<u>Final Report for Ohio Water Resources Center</u>

Title: Quantifying direct groundwater discharge to Lake Erie and vulnerability to hidden nutrient loads

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1. Main Text

<u>Problem and Research Objectives</u>

Elevated nutrient inputs to the Great Lakes contribute to eutrophication and harmful algal blooms [*Michalak et al.*, 2013; *National Wildlife Federation*, 2011]. Harmful algal blooms are a major concern for federal and state governments and local communities because of negative impacts to aquatic ecosystems, fishery and tourism revenues, and essential drinking water resources. For example, a prolonged harmful algal bloom near Toledo, Ohio triggered a ban on tap water for 500,000 people in August of 2014. Lake Erie's shallow depth and short residence times render it particularly susceptible to nutrient contamination and harmful algal blooms [*Richards et al.*, 2010].

Nutrients can enter large lakes through river and groundwater inputs. Nutrient inputs from groundwater to the Great Lakes are poorly constrained, mainly because they are highly heterogeneous and broadly distributed along the coast [*Kornelsen and Coulibaly*, 2014; *Robinson*, 2015]. Groundwater fluxes to lakes can range by over five orders of magnitude [*Rosenberry et al.*, 2015]. Chemical fluxes are also obscured by variations in nutrient concentrations along discharging flow paths [*Frape and Patterson*, 1981; *Kroeger and Charette*, 2008; *LaBaugh et al.*, 1997; *Sawyer*, 2015]. For example, mineralization of organic matter may increase dissolved phosphorus concentrations, while sorption to sediment grains may reduce it [*Lewandowski et al.*, 2015]. Nitrate can be removed via denitrification in anoxic zones with a sufficient supply of organic carbon. Despite the potential for removal, nitrate concentrations in groundwater can exceed nitrate concentrations in rivers by an order of magnitude [*Valiela et al.*, 1990].

If nutrient concentrations in discharging groundwater are high, the groundwater-borne nutrient load can be high even if the rate of groundwater discharge is low [*Valiela et al.*, 1990]. In a review of lake studies, *Lewandoski et al.* [2015] found that typically groundwater-borne P loads across the sediment-water interface vary widely from 0.74 to 2900 mg PO_4-P m^{-2} yr^{-1}, while N loads vary widely from 0.001 to 640 g m^{-2} yr^{-1}. Groundwater inputs of phosphorus have been implicated as a possible contributor to algal fouling along the Lake Huron coast, although loads were not quantified [*Barton et al.*, 2013].

Deteriorating water quality in the Great Lakes and large uncertainties in nutrient sources motivate new studies on groundwater. A 2015 report for the Great Lakes Executive Committee identified several priority science needs for understanding groundwater effects on lake chemical, physical and biological integrity [*Grannemann and Van Stempvoort*, 2015]. The first two priority science needs are: 1) tools to characterize heterogeneity in groundwater/surface water exchanges, and 2) accurate quantification of groundwater discharge to surface water. Our study addresses both needs. ***Our first objective was to use a water budget approach to quantify direct groundwater discharge to Lake Erie and other parts of the Great Lakes coast. Our second objective was to use this information to assess areas that are vulnerable to high groundwater-borne nutrient loads and relate these vulnerability estimates to field***

measurements of groundwater-borne nutrient loads.

<u>Methodology</u>

<u>Geospatial analysis</u>. We estimated direct groundwater discharge rates to the Lake Erie coast using the water budget method of *Sawyer et al.* [2016]. In short, recharge zones for direct groundwater discharge were defined with NHDPlus [*McKay et al.*, 2012], a high-resolution hydrographic data available for the United States portion of the coast (43% of the entire Great Lakes coastline). We assumed that recharge zones are the wedge-shaped land areas outside stream catchments where water flows directly to the coast (Figure 1). We then assumed that recharge across these coastal catchments is the component of precipitation that infiltrates and would become base flow to a stream, if a stream were present, but instead flows to the coast.

Two types of data products from NHDPlus were used in this study: 1) the networks of rivers, streams and coastlines (a polyline product), and 2) their associated contributing catchments (a polygon product). These data products were obtained for the Great Lakes Region (Figure 1). A two-step process was used to estimate the geometry and size of recharge areas. First, coastlines were extracted from the polyline product using the feature type attribute. Second, the contributing catchments corresponding to each of the coastlines were extracted using the common NHDPlus integer identifier

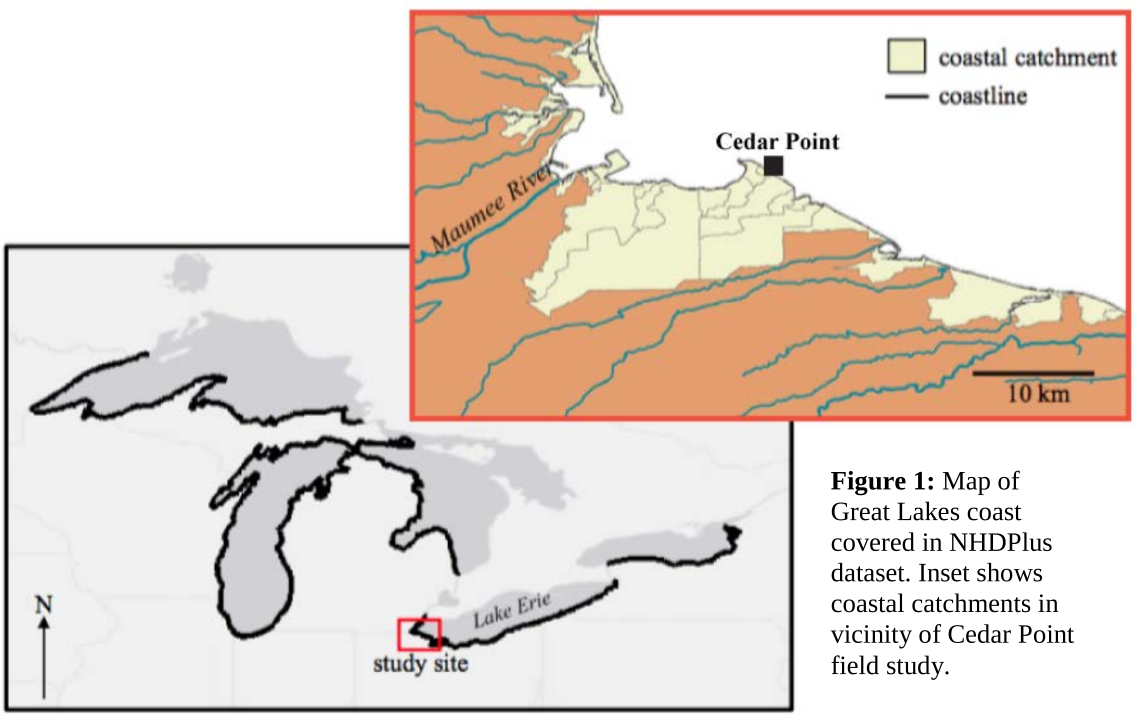

Figure 1: Map of Great Lakes coast covered in NHDPlus dataset. Inset shows coastal catchments in vicinity of Cedar Point field study.

relating polylines and polygons. Coastal catchments were then grouped by reach code. By construction, none of the coastal catchments contained streams, and instead the catchments were wedged between known intersections of streams and coast. The infiltrating precipitation within coastal catchments is assumed to flow to the coast and become direct groundwater discharge.

Infiltrating runoff was acquired from the second phase of NASA's North American Land Data Assimilation System, NLDAS2 [*Xia et al.*, 2012]. NLDAS2 provides a 30-year average monthly (1980-2009) dataset of terrestrial hydrologic quantities on a 1/8th degree (approximately 12.5 km) latitude-longitude grid over North America. We computed the recharge rate at each grid cell as the average of monthly infiltrating runoff from the NLDAS2 output based on the Variable Infiltration Capacity land surface model (VIC) [*Liang et al.*, 1994]. We excluded non-infiltrating runoff (another NLDAS2 product) because it presumably discharges to the coast as overland flow. We calculated annual recharge volume (m^3/y) across each coastal catchment by multiplying the catchment area by the annual recharge rate nearest to the catchment centroid. This calculation assigns the recharge rate at the NLDAS2 grid cell that is closest to the catchment centroid to the entire catchment, which is a valid assumption because the contributing catchments are much smaller than the size of the NLDAS2 grid cell. Finally, we divided the annual recharge volume by the corresponding coastline length to produce a flux (m^2/y). Uncertainty in the direct groundwater discharge rate was estimated using a multi-model ensemble produced with NLDAS2 output from the models VIC [*Liang et al.*, 1994], Mosaic [*Koster and Suarez*, 1994], and Noah [*Chen et al.*, 1997].

Next, we combined our estimates of direct groundwater discharge rates along the United States Great Lakes coast with land use data to map vulnerability to groundwater-borne nutrient loading. Where the direct groundwater discharge rate was above average and the fraction of total developed and agricultural land area was above average, we assumed that potential nutrient fluxes could be above average and designated these coastlines vulnerable to nutrient inputs from direct groundwater discharge. We determined the fraction of developed and agricultural land in each coastal catchment using the 2011 National Land Cover Database (http://www.mrlc.gov/nlcd2011.php). Specifically, we converted the raster dataset to a polygon shape file and summed the areas of developed, crop, and pasture land in each coastal recharge zone.

Field observations. Because vulnerability maps only indicate coastal regions with a greater likelihood of high nutrient inputs from groundwater, we conducted a detailed field study of a vulnerable coastal site to quantify groundwater-borne nutrient loads. The study site was located at Cedar Point Wildlife Refuge in the Western Lake Erie Basin (41°41'57.62"N, 83°19'32.95"W, Figure 1). Cedar Point is underlain by silty glacial till with a thin (1-2 m) veneer of highly permeable sand. The site is bordered by coastal wetlands, but the predominant land use within the entire coastal catchment is agricultural.

At the site, we measured direct groundwater seepage rates with Lee-type seepage meters (Figure 2). Specifically, twenty-four Lee-type seepage meters were deployed in three shore-perpendicular transects on the lake bed. Seepage meters were constructed from the ends of steel drums (internal diameter of 57 cm) modified from the design of *Lee* [1977] (Figure 2). Meters were spaced evenly in 5 or 10 meter intervals within each transect. The use of multiple transects allowed us to explore long-shore variation in seepage rates. We recorded the positions of the meters with a handheld GPS.

After installation of the meters, groundwater flow was allowed to equilibrate for one day prior to measurements. We measured seepage rates at a time with relatively calm nearshore conditions [*Shinn et al.*, 2002]. Measurements were conducted in two rounds and averaged to improve accuracy. Measurements were performed by connecting plastic autoclave bags to the meters via a quick connect valve (Figure 2). Bags were prefilled with 1.89 liters of lake water to allow measurement of recharge in addition to discharge. The prefilled bags were first weighed with a digital scale (±0.05 kg precision). The collection bags were then attached to the seepage meters for 3 hours. After collection, the bags were again weighed, and the volumetric seepage rate was calculated from the difference between the initial and final water mass in the bag and the density of water. The linear seepage rate was then calculated from the known cross-sectional area of the meter.

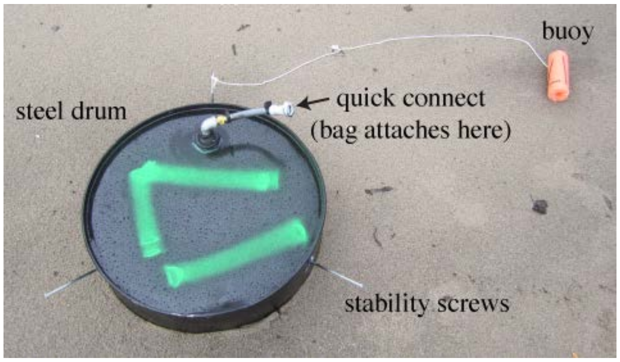

Figure 2: Photograph of a Lee-type seepage meter used by PI Sawyer's laboratory.

To understand fluxes of nutrients across the sediment-water interface, pore water samples were collected near each seepage meter (~1 m away) at 25 cm below the sediment-water interface. The samples were collected next to the meters instead of from the autoclave bags because the large steel meters restrict the supply of oxygen and can influence redox chemistry in the underlying groundwater. The sampling depth of 25 cm is somewhat arbitrary but was chosen to be deep enough to avoid drawing down lake water into the sampler but sufficiently close to the sediment-water interface to reflect the final chemistry of discharging groundwater as it flows through legacy lakebed sediments [*Lewandowski et al.*, 2015]. Pore water was collected by inserting a perforated steel tube with a 0.5-cm inner diameter and 0.6-cm outer diameter into the lakebed. The tube was purged by hand using a syringe, and the contents were discarded. The syringe was then used to collect 12 mL of pore water, which was filtered to 0.45 um and placed immediately in a cooler on ice. Samples were transferred from the cooler to a freezer within 12 hours of collection. Additional samples were collected for end-member waters that mix in shallow lakebed sediments (lake water and onshore groundwater). Onshore groundwater samples were collected from piezometers screened near the water table on the adjacent beach.

Samples were analyzed in the Geochemistry Lab at The Ohio State University for basic anions, including dissolved reactive phosphate (PO_4^{3-}), using Ion Chromatograph (IC). Samples were analyzed for ammonium (NH_4^+), and nitrate plus nitrite (NO_2^-+NO_3^-) using a Skalar flow-injection nutrient analyzer.

We calculated the mass flux of nitrate plus nitrite, ammonium, and dissolved phosphorus per unit length of coast by assuming fluxes are purely advective. This calculation neglects dispersive fluxes and may be an underestimate.

Principal Findings and Results

Estimated rates of direct groundwater discharge along the Great Lakes coast are highly variable, but generally are greatest for Lake Erie and Lake Michigan [*Knights et al.*, 2017] (Figure 3). The average direct groundwater discharge rate for Lake Erie is 477 $m^3\ y^{-1}\ m^{-1}$. At our Cedar Creek field site, measured discharge rates were significantly lower than water budget-based estimates (354 ± 25 m^3 y^{-1} m^{-1} compared to 588 ± 181 m^3 y^{-1} m^{-1}). This comparison underscores the uncertainties in attempting to estimate direct groundwater discharge rates, which can vary by orders of magnitude across different lithologies or sediment types.

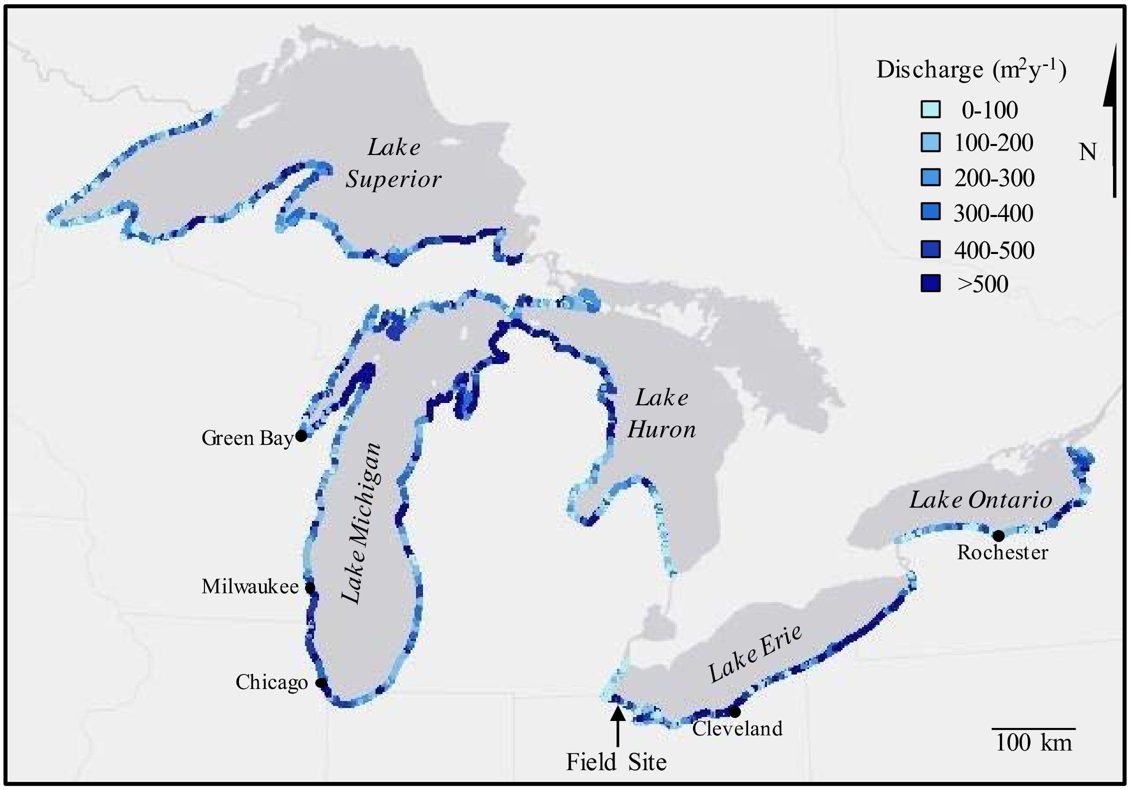

Figure 3: Direct ground water discharge to the Great Lakes. Discharge rates are high along the eastern and central sections of Lake Erie.

Approximately 15% of the analyzed Great Lakes coast is vulnerable to nutrient inputs from groundwater, and Lake Erie shoulders the highest vulnerability [*Knights et al.*, 2017]. Almost one-third of Lake Erie's United States coastline is vulnerable (Figure 4).

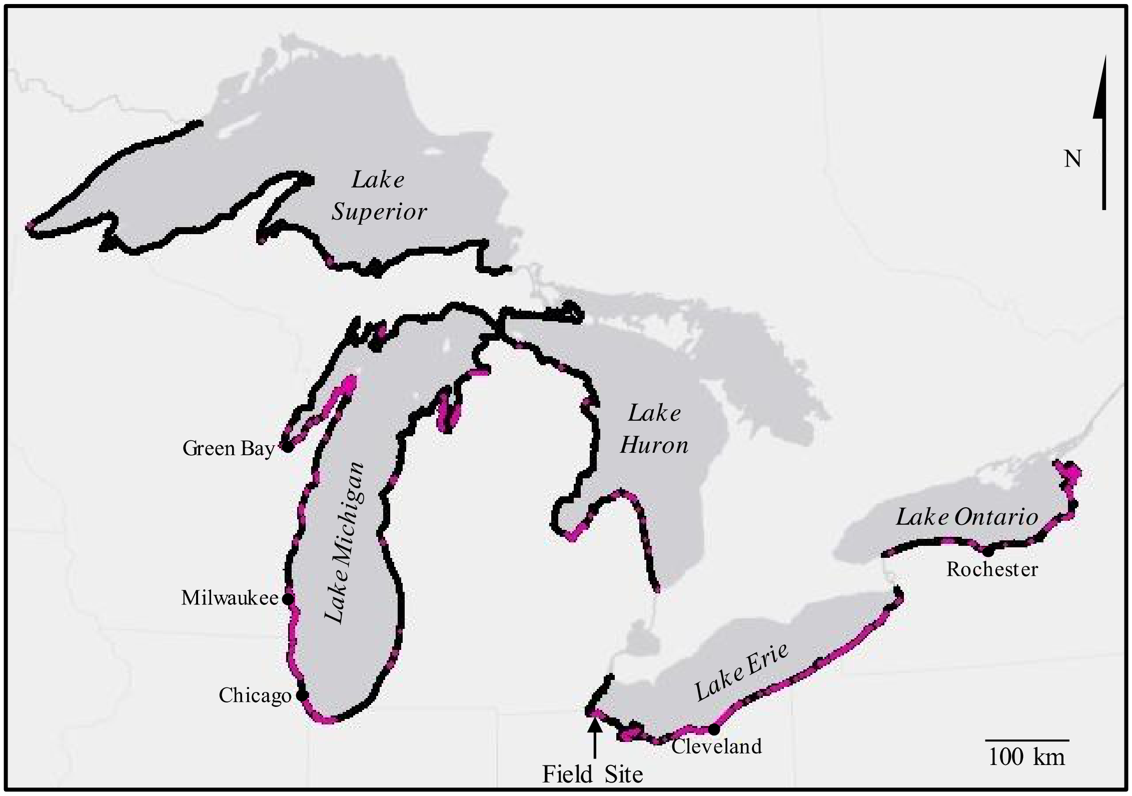

Figure 4: Vulnerability of Great Lakes to contaminant inputs from groundwater. Bright color represents vulnerable areas.

At our vulnerable field site, the mass flux of DP per unit length of shoreline was 86 ± 6.1 mg m^{-1} d^{-1}. Dissolved phosphorous concentrations in lakebed pore waters were elevated (average of 0.12 mg L^{-1}) compared to lake water and onshore groundwater (both below detection). Some of the measured phosphorus may be locally sourced from desorption of legacy P or mineralization of organic matter in the lakebed, which our vulnerability framework does not include.

The mass flux of DIN per unit length of shoreline was 2022 ± 141.3 mg m^{-1} d^{-1}. The average DIN concentration in lakebed pore water was 2.57 mg L^{-1}, which was greater than lake water but less than onshore groundwater. Much of the land-derived nitrogen may be removed by uptake or denitrification along groundwater flow paths prior to discharge.

An important question is whether groundwater is a significant source of nutrients to Lake Erie. We lack distributed chemical data from around Lake Erie to estimate the total flux of groundwater-borne nutrients. However, if we assume nutrient concentrations in groundwater discharge zones around Lake Erie are similar to those at the field site (average DP and DIN concentrations of 0.12 and 2.57 mg L^{-1}, respectively) and use an average direct groundwater discharge rate of 477 m^2 y^{-1} over a coastline length of 1400 km, the total DP and DIN fluxes to Lake Erie are 2.5 and 54.3 g s^{-1}, respectively [*Knights et al.*, 2017]. For comparison, these fluxes represent 13% of the DP load and 4% of the DIN load to Lake Erie by the Maumee River [*Baker et al.*, 2014; *Stow et al.*, 2015]. In summary, groundwater is potentially a small but non-negligible source of nutrients to

Lake Erie. Unlike discharge from a river, direct groundwater discharge is diffuse and exhibits high spatial heterogeneity. The complexity in quantifying direct groundwater discharge as a nonpoint source of contamination makes management difficult compared to point source loading.

Discharging groundwater tends to be nitrogen-rich and can therefore influence primary production [*Lapointe*, 1997; *Weiskel and Howes*, 1992]. Groundwater at our field site delivers a DIN:DP ratio of 147:1, far exceeding the Redfield ratio [*Knights et al.*, 2017]. In comparison, a N:P ratio of 21:1 was reported in lake water within the western basin of Lake Erie near Maumee Bay during the 2008 algal bloom [*Chaffin et al.*, 2011]. Assuming field measurements are representative of average P and N concentrations, discharging groundwater has the potential to exacerbate P limitation.

<u>Finding Significance</u>

We have produced a new understanding of the "hidden" water and nutrient inputs from coastal aquifers to the Great Lakes, which can guide our understanding of coastal water quality and ecosystem health. Our findings are highly pertinent to government officials at federal and state levels, as well as city planners. In a 2015 report, *Granneman and Van Stempvoort* stated: "No conceptual frameworks are available that can be applied as screening tools to evaluate the potential for direct groundwater discharge along a shoreline, and moreover to evaluate if groundwater may be an important pathway in delivering nutrients to nearshore waters" [*Grannemann and Van Stempvoort*, 2015]. This study has provided the highly sought framework. We produced maps of direct groundwater discharge rates and identified coastal areas that are vulnerable to groundwater-borne nutrient loads.

Our map products, which are freely available on Zenodo, can be used by scientists, practitioners, and stakeholders in a number of ways:

1) The groundwater discharge rates can be integrated in improved water budgets for Lake Erie and other Great Lakes. With additional groundwater chemistry information, nutrient fluxes can be estimated and used in nutrient budgets for whole lakes or localized nearshore areas.
2) Maps can be used to target areas for groundwater and lake water quality monitoring.
3) Vulnerability estimates can be improved with local information and used to guide coastal development strategies or best management practices. For example, maps of groundwater discharge rates can be combined with site-specific data on agricultural practices or septic tank distributions to further understand potential nutrient inputs. These areas can then be targeted for improved sewer infrastructure, wetland reconstruction, precision fertilizer application, or a number of other projects designed to improve groundwater quality.

Many factors control nutrient fluxes to the coast (including rates of key reactions such as denitrification, residence times, and the history of land use change or fertilizer applications). Therefore, our vulnerability designation is only a qualitative assessment of areas that may have high groundwater-borne nutrient loads. We recommend more field measurements of groundwater-borne nitrogen and phosphorus loads to provide additional context for our vulnerability maps and determine when and where the vulnerability designation is most reliable (for which nutrients and hydrogeologic conditions).

Highlights:

• 43% of the U.S. Great Lakes' coast is vulnerable to groundwater-borne nutrients.
• Lake Erie has the greatest fraction of vulnerable shoreline.
• Lakebed sediments are a source of dissolved phosphorous at discharge zones.
• Some nitrate removal occurs along groundwater flow paths prior to discharge.

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