FINAL REPORT
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INTERNAL LOADING OF PHOSPHORUS TO LAKE ERIE

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ABSTRACT

Although nutrient abatement strategies implemented in the Lake Erie watershed have reduced nutrient inputs to target levels, phosphorus concentrations in Lake Erie have begun to increase once again and signs of cultural eutrophication are again apparent. Although a number of hypotheses have been suggested to explain the phenomenon, the exact cause(s) are unknown. In particular, one of the poorly known components of the nutrient dynamics in the lake is the amount of phosphorus that is recycled to the water column by internal loading. The objective of this project was to obtain quantitative estimates of the internal flux of phosphorus to Lake Erie. Multiple approaches were employed to obtain these estimates, including 1) Fickian calculations from pore water phosphate concentrations, 2) mass balance calculations on organic phosphorus in the sediment solids, 3) aerobic and anaerobic incubations of whole short cores, 4) batch reactor experiments on slices of varying thicknesses of sediment cores, and 5) an incubation in a circular flume. The diffusive fluxes are in reasonably good agreement with those obtained by other methods (Matisoff et al., in prep) and the data from this study ranged from 0.58-4.93 mg P/m^2/d. Fluxes of resuspended sediment, as measured in batch reactors, were significantly higher, ranging up to 287 mg P/m^2/d.

The project formed the basis of training and theses for two female science students; one obtained a BA and the other a dual BA/MA. The results have been broadly shared with the scientific and management community. The work was presented at institutional poster presentations and at two international meetings and is incorporated into a draft manuscript that has been circulated to interested parties and soon will be submitted to the Journal of Great Lakes Research.

RATIONALE

During the 1960s Lake Erie experienced huge algal blooms, low-oxygen waters, and fish kills reflecting the effects of significant eutrophication. Research and predictions of empirical and computer ecosystem models (e.g., Vollenweider 1976; Schelske and Stoermer 1971; Charlton 1980; Di Toro and Connolly 1980) identified phosphorus control as the best means of controlling eutrophication. Target levels for phosphorus loading were determined by binational collaborative programs that led to the implementation of the Great Lakes Water Quality Agreement (IJC 1978) with a target annual total phosphorus (TP) loading to Lake Erie of 11,000 metric tons and the International Joint Commission (IJC) recommended programs that would achieve those loads (IJC 1983). Phosphorus loadings declined steadily beginning in the late 1970s from over 25,000 metric tons/y (MTA) to their present levels of 8,000-12,000 MTA (Dolan and McGunagle 2001; 2005), phytoplankton biomass and frequency of cyanobacterial blooms had decreased (Makarewicz 1993a), and oxygen depletion rates declined (Bertram 1993). However, since about the mid-1990s, Lake Erie has experienced a number of water quality and ecosystem changes (Matisoff and Ciborowski 2005). For example, although TP loadings have remained at or below the target loading of 11,000 metric tons/y (except during wet years characterized by marked flood pulses), the extent of harmful (*Microcystis)* and nuisance (*Cladophora)* algal blooms has increased (Conroy et al. 2005; Michalak, et. al. 2013), bottom waters in the Central Basin appear to have gone anoxic sooner in the late summer months, and the areal extent of the anoxia has increased relative to previous years (Rockwell and Warren 2003).

There are a number of potential explanations for these ecosystem and water quality changes, including: 1) increased internal loading of phosphorus possibly mediated by Dreissenid mussels (Conroy et al., 2005); 2) underestimation of some phosphorus inputs such as from urban storm water; 3) changes in the ecosystem that have led to altered nutrient uptake mechanisms and nutrient balances in the lake; 4) increases in bioavailable phosphorus loading despite relatively constant loadings of TP (Baker et al., 2014); and 5) weather/climate induced changes that affect lake levels, the timing of nutrient pulses, and water temperatures and wind events that affect sediment resuspension and transport and nutrient release (Ohio EPA 2010). Michalak, et. al. (2013) found similar causes in their analysis of the large 2011 *Microcystis* bloom, and concluded that similar blooms were likely to occur in the future unless changes in agricultural loading sources and climate stressors changed. These uncertainties indicate that a better understanding of the nutrient dynamics in Lake Erie is required before we can implement an appropriately designed Nutrient Management Plan, set target loadings, forecast future water quality and better target remedial actions and best management practices. In particular, one of the poorly known components of the nutrient dynamics in the lake is the amount of phosphorus that is recycled to the water column by internal loading. Not only does this unknown loading create uncertainty in the determination of the quantity of phosphorus delivered to the lake, but it also creates uncertainty in estimating the lag time between reductions in tributary loading and the time frame over which improvements in lake water quality are to be expected. The objective of the project was to obtain estimates of the internal loading of phosphorus to the water column.

APPROACH / KEY FINDINGS

The approach proposed for this project was to obtain quantitative estimates of the internal flux of phosphorus to Lake Erie using 4 different methods. The first approach was to obtain a core from both the central basin and from the western basin, analyze the pore waters and sediments for water content, C, N, TP, exchangable P, Mn, Fe, ^{210}Pb, ^{137}Cs, O_2, NO_3^-, Mn^{2+}, Fe^{2+}, SO_4^{2-}, HCO_3^-, NH_4^+, SRP, and conduct biogeochemical modeling of that data to obtain estimates of the phosphorus flux. These two cores were obtained and analyzed as proposed (and some additional analyses of the sediment P forms were conducted), and the data are reported in the Master's Thesis of a student (Steely 2015). The thesis is not appended to this report (it is 170 pages), but a copy is included on the CD that accompanies this report. It was proposed that those data were to be modeled by Dr. Maria Dittrich (University of Toronto) to obtain pore water and sediment profiles and an estimate of the phosphorus flux. To date those modeling results have not been received (Dr. Dittrich received no funding from this project and consequently her effort has been a low priority for her). However, we obtained phosphate fluxes from this data set using two other approaches. One approach used the pore water phosphate concentrations and obtained the flux using a Fickian calculation. The other approach used some additional P-form analyses in the sediment (developed by Dittrich and performed to provide her with a complete data set) and then the phosphate flux from the sediment was estimated from a mass balance on organic phosphorus. Both of these estimates are included in a manuscript (Matisoff et al., in prep) and in a conference presentation (Matisoff et al. 2015) summarizing these and other estimates of the phosphate flux from sediments in the western basin. For Station 91M in the western basin those values are 0.79 mg P/m^2/d using the Fickian calculation and 4.93 mg P/m^2/d using the mass balance model. At station 43 in the central basin those values are 0.63 and 0.95 mg P/m^2/d, respectively.

The second method to obtain an estimate of the phosphate flux from the sediment was to conduct whole core incubations on short cores that were collected from the same sites. Both aerobic and anaerobic incubations were conducted and analyzed as proposed. It was found that the concentration of phosphate in the water overlying the incubated cores increased nearly linearly with time over the first 8-24 hours permitting phosphate fluxes to be calculated. These results are presented in the Bachelor's Thesis of a student (Hummel 2014). The thesis is not appended to this report (it is 71 pages), but a copy is included on the CD that accompanies this report. These estimates are included in a manuscript (Matisoff et al., in prep) and in a conference presentation (Matisoff et al. 2015) summarizing these and other estimates of the phosphate flux from sediments in the western basin. For Station 91M in the western basin the fluxes under aerobic and anaerobic conditions are 2.67 mg P/m^2/d and 0.58 mg P/m^2/d, respectively. At station 43 in the central basin those values are 1.94 and 1.28 mg P/m^2/d, respectively. It should be noted that the fluxes under anaerobic conditions are probably underestimates because the short duration of the incubations (24 hr) probably did not provide sufficient time for the iron oxides to reduce and dissolve and thereby release their sorbed phosphate (Mortimer 1941).

The third method to estimate phosphate fluxes from the sediment given in the proposal was to conduct batch reactor experiments on cores slices up to 5cm deep. These results are presented in the Bachelor's Thesis of a student (Hummel 2014). The thesis is not appended to this report (it is 71 pages), but a copy is included on the CD that accompanies this report. For a 1 cm slice, for Station 91M in the western basin the fluxes under aerobic and anaerobic conditions are 89.6 mg P/m^2/d and 287 mg P/m^2/d, respectively. At station 43 in the central basin those values are 111 and 103 mg P/m^2/d, respectively. It should be noted that these fluxes are significantly higher than the diffusive fluxes determined by the other methods. No strong relationship between slice thickness and flux or between oxygen conditions and flux were observed. These results are not included with the other data in the internal loading manuscript since that paper focuses only on the diffusive release.

The fourth method proposed to use a circular flume to estimate the internal phosphorus loading to the water column under various rotation rates (bottom shear stresses) to permit an estimate of how the flux is affected by shear stress and sediment entrainment. One experiment of that type was conducted, but the measured phosphorus concentrations in the water column were below detection and no flux estimates resulted from that work. It was determined that this approach was not useful and was abandoned.

ACTIVITIES, TIMELINE AND DELIVERABLES

All proposed activities were completed. Supplies were purchased, students were trained, samples were collected and analyzed, experiments were conducted, data were processed and interpreted, results were presented to a broader audience and written as student theses, and the data and results have been integrated with other data from other projects and other workers to enable a broader interpretation of the results.

All proposed outcomes have been delivered as proposed. As proposed, the samples were analyzed for a broad spectrum of parameters to create a comprehensive data set on sediment chemistry that is suitable for internal loading estimates and biogeochemical modeling. Aerobic and anaerobic core incubation and batch experiments were conducted, circular flume experiments were conducted, and the data from all these data and experiments have been processed to obtain estimates of the phosphate flux from the sediments. The results of the work have been presented to a broader audience, shared with appropriate personnel and a draft publication to be submitted soon will insure wider availability of the results. The original proposal indicated that success would be measured by the project's ability to obtain estimates of the internal loadings of phosphate to the western basin and to the central basin of Lake Erie. Those results have been obtained and are summarized in this report indicating successful completion of the project.

PRODUCTS

Presentations:

Matisoff, G. Sediment Water Exchange Processes in Lake Erie. Lake Erie Millennium Network, October 29-31, 2013, Windsor, ON.

G. Matisoff, R. Steely, E. Kaltenberg, S. Hummel, J. Seo, K. Gibbons, T. Bridgeman, Y. Seo, L. Johnson, M. Dittrich, M.A. Evans, J.D. Chaffin. 2015. Internal Loading of Phosphorus in Western Lake Erie. 58th Conf. on Great Lakes Res., Intern. Assoc. Great Lakes Res., Burlington, VT.

Hummel, S. Effect of resuspension of phosphorus flux to Lake Erie. Source Intersections Fair, Case Western Reserve University, April 18, 2014.

Steely, R. Biogeochemistry of Lake Erie Sediments and Pore Water. Source Intersections Fair, Case Western Reserve University, April 18, 2014.

Steely, R. Biogeochemistry of Lake Erie Sediments and Pore Water. Research ShowCase, Case Western Reserve University, April 17, 2015.

Publications:

G. Matisoff, R. Steely, E. Kaltenberg, S. Hummel, J. Seo, K. Gibbons, T. Bridgeman, Y. Seo, M. Behbahani, W. James, L. Johnson, M. Dittrich, P. Doan, M.A. Evans, J.D. Chaffin. Internal Loading of Phosphorus in Western Lake Erie. To be submitted to the Journal of Great Lakes Research, in preparation.

Student Theses:

Hummel, S. 2014. Sediment Resuspension of Phosphorus Flux to Lake Erie. B.A. Thesis, Case Western Reserve University, 71 pp.

Steely, R. 2015. Biogeochemistry of Lake Erie Sediment and Pore Water. M.S. Thesis, Case Western Reserve University, 170pp.

ADDITIONAL BENEFITS

This small grant project was leveraged with a small grant from Ohio Sea Grant. One student was supported on this project and the other student was supported on the Ohio Sea Grant project. This small grant project led to the successful application of a larger proposal for a USEPA-Great Lakes Restoration Initiative Project, GL-00E01284 Assessment of Nutrient/Eurtrophication Dynamics in Western Lake Erie. The data from this small grant, from the GLRI project, and from other investigators have been combined to provide data for a basin-wide assessment of the internal diffusive flux of phosphate from the sediment. That compilation is being produced as a manuscript for publication (Matisoff et al., in prep). That paper will be useful to the State of Ohio in determining phosphorus loadings to the Lake, in estimating target loadings for maintenance of high water quality, and will provide data that can be used to estimate the time frame over which the lake will take to respond to changes in external loadings.

Two female science students completed their theses on Lake Erie. Stephanie Hummel completed her Bachelor's degree in May 2014 and is currently enrolled in a Master's degree program at Ohio State University. Her career goal is to become a park ranger. Rebecca Steely started this project as a Bachelor's Thesis, but continued on in a dual BA/MA program and received both of her degrees in May 2015. She is currently seeking employment in the environmental consulting field and recently had an interview with the Army Corps of Engineers.

DISSEMINATION

The results of this work have been shared the campus poster fairs, Intersections and Research ShowCase, at the Lake Erie Millennium Conference and at the Conference on Great Lakes Research. Copies of the theses have been made available to Joe DePinto at LimnoTech for inclusion in their Western Basin computer modeling. The draft of the manuscript has been circulated to all participants in the GLRI project, including LimnoTech and the Lake Erie Commission.

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