
Contributions of the BOGLS Steering Committee along with participants of the Workshop and Community Forums at IAGLR and Goldschmidt2013.

Edited by:

Mark Baskaran, Department of Geology, Wayne State University, Detroit, MI-48202; and John Bratton, Great Lakes Environmental Research Laboratory, NOAA, Ann Arbor, MI-48108

Steering Committee:
James Bauer (Ohio State), Ruth Blake (Yale U), Robert Hecky (U. Minnesota-Duluth), Norman Grannemann (USGS), J. Val Klump (U. Wisconsin-Milwaukee), Lawrence Lemke (Wayne State), Nathaniel Ostrom (Michigan State) and Thomas Johnson (U. Illinois, Urbana-Champaign)
Executive Summary:

The pelagic and benthic food webs and associated elemental cycles in the Laurentian Great Lakes have undergone major perturbation over the past 30 years due to factors such as nutrient abatement and introduction of invasive species (zebra and quagga mussels). Such human-induced alterations (directly or indirectly) provide a unique opportunity to document how this natural system has responded and would respond to other such large-scale alterations in the ecosystem. Thus, the Great Lakes System (GLS) could serve as a ‘model laboratory’ to quantify biogeochemical changes caused by humans. The changes in the terrestrial ecosystem and bordering wetlands influence the fundamental biogeochemical processes that take place in the lakes where complex interactions between the adjoining terrestrial environments with that in the aquatic system are integrated. Approximately 37 million people live in the Great Lakes basin with 26 million people relying on the Great Lakes for their drinking water. The water quality has direct impact not only on human health but also on jobs in agriculture, fisheries, manufacturing, shipping, and tourism. In order to assess the scientific needs for process-oriented research in the changes caused by the directly or indirectly human-induced perturbations, a three-day (March 11-13, 2013) workshop was held at Wayne State University, Detroit, Michigan. Sixty scientists mostly from across the Great Lakes states representing 17 universities, five federal agencies, among others, with expertise spanning a spectrum of research areas including nutrients and carbon cycling, key trace elements and isotopes as biogeochemical tracers, geo- and radiochemistry, ecology, hydrogeology, physical oceanography, modeling, remote sensing, and climate change, gathered and discussed the state of the Great Lakes system.

The community identified a number of major changes that have taken place recently in the Laurentian Great Lakes that are remarkable in their scope and speed. The community recognized the urgent need for a long-term process-oriented study coupled with modeling to evaluate ecosystem changes in the Great Lakes system. Food webs in the lower lakes have undergone drastic changes from the expansion of dreissenid mussels, a process that occurred in < 30 years and accelerated greatly in the last 10-15 years. The reengineered ecosystem caused by the dreissenid mussels has resulted in a ‘benthification’ of the system at the apparent expense of pelagic food chains. Drastic decline in the abundance of diatoms, zooplankton, benthic amphipods, forage fish and top piscivorous population have been reported, including ~95% population decrease of benthic amphipod Diporiea. Filtration of water by dreissenids had resulted in water clarity exceeding 20 m secchi depths in Lakes Huron and Michigan, which in turn has resulted in the triggering of resurgence of the submerged macrophyte, Cladophora, in the near-shore causing fouling of beaches throughout the lakes by decaying algal mats. The pelagic primary production in Lake Michigan has decreased by ~70% and other winter and spring blooms have largely disappeared.

The lakes are highly sensitive to climate change, particularly their hydrology (water levels), radiation budgets, stratification and atmospheric forcing. Decrease in areal extent,
thickness and duration of the ice cover, increase in water temperature and the increase in frequency of extreme weather events (resulting in changes in the riverine loading of key macro- and micro-nutrients) have been reported. Summertime thermal stratification is predicted to increase in duration by several weeks, exacerbating issues of hypoxia, benthic metabolism and diagenesis, thermal habitat changes, and the timing of long standing ecological phenomena. Climate change is expected to have a significant impact on regional climate such as changes in ‘lake effect’ precipitation. The recent climate change is felt faster in L. Superior than in many coastal ocean areas.

The concentrations and stoichiometric ratios of key nutrients have been considerably altered during the past century. For example, there has been a net accumulation of nitrate over the past hundred years in Lake Superior which is reported to have an imbalance in NO$_3^-$/PO$_4^{3-}$ ratios (as high as ~10,000). The factors and processes that lead to these alterations in stoichiometric ratios in different lakes of the Great Lakes system are not fully understood. While the chemical reactions (nitrification, denitrification and anammox) are expected to be slower in Lake Superior due to cooler waters compared to Lakes Michigan, Huron, Erie, and Ontario, other factors that control N, C and P cycling, N assimilation, and microbial community structure are not well studied in all the Great Lakes. The degree to which changes result from increases in external sources discharged to the lakes (rivers/streams, atmospheric deposition, submarine groundwater discharge), or active in-lake processes (such as nitrification/denitrification, anammox) is not understood. Despite active removal of PO$_4^{3-}$, Ca$^{2+}$, and key bio-limited elements in the lower lakes and Lake Michigan by dreissenids, answers to questions such as how the NO$_3^-$/PO$_4^{3-}$ ratios have changed the cycling of organic carbon and other micro-nutrients in lakes that are severely impacted remains unknown.

The inland freshwater seas are similar to marine systems in several respects and are unique as well. Many of the dominant physical processes are large scale, such as circulation (affected by the Earth’s rotation), atmospheric forcing mechanisms, upwelling/downwelling, seiches and internal motions, etc. Ecologically they are young (~10 kyr) with relatively simple food webs and low biodiversity. This produces an extreme susceptibility to invasion and perturbation by non-native species.

Lake-wide simultaneous measurements of primary production (PP) and grazing rates in most lakes are lacking; thus, gaps in our understanding of the cycling of N, P, and Si and their link to other key micro-nutrients exist. Lack of data during the cooler periods and deeper waters fuels the uncertainty in PP and grazing estimates. Estimates of PP and respiration rates due to scaling factors are less reliable due to limited data (or lack of data) during winter months and from deeper waters.

The key micronutrients such as Fe play a critical role in nitrate utilization by plankton and thus, the cycling of Fe, Cu, Zn, Cd, Se, V, Mo, Ni, Co are important. Newly-emerging modern isotope tools could serve as powerful tools in quantifying the sources, pathways and transport of these micronutrients. The horizontal and vertical transport of key macro- and micro
nutrients can be investigated using a set of radioactive tracers. Sinkhole vents in some of the lakes offer a unique opportunity to probe how novel microbial communities adapt and thrive in extreme environments.

A concerted and focused research effort will provide new knowledge and improve our fundamental understanding of the processes and yield answers to several key questions. Much of the historical understanding of the ecology and biogeochemistry of the lakes, while relevant and informative, is often no longer operative or has been altered in significant ways. At the same time, the lakes have been the subject of improved physical modeling and forecasting systems and expanding observing platforms under U.S. Integrated Ocean Observing System (IOOS). The breadth of our collective knowledge of these closed systems provides a significant baseline on which to build improved ecological and biogeochemical process models. Both their similarities and their differences provide opportunities to study fundamental ecological/biogeochemical dynamics across time and space scales that are relevant to many aquatic systems, from coastal bays and gulfs, to semi-enclosed seas and estuaries. New and novel approaches, tools, and analytical techniques are also now available that are ideal for process-oriented research on these scales.

This report summarizes number of driving questions, gaps and opportunities for future inquiry that would substantially improve our understanding and ability to sustainably manage these and similar aquatic systems.
1. Introduction to the Great Lakes and their Recent History:

1.1 Introduction to the Great Lakes System:

The largest freshwater seas of the world (244,000 km$^2$), the Laurentian Great Lakes System, has undergone major biogeochemical changes over the past 3 decades due to anthropogenic activities such as nutrient abatement, introduction of invasive species and human-induced climate change. Approximately 37 million (11.8% of US population) people live in the Great Lakes basin of which about 8% of the United States total population relies on the Great Lakes for their drinking water. The water quality has direct impact not only on humans but also the economic activity and vitality of the 8 states that adjoin these lakes.

The Great Lake system is similar to oceans in terms of large scale water mass circulation pattern, discrete coastal zones, shelf breaks and deep basins, yet this system is bounded physically with constrainable inputs and outputs in the mass balance of micro- and macro nutrients, carbon and other radionuclides and tracers. In terms of size, these lakes are intermediate in scale between common lakes and oceans and are complex integrators of watershed changes, biology, biogeochemistry and regional environmental and climate change making these systems unique and attractive for tracking how changes, many anthropogenically induced, reverberate through the system. Relative to more saline waters or ocean basins, the forces controlling the mixing of water masses are, in some cases, weak or absent (e.g. tidal currents), and in some cases stronger (e.g. isothermal mixing). Nutrient concentrations range from hyper-oligotrophic (the P concentrations in Lake Superior are lower than the central North Pacific gyre) to hyper-eutrophic and nutrient limitation is both complex and varied (Sterner et al., 2004; Duhamel et al., 2011). This wide range of conditions is embedded within a system that is logistically accessible to analysis at the appropriate density, geochemically and geologically similar, but not uniform. Important internal differences, e.g. in residence times, physical chemistry, loadings, etc. are known and changes are occurring with a speed which is easily measurable on a scale of years. Thus, the diversity of water depths, differences in the hydrological residence times, temperature differences and diversity in biota in these five freshwater inland seas provide an unparalleled opportunity for focused research on the responsiveness of biogeochemical cycles to human-induced perturbations in ecosystem properties in semi-enclosed systems (Table 1).

1.2 Recent Rapid Changes in the Biogeochemistry of the Great Lakes System:

Historically, changes in the biogeochemistry of the Great Lakes have

Figure 1: Long-term trends of major ions for the Great Lakes (Chapra et al., 2012)
responded rapidly to external stress. The first acceleration in biogeochemical changes in the Great Lakes was observed in changes in the concentrations of major ions in the early to middle part of the 20th century (Beeton, 1965) (Figure 1). The common stressors among great lakes (and many small lakes as well) include: i) eutrophication, ii) fisheries exploitation; iii) exotic species; iv) contaminants; and v) climate change. The major milestones in the alterations of major nutrients to the Great Lakes system include: 1950s to 1970: increases in P loading to the lakes; 1972 to 1990: mandated P reductions resulting in water quality improvements (lower P, Chl and fewer algal blooms); 1988-1997: dreissenid mussels invasion and colonization of all lakes (except Lake Superior), first zebra mussels in shallow regions and then quagga mussels in deeper water; and 2000-2010: quagga mussel populations explode in profundal regions of all lakes, except Lake Superior; 1980-present: a warmer, wetter climate.

Excessive nutrients loading from pulse events (e.g., excessive rains over a short period of time discharging a large amount of nutrients) from the watershed have resulted in eutrophication in some of the lakes. The implementation of the Clean Water Act resulted in significant reduction in loading of nutrients that generated improvements in water quality in tributaries and open waters throughout the lower lakes, in particular. Yet, eutrophication remains an issue with some of the most extensive algal blooms ever observed in some of the lakes. For example, in 2011, ~10% of the surface area of Lake Erie (~2.5 x 10^3 km^2) was covered with bloom concentrations, a historical record. This occurrence is hypothesized to be the consequence of a complex interactions among climate, invasive species, and changing land use practices (Figure 2), and is indicative of how quickly the system can revert to an apparently “previous state” under entirely new conditions.

The rapid, extensive colonization and reengineering of the lower Great Lakes by dreissenid mussels in the last 20-30 years fundamentally altered the cycling of biogeochemically important materials with a speed and magnitude which is remarkable even for the Great Lakes that has resulted arguably in the largest biogeochemical shift in the lakes in recent history (Hecky et al., 2004), despite the long history with nearly 200 non-native invaders (Figures 3, 4). This directly and indirectly human-induced large-scale perturbation is an example of an opportunity to investigate the response of a large land-margin ecosystem which integrates complex interactions among terrestrial, atmospheric and aquatic components.
1.3 Contrasts in the Biogeochemistry Between all Five Lakes:

The highly varying inputs of nutrients among the five lakes, contrasting regeneration of macro- and micro nutrients due to highly differing mean water depths, hydrological residence times (Quinn, and mean annual surface temperatures make each of these lakes unique resulting in differences in the biogeochemical cycling of nutrients within these five lakes. Influence of internal recycling in lakes generally is a function of hydrological residence time both on scale of whole lakes as well as locally within lakes while influence of external loading is associated with the ratio of catchment area to lake area (CA/LA). The values of CA/LA ratios are given for all five lakes in Table 1, Fig. 5. The annual mixing of nutrients from the deep water, which is the primary source of nutrients supporting new production for the deep waters in the lake, can vary substantially from lake to lake and from year to year due to differences in the vertical mixing of waters (Dymond et al., 1996; Hecky et al., 1996). The hydrodynamical regimes of the five lakes are not the same. There are striking contrasts, in terms of ecological status, between the five lakes in the Great Lakes system. A large and predictable hypoxic zone in Lake Erie, differences in the trophic states from ultra-oligotrophic (Superior) to hyper-eutrophic (Sandusky Bay, Lake Erie), eutropic to oligotrophic conditions in Lake Erie, and marked differences in the response to recent climate change in different lakes (e.g., such as Lake Superior warming at twice the rate of the atmosphere), are some of the special features of the Great Lakes system. Due to the size of the lakes, the changes caused by changing climate will be expressed sooner and can be more easily quantified in the Great Lakes than in the oceans and they may be harbingers of climate change impacts, but not an indicator of the direction of those changes in the oceans.
Figure 4: Changes in the P loading in lakes that are reengineered by zebra mussels. The differences in the thickness of the arrows indicate the changes taken from pre-mussel to post-mussel periods (From Hecky et al., 2004).
anthropogenically induced external loading of nutrients to the lake primarily depends on the population density in the watershed surrounding the lake. The population density in the watershed surrounding Lake Superior is the lowest and thus, the input of nutrients from sources such as sewage and fertilizer are relatively minor. Lake Superior is reported to have a century-long buildup of NO$_3^-$ such that nitrate is far in excess of P, with a NO$_3^-$/PO$_4^{3-}$ molar ratio in deep-water of 10,000, more than 600 times the mean requirement ratio for primary producers (Sterner et al., 2007), but the temporal variations for other lakes are less known. The low rates of primary production coupled with low watershed inputs of organic C input and low OC burial rates to sediments limit rates of nitrate removal by denitrification in Lake Superior (Johnson et al., 1982; 2012; Finlay et al., 2007). Rates of N cycling processes in the Great Lakes, however, are nearly lacking thus while changes in nitrate are apparent, the precise causes remain elusive. The concentrations of dissolved organic carbon vary widely, from about 100 µM in Lake Superior to about ~400 µM in Huron, Michigan, Erie and Ontario (Waples et al., 2008). The primary productivity is the lowest in Lake Superior (12-25 mmol C m$^{-2}$d$^{-1}$) and highest in Lake Erie (73-84 mmol C m$^{-2}$d$^{-1}$; Kumar et al., 2008; Sterner, 2010).

2. Rapid and Unexpected Recent Changes in the Large Lake System:

The major drivers of ecosystem change are changes in the flow of macro- and micro-nutrients. The overall loadings of phosphorus to the Great Lakes have decreased due to a combination of regulations to reduce point source loadings and improved agricultural practices to reduce nonpoint source loadings (e.g., Bertram, 1993; DePinto et al., 1986). For example, between 1970 and 1990, the total loading of phosphorus to Lake Michigan from point and non-point sources (such as streams/rivers/tributaries, atmospheric and point sources) decreased by 50% (Miller et al., 2000) and such reductions in the loading of phosphorus have resulted in the decrease in the turbidity and algal blooms in the lake’s water column and increases in the clarity, light penetration, and dissolved oxygen, while the introduction of invasive species in late 1980s (such as zebra and quagga mussels) have bioengineered this ecosystem. The patterns of turbidity in Lake Erie during 1980s and early 2000s were reported to have been altered with near-shore waters often clearer than offshore waters whereas in the western and central basin of the lake there were increases during this period (Cha et al., 2011). Such an increase in clarity has resulted in deepening of euphotic zone which allows biota to have better access to the nutrient-rich deeper water in stratified season (Barbiero and Tuchman, 2004). Earlier studies have documented large changes in productivity and diatom abundance at two stations in Lake Erie, although lake-wide data is not available (Saxton et al., 2012).

The spread of invasive mussels has led concomitantly to alterations in nutrient ratios (e.g., C/N and P/N ratios), increased water clarity, and hardening of formerly soft substrates over large areas, all with implications for shifts in the biogeochemical cycling of both major and minor elements (Fig. 1). These changes have resulted in the alterations of pelagic and benthic food webs and associated elemental cycles. In the near-shore areas of Lakes Huron, Erie, and
Ontario, significant decreases in the concentrations of P, phytoplankton, and chlorophyll and Chl-a/P ratios coincided with the establishment of dreissenid zebra mussels and later quagga mussels (e.g., Fahnsteniel et al., 1995; Nicholls et al., 2002). For example, less dissolved P in the water column, either from the abatement of P loading to lakes or removal of particulate P from the near-shore water column by filter-feeding mussels, led to decreased pelagic productivity, increased benthic macroalgal productivity in littoral waters, less organic material ultimately settling to the bottom and thus less available materials and energy for benthic communities (Eberts and George, 2001; Nalepa et al., 2007). Diatoms, once a dominant component of the spring bloom during the isothermal mixing period, have been significantly reduced in abundance, resulting in disappearance of the spring phytoplankton bloom in Lake Michigan and dramatic decreases in some zooplankton species (Figure 6, Vanderploeg et al., 2010, Kerfoot et al., 2010). Chlorophyll a, phytoplankton carbon biomass, and water column primary production decreased 66%, 87%, and 70%, respectively, in Lake Michigan during 2007-08 as compared to 1995-98 (Fahnenstiel et al., 2010). These changes have affected the annual biogeochemical cycling of nutrients and carbon as well (Mida et al., 2010). Prior to this shift, dissolved silica uptake during the spring bloom lowered silica concentrations to near zero (a few µmolar). Subsequent diatom settling, dissolution and silica regeneration resulted in an annual cycle of depletion and regeneration. Annually about 20% of the silica deposited was ultimately buried, with the remainder recycled back into the overlying water during isothermal conditions. Today, silica concentrations drop by less than half of their winter seasonal maximum, i.e. dissolved silica uptake has been significantly reduced in a shift that has been termed “incidental oligotrophication” (Evans et al., 2011). Gradual increases in spring silica concentration in all basins of Lakes Michigan and Huron between 1983 and 2008 have been recently reported (Barbiero et al., 2006; Evans et al., 2011). This shift has transferred nutrients and energy from the pelagic system to the benthic system in the form of an expanding population of quagga mussels throughout the lake. The consequences of these changes on the nutrient and energy flow for benthic carbon metabolism are unknown, but likely dramatic. Since Si is required by diatoms, the depletion of Si can be used as a measure of diatom and phytoplankton production. The silica drawdown in lakes Michigan, Huron and Superior is compared in Figure 9. It has been reported that after the invasion of quagga mussels, there was much less consumption of silica.
during winter-spring. A widespread observed decline of Ca in lake waters and was attributed to the reduction in the exchangeable Ca concentration in catchment soils (Jeziorski et al., 2008). Such reduction is caused by a number of factors that include acidic deposition, reduction in atmospheric deposition of Ca, Ca loss from forest biomass harvesting (Jeziorski et al., 2008). It has been shown that the dreissenids have caused decreases in Ca and lower lakes due to calcification in producing shells (Chapra et al., 2012). It is estimated that alkalinity concentrations in decline in Ca due to mussels would reduce soluble reactive

Figure 7: closed symbols, northern basin; Open symbols: southern basin (data from EPA_GLNPO).

Figure 8: Total P loading reductions exceeded the target. The standard errors vary from 1.5 to 19% of the total lake load depending on the lake and the year. Lake Superior typically has larger standard errors (9.1% of the load, on average), while Lake Erie has some of the smallest estimates (3.5% of the average load).
phosphorus (SRP) in the waters by approximately 3 mg/L (Arnott and Vanni, 1996; Chapra et al., 2012). Thus, it appears that mussel shells are a major sink of P and Ca in the lakes where the mussel shells have dominated. In Lake Ontario, Ca and alkalinity concentrations have fallen and summer ‘whitings’ are reduced in frequency and in some cases no longer appear (Barbiero et al., 2006).

3. Long-Term Nutrient Concentration Variations in the Great Lakes:

The concentrations of some of the nutrients have varied widely. The total P loading has decreased considerably due to management decisions. The total P loading reductions have exceeded targets in all the 5 lakes and the loading and its variability is now dominated by non-point sources, mainly runoff, which responds to precipitation (Figure 7). From a large database of nitrate concentrations from samples collected spanning over a century for Lake Superior, Sterner et al. (2007) reported a continuous, century-long increase in nitrate whereas phosphate remains at very low levels (Fig. 8). The NO$_3^-$ concentration in Lake Ontario increased by more than a factor of 2 during the last 40 years (Figure 9a,b,c), similar to Lake Superior. There seems no historical P or Si data going back to a century. The cycling of carbon, nitrogen, silica, calcium and other key micro-nutrient trace metals (e.g., Zn, Co, Fe, V) in all five lakes have been affected (Fig. 10). These micro-nutrients play a significant role on the structure of the freshwater ecosystems and their biological activity which are key factors in regulating the carbon cycle. It is not known how the dissolved trace element concentrations have changed over the past 30 years as reliable data based on ultra-clean trace metal sampling are limited. The changes in biogeochemical cycling of nutrients have resulted in the changes of benthic fauna diversity and biomass as well flora (e.g., increased abundance of sea grasses, red macroalgae; Figure 5, Hecky et al., 2004).

3.1 Stoichiometric challenge:

One of the most important differences between freshwater and salt water is stoichiometric paradigm in that C:N:P ratios of different components of the oceanic ecosystem exhibit little temporal and spatial variation (Redfield, 1934; Falkowski, 2000). However, the variations of SRP in lakes are quite large (e.g., Hecky et al., 1993; Elser et al., 2000). The limited spatial and temporal data on the primary productivity (PP) and respiration rates (RR) adds a large uncertainty on the controls of stoichiometric ratios, and data on the seasonal and deep water PP and RR are generally lacking. For example, the elemental ratios of C:P in seston varies dramatically on a multi-year time scale (100-150 in 1996-1997 to 300-350 in 2000, Sterner et al., 2007). Such a change has major consequence on the entire food web, species abundance, secondary production, autotrophy/heterotrophy relationships, etc. (e.g., Elser et al., 2000). Furthermore, decreased pelagic productivity and lower amounts of organic carbon in benthic sediments have been driven by alterations in the sources, pathways and cycling of nutrients in the littoral regions of the Great Lakes system.
Long-term trend of increasing nitrate: other Great Lakes

Rising NO₃- evident in all of the Great Lakes
But not likely to be for the same reasons

Figure 9a: Temporal variations of nitrate and phosphate in Lake Ontario over the past ~40 years and nitrate concentrations in the Great Lakes system

Figure 9b: Nitrate concentration in Lake Superior

Figure 9c: Concentrations of NO₃⁻ in L. Superior Figure 8b: NO₃⁻ + NO₂⁻ and total Mo in L. Ontario (Sterner et al., 2007) & Mo-unpublished data (Twiss, 2013)
The concentrations of nitrate in Lake Superior have been reported to have increased steadily over the past century, from \(~5\) to \(~30 \mu \text{mol L}^{-1}\) (Sterner et al., 2007). While the phosphate concentrations in Lake Superior have decreased over the past 4 decades, the atmospheric deposition of nitrate has remained constant. This has resulted in the present-day severe stoichiometric imbalance in Lake Superior, with the \((\text{NO}_3^-/\text{PO}_4^{3-})\) ratio of \(~10,000\) (molar ratio) in the deeper waters of Lake Superior (Sterner et al., 2007). Continuous gradual increase of spring silica concentration in some of the lakes (e.g., Lakes Michigan and Huron) from 1983 to 2008 has altered the \(\text{N}:\text{P}:\text{Si}\) stoichiometric ratios. These changes in the cycling of key macro-nutrient elements in the Great Lakes system have likely altered key micro-nutrient stoichiometry as well which needs further investigation.

4. Fluxes and Processes of Key Major and Minor Nutrient Elements in the Great Lakes System:

4.1. Atmospheric deposition of key macro- and micronutrients:

Long-term records of atmospheric deposition of N or P or Si emissions in the airshed of the Great Lakes are very limited. The relative percentages of the reduction of the nutrients are different for different nutrients. For example, phosphorus concentrations in precipitation have decreased from an average of 57 mg as P L\(^{-1}\) in 1976 to an average of 6.4 mg as P L\(^{-1}\) for 1994-1995 while the volume-weighted mean concentration of \(\text{NO}_3^-\) in Lake Michigan did not change between 1983 (2.0-2.5 mg as \(\text{NO}_3^-\)) and 1994-1995 (1.9 mg as \(\text{NO}_3^-\)) (Voldner and Alvo, 1989; Miller et al., 2000), thus altering the \(\text{PO}_4^{3-}/\text{NO}_3^-\) stoichiometric ratio of the atmospheric input to Lake Michigan (Miller et al., 2000). The atmospheric emissions of nitrate from U.S. and Canada over a period of 20 yrs (1980-2000) have been reported to be constant, although temporal increases were reported between 1940 and 1980 (EPA, 2000; Chen et al., 2000). Simultaneous year-long measurements of major nutrient elements along with their isotopic ratios are needed in different air sheds in the Great Lakes system.

4.2 Inputs of micro- and macro nutrients through groundwater discharge studies
Over the past 250 years, the geochemistry of the Great Lakes groundwater and surface water systems has been altered by regional land use changes including deforestation, wetland drainage, agriculture, industrialization, and urbanization. Further changes stemming from the “green revolution” in agricultural practices and accelerating climate change beginning in the latter half of the twentieth century are anticipated, but not well constrained. The volume, location, and quality of direct groundwater discharge to the Great Lakes are poorly understood. Coastal areas, where groundwater discharge is expected to be greatest, are largely ungauged. Therefore, the amount and chemistry of groundwater discharging to the Great Lakes are not well known.

Some of the groundwater flow systems in an aquifer system provide base flow to the streams in response to recharge from the precipitation events. Submarine groundwater discharge could be one of the significant sources of nutrients and key trace elements to the lakes. The groundwater component of stream flow (for 195 selected streams in the US part of the Great Lakes Basin) ranges from 25 to 97%, with an average value of ~67%. Although there is no estimate on the total amount of direct groundwater discharge to Lake Huron, Superior, Erie and Ontario, there is an estimate for Lake Michigan. The total groundwater discharge to Lake Michigan was estimated to be $2.7 \times 10^3$ ft$^3$ s$^{-1}$ (~76.5 m$^3$/yr; Grannemann and Weaver, 1998). Highest rates of groundwater discharge were calculated for the northeastern shore of Lake Michigan.

Numerical groundwater flow and transport models are therefore needed, in conjunction with field measurement (seepage meter covering several locations around the lakes) and tracer studies (e.g., $^{234}\text{U}$/$^{238}\text{U}$, $^{223,224,226,228}\text{Ra}$, $^{222}\text{Rn}$, $^{87}\text{Sr}$/$^{86}\text{Sr}$ in aquifers and lakes), to investigate processes controlling nutrient and solute flux across an appropriate range of spatial and temporal scales. Groundwater flow paths vary from local to regional with travel times ranging from days to decades to centuries. Regional flow paths through carbonate, siliciclastic, and crystalline bedrock will likely have different equilibrium chemistries and spatial variability in both the volume and chemistry of submarine discharge to the Great Lakes is expected. Consequently, models will enhance our ability to predict: i) flow paths and discharge regions; ii) estimate geochemical signals; iii) quantify nutrient and solute fluxes; and iv) detect and confirm anomalous regions. Hence, they will contribute to a greater understanding of the role of groundwater and surface water hydrology in the biogeochemical cycling of phosphorous, nitrogen, and micronutrient cycling within Great Lakes ecosystems.

In about 37% of the monitor-well samples in the Lake Erie and Lake St. Clair drainages, the nitrate concentrations indicated evidences of human influence such as fertilizer, manure or septic systems and thus, the contribution of nitrate to base-flow in riverine systems is expected to be significant. Phosphate concentrations in groundwater depend on the bedrock, with siliciclastic bedrock groundwater exhibiting lower concentrations (0.017-0.020 mg/L) compared to carbonate rocks (< 0.1 mg/L). Many of the shallow groundwater aquifers is hydraulically connected to the land surface, based on the presence of tritium in ~83% of the waters from monitor wells which were recharged after 1953 and 53% of the wells contained a pesticide or elevated nitrate.
concentration (Myers et al., 2000). However, there is no estimate on the fluxes of N, P, Si or C or any of the micro-nutrients to the Great Lakes through groundwater discharge.

Recently, three sinkhole vents were discovered in cyanobacterial mats that are similar to extreme and exotic ecosystems. These cyanobacterial mats thrive in low-O$_2$, conduct both oxygenic and anoxygenic photosynthesis and these organisms could serve as sentinels of environmental change (Voorhies et al., 2012). The waters that are discharged in these vents are anoxic, with high concentrations of sulfate and chloride and low concentrations of nitrate and oxygen. It remains unknown if there are more sinkhole vents in other areas of Lake Huron and other lakes in the Great Lakes system, at large. Stable ($\delta^{18}$O and $\delta$H) and radioactive isotope studies ($^{226}$Ra, $^{228}$Ra) in water samples collected near the sediment-water interface at few kilometers from the sinkhole vents indicate that there several effusive fluxes where highly anoxic waters are leaking (Baskaran et al., 2014 – in review). These sinkhole vents can serve as analogs for life in extreme environments.

4.3. Inputs of macro- and micro nutrients from sediments:

The sediment accumulation rates in lacustrine systems are generally higher than the shelf and deep oceans and the degree of bioturbation that causes the loss of temporal resolution of sedimentary record is low and hence usually lacustrine sedimentary records are better candidates for paleo reconstruction studies. There are some sporadic attempts to quantify the transport and burial rates of organic carbon. Quantitative assessment and numerical models of sediment dynamics have been conducted in a limited area (e.g., Edgington and Robbins, 1990). The nature of the bathymetry in the coastal areas in the Great Lakes makes the storm-generated episodic resuspension and horizontal advection of nutrients, carbon, sediments and other biogeochemically key material to be significant, although the trapping of the nutrients, particulate matter containing key elements and isotopes, attenuation and sequestration of key material fluxes are not investigated. Sediment burial of C seems to be more important in the shallower lakes, although the data is very limited in the Great Lakes system. Earlier studies on $^{14}$C in POC indicate presence of resuspended material to be the major source of particulate matter. Data on well-constrained benthic flux estimates of C, N and P are also needed for a better understanding of the biogeochemical cycling of key macro-nutrients in the lacustrine system.

4.4. Internal Cycling and regeneration studies:

The internal cycles of macro- and micro nutrients (both dissolved, particulate and colloidal forms) in the inland sea waters are influenced by a complex set of removal, transport and transformation processes that include removal by invasive species, atmospheric deposition from the industrial belt in the Midwestern states, agricultural industry, etc. The hydraulic residence times of these waters (Table 1) are much lower than the global ocean circulation times of ~2000 yrs and hence the uniform mixing of the water takes place much quickly compared to the oceans (Fee et al., 1996). Some of the trace metals (e.g., Fe) has been found to serve both as
a limiting factor in the growth of phytoplankton in high-nutrient low chlorophyll regions and for its regulation of nitrogen fixation.

It has been estimated that the external loading of nutrients is sufficient to meet the algal demand on a daily basis, while internal cycling meets the overall needs. The influence of internal cycling/recycling on lakes generally is a function of water residence time, both at the scale of whole lakes as well as factors and processes that operate locally within lakes while the influence external loading is associated with the terrestrial catchment to lake area (Table 1). The vertical distribution of a micro- or macro nutrient results from a combination of processes such as physical transport, chemical control, and biological activity. The external loading of nutrients can be relatively easily characterized and quantified, while the internal loading and cycling is difficult, as it involves quantification of several biogeochemical processes that are not well understood in the Great Lakes system. Internal loading estimate would require an estimate of benthic fluxes, rates of particle-recycling of N, P and C, and extent of remineralization of POC, PON and POP. There are very little data on the benthic fluxes of macro- and micro nutrients for the Great Lakes system. Furthermore, data on the remineralization term for POC, PON and POP in the water column from sinking particulate matter are very limited and is confined to a limited area.

To investigate the cycling and transport of N, P, Si, and OC, some of the U-Th series radionuclides (e.g., $^{234}$Th, $^{210}$Pb, $^{210}$Po, $^{210}$Bi), cosmogenic radionuclides (e.g., $^7$Be) and anthropogenic radionuclides (e.g., $^{90}$Y/$^{90}$Sr) have been utilized (e.g., Coale and Bruland, 1985; Murray et al., 1989; Buesseler et al., 1992; Baskaran et al., 2003; Moran et al., 2003; Cochran and Masque, 2003; Murray et al., 2005; Waples et al., 2006; Rutgers van der Loeff and Geibert, 2008). Variations in the nature of particulate matter (biogenic versus lithogenic) due to the presence of dreissenids can be investigated using tracers that trace biogenic particulate matter (e.g., $^{210}$Po) and terrigenous particulate matter (e.g., $^{210}$Pb). They also can be used to constrain rates of scavenging and biological uptake by particles and to quantify processes that regulate the internal cycling and eventual removal of key nutrient elements. Radium isotopes can be used as a tracer of other alkaline elements such as Ca, Ba, Sr, etc. The abundances of Ca and Ba are considerably altered in the many of the lakes due to dreissenids and it is likely that Ra is also altered from the water column. Quantification of sediment resuspension rates using particle-reactive radionuclides ($^{210}$Pb and $^7$Be) in freshwater system has been conducted (e.g., Jweda et al., 2008), and amount of release of organic C, N and P from sediments can be quantified from the sediment resuspension rates.

4.5. Impacts on nutrient cycling due to climate changes:

The major impact of global climate change (or regional climate change) caused by human perturbation will affect the hydrological cycle the most having the most immediate impact on future human welfare of those who twelve in the Great Lakes region. The global climate change has resulted in increasing annual surface air temperature as well changes in the amount and frequency of precipitation in the Great Lakes region. The climate change will affect the
hydrologic balance, biological productivity, and ecosystem structure and water quality. Continued rise of atmospheric CO$_2$, both from measurements and predicted GCMs will have significant impacts on the ecosystem of the Great Lake system. Model-predicted global warming is expected to affect the length of the stratified period in the Great Lakes (by as much as 90 days; Weiss and Sousounis, 1999). Such elongated period of stratification will result in extended isolation of warmer hypolimnion from the atmosphere and could result in lower dissolved oxygen (DO) levels and such lower DO potentially will have enormous impacts on nearly all segments of the lake ecosystem, including nutrient cycling, benthic metabolism and fisheries (SOFIS Report, 2003). Changes in the frequency and amount of precipitation could result in the water level fluctuations, changes in river runoff and lake water evaporation. Changes in the hydrological cycle expected to accompany global warming will likely have an impact on the delivery of lithogenic and nutrient elements to the Great Lakes through several processes that include increased watershed erosion and runoff in several areas. Changes in the wind field resulting from regional climate change, as a result of global climate change, can alter the water and nutrient exchange between semi-enclosed bays and the open lake water. For example, changes in the wind field over the Great lakes basin since 1980 has resulted in a reduced amount of water exchange between Green Bay and Lake Michigan which has led to the formation of intensified bottom water hypoxia, increased benthic metabolism within the bay, and warmer bottom water temperature (Waples and Klump, 2002). Over the last 30 years, the surface water temperatures in Lake Superior have risen twice as fast as air temperatures (Austin and Coleman 2007). In Lakes Michigan and Huron evaporation has increased significantly, equivalent to a nearly 4 meter drop in lake level, but this has been offset by increases in precipitation and runoff (Hanrahan et al. 2010). Decreases in the water levels in Great Lakes and their connecting channels are of major concern not only for recreation industry but also for other sectors including transportation industry.

5. Tools for Biogeochemical Cycling Studies:

5.1 Particle-reactive and stable isotopes:
A major understanding of the biogeochemical cycles of many elements in aqueous system is linked to the understanding of the cycling of particle-reactive radionuclides. Several key biogeochemical processes in the water column including formation, aggregation/disaggregation, dissolution, and scavenging of biogenic particulate matter, exchange of particle-reactive species between particles and solution, and export of particulate organic carbon, nitrogen and other particle-reactive organic matter (e.g., PCBs, PAHs) relies heavily on the natural radioactive clocks provided by the U-Th series radionuclides along with a set of cosmogenic and anthropogenic radionuclides (Ivanovich and Harmon, 1992; Bourdon et al., 2003; Krishnaswami and Cochran, 2008; Hong et al., 2011; Kaste and Baskaran, 2011). While a large body of data exist utilizing U-Th series radionuclides as POC, PON export tracers ($^{234}$Th/$^{238}$U and $^{210}$Po/$^{210}$Pb) in the marine systems (Buesseler, 1998; Moran et al., 2003; Waples et al., 2006), virtually no data exist in the freshwater system. Although the $^{238}$U concentration in freshwater system is very low (~5% of open ocean value) in the Great Lakes (limiting $^{234}$Th/$^{238}$U pair for export studies), the $^{210}$Pb concentrations in surface waters are expected to be significantly higher than that of most other deep ocean basins ($^{210}$Po/$^{210}$Pb pair can be utilized export studies) due to differences in the sources of air masses. The half-lives of these nuclides are short (e.g., $^{234}$Th: 24.1 d; $^{210}$Po: 138.4 d; $^{210}$Bi: 5.1 d) to make these nuclides sensitive to short-term changes that occur (e.g., POC flux integrated over a week to a few months) in upper water column. The deficiencies of these nuclides are created by the scavenging of these onto
biogenic particulate matter and the sinking of such particulate matter out of the euphotic zone. It has been documented that $^{210}$Po traces much more efficiently the biogenic organic matter than Th and hence Po is likely a better tracer for POC and PON export studies (Figure 11, 12; Friedrich and Rutgers van der Loeff, 2002; Verdeny et al., 2007). The lone study in Lake Superior (Chai and Urban, 2004) that reported similar residence time for $^{210}$Po and $^{210}$Pb is in contrast with much longer time of $^{210}$Po compared to $^{210}$Pb in the upper 150 m, due to remineralization of particulate $^{210}$Po in marine system (e.g., Sarin et al., 1999). No other data exists from any of the other lakes in the Great Lake system to compare with. Using $^{210}$Po-$^{234}$Th and $^{210}$Po-$^{210}$Pb as coupled tracers, Friedrich and Rutgers van der Loeff (2012) estimated the sinking velocities of biogenic Si and POC. Particle formation and dynamics can be investigated using the disequilibrium between $^{210}$Po-$^{210}$Bi-$^{210}$Pb pair, similar to aerosol removal in the atmosphere. There are limited attempts to quantify the lateral export suspended particulate matter using radioactive tracers ($^{234}$Th, $^{137}$Cs, $^7$Be) in the Great Lakes system. For example, the Keweenaw Interdisciplinary Transport Experiment in Lake Superior (KITES) focused on a region dominated by a strong coastal jet, and the sister project in Lake Michigan, Episodic Events—Great Lakes Experiment (EEGLE), concentrated on the biogeochemical effects of a major plume of resuspended sediment that occurs annually in the southern portion of the lake (Eadie et al. 2008; see JGR special issue, 2004: http://www.agu.org/journals/ss/EEGLE1/). These studies were limited to one area and had limited scope in terms of using key micro and macro-nutrients study.

The understanding of nitrogen cycle in the Great Lakes system is very limited, although the N/P stoichiometry ratios in many of the lakes have drastically changed, mainly due to increase in N rather than drastic decrease in P values. We have currently a better understanding of N cycle in a small lake in Switzerland compared to the Great Lakes. Although historical data on the nitrification-denitrification at the sediment-water interface and sediment cores are limited, it has been shown that the vertical distribution of $\delta^{15}$N and $\delta^{13}$C of a dated core from
Lake Ontario varied by ~2‰ over the past 140 years while δ¹⁵N values change by ~5-6‰ and it was attributed to active denitrification at the sediment-water interface (Hodell and Schelske, 1998). The classical view that nitrogen cycle is dominated by nitrification and denitrification is changing, and ANAerobic AMMonium OXidation (Anammox: NO₃⁻ + NH₄⁺ → N₂) and Dissimilatory Nitrate Reduction to Ammonium (DNRA: NO₃⁻ → NH₄⁺) are increasingly being recognized as important processes that regulate the nitrogen cycling (Figure 13).

Very limited data is available on denitrification and on DNRA in the Great Lake systems and no nitrification rate data seem to be available from Lake Huron and Ontario.

5.2 New and Newly Emerging Tools:

Key major nutrients (P, N and Si) and some of the essential micro-nutrient trace elements (e.g., Fe, Zn, Co, V, Mo, and Cu) play important roles in the biochemical activity in organisms (e.g., Morel et al., 2003; Morel and Price, 2003). High precision measurements of the isotopes of these micronutrients are available only in the last ~15 years and there is limited data on their distributions in the Great Lakes system. For example, there are vertical profiles of Si isotopes (δ²⁹Si) for Lake Tanganyika (Figure 14). The δ²⁹Si isotopic ratio could be useful in studying environmental changes and particularly recent changes in the diatom utilization (Alleman et al. 2005). Lack of such information prevents the scientific community to get a good handle on the sources, transport and cycling of these essential elements across the lakes.

A large number of isotopes are utilized as a set of powerful tools to map the food webs in terms of the major carbon flows and trophic relationships (Hecky and Hesslein, 1995). For example, the distribution of phosphate and Cd are similar in marine system (Elderfield and Rickaby, 2000) and thus, isotopes of Cd can be used to trace the pathways of P because both species are likely removed from the freshwater sea by biological activity. Zinc which is an essential micronutrient could serve as a tracer for another macro-nutrient, Si, in aqueous system (Ellwood and Hunter, 2000; GEOTRACES Science Plan, 2006). There is very limited data on the
isotopic fractionation of nutrient elements as well as micro-nutrient elements and thus, some of the isotopic tools could serve as powerful tools in assessing nutrient utilization. Isotopes of nitrogen and oxygen in nitrate are used to quantify the sources and dynamics of nitrate, both $\delta^{15}\text{N}$ ($\delta^{15}\text{N}-\text{NO}_3$) and $\delta^{18}\text{O}$ ($\delta^{18}\text{O}-\text{NO}_3$). It has been shown that the $\delta^{15}\text{N}$ values of NO$_3^-$ sources often overlap and thus combined use of N and O isotopes are powerful (Kendall, 1998; Burns and Kendall, 2002; Hastings et al., 2003). The $\delta^{18}\text{O}$ of NO$_3^-$ from nitrification is largely determined by the $\delta^{18}\text{O}$ in water in the ecosystems while $\delta^{18}\text{O}$-NO$_3^-$ values in precipitation is the result of isotopic fractionation taking place during interactions between oxides of nitrogen and O$_3$ in the atmosphere (Hastings et al., 2003; Michalski et al., 2011). Oxygen isotopes in phosphate are used to trace the pathways of phosphate (Jaisi et al., 2011; Paytan and McLaughlin, 2011).

6. Missing Gaps in Knowledge and Key Questions:

A mass balance of C, N, P and Si in the lakes require good estimates on the primary production, grazing, DOC inputs/outputs from rivers/streams and carbon burial rates. Attempts for OC budget have been attempted for L. Superior (Urban et al., 2005). Lake-wide studies on the production and grazing in most lakes are lacking and thus, there are gaps in our understanding of the N, P, and Si cycling and its link to other key macro- and micro nutrients. Earlier PP studies are primarily from certain seasons of the year and lack of data during the colder periods and deeper waters fuels the uncertainty in the C estimate. The uncertainty in the primary production rate for Lake Superior is mainly due to the scaling-up factors used on the vertical temperature and chlorophyll data at measured at depths. The chemical reactions (nitrification, denitrification and anammox) are expected to be slower in Lake Superior due to cooler waters compared to other lakes (Michigan, Huron, Erie, and Ontario); other factors that control the N, C and P cycling and N assimilation and microbial community structure are not studied in all the Great Lakes, whether it is due to increase in external sources discharged to the lakes (rivers/streams, atmospheric deposition, submarine groundwater discharge), or active in-lake processes (such as nitrification/denitrification, anammox).

The first step in the transfer of nutrients and C to food chains is the grazing. In eutrophic environments, the transfer by grazing is less efficient that that observed in oligotrophic waters and hence the settling of nutrients to deeper waters is primarily controlled by grazing. Thus, the relative importance of grazing compared to the export of particulate C, N, and P. During vertical transport of POC, PON, POP, particles undergo remineralization contributing to the dissolved C, N, and P in the water column. Thus, grazing data using some commonly used protocol (e.g., dilution gradient method, Landry and Hassett, 1982) is needed. The small consumers such as picoplankton (<10 um) could play an important role as dominant consumers relative to the whole food web. Lake-wide primary production rates from time-series, vertical profiles, and day/night studies are needed to limit the range of variations on the primary production estimate, using widely accepted method(s), such as $^{14}\text{C}$ methodology. Similarly, an estimate on the grazing on planktons for the whole lake needs to be assessed. It is also essential to measure vertical profiles of production and establish an empirical relation between production, light and temperature.
Establishing such a relationship at different seasons (summer, winter and spring) will help to constrain the estimate on production. Lake-wide efforts on the simultaneous measurements of primary productivity and respiration rate with special emphasis on seasonality, year-around measurements and surface and deep-water measurements of these parameters are important (including under-ice measurements of production and respiration to quantify autotrophic-heterotrophic balance). Sporadic and sparse measurements of primary production and respiration rates most likely have missed the important spatial and temporal variations of the biological activity and thus, it is urgently needed to quantify these rates.

Recent studies in Lake Erie showed that Fe is required for the stimulation of NO$_3^-$ draw down and required for NO$_3^-$ assimilation (Twiss et al., 2005; Havens et al., 2012). Several other trace elements such as Co, Zn, Ni, Mn, Cu, also serve as essential micronutrients, and their distribution, sources, pathways and eventual sinks remain unknown. The biogeochemical cycling of Fe in the Great Lakes system remains poorly characterized. A potential relationship between micro-nutrients and macro-nutrients (e.g., PO$_4$-Cd; Si-Zn) could help in identifying and quantifying processes in the freshwater systems. The trace metal enrichment is likely to play a significant role on the nutrient assimilation in picoplanktons (Twiss et al., 2005). Low availability of Fe and other micronutrients could also constrain the primary productivity in the Great Lakes system. The concentrations of the micronutrients in the lacustrine system are expected to be very low and large-volume of samples may be required.

With the present understanding of the Great Lakes system, there are several knowledge gaps. A systematic process-oriented study is expected to answer the questions listed below:

i) How does the onshore-offshore coupling along with the presence of invasive species affect the coastal trapping, attenuation and sequestration of nutrients, suspended particulate matter, POC and other key micro-nutrients?

ii) How does the vertical and horizontal transport of nutrients due to episodic events affect the lacustrine productivity on different temporal and spatial scales?

iii) How does the cycling and internal of loading of nutrients have impacted the concurrent coastal eutrophication and pelagic oligotrophication in some of the lakes in the Great Lakes system?

iv) In what time scales the stoichiometric ratios vary in different lakes in the Great Lakes system? How does this ratio vary in seston in different Great Lakes system? How do the stoichiometry ratios of nutrients from atmospheric loading compare with that of terrestrial runoff year around in all the lakes?

v) How did the NO$_3^-$/PO$_4^{3-}$ ratios vary over the past 30 years in areas that are severely impacted by invasive species (zebra and quagga mussels), due to active removal of PO$_4^{3-}$, Ca, and key bio-limited elements and their isotopes in the lower lakes?
vi) How does the seasonal variations of the rates of primary productivity and respiration and at deeper waters compare with the other decay of organic matter such as CO₂ production from heterotrophic processes in different spatial and temporal scales?

vii) How we can quantify the horizontal and vertical transport of key macro- and micro nutrients using a suite of newly emerging isotopes of Fe, Cu, Zn, Cd, Se,V, Mo, Ni, Co in conjunction with a suite of particle-reactive radionuclide tracers.

viii) How do the sink terms of P, N, Si, and C vary across the five lakes as a result of varying extent of denitrification due to varying supply terms of labile organic carbon to the lake bottom resulting in nitrate build up.

ix) What factors and processes limit the nutrient utilization in the Great Lakes system? Does it vary from lake to lake? If most lakes are limited by N and P, are there any key micronutrients, such as Fe, that is limiting the nutrient utilization?

x) How have the quantity and quality of groundwater and surface water discharged to the Great Lakes been influenced by deforestation, wetland drainage, farming, industrialization, and urbanization in the Great Lakes watershed? How have these changes contributed to alteration of biogeochemical cycling of nitrogen, phosphorous, and other micronutrients in the Great Lakes?

xi) What is the impact of sinkhole vents in the biogeochemical cycling of nutrients in Lake Huron and other lakes, if they also have sinkhole vents?

xii) How does the filtering activity of dreissenids affect the inorganic nutrient forms of N and P and the organic forms versus particulate forms of C, N and P.

xiii) How do the anthropogenic alterations on nutrients affect the ecological and evolutionary trajectories? How the dreissenid mussel invasion has altered the CO₂ emissions from freshwater system? and

xiv) How does the trace metal speciation and bioavailability of trace metals in freshwater seas vary in different lakes

7. Field Sampling, Remote Sensing and Synergies Among Other Federal Agencies:

In field expeditions, it is essential to collect data of standard hydrographic parameters (e.g., temperature, oxygen, salinity) in all stations and the data quality is should to be comparable to that of WOCE and GEOTRACES. Major nutrients (nitrate, phosphate, silicic acid) should also be measured, again similar to the WOCE and GEOTRACES quality. The field sampling should focus on areas of prominent sources (river/stream discharges), submarine sinkhole vents, etc. From a review of the existing data and monitoring stations, sections should be selected to include major biogeographic regions and gradients of biological productivity. The field sampling should be coordinated with other federal agencies that have interest in the Great Lakes (EPA, NOAA Vessels – NASA remote sensing data) and researchers in Canada.
From the Great Lakes Workshop 2010 conducted by NASA GRC, it was recognized that there are significant opportunities for NASA to improve the understanding of the hydrology and physical limnology of the Great Lakes (e.g., ice, temperature, precipitation, wind velocity, currents, etc.). NASA current interest includes water cycle (quantity, quality, and availability and future changes), limnology, climate, ecology and human effect modeling, and remote sensing.

Coastal processes in the Great Lakes are important for Great Lakes, yet often not considered in national scope. The current interests of NASA include reflectance, surface radiometry, benthic optical characterization and other atmosphere and water column correction factors relevant to remote sensing. NOAA has conducted long-term sediment trap studies to investigate sediment transport along cross and along-shore, benthic nepheloid layers and resuspension. GLNPO/EPA monitors 11-18 stations in offshore regions in lakes Michigan, Huron and Superior collecting a suite of limnological parameters.

The satellite remote sensing provides a synoptic view for the whole Great Lakes region of several parameters of interest that include surface temperature, color, chlorophyll concentration, colored dissolved organic matter, atmospheric aerosol loading, wind speed and direction. Moorings with current meters in several sites have been deployed in Lake Superior from ~2007 to present. Current profilers (ADCPs) and thermisters at a range of depths also have been deployed. The Muskegon Lake Observatory buoy is investigating the metabolism in Lake Michigan and is being compared to the estimate obtained from bottles (McNair et al., 2013). Remote sensing using satellites of optically-sensitive compounds (e.g., colored dissolved organic matter, CDOM) provide valuable information on their sources, fate and transport in lacustrine systems.

8. Link to the Major Ongoing Oceanographic Research:

The biogeochemical changes that have recently taken place in the estuarine and marine coastal environments are useful in informing the key biogeochemical changes that have taken place in inland seas, and vice versa. The distribution of these key macro and micronutrients are being measured as a part of the GEOTRACES project in major ocean basins (North Atlantic: 2010 and 2011; East Pacific: October-December, 2013). During the first phase of the GEOTRACES project two cruises (Atlantic inter-calibration cruise: 2008 and Pacific inter-calibration cruise: 2009) were dedicated to establish the best practices of sampling (particulate and dissolved), storage and analytical protocols for the contamination-prone elements and radionuclides (http://www.obs-vlfr.fr/GEOTRACES/science/intercalibration/222-sampling-and-sample-handling-protocols-for-geotraces-cruises) and thus the best practices of sampling, storage, and analyses are established for the work in the Great Lakes.

9. Broader Impacts:

The water quality has direct impact on human health of about 8% of the US population. These set of lakes in the Great Lakes system have different temperatures, water depths, hydrological residence times, and varying amounts of anthropogenic impacts of macro- and
micro nutrients in the watershed and investigations on the sources, fate and transport of micro- and macro nutrients will yield a dramatically improved knowledge of the nutrient cycles in the world’s largest lake system. The biogeochemical processes as modified by human impact in the Great Lakes system vary considerably due to the differences in the land use between their watersheds. The major human induced perturbations of the nitrogen cycle in the Great Lakes and their present and continuously growing impacts on the aquatic system, such as eutrophication, hypoxia in lakes and streams can provide the changes that are taking place. Investigations in the Great Lakes system provide tools to validate some of the existing models of nutrient transport and cycling. Similar future perturbations in other large lakes worldwide (e.g., East African rift lakes, Lake Baikal, Lake Tanganyika, and the Canadian interior great lakes (Great Bear, Great Slave, Winnipeg, and Athabasca) are likely to happen and hence this study has broader implications for lacustrine systems around the world. Since the extent of inter-watershed human perturbations on the watershed varies, documenting the impact of such changes on these lakes would provide baseline data which can be compared to the future studies, as continued alterations by humans take place.

Acknowledgments: This Report is a product of the Workshop which was financially supported by NSF (OCE-1253310), NOAA, NASA, Wayne State University, CILER, Michigan State University, University of Illinois-Urbana Champaign, University of Minnesota-Duluth, Ohio State University, University of Wisconsin-Milwaukee, Yale University, Sea-Grant-Wisconsin and Sea-Grant-New York. Inputs from participants at the International Association of Great Lakes Research Annual Meeting at West Lafayette, IN, Geochemical Society Meeting at Florence, Italy, and American Geophysical Union Fall-2013 meeting are deeply appreciated.

Enclosed Appendix: A) BOGLS Workshop (11-13 March 2013) Agenda; B: List of Participants at the BOGLS Workshop; C: List of participants at the IAGLR Annual Meeting (June 2013), Geochemical Society Meeting (August 2013) and Fall AGU Meeting (December 2013).
References:


Austin, J. A. and S. M. Colman (2007). "Lake Superior summer water temperatures are increasing more rapidly than regional air temperatures: A positive ice-albedo feedback." Geophysical Research Letters 34(6).


Francis et al. 2007. ISME Journal 1, 19-27.


GEOTRACES science plan (2006). An international study of the marine biogeochemical cycles of trace elements and their isotopes. Baltimore, MD. Scientific Committee on Oceanic Research, GEOTRACES rept. no. 1


JGR special issue J. Geophys. Res. (Oceans) 109 (C10).


SOFIS Report. T. C. Johnson. Duluth, Minnesota 55812, University of Minnesota-Duluth.


Recent Changes in the Biogeochemistry of the Great Lakes System Workshop
McGregor Conference Center
March 11-13, 2013

Agenda

Monday March 11, 2013

07:30 – all day Lobby Registration

07:30 – 08:30 B/C Continental Breakfast

08:30 - 09:15 F/G/H Technical Session 1

Chair, Mark Baskaran

Welcome, Introductions, Workshop Overview

09:15 – 10:30 F/G/H Plenary Session: Disrupted Biogeochemical Cycles in the Great Lakes: Challenges and Opportunities for Aquatic Science. R.E. Hecky, University of Minnesota-Duluth

Presentation: Micronutrient Dynamics in Lakes and Their Investigation Using New Isotopic Tools. T.M. Johnson, University of Illinois at Urbana-Champaign

10:30 – 10:45 B/C Refreshment Break

10:45 - 12:30 F/G/H Technical Session 2

Chair, Val Klump

Presentation: Recent Advances in Understanding the Roles and Reactions of P in Aquatic Systems. R.E. Blake, Yale University


Presentation: Tracing the Biogeochemical Cycling of Key Micro- and Macro-Nutrients in the Great Lakes System Using a Suite of
**Particle-Reactive Radionuclides.** **M. Baskaran,** Wayne State University and **V. Klump,** University of Wisconsin-Milwaukee

12:00 – 12:30  | F/G/H  | Questions and Discussion: Technical Sessions 1 and 2
               |       | Moderated by V. Klump
12:30 – 01:45  | B/C   | Lunch (boxed lunch provided)
01:45 – 03:00  | F/G/H  | **Technical Session 3**
               |       | Chair, Tom Johnson
               |       | Plenary Session: *Recent Changes in Primary Productivity and Phytoplankton Dynamics in the Great Lakes.* **G. Fahnenstiel,** Michigan Technological University
               |       | Presentation: *Spatio-temporal Variability and Potential Long-Term Trends in Great Lakes Carbon Cycling.* **G.A. McKinley,** University of Wisconsin-Madison
03:00 – 03:30  | F/G/H  | Questions and Discussion: Technical Session 3
               |       | Moderated by **T. Johnson**
03:30 – 03:45  | B/C   | Refreshment Break
03:45 – 05:00  | F/G/H  | **Technical Session 4**
               |       | Chair, Norm Grannemann
               |       | Presentation: *Gaps in Understanding of the Role of Groundwater in Great Lakes Biogeochemical Processes.* **J. Bratton,** GLERL-NOAA, **N. Grannemann,** USGS, **L. Lemke,** Wayne State
               |       | Presentation: *Inertial Oscillations as a Primary Ecosystem Driver.* **J. Austin,** University of Minnesota-Duluth
05:00 – 05:30  | F/G/H  | Questions and Discussion: Technical Sessions 1-4
               |       | Moderated by **N. Grannemann**
05:30 – 06:00  | Lobby  | Social Break
05:30 – 06:00  | A      | Steering Committee Meeting: Formative Workshop Assessment
06:00 – 07:30  | B/C   | Catered Dinner
Recent Changes in the Biogeochemistry of the Great Lakes System Workshop
McGregor Conference Center
March 11-13, 2013

Agenda

Tuesday March 12, 2013

07:30 – all day  Lobby  Registration
07:30 – 08:30   B/C  Continental Breakfast
08:30 – 08:40   F/G/H  Technical Session 5
                  Chair, Larry Lemke

Goals and objectives for today’s sessions
M. Baskaran, Wayne State University
J. Bratton, GLERL-NOAA

Guidelines for advocacy presentations
L. Lemke, Wayne State University

08:40- 10:30   F/G/H  15-Minute Introductory Talks

Dreissenid Mussels Have Reengineered the Biogeochemistry of the Great Lakes

H.A. Vanderploeg, GLERL-NOAA

Sediment Trap Studies in the Great Lakes
N. Hawley, NOAA Federal GLERL

5-Minute Advocacy Talks

Important Negative Impacts on the Nitrogen Cycle are Ignored in the Debate About Managing Eutrophication. D. Bade, Kent State University
Microbiogeochemical Ecophysiological Time Series Analysis in Lake Michigan: Key to Distinguishing Between Episodic and Progressive Perturbations. R. L. Cuhel, University of Wisconsin-Milwaukee

A modeling Approach to identify Factors Driving Increased Dissolve Reactive Phosphorous Loss from Agricultural Fields in the Maumee Basin. S. Y. Gerbremariam, Ohio State University

The Effect of Bain Scale Meteorological Events and the Persistence of Major Invasive Species on Biogeochemical Cycling and Ecosystem Function in Lake Michigan. C. Aguilar, University of Wisconsin-Milwaukee

Potential Impacts of Changes in Major Ion Composition on Trace Metal Interactions with Phytoplankton: the Lake Ontario Example. M. Twiss, Clarkston University

The Importance of Iron and Sulfur Cycling in the Great Lakes System. L. Kinsman-Costello, University of Michigan

Great Lakes Traces: A program to Study the Biogeochemical Cycling of Trace Elements and Their Isotopes in the Great Lakes. A. Chappez, Central Michigan University


10:30-10:50 B/C Refreshment Break

10:50 – 12:30 F/G/H Technical Session 6
Chair, Ruth Blake

5-Minute Advocacy Talks

Carbon Dynamics in Response to Environmental Change?. L. Guo, University of Wisconsin-Milwaukee

Using Observations to track Lake Metabolism and Their Role in the Global Carbon Cycle. L. Gereaux, Grand Valley State University

Sediment Biogeochemistry of Great Lakes Sediment. G. Matisoff, Case Western Reserve University

Unique Cyanobacterial Mats in Lake Huron Sinkholes: Sentinels of Environmental Change? G. J. Dick, University of Michigan
Is Climate Change Tuning the Invisible Engine of the Great Lakes?  
V. Denef, University of Michigan

Direct Measurements of Heat, Moisture and Carbon Fluxes on the Great Lakes. J. Lenters, Limno Tech

Variability of Satellite-Derived Chlorophyll Concentrations and Colored Dissolved Organic Matter in Lake Superior. C. Mouw, Michigan Tech University

The Importance of Biogeochemical Water Quality Monitoring.  
M.D. Rowe, NOAA/GLERL

Climate Change Impact on Reservoir Thermal Structure and Turbidity Transport and Some Aspects of Ice Cover Modeling in New York City Drinking Water Reservoir. N. R. Samal, New York City Government

Simulating the 1998 Spring Bloom in Lake Michigan using FVCOM-Ecosystem Model. J. Wang, University of Michigan CILER

Pollutant Loads Generated from Lake St. Clair Metroparks during Dynamic Stormwater Runoff Events. S.P. McElmurry, Wayne State University

Ballast Water Verification and Early Detection of Invasive Species  
J.L. Ram, Wayne State University


12:30-01:30 B/C Buffet Lunch

01:30 – 02:30 F/G/H Technical Session 7  
Chair, Mark Baskaran

Funding Agency Perspectives

NSF- Tele Conference with Don Rice

Larry Liou, NASA

Norm Grannemann, USGS

John Bratton, NOAA
Goals and Expectations for Breakout Sessions

M. Baskaran, Wayne State University

02:30 -04:00  J  Breakout Session 1A – Micro- and macro-nutrient and carbon cycling and tracer studies – field studies

I  Breakout Session 1B – Modeling, environmental/climate change and physical oceanography and how these affect the carbon and nutrient cycling

E  Breakout Session 1C – Exchange of water and nutrients between reservoirs; field and modeling studies; tracer studies

04:00 – 04:15  B/C  Refreshment Break

04:15 -05:30  Technical Session 8

Chair, Nathaniel Ostrom

J  Breakout Session 2A – Nearshore, shallow water dynamics and processes

I  Breakout Session 2B – Offshore, deep water and cross margin processes

E  Breakout Session 2C – Land margin interface and terrestrial aquatic coupling, atmospheric interactions

0:530 – 0:600  A  Steering Committee Meeting: Formative Workshop Assessment

05:30 – 06:30  Lobby  Posters

In Situ Approaches to Assess Sediment Contamination. Allen Burton, Anna Harrison, et al., University of Michigan
The importance of winter plankton assemblages in Lake Erie. **Hunter Carrick**, Central Michigan University

Surface ground Water Exchange. **Lynn Katrib**, Wayne State University

*The Dynamics of Hypoxia in Green Bay, Lake Michigan.* **Val Klump**, University of Wisconsin-Milwaukee

Comparative Effects of Climate on Green Bay Stratification. **Shelby LaBuhn**, University of Wisconsin-Milwaukee

*Sediment Loading Budgets in the Great Lakes Watershed.* **Carol Miller**, Wayne State University

Ecosystem Metabolism and Microbial Sources of $N_2O$ in Muskegon Lake, a Eutrophic Area of Concern. **Kateri Salk**, Michigan State University

Relative Contribution of Hypoxia and Natural Gas Drilling to Atmospheric Methane Emissions From Lake Erie. **Amy Townsend Small**, University of Cincinnati

Radiocarbon Distributions in Lake Superior, the World’s Largest Freshwater Lake. **Paul Zigah**, University of Minnesota-Duluth
**Appendix-A**

**Recent Changes in the Biogeochemistry of the Great Lakes System Workshop**

McGregor Conference Center

March 11-13, 2013

---

**Agenda**

**Wednesday March 13, 2013**

<table>
<thead>
<tr>
<th>Time</th>
<th>Group</th>
<th>Session/Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>07:30 – 08:30</td>
<td>B/C</td>
<td>Continental Breakfast</td>
</tr>
</tbody>
</table>
| 08:30 – 10:30 | F/G/H | **Technical Session 9**
               |       | Chairs, Jim Bauer/Mark Baskaran                        |
|               |       | Presentation of Breakout Group Session Summaries       |
|               |       | Discussion of Breakout Group Sessions                  |
| 10:30-10:50   | B/C   | Refreshment Break                                      |
| 10:50-12:00   | F/G/H | **Technical Session 10**
               |       | Chair, John Bratton                                    |
|               |       | Sensors and Monitoring Networks                        |
|               |       | Logistics for Field Sampling                           |
|               |       | *Ship Capabilities and Ongoing Efforts.* **Russell Kreis,** USEPA |
|               |       | *Blue Heron*                                            |
|               |       | University of Minnesota – Duluth                       |
|               |       | Final Session and Summary of the Workshops             |
| 12:00         | B/C   | Boxed lunch                                            |
|               |       | BOGLS Workshop Ends                                    |
| 12:00         | A     | Steering Committee Meeting: Summative Workshop Assessment |