Extreme Rain Events' Effects on the Biogeochemistry of Lake Superior

A Thesis submitted to the Faculty of the University of Minnesota by

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Abstract

Climate change is expected to profoundly affect the Great Lakes region of North America. An increase in intensity and frequency of rain events is anticipated to deliver more runoff and to increase riverine inputs to Lake Superior's ecosystem. The effects of these changes on key biogeochemical parameters were analyzed by coupling satellite data, water column sensor profiles, and discrete surface-water sampling after two "500-year" flood events in the Lake Superior basin. This study provides both a spatial and a temporal sense of how plumes interacted within the ecosystem. We also determined the significant differences in water quality parameters for plume versus non-plume waters. These two plumes were important for delivery of nutrients, with variable transport of sediments and colored dissolved organic matter (CDOM) as well. Data from the 2012 storm event showed a significant input of total nitrogen (TN), total phosphorous (TP) and CDOM to the system. In the 2016 storm event, carbon cycling parameters (which were not measured in 2012) including acidity, total inorganic carbon (TIC), and dissolved organic carbon (DOC) were elevated in the plume, along with ammonia. In neither storm event was there a significant difference in chlorophyll a between plume and non-plume waters during our sampling cruises. These two plume events were similar in amount of precipitation, but their effect on the biogeochemistry of Lake Superior varied due to the differences in the watersheds where the rain fell. The studied plume events were dynamic, changing with currents, winds and the settling of suspended sediments.

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Chapter 1. Introduction

As climate change becomes a more pressing issue, it is necessary to understand the relationship between lakes and their watersheds to predict the quality of freshwater ecosystems for human recreation and water consumption, for support of biodiversity, and other factors (Schindler 2009). It is anticipated that the average precipitation within the United States will be impacted by climate change to varying degrees depending on the region; changes in precipitation will in turn affect watershed-lake connectivity. The frequency and intensity of storm events are expected to increase in the Southeast, Northeast and Great Lakes region regions of the United States of America (Donat et al. 2016; Groisman et al. 2005; Mallakpour and Villarini 2016; Walsh et al., 2015). Observed extreme daily rainfall events are expected to increase in amount of rain delivered on average by about 7% per degree Celsius of global warming, as a warmer atmosphere can hold more water vapor (Prein et al. 2017). An upward trend in seasonal totals of precipitation and the amount of rain delivered in heavy precipitation events has been observed for most of the continental United States (Easterling et al. 2000). If more of a region's precipitation occurs in extreme rain events, the biogeochemistry of lake systems is likely to be significantly altered, which could also significantly shift lake ecosystems.

Over the last 30 years, Great Lake states have seen increases in heavy precipitation events, about 37% above the average of 1901-1960 (Walsh et al. 2015). These changes are expected to transform watersheds, affecting how they supply nutrients and sediment to lake ecosystems (Schindler 2009). In addition to infrastructure damages, large amounts of runoff from such rain events could increase soil erosion, increase terrestrial inputs of organic matter (e.g., leaves, woody debris, etc) and nutrients, and carry contaminants such as pesticides, herbicides, petroleum products, and fertilizers into lake systems.

Spatial analysis was used to determine how cumulative stress was affecting the Laurentian Great Lakes (Allan et al., 2013). Toxins, runoff from the land, invasive species, depleted fisheries, coastal development, climate change and aquatic habitat, were the most influential stressors for the region (Allan et al, 2013). For much of the Great Lakes the nearshore areas had higher cumulative stress than the offshore areas, with the most stressed areas being at river mouths and wetlands (Allan et al. 2013). Western Lake Superior, the study area for this thesis, is within the top 20% category for cumulative stress, being exposed to 12-20 stressors above the average for the whole Great Lakes ecosystem (Allan et al., 2013). These high stress levels commonly occur where humans also rely on the system to provide many ecosystem services (Allan et al., 2013). These are areas where human uses of the lakes are directly linked to commerce and rely on the health of the ecosystem (Allan et al., 2013). Here we investigate three of these stressors: sediments, nitrogen and phosphorus. It is anticipated that, with more frequent and intense storm events, these three factors could impart more stress on the system.

Lake Superior is the world's largest freshwater lake by surface area, containing 10% of the world's surface liquid freshwater. It is an oligotrophic ecosystem (Matheson and Munawar 1978; Munawar and Munawar 1978) with cold epiliminetic temperatures and low nutrient concentrations (Sterner 2010). It is unclear how fluxes of biogeochemically important compounds into the lake will be affected by large amounts of rainfall, runoff, erosion, and increasingly variable river discharge. The watershed influence is lessened compared to direct precipitation on the lake due to its low watershed to lake surface area ratio (~1.55, Cotner et al. 2004), but its oligotrophic nature may make any changes in watershed inputs more impactful.

At present phytoplankton growth appears to be mainly light limited, and there is evidence that annual primary production in the lake could be changing due to decreased ice cover, warming surface waters, or longer growing season. Based on data from short term incubations, phytoplankton growth in cold, dimictic Lake Superior is thought to be controlled by temperature and light availability, rather than nutrient concentrations (Sterner 2010). With the changing climate, soluble reactive phosphorus may become evident as a new important factor. The primary production in Lake Superior has been rapidly increasing within the last century and is thought to be a result of anthropogenic climate change (O'Beirne et al., 2017). Climate warming has shorted the length of time that ice can form on the lake which has led to increasing surface water temperatures (during the summer) and longer seasonal stratification, allowing for a longer growing season (O'Beirne et al., 2017). We anticipate that extreme storm events affecting key watersheds for nutrient delivery (see Chapter 2) will increase the river contribution of phosphorus and other nutrients, which, along with the changing lake temperatures and stratification times, may increase primary productivity in Lake Superior.

A majority of the phosphorus in lake systems, including that of Lake Superior, is derived from river inputs (Robertson & Saad, 2011). The St. Louis River is the single most significant tributary input to Lake Superior for materials and nutrients (International Joint Commisions, 1977). Considering only loading from the U.S.A., the western arm of Lake Superior has two of the five tributaries with greatest TP loading to whole lake, with the St. Louis River being the largest, delivering 126,934 kg/year phosphorus and the Nemadji River being fourth largest delivering 69,446 kg/year (Robertson & Saad, 2011). During extreme storm events with high levels of precipitation it is expected that high discharge from rivers and bank erosion will cause an increase in phosphorus inputs to the lake. As phosphorus has been shown to limit algal growth in lake water, including that of Lake Superior (Sterner et al., 2004), there could be an increase in primary productivity following these events. Although it was not focused on rainstorm events, a study on river and stream plumes in Lake Ontario's nearshore environment determined that river plumes had higher values of chlorophyll, TP, turbidity, specific conductance, and temperature than non-plume waters (Makarewicz et al. 2012). In situ and enrichment incubations were used to study how spring recurrent coastal sediment and river plumes affected the phytoplankton growth of Lake Michigan (Lohrenz, 2004). It was found that river water (not resuspension events) stimulated lake productivity (Lohrenz, 2004). In fact, the resuspension events reduced the light availability constraining primary production (Lohrenz, 2004). This finding suggests that while increased levels of river discharge may deliver high levels of dissolved phosphorus, extreme storm events can also reduce ecosystem productivity through light limitation as happened in resuspension events (Lohrenz, 2004).

As applied in this study the term "plume" describes when a lotic system, either ephemeral or year-round, enters a lentic system and delivers material, often suspended sediments, organic matter, colored dissolved organic matter (CDOM) and nutrients, from the surrounding watershed to the lake ecosystem. There are many different types of plumes described in aquatic science literature; plumes can be due to winds, wave resuspension, or precipitation (typical and extreme) events. These plumes are caused by different factors and deliver diverse material to lake ecosystems. The literature at present does not distinguish clearly among these several plume types, which makes it difficult to determine how a system will respond to events. Plumes are often visible in lakes, especially after rain events, and are typically characterized by their brownish–red color and overall decrease in light penetration though the water column.

Nearshore areas of lakes are transition zones between the waters most heavily influenced by the terrestrial landscape and anthropogenic inputs and open oligotrophic waters (Chu et al. 2014). The nearshore areas (defined as areas were 1% of incoming surface light reaches the lake bottom) contain about 90% of the biodiversity within Lake Superior (Vadeboncoeur et al. 2011). The nearshore area is more productive than offshore; this is typically attributed to the nutrient loading (mainly phosphorus) that is delivered from the terrestrial watershed (Schindler 1978).

Both positively and negatively buoyant river plumes have been observed in the Laurentian Great Lakes (Rao and Schwab, 2007 and references therein). However, in late spring or early summer, the warmer river discharge that forms the plumes, especially for larger rivers, is often less dense than deep lake water and therefore remains in the surface layer of the lake due to the density difference. Such a buoyant plume was observed by Rao and Schwab (2007), who described how the warm Niagara River influenced the thermal structure of Lake Ontario. This inflow of river water was seen to extend to distances farther than 10 km from the river mouth and to a vertical depth of 10 m (Rao and Schwab 2007). While such a density separation typically leads to an entrapment of nutrients, sediment and anthropogenic inputs in the surface waters, it has been shown that there is exchange from nearshore to offshore ecosystems, which allows these river plumes to affect a greater portion of the lake (Rao and Schwab 2007). The gradient of nutrients and temperature along the thermal front of the plume is dependent on the seasons (Rao and Schwab 2007). It is due to the buoyant properties of these large river plumes that they can be seen by satellites, which facilitates the study of their material transport from nearshore to open water.

The structure of lacustrine autotrophic and heterotrophic biological communities may rely on the transport of dissolved material and sediments from watersheds to lakes and the extent to which this transport is retained in the nearshore or exported to offshore regions (Makarewicz et al. 2012). It has been shown that the Gulf of Mexico (an oligotrophic marine system over an order of magnitude larger in surface area than Lake Superior) is supported by the flow of nutrients from the Mississippi River, especially during times of a higher flow rate (Wawrik and Paul 2004). In a similar manner the Selenga River accounts for over 50% of the nutrient load to Lake Baikal, specifically influencing the southern basin (Müller et al. 2005). The Selenga River input created a significant difference in net ecosystem production between the northern and southern basins of Lake Baikal (1,220 mmol C m^{-2} $year^{-1}$, 1730 mmol C m^{-2} $year^{-1}$, respectively), which suggests that riverine inputs of nutrients and carbon from the river are being used in the southern basin ecosystem to produce a greater annual yield of autotrophic phytoplankton (Straškrábová et al. 2005). Inputs of river nutrients and organic matter have also shown to increase the primary production in Lake Superior near the Ontonagon River on the Keweenaw Peninsula (Auer and Bub 2004). The watershed of western Lake Superior drains a few of the largest phosphorus-delivering tributaries of the lake in the

United States, such as the St. Louis (largest) and Nemadji Rivers (fourth-largest), thus it is suspected that it would be possible to observe an increase in primary productivity during times of high flow (Robertson & Saad, 2011). It has been shown that these plumes can heavily impact the offshore environment if the river inputs travel far enough.

Robertson et al. (2016) simulated the impacts of climate change (+2.6 °C average and -5.1% to 16.7% change in precipitation) on Lake Michigan phosphorus loading. An output of their model was total annual phosphorus loadings for the Lake Michigan area between years 2045-2065; these loadings contained a large amount of variability (-29.6 to 17.2%), (Robertson et al. 2016). While this study projects a decrease in phosphorus loading to the system, with an average value of -3.1%, it does not consider the effect of extreme rain events (Robertson et al., 2016). This demonstrates that further studies of the effects of climate change on nutrient cycling, including multiple impacts from changing hydrology, need to occur to more accurately determine the response of lake systems.

Lake Superior may be susceptible to climate-change related inputs from its watershed due to its currently low concentration of phosphorus. These low total phosphorus (TP) levels (on the order of 0.03 to 0.1 µmol/L) (0.93-3.10 µg/L P) are coupled with high concentrations of total nitrogen (30-32 µmol/L) (0.42-0.45 mg/L N), most of which is in the dissolved form as nitrate (Sterner 2011). Thus, large amounts of phosphorus entering the lake ecosystem due to extreme events could greatly influence the biogeochemical environment and cause an ecosystem response (Carpenter, Booth, and Kucharik 2018; Makarewicz et al. 2012). Not all forms of phosphorus will equally stimulate productivity, however. Dissolved soluble reactive phosphorus is the most bioavailable form, and thus most likely to cause an increase in primary production.

Bioavailable inorganic phosphorus is taken up by organisms and cycled through food webs, and returned to the water column in soluble form by excretion and "sloppy feeding", the loss of soluble prey biomass during the feeding process (Dagg, 1974). The particulate phase of phosphorus, when it is bound to sediment or in iron-oxide complexes, typically settles out of the water column and thus does not contribute to water column production (Heath & Munawar, 2004). The phosphorus cycle is tied tightly to oxic/anoxic conditions in the lake due to the solubility of iron in its different forms. The surface sediments of Lake Superior are well oxygenated, such that the oxidized surface layer acts like a cap keeping the phosphorus in its iron-oxide-bound particulate phase.

In addition to delivering nutrients, rain-driven plumes may have high concentrations of suspended sediments and CDOM, decreasing overall light penetration and thus the volume of the euphotic zone within the lake; the interplay between nutrient delivery and light limitation complicates predicting the impact of plumes on primary productivity (Minor et al. 2014). While autotrophs might be negatively affected by the decrease in light availability in the nearshore, heterotrophic bacteria may utilize the input of allochthonous carbon as metabolic substrate (Azam et al. 1983; Tranvik 1992; Pomeroy et al. 2007). As allochthonous organic material contains high C: N and C: P ratios, these heterotrophic bacteria will also remove usable N and P from the water column for cellular processes, perhaps further decreasing nutrients available for autotrophs.

The amount and composition of river discharge can be affected by the size (Steinman, Chu, and Ogdahl 2009), soil type (Frost et al. 2006) and land-use (Yurista, Kelly, and Miller 2011) of the watershed. It has been specifically shown for the nearshore of Lake Superior that water quality properties were primarily driven by agriculture-chemical usage and land cover attributes (Yurista, Kelly, and Miller 2011). Peak values in temperature, specific conductivity, beam attenuation, fluorescence and zooplankton biomass occurred in the Duluth-Superior to Apostle Island nearshore area. These peaks are highly correlated with watershed areas that had the most altered land use. Loadings from rivers in different land use areas may supply distinct types of nutrients, organic carbon, and suspended matter to lake systems.

Studies of extreme rain events have shown a wide range of effects on ecosystems of small to large lakes and marine estuaries (Carpenter, Booth, Kucharik, & Lathrop, 2015; Havens et al., 2016; Ringuet & MacKenzie, 2005; Lohrenz et al., 2004; Sadro & Melack, 2012; Vanderploeg et al., 2007; Weyhenmeyer et al., 2004; Williamson et al., 2014). A common thread of these studies is the interplay between light limitation and nutrient availability. In many, but not all cases, there was a short-term decrease in primary productivity days to weeks after the storm event. In some cases, this was followed by an increase in primary production or algal biomass months after the storm event. Inputs from an extreme rain event in an alpine oligotrophic lake system resulted in an increase in particulate and dissolved organic matter, a minimization of the photic zone, and reduction of chlorophyll-a (Sadro & Melack, 2012). These led to a 47% decrease for the whole lake gross primary production, as well as a 30% increase in respiration (relative to average fall values), which altered the carbon dynamics from slightly autotrophic to strongly heterotrophic (Sadro & Melack, 2012). Conversely, during storm conditions in Southern Kaneohe Bay Hawaii, it was determined that nutrient loading via runoff generally led to an increase in phytoplankton biomass, but this was followed by a rapid depletion of nutrients that resulted in a decline of algal population (Ringuet & MacKenzie, 2005). Total phosphorus has been determined to be highly correlated with suspended matter and river influences in Lake Michigan during storm events (Vanderploeg et al., 2007). While such plumes do contain nutrients needed to increase primary production, it was observed that chlorophyll concentrations were lower in plume regions than in non-plume areas (Vanderploeg et al., 2007). Studies conducted as part of the Episodic Events Great Lakes Experiment determined that storms and the plumes that they create generally have a negative effect on the planktonic food web. A study in Lake Malaren, Sweden showed that an extremely wet November (with precipitation 71 mm higher than the monthly November average from 1961-1990) led to a spring that had elevated organic carbon, reactive silica (double from pre-storm values), particle concentrations and a doubling of crytptophycean biomass, as well as a decrease in conductivity (Weyhenmeyer et al., 2004).

It is thought that a single extreme climatic event could have a stronger influence on an ecosystem than a fluctuation in the mean values of temperature and precipitation (Parmesan et al. 2000). This thesis investigates and compares the effects of two extreme rain events from the past decade. Both events studied occurred in the southwestern watersheds of Lake Superior. The "500 year" flood events occurred in 2012 and 2016 and supplied about 22-25 cm of precipitation to the St. Louis River watershed and central/eastern Minnesota and Northern Wisconsin, respectively (Czuba, Fallon, and Kessler 2012; www.weather.gov /dlh/flash-flooding-2016-07-11.htm, accessed Feb. 2017; https://hdsc.nws.noaa.gov /hdsc /pfds /pfds_map_cont.html, accessed Sept. 2017). Both of these plume-producing events were classified as "Mega-rain" events by the

Minnesota Department of Natural Resources, which considers a "Mega-rain" event to be when "6 inches of rain falls upon more than 1,000 square miles, with the rainfall at the core of the storm being greater than 8 inches" (http://www.dnr.state.mn.us/climate/summaries_and _publications/mega_ rain_events.html). These storm events produced sediment plumes resulting mainly from rainfall (as opposed to wind or wave action) leading to increased river flow, bank erosion, and overland flow. These plumes were visible in MODIS satellite images for days to weeks after the precipitation events, (MODIS today http://ge.ssec. wisc.edu/modis-today). It was determined that the 2012 storm created large fluxes of terrestrial material, which supplied the western arm of the lake with high nutrient, CDOM, and sediment concentrations (Minor et al., 2014).

Here it is investigated how these two extreme storm events influenced the biogeochemistry of Lake Superior. Thesis goals are: 1. to understand how these storm plumes affect water quality, including nutrient inputs and carbon cycle parameters; and 2. to establish the importance of storm-event plumes to transport of nutrients and carbon species. In this thesis, a combination of satellite, in situ sensor, and wet chemical data is used to estimate nutrient (N and P), chlorophyll a, inorganic and organic carbon inputs from these plumes. These tools allow us to estimate the spatial extent of the plume and the potential impact of plume inputs; where possible we relate these inputs to annual budgets for these chemical species.

Another component of this study was to use geographic information science (GIS) to determine which variables contributed to erosion and what areas in the watershed were most likely to experience erosion. This was completed using the Revised Universal Soil

Loss Equation (RUSLE) in ArcGIS Pro. This technique was first developed by Wischmeier and Smith for the Department of Agriculture to determine how to best protect farmland from erosion and is most accurate when long term averages are used. The equation is as follows:

$$A= R*K*LS*C*P \qquad (1)$$

where A is the estimated average soil loss in tons per acre per year, R is the rainfall-runoff erosivity factor, K is the soil erodibility factor, LS is the slope length/steepness factor, C is the cover management factor and P is the support practice factor. One important thing to note about RUSLE is that "it estimates annual soil loss per unit area from rill and interrill erosion caused by rainfall splash and overland flow, but not from gully and channel erosion; it does not consider the runoff process explicitly, nor soil detachment, transport, and deposition individually" (Renard et al., 1994). Examining the results in our study region it appeared that 3 out of the 5 factors have relatively high values in similar locations. This indicates that their cumulative effect on erosion is great. For this analysis the watershed basins along the north shore and the Wisconsin shore to the Bayfield Peninsula are considered as sources of material for Western Lake Superior. Areas directly along the north and south shore of western Lake Superior have the highest amount of erosivity, when compared to values farther inland. High K values indicate that the soil type is easily eroded. Upon visual inspection Inceptisols, which are commonly found along the north shore of the lake, seem to correlate closely with large K values, indicating that these types of soil are most likely to become eroded material. Through this GIS study we could determine that soil type and landcover are an important factor affecting the source material to the lake ecosystem (see Chapter 2, section 4), and provided us a way to determine the most likely place of origin within the watershed.

Chapter 2 of this thesis discusses the 2012 and 2016 extreme events and is formatted for publication in an academic journal, thus there is some overlap in introductory material and methods. Chapter 3 provides detailed information on sampling sites and parameter data, in the form of supplementary information.

Contributions: Paul McKinney assisted with satellite data processing by giving advice and assisting in editing the manuscript. Gaston Small assisted in editing of the manuscript and contributing to the 2012 water quality data. Robert Sterner assisted by procuring funding, giving lab resources, and contributing water quality data as well as helping to edit the manuscript. Elizabeth Minor assisted by procuring funding, helping to design the study, contributing lab resources and data, and assisting in editing the manuscript.

CHAPTER 2. TALE OF TWO STORMS: IMPACT OF EXTREME RAIN EVENTS ON THE BIOGEOCHEMISTRY OF LAKE SUPERIOR

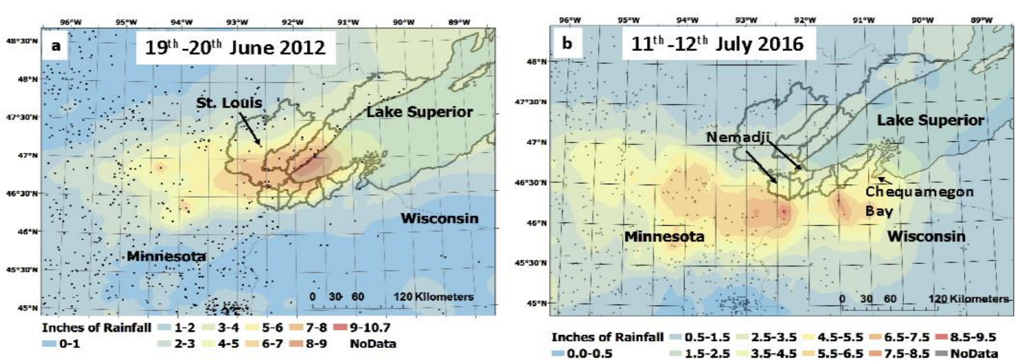
2.1 Introduction

Both the frequency and intensity of extreme weather events are increasing (Donat et al., 2016; Groisman et al., 2005; Mallakpour & Villarini, 2016; Walsh et al., 2014). Most of the continental United States is in the midlatitudes where there is an upward trend in extreme precipitation events (Walsh et al., 2014). The Michigan, Wisconsin, and Minnesota regions of the United States has seen one of the highest increases in heavy precipitation events within the last 30 years, more than 30% above the average of 1901–1960 (Walsh et al., 2014). The western Great Lakes region of the United States has seen severe damages to infrastructure (homes, businesses, and dams), resulting in affected areas being declared as federal disaster areas due to these extreme rainfall events (Czuba et al., 2012; Groisman et al., 2005; Villarini et al., 2011). In addition to these infrastructure damages, large amounts of runoff can cause soil erosion, increase terrestrial inputs of organic matter (e.g., leaves and woody debris), and carry contaminants such as pesticides and fertilizers into lake systems.

Lake Superior, the westernmost Laurentian Great Lake, is the world's largest freshwater lake by surface area, containing 10% of the world's surface liquid freshwater. It is an oligotrophic ecosystem (Matheson & Munawar, 1978; Munawar and Munawar, 1978) with cold epiliminetic temperatures and low nutrient concentrations (Sterner, 2010). It is unclear how the biogeochemical parameters of this lake will be affected by large amounts of rainfall and subsequent runoff, erosion, and enhanced river discharge. On one hand, compared to other lakes, the size of the area draining to Lake Superior is relatively small compared to the surface area of the lake itself (~1.55; Cotner et al., 2004), which could be expected to limit the effect of riverine inputs on the lake's biogeochemistry. On the other hand, the lake is oligotrophic, which might increase the effect of those inputs that do reach the lake relative to lakes with relatively larger watersheds. In 2013, Allan et al. (2012) published an article on the cumulative stress that the Laurentian Great Lakes are experiencing, by using spatial analysis to determine how many factors were above average for a region. The main categories of factors that were considered for sites were toxins, runoff from the land, invasive species, fisheries, coastal development, climate change, and aquatic habitat. The Western arm of Lake Superior has between 12 and 20 of these stressors, three of which are investigated in our plume study (sediments, nitrogen, and phosphorus).

In this study we focus on two "500-year" flood events that have occurred within the past 5 years in Lake Superior's southwestern watershed (Czuba et al., 2012;

Figure 1 Total rainfall amounts for each storm event in inches with the watershed regions for riverine input to far-western Lake Superior outlined in gray. Dots represent rain gauge data collection locations. (a) 2012 storm with St. Louis watershed labeled. (b) 2016 storm with Nemadji upper and lower watershed and Chequamegon Bay labeled.



www.weather.gov/dlh/flash-flooding-2016-07-11.htm, accessed February 2017;

https://hdsc.nws.noaa.gov/hdsc/pfds/pfds_map_cont.html, accessed September 2017). The 2012 flood event occurred on 19–20 June when up to 25 cm of precipitation fell on the watershed of Western Lake Superior, concentrated in the drainage area of the St. Louis River (Figure 1a; Czuba et al., 2012). The 2016 flood event occurred on 11–12 July and supplied up to 22 cm of precipitation centered mainly in central/eastern Minnesota and Northern Wisconsin (Figure 1b; www.weather.gov/dlh/flash-flooding-2016-07-11, accessed February 2017). Both of these plume-producing events were classified as "Mega-rain" events by the Minnesota Department of Natural Resources, which considers a "Mega-rain" event when "6 inches of rain falls upon more than 1,000 square miles, with the rainfall at the core of the storm being greater than 8 inches"

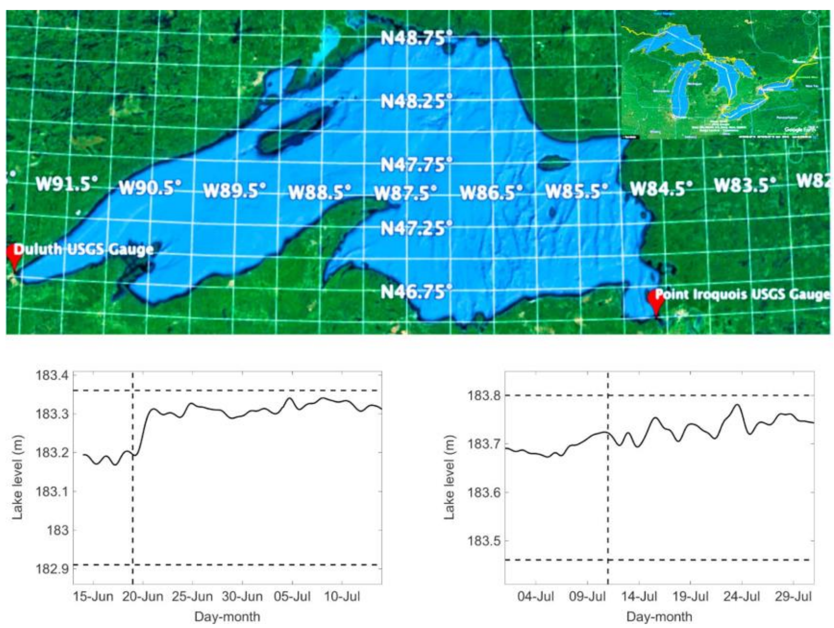


Figure 2 (a) Map of Lake Superior (from Google Earth) showing the location of the NOAA lake level gauges whose data are shown in (b) and (c). Inset to a shows all the Laurentian Great Lakes. (b, c) Water level rise due to storm events based upon the average lake level height data of NOAA gauges 9099064 (Duluth, MN) and 9099004 (Point Iroquois, MI) collected every hour: (b) The 2012 storm event and (c) the 2016 event. Dashed horizontal lines show the low and high for the respective year averaged for the two gauges. The vertical line shows the onset of the extreme rain event studied.

(http://www.dnr.state.mn.us/climate/summaries_and_publications/mega_rain_events.html). The direct rainfall-runoff from rivers and overland flow resulted in sediment plumes visible in satellite images (MODIS today; http://ge.ssec.wisc.edu/modis-today/) for weeks after the precipitation events. The Wisconsin shoreline of Lake Superior consists of highly erodible red clay soils; in general, the erosion of this shoreline contributes 70% of the total suspended load observed in far western Lake Superior (Stortz et al., 1976). Both of these events delivered similar amounts of rain to the watershed of the lake, but the 2012 event resulted in a distinct rise (a measurable amount [8–10 cm]), and the 2016 event showed a more gradual increase in the level of Lake Superior as shown at NOAA water level stations (9099064, 9099004, see Figure 2).

These intense rain events resulted in flooding, erosion of rivers, and direct bank erosion. The 2012 event created large fluxes of sediment (Czuba et al., 2012) and supplied the western arm of the lake with plume water that had high nutrient and sediment concentrations (Minor et al., 2014). Such sudden fluxes of nutrients and sediment may contribute significantly to overall annual inputs of nutrients and sediment in the lake and could potentially alter the biogeochemical cycles of the lake. Aquatic ecosystems, including oligotrophic large lakes, are significantly subsidized by terrestrial inputs of nutrients and organic matter (Cotner et al., 2004). A study conducted by Makarewicz et al. (2012) on river and stream plumes in Lake Ontario's nearshore environment showed that river plumes had higher levels of chlorophyll, total phosphorus (TP), turbidity, specific conductance, and temperature than nonplume waters; however, this study was not focused upon storm events. The effects of storm events are complex and not yet well understood, especially for extreme events, which may be difficult to predict or sample sufficiently.

In freshwater systems, phosphorus is known to be a limiting nutrient (Baehr & McManus, 2003; Downing & McCauley, 1992; Makarewicz et al., 2012), and Lake Superior is an extreme case where low TP levels (on the order of 0.03 to 0.1 μmol/L; 0.93–3.10 μg/L P) are coupled with fairly high concentrations of total nitrogen (TN; 30–32 μmol/L; 0.42–0.45 mg/L N), most of which is in the dissolved form as nitrate (Sterner, 2011). Large pulses of phosphate entering the lake ecosystem could greatly influence the biogeochemical environment and ecosystem response (Carpenter et al., 2017; Makarewicz et al., 2012). A study completed by Robertson et al. (2016) simulated the impacts of climate change (+2.6 °C average and -5.1% to 16.7% change in precipitation) on Lake Michigan phosphorus loading and found a large amount of variability in average phosphorus loading within their model output (-29.6% to 17.2%; Robertson et al., 2016). Such studies demonstrate that further work needs to be done to constrain climate change effects on nutrient cycling (Robertson et al., 2016). In addition to delivering nutrients, plumes, especially after storm events, may have high concentrations of suspended sediments and colored dissolved organic matter (CDOM), decreasing overall light penetration and thus the volume of the euphotic zone within the lake; the interplay between nutrient delivery and light limitation complicates predicting the impact of plumes on primary productivity (Minor et al., 2014).

In this project we investigate the volume of the lake impacted by two extreme-event plumes and relate these data to lake water column data collected after each of these storms. Our goal is to understand how these plumes affect water quality, including nutrient inputs and carbon cycle parameters, and to establish the importance of storm-event plumes to transport of nutrients and carbon species. Transport of dissolved material and sediments from watersheds to lakes may be important in determining the timing and extent of nutrient availability and in structuring lacustrine autotrophic and heterotrophic biological communities (Makarewicz et al., 2012). The plumes of river water into the nearshore zone of large lakes have been shown to deliver variable concentrations of TP, bioavailable phosphorus, and other nutrients (Makarewicz et al., 2012) that may be further transported into deeper waters. We use the combination of satellite, in situ sensor, and wet chemical data to estimate nutrient (N and P), chlorophyll *a*, and inorganic and organic carbon inputs from these plumes. These tools allow us to estimate the spatial extent of the plume and the potential impact of plume inputs; where possible we relate these inputs to annual budgets for these chemical species.

2.2 Materials and Methods

2.2.1 Field Sampling and Water Quality Analysis

One of the challenges with studying storm events on large lakes is that their unpredictability makes it difficult to coordinate work using multiuser research vessels. Thus, the field sampling for these events occurred in two separate, opportunistic sampling campaigns. These campaigns had different goals and objectives, and thus, the parameters measured for each event are somewhat different (see Tables 1 and 2). We therefore limit our comparisons to plume versus nonplume waters from the same event, so that we are comparing samples analyzed by the same methods. For the 2012 plume event, samples were collected on a weekly basis after the storm (see supporting information

(SI) Table S1 for site information). For the 2016 plume event, sites were sampled once approximately 1 week after the plume-producing event over a 3-day time span (see SI Table S5). For both events, water column profiles were taken by Seabird CTD model 911, which measured conductivity, temperature, and depth. The profiling rosette was also equipped with a Wet Labs WETStar fluorometer to detect chlorophyll *a* using an excitation wavelength of 460 nm and emission at 695 nm, while CDOM was determined by using an excitation wavelength of 370 nm (10 nm full width at half maximum) and emission centered at 460 nm (120 nm full width at half maximum). A transmissometer (650 nm, Chelsea/Seatech/WET labs CStar) was used to detect active light attenuation. Eight-liter Niskin bottles were used to collect "surface water" samples at 5-m depth.

Whole water samples were taken and stored frozen until analysis of TP, soluble reactive phosphorus, and TN. Additional whole water was taken for total suspended solids analysis. Dissolved samples were taken for nutrient analysis by passing whole water through a combusted Whatman 0.7-μm glass fiber filter. All sample bottles were rinsed three times with sample (whole or filtered water) before filling. Nutrient samples and filters were stored frozen until analysis. Samples were thawed and brought to room temperature 1 day prior to analysis.

The standard method for determining TP concentration of samples was followed (Murphy & Riley, 1962; Wetzel & Likens, 1991) using sulfuric acid and potassium persulfate to convert other phosphorus forms to orthophosphate. Orthophosphate was reacted with ammonium molybdate in the presence of H_2SO_4, and the complex that formed was reduced by antimony potassium tartrate and ascorbic acid, which created a blue color that is proportional to the concentration of TP in the sample. Soluble reactive phosphorus was analyzed in a similar manner as TP, without the conversion of organic phosphorus to orthophosphate via a sulfuric acid and potassium persulfate digestion. The samples were analyzed on a 10-cm cell at 880 nm on a GeneSys20 spectrophotometer. All samples were run in duplicate, and the average value is reported. The procedure is suitable for concentrations of 0.01 to 6 mg/L PO_4-P.

TN was treated with potassium persulfate to convert reduced nitrogen species to nitrate, which was then reduced to nitrite, converted to an azo dye, and measured colorimetrically. Nitrates/nitrites (NO_3/NO_2) were measured after reduction of nitrate to nitrite and then following the same colorimetric protocol. These nitrogen measurements were performed using a Lachat Quik-Chem 8000 as in Diamond (2000) and had a method detection limit (MDL) of 1.7 µg/L.

Total suspended solid analyses were performed at the Natural Resources Research Institute in Duluth, MN. Protocols set by American Public Health Association (APHA) et al. (1992) were followed. Whole water samples were stored at 4 °C and then filtered in the laboratory onto Whatman GF/C filters of 1.2 µm that had been rinsed with deionized water, dried, combusted, and weighed beforehand. The sample and filter were then dried at 102–105 °C, cooled to room temperature in a desiccator, and weighed.

Chlorophyll *a* samples were extracted from whole water filtered on shipboard through 0.7-μm GF/F filters. These filters were stored frozen and in the dark in 15-ml centrifuge tubes until analysis. Once in the lab, chlorophyll *a* was extracted from the filters by 10 ml of 90% acetone overnight (Welschmeyer, 1994). Samples were measured on a Turner Designs 10-AU fluorometer using an excitation filter of 436 nm and an emission filter of 680 nm. The fluorometer was calibrated prior to reading samples using a solid standard of pure chlorophyll *a*. The Turner Designs 10-AU fluorometer has a range of 0 to 250 μg/L and a detection limit of 0.025 μg/L. The day 5 July 2012 was an exception to this procedure where the whole water was stored at 4 °C in the dark and filtered in the laboratory within 1 day of collection onto GF/C filters. Samples collected on 5 July 2012 were analyzed using a UV-visible spectrometer rather than a fluorometer (APHA et al., 1992; Axler & Owen, 1994).

Methods for the 2016 plume study were as described above with the following changes: TP and total dissolved phosphorus were processed colorimetrically but analyzed on an Aq400 (Seal Analytical).

For pH analyses, water samples were transferred from Niskin bottles to 500-ml Nalgene bottles using silicone tubing and container overflow to minimize air exchange. Samples were analyzed within 24 hr on a Genesys6 UV-visible spectrophotometer using a 10-cm path length cell. Samples (in air-tight cuvets) were allowed to equilibrate to room temperature in a water bath for 10 min. They were then analyzed without indicator to establish a blank value, after which 70 μl of 2 mM cresol red was mixed into the sample as an indicator solution, and samples were measured, and pH determined as described in French et al. (2002). Each sample was run in at least duplicate, and average values at room temperature are reported here.

Total inorganic carbon (TIC) samples, in 40-mL amber VOA vials, were collected from Niskin bottles using silicone tubing. TIC sample containers were rinsed three times each with sample water and then allowed to overflow. Prior to storage, 11 μl of saturated $HgCl_2$ were added to each sample as a preservative, and the TIC samples were stored and refrigerated. Samples were analyzed on a Shimadzu TOC-V autoanalyzer within a week of collection as IC. Before injections of samples, the column was washed two times with Milli-Q water. Three to five injections of each sample were analyzed. The standard deviation maximum allowed for the measurements was 0.1 mg/L, and the critical value maximum is 2%; those injections meeting these criteria were averaged for results. Calibration standards were made fresh with dilutions of 1,000 ppm inorganic carbon (IC) to concentrations of 0.1 to 32 mg/L IC. A check standard of 8.9 mg/L was interspersed every 10 to 14 samples throughout the analytical run, and its measured value was within 5% of the accepted value in all cases.

Dissolved organic carbon (DOC; <GF/F) and TOC samples were collected into 40-ml amber vials. Of the 6 M HCl solution, 40 μl was added to each sample to acidify it to a pH of 2. Samples were analyzed as non-purgeable organic carbon (NPOC) using a Shimadzu TOC-V autoanalyzer. Calibration and check standards were potassium phthalate solutions. A Hansell Lab Deep Sea Reference (DSR) was also used as a check standard. Our values for TOC analyses were within 7.3% of the (DSR) accepted value and within 10% of the known values from our in-house check standards.

Total dissolved nitrogen samples were also analyzed on the Shimadzu TOC-V auto analyzer; these data were collected from DOC samples with a combined carbon/nitrogen standard consisting of potassium phthalate and potassium nitrate in MilliQ water.

A standard-addition, fluorometric method was used for ammonium analysis (Holmes et al., 1999; Taylor et al., 2007). Sodium sulfite solution, borate buffer, and *o*-phthaldialdehyde solution were combined to make a working reagent, which was added to both spiked and unspiked samples. These samples were incubated for 18 hr at room temperature in the dark, prior to analyses by fluorometer.

2.2.2 Satellite Data and Statistics

Plume location and sampling sites are qualitatively shown in Figures 3 and 4. To identify plume versus nonplume waters, we used remote sensing data acquired by the Visible Infrared Imaging Radiometer Suite (VIIRS) aboard the Suomi National Polar-orbiting Partnership satellite and processed by the NASA Ocean Color Processing Group at https://oceancolor.gsfc.nasa.gov/. We used the Ocean Color Processing Group level 2 products, which include the diffuse attenuation coefficient at 490 nm (Kd(490), a widely used parameter for turbidity (Shi & Wang, 2010; Yousef et al., 2017). Cloud cover often obscures remote sensing imagery of Lake Superior; thus, the daily frequency of VIIRS imagery increases the number of usable images relative to other remote sensing platforms with higher spatial resolution, but lower frequency (e.g., Landsat and Sentinel), and in the absence of clouds, makes it possible to track the development of features such as plumes over daily timescales. Comparison with available MODIS imagery, also available daily, showed that the VIIRS imagery provided the best match-up with the in-situ sampling.

As a general guideline, *K*d (490) values above $0.40m^{-1}$ are typical of mesotrophic systems whereas values less than that value are typical of oligotrophic systems (Kirk, 2011; Ringelberg, 2010). Therefore, we used that value as a threshold, and areas where *K*d (490) exceeded $0.40m^{-1}$ were classified as plume impacted whereas areas where *K*d (490) was lower were classified as nonplume impacted. Plume analyses are further complicated by the mismatch of satellite resolution (in this case 0.75 km × 0.75 km grid size at nadir) versus shipbased locational precision, which is about 10 m.

The Microsoft Excel 2010 Data Analysis tool package was used for the *F* test of variance and the *T* test of Means between plume and nonplume impacted groups for the water quality parameters collected from in situ sensors and surface-water samples.

2.2.3. Determination of Plume Volume

For a better understanding of the potential effects of these two plumes on Lake Superior, we wished to estimate the inputs of material from the plumes into the lake system. These inputs can then be compared with annual budgets for these chemical species. To make such a comparison, the volume of the lake impacted as well as the concentration of material within the plume needs to be determined. Here the area of plume-impacted water was determined by creating a layer using SeaDas software in which *K*d (490) values greater than 0.40 m^{-1} were extracted from the image (https://seadas.gsfc.nasa.gov/). These areas were compared to SeaDas's preset layer for turbid water to see how different optical algorithms affected our prediction of plume area and our subsequent estimates of plume inputs of nutrients, etc. SeaDas's layer for turbid water is expressed as *R*lim(555); it uses SeaWiFS channel 5, diffuse attenuation coefficient for downwelling irradiance (*K*d), backscattering coefficient (*b*b), index of refraction ($n \sim 1.341$), Fresnel reflectivity (r), and the additional SeaDAS chlorophyll and phaeopigment algorithms to determine the turbidity of the water (Figueras et al., 2004). We estimated the vertical extent of the plumes visible at the surface using transmissometry data obtained during our cruises. For both events, active light transmission was low at the surface within the plume-impacted areas and increased sharply below 10-m depth. Therefore, we used 10 m as an estimate of the plume's thickness and multiplied it by the area of the plume to determine the plume volume. Our volume estimate assumes that the thickness measured by our limited field sampling was continuous across the area impacted by the plume, which is reasonable for the summer season when the lake is density stratified. For a conservative estimate of how much phosphorus was input into the system by the 2012 plume, the average value for non-plume water was subtracted from the average value for the plume water. This number was then multiplied by the volume of the plume.

2.3 Results

*K*d values (SI Tables S3 and S6) from the VIIRS Suomi were determined for all sites sampled by ship for multiple dates throughout the sampling regime. To provide visual context, these data were compiled and displayed in four panels to show changes in time (Figures 3 and 4). For the 2012 flood, plume impacts appeared highest near the mouths of the St. Louis and Nemadji rivers and also the Wisconsin shoreline. The

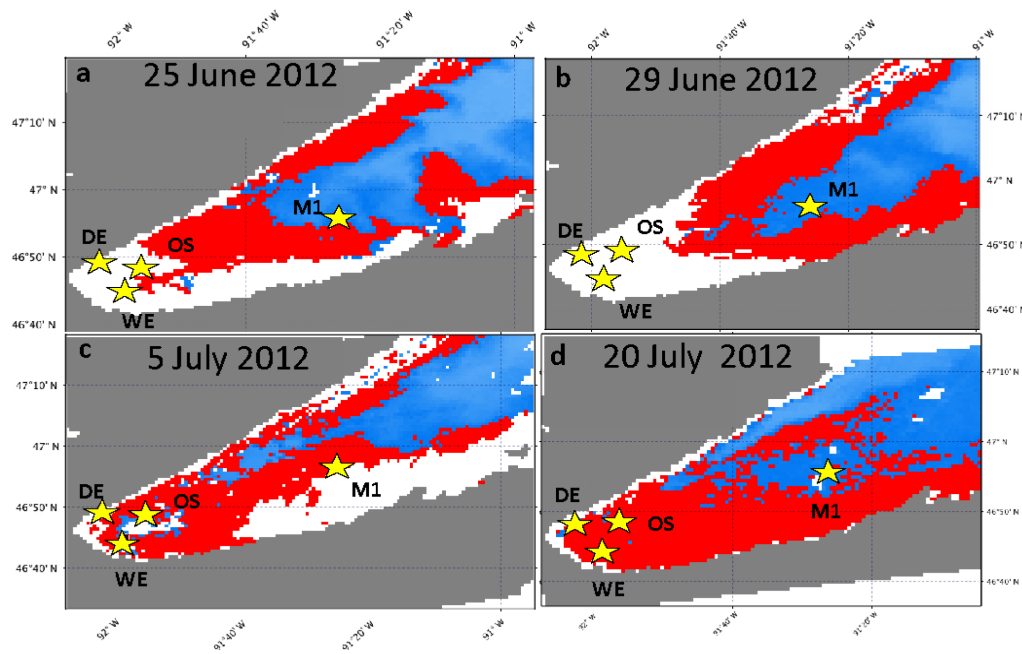


Figure 3 Stars show the locations of plume, and triangles show nonplume sites of ship-based sampling sites overlaid on Kd(490) values in SeaDAS software. Further information on sampling sites DE, OS, WE and M1 can be found in SI, Table S1. Red indicates Kd(490) values equal or over 0.41 m^{-1} (plume), and blue indicates Kd(490) values under 0.41 m^{-1} (nonplume). White shows areas where no data were available mainly due to extensive loading or due to cloud cover. Gray indicates land as determined from preloaded mask in SeaDAS. Pixel size 0.75 km× 0.75 km at nadir.

maximum *K*d(490) value reported was 6.4 m^{-1}. There were areas within the plume impacted region for which the *K*d(490) was unreported, presumably due to the high reflectance of the suspended sediment. For the 2016 event, the Wisconsin shoreline and Chequamegon Bay were strongly impacted. Both plumes were dynamic (e.g., separate panels within Figures 3 and 4) as sediment concentrations moved with currents and wind in the western arm, dispersing and settling in the water column.

Once sites were designated as plume or nonplume, measurements of in situ chemical parameters were separated on the same basis (SI Tables S2, S4, S7, and S8). An *F* test for variance, with an *α* value of 0.05, was conducted to determine if the two data sets (plume versus nonplume) had equal or unequal variances. Once this was determined, a *T* test for means was conducted to analyze if the two data sets had significantly different means with an *α* value of 0.05. In the 2012 storm event, the plume, relative to nonplume waters, was significantly enriched in TN, TP, and CDOM, but not chlorophyll *a* (Table 1, Figure 5). In the 2016 storm event, transmissometry measurements, ammonia, and CDOM concentrations and the additional carbon cycling parameters measured (pH, TIC, TOC, and DOC), were significantly different in plume versus nonplume waters (Table 2 Figure 6 and 7). As in the 2012 plume, there was no significant difference in chlorophyll *a* concentrations between plume and nonplume waters (Table 2).

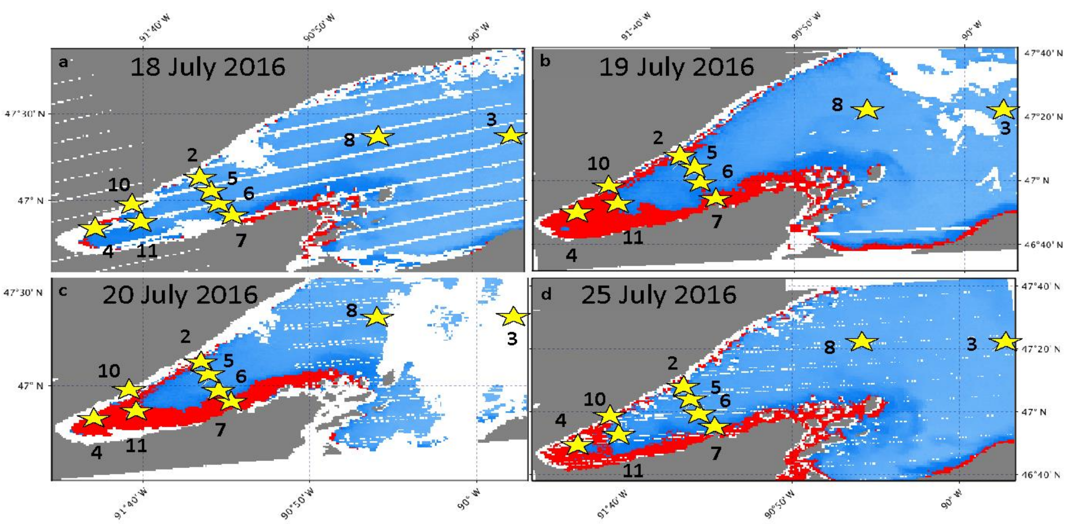


Figure 4 Stars show locations of plume, triangles show nonplume, and squares indicate unclassified sites of ship-based sampling sites overlaid on Kd(490) values in SeaDAS software. Further information on sampling sites 2, 3, 4, 5, 6, 7, 10, and 11 can be found in SI, Table S5 Red indicates Kd(490) values equal or over 0.41 m^{-1} (plume), blue indicates Kd(490) values under 0.41 m^{-1} (nonplume). White shows areas where no data were available mainly due to extensive loading or due to cloud cover. Gray indicates land as determined from preloaded mask in SeaDAS. Pixel size 0.75 km× 0.75 km at nadir.

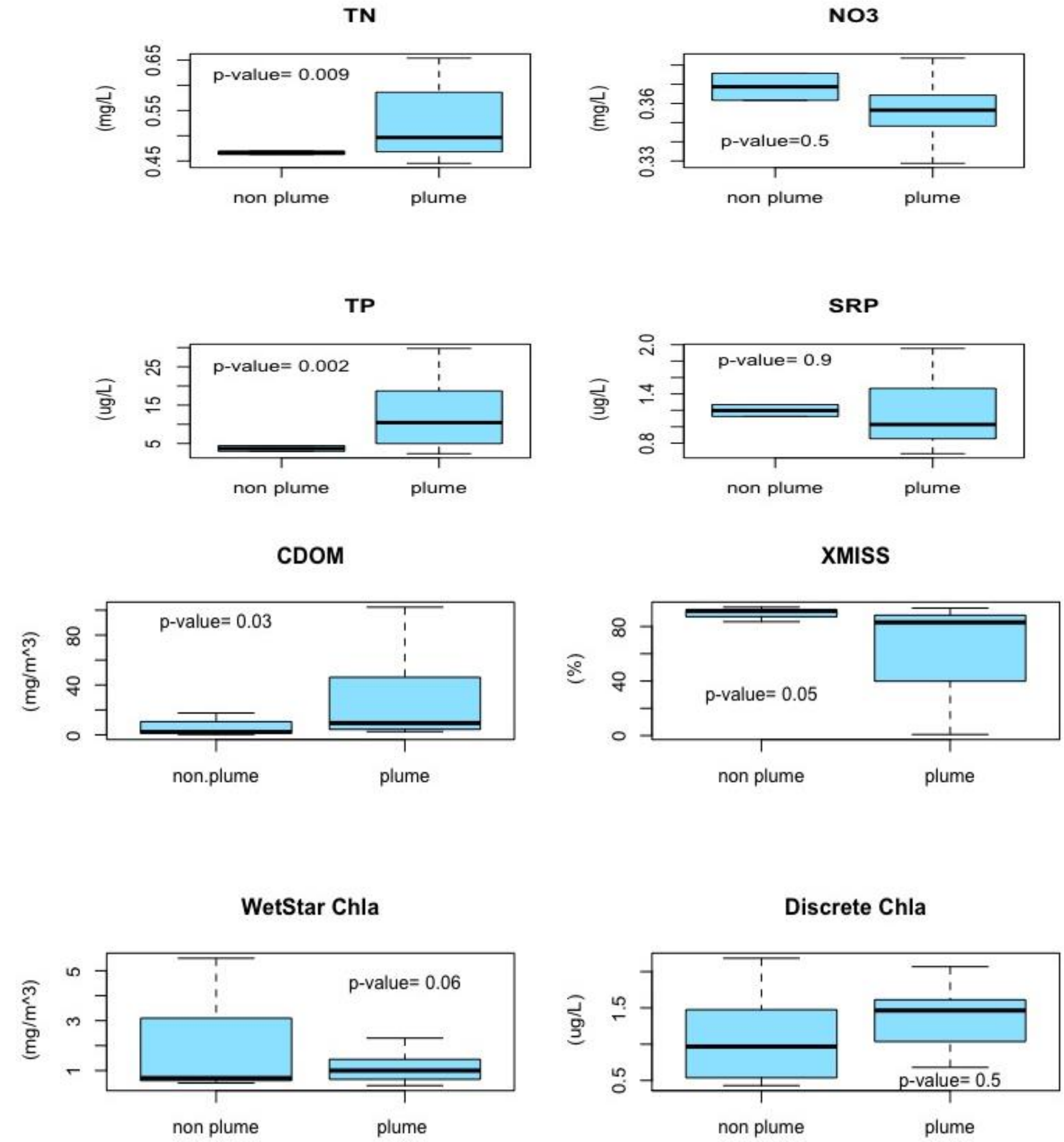


Figure 5 Boxplots of 2012 Data

Table 1

Parameters Measured From Water Collected at Ship-Based Stations for 2012

Parameter	Unit	Plume n	Plume Range	Plume Average	Nonplume n	Nonplume Range	Nonplume Average	F test $<$ or $\geq$ than F critical	T test $<$ or $\geq$ T critical two-tailed	p value
Transmissometry (Xmiss)	%	34	0.83–93.50	65.51	8	36.98–94.18	84.07	2.72 < 3.36	1.57 < 2.02	0.1
Colored dissolved organic matter (CDOM)	**mg/m^3**	**34**	**2.64–275.76**	**42.02**	**8**	**0.33–61.44**	**11.27**	**9.67 > 3.36**	**2.29 > 2.02**	**0.03**
WETStar chlorophyll *a* (CHLA)	mg/m^3	31	0.68–3.50	1.47	10	0.43–2.18	1.11	1.01 < 2.21	1.58 < 2.02	0.1
Chlorophyll *a* (CHLA; discrete)	μg/L	18	0.1–1.9	0.9	2	1.0–1.9	1.5	1.18 < 4.53	1.15 < 2.05	0.3
Soluble reactive phosphorus (SRP)	μg/L	16	0.67–2.41	1.19	2	1.12–1.27	1.20	23.55 < 245.95	0.03 < 2.12	1
Total phosphorus (TP)	**μg/L**	**22**	**2.33–56.65**	**16.43**	**2**	**2.95–4.42**	**3.69**	**252.77 > 248.31**	**3.54 > 2.07**	**0.002**
Nitrate/nitrite (NO_3/NO_2)	mg/L	22	0.13–0.38	0.34	2	0.36–0.38	0.37	26.46 < 248.31	0.74 < 2.07	0.5
Total nitrogen (TN)	**mg/L**	**21**	**0.45–0.97**	**0.54**	**2**	**0.46–0.47**	**0.47**	**558.60 > 248.01**	**2.89 > 2.08**	**0.009**

Note. Data are divided into nonplume and plume categories by a $K_d(490)$ value of 0.4 m^{-1}. Rows in boldface indicate that plume and nonplume averages were statistically significant from one another (α = 0.05); n values indicate the number of data points analyzed for each parameter.

A locational effect is likely to contribute to the differences between the two

Table 2
Parameters Measured From Water Collected at Ship-Based Stations for 2016

Parameter	Unit	Plume *n*	Plume Range	Plume Average	Nonplume *n*	Nonplume Range	Nonplume Average	*F* test < or ≥ than *F* critical	*T* test < or ≥ *T* critical two-tailed	*p* value
Transmissometry (Xmiss)	**%**	**4**	**54.44–73.94**	**64.94**	**5**	**80.36–90.22**	**86.52**	**6.08 < 6.59**	**4.31 > 2.36**	**0.004**
Colored dissolved organic matter (CDOM)	**mg/m^3**	**4**	**5.72–9.18**	**7.30**	**5**	**1.12–5.61**	**2.28**	**1.75 < 9.12**	**4.32 > 2.36**	**0.004**
WETStar chlorophyll *a* (CHLA)	mg/m^3	4	0.81–1.94	1.28	5	0.40–1.40	0.88	1.44 < 6.59	1.33 < 2.36	0.2
Chlorophyll *a* (CHLA; discrete)	μg/L	4	0.7–1.9	1.2	5	0.7–2.0	1.2	1.23 < 9.12	.095 < 2.36	0.9
Total inorganic carbon (TIC)	**mg/L**	**4**	**9.41–9.50**	**9.44**	**5**	**9.01–9.27**	**9.16**	**6.62 < 9.12**	**4.91 > 2.36**	**0.002**
Total organic carbon (TOC)	**mg/L**	**4**	**1.73–1.90**	**1.84**	**5**	**1.33–1.54**	**1.42**	**1.43 < 9.12**	**7.21 > 2.36**	**0.0002**
Dissolved organic carbon (DOC)	**mg/L**	**4**	**1.78–2.11**	**1.96**	**5**	**1.26–1.57**	**1.41**	**3.11 < 9.12**	**6.79 > 2.36**	**0.0003**
pH	**pH**	**4**	**7.83–7.92**	**7.87**	**5**	**7.91–7.98**	**7.95**	**1.57 < 6.59**	**3.70 > 2.36**	**0.008**
Ammonia (NH_3)	**μg/L**	**4**	**2.90–6.82**	**4.77**	**4**	**1.36–2.39**	**1.87**	**11.44 > 9.28**	**3.18 > 2.78**	**0.03**
Total dissolved nitrogen (TDN)	μg/L	4	5.04–7.16	6.65	5	5.46–6.99	6.82	9.29 > 6.59	0.63 > 2.78	0.6
Total phosphorus (TP)	μg/L	4	1.55–4.34	2.48	5	0.31–2.48	1.86	1.65 < 6.59	0.81 < 2.36	0.4
Total dissolved phosphorus (TDP)	μg/L	4	0.93–3.10	1.86	5	1.55–2.48	2.17	10.29 > 6.59	0.63 < 3.18	0.6

Note. Data are divided into nonplume and plume categories by a $K_d(490)$ value of 0.4 m^{-1}. Rows in boldface indicate that plume and nonplume averages were statistically significant from one another (α = 0.05); *n* values indicate the number of data points analyzed for each parameter.

plumes. The 2012 storm event led to high river inputs of water and associated materials.

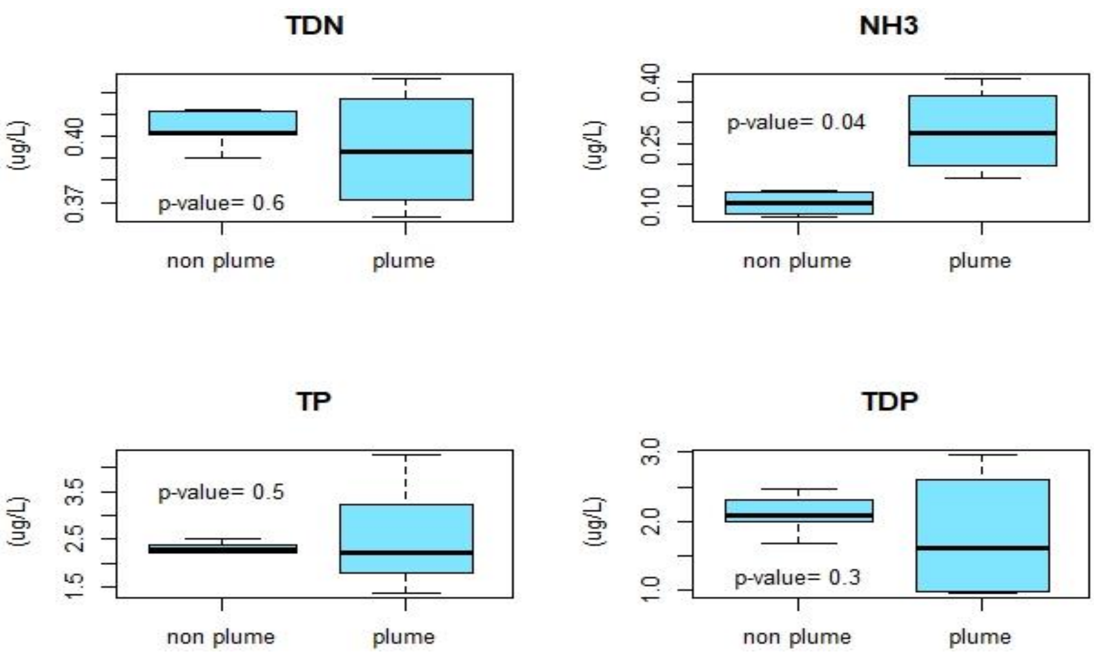


Figure 6 Boxplots of 2016 data with p values

The resulting plume had very high CDOM and total P concentrations (both parameters had plume values over an order of magnitude higher than in nonplume waters) and

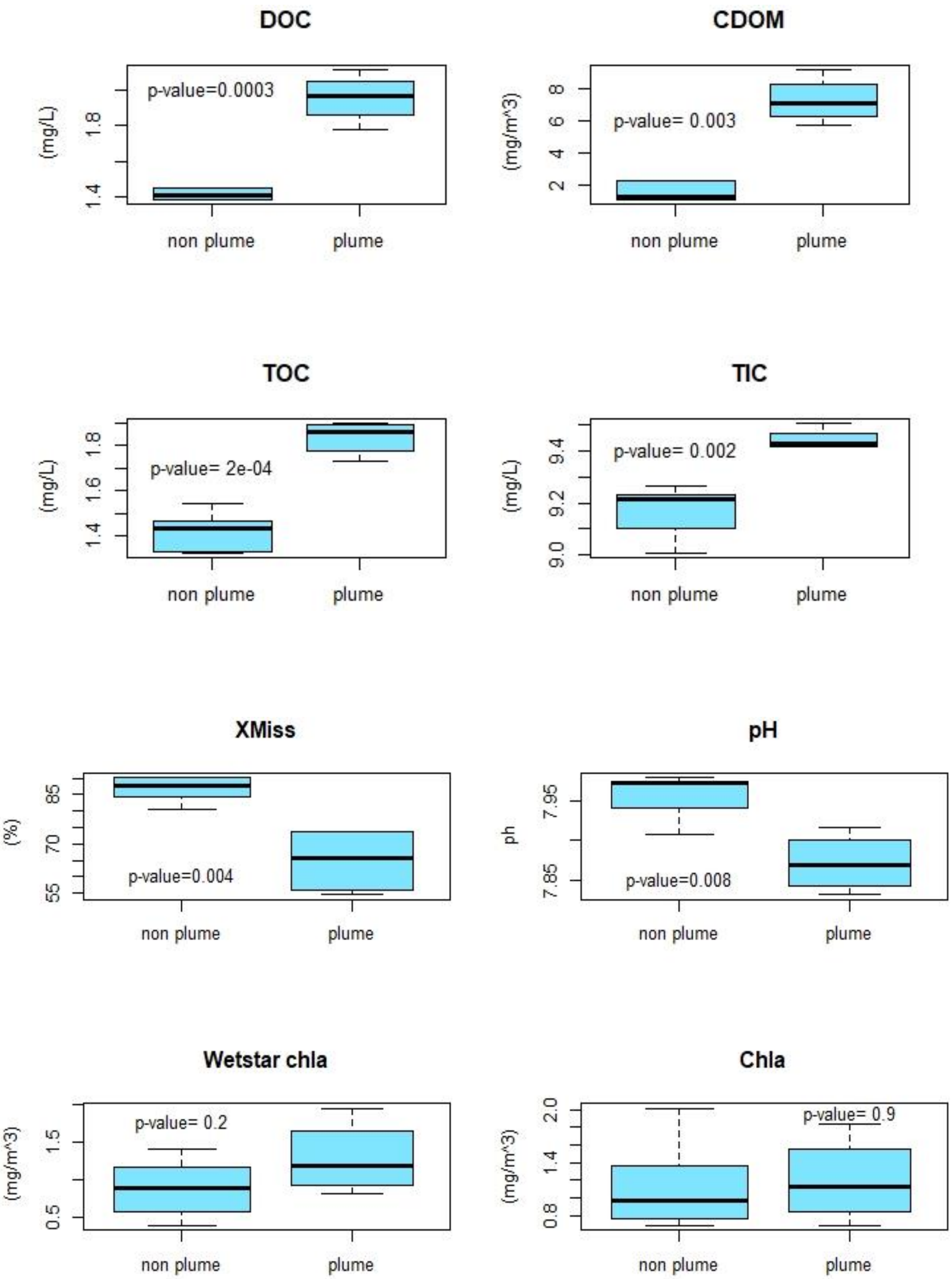


Figure 7 Boxplot of 2016 data with p value.

moderate total N concentrations (Table 1). The 2016 plume, however, appeared to contain much less riverine input and more material from the Wisconsin shoreline of Lake Superior. It was characterized at our sampling locations by a moderate decrease in transmissometry and a moderate increase in CDOM, with maximum plume values of just less than twice maximum nonplume values. Total dissolved nitrogen and TP showed no significant increases in plume waters, but there was a moderate increase in ammonia. For the 2016 event, we also have pH, TOC, DOC, and TIC data (which was missing from our view of the 2012 flood event). In 2016, in-plume pH showed a decrease in value while CDOM, DOC, TOC and TIC, and NH3 show an increase when compared to nonplume values (Table 2). Using satellite and in situ transmissometry data to determine plume volume shows that the 2012 plume delivered 221 to 251 Mg of TP to the lake (Table 3). Between 1994 and 2008, the average annual phosphorus loading of Lake Superior was 3,144 Mg/year (Dolan & Chapra, 2012). Thus, the 2012 plume contributed 7% to 8% of the annual phosphorus loading for the entire lake (Table 3) from one 2-day storm event covering 20% of the lake's terrestrial watershed area. Another way of scaling this is to consider that the 2012 plume delivered 27 days' worth of phosphorus to the lake if phosphorus were delivered equally in space and time across a year. The 2016 plume, in contrast, did not exhibit a significant elevation in P concentrations. Although both the 2012 and 2016 storms were of similar maximum rainfall, the location of rainfall (i.e., differences in the watersheds receiving the rain) appears critical to nutrient delivery to the system (Czuba et al., 2012; www.weather.gov/dlh/flash-flooding-2016-07-11.htm, accessed February 2017). A similar calculation was completed for each in situ parameter where plume and nonplume concentrations were significantly different; these results are shown in Table 4. Annual inputs of TN loading to Lake Superior are 72.2 Gg/ year, where ammonium tributary inputs are 4.8 Gg/year (Sterner et al., 2007). The 2012 plume contributed about 2% of Lake Superior's TN inputs, and the 2016 plume delivered 0.8–1% of the lake's annual ammonium inputs. Nitrate from direct precipitation onto the lake

Table 3
Data Used in Calculations to Determine Phosphorus Delivery to Lake Superior via the 2012 Plume Event

2012	Plume (K_d(490))	Plume (turbid water)
Mask area (km^2)	1,738	1,966
Volume (L)	1.74E+13	1.97E+13
Excess P (Mg)	221	251
% annual P	7.04	7.97

Note. The first "Plume" column is calculated from the K_d(490) method, as is stated in the discussion of plume versus nonplume concentrations in Tables 1 and 2. "Turbid water" uses the preset layer named "turbid water" in SeaDas software to determine the area of the plume.

Table 4
How Much of Each Significant Parameter is Delivered to Lake Superior via Two Plume Events

Year	Parameter	Plume (K_d(490))	Plume (turbid water)
2012	Excess CDOM (Mg)	534.33	604.56
	Excess TN (Gg)	1.30	1.47
	Excess P (Mg)	221.42	250.52
2016	*Excess NH_3 (Mg)*	*37.13*	*50.67*
	Excess DOC (Gg)	*6.79*	*9.27*
	Excess CDOM (Mg)[a]	44.65	60.93
	Excess TIC (Gg)	*2.95*	*4.02*
	Excess TOC (Gg)	*5.21*	*7.11*

Note. Italicized values for 2016 indicate the parameters that were not measured for the 2012 plume. CDOM = colored dissolved organic matter; TN = total nitrogen; DOC = dissolved organic carbon; TIC = total inorganic carbon; TOC = total organic carbon.
[a]In units of mass quinine sulfate dehydrate, which is the calibration standard used to convert CDOM fluorescence into a concentration value (WETStar, 2006).

surface is the largest input of nitrogen to the system (24.1 mmol m^{-2} year^{-1} or 0.336 g N m^{-2} year^{-1}, with organic nitrogen tributary input a close second (22.6 mmol m^{-2}

year^{-1} or 0.316 g N m^{-2} year^{-1}; Sterner et al., 2007). The 2016 plume delivered a significant increase in total organic carbon, of which DOC was the main component and POC contributed a less substantial portion. Annual DOC inputs are approximately 1 Tg/year from terrestrial inputs for Lake Superior (Urban et al., 2005). The 2016 plume studied contained around 0.7–0.9% of Lake Superior's annual terrestrial DOC input. It is a difficult task to determine a carbon budget for a lake system, as there are many possible paths and interactions that it could take. In 2004, Cotner et al. (2004), did complete an organic carbon budget study for Lake Superior. They determined that the lake received 0.54–0.62 Tg of organic carbon per year from rivers. We found that the 2016 storm contributed 5.21–7.11 Gg of TOC. This means that one storm event provided the lake with about 1% of its annual carbon input from rivers. This equates to approximately 20 days' worth of carbon (if there were even delivery of TOC over space and time) delivered in one event.

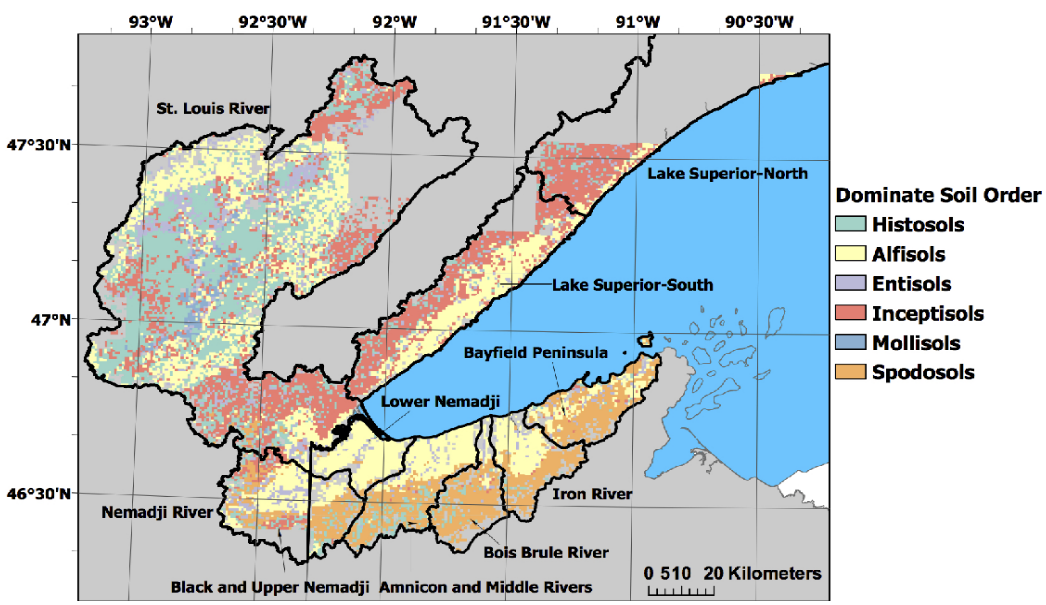


Figure 8 Image shows the dominant soil order in the subwatersheds of western Lake Superior; areas displayed inside the watershed in gray are areas that have not been surveyed yet. The image was produced using ArcGIS Pro.

2.4 Discussion

Plumes are a very dynamic feature of a lake system. They are altered not only by changing currents and winds but also by the settling of suspended sediments and uptake of nutrients. As the timescale of water quality sampling for the two flood events was varied, plume aging could account for some of the differences seen in the affected area. However, it appears that the main reason for the differences in these two plumes is due to the differences in the main watersheds in which the storms occurred. The 2012 plume originated from the St. Louis River watershed (9,453 km2), which is the largest river (in terms of water input) on the United States shoreline of Lake Superior (http://www.dnr.state.mn.us/ watertrails/stlouisriver/index.html). Within the St. Louis watershed, water flows through forests, agricultural land, and urban areas before arriving in the riverbed channel. On its travels, it carries along CDOM, nutrients, sediments, and contaminants from the surrounding area into the river. It is likely that we see a lower concentration of nutrients in the 2016 plume compared to the 2012 plume because the watershed on the Wisconsin shoreline is much closer to the lake basin and much smaller in total area than the St. Louis watershed. The Wisconsin shoreline has multiple small rivers that empty out into the lake basin allowing less time and area for the water to gather nutrients and greater contact of the water within-stream to benthic substrates and their associated bacteria (Ensign & Doyle, 2006), which could lead to greater retention of dissolved nutrients and less alteration of the water due to in-stream primary production (Vannote et al., 1980). In addition, a considerable contribution to the 2016 flood most likely came from direct bank erosion of the Wisconsin clay shoreline, which has low P concentrations relative to riverine inputs (Bahnick, 1977). In addition to the geographic area of the watershed and stream order and length of reach, another factor that may affect plume composition is the different types of soils that are present in the areas affected by the two storms. The soil classifications presented here (Figure 8) were obtained from the Natural Resource Conservation Service soil survey of the area. The dominant soils affected by the 2012 and 2016 rain events differ. The Wisconsin clay shorelines are typically classified as alfisols. Alfisols are generally fertile and have high concentrations in nutrient cations (Ca, Na, Mg, and K). The clay-rich, cation-rich sediments resulting from erosion and river delivery here, coupled with lower DOC concentrations in the plume waters (assuming CDOM is a reasonable proxy for DOC concentrations; for example, Ferrari et al., 1996; Spencer et al., 2012), are likely to impact dissolved nutrient concentrations by sorbing dissolved species (House et al., 1998). In the St. Louis watershed, histosols and inceptisols are the dominant soil condition. Histosols form when organic matter accumulates due to slow decomposition rates and are generally highly acidic. Inceptisols form in many different areas of the world and thus have a wide variety of characteristics. Typically, these types of soil are just beginning to develop horizon lines, with very little clay accumulation. These types of soil in the watershed area differ greatly, indicating that their effect on the biogeochemistry of the lake would also be significantly different. It could be hypothesized that if a rainstorm delivered a large amount of histosol soil, we would likely see a large flux of carbon (total organic, dissolved organic, and colored dissolved organic) and a drop in pH. Our CDOM data for the two storms is consistent with this, with the average in-plume CDOM value for the 2012 storm being approximately six times that of in-plume water in 2016. Unfortunately, we do not have TOC or pH data for the 2012 flood, but such comparisons should be made for future events. Land use is another factor to consider for the two watersheds. The St. Louis watershed is mainly dominated by woody wetland area (https://www.pca.state.mn.us/sites/default/files/wq-ws3-04010201b.pdf) and deciduous forest but also contains the largest urban area in the Lake Superior basin. More urbanized streams have been shown to have higher concentrations of TP and soluble reactive phosphorus than more forested streams in the same area (Brett et al., 2005), and the urbanization near the mouth of the St. Louis River could be a factor in the higher P loadings in the 2012 plume. The high dissolved organic matter delivery within the 2012 plume, however, seems more indicative of forested/undisturbed systems than urban and agricultural watersheds, as urban/agricultural dissolved organic matter has been found to be more labile than dissolved organic matter in undisturbed areas and is thus more likely to be quickly consumed upstream (Williams et al., 2010). The Wisconsin shoreline land cover is predominantly deciduous forest and hay/pasture (Figure 9). The varying dominant land use for the two watersheds, coupled with the other factors described above, helps to explain the different effects we see from the 2012 and 2016 plumes.

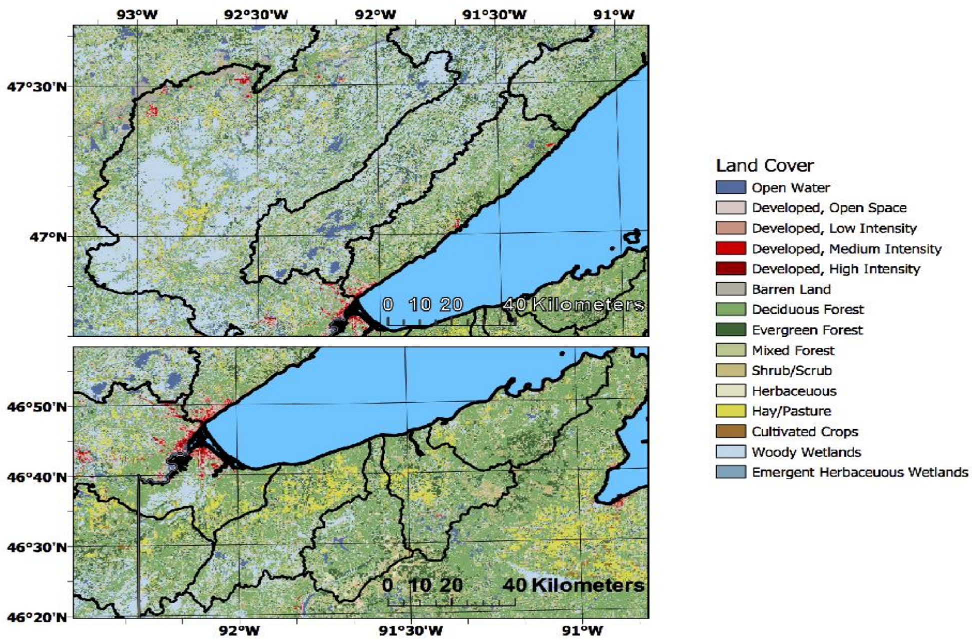


Figure 9 Image shows the varied land use in each of the sub- watersheds of Western Arm of Lake Superior. 6a. focuses on the St. Louis watershed, and 6b. focuses on the watersheds that are on the Wisconsin shoreline. Image was produced in Arc GIS Pro.

Further watershed-specific studies need to be completed in order to determine what specific factor (e.g., land use, watershed area, dominant stream order, and soil type) has the most weight on these outcomes. In the 2012 plume event, a significant input of TN and phosphorus entered the system. As phosphorus is considered a colimiting nutrient with iron in Lake Superior (Baehr & McManus, 2003; Downing & McCauley, 1992), one might hypothesize a response from lake phytoplankton. Unfortunately, no measurements of primary production, the most direct way to determine a response, were performed in plume-affected versus unaffected waters. However, a significant increase in chlorophyll *a* was not observed, indicating that standing stocks of phytoplankton were not increased at our plume-affected sampling sites. Previous study of the 2012 plume data indicates that light availability limited phytoplankton growth and that by the time the suspended solids and CDOM were dissipated sufficiently to relieve the light limitation, the plume delivered increase in nutrients was no longer present in the upper water column (Minor et al., 2014). The limiting nutrient phosphorus could have been sorbed to iron-oxide complexes or otherwise incorporated into the sinking sediment pool or taken up by heterotrophic bacteria (Heath & Munawar, 2004). A lag in response time from algae and/or lack of bioavailable iron could also explain why there was no significant increase in phytoplankton observed in our study. A similar limitation in phytoplankton growth was found in a study of episodic sediment resuspension in Lake Michigan by Millie et al. (2003). They saw that *K*d coefficients and suspended particulate matter were inversely related to production ($p < 0.0001$; Millie et al., 2003). The role of dissolved organic matter in these plume systems needs further study. CDOM absorbs most of the ultraviolet light (UV-A and UV-B) in natural waters (Miller, 1998) and can also absorb a significant proportion of the photosynthetically active radiation. In addition to absorbing portions of light, CDOM also acts as photochemical reactant in processes that can generate dissolved inorganic carbon (Cotner et al., 2004) and can release inorganic nutrients (such as those in Fe-P complexes; Cotner & Heath, 1990; Bushaw-Newton & Moran, 1999). The release of these nutrients and the presence of photodegraded dissolved organic matter are likely to enhance biological decomposition (Cotner et al., 2004) in organic matter rich waters. Chlorophyll *a* could thus have a delayed response to the flux of TP into the system,

as phosphorus adsorbed to sediments and nutrients within dissolved organic matter are later released into the environment (Cotner & Heath, 1990) and as light limitation is relieved due to sedimentation of suspended solids and dispersion or remineralization of CDOM. This highlights the need for studying the evolution of plume water quality and the resulting effects on primary and secondary production over the entire timescale of the event.

2.5 Conclusions

Even though Lake Superior has a very low watershed area to lake surface area ratio (~1.55; Cotner et al., 2004), the two studied "Mega-rain" events had surprisingly impressive effects on lake water chemistry (e.g., the delivery of nutrients, CDOM, and sediments). The 2012 storm delivered a significant proportion of the lake's annual inputs of TP (7% to 8% of annual inputs), TN and CDOM. In the 2016 storm event, for which carbon cycling parameters were measured, pH, TIC, DOC, and NH3, but not chlorophyll *a*, were significantly different in plume waters. We did not see a significant increase for TN or TP as in the 2012 event. This difference is consistent with trends predicted by the soil types, stream orders, and land use in the different watersheds affected by the rain events. Our estimates of plume extent and the effects of plumes on water quality were complicated by the fact that plume characteristics (especially *K*d and transmissometry) can exceed the sensor detection limits (e.g., once there is 0% light transmission, there is no longer a relationship between transmissometry and increased sediment loading). Cloud cover also limited our use of satellite imagery to track the plumes. It would be beneficial to future studies if higher resolution satellite images could be used to determine the areal extent of the plume. The use of autonomous underwater vehicles (AUVs or "gliders") in conjunction with higher resolution satellite data would significantly improve estimates of plume extent. By measuring water column parameters on finer scales, glider data would also give insight into the spatial variability of water quality within these plumes. The timescale of water sampling and the watershed attributes for these two flood events varied. Plume evolution (such as settling of suspended sediments) over these different timescales could explain some of the differences between our 2012 and 2016 results; future studies of plume evolution over time after an event are critical to determining the role of plumes in the lake ecosystem. Further specific studies also need to be completed in order to determine the roles of factors such as land use, soil type, river order, or watershed size in determining the quality and quantity of the material delivered by large storms to lake water.

CHAPTER 3. SUPPLEMENTAL INFORMATION

2012 Data

Table 1 Sampling Site locations

Site Name	Site Initials	Water Column Depth (m)	Latitude, Longitude
Duluth Entry	DE	22	46°47'0.00"N 92° 3'60.00"W
Wisconsin Entry	WE	0	46°43'14.92"N 92° 0'34.08"W
Off Shore	OS	30	46°47'14.92"N 91°57'34.08"W
Middle Western Arm	M1	132	46°55'14.93"N, 91°27'34.08"W

Table S-2. CTD data

CDOM (mg/m^3)	*6/21*	*6/25*	*6/29 (6/30)*	*7/5*	*7/14*	*7/20*	*8/2*	*8/10*	*8/17*	*8/22*	*8/31*	*9/7*	*9/21*
Sites Sampled													
M1						**17.54**	3.84	4.37		**1.51**	**0.33**	**1.00**	**1.59**
OS	28.00	76.47	35.46	**61.44**	34.90	14.13	**3.72**	4.84	7.14	3.24	5.02	3.65	**3.02**
WE	107.54	110.95	275.76	135.72	102.41	38.90	10.37	2.82	5.04	13.69	5.78	7.95	
DE	105.97	226.39	114.27	19.68	78.66	46.17	4.42	4.29	6.52	10.07	4.27	8.85	2.64

Xmiss (%)	*6/21*	*6/25*	*6/29 (6/30)*	*7/5*	*7/14*	*7/20*	*8/2*	*8/10*	*8/17*	*8/22*	*8/31*	*9/7*	*9/21*
Sites Sampled													
M1						**83.48**	91.14	88.26		**91.48**	**91.36**	**94.18**	**91.60**
OS	82.47	1.84	39.90	**36.99**	46.72	86.12	**90.88**	87.78	86.01	88.22	90.35	93.50	**92.60**
WE	4.97	0.97	5.36	25.46	38.11	68.63	81.09	82.49	85.91	79.00	88.86	83.00	
DE	-0.07	0.83	11.66	55.41	34.72	69.61	90.61	87.85	83.05	83.29	90.66	88.76	92.29

Chla Wet Star (mg/m^3)	*6/21*	*7/5*	*7/14*	*7/20*	*8/2*	*8/10*	*8/17*	*8/22*	*8/31*	*9/7*	*9/21*	*9/27*
Sites Sampled												
M1				**1.48**	0.70	0.68		**1.01**	**1.26**	**0.54**	**0.45**	
OS	1.43	**2.18**	1.18	1.00	**0.81**	0.87	0.97	0.95	1.56	0.88	**0.92**	
WE	2.74	3.50	2.07	1.96	1.51	0.71	1.30	1.49	1.88	1.60		2.06
DE	2.74	1.63	1.47	1.65	1.08	1.17	1.53	1.46	1.31	1.48	1.25	0.43

Note: **Bold** indicated values for non-plume, Column headings are month/day, derived from: Minor, E. C., Forsman, B., & Guildford, S. J. (2014), The effect of a flood pulse on the water column of western Lake Superior, USA. Journal of Great Lakes Research, 40(2), 455-462.

Table S-3. 2012 Satellite Data

Kd (1/m)	*6/25*	*6/29*	*7/5*	*7/14*	*7/20*	*8/5*	*8/10*	*8/17*	*8/22*	*8/31*	*9/7*	*9/21*
Sites Sampled												
M1	**0.37**	**0.37**	0.49	0.43	**0.24**	0.47	0.42	1.13	**0.13**	**0.29**	**0.15**	**0.15**
OS			**0.24**	3.35	0.79	0.54	0.66	0.85	3.00	2.24	1.33	**0.21**
WE			0.94	1.60	1.34	1.02	1.08	3.30	0.89		0.88	**0.39**
DE				0.78	2.10	1.70	1.04	0.66	1.73		1.28	0.46

Note: **Bold** indicated values for non-plume, Column headings are month/day

Table S-4. 2012 Water Quality Data.

SRP (ug/L)	6/21	7/14	7/2	8/2	8/10	8/17		
Sites Sampled	n (2)	n (2)	n (2)	n (2)	n (2)	n (2)		
M1			**1.12**	0.88	0.85			
OS	0.93+/- .011	1.3+/-.3	0.98	**1.3+/-.2**	0.67+/-.01	0.86+/-.06		
WE	5.80+/-.06	1.95+/-.08	1.17	1.14+/-.03	0.857+/-.008	0.73+/-.06		
DE	4.7+/-.1	2.41+/-.05	1.69	1.07+/-.09	0.76+/-.03	1.68+/-.02		
NO_2/NO_3 (mg/L)	6/21	*6/25*	*6/29 (6/30)*	7/14	7/20	8/2	8/10	8/17
Sites Sampled	n (3)			n (2)	n (2)	n (2)	n (2)	n (2)
M1					**0.38**	0.35	0.37	
OS	*0.365+/-0.001*	0.33	0.35	0.36	0.37	**0.36**	0.37	0.36
WE	*0.308+/-0.000*	0.30	0.13	0.348+/-0.000	0.350+/-0.001	0.363+/-0.000	0.355+/-0.000	0.358+/-0.000
DE	*0.310+/-0.001*	0.33	0.29	0.38+/-0.02	0.35+/-0.02	0.364+/-0.006	0.361+/-0.001	0.364+/-0.003

Chla discreet measuments (ug/L)								
Sites Sampled	*6/25*	*6/29 (6/30)*	*7/5*	*7/14*	*7/20*	*8/17*	*8/22*	*9/27*
M1					**1.925**			
OS	0.719		**1**	0.4	0.685	1.18	0.66	
WE	0.56	0.50	1.6	0.30	1.786	1.37	1.92	1.7
DE	0.42		1.3	0.1	1.530	1.46	0.36	
TP (ug/L)	6/21	6/25	6/29 (6/30)	7/14	7/20	8/2	8/10	8/17
Sites Sampled	n (3)	n (2)	n (2)	n (2)	n (2)	n (2)	n (2)	n (2)
M1					**4.42+/-0.04**	3.04+/-0.04	5.7+/-0.3	
OS	*7.0+/-0.2*	40.5+/-0.3	15.62+/-.0.04	11.8+/-0.5	2.8+/-0.1	**3.0+/-0.3**	2.3+/-0.1	3.7+/-0.2
WE	*103.6+/-11.9*	52.4+/-0.9	56.65+/-0.30	18.7+/-1.6	9.89+/-0.02	7.4+/-0.5	10.8+/-1.4	5.0+/-0.6
DE	*144.0+/-3.8*	40.8+/-0.1	29.80+/-0.40	12.4+/-1.9	10.27+/-0.01	3.82+/-0.06	10.6+/-1.2	7.6+/-1.4

TN (mg/L)	6/21	6/25	*6/29 (6/30)*	*7/14*	*7/20*	*8/2*	*8/10*	*8/17*
Sites Sampled	n (2)	n (2)						
M1					**0.47**	0.55		
OS	1.28+/-0.01	0.586+/-0.001	0.56	0.50	0.47	**0.46**	0.46	0.46
WE	1.451+/-0.005	0.610+/-0.002	0.97	0.63	0.50	0.48	0.45	0.47
DE	1.41+/-0.01	0.592+/-0.008	0.65	0.50	0.55	0.47	0.45	0.47

Note: Column headings are month/day. This data was included in figures from Minor et al 2014. **Bold** indicates values for non-plume, italicized values are +/- are standard deviations, non italicized +/- are average deviations, number of measurements n ().

Table S-5. 2016 sample site locations and date of CTD profiling and water quality sampling.

Site name	Date Sampled	Latitude	Longitude
Station 4	7/18/16	46º 47.3' N	91º 57.8' W
Station 10	7/18/16	46º 55.0' N	91º 48.0' W
Station 2	7/18/16	47º 3.9' N	91º 25.9' W
Station 3	7/19/16	47º 19.0' N	89º 51.0' W
Station 8	7/20/16	47º 19.0' N	90º 32.6' W
Station 5	7/20/16	46º 59.9' N	91º 22.6' W
Station 6	7/20/16	46º 56.4' N	91º 20.5' W
Station 7	7/20/16	46º 51.7' N	91º 17.0' W
Station 11	7/20/16	46º 50.0' N	91º 45.1' W

Table S-6. 2016 satellite data. Column headings are month/day.

k_d (1/m)	*7/18*	*7/19*	*7/20*
Sites sampled			
4	0.41	0.63	0.80
10		0.81	na
2	**0.13**	**0.21**	**0.26**
3	**0.09**		
8	**0.15**	**0.13**	**0.11**
5	**0.11**	**0.19**	**0.19**
6	**0.17**	**0.32**	**0.35**
7		0.55	0.82
11	**0.32**	0.48	0.53

Note: **Bold** indicates values for non-plume

Table S-7. CTD derived data for 2016 samplings.

Site	*Depth Sampled (m)*	*WetStar chla (mg/m^3)*	*CDOM (mg/m^3)*	*Xmiss (%)*
4	5	1.35	5.72	73.94
10	5	0.81	6.81	57.56
2	5	**0.39**	**1.29**	**87.60**
3	5	**0.89**	**1.13**	**90.23**
8	5	**0.57**	**1.12**	**90.16**
5	5	**1.15**	**2.27**	**84.27**
6	5	**1.40**	**5.61**	**80.36**
7	5	1.94	9.18	73.82
11	2	1.03	7.50	54.44

Note: The complete CTD data for these samplings can be found at the R2R website (http://www.rvdata.us/catalog/Blue_Heron). **Bold** indicates values for non-plume.

Table S-8. 2016 water quality data.

Site	Chla (ug/L) (n=2)	*NH_3 (ug/L)*	DOC (mg/L) (n=3)	*TDN (ug/L)*	*TP (ug/L)*	n (TP)	*TDP (ug/L)*	n (TDP)	*TIC (mg/L)*	TOC (mg/L) (n=3)	pH (n=2)
4	1.00+/-0.04	5.62	*1.69+/-0.02*	5.04	*2.2+/-1.3*	*7*	*1.0+/-0.8*	*5*	9.43	*1.90+/-0.02*	*7.886+/-0.000*
10	0.7+/-0.1	6.82	*1.90+/-0.01*	6.02	*2.2+/-0.4*	*7*	*1.0+/-0.5*	*3*	9.50	*1.89+/-0.02*	*7.852+/-0.003*
2	**0.98+/-0.04**	**1.53**	***1.29+/-0.01***	**5.74**	***2.5+/-1.8***	***4***	***2.5+/-1.1***	***5***	**9.27**	***1.33+/-0.03***	***7.908+/-0.000***
3	**0.76+/-0.02**	**Lost**	***1.15+/-0.01***	**5.46**	***2.2+/-1.9***	***8***	***1.7+/-1.1***	***8***	**9.23**	***1.33+/-0.01***	***7.940+/-0.001***
8	**0.69+/-0.02**	**2.39**	***1.31+/-0.01***	**5.74**	**.23+/-0.05**	**2**	***2.3+/-2.7***	***8***	**9.21**	***1.44+/-0.01***	***7.974+/-0.002***
5	**1.4+/-0.1**	**2.22**	***1.28+/-0.03***	**5.60**	***2.4+/-1.7***	***4***	***2.1+/-2.2***	***8***	**9.10**	***1.47+/-0.02***	***7.979+/-0.000***
6	**2.0+/-0.2**	**1.36**	***1.49+/-0.02***	**5.60**	***2.3+/-0.8***	***3***	***1.99+/-1.0***	***8***	**9.01**	***1.54+/-0.03***	***7.972+/-0.006***
7	1.85+/-0.03	2.90	*1.80+/-0.01*	5.32	*1.4+/-0.4*	*3*	*2.2+/-1.3*	*4*	9.41	*1.83+/-0.02*	*7.832+/-0.001*
11	1.25+/-0.04	3.75	*1.75+/-0.03*	5.74	*4.3+/-2.5*	*3*	*3.0+/-1.7*	*8*	9.42	*1.73+/-0.03*	*7.917+/-0.002*

Note: **Bold** indicated values for non-plume, italicized values are +/- are standard deviations, non italicized +/- are average deviations.

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