



Calcium Concentrations in Lake Superior and South Shore Tributaries and the Implications for Dreissenid Mussel Establishment in the Apostle Islands Area

2014–2017

Natural Resource Report NPS/APIS/NRR—2018/1827



ON THE COVER

A zebra mussel (*Dreissena polymorpha*) attached to the wreckage of the *Sevona* off Sand Island, Apostle Islands National Lakeshore. The white “bubbly” surface in front of the mussel is a freshwater sponge. Photo © T. Lafrancois.

Calcium Concentrations in Lake Superior and South Shore Tributaries and the Implications for Dreissenid Mussel Establishment in the Apostle Islands Area

2014–2017

Natural Resource Report NPS/APIS/NRR—2018/1827

Brenda Moraska Lafrancois¹, Mike McCartney², Toben Lafrancois³, and Josh Delvaux⁴

¹ National Park Service
2800 Lake Shore Drive East
Ashland, Wisconsin 54806

²University of Minnesota
North Central Forest Experimental Station
1992 Folwell Avenue
St. Paul, Minnesota 55108

³Northland College
1411 Ellis Avenue, CB #1247
Ashland, Wisconsin 54806

⁴University of Wisconsin-Milwaukee
Current address: City of Milwaukee Department of Public Works
3000 North Lincoln Memorial Drive
Milwaukee, Wisconsin 53211

November 2018

U.S. Department of the Interior
National Park Service
Natural Resource Stewardship and Science
Fort Collins, Colorado

The National Park Service, Natural Resource Stewardship and Science office in Fort Collins, Colorado, publishes a range of reports that address natural resource topics. These reports are of interest and applicability to a broad audience in the National Park Service and others in natural resource management, including scientists, conservation and environmental constituencies, and the public.

The Natural Resource Report Series is used to disseminate comprehensive information and analysis about natural resources and related topics concerning lands managed by the National Park Service. The series supports the advancement of science, informed decision-making, and the achievement of the National Park Service mission. The series also provides a forum for presenting more lengthy results that may not be accepted by publications with page limitations.

All manuscripts in the series receive the appropriate level of peer review to ensure that the information is scientifically credible, technically accurate, appropriately written for the intended audience, and designed and published in a professional manner.

This report received informal peer review by subject-matter experts who were not directly involved in the collection, analysis, or reporting of the data.

Views, statements, findings, conclusions, recommendations, and data in this report do not necessarily reflect views and policies of the National Park Service, U.S. Department of the Interior. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. Government.

This report is available in digital format from the [Natural Resource Publications Management website](#). If you have difficulty accessing information in this publication, particularly if using assistive technology, please email irma@nps.gov.

Please cite this publication as:

Lafrancois, B. M., M. McCartney, T. Lafrancois, and J. Delvaux. 2018. Calcium concentrations in Lake Superior and south shore tributaries and the implications for dreissenid mussel establishment in the Apostle Islands area: 2014–2017. Natural Resource Report NPS/APIS/NRR—2018/1827. National Park Service, Fort Collins, Colorado.

Contents

	Page
Figures.....	v
Tables.....	vii
Abstract.....	ix
Acknowledgments.....	ix
Introduction.....	1
Methods.....	3
Data Sources and Sampling Locations	3
Data Compilation.....	4
Dreissenid Threshold Analysis.....	8
Results and Discussion	9
Conclusions.....	17
Literature Cited	19
Appendix A. Calcium Concentration Data Tables.....	23

Figures

	Page
Figure 1. Sites sampled for calcium concentrations during 2014 and 2016–2017 in the Apostle Islands area.	5
Figure 2. Graduated symbol map of calcium concentrations sampled at a range of lake, tributary, and other sites in and near the Apostle Islands during May–November, 2014–2017.....	9
Figure 3. Calcium concentrations sampled at Lake Superior sites (“Lake”) and tributary sites (“River”) in the Apostle Islands area during May–November, 2014–2017.	10
Figure 4. Calcium concentrations at Lake Superior sites, approximately clockwise around the Apostles from Port Wing to the Bad River mouth, sampled in 2014 (Lake15–Lake21), 2016 (Lake 1–3, 5–6, and 7–10), and 2017 (Lake 4, 7, and 11).....	11
Figure 5. Calcium concentrations at South Shore tributary sites sampled in 2014 (Bad), 2016 (Brule, Flag, Iron, Sand, and Siskiwit), and 2017 (Brule, Flag, and Siskiwit).	14
Figure 6. Seasonal variation at South Shore tributary sites sampled in 2014 (Bad), 2016 (Brule, Flag, Iron, Sand, Siskiwit), and 2017 (Brule, Flag, Siskiwit).....	15
Figure 7. Calcium concentrations at four sites sampled in two consecutive years (by UWM in 2016 and UMN in 2017).....	16

Tables

	Page
Table 1. Description of sources used to compile calcium concentration data for the Apostle Islands area.	3
Table 2. Site locations, coordinates, and site descriptions for calcium samples collected during 2014 and 2016–2017 in the Apostle Islands area.	6
Table 3. Basic statistics including number of samples (“# Obs), and mean, minimum (“Min”), and maximum (“Max) calcium concentrations, with standard deviation (“Std Dev”), for each site sampled during 2014 and 2016–2017 in the Apostle Islands area.	12
Table A1. Calcium concentrations at lake sites in the Apostle Islands area, compiled from multiple studies spanning 2014–2017.	23
Table A2. Calcium concentrations at river sites in the Apostle Islands area, compiled from multiple studies spanning 2014–2017.	26
Table A3. Calcium concentrations at mixed and lagoon sites in the Apostle Islands area, compiled from multiple studies spanning 2014–2017.	28

Abstract

Zebra and quagga mussels (dreissenids) have caused substantial economic and ecological damage in invaded habitats, but to date have not established extensive populations in Lake Superior. However, dreissenids have recently been detected in low densities in the Apostle Islands National Lakeshore, suggesting that local conditions may be more favorable to their establishment than previously expected. Because low calcium concentrations can limit dreissenid mussel growth and development, calcium conditions can be a useful tool for understanding dreissenid risk. We compiled calcium data from multiple studies and sites in and around the Apostle Islands from 2014–2017, and related calcium concentrations to literature-based thresholds for dreissenid mussel growth and development. All Lake Superior sites had mean concentrations greater than 12 mg/L, suggesting moderate risk of invasive mussel establishment. Further, calcium concentrations were elevated in tributaries relative to Lake Superior, with nearly all river samples exceeding the 15 mg/L threshold and almost half of the river samples exceeding the high-risk 20 mg/L threshold. River plumes likely serve to elevate calcium concentrations in nearshore Lake Superior waters. Given the trend toward increasing calcium concentrations in Lake Superior and the increasing intensity of precipitation and runoff events in this region, continued dreissenid mussel monitoring and prevention work is warranted.

Acknowledgments

We would like to acknowledge the many colleagues from the National Park Service, U.S. Geological Survey, the University of Wisconsin-Milwaukee, and the University of Minnesota-Duluth who made these sampling efforts possible, including J. Glase, T. Gostomski, F. Fitzpatrick, P. Reneau, E. Dantoin, J. Blount, H. Bootsma, S. Leask, and S. Brovold. We thank the University of Minnesota Soil Testing and Research Analytical Laboratories for performing the 2017 calcium analyses. Funding for this sample collection and analysis was provided by the National Park Service and U. S. Geological Survey, largely via project support from the U.S. EPA Great Lakes Restoration Initiative. We're grateful for the helpful comments A. Holdhusen and A. Trebitz provided on a previous version of this report.

Introduction

Dreissenid mussels (zebra and quagga mussels, *Dreissena polymorpha* and *Dreissena rostriformis bugensis*), respectively) are well established in all of the Great Lakes except Lake Superior (Allan et al. 2012). To date, concentrated populations in Lake Superior have been well documented only in the harbor cities of Duluth/Superior and Thunder Bay, Ontario. In the lower Great Lakes, dreissenids have caused extensive economic damage and a cascade of dramatic ecological changes (Vanderploeg et al. 2002, Nalepa et al. 2010), and their spread into the Mississippi River Basin and west of the 100th Meridian has generated significant concern, leading to intensive prevention and containment efforts (Western Panel on Aquatic Nuisance Species 2010).

Calcium ion concentrations are critical to basic metabolic function and shell development in dreissenids and other mollusks (Whittier et al. 2008). As dreissenid mussels are unusually sensitive to calcium levels relative to native mussels (Strayer 1993, MacMahon 1996), calcium concentrations have been used to assess the risk of dreissenid mussel establishment in both regional and continental-scale studies (Cohen and Weinstein 2001, Claudi and Prescott 2011). Lake Superior's relatively low calcium concentrations (approximately 12 mg/L, Vanderploeg et al. 2002) coupled with its cold temperatures, have been assumed to inhibit widespread establishment of dreissenid mussels and other invasive species (Grigorovich 2003). However, most Lake Superior calcium data are from open water locations; less is known about calcium concentrations in Lake Superior nearshore waters and tributaries. Further, isolated zebra mussels have been documented at Lake Superior's Isle Royale National Park since 2009 (Kerfoot 2015) and specimens of both zebra and quagga mussels have been collected in the Apostle Islands area since 2011 (Lafrancois 2017). Consistent detections of adult dreissenid mussel presence suggest that conditions may be more conducive to dreissenid establishment in Lake Superior than previously thought, particularly in ecologically and economically important coastal areas.

National Park Service (NPS) resource managers have expressed concern about the potential for dreissenid mussel establishment throughout the Apostle Islands archipelago (Lafrancois 2017). Here we aim to better characterize calcium concentrations in the Apostle Islands region and clarify implications for persistence of dreissenid mussel populations by compiling calcium data from recent nearshore research projects and relating them to literature-based dreissenid mussel thresholds.

Methods

Data Sources and Sampling Locations

Calcium data for this analysis were compiled from three sources. The first source was a 2014 U.S. Geological Survey study addressing tributary-nearshore interactions in the Bad River and Long Island area (Table 1, “USGS 2014”). This dataset encompasses sites in the eastern Apostle Islands area, including the Bad River as well as river-influenced Lake Superior sites near Long Island and between the mainland, Madeline, and Michigan Islands. Repeated sampling occurred from July through early November 2014. Most samples were analyzed for dissolved calcium concentrations at the USGS National Water Quality Laboratory via Inductively Coupled Plasma atomic emission spectrometry (ICP-AES) following method I-1472-87 in Fishman (1993). Three samples were analyzed for total calcium using in-bottle digestion according to Hoffman et al. (1996) followed by ICP-AES. This dataset is publicly available via the National Water Information System (USGS 2017).

Table 1. Description of sources used to compile calcium concentration data for the Apostle Islands area.

Dataset Name	Year Collected	Number of Samples	Sites Included	Primary Contact(s)
USGS 2014	2014	29	Bad River; Lake Superior near Long, Madeline, and Michigan Islands	Faith Fitzpatrick, Paul Reneau
UWM 2016	2016	93	Brule, Iron, Flag, Siskiwit, and Sand Rivers; Lake Superior from Port Wing to Apostle Islands Sea Caves	Josh Delvaux
NPS 2017	2017	42	Brule, Flag, and Siskiwit Rivers; Lake Superior from Superior to Sand Island	Brenda Moraska Lafrancois, Mike McCartney
Total	–	164	–	–

Additional calcium data were collected during a 2016 project addressing tributary-nearshore interactions in the South Shore-Sand Island area (Table 1, “UWM 2016”, Delvaux 2017). This dataset encompasses tributary sites (Brule, Iron, Flag, Siskiwit, and Sand Rivers), five Lake Superior sites along a nearshore-offshore transect near Sand Island, and four Lake Superior sites spanning a longshore gradient from near Port Wing to the Apostle Islands Mainland Sea Caves. Repeated sampling events occurred from June through October 2016. Calcium concentrations were analyzed on a Thermo Scientific iCE 3300 atomic absorption spectrophotometer at the University of Wisconsin-Milwaukee School of Freshwater Sciences. Prior to analysis, samples were amended with 0.1% LaCl₃ (to inhibit interference from sulfate and phosphate), 1% HNO₃, and 0.1% HCl. The system was calibrated with standards having a matrix similar to that of samples. The calibration curve for calcium was linear from 0 to 10 mg/L. If sample concentrations were outside the linear range of the calibration curve they were diluted in the matrix solution to be in the linear range.

Finally, additional calcium data were collected in 2017 (“NPS 2017”) as part of nearshore monitoring study by the NPS and University of Minnesota-Duluth (UMD) and a unionid and dreissenid survey by the University of Minnesota (UMN) and Northland College (NC). The UMD sites included several rivers sampled previously in 2016 (i.e., the Brule, Flag, and Siskiwit Rivers), and several nearshore Lake Superior sites ranging from as far west as Superior’s Wisconsin Point to as far east as Sand Island. Each of these sites was sampled repeatedly between May and October 2017. Additional one-time sampling was conducted during the UMN-NC mussel study at several sites of native or invasive mussel significance (i.e., Duluth, Stockton Island-Julian Bay, Madeline Island-Krons Reef, and the wreck of the *Sevona*). These one-time samples were taken by divers 1 m above the bottom near unionid mussel beds or dreissenid infested areas, with the exception of the Duluth site where surface water samples were collected. Dissolved calcium concentrations were determined at the UMN Soil Testing and Research Analytical Laboratories using decanted, unfiltered samples analyzed via ICP Optical Emission Spectroscopy, following Fassel and Kniseley (1974) and USEPA (1983).

A majority of sampling locations were categorized as Lake Superior sites (“Lake”) or tributary sites (“River”). Sites near the Duluth and Superior harbors and the Bad River mouth were characterized as “Mixed”, as they were expected to show a mix of lake and river influence. A single site, the Stockton Island Lagoon, was categorized as “Lagoon.”

Data Compilation

Data from all sources and sites were compiled into a single dataset (Figure 1, Table 2). Given that little depth-related variation was apparent at sites where samples were collected across a depth range, data from samples collected at depths >3 m were generally eliminated from the dataset to reduce redundancy. Exceptions include three samples collected by divers during targeted sampling at Stockton Island-Presque Isle Bay, Madeline Island-Krons Reef, the wreck of the *Sevona*, and Stockton Island Lagoon. These samples were collected just above the substrate at depths of 4.4 m, 8.1 m, and 5.4 m, respectively. The compiled dataset, including 164 total samples (Appendix A), was imported into Systat 13 for basic statistical and graphical analysis.

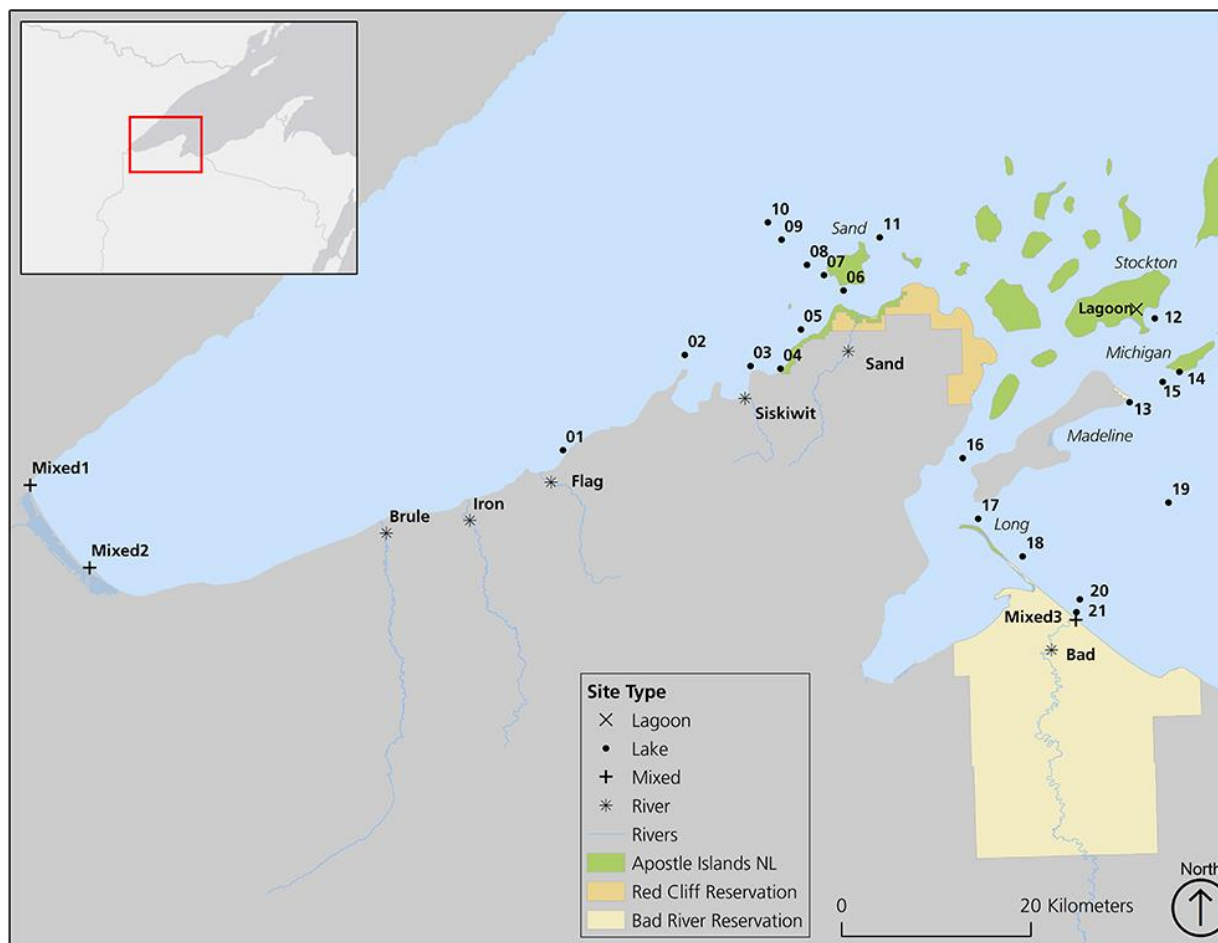


Figure 1. Sites sampled for calcium concentrations during 2014 and 2016–2017 in the Apostle Islands area. See Table 2 for more complete description of sites. Note that “Lake” sites have been abbreviated to the number portion of the “Site ID” found in Table 2.

Table 2. Site locations, coordinates, and site descriptions for calcium samples collected during 2014 and 2016–2017 in the Apostle Islands area. USGS Site Code = site identifier used in the USGS National Water Information System (<http://waterdata.usgs.gov/nwis/>). Data source(s) = agency and year dataset collected; see text for more complete descriptions.

Site Type	Site ID	Latitude	Longitude	USGS Site Code	Data Source(s)	Site Description
Lake	Lake01	46.811750	-91.354972	n/a	UWM 2016	Longshore transect site east of Port Wing
Lake	Lake02	46.899833	-91.183167	n/a	UWM 2016	Longshore transect site near Bark Point
Lake	Lake03	46.887778	-91.092556	n/a	UWM 2016	Longshore transect site near Spirit Point
Lake	Lake04	46.884503	-91.051168	n/a	NPS 2017	Nearshore monitoring site (Meyers Beach)
Lake	Lake05	46.921278	-91.021333	n/a	UWM 2016	Longshore transect site near mainland sea caves
Lake	Lake06	46.957283	-90.960833	n/a	UWM 2016	Nearshore-offshore transect near Sand Island; 0 km from shore
Lake	Lake07	46.972433	-90.987583	n/a	UWM 2016, NPS 2017	Nearshore-offshore transect near Sand Island; 2.67 km from shore (Sand West nearshore monitoring site)
Lake	Lake08	46.982467	-91.010733	n/a	UWM 2016	Nearshore-offshore transect near Sand Island; 4.67 km from shore
Lake	Lake09	47.007117	-91.045083	n/a	UWM 2016	Nearshore-offshore transect near Sand Island; 8.25 km from shore
Lake	Lake10	47.023767	-91.063717	n/a	UWM 2016	Nearshore-offshore transect near Sand Island; 10.79 km from shore
Lake	Lake11	47.006830	-90.908670	n/a	NPS 2017	Wreck of the Sevona, off Sand and York Islands
Lake	Lake12	46.925740	-90.545299	n/a	NPS 2017	Julian Bay, Stockton Island
Lake	Lake13	46.843320	-90.568734	n/a	NPS 2017	Krons Reef, Madeline Island
Lake	Lake14	46.870736	-90.498298	n/a	NPS 2017	Michigan Island docks
Lake	Lake15	46.861667	-90.521944	465142090311901	USGS 2014	Lake Superior between Madeline and Michigan Islands, WI
Lake	Lake16	46.795000	-90.801944	464742090480701	USGS 2014	Lake Superior North Channel between La Point and Bayfield, WI
Lake	Lake17	46.736944	-90.783056	464413090465901	USGS 2014	Lake Superior S Channel between Long and Madeline Islands, WI

Table 2 (continued). Site locations, coordinates, and site descriptions for calcium samples collected during 2014 and 2016–2017 in the Apostle Islands area. USGS Site Code = site identifier used in the USGS National Water Information System (<http://waterdata.usgs.gov/nwis/>). Data source(s) = agency and year dataset collected; see text for more complete descriptions.

Site Type	Site ID	Latitude	Longitude	USGS Site Code	Data Source(s)	Site Description
Lake	Lake18	46.700000	-90.723056	464200090432301	USGS 2014	Lake Superior 0.75 mi N of Bad River Mouth, WI
Lake	Lake19	46.746944	-90.519167	464449090310901	USGS 2014	Lake Superior 9.75 mi N of Bad River Mouth, WI
Lake	Lake20	46.657500	-90.645833	463927090384501	USGS 2014	Lake Superior 1.3 mi N of Bad River Mouth, WI
Lake	Lake21	46.645556	-90.651111	463844090390401	USGS 2014	Lake Superior 0.5 mi N of Bad River Mouth, WI
River	Trib1-Brule	46.736283	-91.601617	n/a	UWM 2016, NPS 2017	Brule River at Weir Riffles (UWM) and McNeils Landing (NPS)
River	Trib2-Iron	46.746850	-91.485933	n/a	UWM 2016	Iron River below Orienta Falls
River	Trib3-Flag	46.781617	-91.372517	n/a	UWM 2016, NPS 2017	Flag River near Highway 13
River	Trib4-Siskiwit	46.856997	-91.101406	n/a	UWM 2016, NPS 2017	Siskiwit River near Highway 13
River	Trib5-Sand	46.899249	-90.956452	n/a	UWM 2016	Sand River near Highway 13
River	Trib6-Bad	46.610278	-90.686944	04027595	USGS 2014	Bad River at Odanah, WI
Mixed	Mixed1	46.786700	-92.093500	n/a	NPS 2017	Duluth, Minnesota, near Lift Bridge
Mixed	Mixed2	46.707421	-92.012656	n/a	NPS 2017	Superior, WI at Wisconsin Point
Mixed	Mixed3	46.638056	-90.652222	04027655	USGS 2014	Bad River at the mouth near Odanah, WI
Lagoon	Lagoon1	46.926074	-90.547659	n/a	NPS 2017	Stockton Island Lagoon

Dreissenid Threshold Analysis

A range of dreissenid mussel thresholds for growth, survival, and population establishment have been proposed in the literature. One commonly cited paper is Mellina and Rasmussen (1994), who found that calcium concentrations <15 mg/L limited distribution of zebra mussels in rivers and lakes near the St. Lawrence River in Ontario and Quebec. Whittier et al. (2008) defined dreissenid risk based on calcium concentrations ranging from very low (<12 mg/L), to low (12–20 mg/L), moderate (20–28 mg/L), and high (>28 mg/L) based on a broader review of literature. In experimental studies, Baldwin et al. (2012) found moderate growth, survival and fertilization and larval developmental success in water with calcium concentrations >13 mg/L and dramatic improvement at >18 mg/L (particularly for larval development). Hincks and Mackie (1997) found negative growth for both species at <8.5 mg/L, and noted that low pH exacerbated the detrimental effects of low calcium. In general, experimental work also shows that while adults may survive cultivation in low calcium water, sublethal effects on growth and reproductive success are commonly observed in water with calcium concentrations <10 mg/L (Cohen and Weinstein 2001). Some have noted that subhabitats with slightly elevated calcium concentrations may allow dreissenid mussel establishment (e.g., nearshore or groundwater-influenced areas of Lake George; Wimbush et al. 2009), and emphasized the potential vulnerability of waters in the 12 to 15 mg/L calcium range (Davis et al. 2015). For our purposes, we assume that sites with calcium concentrations <10 mg/L have a very low probability of supporting dreissenid mussels (e.g., Cohen and Weinstein 2001), but that sites with calcium concentrations of 15–20 mg/L or more have moderate to high potential to support dreissenids (Cohen and Weinstein 2001, Mellina and Rasmussen 1994). We plotted these concentrations on our graphs as a guide.

Results and Discussion

Calcium concentrations at Lake Superior sites averaged 14.30 mg/L (± 1.87 sd), somewhat lower than the average concentration at the sampled river sites (19.64 mg/L ± 5.20 sd) (Figures 2, 3). Overall, the lowest single calcium concentration was measured in the Stockton Island Lagoon in mid-August 2017 (5.83 mg/L), and the highest single concentration was measured in the Sand River in late August 2016 (36.45 mg/L) during a low flow period (Appendix A).

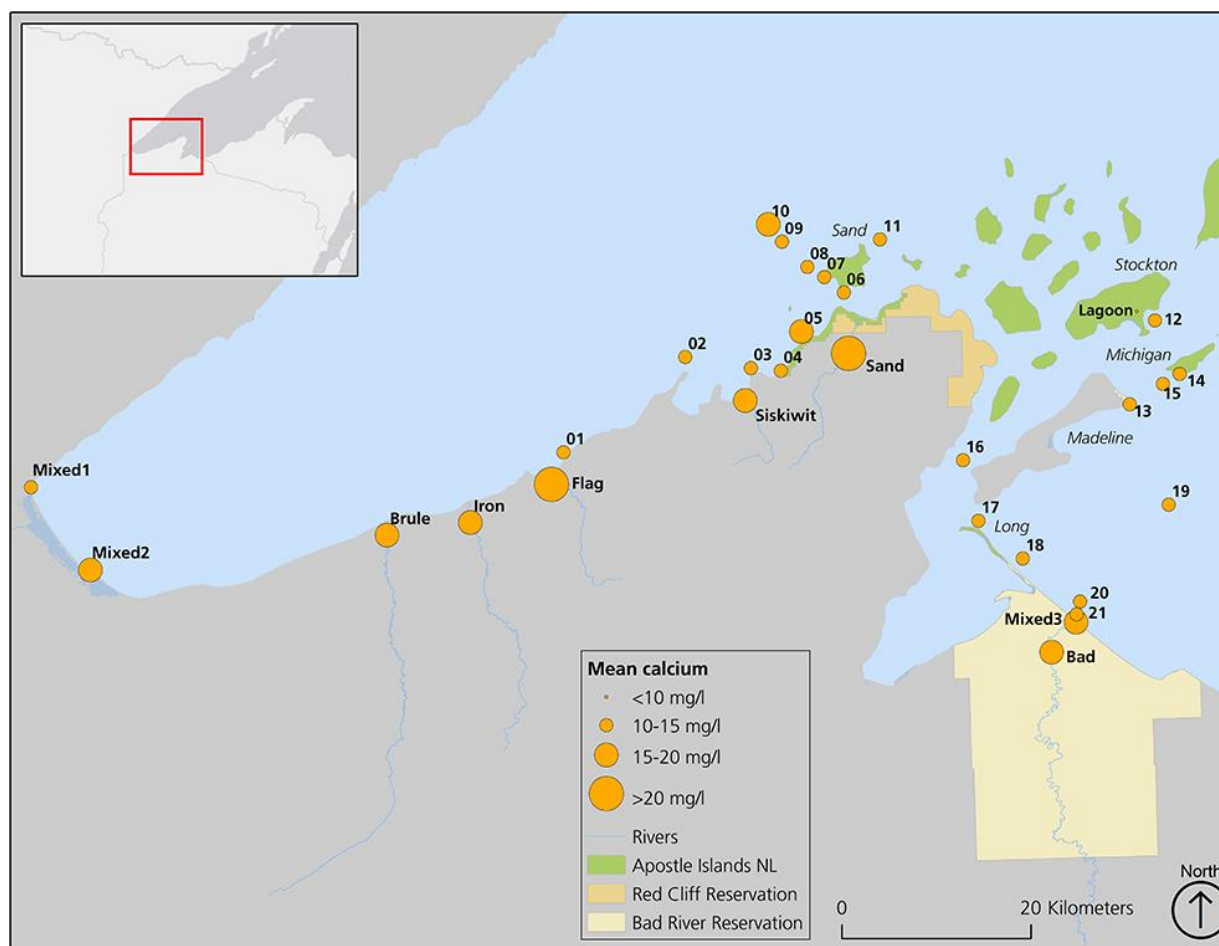


Figure 2. Graduated symbol map of calcium concentrations sampled at a range of lake, tributary, and other sites in and near the Apostle Islands during May–November, 2014–2017.

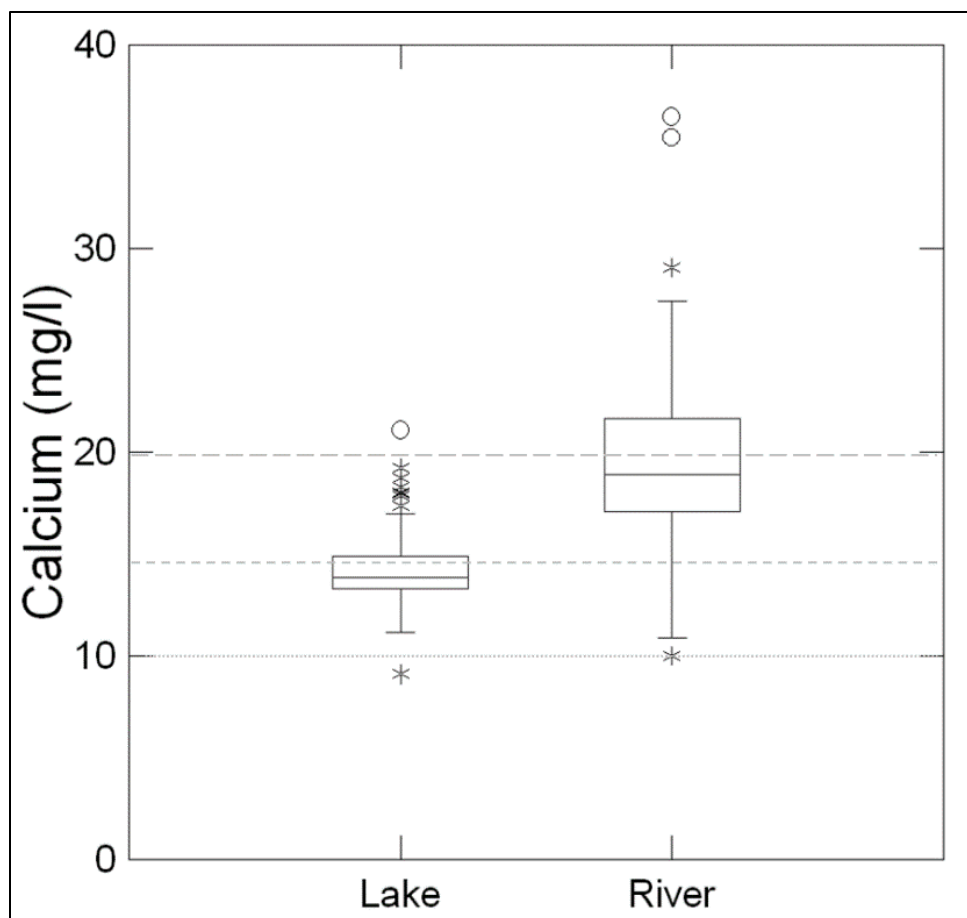


Figure 3. Calcium concentrations sampled at Lake Superior sites (“Lake”) and tributary sites (“River”) in the Apostle Islands area during May–November, 2014–2017. The center line on each box represents the median value for each site, the box length indicates the range within which the central 50% of values fall, and the whiskers represent the first and third quartile values. Asterisks and open circles denote outlying values. Literature-based thresholds for dreissenid mussel establishment and survival are plotted as a long dashed line (Cohen and Weinstein 2001, 20 mg/L), and short dashed line (Mellina and Rasmussen 1994, 15 mg/L). A dotted line denotes threshold below which no dreissenid mussel establishment is likely (Cohen and Weinstein 2001, 10 mg/L).

Among Lake Superior sites, the lowest concentration was observed near Spirit Point (Lake03), on 29 July 2016 (9.10 mg/L), and the highest concentration was observed near the Mainland Sea Caves past Meyers Beach (Lake05), a few weeks later, on 18 August 2016 (21.07 mg/L). The Lake Superior site with the highest mean calcium concentrations was site Lake05 near the Apostle Islands Mainland Sea Caves (16.84 mg/L $\pm$ 3.48 sd). Calcium concentrations were higher and more variable at sites along the South Shore and in the western Apostles (sites Lake01–Lake10) than at sites near Long Island and the eastern Apostles (sites Lake16–Lake20) (Table 3, Figure 4). This pattern likely reflects actual spatial trends and a relatively strong influence of periodic tributary plumes along the South Shore (Delvaux 2017), but may also result from differences in sampling frequency and sampling agency, as the western Apostles sites were sampled in 2016 and 2017 by UMD and UWM, and the eastern Apostles sites were sampled in 2014 by USGS.

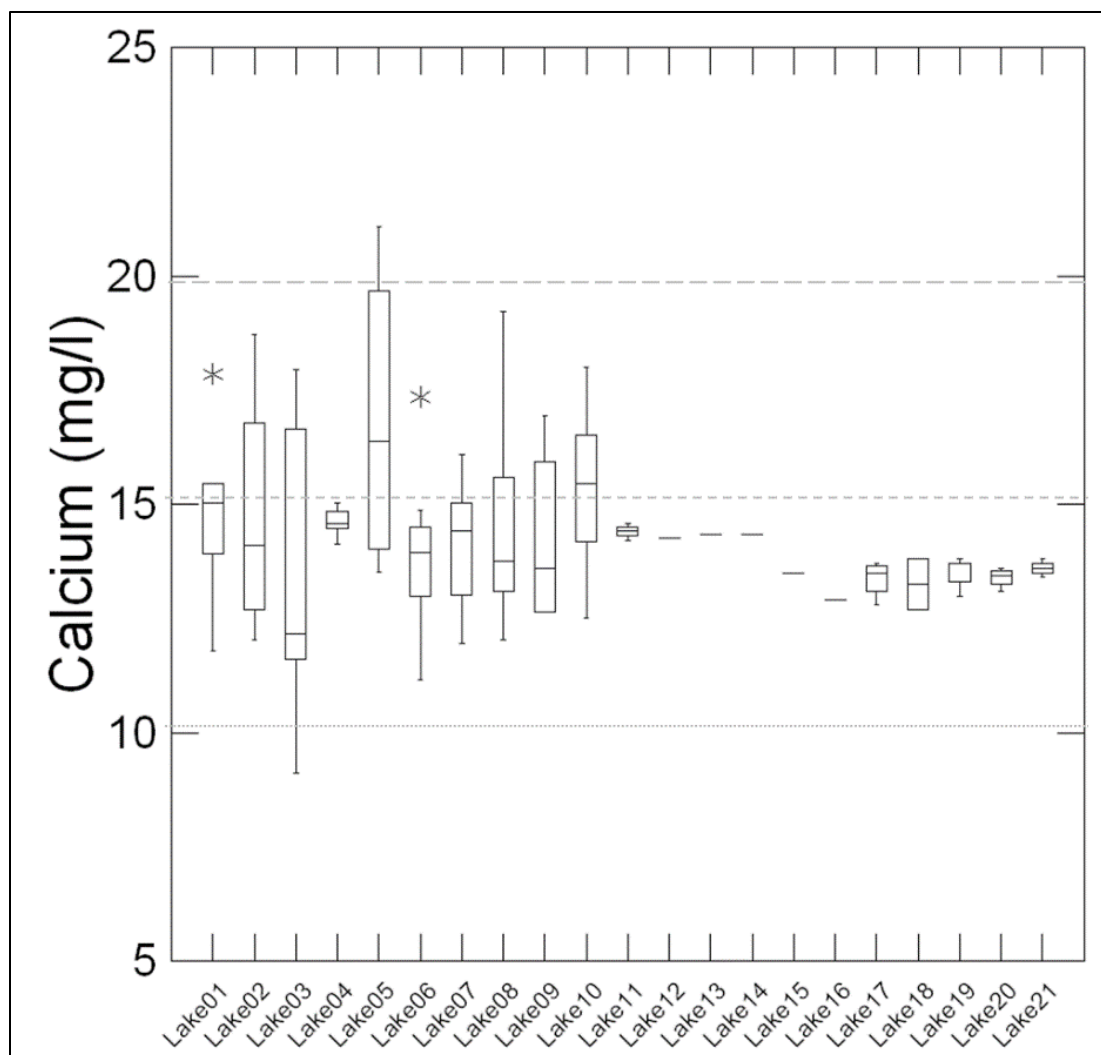


Figure 4. Calcium concentrations at Lake Superior sites, approximately clockwise around the Apostles from Port Wing to the Bad River mouth, sampled in 2014 (Lake15–Lake21), 2016 (Lake 1–3, 5–6, and 7–10), and 2017 (Lake 4, 7, and 11). The center line in each box represents the median value for each site, the box length indicates the range within which the central 50% of values fall, and the whiskers represent the first and third quartile values. Asterisks denote outlying values. Literature-based thresholds for dreissenid mussel establishment and survival are plotted as a long dashed line (Cohen and Weinstein 2001, 20 mg/L), and short dashed line (Mellina and Rasmussen 1994, 15 mg/L). A dotted line denotes threshold below which no dreissenid mussel establishment is likely (Cohen and Weinstein 2001, 10 mg/L).

Table 3. Basic statistics including number of samples (“# Obs), and mean, minimum (“Min”), and maximum (“Max) calcium concentrations, with standard deviation (“Std Dev”), for each site sampled during 2014 and 2016–2017 in the Apostle Islands area.

Site ID	# Obs	Mean	Min	Max	Std Dev
Lake01	5	14.81	11.79	17.85	2.21
Lake02	4	14.74	12.03	18.73	2.90
Lake03	5	13.50	9.10	17.96	3.70
Lake04	7	14.63	14.13	15.02	0.31
Lake05	4	16.84	13.52	21.07	3.48
Lake06	8	13.92	11.15	17.35	1.79
Lake07	11	14.19	11.96	16.08	1.36
Lake08	7	14.62	12.04	19.21	2.42
Lake09	6	14.23	12.64	16.95	1.80
Lake10	7	15.34	12.51	18.01	1.95
Lake11	3	14.41	14.21	14.59	0.19
Lake12	1	14.27	n/a	n/a	n/a
Lake13	1	14.33	n/a	n/a	n/a
Lake14	1	14.35	n/a	n/a	n/a
Lake15	1	13.50	n/a	n/a	n/a
Lake16	1	12.90	n/a	n/a	n/a
Lake17	4	13.38	12.80	13.70	0.40
Lake18	2	13.25	12.70	13.80	0.78
Lake19	5	13.50	13.00	13.80	0.34
Lake20	4	13.40	13.10	13.60	0.22
Lake21	3	13.60	13.40	13.80	0.20
Trib1-Brule	15	16.61	10.94	23.34	3.25
Trib2-Iron	8	19.07	13.54	27.41	3.97
Trib3-Flag	12	21.52	18.59	26.77	2.49
Trib4-Siskiwit	12	17.20	9.99	25.34	4.46
Trib5-Sand	8	26.83	17.31	36.45	6.72
Trib6-Bad	4	19.50	15.00	23.60	3.61
Mixed1	2	14.45	14.43	14.46	0.02
Mixed2	7	17.68	15.20	21.63	2.19
Mixed3	5	16.82	13.90	23.40	3.84
Lagoon1	1	5.83	n/a	n/a	n/a

Among river sites, the Brule River had the lowest mean calcium concentration ($16.61 \text{ mg/L} \pm 3.25$) and the Sand River had the highest ($26.83 \text{ mg/L} \pm 6.72 \text{ sd}$) (Table 3, Figures 2, 5). River calcium concentrations varied seasonally during the May–October sampling period, with the highest mean monthly concentrations observed in August in each river (Figure 6). Rose (1988) analyzed dissolved calcium samples from the Sand River in the early 1980s and documented similar, though overall lower, concentrations in this river, ranging from 10 mg/L to 27 mg/L. Samples from the Raspberry River and Red Cliff Creek showed a similar range of concentrations (Rose 1988). Variation in calcium concentrations among tributaries may result from differences in underlying geology and geomorphology, with higher calcium concentrations likely found in rivers dominated by Lake Superior red clays and prone to bank erosion (USEPA 1980, Bahnick et al. 1978) or during baseflow in rivers with significant groundwater input (Fitzpatrick et al. 2015).

Sites sampled during two different calendar years (i.e., the Brule, Flag, and Siskiwit Rivers and the Lake07 site near Sand Island) showed relatively little interannual variation in calcium concentrations, despite differences in annual hydrology and analytical laboratory during 2016 and 2017 (Figure 7).

With respect to thresholds for dreissenid risk, calcium concentrations in all but one of the Lake Superior samples were greater than the 10 mg/L threshold (i.e., our low-risk threshold for dreissenid mussel establishment), and concentrations in 25% of Lake Superior samples were greater than the 15 mg/L threshold (e.g., our moderate-risk threshold for dreissenid establishment; Appendix A). A single sample exceeded the high-risk 20 mg/L threshold. All Lake Superior sites had mean calcium concentrations greater than 12 mg/L (Table 3). Calcium concentrations were higher in the river sites; all but one of the river samples had concentrations greater than the 10 mg/L threshold. Nearly all of the river samples (85%) had concentrations greater than the 15 mg/L threshold, and almost half (42%) had concentrations greater than the high-risk 20 mg/L threshold. Among the “mixed” sites near Duluth, Superior, and the Bad River mouth, all samples had calcium concentrations greater than the 10 mg/L threshold and 71% of samples were higher than the 15 mg/L threshold. The single “lagoon” site sampled in this study, Stockton Island Lagoon, had very low calcium concentration of 5.83 mg/L, well below the 10 mg/L threshold and similar to calcium levels documented during previous sampling in Michigan and Outer Island Lagoons (Rose 1988). The unique coastal lagoon environments in the Apostle Islands are the least likely aquatic habitats to support dreissenid establishment.

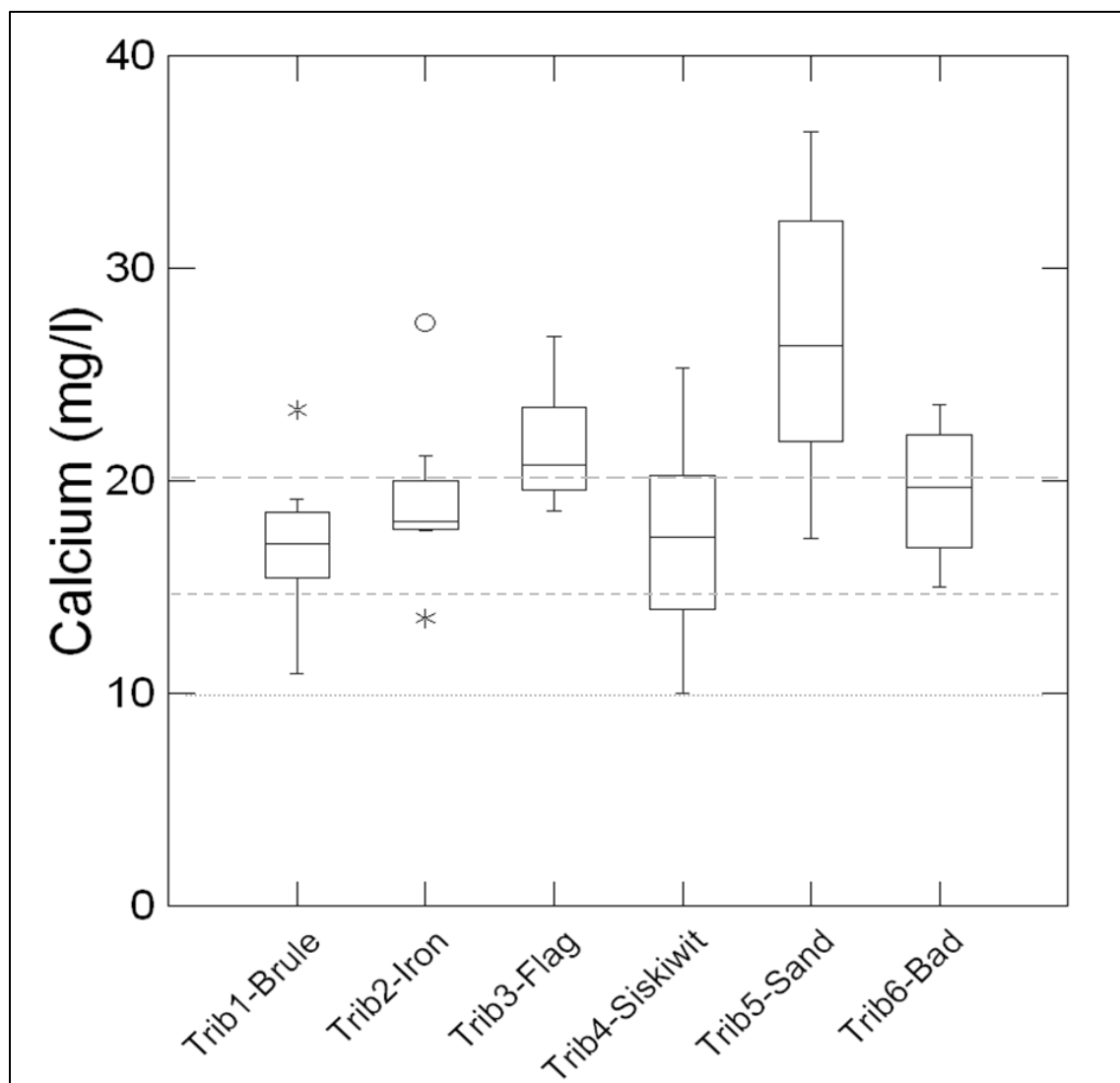


Figure 5. Calcium concentrations at South Shore tributary sites sampled in 2014 (Bad), 2016 (Brule, Flag, Iron, Sand, and Siskiwit), and 2017 (Brule, Flag, and Siskiwit). The center line in each box represents the median value for each site, the box length indicates the range within which the central 50% of values fall, and the whiskers represent the first and third quartile values. Asterisks and open circles denote outlying values. Literature-based thresholds for dreissenid mussel establishment and survival are plotted as a long dashed line (Cohen and Weinstein 2001, 20 mg/L), and short dashed line (Mellina and Rasmussen 1994, 15 mg/L). A dotted line denotes threshold below which no dreissenid mussel establishment is likely (Cohen and Weinstein 2001, 10 mg/L).

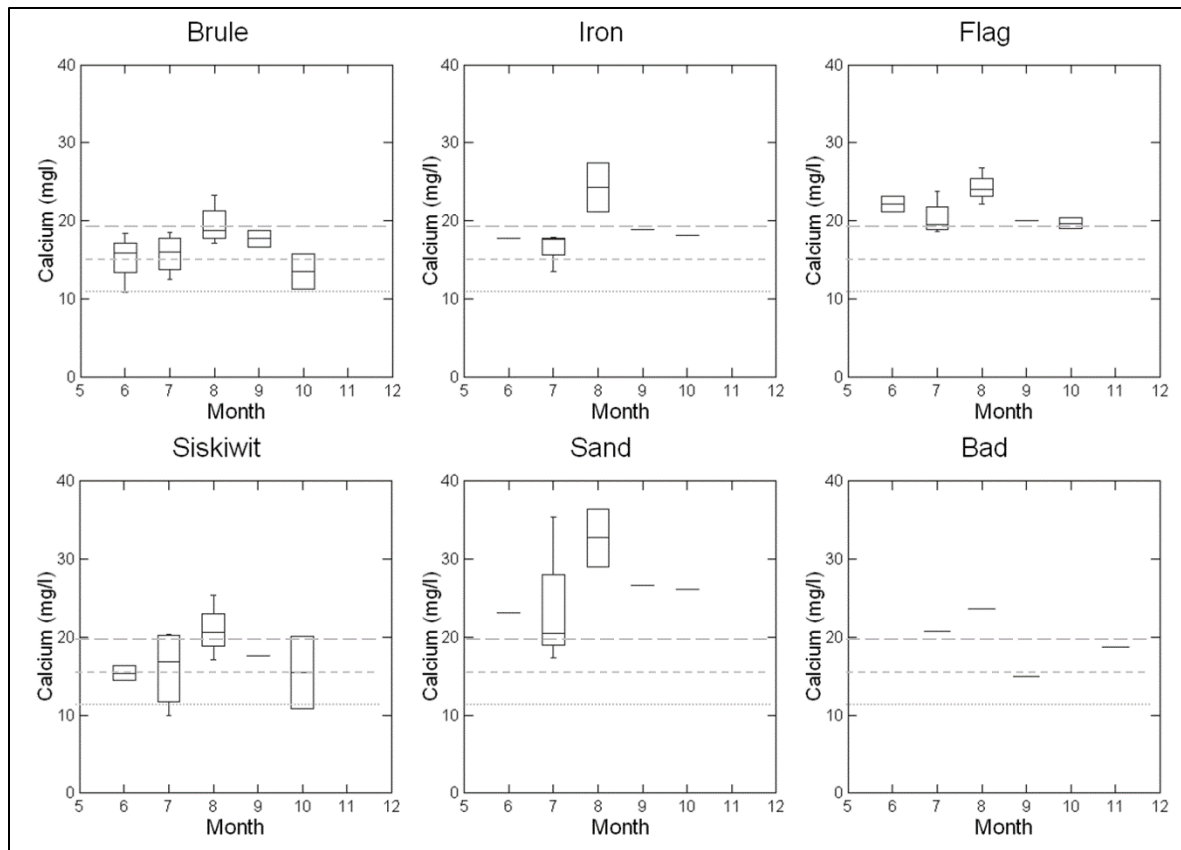


Figure 6. Seasonal variation at South Shore tributary sites sampled in 2014 (Bad), 2016 (Brule, Flag, Iron, Sand, Siskiwit), and 2017 (Brule, Flag, Siskiwit). The center line in each box represents the median value for each site, the box length indicates the range within which the central 50% of values fall, and the whiskers represent the first and third quartile values. Literature-based thresholds for dreissenid mussel establishment and survival are plotted as a long dashed line (Cohen and Weinstein 2001, 20 mg/L), and short dashed line (Mellina and Rasmussen 1994, 15 mg/L). A dotted line denotes threshold below which no dreissenid mussel establishment is likely (Cohen and Weinstein 2001, 10 mg/L).

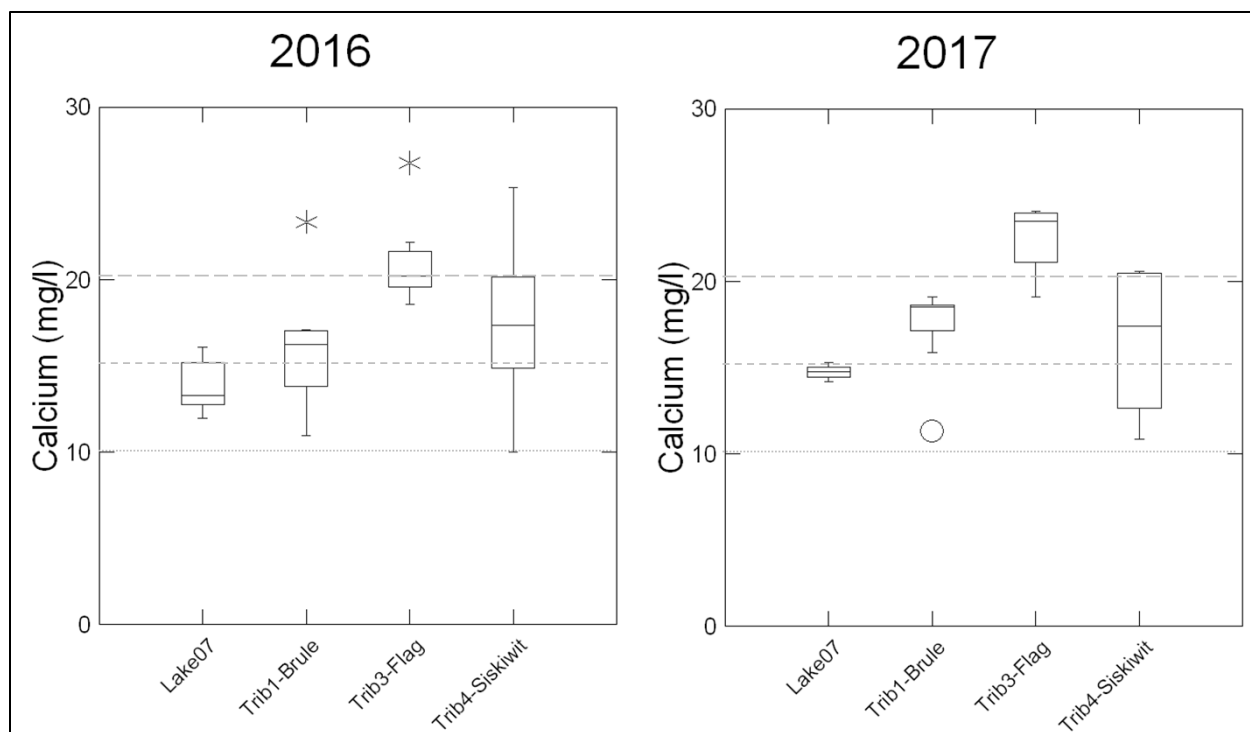


Figure 7. Calcium concentrations at four sites sampled in two consecutive years (by UWM in 2016 and UMN in 2017). The center line in each box represents the median value for each site, the box length indicates the range within which the central 50% of values fall, and the whiskers represent the first and third quartile values. Asterisks and open circles denote outlying values. Literature-based thresholds for dreissenid mussel establishment and survival are plotted as a long dashed line (Cohen and Weinstein 2001, 20 mg/L), and short dashed line (Mellina and Rasmussen 1994, 15 mg/L). A dotted line denotes threshold below which no dreissenid mussel establishment is likely (Cohen and Weinstein 2001, 10 mg/L).

Conclusions

- Detailed data on calcium concentrations are rare in most regions invaded by zebra and quagga mussels. Consequently the compiled Apostle Islands dataset is unique, and provides a valuable opportunity to explore the role of calcium concentrations in the establishment of invasive mussels.
- Calcium concentrations are marginal-to-moderate in Lake Superior waters of the Apostle Islands area, and are potentially sufficient to support dreissenid population establishment.
- Calcium conditions in many of the area's tributaries are elevated relative to Lake Superior (particularly in the Flag and the Sand Rivers, where mean concentrations exceeded 20 mg/L) and are quite favorable to dreissenid mussel establishment.
- Tributary inputs (river plumes) strongly influence nearshore water chemistry and ecology in the region (Delvaux 2017), contain elevated calcium concentrations, and may exacerbate the risk of dreissenid establishment in localized coastal areas of Lake Superior (*sensu* Wimbush et al. 2009). Cooperation with other land management agencies to better address erosion of clays and related minerals would help minimize calcium inputs to Lake Superior via tributaries (Bahnick et al. 1978, WDNR 2007).
- Definitive conclusions about potential dreissenid establishment are limited by a lack of clear consensus on calcium thresholds and a lack of data on populations living near these thresholds. Further studies should address how calcium fluctuations affect survival, physiology, or reproductive traits of dreissenids, particularly in marginal environments like the Apostle Islands area.
- The presence of dreissenid mussels in the Apostle Islands area, coupled with the marginal-to-moderate calcium concentrations documented here and the upward calcium ion trends for Lake Superior since 1965 (Chapra et al. 2012) suggests a need for continued dreissenid mussel monitoring and prevention work.

Literature Cited

- Allan, J. D., P. B. McIntyre, S. D. P. Smith, B. S. Halpern, G. L. Boyer, A. Buchsbaum, G. A. Burton Jr., L. M. Campbell, W. L. Chadderton, J. J. H. Ciborowski, P. J. Doran, T. Eder, D. M. Infante, L. B. Johnson, C. A. Joseph, A. L. Marino, A. Prusevich, J. Read, J. B. Rose, E. S. Rutherford, S. P. Sowa, A. D. Steinman. 2012. Joint analysis of stressors and ecosystem services to enhance restoration effectiveness. *Proceedings of the National Academy of Sciences* 110(1):372–377. Available at: www.pnas.org/cgi/doi/10.1073/pnas.1213841110.
- Bahnick, D. A., T. P. Markee, C. A. Anderson, and R. K. Roubal. 1978. Chemical loadings to southwestern Lake Superior from red clay erosion and resuspension. *Journal of Great Lakes Research* 4(2):186–193.
- Baldwin B. S., M. Carpenter, K. Rury, and E. Woodward. 2012. Low dissolved ions may limit secondary invasion of inland waters by exotic round gobies and dreissenid mussels in North America. *Biological Invasions* 14(6):1157–1175.
- Chapra, S. C., A. Dove, and G. J. Warren. 2012. Long-term trends of Great Lakes major ion chemistry. *Journal of Great Lakes Research* 38:550–560.
- Claudi, R., and K. Prescott. 2011. Examination of calcium and pH as predictors of dreissenid mussel survival in the California State Water Project. California Dept. of Water Resources. Unpublished report by R. Claudy and K. Prescott, RNT Consulting Inc.
- Cohen, A. N., and A. Weinstein. 2001. Zebra mussel's calcium threshold and implications for its potential distribution in North America. Unpublished report. San Francisco Estuary Institute, San Francisco, California. Available at: <https://nrm.dfg.ca.gov/FileHandler.ashx?DocumentID=3870>.
- Davis, C. J., E. K. Ruhmann, K. Acharya, S. Chandra, and C. L. Jerde. 2015. Successful survival, growth, and reproductive potential of quagga mussels in low calcium lake water: Is there uncertainty of establishment risk? *PeerJ* 3:e1276. Available at: <https://doi.org/10.7717/peerj.1276>.
- Delvaux, J. M. 2017. River influence on the nearshore ecosystem of western Lake Superior. Thesis. University of Wisconsin–Milwaukee, Milwaukee, Wisconsin.
- Fassel, V. A., and R. N. Kniseley. 1974. Inductively coupled plasma optical emission spectroscopy. *Analytical Chemistry* 46(13):1110A–1120A.
- Fishman, M. J. (editor). 1993. Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of inorganic and organic constituents in water and fluvial sediments. U.S. Geological Survey Open-File Report 93-125. U.S. Geological Survey, Denver, Colorado. Available at: <https://pubs.er.usgs.gov/publication/ofr93125>.
- Fitzpatrick, F. A., M. C. Peppler, D. A. Saad, D. M. Pratt, and B. N. Lenz. 2015. Geomorphic, flood, and groundwater-flow characteristics of Bayfield Peninsula streams, Wisconsin, and implications

- for brook-trout habitat. U.S. Geological Survey Scientific Investigations Report 2014–5007. Available at: <http://dx.doi.org/10.3133/sir20145007>.
- Grigorovich, I. A., R. I. Colautti, E. L. Mills, K. Holeck, A. G. Ballert, and H. J. MacIsaac. 2003. Ballast mediated animal introductions in the Laurentian Great Lakes: Retrospective and prospective analyses. *Canadian Journal of Fisheries and Aquatic Sciences* 60(6):740–756.
- Hincks, S. S., and G. L. Mackie. 1997. Effects of pH, calcium, alkalinity, hardness, and chlorophyll on the survival, growth, and reproductive success of zebra mussel (*Dreissena polymorpha*) in Ontario lakes. *Canadian Journal of Fisheries and Aquatic Sciences* 54(9):2049–2057.
- Hoffman, G. L., M. J. Fishman, and J. R. Garbarino. 1996. Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—In-bottle digestion of whole-water samples. U. S. Geological Survey Open File Report 96-225. U.S. Geological Survey, Denver, Colorado.
- Kerfoot, S. 2015. 2015 zebra mussel report: Isle Royale National Park. Unpublished Great Lakes Restoration Initiative report submitted to Isle Royale National Park, Houghton, Michigan.
- Lafrancois, B. M. 2017. Unsettling discoveries: Invasive mussels in the Apostle Islands. National Park Service Great Lakes Network Resource Brief. National Park Service, Ashland, Wisconsin. Available at: <https://irma.nps.gov/DataStore/Reference/Profile/2240471>.
- McMahon, R. F. 1996. The physiological ecology of the zebra mussel, *Dreissena polymorpha*, in North America and Europe. *American Zoologist* 36(3):339–363.
- Mellina, E., and J. B. Rasmussen. 1994. Patterns in the distribution and abundance of zebra mussel (*Dreissena polymorpha*) in rivers and lakes in relation to substrate and other physicochemical factors. *Canadian Journal of Fisheries and Aquatic Sciences* 51:1024–1036.
- Nalepa, T. F., D. L. Fanslow, and S. A. Pothoven. 2010. Recent changes in density, biomass, recruitment, size structure, and nutritional state of *Dreissena* populations in southern Lake Michigan. *Journal of Great Lakes Research* 36:5–19.
- Rose, W. 1988. Water resources of the Apostle Islands National Lakeshore, Northern Wisconsin. Water-Resources Investigations Report 87-4220. U.S. Geological Survey, Madison, Wisconsin.
- Strayer, D. L. 1993. Macrohabitats of freshwater mussels (Bivalvia:Unionacea) in streams of the Northern Atlantic Slope. *Journal of the North American Benthological Society* 12(3):236–246.
- USEPA (U.S. Environmental Protection Agency). 1980. Red clay project: Impact of nonpoint pollution control on western Lake Superior. Final Part II. EPA 905/9-79-002-B. U. S. Environmental Protection Agency, Region V, Chicago, Illinois.

- USEPA (U.S. Environmental Protection Agency). 1983. Method 200.7 Methods for chemical analysis of water and wastes. EPA-600 4-79-020. Environmental Monitoring and Support Laboratory, Office of Research and Development, Cincinnati, Ohio.
- USGS (U.S. Geological Survey). 2017. National Water Information System data. Available at: <http://waterdata.usgs.gov/nwis/> (accessed April 2017).
- Vanderploeg, H. A., T. F. Nalepa, D. J. Jude, E. L. Mills, K. Holeck, J. R. Liebig, I. A. Grigorovich, and H. Ojaveer. 2002. Dispersal and emerging ecological impacts of Ponto-Caspian species in the Laurentian Great Lakes. *Canadian Journal of Fisheries and Aquatic Sciences* 59:1209–1228.
- Western Panel on Aquatic Nuisance Species. 2010. Quagga-zebra mussel action plan for western U.S. waters. Unpublished document submitted to the Aquatic Nuisance Species Task Force.
- Whittier, T. R., P. L. Ringold, A. T. Herlihy, and S. M. Pierson. 2008. A calcium-based invasion risk assessment for zebra and quagga mussels (*Dreissena* spp). *Frontiers in Ecology and the Environment* 6. Available at: <https://esajournals.onlinelibrary.wiley.com/doi/10.1890/070073>.
- Wimbush, J. M., E. Frischer, J. W. Zarzynski, and S. A. Nierzwick-Bauer. 2009. Eradication of colonizing populations of zebra mussels (*Dreissena polymorpha*) by early detection and SCUBA removal: Lake George, NY. *Aquatic Conservation: Marine and Freshwater Ecosystems* 19:703–713.
- WDNR (Wisconsin Department of Natural Resources). 2007. Managing woodlands on Lake Superior's red clay plain: Slowing the flow of runoff. PUB-FR-385-2007. Wisconsin Department of Natural Resources, Madison, Wisconsin.

Appendix A. Calcium Concentration Data Tables.

Table A1. Calcium concentrations at lake sites in the Apostle Islands area, compiled from multiple studies spanning 2014–2017. See Figure 1 for site locations.

Site ID	Date Collected	Ca (mg/L)
Lake01	6/24/2016	15.45
Lake01	7/20/2016	13.92
Lake01	7/29/2016	11.79
Lake01	8/18/2016	15.04
Lake01	8/31/2016	17.85
Lake02	7/20/2016	12.03
Lake02	7/29/2016	13.37
Lake02	8/18/2016	14.81
Lake02	8/31/2016	18.73
Lake03	6/24/2016	11.60
Lake03	7/20/2016	12.16
Lake03	7/29/2016	9.10
Lake03	8/18/2016	16.66
Lake03	8/31/2016	17.96
Lake04	5/31/2017	14.83
Lake04	6/21/2017	14.88
Lake04	7/13/2017	14.59
Lake04	8/2/2017	15.02
Lake04	8/23/2017	14.57
Lake04	9/13/2017	14.37
Lake04	10/4/2017	14.13
Lake05	7/20/2016	13.52
Lake05	7/29/2016	14.51
Lake05	8/18/2016	21.07
Lake05	8/31/2016	18.27
Lake06	6/23/2016	12.62
Lake06	7/6/2016	11.15
Lake06	7/18/2016	13.38
Lake06	7/28/2016	13.74
Lake06	8/17/2016	14.86
Lake06	9/1/2016	17.35

Table A1 (continued). Calcium concentrations at lake sites in the Apostle Islands area, compiled from multiple studies spanning 2014–2017. See Figure 1 for site locations.

Site ID	Date Collected	Ca (mg/L)
Lake06	9/21/2016	14.12
Lake06	10/25/2016	14.15
Lake07	5/31/2017	15.28
Lake07	7/13/2017	14.76
Lake07	8/23/2017	14.73
Lake07	10/4/2017	14.18
Lake07	6/23/2016	11.96
Lake07	7/18/2016	13.27
Lake07	7/28/2016	12.77
Lake07	8/17/2016	12.76
Lake07	9/1/2016	15.94
Lake07	9/21/2016	14.41
Lake07	10/25/2016	16.08
Lake08	6/23/2016	15.50
Lake08	7/6/2016	13.76
Lake08	7/18/2016	12.04
Lake08	7/28/2016	13.32
Lake08	8/17/2016	12.88
Lake08	9/21/2016	19.21
Lake08	10/25/2016	15.65
Lake09	7/6/2016	13.75
Lake09	7/18/2016	12.64
Lake09	7/28/2016	13.45
Lake09	8/17/2016	12.64
Lake09	9/21/2016	16.95
Lake09	10/25/2016	15.94
Lake10	7/6/2016	12.51
Lake10	7/18/2016	14.78
Lake10	7/28/2016	13.59
Lake10	8/17/2016	15.67
Lake10	9/1/2016	17.37
Lake10	9/21/2016	18.01
Lake10	10/25/2016	15.45

Table A1 (continued). Calcium concentrations at lake sites in the Apostle Islands area, compiled from multiple studies spanning 2014–2017. See Figure 1 for site locations.

Site ID	Date Collected	Ca (mg/L)
Lake11	5/15/2017	14.43
Lake11	5/15/2017	14.59
Lake11	5/15/2017	14.21
Lake12	8/11/2017	14.27
Lake13	5/19/2017	14.33
Lake14	5/19/2017	14.35
Lake15	9/18/2014	13.50
Lake16	9/18/2014	12.90
Lake17	7/25/2014	13.40
Lake17	8/20/2014	13.60
Lake17	9/18/2014	12.80
Lake17	11/4/2014	13.70
Lake18	7/24/2014	13.80
Lake18	9/18/2014	12.70
Lake19	7/22/2014	13.30
Lake19	7/23/2014	13.80
Lake19	8/19/2014	13.70
Lake19	9/16/2014	13.00
Lake19	11/3/2014	13.70
Lake20	7/23/2014	13.50
Lake20	8/19/2014	13.40
Lake20	9/16/2014	13.10
Lake20	11/3/2014	13.60
Lake21	7/23/2014	13.60
Lake21	9/16/2014	13.40
Lake21	11/3/2014	13.80

Table A2. Calcium concentrations at river sites in the Apostle Islands area, compiled from multiple studies spanning 2014–2017. See Figure 1 for site locations.

Site ID	Date Collected	Ca (mg/L)
Trib1-Brule	6/1/2017	15.90
Trib1-Brule	6/21/2017	18.45
Trib1-Brule	7/14/2017	18.55
Trib1-Brule	8/2/2017	19.13
Trib1-Brule	8/24/2017	18.52
Trib1-Brule	9/13/2017	18.76
Trib1-Brule	10/5/2017	11.32
Trib1-Brule	6/21/2016	10.94
Trib1-Brule	7/6/2016	17.03
Trib1-Brule	7/15/2016	12.49
Trib1-Brule	7/27/2016	15.13
Trib1-Brule	8/16/2016	17.09
Trib1-Brule	8/30/2016	23.34
Trib1-Brule	9/22/2016	16.69
Trib1-Brule	10/26/2016	15.80
Trib2-Iron	6/21/2016	17.80
Trib2-Iron	7/6/2016	17.95
Trib2-Iron	7/15/2016	13.54
Trib2-Iron	7/27/2016	17.63
Trib2-Iron	8/16/2016	21.16
Trib2-Iron	8/30/2016	27.41
Trib2-Iron	9/22/2016	18.90
Trib2-Iron	10/26/2016	18.18
Trib3-Flag	6/1/2017	23.15
Trib3-Flag	7/14/2017	23.79
Trib3-Flag	8/24/2017	24.10
Trib3-Flag	10/5/2017	19.08
Trib3-Flag	6/21/2016	21.11
Trib3-Flag	7/6/2016	18.59
Trib3-Flag	7/15/2016	19.29
Trib3-Flag	7/27/2016	19.84
Trib3-Flag	8/16/2016	22.15

Table A2 (continued). Calcium concentrations at river sites in the Apostle Islands area, compiled from multiple studies spanning 2014–2017. See Figure 1 for site locations.

Site ID	Date Collected	Ca (mg/L)
Trib3-Flag	8/30/2016	26.77
Trib3-Flag	9/22/2016	20.05
Trib3-Flag	10/26/2016	20.35
Trib4-Siskiwit	6/1/2017	14.47
Trib4-Siskiwit	7/13/2017	20.33
Trib4-Siskiwit	8/24/2017	20.59
Trib4-Siskiwit	10/5/2017	10.87
Trib4-Siskiwit	6/21/2016	16.31
Trib4-Siskiwit	7/6/2016	20.18
Trib4-Siskiwit	7/15/2016	9.99
Trib4-Siskiwit	7/27/2016	13.49
Trib4-Siskiwit	8/16/2016	17.12
Trib4-Siskiwit	8/30/2016	25.34
Trib4-Siskiwit	9/22/2016	17.61
Trib4-Siskiwit	10/26/2016	20.10
Trib5-Sand	6/21/2016	23.12
Trib5-Sand	7/6/2016	20.54
Trib5-Sand	7/15/2016	17.31
Trib5-Sand	7/27/2016	35.44
Trib5-Sand	8/16/2016	29.05
Trib5-Sand	8/30/2016	36.45
Trib5-Sand	9/22/2016	26.59
Trib5-Sand	10/26/2016	26.15
Trib6-Bad	7/22/2014	20.70
Trib6-Bad	8/18/2014	23.60
Trib6-Bad	9/17/2014	15.00
Trib6-Bad	11/3/2014	18.70

Table A3. Calcium concentrations at mixed and lagoon sites in the Apostle Islands area, compiled from multiple studies spanning 2014–2017. See Figure 1 for site locations.

Site ID	Date Collected	Ca (mg/L)
Mixed1	10/19/2017	14.43
Mixed1	10/19/2017	14.46
Mixed2	6/1/2017	15.20
Mixed2	6/21/2017	16.69
Mixed2	7/14/2017	18.76
Mixed2	8/2/2017	15.65
Mixed2	8/24/2017	21.63
Mixed2	9/13/2017	18.46
Mixed2	10/5/2017	17.40
Mixed3	7/22/2014	15.90
Mixed3	7/23/2014	14.30
Mixed3	8/18/2014	23.40
Mixed3	9/16/2014	13.90
Mixed3	11/3/2014	16.60
Lagoon1	8/11/2017	5.83

The Department of the Interior protects and manages the nation's natural resources and cultural heritage; provides scientific and other information about those resources; and honors its special responsibilities to American Indians, Alaska Natives, and affiliated Island Communities.

NPS 633/149549, November 2018

National Park Service
U.S. Department of the Interior



[Natural Resource Stewardship and Science](#)

1201 Oakridge Drive, Suite 150
Fort Collins, CO 80525