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Dataset Title: Concentrations and isotope values of nitrogen forms during 2020 Lake Erie Cyanobacterial harmful algal bloom

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RESEARCH OVERVIEW

Nitrogen availability is hypothesized to play a central role in cyanoHAB progression, as well as production of the nitrogen-rich toxin microcystin. Recent work implicated reduced nitrogen substrates like ammonium and dissolved organic nitrogen (DON) in promoting greater bloom biomass and longevity. To examine the relative importance of oxidized and reduced nitrogen substrates to phytoplankton during different bloom stages, we measured concentrations and natural abundance δ15N isotope values of dissolved nitrogen substrates and phytoplankton biomass throughout the entirety of the 2020 cyanoHAB in Western Lake Erie. This is the first data on DON concentrations and isotope values in Western Lake Erie. We measured nitrate concentrations and isotope values to compare with DON and also with particulate organic matter 15N isotope values. This dataset is described and analyzed in the publication, "Patterns in sources and forms of nitrogen during a freshwater cyanobacterial harmful algal bloom".

METHODS

Sample collection:

Samples were collected approximately weekly between mid-June and late September 2020, from three stations in the western basin of Lake Erie (coordinates in 2020LakeErie\_forDeepBlue\_data.csv file).

Sample Processing:

Water samples were collected from 0-1 m below the surface using a peristaltic pump and tubing, then transported in carboys back to the lab. Water quality parameters such as temperature, specific conductivity, and turbidity were measured using an on-board CTD profiler. In the lab, particulate organic matter (POM) was collected by vacuum filtering 2L of water through pre-combusted glass fiber filters (GFF, 0.7 µm nominal pore size). Filters were frozen at -80°C, and the filtrate was subsequently filtered through 0.2 µm polyethersulfone flat filters and collected for nutrient and fluorescence (EEMs) analysis. Nutrient samples were frozen at -20°C until analysis, while EEMs samples were stored at 4°C. All water samples were filtered and stored on the same day they were collected.

Sample analysis:

Dissolved nutrient and microcystin concentrations were determined at the Cooperative Institute for Great Lakes Research (CIGLR) at the University of Michigan. All N substrate concentrations are reported as µM N. Isotope values are reported as δ values, in units of permil (‰).

δ15N values of NO3- and total dissolved N (TDN, includes NO3-, NO2-, NH4+, and DON) were measured using the denitrifier method (Sigman et al. 2001; Casciotti et al. 2002), on a Delta V Advantage isotope ratio mass spectrometer with a custom built purge and trap system. Isotope measurements were standardized to the N2 reference scale using standard reference materials IAEA N3 and USGS 34.

TDN was measured using persulfate oxidation to NO3-, followed by the denitrifier method (Knapp et al. 2005). To oxidize TDN to NO3-, 12 mL of sample was combined with 1.5 mL of fresh persulfate oxidizing reagent (POR) in a pre-combusted 16 mL glass vial with PTFE-lined cap (Wheaton EC sample vials, DWK part #224746), and autoclaved for 45 minutes on a slow-vent or liquid setting. POR consists of 3 g ACS grade NaOH and 3 g of re-crystallized potassium persulfate (K2S2O8) dissolved in 100 mL of ultrapure water. The K2S2O8 was re-crystallized by slowly adding water until all was dissolved, then re-crystallizing on ice for 1 hr, pouring off supernatant, and repeating for a total of three times. After the final recrystallization, the K2S2O8 was vacuum filtered through qualitative filter paper, rinsed thoroughly with methanol, and left to dry for a few minutes under vacuum. Recrystallized K2S2O8 was always stored in a desiccator, protected from light, and used within a week. POR was always prepared immediately before use. Each batch of samples was autoclaved with three vials containing only 12 mL of POR, to determine the size and δ15N value of any N contamination associated with the POR.

Before isotope analysis, the concentration of NO3-in both unoxidized and oxidized samples was measured using a chemiluminescent NOx analyzer (Teledyne NO/NOx Analyzer 200E). The concentration of DON was calculated by subtracting the concentrations of NH4+ and NO3-in the unoxidized samples from the N concentration of the persulfate oxidized TDN samples. TDN concentration was corrected for any N contamination in the POR blanks, but this was always <0.5 µM or below detection. The concentrations and δ15N values of TDN and NO3- were used to calculate the δ15N value of total reduced N (δ15NTRN) by mass balance:

δ15NTRN = (δ15NTDN × [TDN] – δ15NNO3 × [NO3-])/ [TRN]

TRN is mostly DON, but includes some NH4+ as well, especially at the beginning of the sampling season. We were unable to measure the δ15N of NH4+ as part of this study and therefore report isotope values as “δ15NTRN” rather than “δ15NDON”. The average precision for both δ15NNO3 and δ15NTDN was 0.3‰, and propagation of error results in an average precision for δ15NTRN of 0.7‰.

POM analysis: GFF filters were dried at 50°C overnight, then subsampled for isotope analysis using a cork borer. Subsamples were placed into tin capsules (Costech), which were folded and crushed to remove air, then analyzed on a Thermo Scientific Flash IRMS Elemental Analyzer with EA Isolink, coupled to a Delta V Advantage IRMS through a Conflo IV universal interface. Sample δ15N values were calculated using in-house laboratory standards as well as standard reference materials USGS40 and USGS41a.

REFERENCES

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FILE INVENTORY

2020LakeErie\_forDeepBlue\_data.csv : contains all data associated with this entry

Definitions\_of\_terms\_and\_variables.csv : contains explanation of column names and terms for data contained in 2020LakeErie\_forDeepBlue\_data.csv

DEFINITIONS OF TERMS AND VARIABLES

See “Definitions\_of\_terms\_and\_variables.csv” file

Data is organized by station and then by date (in 2020LakeErie\_forDeepBlue\_data.csv)

OTHER

Related publications: Kharbush, J.J., Robinson, R.S., Carter, S.J. “Patterns in sources and forms of nitrogen in a large eutrophic lake during a cyanobacterial harmful algal bloom.” In press. Limnology and Oceanography.

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