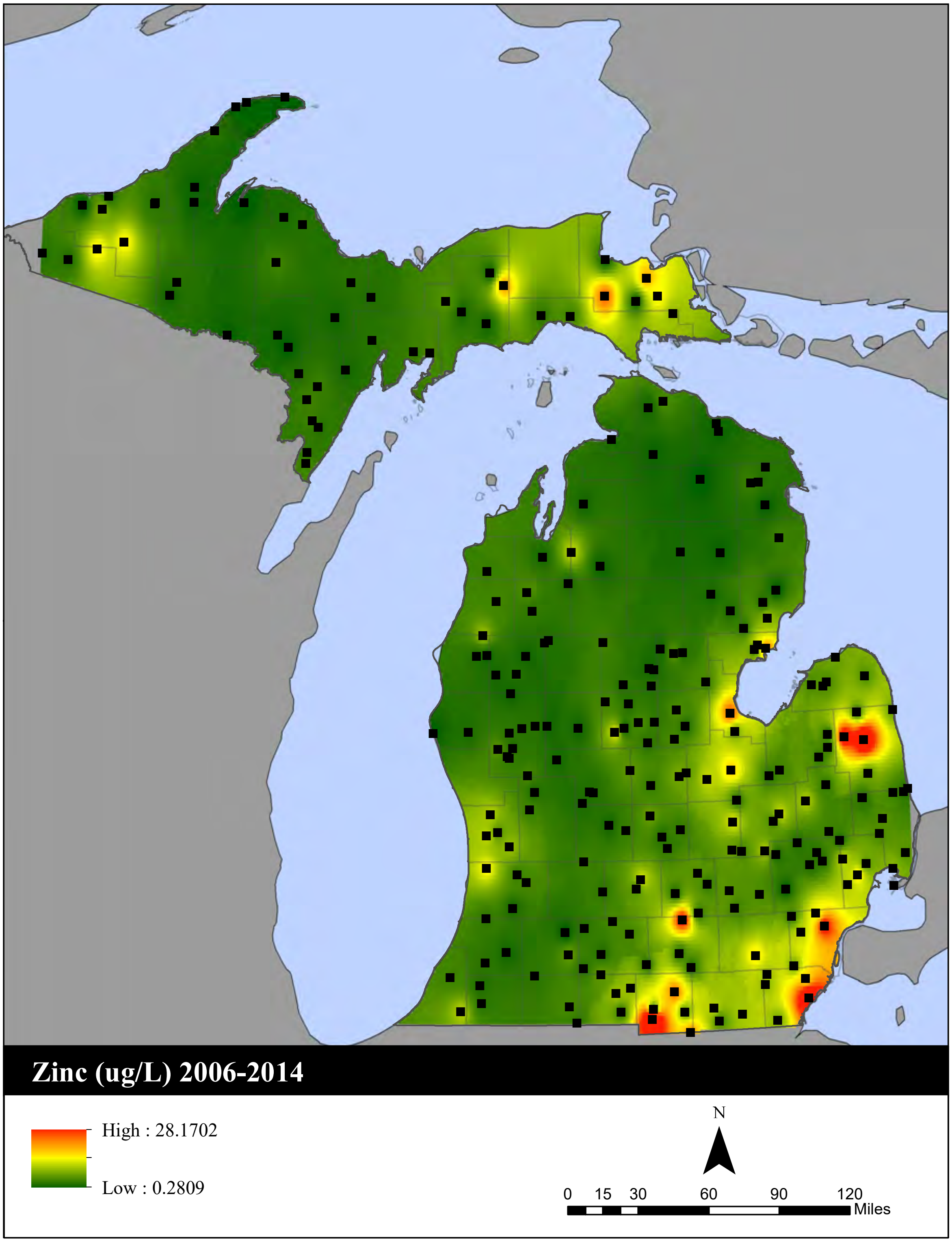


Figure 1-28. Inverse distance weighting interpolation image of median zinc concentrations (µg/L) from 2006-2014.

Zinc is another naturally occurring trace metal, usually found at very low concentrations in the environment (USDHHS, 2005b). Zinc can enter surface water via natural or anthropogenic sources (USDHHS, 2005b). Typically, high concentrations of zinc are the result of anthropogenic sources such as mine tailings, slag, coal, urban runoff, and preservatives (TDC Environmental, 2015; USDHHS, 2005b).

Zinc concentrations were detectable (i.e., above MDL of 0.13 µg/L) in 99.6% of samples and quantifiable (i.e., above RL of 0.43 µg/L) in 92.9% of samples collected at probabilistic sites from 2006 to 2014 (n = 1,878 samples). Zinc sample concentrations ranged from nondetect to 144 µg/L (STORET #830220), and site median concentrations ranged from $0.13 < x < 0.43$ to 30.09 µg/L.

Some of the greatest zinc median concentrations were found in southeast Michigan, but in general, median concentrations varied by site throughout the state (Figure 1-28). The HELP ecoregion had the greatest median concentrations and NLAF had the lowest median concentrations from 2006 to 2014 (Figure 1-29A; $X^2 = 57.39$, $df = 4$, $p = <0.001$). Concentrations did not differ by stream order at a statewide scale (Figure 1-29B; $X^2 = 2.59$, $df = 3$, $p = 0.46$).

Median zinc concentrations were greater at sites where the upstream watershed was dominated by lacustrine clay and silt or lacustrine sand and gravel compared to sites where the upstream watershed was dominated by thin to discontinuous glacial till over bedrock and glacial outwash sand and gravel/postglacial alluvium, but did not differ among other surficial geology types (Figure 1-29C; $X^2 = 62.66$, $df = 11$, $p = <0.001$).

Median zinc concentrations differed by land cover type and were greater in sites where the upstream watershed was dominated by low intensity development, pasture/hay, cultivated crops, and woody wetlands compared to sites where the upstream watershed was dominated by deciduous forests, but did not differ from other land cover types (Figure 1-29D; $X^2 = 69.26$, $df = 9$, $p = <0.001$).

Additionally, when zinc concentrations were compared to the presence of varying levels of development (none, low, medium, and high) in the upstream watershed, median zinc concentrations were greater when development was present relative to when development was absent ($X^2 = 27.454$, $df = 3$, $p = <0.001$). This suggests that presence of development alone may influence zinc concentrations irrespective of the percentage of the watershed in development.

Zinc did not exceed WQS at any site from 2006 to 2014.

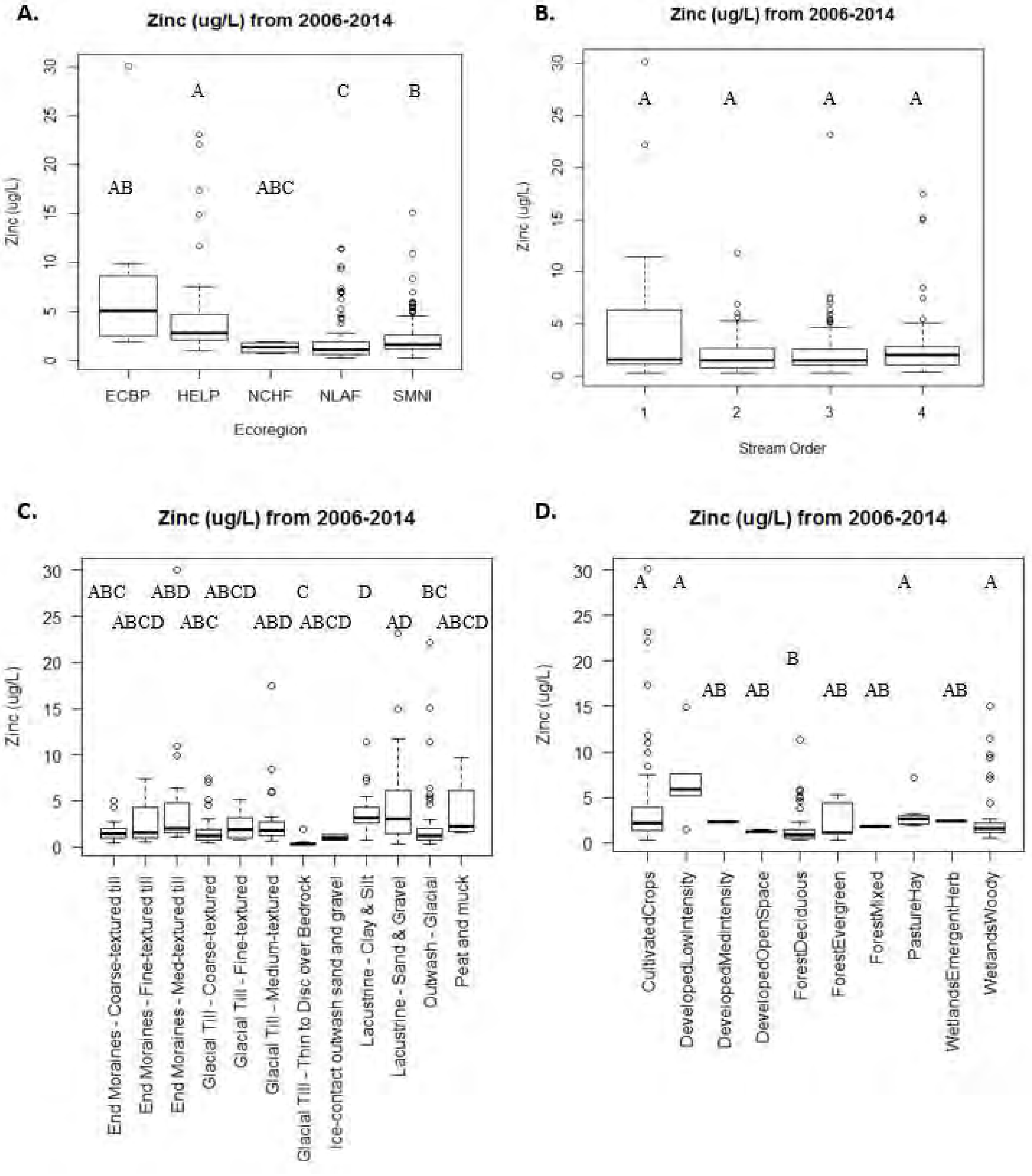


Figure 1-29. Median site zinc concentrations (μg/L) by (A) Ecoregion, (B) Stream Order, (C) Surficial Geology, and (D) Land Use from 2006-2014 (different letters denote significant difference in Kruskal Wallis post hoc Dunn tests at α = 0.05; sample sizes shown in Table 3).

1.4.2.7 Mercury

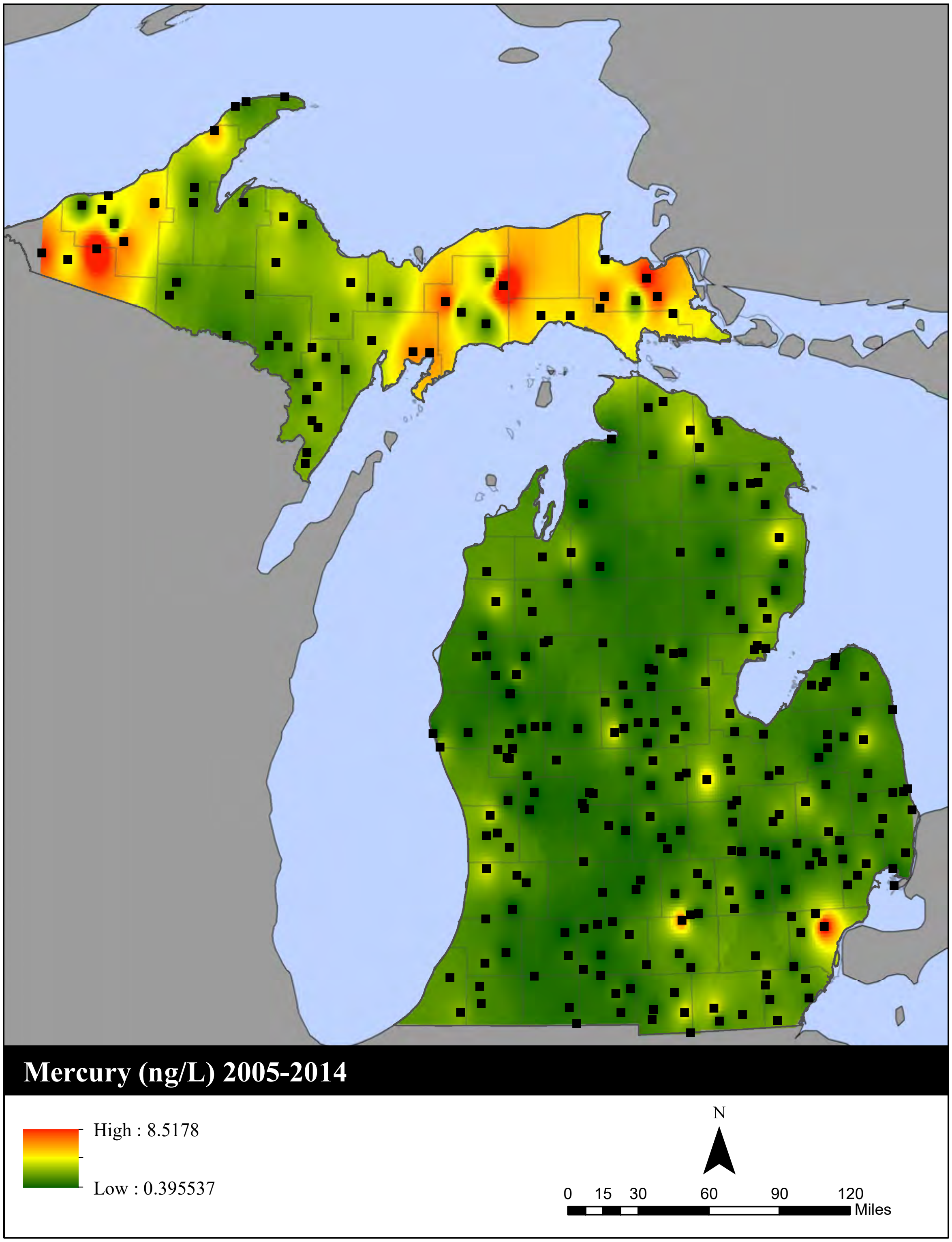


Figure 1-30. Inverse distance weighting interpolation image of median mercury concentrations (ng/L) from 2005-2014.

Mercury is also both naturally occurring and anthropogenically introduced (LimnoTech, 2013). Mercury introduced via anthropogenic pathways is primarily introduced through atmospheric deposition (LimnoTech, 2013). Major sources include fuel combustion, industrial processes, and incineration (LimnoTech, 2013). Mercury is primarily of concern to human health and aquatic life because of its neurotoxic and bioaccumulative properties (LimnoTech, 2013). Michigan developed a statewide Total Maximum Daily Load (TMDL) for mercury (LimnoTech, 2013) (https://www.michigan.gov/egle/about/Organization/Water-Resources/tmdls/statewide-mercury-tmdl).

From 2005 to 2014, mercury concentrations were quantifiable (i.e., above the RL of 0.5 ng/L) in 86.7% of samples collected at probabilistic sites (*n* = 2,090 samples). Mercury sample concentrations ranged from nondetect to 60 ng/L (STORET #030699), and site median concentrations ranged from nondetect to 8.55 ng/L.

Mercury median concentrations were greatest in the western and eastern ends of the Upper Peninsula (Figure 1-30). Sites within the NLAF ecoregion had greater mercury concentrations than sites within the SMNIDP ecoregion; however, concentrations at sites within both the NLAF and SMNIDP ecoregions did not differ from those within the ECBP, HELP, and NCHF ecoregions (Figure 1-31A; X^2 = 32.47, *df* = 4, *p* = <0.001). At a statewide-scale, mercury concentrations were greater in first order streams than second or third order streams; however, they did not differ from fourth order streams (Figure 1-31B; X^2 = 15.68, *df* = 3, *p* = 0.001).

Median mercury concentrations were greater at sites where the upstream watershed was dominated by lacustrine sand and gravel compared to sites where the upstream watershed was dominated by glacial outwash sand and gravel/postglacial alluvium, but did not differ among other surficial geology types (Figure 1-31C; X^2 = 32.53, *df* = 11, *p* = <0.001). Median mercury concentrations were greatest in sites where the upstream watershed was dominated by peat and muck; however, concentrations were also very variable at these sites, leading to no overall difference in median concentrations between sites with peat and muck compared to all other surficial geology types.

Median mercury concentrations varied by land cover type and were greater at sites where the upstream watershed was dominated by woody wetlands compared to sites where the upstream watershed was dominated by cultivated crops, deciduous forest, or emergent herbaceous wetlands (Figure 1-31D; X^2 = 66.67, *df* = 9, *p* = <0.001). The conditions typical of wetlands (e.g., anoxic sediments, large pools of dissolved organic matter, and anaerobic bacteria) are well known to promote the production and export of mercury to surface waters (Windham-Myers et al., 2014) potentially explaining the greater mercury concentrations in watersheds dominated by wetlands and sites with the greatest DOC concentrations. Additionally, mercury deposition measured in throughfall has been shown to be greater when coniferous canopy or deciduous canopy types are present compared to open areas due to the denser canopy's greater ability to accumulate mercury from the atmosphere (Witt et al., 2009). Canopy cover could potentially explain why concentrations were greater in woody wetlands compared to emergent herbaceous wetlands although sample size was very low for emergent herbaceous wetlands (*n* = 2).

Additionally, when mercury concentrations were compared to the presence of varying levels of development (none, low, medium, and high) in the upstream watershed, median mercury concentrations were similar when high, medium, or low intensity development land cover was present compared to when development was absent, and median concentrations were greater when no development was present compared to when low intensity development was present (X^2 =13.291, *df* = 3, *p* = 0.004) suggesting presence of development in a watershed has little influence on mercury concentrations found in that watershed.

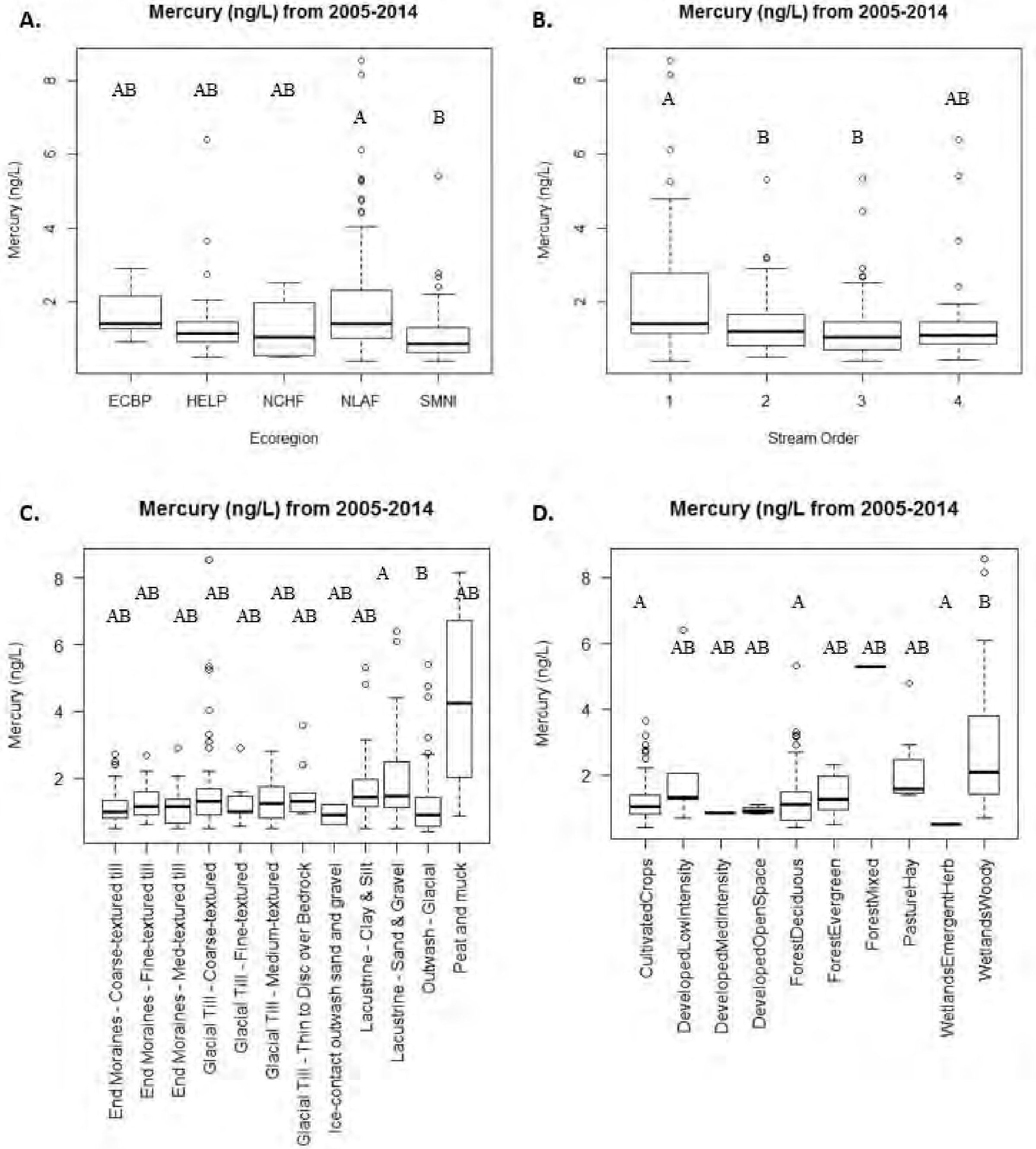


Figure 1-31. Median site mercury concentrations (ng/L) by (A) Ecoregion, (B) Stream Order, (C) Surficial Geology, and (D) Land Use from 2005-2014 (different letters denote significant difference in Kruskal Wallis post hoc Dunn tests at α = 0.05; sample sizes shown in Table 3).

It was determined that 54 ± 7% of the perennial river miles in Michigan met the mercury WQS of 1.3 ng/L using the probabilistic data collected from 2005-2009 (Roush, 2013), and 46 ± 7% of the perennial river miles in Michigan met the WQS using probabilistic data collected from 2010 to 2014 (Figure 1-32). Attainment for other sliding 5-year intervals were 55 ± 7% for 2006 to 2010, 57 ± 7% for 2007 to 2011, 55 ± 7% for 2008 to 2012, and 51 ± 7% for 2009 to 2013.

It is important to note there were differences in sites during the 2005 to 2009 cycle and the 2010 to 2014 cycle. At the start of the second cycle of monitoring (i.e., 2010), 25 of the sites sampled in 2005 were resampled to monitor temporal trends, while 25 new sites were randomly chosen to monitor statewide spatial trends and have a truly random sample design. However, this design was not repeated in 2011. Instead, it was decided the original sites that were randomly chosen from 2005 to 2009 would become fixed (i.e., would be resampled every five years). The differences in sites in 2005 and 2010 could have influenced attainment calculations; however, the drop in attainment cannot be fully explained by the site changes since 10 of the 25 original sites were not attaining in 2005 and only 5 of the 25 replacement sites were not attaining in 2010.

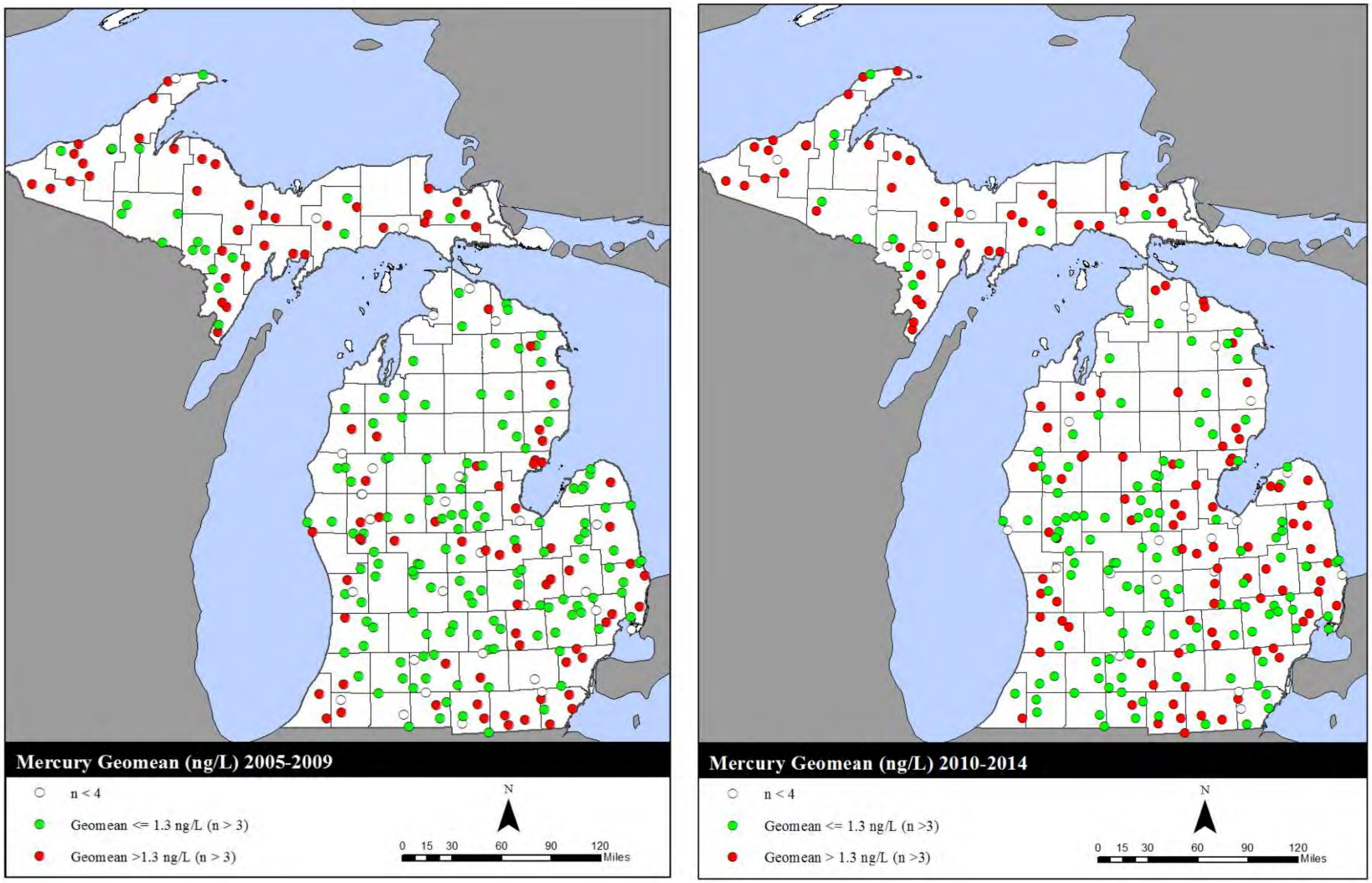


Figure 1-32. Mercury geomean concentrations relative to mercury wildlife value for probabilistic sites from (A) 2005-2009, and (B) 2010-2014 (white points are sites with at least 1, but less than 4 samples taken in 1 calendar year).

Section 2. TRIBUTARY MONITORING: STATUS AND TRENDS

2.1. INTRODUCTION

This section presents 1998-2013 water chemistry results of the Great Lakes tributaries' monitoring sites and discusses the occurrence of temporal trends for select parameters. The goals of this monitoring were to: (1) identify water quality conditions in select Michigan tributaries to the Great Lakes; (2) evaluate the occurrence of spatial and temporal trends; and (3) provide monitoring support to other WRD programs. This WCMP Great Lakes tributary site monitoring effort was completed at the end of 2013.

2.2. MAJOR CONCLUSIONS

Certain rivers at their "main sites" often had the **highest median values for parameters typically considered to be indicative of pollution** (when they are present at elevated levels):

River Rouge and Clinton River

The River Rouge had the highest median concentrations of total ammonia, lead, and cadmium. The Clinton River had the highest median concentrations of total phosphorus, orthophosphate, nitrite, chloride, sodium, chromium, copper, nickel, and zinc. Both of these rivers have largely dense urban watersheds with the Rouge River and Clinton River watersheds having the following ranks in terms of highest % land covered by "developed, high intensity" (first [10.3%] and third [6.8%], respectively), "developed, medium intensity" (first [25.0%] and third [15.6%], respectively), and "developed, low intensity" (second [27.6%] and third [17.3%], respectively). (The Saginaw River watershed ranked second for both "developed, high intensity" and "developed, medium intensity" and first for "developed, low intensity," though this may have partly been an artifact of a relatively smaller watershed area used for the Saginaw River in Geographic Information System (GIS) land use analysis.)

Huron River and Flint River

The Huron River had the highest median concentrations of TDS and specific conductance. The Flint River had the highest median concentrations of nitrate and TSS. The Huron River and Flint River watersheds have a more diverse mix of agricultural, residential, urban, and forested areas and they ranked fourth and fifth highest, respectively, in terms of highest % land covered by "developed, high intensity," "developed, medium intensity," and "developed, low intensity."

Certain other rivers at their "main sites" frequently had the **lowest median concentrations or values for parameters generally considered to be indicative of pollution**, and they tended to be in watersheds dominated by forest or wetland:

Au Sable River

The Au Sable River had the lowest median lead, chromium, copper, mercury, and zinc. The watershed upstream had a combined 72% for deciduous forest, Evergreen forest, shrub/scrub, and woody wetlands and less than 2% each of "developed, low intensity," "cultivated crops," "pasture/hay," "developed, medium intensity," "barren land," or "developed, high intensity."

Thunder Bay River

The Thunder Bay River had the lowest median orthophosphate, nitrate, nitrite, and TSS. The watershed upstream had a combined 66.2% deciduous forest, Evergreen forest, and woody wetlands and less than 6% for all other land use types; "developed, high intensity," "developed, medium intensity," and "developed, low intensity."

Tahquamenon River

The Tahquamenon River had the lowest median TDS, nickel, and specific conductance. The watershed upstream had a combined 90% for deciduous forest, Evergreen forest, emergent herbaceous wetlands, and woody wetlands.

Cheboygan River

The Cheboygan River had the lowest median total phosphorus and turbidity. The watershed upstream had a combined 62.5% deciduous forest, Evergreen forest, and woody wetlands, and less than 6% for most other land use types. Grassland and open water were 8.1% and 6.4%, respectively.

Boardman River

The Boardman River had the lowest median total Kjeldahl nitrogen and TOC[4]. The watershed upstream had a combined 51.5% for deciduous forest, Evergreen forest, and woody wetlands. Grassland was 15.1%. All other land uses were 7% or less.

Trends

Parameter trends were variable:

- For main sites, the majority of significant temporal trends for 1999-2013 was downward for many parameters (e.g., ammonia, copper, lead, nitrate, total phosphorus, and TSS).
- Other parameters that were analyzed may warrant more concern and be a priority for future monitoring because they had more than one river with a significant ($p < 0.05$) upward trend (> 1% per year or higher) amongst the main sites, for example:
    - Chloride (Black, Rouge, Menominee, and Manistique Rivers).
    - Mercury (Cheboygan, Sturgeon, Au Sable, and Pine Rivers).
    - Nitrite (Rouge River); (the Black River had a p value of 0.05).
    - Total Kjeldahl nitrogen (Black, Rouge, and Escanaba Rivers).
    - Orthophosphate (Black, Ontonagon, and lower Grand Rivers).
- Additionally, while no chromium values were detected above WQS in this study, many rivers did have large upward trends, making it a parameter to also consider as a priority moving forward.

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[4] TOC concentrations in some cases may be reflective of industrial, municipal, or agricultural inputs, while in other cases it may be reflective of inputs by wetlands.

Loads

Loads of total phosphorus, chloride, chromium, copper, lead, mercury, and TSS generally were highest in large watershed streams with the largest annual flows, such as the Saginaw River and Grand River. The Saginaw River had the maximum observed loads for total phosphorus, chloride, copper, lead, mercury, and TSS for the time period examined (2002 to 2013); the Ontonagon River had the highest observed load for chromium. Loads were generally lowest in the smaller tributaries sampled as part of this program, such as the Boardman and Thunder Bay Rivers.

Main Sites versus Minimally Impacted Sites

Spatial relationships (e.g., between ecoregions; main sites versus minimally impacted sites) were also examined and discussed; however, study design limited the robustness of conclusions that could be drawn.

2.3. METHODS

2.3.1. Site Selection

Tributary monitoring for the WCMP was performed concurrently with the watershed basin cycle recognized by the WRD Surface Water Assessment Section and National Pollutant Discharge Elimination System (NPDES) Programs. In this 5-year watershed basin cycle, 45 watershed units are used as the framework to divide biological monitoring surveys, NPDES reviews, and other related work.

Of the 45 watershed units, 27 were selected for water chemistry monitoring sites based on a number of criteria, which included: surrounding land use, availability of historical water quality data, proximity to USGS stream flow gauging stations, accessibility, and avoidance of stream reaches subject to flow reversals. More details about study design are provided later.

Sites were located near the mouths of these rivers and were generally limited to one site per watershed; however, four watersheds had an additional mid-reach site to represent the upper reaches of those watersheds, making a total of 31 WCMP Great Lakes tributary sites. Mid-reach sites, called upper tributary sites, in this report, were located on the St. Joseph, Kalamazoo, Grand, and Muskegon Rivers. Additionally, a minimally impacted site was assigned to each tributary site to make within-watershed comparisons, with the exception of the Saginaw River. All monitoring locations are shown in Figure 2-1. Details of each tributary site and minimally impacted site can be found in Table 2-1 and Table 2-2, respectively.

The Black River tributary site in St. Clair County was moved in 2006 when the USGS determined that the original location (Water Street boat launch D/S of RR bridge; also referred to as being in watershed #24 in USGS's report (Hoard et al., 2018) likely represented Lake Huron water chemistry. Therefore, data presented for the Black River main site in this report will cover the years 2006-2013 at the new location (i.e., 450-500 feet upstream of Black River canal, also referred to as being in watershed #32 in Hoard et al. (2018), unless otherwise noted.

Figure 2-1. Locations of the WCMP Great Lakes tributaries monitoring sites with respect to ecoregions. (Ecoregion data source: Ecoregions Level III and IV, US, 2011, USEPA, SEGS; USEPA Office of Research and Development; available at https://edg.epa.gov/metadata/catalog/main/home.page.)

Table 2-1. List of main WCMP tributary sites. Watershed number corresponds to the numbering system in Table 2-2 and Figure 2-1. Integrator Sites were visited 12 times during their basin year, with event-driven sampling during 8 of 12 visits, as possible.

Watershed #	River Name	Intensive or Integrator Site	Years that Sites Were Sampled Intensively	1st Year	STORET ID	Latitude	Longitude
1	Ontonagon River	Integrator	2008, 2013	2000	660038	46.86751	-89.31695
2	Menominee River	Integrator	2002, 2007, 2012	2000	550038	45.10625	-87.63556
3	Escanaba River	Integrator	1999, 2000, 2005, 2010	1999	210102	45.77890	-87.06496
4	Sturgeon River	Integrator	2001, 2006, 2011	2000	210032	45.85063	-86.66925
5	Manistique River	Integrator	1999, 2004, 2009	1999	770073	45.97132	-86.24282
6	Tahquamenon River	Integrator	1999, 2004, 2009	1999	170141	46.55583	-85.03889
7	Pine River	Integrator	2004, 2009	2000	490006	46.05722	-84.65721
8	Cheboygan River	Integrator	2000, 2005, 2010	2000	160073	45.63334	-84.48195
9	Boardman River	Integrator	2003, 2008, 2013	2001	280014	44.67528	-85.63070
10	Manistee River	Integrator	2004, 2009	2000	510088	44.26430	-86.29538
11	Pere Marquette River	Integrator	1999, 2000, 2005, 2010	1999	530027	43.94445	-86.28000
12	Muskegon River (Lower)	INTENSIVE	sampled intensively all years	1999	610273	43.31778	-86.03889
13	Muskegon River (Upper)	Integrator	2001, 2006, 2011	2000	670008	43.84722	-85.43231
14	Grand River (Lower)	INTENSIVE	sampled intensively all years	1999	700123	43.02842	-86.03584
15	Grand River (Upper)	Integrator	2001, 2006, 2011	2000	340025	42.97195	-85.07000
16	Kalamazoo River (Lower)	INTENSIVE	sampled intensively all years	1999	030077	42.65112	-86.10612
17	Kalamazoo River (Upper)	Integrator	2004, 2009	2000	390598	42.32556	-85.35889
18	St. Joseph River (Lower)	Integrator	1999, 2001, 2005*	1999	110628	42.09642	-86.47117
19	St. Joseph River (Upper)	Integrator	2000, 2006**, 2010	2000	750273	41.80003	-85.75694
20	River Raisin	Integrator	2003, 2008, 2013	1998	580046	41.90165	-83.36482

Watershed #	River Name	Intensive or Integrator Site	Years that Sites Were Sampled Intensively	1st Year	STORET ID	Latitude	Longitude
21	Huron River	Integrator	2002, 2007, 2012	1998	580364	42.06407	-83.25419
22	River Rouge	Integrator	2000, 2005, 2010	1998	820070	42.28056	-83.12889
23	Clinton River	INTENSIVE	sampled intensively all years	1998	500233	42.58417	-82.88278
24	Black River	Integrator	2007, 2012	2006	740267	43.01750	-82.45306
25	Flint River	Integrator	2003, 2008, 2013	2000	730285	43.30889	-83.95250
26	Cass River	Integrator	2001, 2006, 2011	2000	730024	43.36500	-83.95473
27	Shiawassee River	Integrator	2000, 2005, 2010	1998	730023	43.25473	-84.10556
28	Tittabawassee River	Integrator	2002, 2007, 2012	1998	730025	43.39278	-84.01112
29	Saginaw River	INTENSIVE	sampled intensively all years	1998	090177	43.61751	-83.84278
30	Au Sable River	INTENSIVE	sampled intensively all years	1998	350061	44.43612	-83.43417
31	Thunder Bay River	Integrator	2000, 2005, 2010	1998	040123	45.06747	-83.43525

* In 2005, the Lower St. Joseph River and Pokagon Creek were sampled out of rotation with their Basin Year.

** In 2006, the Upper St. Joseph River and Coldwater River were sampled out of rotation with their Basin Year.

2.3.2. Study Design

2.3.2.1. Integrator Sites

Twenty-five of the 31 tributary sites were called Integrator Sites (Figure 2-1, Table 2-1). During non-watershed basin cycle years (four of every five years), Integrator Sites were sampled four times annually, regardless of stream flow. This sampling design was meant to discern typical water chemistry concentrations at these locations and determine temporal changes in water quality. During basin year cycles (once every five years), these sites were sampled 12 times beginning with the first significant snowmelt or spring rain event (assuming stream accessibility) and continuing through November. This sampling design was meant to provide loading estimates of various parameters as well as contribute to temporal trend analysis. To estimate flow and loading, field crews attempted to collect 75% of samples during high flow events and 25% of samples during base/low flow. A high flow event was defined by one or more of the following conditions: stream flow at or above the 20% exceedance flow; an increase in stream flow of approximately 100% above the preceding base flow condition; or an increase in stream flow following a lengthy period of discharge at base flow and considered likely to produce a measurable change in the concentration of sampled constituents.

2.3.2.2. Intensive Sites

The remaining 6 of 31 tributary sites (Figure 2-1, Table 2-1) were chosen to be sampled 12 times every year using the same flow-stratified schedule described above. High flow volume and expected contamination were important watershed selection criteria for 5 of the sites in this intensive sampling category, as these factors are associated with significant sources of contaminant loading to the Great Lakes. Intensive Sites were the tributary monitoring locations in the Clinton, Lower Grand, Lower Kalamazoo, Lower Muskegon, and Saginaw River watersheds. A sixth intensive site was also located in the Au Sable River watershed to represent a watershed with relatively few impacts.

In this report, Integrator and Intensive sites are sometimes grouped together and referred to as “main sites” for brevity and convenience.

Table 2-2. List of WCMP minimally impacted sites. Watershed number corresponds to the numbering system in Table 2-1 and Figure 2-1.

Watershed #	Minimally Impacted Site Name	STORET ID	Latitude	Longitude
1	East Branch Ontonagon	310468	46.50555	-88.94861
2	Paint River	360124	46.22945	-88.70008
3	Bryan Creek	520258	46.18541	-87.56603
4	Eighteen Mile Creek	210217	46.01518	-86.69380
5	Fox River	770082	46.40002	-86.02881
6	Tahquamenon River (Headwaters)	480033	46.37281	-85.78184
7	Bear Creek	170154	46.20451	-84.69751
8	Pigeon River	160177	45.37444	-84.51500
9	East Creek	280318	44.62746	-85.50444
10	Anderson Creek	830159	44.48217	-85.62027

Watershed #	Minimally Impacted Site Name	STORET ID	Latitude	Longitude
11	Pere Marquette River (Headwaters)	430578	43.86187	-85.88087
12	Bigelow Creek	630291	43.42833	-85.76833
13	Bigelow Creek	630291	43.42833	-85.76833
14	Bellamy Creek	340186	42.97918	-85.11105
15	Grand River (Headwaters)	380083	42.13889	-84.35306
16	South Branch Kalamazoo River	130331	42.16103	-84.80253
17	South Branch Kalamazoo River	130331	42.16103	-84.80253
18	Coldwater River	120215	42.02848	-85.10663
19	Pokagon Creek	140110	41.91194	-86.05916
20	River Raisin (Headwaters)	380393	42.15583	-84.14361
21	Huron River (Headwaters)	470521	42.47139	-83.75639
22	Johnson Drain	821417	42.42571	-83.48178
23	North Branch Clinton River	500467	42.88360	-83.07840
24	Black River (Headwaters)	760058	43.19362	-82.62417
25	South Branch Flint River	440173	43.01549	-83.25982
26	Evergreen Creek	790157	43.39430	-83.47600
27	Shiawassee River (Headwaters)	631036	42.77175	-83.57903
28	West Branch Tittabawassee	260068	44.10438	-84.38746
29	*no minimally impacted site*			
30	Perry Creek	680056	44.65830	-84.08280
31	Thunder Bay River (Headwaters)	600051	44.97409	-84.09286

2.3.2.3. Minimally Impacted Sites

These were identified by Surface Water Assessment Section biologists with knowledge of the watersheds. Sites were not defined as having no known human disturbance impacts; instead they were sites within the watershed with relatively few known impacts. One minimally impacted site was chosen in 30 of the 31 tributary watersheds to represent the best water quality one might expect based on the consideration of water chemistry and biota. The exception was the Saginaw River; it is the mainstem of the Tittabawassee, Shiawassee, Cass, and Flint Rivers, which are integrator sites with their own minimally impacted sites.

The water chemistry data from these sites allowed for within-watershed comparisons with their (in most cases, downstream) main sites. (*Note*: While minimally impacted sites for the Upper Grand River and Upper Muskegon River were not upstream of their paired main sites, the remaining 93% of the minimally impacted sites were upstream of their respective main sites.) Each minimally impacted site was sampled 4 times per year regardless of flow – only during its basin year cycle – beginning with the first significant snowmelt or spring rain event (assuming stream accessibility) and continuing through November. Information about these sites can be found in Figure 2-1 and Table 2-2.

2.3.3. Regional (Spatial) Analysis

Ecoregions are used in this section to better understand spatial patterns of water chemistry conditions in Michigan. Any general patterns observed amongst the various ecoregions (based upon the limited number of main sites within them) are noted in the Results and Discussion portion of this section, primarily for illustrative purposes.

Water quality parameter results are discussed in this section using the same ecoregion boundaries shown in Section 1.2.4 of Roush (2013) and in Section 1 of this report[5]. Detailed descriptions of the ecoregions relevant to this report and their corresponding hydrology can be found in those sections. A list of those ecoregions and the associated abbreviations used in this report can be found in Appendix A-2. Figure 2-1 of this report shows the WCMP Great Lakes tributary sites and where they fall within each ecoregion.

The effects of quaternary geology and dominant land cover type were also examined at a cursory level. Sites were plotted on a quaternary geology map layer based upon work by Farrand and Bell (1982). For land use analyses, the watershed upstream of each Great Lakes tributary site was first delineated using the Watershed Tool in ArcGIS (watershed delineations are based upon DEMs [digital elevation models], for additional information visit here[6]). The dominant land cover type, or the land cover type making up the greatest percentage of area within each watershed, was then determined using the NLCD (2011) from the Multi-Resolution Land Characteristics Consortium (Homer et al., 2015; NLCD, 2011; Figure 1-4; Table 1-1). (Note: Because the Watershed Tool initially delineated a very small watershed for the Escanaba River main site [STORET 210102] due to topographical characteristics, the decision was made to instead use the 10-digit HUC upstream of the site to delineate the watershed boundary for land use analyses.)

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[5] See also United States Level III and IV Ecoregions (USEPA) and Level III Ecoregions of Michigan at https://edg.epa.gov/metadata/catalog/main/home.page and *(The link provided was broken and has been removed.)* (data date December 23, 2011, publication date April 26, 2012).

[6] http://pro.arcgis.com/en/pro-app/tool-reference/spatial-analyst/how-watershed-works.htm (last visited February 6, 2018)

2.3.4. Loading Rate Estimates

Previous WCMP reports included loading estimates through 2008 (e.g., Aiello, 2008; Roush, 2013). For this report, 2009-2013 loading rate estimates for total phosphorus, chloride, chromium, copper, lead, mercury, and TSS were also included. As before, these estimates were calculated by the USGS Michigan Water Science Center for the WCMP's integrator sites (during their basin years; refer to Table 2-1) and for all intensive sites. Results of the loading calculations for 2001-2013 are presented in Appendix A-3 and discussed briefly in the results and discussion section below; see also Hoard et al. (2018). Flow data used for loading estimates came from USGS gauges near the sampling locations. Loading calculations were performed using the Stratified Beale Ratio Estimator described by Richards (1994) (see also Richards et al. [1996]).

Loading rates are shown as mean kilograms per year (kg/year) (Appendix A-3). All loading estimates have a 95% confidence interval. A "+/-" confidence interval of 20% shows there is a 95% certainty the true values lie within +/- 20% of the estimated loading rate. Also included in Appendix A-3 are mean stream flows (mean period flows) based upon flow measurements taken during the sampling period.

2.3.5. Statistics

2.3.5.1. Spatial

Refer to the Introduction for most of the details on spatial statistical methods employed on this dataset. Note that when a summary statistic (e.g., a median or maximum) is reported for a particular site in this section, it is a statistic derived from all years of data for that site.

Statistical comparisons between each main site (i.e., intensive or integrator) and its respective (within-watershed) minimally impacted site were considered (e.g., Wilcoxon rank-sum tests); however, they were not done because distributions of the main sites and their respective minimally impacted sites were not similar. The Wilcoxon rank-sum test[7] does not assume normality of the data, but it does require both samples to come from distributions with the same shape (Krzywinski and Altman, 2014b). Also, recall that these two different types of sites were not sampled in the same manner.

2.3.5.2. Temporal

Temporal trend analyses were performed by the USGS Michigan Water Science Center on the following parameters: total chloride, TSS, nitrogen (as ammonia, nitrate, nitrite, and Kjeldahl), total phosphorus, total orthophosphate, total chromium, total copper, total lead, and total mercury (Hoard et al., 2018) using Seasonal Kendall (SK) or Tobit Regression (TR) techniques within the computer program S-ESTREND. (Field parameters such as DO, pH, specific conductance, and water temperature were not analyzed for trends for various reasons including the fact that measurements were not collected at a similar time of day across all sites and dates, and these parameters [especially DO, pH, and temperature] typically exhibit diurnal and seasonal patterns.) The TR technique was used to provide some measure of a trend on

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[7] The two-sample Wilcoxon rank sum test is equivalent to the Mann-Whitney test (Sprent and Smeeton, 2001; Krzywinski and Altman, 2014a and 2014b).

streams having more than 5% of their data (for a particular parameter) that was censored (Chris Hoard, USGS, pers. comm., February 4, 2016).

Temporal trend analyses were calculated by the USGS for all intensive and integrator sites when possible. Table 2-3 shows an example of defined seasons for SK analyses. A trend result was considered here to be significant if the p-value of the test was $p \leq 0.05$. Trends are reported here as being upward or downward trends in terms of % *per year*. Refer to the Introduction of this report, Hoard et al. (2009), and Hoard et al. (2018) for additional details regarding temporal statistical methods employed on this dataset.

Table 2-3. Example of definition of seasons used for SK tests. Adapted from Hoard et al. (2009).

	Season Number											
Number of Seasons per Year	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
12	01/01–02/28	03/01–03/24	03/25–04/18	04/19–05/12	05/13–06/06	06/07–06/30	07/01–07/25	07/26–08/18	08/19–09/12	09/13–10/06	10/07–10/31	11/01–12/31
6	01/01–02/28	03/01–04/30	05/01–06/30	07/01–08/30	08/31–10/31	11/01–12/31						
4	01/01–03/31	04/01–06/30	07/01–09/30	10/01–12/31								
3	01/01–04/30	05/01–08–31	09/01–12/31									
2	01/01–06/30	07/01–12/31										

2.3.6. Historical Parameters

2.3.6.1. Base/Neutral Organics; Methyl Tertiary Butyl Ether (MTBE); Benzene, Toluene, Ethylbenzene, and Xylene (BTEX); and Total Cyanide

Several analytes were dropped from the WCMP at the end of the 2004 field season including base/neutral organics, MTBE, BTEX, and total cyanide. Base/neutral organics (e.g., polycyclic aromatic hydrocarbons, phthalates, benzenes, etc.) (USEPA, 1984; Aiello and Smith, 2002) are used by industry in a wide range of applications, many involving petroleum products such as fuels and plastics (Aiello and Smith, 2002). MTBE is an octane-enhancing replacement for lead that sometimes was used as a gasoline additive beginning in 1979. BTEX chemicals are common components of gasoline (Aiello and Smith, 2002).

Sampling for base/neutral organics, MTBE, and BTEX, which began in 1999, and for total cyanide, which began in 2001, had been initiated to support the Strategy's goal to detect new and emerging water quality problems. The majority of results obtained for these analytes were below analytical quantification levels, leading to the decision to drop them from the WCMP (Aiello, 2008). Results of these data can be found in previous reports on the MDEQ Web site at https://www.michigan.gov/egle/about/Organization/Water-Resources/GLWARM/water-chemistry (last visited August 31, 2018).

2.3.6.2. Pesticides

In 2005, EGLE's WCMP and the USGS partnered on a pesticide screening study. Of 320 water samples that were analyzed for the certain herbicides (atrazine, metolachlor, and simazine) and insecticides (chlorpyrifos and diazinon), only one sample, collected in June 2005 from the Black River, exceeded the Michigan Rule 57 water quality value for any pesticide analyzed at any location during that screening study. That sample was collected following herbicide application and recent rainfall, and exceeded the water quality value for atrazine (FCV = 7.3 µg/L) with an atrazine concentration of 10 µg/L (Fogarty and Duris, 2007; Aiello, 2008).

2.3.6.3. Polychlorinated Biphenyls (PCB)

PCB analysis was discontinued after 2007. The goal of this sampling was to determine if PCBs were ubiquitous in Michigan. While concentrations varied widely, PCBs were present in all samples and only met the WQS of 0.026 ng/L on one occasion at the Cheboygan River site. Total PCB concentrations exceeded this standard at this site on all other dates (Roush, 2013). Results of these data can be found in previous reports on EGLE's Web site at https://www.michigan.gov/egle/about/Organization/Water-Resources/GLWARM/water-chemistry (last visited July 11, 2017). Information about a statewide TMDL) being developed for PCBs can be found at https://www.michigan.gov/egle/about/Organization/Water-Resources/tmdls/statewide-mercury-tmdl (last visited July 11, 2017). The purpose of the TMDL is to gather data, identify problems, and develop appropriate goals and reasonable assurance that will work toward restoring the designated uses to the water bodies.

2.3.6.4. Other Historical Parameters

Other organic contaminants of interest (e.g., dioxin, furan, PFOS, PFOA) were occasionally monitored in the past at some locations, and their methods and results can be found in past reports such as Aiello (2005).

2.4. RESULTS AND DISCUSSION

Section 2 of this WCMP report focuses on and presents water chemistry results of Michigan DEQ's Great Lakes tributaries monitoring sites during the years 1998-2013 and it discusses the occurrence of temporal trends for select parameters.

Results of individual water quality parameters are discussed in detail below. At the end, in section 2.3.5, there is some general discussion about any overall spatial (e.g., ecoregional) or temporal patterns that were observed which may be influenced by factors such as broad differences in land use patterns (e.g., extent of urban or agricultural development), population density, geology, etc. Refer to Table 1-2 for an explanation of lab codes that resulted in exclusion of some data from spatial and temporal analyses.

Breakdown of Key Findings within Each Ecoregion

For each of the parameters discussed below, Appendices C-2 and C-3 present summaries of the data broken down by ecoregion, including lists of the three (sometimes more) highest and lowest medians observed *within each ecoregion* plus instances where Minimally Impacted Sites had medians that were higher relative to their respective Main Sites.

Note: Some Minimally Impacted Sites were not located within the same ecoregion as their corresponding "Main Site". Those particular sites are listed below.

	Main Sites		**Minimally Impacted Sites**	
Water-shed #	**River Name**	**Eco-region Abbrev-iation**	**River Name**	**Eco-region Abbrev-iation**
9	Boardman River	NC	East Creek	NL
10	Manistee River	NC	Anderson Creek	NL
11	Pere Marquette River	SM	Pere Marquette River (Headwaters)	NL
12	Muskegon River (Lower)	SM	Bigelow Creek	NL
20	River Raisin	HE	River Raisin (Headwaters)	SM
21	Huron River	HE	Huron River (Headwaters)	SM
23	Clinton River	HE	North Branch Clinton River	SM
25	Flint River	HE	South Branch Flint River	SM
27	Shiawassee River	HE	Shiawassee River (Headwaters)	SM
28	Tittabawassee River	HE	West Branch Tittabawassee	NL

2.4.1. Nutrients

2.4.1.1. Phosphorus

Total Phosphorus

Median total phosphorus concentrations amongst all the Main (Intensive and Integrator) tributary sites ranged from 0.145 mg/L at the Clinton River (HELP ecoregion) to 0.008 mg/L at the Cheboygan River (NLAF ecoregion) (Appendix C-1). The highest median concentrations were typically in the HELP and SMNIDP ecoregions; the top 10 medians amongst Main Sites were observed in these ecoregions. The Pine River had the 11th highest median overall and the highest median out of NLAF and NCHF ecoregion sites (Appendix C-1, Figure 2-2).

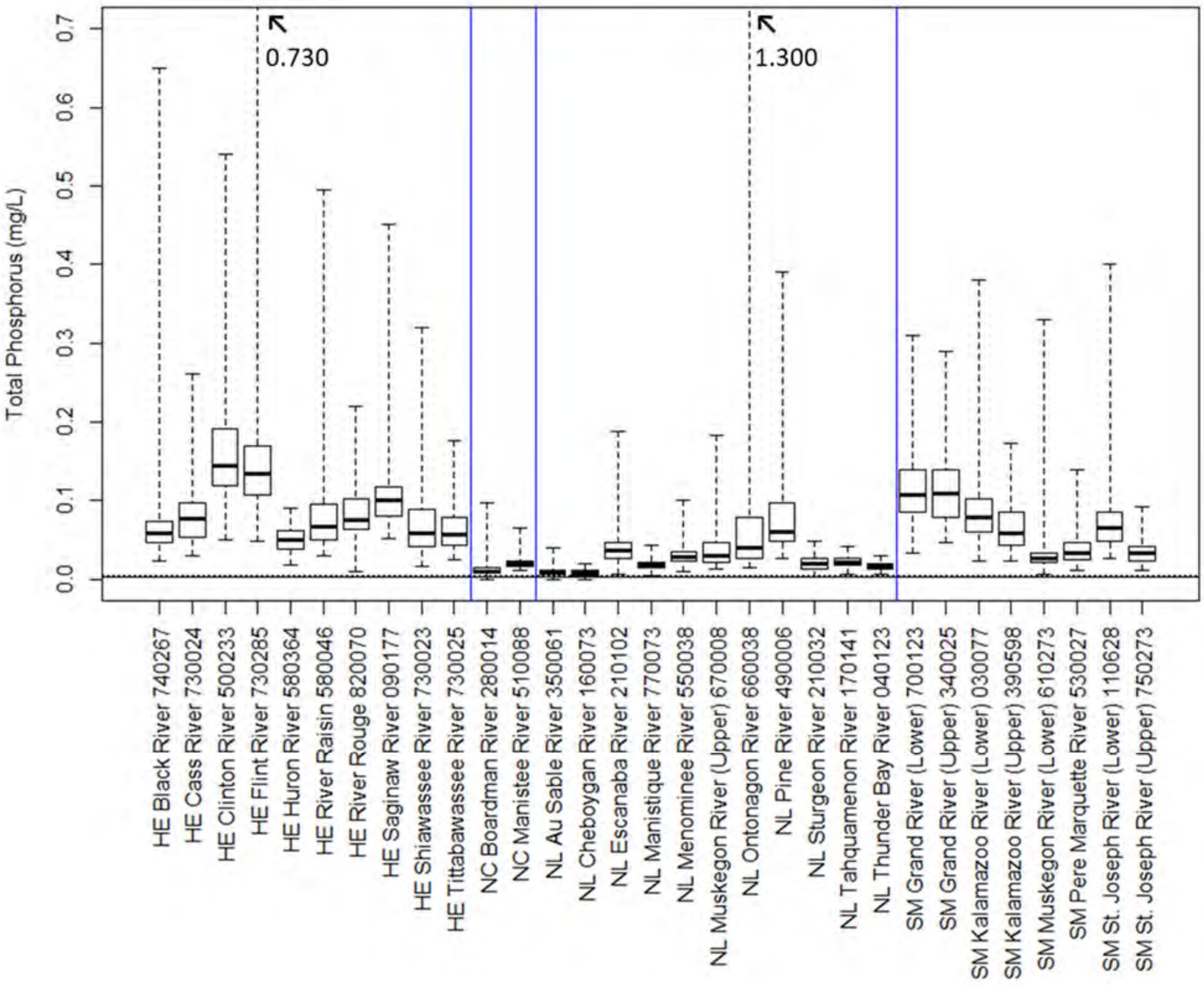


Figure 2-2. Total phosphorus concentrations at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (reporting limit). Blue vertical lines separate ecoregions.

Overall, 83% of the Minimally Impacted Sites had lower median total phosphorus concentrations than their associated (paired) Main Sites (Appendix C-4). In the cases where the Minimally Impacted Sites had higher medians than their respective Main Sites (i.e., negative differences shown in Appendix C-4), all median total phosphorus concentrations were less than 0.060 mg/L (Appendices C-2, C-4). (*Note*: Total phosphorus concentrations below 0.060 mg/L are expected to keep stream chlorophyll levels below 100 milligrams per square meter (mg/m^2) most of the time; levels of filamentous algae that are considered to be "nuisance" may be reached in streams when chlorophyll levels are somewhere between 100 and 200 mg/m^2 [Dodds and Welch, 2000].)

Trends and Loading. There were no significant ($p \leq 0.05$) upward total phosphorus trends observed amongst Main Sites in this study. Significant downward trends ranged from -3.08% (River Raisin) to -4.24% (lower St. Joseph River) per year (Table 2-4; Hoard et al., 2018). As for loading, the Saginaw River and lower Grand River tributary sites consistently had the highest mean phosphorus loadings of sites analyzed since these estimates were made in 2001 (Appendix A-3). Mean annual phosphorus loads ranged from 227,166 to 922,000 kg/year at the Saginaw River and from 256,000 to 746,000 kg/year at the lower Grand River tributary sites from 2001 to 2013 (Appendix A-3). These are generally the largest tributary sites with respect to mean period flows, which ranged from 2,610 to 6,899 cubic feet per second for the Saginaw River and 2,730 to 6,545 cubic feet per second for the lower Grand River between 2001 and 2013 (Appendix A-3).

Orthophosphate

Orthophosphate concentrations followed a general pattern similar to that of total phosphorus. Median orthophosphate concentrations amongst the Main Sites ranged from 0.069 mg/L at the Clinton River (HELP ecoregion) to 0.005 mg/L at a number of sites in both the NLAF ecoregion (Cheboygan, Au Sable, Manistique, Sturgeon, Tahquamenon, and Thunder Bay Rivers) and the NCHF ecoregion (Boardman and Manistee Rivers) (Appendix C-1, Figure 2-3). The top 8 Main Site medians were observed in the HELP and SMNIDP ecoregions. The Pine River had the 9th highest median overall and the highest median out of NLAF and NCHF ecoregion sites (Appendix C-1, Figure 2-3).

Overall, 77% of Minimally Impacted Sites had lower median orthophosphate concentrations than their paired Main tributary sites (Appendix C-4).

Trends. Orthophosphate results were below quantification at a frequency that precluded trend analysis to be run at a number of Main locations (see Hoard et al., 2018). Significant upward trends for orthophosphate ranged from 3.15% (lower Grand River) up to 21.10% (Black River) per year (Table 2-4). (Note that while this Black River site had a large trend that was computed, it had less data [8 years] and samples than the other Main Sites, and it had a number of data points that were censored (12 out of 47 samples, or 26%) [Table 2-4; Hoard et al., 2018]). Significant downward trends ranged from -3.42% (upper Kalamazoo River) to -6.48% (Escanaba River) per year (Table 2-4; Hoard et al., 2018).

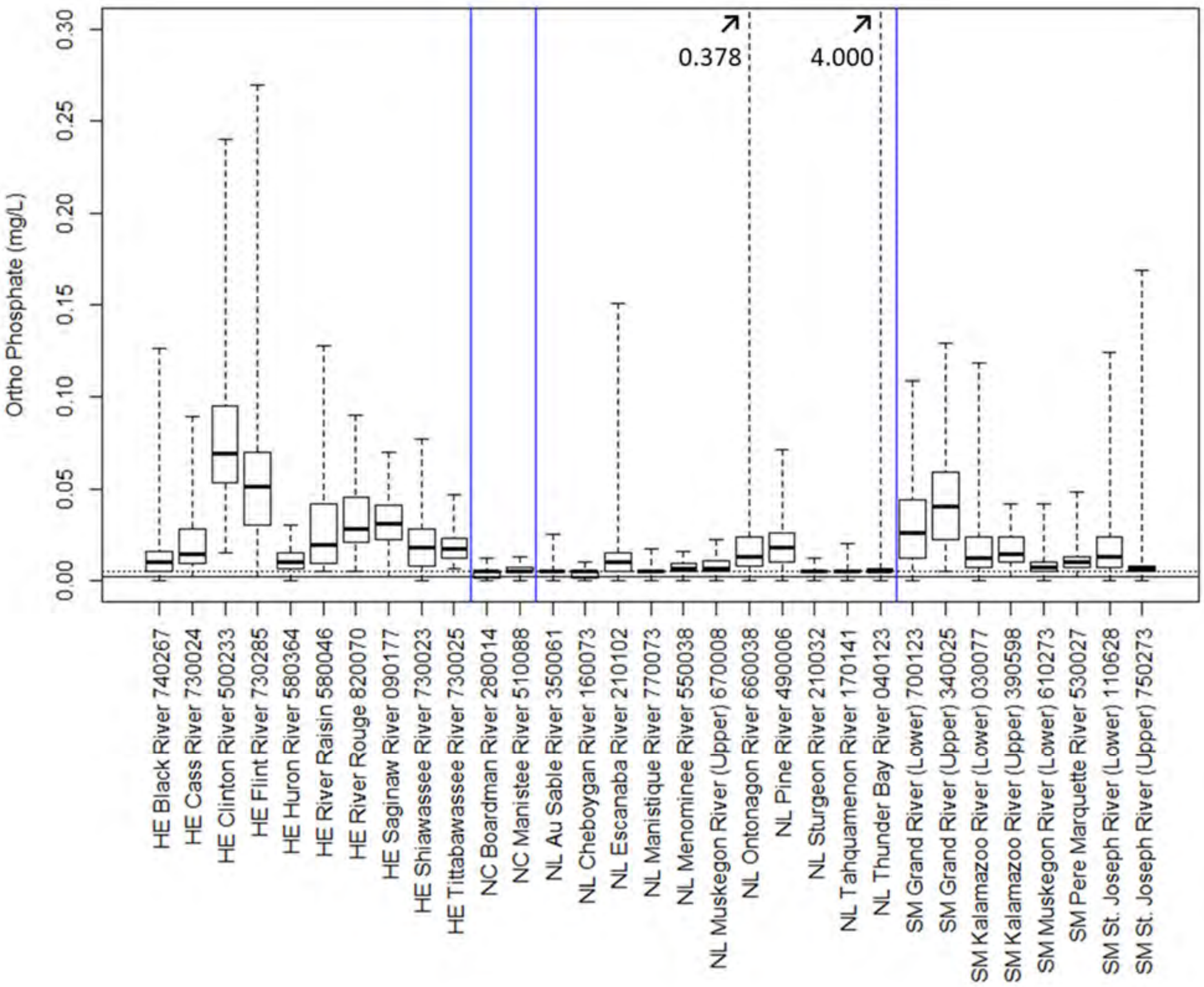


Figure 2-3. Total orthophosphate concentrations at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (reporting limit). Blue vertical lines separate ecoregions.

2.4.1.2. Nitrogen

Nitrate

Median nitrate concentrations amongst all the Main tributary sites ranged from 2.12 mg/L at the Flint River (HELP ecoregion) to 0.01 mg/L at both the Au Sable River and Ontonagon River (NLAF ecoregions) (Appendix C-1, Figure 2-4). The highest median concentrations were typically in the HELP and SMNIDP ecoregions; the top 17 medians amongst Main Sites were observed in these ecoregions. The Boardman River had the 18th highest median overall and the highest median out of NLAF and NCHF ecoregion sites. Nitrate concentrations in the NLAF and NCHF ecoregions were much less variable than those in HELP and SMNIDP ecoregions (Appendix C-1).

Overall, 60% of the Minimally Impacted Sites had lower median nitrate concentrations than their associated (paired) Main tributary sites (Appendix C-4).

Trends. The only significant, upward nitrate trend that was observed was at the River Rouge Main Site (3.90% per year) (Table 2-4; Hoard et al., 2018). The remaining four significant downward trends ranged from -1.65% (upper St. Joseph River) to -7.49% (Huron River) per year.

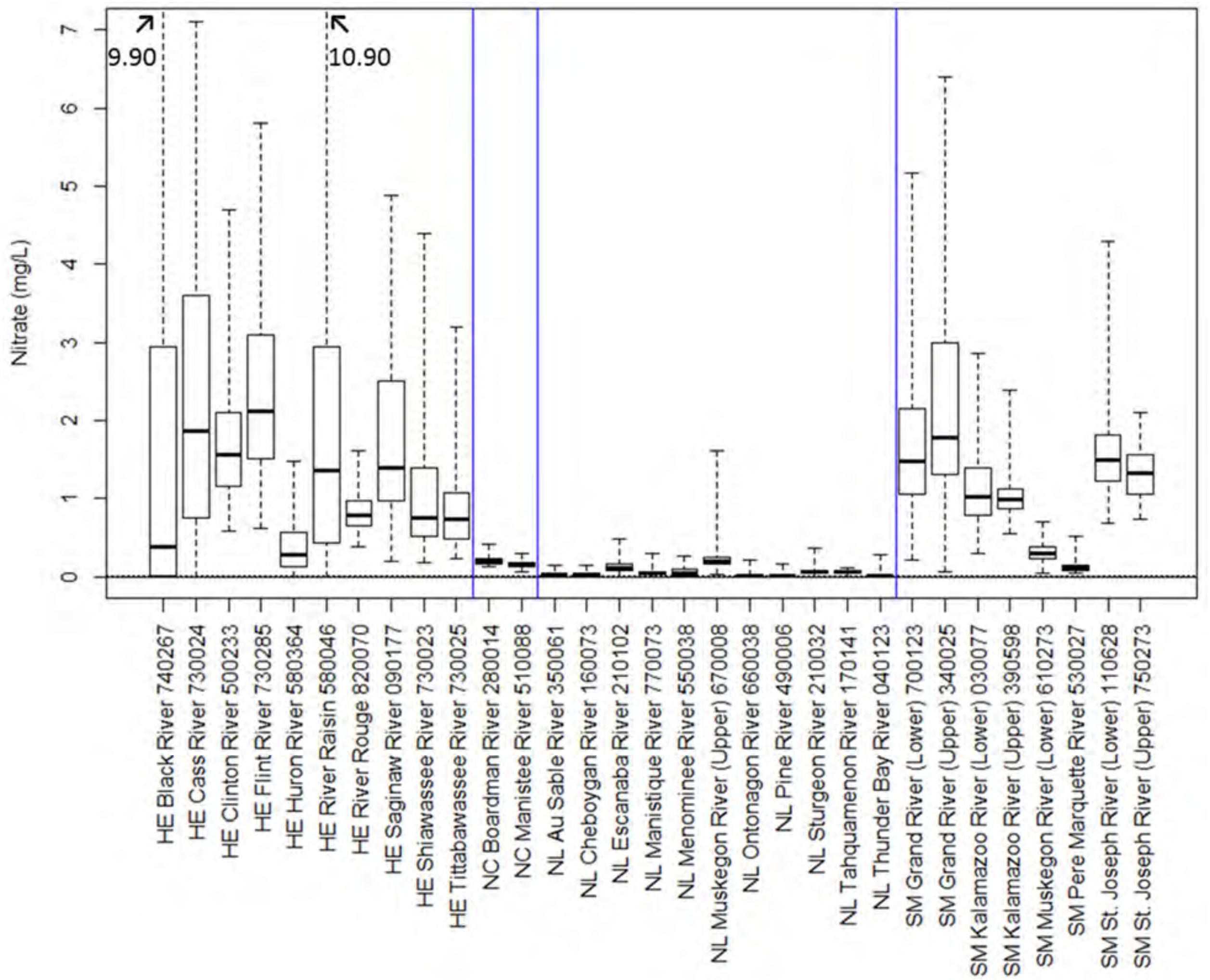


Figure 2-4. Total nitrate concentrations at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (reporting limit). Blue vertical lines separate ecoregions.

Nitrite

Median nitrite concentrations amongst all the Main tributary sites ranged from 0.033 mg/L at the Clinton River (HELP ecoregion) to non-quantifiable (i.e., below the reporting limit; < 0.010 mg/L) at multiple sites in the NCHF and NLAF ecoregions (i.e., the Boardman, Manistee, Au Sable, Cheboygan, Sturgeon, and Thunder Bay Rivers) (Appendix C-1, Figure 2-5). The highest median concentrations were typically in the HELP and SMNIDP ecoregions; the top 13 medians amongst Main Sites were observed in these ecoregions. The Escanaba River had the 14th highest median overall and the highest median out of NLAF and NCHF ecoregion sites (Appendix C-1).

Overall, 80% of the Minimally Impacted Sites had lower median nitrite concentrations than their associated Main tributary sites (Appendix C-4). The remaining 20% of the Minimally Impacted Sites had median values that were equal to the values at their paired Main Sites.

Trends. Nitrite results were below quantification at a frequency that precluded trend analysis to be run at a number of Main locations (see Hoard et al., 2018). The strongest significant, upward nitrite trend was found in the River Rouge (6.40% per year); the strongest significant downward trend was found at the River Raisin (-4.83% per year) (Table 2-4; Hoard et al., 2018). Worth noting was the Black River upward trend (8.93% per year). Similar to orthophosphate, the Black River site trend was computed using only 8 years of data and it had a number of data points that were censored (10 out of 47 samples, or 21%).

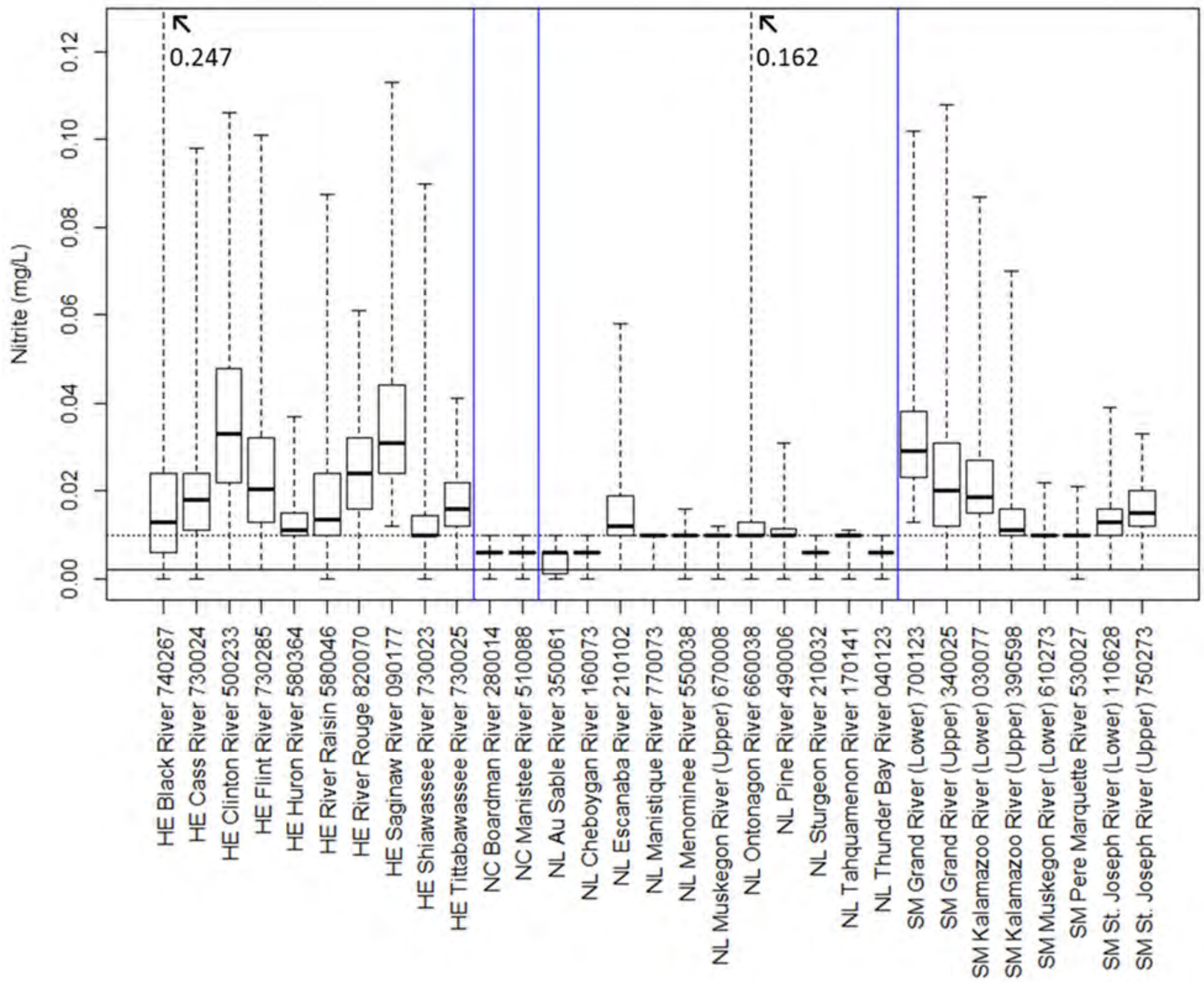


Figure 2-5. Total nitrite concentrations at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (reporting limit). Blue vertical lines separate ecoregions.

Total Kjeldahl Nitrogen

Median total Kjeldahl nitrogen (TKN) concentrations amongst all the main tributary sites ranged from 1.07 mg/L at the Saginaw River (HELP ecoregion) to 0.18 mg/L at the Boardman River (NCHF ecoregion) (Appendix C-1, Figure 2-6).

The highest median concentrations were typically in the HELP and SMNIDP ecoregions; the top 13 medians amongst main sites were observed in these ecoregions. The Escanaba River had the 14th highest median overall and the highest median out of NLAF and NCHF ecoregion sites (Appendix C-1).

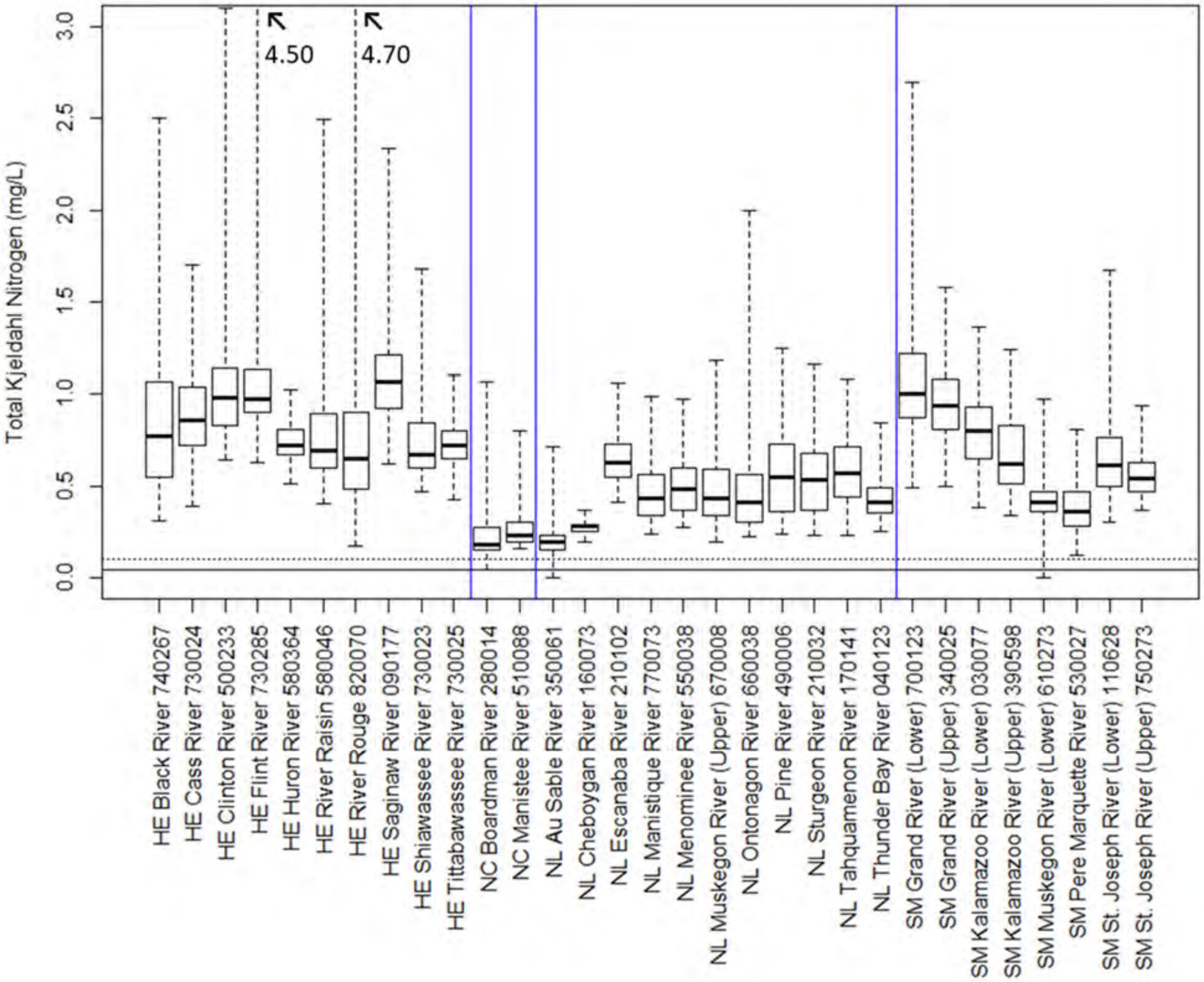


Figure 2-6. Total Kjeldahl nitrogen concentrations at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (RL). Blue vertical lines separate ecoregions.

Overall, 77% of the minimally impacted sites had lower median total Kjeldahl nitrogen concentrations than their associated (paired) main tributary sites (Appendix C-4).

Trends. Significant upward trends for total Kjeldahl nitrogen ranged from 2.66% (Escanaba River) to 5.30% (Black River) per year (Table 2-4; Hoard et al., 2018). Significant downward trends ranged from -1.58% (Clinton River) to -2.46% (lower Grand River) per year.

Total Ammonia

Median total ammonia concentrations amongst all the main tributary sites ranged from 0.153 mg/L at the River Rouge (HELP ecoregion) to nonquantifiable (< 0.010 mg/L) at the Black River (HELP ecoregion) (Appendix C-1, Figure 2-7). The highest median concentrations were typically in the HELP and SMNIDP ecoregions; nearly all the top 16 medians amongst main sites were observed in these ecoregions. The one exception was the Escanaba River, located in the NLAF ecoregion, which had the fifth highest median overall (Appendix C-1).

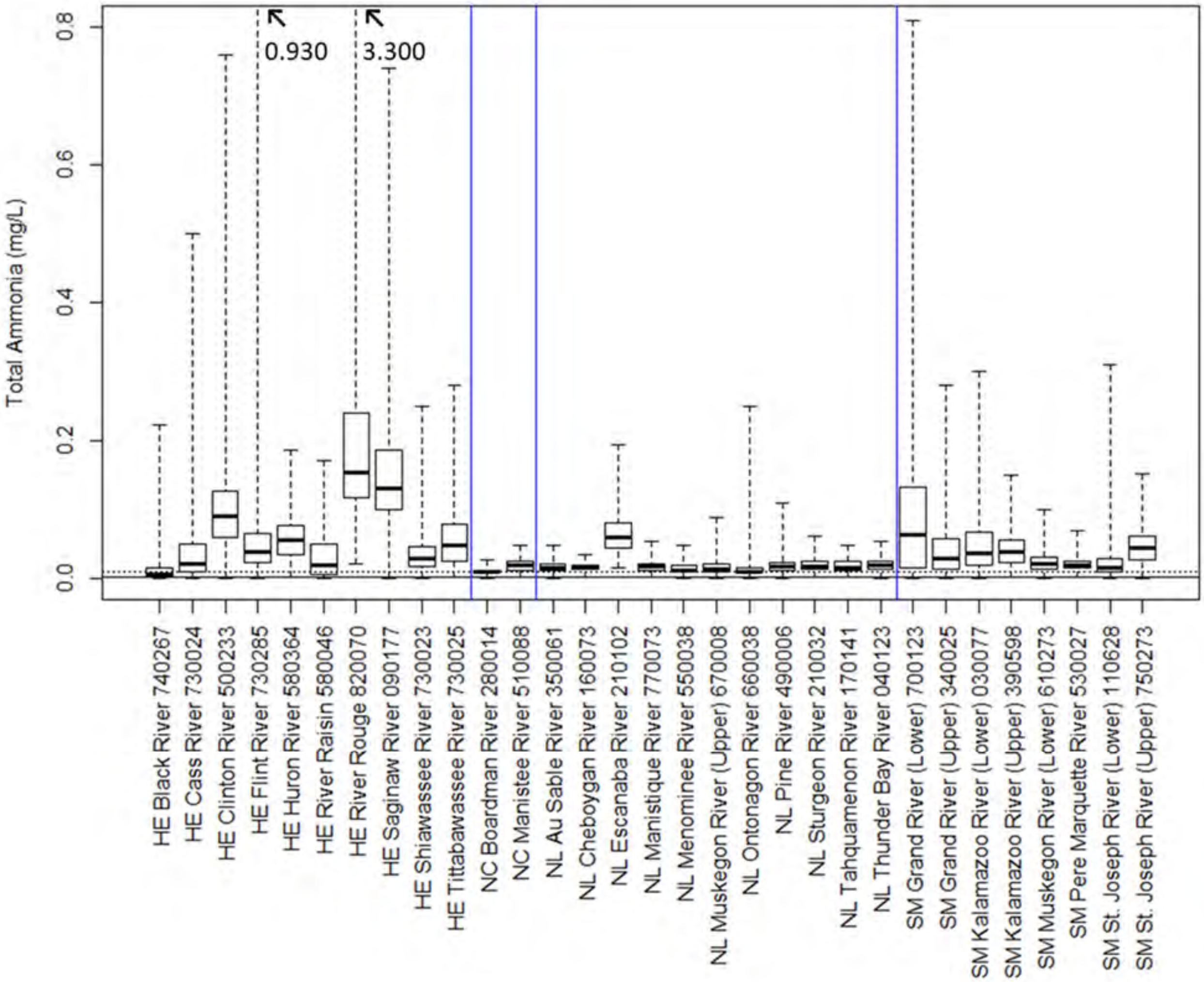


Figure 2-7. Total ammonia concentrations at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (RL). Blue vertical lines separate ecoregions.

Overall, 77% of the minimally impacted sites had lower median total ammonia concentrations than their associated main tributary sites (Appendix C-4). In the cases where the minimally impacted sites had higher medians than their respective main sites (i.e., negative differences shown in Appendix C-4), all median total ammonia concentrations were less than 0.035 mg/L.

Trends. Only one main tributary site had a significant upward trend (River Rouge, 5.44% per year) for total ammonia (Table 2-4; Hoard et al., 2018). The remaining sites had decreasing trends, ranging from -2.68 (Menominee River) to -12.24% (Tittabawassee River) per year.

2.4.2. Conventional Parameters

2.4.2.1. TOC

Median TOC concentrations amongst all the main tributary sites ranged from 19.0 mg/L at the Escanaba River (NLAF ecoregion) to 2.9 mg/L at the Boardman River (NCHF ecoregion) (Appendix C-1, Figure 2-8). The highest median concentrations were typically in the NLAF ecoregion; the top 7 medians amongst main sites were observed in this ecoregion. The Grand River (Upper) site had the eighth highest median overall for the remaining ecoregions (SMNIDP, HELP, NCHF) (Appendix C-1).

DOC often makes up a relatively large portion of the TOC mass in natural fresh waters (e.g., lakes, wetlands, rivers), and the concentrations of DOC tend to be greatest in wetland areas, relative to other types of natural waters, due to the buildup of organic acids in the water resulting from the decay and leaching of abundant moss, plant, and other organic matter (Thurman, 1985). Roush (2013) suggested that the highest TOC concentrations were found at Upper Peninsula tributary sites such as the Escanaba, Tahquamenon, Sturgeon, and Pine Rivers because their headwaters originate from organic wetland soils and are naturally stained due to the leaching of humic substances within the watershed.

Overall, 77% of the minimally impacted sites had lower median TOC concentrations than their paired main tributary sites (Appendix C-4).

2.4.2.2. Turbidity

Median turbidity values did not display a clear pattern associated with ecoregions. The two highest (Pine and Ontonagon Rivers) median values, as well as the three lowest, were all from rivers located in the NLAF ecoregion. Median turbidity values amongst all the main tributary sites ranged from 29.0 Nephelometric Turbidity Units (NTU) at the Pine River (NLAF ecoregion) to 1.0 NTU at both the Au Sable and Cheboygan Rivers (NLAF ecoregion) (Appendix C-1, Figure 2-9). Turbidity in water can be caused by a number of substances such as suspended or colloidal clay, silt, finely divided organic matter, and plankton (APHA et al., 1995). A number of factors can influence the variability of turbidity including land use type/intensity (e.g., agriculture, forestry, and urban development), riparian zone disturbance, streambank erosion, and local geology (Waters, 1995; Allan, 2004; Borok, 2010).

Overall, 83% of the minimally impacted sites had lower median turbidity values their associated main tributary sites (Appendix C-4).

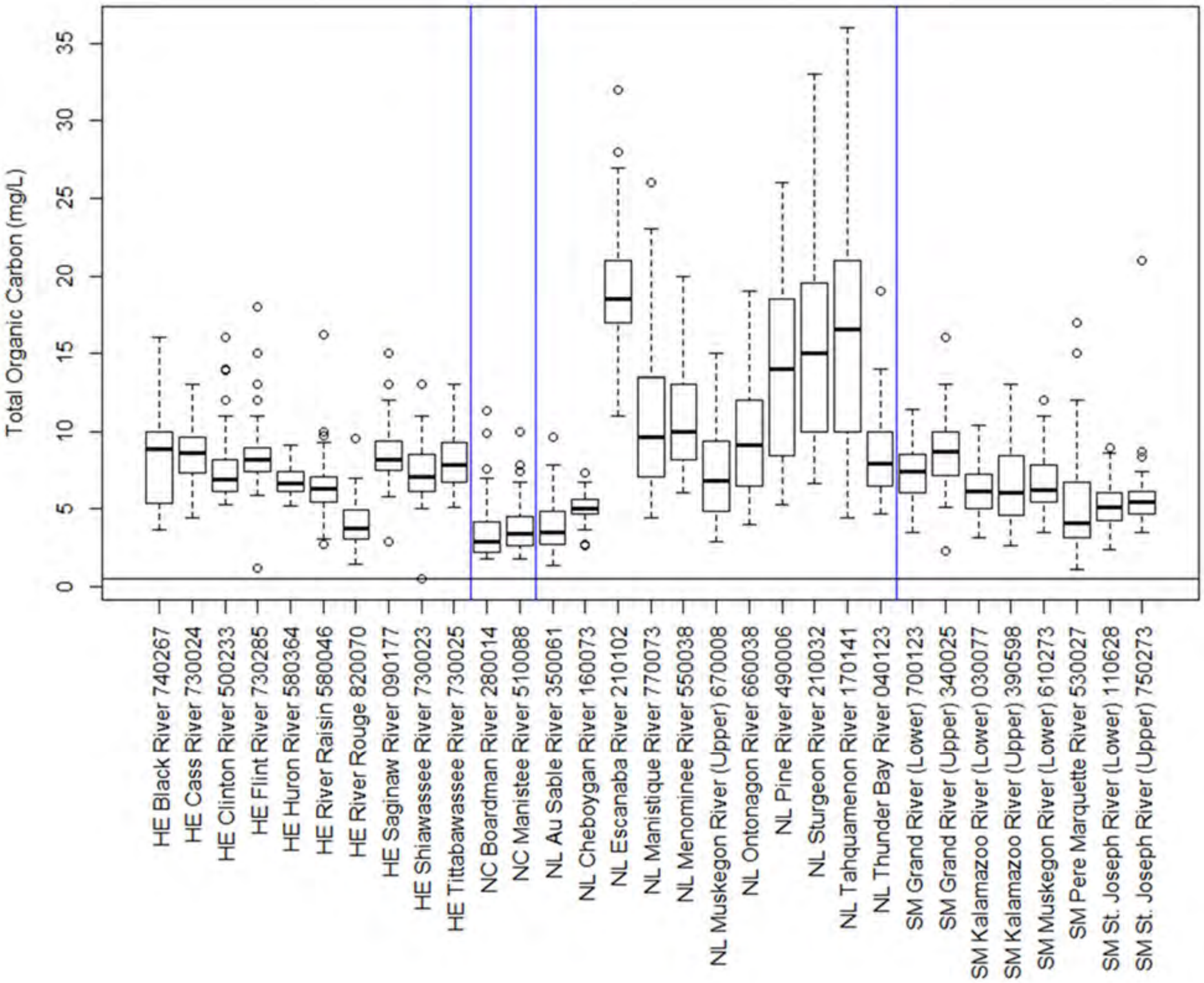


Figure 2-8. TOC at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (RL). (*Note*: The detection limit and RL for TOC were the same [0.5 mg/L].) Blue vertical lines separate ecoregions.

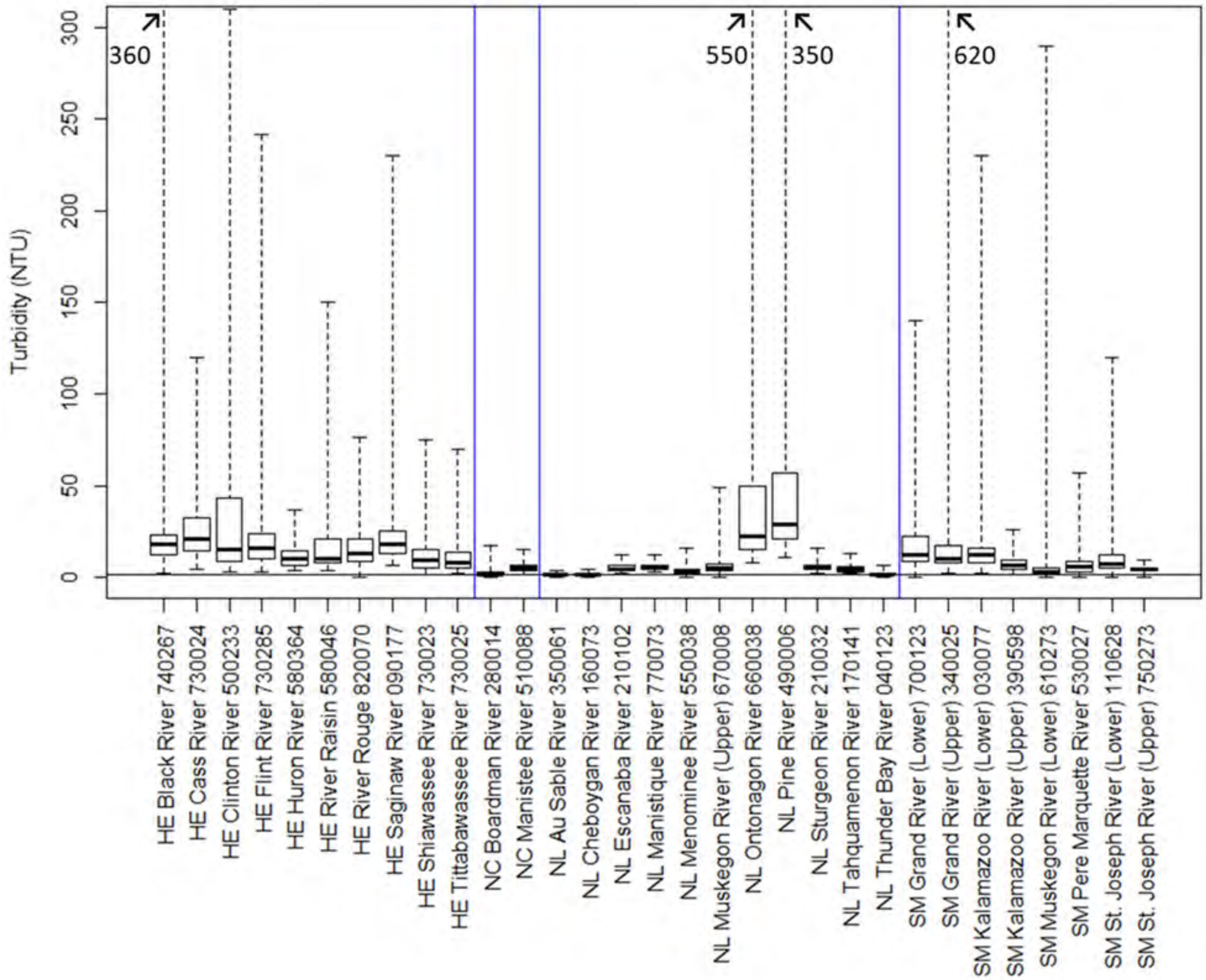


Figure 2-9. Turbidity concentrations at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (RL). (*Note*: The detection limit and RL for turbidity were the same [1 NTU].) Blue vertical lines separate ecoregions.

2.4.2.3. TDS and Major Ions

TDS

TDS is a measurement of inorganic salts. The major constituents measured for the WCMP were chloride and sulfate anions and calcium, magnesium, sodium, and potassium cations. Concentrations of TDS followed the same pattern as many other WCMP water chemistry parameters, with higher values found in the HELP ecoregion and the southern portion of the SMNIDP.

Median TDS concentrations amongst all the main tributary sites ranged from 600 mg/L at the Huron and Clinton Rivers (HELP ecoregion) to 100 mg/L at the Ontonagon and Tahquamenon Rivers (NLAF ecoregion) (Appendix C-1, Figure 2-10). The highest median concentrations were typically in the HELP and SMNIDP ecoregions; the top 16 medians amongst main sites were observed in these ecoregions (the top 8 were all in the HELP ecoregion). The Escanaba River had the 17th highest median overall and the highest median out of NLAF and NCHF ecoregion sites (Appendix C-1).

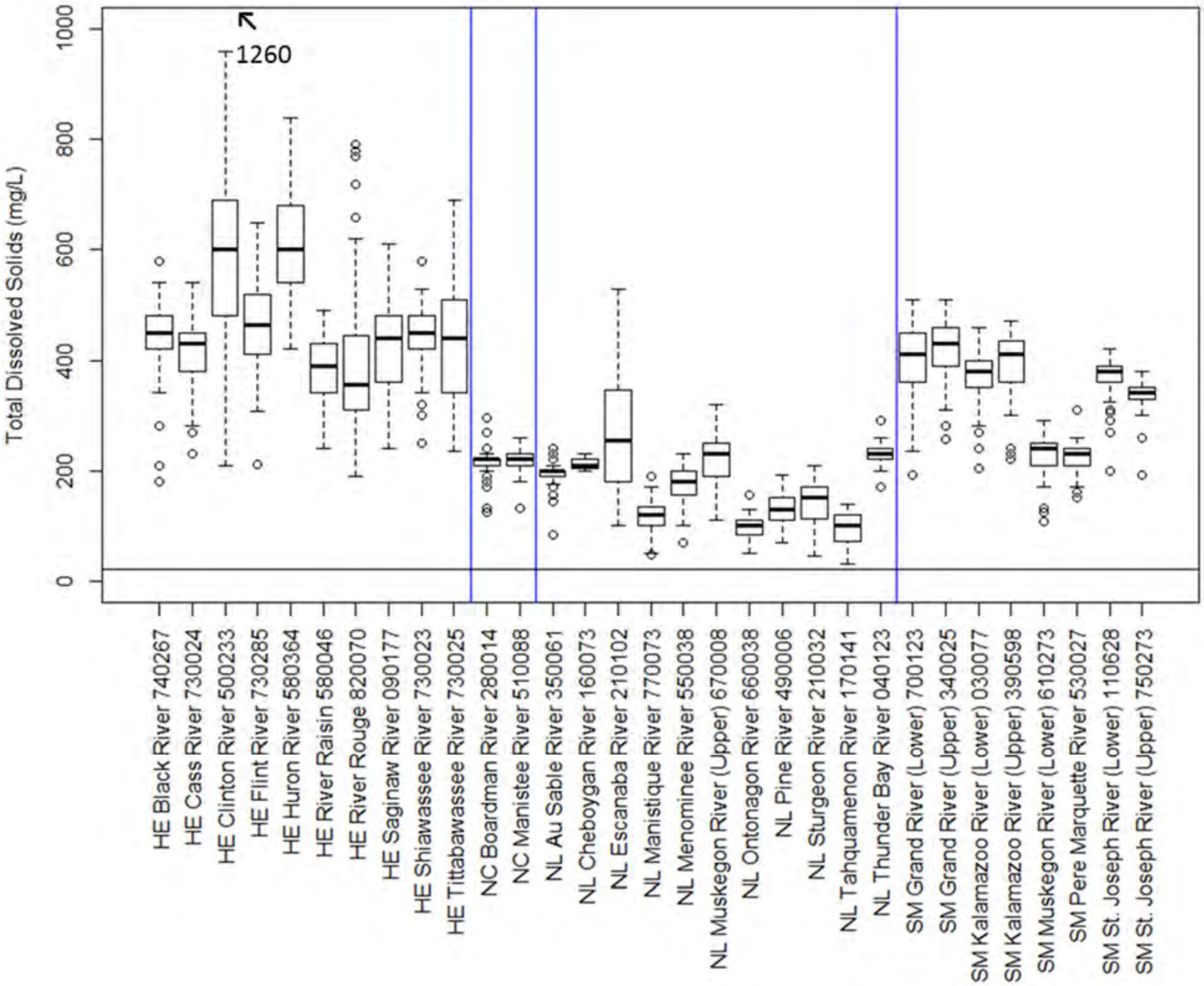


Figure 2-10. TDS concentrations at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (RL). (*Note*: The detection limit and RL for TDS were the same [20 mg/L].) Blue vertical lines separate ecoregions.

Overall, 63% of the minimally impacted sites had lower median TDS values than their associated (paired) main tributary sites (Appendix C-4).

The largest TDS fraction (examining the major constituents mentioned above) was typically calcium (Appendix C-5). There were, however, some exceptions where other constituents were the largest fraction including one case in the NLAF ecoregion (sodium: Escanaba River) and some sites in the HELP ecoregion (chloride: Rouge, Clinton, Flint, Shiawassee, Tittabawassee, and Saginaw Rivers; sulfate: Huron River).

Sodium and chloride data are discussed in greater detail below. The only TDS component analyzed for trends was chloride.

Calcium, magnesium, potassium, and sulfate data are summarized in Appendices C-1 and C-4, and Figures 2-11, 2-12, 2-13, and 2-14.

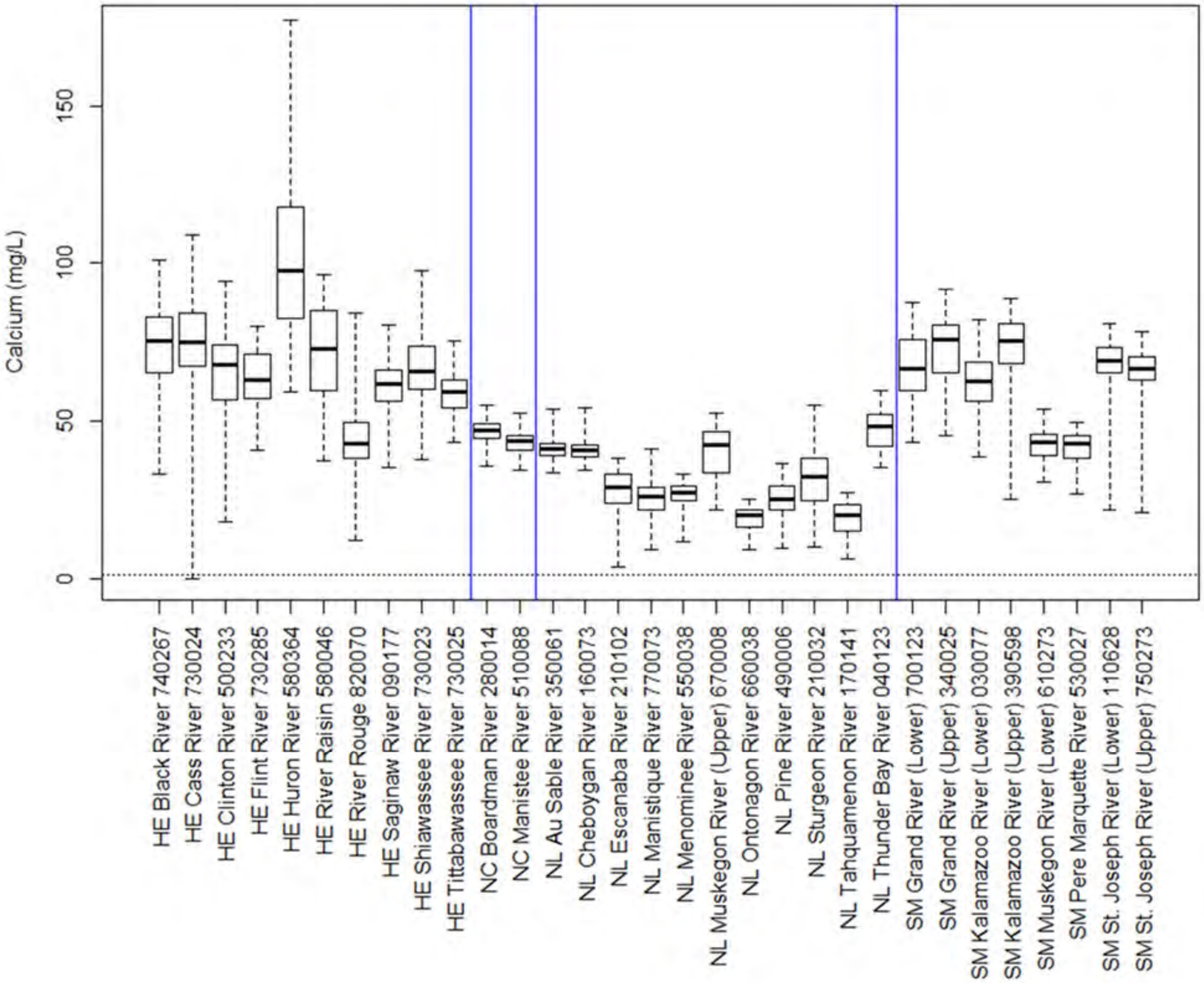


Figure 2-11. Calcium concentrations at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (RL). (*Note*: The detection limit and RL for calcium were the same [1.0 mg/L].) Blue vertical lines separate ecoregions.

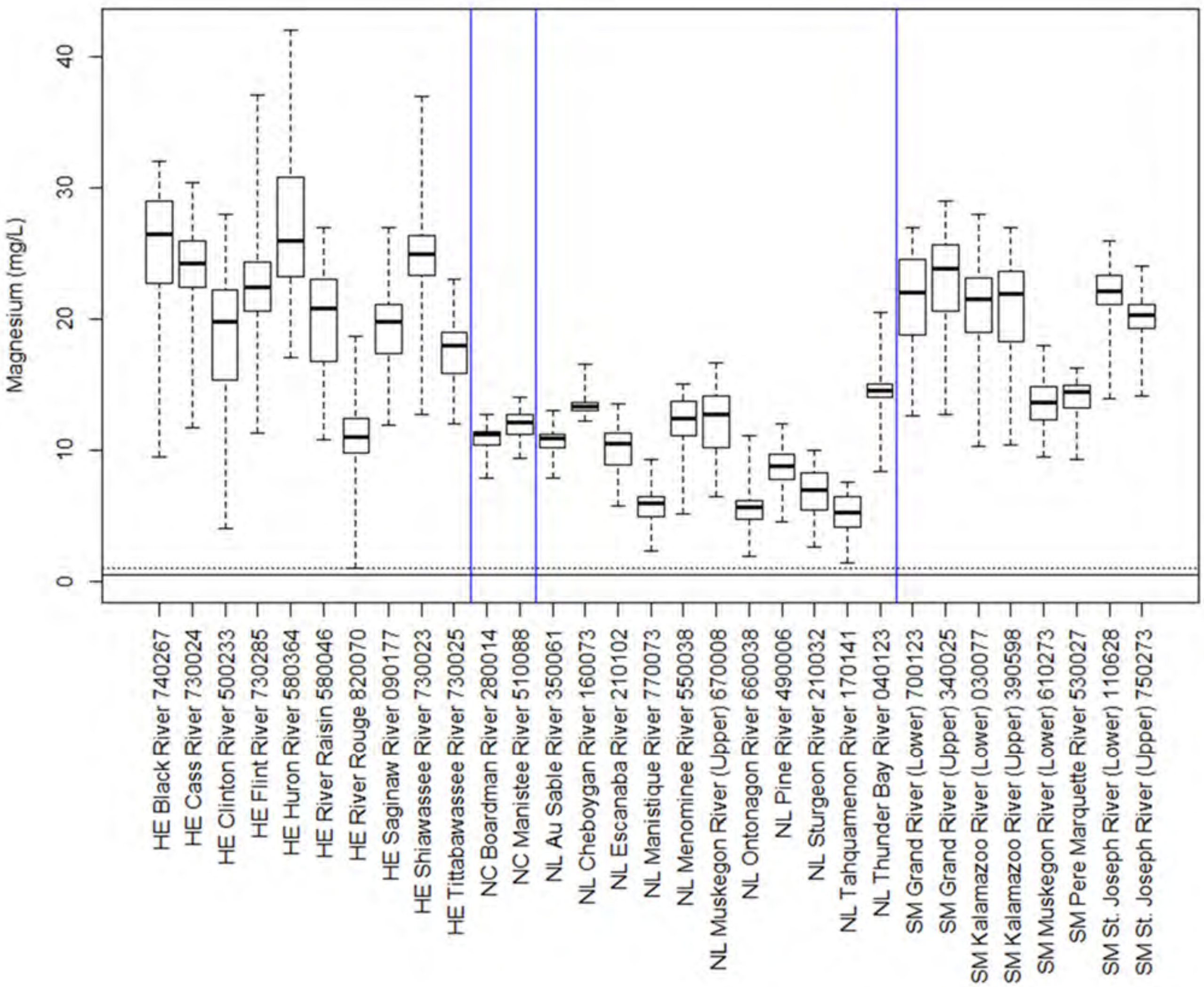


Figure 2-12. Magnesium concentrations at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (RL). Blue vertical lines separate ecoregions.

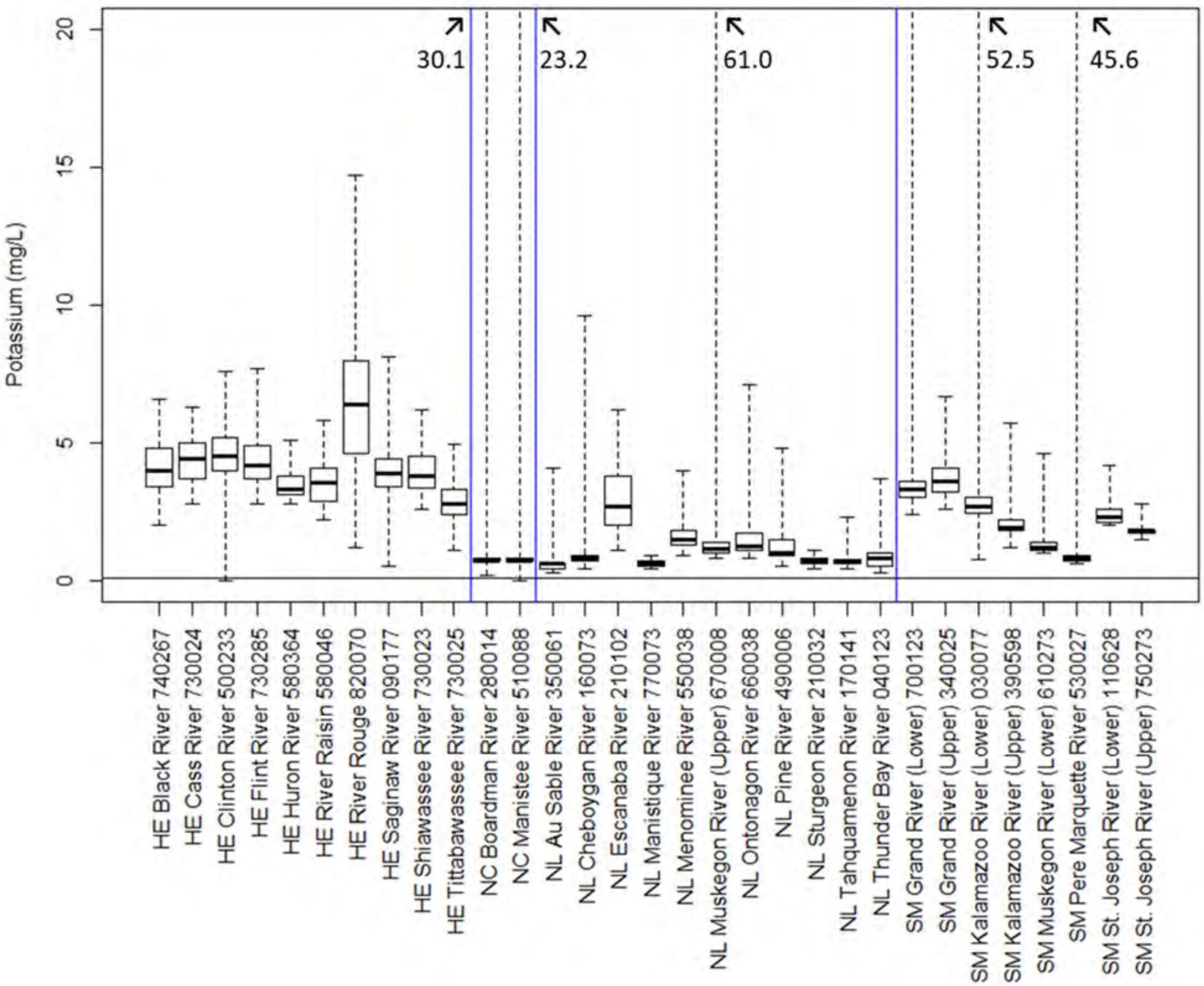


Figure 2-13. Potassium concentrations at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (RL). (*Note*: The detection limit and RL for potassium were the same [0.1 mg/L].) Blue vertical lines separate ecoregions.

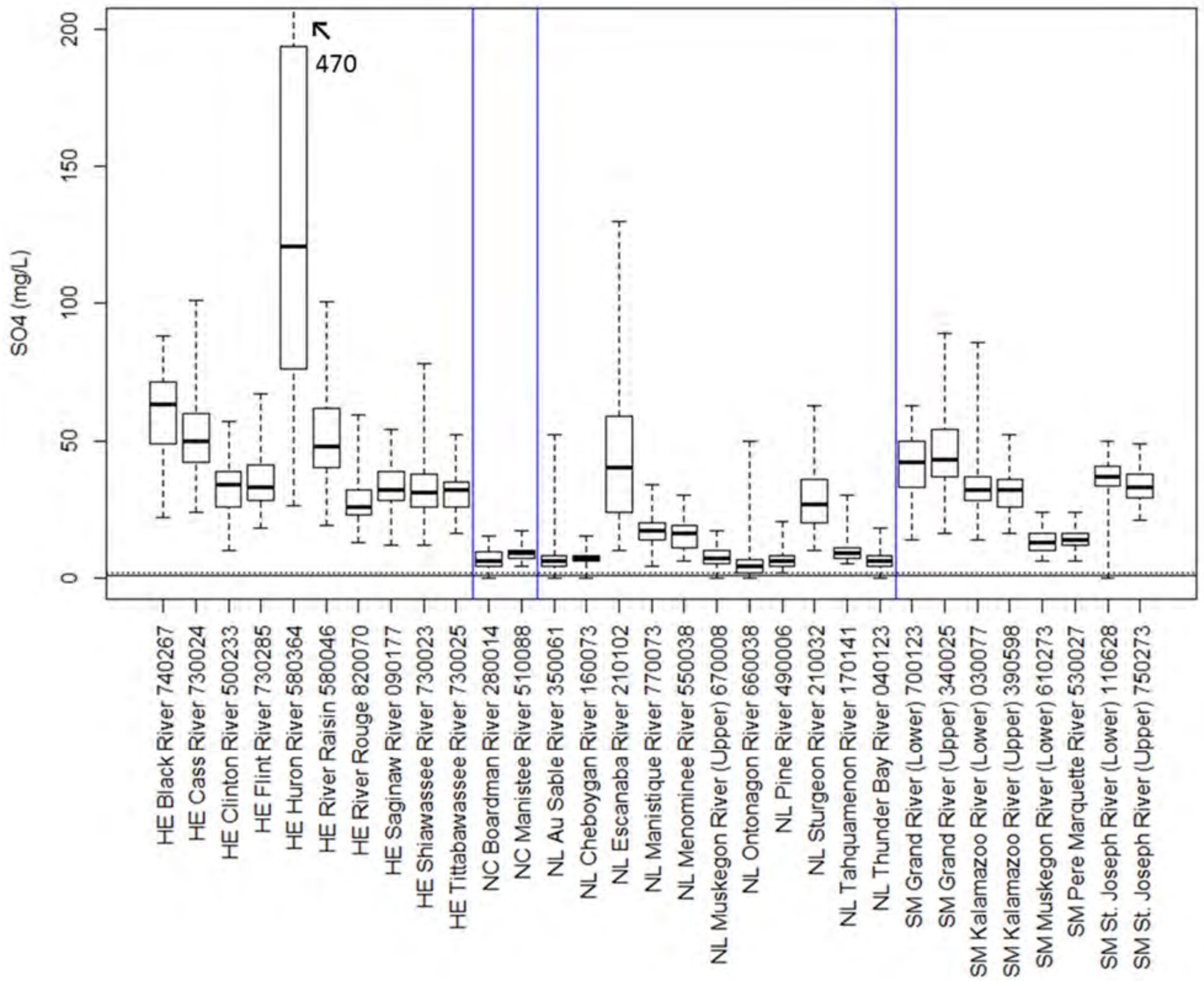


Figure 2-14. Sulfate concentrations at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (RL). Blue vertical lines separate ecoregions.

2.4.2.4. Chloride

Median chloride concentrations amongst all the main tributary sites ranged from 151.0 mg/L at the Clinton River (HELP ecoregion) to 2.0 mg/L at the Manistique, Sturgeon, and Tahquamenon Rivers (NLAF ecoregion) (Appendix C-1, Figure 2-15). The highest median concentrations were typically in the HELP and SMNIDP ecoregions; the top 16 medians amongst main sites were observed in these ecoregions. The Escanaba River had the 17th highest median overall and the highest median out of NLAF and NCHF ecoregion sites. Aside from the Escanaba River, chloride concentrations in the NLAF and NCHF ecoregions were much less variable than those in HELP and SMNIDP ecoregions (Appendix C-1).

Overall, 77% of the minimally impacted sites had lower median chloride concentrations than their associated (paired) main tributary sites (Appendix C-4). There were 7 cases (out of 30) where the minimally impacted sites had higher medians than their respective main sites (i.e., negative differences shown in Appendix C-4), including the River Rouge vs. Johnson Drain (a 71 mg/L difference between the medians).

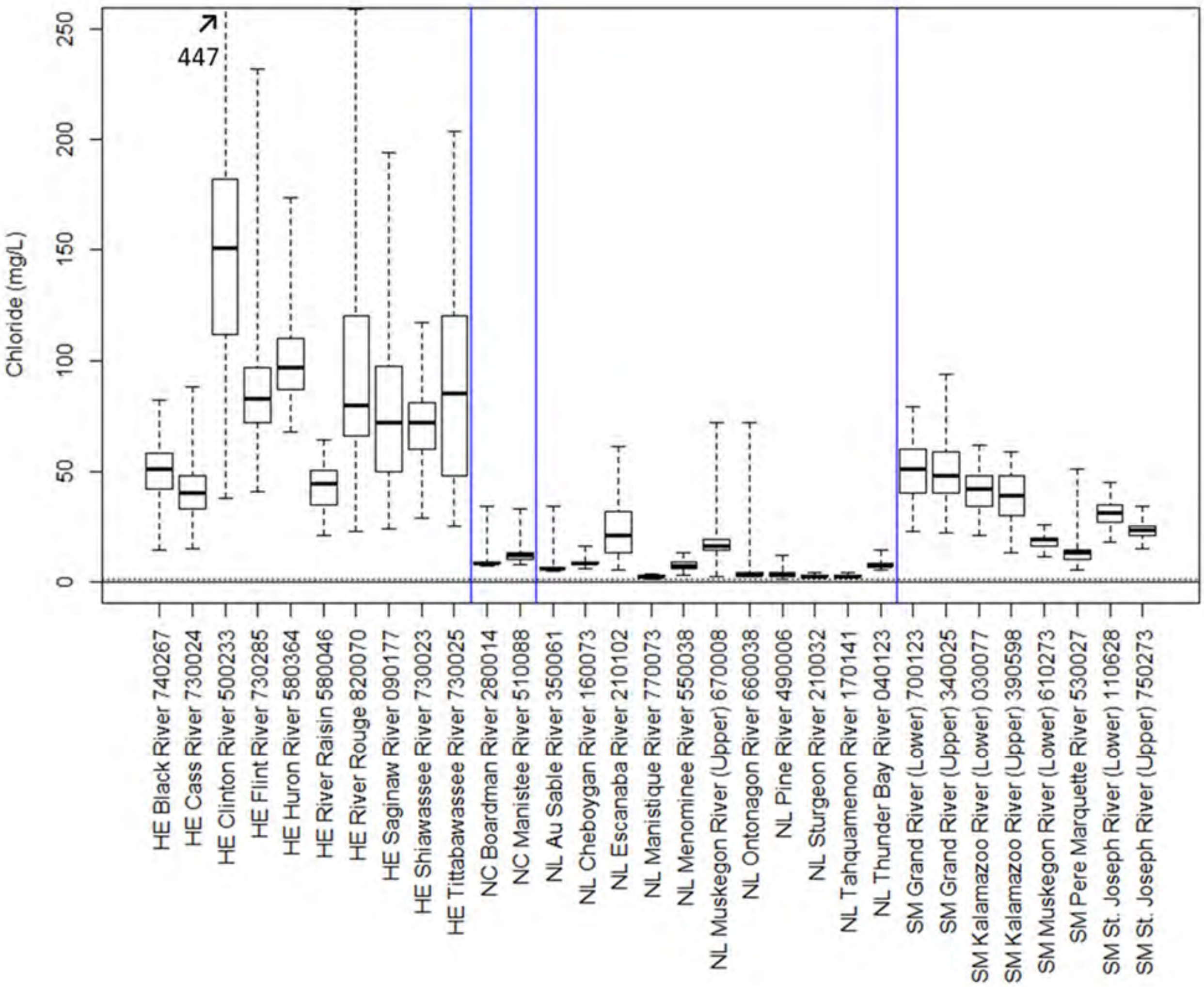


Figure 2-15. Chloride concentrations at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (RL). Blue vertical lines separate ecoregions.

Trends and Loading. Five Main tributary sites had a significant upward trend for chloride, with the strongest trend observed at the Black River site (5.43% per year) (Table 2-4; Hoard et al., 2018). One site, Cass River, had a significant downward trend (-1.70% per year). The highest mean annual loading of chlorides has consistently been found at the Saginaw River tributary site. From 2001-2013, the range was 193,000,000 to 297,000,000 kg/year (Appendix A-3). The Lower Grand River tributary site consistently had the second largest chloride loadings.

Chlorides occur naturally in rivers from the weathering of chloride containing minerals. In developed areas, however, chloride concentrations are dominated by agriculture and urban sources (Sonzogni et al., 1983). Amirsalari and Li (2007) found a positive correlation with impervious surface area and reduced water quality, including increased chloride concentrations. Many of the main sites having the highest chloride concentrations (Appendix C-1) are located in watersheds that have substantial amounts of urban development (and impervious surfaces) and/or agricultural land use (e.g., Clinton River, Huron River, Tittabawassee River, Flint River, River Rouge). Continuing to track chloride concentrations in surface waters in Michigan appears to be important given that continued use of road salts over many decades appears to be raising concerns over increased salinization of fresh waters in at least certain parts of the United States (e.g., the Northeast) (Kaushal et al., 2005), including in more rural parts of the state that may be experiencing growth in road length and other impervious surfaces.

2.4.2.5. Sodium

Median sodium concentrations amongst all the main tributary sites ranged from 88.0 mg/L at the Clinton River (HELP ecoregion) to 1.7 mg/L at the Sturgeon River (NLAF ecoregion) (Appendix C-1, Figure 2-16).

The highest median concentrations were typically in the HELP and SMNIDP ecoregions; the top 18 medians amongst main sites were observed in these ecoregions, with the exception of the Escanaba River. The Escanaba River had the fifth highest median overall and the highest median out of NLAF and NCHF ecoregion sites. Similar to chloride patterns, aside from the Escanaba River, sodium concentrations in the NLAF and NCHF ecoregions were much less variable than those in HELP and SMNIDP ecoregions (Appendix C-1).

Overall, 80% of the minimally impacted sites had lower median sodium concentrations than their associated main tributary sites (Appendix C-4). There were 5 cases (out of 30) where the minimally impacted sites had higher medians than their respective main sites (i.e., negative differences shown in Appendix C-4).

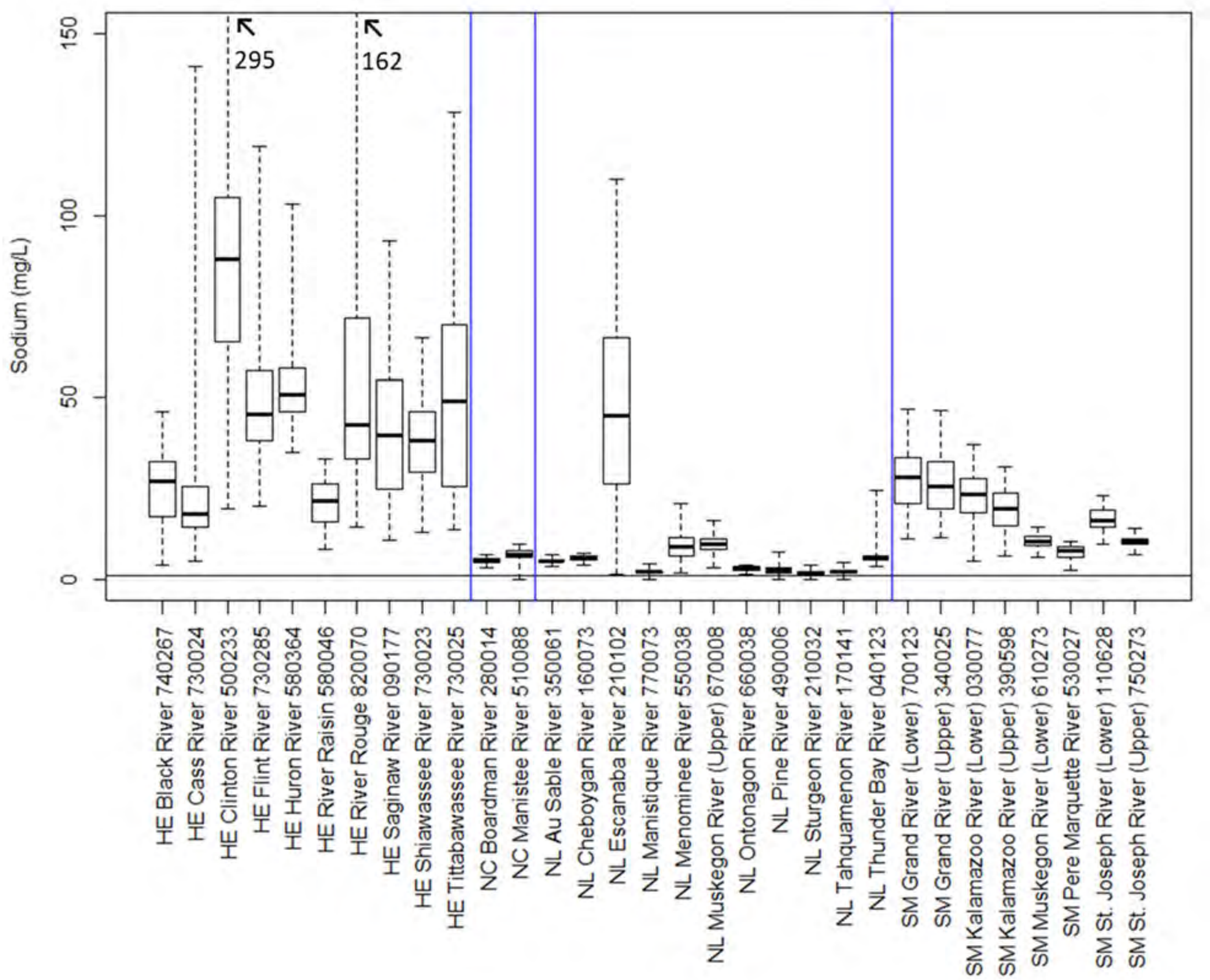


Figure 2-16. Sodium concentrations at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (RL). (*Note*: The detection limit and RL for sodium were the same [1.0 mg/L].) Blue vertical lines separate ecoregions.

2.4.2.6. Hardness and Specific Conductance

Median hardness values amongst all the main tributary sites ranged from 351 mg/L at the Huron River (HELP ecoregion) to 72 mg/L at the Tahquamenon River (NLAF ecoregion) (Appendix C-1, Figure 2-17). The highest median values were typically in the HELP and SMNIDP ecoregions; the top 15 medians amongst main sites were observed in these ecoregions. The Thunder Bay River had the 16th highest median overall and the highest median out of NLAF and NCHF ecoregion sites (Appendix C-1). Overall, 43% of the minimally impacted sites had lower median hardness values than their associated main tributary sites (Appendix C-4).

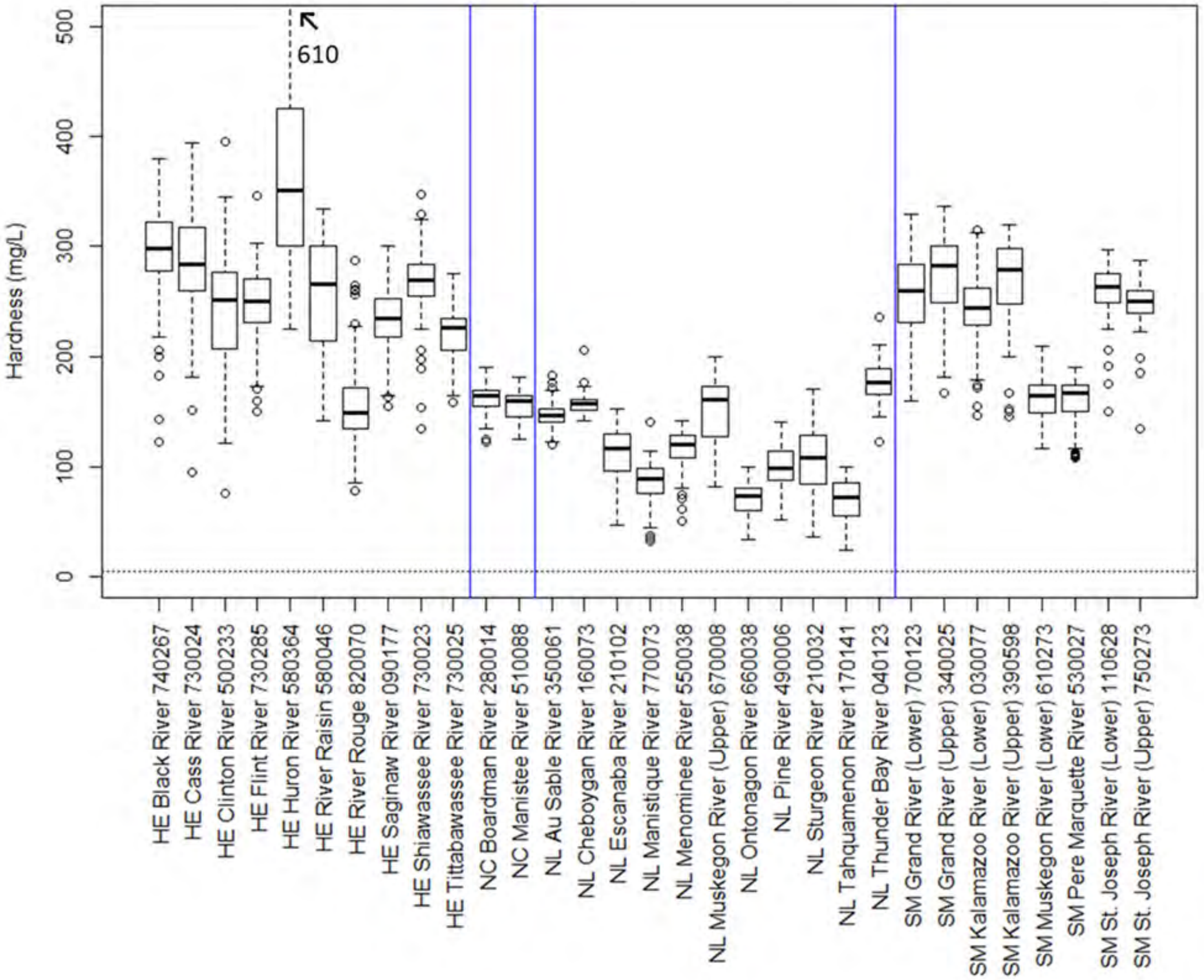


Figure 2-17. Hardness (calculated) at WCMP tributary stations from 1999-2013. Blue vertical lines separate ecoregions.

Median specific conductance values amongst all the main tributary sites ranged from 950 microsiemens per centimeter (µS/cm) at the Huron River (HELP ecoregion) to 149 µS/cm at the Tahquamenon River (NLAF ecoregion) (Appendix C-1, Figure 2-18). The highest median values were typically in the HELP and SMNIDP ecoregions; the top 16 medians amongst main sites were observed in these ecoregions. The Escanaba River had the 17th highest median overall and the highest median out of NLAF and NCHF ecoregion sites (Appendix C-1).

Overall, 67% of the minimally impacted sites had lower median specific conductance values than their paired main tributary sites (Appendix C-4).

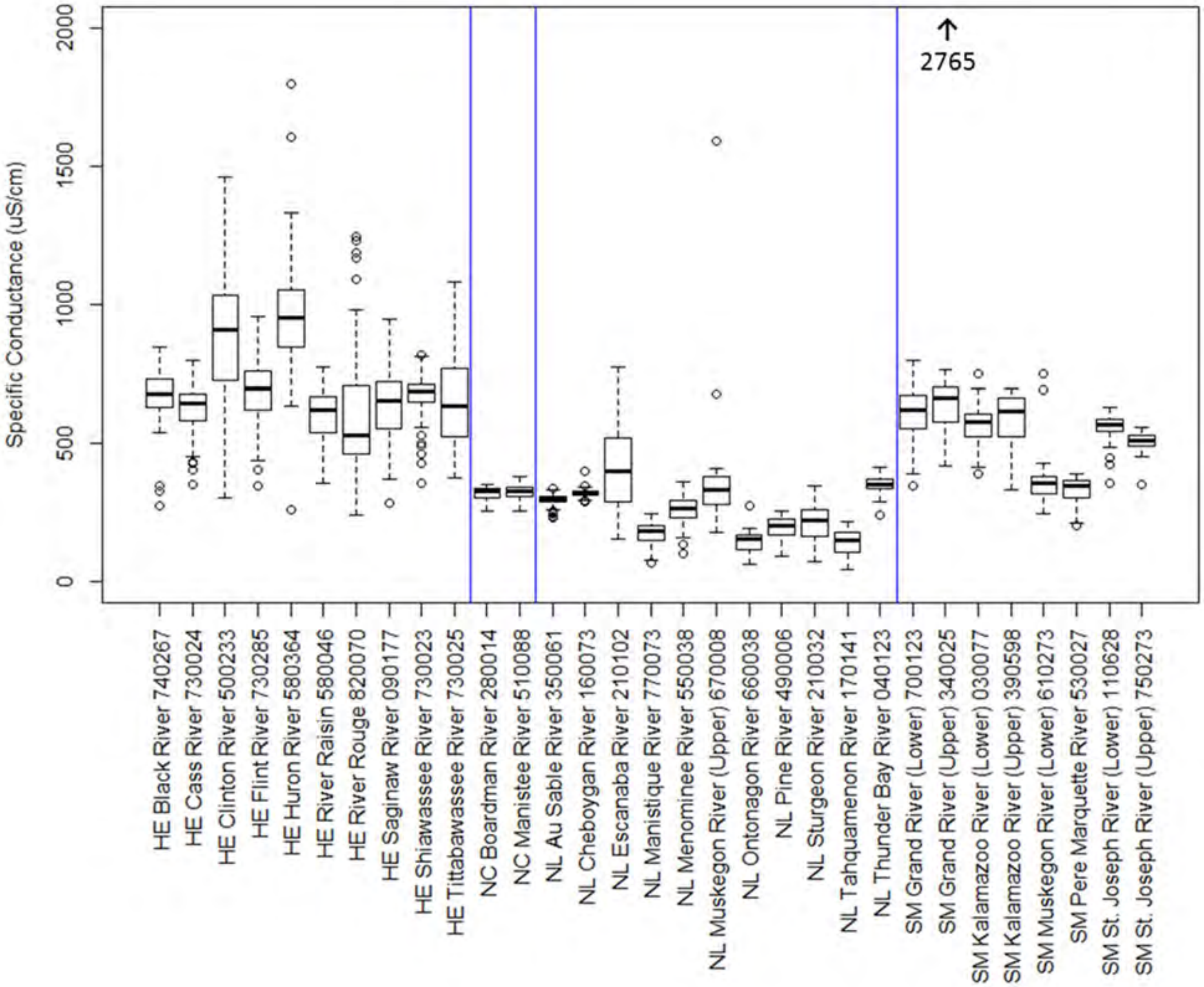


Figure 2-18. Specific conductance at WCMP tributary stations from 1999-2013. Blue vertical lines separate ecoregions.

2.4.2.7. Total Suspended Solids

Median TSS concentrations amongst all the main tributary sites ranged from 25 mg/L at the Flint River (HELP ecoregion) to 4 mg/L at multiple sites in the NLAF and NCHF ecoregions (Appendix C-1, Figure 2-19). The highest median concentrations were typically in the HELP and SMNIDP ecoregions; the top 13 medians amongst main sites were observed in these ecoregions, with the exception of the Pine River (NLAF ecoregion), which had the fourth highest median. The Ontonagon River had the 14th highest median overall and the highest median out of the remaining NLAF and NCHF ecoregion sites (Appendix C-1).

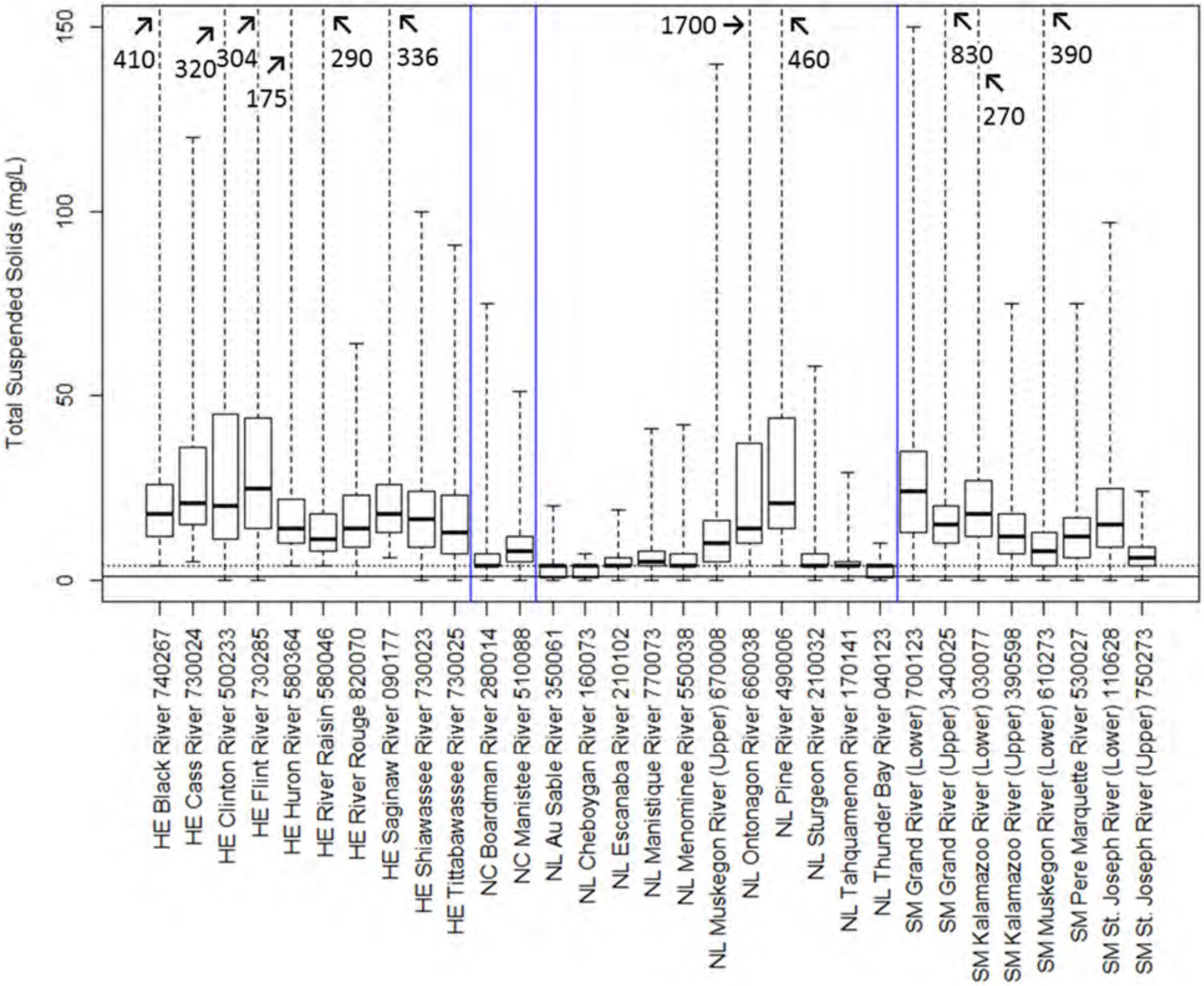


Figure 2-19. TSS at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (RL). Blue vertical lines separate ecoregions.

Overall, 63% of the minimally impacted sites had lower median TSS values than their associated Main tributary sites (Appendix C-4).

Trends and Loading. TSS results were below quantification at a frequency that precluded trend analysis to be run at 5 main locations (see Hoard et al., 2018). The only significant trends that were observed were all downward, ranging from -3.78% (lower Grand River) to -6.76% (upper Grand River) per year (Table 2-4; Hoard et al., 2018). TSS loading estimates were not as precise compared with other parameters given their often large confidence intervals. Results are presented in Appendix A-3; however, it is difficult to draw conclusions based on these data.

2.4.2.8. Alkalinity

Median total alkalinity concentrations amongst all the main tributary sites ranged from 227 mg/L at the Kalamazoo River (Upper) (SMNIDP ecoregion) to 53 mg/L at the Tahquamenon River in the NLAF (Appendix C-1, Figure 2-20). The highest median concentrations were typically in the HELP and SMNIDP ecoregions; the top 14 medians amongst main sites were observed in these ecoregions. The Thunder Bay River had the 15th highest median overall and the highest median out of the remaining NLAF and NCHF ecoregion sites (Appendix C-1). Alkalinity followed the same general pattern as hardness and TDS, generally being higher in the HELP and southern regions of the SMNIDP ecoregions. The lowest median values were found at Upper Peninsula tributary sites of the NLAF ecoregion. (Note: Three alkalinity data points were dropped from the Ontonagon River site [STORET 660038] during the months of May-June 2013 due to sample dilutions by the laboratory that resulted in negative reported results.)

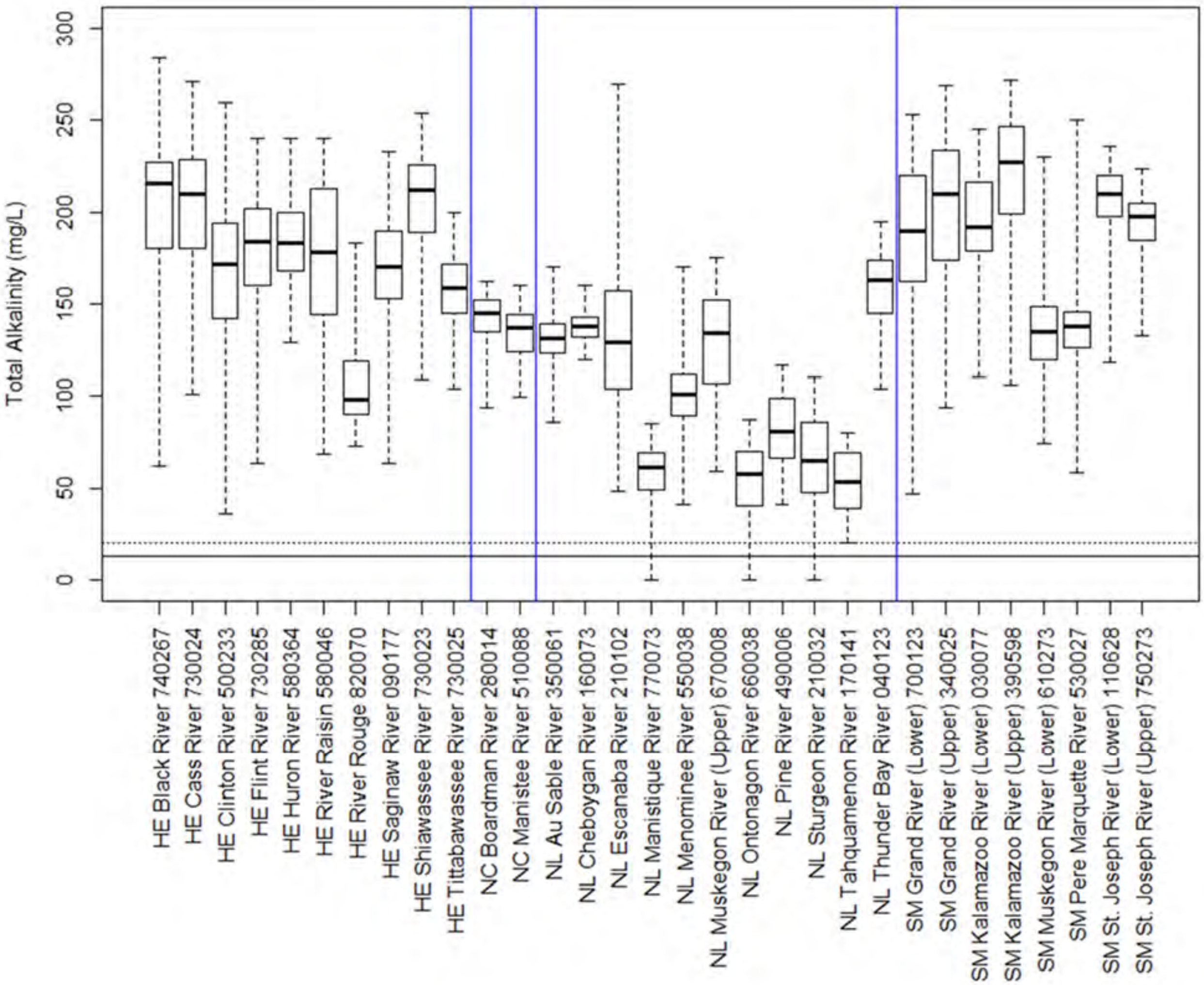


Figure 2-20. Total alkalinity concentrations at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (RL). Blue vertical lines separate ecoregions.

Overall, 73% of the minimally impacted sites had higher median alkalinity values than their paired main tributary sites (Appendix C-4).

2.4.2.9. pH

Median pH amongst all the main tributary sites ranged from 8.3 at the Cheboygan River (NLAF ecoregion) to 7.4 at the Tahquamenon River in the NLAF (Appendix C-1, Figure 2-21). The six sites with the lowest median pH values included 4 sites in the NLAF ecoregion in the Upper Peninsula (Ontonagon, Sturgeon, Manistique, and Tahquamenon Rivers) and two urban sites in the HELP ecoregion (Clinton River and River Rouge) (Appendix C-1).

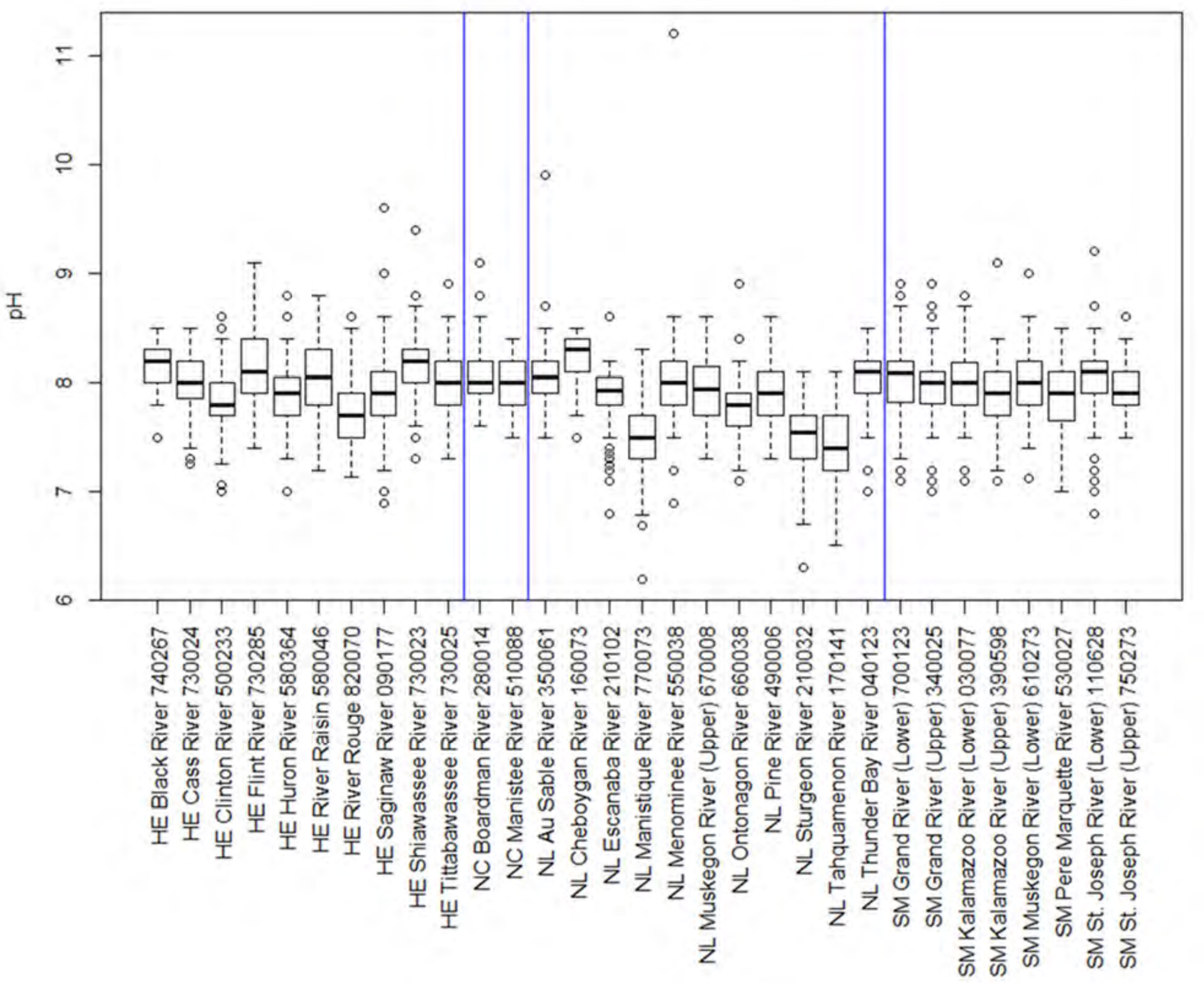


Figure 2-21. pH at WCMP tributary stations from 1999-2013. Blue vertical lines separate ecoregions.

2.4.2.10. DO

Median DO values amongst all the main tributary sites ranged from 10.6 mg/L at the Boardman River (NCHF ecoregion) to 6.4 mg/L at the River Rouge (HELP ecoregion) (Appendix C-1, Figure 2-22). The lowest median values were typically in the HELP and SMNIDP ecoregions; the lowest 7 medians amongst main sites were observed in these ecoregions. Overall, 77% of the minimally impacted sites had higher median DO values than their paired main tributary sites (Appendix C-4).

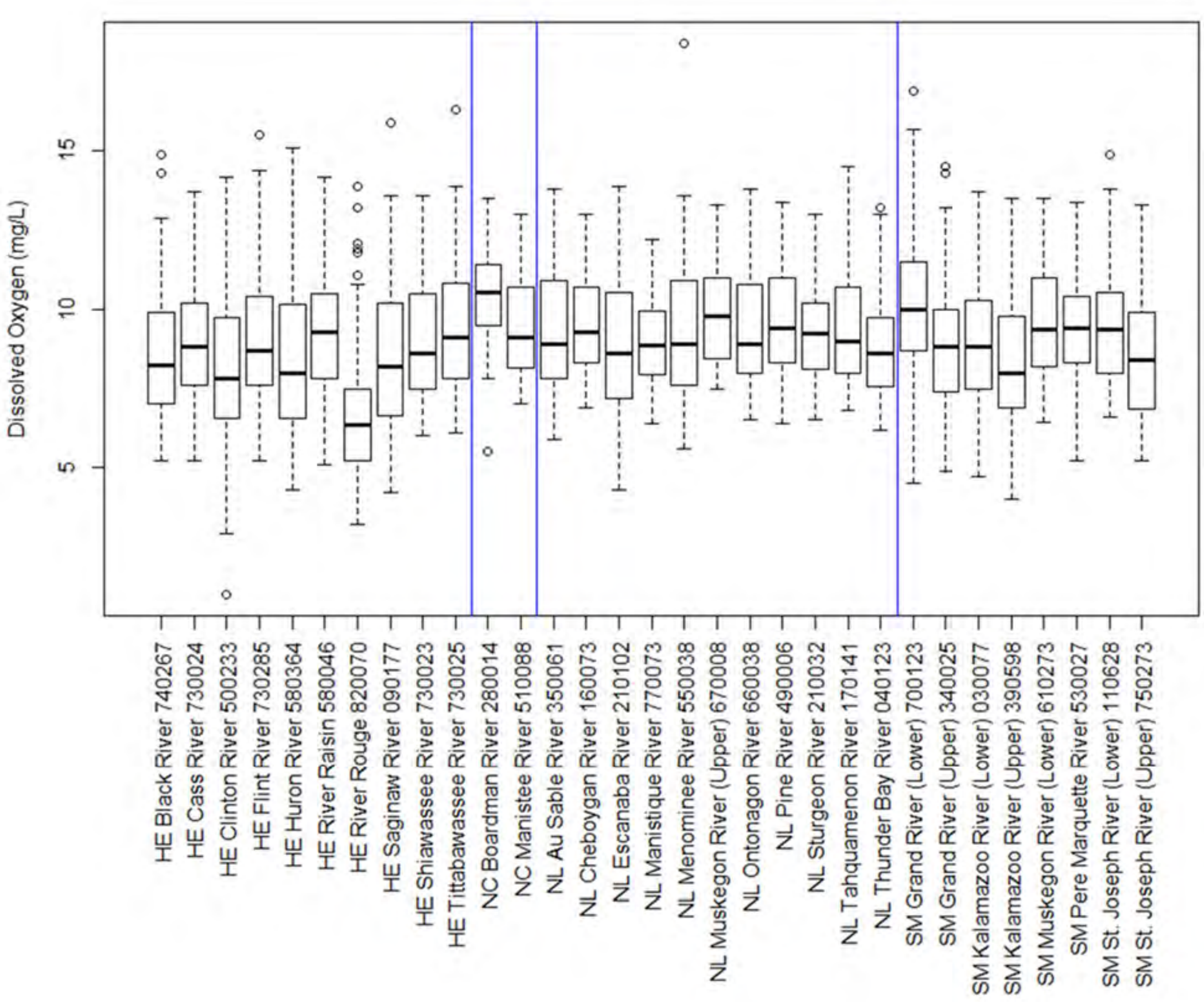


Figure 2-22. DO at WCMP tributary stations from 1999-2013. Blue vertical lines separate ecoregions.

2.4.3. Trace Metals

Overview Regarding Trace Metals and WQS

Using Rule 57 Water Quality Values (MDEQ, 2018) that were last revised December 1, 2015, all ambient data for Great Lakes tributary sites (both main and minimally impacted; see Tables 2-1 and 2-2) from 1998-2013 were compared against existing FCV and AMV WQS for the Other Indigenous Aquatic Life and Wildlife and the Coldwater/Warmwater Fisheries designated uses. (This exercise was done mainly for illustrative purposes only in this report in order to help put the data in context. Per MDEQ [2016b], the latest WQS and assessment methodologies are generally used on the most recent available 2-year dataset when performing official assessments for each biennial Integrated Report, and not on multi-year, historical datasets.) Overall, exceedances of trace metal WQS were found to be rare throughout the 1998-2013 time period. The following is a summary of those analyses.

FCV Exceedances (1998-2013):

Using the Rule 57 Water Quality Values, copper and/or zinc exceeded FCV WQS at a total of 2 sites out of 59 Great Lakes tributary sites from 1998-2013 after taking into account concurrently-collected hardness data, and then only rarely at those 2 sites.

Copper FCVs were exceeded at 2 sites (Clinton River, STORET 500233; Ontonagon River, STORET 660038) out of the 59 sites, though for the Clinton River there were not enough exceedances (2 or more) within a 2-year time frame to list the river reach as impaired. Zinc was exceeded at 1 site on 1 occasion (Clinton River, STORET 500233).

No other measured trace metals (nickel, chromium, lead, cadmium) were observed above WQS values.

Trace Metal	# of Exceedances	# of Samples	% Exceedance
Cadmium	0	1,150	0.00%
Chromium	0	3,070	0.00%
Copper	10	3,104	0.32%
Lead	0	3,169	0.00%
Nickel	0	1,346	0.00%
Zinc	1	1,153	0.09%

AMV Exceedances (1998-2013):

Using the Rule 57 Water Quality Values, copper and/or zinc exceeded AMV WQS at a total of 2 sites out of the 59 Great Lakes tributary sites overall from 1998-2013 after taking into account concurrently-collected hardness data, and then only rarely at those 2 sites.

Copper AMVs were exceeded at 2 of the 59 sites (Clinton River, STORET 500233; Ontonagon River, STORET 660038). Zinc was exceeded at 1 site on one occasion (Clinton River, STORET 500233).

No other measured trace metals (nickel, chromium, lead, cadmium) were observed above WQS values.

Trace Metal	# of Exceedances	# of Samples	% Exceedance
Cadmium	0	1,150	0.00%
Chromium	0	3,070	0.00%
Copper	4	3,104	0.13%
Lead	0	3,169	0.00%
Nickel	0	1,346	0.00%
Zinc	1	1,153	0.09%

2.4.3.1. Chromium

Median total chromium concentrations amongst all the main tributary sites ranged from 1.540 µg/L at the Clinton River (HELP ecoregion) to 0.080 µg/L at the Au Sable River (NLAF ecoregion) (Appendix C-1, Figure 2-23). Regional patterns were not as clear as most of the parameters discussed thus far. The HELP ecoregion had the highest (Clinton River), second highest (River Rouge), and fourth highest (Flint River) median chromium concentrations, while the NLAF ecoregion had the third (Pine River) and fifth (Ontonagon River) highest median values. The Lower Grand River had the sixth highest median value, and the highest median value of all the SMNIDP ecoregion sites (Appendix C-1).

Overall, 80% of the minimally impacted sites had lower median total chromium values than their associated (paired) main tributary sites. In the Au Sable River watershed (NLAF ecoregion), however, Perry Creek had a median that was more than double that of the next largest minimally impacted site median (i.e., 0.874 µg/L at the Paint River in the Menominee River watershed, NLAF), and its median (2.160 µg/L) was 27 times greater than that of its associated main site on the Au Sable River (0.080 µg/L) (Appendix C-4). Per Roush (2013), EGLE is aware that there has been a contaminated groundwater plume that vents into Perry Creek approximately two miles upstream of the minimally impacted site. Some sediment and groundwater cleanup and source removal work was performed in 2008 to deal with contaminants including perchloroethylene, hexavalent chromium, and chlorides (Roush, 2013).

Trends and Loading. Similar to the findings in Roush (2013), a number of main tributary sites (9 in the current report) had a significant upward trend for chromium. The strongest trend was observed at the Au Sable River (26.73% per year) (Table 2-4; Hoard et al., 2018). No significant downward trends were observed among the main sites. Chromium showed many of the strongest upward significant trends (in terms of %) amongst all the water quality parameters that had trends evaluated. (The only other parameter that had a site with an upward significant trend greater than 12% per year was orthophosphate, with a 21% trend at the Black River). Chromium had 5 sites with trend percentages greater than 12% per year; the greatest trend percentage was observed at the Au Sable River (26.73%). Four of these 5 sites were in the NLAF ecoregion; the fifth site (upper St. Joseph River) was in the SMNIDP ecoregion. It is important to point out that the sites with the 5 largest, significant upward trends (Au Sable, Boardman, Thunder Bay, Cheboygan, and upper St. Joseph River) also had the 5 lowest median concentrations (< 0.220 µg/L) (see below and Appendix C-1). According to Schertz et al. (1991), the magnitude of statistically significant trend slopes may not always be environmentally important when compared with criteria such as WQS.

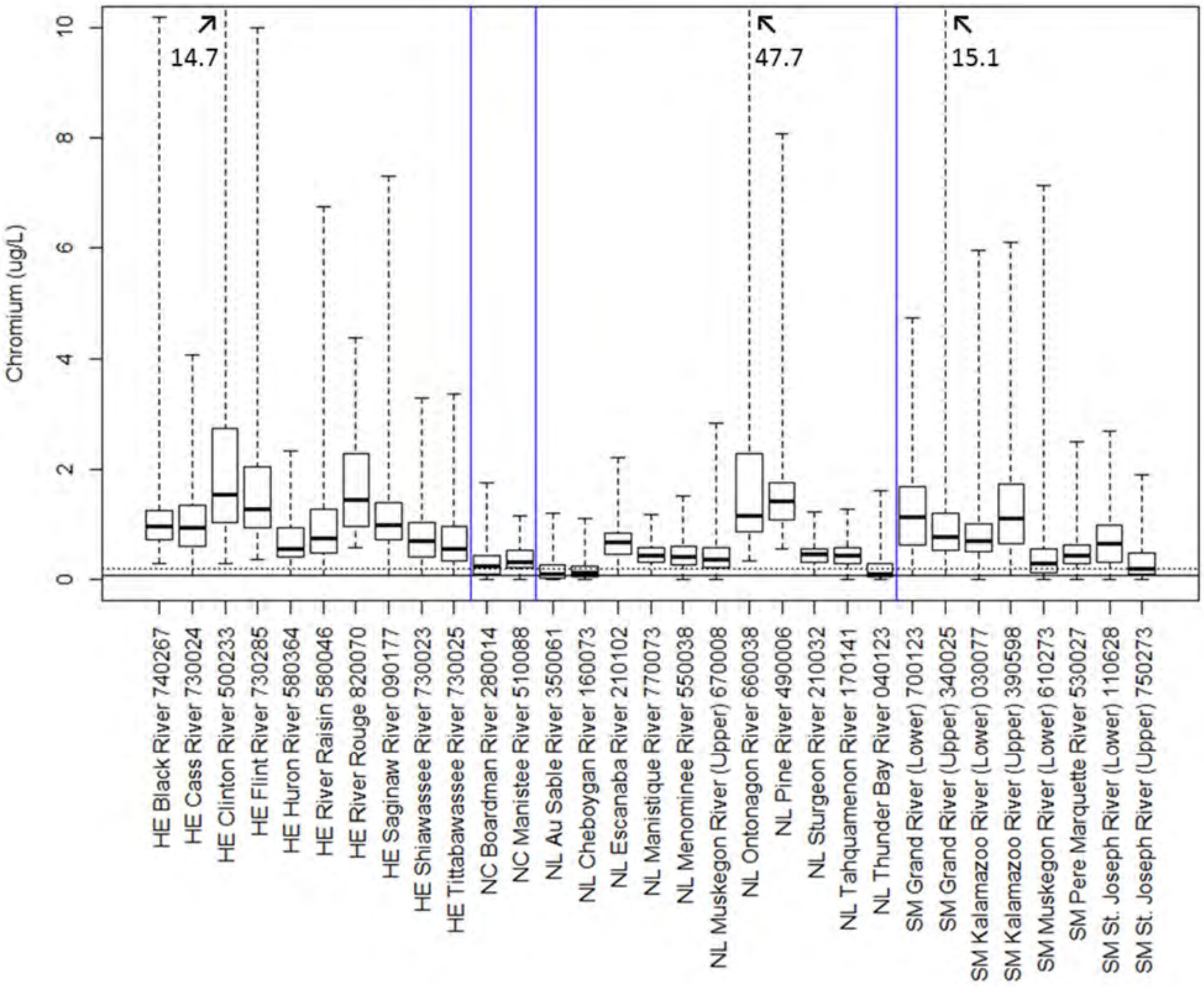


Figure 2-23. Total chromium concentrations at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (RL). Blue vertical lines separate ecoregions.

The highest mean annual chromium loadings were typically from the Saginaw River and Lower Grand River tributary sites, which were as high as 12,100 and 9,144 mean kg/year (confidence intervals 42% and 34%), respectively (Appendix A-3). The exception to the above pattern was in 2008, and to a lesser extent in 2013, when the Ontonagon River tributary site (an integrator site) was sampled intensively. In 2008, this site had the highest mean loading rate of any year at 18,700 kg/year (with a confidence interval of 94%); in 2013 this site's mean loading rate was the ninth highest (of any year) at 9,021 kg/year (with a confidence interval of 59%) (Appendix A-3). The large confidence intervals indicate that loads are highly variable at this site within a year. Per Roush (2013), chromium concentrations appear to increase with rain events at the Ontonagon River tributary site, which makes a loading estimate difficult to ascertain with only 12 data points. This site's overall (2001-2013) median concentration was 1.15 µg/L, with results reaching 47.7 µg/L on May 10, 2006, and 28.5 µg/L on April 17, 2008; both of these high concentration days had considerable rain events. There are no known industries in the area that are associated with chromium processes; and QA/QC data taken on these dates were within acceptable data ranges (Roush, 2013).

Criteria. To illustrate how WCMP concentrations compare to Michigan's WQS, and because there were no WQS exceedances in this dataset, we can examine the highest chromium concentration found at a Great Lakes tributary site in the time period 1998-2013. The main site on the Ontonagon River had a total chromium value of 47.7 µg/L and a hardness value of 70 mg/L on May 10, 2006. At this hardness, the WQS are 83.0 µg/L (FCV) and 638.1 µg/L (AMV), neither of which was exceeded. As a second example (at a lower hardness but still a relatively high chromium value), the main site on the Ontonagon River had a total chromium value of 28.5 µg/L and a hardness value of 40 mg/L on April 17, 2008. At this hardness, the WQS are 52.5 µg/L (FCV) and 403.5 µg/L (AMV), neither of which was exceeded.

Please note these data are for total chromium. In ambient water, trivalent (Cr III) and hexavalent (Cr VI) chromium are the predominant valence states (USEPA, 1980). Trivalent chromium toxicity, like many heavy metals, varies with water quality characteristics and has a WQS dependent on hardness. Hexavalent chromium is not affected by water hardness. The Michigan chronic and acute WQS for the dissolved form of hexavalent chromium are 11 µg/L (FCV) and 16 µg/L (AMV), respectively (MDEQ, 2018).

2.4.3.2. Copper

Median total copper concentrations amongst all the main tributary sites ranged from 3.67 µg/L at the Clinton River (HELP ecoregion) to 0.25 µg/L at the Au Sable River (NLAF ecoregion) (Appendix C-1, Figure 2-24).

The highest median copper concentrations were typically in the HELP and SMNIDP ecoregions. The top 16 medians amongst main sites were observed in these ecoregions, with one notable exception: the Ontonagon River in the western Upper Peninsula of the NLAF ecoregion had the second highest median of all the main sites (3.27 µg/L). The next highest NLAF median was at the Pine River, with the 17th highest median overall and the highest median out of the remaining NLAF and NCHF ecoregion sites (Appendix C-1). Overall, 90% of the minimally impacted sites had lower median total copper values than their paired main tributary sites (Appendix C-4).

The Ontonagon River is located in Michigan's western Upper Peninsula, a region recognized for its important commercial deposits of native copper (Courter, 1992; Wilband, 1978). This condition likely explains the high concentrations found at the Ontonagon River site.

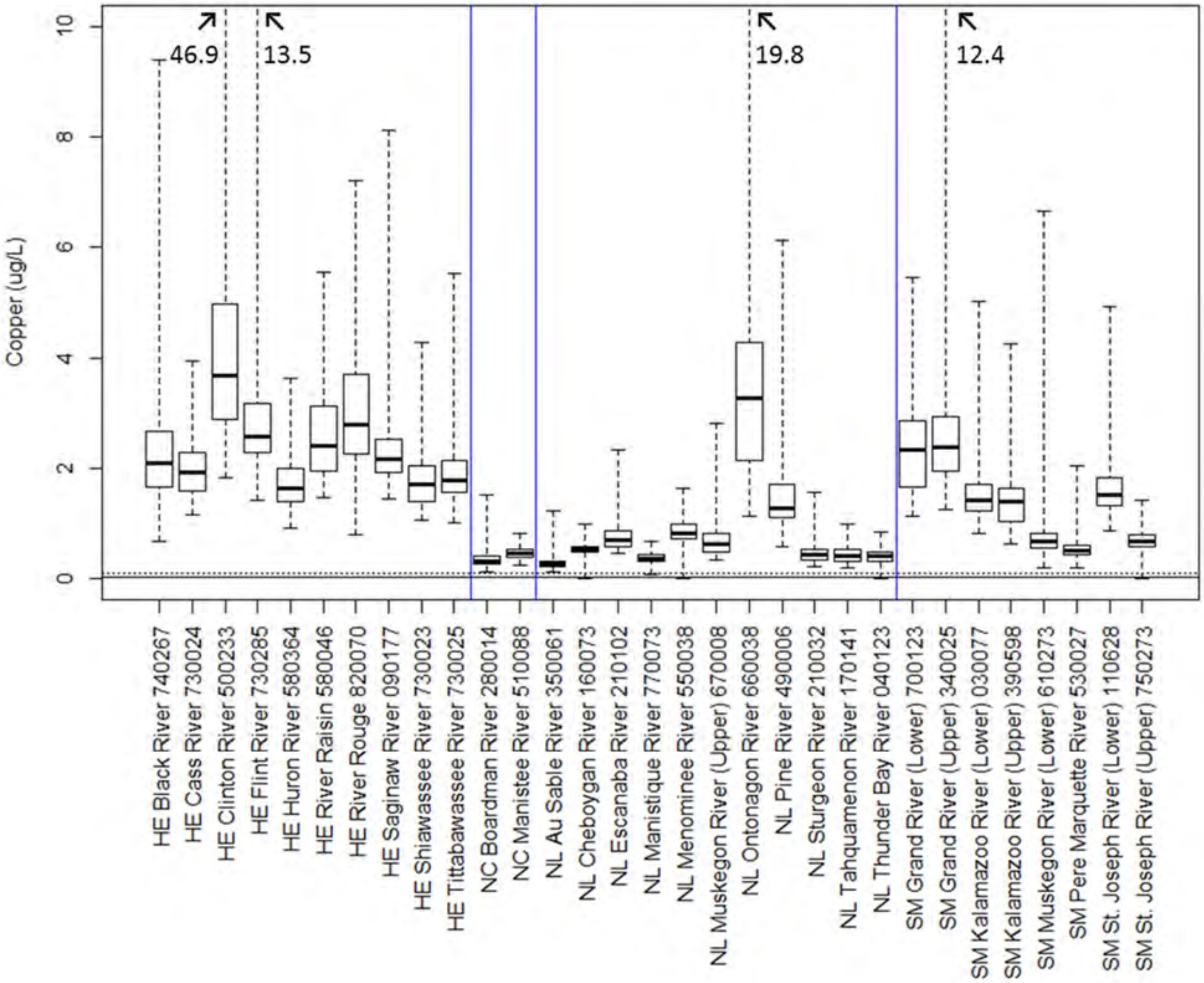


Figure 2-24. Total copper concentrations at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (RL). Blue vertical lines separate ecoregions.

Trends and Loading. The only significant trends observed for copper at main sites were downward, ranging from -1.37% per year at the lower Kalamazoo River site to -3.32% per year at the Escanaba River site (Table 2-4; Hoard et al., 2018). The highest copper loadings were typically from the Saginaw River and Lower Grand River tributary sites, ranging as high as 19,400 kg/year (+/- 31 percent) and 14,856 kg/year (+/- 13 percent), respectively (Appendix A-3). However, similar to chromium, there were some exceptions. The Ontonagon River integrator site was sampled in 2008 for loading estimates and had the second highest mean annual rate (18,300 kg/year) of any year, while the 2013 sampling there had the tenth highest mean annual rate (14,549 kg/year) of any year. Note there is a lot of uncertainty around the load estimates as indicated by their confidence intervals of 85% and 50%, respectively, perhaps due to seasonal variability. Similar to chromium, copper concentrations were variable at this tributary site (ranging from 1.1-46.9 µg/L), which makes a loading estimate difficult to ascertain with only 12 data points (Roush, 2013).

Criteria. To illustrate how WCMP concentrations compare to Michigan's WQS, we can examine the highest copper concentration found at a Great Lakes tributary site in the time period 1998-2013. The main site on the Ontonagon River had a total copper value of 46.9 µg/L and a hardness value of 70 mg/L on May 10, 2006. At this hardness, the WQS are 9.9 µg/L (FCV) and 14.4 µg/L (AMV), both of which were exceeded.

2.4.3.3. Lead

Median total lead concentrations amongst all the main tributary sites ranged from 2.060 µg/L at the River Rouge (HELP ecoregion) to 0.037 µg/L at the Au Sable River (NLAF ecoregion) (Appendix C-1, Figure 2-25). The highest median concentrations were typically in the HELP and SMNIDP ecoregions; the top 14 medians amongst main sites were observed in these ecoregions. The Pine River (NLAF ecoregion) had the 15th highest median overall and the highest median out of the remaining NLAF and NCHF ecoregion sites (Appendix C-1). Overall, 80% of the minimally impacted sites had lower median total lead values than their associated (paired) main tributary sites (Appendix C-4).

Trends and Loading. The only significant upward trend for lead at main sites was 3.83% per year at the Ontonagon River site (Table 2-4; Hoard et al., 2018). The remaining significant trends were all downward and ranged from -1.80% per year at the Menominee River to -6.26% per year at the lower St. Joseph River. The largest loading estimates for lead were for the Saginaw River and Lower Grand River tributary sites; however, the confidence intervals for these estimates were routinely high, especially for the Saginaw River (e.g., 92%, 154%, and 126% in 2006, 2013, and 2002, respectively) (Appendix A-3). Of note, the lower St. Joseph River had the seventh highest loading estimate (of any year) in 2001, with an estimated mean annual load of 8,886 kg/year.

Criteria. To illustrate how WCMP concentrations compare to Michigan's WQS, we can examine the highest lead concentration found at a Great Lakes tributary site in the time period 1998-2013. The main site on the Clinton River had a total lead value of 50.8 µg/L and a relatively low hardness value of 58 mg/L on August 6, 1998. At this hardness, the WQS are 60.2 µg/L (FCV) and 577.6 µg/L (AMV), neither of which was exceeded.

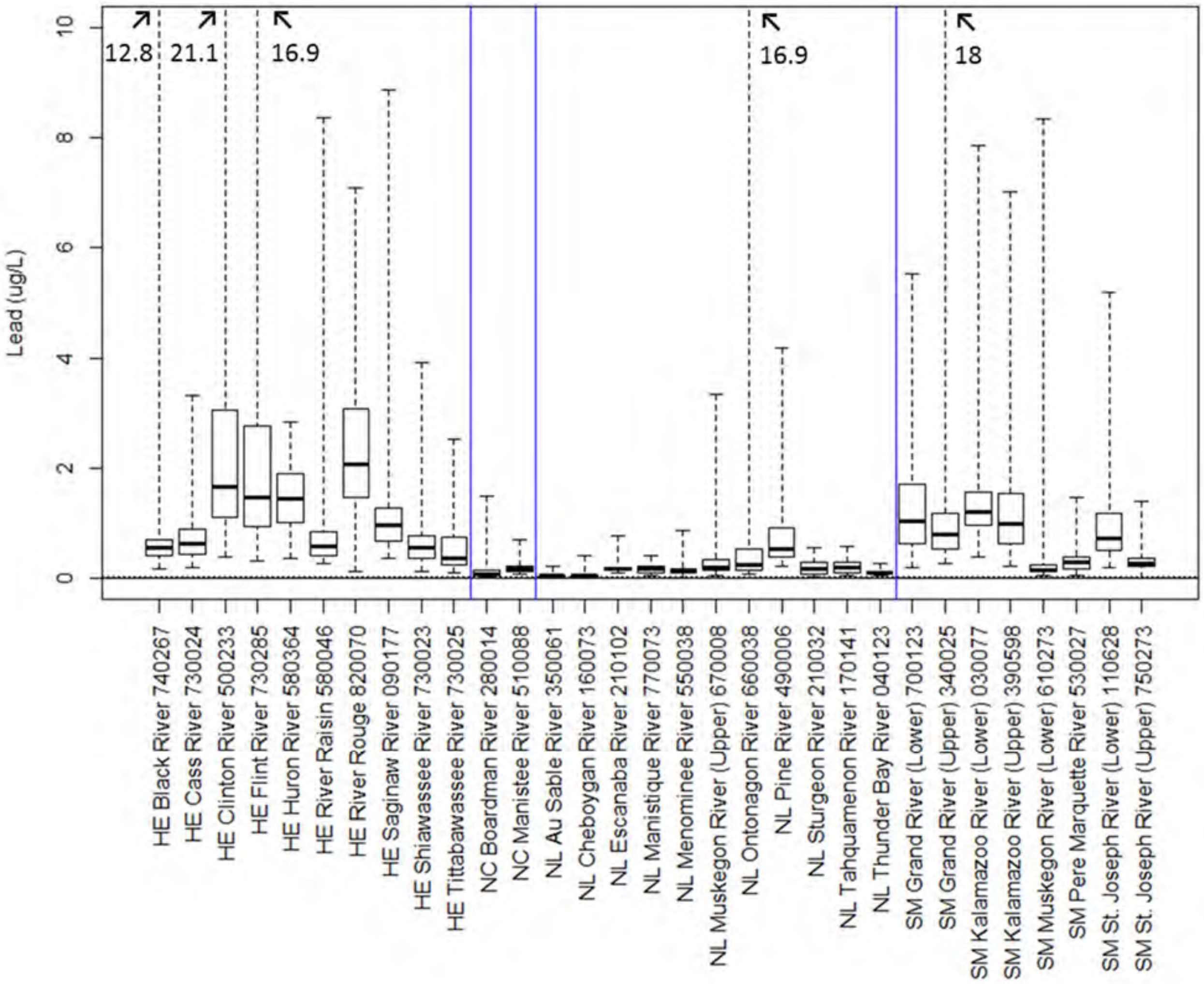


Figure 2-25. Total lead concentrations at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (RL). Blue vertical lines separate ecoregions.

2.4.3.4. Cadmium, Nickel, and Zinc

Sampling for total cadmium, total nickel, and total zinc at Great Lakes tributary sites ceased at the end of 2005; however, highlights of that sampling will still be briefly discussed here.

The Clinton River (HELP ecoregion) had the highest median nickel and zinc concentrations amongst all the main tributary sites, while the River Rouge (HELP ecoregion) had the highest median cadmium concentrations (Appendix C-1; Figures 2-26, 2-27, and 2-28). The highest concentrations of these metals tended to be in the HELP and SMNIDP ecoregions; however, there were some notable exceptions. The Escanaba River (NLAF ecoregion) had the third highest median cadmium concentration and the ninth highest median zinc concentration (Appendix C-1).

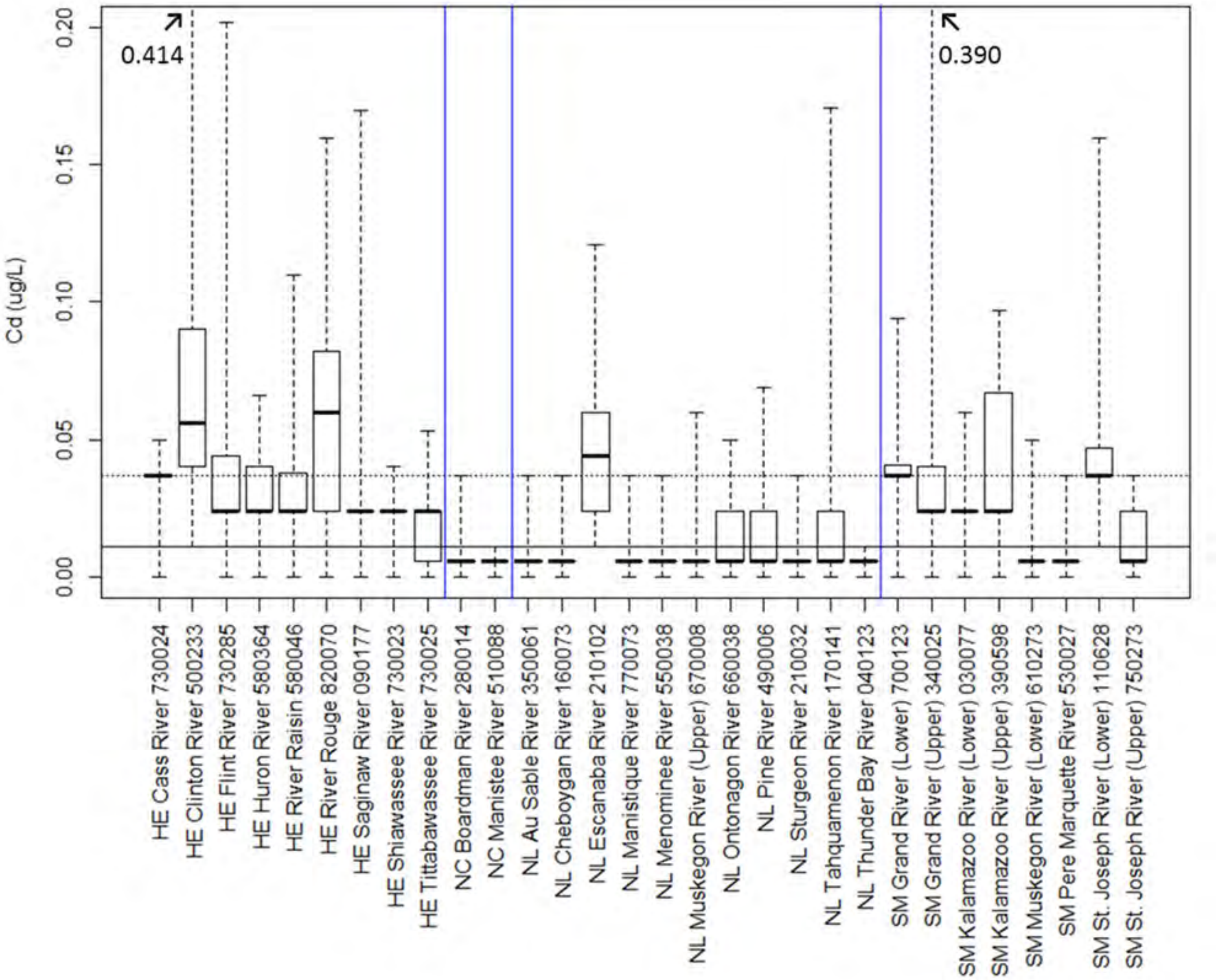


Figure 2-26. Total cadmium concentrations at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (RL). Blue vertical lines separate ecoregions.

Overall, 37%, 73%, and 70% of the minimally impacted sites had lower median cadmium, nickel, and zinc values, respectively, than their associated main tributary sites (Appendix C-4).

Criteria. To illustrate how WCMP concentrations compare to Michigan's WQS, we can examine the zinc concentration found at a Great Lakes tributary site in the time period 1998-2013 that exceeded WQS. (Zinc was the only metal out of cadmium, nickel, and zinc to ever exceed WQS criteria at WCMP tributary sites from 1998-2014.) The main site on the Clinton River had a total zinc value of 222.9 µg/L and a hardness value of 58.0 mg/L. At this hardness, the WQS are 156.4 µg/L (FCV) and 155.1 µg/L (AMV), both of which was exceeded.

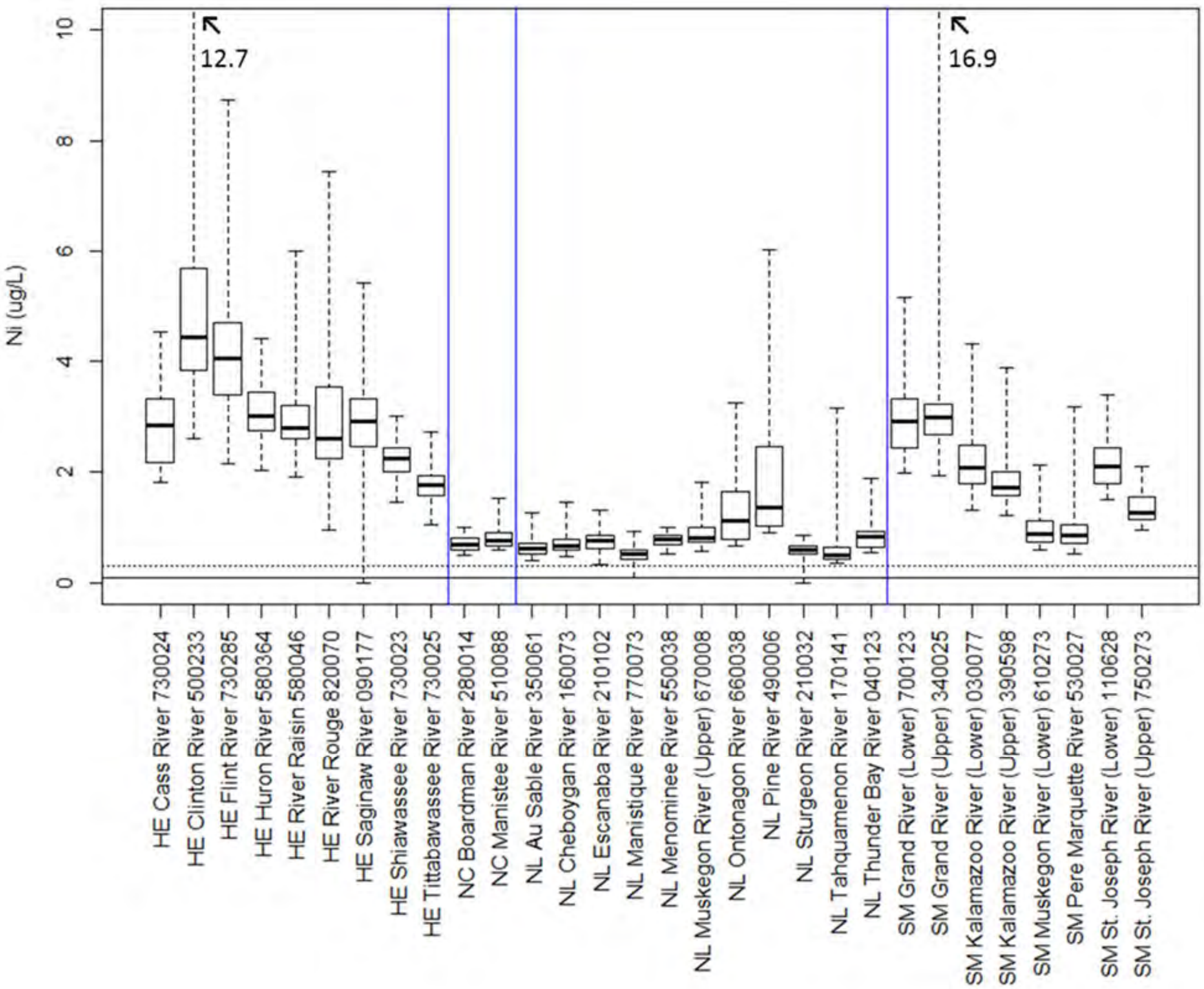


Figure 2-27. Total nickel concentrations at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (RL). Blue vertical lines separate ecoregions.

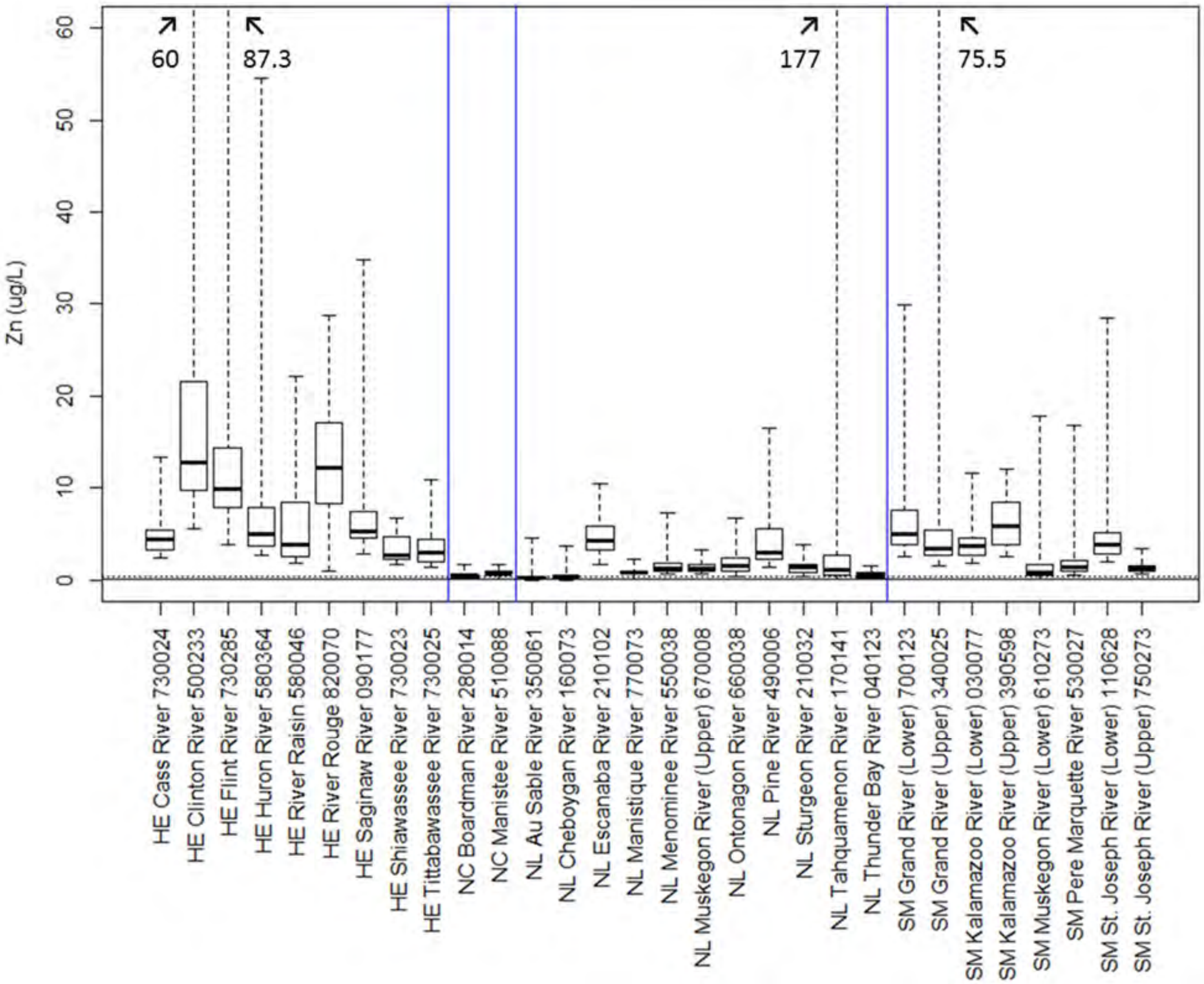


Figure 2-28. Total zinc concentrations at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (RL). Blue vertical lines separate ecoregions.

2.4.3.5. Mercury

Median total mercury concentrations amongst all the main tributary sites ranged from 5.21 ng/L at the Kalamazoo River (Lower) (SMNIDP ecoregion) to 0.45 ng/L at both the Cheboygan River and Au Sable River (NLAF ecoregion) (Appendix C-1, Figures 2-29 [large y-axis] and 2-30 [small y-axis]). The second highest value was at the Kalamazoo River (Upper) (SMNIDP). Unlike many of the other parameters discussed in this report, there was no clear pattern by ecoregion for mercury. The top 2 sites were in the SMNIDP ecoregion, the third and fourth highest were from the NLAF ecoregion, the fifth highest was from the HELP ecoregion. Overall, 80% of the minimally impacted sites had lower median total mercury values than their associated main tributary sites (Appendix C-4).

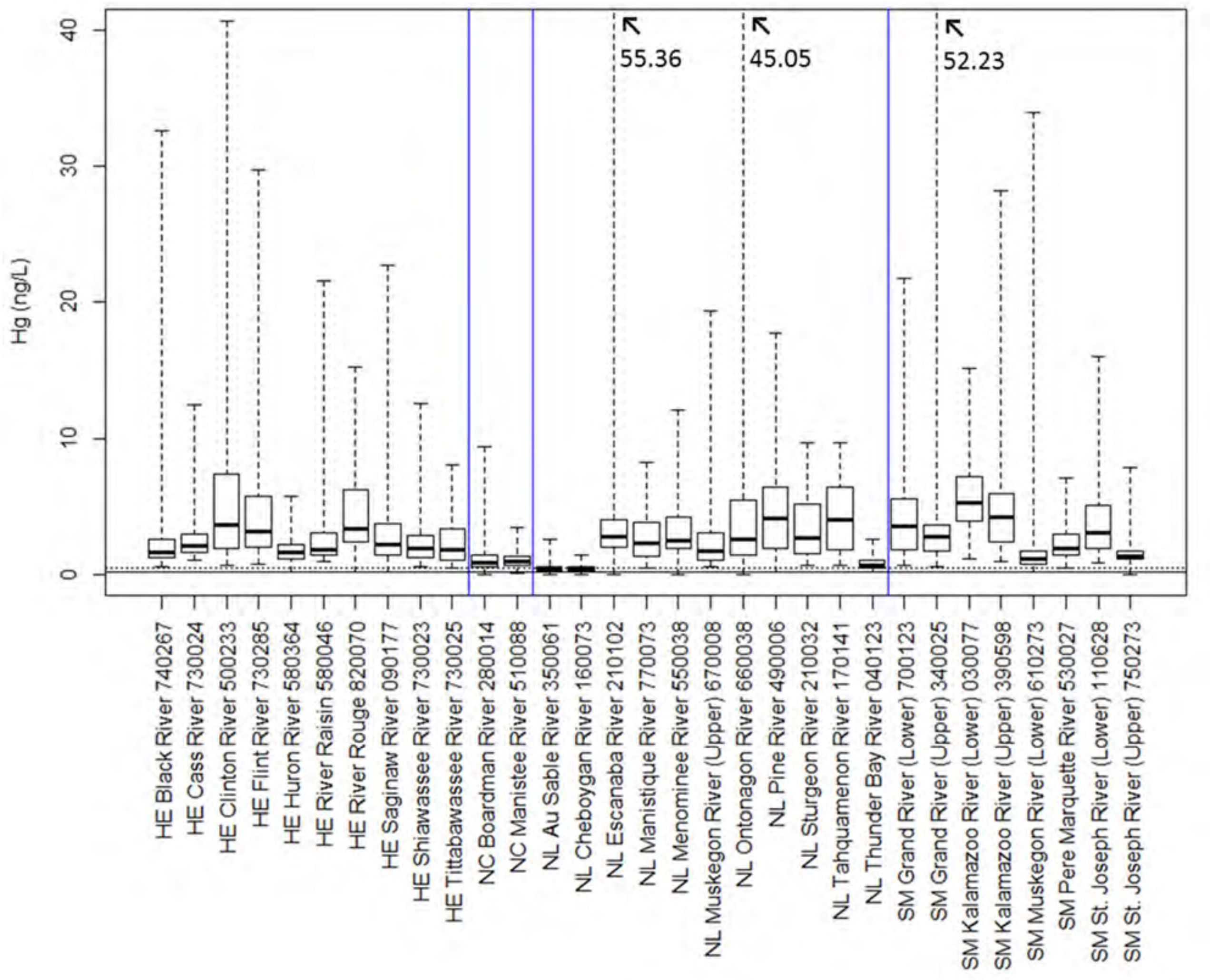


Figure 2-29. Total mercury concentrations, using a large y-axis, at WCMP tributary stations from 1999-2013. The solid horizontal line represents the detection limit; the dotted line represents the quantification limit (RL). Blue vertical lines separate ecoregions.

Trends and Loading. The only significant trends that were observed for mercury were upward. They were all located in the NLAF ecoregion and ranged from 2.99% (Pine River) to 7.12% (Cheboygan River) per year (Table 2-4; Hoard et al., 2018). While not significant (using a criteria of p < 0.05), trends were approaching significance at a few main sites in southern Michigan (-2.15%, p = 0.07, Saginaw River [HELP]; -2.52%, p = 0.10, lower Grand River [SMNIDP]; -2.96%, p = 0.09, Clinton River [HELP]) (Hoard et al., 2018).

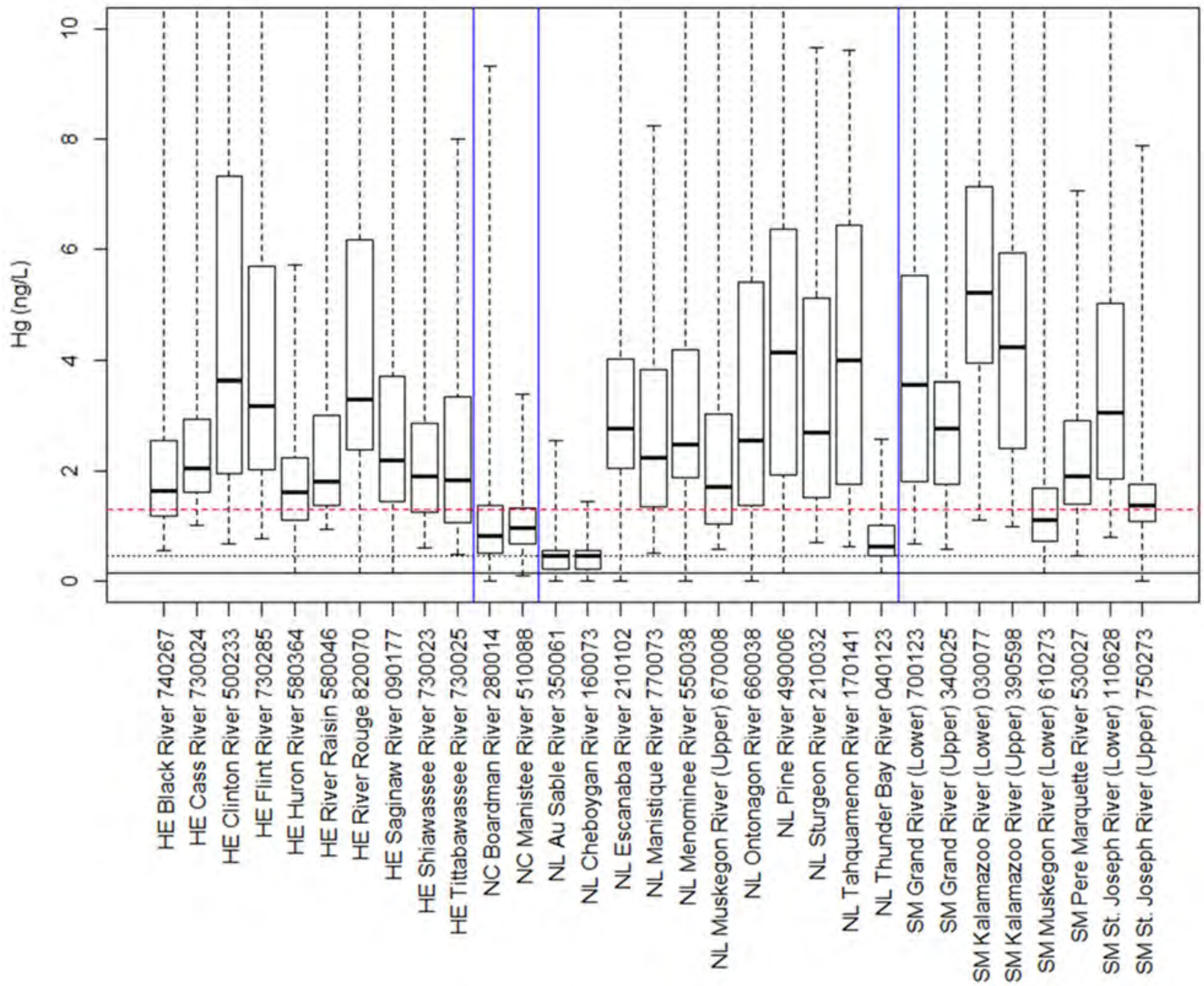


Figure 2-30. Total mercury concentrations, using a small y-axis, at WCMP tributary stations from 1999-2013. The red dashed reference line equals 1.3 ng/L, the WQS criteria (note: criteria is intended for the geometric mean of results at a site). The black, solid horizontal line represents the detection limit; the black, dotted line represents the quantification limit (RL). Blue vertical lines separate ecoregions.

The largest mean annual load estimate for mercury was 69.4 kg/year at the Saginaw River tributary site in 2006 (Appendix A-3). The confidence interval was 67 percent, which shows we are 95% certain that mercury loading at this site was between 23 and 116 kg in 2006. This range is very large, which suggests that seasonal inputs may be important. The highest mercury loadings were typically at the Saginaw River and Lower Grand River tributary sites. The Au Sable frequently had the lowest loading estimates, which were usually less than 1 kg/year. The Boardman River also had a few loading estimates that were less than 1 kg/year.

Criteria

Figure 2-30 contains total mercury boxplots showing median values, 25th and 75th quartile values, minimum and maximum values. Figure 2-30 also includes (for illustrative purposes) a reference line of 1.3 ng/L, which represents the total mercury wildlife value WQS; however, this WQS is typically compared against geometric means for certain smaller time windows.

Mercury is a Bioaccumulative Chemical of Concern, and thus the use of geometric means within 2-year windows at each site is more appropriate for the actual determination of whether WQS are being met for EGLE's biennial Integrated Report (MDEQ, 2006 and 2016b). Two-year window geometric means for each site dating back to 1998 were not computed for this WCMP report.

Information about a statewide TMDL being developed for mercury can be found at https://www.michigan.gov/egle/about/Organization/Water-Resources/tmdls/statewide-mercury-tmdl (last visited September 6, 2018). Additional information about mercury in streams can be found in (Wentz et al., 2014).

2.4.4. *E. coli* Bacteria Monitoring by Other EGLE Programs

E. coli bacteria in surface water are commonly used as a biological indicator for determining whether water has been contaminated by fecal matter and harmful pathogens often associated with fecal matter. While related to water quality, EGLE *E. coli* monitoring is *not* overseen by the WCMP, and therefore not included in this report. For more information on EGLE's *E. coli* monitoring and TMDL efforts, please visit https://www.michigan.gov/egle/about/Organization/Water-Resources/GLWARM/e-coli-in-surface-waters (last visited September 6, 2018).

Table 2-4. Summary of significant trends in water quality data collected at select Michigan WCMP (Great Lakes tributary) stream sites, 1999-2013, as computed by the USGS (Hoard et al., 2018). *Only significant trends (with a p value < 0.05) are shown in this table*. "Trend as a Percentage" is expressed in terms of % per year (Hoard et al., 2018). Refer to Hoard et al., 2018 for more details, including non-significant trends. *Data for the Black River near Port Huron, Michigan, station (for data from 2006-2013) was listed as being in watershed #32 in the USGS report (Hoard et al., 2018) instead of watershed #24 that was used in this table for both the 2000-2005 and 2006-2013 datasets.

Trend as a Percentage	P-value of Trend	Trend Test Used	Watershed Number	Site	Minimum Concentration	Median Concentration	Maximum Concentration	Constituent
5.44	0.016	SK	22	River Rouge	0.010	0.151	3.300	Ammonia (mg/L as N)
-2.68	0.048	TR	2	Menominee River	0.003	0.011	0.047	Ammonia (mg/L as N)
-3.75	0.009	SK	30	Au Sable River	0.001	0.015	0.047	Ammonia (mg/L as N)
-5.52	0.004	SK	14	(lower) Grand River	0.002	0.065	0.810	Ammonia (mg/L as N)
-5.70	0.035	SK	26	Cass River	0.002	0.025	0.500	Ammonia (mg/L as N)
-5.79	0.012	SK	16	(lower) Kalamazoo River	0.004	0.035	0.300	Ammonia (mg/L as N)
-5.95	0.033	SK	25	Flint River	0.005	0.040	0.930	Ammonia (mg/L as N)
-8.05	0.002	SK	23	Clinton River	0.013	0.090	0.760	Ammonia (mg/L as N)
-8.10	0.025	SK	20	River Raisin	0.004	0.025	0.170	Ammonia (mg/L as N)
-10.36	0.013	SK	17	(upper) Kalamazoo River	0.004	0.038	0.150	Ammonia (mg/L as N)
-10.73	0.001	SK	19	(upper) St. Joseph River	0.004	0.044	0.151	Ammonia (mg/L as N)
-12.24	0.007	SK	28	Tittabawassee River	0.003	0.046	0.280	Ammonia (mg/L as N)
5.43	0.047	SK	24 ('00-'05)	Black River	12.0	28.0	70.0	Chloride (mg/L)
3.40	0.045	SK	22	River Rouge	1.0	79.5	259	Chloride (mg/L)
2.81	0.013	SK	2	Menominee River	3.0	7.3	13.0	Chloride (mg/L)
1.40	0.029	SK	5	Manistique River	1.0	2.0	3.7	Chloride (mg/L)
0.90	0.024	SK	18	(lower) St. Joseph River	18.0	31.0	45.0	Chloride (mg/L)
-1.70	0.036	SK	26	Cass River	15.0	40.0	88.0	Chloride (mg/L)
26.73	< 0.0001	TR	30	Au Sable River	0.002	0.090	1.200	Chromium (µg/L)
23.52	< 0.0001	TR	9	Boardman River	0.002	0.214	1.760	Chromium (µg/L)
18.85	< 0.0001	TR	31	Thunder Bay	0.002	0.110	1.600	Chromium (µg/L)

Trend as a Percentage	P-value of Trend	Trend Test Used	Watershed Number	Site	Minimum Concentration	Median Concentration	Maximum Concentration	Constituent
16.81	< 0.0001	TR	8	Cheboygan River	0.002	0.108	1.090	Chromium (µg/L)
12.72	0.001	TR	19	(upper) St. Joseph River	0.002	0.182	1.890	Chromium (µg/L)
7.16	0.012	SK	4	Sturgeon River	0.102	0.452	1.230	Chromium (µg/L)
5.65	0.001	TR	12	(lower) Muskegon River	0.002	0.281	7.140	Chromium (µg/L)
4.65	0.045	SK	2	Menominee River	0.057	0.410	1.510	Chromium (µg/L)
4.18	0.048	SK	5	Manistique River	0.095	0.420	1.180	Chromium (µg/L)
-1.37	0.021	SK	16	(lower) Kalamazoo River	0.806	1.440	5.030	Copper (µg/L)
-2.31	0.022	SK	23	Clinton River	1.820	3.665	19.800	Copper (µg/L)
-2.32	0.010	SK	20	River Raisin	1.470	2.390	7.980	Copper (µg/L)
-3.32	0.002	SK	3	Escanaba River	0.452	0.681	2.330	Copper (µg/L)
3.83	0.016	SK	1	Ontonagon River	0.061	0.235	16.900	Lead (µg/L)
-1.80	0.024	SK	2	Menominee River	0.048	0.125	0.871	Lead (µg/L)
-2.33	0.010	SK	16	(lower) Kalamazoo River	0.387	1.190	7.870	Lead (µg/L)
-3.91	0.026	SK	23	Clinton River	0.377	1.630	21.100	Lead (µg/L)
-4.97	0.008	SK	14	(lower) Grand River	0.187	1.020	5.530	Lead (µg/L)
-5.27	0.005	SK	29	Saginaw River	0.359	0.946	8.870	Lead (µg/L)
-5.38	0.032	SK	25	Flint River	0.311	1.470	16.900	Lead (µg/L)
-5.45	0.009	SK	26	Cass River	0.175	0.607	3.320	Lead (µg/L)
-5.48	0.026	SK	28	Tittabawassee River	0.102	0.363	2.530	Lead (µg/L)
-6.26	0.005	SK	18	(lower) St. Joseph River	0.183	0.709	5.200	Lead (µg/L)
7.12	0.004	SK	8	Cheboygan River	0.14	0.43	1.43	Mercury (ng/L)
5.21	0.005	SK	4	Sturgeon River	0.69	2.76	9.68	Mercury (ng/L)
3.43	0.042	SK	30	Au Sable River	0.01	0.35	2.54	Mercury (ng/L)
2.99	0.023	SK	7	Pine River	0.20	3.98	17.76	Mercury (ng/L)
3.90	0.028	SK	22	River Rouge	0.01	0.78	1.61	Nitrate (mg/L as N)
-1.65	0.046	SK	19	(upper) St. Joseph River	0.73	1.32	2.40	Nitrate (mg/L as N)

Trend as a Percentage	P-value of Trend	Trend Test Used	Watershed Number	Site	Minimum Concentration	Median Concentration	Maximum Concentration	Constituent
-2.17	0.034	SK	10	Manistee River	0.06	0.15	0.30	Nitrate (mg/L as N)
-3.65	0.010	TR	30	Au Sable River	0.00	0.01	0.16	Nitrate (mg/L as N)
-7.49	0.007	SK	21	Huron River	0.01	0.28	1.48	Nitrate (mg/L as N)
6.40	0.032	SK	22	River Rouge	0.001	0.024	0.061	Nitrite (mg/L as N)
-2.66	0.043	SK	14	(lower) Grand River	0.013	0.029	0.102	Nitrite (mg/L as N)
-3.91	0.021	SK	23	Clinton River	0.009	0.033	0.106	Nitrite (mg/L as N)
-4.83	0.002	TR	20	River Raisin	0.002	0.014	0.087	Nitrite (mg/L as N)
21.10	0.000	TR	24 ('06-'13)*	Black River	0.002	0.010	0.130	Orthophosphate (mg/L as P)
9.19	0.001	TR	1	Ontonagon River	0.001	0.013	0.380	Orthophosphate (mg/L as P)
3.16	0.015	TR	14	(lower) Grand River	0.001	0.028	0.110	Orthophosphate (mg/L as P)
-3.42	0.021	TR	17	(upper) Kalamazoo River	0.006	0.015	0.087	Orthophosphate (mg/L as P)
-6.48	0.001	TR	3	Escanaba River	0.002	0.009	0.150	Orthophosphate (mg/L as P)
-3.08	0.038	SK	20	River Raisin	0.030	0.067	0.490	Phosphorus (mg/L as P)
-3.37	0.017	SK	23	Clinton River	0.050	0.144	0.540	Phosphorus (mg/L as P)
-3.38	0.019	SK	7	Pine River	0.026	0.061	0.390	Phosphorus (mg/L as P)
-3.83	0.047	SK	25	Flint River	0.049	0.134	0.730	Phosphorus (mg/L as P)
-4.12	0.021	SK	26	Cass River	0.030	0.077	0.260	Phosphorus (mg/L as P)
-4.24	0.008	SK	18	(lower) St. Joseph River	0.027	0.065	0.400	Phosphorus (mg/L as P)
5.30	0.039	SK	24 ('06-'13)*	Black River	0.31	0.77	2.50	Total Kjeldahl Nitrogen (mg/L as N)
3.61	0.048	SK	22	River Rouge	0.10	0.65	4.70	Total Kjeldahl Nitrogen (mg/L as N
2.66	0.018	SK	3	Escanaba River	0.41	0.63	1.06	Total Kjeldahl Nitrogen (mg/L as N)
-1.58	0.028	SK	23	Clinton River	0.64	0.98	3.10	Total Kjeldahl Nitrogen (mg/L as N)
-1.60	0.020	SK	16	(lower) Kalamazoo River	0.38	0.80	1.36	Total Kjeldahl Nitrogen (mg/L as N)

Trend as a Percentage	P-value of Trend	Trend Test Used	Watershed Number	Site	Minimum Concentration	Median Concentration	Maximum Concentration	Constituent
-2.46	0.011	SK	14	(lower) Grand River	0.49	1.00	2.70	Total Kjeldahl Nitrogen (mg/L as N)
-3.78	0.018	SK	14	(lower) Grand River	4	24	150	TSS (mg/L)
-3.89	0.001	TR	12	(lower) Muskegon River	1	8	390	TSS (mg/L)
-4.08	0.030	TR	13	(upper) Muskegon River	2	10	140	TSS (mg/L)
-4.56	0.003	TR	28	Tittabawassee River	4	13	91	TSS (mg/L)
-4.66	0.011	SK	29	Saginaw River	6	18	340	TSS (mg/L)
-5.69	0.020	SK	23	Clinton River	4	20	320	TSS (mg/L)
-5.80	0.024	SK	26	Cass River	5	21	120	TSS (mg/L)
-6.70	0.020	SK	18	(lower) St. Joseph River	2	15	97	TSS (mg/L)
-6.76	0.000	TR	15	(upper) Grand River	4	15	830	TSS (mg/L)

2.4.5. Summary and Conclusions

(1) Limitations of the Study Design

Minimally Impacted Sites vs. Main Sites

The original selection process for determining minimally impacted sites to pair with main sites had some weaknesses in statistical design, most likely due to budget and time constraints. The minimally impacted sites were not true reference sites, but rather they were selected using available knowledge of each watershed and best professional judgement of EGLE staff. These paired sites frequently had substantial differences (e.g., different longitudinal position within a watershed, differing stream/river size [order], different dominant catchment surficial geologies, etc.) that could explain differences in concentrations irrespective of the level of impact (i.e., minimally impacted vs. main sites). An additional weakness of this comparison approach is that these 2 kinds of sites were not sampled in the same manner (frequency and flow-wise). For main sites, field crews attempted to collect 75% of samples during high flow events and 25% of samples during base/low flow and samples were collected 4-12 times per year every year. For minimally impacted sites, there was no targeting of specific flow conditions; they were essentially sampled under random flow conditions. Also, they were only sampled 4 times during each minimally impacted site's basin year and not during the other 4 years. Therefore, it is likely that at least some of the variability in median concentrations between main sites and minimally impacted sites is due to different sample sizes and differences in the proportion of high flow versus low flow events sampled for these different types of sites.

The intent was to try to monitor sites that were expected to have the least-impacted, best water quality conditions within a watershed against (expected) more-impacted conditions at the main sites. Given time and budget limitations and the reliance on best professional judgement to find sites instead of an exhaustive search to find truly comparable reference sites, this was the most reasonable approach available at the time. Finding real reference sites (of similar size, geology, ecoregion to main sites) when the study was designed likely would have been difficult, particularly in the southern Lower Peninsula, since there are few large rivers there that have been little influenced by densely-populated urban areas, intense agriculture, or both. Thus, while the comparisons between minimally impacted sites and main sites should be treated with caution given the limitations stated above, they do present a rough range of conditions that would be expected to be found within in their respective watersheds.

Regional (Spatial) Analysis

Ecoregions were used in Section 2 to better understand spatial patterns of water chemistry conditions in Michigan, with any general patterns observed amongst the various ecoregions (based upon the limited number of main sites within them) being noted. Since main sites are located on many of the largest river systems (in terms of water volume and, often, pollutant load) in Michigan, and since they are assimilating point and nonpoint source pollution from throughout their drainage area, this information is some of the best available to assist water resource managers with identifying, prioritizing, and targeting regions of the state to do more detailed, local, follow-up monitoring. This information is also useful in deciding where water quality restoration and best management practice efforts ought to be focused in order have the greatest impact.

It must be noted, however, that we cannot draw *statistically-based* statewide and regional conclusions using these data because the selection process for these sites was not random. Any conclusions related to ecoregion patterns about water quality characteristics observed amongst the major Great Lake tributaries described and discussed in this section should be limited to those monitoring locations. No confident predictions or extrapolations should be made regarding water quality conditions of other specific water bodies elsewhere in the ecoregion of one of these main sites. The Probabilistic sites portion of this report (Section 2) is a more appropriate design for that type of objective since those sites were originally chosen randomly.

(2) General Spatial Patterns

As just mentioned, *statistically-based* statewide and regional conclusions (e.g., for ecoregions as a whole) cannot be drawn using the data presented in this section because the site-selection process was not random. Still, there were some general observed patterns that are summarized here.

Concentrations, or values (e.g., for specific conductance), at main sites (intensive and integrator) were generally highest in HELP and SMNIDP ecoregions for many parameters including: total phosphorus, orthophosphate, nitrate, nitrite, total Kjeldahl nitrogen, total ammonia, TDS, chlorides, sodium, hardness, specific conductance, TSS, alkalinity, copper, lead, cadmium, nickel, and zinc (Appendix C-1). Some notable deviations from this pattern were the Ontonagon River (second highest median for copper; NLAF ecoregion, Upper Peninsula) and the Escanaba River (third highest median for cadmium; fifth highest median for ammonia and sodium; NLAF ecoregion, Upper Peninsula).

Concentrations of TOC at main sites were highest in NLAF (i.e., the top 7 medians amongst main sites, and 3 of the top 4 medians amongst minimally impacted sites, were observed in this ecoregion), perhaps because many of their headwaters originate from organic wetland soils and are naturally stained due to the leaching of humic substances within the watershed (Roush, 2013).

Some parameters did not display spatial patterns. For mercury and chromium, sites from 3 (SMNIDP, HELP, NLAF) of the 4 ecoregions were found in the top 5 or 6 median concentrations for each parameter (Appendix C-1). Turbidity was another parameter for which spatial patterns were unclear across the state. It is interesting to note, however, that 2 NLAF ecoregion sites in the Upper Peninsula had the highest turbidity values (Pine River and Ontonagon River). Additionally, while not evaluated statistically in this report, it is worth mentioning that out of 13 main sites located within the NLAF and NCHF ecoregions, the Pine River and/or Ontonagon River (which have predominantly Lacustrine clay and silt quaternary geological conditions [Figure 2-31]) had the highest concentration for half of the pollutant-type parameters listed in Table 2-5, including turbidity, total phosphorus, orthophosphate, TDS, TSS, lead, chromium, copper, mercury, and nickel (Appendix C-1). It is possible that, similar to probabilistic sites discussed earlier in this report, this is due, at least partly, to factors such as dominant quaternary geology type.

(3) Sites with Highest Median Pollutant Concentrations

Some specific sites frequently had the highest values for parameters typically considered to be indicative of pollution (when they are observed at high levels) (Table 2-5). The Clinton River had the highest median concentration for 9 of these parameters (total phosphorus, orthophosphate, nitrite, chloride, sodium, chromium, copper, nickel, and zinc). The River Rouge had the highest median concentration of 3 of these parameters (total ammonia, lead, and cadmium). Both of these rivers have largely dense urban watersheds, with the Rouge River and Clinton River watersheds having the following ranks in terms of highest % land covered by "developed, high intensity" (first and third, respectively), "developed, medium intensity" (first and third, respectively), and "developed, low intensity" (second and third, respectively) (Appendix C-6). (Note: The Saginaw River watershed ranked second for both "developed, high intensity" and "developed, medium intensity" and first for "developed, low intensity" though this may have been an artifact of a relatively smaller watershed area used for the Saginaw in GIS land use analysis [see Figure 2-32a].)

Both the Flint River and Huron River sites each had the highest median concentration of 2 of these parameters (Flint: nitrate and TSS; Huron: TDS and specific conductance). These watersheds have a more diverse mix of agricultural, residential, urban, and forested areas, and they ranked fourth and fifth highest, respectively, in terms of highest % land covered by "developed, high intensity," "developed, medium intensity," and "developed, low intensity" (Appendix C-6). The Flint River site is located more than 20 miles downstream of the Flint urban area. The Huron River watershed urban areas include Rockwood, Flat Rock, Ypsilanti, and Ann Arbor.

All of these sites (Rouge, Clinton, Flint, and Huron Rivers' main sites) were located in the HELP ecoregion.

(4) Urban and Agricultural Land Uses

The spatial patterns described in bullets number 2 and 3 above, that concentrations (or values) at main sites (intensive and integrator) were generally highest in HELP and SMNIDP ecoregions for many parameters, appears to align with the fact that the most dense urban land areas and most intensive agricultural land areas are generally located in the HELP and SMNIDP ecoregions of the state (see Figures 2-32a, 2-32b).

The pollutant-type parameters listed in Table 2-5 are commonly found at elevated concentrations in watersheds that have large, dense urban and intensive agricultural land use areas (Figures 2-32a, 2-32b). In addition to natural inputs, these substances can be contributed to waterways by human activities (e.g., runoff of pollutants deposited on impervious surfaces [e.g., roads, parking lots]; winter road safety maintenance; failing septic systems; erosion from construction, agricultural activities, and logging; application of fertilizers; waste water treatment/discharge) (Paul and Meyer, 2001).

(5) Sites with Lowest Median Pollutant Concentrations

Some sites frequently had the lowest median concentrations (or values) for parameters generally considered to be indicative of pollution. Out of 20 of these types of parameters listed in Table 2-5, the Au Sable River, Thunder Bay River, and Tahquamenon River main sites had the lowest concentration of 5, 4, and 3 parameters, respectively. All of these sites were located in the NLAF ecoregion.

(6) Lower Muskegon River and Pere Marquette River

Even though the lower Muskegon River and Pere Marquette River main sites were located in the SMNIDP ecoregion, they often had water chemistry characteristics that generally were more reflective of those found in the NLAF and NCHF ecoregions (Roush, 2013). The sites often had the lowest median concentrations or values within the SMNIDP ecoregion (Appendices C-1, C-2, and C-3) and generally were more similar to those conditions found at sites within the NLAF and NCHF ecoregion. This appears to be due to the fact that these two tributary sites are located near, and receive most of their flow from, the NLAF ecoregion (Roush, 2013).

(7) Minimally Impacted Sites with Unexpected Conditions

Some minimally impacted sites frequently had median concentrations of parameters (considered here to be pollutant-type) that were greater than their respective main sites. Sites with ≥ 50% of their parameters having larger median values at the minimally impacted sites included: Pokagon Creek (vs. St. Joseph River [Upper]) in the SMNIDP ecoregion and Pigeon River (vs. Cheboygan River), East Creek (vs. Boardman River), and Perry Creek (vs. Au Sable River) (NLAF and NCHF ecoregions) (Table 2-6).

Minimally impacted sites were originally sites that had been identified by Surface Water Assessment Section biologists, with some knowledge of the watersheds, early on in the study. These were sites with relatively few known impacts. As it turns out, some of these sites may have had more impacts than originally believed or known. For example, regarding the case of Perry Creek in the Au Sable River watershed, EGLE became aware that there had been a contaminated groundwater plume that vents into Perry Creek approximately 2 miles upstream of this minimally impacted site after it had already been selected and monitored as part of the WCMP project (Roush, 2013).

Table 2-5. WCMP Great Lake tributary sites with the 3 highest and lowest median concentrations among all main sites (intensive and integrator). River site label includes a 2-letter abbreviation for ecoregion, plus river name and STORET number. This table focuses only on parameters that are considered to be pollutant-type (e.g., key plant nutrients, metals) parameters.

Water Quality Parameter	Highest Median Concentration	Second Highest Median Concentration	Third Highest Median Concentration
Total Phosphorus	HE Clinton River 500233	HE Flint River 730285	SM Grand River (Upper) 340025
Orthophosphate	HE Clinton River 500233	HE Flint River 730285	SM Grand River (Upper) 340025
Nitrate	HE Flint River 730285	HE Cass River 730024	SM Grand River (Upper) 340025
Nitrite	HE Clinton River 500233	HE Saginaw River 090177	SM Grand River (Lower) 700123
Total Kjeldahl Nitrogen	HE Saginaw River 090177	SM Grand River (Lower) 700123	HE Clinton River 500233
Total Ammonia	HE River Rouge 820070	HE Saginaw River 090177	HE Clinton River 500233
TOC[1]	NL Escanaba River 210102	NL Tahquamenon River 170141	NL Sturgeon River 210032
Turbidity	NL Pine River 490006	NL Ontonagon River 660038	HE Cass River 730024
TDS	HE Huron River 580364	HE Clinton River 500233	HE Flint River 730285
Chloride	HE Clinton River 500233	HE Huron River 580364	HE Tittabawassee River 730025
Sodium	HE Clinton River 500233	HE Huron River 580364	HE Tittabawassee River 730025
Total Suspended Solids	HE Flint River 730285	SM Grand River (Lower) 700123	HE Cass River 730024
Lead	HE River Rouge 820070	HE Clinton River 500233	HE Flint River 730285
Chromium	HE Clinton River 500233	HE River Rouge 820070	NL Pine River 490006
Copper	HE Clinton River 500233	NL Ontonagon River 660038	HE River Rouge 820070
Mercury	SM Kalamazoo River (Lower) 030077	SM Kalamazoo River (Upper) 390598	NL Pine River 490006
Nickel	HE Clinton River 500233	HE Flint River 730285	HE Huron River 580364
Zinc	HE Clinton River 500233	HE River Rouge 820070	HE Flint River 730285
Cadmium	HE River Rouge 820070	HE Clinton River 500233	NL Escanaba River 210102
Specific Conductance	HE Huron River 580364	HE Clinton River 500233	HE Flint River 730285

Water Quality Parameter	Highest Median Concentration	Second Highest Median Concentration	Third Highest Median Concentration
Number of Occurences:			
HE Clinton River 500233	9	4	2
HE River Rouge 820070	3	2	1
HE Flint River 730285	2	3	4
HE Huron River 580364	2	2	1
HE Saginaw River 090177	1	2	0
NL Escanaba River 210102	1	0	1
NL Pine River 490006	1	0	2
SM Kalamazoo River (Lower) 030077	1	0	0
HE Cass River 730024	0	1	2
HE Tittabawassee River 730025	0	0	2
NL Ontonagon River 660038	0	2	0
NL Sturgeon River 210032	0	0	1
NL Tahquamenon River 170141	0	1	0
SM Grand River (Lower) 700123	0	2	1
SM Grand River (Upper) 340025	0	0	3
SM Kalamazoo River (Upper) 390598	0	1	0

Table 2-5 cont'd

Water Quality Parameter	Third Lowest Median Concentration	Second Lowest Median Concentration	Lowest Median Concentration
Total Phosphorus	NC Boardman River 280014	NL Au Sable River 350061	NL Cheboygan River 160073
Orthophosphate	NL Sturgeon River 210032	NL Tahquamenon River 170141	NL Thunder Bay River 040123
Nitrate	NL Ontonagon River 660038	NL Au Sable River 350061	NL Thunder Bay River 040123
Nitrite	NL Cheboygan River 160073	NL Sturgeon River 210032	NL Thunder Bay River 040123
Total Kjeldahl Nitrogen	NC Manistee River 510088	NL Au Sable River 350061	NC Boardman River 280014
Total Ammonia	NC Boardman River 280014	NL Ontonagon River 660038	HE Black River 740267
TOC[1]	NL Au Sable River 350061	NC Manistee River 510088	NC Boardman River 280014
Turbidity	NL Thunder Bay River 040123	NL Au Sable River 350061	NL Cheboygan River 160073
TDS	NL Manistique River 770073	NL Ontonagon River 660038	NL Tahquamenon River 170141
Chloride	NL Sturgeon River 210032	NL Tahquamenon River 170141	NL Manistique River 770073
Sodium	NL Tahquamenon River 170141	NL Manistique River 770073	NL Sturgeon River 210032
Total Suspended Solids	NL Sturgeon River 210032	NL Tahquamenon River 170141	NL Thunder Bay River 040123
Lead	NC Boardman River 280014	NL Cheboygan River 160073	NL Au Sable River 350061
Chromium	NL Cheboygan River 160073	NL Thunder Bay River 040123	NL Au Sable River 350061
Copper	NL Manistique River 770073	NC Boardman River 280014	NL Au Sable River 350061
Mercury	NL Thunder Bay River 040123	NL Cheboygan River 160073	NL Au Sable River 350061
Nickel	NL Sturgeon River 210032	NL Manistique River 770073	NL Tahquamenon River 170141
Zinc	NC Boardman River 280014	NL Cheboygan River 160073	NL Au Sable River 350061
Cadmium	NL Manistique River 770073	NL Thunder Bay River 040123	SM St. Joseph River (Upper) 750273
Specific Conductance	NL Manistique River 770073	NL Ontonagon River 660038	NL Tahquamenon River 170141

Water Quality Parameter	Third Lowest Median Concentration	Second Lowest Median Concentration	Lowest Median Concentration
Number of Occurences:			
NL Au Sable River 350061	1	4	5
NL Thunder Bay River 040123	2	2	4
NL Tahquamenon River 170141	1	3	3
NC Boardman River 280014	4	1	2
NL Cheboygan River 160073	2	3	2
HE Black River 740267	0	0	1
NL Manistique River 770073	4	2	1
NL Sturgeon River 210032	4	1	1
SM St. Joseph River (Upper) 750273	0	0	1
NC Manistee River 510088	1	1	0
NL Ontonagon River 660038	1	3	0

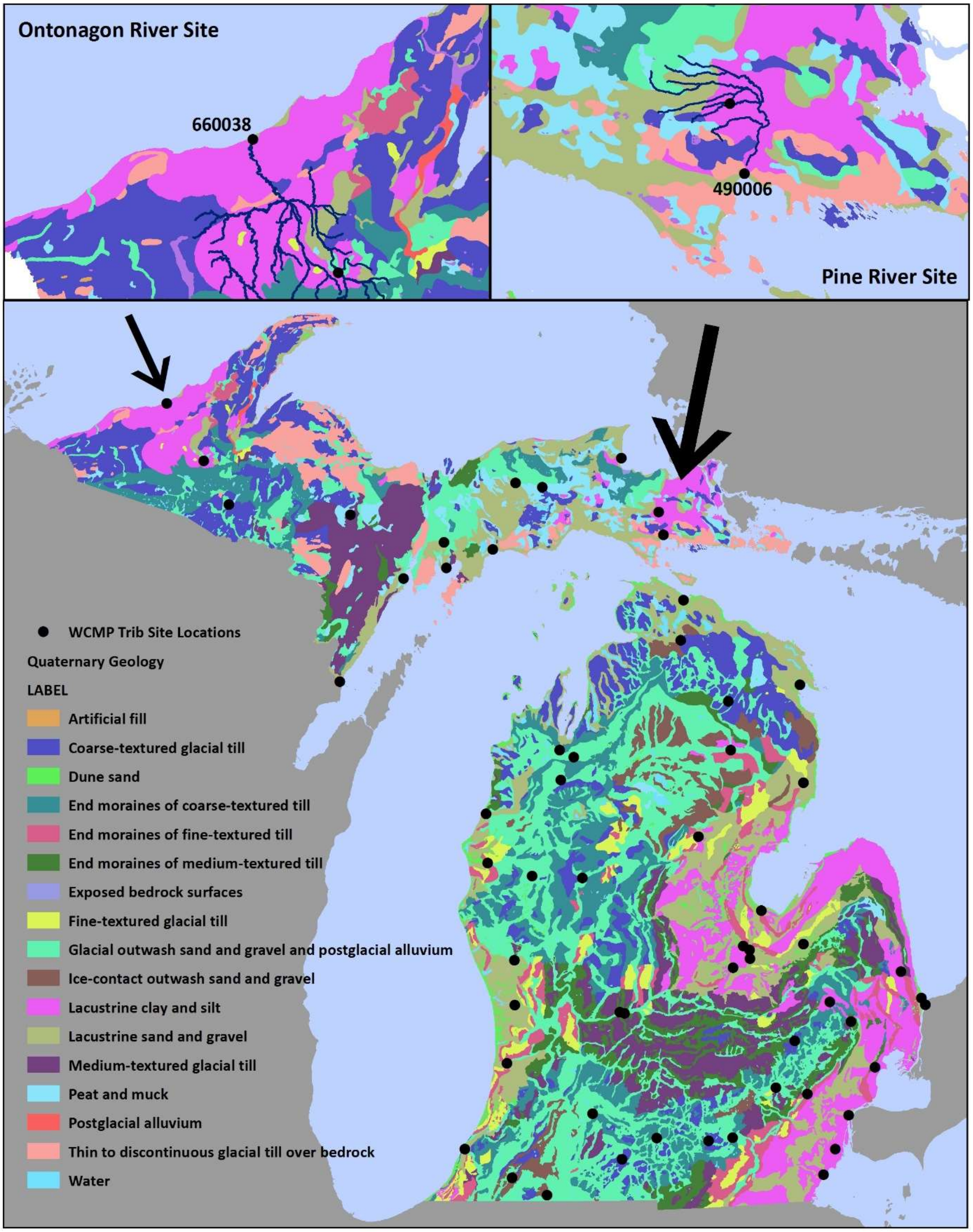


Figure 2-31. Locations of the WCMP Great Lakes tributary sites relative to quaternary geology type. Geology data source: Farrand and Bell (1982).

Michigan Department of Environmental Quality
Water Resources Division
Surface Water Quality Assessment Section
Data Source: US EPA Office of Research and Development
MDEQ Water Resources Divison
Date Created: 1/3/2018

Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community

Figure 2-32a. Locations of the WCMP Great Lakes tributary sites relative to land use type and watershed boundaries.

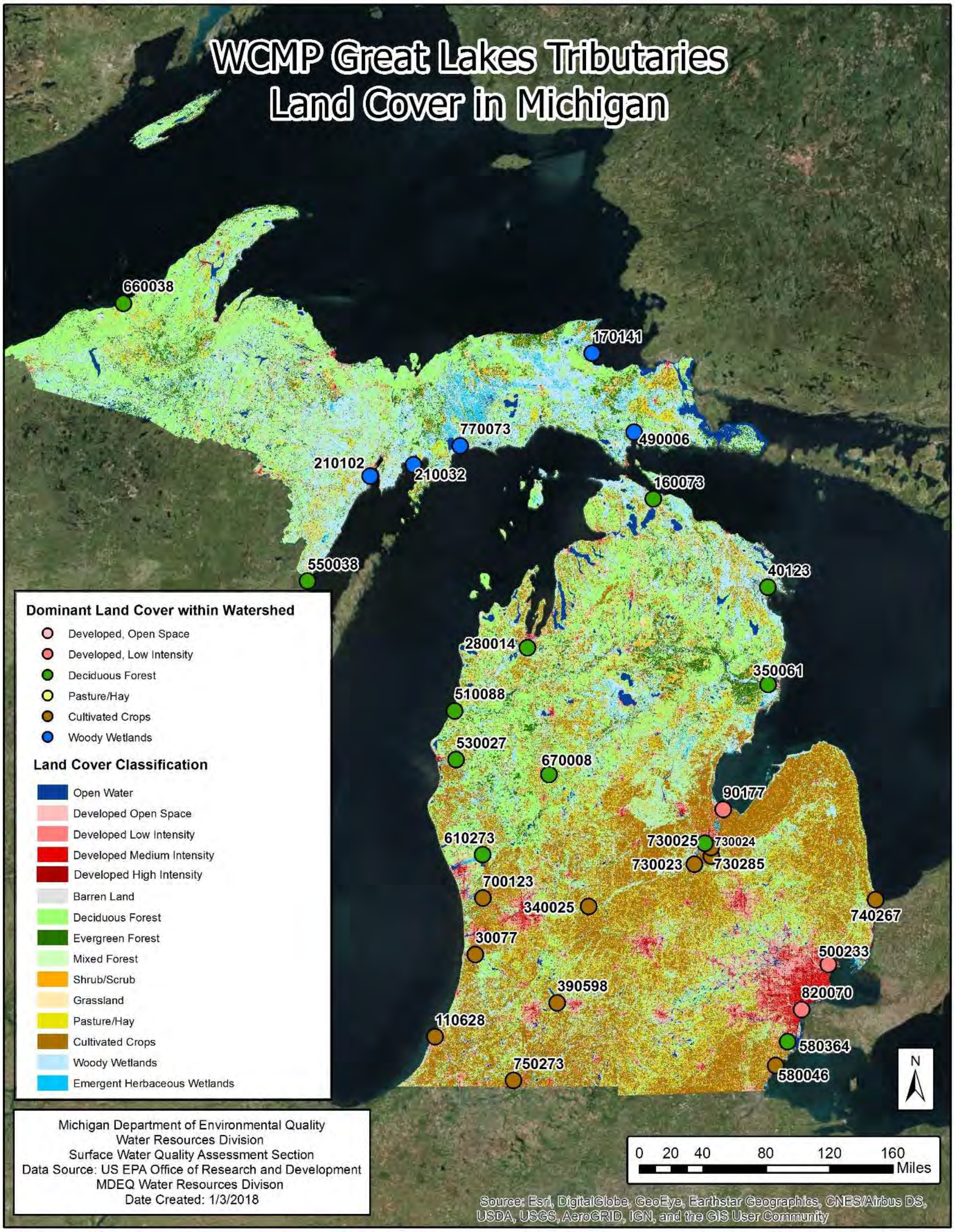


Figure 2-32b. Locations of the WCMP Great Lakes tributary sites relative to land use type.

(8) Alkalinity

Alkalinity is a term that was historically used to refer to the buffering capacity of the carbonate system in water. It is now a term that is used interchangeably with Acid Neutralizing Capacity, which is the capacity to neutralize strong acids (Wetzel, 2001).

Most water quality parameters in this WCMP's Great Lakes tributaries section had greater values at their main sites relative to their associated (paired) minimally impacted sites with the exception of alkalinity. Median alkalinity at 73% of the minimally impacted sites was greater than at their paired main sites (Appendix C-4). In most cases (93%), the WCMP's minimally impacted sites were located upstream relative to their paired main sites.

Alkalinity in aquatic ecosystems can vary widely across a landscape, is complex, and is influenced by multiple factors and processes including local geology, precipitation, biological activity, and human activities (Wetzel, 2001). Also, longitudinal position in a river system may be an important factor in determining alkalinity at a given location on a stream or river.

There is a great variety of geological formations across the state of Michigan, especially when comparing the western half of the Upper Peninsula to the eastern half of the Upper Peninsula and the Lower Peninsula (MDEQ, 2003b; Schaetzl et al., 2009), and the availability of carbonate-rich bedrock and surficial geology can influence regional alkalinity.

Human activities can contribute to acid precipitation in many areas (Allan and Castillo, 2007; USEPA, 2016), which may affect alkalinity patterns. Acid deposition (acid rain), which forms when smokestack and auto emissions either combine with moisture in the air or deposits in dry form (e.g., as part of soot) (USEPA, 2016), can increase the acidity (lower the pH) of water, but it also can lead to increased weathering and leaching of carbonates from local geology (Wetzel, 2001; Kaushal et al., 2013). Upward trends in alkalinity and pH since the early 1990s are common in small headwater systems and indicate a recovery from acidification (Stets et al., 2014). Acid deposition varies across the state of Michigan (see Environment Canada [2015]) and may partially explain the variability in alkalinity across the state.

Biological processes such as photosynthesis by aquatic plants can cause some CaCO3 to precipitate out of the water column as it removes carbon dioxide from the water (Wetzel, 2001).

Temperature affects the solubility of CaCO3; its solubility decreases with increasing temperature (Brezonik and Arnold, 2011). While not universal (see Fullerton et al., 2015), a minimally-disturbed river system often has cooler mean daily water temperatures in its headwater stream areas compared to larger mid- and downstream river sections due to the typically smaller stream widths, greater riparian vegetation shading, and greater relative influence by groundwater inputs in headwaters (Caissie, 2006; Allan and Castillo, 2007). So, if water temperature often increases in the downstream direction, it is possible the solubility of CaCO3 may often decrease in a downstream direction, which would affect alkalinity. (Much more sampling and data would be needed to thoroughly and statistically examine the question of longitudinal patterns in alkalinity.)

Table 2-6. Watersheds in which minimally impacted sites frequently had (i.e., ≥ 50% of the time) median concentrations of pollutant-type parameters greater than the median concentrations at their respective main sites, as indicated by dark-shaded cells. Pollutant-type parameters included here are: total phosphorus, orthophosphate, total Kjeldahl nitrogen, nitrate, nitrite, total ammonia (NH3), turbidity, TSS, TOC, sodium, chloride, lead, chromium, copper, mercury, nickel, zinc, cadmium, specific conductance, and TDS. Refer to Appendix C-4 for more details.

Water-shed #	River Name	Eco-region Abbrev-iation	River Name	Eco-region Abbrev-iation	# of pollutant-type parameters having median concentrations greater at the minimally impacted site rather than the main site	
	Main Sites		Minimally Impacted Sites		#	%
1	Ontonagon River	NL	East Branch Ontonagon	NL	1	5%
2	Menominee River	NL	Paint River	NL	3	15%
3	Escanaba River	NL	Bryan Creek	NL	0	0%
4	Sturgeon River	NL	Eighteen Mile Creek	NL	1	5%
5	Manistique River	NL	Fox River	NL	3	15%
6	Tahquamenon River	NL	Tahquamenon River (Headwaters)	NL	2	10%
7	Pine River	NL	Bear Creek	NL	5	25%
8	Cheboygan River	NL	Pigeon River	NL	10	50%
9	Boardman River	NC	East Creek	NL	11	55%
10	Manistee River	NC	Anderson Creek	NL	9	45%
11	Pere Marquette River	SM	Pere Marquette River (Headwaters)	NL	0	0%
12	Muskegon River (Lower)	SM	Bigelow Creek	NL	4	20%
13	Muskegon River (Upper)	NL	Bigelow Creek	NL	2	10%
14	Grand River (Lower)	SM	Bellamy Creek	SM	3	15%
15	Grand River (Upper)	SM	Grand River (Headwaters)	SM	1	5%
16	Kalamazoo River (Lower)	SM	South Branch Kalamazoo River	SM	3	15%
17	Kalamazoo River (Upper)	SM	South Branch Kalamazoo River	SM	2	10%
18	St. Joseph River (Lower)	SM	Coldwater River	SM	3	15%
19	St. Joseph River (Upper)	SM	Pokagon Creek	SM	12	60%
20	River Raisin	HE	River Raisin (Headwaters)	SM	2	10%

Water-shed #	River Name	Eco-region Abbrev-iation	River Name	Eco-region Abbrev-iation	# of pollutant-type parameters having median concentrations greater at the minimally impacted site rather than the main site	
21	Huron River	HE	Huron River (Headwaters)	SM	2	10%
22	River Rouge	HE	Johnson Drain	HE	8	40%
23	Clinton River	HE	North Branch Clinton River	SM	0	0%
24	Black River	HE	Black River (Headwaters)	HE	7	35%
25	Flint River	HE	South Branch Flint River	SM	0	0%
26	Cass River	HE	Evergreen Creek	HE	1	5%
27	Shiawassee River	HE	Shiawassee River (Headwaters)	SM	0	0%
28	Tittabawassee River	HE	West Branch Tittabawassee	NL	0	0%
29	Saginaw River	HE	*no minimally impacted site*		0	0%
30	Au Sable River	NL	Perry Creek	NL	14	70%
31	Thunder Bay River	NL	Thunder Bay River (Headwaters)	NL	4	20%

The buffering capacity of water is critical to the maintenance of life in streams and rivers (Allan and Castillo, 2007). Alkalinity appears to be a parameter ripe for additional, more intensive monitoring and study on a large geographic scale (e.g., the state of Michigan, the Midwestern United States, etc.) because of its importance to aquatic life and also because more information is needed to help understand any longitudinal, geographic, land-use, and temporal patterns that may exist.

(9) Temporal Trends

For many Great Lake tributary parameters analyzed for temporal trends by Hoard et al. (2018), the majority of significant trends were downward (e.g., ammonia, copper, lead, nitrate, total phosphorus, TSS) (Table 2-4). This report does not attempt to do a detailed analysis to determine what might explain why those trends were observed. A more intensive study design would be needed to confidently determine whether management of point source and nonpoint source pollution and land use practices are reducing pollution loads to water bodies across the state of Michigan. Still, these results might be encouraging to water resources managers. Additional monitoring would be needed to determine if these trends continue.

Some other parameters that were analyzed may warrant more concern and be a priority for further monitoring because they had more than 1 river with an upward trend amongst the main sites in this report. For example, rivers having significant ($p < 0.05$) upward trends > 1% per year, or even higher, included:

- Chloride (Black, Rouge, Menominee, and Manistique Rivers).
- Mercury (Cheboygan, Sturgeon, Au Sable, and Pine Rivers).
- Nitrite (Rouge River); (the Black River had a p value of 0.05).
- Total Kjeldahl Nitrogen (Black, Rouge, and Escanaba River).
- Orthophosphate (Black, Ontonagon, and lower Grand Rivers).

Additionally, while no chromium values were detected above WQS in this study, many rivers had large upward trends, making it a parameter to also consider as a priority moving forward (Table 2-4).

Many interrelated factors may explain why these trends were found in the data. Water quality improvement and protection efforts such as implementation of best management practices in agricultural, urban, and forested watersheds may help to explain decreases in concentrations of certain pollutants that were observed at many of the main river sites. Increases in concentrations of certain pollutants may be occurring due to factors such as changes in land use (e.g., urban, agricultural) or management of these lands or, as was described for pollutant loadings in Maccoux et al. (2016), increases in precipitation amounts. These trends and possible explanations warrant further and more in-depth investigations in the future.

(10) Loads

Loads of total phosphorus, chloride, chromium, copper, lead, mercury, and TSS generally were highest in large watershed streams with the largest annual flows, such as the Saginaw River and Grand River. The Saginaw River had the maximum observed loads for total phosphorus, chloride, copper, lead, mercury, and TSS for the time period examined (2002-2013); the Ontonagon River had the highest observed load for chromium. Loads were generally lowest in the smaller tributaries sampled as part of this program, such as the Boardman and Thunder Bay Rivers.

SECTION 3. BAY MONITORING: STATUS AND TRENDS

3.1 INTRODUCTION

The WCMP sampling in Saginaw Bay and Grand Traverse Bay began in 1998.

Saginaw Bay is a large embayment in eastern mid-Michigan on Lake Huron. Saginaw Bay extends 82 kilometers (km) from Lake Huron proper to the mouth of the Saginaw River and its watershed drains approximately 15% of Michigan's land area (GLEC, 2007; USEPA, 2012). Saginaw Bay can be divided into 2 physical regions; the inner bay and the outer bay (Beeton et al., 1967). The inner bay extends from the mouth of the Saginaw River to Lookout Point on the northwest shore and Sand Point on the southeast shore. The inner bay has an average depth of 4.5 meters and a maximum depth of approximately 14 meters (Beeton et al., 1967). The outer bay includes all of Saginaw Bay northeast of these features. The outer bay has an average depth of 14.6 meters and maximum depth of 40.5 meters and contains 70% of the overall volume of the bay (Beeton et al., 1967). Additional, detailed descriptions of the physical characteristics and hydrologic influences within Saginaw Bay can be found in a previous WCMP report by GLEC (2007) and Roush (2013).

Grand Traverse Bay is a large embayment on Lake Michigan, located in the northwestern Lower Peninsula of Michigan. It consists of 2 deep, narrow basins called west and east Grand Traverse Bay, which are separated by a peninsula. Each bay is approximately 15 km wide and extends approximately 48 km from Lake Michigan. The maximum depth of west and east Grand Traverse Bay is 123 and 187 meters, respectively (Saxton, 2006). A more complete description of the physical characteristics of Grand Traverse Bay can be found in GLEC (2007).

Water chemistry data and trends for samples collected between 1998 and 2014 will be discussed in this report.

3.2 MAJOR CONCLUSIONS

Saginaw Bay

Amendments to the Great Lakes Water Quality Agreement set targets of 15 µg/L for total phosphorus and 3.6 µg/L for chlorophyll a within Saginaw Bay (International Joint Commission, 1978). Based on medians of data collected since 1999, these numerical targets are being met at some, but not all, stations in Saginaw Bay.

<u>Seasonal</u>

In general, water chemistry parameters in Saginaw Bay showed highest concentrations in the spring and/or fall, with the exception of total phosphorus and Kjeldahl nitrogen (discussed below). It is likely that spring and fall spikes reflect a combination of spring and fall turnover (thermal destratification) and high surface runoff triggered by wet weather events. Decreased summer concentrations of major and minor nutrients (i.e., nitrate, nitrite, and ammonia) may also be the result of increased photosynthetic activity associated with plants and algae (Stow et al., 2013; Pillsbury et al., 2002; Heath et al., 1995, and Fahnenstiel et al., 1995).

Total phosphorus and Kjeldahl nitrogen concentrations were highest during late summer and fall. These peaks coincide with the period of highest chlorophyll a. Therefore, it is likely that these seasonal patterns are caused by algal blooms and increased algal biomass in the summer (Stow et al., 2013). However, total phosphorus and Kjeldahl nitrogen may also be influenced by the suspension of sediments within Saginaw Bay during periods of high wave energy, which are typical during fall months (Bierman et al., 1984; Hawley et al., 2014).

Spatial

Nutrient and trace metal concentrations were generally higher at STORET 090252 near the mouth of the Saginaw River and lowest near the north and northeast perimeter sampling locations. Based on hydrologic studies in Saginaw Bay, it is likely that outer-bay locations are heavily influenced by low nutrient offshore waters of Lake Huron through lake seiches, whereas the southwest Saginaw River locations (namely STORET 090952) are influenced heavily by the Saginaw River (Beeton et al., 1967; Danek and Saylor, 1977; Stow et al., 2013).

Temporal Trends

Alkalinity has increased at a rate between 0.98% and 1.82% annually at 6 of the 8 Saginaw Bay stations, with median alkalinity ranging from 86 to 102 mg/L. In general, Great Lakes water bodies have high alkalinity because of natural limestone deposits. As groundwater flows through carbonate rock ($CaCO_3$), the calcium (Ca) and carbonate (CO_3) dissolve into water. The negatively charged carbonate ion (CO_3^-), neutralizes acids by absorbing free H^+ ions. Therefore, an increasing trend in alkalinity may be explained by an increasing proportion of groundwater during recent low water levels and low precipitation years in the Great Lakes region (Gronewold et al., 2013). Regardless, median alkalinity was 91 mg/L, so although this trend was statistically significant, the rate may not be ecologically relevant.

There were increasing trends in sodium at 4 out of 8 sites at a rate between 1.27% and 2.64% annually, with median concentrations ranging from 8.1 mg/L to 9.8 mg/L. This element is required for aquatic plant growth; however, unnaturally high levels can be an indication of anthropogenic pollution from road salts, wastes, and fertilizers. That being said, current levels are well below present screening guidelines (Iowa Department of Natural Resources, 2009).

Concentrations of lead, copper, and chromium are meeting all applicable Rule 57 WQS. That being said, chromium has increased within Saginaw Bay at STORET IDs 060062 and 090252 at a rate of between 5.18% and 8.5% annually. This trend is not consistent with the WCMP tributary site on the Saginaw River. Trends in chromium were not analyzed for in the Great Lakes embayments in the previous WCMP report (Roush, 2013). The trends in Saginaw Bay chromium were at stations near the outer bay; therefore, it is possible the trends identified are the result of the influence of the Saginaw River and changes in hydrologic currents directing the Saginaw River plume toward the outer bay (Beeton et al., 1967; Stow et al., 2013).

EGLE will continue to monitor quality and the environmental and ecological significance of these patterns trends as long as resources allow.

Grand Traverse Bay

Spatial/Seasonal

Unlike Saginaw Bay, the major tributary to Grand Traverse Bay, the Boardman River, does not appear to influence nutrient or metal distributions within Grand Traverse Bay. Trophic status throughout Grand Traverse Bay remains oligotrophic and excellent in quality and total phosphorus has decreased further since WCMP monitoring began.

Temporal Trends

Total phosphorus has been decreasing at the only station meeting data requirements for trend analysis at a rate of -6.15%. In contrast to Saginaw Bay, the water quality in Grand Traverse Bay has been historically classified as oligotrophic and minimally impacted (Saxton, 2006). Chlorophyll a has also been decreasing at all 4 stations at a rate of -6.76% to -10.66% annually. Decreases in total phosphorus and chlorophyll in Grand Traverse Bay may be the result of improved wastewater treatment practices and the introduction of zebra mussels in 1992 (GLEC, 2007).

We also identified significant, increasing trends in magnesium, sodium, chloride and sulfate at stations within Grand Traverse Bay. While these chemicals are required nutrients for plant growth, elevated levels can be indicative of disturbance, such as the increasing development of Grand Traverse Bay (GLEC, 2007). Regardless, all values are meeting relevant screening values and EGLE will continue to monitor quality and the environmental and ecological significance of these patterns trends as long as resources allow.

Trace metals were not analyzed for trend analysis due to limited sample size and high frequency of censored data; however, all samples met Rule 57 criteria.

3.3 METHODS

3.3.1 Study Design

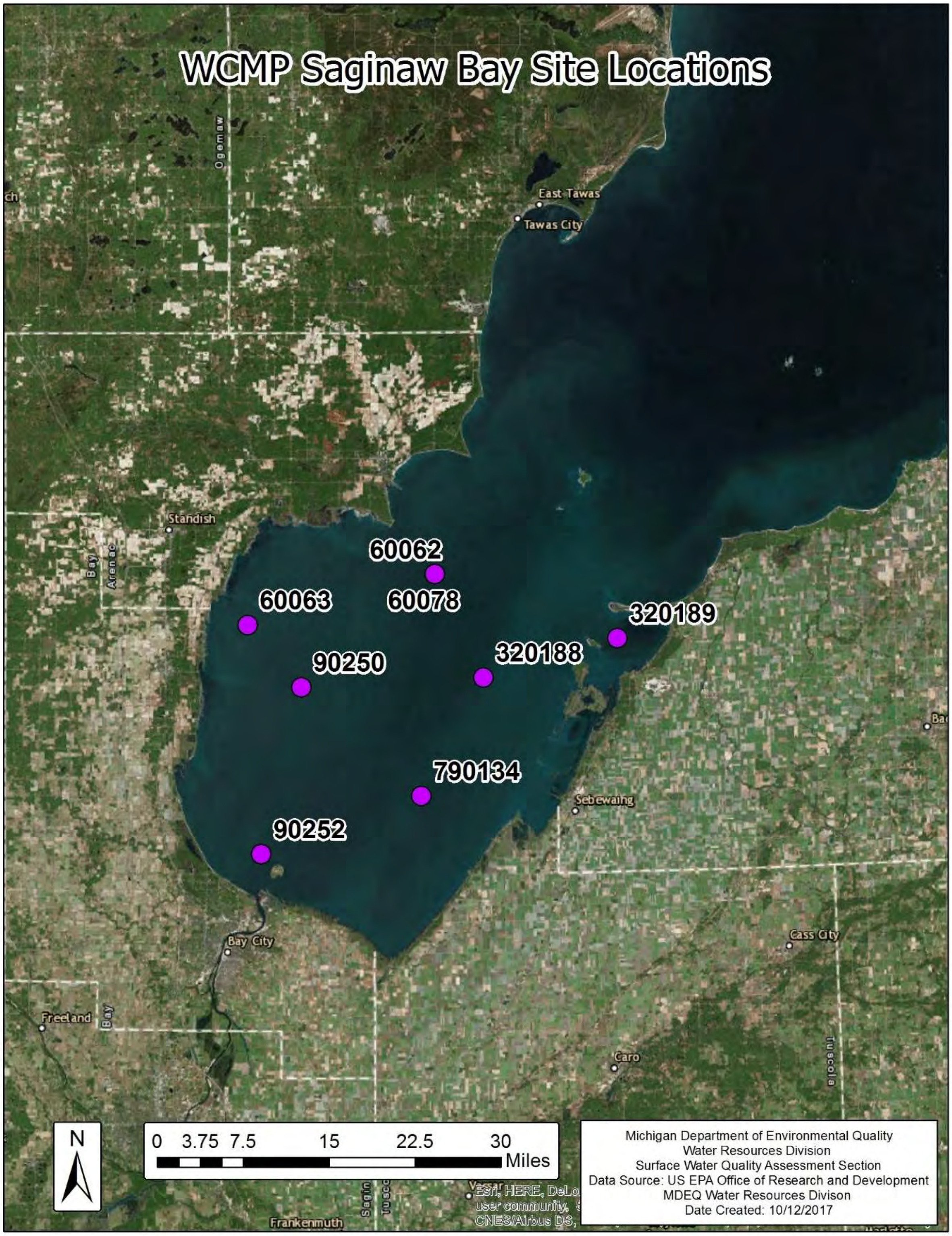
Saginaw Bay

The WCMP for Saginaw Bay consists of 7 monitoring locations spread throughout the inner bay. All 7 locations are monitored with surface grab samples. At 1 of these stations (STORET #060062) a concurrent mid-depth sample is taken. The mid-depth station has its own STORET number, 060078, which makes for a total of 8 monitoring stations (Figure 3-1). Sampling for Saginaw Bay was originally limited to 3 events between May and October. In 2001, sampling in Saginaw Bay was increased to monthly, from April to November. Sampling schedules in the Great Lakes bays have been modified, as necessary, to account for equipment failure or personnel safety.

Grand Traverse Bay

The WCMP for Grand Traverse Bay consists of 4 monitoring locations. Two stations are located in East Bay and 2 are located in the West Bay (Figure 3-2). All 4 locations are monitored with surface grab samples. Sampling in Grand Traverse Bay has continued to occur

3 times per year, typically during the months of April, July, and October. Sampling schedules in the Great Lakes bays have been modified, as necessary, to account for equipment failure or personnel safety.



WCMP Saginaw Bay Site Locations

Michigan Department of Environmental Quality
Water Resources Division
Surface Water Quality Assessment Section
Data Source: US EPA Office of Research and Development
MDEQ Water Resources Divison
Date Created: 10/12/2017

Figure 3-1. WCMP Monitoring locations in Saginaw Bay, an embayment of Lake Huron.

Michigan Department of Environmental Quality
Water Resources Division
Surface Water Quality Assessment Section
Data Source: US EPA Office of Research and Development
MDEQ Water Resources Divison
Date Created: 10/12/2017

Figure 3-2. WCMP locations in Grand Traverse Bay, an embayment of Lake Michigan.

3.3.2 Data Analysis

All results are presented by parameter type. The parameter types used in the Great Lakes Bays chapter include (A) nutrient parameters (total phosphorus, orthophosphate, kjeldahl nitrogen, nitrate, nitrite, ammonia, and chlorophyll a), (B) conventional parameters (TOC, turbidity, TDS, chloride, sodium, hardness, conductance, TSS, alkalinity, pH, DO, potassium, and sulfate) and (C) trace metals (chromium, copper, lead, and mercury).

3.3.3 Statistical Analysis

Results in this chapter are presented, by parameter type, as described above. Statistical methods are covered in-depth within the introduction, but are summarized as follows:

Between group (e.g., STORET and monthly) comparisons were made using Kruskal-Wallis tests for parameters without censored data (Giraudoux, 2016; Helsel, 2012). For parameters with censored data, comparisons among groups were conducted using the interval-censored form of the generalized Wilcoxon test. Summary statistics for parameters with censored data points were generated using Turnbull methods as described in Helsel (2012). For parameters that did not have any values below the laboratory's reporting limits (RL), summary statistics (e.g., minimum, quartile 1, median, quartile 3, and maximum) and boxplots were generated using the base (standard) R environment. Temporal trend analyses were performed using Seasonal Kendall trend analysis for uncensored data (Lorenz, 2015). Trends in parameters with censored data were measured using Tobit linear regression (TR) techniques (Lorenz, 2015; Helsel and Hirsch, 2002).

3.3.3.1 Spatial

Statistical comparisons were made to identify significant spatial (STORET) patterns in the parameters. The results of these spatial comparisons are shown in tables at the end of each section.

3.3.3.2 Temporal

Statistical comparisons in the Great Lakes Bays were made to analyze temporal (monthly) patterns in water quality parameters. Ecologically significant patterns in monthly concentrations are displayed in text with boxplots. Additional figures are available upon request. Potential trends from 1998-2014 were also identified using temporal trend analysis. Temporal trend results are shown in summary tables at the end of each section.

3.4 RESULTS

3.4.1 Saginaw Bay

3.4.1.1 Nutrients

Total Phosphorus

The overall median concentration of total phosphorus in Saginaw Bay was 0.016 mg/L. This concentration suggests that Saginaw Bay is mesotrophic in trophic status. Phosphorus concentrations ranged from nondetectable (< 0.003 mg/L) to 0.184 mg/L. There was a significant difference in concentrations among months and total phosphorus was higher in the fall and lowest in spring and summer ($p < 0.001$; Figure 3-3). Concentrations also varied significantly by location and were highest at the mouth of the Saginaw River and lowest at the northeast stations ($p < 0.001$; Table 3-1). No significant temporal trends were detected (Table 3-1).

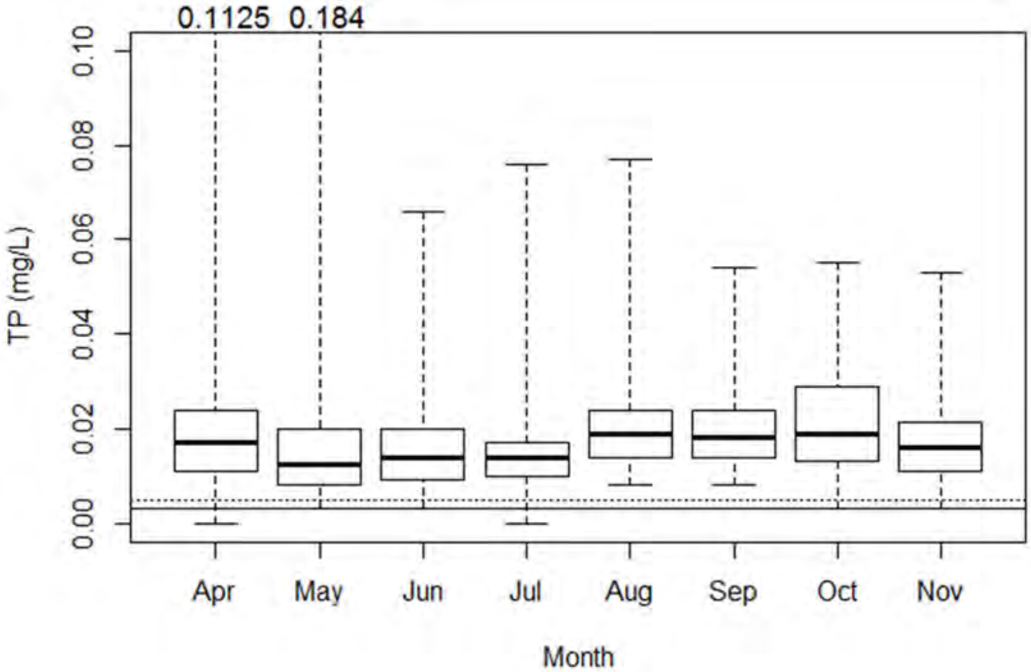


Figure 3-3. Total phosphorus concentrations, by month, 1998-2014. Y axis was cut off at a maximum concentration of 0.10 mg/L. Numbers across top reflect maximum values above this cutoff. Solid line represents detection limit; dotted line represents quantification limit.

Orthophosphate

Nearly 96% (641 of 831) of samples were below the laboratory's quantification limit, suggesting that concentrations of orthophosphate are fleeting in Saginaw Bay. The overall median concentration was 0.005 mg/L and concentrations ranged from nondetectable (< 0.002 mg/L) to 0.087 mg/L. Monthly comparisons and temporal trend analyses were not performed due to the high frequency of samples below quantification level (> 50%).

Kjeldahl Nitrogen

Overall median Kjeldahl nitrogen was 0.37 mg/L and concentrations ranged from 0.120 mg/L to 1.44 mg/L. Kjeldahl nitrogen varied by month and was highest in the summer and lowest in spring and fall ($p < 0.001$; Figure 3-4). Concentrations were also higher at stations near the Saginaw River mouth and lowest at the north and northeast stations ($p < 0.001$; Table 3-1). No significant temporal trends were detected (Table 3-1).

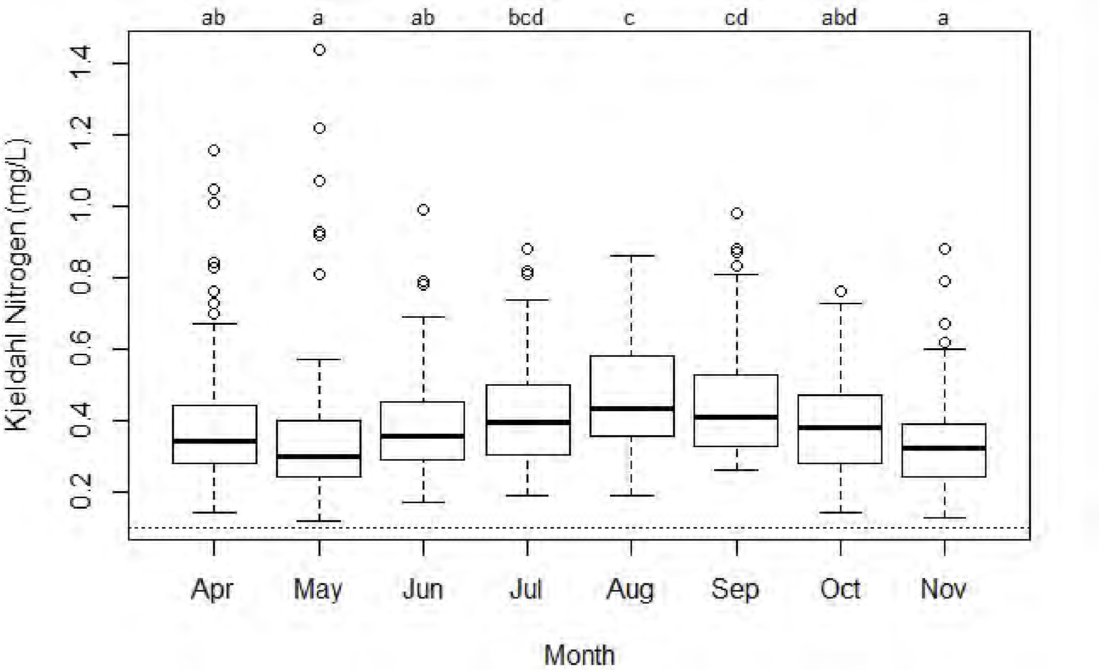


Figure 3-4. Kjeldahl nitrogen concentrations, by month, 1998-2014. Letters across top reflect results of multiple comparisons. Months that do not share a letter are statistically different. The horizontal dotted line represents EGLE Environmental Laboratory quantification limit.

Nitrate Nitrogen

The overall median concentration was 0.270 µg/L. Concentrations ranged from nondetectable (< 0.001 mg/L) to 1.93 mg/L. Nitrate levels were significantly higher in spring and lower in the summer and fall ($p < 0.001$; Figure 3-5). Nitrate was also highest at the Saginaw River mouth ($p = 0.005$; Table 3-1). There were no significant temporal trends in nitrate (Table 3-1).

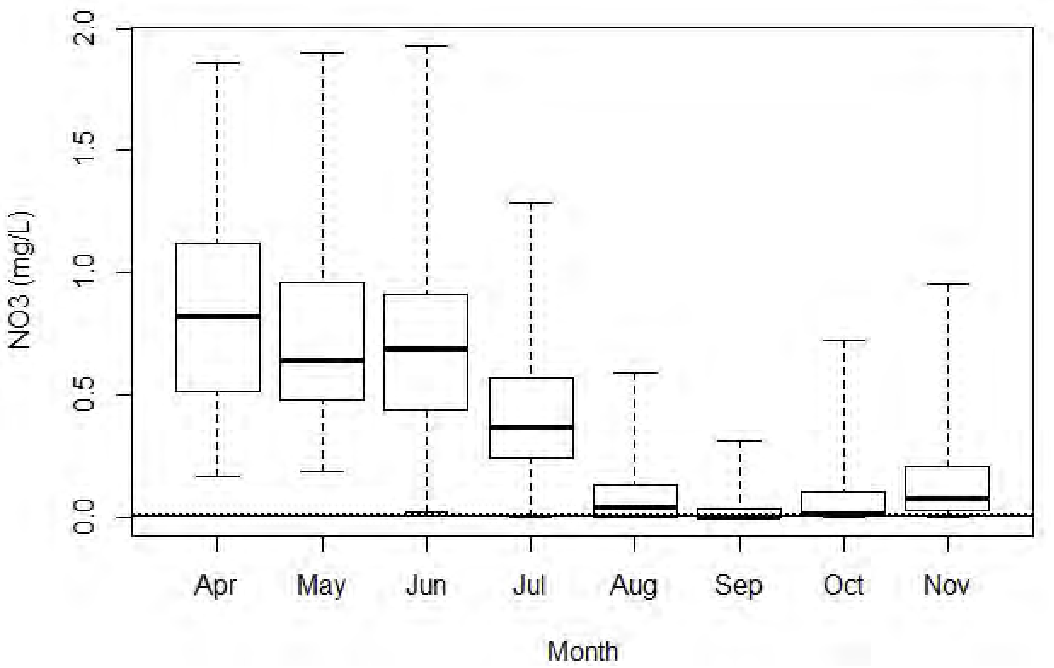


Figure 3-5. Nitrate concentrations, by month, 1998-2014. The solid line represents the detection limit; the dotted line represents EGLE Environmental Laboratory's quantification limit.

Nitrite Nitrogen

Nearly 85% (703 of 831) of nitrite samples were below the laboratory's quantification limit in Saginaw Bay. The overall median concentration of nitrite was 0.01 mg/L and ranged from nondetectable (< 0.002 mg/L) to 0.12 mg/L. No temporal trends were detected. Summary statistics, by station, can be found in Table 3-1.

Ammonia Nitrogen

Nearly 62% (511 of 830) of samples were below the quantification limit in Saginaw Bay. The overall median concentration of ammonia was 0.010 mg/L and levels ranged from nondetectable (< 0.001 mg/L) to 0.194 mg/L. No temporal trends were detected. Summary statistics, by station, can be found in Table 3-1.

Chlorophyll a

The overall median concentration of chlorophyll a was 5.0 µg/L. This concentration classifies Saginaw Bay as mesotrophic, which is in agreement with the estimate using total phosphorus. Concentrations ranged from nondetectable (< 1 µg/L) to 35 µg/L. Chlorophyll a was significantly higher in summer and fall and lower in the spring ($p < 0.001$; Figure 3-6). Concentrations were also higher at southern and western Saginaw Bay and lower at northeast stations ($p < 0.001$; Table 3-1). There was a decreasing trend in chlorophyll a at 5 out of the 8 sites at a rate of -3.44% to -4.74% annually (Table 3-1).

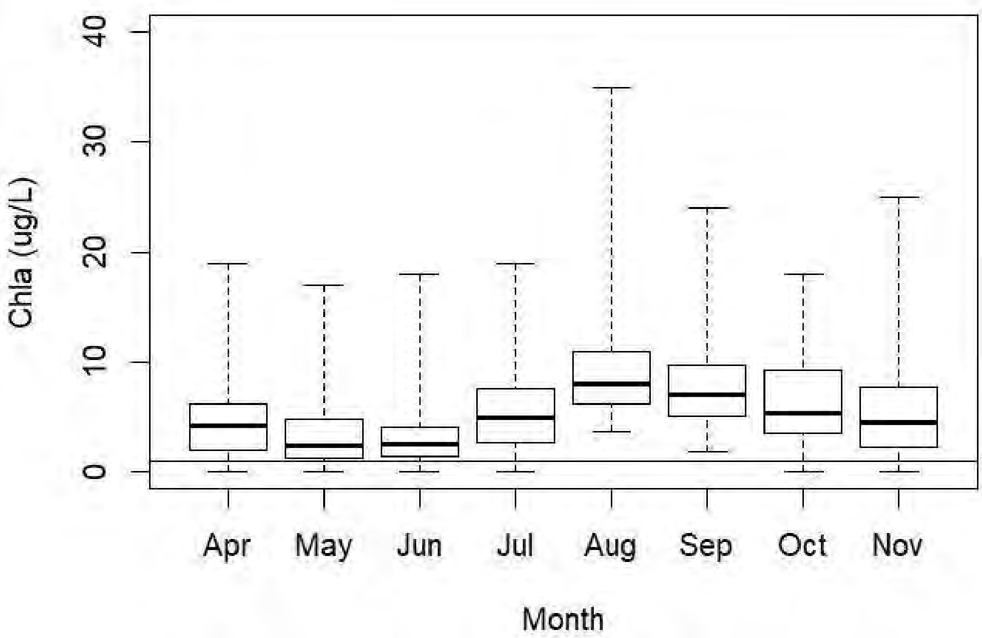


Figure 3-6. Chlorophyll a concentrations, by month, 1998-2014. The solid horizontal line represents the laboratory's detection limit.

Table 3-1. Saginaw Bay nutrients, by station. (Left) Summary Statistics. STORETs with nondetect samples marked with ‘ND;’ STORETs with nonquantifiable samples marked with ‘NQ.’ STORETs that do not share a letter under multiple comparisons are statistically different. Multiple comparisons were not performed on parameters with censored data. (Right) Temporal trends were analyzed using Seasonal Kendal (SK) or Tobit Regression (TR). Parameters censored > 50% marked --.

Summary Statistics							**Trend Analysis**			
****Total Phosphorus (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
060062	NQ	0.010	0.014	0.020	0.100	NA	TR	15.4	-1.5	0.24
060063	NQ	0.010	0.014	0.019	0.038	NA	TR	15.4	-0.4	0.61
060078	0.005	0.010	0.015	0.021	0.106	NA	TR	15.4	-1.2	0.33
090250	ND	0.015	0.020	0.028	0.057	NA	TR	15.4	-2.0	0.10
090252	0.006	0.017	0.024	0.037	0.184	NA	TR	15.4	1.1	0.41
320188	ND	0.009	0.013	0.018	0.113	NA	TR	15.4	0.2	0.86
320189	NQ	0.012	0.017	0.021	0.098	NA	TR	15.4	-1.0	0.35
790134	NQ	0.011	0.015	0.020	0.052	NA	TR	15.4	0.3	0.75
****Orthophosphate (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
060062	ND	0.005	0.005	0.005	0.045	NA	--	--	--	--
060063	ND	0.001	0.005	0.005	0.025	NA	--	--	--	--
060078	ND	0.001	0.005	0.005	0.035	NA	--	--	--	--
090250	ND	0.001	0.005	0.005	0.013	NA	--	--	--	--
090252	ND	0.005	0.005	0.006	0.087	NA	--	--	--	--
320188	ND	0.001	0.005	0.005	0.020	NA	--	--	--	--
320189	ND	0.005	0.005	0.005	0.016	NA	--	--	--	--
790134	ND	0.001	0.005	0.005	0.008	NA	--	--	--	--
Kjeldahl Nitrogen (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
060062	0.130	0.255	0.310	0.370	0.930	ab	SK	16.0	0.25	0.798

** Parameters summarized using interval-censored data analysis. Multiple comparisons were not possible for these parameters.

Table 3-1 (continued).

Summary Statistics							Trend Analysis			
Kjeldahl Nitrogen (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
060063	0.19	0.30	0.38	0.46	0.81	c	SK	16.0	0.68	0.606
060078	0.14	0.25	0.31	0.35	0.92	ab	SK	16.0	0.65	0.397
090250	0.17	0.31	0.35	0.40	0.79	bc	SK	16.0	0.00	0.983
090252	0.18	0.38	0.49	0.66	1.44	d	SK	16.0	0.00	0.923
320188	0.12	0.26	0.35	0.44	1.05	abc	SK	16.0	0.37	0.807
320189	0.18	0.39	0.49	0.65	1.16	d	SK	16.0	0.56	0.651
790134	0.14	0.29	0.40	0.51	0.98	c	SK	16.0	0.74	0.544
****Nitrate Nitrogen (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
060062	ND	0.08	0.28	0.56	1.51	NA	TR	15.4	-1.96	0.448
060063	ND	0.01	0.21	0.53	1.29	NA	TR	15.4	-2.89	0.576
060078	ND	0.09	0.27	0.56	1.93	NA	TR	15.4	-1.39	0.576
090250	ND	0.01	0.29	0.57	1.56	NA	TR	15.4	-6.48	0.177
090252	ND	0.02	0.40	1.09	1.90	NA	TR	15.4	-0.53	0.908
320188	ND	0.03	0.32	0.55	1.86	NA	TR	15.4	-7.24	0.105
320189	ND	0.01	0.11	0.53	1.57	NA	TR	15.4	-5.86	0.268
790134	ND	0.02	0.28	0.75	1.68	NA	TR	15.4	-2.04	0.668

** Parameters summarized using interval-censored data analysis. Multiple comparisons were not possible for these parameters.

Table 3-1 (continued).

Summary Statistics							**Trend Analysis**			
****Nitrite Nitrogen (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
060062	ND	0.006	0.006	0.006	0.051	NA	--	--	--	--
060063	ND	0.010	0.010	0.010	0.031	NA	--	--	--	--
060078	ND	0.010	0.010	0.010	0.036	NA	--	--	--	--
090250	ND	0.003	0.010	0.010	0.025	NA	--	--	--	--
090252	ND	0.010	0.010	0.014	0.120	NA	--	--	--	--
320188	ND	0.010	0.010	0.010	0.025	NA	--	--	--	--
320189	ND	0.006	0.006	0.013	0.048	NA	--	--	--	--
790134	ND	0.010	0.010	0.010	0.040	NA	--	--	--	--
****Ammonia Nitrogen (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
060062	ND	0.010	0.010	0.011	0.032	NA	TR	--	--	--
060063	ND	0.010	0.010	0.010	0.031	NA	TR	--	--	--
060078	ND	0.010	0.010	0.011	0.031	NA	TR	--	--	--
090250	ND	0.010	0.010	0.010	0.051	NA	TR	--	--	--
090252	ND	0.010	0.017	0.039	0.194	NA	TR	15.4	-0.75	0.756
320188	ND	0.010	0.010	0.010	0.117	NA	TR	--	--	--
320189	ND	0.010	0.010	0.019	0.153	NA	TR	15.4	-0.43	0.891
790134	ND	0.010	0.010	0.013	0.028	NA	TR	--	--	--

** Parameters summarized using interval-censored data analysis. Multiple comparisons were not possible for these parameters.

Table 3-1 (continued).

Summary Statistics							**Trend Analysis**			
****Chlorophyll a (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
060062	ND	2.8	5.1	8.3	26.0	NA	TR	15.4	-3.81	**0.016**
060063	ND	1.7	3.2	5.8	25.0	NA	TR	15.4	-4.74	**0.007**
060078	ND	2.0	3.4	5.7	10.0	NA	TR	15.4	-0.897	0.741
090250	ND	4.6	6.8	11.0	24.0	NA	TR	15.4	-4.22	**0.004**
090252	ND	2.1	5.9	11.0	35.0	NA	TR	15.4	-2.60	0.146
320188	ND	1.6	4.0	6.4	15.0	NA	TR	15.4	-3.45	**0.034**
320189	ND	4.3	5.9	8.5	19.0	NA	TR	15.4	-3.43	**0.003**
790134	ND	2.3	4.0	7.3	15.0	NA	Short Record	--	--	--

** Parameters summarized using interval-censored data analysis. Multiple comparisons were not possible for these parameters.

3.4.1.2 Conventional Parameters

TOC

The overall median concentration was 3.7 mg/L and ranged from 1.4 mg/L to 11.0 mg/L. Values for TOC varied significantly by month ($p < 0.001$) and were highest during the summer and lowest in the spring. Concentrations also varied by station and were highest at the Saginaw River mouth station and lowest at the northern locations ($p < 0.001$; Table 3-2). An increasing trend in TOC was detected at STORET 060063 (trend = 2.17%; Table 3-2).

Turbidity

The overall median value for turbidity within Saginaw Bay was 3.3 NTU. Turbidity ranged from nondetectable (< 1 NTU) to a maximum of 78. The frequency of censored (nondetectable) samples precluded the analysis of spatial analysis. Trends were not explored for this parameter due to diurnal and seasonal variability. Summary statistics, by station, are shown in Table 3-2.

TDS

The overall median concentration was 190 mg/L and concentrations ranged from 112 mg/L to 370 mg/L. TDS was highest in the spring and lowest in the fall ($p < 0.001$). Concentrations also varied significantly by station and were highest at the Saginaw River mouth and lowest at the northern sampling locations ($p < 0.001$; Table 3-2). No significant temporal trends were detected (Table 3-2).

Sodium

Median sodium was 9.8 mg/L and ranged from nondetectable (< 0.1 mg/L) to 33.9 mg/L (Table 3-3). Sodium varied by month and was highest in the spring and lowest in the fall ($p < 0.001$). Concentrations also varied by STORET and were higher near the Saginaw River and lower at the northern stations ($p < 0.001$; Table 3-2). There was a significant, increasing trend in sodium at 4 of 8 stations (trend = 1.92%, 1.27%, 1.31%, and 2.64%; Table 3-2).

Chloride

Median chloride was 18 mg/L and concentrations ranged from 6.0 mg/L to 62 mg/L. Chloride varied by month and were higher in spring and lower in the fall ($p < 0.001$; Figure 3-7). Concentrations were also higher at the Saginaw River mouth station ($p < 0.001$; Table 3-2). Trend analyses did not detect any significant temporal patterns (Table 3-2).

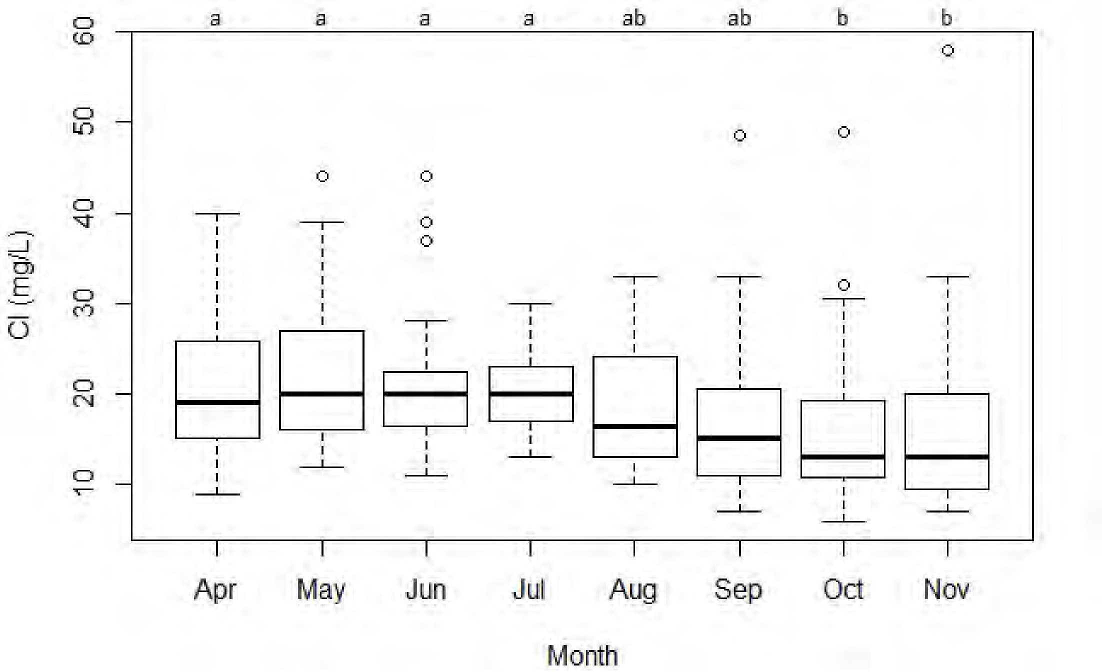


Figure 3-7. Total chloride within Saginaw Bay, 1998-2014. Months that do not share a letter (top) are significantly different.

Hardness

Overall median hardness was 122 mg/L and concentrations ranged from 40 mg/L to 315 mg/L. Hardness varied by month and was highest in spring and lowest in the fall ($p < 0.001$; Figure 3-8). This monthly pattern was similar to the trend for alkalinity and conductivity. Hardness was also highest at southwest stations and lowest at northeast stations ($p < 0.001$; Table 3-2). There was an increasing trend at 2 of 8 sites (trend = 1.20% and 0.55%; Table 3-2).

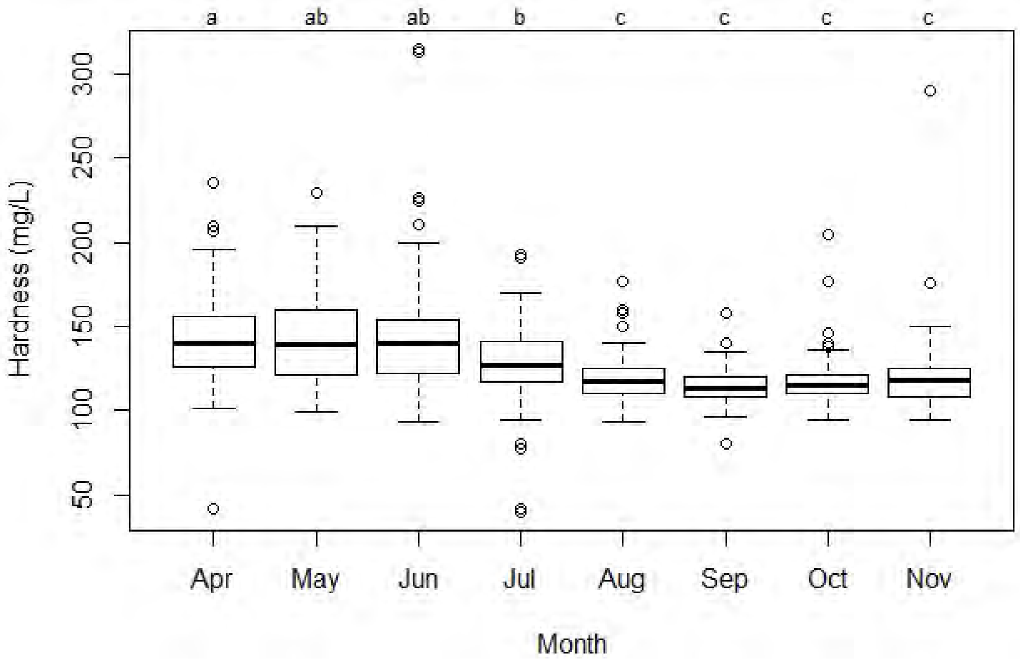


Figure 3-8. Hardness by month. Months that do not share a letter (top) are significantly different.

Calcium

The median concentration was 32.3 mg/L and concentrations ranged from 14.9 mg/L to 65.2 mg/L. Concentrations varied significantly by month and were highest in the spring and lowest in the fall ($p < 0.001$; Figure 3-9). Concentrations were significantly higher at the Saginaw River station and lower at the northern sampling stations ($p < 0.001$; Table 3-2). A significant, increasing trend was found at STORET 060063 (trend = 0.951%; Table 3-2).

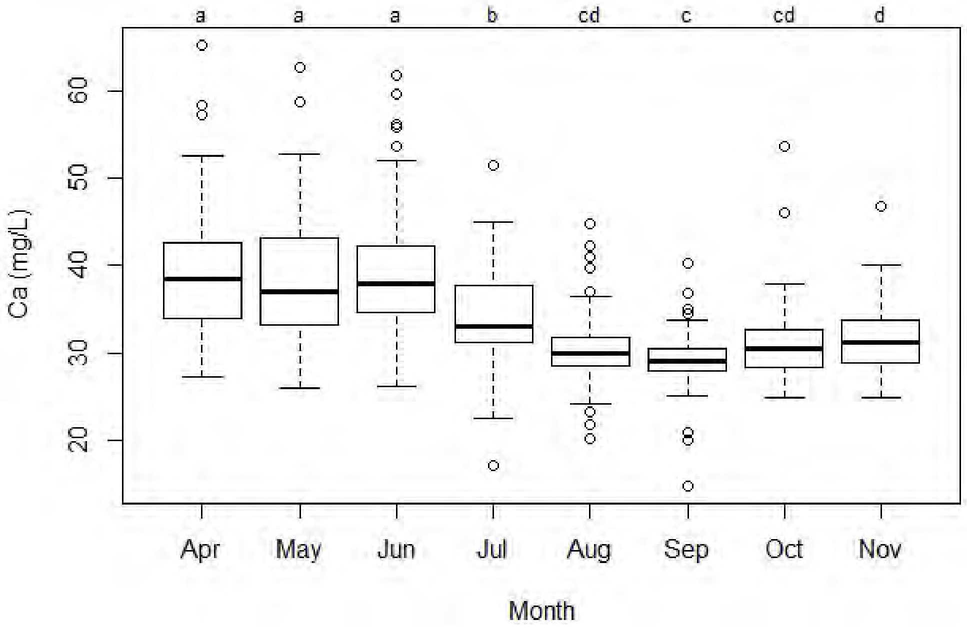


Figure 3-9. Total calcium within Saginaw Bay, 1998-2014. Months that do not share a letter (top) are significantly different.

Magnesium

Overall median magnesium was 10.2 mg/L between 1998 and 2014 and ranged from 6.7 mg/L to 18.2 mg/L (Table 3-3). Magnesium varied by month ($p < 0.001$) and was highest in the spring and lowest in fall. Concentrations also varied by station and were highest near the Saginaw River mouth and lowest at northern stations ($p < 0.001$; Table 3-2). An increasing trend was found at 2 of 8 stations (trend = 1.11% and 0.819%; Table 3-2).

Conductivity

The overall median value for conductivity was 288 µS/cm and concentrations ranged from 186 µS/cm to 559 µS/cm. Conductivity was significantly higher in the spring and lower in the fall ($p < 0.001$). Conductivity also varied by STORET and was highest at southwest stations and lowest at northeast stations ($p < 0.001$; Table 3-2). There was a significant, increasing trend in conductivity at 2 of 8 locations (trend = 1.17% and 0.67%; Table 3-2).

TSS

Overall median TSS was 5 mg/L and ranged from nondetectable (< 1 mg/L) to 60 mg/L (Table 3-3). Values varied by month and were generally highest during the late summer and lowest in late spring ($p < 0.001$). TSS was also highest at the Saginaw River mouth and lowest in the northern sites ($p < 0.001$; Table 3-2). No significant temporal trends were detected in TSS (Table 3-2).

Alkalinity

Median alkalinity was 91 mg/L and alkalinity ranged from 47 mg/L to 200 mg/L. Alkalinity varied by month and was greatest during the spring and lowest in the fall ($p < 0.001$). Alkalinity was also highest at the southwest locations ($p < 0.001$; Table 3-2). There was a significant, increasing trend at 6 of 8 locations (trend = 1.09%, 1.82%, 0.98%, 1.13%, 1.29% and 1.18%; Table 3-2).

pH

Overall median pH was 8.23 within Saginaw Bay and values ranged from 6.6 to 9.54. pH varied by month and was highest in the summer and lower in the fall ($p < 0.001$). pH was also higher near the Saginaw River and lower in the north and east ($p < 0.001$; Table 3-2). There were no statisically significant temporal trends in pH (Table 3-2).

DO

Median DO was 9.755 mg/L and levels ranged from 5.13 mg/L to 15.74 mg/L. DO was highest in fall and lowest in summer ($p < 0.001$). DO did not vary by STORET. Trends were not explored for this parameter due to diurnal and seasonal variability.

Potassium

The overall median concentration of potassium was 1.516 mg/L and ranged from 0.90 mg/L to 5.90 mg/L. Concentrations varied by month and were highest in the spring and lowest in the fall ($p < 0.001$). Concentrations also varied by STORET and were highest at the Saginaw River mouth station ($p < 0.001$; Table 3-2). A significant, increasing trend was found at 1 of 8 stations (trend = 2.38%; Table 3-2).

Sulfate

Median sulfate was 19 mg/L and concentrations ranged from 12 mg/L to 39 mg/L. Concentrations were highest in the spring and lowest in the fall ($p < 0.001$; Figure 3-10). Concentrations also varied by station and were highest at the Saginaw River mouth station ($p < 0.001$; Table 3-2). A significant, increasing trend was found for sulfate at STORET 060078 (trend = 1.76%; Table 3-2).

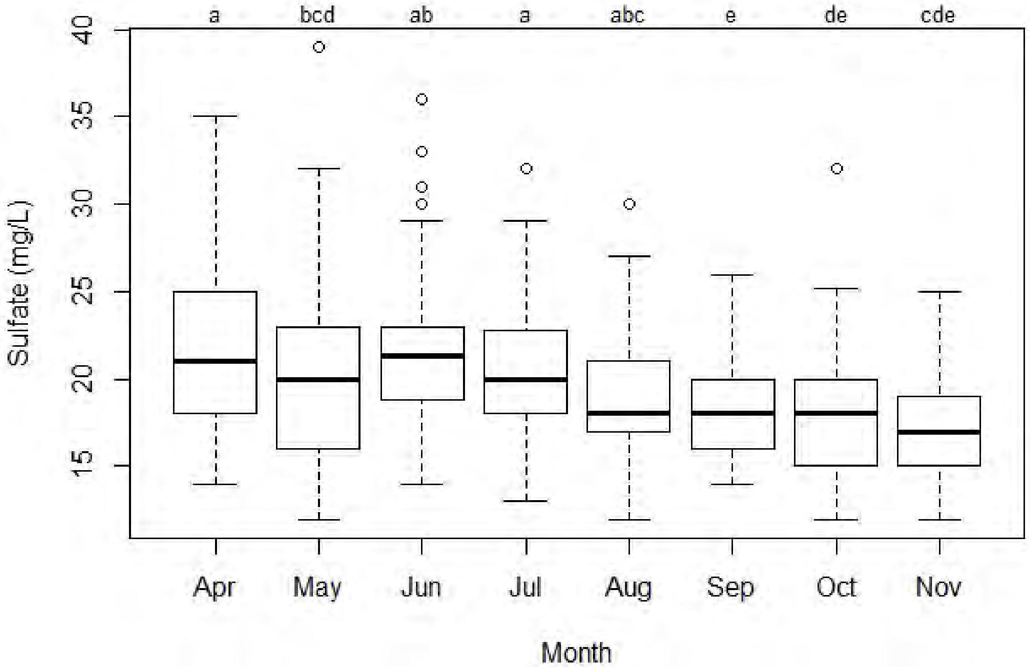


Figure 3-10. Sulfate within Saginaw Bay, 1998-2014. Months that do not share a letter (top) are significantly different.

Table 3-2. Saginaw Bay conventional parameters, by station. (Left) Summary Statistics. STORETs with nondetect samples marked with 'ND;' STORETs with nonquantifiable samples marked with 'NQ.' STORETs that do not share a letter under multiple comparisons are statistically different. Multiple comparisons were not performed on parameters with censored data. (Right) Temporal trends were analyzed using Seasonal Kendal (SK) or Tobit Linear Regression (TR). Parameters censored > 50% marked --.

Summary Statistics							**Trend Analysis**			
TOC (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
60062	1.5	2.8	3.2	3.7	8.5	a	SK	16	0	0.833
60063	2.1	3.3	3.9	4.7	9.3	bc	SK	16	2.17459	**0.039**
60078	1.7	2.8	3.1	3.7	7.9	a	SK	16	0.65309	0.478
90250	2.3	3.1	3.6	4	6.6	abd	SK	16	0.39765	0.585
90252	1.8	3.7	4.7	6.1	11	e	SK	16	1.29605	0.278
320188	1.5	2.6	3.4	4.3	7.8	ad	SK	16	1.4413	0.322
320189	1.5	3.4	4.2	5.4	8.8	ce	SK	16	1.19772	0.24
790134	1.4	3	3.9	5	8.3	bcd	SK	16	1.7107	0.215
****Turbidity (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
060062	ND	1.0	2.6	3.9	57.0	NA				
060063	ND	1.0	2.7	4.6	12.0	NA				
060078	ND	1.0	2.5	4.4	57.0	NA				
090250	ND	2.4	3.9	5.8	33.0	NA				
090252	ND	2.3	4.1	7.7	78.0	NA				
320188	ND	1.4	3.0	5.2	58.0	NA				
320189	ND	2.9	4.1	6.0	40.0	NA				
790134	ND	2.0	3.2	5.3	21.0	NA				

** Parameters summarized using interval-censored data analysis. Multiple comparisons were not possible for these parameters.

Table 3-2 (continued).

Summary Statistics							**Trend Analysis**			
TDS (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
60062	138	164	180	200	300	ab	SK	16	0	0.547
60063	148	180	190	210	310	ab	SK	16	0.45	0.262
60078	139	160	180	200	280	a	SK	16	0.45	0.254
90250	150	179	190	220	310	b	SK	16	0	0.948
90252	150	190	230	280	370	c	SK	16	0.06	0.614
320188	112	160	180	210	310	ab	SK	16	0	0.981
320189	116	172	200	220	270	b	SK	16	-0.5	0.505
790134	116	175	190	228	320	b	SK	16	0	0.912
****Sodium (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
60062	4	6.7	8.4	10.3	17.4	NA	TR	14.3	0.96	0.078
60063	4.6	8.4	9.8	11.7	16.8	NA	TR	14.3	1.92	**0.002**
60078	3.6	6.6	8.1	10.3	16.4	NA	TR	14.3	1.27	**0.031**
90250	5	8	9.6	11.3	17.5	NA	TR	14.3	1.31	**0.007**
90252	ND	10.5	14.3	17.8	33.9	NA	TR	14.3	1.31	0.247
320188	4.2	6.4	8.7	11.8	19.7	NA	TR	14.3	2.64	**0.003**
320189	4.5	8	10.6	13.6	18	NA	TR	14.3	0.44	0.535
790134	4.1	8.4	11	13	23	NA	TR	14.3	1.63	0.068

** Parameters summarized using interval-censored data analysis. Multiple comparisons were not possible for these parameters.

Table 3-2 (continued).

Summary Statistics							**Trend Analysis**			
Chloride (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
60062	6.00	11.0	14.0	19.0	36.0	a	SK	16.0	0.44	0.421
60063	9.00	15.0	18.0	22.0	40.0	ab	SK	16.0	1.89	0.818
60078	6.00	11.0	14.0	19.0	34.0	a	SK	16.0	1.85	0.130
90250	9.00	14.0	17.6	22.0	41.0	ab	SK	16.0	0.64	0.395
90252	7.00	19.3	27.8	38.0	62.0	c	SK	16.0	0.86	0.315
320188	6.00	11.6	16.0	22.0	40.0	ab	SK	16.0	1.57	0.300
320189	8.90	14.0	19.0	27.0	51.0	ab	SK	16.0	-0.79	0.561
790134	7.00	14.5	20.0	26.0	44.0	bc	SK	16.0	0.00	0.907
Hardness (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
60062	94	110	117	135	313	ab	SK	16	0.6	0.086
60063	40	115	124	140	196	ab	SK	16	1.2	**0.004**
60078	94	109	118	132	315	a	SK	16	0.5	**0.017**
90250	42	117	125	140	184	b	SK	16	0.5	0.109
90252	107	122	140	175	235	c	SK	16	0.8	0.06
320188	77	108	118	132	290	a	SK	16	1	0.07
320189	80	114	123	135	178	ab	SK	16	0.7	0.25
790134	97	113	123	143	193	ab	SK	16	0.8	0.104

** Parameters summarized using interval-censored data analysis. Multiple comparisons were not possible for these parameters.

Table 3-2 (continued).

Summary Statistics							**Trend Analysis**			
Calcium (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
60062	25	28.9	31.2	36.7	50.7	ab	SK	16	0.36	0.098
60063	22.6	30.6	32.9	37.5	52.8	ac	SK	16	0.95	**0.010**
60078	25	28.9	31.5	36	48.9	ab	SK	16	0.3	0.147
90250	27	31.3	34	38	48.2	cd	SK	16	0.36	0.193
90252	25.1	32.1	38	46.2	65.2	d	SK	16	0.66	0.062
320188	25.6	28.5	31	35.3	58.3	ab	SK	16	0.85	0.084
320189	14.9	28	31	34.9	47.5	b	SK	16	0.88	0.243
790134	24.8	29.2	32.1	38.6	51.5	abc	SK	16	0.82	0.076
Magnesium (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
60062	7.3	8.8	9.6	10.9	13.2	ab	SK	16	0.86	0.067
60063	7.8	9.6	10.3	11.2	15.8	cd	SK	16	1.11	**0.007**
60078	7.3	8.7	9.4	10.5	12.5	a	SK	16	0.82	**0.039**
90250	8.2	9.4	10	11	15.5	bc	SK	16	0.57	0.127
90252	8.1	10.3	12	13.8	18.2	e	SK	16	0.68	0.131
320188	7.3	8.7	9.7	11.1	15.4	abc	SK	16	1	0.163
320189	8.1	9.8	11.1	12.6	17	de	SK	16	0.13	0.821
790134	6.7	9.5	10.5	12	16	cd	SK	16	0.48	0.177

** Parameters summarized using interval-censored data analysis. Multiple comparisons were not possible for these parameters.

Table 3-2 (continued).

Summary Statistics							**Trend Analysis**			
Conductivity (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
60062	186	247	268	307	442	a	SK	16	0.4	0.189
60063	218	268	294	324	465	bc	SK	16	1.2	**0.011**
60078	190	240	267	298	416	a	SK	16	0.7	**0.026**
90250	199	263	295	323	463	bc	SK	16	0.5	0.149
90252	220	300	352	427	559	d	SK	16	0.6	0.227
320188	194	244	271	311	467	ab	SK	16	0.6	0.227
320189	197	262	290	323	433	abc	SK	16	0.3	0.854
790134	204	262	295	348	477	c	SK	16	0.7	0.107
TSS (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
60062	ND	4	4	6	39	NA	TR	15.4	-2.65	0.313
60063	ND	4	4	8	18	NA	TR	15.4	1.94	0.514
60078	ND	4	4	6	48	NA	TR	15.4	-2.77	0.254
90250	ND	4	5	9	36	NA	TR	15.4	-6.11	0.189
90252	ND	4	6	10	54	NA	TR	15.4	-0.75	0.756
320188	ND	4	6	10	26	NA	TR	15.4	-5.72	0.072
320189	ND	5	7	10	60	NA	TR	15.4	-0.43	0.892
790134	ND	4	5	9	31	NA	TR	15.4	-5.48	0.07

** Parameters summarized using interval-censored data analysis. Multiple comparisons were not possible for these parameters.

Table 3-2 (continued).

Summary Statistics							**Trend Analysis**			
Alkalinity (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
60062	64	80	87	98	200	ab	SK	15	1.1	**0.042**
60063	61	83	94	102	160	ab	SK	15	1.8	**0.002**
60078	64	79	88	97	160	ab	SK	15	1	**0.033**
90250	72	85	94	101	140	a	SK	15	1.1	**0.028**
90252	64	91	109	129	170	c	SK	15	1.3	0.077
320188	69	77	86	97	180	b	SK	15	0.8	0.26
320189	47	80	86	96	170	b	SK	15	1.3	**0.035**
790134	64	81	92	105	170	ab	SK	15	1.2	**0.046**
pH										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
60062	6.6	7.85	8.13	8.35	8.89	a	SK	16	0.22	0.313
60063	7.2	8.14	8.34	8.53	8.97	b	SK	16	0.14	0.279
60078	6.6	7.86	8.13	8.36	8.86	a	SK	16	0.22	0.339
90250	7	8.07	8.25	8.45	8.99	ab	SK	16	0.09	0.531
90252	7	7.97	8.17	8.49	9.17	ab	SK	16	0.08	0.554
320188	7.2	8.05	8.34	8.5	9.17	b	SK	16	0.15	0.265
320189	6.89	8	8.3	8.6	9.54	b	SK	16	0.08	0.673
790134	6.9	8.06	8.31	8.51	9.15	b	SK	16	0.11	0.464

** Parameters summarized using interval-censored data analysis. Multiple comparisons were not possible for these parameters.

Table 3-2 (continued).

Summary Statistics							**Trend Analysis**			
Dissolved Oxygen (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
60062	6.89	8.95	9.71	11.39	14.5	a				
60063	5.13	8.92	9.77	11.18	15.07	a				
60078	6.73	8.84	9.68	11.15	14.03	a				
90250	6.71	8.74	9.75	11.18	14.4	a				
90252	5.37	8.55	9.24	10.81	14.2	a				
320188	6.56	9.01	9.81	11.09	14.5	a				
320189	6.78	8.74	9.93	11.05	15.74	a				
790134	6.8	8.86	9.75	11.14	14	a				
Potassium (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
60062	0.9	1.2	1.4	1.7	5.9	ab	SK	15	0.27	0.472
60063	1.1	1.4	1.6	1.8	2.7	acd	SK	15	2.38	**0.007**
60078	0.9	1.2	1.4	1.6	3.5	b	SK	15	1.39	0.092
90250	1.1	1.4	1.5	1.7	2.8	abcd	SK	15	1.06	0.069
90252	1	1.6	2	2.5	4.2	e	SK	15	0.92	0.215
320188	0.9	1.2	1.4	1.7	3.8	abc	SK	15	2.35	0.152
320189	1	1.4	1.7	2	5	d	SK	15	0.7	0.6
790134	0.9	1.3	1.6	2	3.1	cd	SK	15	1.55	0.136

** Parameters summarized using interval-censored data analysis. Multiple comparisons were not possible for these parameters.

Table 3-2 (continued).

Summary Statistics							**Trend Analysis**			
Sulfate (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
60062	12	16	18	21	39	ab	SK	16	1.3	0.079
60063	12	17	19	21	30	ac	SK	16	0.25	0.483
60078	12	15	18	20	28	b	SK	16	1.76	**0.013**
90250	13	17	19	21	28	ab	SK	16	0.54	0.221
90252	14	18	21	25	36	d	SK	16	0.55	0.45
320188	12	16	18	21	31	ab	SK	16	0.93	0.297
320189	13	19	20	23	33	cd	SK	16	-0.1	0.658
790134	12	17	19	22	31	acd	SK	16	0	0.745

** Parameters summarized using interval-censored data analysis. Multiple comparisons were not possible for these parameters.

3.4.1.3 Trace Metals

Trace metals were collected from 4 of the 8 stations in Saginaw Bay, April through November. Trace metal stations include STORET #060062, #060063, #090252, and #320189. There were no WQS exceedances for metals in the current Integrated Report cycle (2012-2013).

Chromium

Median overall chromium was 0.206 µg/L within Saginaw Bay. Chromium ranged from nondetectable (< 0.057 µg/L) to 3.02 µg/L. Concentrations of chromium varied by month and were generally higher in spring and lower in summer ($p < 0.001$; Figure 3-11). Chromium also varied by location and the station near the Saginaw River had higher concentrations ($p < 0.001$; Table 3-3). An increasing trend was detected at 2 of 4 stations monitored for metals (trend = 8.5%, 5.18%; Table 3-3).

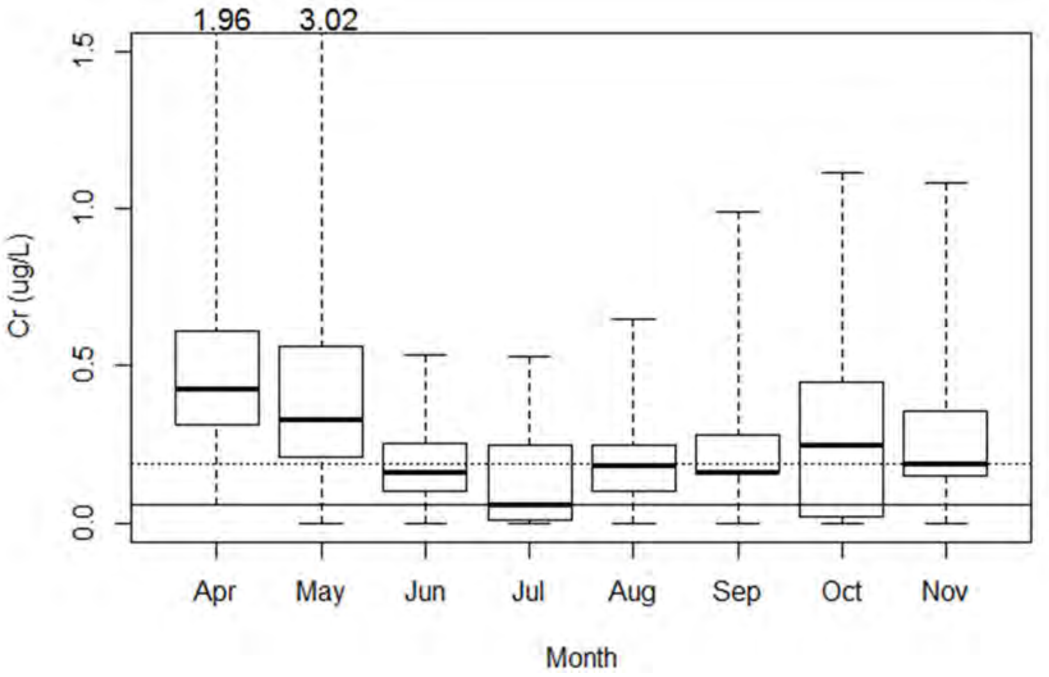


Figure 3-11. Total chromium within Saginaw Bay, 1998-2014. The y-axis was limited to a maximum of 1.5 µg/L chromium. Numbers across top reflect values exceeding this cutoff. The solid horizontal line represents the detection limit; dotted line represents the quantification limit.

Copper

Overall median copper was 0.823 µg/L within Saginaw Bay and ranged from nonquantifiable (< 0.57 µg/L) to 3.88 µg/L. Copper concentrations varied by month and were generally higher in spring and lower in late summer and fall ($p < 0.001$; Figure 3-12). Copper also varied by location and was generally higher at the station nearest the Saginaw River and lower at the north and northeast outer locations ($p < 0.001$; Table 3-3). An increasing trend in copper was detected at STORET 060062 near the outer bay (trend = 1.53%; Table 3-3).

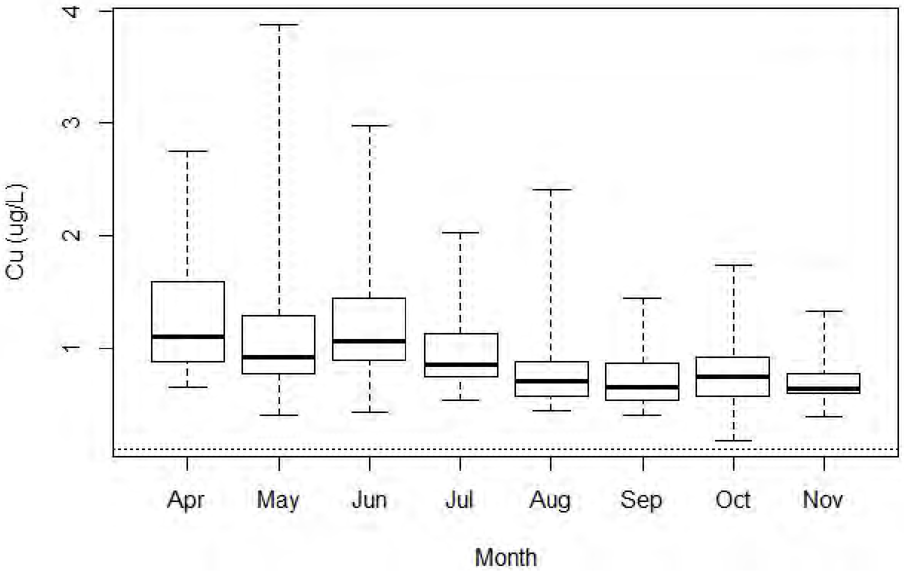


Figure 3-12. Total copper within Saginaw Bay, 1998-2014. Solid horizontal line represents the laboratory's detection limit. The dotted line represents the quantification limit.

Lead

Median lead was 0.158 µg/L. Concentrations ranged from 0.037 µg/L to 3.44 µg/L. Lead concentrations varied by month and were highest in spring and fall and lowest in summer ($p < 0.001$; Figure 3-13). Concentrations were highest at the Saginaw River mouth ($p < 0.001$; Table 3-3). There were no significant temporal trends in lead within Saginaw Bay (Table 3-3).

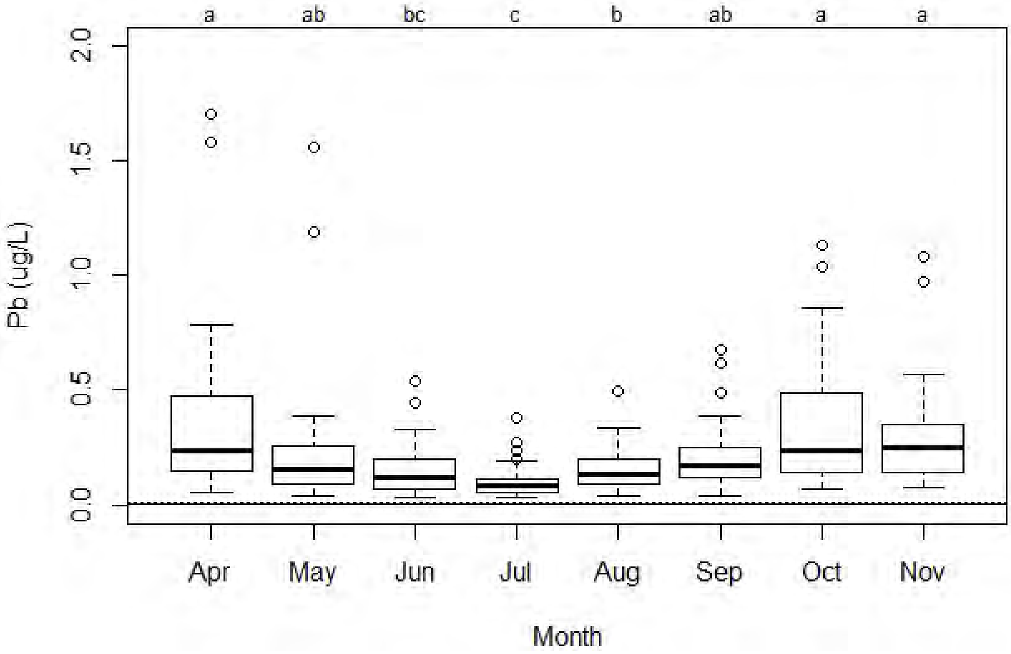


Figure 3-13. Total lead within Saginaw Bay, 1998-2014. The solid horizontal line represents the laboratory's detection limit. Months that do not share a letter (top) are significantly different. The dotted line represents the quantification limit. The dotted line represents the quantification limit.

Mercury

Median mercury was 0.525 ng/L within Saginaw Bay and concentrations ranged from nondetectable (< 0.14 ng/L) to 12.68 ng/L (Table 3-3). Mercury concentrations were higher in spring and fall and lower in the summer ($p < 0.001$; Figure 3-14). Concentrations were also higher at the mouth ($p < 0.001$; Table 3-3). There were no significant temporal trends in mercury for Saginaw Bay (Table 3-3).

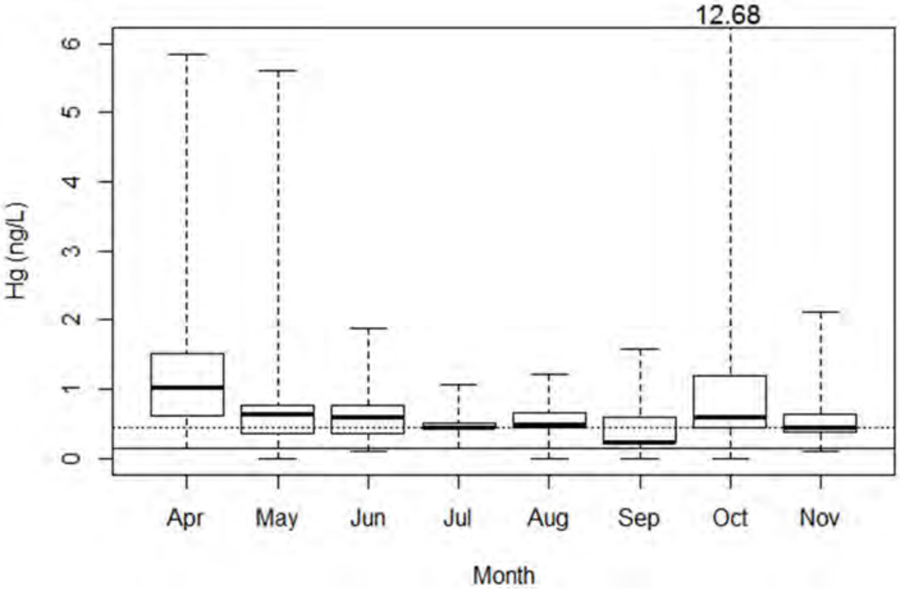


Figure 3-14. Total mercury within Saginaw Bay, 1998-2014. The y-axis was limited to a maximum of 6 ng/L mercury. Numbers across top reflect values exceeding this cutoff. Solid horizontal line represents the laboratory's detection limit; dotted line represents the quantification limit.

Table 3-3. Saginaw Bay trace metal data, by station. (Left) Summary Statistics. STORETs with nondetect samples marked with 'ND;' STORETs with nonquantifiable samples marked with 'NQ.' STORETs that do not share a letter under multiple comparisons are statistically different. Multiple comparisons were not performed on parameters with censored data. (Right) Temporal trends were analyzed using Seasonal Kendal (SK) or Tobit Regression (TR). Parameters censored > 50% marked --.

Summary Statistics							**Trend Analysis**			
Lead (µg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
060062	0.409	0.085	0.141	0.254	3.440	a	SK	16.0	-2.61	0.163
060063	0.037	0.063	0.098	0.158	0.854	b	SK	16.0	-2.89	0.055
090252	0.062	0.127	0.214	0.353	3.050	c	SK	16.0	-1.20	0.386
320189	0.048	0.125	0.201	0.272	1.700	c	SK	16.0	1.35	0.587
****Chromium (µg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
060062	ND	0.150	0.220	0.399	3.020	NA	TR	15.0	8.50	**0.006**
060063	ND	0.100	0.110	0.351	1.057	NA	--	--	--	--
090252	ND	0.190	0.269	0.430	2.890	NA	TR	15.1	5.18	**0.049**
320189	ND	0.100	0.160	0.316	1.550	NA	--	--	--	--
****Copper (µg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
060062	NQ	0.592	0.754	0.953	3.620	NA	TR	15.0	1.53	**0.032**
060063	0.438	0.652	0.820	1.040	2.030	NA	TR	15.0	1.28	0.062
090252	0.408	0.826	1.121	1.700	3.880	NA	TR	15.1	1.29	0.143
320189	0.393	0.569	0.697	0.860	2.130	NA	TR	15.0	0.84	0.240
****Mercury (ng/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
060062	ND	0.220	0.530	0.740	5.420	NA	TR	15.0	-0.35	0.862
060063	ND	0.450	0.450	0.580	12.680	NA	--	--	--	--
090252	ND	0.295	0.670	1.650	5.850	NA	TR	15.1	-1.67	0.465
320189	ND	0.450	0.550	0.690	4.200	NA	TR	15.0	0.40	0.785

** Parameters summarized using interval-censored data analysis. Multiple comparisons were not possible for these parameters.

3.4.2 Grand Traverse Bay

3.4.2.1 Nutrients

Total Phosphorus

The overall median concentration of total phosphorus was 0.005 µg/L, which categorizes Grand Traverse Bay as oligotrophic. Total phosphorus ranged from nondetectable (<0.003 mg/L) to 0.011 mg/L. Concentrations were highest in summer and lowest in the spring (p <0.001). There were no significant differences in concentrations among sampling stations. There was a significant decreasing trend in total phosphorus at 1 station (trend = -6.15%; Table 3-4). The frequency of censored (nondetect) data was > 50% at other sites, so trend analysis was not conducted.

Orthophosphate

Nearly 96% (180 of 188) of orthophosphate samples were below the quantification limit in Grand Traverse Bay. The median overall concentration was 0.001 µg/L and concentrations ranged from nondetectable (< 0.002 mg/L) to 0.026 mg/L (Table 3-4). Spatial and temporal analyses were not performed due to the high frequency of censored data.

Kjeldahl Nitrogen

The overall median concentration of kjeldahl nitrogen was 0.16 mg/L and levels ranged from nonquantifiable (< 0.1 mg/L) to 0.29 mg/L. Concentrations varied by month and were highest in the summer and lowest in the spring (p < 0.001; Figure 3-15). Concentrations were not different among stations and no significant trends were detected (Table 3-4).

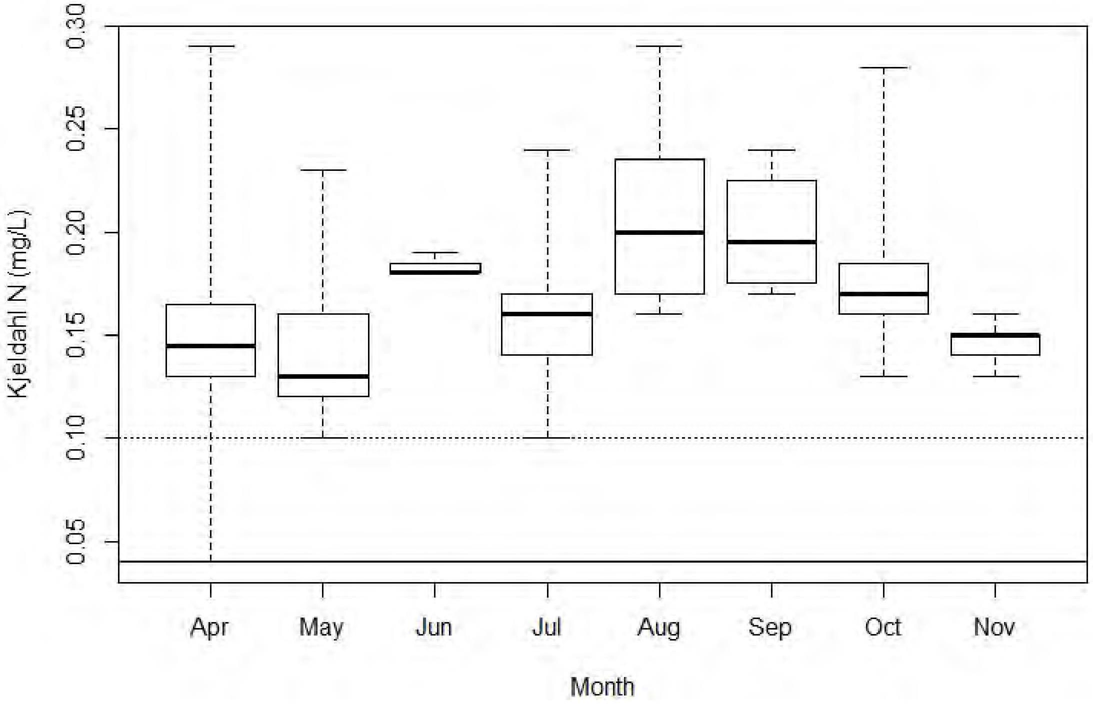


Figure 3-15. Kjeldahl Nitrogen within Grand Traverse Bay, 1998-2014. Solid horizontal line represents the laboratory's detection limit; dotted line represents the quantification limit.

Nitrate Nitrogen

The overall median concentration of nitrate was 0.230 mg/L and concentrations ranged from 0.151 mg/L to 0.720 mg/L. Concentrations varied by month ($p < 0.001$) and were highest in spring and lowest in fall. Concentrations were not statistically different among stations and no temporal trends were detected (Table 3-4).

Nitrite Nitrogen

All (188 of 188) were below the quantification limit in Grand Traverse Bay. The median concentration was 0.006 mg/L and concentrations ranged from nondetectable (< 0.002 mg/L) to 0.01 mg/L. Spatial and temporal analyses were not performed due to the high occurrence of unquantifiable data. Summary statistics, by STORET, are in Table 3-4.

Ammonia Nitrogen

Approximately 83% (145 of 187) of samples were below the quantification limit in Grand Traverse Bay. The median concentration was 0.01 mg/L and ammonia ranged from nondetectable (< 0.001 mg/L) to 0.021 mg/L. Spatial and temporal analyses were not performed due to the high frequency of unquantifiable data. Summary statistics are in Table 3-4.

Chlorophyll a

The median overall concentration was 1 µg/L, which classifies Traverse Bay as oligotrophic. Chlorophyll a ranged from nondetectable (< 1 µg/L) to 5.02 µg/L. Concentrations were highest in the fall and lowest in spring ($p < 0.001$). There was a significant, decreasing trend at all 4 stations at a rate of -6.76% to -10.66% annually (Table 3-4).

Table 3-4. Grand Traverse Bay nutrient data, by station. (Left) Summary Statistics. STORETs with nondetect samples marked with 'ND;' STORETs with nonquantifiable samples marked with 'NQ.' STORETs that do not share a letter under multiple comparisons are statistically different. Multiple comparisons were not performed on parameters with censored data. (Right) Temporal trends were analyzed using Seasonal Kendal (SK) or Tobit Regression (TR). Parameters censored > 50% marked --.

Summary Statistics							Trend Analysis			
****Total Phosphorus (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	ND	0.002	0.005	0.005	0.010	NA	--	--	--	--
280289	ND	0.002	0.005	0.006	0.008	NA	--	--	--	--
450132	ND	0.005	0.005	0.006	0.011	NA	TR	15.3	-6.15	**0.000**
450133	ND	0.002	0.005	0.006	0.009	NA	--	--	--	--
****Orthophosphate (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	ND	0.001	0.001	0.004	0.006	NA	--	--	--	--
280289	ND	0.001	0.001	0.005	0.006	NA	--	--	--	--
450132	ND	0.001	0.001	0.005	0.007	NA	--	--	--	--
450133	ND	0.001	0.001	0.005	0.026	NA	--	--	--	--
****Kjeldahl Nitrogen (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	NQ	0.14	0.16	0.17	0.24	NA	TR	15.3	-0.80	0.089
280289	NQ	0.14	0.16	0.17	0.24	NA	TR	15.3	-1.00	0.057
450132	0.11	0.14	0.16	0.18	0.29	NA	TR	15.3	-0.49	0.437
450133	0.10	0.14	0.17	0.18	0.28	NA	TR	15.3	-0.91	0.111
Nitrate Nitrogen (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	0.15	0.19	0.22	0.25	0.28	A	SK	16.0	-0.74	0.10
280289	0.16	0.21	0.23	0.25	0.28	A	SK	16.0	0.22	0.63
450132	0.15	0.22	0.24	0.25	0.72	A	SK	16.0	-1.42	0.08
450133	0.16	0.21	0.23	0.24	0.27	A	SK	16.0	-0.47	0.22

** Parameters summarized using interval-censored data analysis. Multiple comparisons were not possible for these parameters.

Table 3-4 (continued).

Summary Statistics							**Trend Analysis**			
****Nitrite Nitrogen (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	ND	0.00	0.01	0.01	0.01	NA	--	--	--	--
280289	ND	0.00	0.01	0.01	0.01	NA	--	--	--	--
450132	ND	0.00	0.01	0.01	0.01	NA	--	--	--	--
450133	ND	0.00	0.01	0.01	0.01	NA	--	--	--	--
****Ammonia Nitrogen (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	ND	0.010	0.010	0.010	0.021	NA	--	--	--	--
280289	ND	0.010	0.010	0.010	0.017	NA	--	--	--	--
450132	ND	0.010	0.010	0.010	0.018	NA	--	--	--	--
450133	ND	0.010	0.010	0.010	0.013	NA	--	--	--	--
****Chlorophyll a (µg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	ND	1.00	1.00	2.00	3.41	NA	TR	15.3	-8.97	**< 0.001**
280289	ND	1.00	1.00	1.70	5.02	NA	TR	15.3	-6.76	**< 0.001**
450132	ND	1.00	1.00	2.00	4.21	NA	TR	15.3	-10.66	**< 0.001**
450133	ND	1.00	1.00	1.90	3.94	NA	TR	15.3	-10.47	**< 0.001**

** Parameters summarized using interval-censored data analysis. Multiple comparisons were not possible for these parameters.

3.4.2.2 Conventional Parameters

TOC

The median concentration was 2.029 mg/L and concentrations of TOC ranged from 1.2 mg/L to 3.6 mg/L. TOC concentrations varied by month ($p < 0.001$) and were highest in the summer and lower in the spring and fall. Concentrations were not statistically different among stations (Table 3-5). A decreasing trend was detected at all 4 locations (trend = -0.98%, -0.97%, -1.46%, and -0.77%; Table 3-5).

Turbidity

Nearly 93% (171 of 184) of samples were below the quantification limit in Grand Traverse Bay. Median turbidity was 1 NTU and values ranged from nondetectable (< 1 NTU) to 2.13 NTU (Table 3-5). Trends were not explored for this parameter due to diurnal and seasonal variability. Summary statistics, by STORET, can be found in Table 3-5.

TDS

The median concentration was 190 mg/L and TDS ranged from 120 mg/L to 210 mg/L. Concentrations were not statistically different among months or stations and no temporal trends were detected.

Sodium

The overall median concentration was 6.4 mg/L and concentrations ranged from 3.9 mg/L to 7.9 mg/L. The limited number of samples precluded the statistical analysis of monthly and spatial variability. There was an increasing trend in sodium at all locations (trend = 1.89%, 2.09%, 2.21%, and 2.29%; Table 3-5).

Chloride

The overall median concentration was 11 mg/L and concentrations ranged from 9.00 mg/L to 48.00 mg/L. There was a significant, increasing trend in chloride at 4 locations (trend = 0.87% to 1.20% annually; Table 3-5). Summary statistics can be found in Table 3-5.

Hardness

Median hardness was 130 mg/L and hardness ranged from 121 mg/L to 146 mg/L. Hardness was lowest in late summer and highest in spring and fall ($p = 0.022$; Figure 3-16. Hardness values were not different among stations. No temporal trends were detected (Table 3-5).

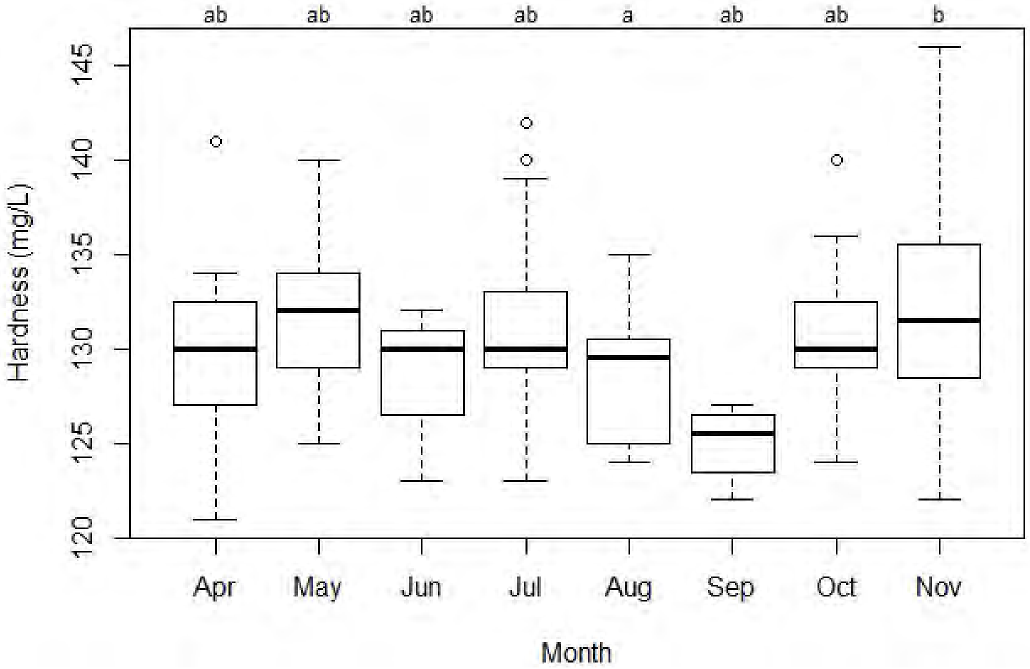


Figure 3-16. Monthly hardness within Grand Traverse Bay, 1998-2014. Months that do not share letters (top) are significantly different.

Calcium

The overall median concentration was 33.8 mg/L and concentrations ranged from 30.2 mg/L to 38.7 mg/L. Concentrations were not statistically different among months or stations and there were no temporal trends in calcium (Table 3-5).

Magnesium

The overall median concentration was 11.2 mg/L and concentrations ranged from 10.4 mg/L to 13 mg/L. Magnesium varied by month and was greatest in the spring and fall and lowest in summer ($p < 0.001$). Concentrations were not statistically different among stations (Table 3-5). An increasing trend was detected at all locations (trend = 0.46%, 0.38%, 0.28%, and 0.52%; Table 3-5).

Conductivity

The overall median concentration was 279 µS/cm and conductivity ranged from 70 µS/cm to 773 µS/cm. Conductivity was not statistically different across months or stations. No temporal trends were detected (Table 3-5).

TSS

Nearly 89% (167 of 188) of samples were below the quantification limit in Grand Traverse Bay. The overall median concentration was 4 mg/L and TSS ranged from nondetectable (< 1 mg/L) to 10 mg/L. The frequency of nonquantifiable data precluded the analysis of spatial and temporal trends. Summary statistics, by STORET, can be found in Table 3-5.

Alkalinity

The overall median concentration was 98.5 mg/L CaCO3 and total alkalinity ranged from 86 mg/L to 123 mg/L. Alkalinity did not vary by month or sampling station and no temporal trends were detected (Table 3-5).

pH

Median pH was 8.10 within Grand Traverse Bay and ranged from 6.52 to 9.09. pH varied significantly by month and was highest in the summer and lowest during the fall ($p < 0.001$). Values were not statistically different among sampling stations. There was a significant, increasing trend in pH at 2 locations (trend = 0.23% and 0.23%; Table 3-5).

DO

The overall median concentration was 10.64 mg/L and levels ranged from 8.01 mg/L to 17.23 mg/L. Concentrations varied and were highest in spring and fall and lowest in the summer ($p < 0.001$). There were no significant differences among stations and trends were not explored for this parameter due to diurnal and seasonal variability (Table 3-5).

Potassium

Median potassium was 1.3 mg/L and concentrations ranged from 1.19 mg/L to 2.10 mg/L (Table 3-5). Median potassium was not statistically different among months or stations and no significant trends were detected in Grand Traverse Bay (Table 3-5).

Sulfate

The overall median concentration was 19 mg/L and concentrations ranged from 11.0 mg/L to 29.3 mg/L. Sulfate was highest in the spring and fall and lowest in summer. Concentrations were not statistically different among stations (Table 3-5). A significant, increasing trend was detected at all 4 locations (trend = 1.54%, 1.64%, 1.60%, and 1.66%; Table 3-5).

Table 3-5. Grand Traverse Bay conventional data, by station. (Left) Summary Statistics. STORETs with nondetect samples marked with 'ND;' STORETs with nonquantifiable samples marked with 'NQ.' STORETs that do not share a letter under multiple comparisons are statistically different. Multiple comparisons were not performed on parameters with censored data. (Right) Temporal trends were analyzed using Seasonal Kendal (SK) or Tobit Regression (TR). Parameters censored > 50% marked --.

Summary Statistics							**Trend Analysis**			
					TOC (mg/L)					
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	1.2	1.8	2	2.2	3.6	a	SK	16	-0.98	**0.01**
280289	1.5	1.8	2	2.1	3.3	a	SK	16	-0.97	**0.014**
450132	1.3	1.9	2	2.3	3	a	SK	16	-1.46	**0.005**
450133	1.6	1.8	2	2.2	2.6	a	SK	16	-0.77	**0.029**
					****Turbidity (NTU)**					
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	ND	1	1	1	1	NA				
280289	ND	1	1	1	1	NA				
450132	ND	1	1	1	1	NA				
450133	ND	1	1	1	2	NA				
					TDS (mg/L)					
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	124	180	190	190	200	a	SK	16	0	0.846
280289	132	180	190	190	200	a	SK	16	0	0.325
450132	128	188	190	190	210	a	SK	16	0	0.353
450133	120	185	190	190	210	a	SK	16	0	0.198
					Sodium (mg/L)					
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	3.9	6	6.45	6.7	7.6	a	SK	15	1.89	**< 0.001**
280289	4.8	6	6.4	6.69	7.6	a	SK	15	2.09	**< 0.001**
450132	4.5	5.75	6.45	6.78	7.9	a	SK	15	2.21	**< 0.001**
450133	4.7	5.93	6.5	6.85	7.6	a	SK	15	2.29	**< 0.001**

** Parameters summarized using interval-censored data analysis. Multiple comparisons were not possible for these parameters.

Table 3-5 (continued).

Summary Statistics							**Trend Analysis**			
Chloride (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	9.00	10.00	10.76	11.00	26.00	a	SK	16	1.06	**0.000**
280289	9.00	10.00	10.00	11.00	48.00	a	SK	16	0.87	**0.002**
450132	9.00	10.00	11.00	11.00	24.00	a	SK	16	1.06	**0.000**
450133	9.00	10.00	11.00	11.00	28.00	a	SK	16	1.20	**0.000**
Hardness (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	121	129	130	133	140	a	SK	16	0.3	0.063
280289	124	129	130	134	146	a	SK	16	0.11	0.16
450132	123	129	131	134	143	a	SK	16	0.13	0.185
450133	122	128	130	132	140	a	SK	16	0.09	0.531
Calcium (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	30.2	32.9	33.9	34.6	37	a	SK	16	0.2	0.300
280289	31	33	33.5	34.3	38.7	a	SK	16	0.09	0.417
450132	31	33.1	34	34.6	36.8	a	SK	16	0.07	0.603
450133	30.2	32.9	33.4	34.3	36	a	SK	16	0	0.965
Magnesium (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	10.5	11.1	11.2	11.5	13	a	SK	16	0.46	**0.006**
280289	10.7	11.1	11.2	11.5	13	a	SK	16	0.38	**0.011**
450132	10.5	11	11.2	11.5	13	a	SK	16	0.28	**0.025**
450133	10.4	11.1	11.2	11.6	12.4	a	SK	16	0.52	**0.009**

** Parameters summarized using interval-censored data analysis. Multiple comparisons were not possible for these parameters.

Table 3-5 (continued).

Summary Statistics							**Trend Analysis**			
Conductivity (micromhos per centimeter [µmhos/cm])										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	98	273	280	285	306	a	SK	16	0.08	0.635
280289	78	272	279	286	314	a	SK	16	0	0.913
450132	99	274	280	288	307	a	SK	16	0.08	0.68
450133	70	271	279	286	773	a	SK	16	0.09	0.807
****TSS (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	ND	1	1	4	10	NA	--	--	--	--
280289	ND	1	1	4	6	NA	--	--	--	--
450132	ND	1	4	4	5	NA	--	--	--	--
450133	ND	1	1	4	6	NA	--	--	--	--
Alkalinity (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	90	95	98	100	116	a	SK	15	0.07	0.511
280289	91	95	98	101	120	a	SK	15	0.17	0.414
450132	86	96	99	102	120	a	SK	15	0.17	0.415
450133	89	94	99	101	123	a	SK	15	0.27	0.323
pH										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	6.53	7.9	8.1	8.22	8.77	a	SK	16	0.14	0.112
280289	6.54	7.9	8.13	8.27	9.09	a	SK	16	0.23	**0.026**
450132	6.55	7.81	8.1	8.22	8.77	a	SK	16	0.14	0.191
450133	6.52	7.88	8.08	8.23	8.75	a	SK	16	0.23	**0.02**

** Parameters summarized using interval-censored data analysis. Multiple comparisons were not possible for these parameters.

Table 3-5 (continued).

Summary Statistics							**Trend Analysis**			
Dissolved Oxygen (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	8.25	9.31	10.48	12.1	15.83	a				
280289	8.01	9.53	10.62	12.22	49.5	a				
450132	8.43	9.44	10.61	13.1	17.23	a				
450133	8.56	9.65	10.8	12.85	15.77	a				
Potassium (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	1.19	1.20	1.30	1.30	2.10	a	SK	15.0	0.00	0.148
280289	1.20	1.20	1.30	1.30	2.00	a	SK	15.0	0.00	0.101
450132	1.20	1.20	1.30	1.31	1.60	a	SK	15.0	0.00	0.602
450133	1.20	1.20	1.30	1.30	1.50	a	SK	15.0	0.00	0.066
Sulfate (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	11.0	17.5	19.0	20.5	28.1	a	SK	16.0	1.54	**0.008**
280289	11.0	18.0	20.0	21.0	28.3	a	SK	16.0	1.64	**0.017**
450132	12.0	18.0	19.0	21.0	28.0	a	SK	16.0	1.60	**0.003**
450133	13.0	18.0	19.0	21.0	29.3	a	SK	16.0	1.66	**0.008**

** Parameters summarized using interval-censored data analysis. Multiple comparisons were not possible for these parameters.

3.4.2.3 *Trace Metals*

Trace metals were collected from all 4 stations in Grand Traverse Bay, in the months of October and November only. There were no WQS exceedances for metals in the current Integrated Report cycle (2012-2013).

Chromium

The overall median concentration was 0.31 µg/L and concentrations ranged from nondetectable (< 0.057 µg/L) to 1.12 µg/L. Concentrations varied by month and were higher in November (p = 0.004). Chromium did not vary significantly by station and the record for chromium was too limited for trend analysis (Table 3-6).

Copper

The overall median concentration was 0.4135 µg/L and copper ranged from nondetectable (< 0.18 µg/L) to 0.570 µg/L. Concentrations did not vary significantly by month or station and the record was too limited for temporal analysis (Table 3-6).

Lead

The overall median concentration of lead was 0.0097 µg/L and concentrations of lead ranged from nondetectable (< 0.0041 µg/L) to 0.106 µg/L. Lead concentrations did not vary significantly by month or station. The record was too limited for trend analysis (Table 3-6).

Mercury

Nearly 91% (58 of 64) of mercury samples were below the quantification limit in Grand Traverse Bay. The median concentration was 0.22 ng/L and concentrations ranged from nondetectable < 0.14 ng/L) to 4.133 ng/L. Concentrations were higher in the month of October (p = 0.037) and did not vary significantly by station. The record for mercury was too limited for temporal analysis (Table 3-6).

Table 3-6. Grand Traverse Bay trace metal data, by station. (Left) Summary Statistics. STORETs with nondetect samples marked with 'ND;' STORETs with nonquantifiable samples marked with 'NQ.' STORETs that do not share a letter under multiple comparisons are statistically different. Multiple comparisons were not performed on parameters with censored data. (Right) Temporal trends were analyzed using Seasonal Kendal (SK) or Tobit Regression (TR). Parameters censored > 50% marked --.

Summary Statistics							Trend Analysis			
**Lead (µg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	NQ	0.010	0.010	0.010	0.025	NA	Short Record	--	--	--
280289	ND	0.005	0.010	0.010	0.106	NA	Short Record	--	--	--
450132	NQ	0.010	0.010	0.019	0.030	NA	Short Record	--	--	--
450133	NQ	0.010	0.010	0.010	0.028	NA	Short Record	--	--	--
**Chromium (µg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	ND	0.12	0.30	0.43	1.12	NA	Short Record	--	--	--
280289	ND	0.12	0.31	0.40	1.00	NA	Short Record	--	--	--
450132	ND	0.12	0.33	0.44	1.01	NA	Short Record	--	--	--
450133	ND	0.16	0.30	0.42	1.04	NA	Short Record	--	--	--
**Copper (µg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	ND	0.38	0.42	0.44	0.57	NA	Short Record	--	--	--
280289	ND	0.38	0.41	0.44	0.57	NA	Short Record	--	--	--
450132	ND	0.39	0.41	0.45	0.57	NA	Short Record	--	--	--
450133	ND	0.39	0.42	0.45	0.57	NA	Short Record	--	--	--
**Mercury (ng/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
280288	ND	0.220	0.220	0.220	4.133	NA	Short Record	--	--	--
280289	NQ	0.220	0.220	0.220	0.723	NA	Short Record	--	--	--
450132	ND	0.220	0.220	0.220	0.450	NA	Short Record	--	--	--
450133	ND	0.135	0.220	0.220	3.388	NA	Short Record	--	--	--

** Parameters summarized using interval-censored data analysis. Multiple comparisons were not possible for these parameters.

SECTION 4. CONNECTING CHANNEL MONITORING: STATUS AND TRENDS

4.1 INTRODUCTION

A total of 6 stations (1 at the headwaters and mouth of each of the connecting channels) are monitored as part of the WCMP. Water chemistry data and trends for samples collected between 1998 and 2014 will be discussed in this chapter.

The St. Marys River connects Lake Superior and Lake Huron and is the northernmost connecting channel (Figure 4-1). The River flows southeast and is approximately 120 km long. Discharge in the river is driven almost entirely by Lake Superior, with a total basin area of over 21,000 square miles. The relative stability of Lake Superior water levels, combined with navigation locks, dams, and hydropower plants, maintains stable flow within the river. Water depths within the St. Marys, St. Clair, and Detroit Rivers have been maintained by dredging since the mid-1800s. Current depths are maintained at 27 feet within the main channel. See Duffy et al. (1985) for a more complete overview of the St. Marys River.

The St. Clair River is approximately 65 km long and flows south from Lake Huron to Lake St. Clair (Figure 4-2). The principle source of water is Lake Huron; however, the St. Clair River gains additional flow from tributaries including the Black, Pine, and Belle Rivers (Herdendorf et al., 1986). There are no major locks or dams across the main channel of the St. Clair River. Flow stability is maintained by the stability of Lake Huron and Lake St. Clair water levels (Herdendorf et al., 1986). See Herdendorf et al. (1986) for a more complete review of the St. Clair River.

The Detroit River is approximately 51 km long and flows in a general southern direction from Lake St. Clair to Lake Erie (Manny et al., 1988). The major source of water in the Detroit River is Lake St. Clair, although the Detroit River gains water from rivers such as the Rouge River and minor tributaries such as the Ecorse River (Manny et al., 1988). Extensive navigational dredging and dumping of these materials has created several numerous artificial islands, leading to complex currents in the Detroit River (Derecki, 1984; Manny et al., 1988). There are no major locks or dams across the Detroit River main channel. Flow velocities are maintained predominantly by surface water levels in Lake St. Clair and Lake Erie, which can be influenced by ice jams and wind-driven seiches (Manny et al., 1988). See Manny et al. (1988) for a more complete review of the Detroit River.

4.2 MAJOR CONCLUSIONS

St. Marys, St. Clair, and Detroit Rivers

Seasonal

In general, the Great Lakes connecting channels do not appear to experience dramatic swings in seasonal water chemistry. Unlike most other rivers in Michigan the St. Marys, St. Clair, and Detroit Rivers are primarily fed by large lakes (Lake Superior, Lake Huron, and Lake St. Clair). As a result, water chemistry in the connecting channels does not appear to be influenced strongly by minor runoff and wet weather events.

That being said, our analyses did identify significant seasonal variability within the Detroit River connecting channel. Several parameters showed a pattern of higher concentrations in the spring and/or fall, including turbidity, alkalinity, hardness, conductivity, TSS, TDS, calcium, potassium, sodium, lead, chromium, and mercury. This is likely the result of the large population centers and high intensity development in the watersheds of the Detroit River tributaries, including the Rouge and Ecorse River watersheds. Urbanized landscapes increase the impact of spring wet weather events by concentrating solutes and decreasing the ability of the landscape to absorb and filter runoff (Weng, 2001; Whitford et al., 2001).

Spatial

Concentrations of most parameters, including nutrients and trace metals, were higher at the downstream sampling location within each connecting channel. The trace metals lead, chromium, and copper were all higher at the downstream location within the St. Marys and St. Clair Rivers. Sampling locations on the Great Lakes connecting channels are positioned upstream and downstream of major cities, so it is likely that downstream areas are a source of nutrients and other water quality parameters. Nonetheless, water samples are meeting relevant WQS in the connecting channels.

Temporal Trends

Some but not all of the connecting channel locations showed a general trend of increasing concentrations of elements such as sodium, chloride, magnesium, and calcium. These trends may be related to application of road salts, which are composed primary of sodium and calcium and related cations bound to chloride (Ramakrishna and Viraraghavan, 2005; Granato, 1996). Concentrations remain well below water quality values, so these trends may not be ecological significant.

We also detected decreasing trends in Kjeldahl nitrogen in the St. Marys and St. Clair River at a rate between 1.73% and 2.00% (median concentrations 0.12 mg/L 0.15 mg/L) and decreasing mercury in the Detroit River at a rate of between -3.33% to -5.57% (median concentrations 1.53 µg/L to 2.40 µg/L), annually. These trends may be related to increasing effectiveness of air and wastewater collection and treatment processes in surrounding residential areas. That being said, these speculations are outside of the scope of the design and analyses of this WCMP report. Trends on the Great Lakes connecting channels are likely the result of several, interrelated factors and processes. Further research would be necessary before we can attribute any of these trends to specific source(s). EGLE, WRD, WCMP will continue to monitor these trends as long as resources allow.

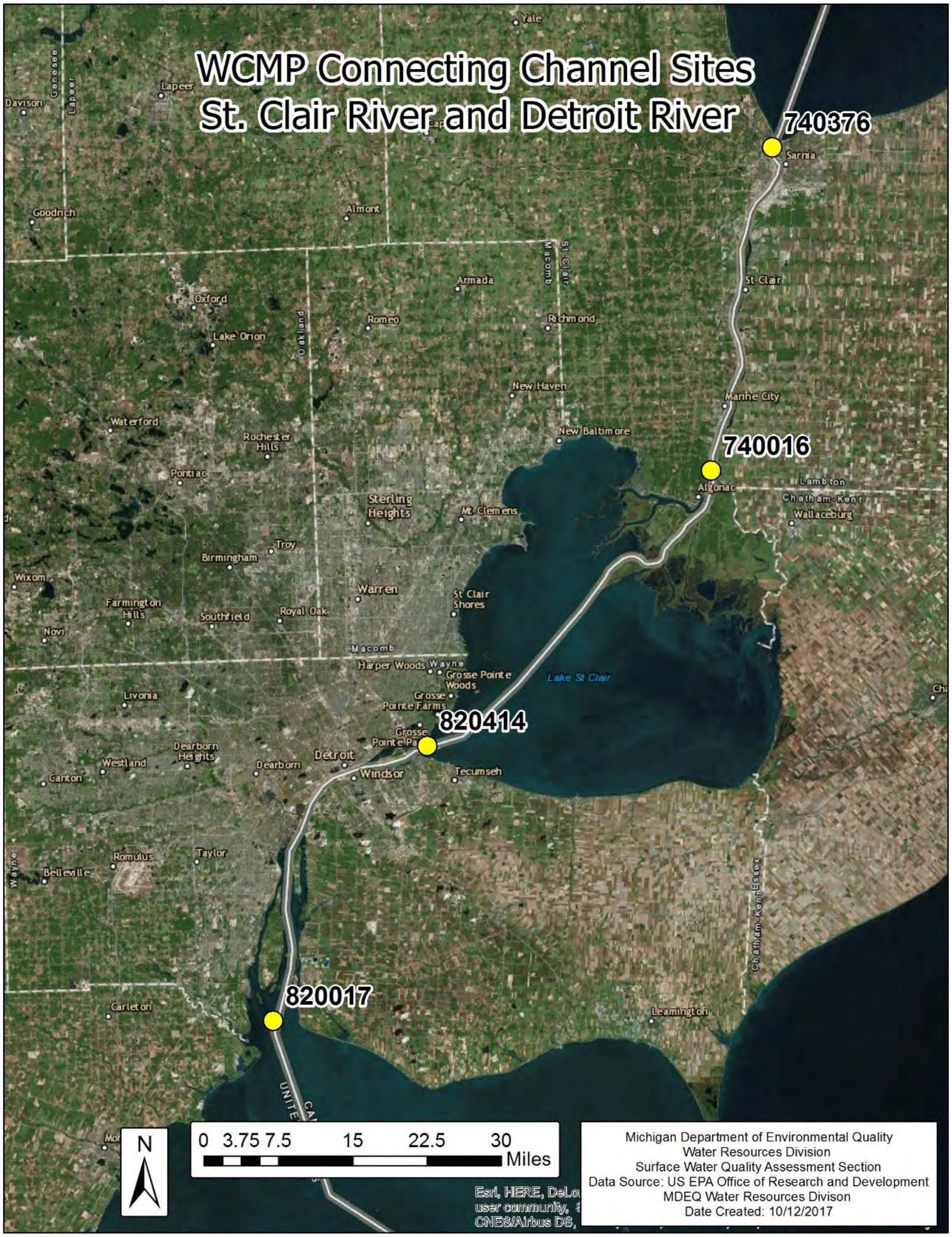
4.3 METHODS

4.3.1 Study Design

Michigan’s Great Lakes connecting channels (the St. Marys, St. Clair, and Detroit Rivers) are important locations for water chemistry monitoring because they carry water between the Great Lakes, directly impacting their water quality. They also represent large watersheds impacted by commercial and industrial activities and geological influences.

All 3 connecting channels are sampled at their upstream and downstream reaches. All locations are sampled with surface grab samples. Sampling for the connecting channels takes place monthly, during open water months. Typically, this includes the months of April to November, although schedules in the Great Lakes connecting channels are modified, as necessary, to account for equipment failure or personnel safety.

Figure 4-1. WCMP monitoring locations, shown with STORET numbers, on the St. Marys River, Michigan.



Michigan Department of Environmental Quality
Water Resources Division
Surface Water Quality Assessment Section
Data Source: US EPA Office of Research and Development
MDEQ Water Resources Divison
Date Created: 10/12/2017

Figure 4-2. WCMP monitoring locations, shown with STORET numbers, on the St. Marys River, Michigan.

4.2.2 Data Analysis

All results are presented by parameter type. The parameter types used in this chapter include: (A) nutrient parameters (total phosphorus, orthophosphate, kjeldahl nitrogen, nitrate, nitrite, ammonia, and chlorophyll a); (B) conventional parameters (TOC, turbidity, TDS, chloride, sodium, hardness, conductance, TSS, alkalinity, pH, DO, potassium, and sulfate); and (C) trace metals (chromium, copper, lead, and mercury).

4.3.3 Statistical Analysis

Results in this chapter are presented, by parameter type, as described above. Statistical methods are covered in-depth within the introduction, but are summarized as follows:

Between group (e.g., STORET and monthly) comparisons were made using Kruskal-Wallis tests for parameters without censored data (Giraudoux, 2016; Helsel, 2012). For parameters with censored data, comparisons among groups were conducted using the interval-censored form of the generalized Wilcoxon test. Summary statistics for parameters with censored data points were generated using Turnbull methods as described in Helsel (2012). For parameters that did not have any values below the laboratory's reporting limits (RL), summary statistics (e.g., minimum, quartile 1, median, quartile 3, and maximum) and boxplots were generated using the base (standard) R environment. Temporal trend analyses were performed using Seasonal Kendall trend analysis for uncensored data (Lorenz, 2015). Trends in parameters with censored data were measured using Tobit linear regression techniques (Lorenz, 2015; Helsel and Hirsch, 2002).

4.3.3.1 Spatial

Statistical comparisons were made to identify significant spatial (STORET) patterns in the parameters. The results of these spatial comparisons are shown in tables at the end of each section.

4.3.3.2 Temporal

Statistical comparisons in the connecting channels were made to analyze temporal (monthly) patterns in water quality parameters. Ecologically significant patterns in monthly concentrations are displayed in text with boxplots. Additional figures are available upon request. Potential trends from 1998-2014 were also identified using temporal trend analysis. Temporal trend results are shown in summary tables at the end of each section.

4.4 RESULTS AND DISCUSSION

4.4.1 St. Marys River

4.4.1.1 Nutrients

<u>Total Phosphorus</u>

The overall median concentration of total phosphorus was 0.007 mg/L and concentrations ranged from nondetectable (< 0.003 mg/L) to 0.039 mg/L. Total phosphorus concentrations were not statistically different among months but were significantly higher downstream

($p < 0.001$; Table 4-1). There was a significant, decreasing trend in total phosphorus at the upstream station ($p = 0.035$; rate = -2.64% annually; Table 4-1).

Orthophosphate

Overall median orthophosphate was 0.005 mg/L and concentrations ranged from nondetectable (< 0.002 mg/L) to 0.017 mg/L. Monthly comparisons and temporal trend analyses were not performed due to the high frequency of samples below quantification level. Summary statistics, by STORET location, are shown in Table 4-1.

Kjeldahl Nitrogen

The overall median concentration was 0.13 mg/L and concentrations ranged from nondetectable (< 0.1 mg/L) to 0.46 mg/L. Concentrations were not statistically different among seasons or between sampling locations (Table 4-1). There was a decreasing trend in Kjeldahl nitrogen upstream and downstream (trend = -2.00% and -1.80% annually; Table 4-1).

Nitrate Nitrogen

Median nitrate was 0.30 mg/L and concentrations ranged from 0.24 mg/L to 0.51 mg/L. Nitrate concentrations were different among months and were highest in spring and lowest in late summer ($p < 0.001$; Figure 4-3). Concentrations were also greater downstream ($p = 0.009$; Table 4-1). A decreasing trend was detected upstream at a rate of -0.62% annually (Table 4-1).

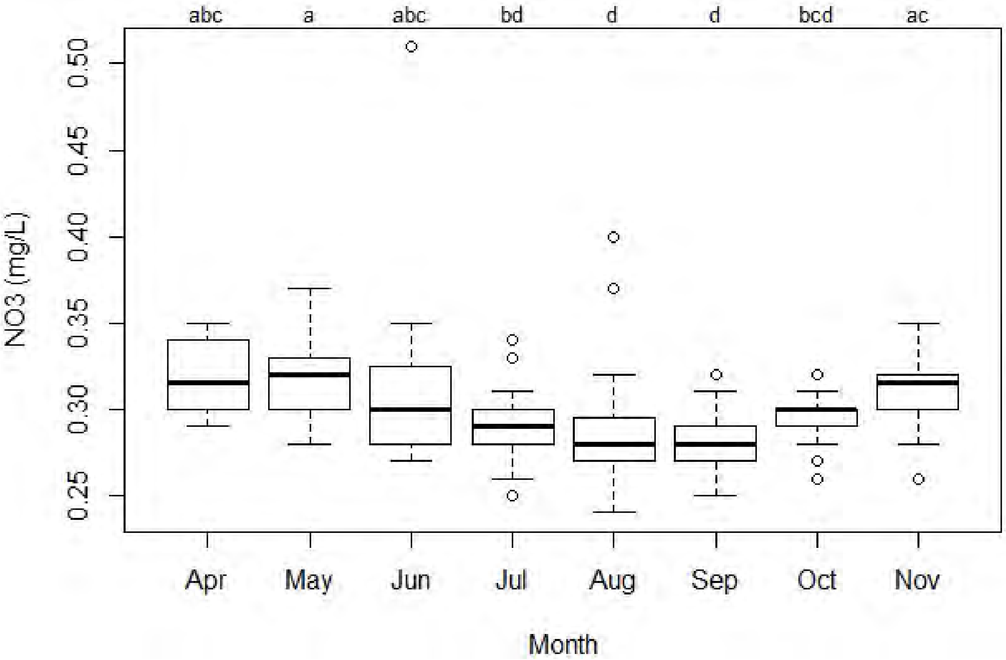


Figure 4-3. Nitrate concentrations, by month. Letters across top reflect results of multiple comparisons. Months that do not share a letter are statistically different.

Nitrite Nitrogen

The overall median concentration was 0.006 mg/L. Nitrite ranged from nondetectable (< 0.002 mg/L) to 0.023 mg/L. Monthly comparisons and temporal trend analyses were not performed due to the high frequency of samples below the quantification level. Summary statistics, by STORET, are shown in Table 4-1.

Ammonia Nitrogen

The overall median concentration was 0.01 mg/L. Concentrations of ammonia ranged from nondetectable (< 0.001 mg/L) to 0.017 mg/L. Monthly comparisons and temporal trend analyses were not performed due to the high frequency of samples below quantification level. Summary statistics, by STORET, are shown in Table 4-1.

Table 4-1. St. Marys River nutrients, by station. (Left) Summary Statistics. STORETs with nondetect samples marked with ‘ND;’ STORETs with nonquantifiable samples marked with ‘NQ.’ STORETs that do not share a letter under multiple comparisons are statistically different. Multiple comparisons were not performed on parameters with censored data. (Right) Temporal trends were analyzed using Seasonal Kendal (SK) or Tobit Regression (TR). Parameters censored with > 50% frequency are marked --.

Summary Statistics							Trend Analysis			
****Total Phosphorus (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	ND	0.005	0.005	0.008	0.017	a	TR	16.4	-2.77	**0.025**
170140	ND	0.007	0.009	0.010	0.039	b	TR	16.4	-1.40	0.095
****Orthophosphate (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	ND	0.001	0.005	0.005	0.017	a	--	--	--	--
170140	ND	0.005	0.005	0.005	0.015	b	--	--	--	--
****Kjeldahl Nitrogen (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	NQ	0.10	0.12	0.15	0.31	a	TR	16.4	-2.00	**< 0.001**
170140	NQ	0.11	0.13	0.15	0.46	a	TR	16.4	-1.80	**0.002**
Nitrate Nitrogen (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	0.25	0.28	0.30	0.32	0.51	a	SK	16.4	0.62	**0.003**
170140	0.24	0.27	0.29	0.31	0.40	b	SK	16.4	0.00	0.496
****Nitrite Nitrogen (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	ND	0.006	0.006	0.006	0.010	a	--	--	--	--
170140	ND	0.006	0.006	0.006	0.023	b	--	--	--	--
****Ammonia Nitrogen (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	ND	0.010	0.010	0.010	0.015	a	--	--	--	--
170140	ND	0.010	0.010	0.010	0.017	b	--	--	--	--

** Parameters summarized using interval-censored data analysis.

4.4.1.2 Conventional Parameters

TOC

Overall median TOC was 1.8 mg/L. Concentrations ranged from 0.7 mg/L to 4.2 mg/L. Values were not statistically different among months or sampling location and no trends were detected (Table 4-2).

Turbidity

Overall median turbidity was 2.4 NTU and ranged from nondetectable (< 1 NTU) to 23 NTU. Turbidity was not statistically different among months but was higher downstream ($p < 0.001$; Table 4-2). Trends were not explored for this parameter due to diurnal and seasonal variability.

TDS

The overall median concentration of TDS was 68.5 mg/L. Concentrations ranged from nondetectable (< 20 mg/L) to 80 mg/L. Concentrations were not different among seasons and were higher downstream ($p < 0.001$; Table 4-2). There were no significant temporal trends in TDS (Table 4-2).

Sodium

The overall median concentration of sodium was 1.5 mg/L and concentrations ranged from nondetectable (< 1 mg/L) to 2.9 mg/L. Sodium was not statistically different among months and was higher downstream ($p = 0.040$; Table 4-2). There was a statistically significant, increasing trend upstream and downstream (trend = 1.62% and 1.87% annually; Table 4-2).

Chloride

The overall median concentration of chloride was 2.0 mg/L and concentrations ranged between nonquantifiable (< 1 mg/L) to 7 mg/L. Chloride was not significantly different among months or sampling location (Table 4-2).

Hardness

Median hardness was 46 mg/L and ranged from 36 mg/L to 52 mg/L. Median hardness was not statistically different among months. Hardness was higher downstream ($p < 0.001$; Table 4-2) and there was an increasing trend in hardness upstream and downstream (trend = 0.33% and 0.43% annually; Table 4-2).

Calcium

Median calcium was 13.5 mg/L and ranged from 10.2 mg/L to 15.9 mg/L. Calcium did not vary by month and was higher downstream ($p < 0.001$; Table 4-2). There was a statistically significant, increasing trend in calcium upstream and downstream (trend = 0.34% and 0.35% annually; Table 4-2).

Magnesium

Overall median magnesium was 2.9 mg/L between 1998 and 2014 and concentrations ranged from 1.94 mg/L to 3.4 mg/L. Magnesium did not vary significantly by season and was higher downstream ($p < 0.001$; Table 4-2). Magnesium was increasing significantly downstream only ($p = 0.005$; trend = 0.66%; Table 4-2).

Conductivity

Overall median conductivity was 95 μS/cm and ranged from 51 μS/cm to 126 μS/cm. Median conductivity was not statistically different among months but was higher downstream ($p = 0.002$; Table 4-2). There were no significant temporal trends in conductivity (Table 4-2).

TSS

Median TSS was 4 mg/L and concentrations ranged from nondetectable (< 1 mg/L) to 18 mg/L. Concentrations were not statistically different among months and were higher downstream ($p < 0.001$; Table 4-2). No temporal trends were detected. The frequency of censored data precluded the use of trend analysis at the upstream location.

Alkalinity

Overall median alkalinity was 39 mg/L CaCO and ranged from 23 mg/L to 74 mg/L. There were no differences in median alkalinity among the seasons or locations and no temporal trends were detected (Table 4-2).

pH

pH ranged from 6.00 to 9.09 and overall median pH was 7.72. pH values were significantly different among months ($p < 0.001$) and was highest during in summer and lowest in spring and fall. pH values at the upstream and downstream locations were not significantly different (Table 4-2). There were no significant temporal trends in pH (Table 4-2).

DO

Median DO was 10.3 mg/L and ranged from 6.2 mg/L to 17.30 mg/L. DO varied by month ($p < 0.001$) and was highest in spring and lowest in fall. There was no difference between upstream and downstream DO. Trends were not explored for this parameter due to diurnal and seasonal variability.

Potassium

Median potassium was 0.60 mg/L and concentrations ranged from 0.4 mg/L to 4.5 mg/L. Potassium did not vary with season and was higher at the downstream location ($p = 0.005$; Table 4-2). No trends were detected (Table 4-2).

Sulfate

The overall median concentration of sulfate was 3 mg/L and concentrations ranged from nondetectable (< 0.6 mg/L) to 8.0 mg/L. Sulfate was not statistically different among sampling months or locations (Table 4-2). There was a significant, increasing trend at upstream and downstream locations (trend = 2.17% and 2.64% annually; Table 4-2).

Table 4-2. St. Marys conventional parameters, by station. (Left) Summary Statistics. STORETs with nondetect samples marked with ‘ND;’ STORETs with nonquantifiable samples marked with ‘NQ.’ STORETs that do not share a letter under multiple comparisons are statistically different. Multiple comparisons were not performed on parameters with censored data. (Right) Temporal trends were analyzed using Seasonal Kendal (SK) or Tobit Regression (TR). Parameters censored with > 50% frequency are marked --.

Summary Statistics							**Trend Analysis**			
TOC (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	0.8	1.6	1.8	2	4.2	a	SK	17	-1.61	0.057
170140	0.7	1.6	1.8	2	3.3	a	SK	17	-0.76	0.176
****Turbidity (NTU)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	ND	1	1	1	9	a				
170140	ND	3	4	5	23	b				
****TDS (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	ND	60	66	70	80	a	TR	16.4	-0.08	0.77
170140	28	66	70	70	80	b	TR	16.4	-0.31	0.149
****Sodium (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	ND	1.3	1.5	1.6	2.9	a	TR	14.3	1.87	**0.002**
170140	ND	1.3	1.6	1.7	2.9	b	TR	14.3	1.62	**0.012**
****Chloride (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	NQ	1.2	2	2	7	a	TR	16.364	-3.221	**< 0.001**
170140	NQ	1.4	2	2	5	a	TR	16.367	-2.573	**< 0.001**
Hardness (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	36	44	45	46	50	a	SK	17	0.33	**0.036**
170140	41	45	46	48	52	b	SK	17	0.43	**0.006**

** Parameters summarized using interval-censored data analysis.

Table 4-2 (continued).

Summary Statistics							**Trend Analysis**			
Calcium (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	10.2	12.9	13.2	13.8	15.4	a	SK	17	0.34	**0.027**
170140	11.8	13.3	13.6	14	15.9	b	SK	17	0.35	**0.045**
Magnesium (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	1.9	2.8	2.8	3	3.1	a	SK	17	0.29	0.052
170140	2.6	2.8	3	3.1	3.4	b	SK	17	0.66	**0.005**
Conductivity (µmhos/cm)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	70	90	94	98	116	a	SK	16	0.08	0.579
170140	51	93	96	100	126	b	SK	16	-0.04	0.78
****TSS (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	ND	1	4	4	9	a	--	--	--	--
170140	ND	4	4	6	18	b	TR	16.4	-3.05	0.104
Alkalinity (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	23	37	39	42	59	a	SK	15	0	0.979
170140	25	38	39	43	74	a	SK	15	0	0.963
pH										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	6	7.49	7.73	7.92	9.09	a	SK	16	0.24	0.213
170140	6.17	7.5	7.7	7.96	8.9	a	SK	16	0.18	0.409

** Parameters summarized using interval-censored data analysis.

Table 4-2 (continued).

Summary Statistics							**Trend Analysis**			
Dissolved Oxygen (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	7.84	9.52	10.44	11.6	16.49	a				
170140	6.2	9.32	10.24	11.24	17.3	a				
Potassium (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	0.4	0.5	0.57	0.6	1.9	a	SK	15	0	0.287
170140	0.5	0.5	0.6	0.67	4.5	b	SK	15	0	0.215
****Sulfate (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	ND	2	3	4	8	a	TR	16.4	2.17	**0.05**
170140	ND	2	3	4	7	a	TR	16.4	2.64	**0.028**

** Parameters summarized using interval-censored data analysis.

4.4.1.3 Trace Metals

There were no WQS exceedances for metals in the St. Marys River for the current Integrated Report (2012-2013).

Chromium

The overall median concentration was 0.298 µg/L and concentrations ranged from nondetectable (< 0.057 µg/L) to 1.350 µg/L. Concentrations were not statistically different among months and were higher downstream ($p < 0.001$; Table 4-3). The frequency of censored data precluded the use of trend analysis at the upstream location. There were no significant trends in chromium (Table 4-3).

Copper

Median copper was 0.8995 µg/L and ranged from 0.678 µg/L to 1.427 µg/L. Copper was not statistically different among months but was higher downstream ($p < 0.001$; Table 4-3). A decreasing trend was identified upstream only ($p = 0.038$; trend = -0.80%; Table 4-3).

Lead

The overall median concentration was 0.0745 µg/L. Lead ranged from nonquantifiable (< 0.014 µg/L) to 0.336 µg/L. Concentrations were not statistically different among months and concentrations were higher downstream ($p < 0.001$; Table 4-3). There was a significant, decreasing trend upstream ($p < 0.001$; trend = -4.53%; Table 4-3).

Mercury

The overall median concentration of mercury was 0.45 ng/L. Concentrations of mercury ranged from nondetectable (< 0.14 ng/L) to 14.165 ng/L. Concentrations were different among months and were highest in spring and lowest in the fall. Concentrations did not vary between upstream and downstream locations. The frequency of censored data precluded the use of trend analysis for Mercury.

Table 4-3. St. Marys trace metal data, by station. (Left) Summary Statistics. STORETs with nondetect samples marked with ‘ND;’ STORETs with nonquantifiable samples marked with ‘NQ.’ STORETs that do not share a letter under multiple comparisons are statistically different. Multiple comparisons were not performed on parameters with censored data. (Right) Temporal trends were analyzed using Seasonal Kendal (SK) or Tobit Regression (TR). Parameters censored with > 50% frequency are marked --.

Summary Statistics							**Trend Analysis**			
****Chromium (µg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	ND	0.100	0.180	0.266	0.932	a	--	--	--	--
170140	NQ	0.328	0.436	0.549	1.350	b	TR	16.4	0.48	0.526
Copper (µg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	0.678	0.782	0.831	0.895	1.260	a	SK	17.0	-0.80	**0.038**
170140	0.794	0.906	0.973	1.042	1.427	b	SK	17.0	-0.27	0.316
****Lead (µg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	NQ	0.0181	0.028	0.0416	0.214	a	TR	16.4	-4.53	**< 0.001**
170140	0.025	0.0873	0.101	0.128	0.336	b	TR	16.4	0.33	0.625
****Mercury (ng/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
170139	NQ	0.30	0.30	0.45	14.17	a	--	--	--	--
170140	ND	0.30	0.41	0.54	13.07	a	--	--	--	--

** Parameters summarized using interval-censored data analysis.

4.4.2 St. Clair River

4.4.2.1 Nutrients

Total Phosphorus

The overall median concentration of total phosphorus was 0.005 mg/L and ranged from nondetectable (< 0.003 mg/L) to 0.106 mg/L. Concentrations were not statistically different among months and were higher downstream ($p < 0.001$; Table 4-4). There was a significant, decreasing trend in total phosphorus upstream (trend = 6.11%; Table 4-4). The frequency of censored data precluded the use of trend analysis at the downstream location.

Orthophosphate

The median overall concentration was 0.005 mg/L and ranged from nondetectable (< 0.002 mg/L) to 0.016 mg/L. Monthly comparisons and temporal trend analyses were not performed due to the high frequency of samples below quantification level. Summary statistics, by STORET, are shown in Table 4-4.

Kjeldahl Nitrogen

The overall median concentration was 0.15 mg/L. Kjeldahl nitrogen ranged from non-quantifiable (<0.1 mg/L) to 0.66 mg/L. Concentrations were not statistically different among seasons or among sampling location (Table 4-4). There was a decreasing trend in Kjeldahl nitrogen upstream and downstream (trend = -1.73% and -1.95% annually; Table 4-4).

Nitrate Nitrogen

Overall median nitrate was 0.31 mg/L and concentrations ranged from 0.22 mg/L to 0.53 mg/L. Concentrations varied by month and were highest in spring and lowest in fall ($p < 0.001$; Figure 4-4). Concentrations were not statistically different between stations and no significant trends were detected (Table 4-4).

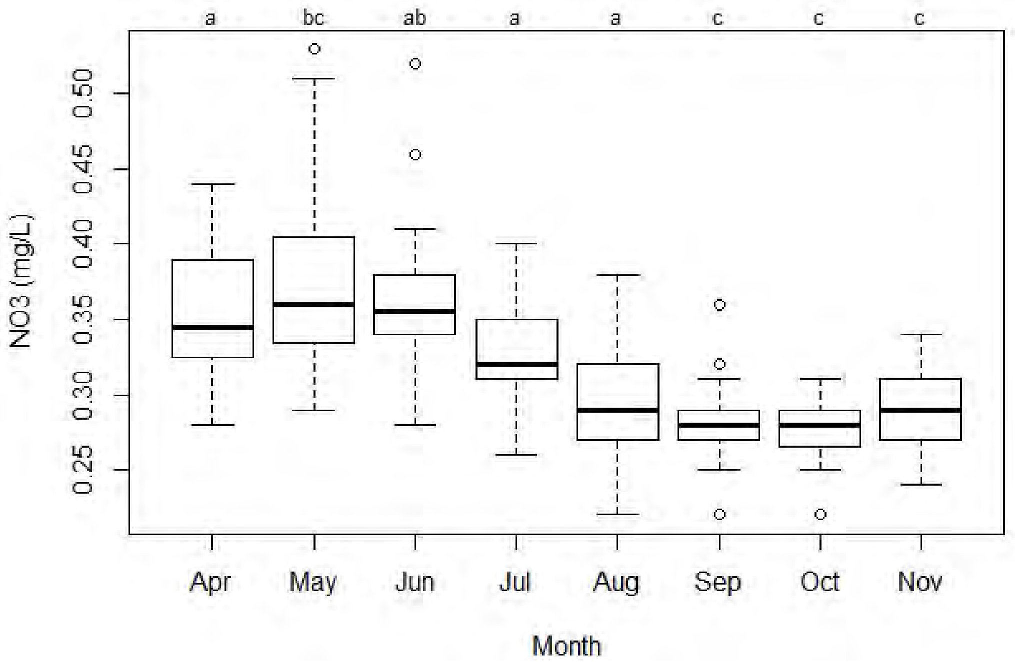


Figure 4-4. Nitrate concentrations within the St. Clair River. Letters across top reflect results of multiple comparisons. Months that do not share a letter are statistically different.

Nitrite Nitrogen

The overall median concentration of nitrite was 0.006 mg/L and concentrations ranged from nondetectable (< 0.002 mg/L) to 0.011 mg/L. Monthly comparisons and temporal trend analyses were not performed due to the high frequency of samples below the quantification level. Summary statistics, by STORET, are shown in Table 4-4.

Ammonia Nitrogen

The overall median concentration of ammonia was 0.01 µg/L and ranged from nondetectable (< 0.001 mg/L) to 0.028 mg/L. Concentrations varied by month ($p < 0.001$) and were highest in early summer and lowest spring and fall. Concentrations were also lower downstream ($p < 0.001$; Table 4-4). There was a significant, increasing trend in ammonia downstream (trend = 0.34% annually; Table 4-4). The frequency of censored data precluded the use of trend analysis at the upstream location.

Table 4-4. St. Clair River nutrients, by station. (Left) Summary Statistics. STORETs with nondetect samples marked with 'ND;' STORETs with nonquantifiable samples marked with 'NQ.' STORETs that do not share a letter under multiple comparisons are statistically different. Multiple comparisons were not performed on parameters with censored data. (Right) Temporal trends were analyzed using Seasonal Kendal (SK) or Tobit Regression (TR). Parameters censored with > 50% frequency are marked --.

Summary Statistics							**Trend Analysis**			
****Total Phosphorus (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	ND	0.005	0.007	0.009	0.025	a	TR	16.4	-6.11	**< 0.001**
740376	ND	0.002	0.005	0.006	0.106	b	TR	--	--	--
****Orthophosphate (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	ND	0.001	0.005	0.005	0.016	a	--	--	--	--
740376	ND	0.001	0.005	0.005	0.010	b	--	--	--	--
****Kjeldahl Nitrogen (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	ND	0.13	0.15	0.19	0.51	a	TR	16.4	-1.95	**0.000**
740376	ND	0.13	0.15	0.19	0.66	a	TR	16.4	-1.73	**0.002**
Nitrate Nitrogen (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	0.22	0.29	0.31	0.35	0.53	a	SK	17.0	-0.49	0.193
740376	0.22	0.28	0.30	0.34	0.46	a	SK	17.0	-0.73	0.060
****Nitrite Nitrogen (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	ND	0.006	0.006	0.006	0.011	a	--	--	--	--
740376	ND	0.006	0.006	0.006	0.011	a	--	--	--	--
****Ammonia Nitrogen (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	ND	0.010	0.012	0.015	0.025	a	TR	17.0	0.34	**0.027**
740376	ND	0.010	0.010	0.010	0.028	b	TR	--	--	--

** Parameters summarized using interval-censored data analysis.

4.4.2.2 Conventional Parameters

TOC

Median TOC was 1.8 mg/L and concentrations ranged from nondetectable (< 0.05 mg/L) to 5.3 mg/L. Concentrations did not vary by month or station. There was a significant, decreasing trend in TOC upstream and downstream (trend = -1.47% and -1.78% annually; Table 4-5).

Turbidity

The overall median value for turbidity was 1.0 NTU and values ranged from nondetectable (< 1 NTU) to 11.6 NTU. Turbidity did not vary significantly by month and was higher downstream ($p < 0.001$; Table 4-5). Trends were not explored for this parameter due to diurnal and seasonal variability.

TDS

Overall median TDS was 140 mg/L and concentrations ranged between 68 mg/L to 220 mg/L. TDS was not statistically different among months or sampling location and no temporal trends were detected (Table 4-5).

Sodium

Median sodium was 4.3 mg/L and concentrations ranged from 1.0 mg/L to 21.0 mg/L. Sodium was not statistically different among months and was higher at upstream stations (Table 4-5). There was a significant, positive trend upstream and downstream (trend = 1.86% and 1.97% annually; Table 4-5).

Chloride

Overall median chloride was 6.70 mg/L and concentrations ranged from 5.90 mg/L to 8.33 mg/L. Concentrations were not statistically different among months and were higher downstream ($p = 0.040$; Table 4-5). There was an increasing trend in chloride at station 740376 at a rate of 0.201% annually ($p = 0.02$; Table 4-5).

Hardness

Median overall hardness was 97.0 mg/L and ranged from nonquantifiable (< 5 mg/L) to 120 mg/L. Hardness did not vary by month or sampling location (Table 4-5). There was a significant, increasing trend downstream only ($p < 0.001$; trend = 0.24%; Table 4-5).

Calcium

Median calcium was 26.3 mg/L and concentrations ranged from nonquantifiable (< 1.0 mg/L) to 36 mg/L. Calcium did not vary significantly by month or station and there were no significant temporal trends in calcium (Table 4-5).

Magnesium

The median concentration of magnesium was 7.6 mg/L and magnesium ranged from nonquantifiable (< 1.0 mg/L) to 9.0 mg/L. Concentrations were not different among sampling months and were higher downstream ($p = 0.032$; Table 4-5). There was a significant, increasing trend in magnesium upstream and downstream (trend = 1.04% and 0.54% annually; Table 4-5).

Conductivity

The overall median conductivity on the St. Clair River was 210 µS/cm and concentrations ranged from 169 µS/cm to 291 µS/cm. Conductivity was not significantly different among months but was higher downstream (Table 4-5). There were no significant trends in conductivity (Table 4-5).

TSS

Overall median TSS was 4.0 mg/L and concentrations ranged from nondetectable (< 1 mg/L) to 29 mg/L. Concentrations were not statistically different among months and were higher downstream ($p < 0.001$; Table 4-5). There were no significant temporal trends, although the frequency of censored data precluded the use of trend analysis at the downstream location (Table 4-5).

Alkalinity

The overall median alkalinity was 73 mg/L CaCO3 and levels ranged from 62 to 98 mg/L. Alkalinity varied by month and was highest in the spring and lowest in the summer ($p = 0.028$). No differences were detected between upstream and downstream alkalinity (Table 4-5). There were no significant temporal trends (Table 4-5).

pH

Median pH on the St. Clair River was 8.06 and ranged from 6.80 to 11.60. Values varied by month and were highest in summer and lowest in fall ($p = 0.002$). Upstream and downstream values were not significantly different (Table 4-5). There were no significant temporal trends in pH in the St. Clair River (Table 4-5).

DO

The median concentration of DO was 10.26 mg/L and levels ranged from 7.35 mg/L to 16.62 mg/L. DO varied by month and was highest in spring and lowest in late summer ($p < 0.001$). Upstream to downstream DO was not statistically different (Table 4-5). Trends were not explored for this parameter due to diurnal and seasonal variability.

Potassium

Median potassium was 1 mg/L and concentrations ranged from nonquantifiable (< 0.10) to 3.9 mg/L. Potassium was not statistically different among months and was higher downstream at 740016 ($p = 0.038$; Table 4-5). There was a slight increasing trend in potassium at the upstream location ($p = 0.025$; trend = 1.29% annually; Table 4-5).

Sulfate

The overall median concentration of sulfate was 14.00 mg/L and concentrations ranged from 7 mg/L to 83 mg/L. Concentrations did not vary by season or by sampling location and no significant temporal trends were detected (Table 4-5).

Table 4-5. St. Clair River conventional parameters, by station. (Left) Summary Statistics. STORETs with nondetect samples marked with 'ND;' STORETs with nonquantifiable samples marked with 'NQ.' STORETs that do not share a letter under multiple comparisons are statistically different. Multiple comparisons were not performed on parameters with censored data. (Right) Temporal trends were analyzed using Seasonal Kendal (SK) or Tobit Regression (TR). Parameters censored with > 50% frequency are marked --.

Summary Statistics							Trend Analysis			
**TOC (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	ND	1.6	1.9	2	5.3	a	TR	16.4	-1.78	**< 0.001**
740376	NQ	1.6	1.8	2	4.3	a	TR	16.4	-1.47	**< 0.001**
**Turbidity (NTU)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	ND	1	2	3	12	a				
740376	ND	1	1	1	10	b				
TDS (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	68	140	140	142	220	a	SK	17.0	0.00	0.779
740376	100	140	140	140	160	a	SK	17.0	0.00	0.586
Sodium (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	2.4	3.9	4.4	4.8	21	a	SK	15	1.97	**< 0.001**
740376	1	3.8	4.3	4.6	6.4	b	SK	15	1.86	**0.002**
Chloride (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	5.9	6.6	6.8	7	8.1	a	SK	15	0.355	0.129
740376	5.9	6.4	6.6	6.8	8.3	b	SK	15	0.201	**0.020**
**Hardness (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	87	95	98	100	112	a	TR	16.4	0.24	**> 0.001**
740376	ND	95	97	99	120	a	TR	16.4	0.94	0.054

** Parameters summarized using interval-censored data analysis.

Table 4-5 (continued).

Summary Statistics							Trend Analysis			
**Calcium (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	21.9	25.8	26.4	27	30	a	TR	16.4	0.15	0.068
740376	ND	25.3	26.2	27.2	36	a	TR	16.4	0.16	0.326
**Magnesium (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	7	7.5	7.6	7.8	9	a	TR	16.4	0.54	**< 0.001**
740376	ND	7.4	7.6	7.8	8.9	b	TR	16.4	1.04	**0.003**
Conductivity (µmhos/cm)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	176	206	211	218	291	a	SK	16	0.07	0.632
740376	169	203	209	215	283	b	SK	16	0.06	0.509
**TSS (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	ND	4	4	5	29	a	TR	16.4	-0.99	0.608
740376	ND	1	4	4	14	b	--	--	--	--
Alkalinity (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	62	71	74	77	98	a	SK	15	0.17	0.37
740376	63	70	73	76	96	a	SK	15	0.19	0.597
pH										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	7	7.83	8.03	8.2	11.6	a	SK	16	0.17	0.247
740376	6.8	7.9	8.1	8.27	9.06	a	SK	16	0.18	0.284

** Parameters summarized using interval-censored data analysis.

Table 4-5 (continued).

STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
Summary Statistics							**Trend Analysis**			
Dissolved Oxygen (mg/L)										
740016	7.35	9.01	10.12	11.19	16.58	a				
740376	7.48	9.3	10.4	11.36	16.62	a				
****Potassium (mg/L)**										
740016	0.8	0.9	1	1.1	3.9	a	TR	14.5	0.22	0.568
740376	ND	0.9	0.92	1	2.8	b	TR	14.5	1.29	**0.025**
Sulfate (mg/L)										
740016	8	12	14	15	83	a	SK	17	3.97	0.071
740376	7	12	14	15	45	a	SK	17	3.12	0.156

** Parameters summarized using interval-censored data analysis.

4.4.2.3 Trace Metals

There were no WQS exceedances for metals in the St. Clair River for the current Integrated Report (2012-2013).

Chromium

The overall median concentration was 0.210 µg/L and ranged from nondetectable (< 0.057 µg/L) to 1.36 µg/L. Concentrations varied by month ($p < 0.008$) and were generally highest in spring and fall and lowest in summer (Figure 4-5). Concentrations were also higher downstream ($p < 0.001$; Table 4-6). No temporal trends were detected (Table 4-6).

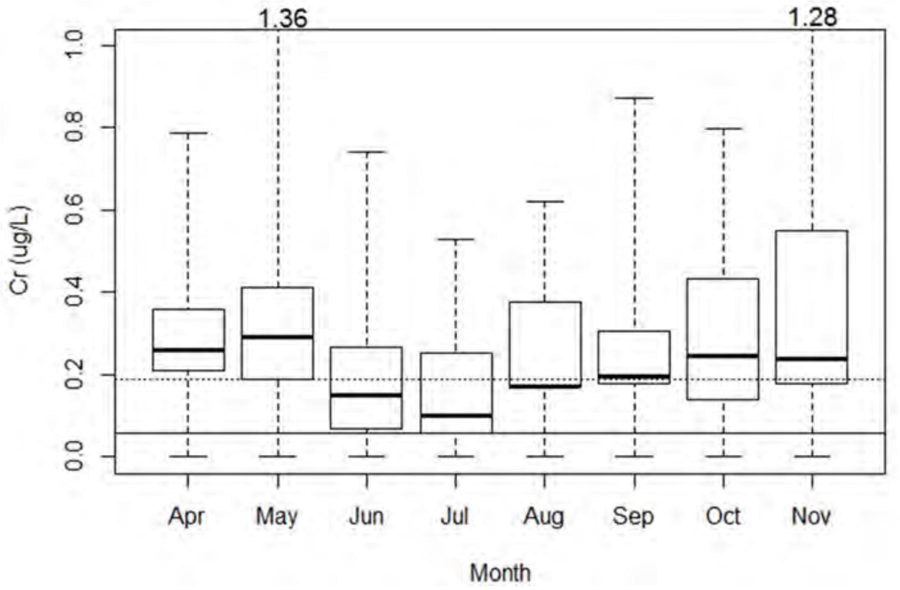


Figure 4-5. Total chromium within the St. Clair River. Y axis was cut off at a maximum concentration of 1.0 µg/L. Numbers across the top reflect values exceeding this cutoff. The solid horizontal line represents the laboratory's detection limit; the dotted horizontal line represents the laboratory's quantification limit.

Copper

The overall median concentration between 1998 and 2014 was 0.502 µg/L. Concentrations ranged from nonquantifiable (< 0.57 µg/L) to 1.36 µg/L. There was no significant variation in copper by sampling month. Concentrations were higher downstream ($p < 0.001$; Table 4-6). No significant temporal trends were detected (Table 4-6).

Lead

The overall median concentration of lead was 0.0522 µg/L and concentrations ranged from nondetectable (< 0.041 µg/L) to 0.6080 µg/L. Concentrations were significantly different among months ($p = 0.009$) and higher in spring and fall and lower in summer (Figure 4-6). Concentrations were also higher downstream ($p < 0.001$; Table 4-6). There were no significant temporal trends in lead (Table 4-6).

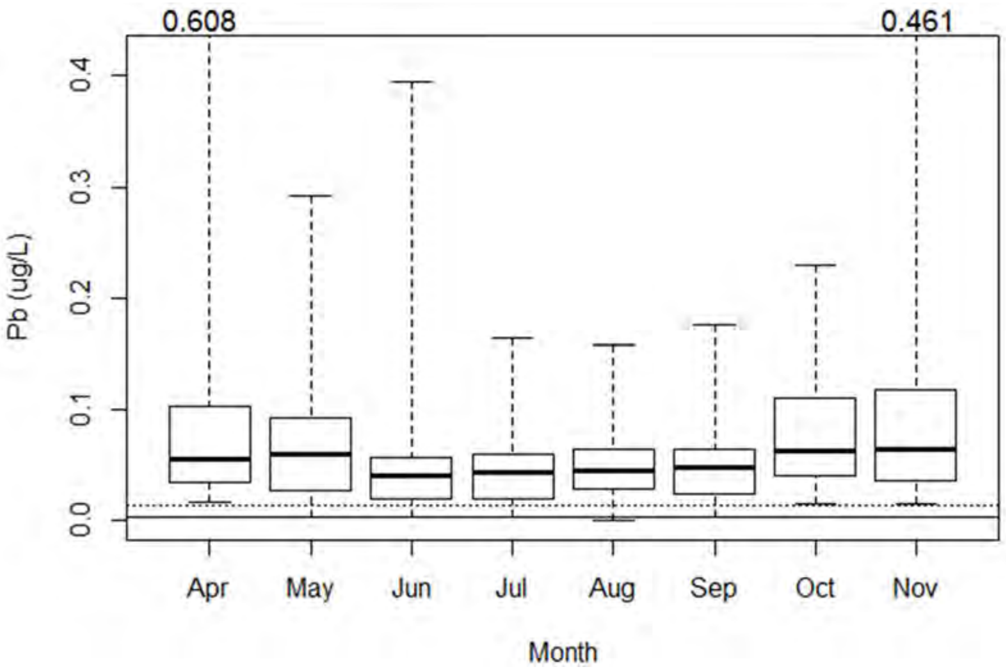


Figure 4-6. Total lead within the St. Clair River. Y axis was cut off at a maximum concentration of 0.4 µg/L. Numbers across the top reflect values exceeding this cutoff. The solid horizontal line represents the laboratory's detection limit; the dotted horizontal line represents the laboratory's quantification limit.

Mercury

The overall median concentration of mercury was 0.39 ng/L. Concentrations ranged from nondetectable (< 0.14 ng/L) to 9.567 ng/L. Concentrations were not statistically different by sampling month and were higher downstream ($p = 0.009$; Table 4-6). The frequency of censored data precluded the analysis of trends in Mercury.

Table 4-6. St. Clair River trace metal data, by station. (Left) Summary Statistics. STORETs with nondetect samples marked with 'ND;' STORETs with nonquantifiable samples marked with 'NQ.' STORETs that do not share a letter under multiple comparisons are statistically different. Multiple comparisons were not performed on parameters with censored data. (Right) Temporal trends were analyzed using Seasonal Kendal (SK) or Tobit Regression (TR). Parameters censored with > 50% frequency are marked --.

Summary Statistics							Trend Analysis			
****Chromium (µg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	ND	0.170	0.254	0.387	1.360	a	TR	16.4	-1.62	0.245
740376	ND	0.140	0.180	0.326	1.130	b	TR	16.4	-2.71	0.209
****Copper (µg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	NQ	0.511	0.564	0.640	1.350	a	TR	16.4	-0.49	0.204
740376	NQ	0.414	0.450	0.493	1.240	b	TR	16.4	0.31	0.449
****Lead (µg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	0.0255	0.0534	0.0654	0.0997	0.608	a	TR	16.4	-1.28	0.196
740376	ND	0.0181	0.0265	0.0463	0.405	b	TR	16.4	1.9	0.186
****Mercury (ng/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
740016	NQ	0.34	0.39	0.56	9.57	a	--	--	--	--
740376	ND	0.30	0.39	0.46	9.30	b	--	--	--	--

** Parameters summarized using interval-censored data analysis.

4.4.3 Detroit River

4.4.3.1 Nutrients

Total Phosphorus

The overall median concentration of total phosphorus was 0.012 mg/L and concentrations ranged from nondetectable (< 0.003 mg/L) to 0.134 mg/L. Concentrations were not statistically different among seasons and were higher downstream ($p < 0.001$; Table 4-7). A significant, decreasing trend was detected upstream (trend = -3.28% annually; Table 4-7).

Orthophosphate

The overall median concentration of orthophosphate was 0.005 mg/L. Concentrations ranged from nondetectable (< 0.002 mg/L) to 0.025 mg/L. Concentrations did not vary significantly by month and were higher downstream ($p = 0.001$; Table 4-7). No temporal trends in were detected.

Kjeldahl Nitrogen

The median concentration of Kjeldahl nitrogen was 0.200 mg/L and concentrations ranged from 0.11 mg/L to 1.41 mg/L. Concentrations of Kjeldahl nitrogen were not statistically different among months and were higher downstream ($p < 0.001$; Table 4-7). No temporal trends were detected at either location.

Nitrate Nitrogen

Median nitrate was 0.300 mg/L and concentrations ranged from 0.191 mg/L to 1.28 mg/L. Nitrate was highest in the spring and lower in fall ($p < 0.001$; Figure 4-7). Concentrations were higher upstream ($p < 0.001$; Table 4-7) and there was a decreasing trend in nitrate at the upstream station ($p = 0.033$; -0.96% annually; Table 4-7).

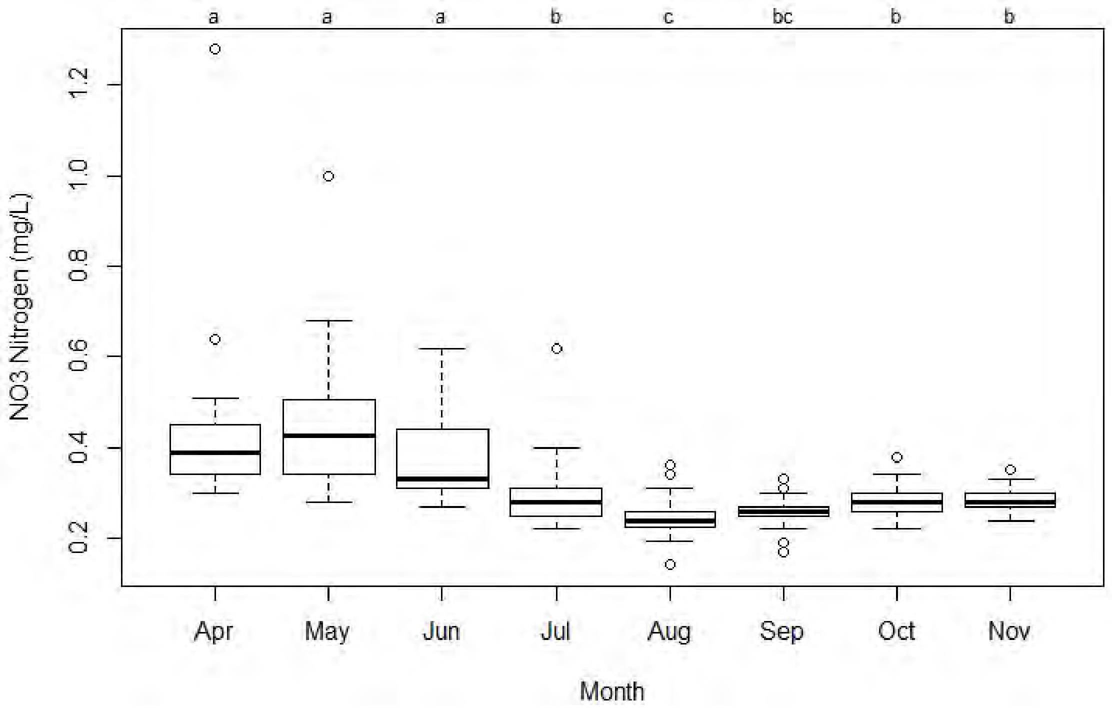


Figure 4-7. Nitrate concentrations, by month, 1998-2014. Months not sharing a letter are significantly different.

Nitrite Nitrogen

The overall median concentration of nitrite was 0.01 mg/L and concentrations ranged from nondetectable (< 0.002 mg/L) to 0.08 mg/L. Monthly comparisons and temporal trend analyses were not performed due to the high frequency of samples below quantification level. Summary statistics, by station, are shown in Table 7.

Ammonia Nitrogen

The overall median concentration was 0.023 mg/L and concentrations ranged from nondetectable (< 0.001 mg/L) to 0.34 mg/L. Concentrations varied by month and were highest in fall and lowest in spring ($p < 0.013$). Ammonia was also higher at downstream ($p < 0.001$; Table 7). No temporal trends were detected within the Detroit River (Table 4-7).

Table 4-7. Detroit River nutrients, by station. (Left) Summary Statistics. STORETs with nondetect samples marked with ‘ND;’ STORETs with nonquantifiable samples marked with ‘NQ.’ STORETs that do not share a letter under multiple comparisons are statistically different. Multiple comparisons were not performed on parameters with censored data. (Right) Temporal trends were analyzed using Seasonal Kendal (SK) or Tobit Regression (TR). Parameters censored with > 50% frequency are marked --.

Summary Statistics							**Trend Analysis**			
****Total Phosphorus (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	ND	0.011	0.014	0.018	0.134	a	TR	16.4	-1.29	0.138
820414	ND	0.010	0.011	0.015	0.116	b	TR	16.4	-3.28	**0.005**
****Orthophosphate (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	ND	0.005	0.005	0.007	0.025	a	TR	16.4	1.16	0.380
820414	ND	0.005	0.005	0.005	0.021	b	--	--	--	--
Kjeldahl Nitrogen (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	0.11	0.19	0.21	0.27	0.70	a	SK	17.0	0.34	0.581
820414	0.11	0.16	0.18	0.21	1.41	b	SK	17.0	-1.05	0.123
****Nitrate Nitrogen (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	0.19	0.26	0.29	0.35	0.67	a	SK	17.0	-0.69	0.106
820414	0.14	0.26	0.30	0.37	1.28	b	SK	17.0	-0.96	**0.033**
****Nitrite Nitrogen (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	ND	0.010	0.010	0.012	0.080	a	--	--	--	--
820414	ND	0.006	0.006	0.006	0.013	b	--	--	--	--
****Ammonia Nitrogen (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	NQ	0.027	0.037	0.054	0.340	a	TR	16.4	0.43	0.709
820414	ND	0.010	0.014	0.019	0.035	b	TR	16.4	-0.18	0.839

** Parameters summarized using interval-censored data analysis.

4.4.3.2 Conventional Parameters

TOC

The median value for TOC was 2.0 mg/L and concentrations ranged from nondetectable (< 0.05 mg/L) to 4.9 mg/L. Concentrations were not statistically different among months but were higher downstream ($p = 0.002$; Table 4-8). There was a significant, increasing trend in TOC upstream (trend = -1.09%; Table 4-8).

Turbidity

The overall median value for turbidity was 3.4 NTU and levels ranged from nondetectable (< 1 NTU) to 73 NTU. Turbidity varied significantly by month and was highest in spring and fall and lowest in summer ($p < 0.001$). There was no statistical difference in turbidity from upstream to downstream (Table 4-8). Trends were not examined for this parameter due to diurnal and seasonal variability.

TDS

Overall median TDS was 150 mg/L and concentrations ranged from 116 mg/L to 350 mg/L. TDS varied significantly across months and was highest in the spring and lowest in the fall ($p < 0.001$). Concentrations were also higher downstream ($p < 0.001$; Table 4-8). No temporal trends were detected in TDS (Table 4-8).

Sodium

Median sodium was 4.9 mg/L and ranged from 2.4 mg/L to 12.0 mg/L. Sodium varied by month and was highest in spring and lowest in the fall ($p = 0.048$; Figure 4-8). It was also higher downstream ($p < 0.001$; Table 4-8). There was an increasing trend in sodium upstream and downstream (trend = 1.73% and 2.40% annually; Table 4-8).

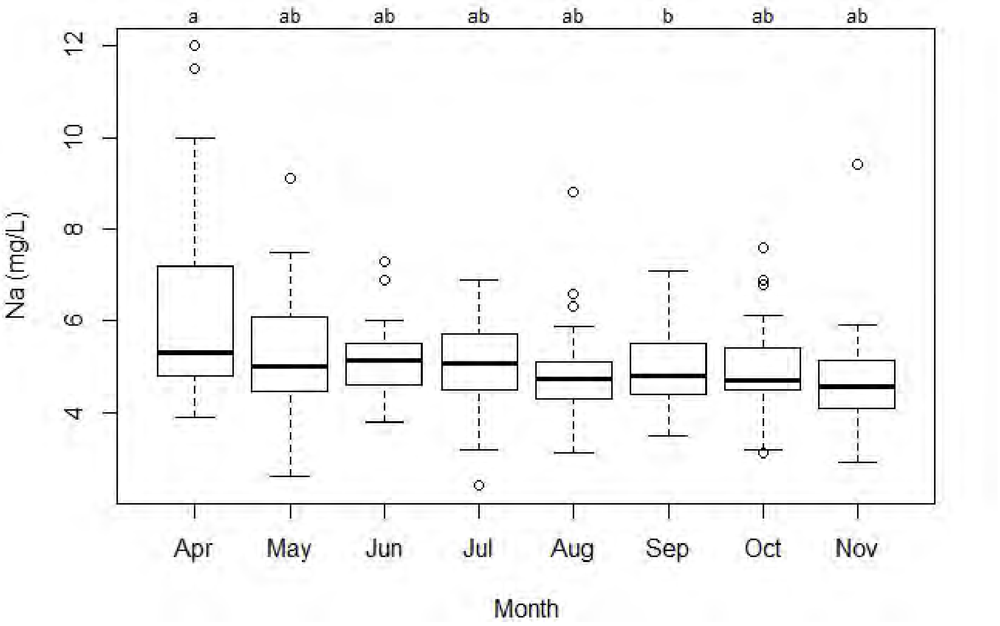


Figure 4-8. Sodium within the Detroit River, by month, 1998-2014. Months not sharing a letter are significantly different.

Chloride

The median concentration of chloride was 7.896 mg/L and concentrations ranged from 6 mg/L to 16.0 mg/L. Chloride was not statistically different among sampling months but was higher downstream ($p < 0.001$; Table 4-8). There was an increasing trend in chloride at station 820017 at a rate of 1.093%, annually ($p = 0.027$; Table 4-8).

Hardness

Overall hardness was 99.6 mg/L and levels ranged from 73 mg/L to 130 mg/L. Hardness varied by month and was highest in spring and lowest in summer ($p < 0.001$). Hardness was not significantly different between upstream and downstream (Table 4-8). There was a significant, increasing trend in hardness downstream (trend = 0.268% annually; Table 4-8).

Calcium

Median calcium was 27 mg/L and concentrations ranged from 16.3 mg/L to 35.1 mg/L. Concentrations varied significantly by month and were highest in May and lowest in July ($p < 0.001$). Calcium was not statistically different between upstream and downstream and there were no significant temporal trends (Table 4-8).

Magnesium

Median magnesium was 7.8 mg/L and concentrations ranged from 6.5 mg/L to 9.5 mg/L. Magnesium did not vary by month or station (Table 4-8). There was an increasing trend in magnesium at both locations (trend = 0.52% and 0.44% annually; Table 4-8).

Conductivity

Median conductivity was 218 µS/cm .and ranged from 171 µS/cm to 342 µS/cm. Conductivity varied by month and was highest in spring and lowest in summer ($p < 0.001$). Conductivity was also higher downstream ($p < 0.001$; Table 4-8). There were no significant temporal trends in conductivity (Table 4-8).

TSS

The overall median value for TSS was 5 mg/L and concentrations ranged from nondetectable (< 1 mg/L) to 130 mg/L. TSS varied by month and was highest in fall and lowest in summer ($p = 0.005$). There was no difference in TSS between upstream and downstream stations (Table 4-8). There were no significant temporal trends in TSS (Table 4-8).

Alkalinity

Median alkalinity was 75 mg/L $CaCO_3$ and ranged from 60 mg/L to 110 mg/L. Alkalinity was highest in spring and lowest in summer ($p < 0.001$). Alkalinity was higher downstream, and no temporal trends were detected at either location (Table 4-8).

pH

Overall median pH on the Detroit River was 7.97 and ranged from 6.23 to 11.2. pH varied by month and was highest during the summmer and lowest in fall ($p < 0.001$). pH was also higher upstream ($p = 0.012$; Table 4-8). There were no significant temporal trends in pH (Table 4-8).

DO

The overall concentration of DO was 9.36 mg/L and DO ranged from 6.1 mg/L to 16.1 mg/L. Concentrations varied by month and were highest in spring and lowest in summer ($p < 0.001$). DO was not statistically different among sampling stations (Table 4-8). Trends were not examined for this parameter due to diurnal and seasonal variability.

Potassium

The overall median concentration of potassium was 1.032 mg/L. Potassium ranged from 0.88 mg/L to 5.00 mg/L. Potassium varied significantly by month and was highest in spring and lowest in the fall ($p < 0.001$). Concentrations were also higher downstream ($p < 0.001$; Table 4-8). There was a significant, increasing trend at the upstream location (trend = 0.84% annually; Table 4-8).

Sulfate

The overall median concentration of sulfate was 14.00 mg/L and concentrations ranged from 8 mg/L to 23 mg/L. There was no significant monthly or spatial variability in sulfate concentrations (Table 4-8). There was an increasing trend upstream (trend = 5.93% annually; Table 4-8).

Table 4-8. Detroit River conventional parameters, by station. (Left) Summary Statistics. STORETs with nondetect samples marked with ‘ND;’ STORETs with nonquantifiable samples marked with ‘NQ.’ STORETs that do not share a letter under multiple comparisons are statistically different. Multiple comparisons were not performed on parameters with censored data. (Right) Temporal trends were analyzed using Seasonal Kendal (SK) or Tobit Regression (TR). Parameters censored with > 50% frequency are marked --.

Summary Statistics							Trend Analysis			
****TOC (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	ND	1.9	2.0	2.2	4.9	a	TR	16.4	-0.73	0.072
820414	ND	1.7	1.9	2.1	3.9	b	TR	16.4	-1.09	**0.013**
****Turbidity (NTU)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	ND	2	3	6	56	a				
820414	ND	2	4	5	73	a				
TDS (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	120	145	150	152	220	a	SK	17.0	0.00	0.332
820414	116	140	140	150	350	b	SK	17.0	0.00	1.000
Sodium (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	3.2	4.8	5.4	6.0	12.0	a	SK	15.0	2.40	**0.004**
820414	2.4	4.0	4.6	4.9	7.6	b	SK	15.0	1.73	**0.003**
Chloride (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	6.0	7.5	8.0	9.0	20.0	a	SK	16	1.093	**0.027**
820414	6.0	6.0	7.0	7.0	14.0	b	SK	16	0.489	0.059
Hardness (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	73	98	100	103	120	a	SK	17	0.27	**0.011**
820414	88	97	99	102	130	a	SK	17	0.1	0.406

** Parameters summarized using interval-censored data analysis.

Table 4-8 (continued).

Summary Statistics							**Trend Analysis**			
Calcium (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	16.3	26.3	27.1	28.2	32.6	a	SK	17.0	0.24	0.146
820414	23.3	26.1	27.0	28.0	35.1	a	SK	17.0	0.05	0.834
Magnesium (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	7.1	7.6	7.8	8.1	9.5	a	SK	17.0	0.52	**0.001**
820414	6.5	7.5	7.7	8.0	9.3	a	SK	17.0	0.44	**0.005**
Conductivity (µmhos/cm)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	176	216	222	231	342	a	SK	16	0.4	0.172
820414	171	208	214	222	320	b	SK	16	0.11	0.416
****Total Suspended Solids (mg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	ND	4	5	8	130	a	TR	16.4	-1.08	0.547
820414	ND	4	6	10	75	a	TR	16.4	-1.88	0.347
Alkalinity (mg/L)										
STORET	Min	Q1	Median	Q3	**Max**	Mult. Comp.	Type	# Years	Trend %	p value
820017	64	72	76	79	110	a	SK	15	0.18	0.269
820414	60	71	75	77	100	b	SK	15	0	0.763
pH										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	6.23	7.7	7.91	8.13	8.68	a	SK	16	0.05	0.766
820414	6.8	7.82	8.05	8.25	11.2	b	SK	16	0.08	0.471

** Parameters summarized using interval-censored data analysis.

Table 4-8 (continued).

Summary Statistics							Trend Analysis			
Dissolved Oxygen (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	6.10	8.25	9.34	10.80	15.50	a				
820414	6.78	8.46	9.38	10.52	16.10	a				
Potassium (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	0.90	1.00	1.10	1.20	3.40	a	SK	15.0	0.00	**0.027**
820414	0.88	0.99	1.00	1.10	5.00	b	SK	15.0	0.84	**0.044**
Sulfate (mg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	8	12	14	16	23	a	SK	17.0	4.16	0.103
820414	9	12	14	16	22	a	SK	17.0	5.93	**0.041**

** Parameters summarized using interval-censored data analysis.

4.4.3.3 Trace Metals

There were no WQS exceedances for metals in the Detroit River for the current Integrated Report (2012-2013).

Chromium

The overall median concentration was 0.34 µg/L and chromium ranged from nondetectable (< 0.057 µg/L) to 4.89 µg/L. Concentrations varied significantly by month and were highest in spring and fall and lowest in the summer ($p < 0.001$). Concentrations were not statistically different between upstream and downstream and there were no statistically significant temporal trends in the Detroit River (Table 4-9).

Copper

The overall median concentration was 0.7075 µg/L and copper ranged from 0.515 µg/L to 5.23 µg/L. Copper was not statistically different among months or sampling stations, but there was a significant, decreasing trend in upstream copper (trend = -1.47% annually; Table 4-9).

Lead

The overall median concentration was 0.2095 µg/L. Lead concentrations ranged from 0.0719 µg/L to 5.14 µg/L. Lead varied significantly by month and was highest in fall and lowest in summer ($p < 0.001$; Figure 4-9). Concentrations were not statistically different between upstream and downstream sampling locations (Table 4-9). There were no temporal trends in lead (Table 4-9).

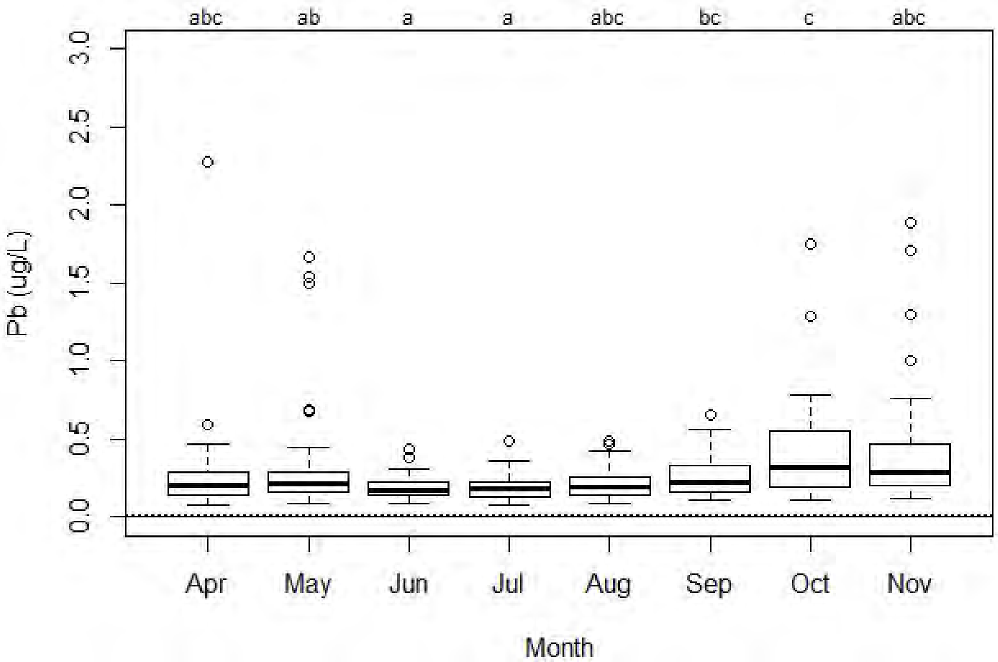


Figure 4-9. Lead within the Detroit River, by month, 1998-2014. Months not sharing a letter are significantly different.

Mercury

The overall median concentration was 1.91 ng/L and concentrations ranged from nondetectable (< 0.14 ng/L) to 37.98 ng/L. Concentrations varied significantly across months ($p < 0.001$) and were highest in the fall and lowest in summer. Concentrations were also higher upstream ($p < 0.001$; Table 4-9). There were significant, decreasing trends in mercury upstream and downstream (trend = -5.41% and -3.32% annually; Table 4-9).

Table 4-9. Detroit River trace metals, by station. (Left) Summary Statistics. STORETs with nondetect samples marked with 'ND;' STORETs with nonquantifiable samples marked with 'NQ.' STORETs that do not share a letter under multiple comparisons are statistically different. Multiple comparisons were not performed on parameters with censored data. (Right) Temporal trends were analyzed using Seasonal Kendal (SK) or Tobit Regression (TR). Parameters censored with > 50% frequency are marked --.

Summary Statistics							**Trend Analysis**			
****Chromium (µg/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	ND	0.236	0.343	0.544	4.890	a	TR	16.4	-0.35	0.762
820414	NQ	0.224	0.338	0.575	3.220	a	TR	16.4	-0.46	0.721
Copper (µg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	0.515	0.657	0.731	0.878	5.230	a	SK	17.0	-0.16	0.806
820414	0.500	0.617	0.685	0.879	3.810	a	SK	17.0	-1.47	**0.014**
Lead (µg/L)										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	0.0719	0.167	0.213	0.305	5.14	a	SK	17.0	-0.31	0.81
820414	0.0719	0.143	0.201	0.302	3.83	a	SK	17.0	-2.33	0.14
****Mercury (ng/L)**										
STORET	Min	Q1	Median	Q3	Max	Mult. Comp.	Type	# Years	Trend %	p value
820017	NQ	0.98	1.53	2.52	37.98	a	TR	16.2	-3.33	**0.010**
820414	ND	1.60	2.40	4.23	35.29	b	TR	16.2	-5.57	**0.001**

** Parameters summarized using interval-censored data analysis.

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