SeaGrant Funding Summary: Rapid Response to the Superior Refinery Fire

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On April 26th, there were multiple explosions and a fire at the Husky Refinery in Superior, WI. Safety measures worked well, with no loss of life and few injuries; however, significant smoke and soot emissions from the fire itself did impact the local airways and may also have impacted local watersheds, the Twin Ports harbor and far western Lake Superior. Our local waters are an important economic driver for the region, supporting tourism and recreation, and we want to ensure that they stay viable for this year and years to come. Thus, we are interested in monitoring water quality in the area in general and, in this case, determining if residual petroleum products and/or black carbon (soot) associated with the refinery fire have entered Lake Superior or Allouez Bay in measurable amounts. We are also interested in whether native microorganisms living in the water can metabolize such inputs, thus cleansing the water and stimulating productivity. By linking both the chemistry and the microbiology we will have a better understanding of how our local freshwater ecosystems are faring.

Sampling

Water samples were taken three times: in the late afternoon of April 26th, while the refinery fire was still actively burning; on April 27th, after the fire had been extinguished; and on on April 30th.

April 26th sampling was performed on the R/V *Blue Heron* at approximately 4:30 PM. Water samples for hydrocarbons, black carbon, particulate organic carbon (POC), dissolved organic carbon (DOC), and total organic carbon (TOC) were taken at the following site (see Figure 1):

1. Superior Entry (Sup Ent)

April 27th sampling was performed on the R/V *Kingfisher*. In addition to the sample types taken for the April 26th sampling, additional samples were also taken, including chlorophyll and nutrient samples collected by a scientist from the Lake Superior National Estuarine Research Reserve. These samples were collected at the following sites:

1. Faxon Creek (FC): site in estuary off the mouth of Faxon Creek
2. Nemadji River (NR): site just inside the Nemadji River entrance into the estuary
3. Allouez Bay (AB): site just into Allouez Bay from the main estuary, is a NERR sampling site.
4. Superior Entry (SE): site just inside the entry as it was too rough to get out to where the Blue Heron sampled April 26. Site is roughly 1 mile from the lake site where we have lipid data from a previous year's sampling
5. Blatnik Bridge (BlBr): site very near to where we have previous lipid data. Is a NERR sampling site.

6. Newton Creek (NC): this site was iced in but was sampled from a land position on April 27 by NERR researchers using bottles we provided.

For the April 27 samplings, in addition to the carbon sampling listed above, NERR collected water for chlorophyll and nutrient analyses at the same sites and did surface water sonde castes. Samples from the R/V *Kingfisher* were collected with 5-L Niskin bottles attached to a rope and triggered via messenger. Bottles were triggered just after submersion. Field blanks were performed for each Niskin at the end of the cruise using deionized water added to the top of each Niskin and dispensed through the nozzle and sample tubing.

Figure 1. Sampling sites. See text for an explanation of acronyms.

The April 30th sampling was again performed with the R/V *Kingfisher*. The following sites were revisited:

1. Faxon Creek (FC)
2. Nemadji River (NR)
3. Allouez Bay (AB)

Additionally, the sites below were added as sampling locations, since these sites have previous data or archived samples which were also analyzed:

1. Park Point (PP), a site in the estuary off of Park Point Park and the airport (this is a site for which have hydrocarbon data from a previous year
2. Wisconsin Entry (WE), approximately 1 mile into to lake from the end of the entry.
3. Offshore site (OS)

Analysis

Total lipid extracts were analyzed for hydrocarbons by GC-MS in the Schreiner lab. Half-liter samples were liquid-liquid extracted three times with hexanes, and the hexane fraction was concentrated via roto-evaporation. Concentrated samples were run through deactivated silica columns to clean any contamintants, and the neutral fraction containing n-alkanes was analyzed via gas chromatography-mass spectrometry.

TOC, DOC, POC, and black carbon (BC) concentrations in water samples were analyzed in the Minor lab following protocols in Zigah et al. (2012). POC refers to samples with a particle size >0.7 μm (isolated onto GF/F filters for analysis), TOC are values of non-volatile OC from whole water (*i.e.*, unfiltered samples), while DOC are samples of non-volatile organic carbon from water that has gone through GF/F filters with a nominal pore size of 0.7 μm.

Results

One of the challenges in this sort of sampling is finding relevant pre-event reference samples for comparison. As this project only measured samples post-event, we provide previous data from our lab and from the literature in an attempt to place these samples in context.

Table 1 below summarizes the results of TOC, DOC, POC, and BC analysis from this sampling effort. None of the water samples analyzed for n-alkanes had concentrations of n-alkanes above the laboratory blank value, so those data are not presented here.

Table 1. Sampling information and the concentrations of TOC, DOC, POC and black carbon as field-blank corrected values in mgC/L. We also present the weight % of black carbon to total organic carbon in POC samples.

sample	date	Lat (N)	Long. (W)	Sample depth	DOC (mgC/L)	TOC (mgC/L)	POC (mgC/L)	BC (mgC/L)	BC as % POC
FC	27-Apr-18	46°43.4300’	92°03.871'	1m	8.3	8.1	1.02	0.061	6.0
NR	27-Apr-18	46°42.092'	92°01.617'	1m	8.9	8.3	3.63	0.232	6.4
AB	27-Apr-18	46°41.895'	92°00.760'	1m	8.7	8.4	1.02	0.022	2.2
SE	27-Apr-18	46°42.639'	92°00.585'	1m	4.6	4.5	0.39	0.082	21.2
BlBr	27-Apr-18	46°44.904'	92°05.924'	1m	8.0	7.9	0.71	0.024	3.4
NC	27-Apr-18	46°42.2795'	92°2.5064'	surface	26.2	29.0	2.48	0	0

FC	30-Apr-18	46°43.422'	92°03.881'	1m	8.5	8.2	1.09	0.022	2.0
NR	30-Apr-18	46°42.099'	92°01.606'	1m	9.2	9.2	1.37	0.191	13.9
AB	30-Apr-18	46°41.900'	92°00.731'	1m	8.2	7.9	1.52	0.09	5.9
PP	30-Apr-18	46°43.804'	92°03.451'	1m	8.2	8.1	1.07	0.029	2.7
WE	30-Apr-18	46°43.297'	91°59.808'	1m	1.2	1.2	0.00	-0.009	0
OS	30-Apr-18	46°47.370'	91°57.813'	1m	1.3	1.3	0.07	0.013	20.0

DOC data from the MPCA sites in the St. Louis watershed (including swampy headwaters sites) sampled in May 2009 yields an average concentration of 21.7 mgC/L (Schminkey and Minor, 2009). Concentrations from Canal Park (near the lift bridge) and Boy Scout Landing on the St. Louis River, both sampled in May 2007 were 9.7 and 16.6 mgC/L (Stephens and Minor, 2010, Stephens, 2008). TOC concentrations from February 2015 for sites FC and NR (Fig 1) were 5.4 and 5.7 mgC/L, respectively. TOC concentrations from site BlBr (Fig 1) in February 2015 and June 2015 were 6 and 20.6 mgC/L, respectively, and exhibit the wide seasonal variability in organic carbon values. Based upon this existing, though admittedly sparse data set, NC stands out as potentially impacted in terms of TOC (29.0 mgC/L) and DOC (26.2 mgC/L). The other samples are within the range seen in our reference samples. Visual observations from those handling the NC sample were that it had a distinct odor and was “frothy”, perhaps indicating contamination with an organic rich material.

Average POC concentration for samples from the St Louis estuary and its headwaters, sampled April 2012 to Sept 2013 1.58 ± 1.74 mgC/L (Loken et al. 2016). In the open-lake, including near-shore and offshore locations, average POC concentrations in September 2011 were 0.308 ± 0.031 mgC/L (with 53 samples analyzed). Based upon this data, the April 27, 2018 samples for NR and possibly NC appear potentially impacted.

Existing BC data for Lake Superior are from four open water sites and exhibited a concentration range of 0.002 to 0.005 mgC/L, which represented between 4 and 9% of the organic carbon in bulk POC samples (Zigah et al., 2012). As this open water data is sparse and less likely to show values representative of nearshore sites impacted by local anthropogenic inputs, we therefore searched in the literature for particulate BC data using the same filter sizes and reporting the %BC for POC samples. In the Gulf of Maine, particulate BC concentrations (>0.7 μm) ranged from <0.0001 to 0.016 mgC/L and were 1 to 20% of the carbon in POC (Flores-Cervantes et al., 2009). In the much more anthopogenically impacted Bohai Rim, which includes regions with the “highest [OC and BC] emission intensities in China” (Fang et al., 2018), particulate BC in river water averaged 0.37 mgC/L (with a standard deviation of 0.67 mgC/L), and represented, on

average 9.0 ± 4.3% of the POC (Fang et al., 2018). In comparison with these literature values, site NR seems impacted, with an order of magnitude higher concentration of BC than seen in the Gulf of Maine and approaching the average river values in the Bohai Rim. In terms of %BC in POC, sites SE, NR, and OS appear impacted. Sites SE and OS may be more sensitive to BC inputs because they have low total POC concentrations. It thus appears that sites SE and NR were most impacted by soot material (most likely aerially deposited) and that site OS may show traces of this as well, most likely due to a low background of other organic particles.

References:

Fang, Y., Chen, Y., Tian, C., Wang, X., Lin, T., Hu, L., et al. (2018). Cycling and budgets of organic and black carbon in coastal Bohai Sea, China: Impacts of natural and anthropogenic perturbations. Global Biogeochemical Cycles, 32, 971–986. https://doi.org/10.1029/2017GB005863

Flores-Cervantes, D.X., Plata, D.L., MacFarlane, J.K., Reddy, C.M., and Gschwend, P.M. (2009). Black carbon in marine particulate organic carbon: Inputs and cycling of highly recalcitrant organic carbon in the Gulf of Maine. Marine Chemistry 113, 172–181. http://dx.doi.org/10.1016/j.marchem.2009.01.012

Loken, L.,Small, G.E., Finlay, J.C., Sterner, R., Runde, E., Brovold, S., and Stanley, E.H. (2016). Saint Louis River Estuary Water Chemistry, Wisconsin, Minnesota, USA 2012 – 2013. DOI: 10.6073/pasta/08fdc0fb8528e37dd7ef6d6ad2b77f99. https://lter.limnology.wisc.edu/dataset/saint-louis-river-estuary-water-chemistry-wisconsin-minnesota-usa-2012-2013

Schminkey, D. and Minor, E.C. Characteristics of Dissolved Organic Carbon within the Lake Superior Watershed, SURP poster presentation, August 2009, University of Minnesota Duluth.

Stehens, B.M. (2008). DOM Characteristics along the Continuum from River to Reservoir: a Comparison of Freshwater and Saline Transects. Master's thesis, Water Resources Science, University of Minnesota.

Stephens, B.M. and Minor, E.C. (2010). DOM characteristics along the continuum from river to receiving basin: a comparison of freshwater and marine transects. Aquatic Sciences, doi: 10.1007/s00027-010-0144-9. https://link.springer.com/article/10.1007/s00027-010-0144-9

Zigah, P.K., Minor, E.C., and Werne, J.P. (2012). Radiocarbon and stable-isotope geochemistry of organic and inorganic carbon in Lake Superior. Global Biogeochemical Cycles 26, GB1023, doi:10.1029/2011GB004132 http://onlinelibrary.wiley.com/doi/10.1029/2011GB004132/pdf

MN SeaGrant awarded $2000:

Amount spent: $500 boat time
Lab analyses: $820.13
Lab supplies: GF/F filters,1 box nitrile gloves, kimwipes, 2 cases of 1-L media bottles, 1 case VOC vials, 1 bottle HCl, pipet tips: $680

Note: we are not pursuing further hydrocarbon analyses or microbial analyses and will not, therefore, be needing to invoice Wisconsin SeaGrant for further sample processing.