

# High-Speed Limnology: Using Advanced Sensors to Investigate Spatial Variability in Biogeochemistry and Hydrology

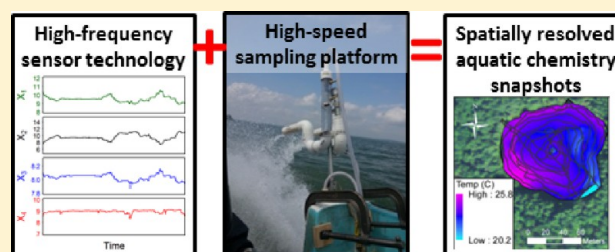
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## S Supporting Information

**ABSTRACT:** Advanced sensor technology is widely used in aquatic monitoring and research. Most applications focus on temporal variability, whereas spatial variability has been challenging to document. We assess the capability of water chemistry sensors embedded in a high-speed water intake system to document spatial variability. This new sensor platform continuously samples surface water at a range of speeds (0 to >45 km h<sup>-1</sup>) resulting in high-density, mesoscale spatial data. These novel observations reveal previously unknown variability in physical, chemical, and biological factors in streams, rivers, and lakes. By combining multiple sensors into one platform, we were able to detect terrestrial–aquatic hydrologic connections in a small dystrophic lake, to infer the role of main-channel vs backwater nutrient processing in a large river and to detect sharp chemical changes across aquatic ecosystem boundaries in a stream/lake complex. Spatial sensor data were verified in our examples by comparing with standard lab-based measurements of selected variables. Spatial fDOM data showed strong correlation with wet chemistry measurements of DOC, and optical NO<sub>3</sub> concentrations were highly correlated with lab-based measurements. High-frequency spatial data similar to our examples could be used to further understand aquatic biogeochemical fluxes, ecological patterns, and ecosystem processes, and will both inform and benefit from fixed-site data.



## INTRODUCTION

Advanced sensor technology has led to new and unexpected insights into ecosystem processes that may not have been possible with previous techniques.<sup>1,2</sup> Powerful networks of semiautonomous sensors (e.g., FLUXNET, NEON) are increasing our ability to measure, model, and develop theory of biogeochemistry, hydrology, and ecosystem function. Meanwhile, lowering sensor costs and increasing the ease of use are enabling smaller groups and individual investigators to observe important parameters at much-needed scales and frequency. Pervasive examples of sensor applications in aquatic systems include monitoring of riverine dissolved oxygen and water discharge (by the U.S. Geological Survey and others) and monitoring of lake chemical and physical characteristics such as dissolved oxygen, wind speed, and water temperature by the Global Lake Ecological Observatory Network (GLEON).

Although sensor technology is becoming common in limnological research, current applications focus almost entirely on temporal pattern and variation. Spatial variability is rarely documented with sensors because of the high investment costs for the spatial replication of such infrastructure.<sup>3</sup> In contrast, spatial patterns have been documented for many years in coastal environments and ocean basins from large networks of sensors (e.g., Global Drifter Program, autonomous underwater vehicles) or from cooperative research cruises. However, unlike the open ocean, there are tens to hundreds of millions of inland

water bodies,<sup>4</sup> and they are extremely diverse,<sup>5,6</sup> thus precluding easily integrated sampling techniques. Similarly, spatial patterns within small inland waterbodies are not observable with current remote-sensing technology (although larger waterbodies are more easily imaged) and may change over short time scales (hours), thus placing them in a challenging intermediate zone in which few automated observation tools are appropriate. Additionally, many important attributes of freshwaters are not detectable with current remote sensing technology, thus necessitating in situ tools.

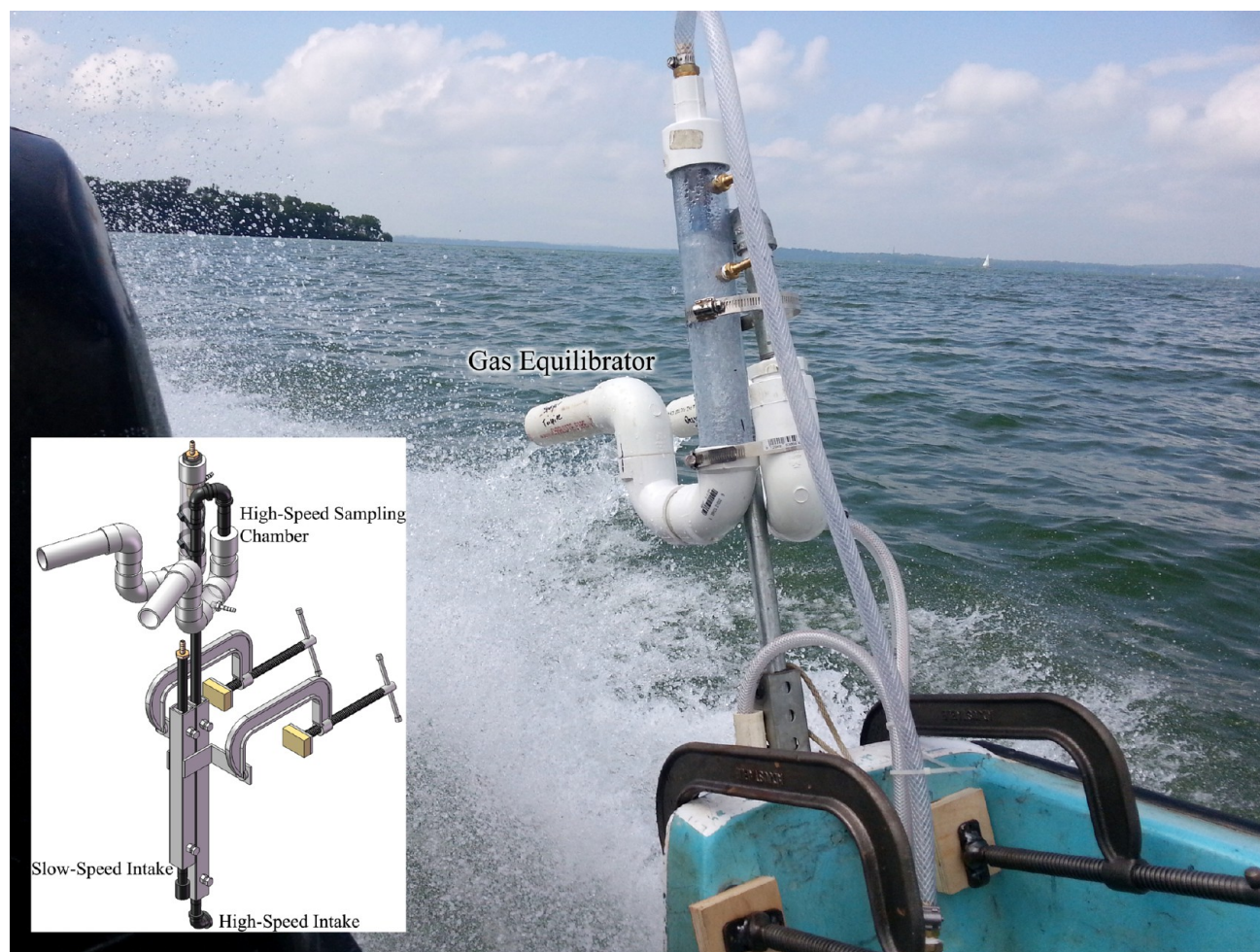
In addition to logistical challenges, conceptualizations and long-held assumptions of aquatic ecosystems limit our ability to understand complex environmental phenomena. Our mental models of lakes and rivers dictate “not only how data are collected but also what data are collected and, most important, what questions are asked”.<sup>7</sup> For example, streams and rivers are typically studied from a fixed location, emphasizing the role of advection and transport of matter and energy. Less attention is given to longitudinal variability despite broad awareness of its influence.<sup>8</sup> Lakes, on the other hand, are typically conceptualized in the vertical dimension, emphasizing the roles

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**Figure 1.** Photograph of the fast limnology automated measurement (FLAME) platform water intake system attached to a moving boat; inset is a computer rendering highlighting the two intake ports not visible in the photograph.

of stratification and vertical mixing, thus partially disregarding horizontal patterns. But what insights can be gained from altering our frame of reference or expanding from single locations? And how might we apply powerful sensor technology to other spatial dimensions?

Past work has highlighted significant spatial variability of water chemistry in individual aquatic ecosystems,<sup>3,9–12</sup> but there is a clear need to address spatial variability in additional freshwater ecosystems<sup>13</sup> and in a more efficient manner. The goal of this paper is to present and evaluate a platform capable of rapid spatial sampling of surface waters using current sensor technology. While we are not the first to use sensor technology on a boat,<sup>14,15</sup> our platform allows for easy integration of multiple sensors and allows for both low-speed and unprecedented high-speed sampling. In addition to describing this new device, our goal is to present and evaluate previously unknown spatial patterns in an array of streams, rivers, and lakes. We also provide suggestions for future applications in support of scientific research, engineering, management, and outreach. Our selected examples also address practical aspects such as the use of spatial statistics, a consideration of aquatic transition zones, and terrestrial–aquatic connections. Each of these examples is geared toward the broad goal of better understanding ecosystem pattern and process.

## ■ MATERIALS AND METHODS

**Instrumentation.** The Fast Limnology Automated Measurement (FLAME) platform is a novel flow-through system designed to sample inland waters at both low (0 to  $\sim 10$  km  $\text{h}^{-1}$ ) and high speeds (10 to  $>45$  km  $\text{h}^{-1}$ ) (Figure 1). The FLAME consists of three components: an intake manifold that attaches to the stern of a boat (having both slow- and high-speed intakes, Figure 1 and Figure S1, Supporting Information); a sensor and control box that contains hoses, valves, a circulation pump and sensor cradles (Figure S2, Supporting Information); and a battery bank to power the electrical components. The boat-mounted intake manifold serves multiple purposes. First, sensors are mounted inside the boat, protecting them from potential damage. Second, the intake system creates a constant, bubble-free water flow, thus preventing any issues for optical sensors due to cavitation. Finally, to analyze dissolved gases, a constant water source is needed on board. Water flow via both the slow- and high-speed intakes is regulated by the onboard impeller pump, allowing for seamless switching between slow- and high-speed operations. Any number of sensors could be integrated into the platform with simple modifications and can be combined with common limnological instruments such as acoustic depth-finders. In our example applications we used a YSI EXO2 multiparameter sonde (EXO2; Yellow Springs, OH) and a Satlantic SUNA V2 optical nitrate ( $\text{NO}_3$ ) sensor (Halifax, NS, Canada), both



Table 1. Survey Location Attributes and Sampling Information

survey location	latitude	longitude	lake area (ha)	max depth (m)	river discharge (m <sup>3</sup> s <sup>-1</sup> )	parameters presented
Trout Bog Lake (Vilas County, WI)	46.04113	-89.68629	1.1	7.9		all EXO2 and UGGA data
Allequash Creek and Allequash Lake (Vilas County, WI)	46.03833	-89.62261	168	8	0.09	pCO <sub>2</sub> , pH
Lake Mendota (Madison, WI)	43.10847	-89.41532	3940	25.3		fDOM
Mississippi River, Navigation Pool 8 (MN and WI)	43.68184	-91.24163		1.8 (mean)	1893.8	conductivity, NO <sub>3</sub>

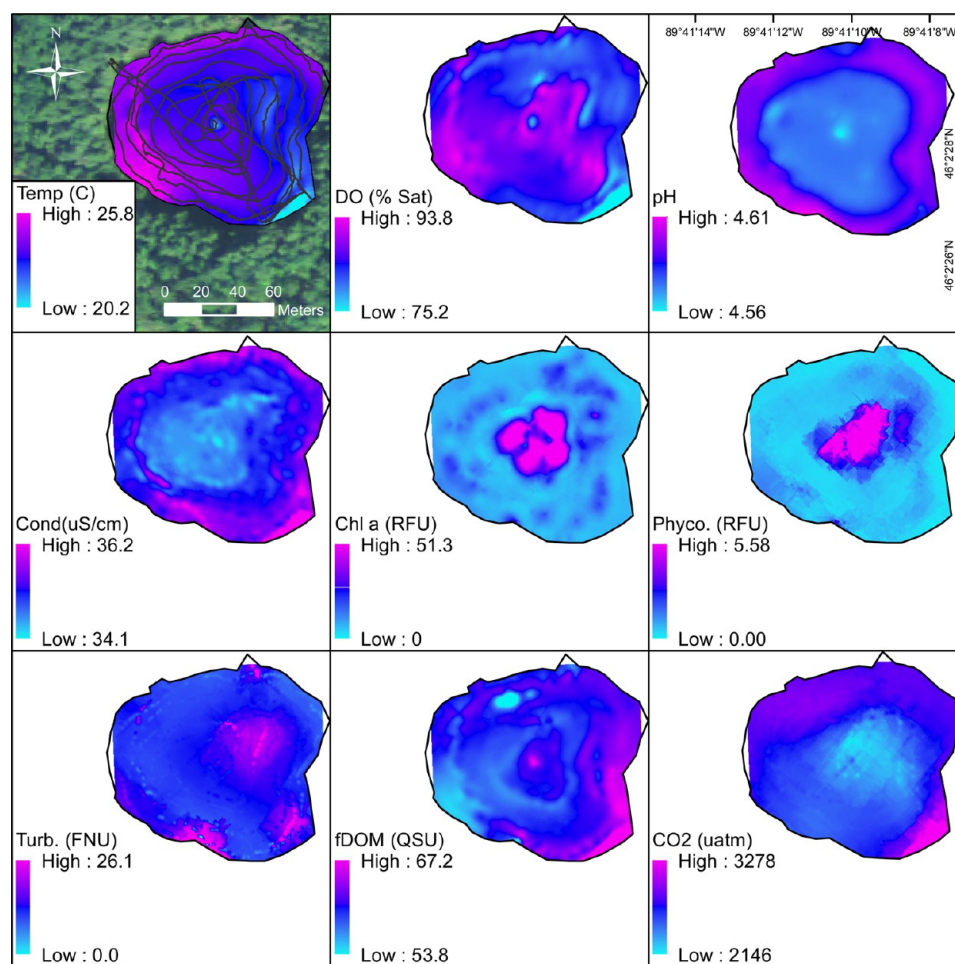
integrated into the control box plumbing with flow-through cells available from the manufacturer. Additionally, a Los Gatos Research ultraportable greenhouse gas analyzer (UGGA) (cavity enhanced absorption spectrometer; Mountain View, CA) was used to measure the dry mole fraction of carbon dioxide (CO<sub>2</sub>) dissolved in surface water by equilibrating water with a small headspace using a sprayer-type equilibration system that has previously been shown to have fast response times relative to other designs<sup>16</sup> (Figure S1, Supporting Information). Both the EXO2 and the UGGA are capable of logging data at 1 Hz. Because the SUNA was operated out of the water and on a boat during warm periods, data were collected less frequently (~0.1 Hz) to minimize lamp-on time and avoid the lamp temperature cutoff of 35 °C. The EXO2 sonde uses a combination of electrical and optical sensors for specific conductivity, water temperature, pH, dissolved oxygen, turbidity, fluorescent dissolved organic matter (fDOM), chlorophyll-*a* fluorescence, and phycocyanin fluorescence. The SUNA instrument measures NO<sub>3</sub> using in situ ultraviolet spectroscopy between 190 and 370 nm and has a detection range of 0.3–3000 μM NO<sub>3</sub>, and a precision of 2 μM NO<sub>3</sub>. The UGGA has a reported precision of 1 ppb (by volume). In order to translate time-series data from the instruments into spatial data, we also logged latitude and longitude at 1 Hz with a global positioning system (GPS) with the Wide Area Augmentation System (WAAS) functionality enabled allowing for <3 m accuracy for 95% of measured coordinates. Synchronized time stamps from the EXO2, UGGA, SUNA, and GPS were used to combine data streams into a single spatially referenced data set.

The FLAME platform was tested with a 5 m long research boat under a wide range of velocities (idling to >45 km h<sup>-1</sup>) and wave conditions on Lake Mendota, WI. We found that the low-draft of the intake system allowed for unencumbered operation of the boat with no noticeable impacts on the boat's handling or top speed. We ran a simple set of experiments to determine the residence time of the system and the overall response time of the EXO2 and UGGA sensors integrated into the platform (Supporting Information). After determining first-order response characteristics of each sensor, we tested and applied an ordinary differential equation method to correct the raw data for significant changes in water input resulting in higher accuracy spatial data (Supporting Information). The goal of this paper was not to evaluate individual sensor accuracy and precision; however, we did address sensor vs wet chemistry (dissolved fraction) measurements in two selected examples to determine the general applicability of the platform. We have not yet assessed the platform's ability to properly collect and analyze larger particles. We used the FLAME throughout the summer of 2014 on four distinct aquatic ecosystems, including a small dystrophic lake, a stream/lake complex, a medium-sized eutrophic lake, and a managed reach of the upper Mississippi River (Table 1). Each of these applications demonstrates the spatial variability of surface water chemistry and the flexibility of

FLAME for limnological research. Although we typically ran all instruments at 1 Hz, we present parameters selectively for brevity.

**Survey 1: Dystrophic Lake Chemical Suite.** In our first example, we sampled a small dystrophic lake (Trout Bog, 1.1 ha) in northern Wisconsin on 15 August 2014 using the slow-speed system attached to a small boat (travel speeds <10 km h<sup>-1</sup>). The sampling took approximately 45 min. We present variables collected with the EXO2 and UGGA in this example. Trout Bog is surrounded by a peat wetland and has a very small contributing watershed area. A maximum depth of 7.8 m combined with high dissolved organic carbon (DOC) concentrations and a limited wind fetch leads to stable thermal stratification in summer. Many chemical and physical parameters are expected to covary in this lake. But how well does a single sampling location (the lake center) represent the lake as a whole? We ask specifically, what is the scale of spatial autocorrelation? To answer this question, we used semivariance analysis and semivariogram modeling (ArcGIS Geostatistical Analyst toolbox). Stable, Gaussian, or spherical empirical semivariogram models were chosen on the basis of their relative ability to fit the data using an iterative approach. We focus our analysis on the empirical semivariogram range, the distance at which variables are no longer spatially autocorrelated, which can also be thought of as the average "patch" size.<sup>9</sup> We used the results of semivariogram modeling to interpolate each parameter for the entire lake surface with ordinary kriging procedures using a 33% randomized subset of the complete data set ( $n = 3760$ ).

**Survey 2: Stream/Lake CO<sub>2</sub> and pH.** In our second example, we present CO<sub>2</sub> and pH data from a stream/lake complex in northern Wisconsin. Sampling occurred in the morning to early afternoon on 24 and 25 July 2014. We used the slow-speed FLAME system attached to a small boat (travel speeds <10 km h<sup>-1</sup>). This ecosystem is a primary study site for the North Temperate Lakes Long term Ecological Research (NTL-LTER) and the U.S. Geological Survey (USGS) Water, Energy and Biogeochemical Budgets program. Water in this set of connected aquatic features originates primarily as upwelling groundwater in the spring ponds to the east, with flow continuing through a wide wetland which then transitions into a forested reach downstream of a USGS gaging station (05357206). Past the gaging station, the stream then flows into the first basin of Allequash Lake, through the second basin to the west, and into the lower section of Allequash Creek before entering the largest lake in the basin, Trout Lake. Surface CO<sub>2</sub> and pH are monitored at the gaging station along Allequash Creek as part of ongoing research objectives regarding cycling of elements such as carbon (C). In order to understand larger scale patterns of ecosystem metabolism and gas flux, we need to understand how temporal data relate to spatial data. We ask how do CO<sub>2</sub> and pH vary along a stream-lake flowpath?



**Figure 2.** Results of FLAME survey of a small dystrophic lake (Trout Bog) showing all measured variables from the EXO2 and UGGA instruments; values were interpolated at the 0.25 m scale using semivariogram analysis (Table 2) and ordinary kriging; top-left panel includes the sampling path and background aerial imagery.

### Survey 3: Lake fDOM and Dissolved Organic Carbon.

In our third example, we present fDOM data collected between 08:00 and 12:00 on 4 July 2014 on Lake Mendota (Madison, WI), a medium-sized eutrophic lake. We sampled the majority of the lake at high speed ( $>40 \text{ km h}^{-1}$ ) in order to capture a full spatial “snapshot”. In addition to the sensor data, we collected discrete water samples for DOC concentration. We predicted that fDOM and DOC would be positively correlated in this ecosystem.<sup>17</sup> Water chemistry samples were collected into plastic bottles while the boat was stopped and free-floating using the slow-speed intake and were then capped and stored on ice. Each sample was filtered ( $0.45 \mu\text{m}$ ) in the lab within 3 h of collection. Filtered DOC samples were analyzed according to protocols established by the NTL-LTER (<https://lter.limnology.wisc.edu>) using a Shimadzu TOC-V-csh total organic carbon analyzer. Using this data set, we ask how homogeneous is the surface mixed layer with respect to DOC concentrations? We again use semivariogram modeling and focus on the range parameter.

**Survey 4: River Conductivity and  $\text{NO}_3$ .** In our final example, we present conductivity and  $\text{NO}_3$  data collected on Navigation Pool 8 of the Upper Mississippi River (near La Crosse, WI) on 21–22 July 2014. We primarily used the high-speed system ( $>30 \text{ km h}^{-1}$ ) to capture spatial variability. Due to the large size of the reach, we combined data collected over the course of 2 days, primarily in the morning and early afternoon

periods. River discharge (measured at Dam 8) during our sampling was  $1893.8$  and  $1775.4 \text{ m}^3 \text{ s}^{-1}$  on the 21st and 22nd, respectively. Our sampling path included sections above and below Lock and Dam 7, the main navigation channel, three tributaries (Black River, La Crosse River, and Root River), two backwater lakes (Target Lake and Lawrence Lake), a backwater channel (Turtle Slough), and immediately upstream from Lock and Dam 8. In this example, we ask how does  $\text{NO}_3$  vary among the major inputs to Pool 8? Additionally, we investigated how  $\text{NO}_3$  compared between the various backwater river sections and the main channel. Using conductivity as a conservative tracer, we identified locations with potentially elevated  $\text{NO}_3$  cycling.

To confirm SUNA measurements, we collected discrete water samples at 10 locations spanning the range of SUNA  $\text{NO}_3$ . River water was filtered ( $0.45 \mu\text{m}$ ) into new 20 mL plastic scintillation vials. Samples were stored on ice and frozen within 6 h of collection. Lab  $\text{NO}_3$  samples were analyzed according to protocols established by the North Temperate Lakes LTER using an Astoria-Pacific Astoria 2 segmented flow autoanalyzer and reported as  $\text{mg NO}_3\text{-N L}^{-1}$ . We assessed the relationship between the traditional lab method and the SUNA sensor using linear regression.

## ■ RESULTS AND DISCUSSION

Novel observations of water chemistry using the FLAME platform revealed both predictable and unexpected spatial patterns among a diverse set of aquatic ecosystems. Key findings included the observation that although water chemistry exhibits spatial autocorrelation, patch size was variable (e.g., ~10 m in Trout Bog to >1000 m in Lake Mendota), and that fixed long-term sampling locations may not adequately account for spatial variability in surface waters (e.g., Allequash Creek). These findings call for a shift toward more extensive spatial characterization of aquatic ecosystems using sensor technology, which can also benefit from and inform current fixed-site applications.

**Survey 1: Dystrophic Lake Chemical Suite.** We observed unexpected high variability in surface water chemistry on Trout Bog Lake in northern Wisconsin (Figure 2). Surface water temperature varied from 20.2 to 25.8 °C with a distinct spatial pattern where warmest temperatures were observed in littoral regions on the western side of the lake, transitioning to cooler temperatures to the southeast. Notably, we found that the temperature variability on this extremely small lake (1.1 ha) was nearly identical to the variability observed on the larger Lake Mendota (39.4 km<sup>2</sup>) on 4 July 2014 (data not shown). Dissolved oxygen was undersaturated with respect to the atmosphere (75.2–93.8%), with least values in the southeastern littoral regions. Surface pH was low ranging from 4.56 to 4.61, with greatest values in the littoral zone and least values in pelagic surface waters. Surface conductivity was relatively low (34.1–36.2  $\mu\text{S cm}^{-1}$ ) but showed distinct spatial patterns with greatest values in the littoral regions gradually decreasing toward the center of the lake. Phytoplankton pigments (chlorophyll-*a* and phycocyanin) had somewhat different patterns relative to other chemical and physical parameters. Both chlorophyll-*a* and phycocyanin fluorescence were elevated in the center of the lake but consistently low elsewhere. Turbidity was relatively low (0 to 26.1 FNU) with elevated values mainly in the lake center. Surface fDOM illustrated a similar littoral-pelagic gradient as other parameters with distinctly elevated values in the southeastern littoral region. Finally, CO<sub>2</sub> also showed a littoral–pelagic gradient and a southeastern littoral maximum. Analysis of spatial autocorrelation (semivariogram modeling) for each parameter revealed a wide array of patch sizes (semivariogram range) between 1.53 m (phycocyanin) and 59.09 m (pH) (Table 2). For most variables, parcels of water ~10 m away were uncorrelated with their neighbors.

Much of the observed variation in Trout Bog Lake can be attributed to pelagic vs littoral differences, as the lake is only

115 m wide. We suspect that spatial gradients are driven primarily by hydrologic interactions with the surrounding wetlands and aquifer, which is spatially distinct (inferred groundwater loading in the southeast). Small seepage lakes such as Trout Bog are typically treated in a 1D framework<sup>18</sup> and are believed to be well-mixed horizontally. However, small lakes have relatively large perimeters relative to their area, which may result in greater relative influence of adjacent terrestrial systems.<sup>19</sup> Together, these high-resolution spatial data challenge conceptions of horizontal homogeneity in the smallest lakes. In a practical sense, these observations could be expanded to other inland waters to understand how typical pelagic (deep-hole) sampling locations reflect the conditions of a lake as a whole. Future research applications could focus on understanding the role of horizontal connectivity with wetland and terrestrial environments to understand the contribution of allochthonous organic matter and discrete nutrient sources fueling primary productivity in the lake center.

**Survey 2: Stream/Lake pCO<sub>2</sub> and pH.** Similar to the findings from the small dystrophic lake, we observed large spatial variability along a stream/lake watercourse. We measured greatest concentrations of CO<sub>2</sub> in the forested reach of Allequash Creek (>3000  $\mu\text{atm}$ ) just before the inlet to Trout Lake (Figure 3). Lowest values were observed in the forested reach upstream of Allequash Lake (<829  $\mu\text{atm}$ ), with intermediate values in the upper wetland reach downstream of the spring ponds and interspersed among small beaver dams. Observed CO<sub>2</sub> concentrations were within the range of seasonal variability previously documented for Allequash Creek and other streams in the region.<sup>20</sup> However, variability during this single sampling (661–4971  $\mu\text{atm}$ ) along a relatively short flowpath (~10 km) was surprisingly large relative to the variability observed for 52 streams (201–15500  $\mu\text{atm}$ ) in the greater Northern Highlands Lake District (NHL; ~6400 km<sup>2</sup>).<sup>20</sup> These patterns are likely driven by a combination of biological in-stream CO<sub>2</sub> production and consumption, groundwater CO<sub>2</sub> delivery, and gas exchange with the atmosphere that are known to vary spatially in NHL streams.<sup>20</sup> In support of our CO<sub>2</sub> data, longitudinal pH patterns were very similar, but opposite to CO<sub>2</sub>, indicating the interrelationship between pH and the carbonate system (Figure 3). Overall variability in pH was high, differing by nearly 2 orders of magnitude (2 pH units) between the upper basin of Allequash Lake and the lower, forested reach upstream of Trout Lake. It is clear that the long-term USGS monitoring site on Allequash Creek is different than upstream and downstream reaches, and transitions between these aquatic features are surprisingly sharp. Knowledge of both temporal patterns (single-station sensor data) and of spatial variability will help inform ongoing investigations of stream C cycling and may lead to improved estimates of aquatic gas flux.

### Survey 3: Lake fDOM and Dissolved Organic Carbon.

Unlike water chemistry patterns observed at other survey sites, we documented relatively consistent patterns in the pelagic zone of Lake Mendota. Surface fDOM was consistently low in the central portion of the lake. However, concentrations along the river inlet were much greater (Figure 4). As expected, measured fDOM was strongly correlated with wet chemical DOC analyses (inset Figure 4). This result suggests that with proper calibration of fDOM/DOC relationships for individual waterbodies,<sup>17,21</sup> the FLAME platform is capable of rapid, high-resolution spatial characterization of DOC in aquatic ecosystems. We speculate that the low fDOM values where

**Table 2. Fitted Semivariogram Range from Trout Bog FLAME Data (See Figure 2)**

parameter	range (m)
temp (C)	15.12
DO (% sat.)	6.44
pH	59.09
conductivity ( $\mu\text{S/cm}$ )	4.429
chlorophyll <i>a</i> (RFU)	11.77
phycocyanin (RFU)	1.532
turbidity (FNU)	1.73
fDOM (QSU)	7.307
CO <sub>2</sub> ( $\mu\text{atm}$ )	2.34



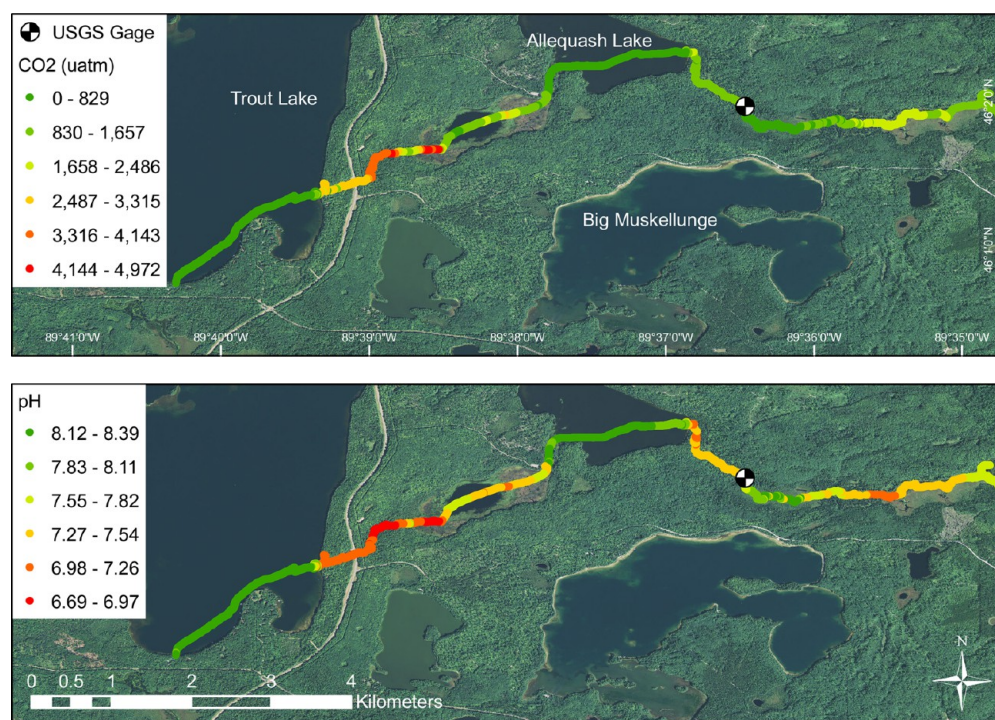


Figure 3. pH and CO<sub>2</sub> map from the Allequash Creek and Allequash Lake FLAME survey.

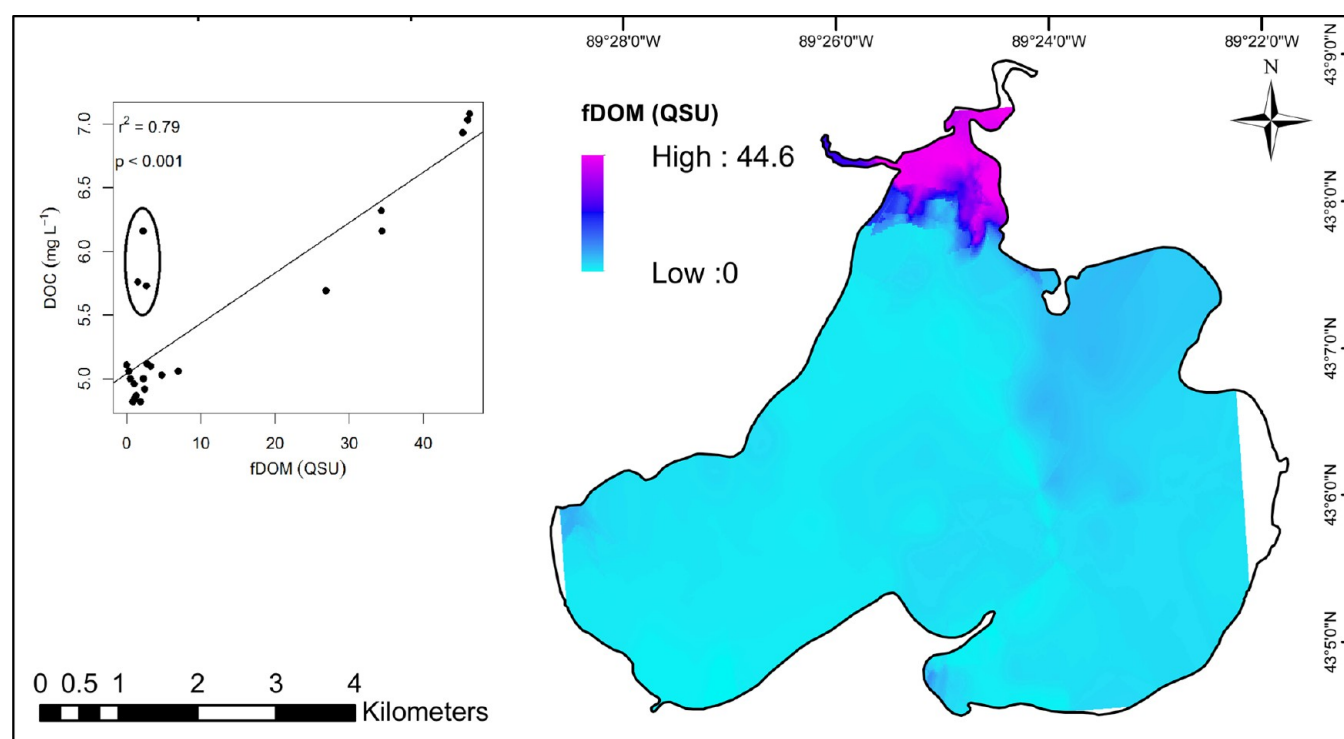
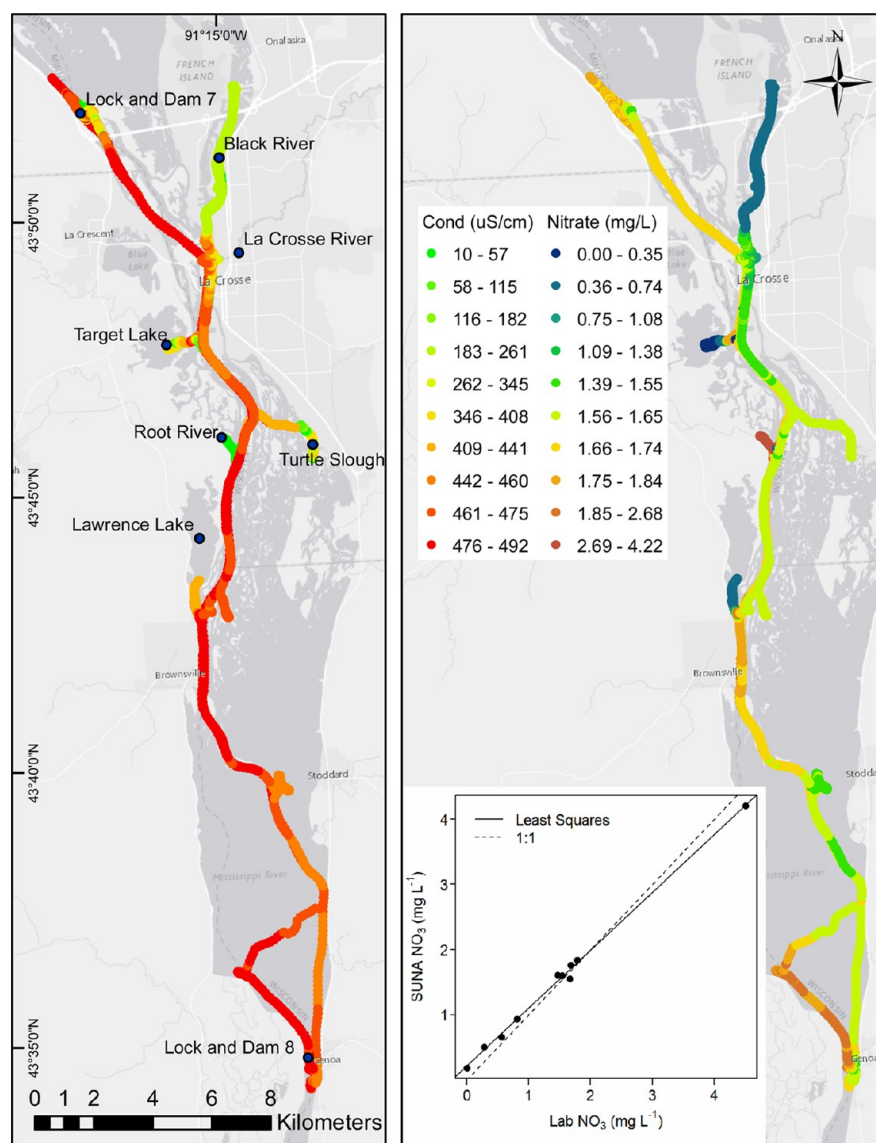


Figure 4. Map of fluorescent dissolved organic matter (fDOM) on Lake Mendota using ordinary kriging; inset shows the linear relationship between fDOM and dissolved organic carbon concentrations (DOC) based on matched discrete wet chemistry samples; potential algal-influenced outliers are circled.

DOC was  $>5.5 \text{ mg L}^{-1}$  indicates the presence of autochthonous (algal-derived) DOM, which typically has lower aromaticity relative to terrestrially derived material.<sup>22</sup> The stark contrast between greatest river fDOM concentrations and least values in the adjacent pelagic zone lead to interesting questions regarding the transport and fate of the presumably terrestrial riverine

carbon load. The entire lake sampling took 4 h. Therefore, much of the variability shown in Figure 4 was likely due to spatial patterns, as opposed to temporal change. Although fDOM varied spatially across the pelagic zone, DOC only varied by  $\sim 1 \text{ mg L}^{-1}$ . In support of our qualitative examination, semivariogram modeling revealed a large range parameter for



**Figure 5.** Map of conductivity and  $\text{NO}_3$  patterns from Navigation Pool 8 of the Upper Mississippi River; inset shows the strong linear relationship between SUNA-derived  $\text{NO}_3$  and laboratory analysis of  $\text{NO}_3$  concentrations.

fDOM (1070 m), suggesting relatively homogeneous fDOM over large scales in this lake. Through repeated spatial sampling and calibration of fDOM/DOC relationships, this approach could be used to understand spatial patterns of DOC production and consumption in lakes. These fDOM/DOC relationships along with fDOM and additional optical spatial snapshots could also be used to ground-truth and/or calibrate powerful remote sensing approaches that are currently limited by the spatial resolution of discrete water chemistry sampling.<sup>23</sup>

**Survey 4: River Conductivity and  $\text{NO}_3$ .** We observed distinct spatial variability in surface water  $\text{NO}_3$  concentrations in Pool 8 of the Upper Mississippi River using high-speed optical techniques. Given that optical  $\text{NO}_3$  was strongly correlated with lab-measured  $\text{NO}_3$  (Figure 5 (inset);  $\text{df} = 8$ ,  $t = 49.4$ ,  $p < 0.001$ ,  $r^2 = 0.99$ ), we can confidently use the optical data set to examine spatial concentration patterns and  $\text{NO}_3$  processing.  $\text{NO}_3$  concentrations outside of the main channel ( $0.35\text{--}2.68 \text{ mg NO}_3\text{-N L}^{-1}$ ) varied more than in the main channel ( $1.09\text{--}1.84 \text{ mg NO}_3\text{-N L}^{-1}$ ; Figure 5). A comparison of  $\text{NO}_3$  in the major tributaries showed least concentrations in

the Black River ( $0.50\text{--}0.93 \text{ mg NO}_3\text{-N L}^{-1}$ ), while the Root River ( $4.20 \text{ mg NO}_3\text{-N L}^{-1}$ ) had much greater concentrations than the main channel. The large differences between tributaries was not surprising as the Root River catchment is dominated by row crop agriculture and is known to have elevated  $\text{NO}_3$  concentrations,<sup>24</sup> whereas the Black River flows through a large lake and wetland before converging with the main river channel.

Using measured conductivity from each location within the river we can assess the relative contribution of multiple  $\text{NO}_3$  sources and assess N cycling using conservative mixing. Deviations between observed and predicted (conservative mixing)  $\text{NO}_3$  concentrations are identified as locations of net consumption or production. For example, the two backwater lakes (Target Lake and Lawrence Lake) had 10–50% of the  $\text{NO}_3$  concentration observed in the proximate main channel. This apparent reduction in  $\text{NO}_3$  could be explained by variation in source water or consumption due to nitrogen cycling processes. Given that conductivity in these backwater lakes was similar to the main channel (80–100%), we can attribute the

reduction of  $\text{NO}_3$  to uptake and removal processes. Backwater regions of Pool 8 have previously been identified as having elevated denitrification capacity due to greater amounts of sediment organic matter and greater biological uptake resulting from N limitation in late summer.<sup>25,26</sup> In contrast, main channel  $\text{NO}_3$  concentrations were more homogeneous, indicating the greater role of advection relative to uptake.<sup>27</sup> Further identification of spatially explicit  $\text{NO}_3$  sources and sinks (as well as process rates) in the Upper Mississippi River may lead to a better understanding of the fate of anthropogenic  $\text{NO}_3$ . Somewhat surprisingly,  $\text{NO}_3$  variability in Pool 8 during a single summer day ( $0.35\text{--}2.68\text{ mg NO}_3\text{--N L}^{-1}$ ) was nearly equivalent to the two-year range ( $0.22$  to  $2.97\text{ mg NO}_3\text{--N L}^{-1}$ ) observed in the Lower Mississippi River with a similar sensor located at a fixed-station.<sup>28</sup> Future work could simultaneously assess the scales of spatial and temporal variability as they relate to biogeochemical processes and ecosystem function.

**Assessment and Future Applications.** We have presented several examples of pervasive spatial variability in aquatic ecosystems using a novel sampling platform. These examples of spatial water chemistry highlight some possibilities of basic biogeochemical mapping that may be useful on their own as a management tool. However, cartographic representations of these data sets are simply the first step in data exploration, similar to making a histogram or scatterplot of typical data. There is a clear need to translate spatial representations of water chemistry into a process-based understanding, and to address fundamental questions regarding spatial variation.

Spatial sampling approaches like the one demonstrated here can supplement and benefit from fixed-station time-series data (streams and rivers), depth profiles (lakes), and other standard aquatic data sets. Integration of these multiple approaches will likely yield new insights and breakthroughs in the study of freshwater ecosystems, but their assimilation will likely be ecosystem and question-specific. The goal should not be to eliminate fixed sensor installations or long-term sampling schemes, but rather to supplement those with spatial snapshots at the surface. Potential combinations include: sampling lake temperature and dissolved oxygen during lake mixing using depth-profiling buoys and spatial surveys to understand mixing processes; tracking nutrient exchange between river channels and backwaters in relation to changes in the hydrograph; and tracing distinct water plumes in transit past observing stations.

Despite the ability to sample aquatic ecosystems at high speeds using the FLAME platform, care must be taken when interpreting these results for larger ecosystems. Sampling events lasting longer than a few hours will inevitably be impacted by temporal variability in addition to spatial variability. For instance, diel oxygen excursions driven by primary production would impact the observed dissolved oxygen variability in space if sampled over longer time periods (e.g.,  $> 4\text{ h}$ ). Our assessments of spatial variability are also limited by the accuracy and precision of the sensors used. While we have provided an example of how to evaluate response times and correct these high-frequency data (Supporting Information), evaluating sensor performance in other applications is essential.

Further insights might be gained by altering reference frames in support of scientific research, engineering, management, and outreach. We suggest that the FLAME platform could be used to rapidly assess spatial variability before and after major events (e.g., storms, stratification) and to inform future and ongoing ecosystem studies. Gridded data (e.g., Figure 2) could be used

to ground-truth remote sensing products<sup>23,29</sup> and ecosystem models. Investigators could use the platform for efficient reconnaissance of discrete chemical influences such as urban discharges and other point sources.<sup>30</sup> Development of innovative calibrations and transfer functions could lead to maps of socially valuable ecosystem metrics that could appeal to the broader public. Further, time-series of spatially explicit data could be leveraged to generate water forecasts (perhaps focused on littoral areas) where there are potential health concerns from harmful algal blooms and other water quality issues.

## ■ ASSOCIATED CONTENT

### Supporting Information

Descriptions of equipment and experiments. This material is available free of charge via the Internet at <http://pubs.acs.org/>

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### Notes

The authors declare no competing financial interest.

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