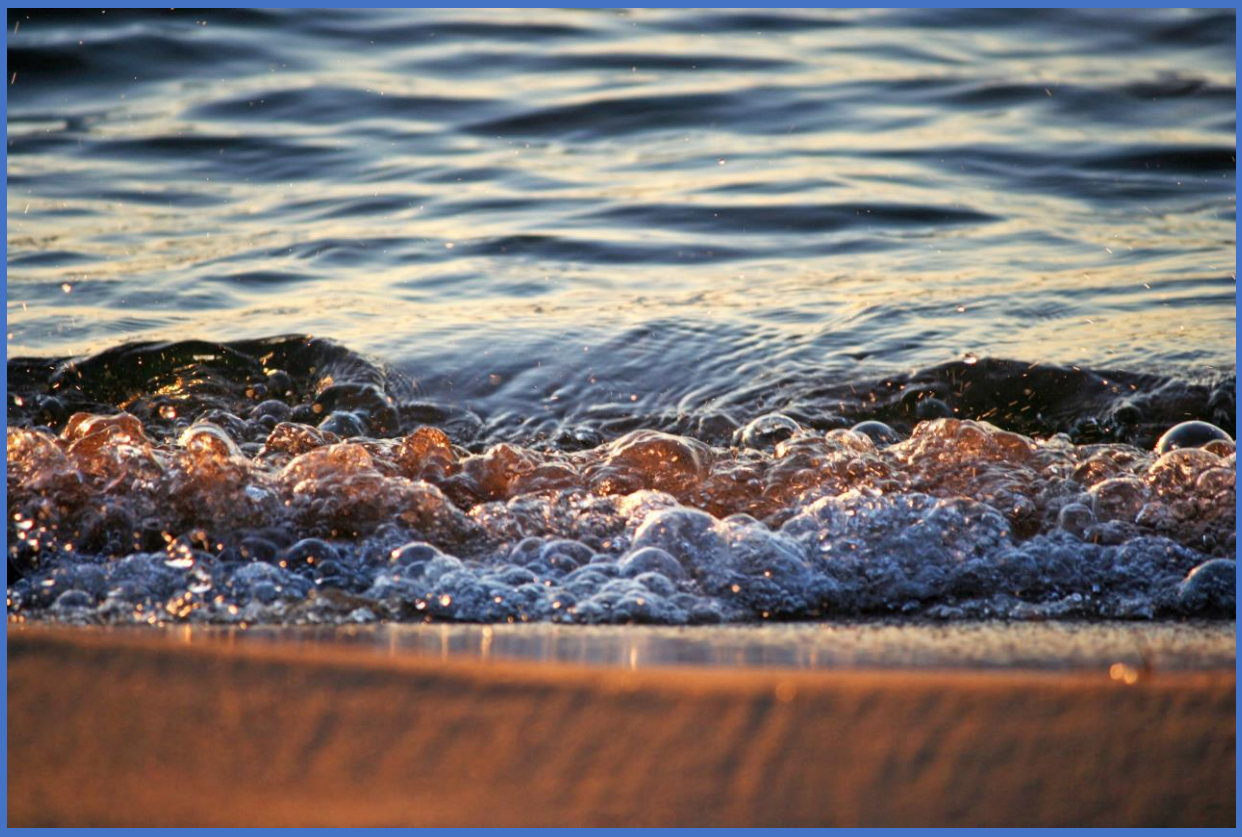
Lake Superior National Coastal Condition Assessment: Additional Water Quality Measurements Report 2021



"Shore Bubbles" by Bill Carroll 2014 Great Lakes Photo Contest

Office of Great Waters -- Northern Region

Wisconsin Department of Natural Resources

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Introduction

Each year EPA conducts a National Aquatic Resources Survey (NARS), which uses a statistical survey design to provide a snapshot of the overall condition of the nation's waters. The use of standardized methods allows for the comparison of data across the nation, as well as through time. On a five-year rotation the nation's coastal waters, lakes and reservoirs, rivers and streams, and wetlands are sampled. This work is done in partnership with states, tribal and federal partners. The work described in this document is a part of the National Coastal Condition Assessment (NCCA). This assessment focuses on coastal waters (Marine and Great Lakes coasts). The two goals of NCCA are to determine "What percent of the Nation's coastal waters are in good, fair, and poor condition for key indicators of water quality, ecological health, and recreation" and "What is the relative importance of key stressors such as nutrients and contaminated sediments?" For the 2021 NCCA, the State of Wisconsin was to sample 6 sites in the Lake Superior nearshore for water quality, sediment quality, benthic community condition, and fish tissue contaminants indices, using standardized methods.

To better characterize Wisconsin's Lake Superior nearshore conditions, Wisconsin DNR intensified efforts and sampled 24 sites for water chemistry in addition to the 6 standard NCCA sites, for a total of 30 sites sampled. There is minimal water quality data for the nearshore of Lake Superior, so this information will begin to address these gaps as well as inform DNR's nearshore monitoring strategy and allow for the calculation of the eutrophication index.

At 10 of the 24 sites, sediments were also collected and examined for dioxin. Sediment samples were collected and analyzed for dioxin to support the State of Wisconsin's efforts on the 2022 Lake Superior Lakewide Action Management Plan (LAMP) priorities. Specifically, LAMP Action 8 from Actions to Prevent and Reduce Chemical Contaminant Pollution Table that states:

Continue outreach and education to the public on impacts of chemical contaminants with a focus on mercury, pharmaceuticals, PFAS and dioxins; the pathways into fish, wildlife and humans; and actions that can be taken to help remove contaminants from the basin.

Dioxin is a chemical of concern in Saint Louis River sediments due to the industry on its shoreline. Sediment transport from the estuary to the nearshore of Lake Superior is evident, especially during large storm events that potentially distribute polluted sediments. These sediments are thought to travel with the prevailing current to the northeast and deposited along the southern shore of the lake. However, there is little data available to determine background concentrations of dioxin in the nearshore regions of Lake Superior. The data collected during this study will support the State of Wisconsin in assessing background concentrations and the fate and transport of dioxin in the Lake Superior nearshore.

This additional data enhancement has two components: (a) additional water quality data collection and (b) sediment sample collection and analysis for dioxin concentrations. Water quality data enhancements consisted of collecting water samples and analyzing for base NCCA water quality parameters (in-situ measurements= dissolved oxygen, pH, Salinity, conductivity, temperature, water column transparency, light attenuation, CHEM= total nitrogen, total phosphorus, pH, conductivity, alkalinity, chloride, sulfate, NUTS= ammonia, nitrate-nitrite, ortho-phosphate and WCHL= chlorophyll-*a).*

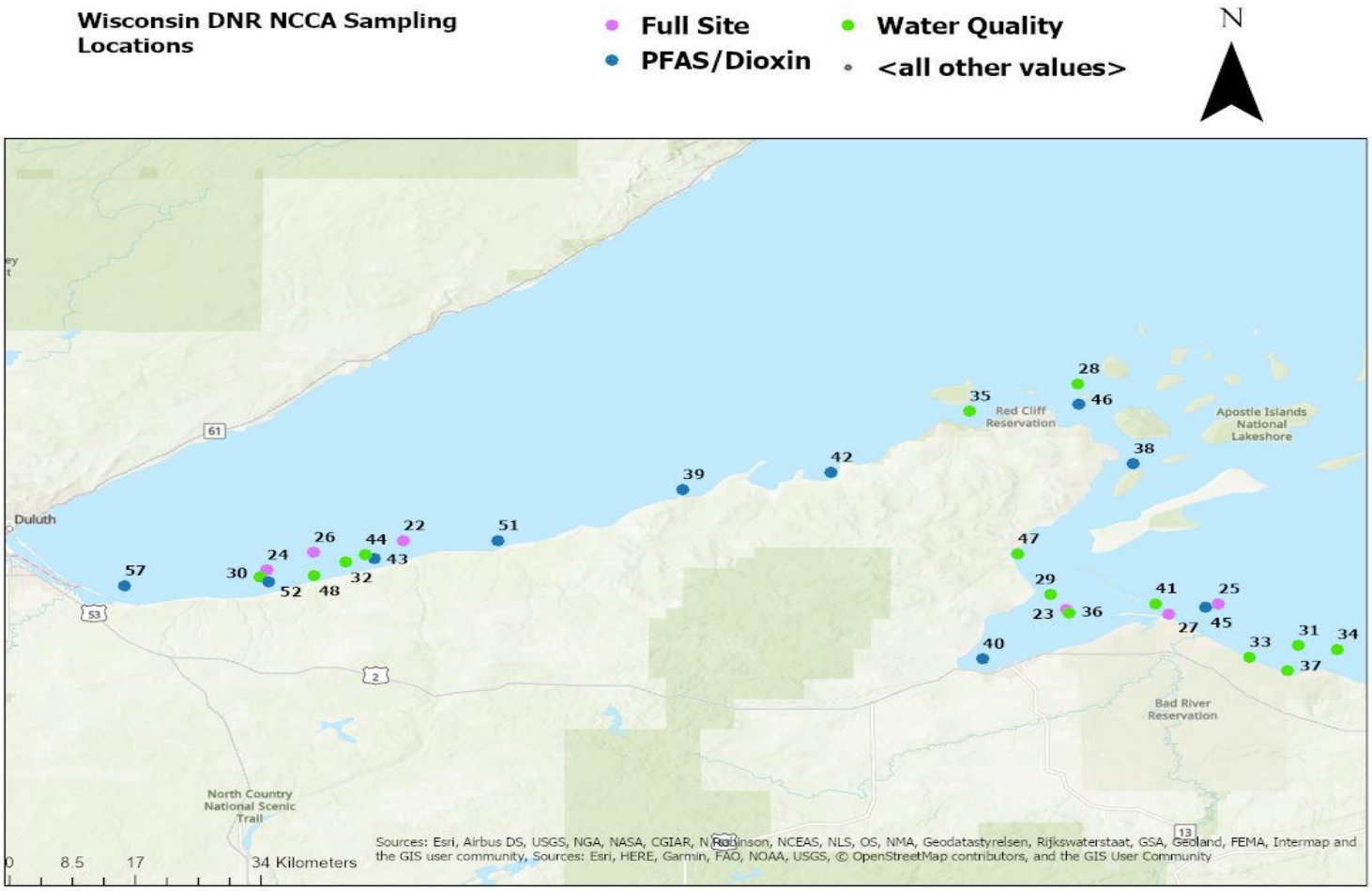

Figure 1 Map of NCCA sampling sites. Purple circles are Full NCCA sites, Blue circles are sites that were sampled for dioxin and water quality parameters. Green circles are where just water quality samples were taken. Numbers refer to the site ID

Methods:

Experimental Design

The NCCA sampling is a probabilistic sampling design, that provides statistically-valid estimates of the condition of all coastal waters with known confidence. Sample sites are selected at random to represent the condition of all coastal waters across each region. A probabilistic survey design allows for the determination of parameters of interest using a representative sample of relatively few members or sites. Using this survey design allows data from the subset of sampled sites to be applied to the larger target population, and assessments with known confidence bounds to be made.

The areas of interest for this assessment are limited to the fringing, shallow band of coastal waters most heavily used by humans and most vulnerable to activities within adjacent coastal watersheds. In the Great Lakes, these are areas 5km from shore and waters 30 meters or less in depth.

Water Quality

WQ, NUTS, and WCHL parameters were analyzed at 23 enhancement sites in addition to the 6 base NCCA sites (Figure 1). Sampling locations for enhancement sites were provided by Mari Nord (EPA) at WDNR's request and were determined following the same random probabilistic study design used in the larger NCCA study. This allows us to extrapolate the condition of these sites to the extent of Wisconsin's Lake Superior coastline (Figure 1).

Dioxin

Out of the enhancement locations requested from EPA, we selected 10 sites to collect additional dioxin sediment samples (Figure 1) (Appendix Table 1). Dioxin is listed as a priority in the Lake Superior Lakewide Action Management plan because it is responsible for fish consumption advisories in some areas of Lake Superior and is a part of the Zero discharge demonstration program. Two objectives drove the dioxin sampling design. First, we want to determine background levels of dioxin in Wisconsin's nearshore of Lake Superior, which will help to inform plans for placement and beneficial use of dredge materials in Lake Superior. The sites selected provide adequate spatial coverage to represent background conditions in the lake. The second was to assess the dispersion of dioxin leaving the St. Louis River estuary and moving along the south shore of Lake Superior. St. Louis River Estuary is a source of sediment-bound dioxin to Lake Superior, but it is not clear how this dioxin moves along the south shore of the lake, or if there may be additional sources of dioxin entering the system contributing to fish consumption advisories and negative ecological impacts. We selected sites that follow the known currents in Lake Superior as we anticipated that sediment from the estuary travels east along the nearshore and slowly settles to the lake bottom. By choosing sampling locations along this gradient, we hoped to determine where deposition of dioxin-contaminated sediment is occurring.

Sampling methods

All samples were collected using NCCA protocols, see the NCCA QAPP for more detailed information. For quality assurance of these samples, all the established steps in the NCCA QAPP will be taken. For in-situ measurements, we followed NCCA QAPP section 5.1, for CHEM, NUTS, and WCHL we will follow section 5.2. We will be using NCCA sediment sampling methods for these parameters QAPP section 5.6.

Sampling handling details are provided in Table 1.

Laboratory analysis

Samples for water quality were sent to the Wisconsin State Laboratory of Hygiene (WSLH). WSLH followed the NCCA Laboratory operations manual for CHEM, NUTS, and WCHL parameters. Dioxin samples were sent to Pace Analytical for analysis using the 1613B method (Appendix A). This is a State of Wisconsin certified laboratory for dioxin analysis. This method targets a Limit of Detection that is related to water quality concerns rather than the remediation of contaminated sediment. This method has a holding time of 1 year, a method detection limit for a Total TCDF of 3.1 pg/L, and doesn't require preservation. The laboratory will follow DNR guidance on the method of reporting limits.

Table 1 Detailed description of sample collection

Parameter	Lab Code	Collection Bottle	Field Filter?	Preservation/Shipping	Hold Time	LOD
Orthophosphate (OrthoP)	ICC53000FF	60 mL polyethylene	Yes 0.45 um	Less than 6C, but not frozen	48 hours	0.0023 mg/L
Total Phosphorus (TP)	ICC52010	250 mL plastic bottle	no	1 mL of 25% H2SO4, Less than 6C, but not frozen	28 days	0.012 mg/L
Total Nitrogen (TN)	ICC46601	250 mL plastic bottle	no	1 mL of 25% H2SO4, Less than 6C, but not frozen	28 days	0.058 mg/L
Nitrate nitrite (NO_3/NO_2)	ICC46000	250 mL plastic bottle	no	1 mL of 25% H2SO4, Less than 6C, but not frozen	28 days	0.055 mg NO3+NO2-N/L
Ammonium (NH_4)	ICC440001	250 mL plastic bottle	no	1 mL of 25% H2SO4, Less than 6C, but not frozen	28 days	0.012 mg/L NH3-N
Chlorophyll a (Chla)	ICC25120	Plastic Quart 500mL	Yes 47 mm, 0.7 um pore, no more than 6 inches of mercury (20kPa)	if filtered 15 mL polypropylene centrifuge tube wrapped in foil on ice. If not packed with ice in a dark cooler	if not filtered 48 hrs. If filtered 3.5 weeks	0.26 ug/L
Conductivity, Alkalinity, pH	ICC30501	Plastic	No	Refrigerated at 4C	14 days for alkalinity and pH 28 days for conductivity	20 mg/L CaCO3 10 uS/cm Conductivity 4 mg/L Alkalinity
Sulfate	ICC36201	60mL polyethylene bottles	no	Refrigerated 4C	28 days	0.16 mg/LI<3I
Chloride	ICC24202	60mL polyethylene bottles	No	Refrigerated 4C	28 days	0.031 mg/L
Dioxin	1613B	4 oz. Amber Wide mouth Jar	No	Refrigerated at 4C	1 year	Total TCDF of 3.1 pg/L

Data Analysis

Eutrophication Index

The eutrophication index is the index that the EPA uses to determine the eutrophic nature of the sampling site. It focuses on assessing parameters indicative of eutrophic status rather than general water quality parameters. There are other indexes related to fish toxicity and sediment quality/toxicity, but we focus on eutrophication, since this was determined to be the most important gap to address at the time. Information from the National Coastal Condition Assessment 2015 Technical Support Document was used to determine the criteria for the calculation of the Eutrophication Index. This index uses 4 parameters to assess Great Lakes water quality: total phosphorus and chlorophyl *a* concentration in surface waters, dissolved oxygen at the bottom of the water column, and Secchi depth (See Appendix Table 2). Some sites were missing dissolved oxygen measurements at the deepest part of the water column, when this occurred the last measurement recorded was used for the index.

Table 2 Indicator Criteria for Eutrophication index specific to Lake Superior

Lake Superior NCCA Eutrophication indicators	Good	Fair	Poor
TP (ug/L)	<5	5 to 10	>10
Chla (ug/L	<1.3	1.3 to 2.6	>2.6
DO (mg/L)	>5	5 to 2	<2
Secchi (m)	>8	8 to 5.3	<5.3

Dioxin

EPA 1613B was used to measure Dioxin. Measurements of individual compound concentrations were reported in ng/Kg. These individual concentrations were multiplied by the Toxic Equivalency Factor (TEF) for that compound, obtained from the Consensus-Based Sediment Quality Guidelines (https://dnr.wi.gov/files/pdf/pubs/rr/RR088.pdf). Reported here is the Sum of the TCDD equivalency of Individual Substituted Dioxin and Furan Congeners.

Results

General Water Quality

A summary of the water quality parameters collected from all NCCA sites gives a general sense of what conditions at these sites were like throughout the summer field season (Table 3). Water quality parameters distribution varied spatially for each parameter (Appendix Figures 1, 2, and 3). OrthoP values were low across all sampling points (Appendix Figure 3). Nitrate showed lower concentrations in Chequamegon Bay and eastern Wisconsin (Appendix Figure 2).

Table 3 Summary Statistics for Water Quality Parameters. This includes standard sites and enhancement sites. Count is number of samples, mean is average concentration of parameter, min is the minimum value observed, max is the maximum value observed and stdev is the standard deviation for each parameter.

Parameter	count	mean	min	max	stdev
Alkalinity (mg/L)	31	43.90	42.80	47.40	0.78
Chla (ug/L)	31	0.78	0.14	1.93	0.34
Chloride (mg/L)	31	1.72	1.55	2.00	0.12
Conductivity (uS/cm)	31	102.4	100.0	108.0	1.6
DO (mg/L)	30	10.05	8.97	11.29	0.61
NO3 (mg/L)	24	0.316	0.243	0.346	0.024
pgTCDD.EQ/kg sed	10	2.4	0	15.5	4.8
pH lab	31	7.61	7.28	7.91	0.14
Secchi (m)	31	6.7	3.3	11.3	1.9
Solids.percent	10	65.5	43.2	79.2	10.8
OrthoP (mg/L)	22	0.004	0.002	0.010	0.001
Sulfate (mg/L)	31	3.69	3.40	3.92	0.12
TN (mg/L)	31	0.416	0.361	0.444	0.018
TP (mg/L)	29	0.004	0.00205	0.018	0.003

Eutrophication Index

The eutrophication index is the index that the EPA uses to determine the eutrophic nature of the sampling site. Data was collected on a variety of days throughout the summer sampling season (June-August), this indicates that a wide variety of conditions are most likely experienced throughout this timeframe not allowing a site to site comparison (Table 1 in Appendix). The majority of sites were categorized as fair, this was typically due to low secchi depths (Figure 2, Table 4). It is thought that the low secchi depth for the nearshore is driven by erosion from the clay shoreline impacting light environment at each site. The sediments entering the nearshore system don't seem to be associated with an increase in TP or chla concentrations, based on a "good" ranking in these categories. Wisconsin's south shore is known to be rich in red clay banks, which can be eroded into the nearshore during rain events or during high water levels. Site 22 was the only site that was sampled twice, once on June 21st and then again on August 30th, 2021, both times it was classified as in good condition.

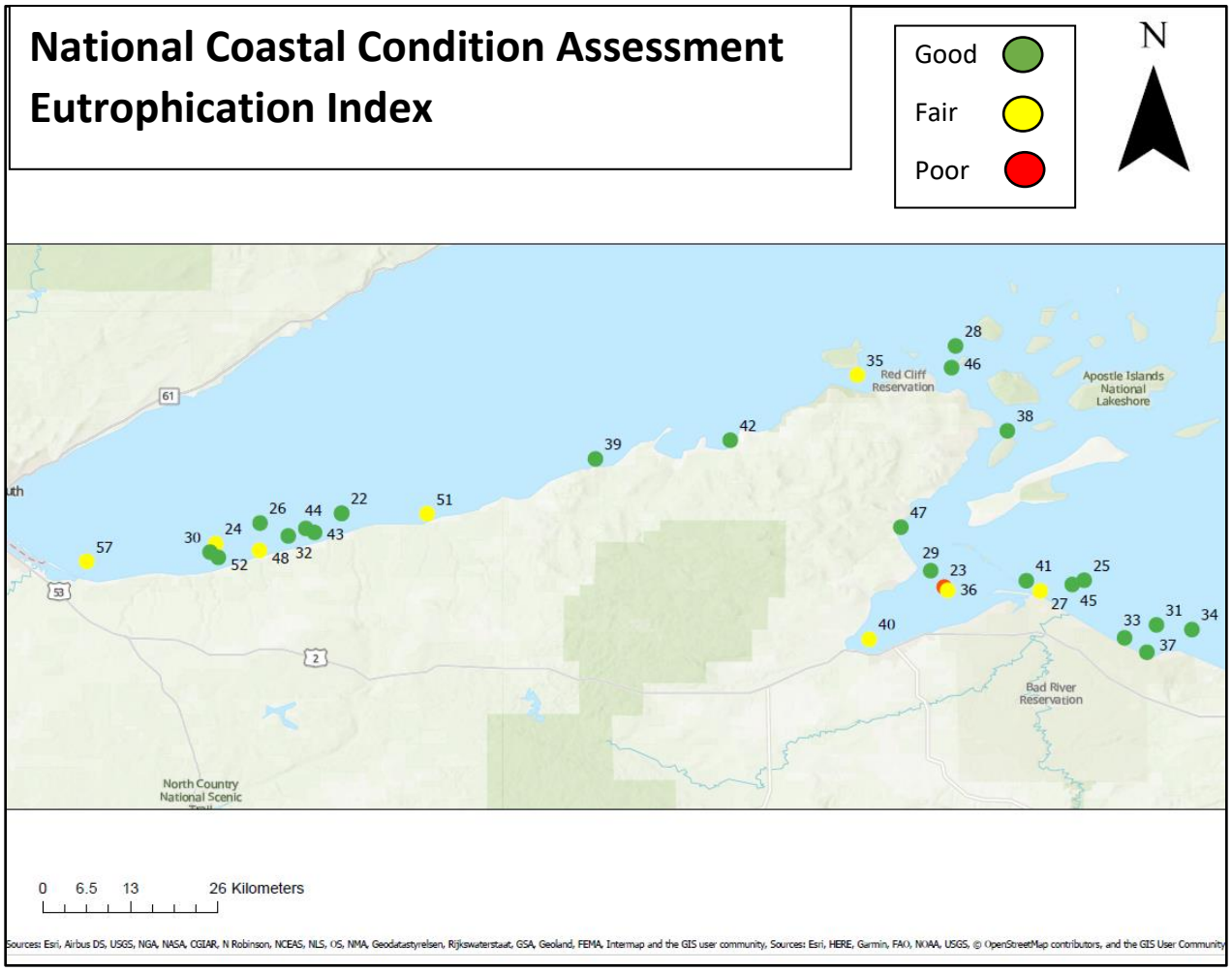

Figure 2 Map indicating the Eutrophication index of sites sampled. Green indicates sites that were designated as good, yellow indicates fair sites and red indicates poor conditions. Numbers are site IDs.

Table 4 Summary of Eutrophication indicators, percent of sites per classification.

	TP	*Chlorophyll a*	*Secchi*	*DO*	*Overall Condition Eutrophication*
% Good	83	94	23	100	71
% Fair	14	6	52	0	26
% Poor	3	0	26	0	3

Dioxin

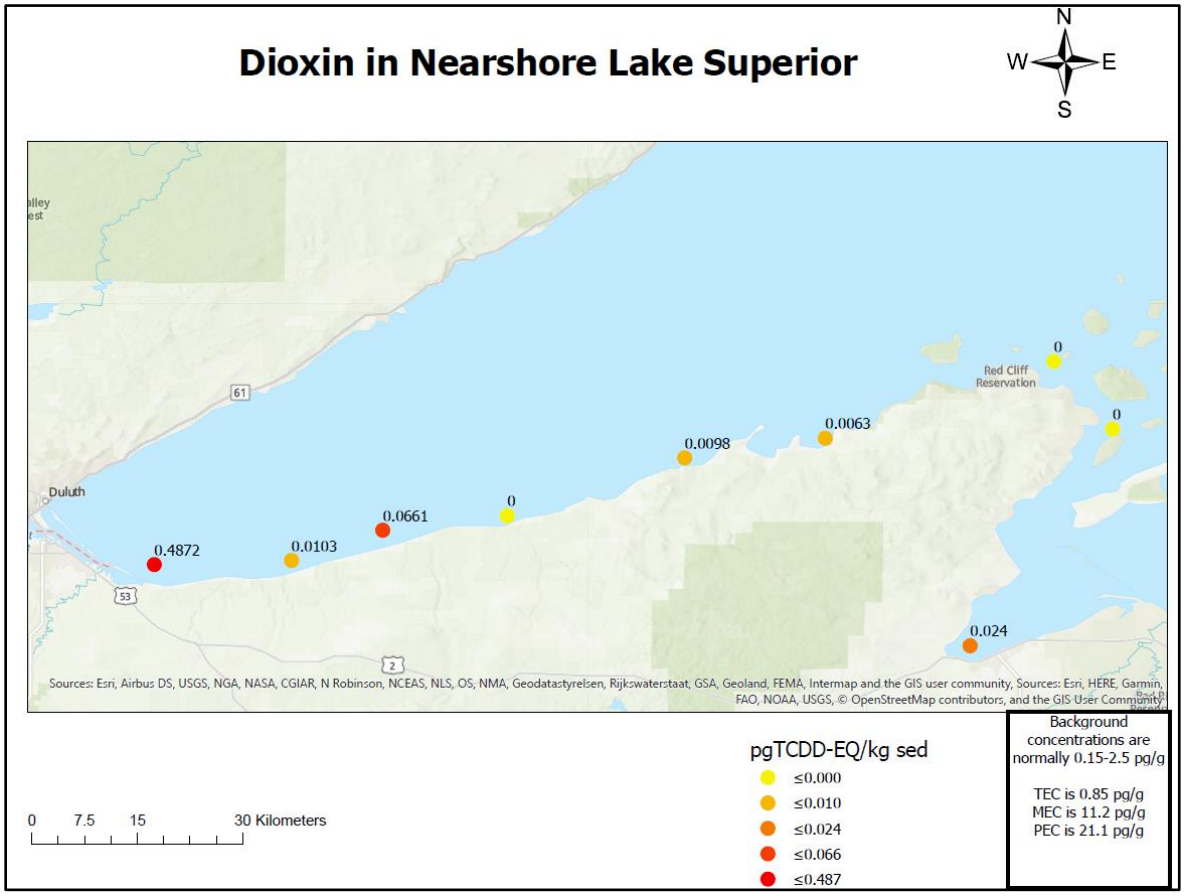

Figure 3 Dioxin Concentrations for 10 locations in Nearshore Lake Superior. Numbers indicate the concentration of TCDD -EQ at each site

All sites have concentrations of dioxins within sediments that are less than Threshold Effects Concentration (TEC), which indicates that benthic macroinvertebrates are most likely not experiencing toxicity due to the presence of dioxin at these sites. The relatively higher concentration outside of the Superior Entry is most likely because of its proximity to the St. Louis River and industrial harbor. Water exiting the Superior entry generally travels along the south shore, up and around the Bayfield peninsula. The sediment that is associated with this flow may fall out of the water column and deposit along the southern shore explaining the pattern observed in dioxin concentrations (Figure 3).

Conclusions

Overall, the nearshore of Lake Superior is characterized as Good to Fair in terms of the eutrophication index. The sites that are designated as Fair are typically in this category because of a lower secchi depth than what the criteria requires. More information regarding the health of other portions of Lake Superior, other Great Lakes, and coastal shorelines will be available through the National Aquatic Resources Survey. The next NCCA is scheduled for 2025, and we intend to lead a similar sampling effort with an intensification of sampling sites. We hope to use these datasets to establish trends of Lake Superior's Wisconsin's nearshore throughout time.

Appendix:

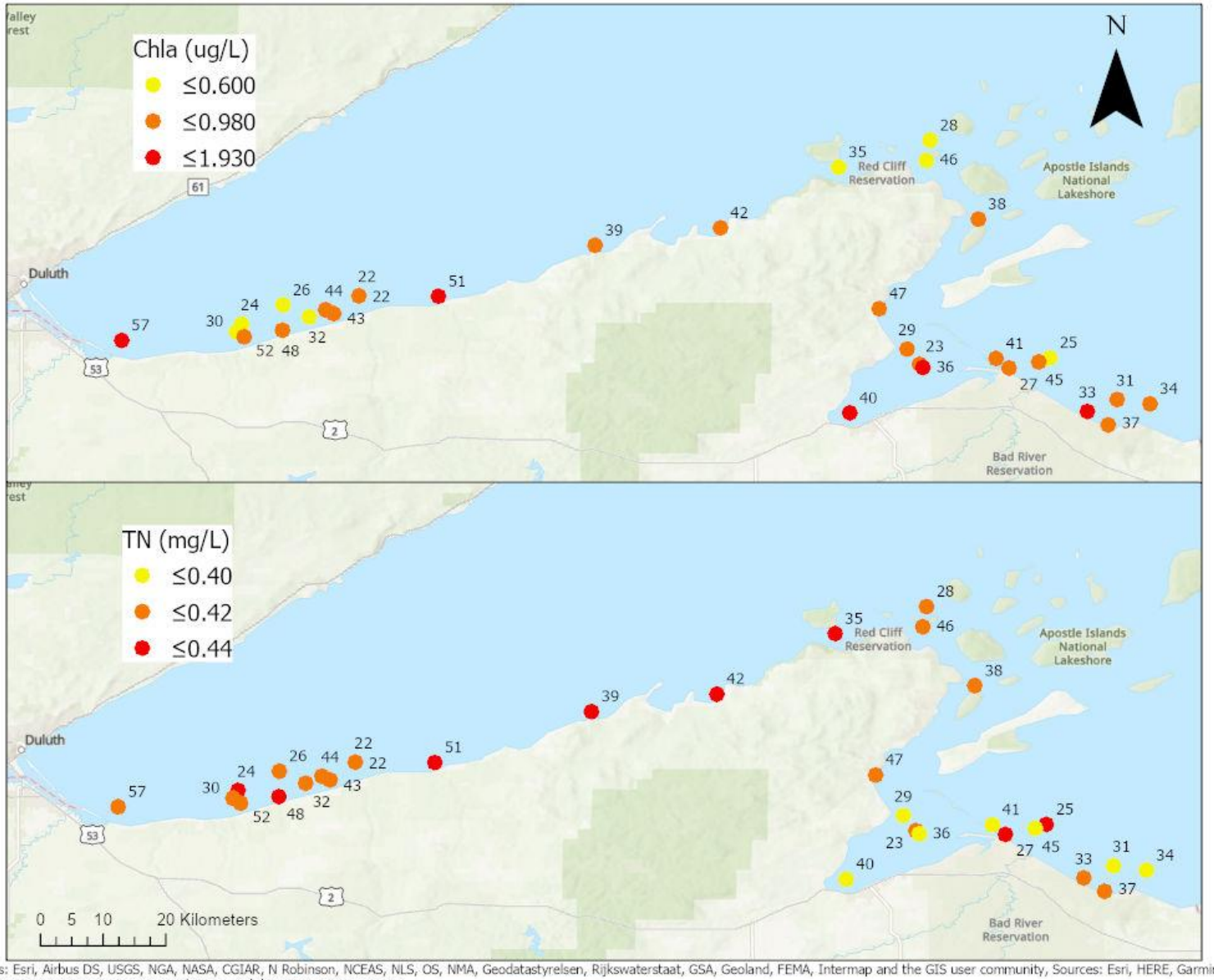

Figure 1 Map depicting concentrations of Chla (top) and TN (bottom) at sampling locations.

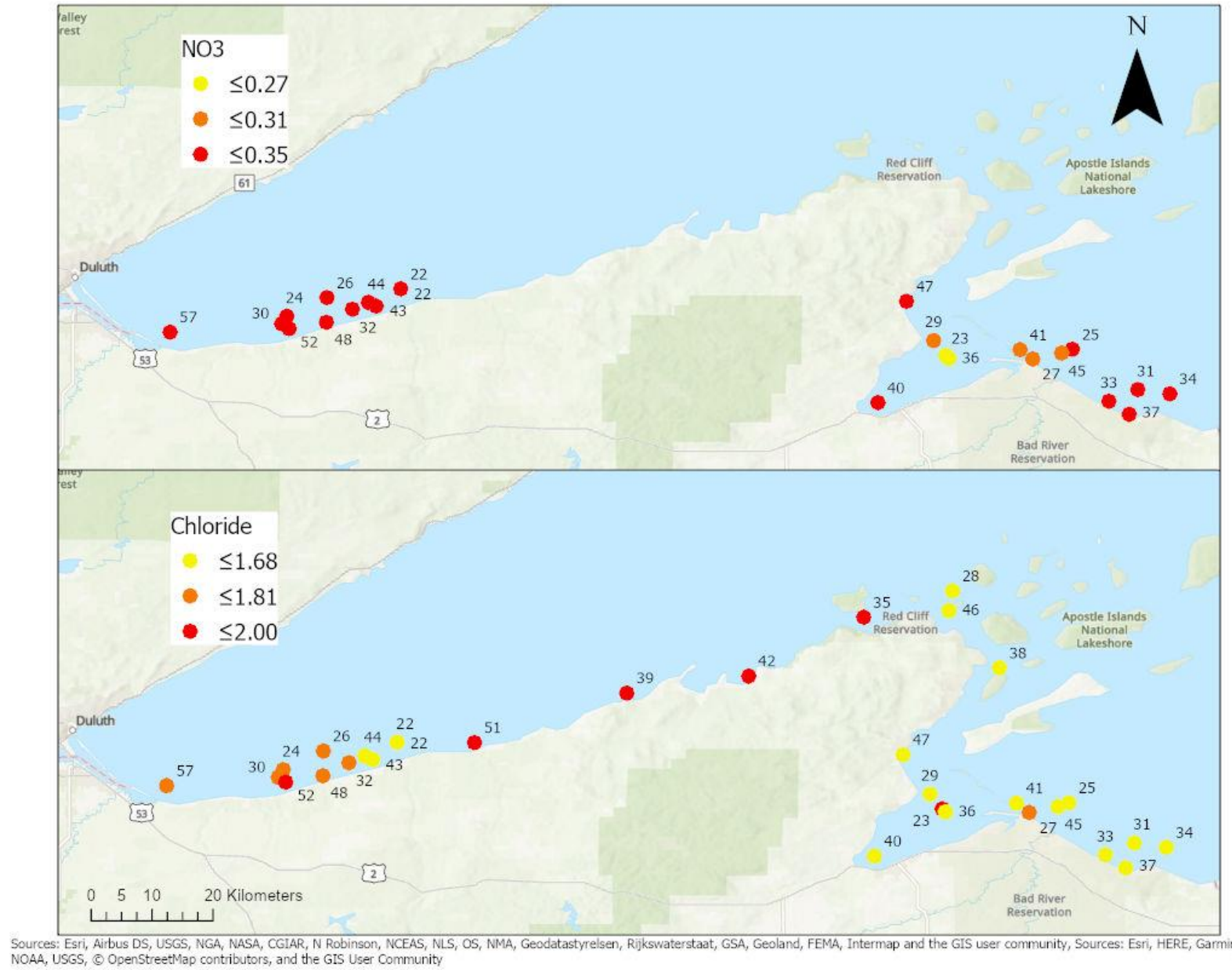

Figure 2 Map depicting concentrations of NO3 (top) and Chloride (bottom) at sampling locations.

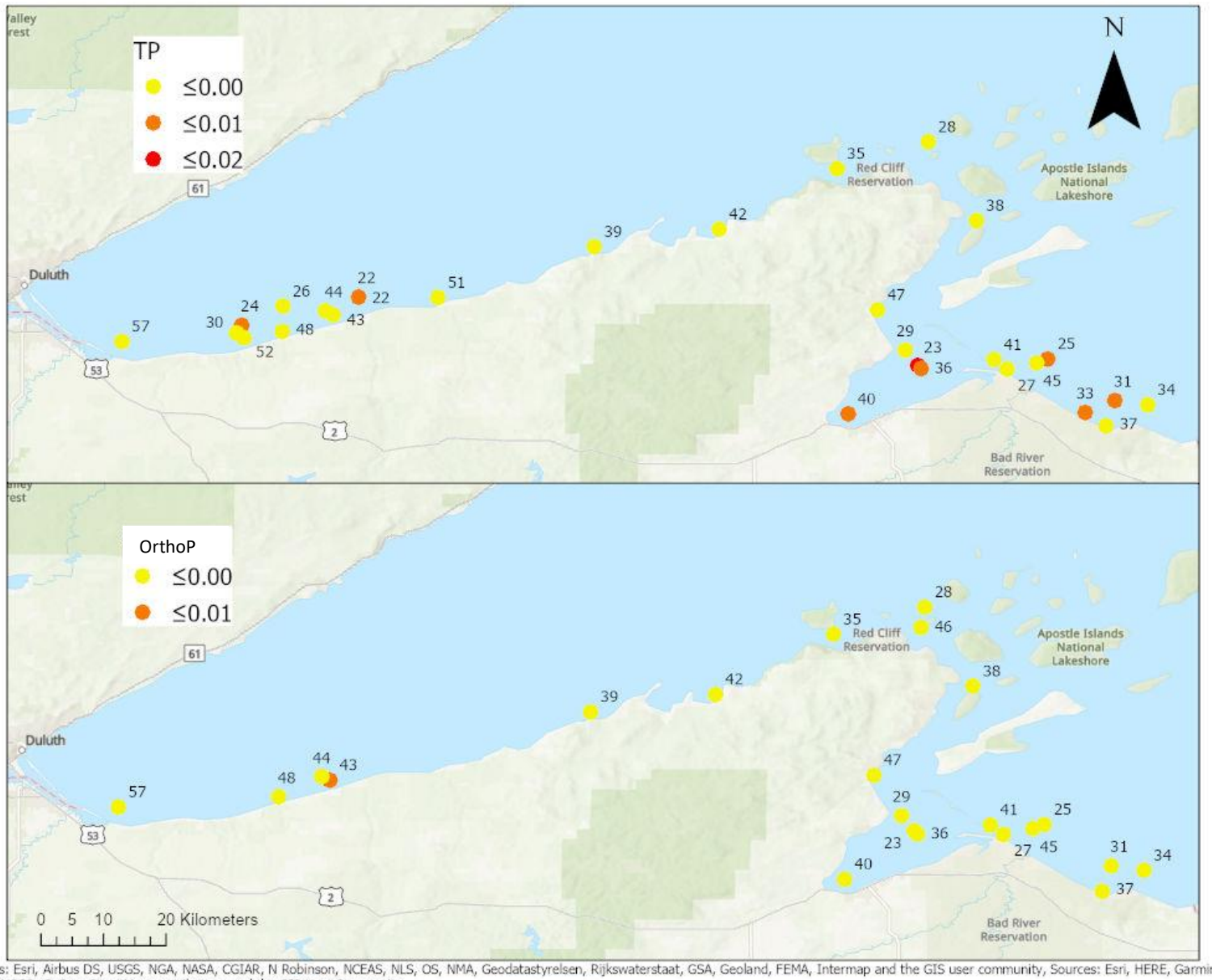

Figure 3 Map depicting concentrations of TP (top) and OrthoP (bottom) at sampling locations.

Table 1 Latitude and Longitude for Sites, with NCCA site IDs, and description. Over20_20 sites are enhancement sites.

Site ID	Classification	Date	Lat	Long
22	Base	21-Jul-21	46.7707	-91.6211
23	Base	29-Jun-21	46.6727	-90.8184
24	Base	21-Jul-21	46.7303	-91.7889
25	Base	29-Jun-21	46.6817	-90.6319
26	Base	21-Jul-21	46.7578	-91.7298
27	Base	29-Jun-21	46.6674	-90.6903
28	WQ	13-Jul-21	46.99342	-90.8032
29	WQ	16-Aug-21	46.6944	-90.8363
30	WQ	4-Aug-21	46.71915	-91.7964
31	WQ	17-Aug-21	46.62227	-90.5356
32	WQ	4-Aug-21	46.74062	-91.6922
33	WQ	17-Aug-21	46.60505	-90.5782
34	WQ	17-Aug-21	46.61603	-90.4884
35	WQ	13-Jul-21	46.9548	-90.9341
36	WQ	16-Aug-21	46.66808	-90.8136
37	WQ	17-Aug-21	46.5859	-90.5484
38	WQ, Sed	13-Jul-21	46.88045	-90.7342
39	WQ, Sed	15-Jul-21	46.84307	-91.283
40	WQ, Sed	16-Aug-21	46.60308	-90.9183
41	WQ	17-Aug-21	46.68097	-90.709
42	WQ, Sed	15-Jul-21	46.86803	-91.1034
43	WQ, Sed	4-Aug-21	46.74523	-91.6572
44	WQ	4-Aug-21	46.75063	-91.6688
45	WQ, Sed	17-Aug-21	46.67602	-90.6478
46	WQ, Sed	13-Jul-21	46.96448	-90.8086
47	WQ	16-Aug-21	46.75223	-90.8761
48	WQ	4-Aug-21	46.72145	-91.7305
51	WQ, Sed	15-Jul-21	46.77013	-91.5073
52	WQ, Sed	4-Aug-21	46.712	-91.7854
57	WQ, Sed	4-Aug-21	46.7068	-91.9607
22 RVT	Base	30-Aug-21	46.7707	-91.6211

Table 2 Summary of Data used to calculate Eutrophication Index

Site ID	TP (mg/L)	TP indicator	ChlA (ug/L)	ChlA indicator	Secchi (m)	Secchi indicator	DO (mg/L)	DO indicator	Overall Eutrophication
22	0.004	Good	0.20	Good	7	Fair		Poor	Good
23	0.018	Poor	0.87	Good	4	Poor		Poor	Poor
24	0.005	Fair	0.14	Good	6	Fair		Poor	Fair
25	0.005	Good	0.45	Good	9	Good		Poor	Good
26	0.004	Good	0.45	Good	9	Good		Poor	Good
27	0.004	Good	0.83	Good	4	Poor		Poor	Fair
28	0.002	Good	0.60	Good	7	Fair	12.55	Good	Good
29	0.004	Good	0.91	Good	7	Fair	10.34	Good	Good
30	0.003	Good	0.49	Good	9	Good		NA	Good
31	0.005	Good	0.80	Good	9	Good	9.65	Good	Good
32	NA	NA	0.58	Good	9	Good	11.23	Good	Good
33	0.005	Good	1.18	Good	8	Fair	10.91	Good	Good
34	0.003	Good	0.73	Good	9	Good	9.36	Good	Good
35	0.002	Good	0.45	Good	3	Poor	10.88	Good	Fair
36	0.006	Fair	1.93	Fair	4	Poor	9.69	Good	Fair
37	0.003	Good	0.70	Good	6	Fair	10.58	Good	Good
38	0.002	Good	0.72	Good	7	Fair	12.34	Good	Good
39	0.002	Good	0.73	Good	7	Fair	11.89	Good	Good
40	0.005	Fair	1.33	Fair	5	Poor	10.60	Good	Fair
41	0.002	Good	0.87	Good	6	Fair	9.67	Good	Good
42	0.003	Good	0.98	Good	6	Fair	12.21	Good	Good
43	0.002	Good	0.74	Good	7	Fair	10.50	Good	Good
44	0.002	Good	0.75	Good	7	Fair	9.21	Good	Good
45	0.003	Good	0.82	Good	8	Fair	10.32	Good	Good
46	NA	NA	0.49	Good	7	Fair	11.41	Good	Good
47	0.004	Good	0.81	Good	8	Fair	10.30	Good	Good
48	0.003	Good	0.87	Good	5	Poor	8.94	Good	Fair
51	0.002	Good	1.14	Good	5	Poor	11..35	Good	Fair
52	0.003	Good	0.67	Good	6	Fair	9.11	Good	Good
57	0.003	Good	1.20	Good	4	Poor	10.68	Good	Fair
22 RVTt	0.008	Fair	0.78	Good	11	Good		Good	Good

Table 3 Summary of data for water quality parameters not summarized in Eutrophication Index calculation

Site ID	OrthoP	TN	NO3	NH3	Chloride	Sulfate	Alkalinity	pH lab	Conductivity	Solids percent	pgTCDD-EQ/kg sed
22	NA	0.42	0.339	NA	1.79	3.79	44.2	7.54	105		
23	0.003	0.42	0.243	NA	2	3.65	44.8	7.68	103		
24	NA	0.43	0.346	NA	1.77	3.75	43.9	7.64	104		
25	0.002	0.44	0.315	NA	1.68	3.53	44.2	7.59	102		
26	NA	0.42	0.337	NA	1.73	3.76	43.7	7.54	103		
27	0.003	0.43	0.285	NA	1.75	3.4	47.4	7.77	108		
28	0.004	0.41		NA	1.57	3.56	43.3	7.35	100		
29	0.004	0.39	0.292	NA	1.68	3.69	43.1	7.72	102		
30	NA	0.42	0.325	NA	1.71	3.76	43.6	7.55	102		
31	0.003	0.40	0.328	NA	1.63	3.67	43.4	7.61	101		
32	NA	0.42	0.332	NA	1.78	3.65	43.7	7.56	101		
33	NA	0.42	0.324	NA	1.6	3.67	43.7	7.68	102		
34	0.004	0.40	0.321	NA	1.6	3.63	43.4	7.75	101		
35	0.004	0.44		NA	1.94	3.91	44.1	7.38	104		
36	0.003	0.36	0.267	NA	1.68	3.68	44.1	7.66	104		
37	0.004	0.41	0.317	NA	1.59	3.64	43.8	7.81	102		
38	0.004	0.41		NA	1.59	3.51	44	7.4	101	57.1	0
39	0.004	0.43		NA	1.85	3.85	44	7.4	102	72.5	1.24
40	0.004	0.40	0.316	NA	1.55	3.58	43.1	7.68	102	59.6	2.63
41	0.004	0.39	0.308	NA	1.65	3.7	43.7	7.67	102		
42	0.004	0.44		NA	1.95	3.92	44.4	7.44	104	71.4	0.13
43	0.010	0.42	0.333	NA	1.65	3.67	43.6	7.6	101		
44	0.004	0.42	0.326	NA	1.68	3.69	43.8	7.67	102	71.8	3.49
45	0.004	0.40	0.298	NA	1.61	3.67	43.7	7.91	102	61.3	0.57
46	0.004	0.42		NA	1.67	3.64	43.5	7.45	101	76.3	0
47	0.0032	0.41	0.332	NA	1.63	3.71	42.8	7.74	102		
48	0.003	0.43	0.322	NA	1.78	3.76	43.9	7.62	103		
51	NA	0.44		NA	1.87	3.86	44.5	7.28	104	63.1	0.02
52	NA	0.42	0.323	NA	1.86	3.73	44.2	7.64	102	79.2	0.46
57	0.004	0.41	0.323	NA	1.81	3.84	44.2	7.7	104	43.2	15.50
22 Revisit	NA	0.41	0.341	NA	1.57	3.65	43.2	7.76	101		