Global Aquatic Research LLC

Canandaigua Lake Foam Research, 2019-2020: Final Report

Photo by Marty Lasher, 9/18/19

For: Canandaigua Lake Watershed Association, November 2020

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Report Notes: This report has been prepared for research purposes only. Please contact us at globalaquaticresearch@gmail.com with any questions.

1. Synopsis

1.1 Project Description

The purpose of this study was to identify the dominant source(s) of foam on Canandaigua Lake, and the extent to which the foam may concentrate algal toxins or persistent organic pollutants. We developed a citizen-scientist based foam sighting and sampling protocol, and gained an understanding of foam-formation dynamics by reviewing the submitted photos and reports. Using this information, we collected samples of several foam events, as well as lake water, stream water, and biota (mussels, phytoplankton, macroalgae), and compared their chemical signatures. We provided a broad organic matter overview by measuring organic carbon and nitrogen concentrations, ratios (C/N), and stable isotopic signatures ($\delta^{13}C$ and $\delta^{15}N$), determined relative amounts of major biological macromolecules (lipids, proteins and carbohydrates) using Fourier Transform Infrared (FTIR) spectroscopy, and analyzed samples for total lipid weight and fatty acid distributions. The results and findings are summarized below and provided in detail throughout this document

1.2 Summary of Findings

The analysis presented here shows that foam in Canandaigua Lake has a fundamentally different chemistry than the surrounding lake water. The chemistry of the foam is also different than water coming from the streams, and did not match the bulk biomass of the macrophytes, mussels, and plankton we examined. Chemical analysis of the foam did suggest that it consists primarily of organic matter produced within the lake, and it appears to be dominated by polysaccharides (biologically produced chains of sugars). A likely explanation for the polysaccharide source is extracellular polymeric substances (EPSs) produced by algae, possibly the cyanobacteria *Microcystis aeruginosa.*

These EPSs are produced during blue-green algae (cyanobacteria) blooms and excreted outside of the cells to serve multiple biological functions. The EPSs, rich in polysaccharides, enter the dissolved organic matter (DOM) pool of the lake, preferentially accumulate at the air-water interface, and create conditions favorable for stable foam formation when the water is agitated by wind, waves, or currents. The foam is therefore likely the end-result of an ecosystem shift onset by the invasion of invasive dreissenid mussels, which have fostered the proliferation of harmful algal blooms (HABs) and promote favorable nutrient conditions for bloom formation and EPS production. In addition to EPS contributions by the HABs, we found that both quagga mussels and macrophytes also have polysaccharides that may contribute to foam formation.

However, more research needs to be done, because it is possible that trace amounts of a yet unidentified chemical(s) contributes to the stability of foam produced in Canandaigua Lake. We still do not know why Canandaigua seems to have larger, more stable foaming events than other Finger Lakes that are also seeing HABs and invasive mussels, and exploring seasonal changes in foam composition as well as working to identify trace chemicals are suggested next

steps. Finally, we found that foam has the potential to concentrate microcystins from HABs and polychlorinated biphenyls (PCBs) from the lake, but the concentrations found were not consistently high (or low) and we did not find any identifiable patterns between different samples.

2. Introduction

Canandaigua lake is the 3rd largest of New York State's Finger Lakes by volume (433 billion gallons of freshwater, CLWA 2014) and the 4th largest by surface area (42.3 km^2, DEC, LMAS, NYSFOLA, 2019). It has a AA water quality rating from the New York State Department of Environmental Conservation (NYSDEC) and is oligo-mesotrophic (low to moderate primary productivity), making it an important resource for recreation, drinking water, and fishing (CLWA 2014). However, in recent years, Canandaigua Lake has seen the emergence of HABs. In particular, *Microcystis aeruginosa*, a cyanobacteria that produces microcystins, a class of hepatotoxins (destructive to liver cells), has resulted in numerous beach closures in the late summer and early fall. Additionally, invasive dreissenid mussels (zebra and quagga) have established themselves in the lake and have resulted in changes to nutrient cycling, phytoplankton ecology, and water clarity (Halfman and Bush, 2005; Karatayev et al., 2014). While many of the Finger Lakes are experiencing these environmental concerns, Canandaigua Lake, in particular, has experienced the production of large quantities of stable surface foam that appears as streaks mid-lake and washes up on the shoreline in thick layers where it may persist for days.

Foam is a frequent occurrence in aquatic systems, and is produced in lakes and rivers from natural biological material or from point-source pollution (Schilling and Zessner 2011, and references therein). In the most basic sense, foam is formed when the rate at which air is injected into water exceeds the rate at which the liquid surrounding the formed bubbles can drain (Napolitano and Cicerone 1999). The chemistry of the very surface of the water, referred to as the surface microlayer (SML) and occupying the uppermost 1mm of the water column, ultimately controls the stability of bubbles and the likelihood of foam formation (Zhang et al., 2003). Lake foam is produced when the SML accumulates foaming agents, or compounds that reduce the surface tension of water, and is agitated by wind, waves, or currents. Foaming agents can be contributed by numerous sources within the lake, including phytoplankton (e g. green algae, cyanobacteria), zooplankton, macrophytes, abundant fauna (e.g. invasive mussels), and bacteria. Additionally, many sources of foaming agents exist in the terrestrial environment and are contributed through creeks or surface runoff, including humic and fulvic substances in soils, lipids from native and invasive plants, detergents and discharge from industry or wastewater treatment.

Based on previous reports that the foam is natural in origin (Boyer 2003, communication), we used an analytical strategy that has been applied to separating organic matter sources in complex mixtures to identify the source of the foam. This strategy combines both a "bulk" approach that examines the elemental signatures of the organic matter pool as a whole, and a "biomarker" approach that examines the distributions of one or more individual

compound classes, in both the unknown matrix (in this case foam) and its possible contributors ("end-members"). This approach has been applied to aquatic systems across the globe where complex organic matter mixtures exist (e.g. Gordon and Goñi 2003, Smith et al. 2010, Bianchi and Canuel 2011, Castañeda and Schouten 2011, Smith et al. 2012, Carlin et al. 2020). Here, the bulk approach measures the organic carbon to nitrogen ratios (C/N) and stable isotope (organic $\delta^{13}C$ and $\delta^{15}N$) values of the entire foam organic matter mixture, and can identify the dominant primary producer(s) that contributed the material. For example, terrestrial producers (vascular plants) have higher C/N ratios than aquatic producers (algae), and more depleted $\delta^{13}C$ and $\delta^{15}N$ values (Hedges & Parker, 1976; Goñi et al., 1997; Perdue & Koprivnjak, 2007; Meyers, 2003). The biomarker approach focused on fatty acid distributions, which also differentiate terrestrial and marine inputs but provide additional source-specific information as individual types of aquatic organisms, terrestrial plants, and bacteria produce different amounts and types of fatty acids (Napolitano 1999). In addition, we used Fourier Transform Infrared Spectroscopy (FTIR), which provides both a signature of the whole organic matter pool and also identifies the relative concentrations of the major classes of biomolecules (lipids, carbohydrates, proteins). Together, these methods provide a powerful way to trace organic matter in the foam back to its original source.

Additionally, we examined the potential for foam to concentrate compounds harmful to human health. SMLs, and thus foam, can concentrate metals and surface-active and lipophilic pollutants from water and sediments (Elzerman and Armstrong 1979, Rice et al. 1982 Napolitano and Richmond 1995). PCBs, a class of toxic persistent organic pollutants with 209 congeners, were produced in large quantities between 1929 and 1979 for a range of industrial purposes and are found contaminating aquatic systems worldwide (Hornbuckle et al. 2006 and references therein). The hydrophobic properties of PCBs cause them to accumulate in the SML of natural waters (Rice et al. 1982), and they can be enriched in lake foam 100-1000 times over background lake water concentrations (Eisenreich et al. 1978). We used an enzyme-linked immunosorbent assay (ELISA) to determine total PCB concentrations in both the lake water and foam samples taken from Canandaigua Lake. Finally, we examined the potential for foam to concentration microcystins. To our knowledge no data exists on the enrichment of microcystins in lake foams, but due to their protein-like structure (cyclic peptides), stability, and the timing of HABs and foam production (Butler et al. 2009 and references therein), we also assessed their concentration in lake and foam samples using an ELISA technique.

3. Foam Sighting Summary

126 foam sightings on the lake were reported from 9/6/19 to 10/26/20 (Figure 1). Foam was observed in nearly all portions of the lake, with more sightings reported in the northern half. September of 2019 had the highest frequency of sightings, with 28 reports submitted. However, when August was included in 2020, more sightings were submitted during that month (26) than in the following September (21). The foam 'season' seems to last from August to November, although foam was observed during all months with the exception of January 2020. We are not yet sure how the total amount of time sighters spent observing the lake

based on the number of volunteers, seasonal changes in lake usage, and the timing of other sighting programs (e.g. HABs), has skewed the observed patterns.

29% of foam sightings were reported to have followed an algae bloom (Figure 1), on average 3 days prior to the observed foam. The former value may be an underestimate as foam reports could be made at any time without a thorough bloom survey beforehand. Foam was most commonly observed as a combination of streaks and/or build-up along shore, and when reported (45/126 events) 56% of the events were considered large (40%) or widespread (16%). The majority of foam was 2" or less thick and contained plant fragments (Figure 2), but accumulations >12" were occasionally observed.

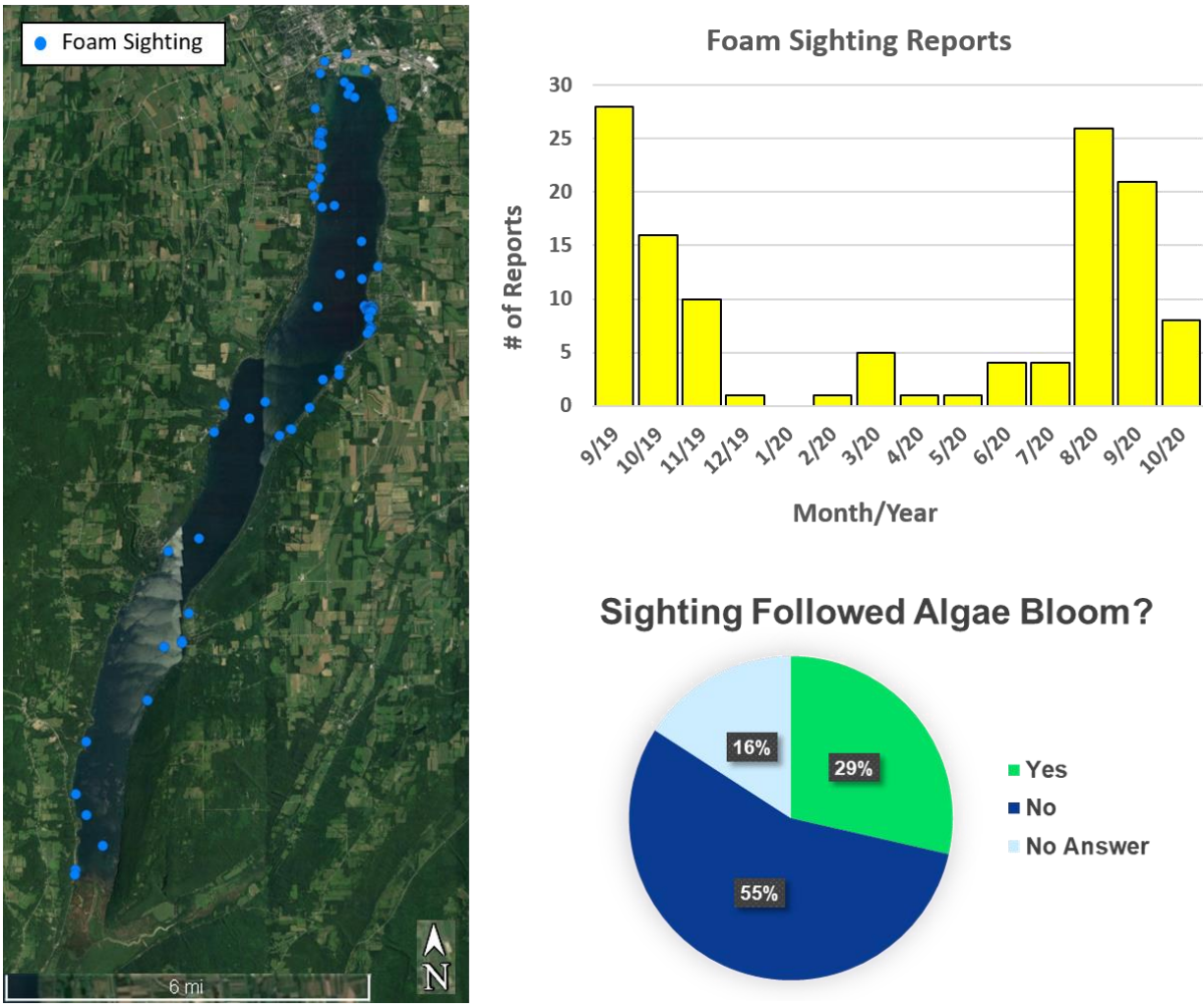

Figure 1 - Foam sighting report locations are indicated by blue dots on the Canandaigua Lake Map. The bar chart shows the total number of reports submitted each month from September 2019 to October 2020. The pie chart shows the distribution of responses when asked if the foam followed an algae bloom.

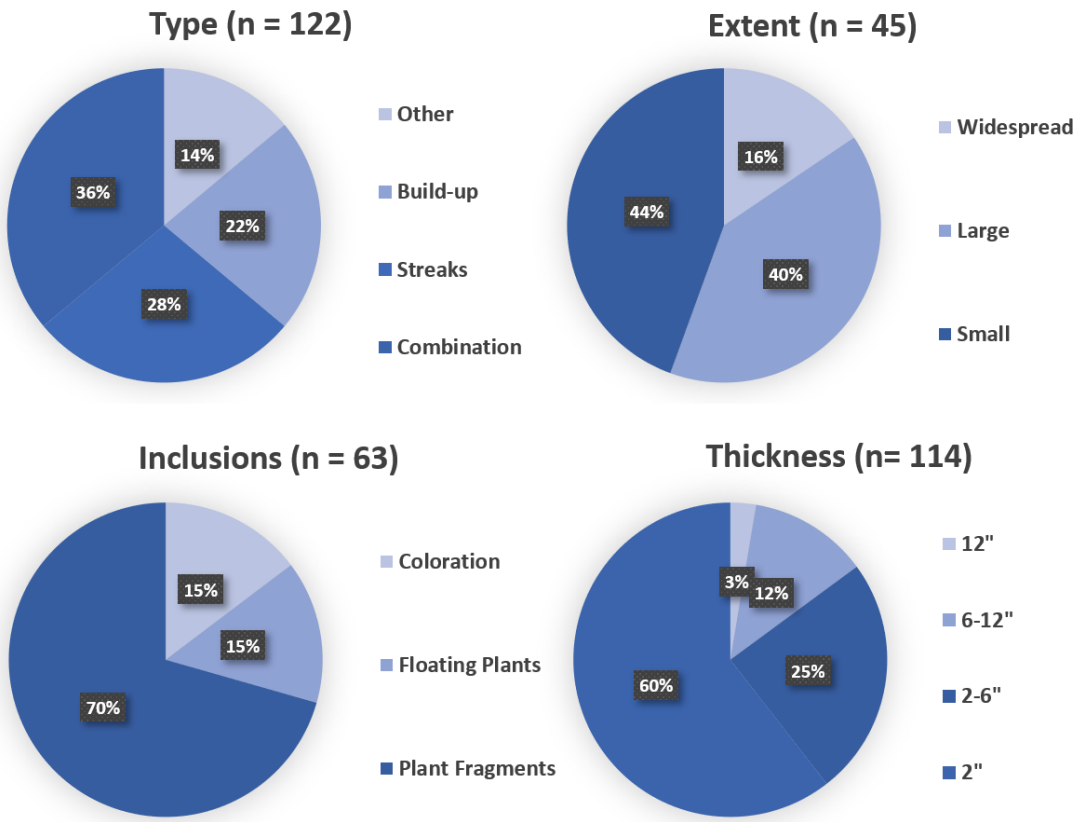

Figure 2 - Foam characteristics as determined from the online reporting tool. The n values show, out of the 126 total reports, how many sightings answered each specific question

4. Sample Descriptions

Eight Foam samples were collected and 6 were chosen for both bulk C and N and fatty acid analysis, with an additional sample analyzed for fatty acids (7 total, Figure 3). The samples were chosen to represent both the northern and southern portions of the lake, as well as a mix of shoreline (Wo_09.13.19, Nap_10.28.19, Klotz_09.07.19) and mid-lake (La_09.18.19, La_09.27.19, Me_10.01.19, Vine_10.08.19, GP_10.08.19) events. The foam IDs contain the dates during which they were sampled, and all were during September and October of 2019. Additionally, we collected a suite of end-members including water from 7 streams (West River, Naples Creek, Cottage City, Bare Hill, Menteth Gully, Seneca Point, and Sucker Brook, Figure 3), a phytoplankton tow, quagga mussels, and 2 macrophyte samples. Zebra mussels were not present in significant quantity in any of our mussel sampling efforts to yield enough material for analysis. The macrophyte samples were taken directly from the foam samples, and the first was primarily eelgrass chop with some other larger seaweeds and the second primarily a mix of watermeal and duckweed.

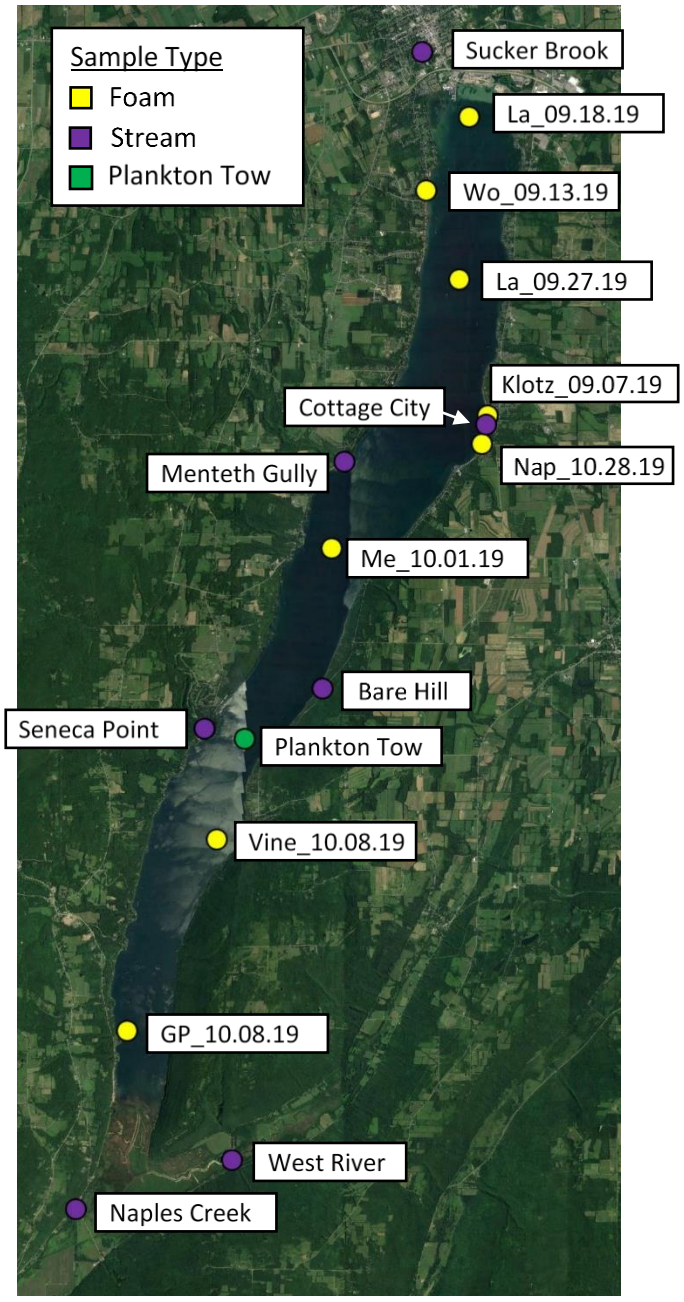

Figure 3 - Foam, stream, and plankton sampling locations. Stream IDs are either common names or the location of their outflow. Lake water samples were taken at the same locations as the foam samples, as well as one near the plankton tow that was not associated with a foam event (Smi_08.19.19)

5. Methods

5.1 Sampling

5.1.1 Aqueous Samples

Foam was sampled by scooping foam from the surface of the water or shoreline with stainless steel strainers into acid-rinsed (2N HCl) 7-gallon HDPE buckets. The buckets were immediately sealed and stored refrigerated until the foam had completely or partially collapsed into a water sample, ranging from 1-3 days. Partially collapsed foam samples were manually agitated to collapse the rest of the foam. The resulting water was coarse-filtered by pouring it through a fine stainless steel mesh (~1mm) into acid-rinsed 1L HDPE bottles in order to remove the macrophytes (typically watermeal and duckweed) and/or macrophyte fragments (typically eelgrass, milfoil, coontail) present. Some combination of these plants was found in all samples. La_09.27.19 was coarse-filtered onboard and immediately processed to observe the effects of storing with these plant inclusions present. A portion (~100-300mls) of the coarse-filtered foam samples was filtered through 0.7uM glass-fiber filters (Whatman GFFs) using vacuum filtration to isolate the dissolved (what passes through the filter) and particulate (what is left on the filter) phases. The filters were stored frozen and freeze-dried for total suspended solids (TSS), C and N analysis. A portion of the filtered foam (FF) was collected into combusted 40ml amber glass DOC vials with PTFE-lined caps, and stored frozen for DOC (concentrations and $\delta^{13}C$), TDN concentrations, and ELISA plate (microcystins and PCBs) analysis. The rest was filtered directly into 500ml combusted glass DO bottles, acidified to a pH of ~2.5 with 12N HCl, and analyzed for lipids within 1-2 days. Klotz_09.07.19 was used to observe potential impacts of storage times, and was kept refrigerated for ~2 months before all

analyses were performed. Of the remaining coarse filtered foam samples (considered 'unfiltered foam,' or UF, as only large plant material was removed), ~500-700mls were frozen and saved for ELISA plate analysis. Two of the UF samples were freeze-dried (La_09.18.19 and Wo_09.13.19) and used for FTIR and C and N analyses

Lake water samples were taken near each foam event in "foam-free" water, and stored refrigerated for ~1-3 days (identical to their corresponding foam sample) in 1L HDPE bottles. 1-2 L of lake water was filtered through 0.7uM filters using a peristaltic pump. Aliquots of both the filtered lake water (FLW) and unfiltered lake water (ULW) were stored in 40ml combusted amber glass DOC vials and acid-rinsed 1L HDPE bottles, respectively, and immediately frozen along with the filters. FLW and ULW samples were used for ELISA plate analysis, and FLW water samples were measured for DOC, TDN, and δ^{13}C-DOC. Filters were analyzed for particulate C and N concentrations and isotopes. The seven streams, chosen to represent diverse watershed usage (see Makarewicz and Lewis 2000 and Makarewicz et al. 2001), were sampled and processed using the same methods as the lake water samples.

5.1.2 Tissue Samples

Surface water plankton were collected offshore near Seneca Point using a plankton tow. The collected plankton were rinsed into acid-rinsed 1L HDPE bottles using ultrapure milli-Q water, and stored refrigerated overnight. The sample was then decanted, frozen, and freeze-dried for fatty acid, FTIR and C and N analysis. Prior to freezing, a sub-sample of the plankton was viewed under a microscope at the Finger Lakes Institute (FLI, Hobart William Smith Colleges). The plankton community was diverse, and the presence of significant amounts of *Microcystis* cyanobacteria was confirmed visually.

Quagga mussels were collected from several sites along the lake spanning a range of depths (20-70 ft). Mussels were stored live and refrigerated in lake water until processing. Larger specimens were selected and thoroughly rinsed with milli-Q water before mussel tissues were mechanically separated from their shells. The tissue samples were then frozen, freeze-dried, homogenized, and subsampled for fatty acid, FTIR, and C and N analysis

Samples of each type of macrophyte inclusion (a mix of watermeal/duckweed, and a mix of eelgrass/coontail chop) were collected from the mesh after foam coarse-filtration, stored frozen and later analyzed as the two macrophyte end-members. These were freeze-dried, homogenized, and subsampled for fatty acid, FTIR, and C and N analysis

5.2 Bulk C and N Analysis

Filtered water samples (lake water, stream, collapsed foam) were analyzed for concentrations of dissolved organic carbon (DOC) and total dissolved nitrogen (TDN), as well as the stable isotopic composition of DOC (δ^{13}C-DOC), based on methods in Zigah et al. (2017). The DOC and TDN concentrations were converted to moles and used to calculate C/N ratios.

Determining the stable isotopic composition of nitrogen ($\delta^{15}N$) in the aqueous samples was not possible due to low concentrations.

Biological tissues (macroalgae, quagga mussels, plankton), freeze-dried foam samples (La_09.18.19, Wo_09.13.19), and particulates (0.7 um filters from water and foam samples) were analyzed for percent organic carbon (%OC), percent nitrogen (%N), and the stable isotopic compositions of organic carbon ($\delta^{13}C$) and total nitrogen ($\delta^{15}N$). Briefly, samples were freeze-dried, homogenized, fumigated with HCl (12N for 8 hours) to remove inorganic carbon, and analyzed via an elemental analyzer – isotope ratio mass spectrometer (EA-IRMS) according to the methods of Hedges and Stern (1984). %OC and %N values were converted to molar quantities and used to determine C/N ratios.

5.3 Lipids

The concentration of total lipids and the distribution of fatty acids was determined for foam and biological tissue samples. Stream and lake water samples did not produce enough lipids for analysis. Lipid analysis was based on the methods in Canuel and Martens (1993).

The biological samples were freeze-dried, homogenized, and extracted with a 65:35% mixture of dichloromethane (DCM) to methanol (MeOH) using an accelerated solvent extractor (ASE). The extracts were purified via a bligh-dyer extraction procedure (Bligh and Dyer 1959), and dried to obtain the total mass of lipids extracted. The lipid extracts were sub-sampled, saponified, transmethylated, and analyzed via gas chromatography/mass spectrometry (GC/MS) as their fatty acid methyl ester (FAME) derivatives according to the methods of Happel et al. (2017). Individual FAs were identified based on a comparison of their mass spectra and retention times to an analytical standard (Supelco 37 component FAME mix, CRM 47885). All identified FA peaks were summed, and each compound is reported as % relative abundance based on the fractional area of its peak to the total.

Foam samples were acidified to a pH of 2.5 using 12N HCl, and FAs in the foam samples were directly extracted based on methods in Canuel and Martens (1993) by adding methanol and dichloromethane directly to the foam sample to reach the desired DCM:MeOH:H_2O ratio. Subsequent procedures were identical to the biological samples.

5.4 FTIR

FTIR characterizes the macromolecular composition of a bulk sample. In other words, this imaging technique produces a qualitative assessment of the relative amount of proteins, lipids, and carbohydrates (Fanesi et al. 2019). The theory behind this technique is that different molecular structures absorb different amounts of IR at specific wavelengths, and FTIR analysis produces peaks of higher IR absorbance that are proportional in size to the macromolecular class or chemical functional group known to produce a response at that wavelength. FTIR was performed on solid samples (freeze-dried foam, biological tissues) based on methods in Hendrickson et al. (2018).

5.5 Microcystins

To measure concentrations of microcystins, we used the Microcystins-ADDA ELISA microtiter plate method (Eurofins Abraxis #520011). The test is congener-independent, and thus the concentrations reported reflect the sum of all microcystin congeners, given as microcystin-LR equivalents. The detection limit for this method is 0.1 ppb, and reproducibility is typically within 10 % (% CV). Sample collection, storage, processing, and quantification were based on EPA method 546, and manufacturer provided directions were closely followed. Both filtered and unfiltered lake water and foam samples were stored frozen. The unfiltered samples thus had lysed cells, and determined concentrations are the sum of intracellular, extracellular, and particle-associated toxins. For filtered samples, the filtering was performed before freezing, and thus these reflect extracellular microcystins (dissolved) only. Samples were analyzed in duplicate, and quantified based on comparison to a standard curve. Standards ranged from 0.15 to 5.0 ppb and were also analyzed in duplicate. Samples with responses lower than the lowest standard were reported as < 0.15 ppb or below detection. Samples with responses higher than the highest standard were diluted and re-analysed until they were within range. A standard blank (Std 0 in ELISA kit) and a field blank (milli-q water stored in a sampling bucket) as well as a quality control sample with a known concentration (0.75 +/- 0.185 ppb), were also included in the analysis. The control had an acceptable mean value (0.655 ppb) and both blanks were below the limit of detection (< 0.1 ppb).

5.6 PCBs

To measure concentrations of PCBs, we used the PCB ELISA microtiter plate method (Eurofins Abraxis #530041). The test shows good cross-reactivity with several Aroclor mixtures, particularly Aroclors 1254, 1243, and 1242. The detection limit for this method is 2 ppb, and reproducibility is typically within 5-13 % (% CV). Sample collection, storage, processing, and quantitation were performed following manufacturer provided directions. Both filtered and unfiltered lake water and foam samples were stored frozen, diluted 50/50 with ACS grade methanol, analyzed in duplicate or triplicate, and quantified based on comparison to a standard curve. Standards of Aroclor 1254 with PCB concentrations ranging from 1 to 250 ppb were also analyzed in duplicate, along with a standard blank (Std 0 in ELISA kit). Samples with responses lower than the lowest standard were reported as < 2 ppb and samples with responses higher than the highest standard are reported as > 500 ppb (double the lowest/highest standards based on the initial dilution).

6. Results and Discussion

6.1 Dissolved Organic Matter

Here, DOM is defined as organic material in the lake, streams or foam that is smaller than 0.7 microns in size (0.45 microns is the technical cutoff but 0.7 is commonly reported based on nominal filter pore size). This material may be truly dissolved (surrounded by water molecules) or exist as colloids, which are small aggregations of molecules. It is primarily the

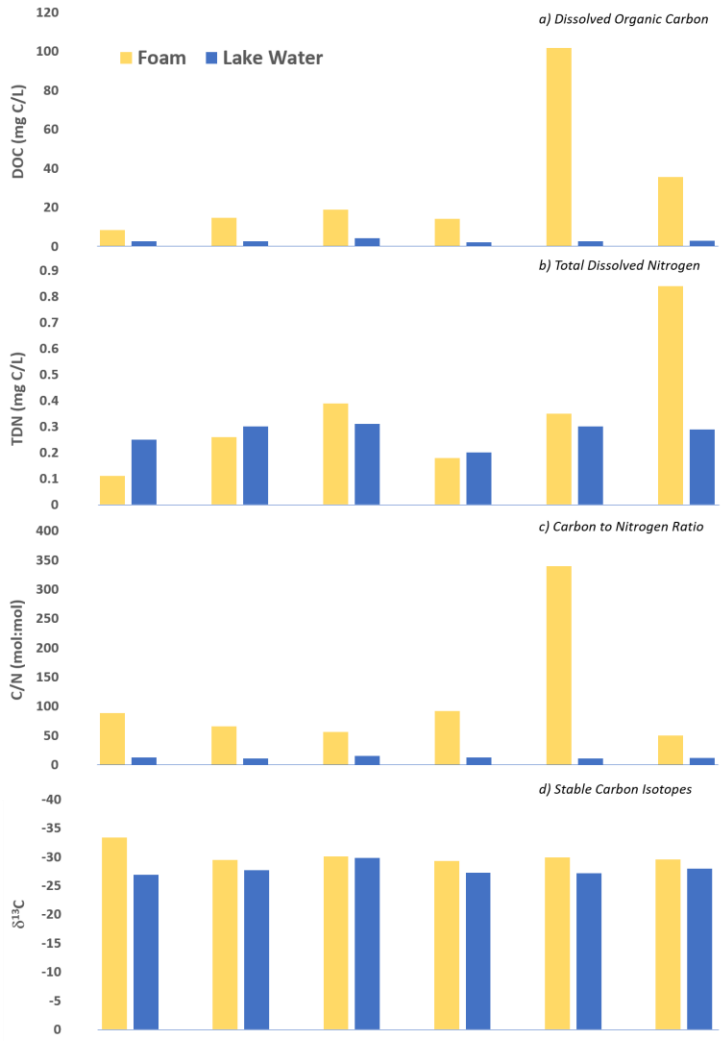

Figure 4 – Comparison between foam and nearby lake water samples of a) dissolved organic carbon (DOC) concentrations, b) total dissolved nitrogen (TDN) concentrations, c) carbon to nitrogen (C/N) ratios, and stable carbon isotope values of DOC (δ^{13}C-DOC). All measurements were made after filtering out particulates with a 0.7um glass-fiber filter (GFF)

DOM that changes the chemistry of the water in terms of foam formation (specifically, by reducing the surface tension of the water), and thus here we focus on the source of the DOM separately from particulates that are trapped in the foam.

6.1.1 C and N concentrations and ratios

The lake water had relatively low values of DOC and TDN, ranging from 2.7-4.1 mg C/L and 0.11-0.84 mg N/L, respectively (Figure 4). The C/N values, ranging from 10.4-15.5, are indicative of a mix of low C/N inputs such as phytoplankton (~6.6, Redfield et al. 1958) and higher C/N inputs such as soils or macroalgae, which is expected in a lacustrine system. Stream water had a similar DOC range (1.5-8.6 mg C/L) but was elevated in TDN (0.5-1.6 mg N/L). The enrichment in dissolved N is likely from fertilizer and soil runoff, as TDN includes inorganic nitrogen.

Foam samples on the other hand were very enriched in DOC (8.4-102 mg C/L) relative to nearby lake water, but had similar TDN concentrations (0.1-0.8 mg N/L, Figure 5). This results in much higher C/N ratios in the foam (49.6 – 339). The foam values are more similar to pure leafy or woody material, which are very depleted in N, but based on other analysis (e.g. fatty acids), terrestrial contributions to the foam do not seem to be large. Instead, the high C/N ratios in the foam suggest the selective concentration of a particular type of biomolecule that is poor in nitrogen. This rules out proteins or nucleic acids as the dominant compounds in the foam, and instead suggests lipids or carbohydrates.

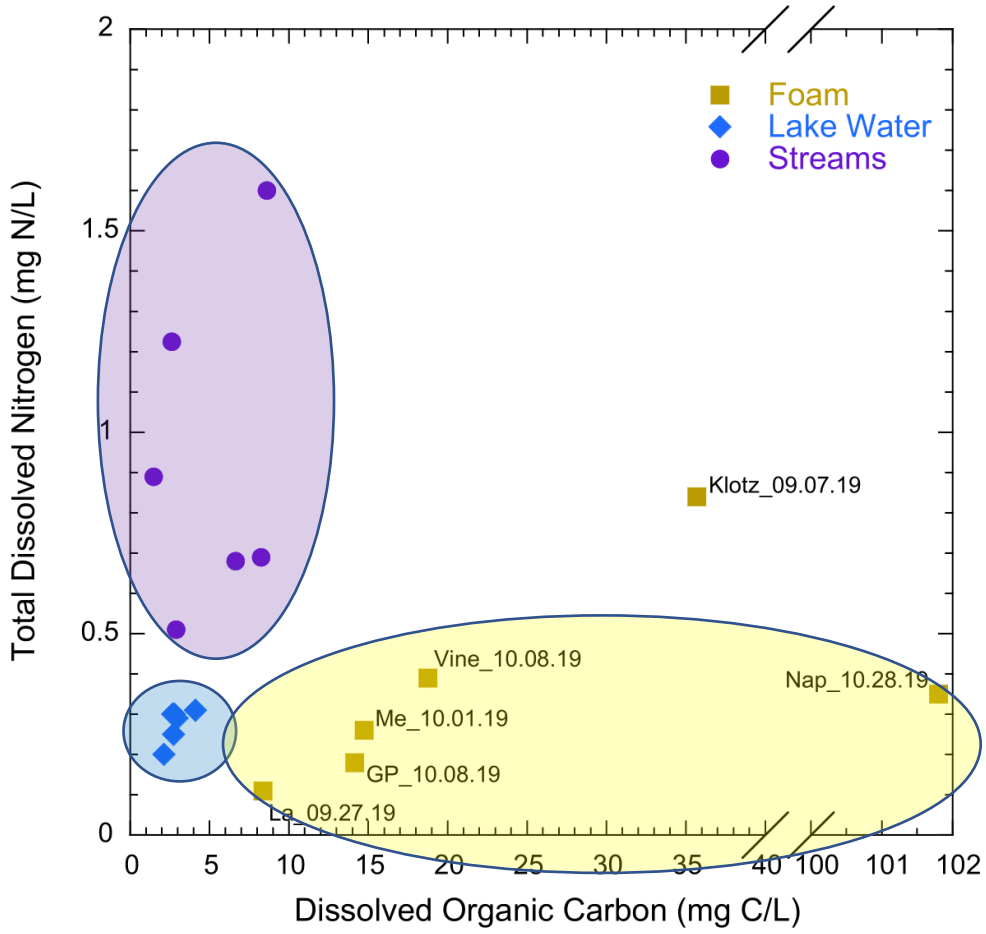

Figure 5 – Total dissolved nitrogen (TDN) and dissolved organic carbon (DOC) concentrations (mg C or N/L) in streams (purple circles), lake water (blue diamonds) and filtered foam (yellow squares), showing the enrichment in DOC in the foam and enrichment of TDN in the streams relative to lake water.

6.1.2 C and N Isotopes

δ^{13}C-DOC values in lake water ranged from -26.9‰ to -29.8‰, and were consistently more depleted (more negative) in the foam, ranging from -29.3‰ to -33.4‰ (Figure 6). The foam had the most depleted δ^{13}C-DOC in the dataset, supporting the finding from C/N ratios that there is the fractionation of a specific type of organic matter from the lake to the foam. Values from the streams were similar to lake water, ranging from -27.4‰ to -29.4‰, while quagga mussels and algae (mixed algal community in the plankton tow) had more depleted values of -30.3‰ and -31.5‰, respectively. While the overlap in the δ^{13}C values and the likelihood of select biomolecules as opposed to bulk biomass from biological sources entering the foam makes distinguishing the source of the foam using this technique difficult, on average the foam most closely resembles the bulk tissues of phytoplankton and quagga mussels. Additionally, the two samples of macroalgae we collected had very different δ^{13}C signatures, -27.6‰ and -15.6‰, reflecting different C assimilation pathways in vascular plants (C3 vs C4, respectively). Thus, we can at least rule out contributions from grass-like macrophytes (e.g. eelgrass) based on δ^{13}C values.

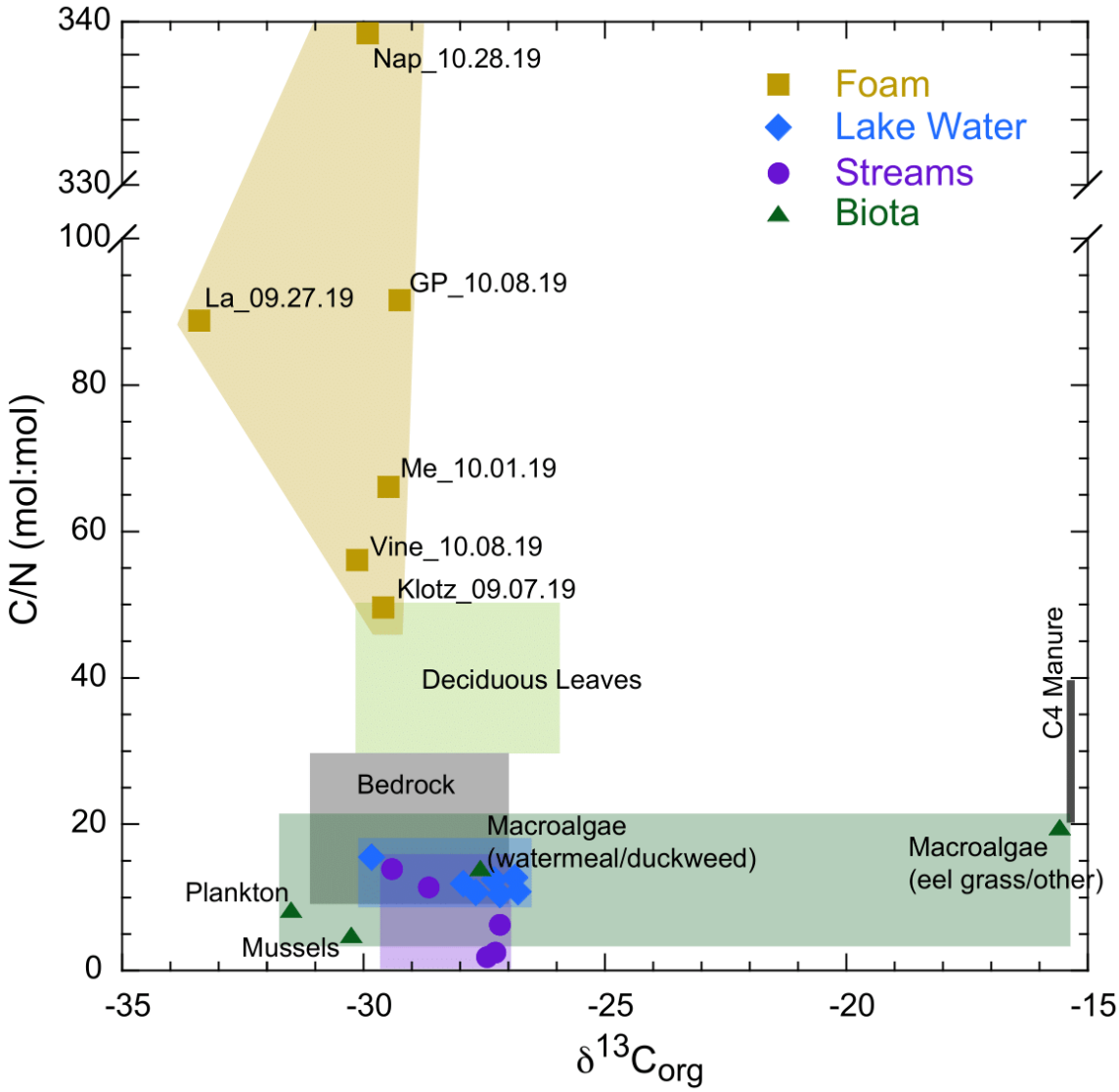

Figure 6 – Carbon to nitrogen (C/N) ratios versus stable carbon isotope ($\delta^{13}C$) values for foam samples and end-members (potential organic matter sources). The measurements were on the dissolved (filtered) phase for foam, lake water, and streams. Biota samples are bulk homogenized tissues. Samples were decarbonated to remove inorganic carbon. The values for bedrock, deciduous leaves, and C4 manure are obtained from the literature. Shaded boxes show the range of values of individual organic matter types. Many of the end-member values overlap, especially their $\delta^{13}C$ values, but the foam values have distinctly high C/N ratios.

6.1.3 Fatty Acids

Lipids, one of the most abundant types of biological molecules, are relatively insoluble in water and thus are often major components of SMLs in lakes (Napolitano and Cicerone 1999). The high C/N ratios in Canandaigua Lake foam are suggestive of enrichment of biomolecules that are low in N, and lipids fit this description (Hedges et al. 2002). However, lipid concentrations in foam were often undetectable. Three samples, one mid-lake (La_09.18.19) and two shoreline (Nap_10.28.19 and Klotz_09.07.19), had an undetectable lipid

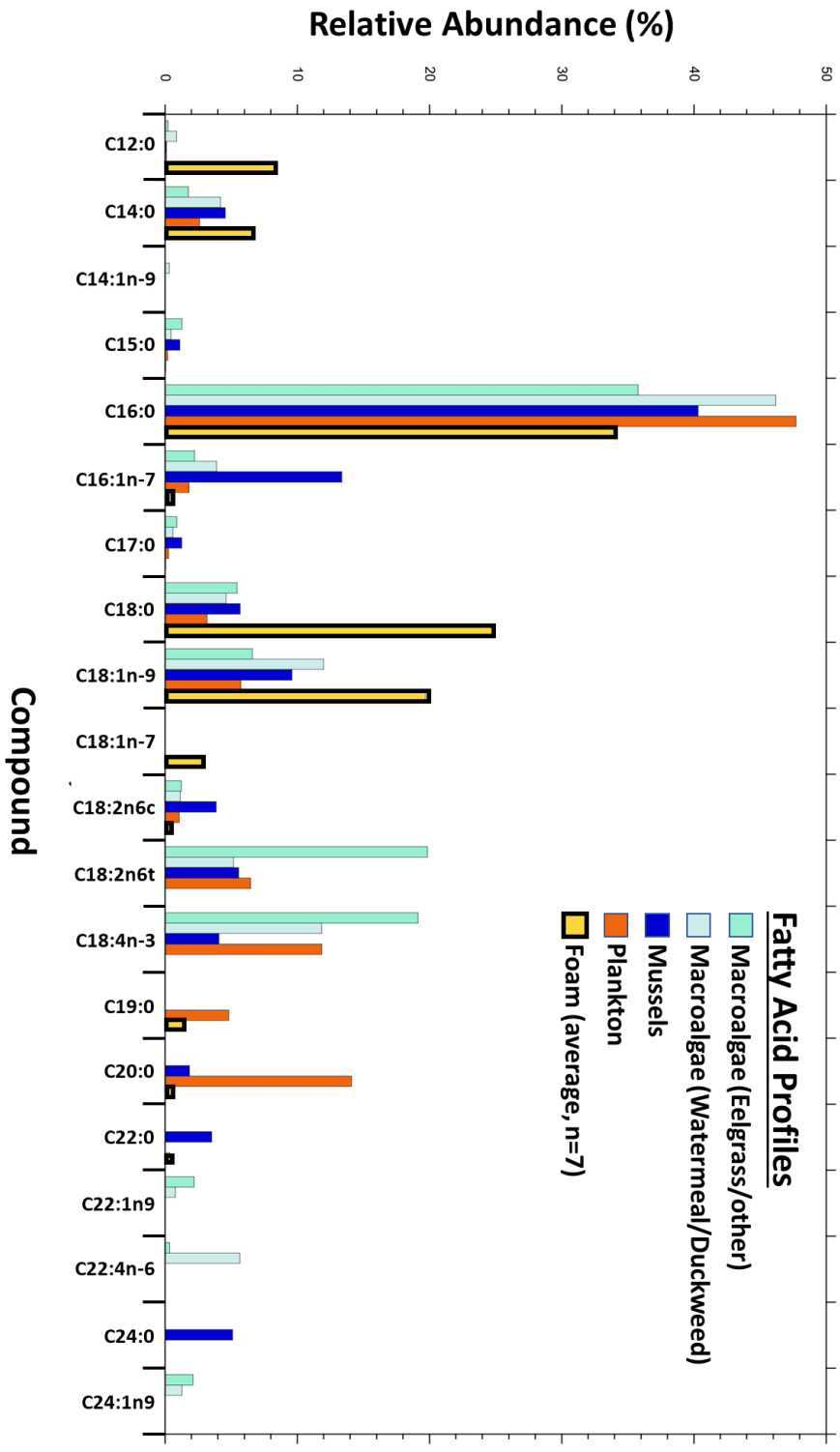

Figure 7 - Fatty acid profiles of foam and biota. Values are shown as % relative abundance, where the peak area of an individual compound measured via GC/MS is calculated as the percentage of total fatty acid peak area for that sample. Compound names are represented as CX:Yn-Z, where X represents the number of carbon atoms in the fatty acid tail (i.e. carbon chain length), Y represents the total # of double bonds in the carbon chain (degree of saturation), and Z represents the carbon position of the start of the first double bond counting from the end of the carbon chain (furthest away from the carboxyl group)

mass after extraction (< 1.5 mg/L). Nap_10.28.19 in particular highlights the lack of importance of lipids in foam formation: This very stable foam that accumulated on the shoreline along Cottage City had a DOC concentration of 102 mgC/L, meaning lipids composed less than ~1% of the organic carbon pool.

We did, however, obtain high weights of lipid extracts for other samples: La_09.27.19 (63.7 mg/L), Me_10.01.19 (24.6 mg/L), Vine_10.18.19 (7.9 mg/L), and GP_10.08.19 (136 mg/L). These values are often unrealistically and/or impossibly high based on measured DOC values. Assuming lipids are 77% C by weight (Hedges et al. 2002), our extracts suggest lipids in these 4 samples compose 586, 128, 32, and 742% of the DOC pool, respectively. The reason for this is the emulsion produced during lipid extraction. The samples reacted with hexane to form a thick, gel-like substance that was difficult to physically separate from the lipid extracts. This gel-like substance, that we think is a foaming agent, was not soluble in hexane and thus not composed of lipids. Thus, the lack of any measurable lipids in several samples is more indicative of their actual abundance, which is supported by other analyses as well (*see* 'FTIR' section). The high lipid weights in the other samples were due to our inability to separate out the non-lipid foaming agent before weighing. It is not clear if lipid extractions were influenced by other factors such as association with other biological molecules (e.g. carbohydrates) and/or the emulsion.

Fatty acids are an abundant type of lipid in aquatic systems, and distributions of fatty acids (chain length and double bond # and location) in an organic matter pool provide source-specific information (Napolitano 1999, Bianchi and Canuel 2011). For example, even-C numbered, long-chain fatty acids (C20-C32) are indicative of terrestrial plant inputs, while even C-numbered medium-chain fatty acids (C12-C18) and C16 and C20 polyunsaturated fatty acids (PUFAs, two or more double bonds in the C chain) are useful markers of phytoplankton. Bacterial inputs can be identified by the presence odd-chain, hydroxy and branched FAs.

Fatty Acids are common components of aquatic foams, having both polar and non-polar regions, which is the ideal chemistry to accumulate at the air-water interface (Napolitano and Cicerone 1999). Despite overall low lipid yields, we detected fatty acids in all the foam samples and were able to gain useful source information (Figure 7). FAs in the foam samples did not match any of the biological tissues measured, and a lack of longer-chained FAs and odd-chained FAs suggested minimal terrestrial and bacterial inputs, respectively. Calculated values of the Terrestrial to Aquatic Ratio of Fatty Acids (TAR_{FA} = C24+C26+C28/C12+C14+C16) were zero, showing that FAs were derived from a source within the lake (Bianchi and Canuel 2011). Foam samples consisted primarily of medium-chain (C12-C18), saturated (no double bonds) fatty acids (Figure 7), with the presence of some monounsaturated (one double bond) C18 FAs (C18:1n-9 and C18:1n-7). With the exception of C16:0, which was the dominant FA in all samples measured, the biological tissues contained significantly lower concentrations of the dominant FAs found in the foam, and instead were found to have higher concentrations of mono- and poly-unsaturated fatty acids (PUFAs), as well as FAs with longer chain lengths (C20-C24). While other types of plankton including diatoms, chrysophytes, and green algae produce more complex fatty acid profiles (Olsen 1999), cyanobacteria lack C20 and C22 PUFAs

altogether, and only some taxa have C18 PUFAs. Additionally, C18:1n-7 has been used as a FA marker for cyanobacteria (Fredrickson et al. 1986), and we found this compound in the foam but not in the biological samples. Overall, this data supports cyanobacteria as the most likely source of FAs in the foam. More specifically, the FA distributions are similar to what we found in the literature for *Microcystis* cyanobacteria (Matsuda and Koyoma, 1977).

The carbon preference index (CPI_{low}), defined as the ratio of even to odd numbered saturated FA carbon chains in the C12-C18 range, is a useful proxy to assess contributions of organic material from different biological sources (Matsuda and Koyama, 1977), and here it also supports a *Microcystis* source of FAs. Aquatic sources typically range from ~6 (Zooplankton) to 46 (Diatoms), while soils have lower values (5, Matsuda and Koyoma 1977). In this study, our macroalgae and mussel samples had a chain-length preference similar to those previously found for aquatic organisms, with values of ~30-70 and 30, respectively. Our foam samples, in contrast, contained almost no odd-chained FAs, resulting in a very high average CPI_{low} value of 641. This is more comparable to reported values for *Microcystis*, which are indeterminate (infinitely high) due to a complete absence of odd-chained FAs. This also explains our CPI_{low} value for the plankton tow (145), which is elevated above normal aquatic values and was confirmed via microscopy to contain a mixed phytoplankton community with significant amounts of *Microcystis*.

Finally, by comparing saponified and unsaponified fatty acid extracts, we determined that the fatty acids are present in the form of triacylglycerides (TAGs), which is how fatty acids are stored in cells. The presence of TAGs and not free fatty acids suggests the material is fresh, as TAGs break down quickly in the environment, particularly at the surface where oxygen and sunlight is plentiful. This suggests a fresh local source to the foam in the lake and that the material forming the foam has experienced limited degradation.

6.2 FTIR

We utilized FTIR on two freeze-dried foam samples: one mid-lake sample (La_09.18.20) and one shoreline sample (Wo_09.13.19). FTIR data is shown in Figure 8, and shaded regions define the regions of the spectra corresponding to lipids, proteins and carbohydrates (Minor and Stephens 2008, Fanesi et al. 2019). More significant responses in these regions translate to relatively more of that compound class being present.

Both the shoreline and the mid-lake sample showed similarly large absorbance peaks in the 1040-1185 cm^{-1} region of the spectrum, corresponding to significant concentrations of carbohydrates. Smaller peaks were observed in the lipid and protein regions of the spectrum, although they were larger in the shoreline sample. The wide band centered at 3400 cm^{-1} has been attributed to carboxylic acids produced from the photochemical degradation of humic substances (Bertilsson and Tranvik, 1998), a common component of SMLs. The larger carboxylic acid band in the shoreline relative to the mid-lake sample is suggestive of photochemical alteration during transport. Together, these profiles suggest fresh foam is composed primarily of carbohydrates, and the chemical signature is altered during transport

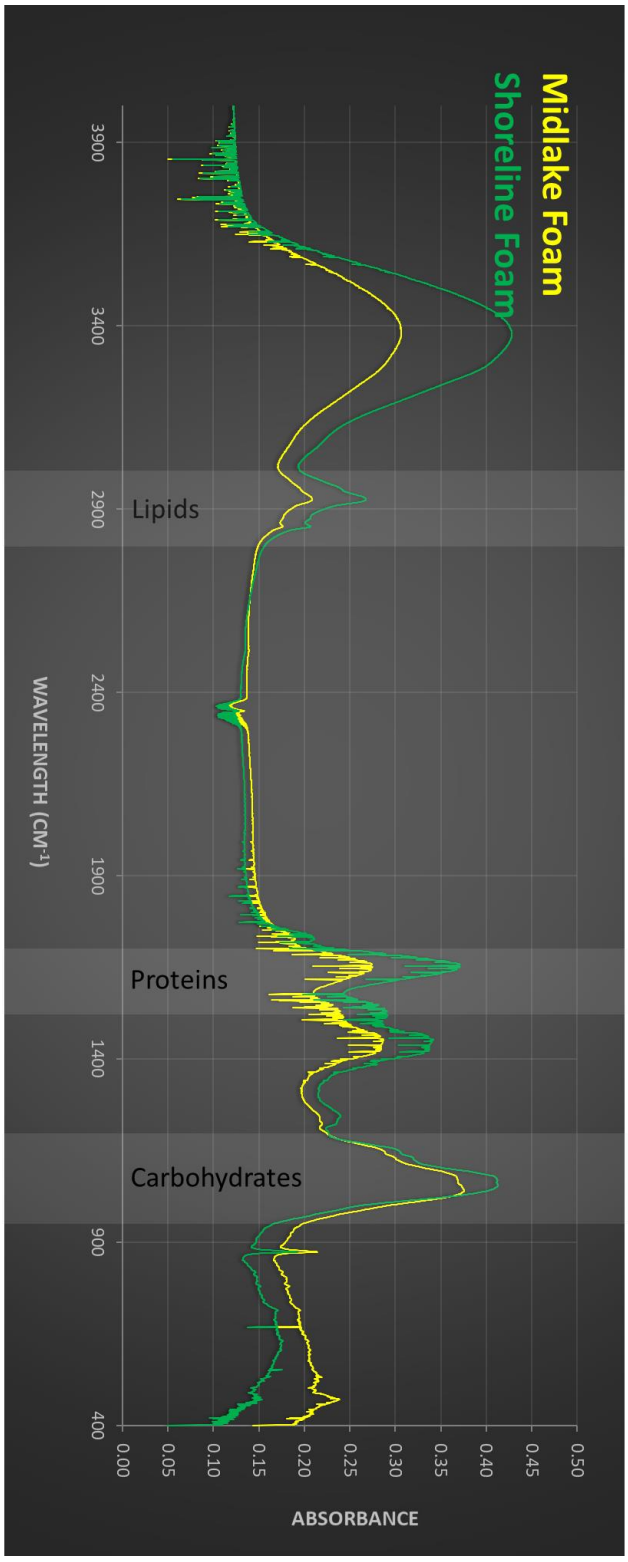

Figure 8 - FTIR spectra of two freeze-dried foam samples: one mid-lake (La_09.18.19) and one shoreline (Wo_09.13.19). The magnitude of responses in absorbance in the shaded regions are relative to the abundance of the indicated class of biomolecule

due to the accumulation of additional material (e.g. plant fragments) as well as limited breakdown processes.

Examining the FTIR signatures of the biological samples (Figure 9), we see peaks corresponding to all 3 macromolecular types in each sample, with some important differences. The quagga mussel tissues had a large protein peak but a smaller carbohydrate peak than any of the other samples. The plankton had an equally large protein peak, and also a large carbohydrate peak. The mixed watermeal/duckweed sample had a small protein peak but a large carbohydrate peak. The lipid peak was largest in plankton, followed by the mussels and then the watermeal/duckweed mixture.

Due to the dominance of carbohydrates in the foam and observable carbohydrate peaks in each biological sample (although a much smaller peak in the mussels), we more closely compared the FTIR spectra in this region. Figure 10 zooms in on the response from 950 to 1200 cm^{-1}, and wavelengths attributed to specific aquatic polysaccharides (chains of sugars) are noted (vertical blue lines), taken from Fanesi et al. 2019. We found that the peaks from both foam samples are nearly identical at all 4 wavelengths, once again supportive of carbohydrates (and specifically polysaccharides) as the source of the foam. Overall, the foam and plankton carbohydrate peaks matched known reports of *Microcystis aeruginosa* (Kansiz et al., 1999, Fanesi et al., 2019), indicated by the strongest IR responses (size of peaks or presence of inflection points) at 1153, 1080 and 1020 cm^{-1}. The quagga mussel peak matched at 1080, 1020 cm^{-1}, but did not have the same response around the 1153 cm^{-1} region. The macroalgae peak had a largely different

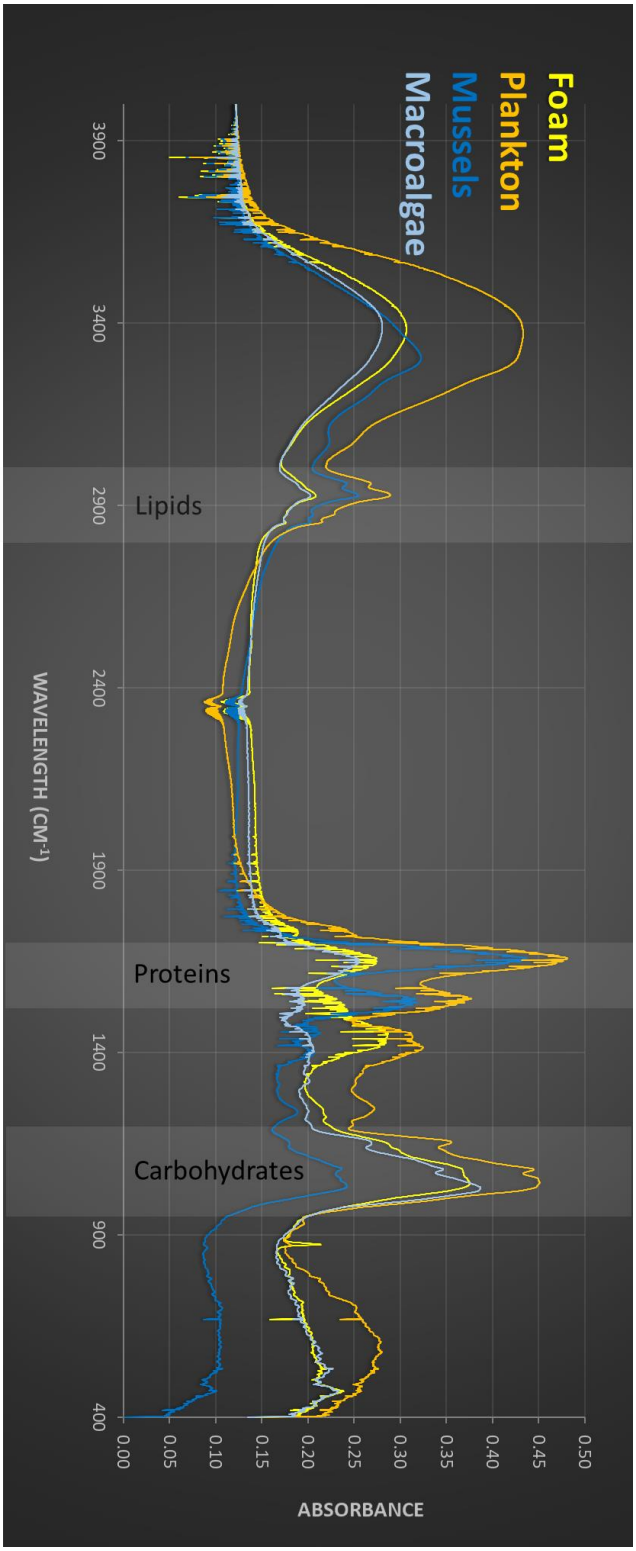

Figure 9 - FTIR spectra of a freeze-dried, mid-lake (La_09.18.19) foam sample, compared to FTIR spectra of biota in the lake. The magnitude of responses in absorbance in the shaded regions are relative to the abundance of the indicated class of biomolecule

shape, with a strong response at 1020 cm^{-1} but less significant responses at 1080 and 1153 cm^{-1}.

6.3 Particulate Organic Matter

While we focused on the dissolved phase to identify the source of the foam, we also analyzed the filters containing all material > 0.7um in size ('particulate' organic matter, or POM). The POM in the foam was compared to two freeze-dried foam samples (La_09.18.19 and Wo_09.13.19) that contained both dissolved and particulate material, freeze-dried biological samples (mussels, macrophytes, plankton), and POM collected from the stream and lake water samples

Concentrations of total suspended solids (TSS), determined as the weight of particulates loaded on filters normalized to the volume of water filtered, were the highest in foam, followed by streams and then lake water. TSS in foam was generally two orders of magnitude more concentrated than in lake water, showing the propensity of foam to accumulate particulate material (Figure 11). Source plots using %OC vs %N (Figure 12), C/N vs. $\delta^{13}C$ (Figure 13A), and C/N vs. $\delta^{15}N$ (figure 13B) all show that the POM in the foam is more similar to the macrophyte and plankton tow samples than the quagga mussels, stream POM or lake POM. This is consistent with the foam being derived from an algal material, and also with the visual confirmation of macrophytes, particularly duckweed and watermeal or chop from eelgrass or other species, in every foam sample.

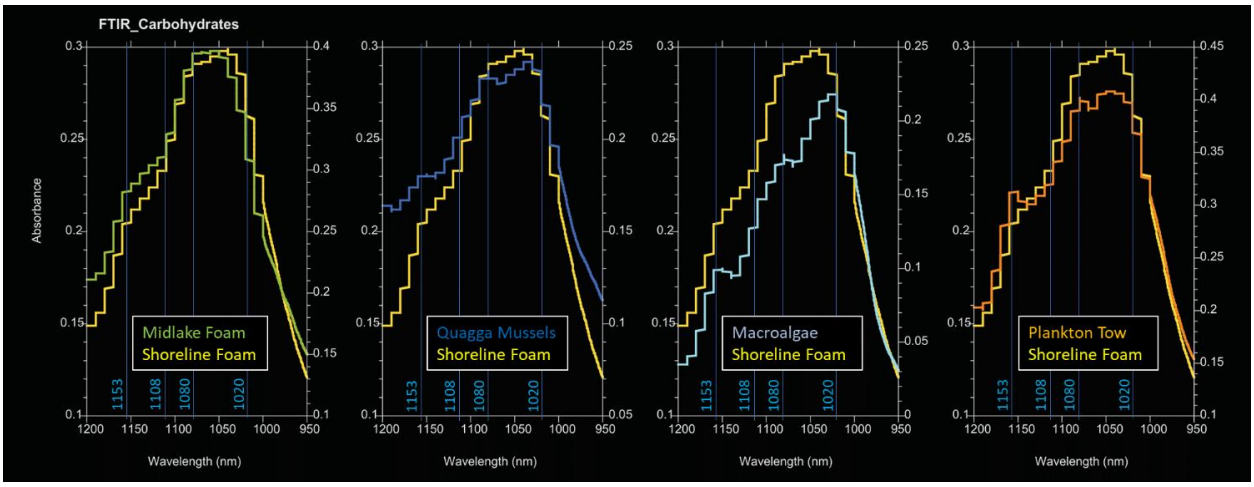

Figure 10 – Comparison of the FTIR spectra of foam and biota samples, zoomed in on the carbohydrate peaks. Vertical blue lines show specific wavelengths where polysaccharides have been shown to give absorbance responses, particularly in phytoplankton

The plots also show the influence of POM on freeze-dried foam signatures. The bulk freeze-dried foam has signatures more similar to the POM in the sample than the DOM that is causing the foam. This analysis supports our choice of filtering the foam samples and treating them as aqueous samples, whenever possible, as opposed to freeze-drying them whole. The filtering step is laborious, uses several filters (which clog easily) and only provides minimal sample amounts (~100-300mls), but is necessary to provide a clean signature. The agreement between freeze-dried foam and watermeal/duckweed samples in the non-carbohydrate region of the FTIR spectra also likely reflects the influence of POM. The differentiation in foam DOM and POM signatures shows that storage effects were minimal, as we would expect significant breakdown to make the chemical signature of the DOM pool more similar to the POM present.

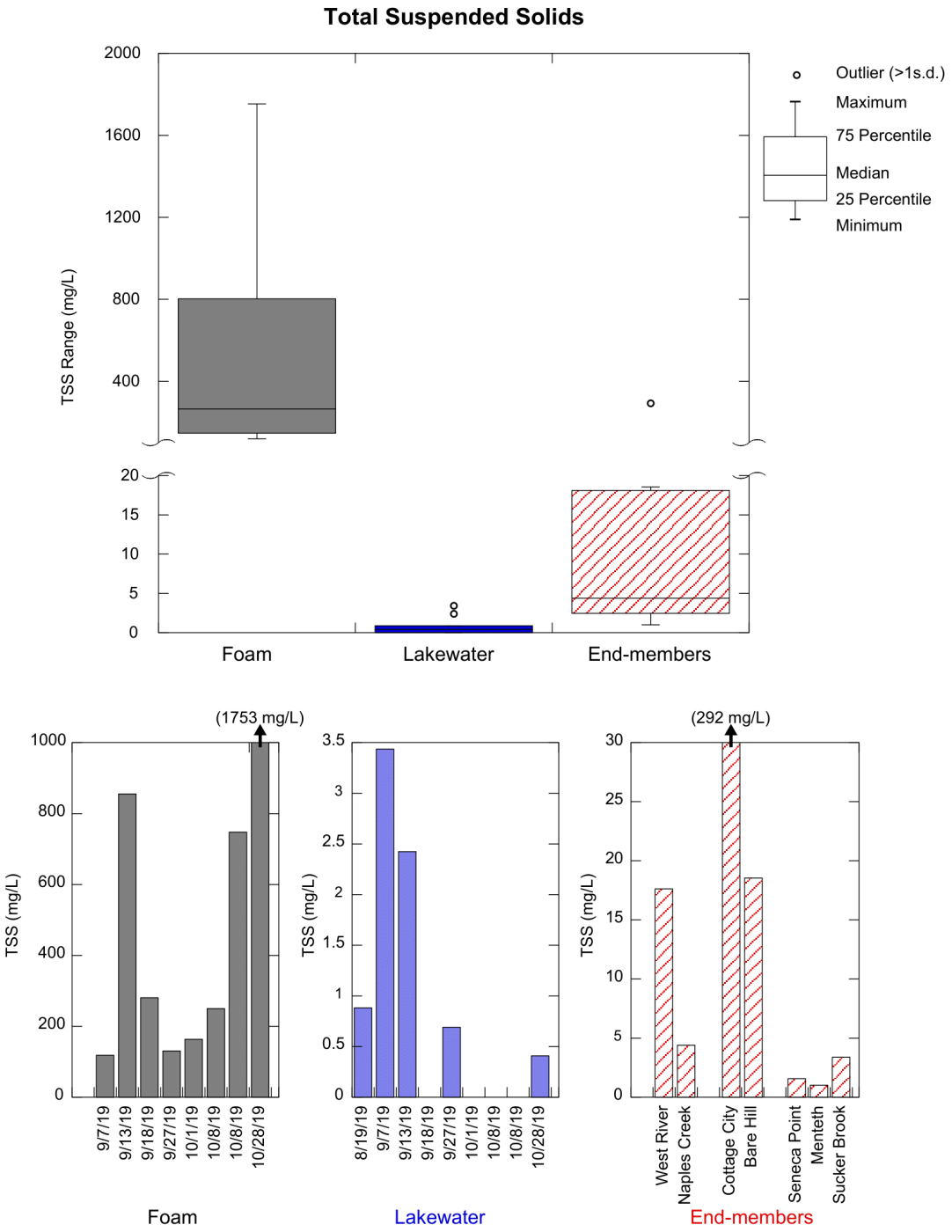

Figure 11 – Concentrations of total suspended solids (TSS) in foam, lake water, and streams ("end-members"). The boxplot at the top of the figure shows the minimum, maximum, median, and 25 and 75 percentile values. The barcharts at the bottom of the figure show individual samples of each type (foam in grey, lake water in blue, streams diagonal red lines), with foam and lake water samples labeled by date and streams labeled by name (if available) or outflow location

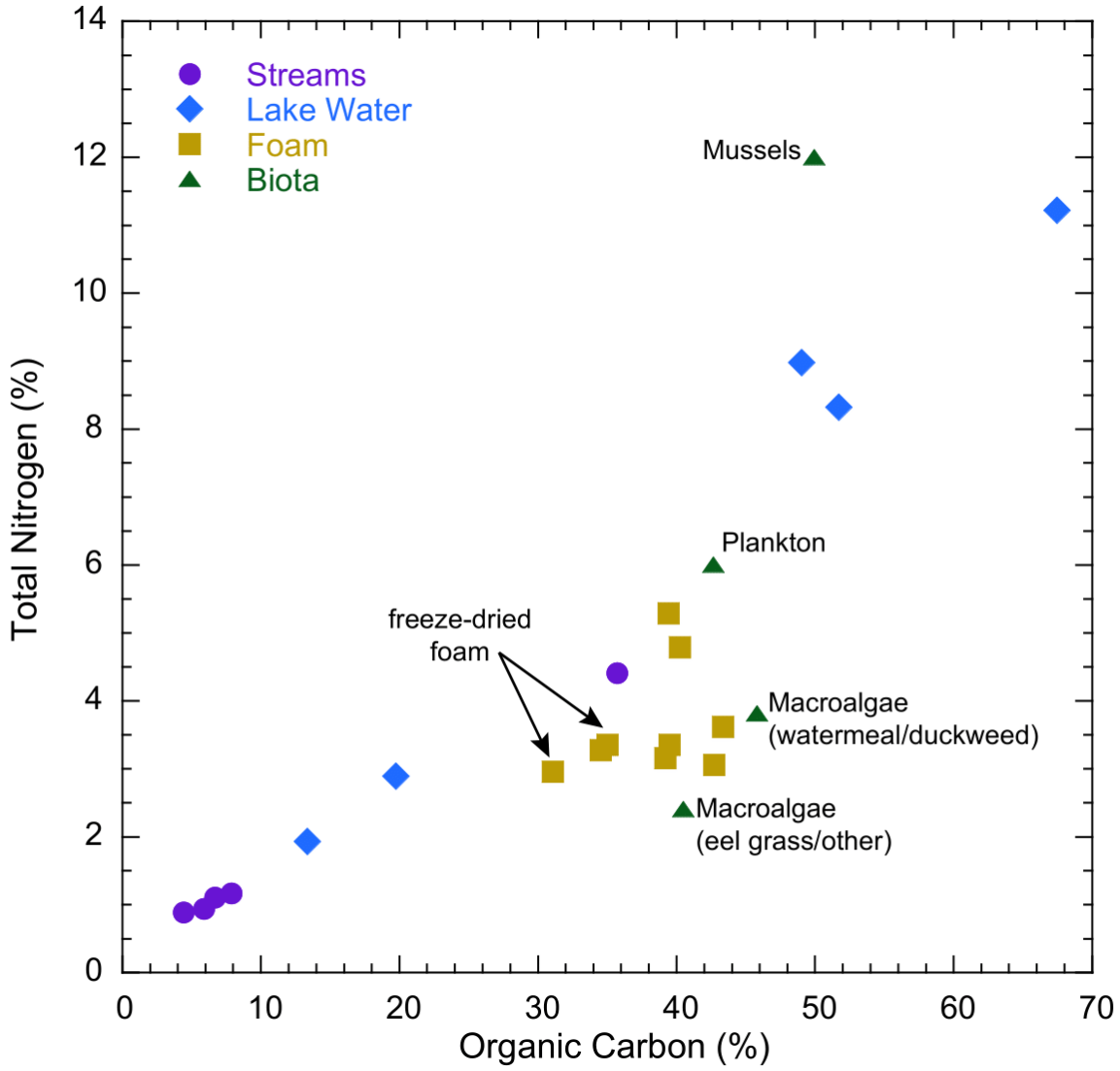

Figure 12 – Percent abundance by weight of total nitrogen and organic carbon of particulates filtered (> 0.7um) from foam, lake water and stream samples, compared to values in freeze-dried homogenized tissues of biota. Also shown are values of bulk freeze-dried foam, which contain both dissolved and particulate material. While the particulate material is not thought to cause the foam, it can provide important information on organic material trapped in the foam during formation or transport.

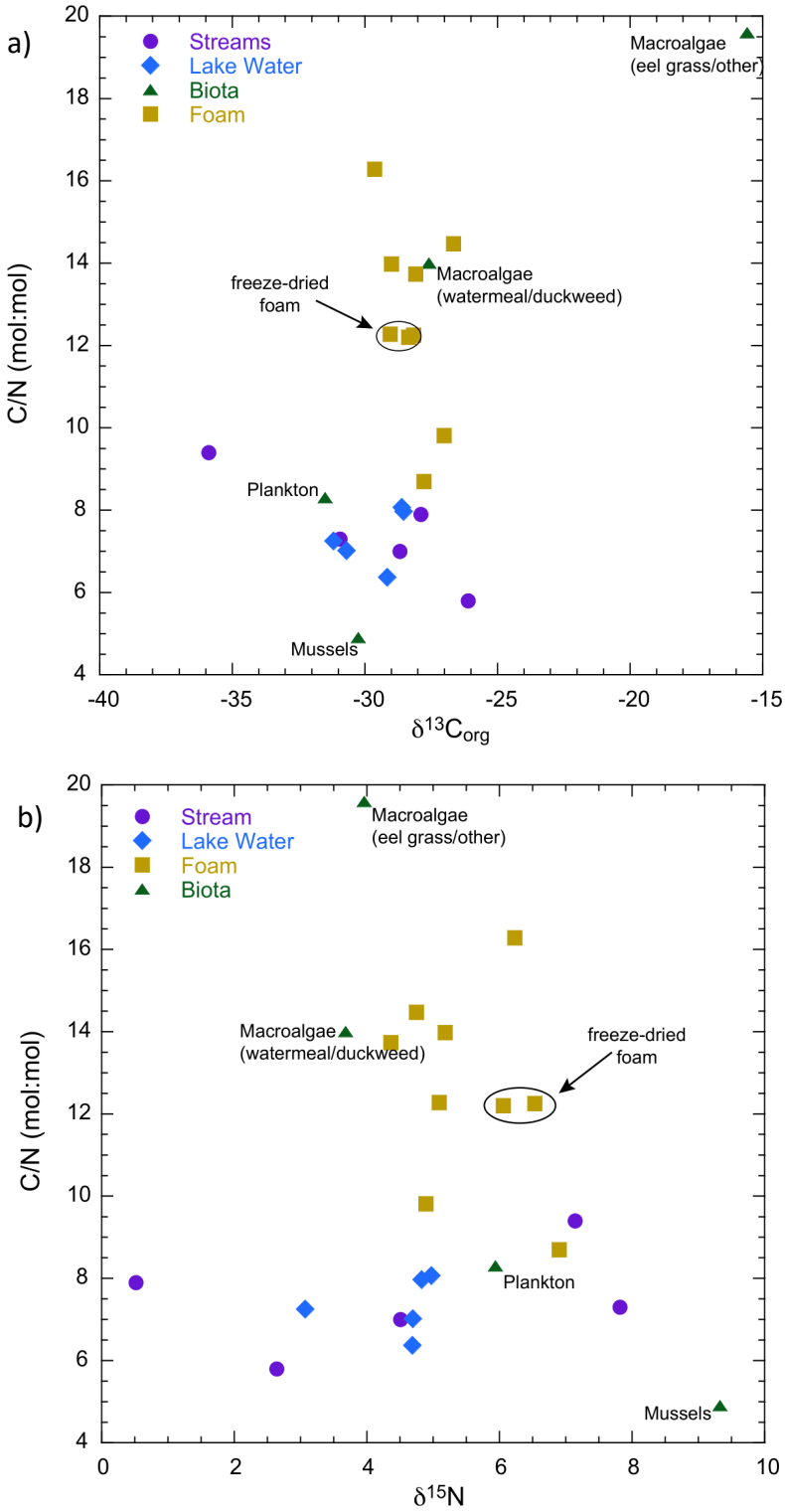

Figure 13 – Source plots comparing particulates in foam (filter analysis), streams, and lake water, as well as freeze-dried foam (dissolved and particulate organic matter) and bulk homogenized tissues from biota in the lake. Both a) C/N vs $\delta^{13}C$ and b) C/N vs $\delta^{15}N$ plots show that particulates in the foam, as opposed to the dissolved fraction previously shown, are more similar to biological sources. Overall, the particulates in the foam are primarily macroalgae and plankton, and there is little evidence of mussel inputs

6.4 Toxins

6.4.1 Microcystins

Lake water and foam samples showed similar overall patterns in microcystins (LR-equivalents) toxin concentrations (Figure 14). In general, filtered samples had lower concentrations than their unfiltered counterparts. Microcystins concentrations in lake water samples ranged from below detection to 2.8 ug/L. All filtered lake water samples were below the detection limit (0.1 ug/L) except one (La_09.18.2019, 1.4 ug/L), and all but two unfiltered lake water samples had microcystins concentrations below the World Health Organization (WHO) drinking water limit (1 ug/L).

In every case, unfiltered foam had higher concentrations of microcystins than lake water samples, filtered or unfiltered, taken nearby. In filtered foam samples, microcystins concentrations ranged from below detection to 6 ug/L, except for one sample that had a much higher value of 38 ug/L. Microcystins concentrations in unfiltered foam were higher in most samples, ranging from 0.5-16.9 ug/L. It should be noted that the highest value, 38 ug/L, was obtained on a filtered foam sample (La_09.27.2019), but an unfiltered sample of that foam was not available for analysis. This sample was also coarse-filtered immediately after collection, and the sample was frozen the same day instead of allowing the foam to collapse for 1-3 days. Therefore, impact of allowing the foam to collapse on microcystin concentrations should be further evaluated.

The microcystins concentration in most foam samples fell below the NYS Department of Health (NYSDOH) limit for safe recreational water use (10 ug/L). However, two of the 7 foam samples measured, Nap_10.28.2019-unfiltered and La_09.27.2019-filtered, were above the recreational use limit (16.9 and 38 ug/L, respectively). One of these samples was taken from a shoreline accumulation, while the other was sampled from a mid-lake streak as the foam formed. This highlights the uncertainty in predicting the presence of high levels of microcystins in foam based on its location in the lake. The tendency for foam to accumulate particulates may partially explain the elevated microcystins concentrations relative to surrounding water, since algal cells from HABs may be entrained in the foam as it is transported at the lake's surface. It remains unclear if microcystins toxins are actively produced within the foam.

6.4.2 PCBs

The measured total PCB concentrations of filtered foam ranged from 2.3 to > 500 ppb, indicating content varies widely amongst different samples (Figure 15). A shoreline foam sample (Klotz_09.07.2019, 71.8 ppb) and a "fresh" foam sample taken mid-lake (La_09.27.2019, >500 ppb) had the highest concentrations, 3-100x greater than any other samples. Two unfiltered foam samples were analyzed and had higher PCB levels than their filtered foam counterparts, suggesting filtering may remove PCBs. This makes sense, as PCBs are known to be particle-reactive, and preferentially associated with particulates (Nellier et al., 2015). Additionally, finding the highest concentration in the mid-lake foam sample that was filtered

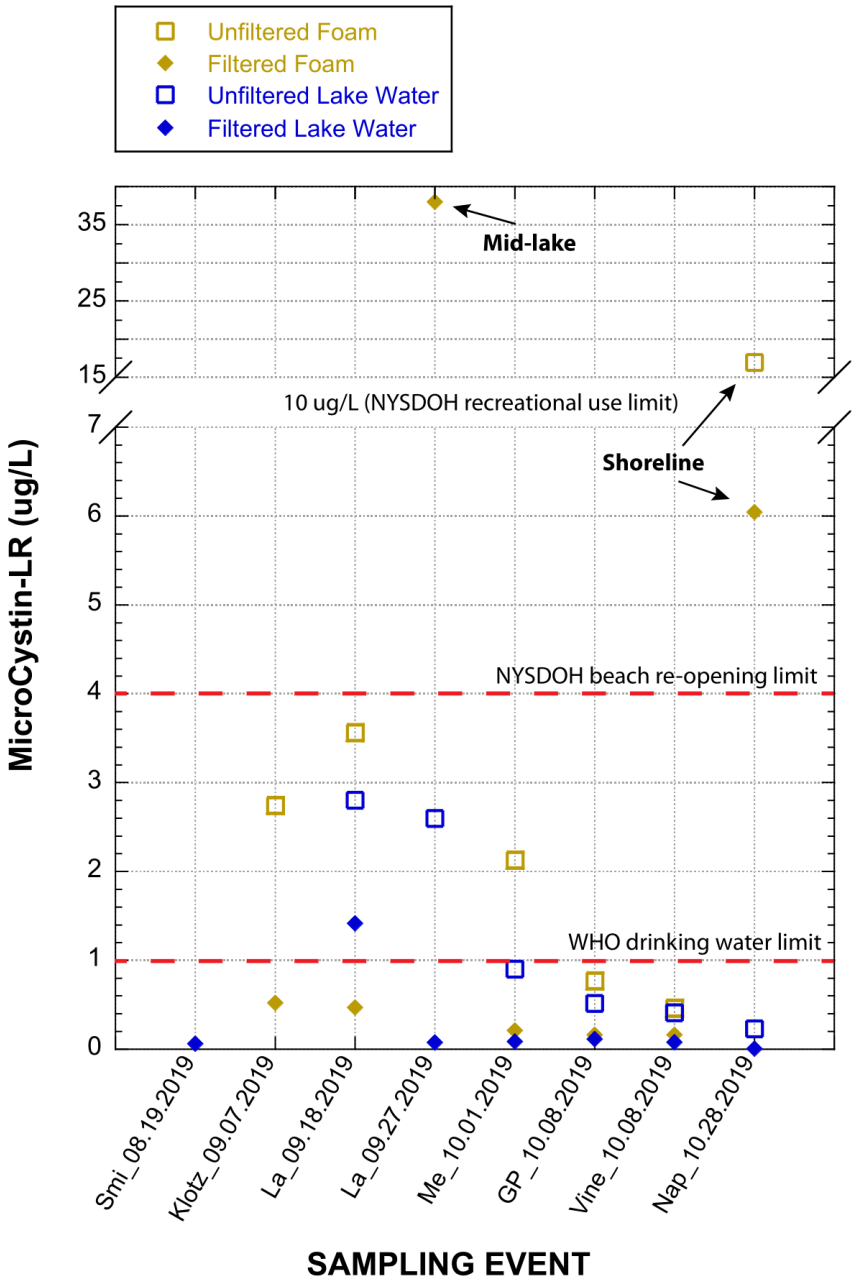

Figure 14 – Concentrations of total microcystins (LR-equivalents) in foam (yellow) and lake water (blue) samples. Closed diamonds show values of filtered samples, which contained only dissolved (extracellular) microcystins, while open square show values of unfiltered samples, which contained both dissolved and particulate (intracellular and sorbed) microcystins. Foam IDs are shown along the x-axis, which also represent corresponding water samples. Smi_08.19.19 however was a lake water sample taken near the plankton tow and does not have a corresponding foam sample. La_09.18.19 was coarse-filtered onboard and does not contain a corresponding unfiltered foam sample

onboard (La_09.27.19), as we observed for microcystins, suggests some PCBs may have been lost from the other samples while allowing the foam to collapse. During this 1-3 day storage period, particulates in the foam were present and may have sorbed PCBs, increasing the amount lost during coarse-filtering.

Two lake water samples were analyzed and in general had PCB levels lower than foam sampled nearby, except for one sample, Me_10.01.2019 (31.6 ppb), which appears to be an outlier and should be interpreted with caution. The PCB concentrations of the other lake water samples ranged from below detection (two samples) to 7.3 ppb (unfiltered lake water sample: Nap_10.28.2019). The NYSDOH maximum contaminant level for PCBs in drinking water, 0.5ppb, is below the minimum detection limit of our analysis, therefore most samples analyzed had PCB concentrations higher than this safe threshold. It should be noted that the highest

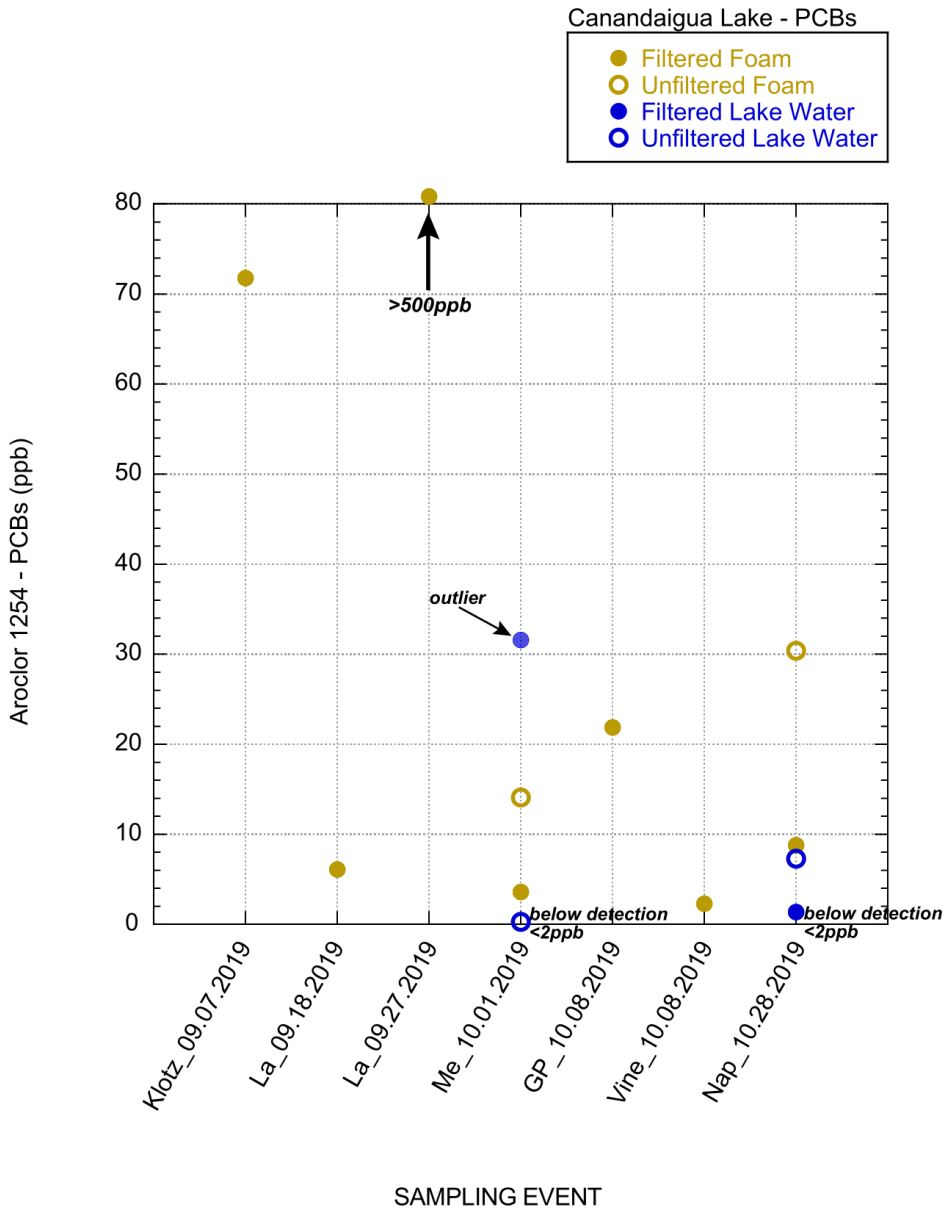

Figure 15 - Concentrations of total PCBs (calculated based on Aroclor 1254 standards) in foam (yellow) and lake water (blue) samples. Closed circles show values of filtered samples, which contained only dissolved PCBs, while open circles show values of unfiltered samples, which contained both dissolved and particulate (intracellular and sorbed) PCBs. Foam IDs are shown along the X-axis, which also represent corresponding water samples.

concentrations were measured as “water” samples derived from collapsing foam samples, and a large amount of foam collapses into a small volume of water, effectively concentrating the PCBs. Elevated PCBs levels have been observed in the SML of large freshwater lakes (e.g. Rice et al., 1982), and since compounds in this layer are responsible for generating foam, the high concentrations we observe might be expected. Removal and disposal of foam may be a way to decrease concentrations of this legacy contaminant in Canandaigua Lake.

The wide range in values amongst the different sample types suggests the foam may concentrate PCBs. However, more work should be done to better quantify concentrations and characterize the distribution of PCB compounds (congeners). The ELISA plate method we used has been tested for several potential interferences but not all matrices, and relatively novel matrices such as foam-forming “water” should be further evaluated with additional techniques.

7. Conclusions

Chemical analysis provided a wealth of information on the source of the foam. Bulk organic matter measurements showed that the foam is enriched in DOC relative to lake water, and high C/N ratios suggest the dominance of a biological macromolecule that contains little N (lipids or carbohydrates). Fatty acid profiles revealed a local aquatic source of the organic material and were consistent with a *Microcystis* signature, but low lipid yields suggested carbohydrates as the dominant component. FTIR provides additional evidence that carbohydrates are the dominant component in freshly produced foam, in particular polysaccharides.

A likely explanation for the polysaccharide-rich chemical signatures consistent with *Microcystis* cyanobacteria are extracellular polymeric substances (EPSs) (Li et al. 2013, Liu et al. 2018, Chen et al. 2019, Xiao and Zheng 2016). During blooms, cyanobacteria such as *M. aeruginosa* embed themselves in a ‘gel-like’ EPS matrix, which aids in defense against grazing, regulating buoyancy, and aggregate formation (Liu et al. 2018, Chen et al. 2019). *M. aeruginosa* EPSs are composed of 70-80% proteins and polysaccharides, with polysaccharides often the dominant component (Wang et al. 2020). Studies have shown both EPS and polysaccharide production increase with nutrient levels (Wang et al. 2020), and have also observed the production of surface foam during *M. aeruginosa* blooms, about 6-8 days after water clarity is first reduced. Furthermore, *M. aeruginosa* may indirectly contribute to increasing polysaccharides in the lake by inducing a toxic stress response in other types of phytoplankton that results in enhanced EPSs production as a defense against microcystins toxins (El-Sheekh et al., 2012).

The role of micro-algae in generating foam has been documented in other aquatic systems. For example, *Phaeocystis pouchetii* blooms along the East Frisian coast are known to produce large quantities of foam that cover local beaches (Batje and Michaelis 1986). Similar to our study, the foam was found to be produced when *P. Pouchetti* reached its colony phase and excreted 15-64% of its produced carbon, primarily as carbohydrates (Eberlein et al. 1985). Along the North Sea and the Eastern English Channel, spring *Phaeocystis globosa* blooms

surround themselves in a thick 'mucopolysaccharide' matrix that changes the viscosity of the water so drastically it has been likened to egg whites (Seuront et al. 2006). Likewise, the end result is large amounts of foam produced along the shore.

Invasive dreissenid mussels (zebra and quagga) may play both a direct and indirect role in foam formation. They have been known to selectively filter feed on non-*Microcystis* types of phytoplankton (Vanderploeg et al. 2001). In low nutrient lakes, a shift in the phytoplankton community has been documented after the establishment of these invasive mussels resulting in increased abundance of *Microcystis aeruginosa* in the water column and promoting blooms (Woller-Skar, 2009). Additionally, the mussels increase the proportion of soluble reactive phosphorus (SRP) in the lake, the bioavailable form of the limiting nutrient for primary production, which both further promotes blooms and EPS formation (Wang et al. 2020, K. Schulz 2020 communication). Finally, when feeding on toxic *Microcystis* algae, dreissenid mussels become sick and produce large amounts of mucous that the organisms expel from various parts of their shells rather than through the normal ciliary tracts (Juhel et al., 2006). The expelled mucous often contains still viable toxic *Microcystis* algal cells which may enhance their presence in the lake relative to other phytoplankton over time. Furthermore, studies investigating the composition of material excreted by quagga mussels indicate the soluble organic matter portion is composed largely of polysaccharides (DeVilbiss and Guo, 2017). This suggests that the interplay between invasive mussels and the toxic *Microcystis* algae on which they feed may increase polysaccharides in the lake, thereby contributing to foam formation. However, our analyses shows little evidence of large amounts of mussel tissues in the foam.

The abundance of different molecular classes (e.g. carbohydrates, lipids, proteins) in a lake's phytoplankton pool can change not only based on a community shift, but also in response to environmental conditions (Fanesi et al. 2019 and references therein). Therefore, the propensity of a system to create foam, and the stability of that foam, can be dependent on both the type of phytoplankton present and how those species are responding to their surroundings. Ultimately this could be the key to why Canandaigua Lake appears to have more foam with increased stability than similar systems nearby that are also experiencing *Microcystis* HABs. To better understand this phenomenon, we recommend comparative studies in other Finger Lakes, and more seasonal sampling of Canandaigua Lake foaming events. We also recommend that future studies specifically target the identified polysaccharide component to better determine its structure and biological associations, which will provide additional perspective on the ecological drivers of foam production.

Finally, this study shows that foam has the potential to concentrate toxins above background lake water concentrations, consistent with other studies in natural foam (Schilling and Zessner 2011). While the findings were variable, microcystins and PCB concentrations were generally higher in foam, with no discernable patterns other than higher concentrations in unfiltered samples. This suggests these toxins may both partition into the SML and/or foam during its formation, as well as be included in association with particulates or cells that the foam concentrates during transport. Future research should further characterize microcystins and PCB congener distributions using techniques such as liquid chromatography/mass

spectrometry (LC/MS) and GC/MS, respectively, and monitor their presence more routinely to determine the environmental factors contributing to their enrichment in foam. We also suggest a more thorough review of different types of trace pollutants, which may identify compounds that contribute to the overall stability of the foam, in addition to the biological components identified here.

8. Acknowledgements

Thank you to the Canandaigua Lake Watershed Association (CLWA) for funding this project and providing scientific support, including but not limited to Lindsay McMillan, Nadia Harvieux, Susan Carpenter, Lynn Klotz, Sally Napolitano, Neil Atkins, Ted Carman, Dr. Joel Pasternack, Dr. Doug Merrill, Marty Lasher, and all the CLWA citizen scientists that were foam sighters/samplers. Our thanks also extends to the State University of New York (SUNY) at Brockport, including Dr. Mark Noll, Dr. Nandini Kar, Dr. Jacques Rinchard, and the Chemistry Department for scientific support, as well as other scientists throughout the western NYS region that we have had foam-related discussions with and input from, including Kevin Olvany at the Canandaigua Lake Watershed Council, Patty Thompson at Finger Lakes Community College (FLCC) for helping with the plankton tow and mussel sampling, Dr. Lisa Cleckner at the Finger Lakes Institute (FLI) for microscopy of the plankton tow, Dr. Liz Minor at the Large Lakes Observatory (LLO) for foaming-agent discussions and analytical support, and the Greater Canandaigua Civic Center for allowing us to store sampling buckets. We also appreciate all others not listed here who have helped this research project come to fruition.

9. Author Information

Global Aquatic Research (GAR) LLC is a local (Sodus, NY) small business that provides academic-level research services to help manage and protect earth's freshwater and marine resources. Our research examines the chemical signatures of water and sediments from lakes, rivers, estuaries and the ocean to assess modern and historical environmental change. We specialize in designing and conducting research projects, including sampling, data analysis and interpretation, and report writing, tailored to address specific environmental concerns. We also provide expert consulting in several fields related to the aquatic sciences.

Dr. Stella C Woodard

Dr. Woodard earned a B.A. in English and Writing from SUNY Oswego in 2001, where she received the Academy of American Poet's prize. She then worked for several years with local youth as an after school program coordinator and 4-H Community Educator in Wayne County. After pursuing additional science coursework at SUNY Brockport, she went on to earn her Ph.D. in Geological Oceanography from Texas A&M University in 2011. In addition to being awarded a Merit Fellowship at Texas A&M, she was the recipient of a national Schlanger Ocean Drilling Fellowship in 2009. Dr. Woodard has logged over 150 days at sea by working on several oceanographic research cruises, including as a sedimentologist for the International Ocean Discovery Program (IODP). She has travelled in the Northwestern and Equatorial Pacific Ocean

as well as to Baffin Bay in the Arctic Circle off western Greenland. Her methods primarily use geochemical and physical properties measurements of sediments, biota and water to reconstruct environmental conditions from deep geologic time to near present day. As a postdoctoral researcher at the Institute of Marine and Coastal Sciences at Rutgers University, her work investigating the role deep ocean currents and temperatures play in affecting global climate and sea-level during the Pliocene (the most recent geologic period when atmospheric CO_2 levels were similar to modern) was featured in *Science Magazine*.
As part of Global Aquatic Research, Stella has focused primarily on questions related to climate, water quality and erosion. She has designed shoreline protection structures along Lake Ontario, and is collaborating with SUNY Brockport to develop a HAB research/monitoring laboratory. Presently she is completing work for the Department of Energy at the Smithsonian Environmental Research Center, designing and building a large scale irrigation system that will flood two half-acre forest plots to simulate storm surge events related to hurricanes and exacerbated by sea level rise.

Dr. Richard W Smith

Dr. Smith earned a B.S. degree with a dual major in Chemistry and Environmental Science from SUNY Brockport in 2007. He was awarded a Ph.D in Chemical Oceanography from Texas A&M University in 2011, and his dissertation research on the natural carbon storage capacity of fjords in New Zealand has been featured in *National Geographic* and *Wired* magazine. Dr. Smith has 3 years of postdoctoral research experience at the University of Connecticut's Department of Marine Sciences. There his research using stable isotopic tracer molecules to determine the fate of explosive compounds (TNT and RDX) leaked from bomb disposal sites in the marine environment received a Project of the Year Award in Environmental Restoration from the Department of Defense. Dr. Smith has published over 30 peer-reviewed articles and has participated in oceanographic research expeditions to the Arctic Ocean, Gulf of Mexico, and coastal New Zealand. After starting Global Aquatic Research in 2014, he has spent the last several years researching the effect of hurricanes on earth's carbon cycle, manufacturing and installing custom lab equipment in government and academic labs, developing an aquatic geochemistry research lab in collaboration with SUNY Brockport, mentoring students, and building infrastructure at the Smithsonian Environmental Research Center to study large storms and sea-level rise.

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