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Potential non-carbonate buffering in an interdunal wetland/slack along Lake Michigan

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ABSTRACT

Interdunal wetlands/slacks occur in Lake Michigan's coastal dunes where the wind scours the sand to the water table. Since May 2016 we have performed ecohydrological studies on the largest interdunal wetlands/slack, ~1.25 ha in size, lying within a deflated parabolic dune east of Lake Michigan at the Saugatuck Harbor Natural Area, Michigan. The slack's hydrology is influenced by Lake Michigan-Huron, appearing and increasing in size and water depth with rising lake levels and decreasing in size to drying with low levels. Prior to 2014, the slack was completely dry and dominated by upland dune species due to low lake levels. In 2014, rising lake levels rewetted the slack. Pools of standing water and hydrophytic vegetation appeared and expanded. While the surface waters of the pools are often supersaturated with O_2 due to photosynthesis, bottom waters at the sediment interface exhibit low O_2 saturation, allowing for the accumulation of organic matter from algae and cyanobacteria as well as emergent wetland vegetation. Surface and groundwater sampling indicate denitrification and sulfate reduction processes in the wetlands. Average total alkalinity in the slack pools, determined by titration, ranged from 3.57 meq/L (winter 2021) to 2.55 meq/L (June 2023) with a low of 1.67 meq/L (July 2021). Beginning in July 2021 and continuing to summer 2023, the titration data exceeded the acceptance criteria for carbonate speciation, suggesting that accumulating organic matter and the associated organic acids were a potential source of non-carbonate alkalinity. Many total alkalinity models assume a carbonate-based system wherein non-carbonate/organic alkalinity is discounted. However, our research finds that the organic fraction of total alkalinity can be considerable. Hence, care must be taken in using total alkalinity values to assess the buffering capacity, especially with respect to CO_2 calculations, for these freshwater systems.

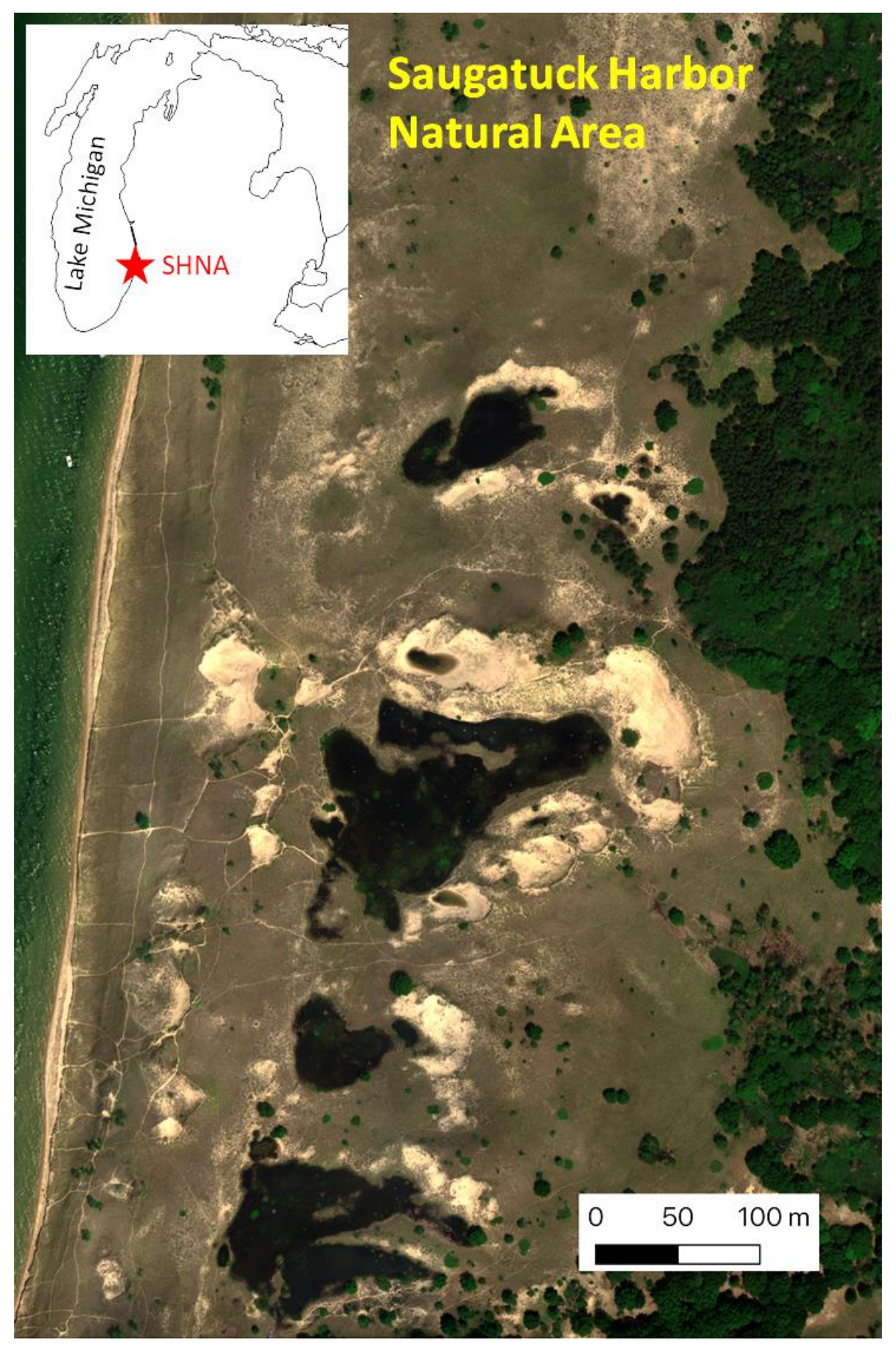

Fig. 1. Location map of study area. Orthomosaic constructed from July 2019 drone imagery.

INTRODUCTION AND STUDY AREA

Interdunal wetlands/slacks are found amongst the coastal dunes of Lake Michigan. These areas tend to be ecologically diverse, albeit rare in occurrence. Our area of study is located at Saugatuck Harbor Natural Area on the eastern shore of Lake Michigan (Fig. 1). The Michigan Natural Features Inventory (MNFI) ranks their status as G-2, meaning they are "imperiled and at high risk of extinction due to a very restricted range…" (MNFI 2016).

The hydrology of these slacks is influenced not only by the levels of Lake Michigan-Huron, but by precipitation and evapotranspiration (DeVries-Zimmerman et al., 2021). Lake level data collected for the Lake Michigan-Huron basin since 1918 show fluctuations of ~2m (USACOE, 2023). These fluctuations can profoundly change the ecosystem. The wetlands appear and expand in times of higher lake levels and contract to disappear during periods of lower lake levels (DeVries-Zimmerman et al., 2020).

During the 16-year period of low lake levels from 1998 – 2014 (Fig. 2), most of the surface water pools wetlands at SHNA dried (Fig. 3). In 2011 and 2013, even the deepest pools in the north dried (Fig. 3). In response to prolonged dryness, the ecological community inhabiting the wetland's footprint transitioned to one dominated by upland dune species. Furthermore, organic material that had accumulated in the wetlands' basin, was exposed, oxidized, and blown away from the area. Soil cores collected within the wetlands' footprint in 2017 did not show accumulated organic material remaining in the surface sediments.

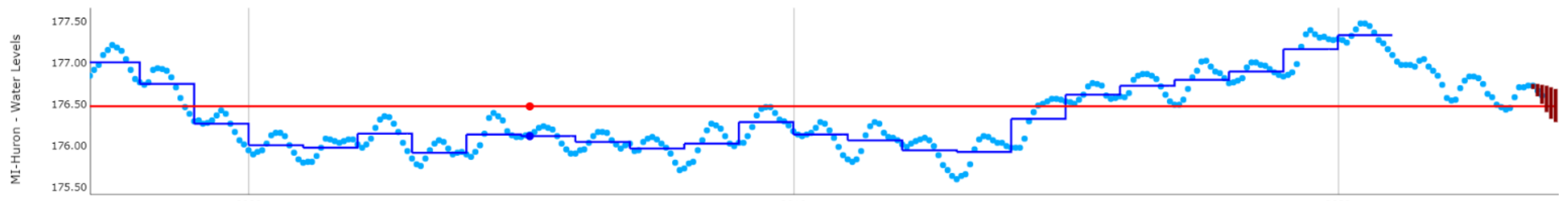

Fig. 2. Lake level curve for Lake Michigan–Huron. Blue line denotes monthly lake-wide averages. Redline denotes lake-wide period of record average (1918 – present). (USACOE, 2023). Elevations referenced to IGLD85 datum.

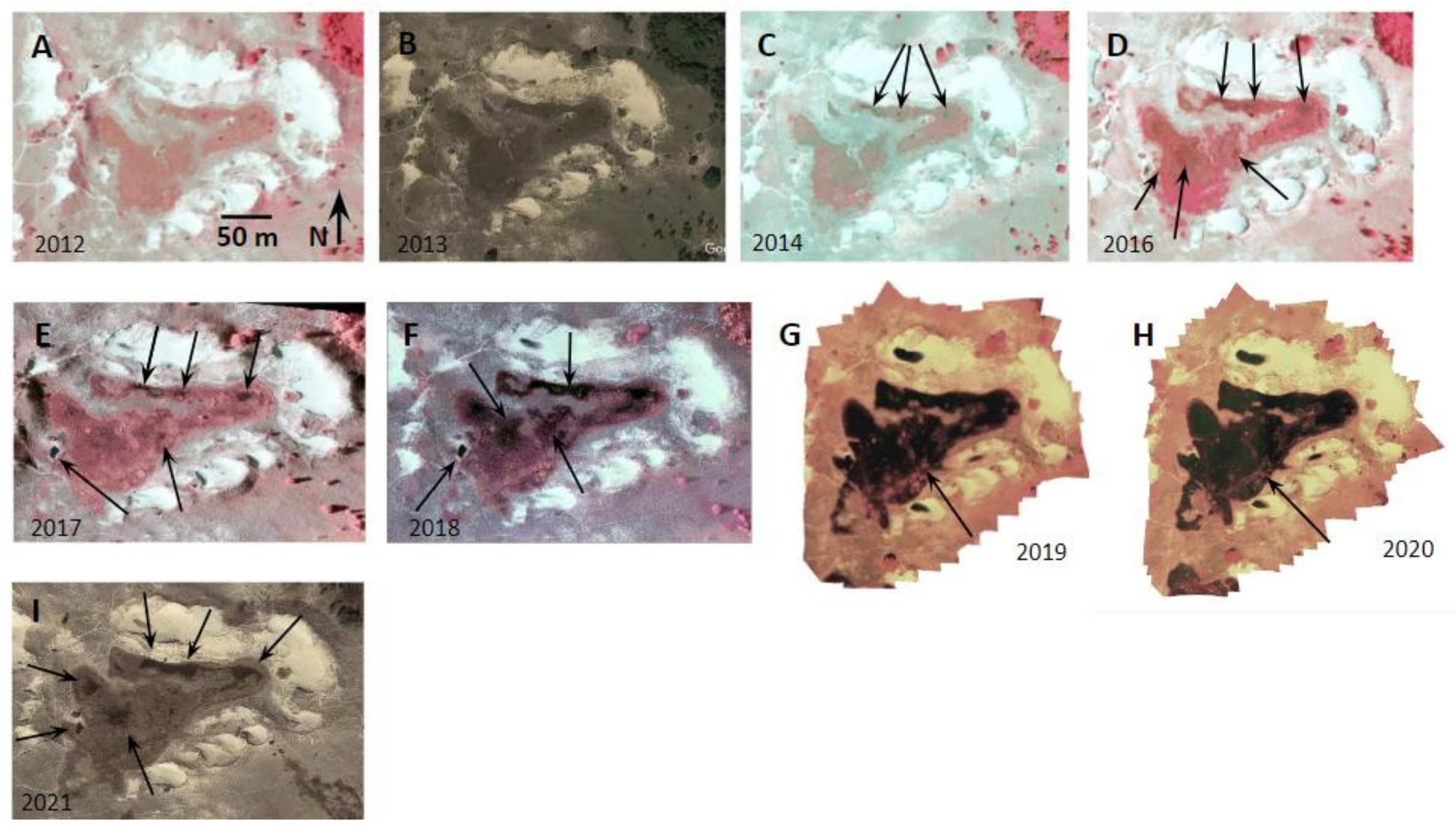

Fig. 3. Images of SHNA wetlands. Images for 2012, 2014, 2016, 2017, 2018, 2019, and 2020 are color-IR. Arrows indicate locations of standing water (pools) within main wetland. 2012, 2014, 2016 images obtained from NAIP, 2013 and 2021 images are from Google Earth. 2017–2020 images obtained from small, unoccupied aerial systems (drone) by Michigamme Group (2017, 2018) and the Hope College Coastal Research Group (2019, 2020).

METHODS

Groundwater sampling of the monitoring well network, together with surface water sampling in the wetland pools, was conducted in winter 2021, 2022, and 2023 (Fig. 4). A bailer was used to collect approximately 500 mL of groundwater in an acid-rinsed 500 mL HDPE bottle for more detailed laboratory analysis following the evacuation of three well volumes from the well. The field parameters, temperature, pH, and dissolved oxygen (DO) were measured using a YSI ProDSS Digital Water Quality Meter (YSI Inc., Yellow Springs, OH, USA) after sample collection. Surface water samples were also collected in 500 mL acid-rinsed HDPE bottles after the bottle was rinsed three times with water in the collection area. Field parameters in the surface water samples were measured within the pools using the YSI Water Quality Meter.

Samples were filtered within 24 hours of collection through 0.45 µm mixed ester cellulose membrane filters (Fisher Scientific). Total alkalinity was determined by titrating filtered samples with 0.02 N H_2SO_4 to a pH of 4. The USGS Alkalinity Calculator was used to analyze the titration data using the inflection point method for the total alkalinity values. Analyses for the inorganic anions NO_3^-, and SO_4^{2-} were performed simultaneously using a Dionex Integrion ion chromatography system with a Dionex IonPac AS11-HC column and conductivity detector.

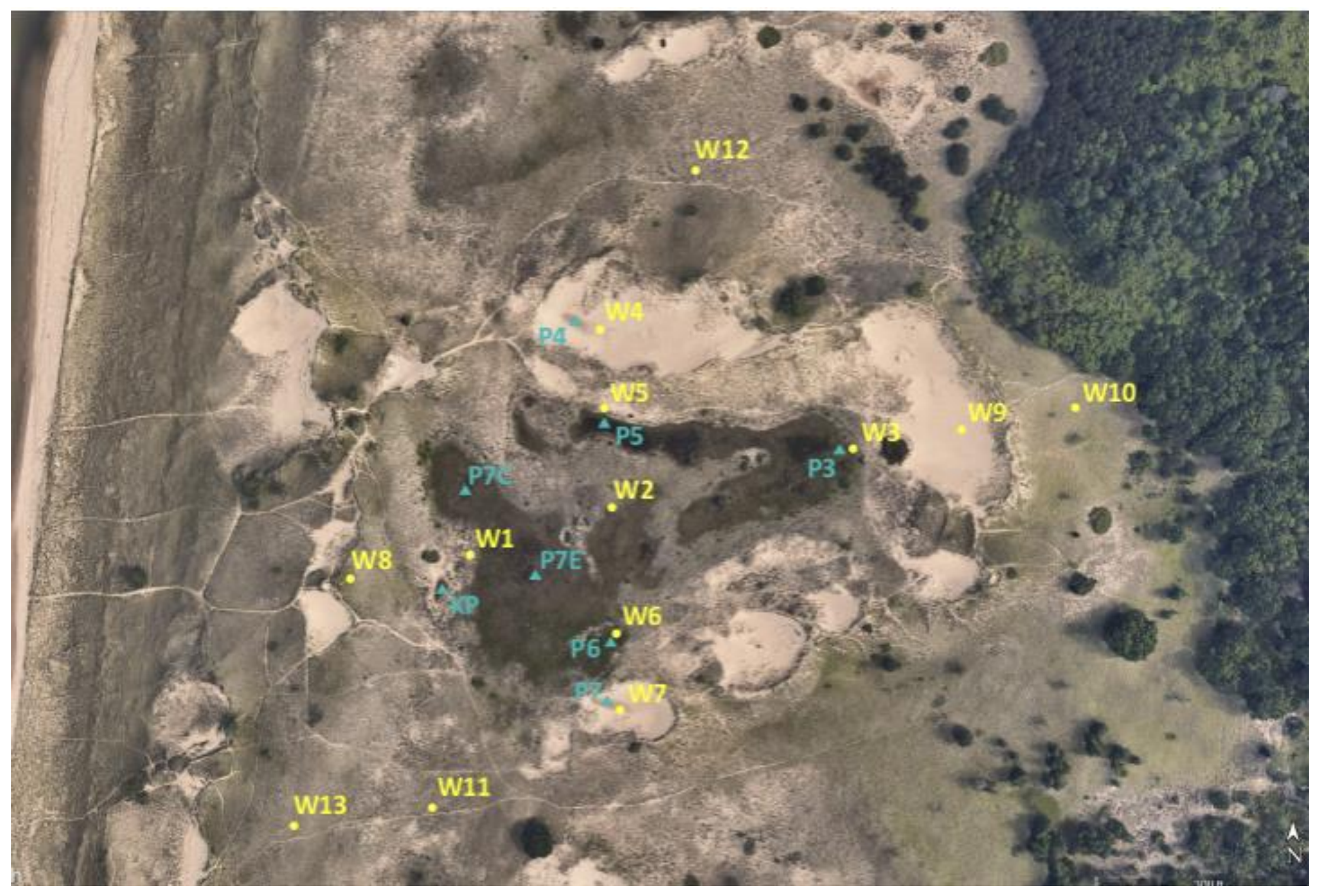

Fig. 4. Location map of the ponds and monitoring wells located within and around the wetland.

RESULTS AND DISCUSSION

The C content of the soil was likely negligible prior to 2013, as the site was mostly dry and had dominant upland/open dune vegetation (DeVries-Zimmerman et al., 2021), conditions not conducive to accumulating organic matter. Hence, 2013 can be used as the earliest date for the beginning of C accumulation. Rising lake levels have caused ponding to occur in the wetlands, creating pools with dominant hydrophytic vegetation and differing depths throughout. While the surface waters of the pools were often supersaturated with O_2 due to autochthonous productivity, bottom waters at the sediment interface exhibited low O_2 saturation, allowing for the accumulation of organic matter from algae and cyanobacteria as well as emergent wetland vegetation.

NO_3^- concentrations are higher around and outside the wetland, indicating N removal through plant uptake by the emergent wetland vegetation and denitrification within the wetland (Fig. 5). Similarly, SO_4^{2-} concentrations are lower inside the wetland than out, indicating sulfate reduction within the wetland (Fig. 5). These conditions also contribute to the anoxic preservation of organic matter (Lukawska-Matuszewska, 2016).

Total alkalinity values (Table 1) obtained using the USGS Alkalinity Calculator assume that the only compounds neutralized during the titration are hydroxide, carbonate, and bicarbonate. Initial total alkalinity values in February 2021 were within the calculated concentrations for these compounds by this method. However, subsequent sampling events showed increasing numbers of samples outside of these limits until late summer 2021 when all samples from that and subsequent sampling events exceeded the acceptance criteria for carbonate speciation. This indicates non-carbonate compounds, potentially organic acids, are contributing to the total alkalinity. It is hypothesized that increasing quantities of accumulated organic matter (Fig. 6) and the associated organic acids may be the source of the increasing non-carbonate alkalinity.

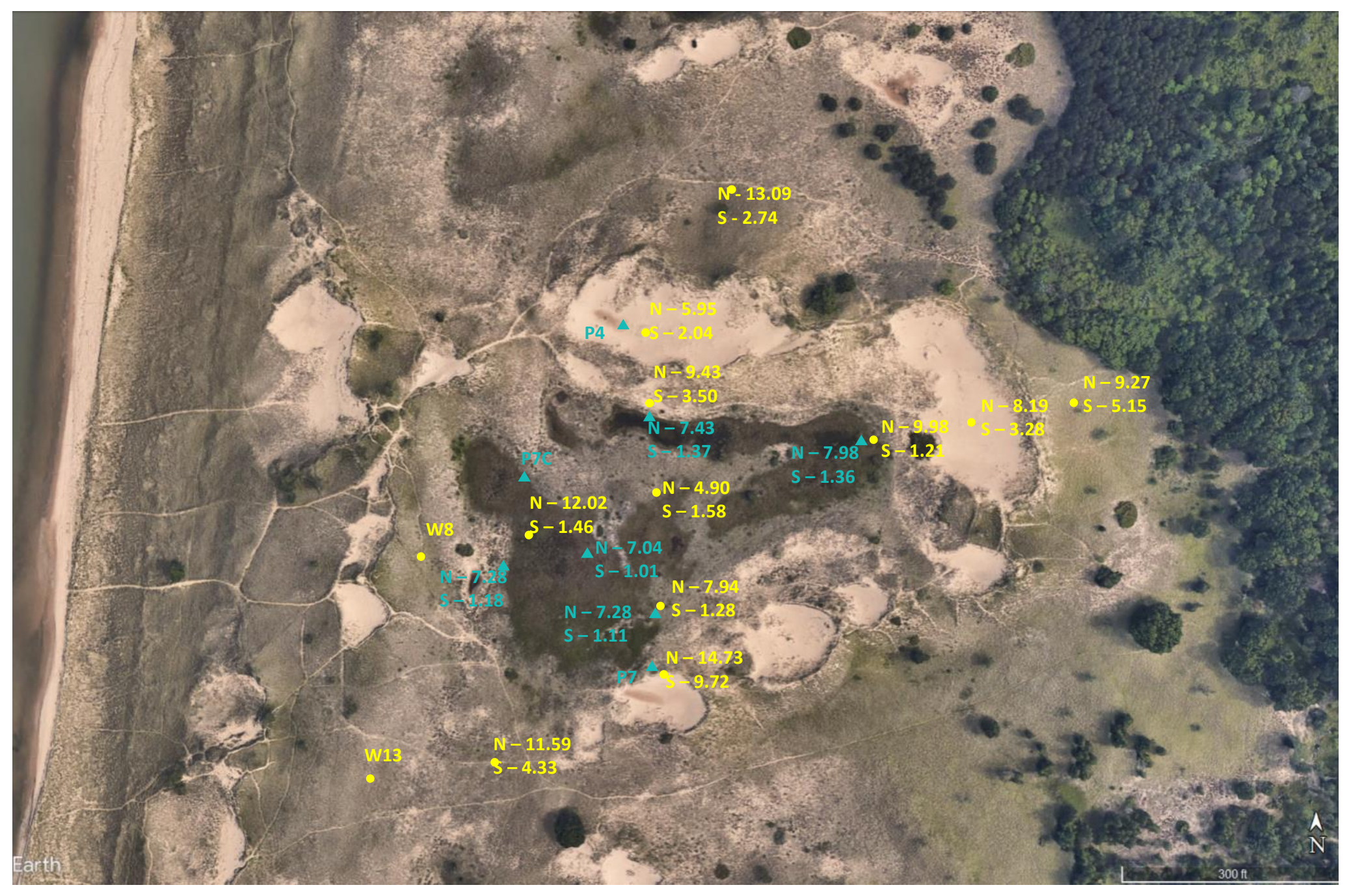

Fig. 5. Map of NO_3^- (N) and SO_4^{2-} (S) concentrations in mg/L for monitoring wells (yellow) and surface water pools (blue).

Inflection Point meq/L							
	2/21/2021	6/3/2021	7/1/2021	7/26/2021	7/19/2022	3/1/2023	6/23/2023
Pool 3	3.28	6.58	3.49	2.21	2.46	1.48	1.92
Pool 4		3.38	3.11	1.12	3.25		
Pool 5	3.56	3.68	4.11	2.03	2.53	1.83	2.12
Pool 6		5.48	3.7	1.75	3.2		
Pool 7			3.06	1.26			
Pool 7C	3.35	5.18	3.41	1.18	4.62	2.17	
Pool 7E	4.08	4.84	3.22		4.24	1.15	
Pool 7E Unfiltered			3.3				
Kermit's Pond		3.7	3.41	2.11	4.38	1.85	3.6

Table 1. Total alkalinity in meq/L in surface water pools at SHNA based on inflection point method. Grey box indicates the titration data exceeded the model's theoretical carbonate titration curve.

Total alkalinity is used to determine the ability of an aquatic system to buffer acid input. The higher the total alkalinity, the more buffering capacity the system has. Many total alkalinity models assume a carbonate based system wherein the contribution of organic alkalinity to total alkalinity is often discounted. However, more research is focusing on the contributions of non-carbonate alkalinity, especially the role of organic matter in aquatic systems (e.g., Hunt et al., 2011; Lukawska-Matuszewska, 2016; Liu et al., 2020; Kerr et al., 2021). This research is showing that the organic fraction of total alkalinity can be considerable. Consequently, it has been demonstrated that CO_2 calculations for marine and freshwater systems can be significantly influenced by assuming that the total alkalinity is solely based on the carbonate system.

Hence, given the ability of marine and freshwater coastal systems to sequester and/or release C in various forms, it is important to accurately understand the many aspects of these systems. Future work will focus on determining the source of the non-carbonate alkalinity, especially quantifying the contribution of organic matter or organic alkalinity to the total alkalinity. Additional analyses for other potential contributors to the total alkalinity, including silica, boron, and ammonia are also being planned.

Fig. 6. Wetland vegetation and accumulated organic matter in surface water pools on north side of wetlands.

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